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UNIVERSITY OF ALBERTA

EVALUATION OF THE RECLAMATION OF DECOMMISSIONED WOOD PRESERVING PLANT SITES IN ALBERTA

BY

ROBERT E. HOFFMANN ©

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND
RESEARCH IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
MASTER OF SCIENCE

DEPARTMENT OF CIVIL ENGINEERING

EDMONTON, ALBERTA
FALL, 1990

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GOVERNMENT OF ALBERTA

HELP
PROJECT
Help End Landfill Pollution
A Project of the Department of Environment

Room 1443, Standard Life Centre, 10405 Jasper Avenue, Edmonton, Alberta, Canada T5J 3N4 Telephone: 403/427-3946 Fax: 403/427-0413

March 5, 1990

Faculty of Graduate Studies
2-8 University Hall
University of Alberta
Edmonton, Alberta
T6G 2J9

Dear Sir:

RE: Use of Consultant's Reports
<u>Prepared for HELP Wood Preserving Operation Sites</u>

Enclosed is a list of Consultant's reports used in the [redacted] report entitled "Evaluation of the Reclamation of Decommissioned Wood Preserving Plant Sites in Alberta - Phase II Report".

According to contracts held with the consultants in question, "all data, documents and materials which are acquired under this Agreement become the sole property of the Department" (of Environment). Therefore, the Department has no objection to these reports being utilized in Mr. Hoffman's study.

Yours truly,

H.A. Kerr
Head
Groundwater Protection Branch

te/ck

Encl.

TASK 1 - TREATMENT PROCESSES, PRESERVATIVE CHARACTERISTICS

1. Anon., (1989), "Docket for the Listing of Wood Preserving Wastes." RCRA Listings.

2. Environmental Protection Service, "Creosote/Chromated Copper Arsenate (CCA)/Pentacholorophenol (PCP)/Pentachlorophenol (PCP) Thermal/Ammoniacal Copper Arsenate (ACA) Wood Preservation Facilities: Recommendations for Design and Operation." Report EPS2/WP1-5.

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8. Thurber Consultants., (1989), Deep Basin Wood Preservers Ltd. Facility. Elmsworth, Alberta. (SW 1/4, 8-70-12-WGM) Site Assessment Study.

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Head, Waste Management Group
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EK:mvw
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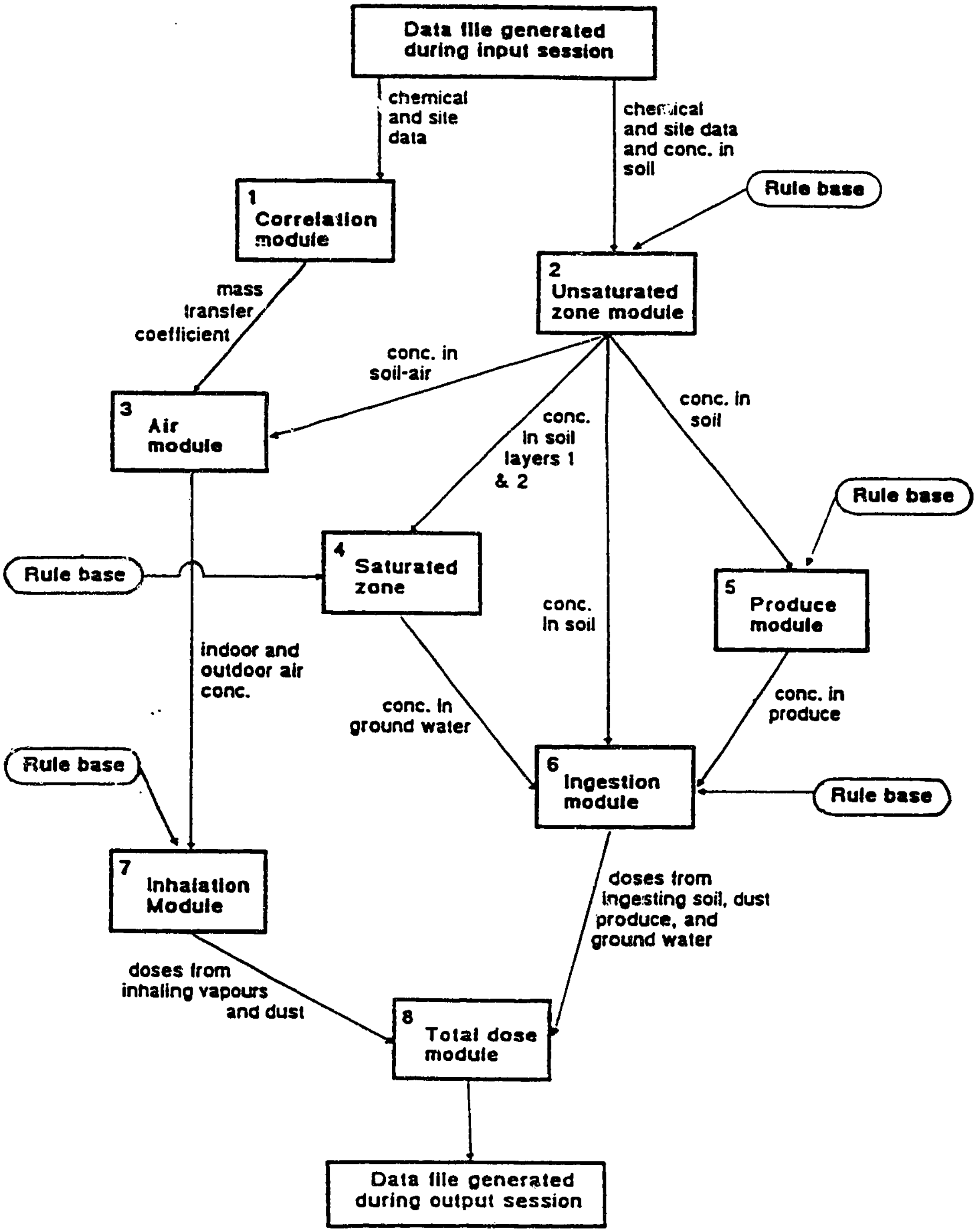
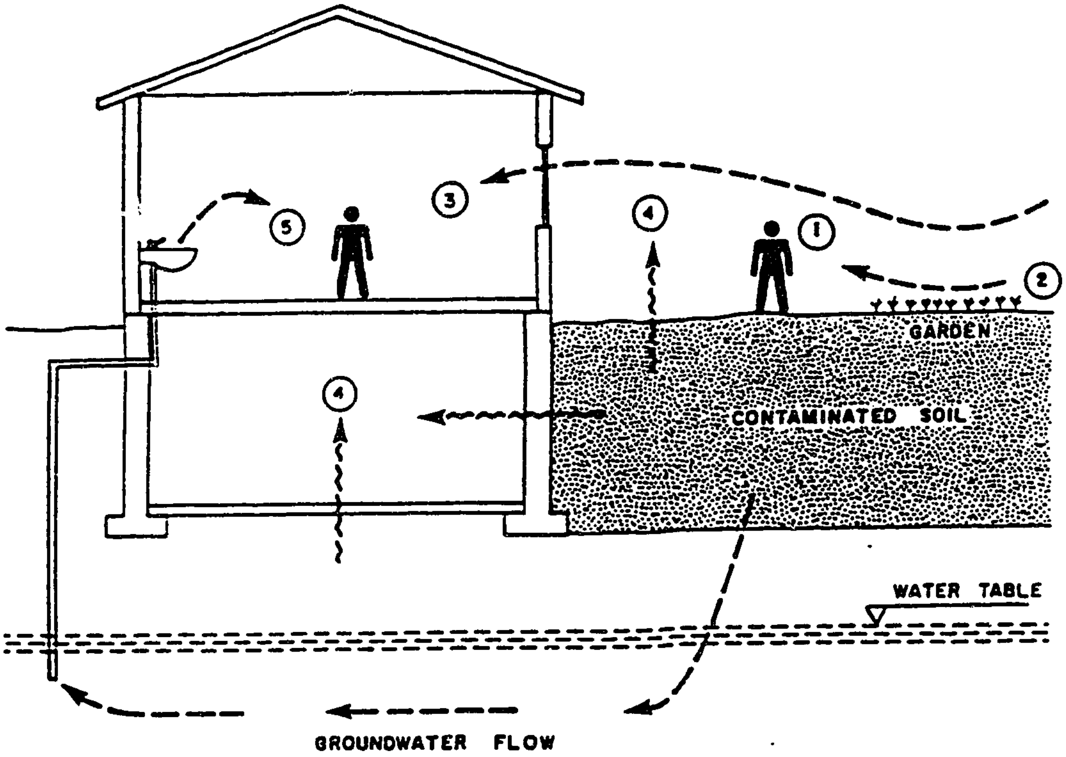


FIGURE 2.3-5 : COMPONENT MODULES AND INFORMATION FLOW (SENES, 1988)



POTENTIAL PATHWAYS:

① DIRECT INGESTION OF SOIL
INHALATION OF PARTICULATE MATTER

② INGESTION OF GARDEN PRODUCE

③ DIRECT INGESTION OF DUST
INHALATION OF PARTICULATE MATTER

④ INHALATION OF VAPOURS (BOTH OUTDOORS AND INDOORS)

⑤ INGESTION OF GROUNDWATER

FIGURE 2.3-6 : EXPOSURE PATHWAYS CONSIDERED IN AERIS (SENES, 1988)

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Engineers
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Economists
Scientists

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Rob Hoffman
Rural Route No. 1 St. Albert
Alberta, Canada
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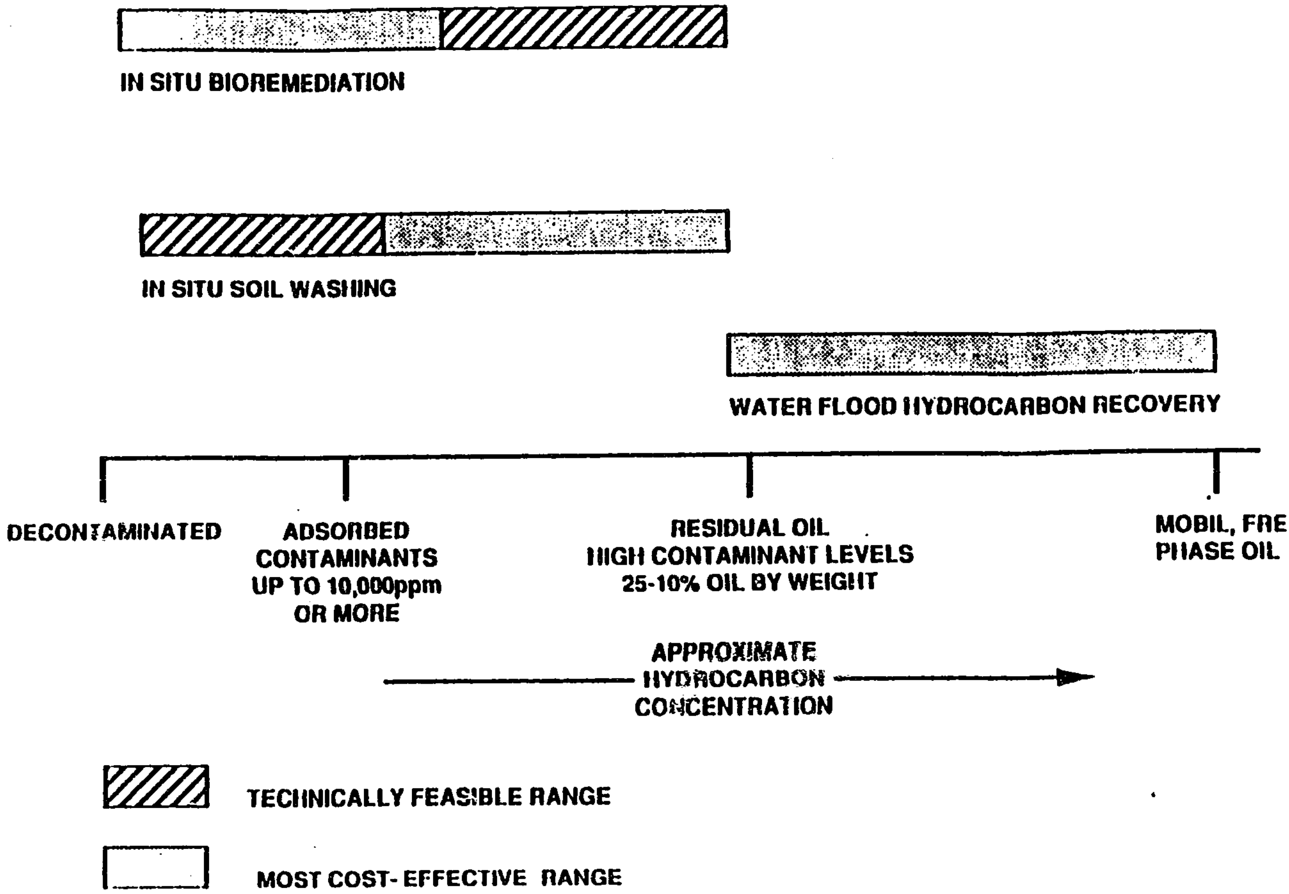

FIGURE 3.3-1 : PROBABLE RANGE OF EFFECTIVENESS FOR SELECTED IN SITU HYDROCARBON REMEDIATION TECHNIQUES (SALE AND PIONTEK, 1988)

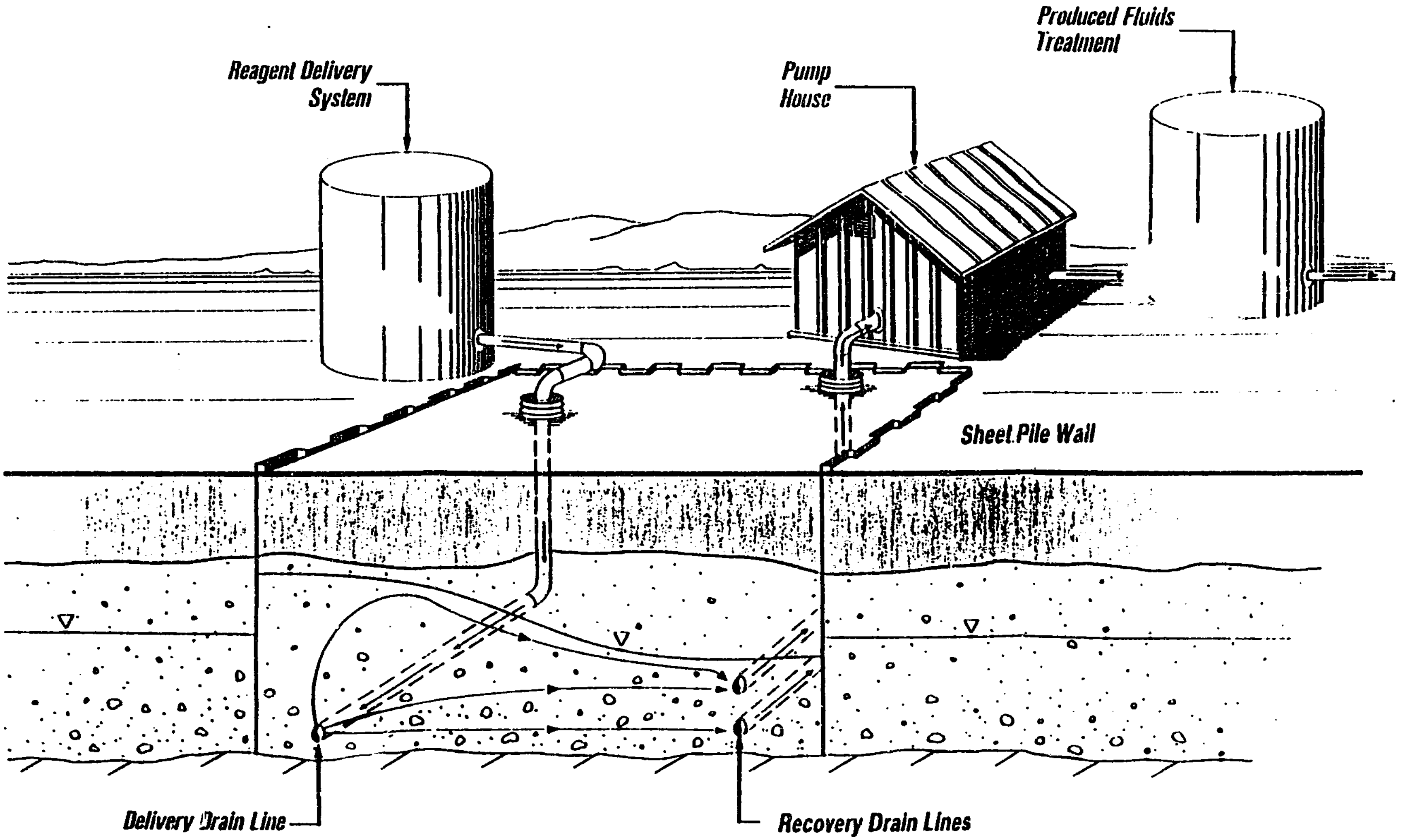

FIGURE 3.3-2 : PILOT-TEST OF IN SITU SOIL WASHING (SALE ET AL., 1989)

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DEGREE FOR WHICH THESIS WAS PRESENTED: MASTER OF SCIENCE

YEAR THIS DEGREE GRANTED: FALL, 1990

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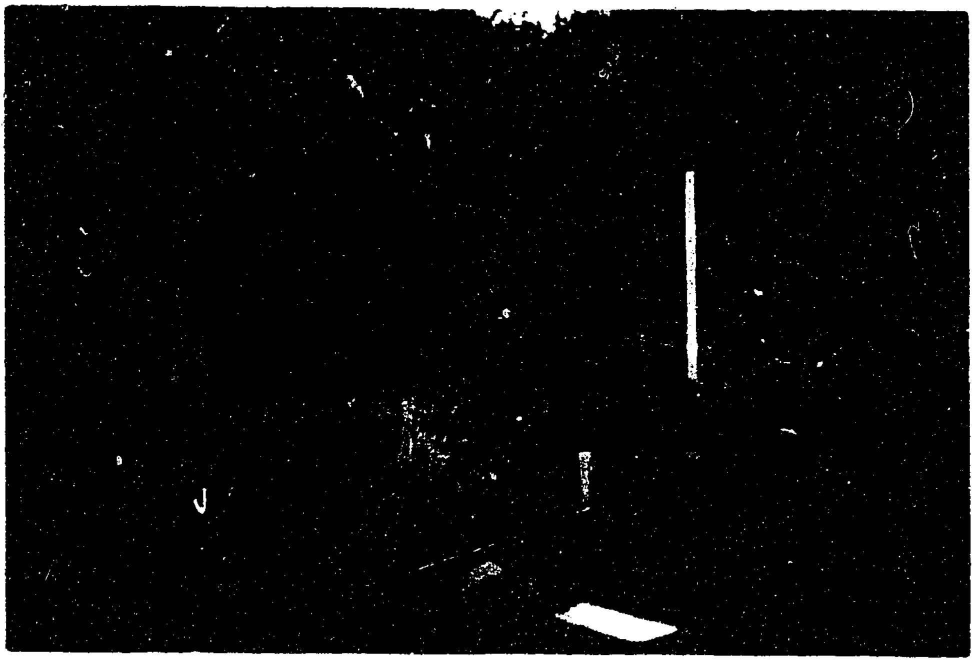

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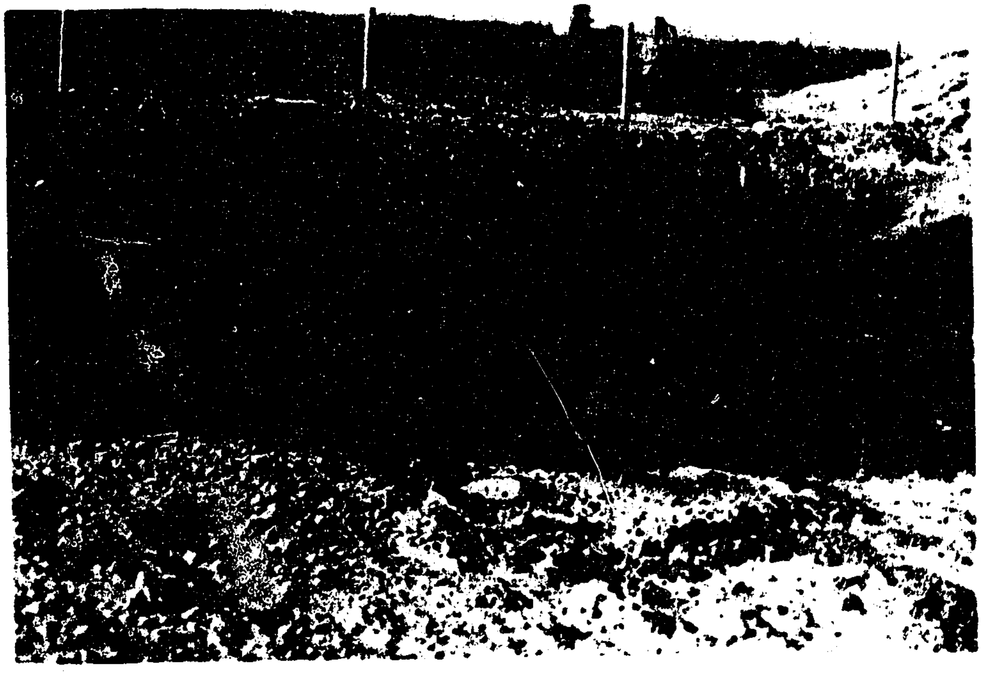

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DR. S.E. HRUDEY (SUPERVISOR)

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DR. P.M. HUCK

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DR. C. ZEISS

Alan Hingston

MR. A.M. HINGSTON

DATE: Sept. 21/90

ABSTRACT

The Help End Landfill Pollution (HELP) Project of Alberta Environment has identified five inactive wood preserving sites in Alberta. These sites were abandoned by their owners without being properly decommissioned. Alberta Environment is concerned these sites may pose an unacceptable hazard to human health or the environment.

This study is directed at evaluating assessment strategies and remediation alternatives for wood preserving sites in Alberta, with specific application to the five abandoned sites. An accurate assessment of hazard at wood preserving sites must consider the chemicals used, and their environmental behaviour. With this knowledge, the predominant pathways by which humans may be exposed to these chemicals may be determined. Site assessment strategies consider whether unacceptable exposures occur through these routes. If so, remediation alternatives can be selected to reduce the exposure to acceptable levels.

Three wood preserving mixtures were used at the five sites, and are typically used in Alberta: pentachlorophenol (PCP)-based, creosote-based, and chromated copper arsenate (CCA)-based. Released to the environment as wastes, compounds in these mixtures partition largely to soil, though some constituents are quite volatile and/or water soluble. Consequently, several exposure pathways may be significant at wood preserving sites, depending on the constituent considered. Bioaccumulation pathways,

where exposure occurs through consumption of contaminated plants or animals, are also likely to be significant for some compounds.

Of the assessment strategies considered, risk assessment/risk management, fixed criteria, and a modified risk assessment model were found to have the widest range of capabilities. These strategies were combined along with bioassay requirements to form a recommended approach for assessing site contamination and developing cleanup standards at wood preserving sites.

Remediation technologies are used to achieve cleanup levels at contaminated sites. Eight alternatives were evaluated for their ability to remediate the different contamination forms existing at wood preserving sites: landfill disposal, solidification/stabilization, incineration, enhanced land treatment, in situ bioreclamation, vapour extraction, in situ soil washing, and pump and treat. An analysis of these methods indicated that no one technology could effectively remediate all contamination forms present at wood preserving sites; a treatment scheme, incorporating several technologies, will be required for complete remediation.

Finally, study results were used to evaluate conditions at the five abandoned sites, and to recommend remediation alternatives.

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I would like to acknowledge several people and agencies who assisted in the development of this thesis:

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- Ms. Nola Shaw, Mrs. Dianne Sergy and Ms. Elaine Hebert for typing the manuscript and drafting figures;
- Ms. Marilyn Kotylak, for cataloging references and rush typing; and
- my parents, Walter and Linda Hoffmann, and Marilyn for their personal support and understanding.

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LIST OF SYMBOLS AND ABBREVIATIONS

a	annum (year)
ACS	American Chemical Society
AERIS	Aid for Evaluating the Redevelopment of Industrial Sites
API	American Petroleum Institute
As	arsenic
CCA	Chromated Copper Arsenate
Cr	chromium
Cu	copper
ha	hectare
HELP	Help End Landfill Pollution
Hg	mercury
IFT	Interfacial Tension
LTU	Land Treatment Unit
NRCC	National Research Council of Canada
OTA	Office of Technology Assessment
PCDD	Polychlorinated Dibenzo[p]dioxin
PCDF	Polychlorinated Dibenzofuran
PCP	Pentachlorophenol
PIC	Product of Incomplete Combustion
POHC	Principal Organic Hazardous Contaminant
q_1^*	carcinogenic potency factor (slope factor)
RfD	Reference Dose (noncarcinogens)
RSD	Risk Specific Dose (carcinogens)

1. Project Overview

A number of wood preserving plant sites in Alberta have been abandoned by their owners. These orphan sites are in addition to other wood preserving plants which have been, or are in the process of being, permanently decommissioned or temporarily closed.

Wood preserving plants have a large potential to cause environmental harm because the chemicals used severely impair biological activity. Alberta Environment and the Help End Landfill Pollution (HELP) project are concerned about the hazards posed by these sites, particularly the orphan sites at which proper plant decommissioning did not likely occur. The five orphan wood preserving plant sites identified are listed in Table 1-1 and shown in Figure 1-1.

This study is intended to provide Alberta Environment and the HELP project with information required to deal with the abandoned and decommissioned wood preserving sites in Alberta. The study is organized into four main areas.

1. Background information, including: a description of the wood preserving industry, properties of the chemicals used, transport and fate of these chemicals in the environment, and the hazards posed by these chemicals distributed in the environment.
2. Information on assessing the contamination at wood preserving sites, and the criteria which can be used to select cleanup levels. One computer risk assessment model is also evaluated.

Table 1-1 Five Abandoned Wood Preserving Sites

Site	Location	Suspected Preservatives Used
Alberta Western Post and Timber Treating Ltd.	Blackfalds	PCP
Canada Creosoting Ltd.	Calgary	Creosote, PCP
Peerless Wood Preservers Ltd.	Cayley	PCP
Deep Basin Wood Preservers Ltd.	Elmworth	CCA
Alberta Osmose Pressure Preserving Ltd.	Faust	PCP, CCA

Notes:

- PCP = Pentachlorophenol Preserving Solution
- CCA = Chromated Copper Arsenate Solution

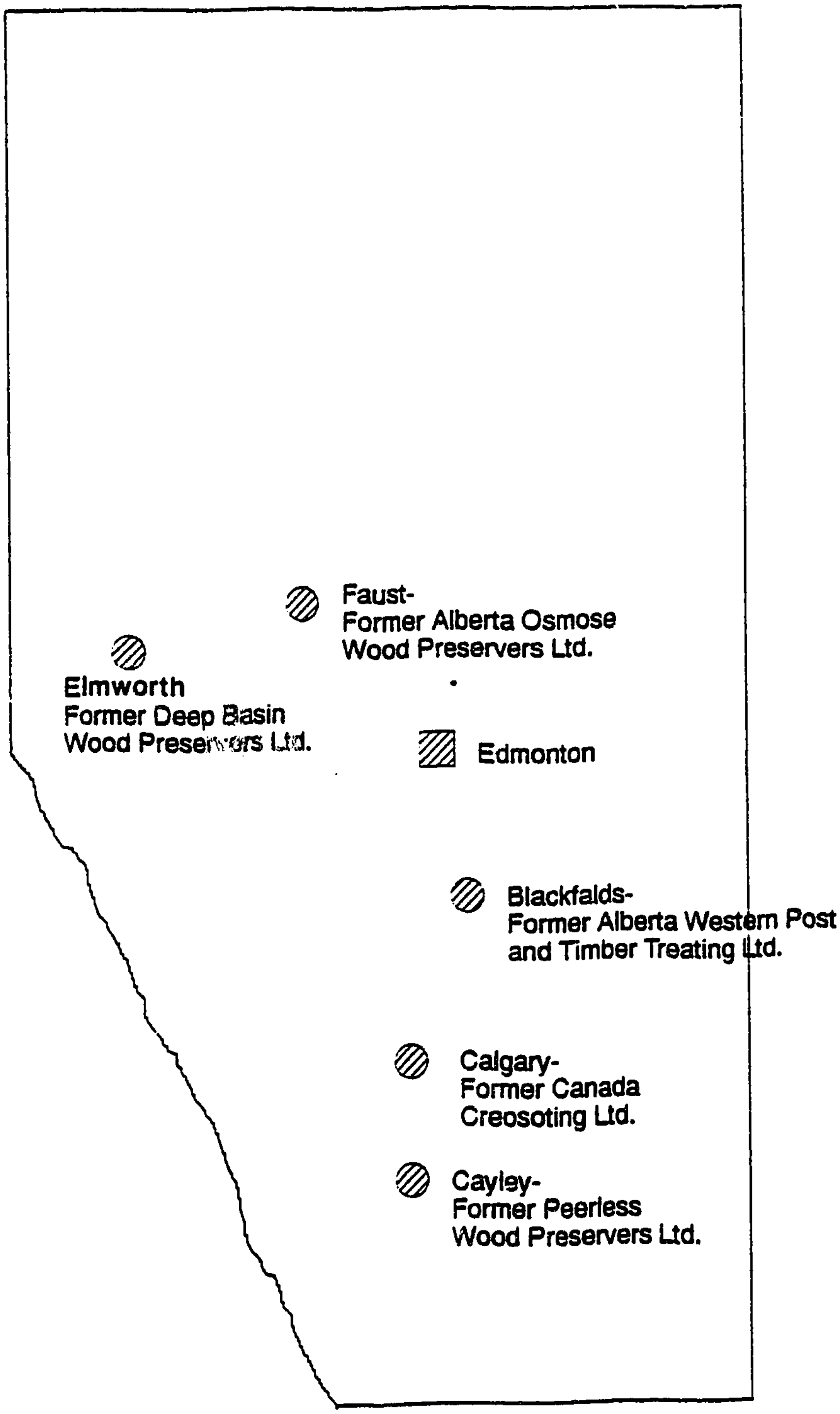


FIGURE 1-1 : LOCATIONS OF THE FIVE HELP SITES

3. Remediation technologies which may be implemented to achieve selected cleanup levels.
4. Application of the foregoing information to the five orphan sites.

By reviewing the relevant background, scientific and technical knowledge concerning characterization and risk management of wood preserving sites, this study should provide a rational and consistent basis for dealing with the five orphan sites in Alberta.

1.1 Need for Wood Preservation

The growth and decay of trees is an essential component in the nutrient cycle of our environment. Insects, bacteria and fungi are the major organisms responsible for the degradation of wood in this cycle.

Insects such as wood wasps, beetles, and marine borers tunnel through tree bark, producing galleries in which eggs are laid. These extensive attacks weaken the wood surface, which in time becomes worn away, exposing fresh surfaces to attack. Additionally, hatched larvae consume sugar and starch from the wood, loosening the bark and reducing cellulose formation (Richardson, 1978). Wood can also be consumed directly by insects such as termites.

Bacteria are normally present in both living trees and wood products (Smith, 1975). The majority of these bacteria do not adversely affect wood, but some can reduce structural integrity by degrading cellulose and pectin, while producing organic acids (Smith, 1978).

In the temperate parts of the world, fungi are the most abundant and significant organisms responsible for wood deterioration (Smith, 1978). Wood-degrading fungi have been grouped into four overlapping categories by Smith (1978).

1. **True wood-destroying fungi**: these generally are Basidiomycetes, which have the ability to consume both the structural cellulose and lignin in wood. This group can be further divided into fungi causing

brown rots and those causing white rots. Attack by true wood-destroying fungi is often very rapid, with a significant loss in strength noticed over a period of a few weeks.

2. **Soft-rot fungi**: these are generally Ascomycetes, which have the ability to attack both cellulose and lignin. In contrast to true wood-destroying fungi, attack of wood in service by soft-rot fungi is generally slow. However, these fungi can thrive under adverse conditions toxic to Basidiomycetes, such as around pilings in sea-water.

3. **Sapstain fungi**: this group of fungi grow preferentially in the sapwood of green lumber, where they utilize sap rich in sugars. These fungi do not degrade cellulose and lignin, which comprise the structural components of wood. Sapstain fungi are a concern because they impact the appearance of wood and its amenability to subsequent treatment (for example, painting or varnishing).

4. **Mould fungi**: these are generally Physomycetes, which grow superficially on wood, rarely penetrating to any depth. These fungi do not degrade structural cellulose or lignin, and therefore, do not structurally weaken the wood. In contrast to sapstain fungi, attacked wood can be refinished to a clean surface.

Wood-destroying fungi have four major requirements for growth: a food source such as cellulose or lignin, a suitable moisture content, a suitable temperature, and an adequate supply of oxygen (Smith, 1978). Removal of any one of these requirements results in the cessation of fungal activity. Because of the utility of wood, it is used in a number of environments, and controls on temperature, moisture level or oxygen supply are not always easily achieved. Consequently, the most widely-applicable treatment mechanism is to "poison" the wood food source through the use of chemicals, termed wood preservatives. The use of these chemicals can also limit destruction cause by insects and bacteria (Environment Canada, 1988a).

Studies have shown that the use of wood preservatives increases the useful life of wood in service by 5 to 10 times, depending on the wood species, use and efficacy of treatment (Environment Canada, 1988b). For example, untreated railway ties are expected to have a useful life of about five years, while the "apparent life" of treated ties in U.S. Class 1 railroads is about 47 years (Arsenault, 1978). Additionally, wood preservation enables the use of smaller and more rapid growing trees, as no dimensional compensation for decay has to be included in structural calculations (Environment Canada, 1988a). It has been estimated that without the use of wood preservation chemicals, timber requirements would increase by three- to six-fold (Environment Canada, 1988b). Consequently, the practice of wood preservation reduces the demand for replacement wood, thereby conserving forests. This makes sense from both an environmental and economic standpoint.

1.2 The Wood Preserving Industry

The use of chemicals to preserve wood dates back to many centuries before Christ. The earliest reference to wood preservation occurs in Genesis 6, when God instructed Noah to "make yourself an ark ... and cover it inside and out with pitch". The Greeks, Egyptians, Chinese and Romans are all believed to have practised chemical wood preservation of some form in the centuries before Christ (Richardson, 1978; Hunt and Garratt, 1967). Developments in wood preservation were stymied in the Dark Ages by strict religious controls on scientific thought. It was not until the industrial revolution that technology was again applied to wood preservation. In Canada, wood treating began on a commercial scale in 1910 with the construction of a creosoting facility in British Columbia (Shields and Stranks, 1978). By 1976, 37 pressure wood preserving plants existed throughout Canada with eight in Alberta (Shields, 1976). A list of wood preserving plant sites in Alberta as of 1989 is included as Table 1.2-1.

Three different wood preserving mixtures have been, and continue to be, predominant in use in Alberta: mixtures using pentachlorophenol (PCP), mixtures using creosote, and those using chromated copper arsenate (CCA). The use of these chemicals is governed by the Canadian Standards Association Standard 080 (CSA, 1989) which stipulates treatment fluid composition, process parameters, analysis methods and allowable uses of treated wood.

When cut timber is brought to the wood treating plant, the initial treatment step is debarking. After this step, the moisture content of the wood is

Table 1.2-1 Wood Preserving Plant Sites in Alberta as of 1989

Company	Location	Preservative(s) Used	Status
Alberta Osmose Ltd.	Faust	PCP, CCA	Abandoned (HELP site)
Alberta Western Post Ltd.	Blackfalds	PCP	Abandoned (HELP site)
Bell Pole Company Ltd.	Carsland	PCP, CCA	Operating
Branch Pole Company Ltd.	Edson	CCA	Operating
Canada Creosoting Ltd.	Calgary	PCP, Creosote	Abandoned (HELP site)
Deep Basin Ltd.	Elmworth	CCA	Abandoned (HELP site)
Domtar Chemicals Ltd.	Camrose	CCA	Shut down
Domtar Chemicals Ltd.	Cochrane	PCP, Creosote	Shut down
Domtar Chemicals Ltd.	Edmonton	ACA	Operating
Natal Forest Products Ltd.	Coleman	PCP, CCA	Operating
Peerless Wood Preservers Ltd.	Cayley	PCP	Abandoned (HELP site)
Pine Ridge Wood Preservers Ltd.	Cherry Grove	PCP, CCA	Operating
Rocky Wood Preservers Ltd.	Rocky Mountain House	PCP, CCA	Operating
Spray Lakes Sawmills Ltd.	Cochrane	CCA	Operating
Sunpine Forest Products Ltd.	Sundre	CCA	Operating

<u>Notes:</u>

- this table was adapted in part from a list compiled by the HELP project.
- plants applying fire retardants, waxes or resins are not included in this list.
- ACA = Ammoniacal Copper Arsenite Preserving Solution.

reduced by air seasoning, kiln drying, or by a pre-treatment step in the retort, such as steaming. Drying is intended to enhance preservative penetration of the wood cell wall by removing cell water, which is much less compressible than air. Conditioning procedures for given wood products are stipulated by the Canadian Standards Association (CSA, 1989). After drying, the wood is ready for preservative treatment. Pressure treatment is used instead of surficial treatment alone to ensure chemical penetration deep into the wood.

1.2.1 Wood Preservation Using Creosote-Based Mixtures

A creosote-based wood preserving mixture was used at one of the five HELP sites. The treating fluid in creosote wood preservation is either a mixture of 50:50 creosote/petroleum oil or 100% creosote (full strength) (Environment Canada, 1988b).

Conditioned timber is loaded onto metal trams and rolled into the treating cylinder (retort) on steel tracks. The hinged retort door is closed and locked. Treatment cylinders may be up to 45 m long and 2 m in diameter (Environment Canada, 1988b). A schematic illustration of a modern-day creosote pressure treating facility is shown in Figure 1.2-1.

Either the full- or empty-cell treatment process may be applied to wood within the retort. The full-cell treatment process completely fills the wood cells with preservative, and consequently results in thorough treatment. The full-cell process is illustrated in Figure 1.2-2 and is described below (Environment Canada, 1988b; McGinnis et al., 1980):

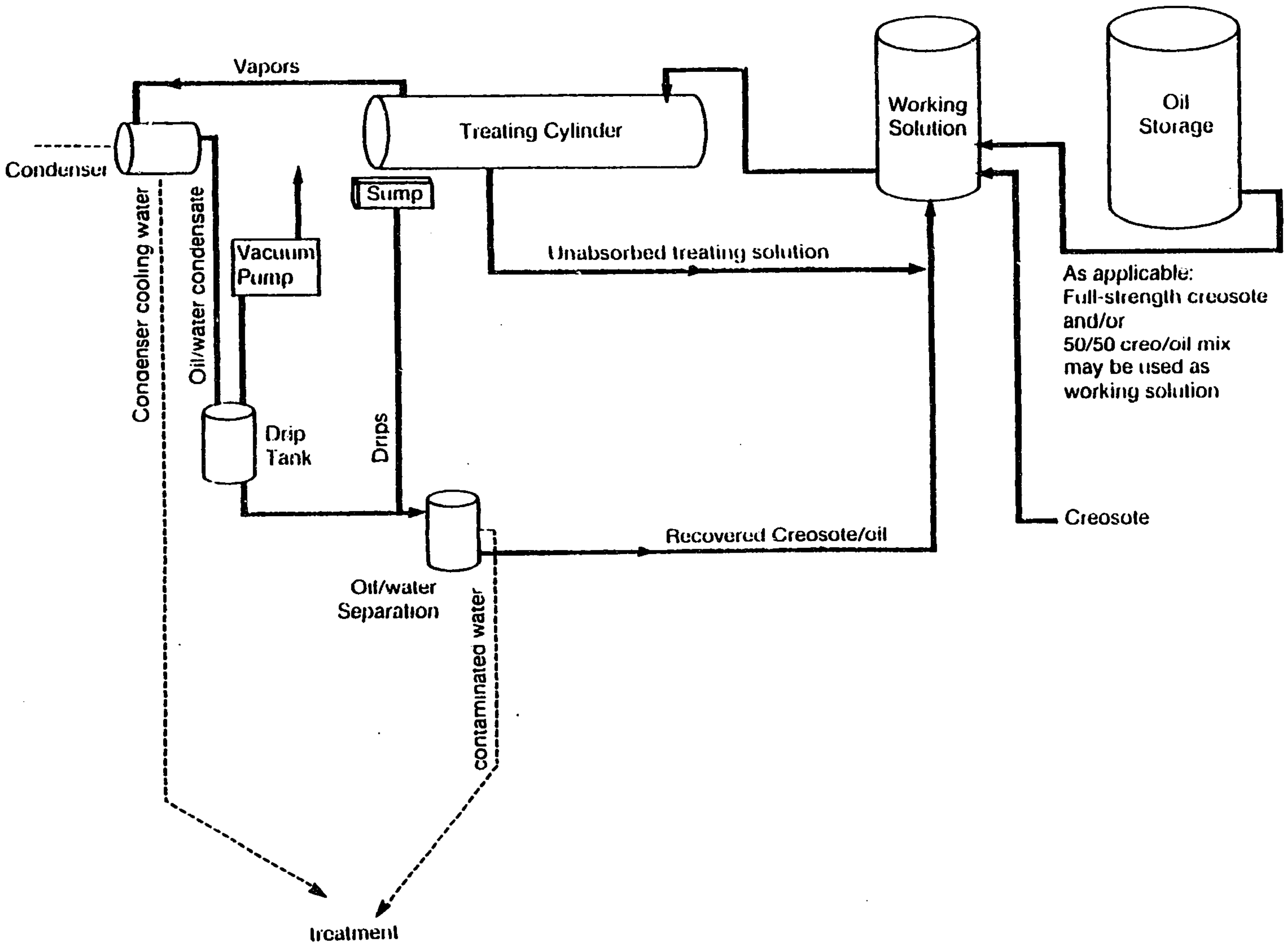


FIGURE 1.2-1 : PROCESS FLOW DIAGRAM OF A CREOSOTE PRESSURE TREATMENT PLANT (ADAPTED FROM ENVIRONMENT CANADA, 1988B)

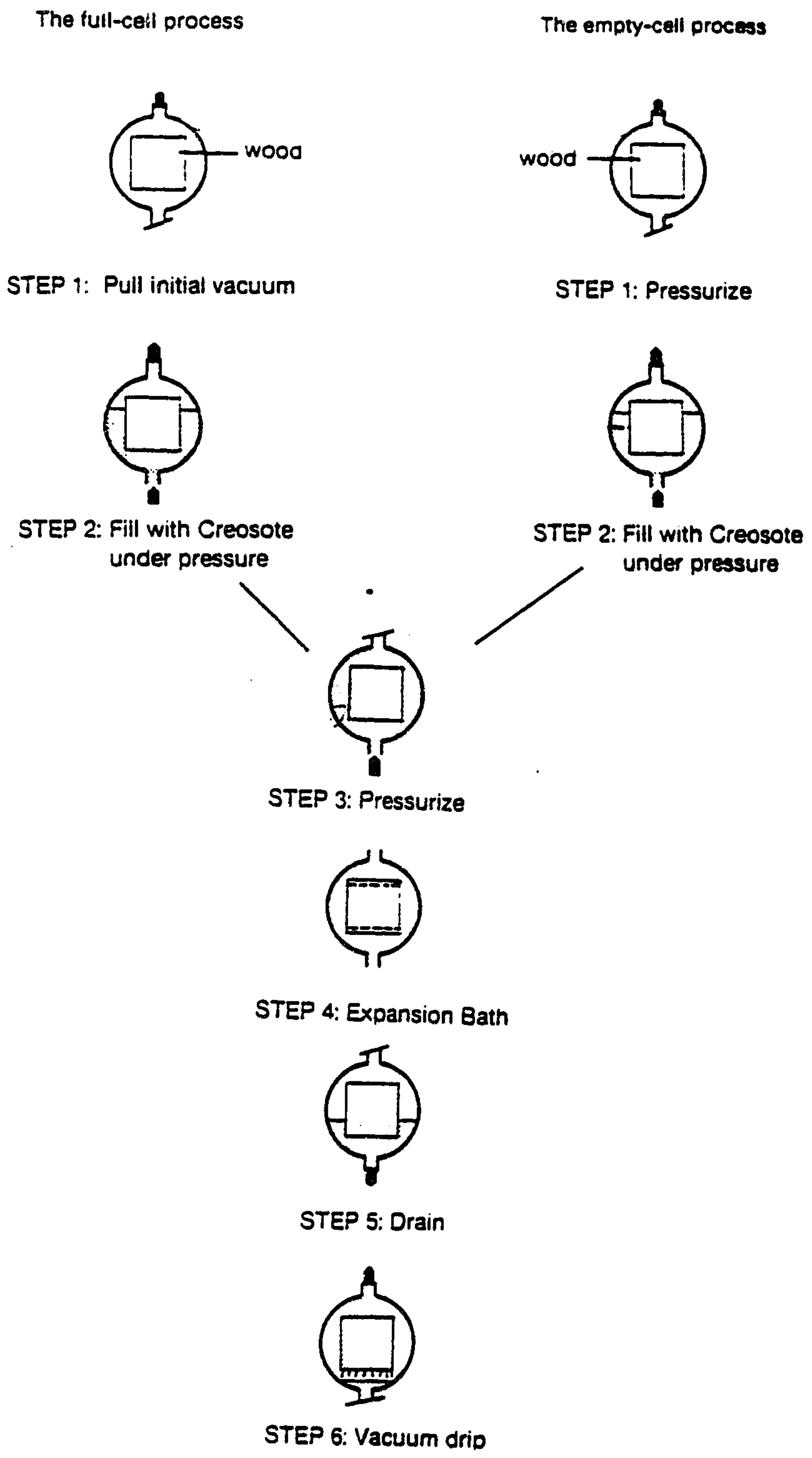


FIGURE 1.2-2 : CREOSOTE WOOD PRESERVATION PROCESS

- a vacuum is initially applied to remove air trapped in the wood cells.
- the cylinder is then filled with heated creosote fluid. The fluid is heated to reduce its viscosity, enhancing its penetration into the timber.
- air or fluid pressure is then applied to drive the preservative mixture into the wood. The pressure is applied until the target preservative retention level is achieved, as measured by the height of free fluid within the retort.
- oil surrounding the wood is then heated in the "expansion bath" step.
- in the final step, residual treating fluid is drained from the retort and a vacuum applied to collect mobile preservative.

The empty-cell and full-cell treatment processes are illustrated in Figure 1.2-2. Empty-cell treatment involves pressurization to retain trapped air in the wood, limiting preservative retention. Full-cell treatment involves application of a vacuum to liberate trapped air before pressurization with creosote, allowing greater penetration.

Operating parameters, preservative standards and product quality requirements for creosote wood preservation are stipulated by the Canadian Standards Association (CSA) Wood Preservation Guidelines (1989).

Wood treated with creosote has been used for railway ties, marine pilings, and in bridge construction. In addition to being a wide-spectrum fungicide, creosote's oily nature makes treated wood somewhat hydrophobic, and consequently increases dimensional stability in the presence of moisture (Smith, 1978). Wood treated with the full-cell process is more resistant to decay than wood produced from empty-cell treatment, and is thus more amenable to use in adverse conditions.

1.2.2 Wood Preservation Using PCP-Based Mixtures

PCP-based wood preserving mixtures were used at four of the five HELP sites. In PCP wood preservation, technical-grade pentachlorophenol (PCP) is blended with a diesel fuel or No. 2 fuel oil carrier to produce a 3 to 6% strength working fluid (Environment Canada, 1988a).

Conditioned timber is then loaded onto metal trams which are rolled into the treating cylinder on steel tracks. After a charge of timber has been placed in the retort, the hinged door is closed and sealed. Treatment cylinders may be up to 45 m long and 2 m in diameter (Environment Canada, 1988a).

Either full- or empty-cell treatment processes may be applied to wood within the retort. These processes were described in section 1.2.1. In short, the empty-cell process utilizes air trapped in the wood cells to limit preservative retention, while full-cell treatment uses an initial vacuum to liberate trapped air, enabling greater preservative penetration.

Operating parameters, preservative standards and product quality requirements for PCP wood preservation are stipulated by the Canadian Standards Association (CSA) Wood Preservation Guidelines (1989).

Wood treated with PCP-based mixtures has been used for telephone and utility poles, railway ties, and as construction timber. The carrier oil used in PCP-based mixtures makes the treated product water-repellent, which reduces preservative leaching, and also makes the wood more resistant to splitting in the presence of moisture.

1.2.3 Wood Preservation Using CCA-Based Mixtures

CCA-based wood preserving mixtures were used at two of the five HELP sites. In CCA wood preservation, a premixed concentrate containing chromated copper arsenate (CCA) is diluted with water to produce a 1.5 to 4.0% strength working fluid (Environment Canada, 1988c).

Conditioned timber is loaded onto metal trams and rolled into the treating cylinder along steel tracks. After the charge of timber has been placed in the retort, the hinged door is closed and sealed. A conceptual diagram of a modern-day CCA pressure treating facility is presented as Figure 1.2-3.

Within the retort, the full-cell treatment process is used for CCA wood preservation (Environment Canada, 1988c; Arsenault, 1978). This treatment approach consists of the following steps (Environment Canada, 1988c):

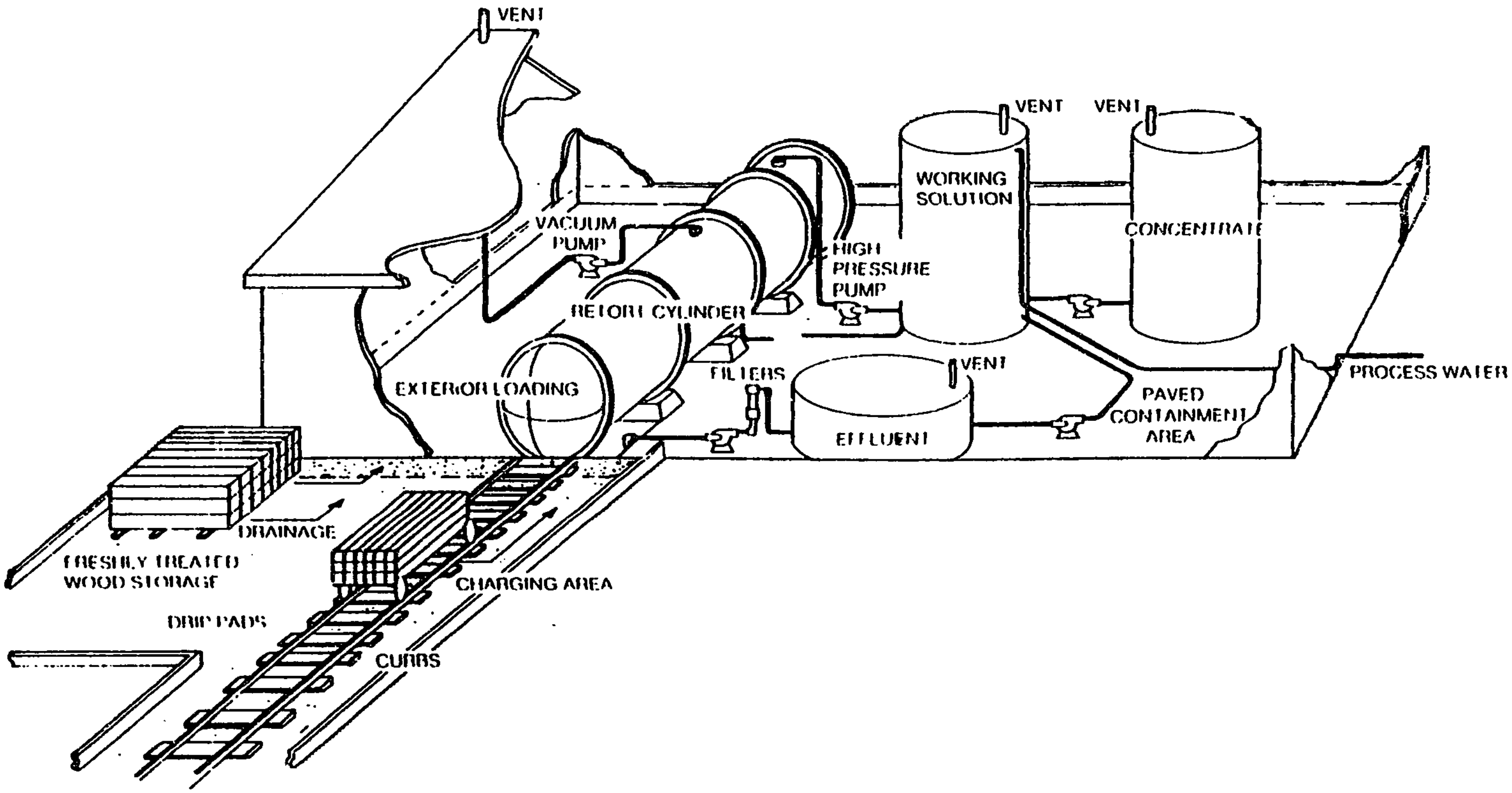


FIGURE 1.2-3 : CONCEPTUAL DIAGRAM OF A CCA PRESSURE TREATING FACILITY (ADAPTED FROM ENVIRONMENT CANADA, 1988C)

- application of an initial vacuum to remove air trapped in the wood cells;
- flooding the retort with CCA working fluid and pressurization until the desired preservative retention level is obtained;
- draining of the excess CCA fluid; and
- application of a final vacuum to recover unfixed preservative.

In contrast to the full-cell treatment approach used for creosote and PCP-based mixtures, CCA fluid is not heated. Heat is used for creosote and PCP to reduce fluid viscosity, enhancing wood cell penetration. For CCA, elevated temperatures increase the rate of chemical fixation between CCA and wood constituents, which may consequently occur before adequate penetration is achieved. This may block further preservative penetration and cause solution sludging in the cylinder (Arsenault, 1978). For this reason heat is not used in CCA treatment, and recently dried timber must be cooled prior to treatment.

Operating parameters, preservative standards and product quality requirements for CCA wood preservation are stipulated by the Canadian Standards Association (CSA) Wood Preservation Guidelines (1989).

CCA-based preserving mixtures use water as the carrier fluid. This water evaporates when the treated wood is dried, leaving the affixed chemicals behind. Consequently, CCA treated wood has a much cleaner appearance than wood treated with oil-based formulations such as creosote and PCP. CCA treated timber may also be stained and painted. Because of these properties, CCA treated wood has been used for landscaping, patio construction, playground equipment, fence posts and preserved-wood foundations (Smith, 1978; Environment Canada, 1988c). CCA treated wood has also been used successfully in industrial applications, such as marine pilings.

1.2.4 Chemical Releases from Wood Preservation Processes

Wood preserving chemicals can be released to the environment at several junctures in the treatment process. The properties of the waste streams are notably different for oil-based and water-based processes.

1.2.4.1 Oil-Based Processes

The treatment processes and preservative fluid properties are very similar for creosote- and PCP-based processes. Consequently, the sources of waste are also quite similar. Chemical releases from wood preserving plants using creosote- or PCP-based mixtures can be divided into spills, vapours, drips and sludges.

Spills may occur during chemical delivery, chemical storage and mixing, as well as during filling and draining of the retort. Vapours may be released from chemical storage, chemical mixing, and from the treating cylinder during vacuum or pressure release cycles.

Drips of preservative fluid are released from leaking pipes. However, the chemical contribution from this source is generally insignificant compared to the drippage released during storage of treated timber. When wood is removed from the retort, excess pressure in the wood cells escapes, releasing large amounts of trapped preservative fluid. For this reason, freshly treated timber is initially moved to an area designated as the "drip pad" and held there for a number of hours. Once the wood is reasonably dry, it is transferred to storage, where it continues to drip. In modern plants, the drip pad is generally made of concrete and sloped towards a sump where drippage is collected and recycled. In older plants however, including the five HELP sites, the drip pad was located on unprotected soil.

Sludges are produced from the retort sump as well as from filters which recycle unused fluid. In pressure treatment of wood, preservative fluid replaces water and sap in the wood cells. Bark, dirt and wood chips also contaminate the fluid. At the end of a treatment cycle then, the preservative fluid for oil-based processes is an oil/water/sap emulsion containing other solid contaminants. In modern plants the emulsion is broken, and the components are sent for treatment and re-use. In older plants however, including the five HELP sites, the process sludge was dumped in lagoons with limited or non-existent liners. Shields (1976) reported that, even in 1976, twenty of the thirty-six pressure preserving plants in Canada discharged process sludge to lagoons.

Experience at creosote and PCP wood preserving plants has shown that chemical releases as spills or vapours may pose a significant hazard to occupational personnel (Henning and Konasewich, 1984), but these sources seldom represent a long-term environmental hazard at decommissioned plants. For such sites, chemical releases as drips or sludges represent the most significant long-term environmental concern. Soil used as a drip pad is generally heavily contaminated for at least a one-metre depth. Leaking lagoons have contaminated soil and groundwater to as much as one-hundred metres deep.

1.2.4.2 Water-Based Processes

Water is the carrier fluid in CCA-based wood preserving mixtures. Consequently, CCA-based treatment has several advantages over oil-based processes:

- the viscosity of water is lower than that of oil, even when the oil is heated. As a result, there is less blockage of wood cell pores and subsequent sludging. Much less sludge is therefore generated in CCA-based processes (McGinnis, 1988). This general observation is consistent with findings at the Faust site, where both PCP- and CCA-based processes were used.
- the oil/water/sap emulsion which forms for oil-based processes does not form within the retort for CCA-based processes. Consequently, residual treating fluid is more easily treated and recycled, and less is disposed.
- creosote- and PCP-based preserving mixtures are heated during application, whereas CCA is applied at ambient temperatures. The constituents of CCA are also not volatile. Consequently, chemical releases as vapours are more substantial for the oil-based processes.

- the solvent nature of creosote and diesel fuel cause more piping leaks than occur with CCA mixtures, as rubber and plastic seals and gaskets may gradually be solubilized.

A comparison of treating process residual volumes is presented in Table 1.2-2. Testing at CCA wood preserving facilities has generally shown that chemical releases as spills or vapours do not represent a hazard to occupational personnel (for example; Henning and Konasewich, 1984), or represent a long-term environmental concern at decommissioned facilities. As for sites utilizing oil-based processes, chemical releases as drips or sludges represent the most significant long-term environmental hazard at CCA facilities. For example, surficial soil used as a drip pad is generally heavily contaminated, while non-secure lagoons holding CCA sludge have contaminated both vadose and saturated soil zones.

Table 1.2-2 Treating Process Residual Volumes

Process	Volume of Treating Process Residual Generated per Cubic Metre of Preserved Wood (litres)
PCP-based	0.85
Creosote-based	0.54
CCA-based	0.05

Notes:

- source: U.S. EPA (1987c).

1.3 Important Characteristics of Wood Preserving Mixtures

Oil-based wood preserving fluids contain hundreds or even thousands of different chemicals. The environmental and toxicological behaviour of mixtures containing these chemicals is much different from the behaviour of the chemicals acting individually. This concept is best illustrated using a number of examples.

- By itself, pentachlorophenol (PCP) is heavier than water, and will sink to the bottom of a container when both phases are present. In PCP-based wood preserving mixtures, PCP is dissolved in diesel fuel, which is lighter than water. Consequently, PCP-based preservative fluids "float" on the groundwater table in aquifers where both phases are present. The actual density of the treating fluid is neither that of technical-grade PCP nor diesel, but of the mixture. In PCP preserving mixtures, diesel comprises more than 95% of the fluid, so the density of the fluid most closely resembles that of the diesel fuel.

- By itself, benzo[a]pyrene is strongly adsorbed to soil organic matter. In creosote-based wood preserving mixtures, benzo[a]pyrene is just one of hundreds (or even thousands) of polynuclear aromatic hydrocarbons (PAHs) present, and is known to be a potent carcinogen. Strong competition exists among the PAHs in creosote for adsorption sites in soil as well as for receptor sites in organisms. Consequently, the mobility and effective toxicity of benzo[a]pyrene in creosote is different from its behaviour as a pure compound.

- By themselves, PAHs are hydrophobic. They preferentially partition to organic solids in an aqueous environment such as an aquifer. Consequently, the movement of a contaminant plume containing a single PAH is very slow in most soils. However, facilitated transport occurs when many PAHs are present because of cosolvent effects. As a result, PAHs in creosote may be much more mobile in groundwater systems than predicted by the behaviour of individual constituents. Likewise the transport across cellular membranes may be altered.

Unfortunately, very little research has been done on the environmental fate and toxicology of whole wood preserving fluids. In this review, results from such research have been emphasized. In most areas, information has been taken from individual-compound studies. From a practical standpoint, single-compound studies provide general expectations for behaviour, but actual behaviour may differ because of influences from the chemical mixture.

1.4 Characteristics of Chemicals in Wood Preserving Mixtures

The physical, chemical, biodegradation and toxicological properties of chemicals used in wood preserving mixtures have been reviewed. The properties of the treating fluid, as a whole, will also be presented where the information is available.

1.4.1 PCP-Based Wood Preserving Mixtures

1.4.1.1 Physical and Chemical Properties

Working mixtures in PCP wood preservation contain from 3 to 6% technical-grade PCP dissolved in petroleum oil. The petroleum carrier forms the major component of the mixture, and consequently, the fluid properties most closely resemble those of the carrier. These properties are specified in CSA Standard 080 (1989), which segregates hydrocarbon solvents into four classes. The diesel fuel carrier used at the HELP sites would most likely have conformed to Type A specifications (Table 1.4-1).

Properties of major concern are the density and viscosity. At 15.5°C, the density of water is 1.00 kg/L, whereas that of diesel fuel is 0.85 kg/L. Diesel fuel is thus lighter than water. At 37.8°C, the kinematic viscosity of water is 6.9×10^{-7} m^2/s (0.69 centistokes), whereas that of Type A hydrocarbon solvent is 1.3×10^{-5} m^2/s (13.0 centistokes). Consequently, water is much less viscous than diesel fuel. The differences in density and viscosity between water and diesel fuel significantly influence the behaviour of a PCP-plume in groundwater.

Table 1.4-1 Properties of Type A Hydrocarbon Solvent

Property	Maximum	Minimum
density at 15.5°C (kg/L)	-	0.85
flashpoint (°C)	-	66
% volume of fractions distilling below 315.5°C	90	-
kinematic viscosity at 37.8°C (centistokes)	13	-
% weight solvency at 34.9°C	-	10

Notes:

- source : CSA Standard 080 (1989) - Wood Preservation

The other component in PCP-based wood preserving mixtures is technical-grade pentachlorophenol (PCP), a synthetic organic chemical produced by reacting chlorine with phenol in the presence of a catalyst. During the chlorination reaction, the temperature must be kept above the melting point of the products formed. This is believed to lead to the formation of contaminants in technical PCP, including lower chlorophenols and chlorinated phenoxyphenols, as well as several microcontaminants, of which polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) warrant the greatest concern. Only dioxins containing six to eight chlorine atoms have been consistently found in technical-grade PCP, though the highly toxic 2,3,7,8-tetrachlorodibenzo[p]dioxin (2,3,7,8-TCDD) was reportedly found in one European sample (World Health Organization, 1987). Furans containing four to eight chlorines are commonly found in technical-grade PCP.

A typical composition of technical-grade PCP is presented in Table 1.4-2. The actual composition of any PCP depends on the source material and date of manufacture (Crosby, 1981). The physical and chemical properties of "pure" pentachlorophenol (in contrast to "technical" PCP which contains production impurities) are summarized in Table 1.4-3. These properties are repeated on Appendix A, along with those of some of the other constituents in PCP and creosote preserving mixtures.

Pure PCP is considered to be a relatively stable organic compound, which is moderately volatile, sparingly soluble in water and highly soluble in organic solvents (Environment Canada, 1988a; McGinnis et al., 1988). It is

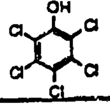
Table 1.4-2 Typical Composition of Technical Grade Pentachlorophenol (PCP) and Working Solution

Compound Family	Component	Typical % in Technical Grade PCP	Typical % in 5% Strength PCP Preserving Solution
Diesel Carrier	-	0	95
Chlorinated Phenols	Pentachlorophenol (PCP)	84.6 - 90.4	4.2 - 4.5
	Tetrachlorophenol	3.0 - 10.4	0.15 - 0.52
	Trichlorophenol	0.002 - 0.100	0.0001 - 0.005
	Chlorinated phenoxyphenols	6.2 - 7.0	0.31 - 0.35
Dibenzo[p]dioxins	Octachloro-	0.0015 - 0.33	0.000075 - 0.0165
	Heptachloro-	0.0007 - 0.087	0.000033 - 0.0044
	Hexachloro-	0.0001 - 0.0038	0.000005 - 0.000045
	Pentachloro-	nd - 0.000008	nd
	Tetrachloro-	nd - 0.000125	nd
Dibenzofurans	Octachloro-	nd - 0.0300	nd - 0.0013
	Heptachloro-	0.00028 - 0.0400	0.000009 - 0.002
	Hexachloro-	0.00034 - 0.0090	0.000017 - 0.00045
	Pentachloro-	nd - 0.0040	nd - 0.0002
	Tetrachloro-	nd - 0.0125	nd - 0.00063

<u>Notes:</u>

- Sources: Monenco, 1989; McGinnis et al., 1988; World Health Organization, 1987; Crosby, 1981; U.S. EPA, 1986b.
- nd = below detection limits (i.e. none detected).
- tetrachlorodibenzo[p]dioxin values are for the 1,2,3,4 isomer.
- properties of some of these compounds are presented in Appendix A.

Table 1.4-3 Properties of Pure Pentachlorophenol (PCP)

Property	Value	Significance
chemical formula	C_6Cl_5OH	
CAS Registry number	87-86-5	
chemical structure		
molecular weight (g/mol)	266.74	
specific gravity at 22°C	1.85 - 1.99	heavier than water
solubility in water (ppm)		slightly soluble in water
at 0°C	5	
at 20°C	14	
at 50°C	35	
melting point (°C)	188 - 191	solid at ambient temperatures
boiling point (°C)	293 - 310	
vapour pressure at 20°C (mm Hg)	0.00017 - 0.000015	PCP is moderately volatile
dimensionless Henry's Law constant	0.00015	
flashpoint	not flammable	
pKa at 25°C	4.70 - 4.80	PCP is a weak acid, of roughly the same strength as acetic acid
physical appearance at ambient temperatures	light brown solid	
log-octanol/water partition coefficient at pH = 1.2	4.84	
at pH = 6.5	3.56	
at pH = 7.2	3.32	
at pH = 13.5	3.86	

Notes:

- Sources: U.S. Department of Agriculture, 1980; McGinnis et al., 1988; Environment Canada, 1983; Environment Canada, 1988a; World Health Organization, 1987.

a solid at room temperature. An important property of PCP is its pH sensitivity. PCP is a weak acid whose conjugate base is the pentachlorophenate ion. A distribution diagram for the two species is presented in Figure 1.4-1. As pH increases, PCP ionizes to the pentachlorophenate ion form, which is much more soluble in water. For example at 20°C, PCP is soluble to only 14 ppm, whereas the pentachlorophenate ion is soluble to 330 000 ppm (33% by weight) (Environment Canada, 1983). At a pH of 2.7, PCP is only 1% ionized, but at a pH of 6.7, PCP is 99% ionized. Consequently, the pH of surface or groundwater is very influential on PCP solubility, and thus mobility.

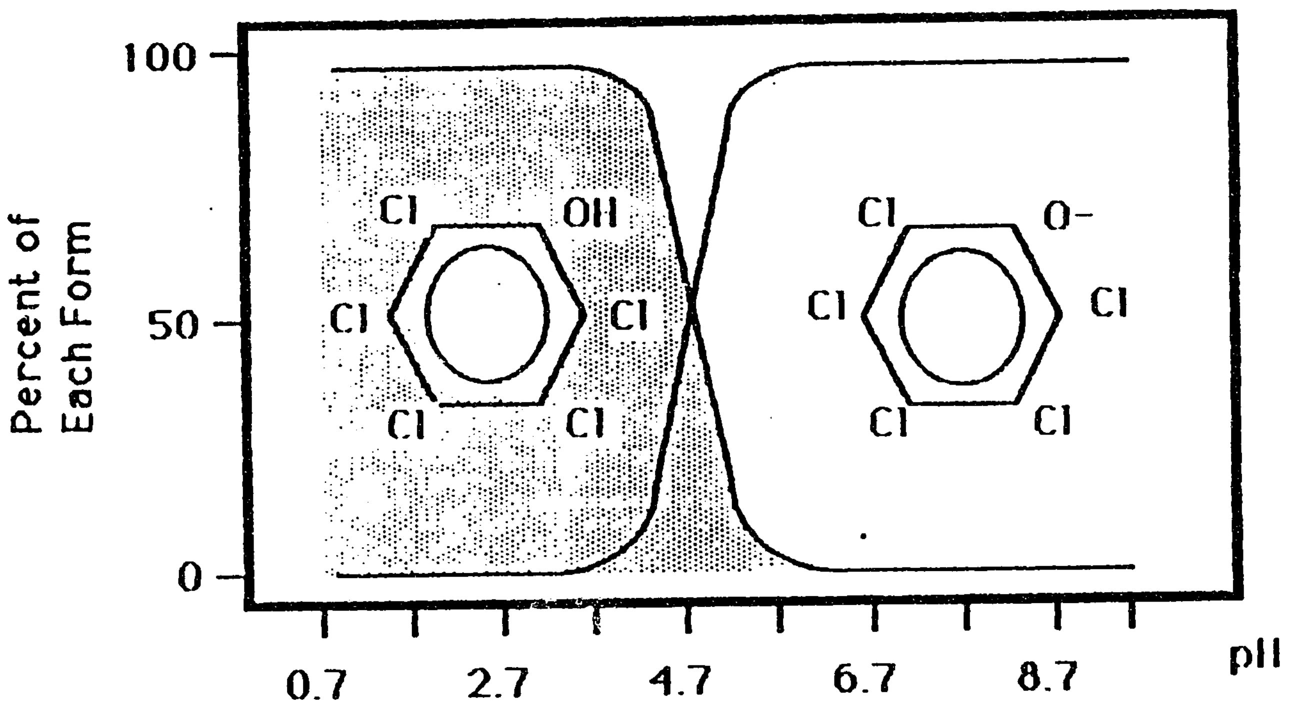
1.4.1.2 Biodegradability

Wood preservative chemicals are used because they are biocidal. Consequently, biological degradation of these compounds is difficult.

In PCP-based wood preservation, the aliphatic and aromatic hydrocarbons which comprise the diesel carrier are much more amenable to biological degradation than those associated with technical-grade pentachlorophenol. Consequently, this section will focus on the biodegradability of the remaining components: chlorinated phenols, dioxins and furans.

1.4.1.2.1 Chlorinated Phenols

Sequential dechlorination is the primary biodegradative mechanism of chlorophenols in the environment. Consequently, PCP is located at the front of the process, as it is the most highly chlorinated compound of the group. Phenols with less chlorine substitution exist as both degradation



- rising pH increases the amount of pentachlorophenol existing in the ionized (pentachlorophenate) form, which is much more soluble in water than the protonated compound.
- at a pH of 4.7, 50% of the total pentachlorophenol mass exists in each form.

FIGURE 1.4-1 : DISTRIBUTION DIAGRAM FOR THE PENTACHLOROPHENOL - PENTACHLOROPHENATE SYSTEM (PKA = 4.7) products of higher chlorophenols as well as impurities from technical-grade PCP. For example, 2,4-dichlorophenol may be present as a degradation product of a higher chlorophenol, or as a product contained in the original PCP formulation. This makes identification and quantification of degradation products difficult.

The biocidal activity of chlorophenols increases with the degree of chlorination (Environment Canada, 1983). Consequently, PCP is the most difficult chlorophenol to biologically degrade because it is the most highly chlorine substituted. This observation, in conjunction with the common degradative pathway shared by all chlorophenols following dechlorination, implies that a study of the biodegradation of PCP will reveal processes and pathways common in all chlorophenol degradation.

The biodegradability of PCP has been demonstrated. A sample of relevant literature is presented in Table 1.4-4. The remainder of the discussion in this section is based largely on this literature.

Though PCP is a biocide, there are many types of bacteria, fungi and yeasts that are capable of degrading it, including *Pseudomonas*, *Aspergillus*, *Trichoderma*, *Arthrobacter*, *Flavobacterium*, *Paecilomycetes*, *Penicillium*, *Scopulariopsis*, *Rhodotorula glutinis*, and *Phanerochaete chrysosporium*. All of the chlorophenols have been shown to be metabolized by pure or mixed cultures of these microorganisms either aerobically or anaerobically. The sequence of reactions occurring in PCP degradation is summarized in Figure 1.4-2. Some debate exists over whether PCP is more

TABLE 1.4-4 : Research on the Biodegradation of PCP

AUTHOR(S)	PAPER TITLE AND YEAR	COMMENTS
S.L. Woods, J.F. Ferguson, M.M. Benjamin	Characterization of Chlorophenol and Chloromethoxybenzene Biodegradation During Anaerobic Treatment (1989)	PCP was rapidly degraded under anaerobic conditions to 2,3,4,5-tetrachlorophenol and 3,4,5-trichlorophenol.
M.L. Rochkind, J.W. Blackburn	Microbial Decomposition of Chlorinated Aromatic Compounds (1986)	PCP was metabolized by a variety of microorganisms, including *Pseudomonas sp.* Dioxins and furans were not used as primary substrates, but were cometabolized.
M.D. Baker, C.I. Mayfield	Microbial and Non-Biological Decomposition of Chlorophenols and Phenol in Soil (1980)	Chlorophenols (including PCP) were found to undergo both biotic and abiotic degradation in soil.
G.J. Stanlake, R.K. Finn	Isolation and Characterization of PCP Degrading Bacterium (1982)	Isolated an *Arthrobacter sp.* capable of utilizing PCP as a primary substrate.
L.P. Moos, E.J. Kirsch, R.F. Wukasch, C.P.L. Grady	PCP Biodegradation - I (Aerobic) (1983)	PCP degradation was found to follow first order kinetics.
M.A. Guthrie, E.S. Kirsch, R.F. Wukasch, C.P.L. Grady	PCP Biodegradation - II (Anaerobic) (1984)	PCP degradation during anaerobic digestion occurred, but only after an acclimation period.
R.U. Edgehill, R.K. Finn	Isolation, Characterization and Growth Kinetics of Bacteria Metabolizing PCP (1982)	A soil bacterium capable of utilizing PCP as a sole source of carbon was isolated and characterized.
S. Kawatsuka, M. Igarashi	Degradation of PCP in Soils (1975)	PCP was found to be microbially degraded in soils.
M.D. Mikesell, S.A. Boyd	Enhancement of PCP degradation in Soil through Induced Anaerobiosis and Bioaugmentation with Anaerobic Sewage Sludge (1988)	The addition of anaerobic sewage sludge, which had previously been shown to dechlorinate chlorophenols, to PCP contaminated soil greatly increased the rate of PCP degradation.
V.H. Kitunen, R.J. Valo, M.S. Salkinoja-Salonen	Contamination of Soil around Wood-Preserving Facilities by PAHs (1987)	Chlorophenols were found to be metabolizable and mobile in soil while polychlorinated dibenzofurans were persistent and immobilized in the top layer of soil.
N.J. Hutzler, C.R. Baillod, P.A. Schaepe, R.M. Mauno, C.J. Perram	Biological Reclamation of Contaminated Soil at Wood Preserving Sites (1989b)	PCP degradation was shown in both laboratory and pilot-scale land treatment demonstrations.
R.C. Sims, J.L. Sims, D.L. Sorenson, W.J. Doucette, L.L. Hastings	Waste/Soil Treatability Studies for Four Complex Industrial Wastes: Methodologies and Results (1986)	Both PCP and creosote wood preserving wastes were shown to be biologically degradable.
G. McGinnis, H. Borazjani, L. McFarland, D. Pope, D. Strobel	Characterization and Laboratory Soil Treatability Studies for Creosote and Pentachlorophenol Sludges and Contaminated Soil (1988)	Degradation of PCP and PAHs was observed in both amended and unamended soils.

TABLE 1.4-4 : continued

AUTHOR(S)	PAPER TITLE AND YEAR	COMMENTS
R.L. Crawford, W.W. Mohn	Microbiological Removal of Pentachlorophenol from Soil using a *Flavobacterium* (1985)	A *Flavobacterium* was shown to degrade PCP from soil.
B.J. Brown, J.J. Pignatello, M.M. Martinson, R.L. Crawford	PCP Degradation: A Pure Bacterial Culture and an Epilithic Microbial Consortium (1986)	A *Flavobacterium* strain utilizing PCP as a primary substrate was examined.
R.U. Edgehill, R.K. Finn	Microbial Treatment of Soil to Remove PCP (1983)	Direct Innoculation of PCP-utilizing *Arthrobacter* into contaminated soil rapidly increased rate of PCP degradation.
J.D. Bogart, J.R. League	Biological Remediation of Underground Storage Facilities (1988)	Enhanced landfarming (using a proprietary technology) showed significant degradation of creosote and PCP
J.R. Ryan, J. Smith	Land Treatment of Wood Preserving Wastes (1986)	Field and pilot-scale studies at four wood preserving plants showed that land treatment of PCP and creosote wastes was feasible.
J.A. Glaser	Promising Technologies For the Biological Detoxification of Hazardous Waste (1988)	Use of the White Rotting Fungus *P. chrysosporium* to degrade PCP and creosote in contaminated soils and process waters.
W.L. Ramsay, R.R. Steimle, J.T. Chaconas	Renovation of a Wood Treating Facility (1981)	Sewage sludge was mixed with creosote and PCP contaminated soils, resulting in accelerated biological degradation.

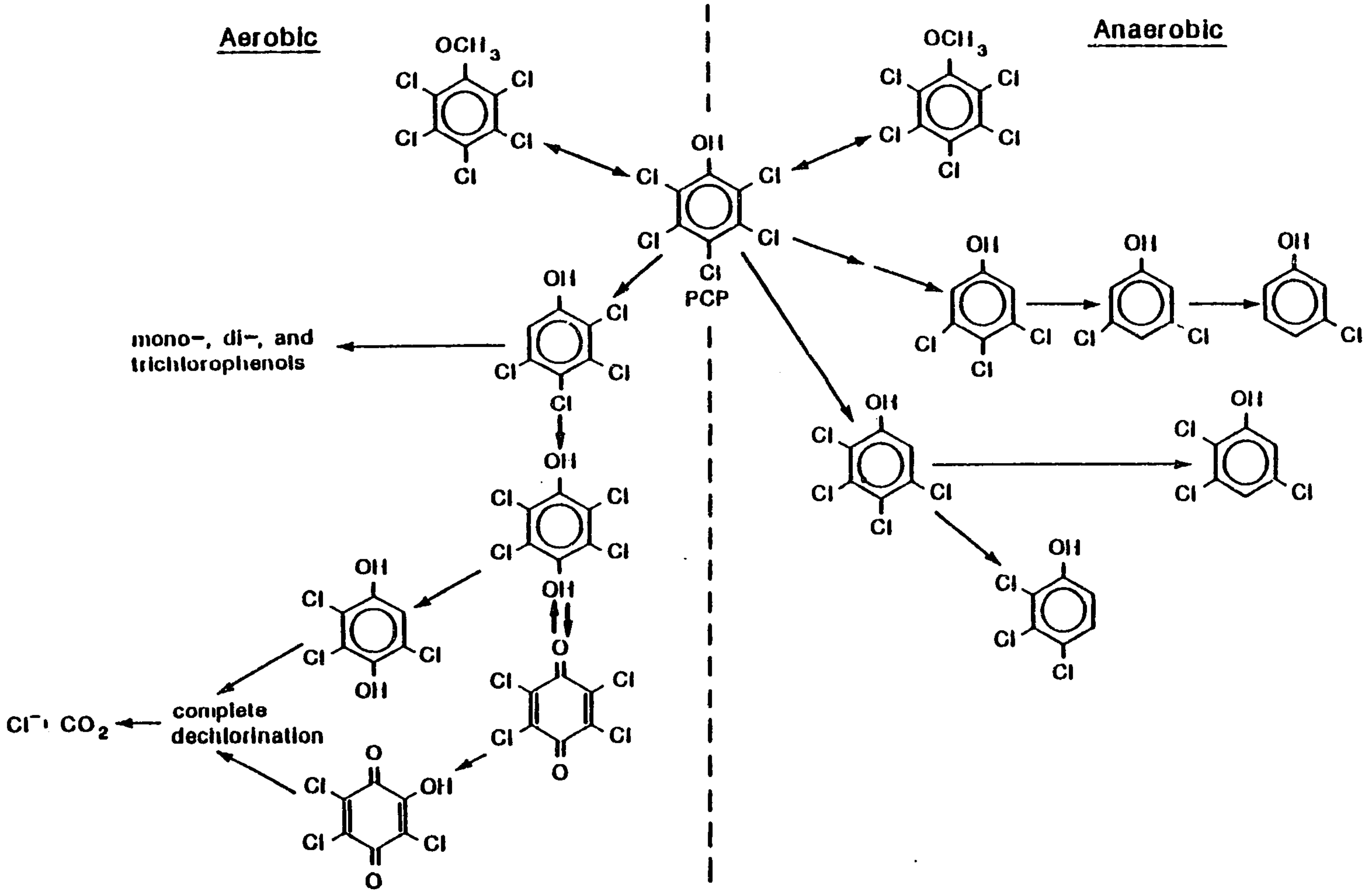


FIGURE 1.4-2 : TYPICAL DEGRADATION PATHWAYS OF PENTACHLOROPHENOL (PCP) IN AEROBIC AND ANAEROBIC ENVIRONMENTS (ADAPTED IN PART FROM BOYD ET AL., 1989)

rapidly degraded under aerobic or anaerobic conditions. Part of the problem arises from which reaction in the sequential degradation of PCP is being considered; the successive dechlorination reactions are believed to be more rapid under anaerobic conditions, though the final conversion to mineralized end products is favored under aerobic conditions. In both aerobic and anaerobic processes, PCP can be converted to pentachloroanisole. However, this reaction is reversible and does not proceed further towards mineralization. The main route for PCP degradation involves successive dehalogenation to simpler chlorophenols. The second step in the aerobic process involves an oxidation step to form substituted hydroquinones or catechols. This oxidation product then undergoes ring cleavage, ultimately forming carbon dioxide and inorganic chlorine. These oxidative reactions are illustrated using tetrachlorophenol in Figure 1.4-2. The products of chlorophenol degradation are generally less toxic and more water soluble than the parent compound. One exception is 2,4,6-trichlorophenol, which is believed to be a degradation product of PCP, and is a carcinogen (Crosby, 1981).

While the number of species of microbes that utilize chlorophenols as a primary carbon source is small, many chlorophenols are co-metabolized by a variety of other species. Co-metabolism is the transformation of a non-growth substrate in the presence of a growth substrate. Co-metabolism is especially important for higher chlorophenols, which are more resistant to biological decay.

1.4.1.2.2 Dioxins and Furans

Only dioxins and furans with four or more chlorine atoms have been detected in technical-grade PCP (Table 1.4-2). Consequently, only these compounds will be studied. It should be noted that the tetrachlorodibenzo[p]dioxin (TCDD) consistently found in technical PCP formulations is the 1,2,3,4 isomer; the highly toxic 2,3,7,8-TCDD has only been conclusively found once, and is not considered to be normally present (World Health Organization, 1987).

The polychlorinated dibenzo[p]dioxins and furans (PCDDs and PCDFs) present in technical-grade PCP have not been shown to undergo biodegradation in the natural environment or in optimized treatment systems (Rochkind et al., 1986; U.S.EPA, 1984b; U.S.EPA, 1986a). Studies on the biodegradation of PCDDs and PCDFs are complicated by a number of factors:

- the compounds are highly hydrophobic and consequently adsorb strongly to suspended particulates and glassware.
- the concentrations of concern begin at the part per trillion level.
- artifacts may arise from the complicated extraction and analytical procedures involved (Rochkind, 1986). For example, technical-grade PCP contains chlorinated phenoxyphenols (Table 1.4-2), which are important dioxin precursors or "pre-dioxins". These compounds may react to form dioxins during photolytic decomposition or during gas chromatography (Baker and Matheson, 1981; World Health Organization, 1987; Nilsson, 1974).

These complications often result in poor analytical recoveries and erroneous conclusions concerning biodegradation. The use of radiolabelled compounds in dioxin and furan analysis has greatly improved analytical accuracy.

2,3,7,8-TCDD has been studied in much greater depth than other dioxins or furans because of its extreme toxicity. Research has shown that only five of the approximately 100 microbial strains tested had any ability to metabolize the compound (U.S.EPA, 1984b). The most successful organism found to date is a wood-degrading fungus, *Phanerochaete chrysosporium*, which degraded approximately 25% of 14 pmol of 2,3,7,8-TCDD (Bumpus, 1985).

As mentioned previously, 2,3,7,8-TCDD is not found in technical-grade PCP. However, its recalcitrance to biological degradation provides an indication of the biodegradability potential of the less-researched PCDDs and PCDFs present in technical PCP, which are expected to be even more resistant to biodegradation due to greater chlorine substitution (U.S.EPA, 1984b; Klecka and Gibson, 1980).

1.4.1.3 Toxicological Properties

PCP-based wood preserving fluids contain technical-grade pentachlorophenol (and associated production impurities), as well as a diesel carrier (Table 1.4-2).

1.4.1.3.1 Diesel Fuel Carrier

Diesel fuel is a complex mixture of aliphatic and aromatic hydrocarbons, and a complete evaluation of its toxicological properties is beyond the scope of this study. Consequently, only a qualitative evaluation of diesel fuel toxicity will be made, by considering its effect on aquatic biota.

Bioassay results from tests using No. 2 fuel oil (diesel fuel) vary widely, depending on both the physical form and animal species used. For example, Vandermeulen (1987) reported no mortality of flagfish, fathead minnow or snail when exposed to the water-soluble fraction (WSF) of No. 2 fuel oil in a 96-hour acute toxicity test. Ninety-six hour LC_{50} (96 h LC_{50}) values for frog larvae and *Daphnia* exposed to the WSF were in the part-per-thousand (ppt) range. In contrast, 48 h LC_{50} values for larval rainbow trout exposed to the WSF of diesel oil were shown to be about 2.5 ppm (parts-per-million) by Lockhart and coworkers (1987). Consequently, there is a thousand-fold difference in acute toxicity values for aquatic biota exposed to the WSF of diesel fuel. In addition, toxicity variations exist for different aqueous forms of the diesel oil. For example, Vandermeulen (1987) reported 96 h LC_{50} values in the ppt range for biota exposed to the WSF of fuel oil. Ninety-six hour LC_{50} values were also in the ppt range for the same species exposed to a floating layer of No. 2 fuel oil, but decreased to ppm levels when exposed to a diesel oil emulsion. Consequently, chemical form also affects the aquatic toxicity of diesel.

Chlorinated phenols typically display LC_{50} values in the ppm or ppb (parts-per-billion) range, suggesting they are more toxic than diesel fuel for most aquatic species. This comparison, in conjunction with a qualitative assessment of the toxicity of diesel fuel constituents, provides reasonable justification for assuming the compounds present in technical-grade PCP present a greater toxicological danger than those associated with the diesel carrier.

1.4.1.3.2 Technical Grade PCP

Assessing the toxicity of technical-grade PCP is complicated by a number of factors:

- toxicological data exist for technical-grade PCP, but conclusions on uptake, metabolism and excretion cannot be made for such a heterogeneous mixture of chemicals. Uptake, metabolism and excretion data do exist for the individual components in technical-grade PCP, but this data does not reflect any chemical synergism or antagonism present in the mixture.
- technical PCP as a whole has both acute and chronic toxicological effects, as do the individual components.
- technical PCP as a whole elicits different responses from different species, as do the individual components.

A complete examination of the toxicity of PCP-based preserving fluids must incorporate all of these aspects. Such an examination is beyond the scope of this study, and some generalizations must be made, namely:

- median lethal concentration (LC_{50}) values will be taken from studies which used technical-grade PCP.
- discussion on uptake, metabolism and excretion will involve "typical" compounds.

- only data from fish and mammals will be used.
- both acute and chronic effects will be considered.

Uptake, Metabolism, Excretion

The uptake, metabolism and excretion of pentachlorophenol is typical of that experienced by all chlorophenols. The uptake of PCP by animals (including humans) is pH-dependent; penetration of cell membranes increases as pH decreases, as un-ionized PCP is preferentially transmitted over ionized forms, which possess low lipid solubility (Klaassen, 1986b; Sims et al., 1986). The ionization of PCP was discussed in section 1.4.1.1. It is generally held that chlorophenols are readily adsorbed through the skin, as well as through the gastrointestinal tract and respiratory system (World Health Organization, 1987; Agriculture Canada, 1987; U.S.EPA, 1986b; Murphy, 1986).

Once in an animal, PCP is metabolized, either to tetrachlorohydroquinone through oxidation or it is conjugated to PCP-glucuronide (World Health Organization, 1987). PCP is rapidly eliminated in both free and conjugated forms by mammals through urinary excretion (World Health Organization, 1987; Environment Canada, 1983; Crosby, 1981). Therefore, significant bioaccumulation of PCP in plants, fishes and mammals is not likely to occur (U.S. Department of Agriculture, 1980; Environment Canada, 1988a; Geyer et al., 1987).

The second group of chemicals present in technical-grade PCP is comprised of polychlorinated dibenzo[p]dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Less is understood about the uptake, metabolism and excretion of these compounds. In general, PCDDs and PCDFs are lipid soluble (high k_{ow} values), and are therefore easily absorbed by passive diffusion across cell membranes (U.S.EPA, 1986a; U.S.EPA, 1984b). After absorption, PCDDs and PCDFs preferentially partition to tissues with a high lipid content (for example, fat, skin, adrenals). Some metabolic transformation may also occur for these compounds (Williams and Weisburger, 1986; U.S.EPA, 1986a; U.S.EPA, 1984b). The lipophilic nature of PCDDs and PCDFs, in conjunction with negligible metabolic transformation, result in extremely high retention of these compounds by mammals. Highly chlorinated isomers of these compounds have been found to persist in the liver and adipose tissue for many years (U.S.EPA, 1986a; U.S.EPA, 1984b). Consequently, PCDDs and PCDFs have extremely large bioaccumulation factors, consistent with their large k_{ow} values (Appendix A).

Acute and Chronic Toxicity

All chemicals can induce toxic effects in sufficient dose. Simply put: the dose makes the poison. Consequently, general classifications of toxicity cannot be made without dose-response information.

Chemical effects are generally separated into two classes: acute and chronic. Acute lethality tests measure responses over a short-term period, usually 1 to 14 days. Chronic studies measure responses for a longer duration, usually from six months to two years. Bioassays for chemical carcinogenicity involve chronic studies because of the time required for neoplastic development.

The acute lethality effects of technical-grade PCP arise from the chlorophenols present, whereas chronic exposure effects are mediated via the dioxin and furan contaminants (National Research Council of Canada [NRCC], 1982; Environment Canada, 1983; World Health Organization, 1987). An exception to this generalization is chloracne, an acute skin condition (acne) linked to dioxin contaminants in technical PCP (World Health Organization, 1987; Crosby, 1981; Environment Canada, 1988a; Murphy, 1986). If sufficient concentrations of dioxins and/or furans were present in technical-grade PCP, they would also be capable of causing acute lethality. The toxic effects initiated by all chlorophenols in animals appear to result from a common mechanism; uncoupling of oxidative phosphorylation in the mitochondria (NRCC, 1982; Murphy, 1986). This uncoupling causes an interference in the metabolic process of energy production, leading to energy starvation (Environment Canada, 1983). Acute toxic effects of chlorophenols tend to increase with increasing chlorine substitution, making PCP the most lethal (NRCC, 1982; World Health Organization, 1987; Environment Canada, 1983). Acute chlorophenol poisoning in animals is symptomized by increased blood pressure, elevated respiratory rate, elevated body temperature, rapidly developing weakness, and convulsions. In addition to systemic effects, chlorophenols can also initiate localized effects such as swelling, chloracne and hair loss from topical applications (Environment Canada, 1983; World Health Organization, 1987). Oral median lethal dose (LD_{50}) values for acute toxicity tests of PCP range between 27 and 205 mg/kg-body weight for a variety of species, regardless of the vehicle of administration and the purity of PCP (World Health Organization, 1987). In mammals, over a spectrum of species ranging from mouse to bovine calf, the LD_{50} values are all close to 150 mg/kg-body weight (NRCC, 1982). The LD_{50} values for technical PCP imply that the mixture is very toxic, using the guideline values of Klaassen (1986a) (Figure 1.4-3).

As mentioned previously, chronic effects from exposure to chlorophenol formulations are believed to arise in part from dioxin and furan impurities. This belief is held partially because chlorophenols do not significantly accumulate in animal tissues (Environment Canada, 1983). Consequently, chronic effects must arise either from compounds other than chlorophenols, or result from relatively high levels of continuous exposure to chlorophenols. Most chlorophenols initiate similar effects in acute toxicity tests, though a noticeable difference in chronic effects exists between the different compounds. PCP will be discussed here because it is the major chlorophenol in technical-grade PCP. In studies with rats, PCP has been shown to be both embryotoxic and fetotoxic, though not teratogenic (World Health Organization, 1987; U.S.EPA, 1986b; Agriculture Canada, 1987). Embryotoxicity and fetotoxicity refer to death in the embryonic and fetal stages of offspring development, respectively, while teratogenicity refers to physical defects induced during offspring development between conception and birth. Bioassay results have shown that purified PCP does not cause point mutations, which is consistent with rat studies indicating

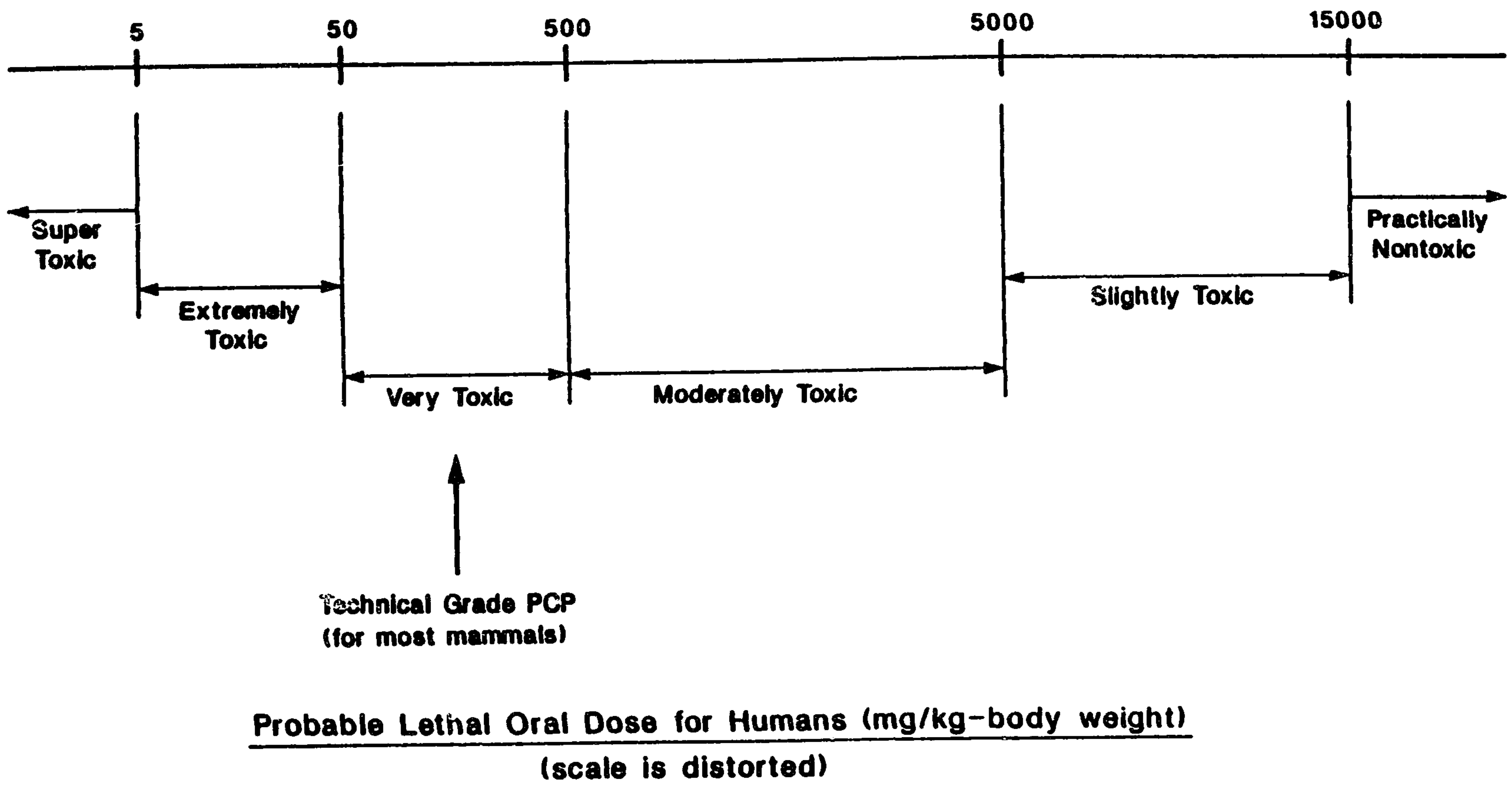


FIGURE 1.4-3 : TOXICITY RATING SCALE (DEVELOPED FROM DATA PRESENTED IN KLAASSEN, 1986A)

PCP is neither an initiator nor a promoter carcinogen (World Health Organization, 1987; U.S.EPA, 1986b; World Health Organization, 1982).

Polychlorinated dibenzo[p]dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) with four to eight chlorines exist in technical-grade PCP. The most potent carcinogen listed by the U.S.EPA (1988c), 2,3,7,8-TCDD, has not been identified in any North American PCP formulations. Acute and chronic effects have been shown to vary widely for PCDDs and PCDFs, even among isomers. For example, 2,3,7,8-TCDD produces chloracne, is teratogenic and embryotoxic, whereas the 1,2,3,4 isomer displays none of these effects (Baker and Matheson, 1981). Compound symmetry, chlorination of two adjacent carbon atoms, and the availability of unsubstituted positions all enhance PCDD and PCDF lethality (World Health Organization, 1987; Baker and Matheson, 1981). The acute and chronic effects of the most prevalent PCDDs and PCDFs in technical PCP are presented with those of chlorophenols in Table 1.4-5

TABLE 1.4-5: Toxicological Properties of Chemicals Present in Technical Grade PCP

Compound Family	Component	Acute Toxicity to Animals (LD_{50}) (mg/kg-body weight)	Chronic Behavior		Bioconcentration Factor in Fish
			Effects	q1* (kg-d/mg)	
Chlorinated Phenols	Pentachlorophenol (PCP)	27 - 205	embryotoxic, fetotoxic (group E)	-	890 - 4000
	2,3,4,6-tetrachlorophenol	-	embryotoxic, fetotoxic (group D)	-	160 - 1000
	2,4,5-trichlorophenol	-	inadequate evidence of carcinogenicity in humans and animals (group D)	-	80 - 1900
	2,4,6-trichlorophenol	-	inadequate evidence of carcinogenicity in humans but sufficient evidence in animals (group B_2)	1.99 x 10^{-2}	20 - 200
Dibenzo[p]dioxins (PCDDs)	octachloro-	1000 - 4000	embryotoxic but not teratogenic or acnegenic. Its carcinogenicity has not been assessed (Group D)	-	4 000 000
	heptachloro-	0.6	effects have not been assessed (group D)	-	1 000 000
	hexachloro-	0.06 - 1.8	teratogenic, embryotoxic and acnegenic. Sufficient evidence of carcinogenicity in animals but inadequate data in humans (group B_2)	6.2 x 10^3	30 000
Dibenzofurans (PCDFs)	hexachloro-	0.001 - 0.100	chronic exposure effects have not been studied (group D)	-	2 000 000
	pentachloro-	0.001 - 0.100	(group D)	-	500 000
	tetrachloro-	0.005 - 0.010	(group D)	-	100 000

Notes:

- Sources: Battelle (1989), U.S. EPA (1987c), U.S. EPA (1988c), U.S. EPA (1986a), Agriculture Canada (1987), World Health Organization (1987), World Health Organization (1982), U.S. EPA (1986b), U.S. EPA (1984b), U.S. Department of Agriculture (1980), Baker and Matheson (1981).
- Bioconcentration factor = concentration of chemical at equilibrium in whole organism divided by concentration of chemical in enveloping media (water for fish)
- For carcinogenic effects, the U.S. EPA's categorization scheme for ranking carcinogens has been adopted:
  - group A - Human carcinogen (sufficient evidence)
  - group B - Probable human carcinogen group B1 - limited evidence in humans group B2 - combination of sufficient evidence in animals and inadequate data in humans
  - group C - Possible human carcinogen (limited evidence in animals)
  - group D - not classified (inadequate animals evidence)
  - group E - no evidence of carcinogenicity for humans (no evidence in at least two species of animal or in both epidemiological and animals studies).
- q_1* = slope of the line drawn from the origin to the upper 95% confidence interval at the lowest dose of a dose-response plot. This slope is a measure of carcinogenic potency. A q1* value is not generated for non-carcinogenic chemicals.

1.4.2 Creosote-Based Wood Preserving Mixtures

1.4.2.1 Physical and Chemical Properties

Creosote is used either full-strength or as a 50:50 creosote/petroleum oil mixture in wood preservation. Creosote is produced in the destructive distillation of coal tar, and is comprised of the 200°C to 400°C fractions. Over 300 compounds have been identified in creosote, though it is generally agreed that several thousand compounds are present (U.S. Department of Agriculture, 1980; Domtar Chemicals Inc., 1986). Coal tar creosote contains approximately 85% polynuclear aromatic hydrocarbons (PAHs), 10% phenolic compounds, and 5% nitrogen- sulfur- and oxygen-containing heterocycles (Mueller et al., 1989). The range in composition of creosote is presented in Table 1.4-6. The exact composition and properties of creosote depend upon the characteristics of the coal from which the tar originated, as well as the distillation process used (Richardson, 1978).

Creosote is an oily, dark brown to black liquid, with a sharp smokey or tarry odour. The data in Table 1.4-6 demonstrate that chemical composition of creosote is quite variable, which makes chemical classification difficult. Consequently, creosote is normally described in terms of its physical properties. Table 1.4-7 summarizes properties that have been compiled from various sources. The physico-chemical properties of some creosote constituents are presented in Appendix A. Physical properties of creosote that have environmental significance are its specific gravity and solubility. Creosote is only slightly soluble in water and heavier than water, which

Table 1.4-6 Typical Creosote Composition

Compound Family	Component	Typical % in Creosote
Polynuclear Aromatic Hydrocarbons (PAHs)	Naphthalene	1.3 - 17.5
	1-methylnaphthalene	0.9 - 3.5
	2-methylnaphthalene	1.2 - 6.5
	Dimethylnaphthalenes	2.0 - 2.3
	Biphenyl	0.8 - 1.9
	Acenaphthene	5.6 - 14.7
	Acenaphthylene	0.5 - 2.0
	Carbazole	1.2 - 5.1
	Fluorene	5.1 - 10.0
	Phenanthrene	10.2 - 21.0
	Anthracene	2.0 - 2.52
	Methylfluorenes	2.3 - 3.0
	Fluoranthene	7.6 - 11.8
	Pyrene	4.4 - 8.5
	Chrysene	1.0 - 3.0
	Benzofluorenes	1.0 - 2.0
	Methylanthracenes	4
	Methylphenanthrenes	3
	Benzo[a]pyrene	-
	Benzo[a]anthracene	1.1
	Benzo[e]pyrene	-
	Benzo[b]fluoranthene	0.6
	Benzo[j]fluoranthene	-
	Benzo[k]fluoranthene	0.4
	Perylene	-
	Benzo[b]chrysene	-
	Benzo[g,h,i]perylene	0.1
	Dibenzo[a,h]anthracene	0.2
	Indeno[1,2,3-c,d]pyrene	0.1
Phenolics	Phenol	-
	o,m,p-cresol	-
	Pentachlorophenol (PCP)	-
	Xylenol	-
	Trimethylphenol	-

.....continued

Table 1.4-6 Typical Creosote Composition (continued)

Compound Family	Component	Typical % in Creosote
Nitrogen-Containing Heterocycles	Quinoline	-
	Isoquinoline	-
	Dimethylpyridine	-
	Acridine	-
	Aniline	-
	Methylquinoline	-
	Pyrrole	-
	Pyrrolidine	-
Sulfur-Containing Heterocycles	Benzo[b]thiophene	-
	Dibenzothiophene	-
Oxygen-Containing Heterocycles	Dibenzofuran	5.0 - 7.5

Notes:

- **Sources. U.S. Department of Agriculture, 1980; McGinnis, 1984; U.S.EPA, 1988b; Sims et al., 1986; Environment Canada, 1988b; Mueller et al., 1989.**
- **Those compounds whose % in creosote is listed as a dash ("-") have been conclusively identified in creosote, but their exact amounts are unavailable.**

Table 1.4-7 Properties of Creosote

Property	Value	Significance
CAS Registry Number	8001-58-9	Material derived from coal tar distillation
CAS Registry Number	8021-39-4	Material derived from coking of wood (not in common use)
Solubility	Varies, depending on constituent considered.	
Specific gravity at 15°C	1.05 to 1.10	Sinks in surface water, groundwater and seawater.
Melting point (°C)	- 60 to -20	Liquid at ambient temperatures.
Boiling point (°C)	200 to 450	
Flashpoint (°C)	>74	Combustible liquid

<u>Notes:</u>

- Sources: Environment Canada, 1988b; U.S. Department of Agriculture, 1980; U.S.EPA, 1987b.

implies that a distinct creosote phase will migrate to the bottom of an aquifer.

1.4.2.2 Biodegradability

Creosote is used in wood preservation to "poison" the wood for microorganisms which consume cellulose and lignin as substrate. Consequently, biological degradation of the compounds in creosote is difficult.

Creosote is comprised of polynuclear aromatic hydrocarbons (PAHs), phenolics, and nitrogen-, sulfur-, and oxygen-containing heterocyclics (Table 1.4-6). The microbial decomposition of some of the phenolic compounds (chlorophenols) and oxygen-containing heterocycles (dibenzofurans) was evaluated in section 1.4.1.2. Consequently, only degradation of PAHs as well as nitrogen and sulfur heterocycles requires examination in this section.

1.4.2.2.1 Nitrogen- and Sulfur-Containing Heterocycles

The nitrogen-containing heterocycles identified in creosote can be organized into three different chemical classes:

- pyridine derivatives (quinoline, isoquinoline, methylquinoline, and dimethylpyridine);
- indole derivatives (pyrrole, pyrrolidine, and carbazole); and
- aromatic amides (acridine and aniline).

Selected compounds in these classes have been shown to be microbially degraded, as summarized by Fedorak and Westlake (1984b), and Verschueren (1983):

- quinoline served as the sole carbon source for a bacteria isolated by Grant and Al-Najjar (1976);
- carbazole was used as the sole substrate by four bacterial strains in studies reported by Finnerty and coworkers (1983); and
- aniline was microbially degraded in soil (Verschueren, 1983).

Fedorak and Westlake (1984b) examined the microbial degradation of alkyl carbazoles in crude oil. They found that a mixed bacterial culture enriched on carbazole could degrade several of the alkyl carbazoles present. Compound susceptibility to degradation was observed to decrease with increasing alkylation. Degradation was observed to cease after eight days, at which point the carbazole-enriched culture was still able to degrade aromatic hydrocarbons and sulfur heterocycles. These results suggest that nitrogen-containing heterocycles (particularly alkylated carbazoles) may be more recalcitrant to biological degradation than some of the PAHs and sulfur heterocycles present in creosote.

Both of the sulfur-containing heterocycles identified in creosote have been shown to undergo microbial decomposition. Fedorak and Westlake (1984a) incubated soil with crude oil in shaker flasks. Alkyl benzothiophenes and dibenzothiophene were both found to be microbially degraded in these microcosms, even without nutrient supplementation. The alkylated benzothiophenes were observed to be more susceptible to microbial attack than dibenzothiophene.

1.4.2.2.2 PAHs

The number of PAHs in creosote has prevented clear understanding of the degradative processes involved. Those studies that have attempted to describe the biodegradability of mixtures of PAHs are complicated by the number of compounds and degradation products present, and the results have generally been ambiguous and inconclusive (Mueller et al., 1989). On the other hand, biodegradation of single PAHs by pure cultures is well documented. However, these studies likely do not accurately reflect PAH degradation occurring at wood preserving sites, where many carbon sources exist for consumption by mixed cultures of microorganisms. It is also quite likely that the biocidal activity of creosote arises from the interactions of a number of PAHs. This behaviour is not apparent in single-compound studies, further reducing their applicability to PAH mixtures.

The biodegradability of PAHs as single compounds or mixtures has been demonstrated. A sample of relevant literature is presented in Table 1.4-8. The remainder of the discussion in this section is based largely on this literature.

A variety of bacteria and fungi capable of degrading PAHs have been isolated, including *Aeromonas*, *Alcaligenes*, *Beijerinkia*, *Cunninghamella elegans*, *Cyanobacter*, *Flavobacterium*, *Micrococcus*, *Mycobacterium*, *Nocardia*, *Pseudomonas*, *Vibrio*, and *Phanerochaete chrysosporium* (Mueller et al., 1989; Cerniglia et al., 1980). In addition to pure-culture

TABLE 1.4-8 : Research on the Biodegradation of PAHs

AUTHOR(S)	PAPER TITLE AND YEAR	COMMENTS
S.E. Herbes, L.R. Schwall	Microbial Transformation of PAHs in Pristine and Petroleum-Contaminated Sediments. (1978)	Smaller PAHs were degraded faster than larger PAHs. Degradation was faster in acclimated sediments.
C.E. Cerniglia, R.H. Dodge, D.T. Gibson	Studies on the Fungal Oxidation of PAHs (1980)	Benzo [a] pyrene and Benzo [a] anthracene were degraded by the fungi *C. elegans.*
M.A. Heitkamp, C.E. Cerniglia	Effects of Chemical Structure and Exposure on the Microbial Degradation of PAHs in Freshwater and Estuarine Ecosystems (1987)	Microbial degradation of PAHs was observed in two aqueous environments.
M.A. Heitkamp, C.E. Cerniglia	Mineralization of PAHs by a Bacterium Isolated from Sediment below an Oil Field (1988)	A pure culture bacteria was isolated which degraded a number of PAHs.
J.T. Wilson, J.F. McNabb, J.W. Cochran, T.H. Wang, M.B. Tomson, P.B. Bedient	Influence of Microbial Adaptation on the Fate of Organic Pollutants in the Groundwater (1985)	Creosote wood preserving wastes were degraded rapidly in contaminated soil. Diffusion of oxygen through the soil was determined to be the limiting factor in PAH degradation.
J.R.Mihelcic, R.G. Luthy	Degradation of PAH Compounds Under Various Redox Conditions in Soil-Water Systems (1988)	Degradation of PAHs under aerobic, anaerobic, and denitrification conditions was studied.
R.C. Sims, J.L. Sims, D.L. Sorenson, W.J. Doucette, L.L. Hastings	Waste/Soil Treatability Studies for Four Complex Industrial Wastes: Methodologies and Results (1986)	Both PCP and creosote wood preserving wastes were shown to be biologically degradable.
G. McGinnis, H. Borazjani, L. McFarland, D. Pope, D. Strobel	Characterization and Laboratory Soil Treatability Studies for Creosote and Pentachlorophenol Sludges and Contaminated Soil (1988)	Degradation of PCP and PAHs was observed in both amended and unamended soils.
I. Bossert, W.M. Kachel, R. Bartha	Fate of Hydrocarbons During Oily Sludge Disposal in Soil (1984)	A laboratory simulation of landfarming confirmed that PAHs are removed from sludge by the microbially mediated processes of mineralization and humification.
J.D. Bogart, J.R. League	Biological Remediation of Underground Storage Facilities (1988)	Enhanced landfarming (using a proprietary technology) showed significant degradation of creosote and PCP
J.R. Ryan, J. Smith	Land Treatment of Wood Preserving Wastes (1986)	Field and pilot-scale studies at four wood preserving plants showed that land treatment of PCP and creosote wastes was feasible.
J.A. Glaser	Promising Technologies For the Biological Detoxification of Hazardous Waste (1988)	Use of the White Rotting Fungus *P. chrysosporium* to degrade PCP and creosote in contaminated soils and process waters.
W.L. Ramsay, R.R. Steimle, J.T. Chaconas	Renovation of a Wood Treating Facility (1981)	Sewage sludge was mixed with creosote and PCP contaminated soils, resulting in accelerated biological degradation.
T.L. Bulman, S. Lesage, P. Fowlie, M.D. Webber	The Fate of Polynuclear Aromatic Hydrocarbons in Soil (1987)	A mixture or eight PAHs was shown to biodegrade in an unacclimated soil.

studies, biodegradation of PAHs by mixed microbial cultures has been demonstrated (for example: Hutzler et al., 1989b; McGinnis et al., 1988).

The general mechanism of PAH degradation involves the initial hydroxylation of one of the terminal aromatic rings (Figure 1.4-4). This hydroxylation is illustrated for anthracene in Figure 1.4-5. The hydroxylation of PAHs requires molecular oxygen, signifying that biodegradation of PAHs is typically an aerobic process. However, selected PAHs have been shown to be degraded under anaerobic conditions, though at slower rates than aerobic processes, and using other pathways than hydroxylation (for example: Mihelcic and Luthy, 1988).

The following generalizations have arisen from research into PAH degradation:

- degradation rates decrease as the molecular weight increases, possibly because of decreasing water solubility and corresponding limitations on accessibility (McGinnis, 1984; Herbes et al., 1980; Sims and Overcash, 1983).
- degradation rates are larger in unsaturated soil than in saturated soil or water, likely because PAH degradation is an aerobic process, and oxygen is only slightly soluble in water (Herbes et al., 1980).
- degradation is faster where an acclimated microbial population exists (McGinnis, 1984; Heitkamp and Cerniglia, 1987; McGinnis et al, 1988; Sims and Overcash, 1983).

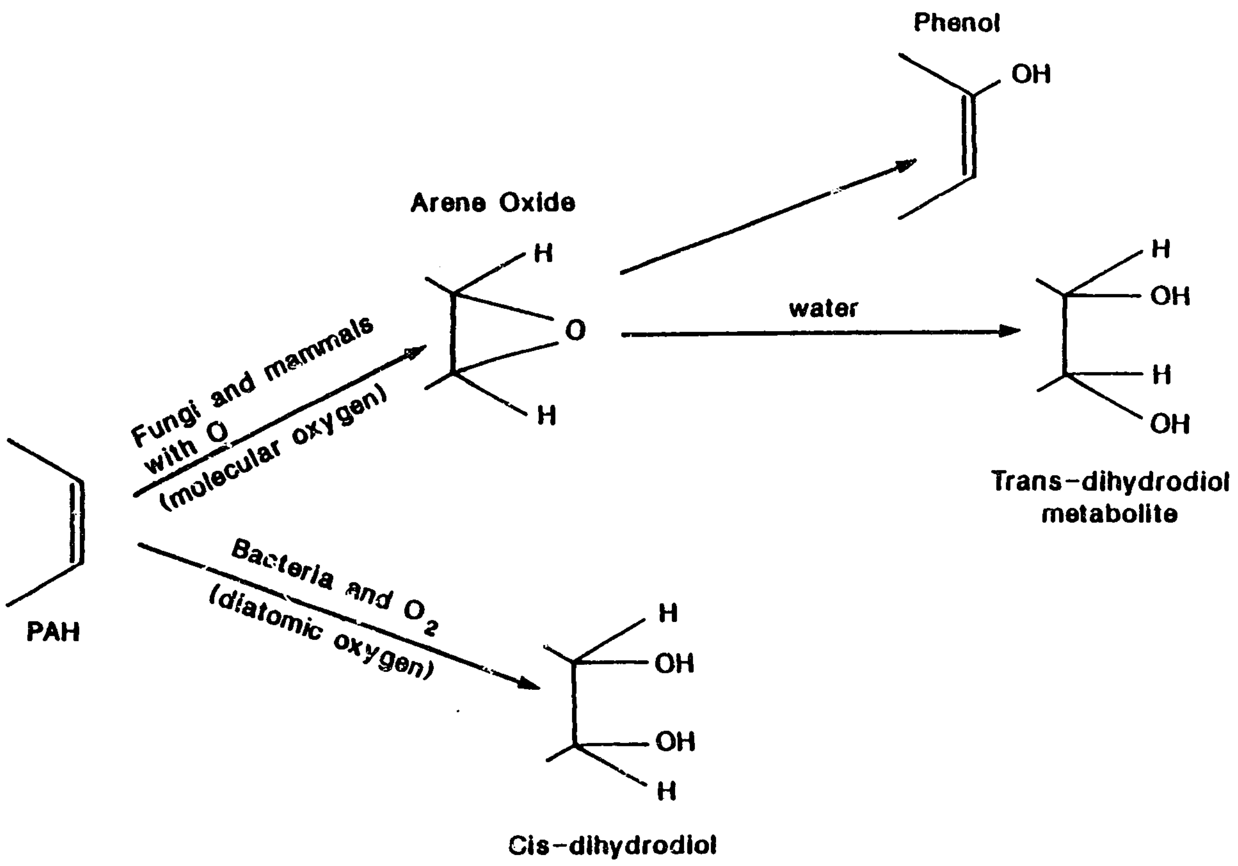


FIGURE 1.4-4 : INITIAL REACTIONS USED BY BACTERIA, FUNGI AND MAMMALS TO OXIDIZE PAHS (ADAPTED FROM CERNIGLIA ET AL., 1980)

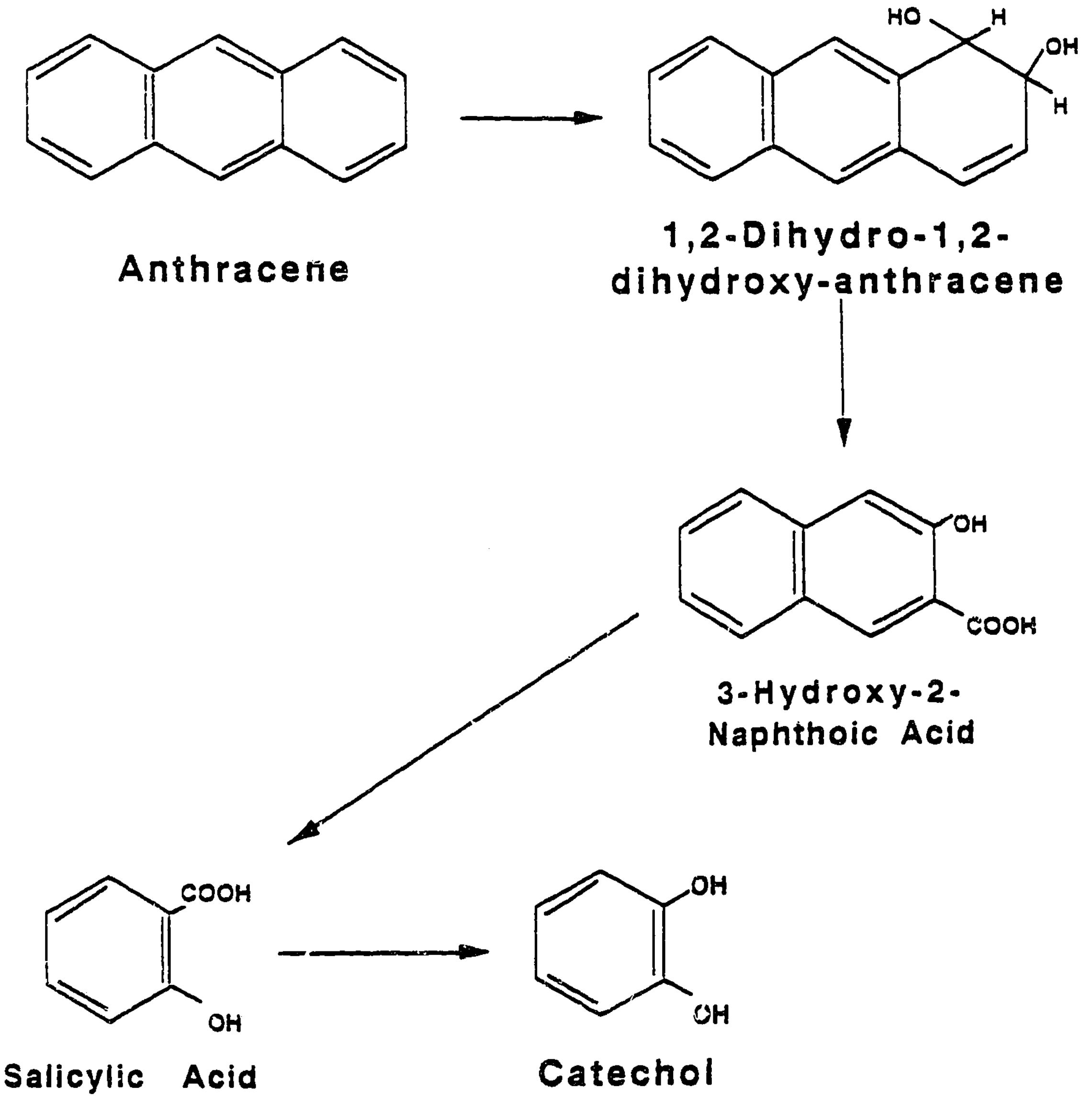


FIGURE 1.4-5 : PROPOSED MECHANISM FOR THE BACTERIAL DEGRADATION OF ANTHRACENE (ADAPTED FROM ROGOFF, 1961)

- two- and three-ring PAH compounds can be utilized by soil microorganisms as a sole carbon source and are usually rapidly degraded (i.e. half lives less than 100 days) (McGinnis, 1984; McGinnis et al., 1988; Heitkamp and Cerniglia, 1987; Sims et al., [illegible]
- four- and five-ring PAHs are not known to be utilized as a sole carbon source by bacteria, but can be co-metabolized with smaller, more degradable organics (Perry, 1979; Mueller et al., 1989). However, certain types of fungi are capable of achieving the initial biotransformation of these compounds, producing metabolites more amenable to further transformation by bacteria. For example, *Cunninghamella elegans* and *Phanerochaete chrysosporium* have been shown to transform benzo[a]anthracene and benzo[a]pyrene in single-substrate pure-culture tests (Enzminger and Ahlert, 1987; Cerniglia et al., 1980).

1.4.2.3 Toxicological Properties

Creosote-based wood preserving mixtures contain polynuclear aromatic hydrocarbons (PAHs), phenolics, and heterocycles (Table 1.4-6). As with PCP-based fluids, creosote exhibits acute and chronic effects as a whole, but uptake, metabolism and excretion can only be evaluated using individual compounds. The toxicity of some of the phenolic compounds (chlorophenols) and oxygen-containing heterocycles (dibenzofurans) was evaluated in section 1.4.1.3. Consequently, only the toxicity of PAHs as well as nitrogen and sulfur heterocycles requires consideration in this section.

1.4.2.3.1 Toxicological Properties and Fish-Tainting Potential of Nitrogen and Sulfur Heterocycles

Toxicological concerns related to nitrogen- and sulfur-containing heterocycles in creosote are primarily associated with their human and aquatic toxicity. Nitrogen heterocycles such as quinoline compounds and aniline are suspected human carcinogens, and are quite toxic to fish. Sulfur heterocycles such as thiophene and dibenzothiphene have been associated with the tainting of fish flesh.

In mammals, aniline undergoes an activation reaction after absorption, resulting in the formation of a hydroxylamine metabolite. This intermediate is a powerful hematopoietic agent, which is believed to produce methemoglobinemia, possibly resulting in chronic splenic congestion and sarcoma (cancer) formation (Williams and Weisburger, 1986). Exposure to aniline has also been associated with reproductive dysfunctions in women (Dixon, 1986).

Some quinoline compounds initially undergo an epoxidation reaction after absorption, transforming the parent compound into an active metabolite. Ring epoxidation is believed to be responsible for the carcinogenic responses observed in some mammals exposed to quinoline and certain methylquinoline isomers (Williams and Weisburger, 1986). Isoquinoline, which is also present in creosote, is not carcinogenic (Williams and Weisburger, 1986).

Nitrogen-containing heterocycles are also quite toxic to fish. For example, Birkholz and coworkers (1990) reported 48h LC_{50} values of about 5 mg/L for rainbow trout (*Salmo gairdneri*) exposed to various dimethylquinoline isomers.

Sulfur-containing heterocycles have been associated with the tainting of fish flesh at low concentrations. Jardine and Hrudey (1988) quantified detection thresholds for several volatile components in walleye (*Stizostedium vitreum*) tissue. Of the compounds tested, benzothiophene had the lowest detection threshold (0.09 ppm), implying it has the greatest capability for causing taint in fish. Dibenzothiophene demonstrated a significantly higher threshold.

1.4.2.3.2 Uptake, Metabolism, Excretion of PAHs

As a class of compounds, PAHs are highly lipid soluble and are believed to be readily absorbed across plasma membranes by passive diffusion (Enzminger and Ahlert, 1987; U.S.EPA, 1984c). For example, rapid PAH absorption has been reported from the gastrointestinal tract (U.S.EPA, 1984c), through the lungs (Vainio et al., 1976), as well as across skin and the placenta (Enzminger and Ahlert, 1987). Internal absorption of PAHs is believed to occur rapidly, as complete bodily distribution of the compounds occurs within minutes to hours after ingestion (Enzminger and Ahlert, 1987).

Metabolism of PAHs may lead to a number of acute and subchronic effects, which will be discussed in the next section. Of greater importance are the metabolic pathways which transform PAHs to carcinogens. Williams and Weisburger (1986) classify PAHs as activation-dependent, DNA-reactive carcinogens. This means PAHs as parent compounds are not carcinogenic, but must undergo enzymatic activation to a reactive ultimate carcinogen which binds covalently with DNA. In this way PAHs are precursor compounds, often called pre-, or procarcinogens.

Following internal absorption, PAHs undergo a multistep bioactivation process in mammals, mediated by the liver-based cytochrome P-450 enzyme system. The first reaction involves an epoxidation of the parent PAH to a corresponding arene oxide (epoxide). In the second reaction, arene oxides are hydrated to stereoisomeric diols by the epoxide hydrolase enzyme. In the final step, diols undergo a further epoxidation to a diol epoxide. The ultimate carcinogen will be a diol epoxide in one of several possible stereoisomeric forms, as cancer induction results from a highly stereospecific chemical interaction (Williams and Weisburger, 1986). The remaining biotransformation products consist of detoxified metabolites which are linked with endogeneous molecules (conjugated) and rapidly excreted (Williams and Weisburger, 1986). The biotransformation of benzo[a]pyrene is illustrated in Figure 1.4-6.

The biotransformation of PAHs by mammalian enzyme systems to ultimate carcinogens is the initial step in the carcinogenic process, as outlined below (Williams and Weisburger, 1986).

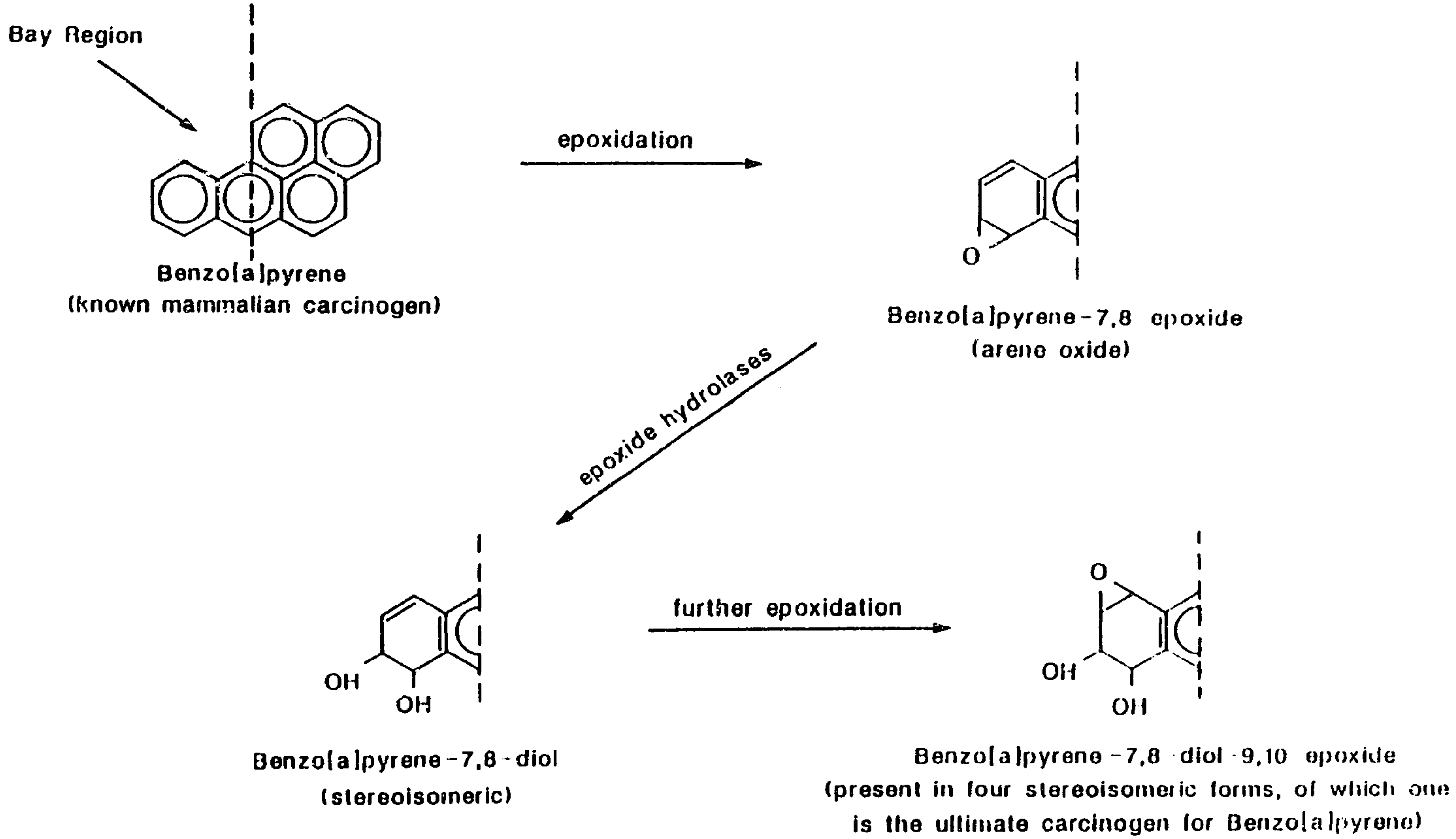


Figure 1.4-6 : Biotransformation of Benzo[a]pyrene to Diol Epoxide (Ultimate Carcinogen) (Adapted from Williams and Weisburger, 1986)

1. **Neoplastic Conversion**
    - metabolic activation (biotransformation to ultimate carcinogen)
    - covalent reactions between the ultimate carcinogen and cellular constituents
    - fixation of carcinogen damage
    - multiplication of altered cells
2. **Neoplastic Development and Progression**
    - progressive cell growth leads to neoplasm formation
    - progression of differentiated neoplasm
    - undifferentiated cancer

PAHs can be biotransformed to carcinogens following ingestion or inhalation, but some are also known to be local carcinogens, which initiate skin cancer at the site of application (Williams and Weisburger, 1986; Environment Canada, 1988b). A U.S.EPA (1984c) study concluded that creosote components benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[b]fluoranthene, benzo[a]anthracene, indeno[1,2,3-c,d]pyrene and chrysene produce excess tumors in mouse skin when applied topically. This data for individual PAHs is consistent with the documented local carcinogenic effect of creosote, discussed in the next section.

Not all PAHs are biotransformed to carcinogenic metabolites; many are detoxified, and others have even been shown to inhibit neoplasm development (inhibitors) (Sims et al., 1986). Conney (1982) initially proposed the now well-accepted theory that the existence of a "bay" region on a PAH molecule facilitates covalent binding of the ultimate carcinogen with DNA. The "bay" region for benzo[a]pyrene is illustrated in Figure 1.4-6. It is postulated that PAHs without this "bay" region are not biotransformed to carcinogens. Toxicological evidence to date on individual PAHs supports this premise (Utah State, 1989). For example, naphthalene and anthracene do not contain a bay region and have not been shown to be carcinogenic in mammals.

In addition to carcinogenic properties, a number of individual PAHs exhibit mutagenic, teratogenic or fetotoxic effects, as summarized in Table 1.4-9. An asymmetrical relationship exists between mutagenicity and carcinogenicity; an initiator carcinogen requires a DNA mutation, but all mutations do not lead to carcinogenicity (Utah State, 1989; Williams and Weisburger, 1986).

1.4.2.3.3 Acute and Chronic Toxicity of Creosote to Aquatic Species and Humans

More toxicological data exists for creosote-based wood preserving mixtures than for PCP-based ones because of a greater period of use. Consequently, a more realistic assessment of acute and chronic effects arising from exposure to residual treating fluid at the HELP sites can be made for creosote.

An assessment of creosote's toxicity to aquatic species is complicated by a number of factors:

Table 1.4-9: Systemic, Chronic Toxicological Properties of PAHs Present in Creosote

PAH Compound	Toxicology		Bioconcentration Factor in Fish
	Behavior	Carcinogenic Classification	
naphthalene	inhibitor	E	32 - 170
1-methylnaphthalene	inhibitor	E	-
2-methylnaphthalene	inhibitor	E	100 - 510
dimethylnaphthalene	inhibitor	D	-
acenaphthene	-	D	130 - 1000
acenaphthylene	-	D	77 - 300
carbazole	mutagenic	C	-
fluorene	mutagenic, noncarcinogenic	E	3 - 800
phenanthrene	initiator, mutagenic	D	200 - 1400
anthracene	mutagenic	C	320 - 1400
fluoranthene	co-carcinogenic, initiator, mutagenic	D	740 - 5000
pyrene	co-carcinogenic, mutagenic	D	1600 - 6000
chrysene	mutagenic, initiator, carcinogenic	C	2800 - 11 000
benzo[a]pyrene	mutagenic, carcinogenic, fetotoxic, teratogenic	B_2	6600 - 40 000
benzo[a]anthracene	mutagenic, carcinogenic	B_2	2800 - 12 000
benzo[e]pyrene	carcinogenic, mutagenic	D	-
benzo[b]fluoranthene	sufficient evidence of carcinogenicity in animals but inadequate data for humans	B_2	6600 - 24 000
benzo[j]fluoranthene	carcinogenic, mutagenic	B_1 or B_2	-
benzo[k]fluoranthene	-	B_1 or B_2	6600 - 90 000
perylene	-	D	7191
benzo[g,h,i]perylene	-	D	200 000
dibenzo[a,h]anthracene	mutagenic	B_2	70 000
indeno[1,2,3-c,d]pyrene	-	B_2	300 000

Notes:

- Sources: Enzminger and Ahlert (1987), Vandermeulen (1987), U.S.EPA (1984a), Sims et al., (1986), U.S.EPA (1984c), U.S.EPA (1987c), Battelle (1989).
- bioconcentration factor = concentration of chemical at equilibrium in whole organism divided by concentration of chemical in enveloping media (water for fish)
- the U.S.EPA's categorization scheme for ranking carcinogens has been adopted for this table:

  group A - Human carcinogen (sufficient evidence)
  group B - Probable human carcinogen, group B_1 - limited evidence in humans, group B_2 - combination of sufficient evidence in animals and inadequate data in humans
  group C - Possible human carcinogen (limited evidence in animals)
  group D - not classified (inadequate animal evidence)
  group E - no evidence of carcinogenicity in humans (no evidence in at least two species of animals or in both epidemiological and animal studies)

- the chemical composition of creosote varies widely, depending on the coal tar from which the creosote was derived.
- as a whole, creosote is quite insoluble in water, and some tests utilize organic carrier solvents to increase the aqueous solubility of creosote to toxic levels. The applicability of these test results to wood preserving sites where creosote exists by itself is difficult to determine.

A summary of data on the toxicity of creosote to aquatic organisms is presented in Table 1.4-10. The acute toxicity of creosote to aquatic species has been held to be due to the smaller (three rings or less) PAHs, as the toxicity of larger PAHs generally exceeds their aqueous solubility (Landrum et al., 1987; Environment Canada, 1988b). However, the majority of the studies upon which this premise was based were conducted under laboratory conditions that minimized photolytic reactions. Landrum and coworkers (1987) showed that in the presence of natural and simulated sunlight, anthracene and other PAHs are acutely toxic to aquatic organisms at concentrations well below aqueous solubility limits. In one test using an illuminated artificial stream, the toxicity of anthracene was over 400 times greater than reported in other studies. The drastic increases in PAH toxicity were attributed to interactions of bioaccumulated parent PAH and light, and not to the action of externally formed photodegradation products. As a result of these new findings, the mechanisms and components of creosote which lead to its aquatic toxicity are unclear, but it is likely that photoreactivity is a significant component.

Table 1.4-10: Acute Toxicity of Creosote to Aquatic Organisms

Creosote Concentrations Tested (mg/L)	Aquatic Species Used	96-hour LC_{50} (mg/L)	Comments	Reference
0.08 - 0.32	rainbow trout	-	no effect level	Environment Canada (1988b)
0.20 - 0.56	rainbow trout	0.38	-	Environment Canada (1988b)
>10	rainbow trout	-	mortality inadequate to measure LC_{50}	Domtar (1986)
-	larval lobsters	0.020	saltwater species	Environment Canada (1988b)
-	mysid shrimp	0.018	saltwater species	U.S. EPA (1987c)

Notes:

- 96-hour LC_{50} is the creosote concentration at which 50% of the test organisms die within 96 hours.

Creosote has been used in North America for wood preserving since the mid 1800's. As a result, the acute and chronic effects of creosote on humans are well documented through occupational exposure. Short-term inhalation of vapours results in irritation of the nose and throat, whereas more prolonged vapour inhalation can lead to vomiting, convulsions or coma (Environment Canada, 1988b). Ingestion of creosote may result in sweating, vomiting, respiratory difficulties, and in severe poisonings, circulatory collapse and respiratory failure leading to death (International Labour Organization, 1983; Environment Canada, 1988b). The fatal dose of creosote for humans by ingestion is about 0.1 g/kg (International Labour Organization, 1983; Environment Canada, 1988b). The most common acute effect resulting from contact with creosote is dermatitis, characterized by reddening and itching of affected skin. More severe contact may cause progression of dermatitis to ulceration. Exposed skin may exhibit an enhanced sunburn response (photosensitization), as well as hyperpigmentation (Dusich et al, 1980; Domtar, 1986; Environment Canada, 1988b; International Labour Organization, 1983). Chemical burns may result if creosote is not removed from the skin (Wisconsin Division of Health, 1988; Todd and Timbie, 1983).

Creosote has been causally associated with increased incidence of lung, bladder, breast and skin cancers in humans. Sims et al. (1986) and the National Cancer Institute (1985) provide reviews of documented cases. U.S.EPA (1987b) concluded that creosote contains several known carcinogens as well as related chemicals that may act as cocarcinogens, initiators, promoters or potentiators of carcinogenesis, and correspondingly classified it as a Group B_1 carcinogen (probable human carcinogen - see Table 1.4-9 for an explanation of the carcinogenic groupings). U.S.EPA (1987c) however, implies creosote is a Group A carcinogen (known human carcinogen). Neither the Group B_1 or A classifications have been confirmed in other sources. U.S.EPA (1982) concluded that assessing the carcinogenicity of creosote as a whole using the carcinogenic potency of individual components is not appropriate because of the possibility of chemical synergism. For the same reason the acute and chronic effects of individual components are not discussed further in this section.

1.4.3 CCA-Based Wood Preserving Mixtures

1.4.3.1 Physical and Chemical Properties

CCA-based wood preserving fluids typically contain 1.5 to 4.0% CCA dissolved in water. At least 95% of CCA-based mixtures is the carrier, and consequently, the fluid properties most closely resemble those of water. Copper, chromium and arsenic in CCA all exist as oxides, and any noteworthy production impurities have not been reported. Three types of CCA concentrate are available from manufacturers (Types A, B, C), though Type C is predominantly used in Canada (Arsenault, 1978; Environment Canada, 1988c). A typical composition of CCA concentrate and working fluid is presented in Table 1.4-11.

CCA-based wood preserving mixtures are yellow-green in color, odourless, freely soluble in water, acidic, and heavier in water. The properties of CCA preserving fluids are summarized in Table 1.4-12.

Table 1.4-11 Typical Composition of CCA Concentrate and Working Mixture

Compound Family	Component	Typical % in CCA Concentrate	Typical % in 2% Strength CCA Preserving Solution
Water (carrier fluid)	-	50.00	98.00
Inorganics	CrO_3	23.75	0.95
	CuO	9.25	0.37
	As_2O_5	17.00	0.68

<u>Notes:</u>

- Adapted in part from Environment Canada, 1988c.
- A 50% strength concentrate is typically used in industry, and was used for calculation purposes here.

Table 1.4-12 Properties of CCA-Based Preserving Mixtures

Property	Value	Significance
Physical state at 20°C	liquid	
Solubility	freely soluble in water	
pH	2.9 to 4.3	acidic
Freezing point	-30°C	
Flashpoint	not flammable	
Vapour pressure	non-volatile	
Odour	odourless	
Colour	yellow-green	
Specific gravity	1.03	slightly heavier than water

Notes:

- Values in this table were extracted from, or calculated from, data presented in Environment Canada (1988c).
- A 5% strength CCA working solution was used for calculations in this table.

1.4.3.2 Biodegradability

CCA-based wood preserving fluids contain water, as well as inorganic oxides of copper, chromium and arsenic. All of these components are inorganic, and consequently cannot be biodegraded.

However, inorganic compounds can participate in a biological cycle through valence changes and methylation reactions. For example, Woods (1974) documents the biological cycle of arsenic, in which inorganic arsenate is reduced to arsenite and methylated by microorganisms to form both trimethyl and dimethylarsine.

1.4.3.3 Toxicological Properties

The components of CCA all exhibit different environmental behaviours. Consequently, ratios of Cu, Cr and As in environmental media at CCA facilities are not consistent with their ratios in the working mixture. As a result, the toxicity of each of the components, as well as that of the CCA mixture, must be reviewed to adequately assess environmental hazards posed by CCA releases (Environment Canada, 1988c).

1.4.3.3.1 Copper

Copper is essential to human life and health, and a daily dose of at least 2 milligrams is required (Owen, 1982). In particular, copper is the prosthetic element (nonprotein portion) of 12 specific enzymes (National Academy of Sciences, 1977; Goyer, 1986). As a result, copper poisoning in humans is rare, because the toxicity [illegible] metals is sharply diminished when bound to proteins or other macromolecules (Goyer, 1986; National Academy of Sciences, 1977). Ingestion of large amounts of copper (several grams) is required to overwhelm the body's homeostatic mechanisms of conjugation and excretion (Scheinberg, 1979; Environment Canada, 1988c). For example, drinking water limits of 1 mg/L for copper were not established because of toxicological concerns, but for aesthetic reasons, such as palatability and to prevent the staining of plumbing fixtures (National Academy of Sciences, 1977; Health and Welfare Canada, 1989).

In addition to the body's resistance to copper poisoning by ingestion, poisoning by inhalation of vapours or dust containing copper has not been shown to occur. The National Academy of Sciences (1977) and Scheinburg (1979) discuss a case in which vineyard workers chronically exposed to copper sulfate developed malignant lung and liver tumors. However, the results of this study are inconclusive, because the workers were also exposed to arsenic-based insecticides as well as arsenic-contaminated groundwater (World Health Organization, 1981; Scheinberg, 1979).

Toxicological information for copper implies that dust, vapours and groundwater from the HELP sites which used CCA will not present a copper-based hazard to human health. At the CCA sites, human health risks will likely be associated with the chromium or arsenic content of dust, vapours or groundwater.

While humans can withstand large amounts of copper without toxic effects, aquatic species are quite sensitive to copper compounds. The National

Research Council of Canada (NRCC) (1979) postulated that copper toxicity to fish results from a decrease in the quantity of antibody produced for specific antigens, making the fish more susceptible to disease. Water hardness is the major factor modifying fish tolerance to copper, possibly because calcium/magnesium hardness alters cell-membrane permeability at gills (NRCC, 1979), or because copper speciation with hardness-based compounds affects the availability for uptake. Relationships between 96-hour median lethal concentrations (96-h LC_{50}) and water hardness have been developed for many taxonomic orders of fish by the NRCC (1979). A typical range of 96-h LC_{50} values for aquatic species exposed to copper is from 0.04 mg/L (fathead minnow) to 0.89 mg/L (rainbow trout) (U.S.EPA, 1987c; Environment Canada, 1988c). The International Joint Commission (IJC) adopted 0.005 mg/L as the maximum allowable copper concentration in the Great Lakes (Environment Canada, 1988c). This value was selected to protect the most sensitive species within the Great Lakes ecosystem, and is independent of water hardness. Copper is also only moderately bioconcentrated in fish flesh, with bioconcentration factors ranging from 50 to 400 (Battelle, 1989).

1.4.3.3.2 Chromium

Chromium (Cr) is a transition metal, whose valence can range from 0 to +6. However, the +3 and +6 forms predominate in the environment, and are consequently the only valences with toxicological significance (NRCC, 1976; Goyer, 1986).

Trivalent and hexavalent chromium elicit drastically different toxicological responses in humans; Cr^{3+} is an essential trace nutrient which maintains efficient glucose, lipid and protein metabolism, and is also a cofactor for insulin action, whereas Cr^{6+} can cause cancer of the lung and upper respiratory tract (World Health Organization, 1988; NRCC, 1976; Goyer, 1986). Trivalent chromium is the naturally occurring form of Cr, with almost all the hexavalent form arising from industrial and domestic emissions (World Health Organization, 1988; Goyer, 1986; NRCC, 1976). Chromium in CCA-concentrate exists in the +6 valence (Table 1.4-11). Part of the Cr^{6+} may be reduced to Cr^{3+} in the working fluid, depending on the oxidation/reduction (redox) potential of the water carrier. Once released to the environment, it is expected the remaining Cr^{6+} in the fluid will be converted to Cr^{3+} under the reducing conditions of soil and groundwater (World Health Organization, 1988). However, work by Environment Canada (1988c) and Bartlett and James (1979) suggest Cr^{6+} may remain in the oxidized form in many soil environments. Consequently, it is possible that chemical forms of both Cr^{3+} and Cr^{6+} exist at the HELP sites which utilized CCA.

The uptake and metabolism of chromium after ingestion or inhalation depend largely on its oxidation state and the chemical form within the oxidation state (World Health Organization, 1988; Goyer, 1986). Consequently, the speciation of chromium released in the environment is relevant to any human health risks. For example, it is assumed that calcium and zinc chromate are two of the most carcinogenic forms of Cr^{6+} because they are only slightly soluble, and consequently remain in contact with tissues for long periods of time (depot effect) (World Health Organization, 1988). In general, compounds of trivalent chromium are poorly absorbed, whereas those containing the hexavalent form easily cross cell membranes (NRCC, 1976; World Health Organization, 1988; Goyer, 1986). Once biologic membranes are crossed, Cr^{6+} is reduced intracellularly to Cr^{3+}, which is the predominant form in biologic materials (Goyer, 1986; World Health Organization, 1988). There is no evidence that trivalent chromium is oxidized to hexavalent forms in biologic systems (World Health Organization, 1988; Goyer, 1986). It has been speculated that the harmful health effects of hexavalent chromium are related to the reduction to trivalent chromium and subsequent binding to genetic material (Goyer, 1986).

<u>Hexavalent</u> chromium compounds have been causally associated with the following human health effects: cancers of the respiratory tract, chronic ulceration and performation of the nasal septum, kidney damage, as well as dermal sensitization and skin ulceration (NRCC, 1976; World Health Organization, 1988; Goyer, 1986). <u>Trivalent</u> chromium compounds are not carcinogenic, and do not elicit adverse responses from the skin or respiratory tract (World Health Organization, 1988; Goyer, 1986). The U.S.EPA (1987c) classified all compounds containing hexavalent chromium as Group A carcinogens (sufficient human evidence).

Both valences of chromium can be toxic to aquatic species, though for any given concentration chromium compounds are generally less toxic than copper compounds. Median lethal concentrations (96-h LC_{50}) for freshwater fish range from 3 to 72 mg/L of Cr^{3+} and from 18 to 133 mg/L of Cr^{6+}. The 96-h LC_{50} value for rainbow trout exposed to Cr^{6+} is 69 mg/L (Environment Canada, 1988c). For both chromium forms, as well as for copper, water hardness modifies fish susceptibility to poisoning (U.S.EPA, 1987c; NRCC, 1976). Both chromium valences are moderately bioconcentrated in fish and benthic organisms (bioconcentration factors range from 20 to 2000 [Battelle, 1989]), and the bioconcentrated product can lead to toxic effects (NRCC, 1976).

1.4.3.3.3 Arsenic

Arsenic (As) exists in an inorganic, pentavalent form (As_2O_5) in CCA concentrate. As^{5+} would typically be expected to be reduced to As^{3+} under the reducing conditions prevalent in most soil and groundwater. However, a study by Environment Canada (1988c) concluded that over 97% of arsenic contained in soil and water near a CCA facility was in the original pentavalent form. It is likely that arsenic will exist in both trivalent and pentavalent forms at HELP sites which used CCA. In addition, inorganic arsenic compounds can undergo valence changes and methylation reactions to form organic methylarsines and organo-arsenic acids (Woods, 1974; Woolson, 1977). The environmental chemistry of arsenic is extremely complex, and the different arsenic forms exhibit different patterns of uptake, metabolism, and toxicity. Consequently, speciation of arsenic released in the environment is relevant to potential human health effects. The National Research Council of Canada (NRCC) (1978) devised the following toxicological ranking of arsenic forms (in order of decreasing toxicity):

arsine compounds (-III) > organo-arsine derivatives > arsenites (+III) > arsenoxides (+III) > arsenates (+V) > pentavalent organic compounds (+V) > arsonium metals (+I) > metallic arsenic (0)

Arsenic may enter the body by ingestion, inhalation or dermal contact. Absorption through plasma membranes into organ cells occurs readily by active transport (NRCC, 1978; World Health Organization, 1981). Once absorbed, pentavalent arsenic compounds are reduced to more toxic trivalent forms, which may combine with sulfhydryl and disulfide protein groups, inhibiting these systems (Goyer, 1986; NRCC, 1978; World Health Organization, 1981). Chromosomal breakage, impaired tissue respiration, and an uncoupling of mitochondrial oxidative phosphorylation are the common cellular effects resulting from arsenic absorption (Goyer, 1986; NRCC, 1978; World Health Organization, 1981). The uncoupling of oxidative phosphorylation is the toxic mechanism demonstrated by chlorophenols (section 1.4.1.3.2). Inorganic arsenic undergoes a methylation reaction prior to urinary excretion, though organic arsenicals are excreted without conversion to inorganic or simpler methylated forms (World Health Organization, 1981; Goyer, 1986; NRCC, 1978).

Inorganic arsenical compounds of both valences have been causally associated with a number of human health effects (World Health Organization, 1981; Goyer, 1986; NRCC, 1978; Balazs et al., 1986);

- cancer of the skin, liver, lymph nodes, respiratory tract;
- cardiovascular effects;
- skin lesions, hyperpigmentation;

- lesions of the upper respiratory tract;
- disturbances in central nervous system function;
- possible teratogenic effects; and
- arteriosclerosis.

Significantly less research has been devoted to the toxicological effects of organic arsenicals. To date, these compounds have not been reported to be carcinogenic in animals, and are less toxic than their inorganic counterparts (World Health Organization, 1981; NRCC, 1978). The U.S.EPA holds that an adequate amount of research demonstrates the in vivo (in organism) reduction of As^{5+} to As^{3+}, and accordingly regulates both chemical forms together as one entity (Environment Canada, 1988c). Arsenic in both +3 and +5 forms is classified as a Group A carcinogen (sufficient human evidence) (U.S.EPA, 1987c).

Arsenic can also be toxic to aquatic species. In surface water, the inorganic form of arsenic will depend on the pH and redox potential of the water, though it will predominantly exist in the +5 valence for most systems. Median lethal concentrations (96-h LC_{50}) for freshwater fish exposed to As^{5+} range from 1.0 to 10.8 mg/L (U.S.EPA, 1987c; Environment Canada, 1988c). Aquatic organisms absorb arsenic through the gills and the gut, and benthic organisms accumulate more arsenic than fin fish. Arsenic from pollution sources is also more readily absorbed by fish than naturally occurring forms (NRCC, 1978). Arsenic is negligibly bioconcentrated in fish; reported bioconcentration factors range from 1 to 40 (Battelle, 1989).

1.4.3.3.4 CCA

In addition to toxicological information on the individual components of CCA, some data exists for the mixture. Human health effects arising from CCA exposure are described by Environment Canada (1988c) based on information from material safety data sheets for Wolmanac 50% Concentrate. Some discussion of potential health effects is also presented by Takahasi et al. (1983). In general, skin contact can lead to irritation, inflammation, and possible skin cancer; inhalation of CCA vapours can cause severe irritation of the nose, throat and eyes, ulceration and perforation of the nasal septum, and possible carcinogenesis; ingestion of CCA can result in nausea, vomiting, shock or coma, liver and kidney damage, jaundice and possible carcinogenesis.

In addition to human health effects, CCA can also be toxic to fish. Environment Canada (1988c) lists a 96-h LC_{50} value of 0.26 mg/L for Rainbow trout exposed to a 50%-strength CCA concentrate. A description of which constituents the 0.26 mg/L value refers to is not provided. The 0.26 mg/L value means that a 4 000 000-fold dilution of 50% concentrate or a 230 000-fold dilution of a 3%-strength working mixture would still be acutely toxic to salmonid species (salmon, trout). Consequently, CCA based wood preserving mixtures have a large potential to cause damage in aquatic environments. A comparison of the human and aquatic toxicity of CCA and its components is presented in Table 1.4-13. CCA concentrate is more acutely toxic to rainbow trout than any of its components (i.e. CCA has the lowest 96-h LC_{50}). This implies that the aquatic toxicities of the compounds in CCA are enhanced in the mixture.

Table 1.4-13: Comparison of the Toxicity of CCA and its Components

CCA Component	Chemical Form	Human Toxicity	Aquatic Toxicity		Bioconcentration Factors for Aquatic Organisms
			96-h LC_{50} for rainbow trout (mg/L)	Description	
CuO	Cu^{2+}	essential element, no toxic effects exhibited unless gross amounts are ingested	0.89	quite toxic	50 - 400
CrO_3	Cr^{6+}	potent human carcinogen, causally associated with cancers of the respiratory tract, kidney damage and skin ulceration (Group A carcinogen)	69	mildly toxic	20 - 2000
As_2O_5	As^{5+}	potent human carcinogen, causally associated with skin, liver, and lung cancer. Classified together with As^{3+} as a Group A carcinogen	10.8	moderately toxic	1 - 40
CCA concentrate (50% strength)	-	skin contact can lead to irritation and possible chronic effects such as cancer; inhalation can lead to ulceration of the nasal septum; ingestion can cause shock, liver and kidney damage and possible carcinogenesis	0.26	very toxic	-

Notes:

- Information presented in this table is discussed in the text.

1.5 Transport and Fate of Wood Preserving Chemicals in the Environment

In the last section, the properties of wood preserving chemicals were evaluated. In section 1.2 the process locations from which these chemicals could be released to the environment were assessed. In this section both areas will be used to determine the fate and transport of wood preserving mixtures in the environment.

1.5.1 Oil-Based Wood Preserving Mixtures

PCP-based wood preserving mixtures contain 3 to 7% technical-grade PCP dissolved in a diesel fuel carrier. Creosote-based mixtures are comprised either entirely of creosote or of a 50% creosote:50% petroleum oil mixture. Both creosote- and PCP-based fluids classify as bulk hydrocarbon fluids.

These mixtures, when released to the environment as drips or process sludges, exhibit an environmental behaviour much different from that of the constituent chemicals acting alone. Consequently, a study of the environmental transport and fate of oil-based wood preserving chemicals must consider two areas: the macroscopic behaviour of the bulk hydrocarbon fluid, as well as the microscopic partitioning of the individual chemicals which comprise the mixtures.

1.5.1.1 Transport and Fate of Bulk Hydrocarbon Phase

Creosote and PCP drips or sludges released on the ground surface will percolate down through the soil in response to gravity. The rate of infiltration will depend on soil porosity, moisture content as well as the viscosity of the bulk hydrocarbon phase. Interfacial tension in the form of capillary forces resists the downward progression of the oil-based mixture. As a mass of hydrocarbon migrates through a mass of soil, some of the hydrocarbon will remain affixed to the soil matrix by capillary forces. The hydrocarbon retained by a soil matrix is termed "residual saturation". If the hydrocarbon mass is small relative to the affected soil surface area, downward migration will cease as the free hydrocarbon mass is exhausted through conversion to residual saturation. This exhaustion generally occurs for the "drip-pad" area at wood preserving sites (Figure 1.5-1).

If the mass of hydrocarbon fluid is sufficient to satisfy the capillary forces of the affected soil, free fluid will reach the capillary fringe. In this situation, the soil's ability to retain a hydrocarbon fluid has been overwhelmed by the volume present. At this point the environmental behaviour of PCP and creosote wastes diverges.

PCP-based wood preserving mixtures are less dense (lighter) than water and have low aqueous solubility (Table 1.4-1). As waste mixture from PCP wood preservation enters the capillary fringe, the PCP-hydrocarbon mixture will bypass the smaller pores, which contain more water because of larger capillary forces, and continue migrating downward through the larger pores. This progression will end when the PCP-hydrocarbon reaches the water table, where all pores are completely filled with water. If the rate of arrival of hydrocarbon mixture at the water table exceeds the rate at which the mixture is removed by solubilization in water, a distinct PCP-hydrocarbon phase will exist, floating on the groundwater surface.

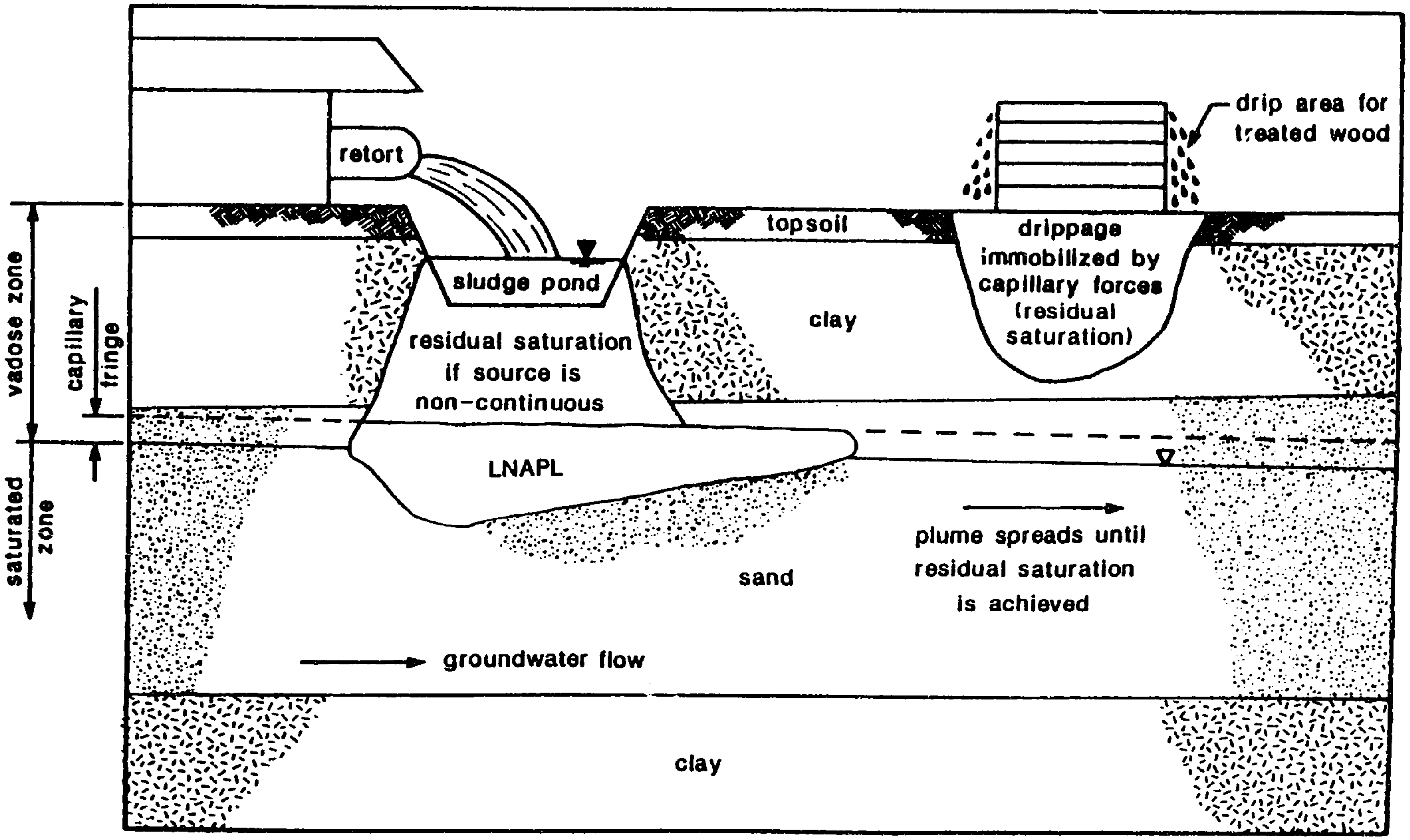


FIGURE 1.5-1 : ENVIRONMENTAL FATE OF EMISSIONS FROM PCP-BASED WOOD PRESERVATION

Such mixtures are labelled light non-aqueous phase liquids (LNAPLs). They may also be referred to as pure- or distinct-phase liquids. An LNAPL will then migrate laterally over the water table in a layer about as thick as the capillary fringe (Dragun, 1988). A sufficient fluid head may exist to drive the LNAPL a small distance up gradient, though the greatest migration will occur in the down gradient direction. A LNAPL will continue to spread in the transverse and lateral directions until the distinct phase is exhausted through conversion to residual saturation. Depression of the water table may also occur if the LNAPL mass is sufficient (Figure 1.5-1).

Creosote-based wood preserving mixtures are more dense (heavier) than water and have low aqueous solubility (Table 1.4-7). If the rate of arrival of waste creosote mixture at the water table exceeds the rate at which the mixture is removed by solubilization in water, a separate phase will exist. Because this phase is heavier than water, it will continue to migrate downwards after contacting the water table (density flow). Density flow occurs by front displacement, in which the hydrocarbon fluid progresses downwards by displacing groundwater (Dragun, 1988). This separate phase is called a dense non-aqueous phase liquid (DNAPL). It may also be referred to as a pure or distinct phase. The downward progression of a DNAPL will cease if the mass of the distinct phase is exhausted by conversion to residual saturation, or if the DNAPL encounters a formation of extremely low permeability (Figure 1.5-2).

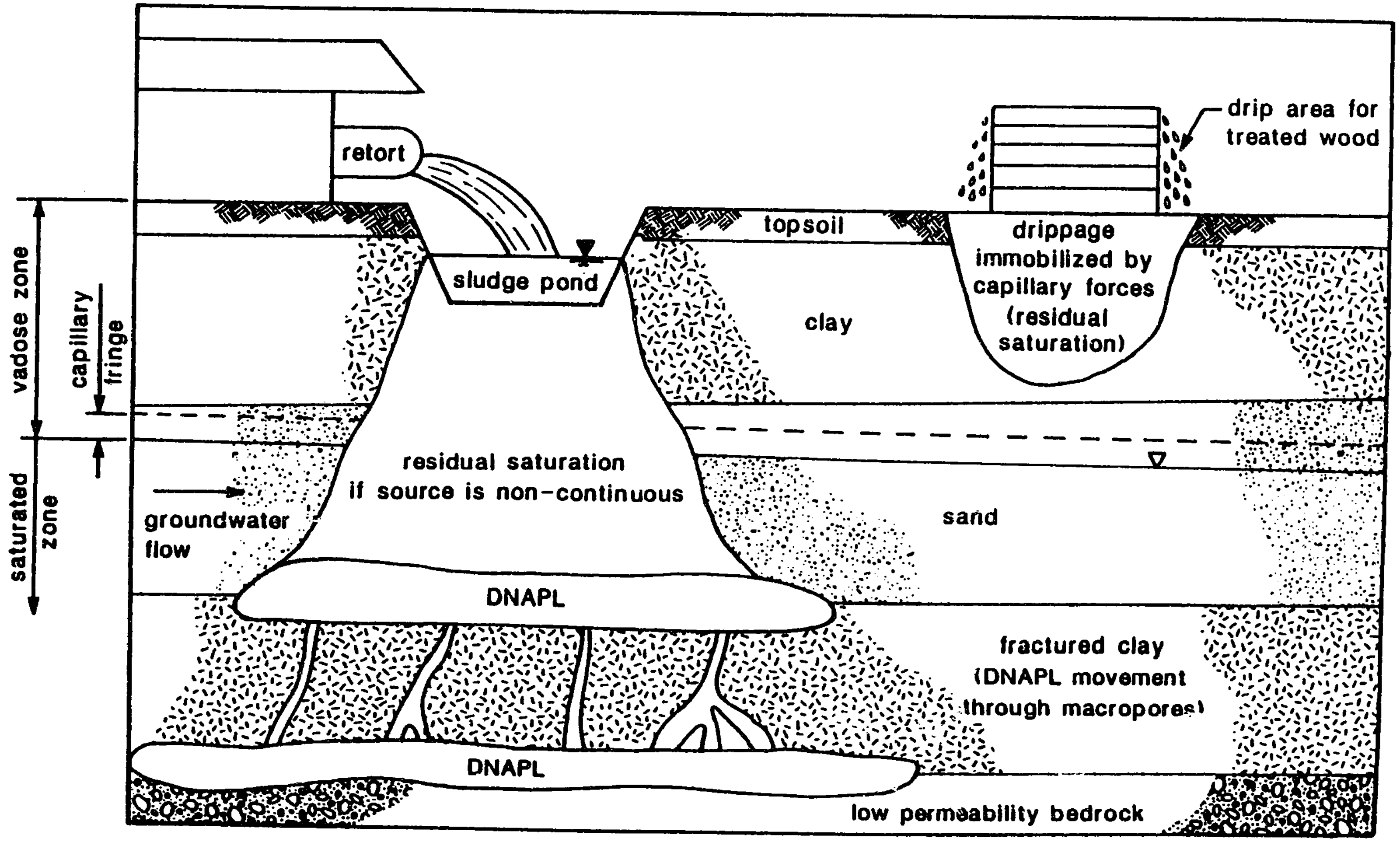


FIGURE 1.5-2 : ENVIRONMENTAL FATE OF EMISSIONS FROM CREOSOTE-BASED WOOD PRESERVATION

A pressure ridge of accumulating oil may form in the capillary fringe for LNAPLS, causing a lateral spreading of the LNAPL contamination. A pressure ridge does not form for DNAPLs, because they concentrate on the bottom of aquifers. Consequently, the lateral migration of DNAPLs is generally much less than that of LNAPLs (Dracos, 1987).

Residual saturation hydrocarbon can be remobilized from the vadose zone by percolating water. This phenomenon will continue until the amount of hydrocarbon which can migrate by this process is depleted. At this point a new level of residual hydrocarbon saturation is achieved, and additional percolating water will generally move around the hydrocarbon with minimal disturbance (Dragun, 1988). For example, Sale and Piontek (1988) discuss a study in which an alluvial sand was flooded with water, with creosote-based preserving mixture, and finally with water again. The maximum residual saturation achieved was about two-thirds of the pore space, with the other one-third comprised of water. The final water flooding displaced about one-half of the creosote oil mixture, leaving about one-third of the pore space filled with oil. This new level of residual saturation was held by interfacial tension between the oil and water, as well as by capillary forces associated with the soil matrix, and could not be mobilized by further flushing.

Another factor enhancing the mobility of bulk hydrocarbon mixtures is their effect on soil permeability; silty and clayey soils, which often possess low permabilities to water, can possess higher permeabilities to hydrocarbons (Dragun, 1988). There are two main ways by which hydrocarbons increase soil hydraulic conductivity. The first mechanism arises from a change in dielectric constant of the pore fluid. Bulk hydrocarbon fluids have a lower ability to transmit charge than water (lower dielectric constant). As a result, electrostatic repulsion forces between adjacent soil particles are reduced as the hydrocarbon fluid replaces water in the soil matrix. Consequently, average interparticle spacing will decrease, and cracks and fissures will form in space previously occupied by soil particles (Dragun, 1988). These new macropores will greatly enhance hydrocarbon mobility.

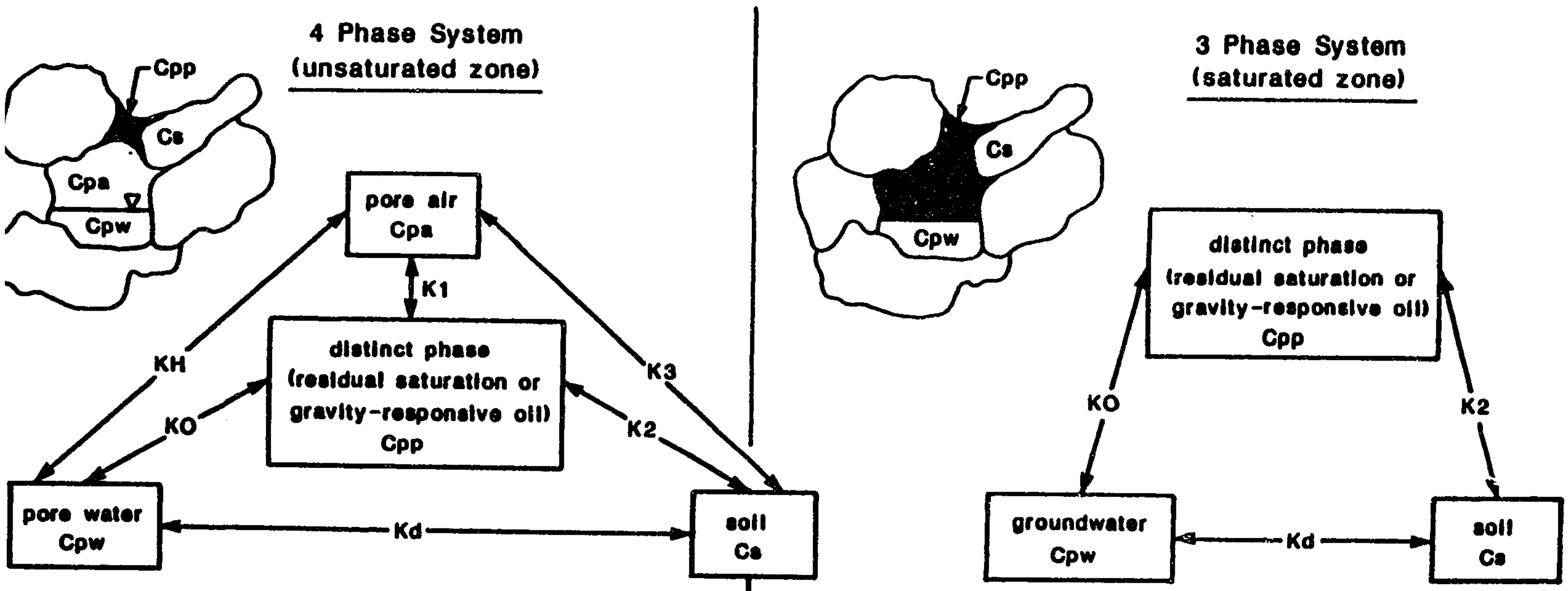
A second way hydrocarbon fluids can increase hydraulic conductivity is that average interparticle spacing decreases when the bulk hydrocarbon, which does not orient itself with surface oxygen atoms on clays, replaces dipolar water, which orients itself outwards from the particle surface (Dragun, 1988). Brown and Thomas (1984) concluded that diesel fuel can increase the hydraulic conductivity of clay-sand mixtures from 40 to 1800 times. Diesel fuel is the carrier in PCP and creosote wood preservation. It is likely that this hydrocarbon-mediated increase in hydraulic conductivity of clay soils and glacial tills enhanced the mobility of creosote- and PCP-based wood preserving mixtures at the HELP sites.

1.5.1.2 Environmental Partitioning of Chemicals in PCP-Based Mixtures

PCP-based wood preserving fluids are oil-based mixtures containing many different types of chemicals, including chlorinated phenols, polychlorinated dibenzo[p]dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) (Table 1.4-2). The environmental behaviour of these chemicals in the mixture is much different from that of the individual chemicals acting alone, because of competitive and inhibitory interactions within the mixture. The behaviour of these chemicals in a multimedia system is best determined by partition coefficients, which describe the relative affinity of a particular chemical for a particular phase at equilibrium (Figure 1.5-3). The use of partition equilibria is the best way of qualitatively determining in which phase of a multimedia system the contaminants will be concentrated, though the approach does possess quantitative limitations. These limitations are primarily associated with the assumption of equilibrium, the reactions which occur subsequent to partitioning, the existence of emulsions rather than true solutions, and interactive effects of other organic substances present.

Partition coefficients are derived in laboratory studies where two or more of the phases are contacted in a closed reactor until equilibrium between or among the phases is established. Equilibrium is defined as the point at which there is no <u>net</u> transfer of contaminant between phases. Coefficients derived in this manner poorly represent conditions in the environment, where interphase equilibrium may not be established because soil, air, and water are continually in flux, being replaced with fresh material (Wu and Gschwend, 1986).

A second disadvantage in the use of partition equilibria is that the approach cannot incorporate repartitioning which arises from chemical reactions occurring subsequent to the original partitioning. The arsenic cycle is a good example of this inadequacy. Arsenic from CCA mixtures which



Legend:

- Cpa–concentration of contaminant in pore air
- Cpp–concentration of contaminant in pure phase
- Cs –concentration of contaminant in soil
- Cpw–concentration of contaminant in pore water

- $Kd = \frac{Cs}{Cpw}$
- $K1 = \frac{Cpp}{Cpa}$
- $K2 = \frac{Cpp}{Cs}$
- $K3 = \frac{Cpa}{Cs}$

- KH–Henry's constant–$\frac{Cpa}{Cpw}$
- $KO = \frac{Cpp}{Cpw}$

FIGURE 1.5-3 : PARTITION EQUILIBRIA RELATIONSHIPS partitions to the soil phase can undergo reactions to form organic and inorganic acids, as well as methylarsine gases. These compounds will undergo a repartitioning after formation.

Partition equilibria relationships require distinct environmental media and contaminant phases. However at wood preserving sites, several combined phases may exist. For example, emulsions may exist rather than true solutions, or the groundwater may be so contaminated it exhibits solvent behaviour, resulting in cosolvent interactions between dissolved and sorbed species. Partition relationships poorly predict phase distribution behaviour in mixed-media environments.

Effective partition coefficients will be site-specific, as they depend on the interaction of soil matrix and waste. Consequently, the following sections will focus on the general mechanisms which cause the partitioning, rather than presenting specific values.

1.5.1.2.1 Behaviour of Chlorophenols, PCDDs and PCDFs in Soil

The adsorption of chlorophenols to soil depends primarily on the amount of organic matter present, as well as on the pH of the soil-water system. Chlorophenols are incorporated into soil organic matter through oxidative coupling. The coupling reaction is believed to be catalyzed by plant and microbial enzymes, as well as by various soil minerals (Boyd et al., 1989). It is possible that chlorophenols may eventually undergo complete chemisorption to soil humic materials through covalent bonding (Boyd et adsorption is pH. Chlorophenols are all weak acids, with pKa's ranging from 4.7 (PCP) to 7.9 (2,4-dichlorophenol). Consequently in basic environments, chlorophenols may be largely ionized, and much more soluble in water (refer to section 1.4.1.1). As a result, chlorinated phenols are more mobile in high pH soils than in acidic soils (Sims et al., 1986). However, the ionized chlorophenol forms may undergo some adsorption to soil as exchangeable anions (McGinnis, 1988). Conflicting viewpoints exist as to the relationship between, and relative effect of, pH and organic matter content upon chlorophenol adsorption, but virtually all studies conclude that these are the paramount parameters. Consistent with partition equilibria theory, adsorbed chlorophenols can be slowly released when cleaner water containing non-equilibrium chlorophenol concentrations passes through the soil (Banerji et al., 1986). The compounds adsorbed to soil will be biologically degraded as an acclimated microbial culture develops.

PCDDs and PCDFs have extremely low aqueous solubilities, as well as an affinity for organic solids. Consequently, these compounds largely partition to t[illegible] subsurface environments. PCDDs and PCDFs have been consi[illegible] completely immobilized in soil, and not subject to any signific[illegible]ching (U.S.EPA, 1984b; U.S.EPA, 1986a). Some studies of contaminant distributions at wood preserving sites have supported this premise (Kitunen et al., 1987), whereas others have reported considerable dioxin and furan migration (Pereira et al., 1985). A comprehensive study (Walters et al., 1989) on dioxins containing four to eight chlorine atoms

- the location of chlorine atoms on the dioxin molecule rather than the amount of chlorination controls partitioning.
- codisposed materials such as PCP reduced the sorptive retention of PCDDs in soil by as much as three times. The decreased attenuation was attributed to cosolvent effects, where the aqueous solubility of PCDDs was increased by the presence of PCP in water/methanol solutions. The effects of diesel fuel on mobility could not be ascertained because of the formation of stable emulsions, and the conversion of diesel to residual saturation.
- sorption equilibria occurred within two days for all PCDDs studied. Desorption of PCDDs was also noted, though the process was limited by kinetics, with 30 to 50 days required for 90% desorption.

This study illustrated that dioxins largely partition to soil, but can slowly desorb if conditions change. Additionally, dioxins are more mobile in mixtures of organic chemicals than they are acting alone. It is likely that this facilitated transport of PCDDs and PCDFs has occurred at wood preserving sites where both PCP and diesel are present.

1.5.1.2.2 Behaviour of Chlorophenols, PCDDs and PCDFs in Air

Chlorinated phenols can exist in the air above abandoned wood preserving sites as vapours or as molecules adsorbed to suspended particulate matter. Waste PCP-based mixtures contain a mixture of chlorophenols, and Henry's Law values (K_H) for individual components can be used to qualitatively assess which compounds may vaporize. Quantitative estimations will not be reliable, because of the influence of the mixture on individual components.

Chlorophenols can be considered to be negligibly volatile, with Henry's Law Constants ranging from 10^{-8} to 10^{-6} atm·m^3/mol (Appendix A). Consequently, volatilization of chlorophenols from water is not expected to be significant using the guideline value of 10^{-5} atm·m^3/mol outlined by Thomas (1982). Chlorophenols existing as vapours and as part of particulate matter are subject to photochemical degradation. Photolysis of chlorophenols occurs by excitation and disruption of carbon-halogen bonds, and involves sequential dechlorination to lower chlorophenols, with eventual conversion to carbon dioxide and inorganic forms of chlorine (Miller et al., 1988; Crosby, 1981; U.S.EPA, 1987c). Some chlorophenols and phenoxyphenols can undergo photochemical ring closure to form PCDDs (U.S.EPA, 1987c; Wong and Crosby, 1978). The photochemical decomposition of chlorinated phenols adsorbed to particulate matter will depend on the light scattering/adsorbing properties of the solid (U.S.EPA, 1987c).

Dioxins and furans can also be transported through air as vapours or adsorbed to airborne particulate matter. The volatility of PCDDs and PCDFs decreases with increasing chlorine substitution. These compounds are approximately as volatile as chlorophenols (Appendix A). For example, the Henry's Law Constant for 2,3,7,8-TCDD and PCP are both about 10^{-6} atm·m^3/mol. Volatilization of PCDDs and PCDFs, even the least volatile forms, has been measured in the gas of unsaturated soil (U.S.EPA, 1987c).

Volatilization of these compounds is enhanced when the molecules are incorporated into thin films of water (Freeman and Shroy, 1986; U.S.EPA, 1987c), as gaseous partitioning is greater from the aqueous as opposed to solid phases, as predicted in comparing the respective Henry's Law Constants and vapour pressures.

Dioxin and furan vapours, as well as molecules adsorbed to airborne material, are believed to undergo photolytic decomposition through successive dechlorination, though the rates are expected to be slower than in the aqueous phase (U.S.EPA, 1987c; U.S.EPA, 1984b). Increasing chlorine substitution is believed to decrease the rate of photodecomposition (U.S.EPA, 1984b). No information on the half-life of gaseous and particulate-sorbed forms is available in the literature.

1.5.1.2.3 Behaviour of Chlorophenols, PCDDs and PCDFs in Surface Water

Chemicals from abandoned PCP wood preserving sites may contact surface water bodies through the erosion and transport of contaminated sediment, and from the discharge of contaminated groundwater. The compounds discharged from groundwater may be in soluble forms, adsorbed to suspended particulates, or be part of a separate phase such as an emulsion, droplet, or LNAPL. Regardless of the physical form, chlorophenols in surface water undergo adsorption, volatilization, photodegradation and biodegradation.

Chlorophenols are hydrophobic in the protonated form, but much more water soluble in the ionized form (section 1.5.1.2.1). Consequently, the amount of adsorption of chlorophenols to aqueous sediments will depend on the pH of the environment. Another important factor is the organic carbon content of the sediment. Karickhoff and coworkers (1979) concluded that the sediment partition coefficient (K_p) for chlorinated hydrocarbons was directly related to the organic carbon content of the sediment. They also concluded that the fines fraction (<50 μm particles) was a much better sorbent than the sand fraction. Within the range of fine particles, differences in sorption were largely related to differences in organic carbon content.

Contaminated sediment may settle on the bottom or be suspended, depending on the flow velocity, as related to bed shear. Suspended particulates may be transported across large distances. Contaminants adsorbed to settled particulates may be incorporated into the food chain by bottom dwellers (benthic organisms), which are subsequently eaten by fish. Contaminated sediment, as well as blobs and micelles (emulsified microdroplets) which settle, continuously partition chemicals to the aqueous phase, and consequently represent a long-term contamination source (Pierce and Victor, 1978). Pierce and Victor (1978), as well as Hwang and Hodson (1986) hold that biodegradation of chlorophenols is faster in the sediment than in the water because of greater microbial activity.

Chlorophenols are negligibly volatile (section 1.5.1.2.2), though significant losses of chlorophenols from water bodies have been reported to occur (U.S.

Department of Agriculture, 1980). Volatilized chlorophenols are subject to photolytic decomposition, as discussed in section 1.5.1.2.2.

Soluble, adsorbed and distinct-phase chlorophenols in aqueous environments are all subject to photodecomposition. Hwang and Hodson (1986) made several conclusions about the photodecomposition of chlorophenols in estuarine water:

- photolysis was a more significant <u>primary</u> transformation process than biodegradation. However, the photoproducts were rapidly degraded by microbes.
- photodecomposition rates were most sensitive to depth, as well as to the presence of dissolved substances and suspended particulates which absorb light. In general, photodecomposition rates decreased with depth because of reduced light penetration. For example, the half-life of PCP was 2.4 h at 3.8 cm depth, and increased exponentially to 22 d at 5.5 m depth. Dissolved and suspended matter such as humic substances can contribute to decomposition by mediating photosensitized reactions or decrease photodecomposition by absorbing light.
- at depths below 20 cm in their study estuary, degradative processes other than photolysis predominated.

Studies on the photolysis of chlorophenols in water have identified successive dechlorination, hydroxylation and ring cleavage as the processes leading to mineralized end products (Wong and Crosby, 1978; U.S.EPA, 1987c).

Finally, Pierce and Victor (1978) discuss a case in which wastewater from PCP wood preservation was spilled into a freshwater lake. These authors made the following observations:

- extensive fish kills occurred.
- the major PCP degradation products observed were pentachloroanisole and two tetrachlorophenol isomers. The relative amounts of tetrachlorophenol and PCP implied that photodecomposition of PCP to tetrachlorophenol had occurred in the wastewater holding pond. Pentachloroanisole was believed to have arisen from microbial decomposition of PCP in the sediment.
- The fish were observed to bioconcentrate PCP and its degradation products rapidly. The concentration in fish decreased as the concentration in water decreased. It took 10 months for concentrations in water and fish to return to background levels.
- Sediment and leaf litter retained high concentrations of PCP and its degradation products throughout the two-year investigation period.

This study, as well as one by Fox and Joshi in U.S.EPA (1987c), highlight the differences in chlorophenol photolysis between laboratory single compound studies and that observed in wastes from PCP wood preservation. Specifically, PCP and its photodecomposition products are apparently more persistent in the environment than predicted in laboratory studies.

Little research has been done on the aquatic fate of the PCDDs and PCDFs present in PCP-based wood preserving mixtures. Some work has been done on the highly toxic 2,3,7,8-TCDD, but this compound is not present in North American PCP formulations. U.S.EPA (1984b) postulated that PCDDs are subject to volatilization and sorption to sediment in aquatic environments, though no quantitative volatilization data were presented. Volatilized PCDDs would presumably undergo photodecomposition. U.S.EPA (1986a) concluded that abiotic reactions such as photodecomposition and hydrolysis, as well as biodegradation were not likely to occur to PCDFs in aquatic environments, and that adsorption to sediment would likely be the ultimate furan sink.

1.5.1.2.4 Behaviour of Chlorophenols in Groundwater

Waste PCP mixtures form a distinct oily layer (LNAPL) on the water table in an unconfined aquifer (section 1.5.1.1). An LNAPL will migrate with the hydraulic gradient as a continuous distinct phase until the plume mass is converted into residual saturation. During this migration, distinct phase droplets (blobs) may break off from the continuous phase because of the shear of the underlying groundwater on the less mobile hydrocarbon phase. The velocity differences between the two phases are due to viscosity differences. Additionally, a continuous partitioning of the components in waste PCP fluid to groundwater will occur by molecular diffusion in response to concentration gradients. Walters and coworkers (1989) also found that stable diesel oil/water emulsions may form at realistic flow rates in an aquifer as a result of soil-diesel contact, presumably due to the tortuosity of the flow path. This finding contradicts the generally-held belief that groundwater systems cannot generate sufficient turbulence to form stable emulsions.

In summary, waste PCP mixtures may exist in an aquifer as a continuous distinct phase (LNAPL), discontinuous distinct phase (blobs), emulsion, residual saturation, and as molecules dissolved in solution and adsorbed to soil. The relationship between the different forms is illustrated in Figure 1.5-4.

Molecules partitioned to the solid or aqueous phases may undergo some subsequent reaction such as complexation or biodegradation. Movement of aqueous phase chlorophenols will be pH-dependent, as the ionized form is more soluble than the protonated form.

All of the forms that waste PCP wood preserving mixtures may take in groundwater can undergo facilitated transport. Facilitated transport refers to any process which speeds the transport of a pollutant beyond what is predicted by idealized Darcian flow and equilibrium sorptive interactions with an immobile solid phase (Huling, 1989). U.S.EPA (1987c) postulated that facilitated transport is occurring at a number of PCP-based wood preserving sites. Two mechanisms may act to facilitate transport at PCP sites: cosolvation and particle transport (Keely, 1989; Huling, 1989).

Cosolvation is the process where a hydrophobic contaminant dissolves in groundwater above its aqueous solubility because of the presence of another solvent. For example, the presence of PCP in groundwater increases the aqueous solubility of PCDDs (Walters et al., 1989). Cosolvent effects are believed to only be significant at cosolvent concentrations above a few

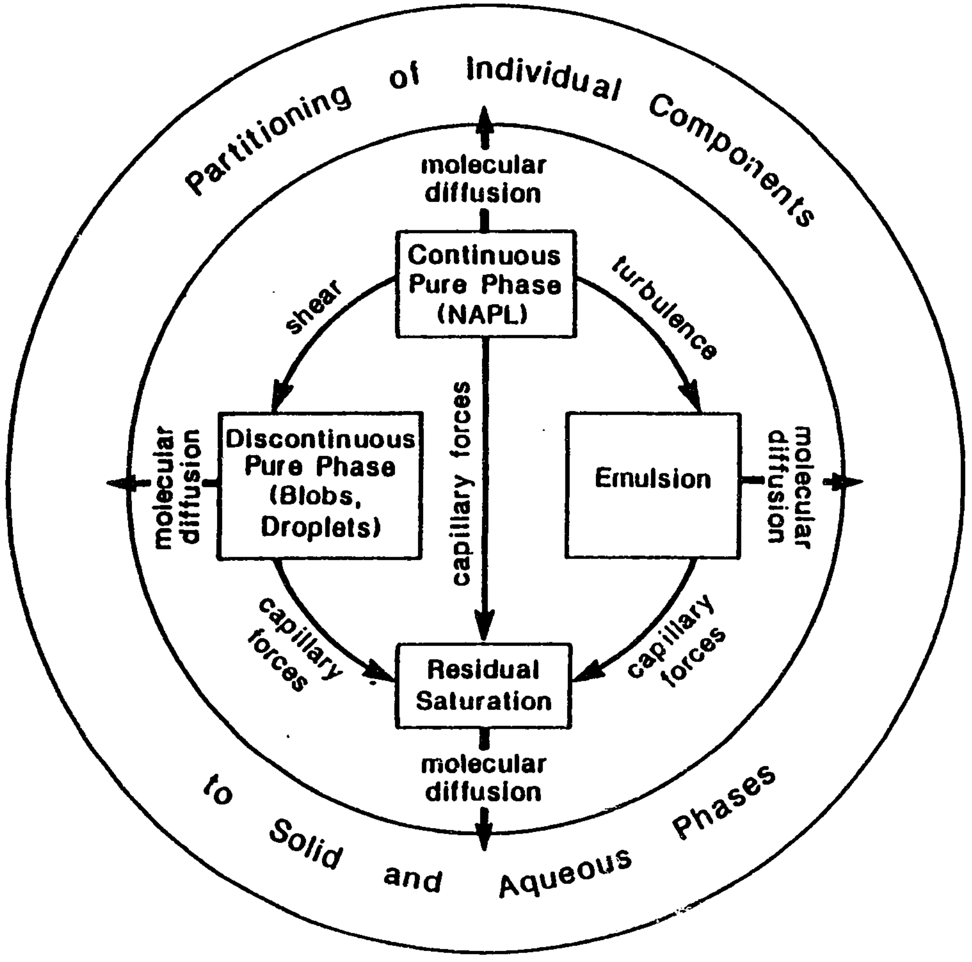


FIGURE 1.5-4 : RELATIONSHIP BETWEEN THE DIFFERENT FORMS OF ORGANIC WOOD PRESERVING CHEMICALS IN AN AQUIFER

percent (note: 1 percent = 10 000 ppm) (Huling, 1989; Keely, 1989). At PCP wood preserving sites, creosote and diesel fuel are the likely cosolvents. However, it is unlikely that their concentrations would be sufficient to cause significant cosolvent effects. Adequate levels may be achieved directly beneath the sludge pond, but these concentrations would decrease with depth through dispersion and dilution.

A more likely mechanism of facilitated transport at wood preserving sites involves colloidal particles. Colloids (particles with diameters less than 10 µm) are mobile in aquifers, and may be organic or inorganic in nature. Organic colloids can be divided into biocolloids, such as spores and viruses, macromolecules, such as humic substances, and oil droplets. Inorganic colloids include clay particles, metal oxides and inorganic precipitates (Huling, 1989). Distinct-phase hydrocarbon or hydrophobic contaminants may partition to colloids in aqueous solutions rather than to immobile aquifer material, facilitating greater contaminant migration.

1.5.1.2.5 Overall Partitioning of Waste PCP-Based Wood Preserving Mixtures in the Environment

Sims and coworkers (1986) performed a study on the partitioning of PCP sludge waste between three different environmental media. The constituent concentrations in this study were generally in the ratio of 10 000:10:1 for oil:water:air phases. Hattemer-Frey and Travis (1989) used a partitioning model to evaluate the transport and fate of pure PCP. Their results showed that in the environment PCP partitions mainly into soil (96.5% of the total PCP released).

In addition, a qualitative description of constituent partitioning can be completed by considering the physico-chemical properties outlined in Appendix A. These properties imply:

- chlorophenols are moderately to highly soluble, with some solubilities exceeding 1000 mg/L. Consequently, partitioning to the aqueous phase may be significant;
- chlorophenols partition largely to organic matter in soil, as indicated by the range of log k_{oc} values (3 to 5);
- chlorophenols are negligibly volatile from water, as their k_H values are all below 10^{-6} atm·m^3/mol. They are also negligibly volatilized from the solid phase, as implied by their vapour pressures;
- chlorophenols partition predominantly to the distinct (oil) phase, as predicted by the range of log k_{ow} values (3 to 6). These values also imply significant bioconcentration of chlorophenols in lipid-rich tissue; and
- dioxins present in PCP-based mixtures possess extremely low aqueous solubilities, moderate volatilities from water, and large affinities for organic (oil, lipid) phases. The k_{ow} values imply much greater bioconcentration of dioxins in lipid-rich tissue compared to chlorophenols.

The study results and qualitative predictions, in conjunction with observations at contaminated wood preserving sites, imply that the constituent chemicals in PCP-based mixtures preferentially exist in the oil phase, but will partition in decreasing amounts to soil, water and air. Significant bioconcentration of most constituents is also likely to occur.

1.5.1.3 Environmental Partitioning of Chemicals in Creosote-Based Mixtures

Creosote is comprised of polynuclear aromatic hydrocarbons (PAHs), phenolics and heterocyclic compounds (Table 1.4-6). The environmental behaviour of the constituent compounds in the mixture is much different from that of the individual chemicals acting alone, because of competitive and inhibitory interactions within the mixture. The behaviour of these chemicals in a multimedia system is best determined by partition coefficients, as discussed in section 1.5.1.2. In general, partition equilibria provides a qualitative indication of which phase in a multimedia environment will concentrate contaminants. Partition coefficients are derived for each constituent in a mixture, but effective partitioning will be site-specific. Consequently, this section will focus on the general mechanisms which cause the partitioning, rather than present specific values. Significant differences exist in the environmental behaviour of PAHs, phenolics and heterocycles. Partitioning of some of the phenolic compounds (chlorophenols), as well as that of the oxygen-containing heterocycles (dibenzofurans) was evaluated in section 1.5.1.2. Consequently, the environmental behaviour of PAHs as well as nitrogen- and sulfur-containing heterocycles requires assessment here. PAHs comprise roughly 85% of creosote, so the majority of this section will focus on their partitioning.

1.5.1.3.1 Behaviour of PAHs in Soil

PAHs are neutral, nonpolar organic molecules containing two or more fused benzene rings. These compounds generally have low aqueous solubilities, and a corresponding affinity for solid surfaces. Two major types of soil surface are responsible for PAH adsorption: organic macromolecules adsorbed to soil particles, and soil mineral surfaces alone.

Organic macromolecules such as humic material are electrostatically neutral as a whole. However these large molecules can contain localized dipoles, due to electron movement. These dipoles can induce momentary electrostatic polarizations on the soil surface, resulting in van der Waals binding between macromolecule and soil surface. In general, van der Waals forces are weak. However, because of the proximity of the molecule and soil surface, as well as the many points of contact possible, strong bonding may result (Dragun, 1988). PAHs preferentially partition to bound organic matter such as humic material, though the specific interactions are not well understood.

Soil mineral surfaces alone, especially clays, are also capable of adsorbing PAHs from solution. It is believed that mineral surfaces possess hydrophobic regions to which PAHs bind, though the actual mechanisms are also not well understood (Dragun, 1988).

Larger PAHs are more strongly adsorbed to soil than smaller PAHs, possibly because of greater van der Waals binding (Mahmood and Sims, 1985; Dragun, 1988; Rosenfeld and Plumb, 1988). Several investigators have developed empirical equations which relate PAH adsorption to the compound's octanol/water partition coefficient and aqueous solubility (for example: Dzombak and Luthy, 1984). The applicability of these relations to PAHs in mixtures has not been evaluated.

Most PAHs do not possess functional groups which can ionize with changing pH. Consequently, PAH adsorption is not affected by moderate pH changes. For extreme pH fluctuations however, adsorption to clay particles may be affected by the change in net surface charge resulting from interactions with ions in solution.

Within the soil, PAHs may repartition to pore gases or soil water if environmental conditions change. Adsorbed and dissolved PAHs are subject to microbial degradation (U.S.EPA, 1984c).

1.5.1.3.2 Behaviour of PAHs in Air

Several PAHs in creosote have been found to be volatile at wood preserving sites. For example, McGinnis (1984) found that four major components are volatilized from waste creosote fluids: naphthalene, methyl naphthalenes, acenaphthene, and fluorene. This finding is consistent with what would be expected considering compound vapour pressure alone (Appendix A). Naphthalene was by far the most volatile, comprising 83% of the volatile PAH fraction. A study by Sims and coworkers (1988) using PAHs individually or in mixtures confirmed that naphthalene and isomers of methylnaphthalene are the most volatile PAHs. In addition, less volatile PAHs can enter the atmosphere adsorbed to suspended particulate matter.

Vapour-phase PAHs are subject to photochemical degradation, as well as chemical reactions with hydroxide radicals, ozone, and gaseous nitrous oxides (U.S.EPA, 1984c). PAHs adsorbed to suspended particulate matter can be removed from the atmosphere by wet or dry deposition, as well as by photochemical degradation (U.S.EPA, 1984c).

Photo-oxidation of vapour-phase PAHs has been well documented. PAHs readily absorb solar radiation and undergo direct photolysis (Sims et al., 1986). Some PAHs are photo-transformed into cytotoxic and mutagenic intermediates (Sims et al., 1986). Both gaseous PAH molecules and PAHs adsorbed to airborne particulates are subject to photodecomposition. In the vapour phase, PAHs exhibit half lives of less than one day (U.S.EPA, 1984c). Some evidence exists that PAHs adsorbed to airborne particulate matter may be more recalcitrant to photodecomposition than their vapour-phase counterparts (Korfmacher et al, 1980). Consequently, particulate-sorbed PAHs may be more environmentally stable, and could be transported off-site.

1.5.1.3.3 Behaviour of PAHs in Surface Water

Chemicals from abandoned creosote wood preserving sites may contact surface water bodies through the erosion and transport of contaminated sediment, and from the discharge of contaminated groundwater. PAHs discharged from groundwater may be in soluble forms, adsorbed to suspended particulates, or be part of a separate oil phase such as an emulsion, droplet or DNAPL. Regardless of the physical form, PAHs in surface water undergo adsorption, volatilization, photodegradation and biodegradation.

PAHs are hydrophobic compounds, and consequently largely partition to the solid (sediment) phase in aquatic environments (Heitkamp and Cerniglia, 1987). Karickhoff and coworkers (1979) concluded that the sediment partition coefficient (K_p) for aromatic hydrocarbons was directly related to the organic carbon content of the sediment. They also concluded that the fines fraction (<50 μm particles) was a much better sorbent than the sand fraction. Contaminated sediment may settle on the bottom or be suspended, depending on the flow velocity, as related to bed shear. In addition to sorption to sediment, PAHs in aquatic environments also bind with dissolved humic material (DHM). McCarthy and Jimenez (1985) observed a direct relationship between the hydrophobicity of a PAH and the affinity for binding to DHM. Enfminger and Ahlert (1987) postulated that DHM facilitates transport of PAHs in aquatic environments because it competes for PAHs with less mobile sediments.

Contaminants adsorbed to settled particles may be incorporated into the food chain by bottom dwellers (benthic organisms), which are subsequently eaten by fish. Contaminated sediment, as well as blobs and DNAPL which settle, continuously partition chemicals to the aqueous phase, and consequently represent a long-term contamination source. Sediment-bound PAHs may undergo microbial degradation, though the rates may be very slow. For example, Heitkamp and Cerniglia (1987) studied the microbial mineralization of six PAHs in sediment:freshwater microcosms.

Study half lives varied from 2.4 weeks for naphthalene to over 300 weeks (6 years) for benzo[a]pyrene. PAHs were much more persistent in microcosms using pristine sediment than in those using sediment chronically exposed to PAHs.

Some of the constituents of creosote are volatile, and may move from the aqueous to gaseous phases in surface water bodies, as predicted by the Henry's Law Constants. Volatilized PAHs are subject to photolytic decomposition, as discussed in section 1.5.1.3.2. Aqueous phase and particulate sorbed PAHs in surface water bodies also undergo photodegradation (U.S.EPA, 1984c). Some evidence exists that intermediate products arising from photolysis of PAHs accumulated in plants and fish may be toxic. For example, Landrum and coworkers (1987) noted marked increases in anthracene toxicity to fish in illuminated artificial stream microcosms. The toxicity increase was attributed to the interaction of bioaccumulated parent PAH and light, and not to the action of externally formed photodegradation products.

1.5.1.3.4 Behaviour of PAHs in Groundwater

Waste creosote mixtures form a distinct oily phase (DNAPL) on the bottom of an aquifer when present in amounts in excess of their aqueous solubility (section 1.5.1.1). DNAPL movement is controlled by gravity, and DNAPLs will attempt to achieve the lowest elevation in an aquifer, regardless of the prevailing hydraulic gradient (Keely, 1989). DNAPL migration ceases when the plume mass is converted into residual saturation or when a confining geologic formation is encountered. During DNAPL migration, distinct phase droplets (blobs) may break away from the continuous phase because of the shear of the overlying groundwater on the less mobile hydrocarbon phase. The velocity differences between the two phases are due to viscosity differences. Additionally, a continuous partitioning of the components in waste creosote fluid to groundwater will occur by molecular diffusion in response to concentration gradients. Creosote/water emulsions are also believed to occur at creosote wood preserving sites (U.S.EPA, 1987c; Rosenfeld and Plumb, 1988).

In summary, waste creosote fluid may exist in an aquifer as a continuous distinct phase (DNAPL), discontinuous distinct phase (blobs), emulsion, residual saturation, and as molecules dissolved in solution and adsorbed to soil. The relationship between the different forms is illustrated in Figure 1.5-4. Molecules partitioned to the solid or aqueous phases may undergo some subsequent reaction such as complexation or biodegradation.

All of the forms that waste creosote wood preserving mixtures may take in groundwater can undergo facilitated transport. U.S.EPA (1987c) postulated that facilitated transport is occurring at a number of creosote-based wood preserving sites. Two mechanisms may act to facilitate transport at these sites: cosolvation and particle transport. These processes are described in greater detail in section 1.5.1.2.4.

Cosolvent effects are only believed to be significant at cosolvent concentrations above a few percent (Huling, 1989; Keely, 1989). At creosote wood preserving sites, PCP-based fluids and diesel fuel are the likely cosolvents. However, it is unlikely that their concentrations would be sufficient to cause significant cosolvent effects at any location other than directly beneath the sludge pond.

A more likely mechanism of facilitated transport at creosote wood preserving sites involves organic and inorganic colloids, such as humic substances and clay particles. For example, the binding of PAHs to dissolved humic material has been shown to occur (section 1.5.1.3.3). Droplets or dissolved molecules bound to inorganic or organic colloids will migrate much greater distances in an aquifer than those adsorbed to immobile solids.

Because of the chemical complexity of waste creosote mixtures, studies on the behaviour of individual PAHs in groundwater may not reflect the behaviour of the compound when part of creosote. Consequently, observed contaminant distributions at former creosote facilities are the best predictors of PAH mobility in groundwater at other wood preserving sites. In one study, Rosenfeld and Plumb (1988) compared the contaminant distributions in groundwater at five wood treatment facilities. All of the facilities used creosote, and some also used PCP- and CCA-based fluids. Relevant study findings were:

- a significant consistency in organic compound detection was noted between the sites; twenty-seven organic compounds were consistently found at the five locations. These results suggest a fairly strong industry-specific chemical fingerprint in groundwater.

- at one site distinct phase creosote was sampled, and the results compared with those of the overlying groundwater. The results indicated a wide range of distinct phase/aqueous phase partitioning between the PAHs. For example, the ratio of naphthalene in the oil phase to that in the groundwater was 2000, whereas the ratio for benzo[a]pyrene was 19 000.

The observed differences in PAH partitioning between oil and aqueous phases are likely due to differences in octanol/water partition coefficients (Enzminger and Ahlert, 1987; Sims et al., 1986).

1.5.1.3.5 Overall Partitioning of PAHs in the Environment

Sims and coworkers (1986) performed a study on the partitioning of creosote sludge waste between three different environmental media. Their results indicate that PAHs partition between oil:water:air phases in the range of 10 000:10:1 to 100 000:100:1. These results imply that creosote-based PAHs preferentially remain in the waste (oil) phase.

In addition, a qualitative description of constituent partitioning can be completed by considering the physico-chemical properties outlined in Appendix A. These properties imply:

- the aqueous solubility of PAHs decreases with increasing molecular size. PAHs range from negligibly to moderately soluble, with few values exceeding 1 mg/L. Consequently, PAHs are significantly less soluble than chlorophenols;
- corresponding to decreasing aqueous solubilities, k_{oc} values for PAHs increase with increasing mass. The range of log k_{oc} values

(1 to 8) implies significant accumulation of most PAHs in the soil phase;

- k_H and vapour pressure values imply that volatilization of some PAHs from water and a pure phase may be substantial. However an entire range of values exists, where some of the larger PAHs are of extremely low volatility;
- log k_{ow} values range from 3 to 8, implying PAHs partition predominantly to the oil phase, and that significant bioconcentration of PAHs in lipid-rich tissue is likely to occur.

The results of the Sims and coworkers (1986) study, in conjunction with the qualitative predictions and observations at contaminated wood preserving sites, imply that the PAHs in creosote preferentially exist in the oil phase, but will partition in decreasing amounts to soil, water and air. Significant bioconcentration of most PAHs is also likely to occur.

1.5.1.3.6 Environmental Partitioning of Nitrogen and Sulfur Heterocycles

A qualitative evaluation of nitrogen and sulfur heterocycle partitioning can be accomplished by considering the environmental properties of the contaminants outlined in Appendix A:

- quinoline and aniline are both highly water soluble, which implies they may preferentially partition to the aqueous rather than soil phases at a site, and would thus be more mobile than compounds such as chlorophenols and PAHs, which are largely affixed to soil;
- using the guideline values of Thomas (1982), nitrogen heterocycles such as quinoline and aniline are negligibly volatile in water (k_H

$= 10^{-6}$), whereas sulfur heterocycles such as benzothiophene and dibenzothiophene would undergo significant volatilization from water ($k_H = 10^{-4}$); and

- quinoline and aniline possess low k_{ow} values, consistent with their large aqueous solubilities. In contrast, benzothiophene and dibenzothiphene possess larger k_{ow} values, similar to those of three-ring PAHs. Consequently, quinoline and aniline would not be expected to remain in significant amounts in the oil phase at a creosote site, or bioconcentrate in animal tissue. However, the thiophenes would typically be expected to bioconcentrate in lipid-rich tissue, which is of concern considering their low threshold detection levels for tainting (section 1.4.2.3.1).

1.5.2 Environmental Transport and Fate of Water-Based Wood Preserving Mixtures

Chromated copper arsenate (CCA) wood preserving mixtures contain from 1.5 to 4.0% CCA dissolved in water. The inorganic forms of copper (Cu), chromium (Cr) and arsenic (As) generally comprise less than 1% of the working fluid (Table 1.4-11). Consequently, the environmental behaviour of waste CCA preservative most closely resembles that of water. Some differences in behaviour may exist because of the ionic strength of the CCA mixture, which does not exist with dilute pore water. A complete evaluation of the environmental behaviour of waste CCA fluid must consider the movement of the bulk fluid, as well as the partitioning of the individual components.

1.5.2.1 Transport and Fate of the Bulk Solution

CCA drips and sludges released on the ground surface will percolate down through the soil in response to gravity. The rate of infiltration will depend on soil porosity and moisture content. For any given soil, CCA wastes will generally infiltrate faster than would creosote or PCP wastes, because of much lower viscosity. CCA wastes also generally migrate quicker because their progression is not resisted by any interfacial tension.

Soil particles are surrounded by an extremely thin film of water called adhesive or hygroscopic water. This class of water may occupy from 3 to 16% of the pore volume, but is not mobile, as it is held under tensions varying from 31 to 10 000 atm (Dragun, 1988). The next layer of water surrounding soil particles is called capillary water. This class of water can occupy from 4 to 18% of the pore volume, and is also unresponsive to gravity, as it is held under tensions ranging from 0.1 to 31 atm (Dragun, 1988). The matric potential is the dominant potential holding hygroscopic and capillary water adjacent to the soil particle surface, and is defined as the molecular electrical attraction pressure potential between the soil and surrounding water (Utah State, 1989). This potential weakens with distance from the particle (Utah State, 1989). Additional water added to soil containing hygroscopic and capillary water cannot be held by the matric potential against gravity, and is correspondingly termed free water. The relationship between the different types of soil water is illustrated in Figure 1.5-5.

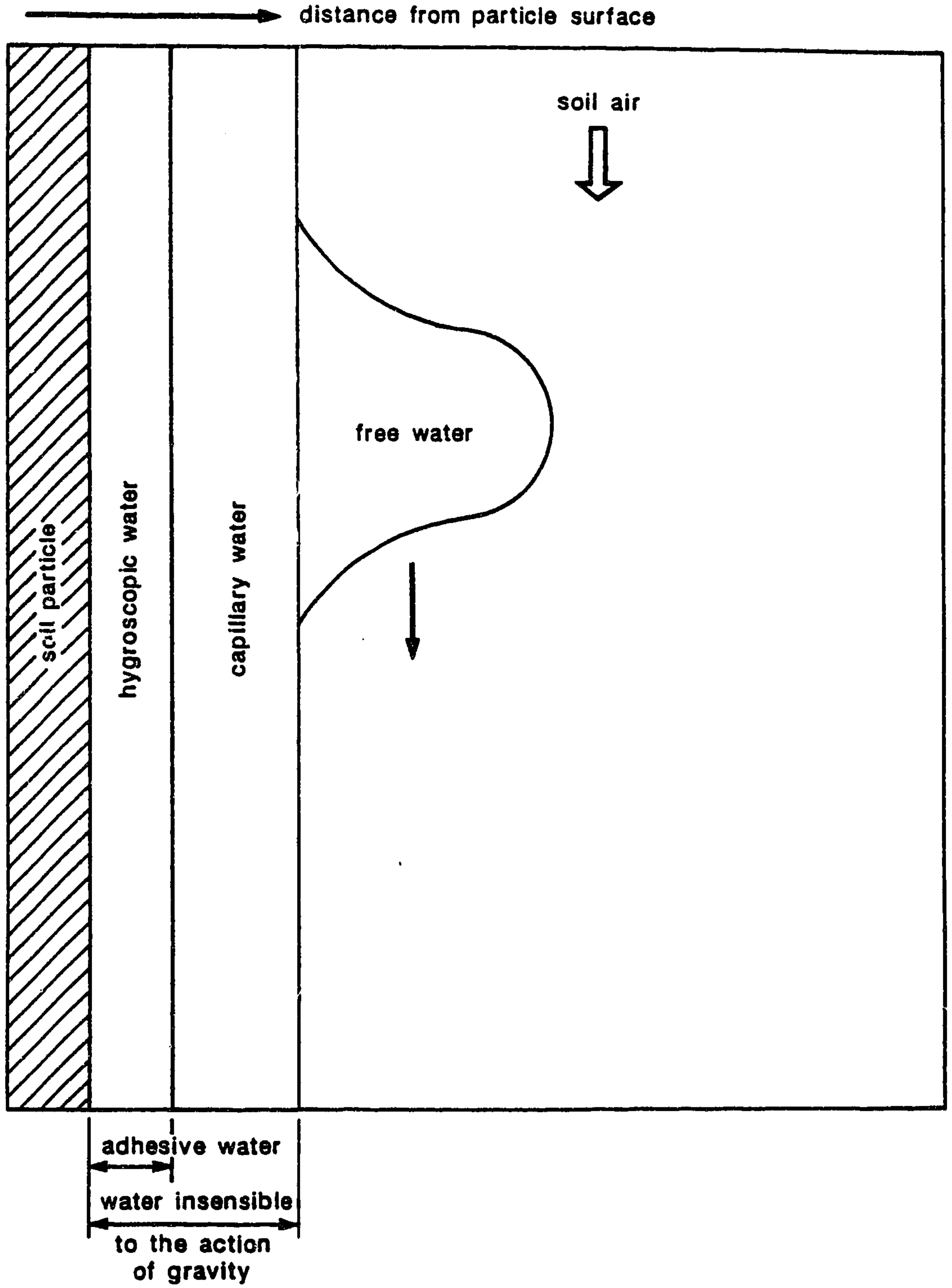


FIGURE 1.5-5 : RELATIONSHIP BETWEEN THE CLASSES OF SOIL WATER (ADAPTED FROM DRAGUN, 1988)

As waste CCA preservative percolates down through the soil, its behaviour will depend on the amount of capillary and hygroscopic water present. In most soils, evaporation eliminates some fraction of the capillary water (hygroscopic water is adsorbed too tightly to be liberated by evaporation). As a result, free CCA mixture will be converted to capillary water by the matric potential. Depending on the soil moisture content and the amount of percolating fluid, two scenarios are possible:

- **the mass of free fluid may be exhausted through conversion to capillary water, in which case downward progression will cease. This situation usually occurs for the soil drip pad at CCA sites (Figure 1.5-6).**
- **the mass of CCA mixture may exhaust the matric potential, and free mixture will continue migrating towards the water table. This situation generally occurs for the sludge pond at CCA sites (Figure 1.5-6).**

CCA preserving mixture is freely soluble in water, and also has the same viscosity. Consequently, CCA preservative arriving at the water table is completely solubilized by groundwater. This is in contrast to oil-based preservatives such as creosote and PCP, which form distinct phases in most groundwater systems.

1.5.2.2 Environmental Partitioning of Individual CCA Components

The use and limitations of partition equilibria were discussed in section 1.5.1.2. In general, partition equilibria provides a qualitative indication of which phase in a multimedia system will concentrate contaminants.

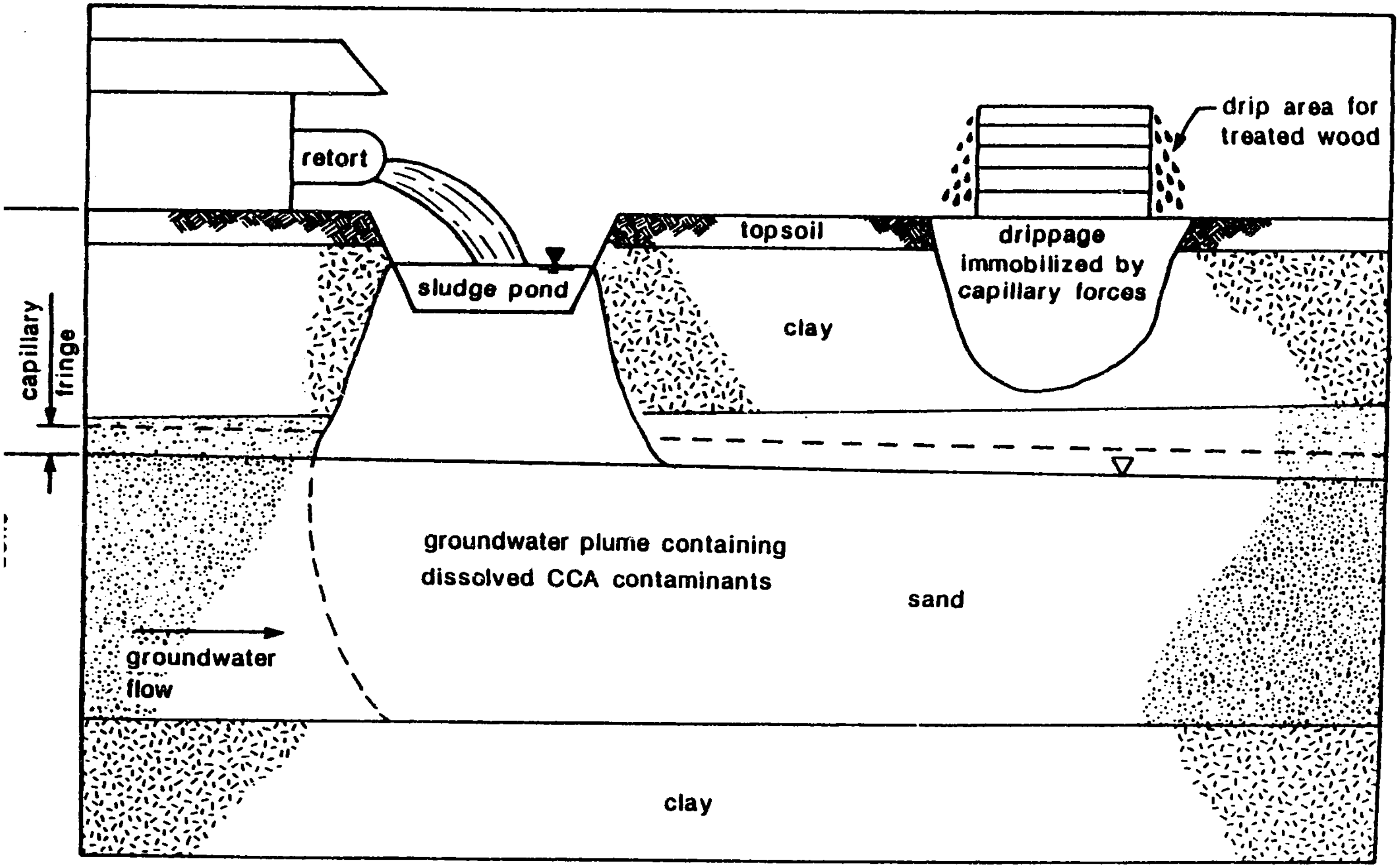


FIGURE 1.5-6 : ENVIRONMENTAL FATE OF EMISSIONS FROM CCA-BASED WOOD PRESERVATION

Because partition coefficients are site-specific, the general mechanisms which cause the partitioning will be discussed in this section.

1.5.2.2.1 Behaviour of Cu, Cr, As in Soil

Behaviour of Cu in Soil

At pH values and oxygen concentrations which predominate in most soils, copper (Cu) exists as a divalent cation (Cu^{2+}) (Bolt and Bruggenwert, 1976). This is also the valence of copper in CCA concentrate. Copper is strongly bound to silicate clays, oxides of iron, aluminum and manganese, and organic matter in soil (Pickering, 1979; Environment Canada, 1988c; Bolt and Bruggenwert, 1976; McBride, 1981; Benjamin and Leckie, 1981). The adsorption of Cu by clay minerals is believed to be due to the attraction between cationic copper and the minerals, which have a bulk negative charge resulting from isomorphous substitution. In isomorphous substitution, cations in the clay lattice are replaced with cations of similar size, but lesser charge, leaving unsatisfied negative valences from oxygen atoms. The attraction between copper and organic (humic) matter is due to the presence of anionic functional groups on the humic molecules.

Copper may be adsorbed from soil solutions as an exchangeable cation, and may subsequently be replaced by another cation if dictated by the chemical potential of the soil solution (typically in response to greater concentrations). However, more permanent copper binding in soils is possible. For example, Cu^{2+} ion can be directly bonded to carboxylic and phenolic functional groups on humic molecules (McBride, 1981). Copper may also be more permanently removed from solution through isomorphous substitution in primary or secondary minerals. McBride (1981) concluded that exchangeable copper represents a small part of the total copper in most soils, and that the bulk of the copper is bound to organic matter, occluded in oxides, and substituted in minerals.

The sorption of copper to clay minerals and organic matter is pH-dependent; copper adsorption decreases with decreasing pH, because of competition from H^+, as well as from Mg^{2+}, Fe^{3+} and Al^{3+} released from minerals in acidic environments (Pickering, 1979; Benjamin and Leckie, 1981).

No studies have indicated that copper undergoes any valence change or methylation reaction once adsorbed to soil. Consequently, the copper cycle in soils is quite simple.

Because fine-grained soils have a net negative charge, cations are more strongly bound to them than anions. Therefore, Cu^{2+} is generally less mobile in soils than other metals such as As and Cr, which predominantly exist as anionic complexes (McBride, 1981; Bolt and Bruggenwert, 1976).

Behaviour of Cr in Soil

Chromium (Cr) exists in the +6 valence in CCA concentrate, and may exist in the +3 and/or +6 valences in soil. The actual chromium form will depend on the redox potential and pH of the soil environment.

It has been widely held that Cr^{6+} forms are not stable in soil environments due to the presence of readily oxidizable organic material, and that reduction to Cr^{3+} compounds will occur (for example: Bolt and Bruggenwert, 1976; NRCC, 1976; Bartlett and Kimble, 1976). However, a study by Bartlett and James (1979) demonstrated that under conditions prevalent in many soils, Cr^{3+} can be oxidized to Cr^{6+}. The oxidation reaction in the study was mediated by the presence of oxidized manganese (Mn), which served as the electron acceptor. Consequently, compounds containing Cr^{6+} as well as those containing Cr^{3+} may exist at CCA wood preserving sites, and the mobility of each form in soil must be considered.

Hexavalent chromium (Cr^{6+}) can exist as either chromate (CrO_4^{2-}) or dichromate ($Cr_2O_7^{2-}$) in soil. Because these complexes are anionic, sorption is limited in fine-grained soils. Chromate (CrO_4^{2-}) is adsorbed by soil colloids including iron and aluminum oxides, kaolinite and montmorillonite (Zachara et al., 1989). Soil colloids bind chromate by surface coordination, and competition for coordination sites with other anions such as SO_4^{2-} occurs (Zachara et al., 1989). Adsorption increases with decreasing pH, because hydrogen ions (H^+) neutralize some of the negatively-charged surface hydroxyl sites (Zachara et al., 1989). Compounds containing Cr^{6+} are generally considered to be highly mobile in soil (Sims et al., 1984; Thorsen and Stensby, 1982; NRCC, 1976; Bartlett and James, 1979). This observation is of some concern, because Cr^{6+} is generally more toxic than Cr^{3+} (section 1.4.3.3.2).

Trivalent chromium (Cr^{3+}) can exist as either a cation (Cr^{3+}) or as part of an anionic complex (CrO_2^-) in soil, depending on the pH and redox potential. Trivalent chromium compounds are believed to undergo much greater adsorption in soil than hexavalent forms (Bartlett and James, 1979). Cr^{3+} is adsorbed by clay particles, organic matter, and also forms low solubility precipitates (Thorsen and Stensby, 1982; NRCC, 1976; Bolt and Bruggenwert, 1976). However, CrO_2^- is likely more mobile than Cr^{3+} in fine-grained soils because of repulsion with the negative surface charges. Sims and coworkers (1984) concluded that <u>all</u> forms of Cr^{3+} are readily sorbed by soils.

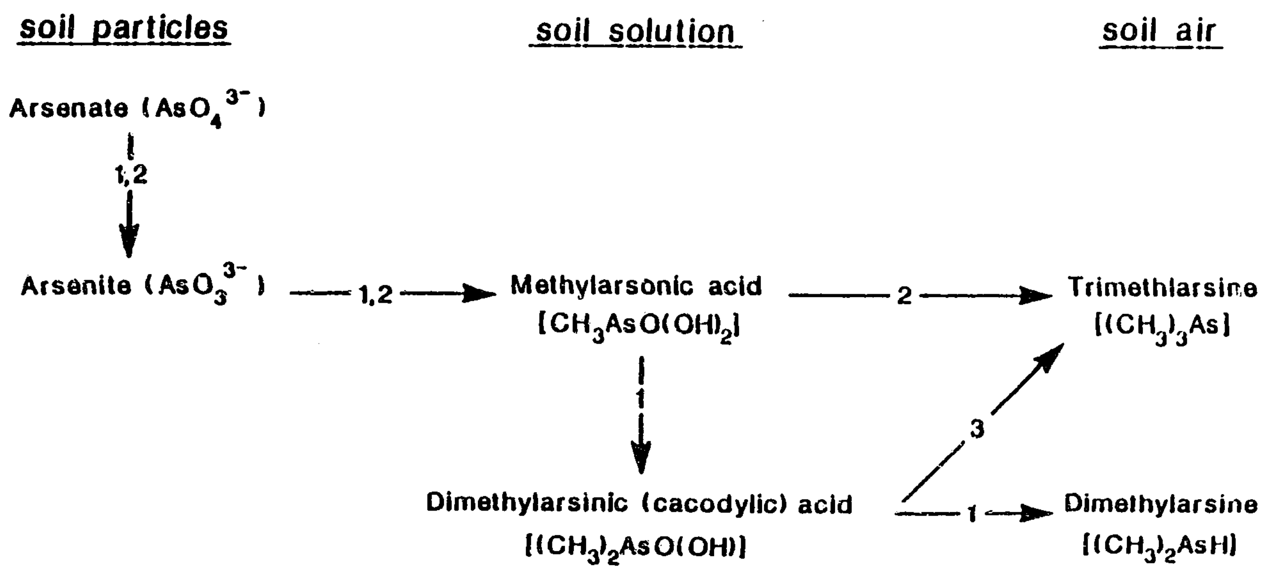
Behaviour of As in Soil

Arsenic (As) exists in the pentavalent form (As^{5+}) in CCA concentrate, and as part of the arsenate anion (AsO_4^{3-}) in soil solutions (World Health Organization, 1981). Arsenate is readily immobilized in soil through precipitation with iron and aluminum hydrous oxides, which comprise the oxide coating of clay particles (Sims et al., 1984; World Health Organization, 1981; Kotuby-Amacher et al., 1988; NRCC, 1978; Bolt and Bruggenwert, 1976; Menzer and Nelson, 1986). Arsenate may also be adsorbed directly as an anion, or complexed with functional groups in soil organic matter (NRCC, 1978). Arsenate (AsO_4^{3-}) and phosphate (PO_4^{3-}) compete for the same oxides on clay particles, so an excess of one form increases the mobility of the other (Sims et al., 1984; Bolt and Bruggenwent, 1976; NRCC, 1978). Therefore, phosphate fertilization of arsenic-contaminated soils may increase the amount of arsenic moving towards groundwater (Bolt and Bruggenwert, 1976).

Arsenate complexes and precipitates can become incorporated into the biological cycle under conditions conducive to microbial activity, such as large amounts of organic matter, warm temperatures, and adequate levels of moisture and nutrients (Sims et al., 1984; NRCC, 1978). First, arsenate is bioreduced to arsenite by microorganisms. Then, arsenite is biomethylated to methylarsonic acid and dimethylarsinic (cacodylic) acid, and finally, to volatile methylarsines (Figure 1.5-7) (NRCC, 1978; Shields and Stranks, 1978; World Health Organization, 1981; Woolson, 1977). These biologically-mediated reactions enhance the mobility of arsenic in soil:

- arsenite (AsO_3^{3-}) forms moderately soluble precipitates with clay minerals, and is therefore more easily leached from soils into groundwater. This observation is of some concern, because As^{3+} is generally more toxic than As^{5+} (section 1.4.3.3.3) (Sims et al., 1984; Shields and Stranks, 1978).
- methylarsines are volatile, and vapours may be released from contaminated soil (NRCC, 1978; Menzer and Nelson, 1986).

The biologically mediated reduction and methylation of arsenate may occur slowly at Canadian CCA facilities because of lower soil temperatures, and also because of the toxicity of the CCA mixture to microbes. For example, a study by Environment Canada (1988c) indicated that soil samples in the vicinity of CCA facilities contained at least 97% of the original pentavalent form of arsenic, indicating that bioreduction to As^{3+} had not substantially occurred.



Legend:

1 = *Methanobacterium* spp.
2 = *Candida humicola*
3 = *Scopulariopsis* spp., *Aspergillus* spp., *Mucur mucedo*, *Lenzites trabea*, *Monilia sitophila*

FIGURE 1.5-7 : BIOLOGICALLY-MEDIATED REACTIONS OF ARSENIC IN SOIL (ADAPTED FROM WOOD, 1974 AND WOOLSON, 1977)

1.5.2.2.2 Behaviour of Cu, Cr, As in Air

Volatilization of copper (Cu) compounds from soil or water has not been reported in the literature. This is consistent with the chemistry of copper, which indicates that copper is strongly fixed to soil and sediments, and is not alkylated by microorganisms. It is most likely that copper enters the atmosphere at CCA sites due to wind and water erosion of contaminated soil. Copper in this form would be environmentally stable, as it would be bound to the soil particles.

Volatilization of chromium (Cr) compounds from soil or water has not been reported. Gaseous chromium forms have been synthesized, but are not likely produced in nature (NRCC, 1976). This is consistent with the chemistry of chromium, which indicates that it is not methylated by microorganisms (API, 1981). It is most likely that chromium enters the atmosphere at CCA sites due to wind and water erosion of contaminated soil. The World Health Organization (1988) postulated that particulate-sorbed Cr^{6+} would be environmentally stable while suspended in the air. This warrants some concern at CCA facilities, because Cr^{6+} is present in CCA concentrate, and Cr^{6+} has been conclusively linked with a number of respiratory ailments, including lung cancer (section 1.4.3.3.2).

Arsenate is reduced and alkylated by microorganisms in soil to volatile methylarsines (section 1.5.2.2.1). Methylarsines are found immediately over arsenic-contaminated soils, but are not stable in the atmosphere, as they are readily oxidized in the presence of sunlight to dimethylarsinic acid and arsenious oxides (World Health Organization, 1981; NRCC, 1978;

Shields and Stranks, 1978; U.S. Department of Agriculture, 1980). These intermediates condense in air and are adsorbed onto particulate matter (NRCC, 1978). Numerous studies have confirmed that arsenic is stable in the atmosphere as oxides and arsenates bound to particulate matter (NRCC, 1978). Consequently, it appears that both methylarsine vapours and arsenic-containing dust may exist on abandoned CCA plant sites, but that only arsenic-containing particulate matter is stable enough to be transported off-site. The existence of airborne arsenic at abandoned CCA facilities warrants some concern, because arsenic has been conclusively linked with a number of respiratory ailments, including lung cancer (section 1.4.3.3.3).

1.5.2.2.3 Behaviour of Cu, Cr, As in Surface Water

Copper, chromium and arsenic from CCA wood preservation may contact surface water bodies through the erosion and transport of contaminated sediment, and from the discharge of contaminated groundwater. These metals may undergo a variety of reactions in surface water. Predominance area diagrams, which relate chemical form to the redox potential and pH of the water, indicate what form a metal <u>may</u> be in. Such diagrams can only be developed for specific, defined water composition, and they will not be directly applicable to natural water composition. Consequently, a qualitative discussion of metal speciation in freshwater will be presented.

In freshwater, 60 to 98% of copper exists as copper-organic complexes (NRCC, 1979). Consequently, copper speciation in aquatic environments is largely influenced by levels of dissolved organic carbon. Copper may also form aquo, carbonato and hydroxo complexes (NRCC, 1979). The complexation of copper with both organic and inorganic ligands depends on pH, alkalinity and redox potential (NRCC, 1979). Copper exists as a cation in aqueous systems, and is therefore also adsorbed to clay minerals in suspension or in sediments (NRCC, 1979).

Chromium (Cr) exists in two valences in natural waters: Cr^{3+} and Cr^{6+}. Trivalent chromium remains as a cation (Cr^{3+}), whereas hexavalent chromium forms anionic complexes (CrO_4^{2-} and $Cr_2O_7^{2-}$) in water. Compounds containing Cr^{6+} are powerful oxidizing agents, and will readily oxidize dissolved organic matter, while being reduced to Cr^{3+}. The actual distribution of Cr^{3+}, CrO_4^{2-} and $Cr_2O_7^{2-}$ in aquatic environments will depend on the dissolved oxygen levels, pH, amount of dissolved organic matter, and the presence of other oxidizing compounds such as MnO_2 (NRCC, 1976; World Health Organization, 1988; API, 1981).

Trivalent chromium (Cr^{3+}) in water readily complexes with a variety of organic and inorganic ligands, such as water, ammonia, urea, and organic acids (humic and fulvic) (API, 1981; NRCC, 1976). Trivalent chromium is also a cation, and therefore adsorbs to suspended and settled clay particles. Negligibly soluble chromium hydroxide precipitates may form with sorbed or dissolved Cr^{3+} (API, 1981).

Hexavalent chromium (Cr^{6+}) exists as oxo anions in natural waters (CrO_4^{2-} and $Cr_2O_7^{2-}$), which are readily reduced to Cr^{3+} in the oxidation of organic matter. However, any Cr^{6+} remaining is expected to be quite mobile in aquatic systems, because CrO_4^{2-} and $Cr_2O_7^{2-}$ do not bind to clay minerals or negatively charged ligands (API, 1981; NRCC, 1976). Hydroxide precipitates containing hexavalent chromium are also more soluble than their trivalent counterparts (API, 1981).

The biologically-mediated reduction and methylation of arsenate that occurs in soils (section 1.5.2.2.1) also occurs in natural waters, though different microorganisms are responsible (Menzer and Nelson, 1986). Thermodynamic considerations which ignore microbial activity predict that As^{5+} should predominate over As^{3+} in well-aerated aquatic systems. However, the ratio between the two species is much lower than expected, implying bioreduction of arsenate (AsO_4^{3-}) to arsenite (AsO_3^{3-}) (NRCC, 1978; Menzer and Nelson, 1986). Methylation of arsenite is also believed to occur in freshwater systems, because the predominant arsenic forms in contaminated water are methylarsonic acid and dimethylarsinic acid (World Health Organization, 1981; Braman and Foreback, 1973). In fresh water, phytoplankton activity has been correlated with the presence of methylarsenic compounds, and concentrations of these compounds are especially high where nutrients from fertilizers have accumulated (World Health Organization, 1981). The hypothesis that arsenic reduction and methylation is mediated by phytoplankton rather than bacteria is supported by the low levels of methylarsenic compounds in sediments of contaminated water bodies (World Health Organization, 1981).

1.5.2.2.4 Behaviour of Cu, Cr, As in Groundwater

CCA-based wood preserving fluids are freely soluble in water (Table 1.4-12), and presumably so are the waste treating mixtures. Consequently, waste CCA fluid contacting groundwater will be converted into a plume of solubilized contaminants. The contaminants will move by advection with the groundwater, and spread throughout the saturated zone by dispersion and molecular diffusion. Plume growth will not be limited by density or viscosity effects, as may occur with oil-based mixtures.

Copper, chromium and arsenic will be adsorbed to aquifer materials by the same processes which caused immobilization in the vadose zone. However, in the saturated zone, the pore water tends towards reducing conditions, and different chemical forms may predominate. In the vadose zone, oxidizing conditions can be maintained by the continual replenishment of pore air, whereas in the saturated zone, oxygen consumed by hydrochemical and biochemical reactions is not replenished (Freeze and Cherry, 1979). This results in low dissolved oxygen levels in groundwater and reducing conditions. Consequently, a different form of the metal may predominate in groundwater than in the vadose zone, affecting adsorption characteristics.

The movement of dissolved copper, chromium and arsenic in groundwater will be retarded by sorption to aquifer materials. However, facilitated transport can increase metal migration. Dissolved CCA constituents may undergo facilitated transport with codisposed materials, adsorbed to colloids, or because of phase shifting.

Most wood preserving plants utilize more than one type of preservative, and the different wastes are generally disposed of together. Consequently, CCA wastes may be mixed with creosote or PCP sludges. As discussed in section 1.5.1.1, hydrocarbon fluids increase the permeability of fine-grained soils. The codisposal of CCA wastes and hydrocarbon mixtures may thus enhance the migration of CCA constituents. The HELP site at Faust is the only site where both organic and inorganic wood preservatives were used. However at this site, the CCA and PCP sludges were diverted into separate ponds (section 4.5.4).

CCA migration in groundwater can also be facilitated by the presence of organic and inorganic colloids, which are mobile particles in aquifers. Copper, chromium and arsenic exist as ions in solution, and may be adsorbed through charge interaction to humic substances and clay minerals, or form mobile inorganic precipitates.

CCA migration in groundwater may be facilitated or retarded due to changes in pH or redox potential which change the predominant chemical species. Dissolved oxygen in groundwater can be depleted through biological activity, leading to reducing conditions and a drop in Eh. In addition, the pH of groundwater can decrease due to the production of hydrogen ion (H+) during aerobic and anaerobic decomposition of organic matter. These effects may increase contaminant mobility by ionizing neutral compounds and reversing precipitation reactions (Keely, 1989). Contaminant mobility may also be decreased if less mobile compounds are formed. For example, a predominance area diagram for chromium is presented in Figure 1.5-8. In this figure, decreasing Eh levels do not alter the predominant chemical form, a stable chromium precipitate. However, the decreasing pH facilitates a phase shift, causing the solubilization of the hydroxide precipitate to the more mobile chromium ion.

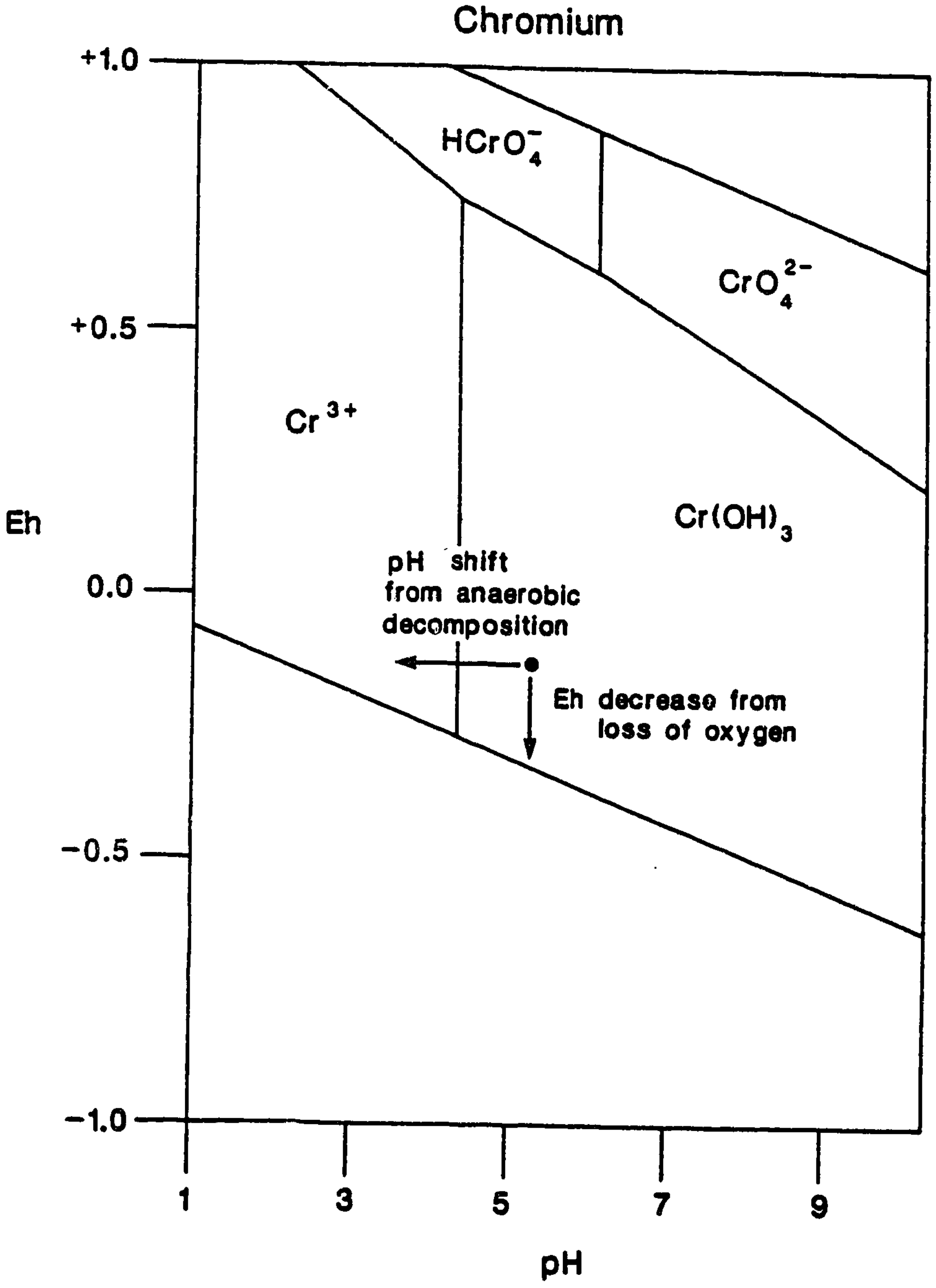


FIGURE 1.5-8 : HYPOTHETICAL FACILITATED TRANSPORT BY PHASE DIAGRAM SHIFTS

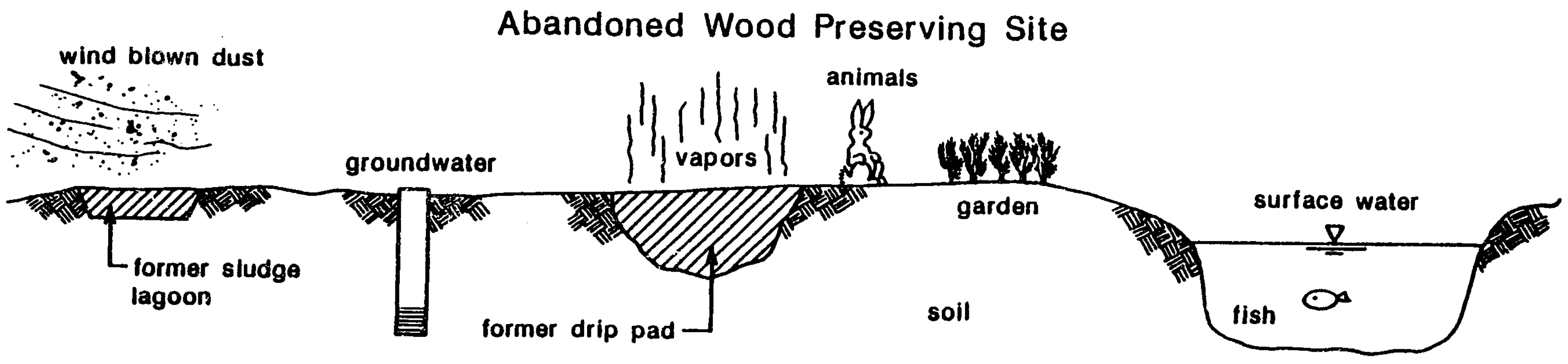
1.6 Exposure Pathways of Contaminants in the Environment

In section 1.5, the transport and fate of wood preserving chemicals in the environment were examined. In this section, the hazards posed by these chemicals in the environment will be considered.

At wood preserving sites, environmental damage from chemical releases begins long before off-site humans are affected. Humans may assign some value to this damage, but as an egocentric species, our greatest concern is how the contamination will affect ourselves. Consequently, humans are the model receptors at contaminated sites. This position, while partially due to our egocentric nature, is supported by the fact that humans comprise the highest trophic level in the food chain, and are therefore most likely to suffer from contaminant biomagnification along this chain, when biomagnification is relevant.

Figure 1.6-1 illustrates the exposure pathways by which humans may contact contaminants at abandoned wood preserving sites. In general, humans may absorb contaminants from environmental media through ingestion, inhalation, and topical contact. Pollutants absorbed from any of these three routes can adversely affect human health (section 1.4).

However, these routes are not equally relevant for all wood preserving contaminants, because of the wide variation in partitioning behaviours. A summary of the relevance of each exposure route for each contaminant is presented in Table 1.6-1, based on information in section 1.5. The classification scheme used in this table is somewhat arbitrary, and may be



Human Exposure Pathways

ingestion

- eating contaminated animals (fish, grazing animals)
- eating garden produce grown in contaminated soil
- drinking contaminated water (from surface or ground)
- ingesting contaminated soil from hands, produce or animals

inhalation

- inhaling contaminant vapours
- breathing dust to which contaminants are adsorbed

topical contact

- dermal (skin) contact with contaminated soil and water

FIGURE 1.6-1 : EXPOSURE PATHWAYS BY WHICH HUMANS MAY CONTACT CONTAMINANTS AT ABANDONED WOOD PRESERVING SITES

Table 1.6-1: Relative Importance of Exposure Pathways for Wood Preserving Chemicals

Preserving Mixture	Compound	Water-Based Pathways	Soil-Based Pathways	Air-Based Pathways	Bioaccumulation Pathways
Diesel Carrier (used for both creosote and PCP processes)	2-methylnaphthalene	2	2	2	2
	benzene	1	3	1	3
	toluene	1	3	1	3
PCP-based	pentachlorophenol (PCP)	2	1	3	2
	2,3,4,6-tetrachlorophenol	1	2	3	2
	2,4,5-trichlorophenol	1	2	2	2
	2,4,6-trichlorophenol	1	2	2	2
	hexachlorodibenzo[p]dioxin	3	1	3	1
Creosote-based	naphthalene	2	2	1	2
	acenaphthene	2	3	1	2
	carbazole	2	2	2	2
	fluorene	2	2	1	2
	phenanthrene	3	1	2	2
	anthracene	3	1	2	2
	fluoranthene	3	1	2	2
	pyrene	3	1	2	2
	chrysene	3	1	3	2
	benzo[a]pyrene	3	1	3	1
	benzo[a]anthracene	3	1	3	2
	benzo[b]fluoranthene	3	1	3	1
	benzo[k]fluoranthene	3	1	3	1
	benzo[g,h,i]perylene	3	1	3	1
	dibenzo[a,h]anthracene	3	1	3	1
	indeno[1,2,3-c,d]pyrene	3	1	3	1

continued

Table 1.6-1: Continued

Preserving Mixtures	Compound	Water-Based Pathways	Soil-Based Pathways	Air-Based Pathways	Bioaccumulation Pathways
Creosote-based	phenol	1	3	2	3
	2,4,6-trimethylphenol	2	3	2	2
	quinoline	1	3	2	3
	aniline	1	3	2	3
	benzothiophene	2	2	1	2
	dibenzothiophene	2	2	2	2
CCA-based	copper	1	1	3	3
	chromium	1	2	3	2
	arsenic	1	2	2	3

Notes:

- this table was derived from information presented in section 1.5, and Appendix A.
- water-based pathways include the ingestion of contaminated ground or surface water, as well as topical contact with contaminated water.
- soil-based pathways include the ingestion of contaminated soil, the inhalation of contaminated soil (airborne particulates), and dermal contact with contaminated soil.
- air-based pathways include the inhalation of contaminant vapours.
- bioaccumulation pathways include the consumption of contaminated plants and animals. These pathways were not considered in section 1.5, and will be assessed solely on k_{ow} values for organic chemicals (Appendix A), which is consistent with uptake equations for organic chemicals in plants (SENES, 1988), and animals (U.S.EPA, 1989b). Bioconcentration potential for inorganics was assessed using Table 1.4-13 and a report by Grant and Dobbs (1977).
- rating scale for water, soil, and air pathways:
  1 = most likely medium to concentrate the compound;
  2 = moderate partitioning of compound to medium; and
  3 = negligible partitioning of compound to medium.
- rating scale for bioaccumulation pathways:
  1 = high bioconcentration in animals, negligible bioconcentration in plants expected;
  2 = moderate bioconcentration anticipated for both plants and animals; and
  3 = negligible bioconcentration expected in animals, high bioconcentration in plants.

modified by constituent behaviour in chemical mixtures differing from constituent behaviour in isolation.

2.0 Assessment and Cleanup Criteria

2.1 Basic Concepts

Assessment criteria or processes are used to gauge the level of contamination at industrial sites; they are used to distinguish contaminated sites from uncontaminated ones, and in the former case, to assess the magnitude of contamination. Assessment criteria or processes may also define, or be used to develop, cleanup guidelines for contaminated sites.

The use of assessment criteria and the development of cleanup guidelines should occur subsequent to site characterization but prior to final selection of remediation options, for three reasons:

- site-specific information is often required for assessment processes;
- assessment criteria or procedures define the boundary across which "clean" sites become considered "contaminated" ones; and
- cleanup criteria are required during evaluation of remediation alternatives; the selected alternative must be able to achieve required cleanup levels.

Assessment and cleanup criteria can be divided into three general classes.

- **absolute methods**: absolute, or fixed criteria are adopted by the regulatory agency, and define the boundary between "clean" and "contaminated" media (Brown, 1986). The Quebec assessment criteria and statutory cleanup levels are examples of absolute methods.

- **relative methods**: site-specific factors are incorporated in site assessment and cleanup criteria development. Regulatory agencies may implement relative methods by specifying a <u>process</u> to be followed in site assessment or cleanup level selection. Restoration to background levels, best practical technology-devised standards, cost-benefit analysis, risk assessment, and computer models such as AERIS are all examples of relative methods.
- **ad hoc methods**: many jurisdictions assess contamination at industrial sites on a case-by-case basis. The approach currently used in Alberta is an example of this type of method.

All assessment criteria can be seen as utilizing basic risk assessment and risk management principles (section 2.3.4); regulatory agencies utilize fixed criteria or relative methods to indicate when the risk posed by a contamination hazard is at an "acceptable" level.

In any case, assessment and cleanup criteria must conform to certain requirements in order to become widely accepted, and to adequately reflect the hazards of contaminated media.

- **scientifically defensible**: both fixed and relative methods must incorporate data which is some measure of environmental harm, such as experimental doses associated with observed adverse effects in humans, lower animals, plants, or microorganisms. The use of such data ensures that cleanup criteria developed from it have a scientific basis in reducing the risk posed by a contamination hazard.

- **legally defensible**: site assessment and cleanup criteria development is an imperfect science because of toxicological data gaps and knowledge gaps related to contaminant uptake. Consequently, several factors could be questioned in a legal challenge. However, the most obvious challenge would arise in regards to process consistency; consistent values or a consistent process must be used to assess site contamination. Legal challenges may result if different absolute criteria or a different approach were adopted from site to site.
- **incorporation of non-technical concerns**: the primary goal of site assessment is to determine whether contamination at a site represents an unacceptable hazard to the public, or to objects of public interest (eg. nearby wetlands). In accordance, cleanup criteria specify concentrations at which the hazard is deemed to be "acceptable". Potentially affected populations should provide input as to what level of hazard is deemed to be acceptable by them. This element of hazard assessment is often neglected or mismanaged, and a failure to distinguish real and perceived risk may arise, possibly resulting in site cleanup based on notoriety rather than hazard.
- **assessment of background hazard**: many contaminants, such as PAHs, are ubiquitous in the environment (section 2.3.1). For such compounds, the risk posed by background levels should be assessed along with that of contaminants at the site. Comparison

of these risk levels may aid potentially-affected populations in placing site contamination in the proper perspective.

- **consideration of both chemical concentrations and toxicity levels:** as discussed in section 3.2.2.1.4, a combined chemical/biological monitoring protocol is required during site remediation. Chemical analyses monitor the disappearance of priority pollutants, whereas biological analyses (bioassays) reflect the toxicity of the chemical mixture, as well as detect adverse biological responses resulting from chemical interactions or compound degradation. In this way, bioassays provide essential additional assessment of the potential hazard of site contamination to humans beyond what can be determined strictly from chemical concentrations. Consequently, site assessments and cleanup levels should incorporate bioassay data. In fact, Fitchko (1989) proposed cleanup criteria based solely on different bioassay tests. The rationale for this recommendation was that bioassays are effects-based approaches, and are therefore more defensible from an environmental protection standpoint. At one time the U.S.EPA also considered using bioassay values alone as cleanup criteria, though that approach was not adopted (Dom DiGiulio, R.S. Kerr Environmental Research Laboratory; personal communication).
- **consideration of site-specificity:** both the public and industry generally desire that assessment processes and cleanup criteria reflect the characteristic uniqueness of each contaminated site by

incorporating site-specific data and concerns (Richardson, 1987; O'Connor, 1989a; Monenco, 1988).

- **incorporation of all environmental media and contaminant types:** assessment criteria or processes must consider all potentially-exposed media (air, surface water bodies, aquifers, vadose zone soil), as well as all types of contaminants (organic, inorganic, organometallic, radionuclides). This requirement relates to the need for assessment criteria and cleanup levels to be applicable to the widest possible range of contamination scenarios.
- **speed of implementation:** site assessment and cleanup criteria development should be quickly achieved, because in most cases, contaminant migration is not prevented during the characterization process.
- **incorporation of future land use:** use of the site following reclamation will affect the exposure pathways for residual contamination as well as the potentially-affected populations, and should be considered in the formulation of cleanup levels. For example, different pathways and populations will be affected if a remediated site is redeveloped as a subdivision rather than as a paved parking lot.

All strategies considered in this section will be evaluated using these criteria, as well as for their applicability to wood preserving sites.

2.2 Absolute Methods

2.2.1 Statutory Guidelines

Statutory guidelines exist where regulatory agencies have enacted legislation outlining acceptable contaminant levels in various environmental media. These levels would be the same for all sites and do not consider site-specific conditions. Several approaches could be used in guideline establishment:

- existing standards such as drinking water guidelines and industrial hygiene standards (drinking water guidelines for chemicals used in wood preservation are presented in Appendix B);
- inherent hazard of the pollutant (for example: reference dose [RfD] for non-carcinogens or carcinogenic potency [q_1^*] for carcinogens);
- risk assessment using "average" environmental media properties and large safety factors; and
- concentrations associated with observed adverse effects in plants, lower animals, or humans.

In addition to hazard consideration, additional concerns such as cost or potential of existing technologies to achieve cleanup levels may also be considered (Monenco, 1988; Office of Technology Assessment [OTA], 1985). However, guidelines developed primarily using technology or cost considerations may be unfavorably viewed by the public, as human health and environmental protection would correctly be perceived as secondary considerations.

The advantages and disadvantages of statutory guidelines are presented below and summarized in Table 2.5-1.

- Advantages:
  - application of guideline values is simple and quickly achieved once the standard is adopted (Beaulieu, 1989; Brown, 1986; Richardson, 1987);
  - may be both scientifically and legally defensible (Brown, 1986);
  - applicable to wood preserving chemicals;
  - could incorporate bioassay values; and
  - considers all environmental media and contaminant types
- Disadvantages:
  - would likely take a long time to assimilate relevant data for all environmental pollutants, delaying guideline development.
  - does not consider site-specific conditions, background hazard, or allow for non-technical input related to site-specific concerns.

The Quebec Assessment Criteria are the only statutory assessment criteria currently used in North America.

2.2.2 Quebec Assessment Criteria

Prior to 1985, site assessment criteria and cleanup levels were developed in Quebec on an ad hoc (case-by-case) basis (Beaulieu, 1989). This approach was deemed to be unacceptable, and criteria developed in the Netherlands and France were modified to reflect Quebec conditions, becoming the "Contaminated Sites Rehabilitation Policy" (1988). This policy was

developed on the premise that redevelopment of contaminated industrial sites is desirable, but that the land must be properly managed, using set procedures and criteria. Specific policy objectives seek to (Ministére de l'Environnement du Québec, 1988):

- **prevent the use of contaminated land to the detriment of health, the environment and property;**
- **facilitate redevelopment of contaminated sites such that residual contaminant levels are compatible with the desired end use; and**
- **ensure that contaminated soil is handled safely.**

In general, industrial sites suspected of being contaminated, or listed in the policy as likely to be polluted, must be characterized using specific criteria prior to redevelopment. If the assessment criteria indicate that the site is contaminated, various land use restrictions apply, and remediation must occur prior to redevelopment. The assessment criteria are intended solely to provide an <u>indication</u> of contamination; it is explicitly stated that they are not to be regarded as <u>standards</u> or cleanup criteria (Ministére de l'Environment du Québec, 1988):

The assessment grid for chemicals used in wood preservation is presented in Appendix B, and a discussion of the significance of the various levels is presented below (Ministére de l'Environnement du Québec, 1988).

Value A:	**represents background concentrations for naturally-occurring contaminants and the detection limit for man-made organic chemicals.**
Level A-B:	**soil or groundwater concentrations are elevated above background levels. At this level, groundwater does satisfy**

drinking quality standards, and remediation is not required except for the most sensitive end uses.

Value B: threshold of contamination, and thorough analyses are required.

Level B-C: soil or groundwater is contaminated. At this level, contamination of groundwater exceeds quality standards for human consumption. Restrictions on land use may be imposed on the site, and remediation will likely be required for most end uses.

Value C: At this threshold, it may be necessary to take prompt remedial action.

Level C+: the soil or groundwater is contaminated. Groundwater cannot be used for human consumption. Concentrations of many contaminants exceed standards governing storm sewer runoff. All uses of such land will be restricted. A thorough site investigation must be conducted. Most likely, site remediation will be required prior to any redevelopment.

As mentioned before, the Quebec Assessment Criteria are indicator ("threshold") values; to establish specific cleanup guidelines, risk assessment or some other (undefined) alternative may be required (Monenco, 1988; Richardson, 1987).

2.3 Relative Methods

2.3.1 Restoration to Background Levels

This approach for site assessment and cleanup criteria development is founded on two basic assumptions (OTA, 1985):

- any level of contaminant above background or pristine concentrations presents an unacceptable risk; and
- levels at or below background or pristine are acceptable.

These assumptions may not be justified, as discussed subsequently. In any case, site cleanup using this approach would continue until the levels of all contaminants were indistinguishable from those of the surrounding background. A variation of this approach would require that the cleanup continue until the site were pristine (as if contamination had never occurred) (OTA, 1985). Before the differences between these two variations can be considered, the types of chemical backgrounds must be discussed.

Pristine media (soil, groundwater) contain naturally-occurring organics (humics) and inorganics (minerals), and have not been influenced by human activity. A second type of background chemical arises from human activity from off-site sources (anthropogenic background). Localized anthropogenic background is often caused by a point source such as a nearby factory. Ubiquitous anthropogenic background generally arises from non-point sources such as automobiles (U.S.EPA, 1989b). When contaminant concentrations in environmental media are greater than those of the anthropogenic and pristine background, site contamination has occurred. Restoration to background levels requires cleanup of site contamination to anthropogenic levels, while restoration of pristine conditions requires cleanup to pristine levels (Figure 2.3-1).

The assumptions upon which restoration to background levels is based may not be justified. Specifically, reduction of contaminant concentrations to anthropogenic or natural levels may not sufficiently mitigate the inherent media hazard; in industrial areas, anthropogenic concentrations may still pose a risk to human health, and in some cases, pristine metal concentrations may also present a hazard (Environment Ontario, 1989; U.S.EPA, 1989b). The underlying objective of site remediation is hazard reduction, and this goal may not necessarily be achieved through restoration to background levels. This approach may therefore not be scientifically defensible. Other concerns in the use of this approach for site assessment and remediation are:

- The approach may not be legally defensible, as there would be inconsistencies among cleanup of sites with similar wastes, depending on their location (OTA, 1985).
- It is difficult to determine natural and anthropogenic background levels in developed areas, where native soil has been replaced and many contamination sources exist.
- It may be difficult to distinguish wood preserving contaminants from anthropogenic and natural sources; CCA constituents are normally present as trace metals in soil, while PAHs are formed naturally during forest fires and as incomplete combustion products during industrial burning of fossil fuels (Environment Canada, 1988b). Chlorophenols may also be considered as

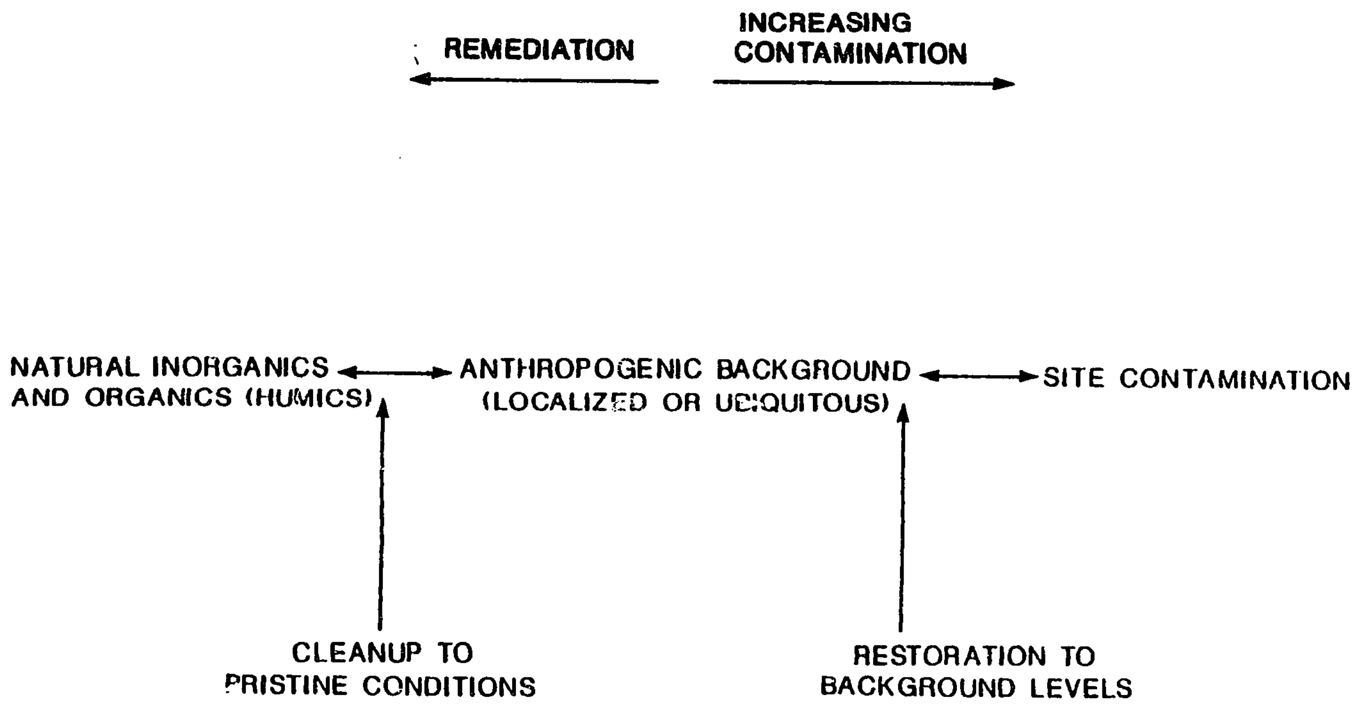


FIGURE 2.3-1 : LEVELS OF SITE CONTAMINATION AND ASSOCIATED RESTORATION ALTERNATIVES

ubiquitous anthropogenic pollutants due to their formation during the chlorination of water and their occurrence as decomposition products of the common chlorophenoxy herbicides (U.S. Department of Agriculture, 1980).

- Restoration to pristine levels would likely be prohibitively expensive and technically unachievable for contaminants that do not exist naturally in the environment, and whose pristine levels would thus be zero (OTA, 1985; Monenco, 1988). For wood preserving contaminants, this situation would exist for chlorophenols, whose pristine concentration is zero (Environment Canada, 1988a). CCA constituents and PAHs are considered to be naturally-occurring compounds because of their presence prior to the existence of man.

In summary, establishing assessment or cleanup criteria on the basis of background or pristine contaminant levels does not make environmental, technical or economic sense (OTA, 1985); the approach does not assure protection of health or the environment, may not be technically feasible, and is likely to be prohibitively expensive. In addition, the intensity of the effort required to attain background or pristine levels grows as the goal is approached, and can be disproportionate to the gains realized (Beaulieu, 1989).

Despite the limitations of this assessment approach, some jurisdictions have adopted it. For example, both Colorado and Texas specify that site remediation must achieve background levels (Dames and Moore, 1986). The approach was also used at a site in Kentucky contaminated with both organic and inorganic chemicals (documented in Booz and Hamilton, 1989).

2.3.2 Technology-Devised Standards

A practical limitation of cleanup criteria is whether a remediation technology exists which can attain the selected values. Cleanup levels derived from complicated risk assessments are of no use if no practical restoration alternative exists to achieve them. Consequently, technology-devised standards are pragmatic, and reflect the belief that by using the best available technology, the risks posed by a contaminated site will be reduced to the lowest level technically achievable (OTA, 1985).

A detailed analysis of the inherent hazard posed by contaminants at a site is <u>not</u> an integral part of this approach (Monenco, 1988; OTA, 1985), because remediation is controlled by technological limitations, not by hazard mitigation. Consequently, site-specific parameters affecting technology implementation (such as hydrogeology) are of greater importance than information related to hazard assessment (such as soil vapour concentrations).

Unfortunately, use of technology-devised standards without a thorough hazard assessment poses a number of concerns.

- without a risk assessment, there would be no indication as to what constituted a complete cleanup, resulting in open-ended time frames and costs (Richardson, 1987; OTA, 1985). Additionally, advances in technology may have to be incorporated to maintain the objective of contaminant removal to the lowest level technically achievable.

- without a risk assessment, the most cost-effective technology could not be selected from the remediation alternatives available, because a comparison of the incremental benefits in risk reduction afforded by the various technologies could not be completed.

Though the use of technology-devised standards is convenient, their use often does not offer environmental protection commensurate with the high costs of implementation (OTA, 1985). This approach does not incorporate risk assessment, and consequently, remediation is dictated by technological limitations, not by hazard reduction. In spite of these shortcomings, this approach is, by default, an extensively utilized alternative in Canada and the U.S. (OTA, 1985), where remediation alternatives are generally designed and implemented before regulatory agencies have dictated a preferred assessment approach or required cleanup levels.

2.3.3 Cost/Benefit Analysis

A cost/benefit approach to establishing cleanup criteria would require the costs of any incremental site remediation be compared with the incremental benefits derived from the expenditure (OTA, 1985). Cleanup criteria would be defined by the concentrations at which incremental costs just equal the incremental benefits realized (in consistent units). Costs for site remedation include initial expenditures plus operation and maintenance costs, while benefits are defined as the reduction of potential adverse human health and/or environmental effects (Monenco, 1988).

Incremental costs associated with increasing site remediation would be reasonably straightforward to calculate. Quantification of the associated incremental benefits requires an understanding of the reduction in risk to public health or the environment those measures are likely to produce. This quantification requires a risk assessment (section 2.3.4) (OTA, 1985). In cost/benefit analysis, risk assessment data are used to balance the incremental risk reduction and incremental increase in remediation costs. Consequently, with cost/benefit analysis cleanup criteria are based on cost optimization rather than hazard reduction.

In order for the optimization to be achieved, costs and benefits must be converted to consistent units (usually dollars). Unfortunately, this conversion is not easily obtained; health effects are often intangible (and very often not quantifiable), while the cost of restoration is specific (and exactly quantifiable) (Monenco, 1988). For example, what dollar value is associated with decreasing the number of cancers arising from site contamination by one person in a million (incremental risk reduction = 1×10^{-6})? The cost of achieving the necessary reduction in contaminant concentration would be more easily determined. Additional concerns associated with cost/benefit analysis are:

- the approach is attractive in theory, but is not likely to be adopted by regulatory agencies because of the value judgements required. Specifically, decision makers will be questioned as to how they judge costs versus human health benefits, and such decisions may be politically difficult (Richardson, 1987; OTA, 1985).

- cleanup criteria from cost/benefit analysis represent the concentrations at which incremental benefits are exactly offset by incremental costs. This optimization of cleanup with respect to cost may generate cleanup concentrations above those required for adequate hazard reduction.
- inconsistent cleanup levels between sites of similar contamination may result if remediation costs or perceived benefits are different.

2.3.4 Risk Assessment/Risk Management

Risk assessment, incorporating site-specific data, quantifies the relationship between contaminant concentrations in environmental media and human exposure. If exposure is deemed to be unacceptable, cleanup levels can be back-calculated knowing the acceptable level. Risk assessment is the most scientifically-rigorous way available of assessing the health hazard posed by site contamination. However, non-technical concerns, such as public opinion and costs versus benefits, are also incorporated into the overall process, specifically in the risk management portion (Figure 2.3-2). Risk assessment is a scientific and technical activity, whereas risk management is a policy- and value-oriented process (Deisler, 1988). Consequently, only risk assessment will be evaluated in this section.

2.3.4.1 Site Characterization

In risk assessment, the site must initially be characterized so that the extent and magnitude of contamination can be quantified, as well as the media properties controlling the transfer of contaminants to receptor

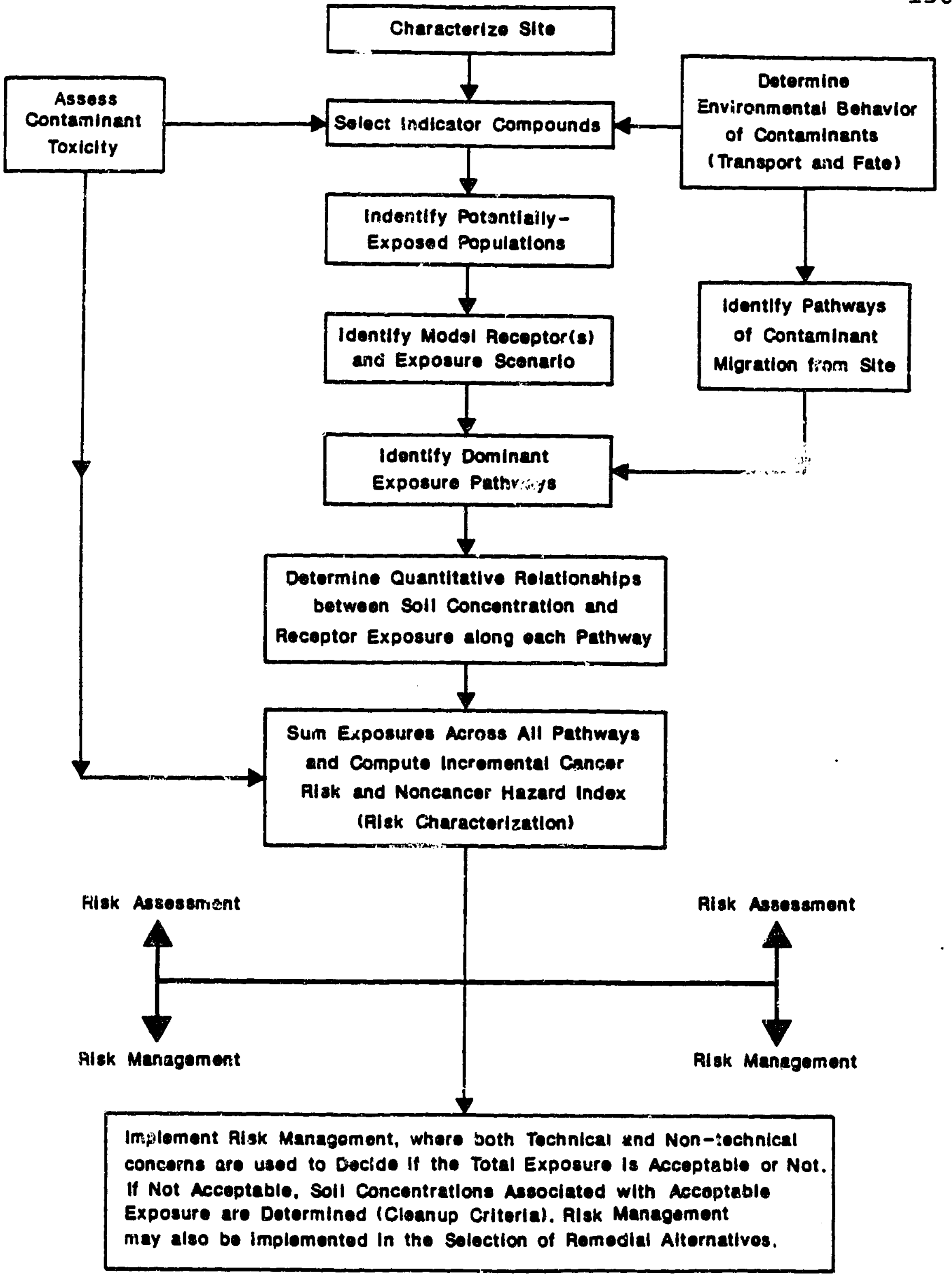


FIGURE 2.3-2 : RISK ASSESSMENT / RISK MANAGEMENT PROCESS

organisms (ultimately humans). Specific data requirements are summarized in Table 2.3-1.

2.3.4.2 Contaminant Toxicity

One of the outputs of site characterization is a list of the potential contaminants present in the various site media and their concentrations. Potential contaminants are identified through comparison of data from site and background samples. At most sites, the number of potential contaminants will be large, possibly limited only by analytical constraints. For example, roughly 300 PAHs have been identified in creosote, though it is generally held that thousands of PAHs will eventually be identified as analytical techniques improve (McGinnis, 1988). All of these compounds could be present at a wood preserving site. It is not possible to include each potential contaminant in the risk assessment because of analytical constraints and limitations in the toxicological data base. Instead, indicator contaminants may be used to represent the mixture of compounds present at the site (section 2.3.4.4). Information on compound toxicity is necessary to properly select indicator contaminants, as well as to calculate incremental cancer risk and the noncancer hazard index during risk characterization.

Contaminants are classified as either noncarcinogens or carcinogens. For noncarcinogenic effects, humans are believed to possess protective mechanisms that must be saturated (overwhelmed) before an adverse effect can be manifested (U.S.EPA, 1989b). As a result, a range of exposures exists from zero to some finite value at which no adverse effect occurs. The

Table 2.3-1: Data Required for Site Characterization

Data Class	Data	Specifics/Comments
Site	climate	temperature, precipitation
	meteorology	wind speed and direction, particulate concentrations and size distribution
	geology	location and characterization of underlying strata
	vegetation	
	current use	residential, industrial
	soil type	minerology, pH, organic content, cation exchange capacity, density, porosity
	groundwater hydrology	aquifer type, hydraulic conductivity, saturated thickness, hydraulic gradient
	groundwater chemistry	
	location of surface water and chemistry	
	biota	plate counts, classification
Contamination	background contaminant levels in all media	so that background risk can be calculated
	areal distribution and magnitude of contamination in all site media	includes plants and animals

Notes:

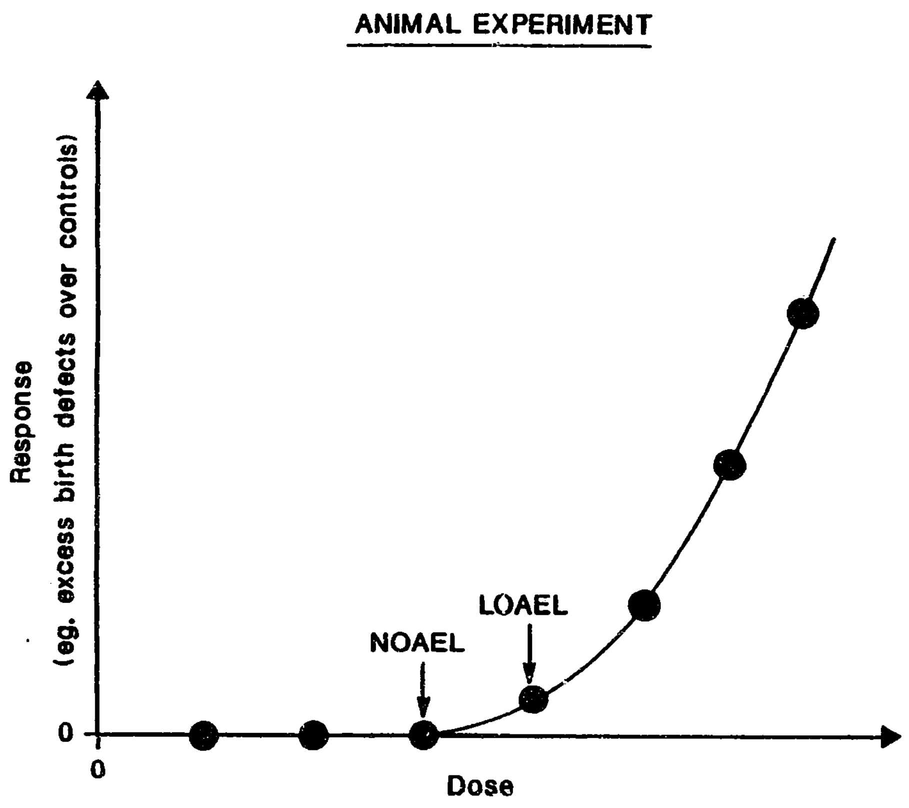
- Sources: Severn (1987), U.S.EPA (1989b).

toxicity parameter for noncarcinogenic effects is called the reference dose (RfD), and represents the upper bound of the no effect range divided by uncertainty factors, used to incorporate mitigating circumstances. Specifically, an RfD is derived by dividing the no-observed-adverse-effect level (NOAEL) or lowest-observed-adverse-effect level (LOAEL) from a dose-response test by uncertainty factors, as illustrated in Figure 2.3-3. The following uncertainty factors (UFs) have been recommended for use by the U.S.EPA (1989b):

- a UF of 10 is used to account for variation in the general population, and is intended to protect sensitive subpopulations (eg. the infirm, children);
- a UF of 10 is used when extrapolating from animal tests to human values, and is intended to account for interspecies variability; and
- a UF of 10 is used when the RfD is derived from a LOAEL rather than a NOAEL, and is intended to account for the uncertainty in extrapolating from LOAELs to NOAELs.

Reference doses (RfDs) are similar to acceptable daily intakes (ADIs), which is an older terminology, except that RfDs have been derived using a more strictly defined methodology, and should replace ADIs in use (U.S.EPA, 1989b). RfDs are generally considered to be uncertain to an order of magnitude or more, and therefore should not be viewed as a strict demarcation between adverse and nontoxic effects (U.S.EPA, 1989b).

Initiation of carcinogenesis, unlike noncarcinogenic health effects, is believed to be a nonthreshold phenomenon (Lincoln, 1987; U.S.EPA, 1989b; American Chemical Society [ACS], 1984). Specifically, one molecule of a



Legend

•RFD = $\dfrac{\text{NOAEL or LOAEL}}{\sum_{i=1}^{n} (\text{UF})_i}$

•RFD = reference dose

•NOAEL = no-observed-adverse-effect-level
=highest dose at which there is no statistically significant increase in the frequency of adverse effects between the exposed population and control group.

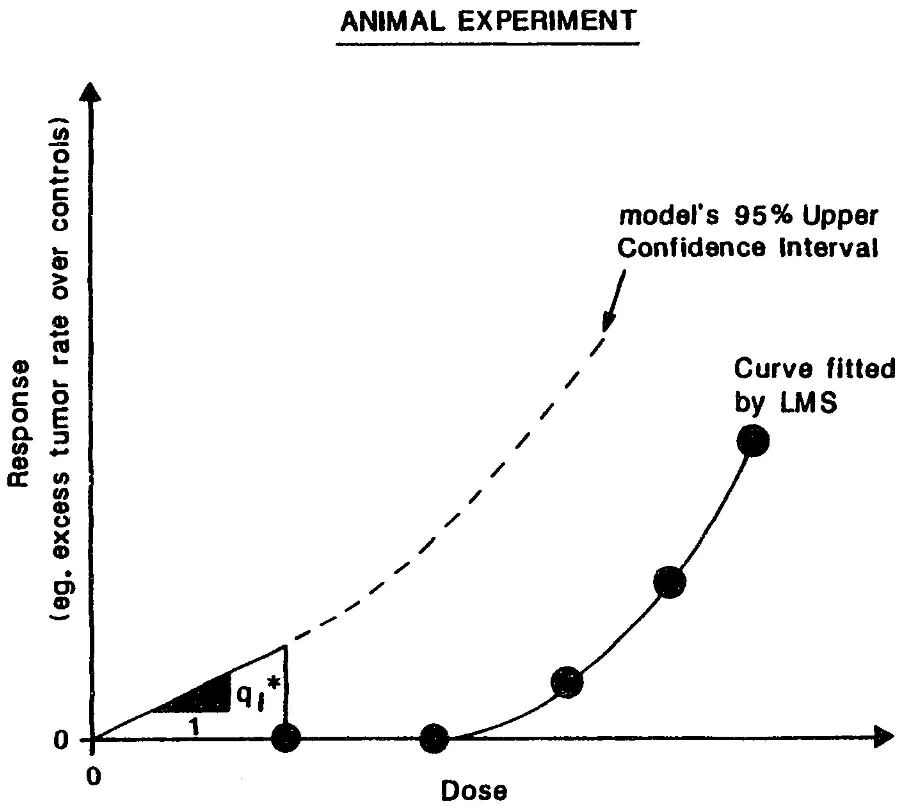
•LOAEL = lowest-observed-adverse-effect-level
=lowest dose at which there is a statistically significant increase in the frequency of adverse effects between the exposed population and control group.

•UF = uncertainty factor, used to incorporate mitigating circumstances (see text).

FIGURE 2.3-3 : CALCULATION OF AN RFD FOR NONCARCINOGENIC EFFECTS carcinogen can cause a change in a nucleic acid, which may result in an altered gene, which in the right environment can lead to uncontrolled cellular proliferation and cancer (Lehr, 1990b). Consequently, any exposure to a chemical carcinogen is associated with some incremental increase in cancer risk. The levels of exposure (doses) of interest to humans generally fall well below those at which animal tests are run, for two reasons (ACS, 1984):

- the test results must be statistically significant, requiring a measurable number of cancers (hits) within a practical size of exposed population; and
- cancer must develop over the relatively short life-span of the lab animal.

Consequently, extrapolation models are used to extend dose-response data from the high doses administered to experimental animals to the low exposure levels (and corresponding low risk levels) expected for human contact in the environment. The U.S.EPA uses the linearized multistage model (LMS), where curve-fitting is done by maximum likelihood estimate (Stara et al., 1986; U.S.EPA, 1989b; Dowd, 1988). After extrapolation, a slope factor (q_1*) is calculated to quantitatively define the relationship between dose and response in low dose regions. The slope factor (q_1* or carcinogenic potency) is the slope of the line drawn from the origin to the upper 95% confidence interval at the lowest dose (Figure 2.3-4). The LMS model is more conservative than most other extrapolation models, and q_1* is also calculated using the upper 95% confidence interval (U.S.EPA, 1989b; Dowd, 1988). As a result, q_1* is a plausible upper-bound (conservative) estimate of the probability of a response. A q_1* value calculated from animal



Legend

$$\bullet q_I^*(\text{animal}) = \frac{\text{Upper 95\% Confidence Interval at lowest dose}}{\text{lowest dose}}$$

$$\bullet q_I^*(\text{human}) = \frac{q_I^*(\text{animal})\,[W_H/W_A]^{1/3}}{(le/Le)\,(Le/L)^3}$$

- above equation from Stara et al.,1986
- q_I^*(animal) = carcinogenic potency for animals
- q_I^*(human) = carcinogenic potency for humans
- W_A = animal weight
- W_H = human weight
- le = length of exposure
- Le = length of observation period
- L = lifespan of animal

FIGURE 2.3-4 : CALCULATION OF q_1^* FOR CARCINOGENIC EFFECTS experiments must be converted into a value for humans, as shown in Figure 2.3-4. The conversion is based on the assumption that different species are equally sensitive to the effects of a toxicant if they absorb the same amount of chemical per unit of body surface area, which is roughly proportional to the 1/3 power of body weight for doses expressed as mg/kg-d (Stara et al., 1986; U.S.EPA, 1989b). Several criticisms have been directed at the use of this process for quantifying carcinogenic hazards, as summarized below.

- **procedure is too conservative**: The linearized multistage model is generally the most conservative extrapolation model (U.S.EPA, 1989b; Dowd, 1988). In addition, q_1^* is calculated from the upper 95% confidence interval of the model fit, rather than from the "best-fit" line. This process also assumes that no threshold for cancer exists, and that constant exposure to the carcinogen will occur over a 70-year lifetime. Carcinogenic potencies derived using this procedure are extremely conservative as a result of these assumptions. Some have argued that the cumulative effect of these conservative assumptions produces risk estimates too safe by several orders of magnitude, and possibly unrelated to the actual risk (Paustenbach, 1987; Lehr, 1990b; Deisler, 1988; Dowd, 1988).
- **LMS is not a biological model**: LMS is a probabilistic representation of a complex biological phenomena; it is a statistical rather than biological model (Sielken, 1987). A better method of extrapolating to low-dose ranges is the use of pharmacokinetic models, which incorporate mathematical

descriptions of physiologically meaningful processes to model the disposition of a contaminant and its metabolites in the body over time, including absorption, distribution, biotransformation and excretion (Cothern, 1989; Sielken, 1987; Dowd, 1988). However, the required data for such models is only available for very few contaminants.

- **LMS poorly extrapolates to low dose data:** Sielken (1987) compared several dose-response extrapolation models, with a particular emphasis on the linearized multistage model (LMS). Sielken found that the models provided similar fits to high-dose data, but dissimilar projections of risk at the lower doses of interest to man. For example, the ratio of risk estimated by the multistage model to that predicted by the probit model ranged through 9 orders of magnitude for low doses. In addition, Sielken observed that the upper 95% confidence interval of the LMS can be as much as 9 orders of magnitude larger than the best-fit model value. Finally, Sielken concluded that the upper confidence limit of the LMS, which defines q_1^* at the lowest experimental dose, was not responsive to the dose-response data (i.e. calculated q_1^* values were very similar for vastly different dose-response patterns).
- **possibility of a threshold:** several researchers believe that cancer is a threshold phenomenon; metabolic detoxification, DNA repair, and other mechanisms may act to overcome the effects of potential carcinogens at low doses (Cohrssen and Covello, 1989; Lehr, 1990b). The existence of a threshold is generally accepted for promoting carcinogens, those which are not capable of reacting

adversely with DNA, but which can promote the proliferation of transformed cells (Cohrssen and Covello, 1989).

From this discussion, it is apparent that q_1^* values (derived using the LMS model) provide a conservative indication of the carcinogenic potency of a compound; it is likely that the true risk is less than that calculated using the potency factors, and may even be zero (Dowd, 1988).

Slope factors (q_1^*s) and reference doses (RfDs) for chemicals used in wood preservation are presented in Table 2.3-2.

2.3.4.3 Environmental Behaviour and Exposure Pathways

The second type of information required in selection of indicator compounds is the environmental behaviour of potential contaminants. Specifically, knowledge is required on the partitioning, transport and fate of potential contaminants, so that compounds with a wide range of environmental behaviours can be selected to represent the mixture. Quantifying contaminant transport and fate also facilitates identification of exposure pathways. For example, if a compound is volatile in soil, and predominantly exists in the atmosphere above the site, vapour transport will be the predominant pathway by which humans may be exposed to the contamination.

The environmental behaviour of wood preserving chemicals and predominant exposure pathways from abandoned preserving sites are discussed in sections 1.5 and 1.6 of this thesis, respectively.

Table 2.3-2: Reference Doses (RfDs) and Carcinogenic Potencies (q_1*s) for Chemicals Used in Wood Preservation

Preservative	Compound	RfD (mg/kg-d)	q_1* (kg-d/mg)	Comments
PCP-based	Hexachlorodibenzo[p]dioxin		$6.2\text{x}10^{3}$	Group B_2 carcinogen
	Pentachlorodibenzofuran	3×10^{-9}		
	Pentachlorophenol	3×10^{-2}		
	2,3,4,6-Tetrachlorophenol	1×10^{-2}		
	2,4,5-Trichlorophenol	1×10^{-1}		
	2,4,6-Trichlorophenol		1.99×10^{-2}	Group B_2 carcinogen
	2,4-Dichlorophenol	3×10^{-3}		
Creosote-based	Anthracene	5.7×10^{-5}		Based on indeno[1,2,3-cd] pyrene
	Benzo[a]anthracene		3.1	Group B_2 carcinogen
	Benzo[k]fluoranthene	1.1×10^{-4}		
	Benzo[a]pyrene		11.5	Group B_2 carcinogen
	Fluorene	5.7×10^{-5}		Based on indeno[1,2,3-cd] pyrene
	Indeno[1,2,3-cd]pyrene	5.7×10^{-5}		
	Pyrene	1.1×10^{-1}		
CCA-based	Arsenic		15	Group A Carcinogen
	Chromium (6+)		41	Group A Carcinogen

Notes:

- Sources: Table 1.4-5, Table 1.4-9, U.S.EPA (1986a), U.S.EPA (1987c).

2.3.4.4 Selection of Indicator Compounds

With information on the toxicity and environmental behaviour of the potential contaminants, indicator compounds can be selected. Several factors should be considered in the selection of indicator contaminants, as summarized below.

- **historical relevance:** indicator compounds should be chemicals reliably associated with site activities based on historical information (U.S.EPA, 1989b).
- **concentration and identification:** indicator compounds should exist at detectable concentrations in most process areas on site, and should be readily identified in analysis. For example, the compound's peak in a chromatogram should not be masked by that of any other chemical (Hertzman et al., 1989).
- **toxicity:** the slate of indicator compounds selected should include both carcinogens and noncarcinogens to incorporate both threshold and nonthreshold effects. Indicator compound toxicity should be well quantified, including toxicity parameters (RfD or q_1*) as well as weight-of-evidence classification (eg. carcinogen grouping) (Hertzman et al., 1989; U.S.EPA, 1989b). For compounds equally well quantified, and with similar weights-of-evidence, the more toxic compound should be selected, as it will contribute a greater amount to the site hazard.
- **mobility, persistence and bioconcentration:** the group of indicator contaminants should contain mobile as well as persistent compounds. Mobile compounds allow quantification of the risk contamination poses to off-site receptors. Persistent compounds

are related to the hazard posed by contamination to on-site individuals. Compounds readily bioconcentrated are indicative of the food-chain risk presented by site contamination to both on- and off-site populations. At wood preserving sites, naphthalene is a typically mobile compound, benzo[a]pyrene is a typically persistent compound, and dioxins are readily bioconcentrated (section 1.4).

Several methods have attempted to incorporate these parameters into a unified procedure for selecting indicator compounds. Two of the most commonly used approaches are outlined by Rodricks (1984) and U.S.EPA (1989b). In the first method, potential contaminants are assigned a score in each of the following categories: toxic potential, probability of release (based on water solubility, volatility and soil mobility), and environmental persistence. The compound scores are then summed, and those with the highest are selected as indicator contaminants.

In the U.S.EPA (1989b) approach, only a compound's concentration and toxicity are considered in the analysis. In this approach, the compound's toxicity value (q_1^* or 1/RfD) is multiplied by its maximum detected concentration in the medium to produce a medium-specific risk factor. Medium-specific risk factors are then summed to obtain the total risk factor for all potential contaminants in that medium. Separate total risk factors should be calculated for carcinogenic and noncarcinogenic effects, as well as for each medium. Finally, the ratio of the risk factor for each chemical to the total medium risk factor is calculated. Compounds with lower ratios may not be suitable for use as indicator compounds, unless they possess other desirable indicator compound qualities. The risk factors developed in this screening are only for use in selection of indicator compounds, and have no meaning outside this context.

Several chemicals have been used as indicator compounds in risk assessments at wood preserving sites:

- benzo[a]pyrene, naphthalene and benzene were used at a former creosote site in British Columbia (Hertzman et al., 1989); and
- benzo[a]pyrene, naphthalene, carbazole, fluorene, phenanthrene, hexachlorodibenzo[p]dioxin, and pentachlorophenol [PCP] were used at a mixed creosote-PCP site in Alberta (Golder, 1990).

2.3.4.5 Identification of Model Receptor and Exposure Scenario

To this point, site contaminants have been evaluated for both toxicity and environmental behaviour. The next requirement of risk assessment is identification of populations who may be exposed to these contaminants and the likely exposure routes. This requires evaluation of both current and future site use. Current site use determines whether an unacceptable risk exists for populations exposed to present site conditions. Future site use is used to formulate cleanup levels such that future populations will not be exposed to an unacceptable hazard.

Site use influences both the potentially-exposed population and the exposure scenario (pathway and duration). For example, a hypothetical-scenario risk assessment conducted by Tucker and Poppell (1986) indicated that the land use scenario adopted for the analysis affected the magnitude of soil cleanup levels by more than three orders of magnitude. Knowledge of site use is used to define a model receptor. The model receptor selected should be a sensitive member of the potentially-exposed population, as sensitive persons (children, pregnant women, elderly, infirm) would presumably be the most likely individuals affected by site contamination. Multiple receptors may have to be modelled if future site use is uncertain, or if several sensitive receptors exist in a potentially-exposed population.

Potential exposure pathways are identified during examination of the environmental behaviour of the contaminants (section 2.3.4.3). These pathways can be refined to the dominant ones knowing probable site use and the model receptor. For example, the study of a contaminant's environmental partitioning may indicate that it is strongly adsorbed to surface soil horizons, and accumulates in garden vegetables. Consequently, consumption of garden produce is a potential exposure pathway. However, if the site is to be redeveloped for industrial purposes, and the model receptor is a factory worker, this exposure pathway is not tenable and can be excluded from the exposure assessment.

2.3.4.6 Quantification of Exposure

A model receptor will be exposed to indicator contaminants at a site through the defined exposure pathways. The amount of exposure (intake) must be quantified so that the probable response can be predicted. Exposure quantification is generally conducted in two stages: determination of media concentrations and calculation of intakes.

Before chemical intakes can be determined, the contaminant concentrations in media along the exposure pathways must be estimated (exposure concentrations). These concentrations may be estimated using monitoring data alone, or using a combination of monitoring data and environmental models. One of the requirements of site characterization is a knowledge of the areal distribution and magnitude of contamination in all site media (section 2.3.4.1). This information is obtained from site monitoring, which includes sampling and analysis. The resulting data could be used to define exposure concentrations. However in some cases, monitoring data alone may not be sufficient, and fate and transport models may be required. These models require monitoring data which describe site conditions (Table 2.3-1), as well as the source and strength of contamination. Specific instances where monitoring data may be supplemented by fate and transport models are (U.S.EPA, 1989b):

- where exposure points exist in areas not evaluated during monitoring.
- where a knowledge of media concentrations with time is required (temporal distribution). Monitoring data are generally collected over a short period relative to the time frames of contaminant migration, and may not accurately reflect exposure concentrations at some future period.
- where monitoring data are restricted by analytical limits. Potentially adverse effects, such as bioconcentration, still occur below the contaminant quantitation limit. These effects can be considered in models, but are not detected during monitoring.

Two types of fate and transport models exist: single-medium dispersion models and compartmental models. Dispersion models incorporate mathematical descriptions of environmental processes which affect the distribution of a contaminant in time and space within one medium. Groundwater transport models are an example of this type of model. Compartmental models use partitioning relationships to predict the contaminant distribution between environmental compartments (air, soil, water, sediment, biota) assuming homogeneous concentrations within any one phase. Dispersion models generally produce a more accurate estimate of the contaminant concentration in the medium considered, but cannot predict the environmental distribution of the contaminant. Consequently, compartmental models are typically used in exposure assessments.

Monitoring data and environmental models characterize the distribution of contamination in media across a site. Concentrations will not generally be uniform throughout any one medium, and so a decision must be made as to what concentrations should be used in the estimation of chemical intake. The largest medium concentration will predict the greatest contaminant intake, and the most severe estimation of hazard. The smallest concentration will similarly produce the lowest site risk. U.S.EPA (1989b) holds that when estimating exposure concentrations, the objective is to provide a conservative estimate of the average site contamination, and thus they use the upper 95% confidence limit on the arithmetic mean chemical concentration in a particular medium.

The second component of exposure quantification is the estimation of chemical intake. In this stage, exposure concentrations are combined with receptor data to estimate the intake of indicator contaminants from the exposure pathways. Two types of intake exist: administered dose ("intake") and absorbed dose. Administered dose is defined as the amount of contaminant at an exchange boundary and available for absorption, whereas absorbed dose refers to the amount of contaminant actually penetrating the boundary. Exchange boundaries are plasma membranes which surround human organs such as the lungs, gastrointestinal tract and skin. Chemical exposures are expressed as intakes (administered doses) for all pathways except dermal contact, in which case the calculated exposure is actually the absorbed dose (U.S.EPA, 1989b). The use of administered doses (intakes) is consistent with toxicity values for carcinogens and noncarcinogens (q_1^*, RfD), which are generally calculated from critical effect levels based on administered rather than absorbed doses (U.S.EPA, 1989b).

Generalized equations for estimating human intakes from several exposure routes are presented in Table 2.3-3. The results of this assessment are pathway-specific intakes for current and future exposures to individual contaminants.

2.3.4.7 Risk Characterization

In the final risk assessment stage, contaminant intake and toxicological data are integrated to predict the probable response of affected individuals.

Table 2.3-3: Generalized Equations for Estimating Chemical Intakes by Humans

Exposure Route	Equation
Ingestion of chemicals in drinking water	Intake (mg/kg-d) = (CW x IR x EF x ED)/(BW x AT)
Dermal contact with chemicals in water	Absorbed Dose (mg/kg-d) = (CW x SA x PC x ET x EF x ED x CF)/(BW x AT)
Dermal contact with chemicals in soil	Absorbed Dose = (CS x CF x SA x AF x ABS x EF x ED)/(BW x AT)
Inhalation of vapour-phase chemicals	Intake (mg/kg-d) = (CA x IR x ET x EF x ED)/(BW x AT)
Ingestion of contaminated fruits and vegetables	Intake (mg/kg-d) = (CF x ER x FI x EF x ED)/(BW x AT)

Notes:

- Source: U.S.EPA (1989b)
- ABS = absorption factor (unitless)
- AF = soil to skin adherence factor (mg/cm^2)
- AT = averaging time = period over which exposure is averaged (d)
- BW = body weight (kg)
- CA = contaminant concentration in air (mg/m^3), measured or modelled
- CF = contaminant concentration in food (mg/kg), measured or modelled
- CF = conversion factor for units
- CS = contaminant concentration in soil (mg/kg), measured or modelled
- CW = contaminant concentration in water (mg/L), measured or modelled
- ED = exposure duration (a)
- EF = exposure frequency (d/a)
- ET = exposure time (h/d)
- FI = fraction ingested from contaminated source (unitless)
- Intake = administered dose
- IR = ingestion/inhalation rate (L/d) or (m^3/h) or (kg/meal)
- PC = chemical-specific dermal permeability constant (cm/h)
- SA = skin surface area available for contact (cm^2)

Risk characterization as performed by the U.S.EPA (1989b) is comprised of three distinct processes:

- quantify risks from individual chemicals in single pathways;
- quantify risks from multiple chemicals in single pathways; and
- combine risks across exposure pathways.

In the first process, incremental cancer risks and noncancer hazard quotients are calculated for the indicator compounds in each pathway. For carcinogens, risks are estimated as the incremental probability of developing cancer over a lifetime as a result of exposure to a potential carcinogen (U.S.EPA, 1989b). This incremental cancer risk is in excess of the background risk sustained by all humans, which is about 0.20 to 0.25 (20 to 25%) (Lehr, 1990a; ACS, 1984; Golder, 1990). The incremental cancer risk associated with exposure to a potential carcinogen is calculated using the amount of exposure as well as the compound's carcinogenic potency:

$$R_{ij} = I_{ij} \times q_1{}^*{}_i \qquad (2.3\text{-}1)$$

where: R_{ij} = incremental cancer risk associated with compound i in exposure pathway j (a unitless probability)

I_{ij} = daily intake of contaminant i from exposure pathway j, averaged over 70 years (mg/kg-d)

$q_1{}^*{}_i$ = carcinogenic potency of compound i (kg-d/mg).

Noncarcinogenic effects are characterized by a threshold (section 2.3.4.2). Exposure below this threshold (doses less than RfD) is believed to cause no adverse effects, even in sensitive populations (U.S.EPA, 1989b). Above this threshold, adverse noncancer effects may occur. For these compounds, a hazard quotient is calculated, based on intake and reference dose:

$$NHQ_{ij} = I_{ij}/RfD_i \qquad (2.3\text{-}2)$$

where: NHQ_{ij} = noncancer hazard quotient associated with compound i in exposure pathway j. Values greater than 1 imply that intake is greater than the threshold value.

I_{ij} = daily intake of contaminant i from exposure pathway j (mg/kg-d)

RfD_i = reference dose of compound i (mg/kg-d).

Because noncarcinogen toxicity is not modelled by a probabilistic approach, NHQ values are simple ratios, and not an estimate of the probability of an effect occurring.

The second process in risk characterization is to quantify risks associated with multiple chemicals in single exposure pathways. This is accomplished by assuming dose additivity in the absence of toxicological data on chemical mixtures (Stara et al., 1986; Beaulieu, 1989; U.S.EPA, 1989b). Dose additivity neglects potential toxicity modification due to chemical synergism or antagonism between individual compounds, and is a reasonable compromise in neglecting these potentially off-setting effects. For carcinogenic chemicals, a total incremental cancer risk is calculated for each exposure pathway by summing the individual cancer risks:

(2.3-3) $$R_j = \Sigma R_{ij}$$

where: R_j = total incremental cancer risk for pathway j

R_{ij} = incremental cancer risk associated with compound i from exposure pathway j.

For noncarcinogenic effects, a hazard index is calculated by summing the individual noncancer hazard quotients:

(2.3-4) $$HI_j = \Sigma NHQ_{ij}$$

where: HI_j = hazard index for pathway j

NHQ_{ij} = noncancer hazard quotient associated with compound i in exposure pathway j.

If any NHQ value exceeds unity, the toxicity threshold may have been exceeded, and possible adverse effects may result. The summation in equation 2.3-4 is made assuming that simultaneous <u>subthreshold</u> exposures to several contaminants could also result in adverse health effects. Therefore, HI_j values greater than unity are a cause for concern, even if none of the constituent NHQ values are above 1 (U.S.EPA, 1989b). As discussed in section 2.3.4.2, RfDs are generally uncertain to an order of magnitude or more, due to the uncertainty factors incorporated and the difficulty in extrapolating from animal tests to humans. Consequently, RfDs are not a strict demarcation between adverse and nontoxic effects, meaning adverse effects could occur well below HI and NHQ values of 1, and may not occur at parameter values in excess of 1.

In the final stage of risk characterization, incremental cancer risks and noncancer hazard indices are combined across all exposure pathways. An additive approach is used again, assuming the model receptor is exposed to all pathways (U.S.EPA, 1989b). This summation must occur separately for each receptor modelled, incorporating the specific exposure routes. For carcinogens:

(2.3-5) $$\text{Total Incremental Cancer Risk} = \Sigma R_j$$

where: R_j = total incremental cancer risk for pathway j.

For noncarcinogens:

(2.3-6) $$\text{Total Noncancer Hazard Index (THI)} = \Sigma HI_j$$

where: HI_j = total hazard index for pathway j.

If the THI exceeds unity, there may be concern for potential noncancer effects, even if none of the constituent HI_j values exceeds 1 (U.S.EPA, 1989b). If the THI does exceed unity, and if combining exposure pathways has resulted in combining HI values based on different compounds, the contributions of the different chemicals should be segregated according to major effect (U.S.EPA, 1989b). Specifically, a variety of adverse noncancer responses exist, and a segregation by effect can indicate the most likely effect to occur. In the case of carcinogenic effects, there is only one endpoint (cancer), and a segregation of incremental risks by effect is not required.

The product of risk characterization is the incremental cancer risk sustained by the model receptor arising from exposure to carcinogenic indicator compounds, as well as a numerical indication of the potential for adverse noncancer effects arising from exposure to noncarcinogenic indicator compounds. In presenting these results to those responsible for risk management, several points should be emphasized:

- the relative magnitude of site risks and the background or natural occurrence rates of the responses (Deisler, 1988).
- the use of indicator compounds in hazard assessment. The risk posed by all contaminants at a site would presumably be significantly larger than that calculated using indicator compounds alone.
- the uncertainties incorporated throughout the process, which limit the precision of the final risk estimates. Uncertainties are factored into calculation of q_1^* and RfD values, as well as in the assumptions of risk and hazard additivity across compounds and pathways. Risk assessment uncertainties are usually so large that the actual (but unknown) risk may commonly be two orders of magnitude greater or smaller than the estimated value (ACS, 1984; Deisler, 1988).

2.3.4.8 Evaluation of Process

In this section, the risk assessment process is evaluated using the criteria outlined in section 2.1. A summary of its capabilities in comparison to other strategies is presented in Table 2.5-1.

- **applicable to wood preserving chemicals**: sufficient data is available on appropriate indicator chemicals.
- **scientifically defensible**: risk assessment is the most scientifically rigorous way of quantifying the exposure of humans to site contaminants.
- **not quickly implemented**: A full risk assessment, from site characterization to risk quantification, may take years to complete (Hertzman et al., 1989). An additional period is also required for risk management, in which acceptable risk levels are determined and cleanup levels formulated. This delay presents a serious concern, because exposure is still occurring during the assessment and management stages.
- **not legally defensible**: the uncertainties incorporated in risk assessment lead to risk estimates that may be orders of magnitude different from the true but unknown value. In addition, the process includes many subjective decisions. Both of these factors may be legally challenged.
- **incorporates non-technical concerns**: non-technical concerns are incorporated into the risk management process, once risk assessment has been completed.
- **assesses the background hazard**: comparison of site risks with background (natural) levels is an integral part of risk assessment.
- **bioassay values are not considered**
- **site-specificity is considered**
- **all environmental media and contaminant types are incorporated**
- **future land use is incorporated.**

2.3.5 AERIS Model

The exposure assessment and risk characterization phases of risk assessment (sections 2.3.4.6 and 2.3.4.7) are amenable to representation in a computer algorithm. AERIS (Aid for Evaluating the Redevelopment of Industrial Sites) is a computer model developed by SENES Consultants Ltd. which incorporates such an algorithm.

In AERIS, an input file is initially generated, incorporating information about the contaminant, redevelopment scenario, model receptor, and site properties.

- **contaminant**: physico-chemical properties such as molecular weight, aqueous solubility, liquid diffusivity, and octanol-water partition coefficient; toxicological properties, specifically the reference dose (RfD - for noncarcinogens), risk specific dose (RSD - for carcinogens), and bioavailability factors for various media. An RSD value is calculated from equation 2.3-1 using the contaminant's q_1^* value and a specified risk level.
- **redevelopment scenario**: residential, agricultural, commercial or parkland.
- **model receptor**: physical attributes of the individual such as weight, breathing rate, soil intake rate, and amount of time spent outdoors.
- **site properties**: climatological data, site dimensions, soil types (saturated and unsaturated zone), soil organic carbon content and pH, aquifer properties (hydraulic gradient, permeability

thickness), properties related to vegetable growth such as vegetative productivity and length of growing season, a representative depth and magnitude of soil contamination, as well as specific media concentrations (air, produce, groundwater).

The input file is generated using "expert system" technology, where default values as well as guidance in selecting values are provided by the rule base along with prompts for each piece of required data.

Once the input file is generated, the contaminant data, site data and soil concentrations are passed to several modules, where media concentrations are calculated (Figure 2.3-5). This is the first step in quantifying exposure (section 2.3.4.6). Only some of the modules may be invoked, depending on the redevelopment scenario selected and whether media-specific contaminant concentrations were entered as input. The way in which media concentrations are calculated in the various modules is summarized below.

- **correlation module**: generates mass transfer coefficients for the air module. These coefficients describe the rate at which a gaseous contaminant moves across various vapour-phase interfaces. For example, this module generates mass transfer coefficients for the transfer of vapours from soil pore spaces to the ground surface, for the transfer from the soil surface to the laminar sublayer, from the laminar sublayer to the turbulent breathing zone, as well as from concrete to indoor air.
- **air module**: uses mass transfer coefficients generated in the correlation module to calculate the flux of gaseous contaminants

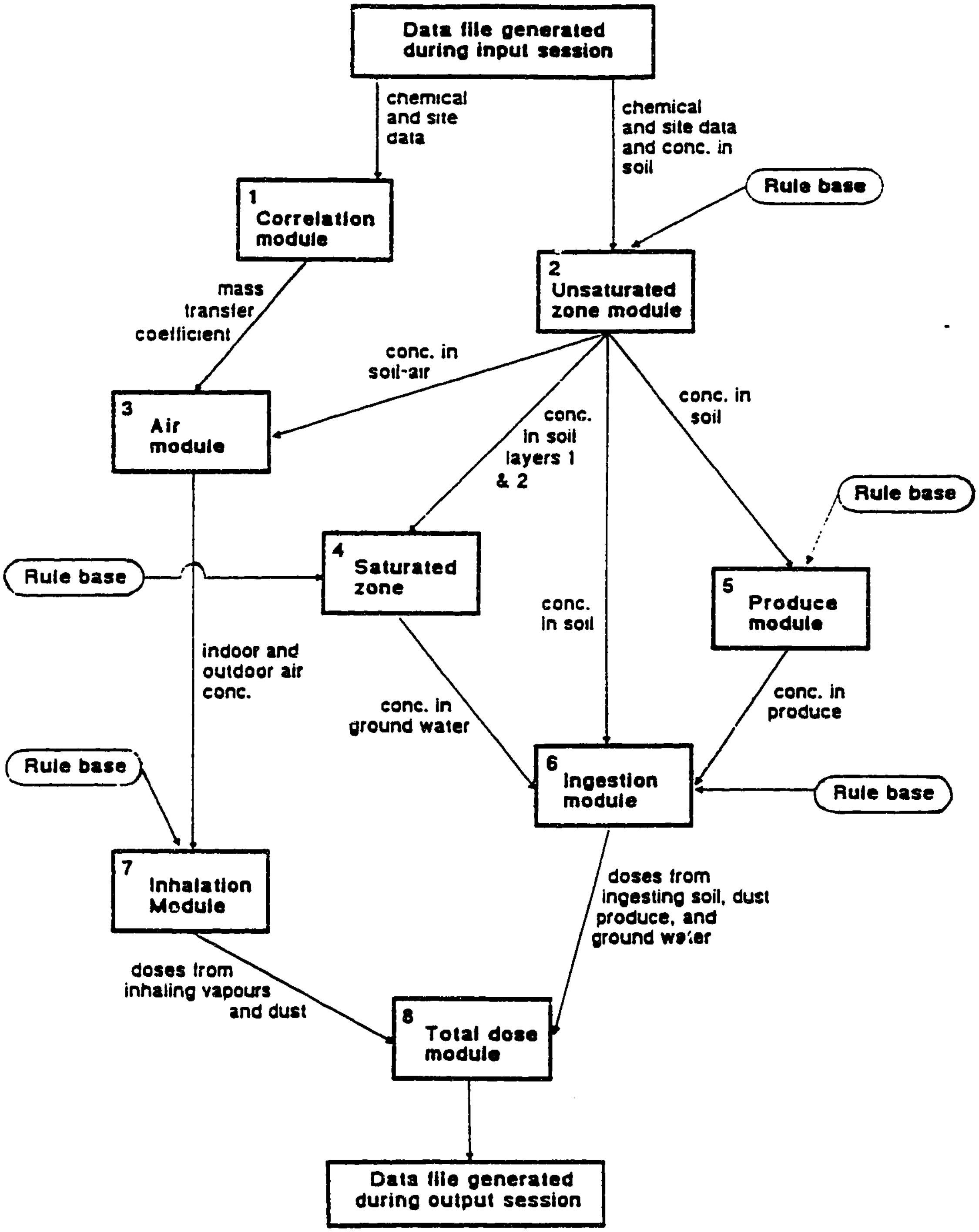
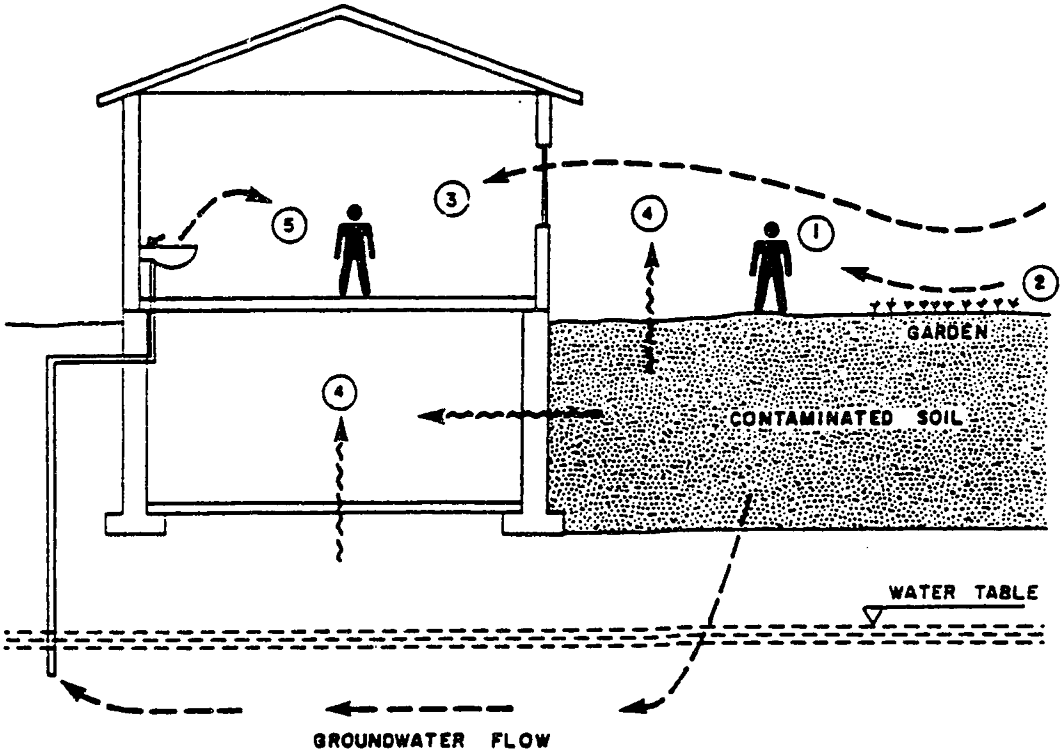


FIGURE 2.3-5 : COMPONENT MODULES AND INFORMATION FLOW (SENES, 1988)

into the receptor's breathing zone while outdoors, and into the receptor's on-site dwelling/business.

- **unsaturated zone module**: calculates soil vapour concentrations for the air module, as well as pore-water concentrations and percolation rates for the saturated zone module. For the purposes of this module, the unsaturated zone can be divided into an upper (contaminated) zone and a lower (uncontaminated) zone if appropriate.
- **saturated zone**: calculates groundwater concentrations for two scenarios: when the entire soil column is contaminated, and when only the unsaturated zone is contaminated. One scenario is neglected in this module, as discussed in section 2.3.5.2.7.
- **produce module**: the soil concentration entered by the user is used to estimate contaminant concentrations in produce grown on-site. Contaminant uptake by produce is assumed to occur by root uptake and foliar deposition in this module.

Once the contaminant concentrations in all environmental media are calculated, these concentrations can be used with receptor and redevelopment scenario properties to quantify the intake of contaminants by receptor organisms. This step comprises the second phase of an exposure assessment (section 2.3.4.5). Calculation of intakes is performed in the ingestion and inhalation modules, using equations similar to those listed in Table 2.3-3. The exposure pathways considered in AERIS are illustrated in Figure 2.3-6.



POTENTIAL PATHWAYS:

① DIRECT INGESTION OF SOIL
INHALATION OF PARTICULATE MATTER

② INGESTION OF GARDEN PRODUCE

③ DIRECT INGESTION OF DUST
INHALATION OF PARTICULATE MATTER

④ INHALATION OF VAPOURS (BOTH OUTDOORS AND INDOORS)

⑤ INGESTION OF GROUNDWATER

FIGURE 2.3-6 : EXPOSURE PATHWAYS CONSIDERED IN AERIS (SENES, 1988)

In risk characterization, the contaminant intake is summed across exposure pathways, producing a total receptor dose. This summation is accomplished in the total dose module of AERIS.

Following risk characterization, media concentrations associated with a total receptor dose equal to the RfD (for noncarcinogens) or RSD (for carcinogens) are calculated. These levels define the cleanup criteria, and are calculated in two steps.

- a linear relationship between total receptor dose and soil concentration is assumed to exist. The total dose (Y_0) and soil concentration (C_{so}) from the model run are used in conjunction with the acceptable dose (RfD or RSD) to determine the acceptable soil concentration:

$$C_{sall} = (C_{so}/Y_0) \cdot (\text{RfD or RSD}) \tag{2.3-7}$$

where: C_{sall} = allowable soil concentration (cleanup level)

C_{so} = input soil concentration

Y_0 = total receptor dose associated with C_{so} (Y_0 calculated in AERIS)

- the correlation, air, unsaturated and saturated zone modules are then invoked to calculate air and groundwater concentrations associated with the computed soil cleanup level.

As a risk assessment model, AERIS possesses many of the inadequacies of a conventional risk assessment. AERIS also contains additional limitations due to the generalized design of the model, which facilitates use at a wide variety of sites, but limits the representation of complex conditions. Accordingly, AERIS should not be used to set specific cleanup objectives, but to identify factors likely to be major contributors to potential exposures, to identify those aspects of site redevelopment requiring more thorough quantification, and to indicate the extent to which remedial action may be required (SENES, 1988).

2.3.5.1 Sensitivity Analysis

Several of the data required by AERIS could vary significantly across a site (for example: soil pH, depth of contamination). However, only one value is allowed as input. The sensitivity of total receptor dose to these parameters should be quantified, so that the significance of the variation with respect to receptor exposure can be assessed.

Unfortunately, many of the potentially-variable parameters in AERIS are used in convoluted ways by the modules, so that the actual impact of the parameters on total dose is difficult to determine. Consequently, a statistical sensitivity analysis, using factorial design, was used to assess the importance of potentially-variable parameters.

First, the parameters to be assessed had to be selected. SENES (1988b), who developed AERIS, compiled a list of typically important and minor parameters based on how they influenced the cleanup levels generated (Table 2.3-4). These parameters were excluded from further study so that uncategorized parameters could be evaluated. To this end, approximately thirty preliminary AERIS runs were conducted, using hypothetical site and redevelopment conditions. These preliminary tests qualitatively confirmed the SENES parameter assessment (Table 2.3-4), and implicated several other parameters as having a possible significant effect on receptor dose. Of these parameters, five were selected for full characterization, based on the relative difficulty of determination, as well as on the likelihood of finding significant parameter variation across a site.

A full 2^5 factorial design was selected to quantify the effect of the five parameters on total dose. The parameters and their respective test levels are listed in Table 2.3-5. The Cayley site was selected for use in the analysis because of the large amount of information available relative to that of other sites. A complete description of test settings and data analysis is presented in Appendix C. The conclusions of the sensitivity analysis are summarized below.

- The effect of other variables, not considered in this analysis, had the greatest impact on total receptor dose (β_0^* is the largest β_i^*). Practically, this means the independent variables tested, and their interactions, cannot adequately describe the model alone; other variables must be considered. In spite of this, the fitted model, utilizing one aggregate parameter for all other effects (β_0^*), adequately described the output response surface.
- Groundwater concentration had the largest effect on total dose of the parameters considered ($\beta_5^* = 0.3490$). Concentrations of a contaminant in groundwater can vary significantly across a site. For example, PCP concentrations at the Cayley site varied from

Table 2.3-4: Typically Important and Minor AERIS Parameters

Parameter	Typical Significance	Comment
RfD (noncarcinogens) RSD (carcinogens)	Important	Important for all compounds
Bioavailability Factors	Important	Important for all compounds
Dose Percentage Factor	Important	Only affects cleanup levels; has no effect on total dose
Degradation Factor	Important	Only affects cleanup levels; has no effect on total dose
Duration Factor	Important	Only affects cleanup levels; has no effect on total dose
Receptor's Body Weight	Important	Important for all compounds
Amount of Produce Eaten or Groundwater Consumed	Important	For relatively non-volatile compounds
Time Spent Indoors	Important	For volatile compounds
Solubility, k_{ow}, Vapour Pressure	Important	For organic compounds
Soil Organic Carbon Content	Important	For organic compounds
Site Length	Minor	-
Aquifer Thickness	Minor	-
Compound Half-life	Minor	-
Inhalation of Suspended Particulates	Minor	Typically minor exposure pathway

<u>Notes:</u>
- Source: SENES (1989b).

Table 2.3-5: Parameters Used in Sensitivity Analysis

Parameter		Reason for Selecting This Value	-1 Level	Reason for Selecting This Value
il Ingestion Rate (summ outdoors) (mg/d)		AERIS default value.	100	Paustenbach (1987) concludes that a consensus estimate for soil ingestion by children (to age 4) is about 100 mg/d. This value is similar to the U.S.EPA (1989b) estimate of 200 mg/d for children to age 6.
Vegetative (garden) productivity (g/m^2)	4090	Productivity of cabbage (SENES, 1988).	280	AERIS default value.
epresentative depth of PCP contamination (m)	3.3	Upper 95% confidence limit on arithmetic mean of depths of contamination (assuming these depths are normally distributed). Only samples containing PCP above the detection limit are considered.	1.1	Arithmetic mean of contamination depth.
epresentative level of PCP contamination (ppm)	5794	Upper 95% confidence limit. U.S.EPA (1989b) holds that when estimating chemical exposures, the objective is to provide a conservative estimate, and thus mandates the use of the upper 95% confidence limit on the arithmetic mean chemical concentration (section 2.3.4.6).	1190	Arithmetic mean of PCP contamination. Only values above the detection limit are considered in computation.
Groundwater PCP concentrations (mg/L)	7.0	One groundwater sample contained PCP concentrations several times the compounds aqueous solubility. Two other samples were similar to, but less than, the solubility limit. Consequently, some pure phase preserving fluid must exist in the aquifer (see also section 4.3.2). Presumably, groundwater containing these fluids would be rejected by users because of its odour and appearance. These liquids may also be removed during pumping and subsequent treatment. However, it is possible that groundwater containing dissolved PCP may be sufficiently palatable to be consumed. Consequently, it is reasonable to assume the maximum concentration of PCP that would be consumed by humans at this site is the aqueous solubility limit, which is 7 mg/L at 5°C.	0.0004	Minimum PCP concentration detected in any site piezometer.

0.4 to 33000 ppb. Given this variation and the parameter's effect on receptor dose, the input value selected must be carefully considered.

- With the groundwater concentration fixed at the lower level (0.4 ppb), the calculated soil cleanup level varied by less than a factor of two in response to all other variables. At the higher level (7000 ppb), the soil cleanup level varied within a factor of about 4 in response to all other variables.
- Soil concentration had the second most significant effect on total dose of the parameters considered ($\beta_4^* = 0.0656$). The importance of this parameter appears logical, as soil-phase contamination is used with partition equilibria relationships to predict vapour-phase, dust and produce concentrations. Direct ingestion of soil is also an exposure pathway. Consequently, the contaminant concentration in soil, which can vary by several orders of magnitude across a site, is an important AERIS input parameter.
- The importance of soil concentration on receptor dose is also apparent in considering interactive effects. The interactions of all variables tested in this analysis had no effect on receptor dose, except two interactions associated with soil concentration. Specifically, a significant interactive effect existed between soil concentration and soil ingestion rate ($\beta_{14}^* = 0.0186$), and between vegetative productivity and soil concentration ($\beta_{24}^* = -0.0016$). For the first interaction, the relationship appears logical, as direct ingestion of soil is an exposure pathway. In the second case however, an interaction should logically exist, but its effect on

receptor dose should be positive; increasing soil concentration combined with greater garden productivity should result in higher plant concentrations, and greater exposure.

- Soil ingestion rate (summer, outdoors) had the third greatest impact on receptor dose of the parameters considered ($\beta_1^* = 0.0282$). Determination of an actual ingestion rate is difficult, and several estimates have been proposed. For example, AERIS uses 477.75 mg/d for adults, U.S.EPA (1989b) recommends 100 mg/d, while Paustenbach (1987) suggests 10 mg/d as a supportable estimate.
- Vegetative productivity had a small negative effect on total dose ($\beta_2^* = -0.0024$), meaning receptor intake decreased as productivity increased. At first glance, this result appears illogical, as higher productivities would presumably lead to greater root uptake of contaminants in soil, as well as a greater leaf area available for deposition of contaminated particulate matter and absorption of vapours. However, a dilution effect may also be occurring, where a given mass of contaminant is distributed in a greater mass of vegetable as productivity increases.
- Representative depth of soil contamination had no effect on receptor dose ($\beta_3^* = 0.0$). This depth is used in AERIS in both the calculation of soil vapour and groundwater concentrations, and would be difficult to assess at wood preserving sites, where several different depths of contamination typically exist.

This sensitivity analysis was completed using pentachlorophenol as the contaminant and data from the Cayley site. Use of a different indicator compound or site scenario could significantly vary the relative importance of the parameters considered in this analysis.

2.3.5.2 Application of AERIS to Wood Preserving Sites

In AERIS, the traditional risk assessment process is translated into a structured set of relationships, represented in a computer algorithm. In this conversion, various assumptions and simplifications are used, leading to model limitations. This section will consider how these limitations affect the application of AERIS to wood preserving sites. Seven areas of application will be evaluated: exposure pathways, partition equilibria, site representation, compound data, temporal concerns, produce uptake, and saturated zone treatment.

2.3.5.2.1 Exposure Pathways

The exposure pathways incorporated in AERIS are illustrated in Figure 2.3-6, whereas those actually existing at wood preserving sites are presented in Figure 1.6-3. In comparing these figures, it is apparent that AERIS neglects three exposure pathways:

- dermal contact with soil and water;
- ingestion of contaminated animals, such as fish; and
- consumption of contaminated surface water.

The significance of these omissions will depend on site conditions and the redevelopment scenario selected. For example, consumption of contaminated surface water and fish were determined to be the two most significant exposure pathways at a former creosoting site in Calgary, Alberta (Golder, 1990). AERIS does not incorporate these pathways, and would have seriously understimated receptor doses for this site.

2.3.5.2.2 Partition Equilibria

AERIS utilizes partition equilibria relationships to quantify how much of a soil-phase contaminant will migrate to other environmental compartments at equilibrium. The use of partition equilibria for wood preserving chemicals was discussed in section 1.5.1.2, and several of the concerns outlined in this section are not addressed in AERIS. Specifically, AERIS requires chemical equilibrium, does not include the presence of a distinct organic phase, and uses partitioning behaviour which is inaccurate for some components (eg. chlorophenols).

Multiphase chemical equilibrium is defined as the point at which there is no net transfer of contaminant among phases. In some instances, partitioning kinetics may be slow relative to the media flux, and equilibrium may not be established (Wu and Gschwend, 1986). For example, the desorption of a chemical from soil may be slower than the rate at which groundwater is migrating past the soil. In such instances, partition equilibria relationships will not accurately predict media concentrations, which are subsequently used in exposure calculations. The significance of using partition equilibria relationships in non-equilibrium environments will be dependent on media flux relative to partitioning kinetics.

In considering compound partitioning in the saturated and unsaturated zones, AERIS neglects the contribution of a separate hydrocarbon phase. As discussed in sections 1.5.1.1 and 1.5.1.2, creosote and PCP wood preserving mixtures are bulk hydrocarbon fluids. Released into a soil environment, these fluids move as a distinct phase, whose rate and extent of migration is controlled by the mixture properties. Chemical equilibrium is the lowest chemical potential attainable by a system, and a soil environment containing a separate phase will attempt to obtain this potential by partitioning compounds from the distinct phase to other environmental compartments (soil, air, pore water). Once the constituents of the distinct phase are partitioned to the different compartments, subsequent transport and fate of these chemicals are dictated by the properties of the individual compounds rather than by those of the mixture. In AERIS, partitioning from the separate phase is neglected, and soil air and pore water concentrations are calculated solely on partitioning from the soil-sorbed phase (Figure 2.3-7). Additionally, partitioning directly from the soil to pore air is not considered. As a result of these omissions, soil and water concentrations predicted by AERIS are likely lower than those actually existing at sites containing a distinct phase, resulting in an underestimation of exposure. The significance of this underestimation will depend on the amount of partitioning which occurs from the distinct phase to air and water (k_0 and k_1), and from soil to pore air (k_3).

A final partition concern associated with AERIS is related to the soil partition coefficient (k_d) used for organic compounds. This coefficient, as

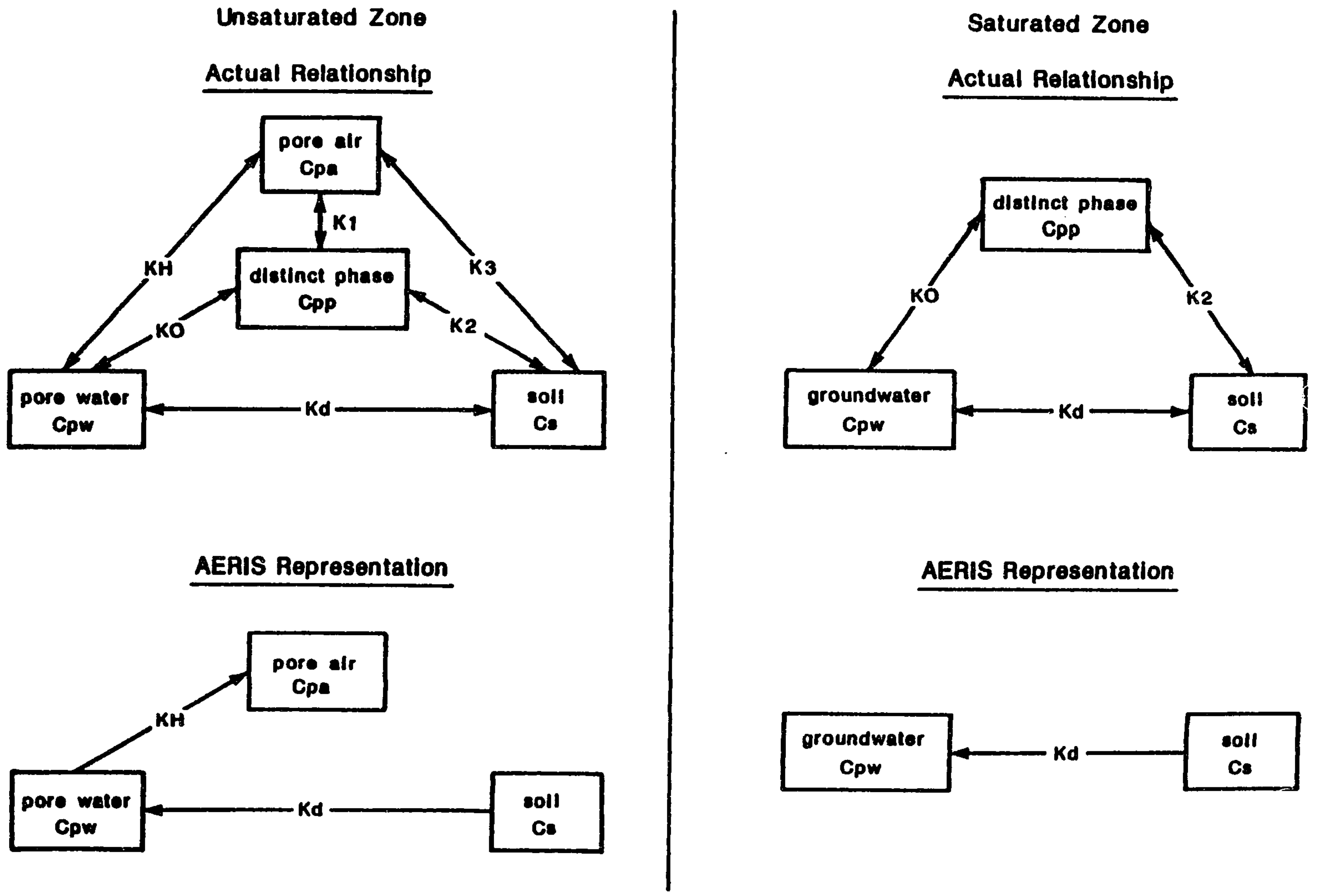


FIGURE 2.3-7 : COMPARISON OF ACTUAL PARTITION EQUILIBRIA RELATIONSHIPS AND THOSE USED IN AERIS (SEE FIGURE 1.5-3 FOR AN EXPLANATION OF THE TERMINOLOGY)

used in AERIS, is based solely on the relative affinity of a compound for solid phase organic carbon:

(2.3-8) $k_d = f_{oc} \times k_{oc}$

where: k_d = soil partition coefficient

f_{oc} = fraction of organic carbon present in soil

k_{oc} = organic carbon partition coefficient, which indicates the extent of chemical partitioning between organic carbon and water at equilibrium.

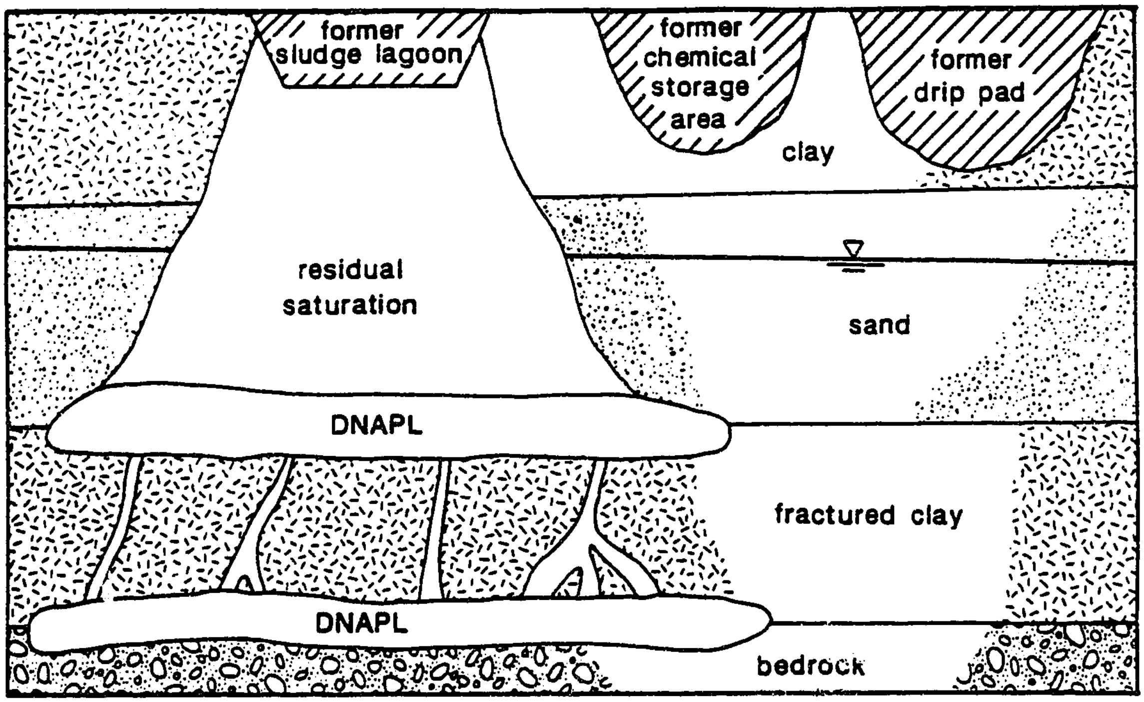
This representation fails to incorporate the solid phase/aqueous phase partitioning of organic compounds which bind to inorganic fractions of soil. In wood preserving mixtures, inorganic sorption specifically occurs for pH-sensitive compounds such as chlorophenols, cresols and some heterocycles, such as pyrrole. For example in section 1.5.1.2.1, both pH and organic matter content were assessed to be the paramount parameters governing chlorophenol adsorption to soil. At low pH values, chlorophenols, creosols and pyrrole exist in protonated forms, which partition significantly to organic matter in soil. However with increasing pH, an increasing fraction of the compounds exists in the ionized state, which may be affixed to exchangeable cations adsorbed to the soil surface, or may be absorbed directly as exchangeable anions. The soil/water partitioning of these compounds is poorly predicted by relationships which simply consider their affinity for organic carbon. Consequently, AERIS should allow the input of site-specific k_d values for organic compounds, as it does for inorganic compounds, or else utilize compound-specific adsorption equations.

2.3.5.2.3 Site Representation

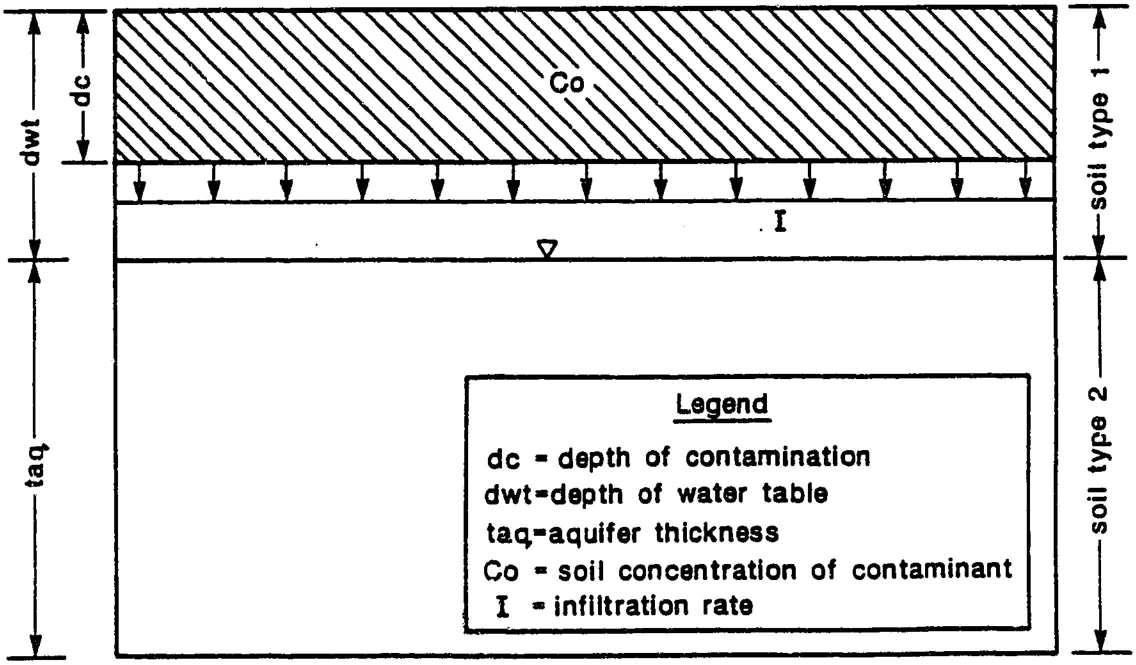
AERIS assumes that soil at a site is contaminated to a uniform magnitude and depth, and that only two formations exist at a site: one in the unsaturated zone and one in the saturated zone. This representation does not accurately reflect observed patterns of contamination at wood preserving sites, where various magnitudes and depths of contamination exist, possibly over several geologic formations (Figure 2.3-8). The simplification of site conditions used in AERIS likely affects the accuracy of exposure estimates, as these simplifications are used in various ways to estimate concentrations in other media. For example, groundwater concentrations are calculated based on the infiltration rate from the contaminated unsaturated zone, which is represented by a uniform depth and magnitude of contamination. Groundwater concentrations computed in this way are subsequently used in exposure calculations, though these concentrations may be significantly different from actual values at sites with a heterogeneous contaminant distribution. Work by Kimbrough and coworkers (in Paustenbach, 1987) has shown that the assumption of a uniform level of soil contamination has the greatest effect of any assumption on exposure concentrations.

2.3.5.2.4 Compound Data

AERIS is designed to be run with only one chemical at a time (SENES, 1989a). Therefore mixtures of chemicals cannot be considered. As discussed in section 1.3, mixtures of chemicals exhibit distinct environmental and toxicological properties, different from those of the



Observed Pattern of Contamination



AERIS Representation

FIGURE 2.3-8 : AERIS REPRESENTATION OF CONTAMINATION AT WOOD PRESERVING SITES constituent compounds. Unfortunately, neither AERIS nor a conventional risk assessment can incorporate data from mixtures.

AERIS contains a database with information on 36 compounds, though any organic compound can be modelled if its physico-chemical properties are known. The wood preserving chemicals included in the database are listed in Table 2.3-6. The constituents of CCA are not present in the database, and cannot be entered as new compounds, as inorganic chemicals require compound-specific partitioning algorithms (SENES, 1988).

The AERIS database erroneously classifies pentachlorophenol (PCP) as a carcinogen. While tests using technical-grade PCP may have produced carcinogenic responses, these are generally attributed to carcinogenic impurities such as 2,4,6-trichlorophenol and hexachlorodibenzo[p]dioxin (section 1.4.1.3.2); studies on pure PCP have indicated that it is neither an initiator nor a promoter carcinogen (World Health Organization, 1987; U.S.EPA, 1986b; World Health Organization, 1982).

2.3.5.2.5 Temporal Concerns

Chemical exposures at abandoned wood preserving sites have a time-dependent (temporal) aspect; contaminants can chemically and biologically degrade, intake patterns may change as a receptor ages, or a person may move from the site. This time dependent nature of exposure is incorporated in AERIS by three parameters: degradation factor, compound half-life, and duration factor.

Table 2.3-6: Wood Preserving Chemicals in AERIS Database

Mixture	Compound
Diesel carrier for PCP and creosote mixtures	benzene 2-methylnaphthalene toluene xylenes
PCP	pentachlorophenol
Creosote	anthracene benzo[a]anthracene benzo[a]pyrene benzo[b]fluoranthene chrysene dibenzo[a,h]anthracene indeno[1,2,3-cd]pyrene phenanthrene phenol pyrene
CCA	none

Notes:

- Organic compounds not in the database can be used in AERIS if the compound's properties are known.
- Inorganic compounds not in the database cannot be used in AERIS, as compound-specific algorithms are required.

AERIS incorporates compound degradation by using a first-order biodegradation rate constant (k) in layer 2 calculations of the pore water concentration. The rate constant, k, is related to compound half-life by equation 2.3-9:

(2.3-9) $k = 0.693/(t_{1/2})$

where: k = biodegradation rate constant (1/h)

$t_{1/2}$ = compound half-life in soil (h).

Unfortunately, this constant is only used in calculations when layer 2 exists at a site. Layer 2 is an uncontaminated layer between the upper contaminated layer and water table. If the depth of contamination exceeds the depth of the water table, AERIS assumes layer 2 does not exist. Compound degradation is not incorporated in any of the other compartments: contaminated zone, saturated zone or atmosphere. In addition, compound half-life has a typically insignificant effect on cleanup levels (Table 2.3-4). This insignificance was qualitatively verified during preliminary AERIS runs, in which half-life was varied over three orders of magnitude with no concomitant effect on receptor dose.

Chemical and biological contaminant degradation are also addressed in AERIS through the degradation factor. The degradation factor selected in AERIS is simply multiplied by the allowable media concentrations to produce new allowable concentrations; the degradation factor has no effect on receptor dose, and has the same effect for both carcinogens and noncarcinogens. This approach poorly reflects the actual situation occurring on-site. A linear relationship is assumed to exist between soil concentration and total receptor dose in AERIS and other risk assessment models (SENES, 1988; Paustenbach, 1987). The compound's half-life in soil could be used to formulate a relationship between soil concentration and time using the biodegradation rate constant (eqn. 2.3-9), which could then be used with the assumption of linearity to generate a relationship between receptor dose and time:

(2.3-10) $Y = (Y_0/C_{s0}) \exp [\ln C_{s0} - kt]$

where: Y = total receptor dose (mg/kg-d)

Y_0 = receptor dose associated with input soil concentration C_{s0} (Y_0 calculated in AERIS)

C_{s0} = input soil concentration (mg/kg)

(Y_0/C_{s0}) = constant relating receptor dose and soil concentration

k = biodegradation rate constant, calculated using equation 2.3-9, where $t_{1/2}$ is also input

t = time.

This relation could be used to assess the variation in receptor exposure with time due to decreasing media concentrations. In this approach, compound degradation is associated directly with receptor dose, which is a more rigorous representation of the actual phenomena than that presently used in AERIS, where degradation is incorporated by arbitrarily increasing cleanup levels. While a more realistic representation, the use of relation 2.3-10 in a computer model would be difficult for noncarcinogenic effects, where the variation of receptor dose with time would have to be applied to the probable time frames of acute and chronic effects.

For carcinogens, the q_1^* value is an upper-bound estimate of the probability of developing cancer from a lifetime exposure to a chemical (U.S.EPA, 1989b). At abandoned sites, exposure seldom occurs over a lifetime, as intake patterns may change or a receptor may move. The duration factor is used in AERIS to account for less-than-lifetime exposure to a potential carcinogen. As with the degradation factor, the duration factor has no effect on receptor dose, but is simply multiplied by the allowable media concentrations to produce new allowable levels. The duration factor is only invoked for carcinogens. This factor poorly reflects the mechanics of chemical carcinogenesis, where risk is not equally distributed over a receptor's life span; Williams and Weisburger (1986) conclude that for many carcinogens, including PAHs, younger members of the species are more susceptible to carcinogens than older members. Consequently, a distinction must be made between less-than-lifetime exposures for adults and children. The duration factor used in AERIS does not incorporate this distinction.

2.3.5.2.6 Produce Uptake

Produce grown in contaminated soil can accumulate pollutants via three mechanisms (SENES, 1988; Paustenbach, 1987):

- **root uptake of soil contaminants.** This pathway is especially significant for root crops (tubers) such as carrots and potatoes;

- **foliar deposition of contaminated particulate matter.** This mechanism may be important for leafy vegetables such as lettuce; and
- **vapour absorption through leaf pores.** This pathway may be significant for volatile contaminants.

In AERIS, the first two mechanisms are incorporated, but the last one is assessed as insignificant and omitted.

Paustenbach (1987) concludes that particulate matter settled on leaves is readily removed during harvesting, rain or washing, and as a result, foliar deposition of contaminated particulate matter rarely presents a health concern. Consequently, the second uptake mechanism may not be as significant as assumed in AERIS.

The significance of omitting the third uptake mechanism is related to the volatility of the contaminant. The volatility of wood preserving chemicals varies widely (Appendix A), so the importance of leaf absorption relative to that of other uptake routes is uncertain.

2.3.5.2.7 Saturated Zone

AERIS considers two scenarios in calculating groundwater concentrations:

- **case 1** - the contaminant source is present in the saturated zone; and
- **case 2** - the contaminant source is not present in the saturated zone.

In case 1, equilibrium sorption-desorption is assumed to dictate groundwater concentrations:

(2.3-11) $C_{gw} = C_s/k_d$

where: C_{gw} = contaminant concentration in groundwater

C_s = contaminant concentration in soil

K_d = soil partition coefficient.

In case 2, groundwater concentrations are computed assuming instantaneous dilution of contaminated water infiltrating from the unsaturated zone:

(2.3-12) $C_{gw} = C_I \, L \, I \, / \, [Q_{in} + L \, I]$

where: C_I = contaminant concentration in infiltrating water

L = length of the site

I = infiltration rate

Q_{in} = hydraulic flowrate entering contaminated zone.

AERIS neglects an alternative case 1 scenario: when the contaminant source is present in the saturated zone but does not extend the full aquifer depth. Equation 2.3-11 is only valid when the entire soil column is contaminated. An equation for the omitted case is derived in Appendix D. This equation actually represents the most generalized situation, from which equations 2.3-11 and 2.3-12 can be derived (Appendix D). The significance of this omission depends on the thickness of the portion of the contaminated layer in the saturated zone relative to the total aquifer thickness.

In both case 1 and case 2 scenarios, groundwater concentrations are calculated assuming equilibrium sorption-desorption from a contaminated soil layer of uniform depth and concentration, extending the full length of the site. Some of the limitations of this representation were discussed in section 2.3.5.2.3. In general, more accurate groundwater concentrations could be predicted using mass transport (dispersion) models, which quantify plume migration from a source of finite extent, such as from a sludge pond. These models characterize the migration of a soluble-component plume considering the processes of advection, dispersion, and diffusion, as well as sorption-related retardation and degradation. Groundwater concentrations predicted from such models would inevitably be more accurate than those generated by AERIS, and consequently, so would the exposure estimates. In addition, mass transport (dispersion) models are capable of predicting groundwater concentrations at off-site locations, and at different periods of time, whereas AERIS can only predict steady-state concentrations directly beneath the contaminated soil layer.

2.3.5.3 Additional Comments

A number of other technical concerns, not specifically related to wood preserving sites, have been noted in the use of AERIS.

- Bioavailability factors can be specified for each exposure pathway in AERIS. These factors attempt to model the difference in "availability" of contaminants in different media for uptake at exchange boundaries (plasma membranes). U.S.EPA (1989b) recommends that these relative absorption efficiencies should not be used, as toxicity values (RfD, q_1*) are generally calculated from critical effect levels based on administered rather than absorbed doses. Consequently, the use of bioavailability factors may result in comparing absorbed doses with toxicity values based on administered doses.

- AERIS assumes that 75% of airborne particulate matter reaches the lower lung (alveoli). In contrast, Paustenbach (1987) holds that only 50% of airborne particulates are in the respirable size range, and that 50% of the respirable fraction is deposited in the upper airways and ultimately swallowed. Consequently, only 25% of suspended particulate matter is believed to reach the lower lung.
- Some parameters that the user should be able to modify are fixed in AERIS. For example:
  - fraction of airborne particulate matter reaching the lower lung; and
  - dimensions of on-site building and air-exchange rate.
- Some inconsistencies exist between values listed in the AERIS documentation and those used in the model. Specifically, SENES (1988) states that a child consumes 250 mg of soil per day when outdoors, but uses 477.75 mg/d in the model. In addition, an AERIS explanation screen states that a child drinks 0.7 L of water per day, but 1.0 L/d is used in calculations.

- AERIS assumes an adult ingests 477.75 mg of soil per day when working outdoors, and 110 mg/d when indoors. Paustenbach (1987) concludes that ingestion rates of 0 to 10 mg/d are reasonable and supportable for adolescents and adults.
- A number of less significant concerns also exist:
    - AERIS does not print the input file, which makes it difficult to confirm data was entered correctly;
    - the first output table is too long for the page, and consequently prints onto the next line; and
    - after editing a context file value, AERIS should return the user to the location in the context file where the change was made, rather than directly to the start of the file.

2.3.5.4 Overall Assessment

A conclusion of the risk assessment discussion was that the uncertainties involved were so large that the actual (but unknown) risk could be two orders of magnitude greater or smaller than the calculated value (section 2.3.4.7). Considering the limitations of AERIS with regards to conditions at wood preserving sites, the risk estimates provided by AERIS (as calculated from doses) would be at least this uncertain. Specifically, the dose estimates produced by AERIS may be completely inaccurate at wood preserving sites where:

- dermal contact with soil or water, ingestion of contaminated animals, or consumption of contaminated surface water are significant exposure pathways;

- significant partitioning from a distinct hydrocarbon phase occurs;
- compound sorption-desorption is poorly predicted by correlations with organic carbon levels;
- site contamination cannot reasonably be represented by a soil layer of uniform contamination and depth;
- compound degradation is rapidly occurring;
- significant contaminant uptake is occurring by vapour absorption through leaf pores; and where
- groundwater concentrations are not accurately predicted by equilibrium desorption from a contaminated soil layer of infinite extent.

As a result of these limitations, the current version of AERIS should not be used at wood preserving sites as the sole resource in quantifying doses resulting from site contamination, or in establishing cleanup objectives. This recommendation is consistent with the intended use of AERIS, which is as an aid.

AERIS can also be evaluated using the criteria outlined in section 2.1. A summary of its capabilities in comparison to other strategies is presented in Table 2.5-1:

- the current version of AERIS cannot model CCA contamination, and is therefore not completely applicable to wood preserving chemicals;
- AERIS is not scientifically defensible for defining ultimate cleanup levels, considering the limitations outlined in this section;

- **AERIS could be quickly implemented, as its data requirements are minimal;**
- **AERIS is not likely to be legally defensible, given its limitations;**
- **AERIS cannot incorporate non-technical concerns;**
- **AERIS can assess the background hazard using background chemical concentrations;**
- **AERIS cannot incorporate bioassay values;**
- **AERIS does consider site-specificity;**
- **AERIS does not incorporate all environmental media or contaminant types; and**
- **AERIS does consider future land use.**

2.4 Ad Hoc Approaches (Alberta)

Most jurisdictions in Canada rely on ad hoc (case-by-case) approaches in assessing site contamination and developing cleanup guidelines. Some examples will be illustrated by considering current approaches in Alberta. Alberta currently has no systematic approach for developing assessment or cleanup criteria for organic contamination, but has developed assessment criteria for inorganics in acidic soils (Table 2.4-1) (Richardson, 1987). For either type of contamination, the province requires the responsible party to specify what contaminants are present, which are of concern, and what residual levels for these compounds should be acceptable (Monenco, 1988). Residual contamination must not present a hazard to any subsequent site user, or migrate beyond site boundaries. The specific criteria selected for identified compounds must be supported by appropriate, scientifically defensible data (Richardson, 1987).

To assist with this task, the province commissioned Monenco Consultants Limited to develop criteria for <u>metals</u> in acidic soils (Table 2.4-1). This study produced suggested cleanup guidelines for various metals, but concluded that site-specific conditions must be considered, and therefore the criteria are only to be used as guidelines towards selecting final cleanup levels. The criteria are based on a number of factors, including the uptake of heavy metals by plants from soil, the phytotoxic limits for native plants, and the bioaccumulation of contaminants from foraging animals to humans.

No guidelines have been formally adopted for <u>organic</u> contaminants in soil, though there is some indication the Quebec assessment criteria are being

Table 2.4-1 : Suggested Cleanup Guidelines for Inorganic Contaminants in Acidic Soils in Alberta

Element	Determining Factor	Acceptable Level for Acidic Soils (pH<6.5) (ppm)
Cadmium		1
Chromium		600
Cobalt (preliminary)		100
Copper		200
Lead		800
Manganese		-
Nickel		250
Zinc	sheep diet	700
Zinc	others	100

Notes:

- source: Monenco, 1985b.
- no limit was recommended for manganese due to high naturally occurring levels.

used informally during site evaluation (Hingston, 1990). In addition, Alberta Environment has drafted a document for discussion, outlining proposed cleanup levels for organic contaminants in soil.

In 1984, prior to the development of cleanup guidelines for heavy metals in soil, Monenco Consultants Limited decommissioned a wet cell battery plant as well as a sour gas processing facility. Case studies are provided by Monenco (1985a), Richardson (1987) and Monenco (1988). These decommissionings illustrate concerns seen as important by Alberta Environment.

The Exide Battery Plant, located in Calgary, produced wet cell lead batteries for approximately 30 years. The plant was closed in 1982 and decommissioning initiated. Site characterization revealed high levels of lead in the upper 10 to 15 cm of soil, with concentrations as high as 114 000 ppm (11.4% of soil on a dry weight basis). The cleanup level selected for site soils was 2600 ppm lead, based on the potential for re-entrainment of lead dust, as well as potential ingestion of contaminated soil by children. This level had been adopted by Ontario and Manitoba for cleanup in the vicinity of secondary lead smelters. Remediation was completed by excavating soils contaminated above the 2600 ppm guideline. Soils with average concentrations below 4000 ppm lead were landfilled in a regional facility, while soils exceeding the 4000 ppm limit were transported to a hazardous waste facility in the U.S. for disposal.

The Pincher Creek Sour Gas Plant operated from 1957 to 1983, at which time decommissioning was initiated due to declining gas reserves. Site investigation revealed joint organic/inorganic contamination in soil, including such compounds as chromium, mercury, lead, sulfur, PAHs and phthalates. Groundwater was also found to be contaminated with sulfate, iron and manganese. While probable future site use included both industrial and agricultural, cleanup levels were based on agricultural use because more stringent criteria would result. Recommended maximum metal concentrations were determined from evaluation of phytotoxic limits (plants), tolerable concentrations (livestock), and soil/crop metal levels. The criteria selected for organic contaminants was 2.0 ppm total hydrocarbons. Site reclamation involved transport of heavily contaminated wastes to a hazardous waste facility in the U.S., and disposal of moderately contaminated material in a regional landfill.

2.5 Recommended Approach

A comparison of the capabilities of the assessment strategies considered in this study is presented in Table 2.5-1. From this comparison, it appears that statutory guidelines, risk assessment/risk management, and AERIS have the widest range of capabilities of the alternatives considered. Each of these strategies possesses advantages and disadvantages for use at wood preserving sites.

- **Statutory Guidelines:**
    - quickly implemented and require minimal data, and are therefore economical, but
    - cannot incorporate site-specific concerns.
- **Risk Assessment/Risk Management:**
    - most scientifically rigorous way of quantifying the human health risks associated with site contamination, but
    - requires large amounts of data and a long time to complete the technical and non-technical aspects, during which exposures are still occurring.
- **AERIS:**
    - quickly implemented and requires minimal data due to expert system design, but
    - is not applicable to wood preserving sites in its present form (section 2.3.5.4).

An alternate strategy has been developed for assessing contamination at wood preserving sites and deriving cleanup levels. This approach uses the best aspects of the three strategies, and modifies some of the less desirable attributes. Two separate levels, or tiers, are incorporated in the approach.

Table 2.5-1 : Comparison of the Capabilities of Existing Assessment/Cleanup Strategies

Strategy	Applicable to Wood Preserving Chemicals?	Scientifically Defensible?	Quickly Implemented?	Legally Defensible?	Incorporation of Non-Technical Concerns?	Assessment of Background Hazard?
Statutory Guidelines	√	√	√	√	x	x
Quebec Assessment Criteria	√	√	√	√	x	x
Restoration to Background Levels	√	x	?	√	x	x
Technology-Devised Standards	√	x	√	?	x	x
Cost/Benefit Analysis	√	√	x	?	x	√
Risk Assessment/Risk Management	√	√	x	x	√	√
AERIS	?	x	√	x	x	√
Alberta	x	?	x	?	?	?
Recommended Approach	√	√	?	√	√	√

continued ...

Notes:

- information presented in this table is discussed in the text.
- √ signifies the strategy deals with the concern.
- x signifies the strategy does not incorporate the concern.
- ? signifies situations for which no definitive answer exists.

Table 2.5-1 : continued

Strategy	Consideration of both Chemical Concentrations and Bioassay Values?	Consideration of Site-Specificity?	Incorporation of all Environmental Media and Contaminant Types?	Incorporation of Future Land Use?
Statutory Guidelines	√	x	√	?
Quebec Assessment Criteria	x	x	x	√
Restoration to Background Levels	√	x	√	x
Technology-Devised Standards	√	√	√	x
Cost/Benefit Analysis	x	√	√	x
Risk Assessment/Risk Management	x	√	√	√
AERIS	x	√	x	√
Alberta	x	√	x	?
Recommended Approach	√	√	√	√

Notes:

- information presented in this table is discussed in the text.
- √ signifies the strategy deals with the concern.
- x signifies the strategy does not incorporate the concern.
- ? signifies situations for which no definitive answer exists.

2.5.1 Level 1

A Level 1 treatment would be used for sites where no imminent hazard to human health or the environment is suspected or has been observed. A typical Level 1 site would be one where groundwater contamination has not been observed in nearby wells, or where seeps of wood preserving mixtures to nearby water bodies have not been noted.

An assessment of the contamination at a Level 1 site would be conducted using a modified version of AERIS. Modifications to AERIS are required for the model to accurately assess exposures at wood preserving sites, and several new aspects should be incorporated:

- exposure pathways for dermal contact with contaminated soil and water, for consumption of contaminated animals, and for consumption of contaminated surface water;
- partitioning from a separate hydrocarbon phase;
- compound-specific sorption equations;
- algorithms for multiple depths and magnitudes of contamination across a site; and
- sorption algorithms for the constituents of CCA.

The modified version of AERIS would be run numerous times for several different indicator compounds, with the most influential parameters varied throughout their site range. The product of these runs would be several different dose estimates for each indicator compound. In keeping with the U.S.EPA's practice of using the upper 95% confidence interval in exposure assessments, the upper 95% confidence interval of the mean receptor dose would be calculated for each indicator compound. If these upper-bound estimates of total receptor dose are much larger than their respective reference doses (RfDs) or risk specific doses (RSDs), the site may pose an imminent hazard and should be upgraded to a Level 2 analysis. The ratio of receptor dose to reference criteria at which Level 1 sites should be considered for Level 2 analysis is arbitrary, though a ratio of 2 or 3 appears reasonable. If this ratio is greater than 1 but below the arbitrary value selected, a Level 1 analysis is adequate and cleanup criteria can be generated.

To develop cleanup criteria, the lower 95% confidence interval of the soil cleanup levels generated in the AERIS runs could be used for each indicator compound. This value would be compared with some statutory level, such as the Quebec C criteria. If the value is below statutory criteria for that compound, the value can be adopted for use. If the value exceeds statutory guidelines, it should undergo a specific review prior to use, ensuring the value was rationally developed, and incorporates all major exposure pathways. A relevant battery of bioassay procedures should also be incorporated into the cleanup criteria, ensuring that toxicity reduction occurs along with contaminant removal. Several bioassays which could be used for various exposure pathways at contaminated sites are outlined by Fitchko (1989).

2.5.2 Level 2

A Level 2 treatment would be used for sites where an imminent hazard to human health or the environment is suspected, observed, or predicted in a

Level 1 analysis. A typical Level 2 site would be one where wood preserving mixtures have been observed seeping into nearby waterways, or where off-site groundwater wells are believed to be contaminated. The potential hazard posed by such sites dictates that a full risk assessment be conducted, in order for the human health risks associated with the contamination to be quantified as accurately as possible.

However, a full risk assessment, from site characterization to risk characterization, takes a long time to complete, during which exposures are still occurring. Consequently, some modifications must be made to the process. Specifically, the first step in risk assessment is site characterization (section 2.3.4.1). Information gathered in this stage should be used to implement containment and source control strategies to minimize exposures during the assessment process. These strategies would be based on a qualitative assessment of what the most significant exposure pathways are likely to be. This process can be considered a preliminary risk assessment to guide the need and selection of containment actions. For example, if wells near a wood preserving site have been shown to be contaminated, and a non-secure sludge lagoon is suspected as the source, sludge pond liquids should be removed, and a downgradient extraction well system installed. The full risk assessment, which must consider long-term risks to human health and the environment, will provide guidance concerning the need for and extent of final cleanup. The risk assessment should recommend a relevant battery of bioassay procedures which can be incorporated into the cleanup levels.

3. Remediation Technologies

In section 2, various ways of assessing the contamination at wood preserving sites and determining acceptable residual contaminant levels were examined. In this section, methods of reducing the hazards posed by these contaminants will be evaluated. Remediation strategies for soil and groundwater contaminated with wood preserving chemicals can be divided into four main categories: containment, destruction, concentration, and dilution.

Containment strategies attempt to reduce the hazards posed by residual chemicals using some encapsulation technology which physically separates contaminated soil and groundwater from natural processes which would tend to disperse the contamination. This encapsulation can occur on a macroscopic scale using isolation methods such as capping, slurry walls or landfill disposal, or on a smaller scale using solidification/ stabilization.

Destruction alternatives "destroy" the contaminants by converting them to less toxic forms. For example, incineration thermally oxidizes organic contaminants to mineralized products, whereas bioreclamation facilitates the microbial decomposition of organic pollutants to nontoxic byproducts.

Concentration strategies involve a separation process by which contaminants are separated from the bulk soil or groundwater phases. The resulting concentrated chemical residue will then require containment or destruction. Vapour extraction, soil washing, and pump and treat are all examples of concentration strategies.

The fourth category of reclamation alternative is dilution. Contaminants added to soil systems will migrate with the bulk groundwater flow (advection), while spreading in all directions as a result of soil heterogeneities (dispersion) and concentration gradients (molecular diffusion). In other words, natural processes attempt to disperse the contaminants throughout the soil system, thereby minimizing the system's chemical potential (Dragun, 1988). At some sites, water-flushing has been used to enhance contaminant spreading. Although there may be conceptual grounds for using such an approach to reduce threshold health risks by dilution below threshold response levels, such an approach would be highly suspect for non-threshold health risks, such as cancer. Consequently, dilution strategies will not be pursued further.

3.1 Containment Strategies

3.1.1 Landfill Disposal

A landfill is an engineered underground structure where wastes are placed in perpetuity. Soil and sludge at the five sites containing PCP, creosote or CCA at concentrations below limits outlined in the Hazardous Waste Regulations could be excavated and disposed in a suitable landfill.

3.1.1.1 Landfill Categories

Two types of landfill exist in Alberta: sanitary, which may also be labelled municipal or regional, and industrial. Sanitary landfills store domestic wastes whereas industrial landfills are used for industrial refuse. Because more dangerous substances are generally involved, greater care is taken in industrial than in sanitary landfills to segregate incompatible wastes. Three different classes of industrial landfill exist in Alberta, each differing by the level of protection afforded and a corresponding list of permissible substances (Alberta Environment, 1987).

- Class I

  This class of industrial landfill may not accept hazardous wastes prohibited from landfill disposal by regulation, and must provide:

  - two liners, one of which must be synthetic
  - a leachate collection and removal system
  - a leak detection system between the two liners
  - surface run-on and run-off control systems
  - gas interception and venting systems

  - groundwater monitoring systems

- Class II

  In addition to Class I restrictions, Class II landfills may not accept for disposal any liquid hazardous waste or hazardous waste containing free liquids. Class II landfills must provide:

  - a synthetic or clay liner
  - surface run-on and run-off control systems
  - gas interception and venting systems
  - groundwater monitoring systems

- Class III

  This class of industrial landfill is limited to accepting inert solid wastes. Landfill-restricted hazardous wastes, wastes containing free liquid, and putrescible wastes are not permitted at Class III landfills. Favourable geologic conditions and a surface drainage control system are also required.

Sanitary landfills designed and operated according to the Waste Management Regulations issued under the Public Health Act are equivalent to Class II industrial landfills. A sanitary landfill containing a synthetic liner and leachate collection system may also be considered equivalent to a Class I industrial landfill (Alberta Environment, 1987). Regardless if some sanitary landfills are viewed as equivalent to industrial landfills, the Waste Management Regulation of the Public Health Act prohibits disposal of any hazardous waste into a modified sanitary landfill or dry waste site (Alberta Environment, 1988a). Excavated soil from any HELP site which is classified as a hazardous waste (section 3.1.1.2) can therefore only be disposed in an industrial landfill. At present, five publically-operated Class II industrial landfills and one Class I facility exist in Alberta, plus a number of private landfills on industrial sites.

3.1.1.2 Regulatory Limits on Landfill Disposal

Regulatory limits on landfill disposal are set out in section 17 of the Hazardous Waste Regulations under the Hazardous Chemicals Act of Alberta. In general, hazardous waste may be landfilled under two conditions:

- the waste is not included on a list contained in section 17(3), and
- the landfill is approved for that purpose by the Director of Standards and Approvals.

The list of hazardous wastes prohibited from landfill disposal contained in section 17(3) of the Hazardous Waste Regulations does affect the disposal of PCP-contaminated soil and sludge. Specifically, section 17(3)(a) prohibits landfill disposal of liquid and solid hazardous wastes containing tri-, tetra- and pentachlorophenol (PCP) in a concentration greater than 1000 ppm. Residual sludge pond liquids and some surrounding soil at the Cayley, Calgary, Blackfalds and Faust sites all exceed this 1000 ppm limit, and are correspondingly prohibited from landfill disposal. Incineration at Swan Hills is likely the only alternative for these materials.

Creosote composition was described in Section 1.4.2. The 26 most prevalent compounds in creosote (from Table 1.4-6) are not listed in section 17(3) of the Hazardous Waste Regulations as chemicals restricted during landfill disposal. Some of the remaining compounds in creosote, such as cresol, are included on the restricted substances list, but would not be present in concentrations near the 1000 ppm limit. There appears to be then no specific regulations under the Hazardous Chemicals Act prohibiting disposal of creosote contaminated soil into landfills approved by the Director of Standards and Approvals for disposal of hazardous wastes.

Liquid wastes arising from the use of chromated copper arsenic (CCA) are also subject to landfill disposal restrictions. Specifically, section 17(3)(f) of the Hazardous Waste Regulations prohibits the disposal of <u>liquid</u> wastes containing arsenic or chromium (+6 valence) in concentrations greater than 500 ppm. This restriction affects the disposal of residual CCA sludge. Soil containing CCA is not explicitly restricted from landfill disposal in these regulations. A more detailed discussion of this point is presented in section 7.4.2 of this thesis. The failure of the Hazardous Waste Regulations to designate wood preserving contaminants as hazardous wastes prohibited from landfill disposal is an oversight when the mobility and toxicity of these chemicals is considered.

On the basis of existing regulations, soil at the five sites is classified as a hazardous waste if it fulfils the definition of a hazardous waste presented in the schedule of the Hazardous Waste Regulations. Mildly contaminated soil may not satisfy the requirements of these regulations, and could therefore legally be disposed in a municipal landfill.

3.1.1.3 Advantages

Landfill disposal of contaminated soil and sludge from wood preserving sites is an attractive alternative for a number of reasons. First, landfill disposal is well-understood and can be quickly implemented. Excavation of contaminated material could begin immediately and remediation would only be limited by the rate at which the material is hauled off the site.

Secondly, landfill disposal requires no residual monitoring at the site provided that thorough remediation is achieved. Soil contaminated above a selected residual value would be excavated and removed, allowing site re-development consistent with the cleanup level.

Finally, costs for landfill disposal of contaminated material may be lower than for other alternatives such as incineration. Any economic benefits from the use of this approach will depend directly on the hauling distance to an approved landfill and the landfill charges. Consequently the economic advantages of landfill disposal will vary from site to site. At the Blackfalds site, soil containing PCP below 1000 ppm was excavated and landfilled in the Class II facility at Rocky Mountain House. Landfill charges, excluding transportation costs, were \$10/tonne (\$15/m^3 for soil of density 1500 kg/m^3).

3.1.1.4 Disadvantages

Landfill disposal of contaminated soil and sludge from wood preserving sites also presents a number of concerns. First, the mobility of wood preserving chemicals is pH-dependent. A landfill leachate of non-neutral pH may thus mobilize and transport contaminants into the environment if the landfill is not secure. Generally, landfill leachates will be somewhat acidic because of the organic acids generated by anaerobic decomposition of degradable organic matter. The following relationships between pH and preservative mobility exist:

- the solubility of CCA components copper, chromium and arsenic increases as pH decreases. These metals are susceptible to leaching from CCA contaminated soil by acidic leachate.
- as pH increases, PCP ionizes to the pentachlorophenate ion form, which is much more soluble in water. The pH-dependent equilibrium between these two species is illustrated in Figure 3.1-1, and was discussed in section 1.4.1.1. A landfill leachate of high pH may mobilize adsorbed PCP from contaminated soils.
- a number of components in creosote also experience increased mobility with changes in pH. For example, cresol and pyrrole mobility is enhanced at high pH values.

The major long-term environmental threat from hazardous waste landfills is leachate migration to ground or surface waters. Consequently, competent facilities minimize leachate formation by liquid waste/solid waste segregation and liquid waste dewatering, while containing and collecting any leachate which does form. The risks posed by soil

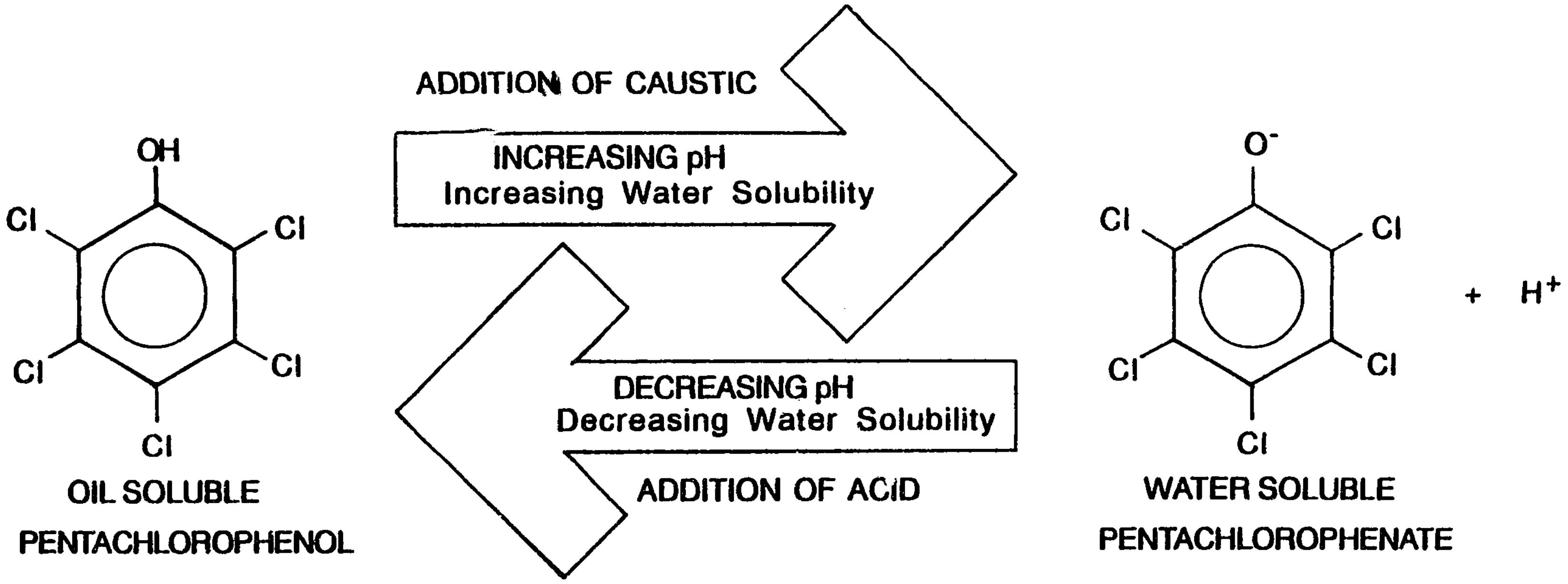


FIGURE 3.1-1 : THE PH-DEPENDENT EQUILIBRIUM BETWEEN PENTACHLOROPHENOL AND PENTACHLOROPHENATE (ADAPTED FROM ENVIRONMENT CANADA, 1983)

contaminated with wood preserving chemicals may be greater in landfills not implementing such strategies than in the natural soil environment.

Another concern regarding landfill disposal of contaminated soils relates to liability. This discussion cannot provide a rigorous legal evaluation of landfill disposal in Alberta. However, issues which should be considered while assessing this technology for the HELP sites include:

- **ownership**: legal precedents have generally followed the premise that whoever owns the land is responsible for the contamination on that property, even if it was generated by a previous owner or tenant (i.e. buyer beware).
- **excavation**: the contractor performing the excavation operation would normally be responsible for the safety of his employees under the Workers Compensation Act.
- **transportation**: joint liability is generally held between owner and transporter of a hazardous waste under the Transportation of Dangerous Goods Act. This issue is significant because some of the HELP sites are isolated, and transportation of contaminated soil may occur over several hundred kilometres to an approved facility.
- **residual liability for landfilled material**: currently no unified approach exists for assessing the liability of landfilled hazardous waste in Alberta. In the absence of specific legislation on this issue, the owner might maintain liability for the material unless that liability was expressly transferred to the Department of Health, which regulates landfills. This issue is significant

because landfill disposal involves no action to decontaminate the soil, and resultingly, the danger of contamination arising from leachate releases remains indefinitely. The issue of residual liability is clearly defined for disposal at the Swan Hills facility, where the Alberta Special Waste Management System contractually assumes perpetual liability. From the viewpoint of the Alberta government, it ultimately assumes the liability for the Alberta Special Waste Management System beyond the limits and restrictions of its environmental impairment liability insurance. Consequently, there are very limited benefits for any Alberta government agency in transferring liability to the Alberta Special Waste Management System.

3.1.2 Solidification/Stabilization

Solidification/Stabilization of contaminated soil seeks to render the contaminants in the soil immobile, insoluble and unreactive. This objective is pursued by mixing the soil with some reagent to produce a monolithic mass of high compressive strength, low permeability, and small contaminant leaching potential.

The stabilization component of solidification/stabilization involves conversion of the contaminants to a chemical form that is more resistant to leaching and more amenable to solidification. The most common stabilization mechanisms are precipitation (as hydroxides, silicates or sulfides), complexation and organic binding (Barth, 1988). The objective of stabilization is to provide additional protection against the possibility of physical or chemical breakdown of the solidified mass; if the solid matrix were to collapse, the waste would be stabilized, thus limiting any contaminant release (Pojasek, 1978).

Solidification is the incorporation of a stabilized waste into a solid mass, thus reducing the exposed surface area of the waste available for leachate attack. Solidification can be accomplished by one of two modes: microencapsulation or macroencapsulation. Microencapsulation involves a chemical reaction between the contaminant and the solid matrix, whereas macroencapsulation is the physical incorporation of the waste into the inert solid matrix. Microencapsulation is more desirable from a contaminant immobilization standpoint, but is rarely achieved in solidification/stabilization of contaminated soils. Solidification/stabilization of residual process sludges is also possible, though the moisture may interfere with matrix setting for some technologies. In such cases a dewatering pre-treatment step is required.

3.1.2.1 Objectives of Solidification/Stabilization

Solidification/stabilization of contaminated soils and sludges at wood preserving sites is intended to achieve the following objectives:

- eliminate contaminated soil as a source of groundwater contamination by immobilizing the adsorbed chemicals;
- minimize the danger of dermal contact and/or potential inhalation of contaminated soil as dust; and

- reduce the hazard classification of the soil. If the contaminated soil qualifies as a hazardous waste, solidification/stabilization might yield a product which could be landfilled.

In order to achieve these intentions, the final product should be a monolithic mass with good dimensional stability, large freeze-thaw resistance, low permeability, minimal leaching potential, high load bearing capacity, and resistant to attack by biological agents (U.S. Army, 1982). The stabilized mass should be evaluated for these qualities by the following tests (Wiles, 1987):

- bulk density
- unconfined compressive strength
- water content
- falling-head permeability test
- equilibrium leach test
- dynamic leach test
- acid neutralization capacity
- sequential chemical extraction
- toxicity characteristic leaching procedure (TCLP)
- freeze/thaw weathering test
- wet/dry weathering test

The unconfined compressive strength parameter is a direct measure of a material's ability to support a load. Strengths greater than about 210 kPa (30 psi) are generally adequate for stabilized wastes placed in a capped landfill with heavy equipment operating above the cap (Weston Inc., 1989).

3.1.2.2 Solidification/Stabilization Technologies

Seven basic divisions of solidification/stabilization technology have been described (U.S.EPA, 1984e; U.S. Army, 1982):

1. solidification through cement addition
2. solidification through the addition of lime and pozzolanic materials
3. techniques involving embedding wastes in thermoplastic materials such as bitumen, paraffin, or polyethylene
4. solidification by addition of an organic polymer
5. encapsulation of wastes in an inert coating
6. self-cementing processes for wastes containing large amounts of calcium sulfate and calcium sulfite
7. formation of a glass capsule by fusion of wastes with silica.

Technologies 3 through 7 are not feasible for solidification/stabilization of contaminated soils and sludges at wood preserving sites as shown in Table 3.1-1. Only the cement and pozzolanic technologies are practical for solidification/stabilization of soils and sludges at the five HELP sites.

3.1.2.2.1 Cement Based Solidification/Stabilization

Cement based solidification/stabilization occurs when anhydrous portland cement powder is mixed with contaminated soil slurried in water. Portland cement is comprised of tri- and dicalcium silicates as well as tricalcium aluminate and calcium aluminoferrite. Stabilization occurs when cations precipitate as hydroxides due to the high pH of cement.

Table 3.1-1 Suitability Matrix for Solidification/Stabilization Alternatives

Technology	Applicable for Wood Preserving Chemicals in Soil?	Practical for Large Volumes of Soil?	Equipment and Specialized Labour Readily Available?	Reasonable Energy Requirements?	Stabilized Product Resistant to Biological Degradation?	Proven in Full-Scale Applications Using Soil?
1. Cement-Based Processes	√	√	√	√	√	√
2. Pozzolanic Processes	√	√	√	√	√	√
3. Thermoplastic Processes	√	x	x	x	√	x
4. Organic Binding Processes	√	√	√	√	x	x
5. Use of Inert Coatings	√	x	x	x	√	x
6. Self-Cementing Processes	x	-	-	-	-	-
7. Glass-Capsule Formation	√	x	x	x	√	x

Notes:

- Sources: U.S. Army (1982), Barth (1988), Weston Inc. (1989)
- √ = technology satisfies criteria
- x = technology does not satisfy criteria

Solidification occurs through the interlacing of thin, densely packed, silicate fibres growing from the individual cement particles. This fibrillar matrix surrounds and isolates the contaminated soil particles, producing a monolithic, rock-like mass (U.S. Army, 1982). Type I, and to a smaller extent, types II and V portland cements have been used for waste solidification. The advantages and disadvantages of cement based processes are outlined below (U.S. Army, 1982).

Advantages:

- raw materials are plentiful and inexpensive;
- the technology of cement mixing and handling is well known, the equipment is commonplace, and specialized labour is not required; and
- drying and dewatering of wastes are not required.

Disadvantages:

- the weight and volume of the stabilized product are roughly double that of the contaminated soil, because relatively large amounts of cement and water are required for the process. This drastically increases the area required for ultimate disposal;
- uncoated cement-based products may require a well designed landfill for burial, because some wastes are leached from solidified concrete by acidic solutions. Coating the product with a sealant is a way of minimizing this potential; and
- high sulfate wastes may cause spalling of the stabilized product.

3.1.2.2.2 Pozzolanic Solidification/Stabilization

Pozzolanic processes involve the reaction of lime with fine-grained siliceous (pozzolanic) material and water to produce a concrete-like solid. Readily available siliceous materials are fly ash, ground blast furnace slag, and cement-kiln dust (U.S. Army, 1982). All of these materials are themselves waste products with little commercial value. The advantages and disadvantages of pozzolanic processes are similar to those for cement based processes, with the exception of two additional advantages (U.S. Army, 1982):

- the reagents are cheaper than for cement based processes because they are waste products themselves; and
- high sulfate wastes do not cause spalling or cracking.

3.1.2.3 Process Alternatives

Three different solidification/stabilization processing alternatives are available for contaminated soils and sludges (Wiles, 1986).

- **in situ processing**: solidifying agents are injected into the ground to stabilize contaminated soils in place.
- **in plant processing**: solidification/stabilization occurs in a plant specifically designed for stabilization of wastes from external sources.
- **mobile plant processing**: solidification/stabilization occurs on-site using equipment easily transported from place to place.

3.1.2.3.1 In Situ Processing

Successful in situ processing would be difficult to achieve at the HELP sites because of soil conditions. All sites, excluding Calgary and Faust, are underlain by highly plastic, low permeability clays, which would severely limit contact between soil and stabilizing agent. The non-homogeneity of soil formations would also produce different depths and levels of treatment across a site. Soil stabilized in place would require some form of capping to prevent surface water infiltration and provide sufficient load bearing capacity. Additionally, a long-term monitoring program would be required to ensure sufficient stabilization occurred, as well as to monitor for a breakdown in the solidified mass.

3.1.2.3.2 In Plant Processing

For in plant processing, only one facility exists in Alberta which is licensed to stabilize hazardous wastes: the Special Waste Management Facility in Swan Hills. A possible reclamation scenario using this facility would require:

- excavation of contaminated soil and sludge by a contractor. This material would then be loaded onto Alberta Special Waste System trucks. At this point the Alberta Special Waste System would assume all liability for the material, as discussed in section 3.2.1.2.
- the material would be transported to Swan Hills, solidified/stabilized, and landfilled in the secure facility.

The cost of such an alternative would be about $\$590/m^3$ ($0.29/kg base cost + approximately $0.20/kg reagent cost for soil of density 1200 kg/m^3) (Mr. Gary Michalchuk, Chem-Securities (Alta.) Ltd.; personal communication).

An advantage of this alternative is that it could be quickly implemented and completed. This alternative would also reduce concerns with residual site monitoring. On the other hand, the unit cost for this alternative is quite high, and large volumes of stabilized waste would require disposal in the secure Swan Hills landfill.

3.1.2.3.3 Mobile Plant Processing

Mobile plant processing involves stabilizing the material on-site. Such systems are generally constructed from readily available construction equipment such as industrial mixers (pugmills), a solids conveyor and sludge pumps. An on-site system capable of handling both soils and sludges is illustrated in Figure 3.1-2. Any advantages of on-site solidification/stabilization relate directly to the ultimate disposal scheme for the solidified waste. This waste will likely occupy a greater volume than the influent soil because of the additives. If the solidified material cannot be landfilled on-site and must be hauled to a secure facility, the economic advantages of on-site treatment would be minimal. In addition, the whole concern of residual liability and monitoring for the solidified waste must be addressed. On-site landfilling of treated soil also possesses disadvantages:

- the volume increase occurring during solidification could make it difficult to find sufficient landfill space; and
- the landfilled waste requires monitoring.

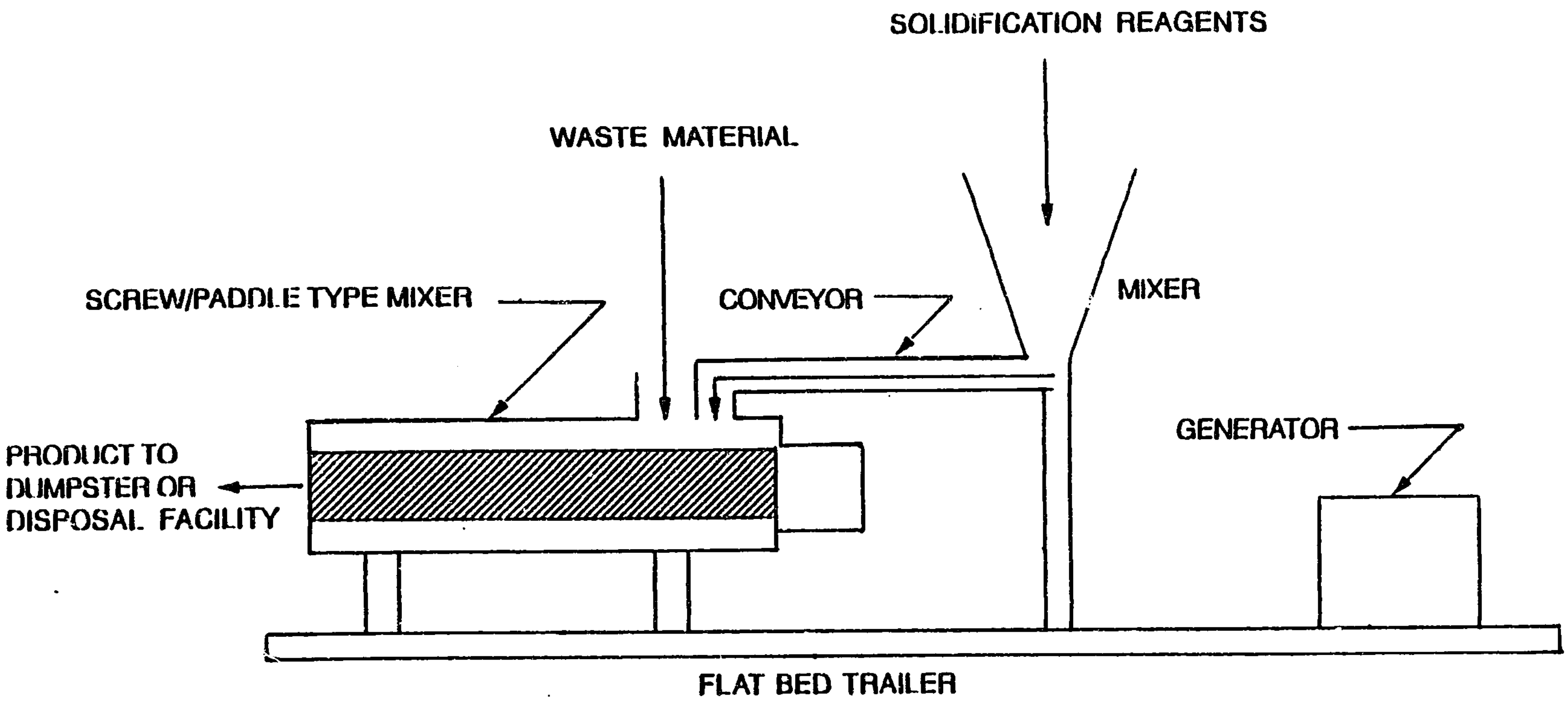


FIGURE 3.1-2 : PROPOSED ON-SITE SOLIDIFICATION/STABILIZATION DESIGN (ADAPTED FROM STANCZYK ET AL., 1982)

3.1.2.4 Use of Solidification/Stabilization for Wood Preserving Wastes

The effectiveness of solidification/stabilization of contaminated soils and sludges at the former wood preservers depends on the extent to which the contaminants participate in the solidification/stabilization reactions. This extent will be site-specific, depending on how background chemicals in the soil and pore water compete for the reagents. However, some generalizations between contaminant type and solidification/stabilization efficacy can be made. Specifically, differences exist between the organic wood preservatives PCP and creosote, and the inorganic CCA.

3.1.2.4.1 Solidification/Stabilization of Creosote and PCP Wastes

Creosote- and PCP-based wood preserving mixtures are comprised of organic chemicals. The physical and chemical nature of these compounds makes solidification/stabilization of such wastes difficult to achieve. Specific difficulties are:

- the organic chemicals do not enter into chemical reactions to form new organic-inorganic compounds or complexes which can bind organic contaminants. Creosote and PCP-contaminated soils are solidified by physical entrapment but are not stabilized (Wiles, 1987). This lack of stabilization means that if the solidified mass disintegrates, contaminants would be free to migrate.
- the diesel fuel carrier used in PCP wood treatment, and the solvent-like nature of creosote interferes with curing of the solid matrix (Barth, 1988). A report by Wiles (1987) also concluded that chlorinated hydrocarbons act as matrix disrupters for both

cement and pozzolanic processes. Both of these effects act to interfere with the solidification process, and significantly reduce the compressive strength of the product.

- the mobility of PCP and creosote in solidified/stabilized soils is the same or <u>greater</u> than in the undisturbed state. An unpublished study performed at the Mississippi State Forest Products Lab in 1989 showed that the mobility of polynuclear aromatic hydrocarbons (PAHs - from creosote) and PCP was 2 to 7 times greater in stabilized wastes compared to undisturbed soils. In general, stabilized PCP was more mobile than stabilized PAHs for all soil concentrations tested. Another study, performed by Weston Inc. (1989) concluded that no significant reduction in PCP mobility was achieved by solidification/stabilization. The enhanced mobility of PCP and creosote in solidified/stabilized soils is caused by the high pH. The pH of solidified/stabilized wastes ranges from 8-11 (Stanczyk et al., 1982). For such pH values, pentachlorophenol exists largely in the water soluble pentachlorophenate ion form, and the mobility of several creosote components is also enhanced (sections 1.4.1.1 and 3.1.1.4). Because of the mobility of organic wood preserving chemicals in stabilized wastes, solidification/stabilization of creosote or PCP-contaminated soils will not significantly reduce any hazard posed by these chemicals.

Various additives such as powdered activated carbon (Kyles et al., 1987) and an organophilic binder (Barth, 1988) have been used in solidification/stabilization processes in an attempt to reduce organic mobility, and to prevent organics from disrupting matrix formation. Although preliminary results are impressive, the products have not been evaluated for long-term physical stability, and in the case of the organophilic binder, products have not been evaluated for resistance to biological decay.

3.1.2.4.2 Solidification/Stabilization of CCA Wastes

Soil and sludge contaminated with chromated copper arsenate (CCA) are amenable to solidification/stabilization, though some concerns exist. These concerns mainly center on the relationship between metal valence state and mobility.

The predominant valence states of copper, chromium and arsenic in soil/water environments are outlined below (from section 1.5.2.2):

- **arsenic:** As^{5+} (as AsO_4^{3-}) and As^{3+} (as AsO_3^{3-})
- **copper:** Cu^{2+}
- **chromium:** Cr^{6+} (as CrO_4^{2-} or $Cr_2O_7^{2-}$) and Cr^{3+} (as CrO_2^- or Cr^{3+})

Studies have shown that Cr^{6+} as well as both As^{3+} and As^{5+} are not easily stabilized. These valences do not stabilize readily because they exist as oxo anions, which do not generally form stable precipitates (Barth, 1988; Stanczyk et al., 1982; Freeze and Cherry, 1979). In general, As^{5+} is less mobile than As^{3+}. On the other hand, Cu^{2+} and Cr^{3+} have been effectively stabilized through precipitation and adsorption, as these valences predominantly exist as cations in soil/water systems (Barth, 1988; Stanczyk et al., 1982). The valence state of metals in soil is determined by the redox potential and pH of the soil/water environment at a site, which may be altered during solidification/stabilization. This makes it difficult to determine if metal contaminants will be mobile in the stabilized waste without performing pilot-scale tests. For this reason, pilot-scale solidification/stabilization tests are generally performed, and the product analyzed for the parameters outlined in section 3.1.2.1. If arsenic and chromium are not sufficiently immobilized in the solidified/stabilized product, a sealant may be used. However, sealants provide no benefit if the solidified mass is broken down.

Despite the concern with metal mobility, successful solidification/ stabilization of CCA contaminated soils has been achieved without pretreatment or the use of sealants at a number of wood preserving sites (for example: Barth, 1988; Weston Inc., 1989).

3.2 Destruction Alternatives

3.2.1 Incineration

Incineration refers to the use of high temperatures to destroy or detoxify hazardous wastes. In order to achieve adequate thermal oxidation, organic matter must be present to sustain combustion, and only organic compounds can be destroyed by incineration. Incineration cannot effectively alter the chemical structure of inorganic compounds to either reduce their volume or toxicity. Consequently, incineration is only relevant for creosote and PCP mixtures.

In general terms, incineration is a process where POHCs (Principal Organic Hazardous Contaminants) in soil and sludge are thermally oxidized to primary and secondary combustion products. Primary combustion products are carbon dioxide, water vapour and inorganic ash. They are the result of complete mineralization of the carbon and hydrogen atoms from the organic contaminant. Secondary combustion products are inorganic compounds such and HCl and Cl_2 which arise from the substituted elements present in the contaminant. To illustrate this terminology, a possible pathway for PCP incineration is:

$$\begin{aligned} 3\,C_6OHCl_5 + 17\,O_2 &\xrightarrow{heat} 18\,CO_2 + H_2O \text{ (primary combustion products)} \\ &\quad + HCl + 7\,Cl_2 \text{ (secondary combustion products)} \end{aligned}$$

3.2.1.1 Factors Affecting Incineration Efficacy

Incineration is capable of destroying the hazardous organic compounds in wastes, while reducing their volume. The destruction and removal efficiency achieved for POHCs in properly incinerated waste streams often exceeds 99.99 percent (U.S.EPA, 1988e). The effectiveness of solids incineration depends on three factors (Oppelt, 1981): residence time, combustion temperature and kiln turbulence.

Sufficient residence time in both the primary combustion chamber and afterburner are required for complete combustion of the POHCs. The combustion chamber temperature, in conjunction with the chamber residence time, must be sufficient to volatilize even the most stable organics. In general, the combustion chamber temperature should be around 1200 °C. A test burn on PCP treated wood indicated that dioxins and furans can be emitted from the incinerator stack for temperatures below 1000 °C (Oberacker, 1988a). Finally, turbulence in the combustion chamber promotes intimate contact between the solids and combustion gases. The stoking action of rotary or rocking kiln incinerators generates turbulence which provides access for oxygen to the burning material. Insufficient oxygen transfer to the combusting surface leads to only partial decomposition of POHCs to Products of Incomplete Combustion (PICs). PICs are undesirable because they are often harmful substances such as carbon monoxide or intermediate organics. For illustration, a possible PIC of pentachlorophenol would be a phenol with less chlorine substitution such as the carcinogenic 2,4,6-trichlorophenol, or chlorinated dioxins and furans. Incinerator residue containing harmful PICs is itself a hazardous waste requiring some form of treatment, such as re-incineration or solidification/stabilization, prior to disposal.

3.2.1.2 Process Alternatives

Two incineration process alternatives exist for contaminated soil and sludge at wood preserving sites: incineration at the Swan Hills facility or on-site incineration with a mobile facility.

The Alberta Special Waste Treatment Centre at Swan Hills is owned in a joint venture by Bovar Inc. and the Alberta Special Waste Management Corporation (ASWMC). The facility is operated by Chem-Securities (Alta.) Ltd., and is the only facility in Alberta licensed to incinerate contaminated soil. At present, the Swan Hills facility operates two small rocking kiln incinerators used to incinerate both liquids and solids. For incineration of contaminated soil, rocking kiln furnaces possess a number of limitations:

- material must be fed in 45 gallon drums;
- incinerators have a small diameter; and
- influent feed is restricted because of mixing limitations from the rocking motion.

Because of these limitations and the increasing demand for soil incineration, a rotary kiln incinerator has been purchased and will be operational some time in 1990. Rotary kiln furnaces have a greater capacity for solids incineration compared to rocking kiln models because loose material can be fed to the furnace using a screw auger, and the full rotary motion induces greater turbulence (Dr. Chris Zeiss, ASWMC; personal communication). For incineration of contaminated soil and sludge from the HELP sites at Swan Hills, a contractor would be required to excavate the soil contaminated above acceptable residual levels and drum it (for incineration in the rocking kiln furnace) or load it loose onto Alberta Special Waste System trucks (for incineration in the rotary kiln furnace). The contaminated material would then be incinerated, producing a mass of residue similar in quantity to that of the influent solids (section 3.2.1.4). Because of turbulence limitations during solids combustion, incinerator residue often contains PICs. For this reason, residue at the Swan Hills facility is characterized by the following tests (Mr. Bob Rutberg, Chem-Securities (Alta.) Ltd.; personal communication):

- the residue is analyzed for polychlorinated biphenyl (PCB) content if PCB was an original contaminant or possible PIC. If any PCB is found, the residue is re-incinerated.
- the residue is tested for metal mobility by an acidic leaching procedure. If significant concentrations of heavy metals are leached in the test, the waste is stabilized and landfilled in the secure Class I facility on-site. Batch stabilization tests are used to select the most effective solidifying agent.

Residue which passes both tests is landfilled as is. While neither of the two tests specifically deals with any PICs or residual POHCs which may exist in expected residues from wood preservative contaminated soil, the security of the Class I landfill is relied upon to provide a sufficient margin of safety.

Incineration of contaminated soil at special waste facilities is expensive (section 3.2.1.4). To reduce costs, companies have developed transportable/mobile incineration units. Mobile systems are mounted on semi-trailers which meet legal over-the-road specifications. These systems require minimal on-site construction. Transportable incinerators involve field assembly of truck-transported components. These incinerators require significant on-site preparation (Oberacker, 1988b). While transportable/mobile systems may possess economic advantages, a number of concerns also exist, including:

- **availability**: on-site incineration units have not been used at sites in Alberta, though test-burns were conducted with a portable unit at the Swan Hills facility. These units are rare in Canada, and would likely have to be contracted from the U.S. (Mr. Hubert Bourque, Alberta Special Waste Services Association [ASWSA]; personal communication).
- **public acceptance**: public resistance to stack discharge from a portable incineration unit may be significant, especially with the existence of literature documenting the discharge of polychlorinated dioxins and furans from improperly run units (eg. Morrill, 1984).
- **potential releases**: because mobile/transportable units are frequently moved from site to site, it is difficult to achieve optimized operation. These units may also have fewer alarms, failsafe mechanisms and exhaust monitors than permanent systems. A risk therefore exists that these units may discharge harmful PICs to the atmosphere, especially during start-up.
- **residue**: incinerator residue would require hazard assessment prior to disposal. It is possible this residue may be classified as a hazardous waste requiring further treatment or disposal in Swan Hills. In some situations incinerator residue from portable units

has been used "as is" for fill material on the site (for example: Oberacker, 1988a; U.S.EPA, 1986e).

3.2.1.3 Advantages

Incineration of contaminated soil and sludge from wood preserving sites is an attractive technology for a number of reasons.

First, incineration is a technical solution which could be quickly implemented and completed. Excavation of contaminated soil could begin immediately, and would be only limited by the rate at which the soil is drummed and shipped to Swan Hills

Secondly, incineration presents no residual monitoring costs or liability if complete remediation is achieved. Soil contaminated above the selected residual level would be removed from the site, allowing development consistent with the cleanup levels.

3.2.1.4 Disadvantages

Incineration of soil and sludge contaminated with wood preserving chemicals does possess drawbacks. First, incineration of soil produces a large volume of residual material requiring disposal. Soil in Alberta typically contains about 5% organic matter and 95% inorganic (non-combustible) material by mass. Pore moisture is included in the inorganic fraction. Combustion of soils converts the organic matter, pore moisture and a small fraction of inorganic material to gases, leaving the non-combustible inorganic fraction as a residual. Consequently, the residual mass quantity from combusted soils is similar to that of the influent soil (the combusted volume is usually substantially less however, because of densification which occurs during combustion). As discussed in section 3.2.1.2, incinerator residue at Swan Hills is disposed in the secure landfill, often after solidification/stabilization. Table 3.2-1 presents a summary of remediation alternatives, soil volumes requiring remediation and anticipated costs for the five sites. From this table it is clear that if all of the contaminated soil were incinerated at Swan Hills, thousands of cubic metres of incinerator residue would require disposal in the secure landfill. This is undesirable because space in this Class I landfill is limited. The use of on-site incineration systems may not mitigate this concern as the residue from such units would still be subject to Hazardous Waste Regulations, and may subsequently require landfill disposal at Swan Hills.

A second drawback of incineration is the cost. Table 3.2-1 presents the incineration costs used by the different consultants. The prices range from $1225 to $3500 per cubic metre of contaminated soil. This variability in unit costs is understandable given the non-specific nature of Chem-Securities (Alta.) Ltd. quotes. Personal communication with Mr. Gary Michalchuk of Chem-Securities (Alta.) Ltd. produced a quote of $1800/m^3 ($1.50/kg for soil of density 1200 kg/m^3) for soil in the following category:

- chlorinated organic concentrations below 5000 ppm; and
- soil volume between 5000 and 15 000 m^3.

Almost all of the contaminated soil at the five sites fits into this category. However, sludge pond liquids and surrounding soil will likely exceed the

TABLE 3.2-1 : Site Summary

HELP Site Location	Preservative Used	Consultant For Preliminary Study	Recommended Remediation by Consultant	Soil Volume (m^3) Requiring Remediation	Consultant's Estimated Incineration Cost (1989\$/m^3 contaminated soil)
Cayley	PCP	Monenco	• Incineration • Regional Landfill Disposal • Bioreclamation	5335*1	\$2550.*2
Calgary	Creosote, PCP	O'Connor	no options discussed	no estimate given	no estimate given
Blackfalds	PCP	Stanley Associates	• Incineration • Landfill Disposal	1600*3	\$1225.*4
Faust	PCP, CCA	Hardy BBT	• Incineration at Swan Hills	10600*5	\$3500.
Elmworth	CCA	Thurber	• Landfill at Swan Hills • Landfill at a secure facility	1200*6	no estimate given
				Chem-Securities (Alta.) Ltd. estimate	\$1800

*1 Calculated from Monenco's estimate of 8000 tonnes of soil contaminated with PCP concentrations greater than 50 ppm (p. 2-16, volume II of Monenco report), and assuming a soil density of 1500 kg/m^3.

*2 Calculated from Monenco's estimate of \$1700/tonne including excavation (p. 2-17, volume II of Monenco report), and assuming a soil density of 1500 kg/m^3.

continued...

TABLE 3.2-1 : continued

*3 Based on Stanley Associates' estimate of 1600 m^3 for the sludge lagoon. Volume estimate is based on contamination in excess of 100 ppm PCP (page 6.4 of the Stanley report)

*4 Calculated from Stanley Associates' estimate of $250 per 45 gallon drum (page 6.4 of Stanley report)

*5 Based on Hardy BBT's estimate of 10 000 m^3 of PCP contaminated soil, and 600 m^3 of soil contaminated with both PCP and arsenic. Volume estimates are based on contamination in excess of the Quebec Guidelines level C (page 15 of the Hardy BBT report).

*6 Based on Thurber's estimate of 300 m^3 of highly contaminated soil in zone 1 and 900 m^3 of moderately contaminated soil in zone 2. Volume estimates are based on contamination in excess of the Quebec Guidelines level C (pages 16-18 of the Thurber report).

limit for chlorinated organics. Specifically, soil samples at the Blackfalds, Cayley and Faust sites near the sludge ponds exceeded 5000 ppm PCP. Elevated chlorinated organic levels present a concern because chlorinated organics form acid gases such as HCl which may attack the refractory lining on the combustion chamber, and air emissions require greater acid gas scrubbing to control (U.S.EPA, 1988e).

The cost of incinerating 10 000 m^3 of contaminated soil (a reasonable estimate for one HELP site) at $1800/$m^3$ is $18 000 000. This price includes transportation, incineration and disposal, but not excavation, groundwater remediation, replacement of fill material or engineering fees. The cost of remediating a HELP site using incineration at Swan Hills could thus exceed $20 000 000. While Table 3.2-1 presented incineration costs per unit volume of soil, it should be noted that actual costs at the Swan Hills facility are based on mass.

Portable incineration units operating on-site are viewed as being more economical than incineration at special waste facilities. However, any cost benefits from portable incineration will depend directly on how the residue is classified. If the residual is a hazardous waste according to Hazardous Waste Regulations, disposal costs may be large. Because the residue characteristics will depend directly on the influent soil type and incinerator operation, residue classification will vary from site to site, and correspondingly, so will the economic advantages.

A third drawback of incineration is the potential release of airborne contaminants such as gases or particulates. As mentioned previously, combustion of PCP-contaminated soil produces acid gases which may impact air emissions. Volatile metals such as arsenic (either pure or as oxides, hydroxides or salts) may also vaporize during incineration (U.S.EPA, 1988e), though Carroll and coworkers (1990) imply that, contrary to predictions, arsenic does not significantly impact air emissions and is well recovered with the ash fraction. Additionally, trivalent chromium (Cr^{3+}) can be oxidized to a more toxic valence state, hexavalent chromium (Cr^{6+}), in combustion systems with oxidizing atmospheres (U.S.EPA, 1988e). This has significant consequences for incineration of soil contaminated with CCA (copper, chromium, arsenic). Consequently, incineration of soils contaminated with PCP and/or CCA is not risk-free.

3.2.2 Bioreclamation

Bioreclamation strategies use biologically-mediated chemical reactions to transform contaminants to less toxic forms. In essence, heterotrophic microorganisms consume organic contaminants as substrate to sustain their metabolism and the synthesis of new cell mass. Only organic chemicals can be decomposed by these microorganisms. Therefore, only pentachlorophenol (PCP) and creosote, and not chromated copper arsenate (CCA), are subject to biological degradation (sections 1.4.1.2, 1.4.2.2, and 1.4.3.2).

Three general categories of bioreclamation exist: enhanced land treatment, in situ bioreclamation and slurry bioreactors. In situ bioreclamation involves degrading the contaminants in soil and groundwater in place. Nutrients, an electron acceptor and other additives are provided by injection wells or infiltration galleries. In situ bioreclamation is only practical in very permeable formations. This process also involves concerns over additives which remain unused in the aquifer.

A slurry bioreactor uses a biologically-enhanced soil/water slurry to degrade the contaminants in a reactor. This alternative may provide quicker remediation than either land treatment or in situ bioreclamation if the soil is workable. The closed reactor also minimizes releases of additives to the environment.

Finally, land treatment is used for low permeability, nonworkable soils, and may be considered as batch biological treatment in an open reactor.

Bioreclamation, using any of the alternatives discussed, possesses a number of advantages:

- unit treatment costs are generally lower than for other technologies;
- contaminated soil and sludge are treated on-site;
- remediated soil can be replaced on-site; and
- remediated soil presents little residual threat of contamination, assuming selected cleanup levels are corrected.

Unfortunately, bioreclamation requires time to implement because of necessary pilot tests, and requires significant time to be completed. The technology has also not been commonly applied in Canada, and concerns exist over residual additives in the soil and the effects of low temperatures on treatment efficiency.

3.2.2.1 Enhanced Land Treatment

Much of the surficial soil in Alberta is underlain by glacial clay tills of low permeability. At wood preserving sites, these soils limit the migration of preservatives released on the ground surface, but also hinder recovery of these contaminants during site reclamation. These low permeability soils limit transfer of oxygen, nutrients, water and energy (as related to temperature). Slow mass transfer limits the practicality of remediation alternatives such as pumping contaminated groundwater, in situ bioreclamation, vacuum extraction, soil washing, and steam stripping. These options may work, but they would be slow, expensive, and may leave significant residual contamination in low permeability pockets around which short-circuiting has occurred.

Thomas et al. (1987a) concluded that permeabilities greater than 10^{-4} cm/s are required for successful in situ biorestoration. Table 3.2-2 presents saturated horizontal hydraulic conductivities for the five HELP sites. Considering these values and the guideline value of Thomas, only one or two of the sites will be amenable to in situ bioreclamation. The high plasticity of site soils will also affect the practicality of bioreactor treatment.

For sites underlain by low permeability soils, above ground biological treatment (land treatment) can be used to overcome mass transfer limitations in the undisturbed material. Land treatment in a closed facility involves a batch reactor utilizing aerobic biological processes to treat contaminated soil. Land treatment requires the addition of nutrients, easily degradable substrate, and other additives to improve soil workability (tilth) and drainage. This soil mixture is then tilled, to provide aeration and mixing, and watered. The system is intended to reduce contaminant concentrations by biodegradation. However, abiotic processes such as volatilization and photolysis can also produce significant contaminant losses.

If land treatment of soils and sludges contaminated with wood preserving wastes is to be considered, the contaminants must be biologically degradable at adequate rates. The biodegradability of PCP, PAHs, and selected heterocycle compounds was examined in section 1.4. In short,

TABLE 3.2-2 : Site Hydrogeology

H.E.L.P. SITE	PRESERVATIVES USED	UNDERLYING SOIL	SATURATED HORIZONTAL HYDRAULIC CONDUCTIVITY (cm/s)	COMMENTS
Cayley	PCP	Clayey silt till with minor amounts of sand and gravel	7.5×10^{-8}	From page 3-25 of the Monenco report.
Calgary	Creosote,PCP	Silts and/or fill materials overlying alluvial gravels	4×10^{-2}	From page 10 of the Golder Associates report.
Blackfalds	PCP	Glaciolacustrine sequence of clay and silt	2×10^{-5}	Pages 5.6 and 5.7 of the Stanley Associates Ltd. report.
Faust	PCP, CCA	Sequence of interbedded deltaic and outwash sands, silts and clays	no calculation of hydraulic conductivity was made	Site geology is summarized on page 6 of the Hardy BBT report.
Elmsworth	CCA	Sequence of highly plastic lacustrine clay and silt	no calculation of hydraulic conductivity was made	Site geology is summarized on page 17 of the Thurber report. Saturated horizontal conductivity was not determined because some of the piezometers had not stabilized (p.7). From this information it is assumed the hydraulic conductivity will be quite low.

research has shown that organic wood preserving chemicals are biodegradable, though the rates depend on the particular soil and amount of contamination present.

3.2.2.1.1 Necessity of a Diverse Microbial Culture

PCP, PAHs, and heterocycle compounds are sequentially transformed to mineralized end products. No single type of microorganism can accomplish all of the required steps. To achieve inert end products, an active, diverse microbial community is required, where the degradation products of one species are substrate for another (Canter et al., 1987; U.S.EPA, 1988d). Without this consortium of microorganisms, intermediate metabolites may accumulate, halting consumption of the parent compound. These intermediate products may also be contaminants themselves.

Commercially available mixtures of organisms used to inoculate soil and groundwater often cannot provide the necessary diverse microbial culture, and thus fail to enhance contaminant degradation rates. Instances where this occurred are documented by Ryan and Smith (1986), and Linkenheil (1987). Better results are generally obtained when selective enhancement is used to develop specific PCP-, PAH-, and/or heterocycle-degraders from microflora at the site, which will be used to enhance the native microbial population during land treatment. Selective enhancement will be discussed in section 3.2.2.1.5.

3.2.2.1.2 Amendments

Certain substances, called amendments, are added to soil prior to land treatment to improve workability or contaminant degradation. The following amendments have been used in land treatment of soil contaminated with wood preservatives.

- **sand:** sand can be added to plastic soils to increase their workability (tilth), drainage and porosity (for oxygen transfer).
- **straw, wood chips:** addition of these materials improves soil tilth, drainage and oxygen transfer. Straw and wood chips also act as substrate, thereby enhancing the microbial population. Frequently, these materials are soaked in a nutrient solution prior to incorporation in the soil.
- **nutrients:** nutrients are required to sustain biological activity. Both macronutrients (nitrogen and phosphorus) and micronutrients (trace metals such as potassium, iron and zinc) are required by microorganisms. The large nitrogen and phosphorus demands can usually be satisfied with commercially available fertilizers. The smaller demand for micronutrients may be satisfied by the addition of manure or municipal sewage sludge.
- **manure, sewage sludge:** addition of these materials improves soil workability, as well as provides readily degradable substrate, nutrients, and an active microbial community.
- **solubility enhancers:** emulsifiers or other additives which increase the aqueous solubility of organics are often incorporated into the soil to move contaminants from the adsorbed to aqueous

phases. An example of such an addition would be adding lime to PCP-contaminated soils. Liming would raise the pH, causing PCP to ionize to the more soluble pentachlorophenate ion form, though the effect of enhanced solubility may be offset by microbial inhibition at high pH values. As with other amendments, an optimum dosage for the particular additive must be determined in a laboratory study. Any land treatment unit utilizing solubility enhancement techniques should be lined to prevent contaminated water from entering the environment. The value of solubility enhancing chemicals is questionable, because degradation is believed to be faster in soil than water (Herbes et al., 1980).

- **bacterial inoculations**: research has shown that inoculating soil in land treatment units (LTUs) with PCP-, PAH-, and heterocycle-degrading bacteria isolated from the particular site results in improved contaminant degradation. The means of isolating such bacteria will be discussed in section 3.2.2.1.5.

3.2.2.1.3 Treatability Limits

The next two sections outline the maximum contaminant concentrations which can be treated at practical rates, as well as the minimum contaminant levels attainable.

Upper Limits

Certain concentrations of contaminants in soil hinder biodegradation to the point that land treatment would no longer be practical. This situation likely occurs because many wood preserving contaminants do not serve as primary substrate for most microorganisms, and are usually only co-metabolized with more easily degradable material. The absence of such alternative substrate in heavily contaminated soils thus leads to a state of microbial dormancy.

Limiting contaminant concentrations have been found to be site-specific, and to change as an acclimated microbial population develops. An acclimated microbial culture is resistant to or thrives on the contaminant, and will develop by a continual exposure of a microbial system to the hydrocarbon pollutant. For example, PCP half lives in the McGinnis study (1988) varied from 20 to over 1000 days in different soils; prior exposure to PCP was believed to be the critical factor.

Certain contaminant concentrations have been quoted in literature or used in practice as limits above which degradation is inhibited:

- PCP concentrations in excess of 150 ppm inhibited microbial growth (Edgehill and Finn, 1981).
- PCP degradation was hindered at a concentration of 500 ppm (Crawford and Mohn, 1985)
- PCP degradation generally occurs at adequate rates for concentrations below 700 ppm (Dr. Gary McGinnis, Mississippi State Forest Products Utilization Lab; personal communication)
- PAH degradation in creosote contaminated soils generally occurs at adequate rates for total PAH values below 9000 ppm (Dr. Gary McGinnis, Mississippi State Forest Products Utilization Lab; personal communication).

The Edgehill and Finn and Crawford and Mohn values were derived for laboratory-scale tests, whereas the limits specified by Dr. McGinnis were based on laboratory, pilot and full-scale experiments at 11 wood preserving sites throughout the U.S. The exact contaminant concentration at which land treatment becomes impractical will vary from site to site. However, the limits quoted here can be used to provide an estimate of how much soil at a site will require dilution with clean soil to be treatable, or require remediation using some other technology.

Lower Limits

Research at wood preserving sites has shown that a minimum contaminant concentration exists for each site, and that this limit cannot be modified, regardless of the amendments used. Modifications to process variables (temperature, amendments, inoculations) only alter the rate at which the limiting concentration is achieved, and not the minimum value itself. Figure 3.2-1 illustrates this phenomena.

Minimum concentrations attainable through bioreclamation may correspond to levels at which other substrate or even dormancy become more thermodynamically appealing to the microbes than continued contaminant degradation.

It is imperative that initial laboratory tests identify lower degradation limits, because these limits may be at concentrations above required

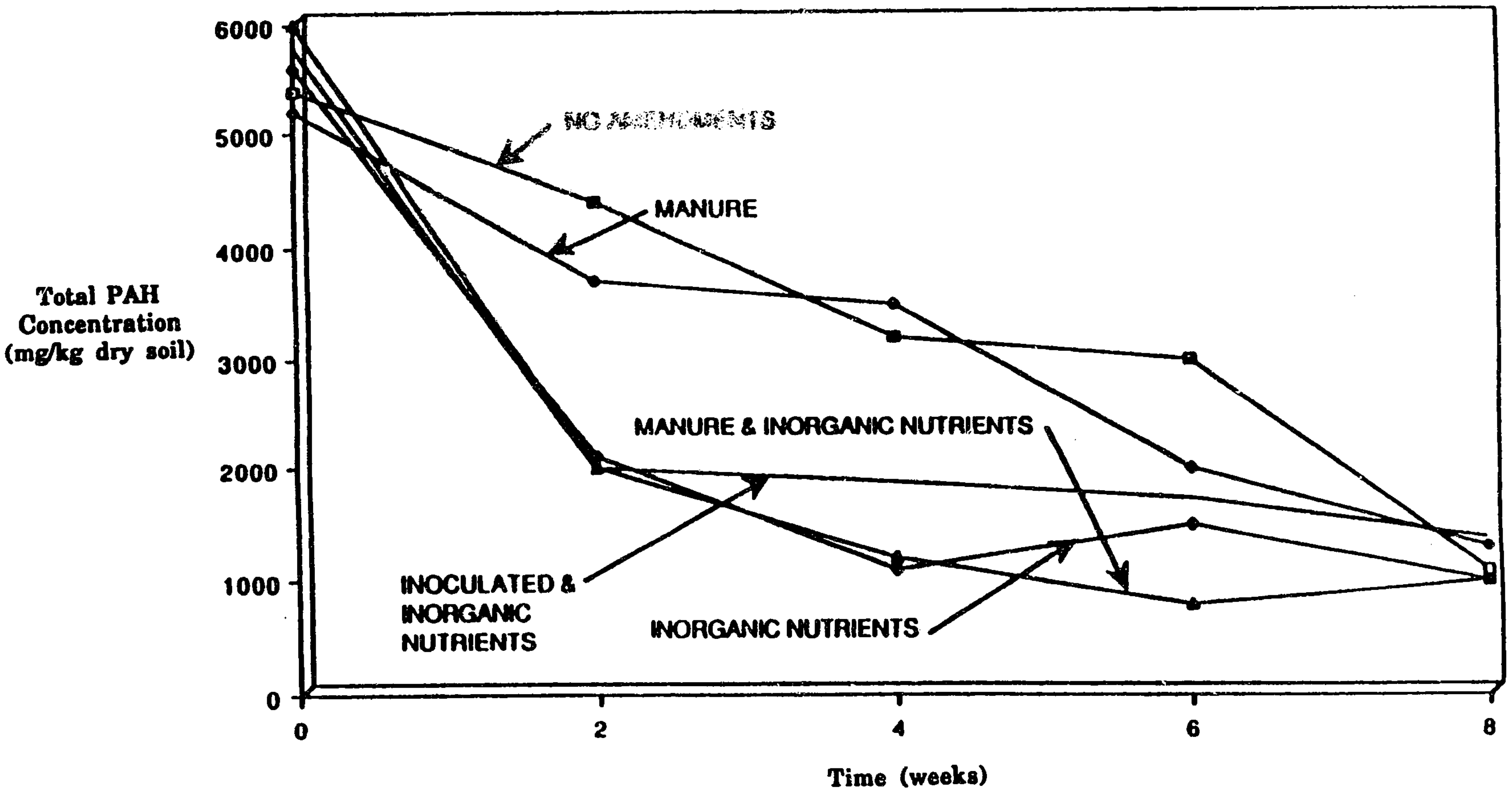


FIGURE 3.2-1 : POLYNUCLEAR AROMATIC HYDROCARBON REMOVAL RESULTS (ADAPTED FROM FLECHAS, 1989)

cleanup levels, thus eliminating bioreclamation as a remediation alternative.

3.2.2.1.4 Monitoring

PCP wood preserving mixtures contain chlorinated phenols, dioxins, furans, and compounds present in the diesel fuel carrier (Table 1.4-2). Creosote is comprised of PAHs, phenolics and heterocycle compounds (Table 1.4-6). This chemical diversity leads to a number of concerns regarding monitoring of bioreclamation systems. These concerns should be addressed during laboratory testing to ensure that all phases of a bioreclamation study can be related to one another. The concerns are:

- what compounds should be used in monitoring for degradation? This issue is complicated by the fact that some compounds degrade faster than others, and some are more toxic than others.
- should monitoring tests include degradation products, which may be pollutants themselves?
- how to monitor for composite effects of the thousands of chemicals present?

Chemical analyses alone, even if performed for hundreds of compounds, could not address all of these concerns. For this reason a combined biological and chemical testing protocol should be adopted for wood preserving sites. Chemical analyses monitor the disappearance of priority pollutants, whereas biological analyses (bioassays) detect a variety of adverse biological responses which may arise from chemical interactions or from degradative pathways (U.S.EPA, 1984f).

Bioassays use organisms (both microbes and higher forms) and their activity in the presence of contaminants to determine the environmental effect and biodegradability of contaminants. A list of bioassays which have been used for soils contaminated with wood preserving chemicals is presented in Table 3.2-3. From this literature, it is apparent that the Microtox assay has been used successfully, and shows appropriate sensitivity, in making treatability decisions and selecting loading rates for soils contaminated with wood preserving chemicals.

The Microtox assay is a simple proprietary acute toxicity test which utilizes a suspension of marine luminescent bacteria (*Photobacterium phosphoreum*) as bioassay organisms (Bulich, 1979). Suspensions of about one million bioluminescent organisms are "challenged" by addition of serial dilutions of the water-soluble fraction (WSF) of a contaminated soil sample. A reduction of bioluminescence after WSF addition reflects physiological inhibition, indicating the presence of toxic constituents (Sims et al., 1986). Bioluminescence results from the Microtox test can be correlated with toxicity data for higher life forms such as fish (Bulich, 1979). Consequently, the Microtox assay can provide an indication of both the microbial inhibition and acute toxicity associated with contaminants in a soil environment.

Application of a combined chemical/biological monitoring protocol will ensure that treated soil does not contain unacceptable concentrations of

TABLE 3.2-3 : Use of Bioassays for Soil Contaminated with Wood Preserving Chemicals

AUTHOR(S)	PAPER TITLE AND YEAR	BIOASSAYS USED/EVALUATED	COMMENTS
N.J. Hutzler, C.R. Baillod, P.A. Schaepe, R.M. Mauno, C.J. Perram	Biological Reclamation of Contaminated Soil at Wood Preserving Sites (1989b)	• Ceriodaphnia	Ceriodaphnia is a small aquatic crustacean sensitive to PCP. Tests are performed on the water-soluble fraction (WSF) of soil.
L.A. Athey, J.M. Thomas, W.E. Miller, J.Q. Word	Evaluation of Bioassays for Designing Sediment Cleanup Strategies at a Wood Treatment Site (1989)	WSF of soil or water samples: • Selenastrum Capricornutum (alga) • Daphnia Magna (microinvertebrate) • Microtox (Photobacterium phosphoreum) • Lactuca sativa (lettuce) Sediment samples: • Eisenia foetida (earthworm) • Modified Neubauer bioassay	Daphnia and Microtox bioassays were the most sensitive to wood preserving wastes.
R.C. Sims, J.L. Sims, D.L. Sorenson, L.L. Hastings	Waste/Soil Treatability Studies for Four Complex Industrial Wastes: Methodologies and Results. Volumes I and II. (1986)	• Microtox • Soil respiration • Soil dehydrogenase • Soil Nitrification • Microorganism plate counts • Ames mammalian mutagenicity	Microtox, soil dehydrogenase and soil nitrification were most sensitive to wood preserving chemicals. Microtox was the most sensitive assay for determining waste loading rate.
J.E. Matthews	Evaluation of Toxicity Test Procedure for Screening Treatability Potential of Waste in Soil (1987)	• Microtox	Microtox assay was used to select initial loading rates for creosote and PCP contaminated soils.
J.R. Ryan, J. Smith	Land Treatment of Wood Preserving Wastes (1986)	• Microtox • Ames mammalian mutagenicity • 96-hour static acute fish bioassay.	-
B.D. Symons, R.C. Sims	Assessing Detoxification of a Complex Hazardous Waste, Using the Microtox Bioassay (1988)	• Microtox	Microtox assay was used for assessing the extent and rates of detoxification of a PAH waste in two soils.

TABLE 3.2-3 : continued

AUTHOR(S)	PAPER TITLE AND YEAR	BIOASSAYS USED/EVALUATED	COMMENTS
W. Aprill, R.C. Sims, J.L. Sims, J.E. Matthews	Assessing Detoxification and Degradation of Wood Preserving and Petroleum Wastes in Contaminated Soil (1990)	• Microtox • Ames	Microtox and Ames assays were used in monitoring in situ soil bioremediation of creosote and PCP contaminated soils.
J.M. Thomas, L.A. Athey, J.R. Skalski	Statistical Approaches to Screening Hazardous Waste Sites for Toxicity (1987b)	WSF tests: • Algae • Daphnia • Microtox • Root Elongation Sediment samples: • Modified Neubauer • Earthworm	Different bioassay organisms displayed different sensitivities to creosote contamination.

pollutants or any other compounds which may pose a hazard to the environment.

3.2.2.1.5 Laboratory Treatability Studies

The first step in assessing the feasibility of land treatment is a laboratory soil treatability study. This study is intended to determine process variable settings which lead to maximum contaminant degradation and toxicity reduction rates. The maximum degradation rate is used in conjunction with the estimated volume of contaminated soil to generate an estimate of remediation time and cost, which can then be compared with that of other technologies.

Treatability studies generally involve mixing contaminated soil with water and amendments, and incubating the mixture at a constant temperature. These microcosms are mixed periodically and analyzed, using a combined chemical/biological protocol, as discussed in section 3.2.2.1.4. Contaminant disappearance rates from such a study are "apparent" degradation rates rather than biodegradation rates because both biotic and abiotic (eg. volatilization) processes are responsible for contaminant removal.

Experimental amendment quantities are selected from previous practice or based on what would be practically achievable in the field. Factorial experimental design may also be used to determine the parameters to which degradation rate is most sensitive. Amendments used at wood preserving sites and their typical optimum levels are summarized below.

- **sand, straw, wood chips and manure**: these materials are added until the soil is of proper consistency to be easily tilled.
- **nutrients**: the soil carbon : nitrogen : phosphorus ratio in a land treatment unit should be around 300 : 12 : 7.5 (derived from Linkenheil et al., 1986; McGinnis, 1986; Ryan and Smith, 1986).
- **solubility enhancers and bacterial inoculations**: optimum levels of these additives vary widely.
- **soil moisture content**: in general, optimum soil moisture content is between 25 and 85% of field capacity, with 70% as the norm (Huddelston et al., 1986; U.S.EPA, 1989c; Dr. Dan Pope, Mississippi State Forest Products Utilization lab; personal communication)
- **temperature**: for the normal range of soil temperatures, microbial activity increases with increasing temperature. However, if land treatment in Alberta is intended to be used year-round, test levels will be limited by what is practically achievable. A suggested range is 10 to 30°C (Coover and Sims, 1987).

Optimum amendment levels are selected from the resulting test data.

A second objective of the laboratory study is to isolate or develop site-specific contaminant degraders. If the bacterial population at a site has acclimated to the contamination, specific organisms can be isolated. Extract from contaminated soil is incubated on petri dishes containing standard agar. After incubation, any organisms present on the agar are streaked onto another agar containing some concentration of PCP or creosote. This process is continued, using a PCP and/or creosote gradient in the agar, until one or two pure cultures remain. These cultures either thrive on wood preservative chemicals or are highly resistant to them. In any case, these species are grown in bulk, and used to inoculate contaminated soil, enhancing the native microbial population. For the case where soil microorganisms have not become acclimated to the contaminants, specific PCP- and/or PAH-degraders can be derived through a process called selective enhancement, where a bacterial population is developed by acclimating an uncontaminated sample of soil from the site to ever-increasing amounts of the contaminants.

In the U.S., laboratory studies often include a leachability assessment, which examines the mobility of contaminants in the soil treatment zone for unlined facilities. However, due to the mobility of wood preserving chemicals under proper conditions (section 3.1.1.2.5), most new land treatment facilities in the U.S. require liners. Because of the mobility of these contaminants and the amount of precipitation received in Alberta, I strongly recommend that land treatment be performed in lined, covered facilities possessing leachate collection systems. This issue will be further discussed in section 3.2.2.1.7.

The final aspect of the laboratory study is to select a loading rate for the pilot-scale test. Loading rates are expressed as mass or volume of contaminated soil per unit treatment area per application, and are derived using contaminant degradation and toxicity reduction data from the laboratory tests. Loading rates determined from laboratory studies are usually preliminary in nature; greater rates are possible in the full-scale unit as an active bacterial population develops (Ryan and Smith, 1986).

3.2.2.1.6 Pilot-Scale Tests

If results of the laboratory treatability study are promising, a pilot-scale land treatment unit (LTU) may be constructed. These field-scale units are intended to identify operational problems and to provide a better estimate of degradation rates which can be expected in a full-scale LTU. The operational concerns to be addressed include irrigation method, leachate collection system operation, and fertilizer application method. As opposed to the constant-temperature laboratory study, soil in the field study will be subjected to temperature fluctuations; cycles of heating and cooling as would occur in a heated full-scale LTU. As a result, the degradation and toxicity-reduction rates will be different in the laboratory and field studies. In general, loading rates determined from pilot studies are larger than those from laboratory studies (Dr. Gary McGinnis, Mississippi State Forest Products Utilization Lab; personal communication).

Current practice in land treatment studies is the laboratory/pilot/full-scale testing sequence. Recently however, there has been movement towards combining laboratory and pilot-scale studies (Utah State, 1989). This modification is intended to decrease the time and cost of land treatment studies, and is based on the logic that an abundance of technical and operational literature exists on the land treatment of hydrocarbon contaminated soils. In essence, these proponents believe that it is not necessary for every study to "re-invent the wheel", but that information on amendment quantities, required environment, loading rates and operational concerns can be extracted from available literature.

A typical pilot-scale LTU is illustrated in Figure 3.2-2.

3.2.2.1.7 Land Treatment in Alberta

In Alberta, the soil is generally frozen for five months of the year (November through March) and significant amounts of precipitation also occur in short periods. In an uncovered land treatment unit (LTU) then, biodegradation of the contaminants would essentially stop for half of every year. In addition, rain and melting snow would wash away contaminated soil and bacteria, further dispersing the contamination.

These concerns could be mitigated if land treatment were to occur in a closed, lined, heated facility:

- heat in the LTU would promote microbial activity, and allow treatment of contaminated soils year-round;
- the enclosure would retain heat, and prevent the influx of precipitation; and
- a liner and leachate collection system would prevent discharges of contaminants to the environment. Collected leachate could also be used to irrigate the LTU, maintaining the soil at the optimum moisture level for biological degradation.

The closed, lined, heated LTU could be considered a batch reactor using aerobic biological processes to treat contaminated soil. The structure

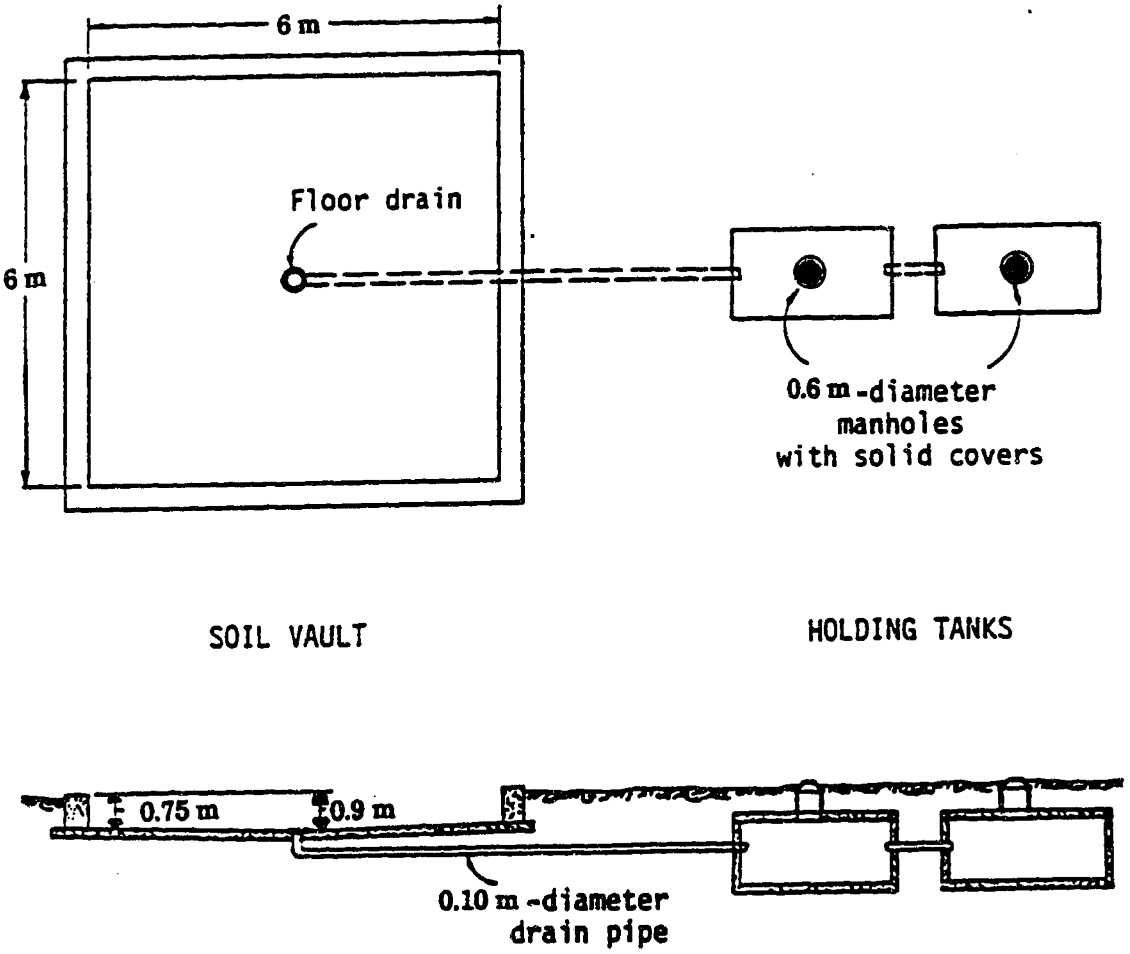


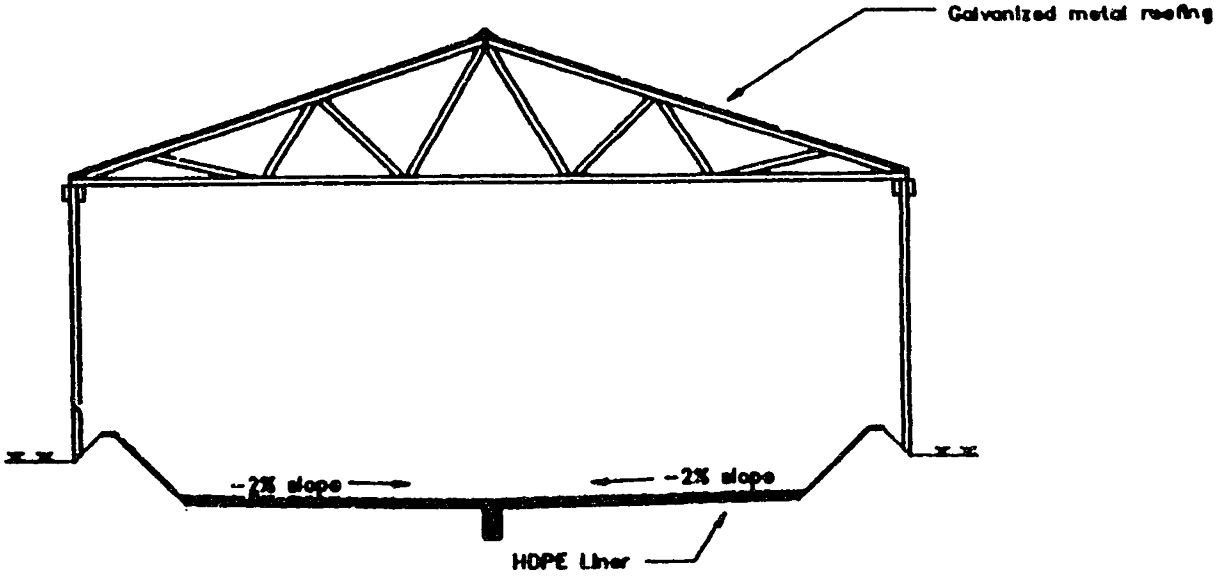
FIGURE 3.2-2 FIELD-SCALE LAND TREATMENT UNIT (ADAPTED FROM HUTZLER ET AL., 1989B)

housing the LTU could be constructed using available packages, such as for farm sheds. Farm sheds possess large doors on both ends which would facilitate hauling of the contaminated soils. A typical LTU before soil placement is illustrated in Figure 3.2-3.

3.2.2.1.8 Full-Scale Land Treatment

A general land treatment scenario, from excavation to decommissioning, is outlined below. This description assumes treatment will occur in a closed, heated facility. Soils are classified as contaminated in this scenario if they possess contaminant concentrations in excess of selected cleanup levels.

- residual process sludge and soil contaminated above practically treatable limits should be diluted with cleaner soil or remediated using another technology.
- the remaining contaminated soil would then be excavated, and mixed with sand, straw, wood chips, nutrients and manure in quantities selected from the laboratory tests. This amended soil would then be stockpiled in an uncontaminated area of the site, and should be surrounded by high density polyethylene to prevent contaminant leaching by snow and rain. Many systems stockpile unamended soil, and add amendments in the LTU. However, site reclamation using land treatment in an LTU generally takes a number of years, and storing amended soil in the stockpile makes use of enhanced biological activity for that period. It is possible that after some period, the remaining stockpiled soil would already be at acceptable concentrations, and the LTU could be decommissioned ahead of schedule. The advantage of an early



(Shown before the placement of soil to be treated)

FIGURE 3.2-3 : CROSS-SECTION OF A TYPICAL LAND TREATMENT UNIT (LTU)
(ADAPTED FROM HUTZLER ET AL., 1989B)

decommissioning would likely outweigh the extra effort of incorporating amendments into the soil prior to stockpiling.

- the site would then be capped with a clean fill, and the LTU constructed near the stockpile.
- Upon construction of the LTU, the first lift of soil would be transferred from the stockpile into the unit. Lifts of about 0.30 m (1 ft) are typically used, as this depth is easily mixed and aerated (Hutzler et al., 1989b; Dr. Gary McGinnis, Mississippi State Forest Products Utilization Lab; personal communication). In the LTU, the soil would be periodically tilled and watered. Tilling is intended to mix and aerate the soil. Tilling should not be excessive because it can modify the soil structure and compact the soil, limiting oxygen transfer. Watering should keep the soil at the optimum moisture level for biological action. The water used may be contaminated groundwater from the site. It should be noted that at moisture contents below field capacity, all water is bound by the matric potential of the soil, and no mobile water exists (section 1.5.2.1). The existence of leachate in the collection system thus implies that the unit has been overwatered and is above field capacity (Utah State, 1989).
- additional amendments such as solubility enhancing chemicals, bacterial inocula or nutrients may also be added to soil in the unit. While the stockpiled soil already contains nutrients, periodic nutrient additions have been shown to enhance contaminant degradation (Hutzler et al., 1989b; McCarty et al., 1981). Bacterial inoculations are generally made by mixing the microorganisms

with water and applying this mixture to the soil through the irrigation system.

- the LTU would be monitored for contaminant degradation and toxicity reduction using the combined chemical/biological protocol developed for the laboratory study. Once the soil in the LTU was at acceptable levels, the next lift could be applied. Some soil from the existing lift should remain in the LTU with the subsequent lift to transfer an acclimated bacterial culture from lift to lift. The cleaned soil removed from the LTU could be replaced on the site.
- this cycle would continue as subsequent lifts would be added to the LTU, treated, removed and returned to the site. The final lift from the stockpile may remain in the LTU, and the bed graded to the original site elevation. The LTU could then be disassembled, and the site covered with topsoil. At this point, soil reclamation would be complete, and the site could be developed for a use consistent with selected cleanup levels.

3.2.2.1.9 Additional Literature

The following list of general references may provide guidance when considering land treatment as a remediation alternative.

- Alberta Environment. 1988b. Guidelines for Land Treatment of Industrial Waste.
- U.S.EPA. 1986d. Permit Guidance Manual on Unsaturated Zone Monitoring for Hazardous Waste Land Treatment Units. EPA/530-SW-86-040.

- U.S.EPA. 1986c. Permit Guidance Manual on Hazardous Waste Land Treatment Demonstrations. EPA/SW-86-032.
- U.S.EPA. 1987a. Guidance Manual on Hazardous Waste Land Treatment Closure.

3.2.2.2 In Situ Bioreclamation

In situ bioreclamation enhances the biological transformation of organic pollutants in vadose and saturated soil zones. Microorganisms are a normal constituent of soil systems, and sustain their metabolism through the consumption of organic matter. The addition of organic contaminants can stress such a system by increasing the microbial demand for complementary substances such as nutrients and an electron acceptor. The supply of these elements will be the rate limiting factor in soil systems abundant in organic substrate. Nutrient and electron acceptor transport is very slow in most soil environments, and as a result, microbes generally exist in a dormant or low activity mode in heavily-contaminated soils (Thomas and Ward, 1988). This is especially true at wood preserving sites where the contaminants are also biocidal.

In situ bioreclamation attempts to stimulate the metabolic activities of the dormant microorganisms by supplying the rate-limiting substances to the subsurface. Nutrients, an electron acceptor, and in some cases, easily degradable substrate and a bacterial seed, are incorporated into soil upgradient of the contaminated zone by wells, infiltration galleries or horizontal pipelines. These soluble additives move with pore water through the vadose and saturated soil zones, enhancing contaminant biodegradation. Electron acceptor transport is generally most crucial, and additional amounts may be supplied by wells located at intervals in the contaminated area. Unused nutrients, mobilized contaminant, as well as soluble degradation products move with groundwater towards a downgradient recovery system, which is comprised of wells or horizontal drainlines. Extracted groundwater is treated if necessary, prepared, and re-injected upgradient of the contamination.

This treatment approach attempts to hydrologically isolate the contaminated zone from the remaining soil system, and develop a treatment cycle involving injection of amendments, circulation through the contaminated zone, extraction of groundwater, treatment and preparation of recovered water, and re-injection. The formation of such a closed loop depends largely on the groundwater injection and recovery system (section 3.3.3). Consequently, in situ bioreclamation can be viewed as an enhanced pump and treat technology. Contaminant removal is greater for bioreclamation for two reasons:

- in situ bioreclamation can remediate both saturated and vadose zones, whereas pump and treat can only recover contaminants mobile in groundwater.
- in situ bioreclamation can remediate bulk hydrocarbon contaminants trapped by capillary forces (residual saturation). Residual saturation hydrocarbon is generally not mobilized under enhanced hydraulic gradients, and is therefore not recovered by pump and treat technologies.

Additional advantages of in situ bioreclamation at wood preserving sites will be discussed in section 3.2.2.2.6.

3.2.2.2.1 Amendments

Nutrients, an electron acceptor, easily degradable substrate, and inoculant microorganisms may be used during in situ bioreclamation to enhance subsurface contaminant degradation.

Nutrients

Inorganic nutrients are required by microorganisms to sustain metabolic activity. After the electron acceptor, nutrients generally limit subsurface contaminant degradation (Piontek, 1989). Microbes require larger amounts of some nutrients (macronutrients) than others (micronutrients). Phosphorus and nitrogen are the primary macronutrients (U.S.EPA, 1990). Micronutrients are comprised of metals such as potassium, iron, calcium, magnesium, copper and zinc (U.S.EPA, 1990; Mueller et al., 1989). Nutrients are provided to the subsurface by dissolving fertilizers or low-grade chemicals in water, which is subsequently injected into the contaminated formation.

No wide agreement exists on the necessary ratio of nutrients in a contaminated aquifer. The recommended soil carbon:nitrogen:phosphorous ratio of 300:12:7.5 for land treatment (section 3.2.2.1.5) could be used, whereas U.S.EPA (1990) recommends a maximum ratio of 300:15:1. U.S.EPA (1989c) postulates that the ratio of oxygen:nitrogen:phosphorous may be more relevant in subsurface environments, where oxygen, and not organic carbon, typically limit biodegradation. In any case, most studies have concluded that required nutrient levels vary from site to site, and must be determined in a laboratory study (for example: Canter et al., 1987; Wilson et al., 1986; Thomas and Ward, 1988).

Electron Acceptor

In both aerobic and anaerobic environments, an electron acceptor is required for the biotransformation of a pollutant. Electron acceptor transport generally limits contaminant degradation rates, even more than nutrient transport (Thomas and Ward, 1988; Wilson et al., 1985; Piontek, 1989). Specifically, the carbon atoms in a hydrocarbon pollutant are biochemically oxidized to a more positive valence, in both aerobic and anaerobic systems, thus donating electrons. The electron acceptor, which is the oxidizing agent, accepts the electrons, being reduced in the process.

Many chemicals can act as electron acceptors, though some forms predominate. In aerobic environments, oxygen is the electron acceptor. In anaerobic systems, sulfate and carbon dioxide predominate (Parkin and Calabria, 1986).

Both chlorophenols and PAHs can undergo biotransformation in aerobic and anaerobic environments, though aerobic processes are better understood and generally considered to be faster than anaerobic processes. In accordance, oxygen is the preferred electron acceptor for in situ bioremediation of wood preserving sites (Piotrowski, 1989; Piontek, 1989; Thomas and Ward, 1988).

However, the use of oxygen as an electron acceptor does possess limitations: oxygen is only slightly soluble in water (8 to 12 mg/L) and is rapidly consumed in the subsurface by both abiotic (hydrochemical) and biotic reactions. Consequently, more soluble forms of oxygen such as hydrogen peroxide (H_2O_2) and ozone (O_3) have been tried. Both of these forms are soluble to several hundred milligrams per litre, but can also adversely impact subsurface remediation. Ozone and H_2O_2 are extremely strong oxidants, which can kill microorganisms; ozone is used to disinfect some municipal water supplies at ppm (mg/L) dosage levels, and H_2O_2 can be toxic to microbes at concentrations as low as 200 ppm (Lee et al., 1987). In addition, ozone and H_2O_2 are unstable molecules in the environment, and readily revert back to molecular oxygen. This "degassing" can produce air bubbles that block the formation (Lee et al., 1987). A study on in situ biodegradation by the U.S. Air Force (Downey, 1989) concluded that the instability of H_2O_2 resulted in degassing at the point of injection, and that there was no peroxide transport in the test aquifer. However Piotrowski (1989) presents a case in which subsurface contaminant degradation at a wood preserving site was greatly enhanced by the injection of H_2O_2. Whether compressed air, ozone or H_2O_2 is used, the electron acceptor is generally injected both upgradient of the contaminated zone as well as at spaced intervals through it.

Easily Degradable Substrate

The success of in situ bioreclamation depends on an active, diverse microbial culture. In heavily contaminated soils, microorganisms lie dormant because of limiting nutrients or electron acceptor, or because of the toxicity of the contaminants. The transformation from dormant to active microbial culture requires the limiting substances, plus carbonaceous material (substrate). Often a substrate more easily degraded than the contaminant is provided to enhance microorganism growth. Glucose, citrate and acetate are frequently used during in situ bioremediation as substrate supplements (U.S.EPA, 1990). In addition to aiding microbial growth, these additives may enhance the degradation of pollutants which are only degraded by co-metabolism. However, they may also decrease the degradation of contaminants present as secondary substrates (secondary substrates are only consumed when the primary source is exhausted).

Waste wood preserving mixtures contain a wide variety of chemicals, some more amenable to biodegradation than others. It is likely that the more easily degraded fractions can sustain a microbial culture when nutrients and an electron acceptor are present. Degradation of these compounds may assist in the co-metabolism of the more recalcitrant components. In addition, material which serves as secondary substrate will be degraded when the primary substrate is depleted. For example, benzo[a]pyrene from a waste creosote mixture may be co-metabolized with some of the smaller aromatic hydrocarbons in the diesel carrier (primary substrate). Once the primary substrate is exhausted, compounds such as anthracene and phenanthrene will be metabolized (secondary substrate). It should be noted that specific microbial strains only possess the enzymatic capabilities to degrade certain types of compounds, and that a diverse population involving many strains will be required for degradation of all creosote fractions. As an example, Foght and coworkers (1990) found that in 138 bacterial isolates, some mineralized aliphatic compounds while others degraded aromatic compounds, but none of the 138 isolates mineralized both types of compounds. As a result of the chemical variety in waste wood preserving mixtures, a substrate supplement will not likely be required for in situ bioremediation. These supplements were not required during pilot-scale bioreclamation studies at two former wood preserving sites (Piontek, 1989; Piotrowski, 1989).

Microbial Amendments

The microbial requirements for in situ bioreclamation are the same as those of land treatment (section 3.2.2.1.1). In situ bioreclamation attempts to develop an active, diverse microbial culture by enhancing the indigenous population, though special microbial strains may also be injected. The effectiveness of these inoculant organisms depends on a number of factors (Wilson et al., 1986; Dragun, 1988; Lee et al., 1987; Thomas and Ward, 1988):

- the added microorganisms must be able to survive in a foreign environment and compete with indigenous organisms for nutrients.
- oculant microbes must be able to be transported from the [illegible] of injection to the contaminated zone, especially to fine-grained materials, where most of the residual saturation exists because of greater capillary forces. Bacteria are similar in size to clay and silt particles, and rely upon the larger micropores or macropores for transport.

- the added microorganisms must be able to retain their selectivity for compound degradation in a multi-substrate environment.

Inoculant organisms may be genetically-manipulated commercial strains or developed from site soils through selective enhancement (section 3.2.2.1.5). One or both types of microbes have failed to enhance contaminant degradation at wood preserving sites (Piontek, 1989; Mueller et al., 1989; Ryan and Smith, 1986; Linkenheil, 1987).

In areas of recent contamination, an acclimation period may be required by the microbes prior to pollutant degradation. Adaptation results from an increase in the population of contaminant degraders, from the induction of specific enzymes, or from a mutation which alters metabolic capabilities (Thomas and Ward, 1988). A study by Wilson and coworkers (1985) observed that subsurface microbes required an acclimation period prior to degrading a series of PAHs in a groundwater plume originating from a creosote sludge pond. Following adaptation, oxygen limited plume degradation. Therefore, at wood preserving sites where the contamination is recent, an acclimation period will be required after amendment injection. Piontek (1989) concluded that unamended microbial populations had adapted to wood preserving chemicals at a chronically-contaminated site.

3.2.2.2.2 Additional Factors

In addition to required nutrients and an electron acceptor, other factors influence the efficacy of in situ bioremediation at wood preserving sites.

- **pH**: microorganism activity is hindered at extreme pH values. The optimum pH range for in situ biodegradation is reported to be from 4.5 to 7.5 by U.S.EPA (1988e), and from 6.5 to 8.5 by Parkin and Calabria (1986). The pH of the soil system will tend to decrease during bioreclamation, as some biotransformation reactions produce organic acids.

- **temperature:** biological reaction rates decrease with decreasing temperature. U.S.EPA (1988e) reports that in situ bioreclamation will be severely impaired at temperatures below 25°C. In Alberta, groundwater temperatures range from 1 to about 10°C, well below the suggested range. However, Freeman and Innes (1986) conclude that bioreclamation is possible in Alberta, through careful selection of native organisms. The viscosity of groundwater also increases with decreasing temperature, impairing the movement of amendments. The effect of a viscosity increase can be expressed in terms of a hydraulic conductivity decrease, as hydraulic conductivity is a function of both media and fluid (Freeze and Cherry, 1979; Thomas and Ward, 1988).
- **moisture content:** excessive moisture decreases microbial activity because of the low solubility of oxygen in water (U.S.EPA, 1988e). However, some free water is required because a contaminant must be in the aqueous phase to enter a microbial cell and be degraded (Mueller et al., 1989). U.S.EPA (1988e) recommends a moisture content between 40 and 79% for in situ biodegradation.
- **presence of toxic substances and competing agents:** at wood preserving sites, in situ bioreclamation could be hindered by the presence of toxic substances such as CCA, which inhibit microbial activity. In addition, other aquifer components can

compete with microorganisms for the amendments. For example, nutrients may be adsorbed by organic matter in the soil matrix. Some of the competing reactions may also produce secondary adverse effects. For example, hydrogen peroxide (H_2O_2) can oxidize Fe^{2+} to Fe^{3+}, which subsequently forms a low solubility iron hydroxide precipitate (U.S.EPA, 1989c). This reaction not only consumes H_2O_2, but plugs the geologic formation with precipitate. Copper and chromium (present in CCA), may also catalyze peroxide decomposition (Thomas and Ward, 1988).

- **method of treating recovered groundwater:** Any conventional wastewater treatment process could be used to treat recovered groundwater at wood preserving sites, though some processes possess distinct advantages. For example, a biological treatment process such as activated sludge will provide a supply of acclimated organisms for re-injection, while air stripping or enhanced oxidation will oxygenate the water (Canter et al., 1987).
- **formation permeability:** the hydraulic conductivity (permeability) of the contaminated formation will affect the movement of microorganisms, nutrients and the electron acceptor. Pollutant biodegradation will be negligible in low-permeability aquifers where transfer of the required amendments is slow. Thomas and coworkers (1987a) concluded that hydraulic conductivities of 10^{-4} cm/s or greater were required for successful in situ biorestoration. Using this guideline value and Table 3.2-2, it appears that only one, or at most two, of the HELP sites will be amenable to in situ bioreclamation. Freeman and Innes (1986)

concluded that low permeability glacial tills would be a significant limiting factor in the application of bioreclamation in Alberta. Increased groundwater viscosity, microbial buildup and precipitates can all reduce formation permeability. In addition, oily-phase contaminants concentrate in the fine-grained portion of aquifers, because of greater capillary forces. These areas may not be effectively contacted by amendments moving with the bulk groundwater flow.

- **degree of hydraulic control**: the success of in situ bioreclamation depends on the ability to hydrologically isolate the contaminated zone from the surrounding groundwater regime, and drive the amendments through the zone along a steep hydraulic gradient. However, bedrock fractures, low permeability lenses and preferential flow paths all act against hydraulic control, reducing treatment efficacy.

3.2.2.2.3 Monitoring

Monitoring concerns for bioreclamation systems are similar to those of land treatment (section 3.2.2.1.4). In general, a combined biological and chemical testing protocol should be adopted at wood preserving sites. In addition to this combined protocol, a number of other parameters may be used to monitor in situ bioreclamation systems.

- **dissolved oxygen levels in groundwater**: dissolved oxygen (DO) levels in groundwater can indicate the amount of biochemical oxidation occurring in the subsurface, and therefore reflect the amount of contaminant degradation. A number of high DO levels after a series of low values imply that remediation is complete, or that some substance is limiting degradation (eg. nutrients), or interfering with microbial activity (eg. toxic intermediate) (U.S.EPA, 1989c; Thomas and Ward, 1988; Piotrowski, 1989).

- **microorganism activity:** an increase in microorganism number and activity is expected during successful in situ bioremediation. The majority of growth will occur attached to the soil substrate rather than in the free liquid. As well, the contaminant degraders may represent only a small fraction of the total microbial population. Accordingly, a study by McGinnis and coworkers (1988) concluded that microbial plate counts from the liquid phase were not related to transformation rates of wood preserving chemicals. This study agrees with the conclusions of U.S.EPA (1989c), which suggest that microorganism activity is a much better indication of contaminant degradation. Consequently, tests of microorganism activity (such as CO_2 evolution) should be used in place of plate counts to monitor bioreclamation at wood preserving sites.
- **presence of degradation products:** the presence and amount of contaminant degradation products can be used to monitor in situ bioreclamation (U.S.EPA, 1989c).
- **disappearance of electron acceptor and nutrients:** both of these phenomena imply enhanced biological activity, and their concentrations can be used as monitoring parameters (U.S.EPA, 1989c; Thomas and Ward, 1988).

- **nitrification:** nitrogen is often provided to aquifers as ammonia. The oxidation of ammonia to nitrate or nitrite implies that the carbonaceous substrate is depleted, and nitrification is occurring. Consequently, these three nitrogen forms can be used as monitoring parameters.

3.2.2.2.4 Laboratory- and Pilot-Scale Studies

The applicability of in situ bioreclamation to wood preserving plants is site-specific. Consequently, laboratory- and pilot-scale studies must be completed to assess the feasibility of in situ bioreclamation for a specific site. Laboratory-scale tests, or "treatability" studies, determine the amendment quantities which lead to maximum rates of contaminant degradation and toxicity reduction. If these rates are sufficient, a pilot-scale study is generally undertaken to determine the most efficient way of providing amendments to the subsurface.

Laboratory-scale tests are generally conducted in shaker flasks or beakers, in a manner similar to that used in treatability studies for land treatment (section 3.2.2.1.5). However for in situ bioreclamation, the oxygen content of headspace gases or pore water is an amendment quantity to be assessed, so the containers are sealed to form closed systems. In general, contaminated soil is incubated with various amounts of nutrients and other amendments. Oxygen is provided by bubbling air through the pore water or circulating it through the headspace, depending if the saturated or vadose zones are being considered. Periodic sampling and analysis is conducted to determine rates of contaminant degradation and toxicity reduction.

Optimum amendment levels are selected from this data. Factorial experimental design may be used to determine the parameters to which the rates are most sensitive. Upper and lower limits of treatability are generally also determined from the test data. In addition, contaminant-degrading microbes may be isolated from the treatability study soil. These microorganisms may be grown in bulk and used to inoculate the subsurface. The means of isolating such organisms are discussed in section 3.2.2.1.5.

If test results from the laboratory study are favourable, a pilot-scale in situ bioreclamation system may be constructed at the site. This system is generally a smaller version of the proposed full-scale system, and is intended to determine the most efficient way of providing amendments to the subsurface and other operational concerns. For example, the ability of injection wells, horizontal pipelines, and infiltration galleries to provide nutrients to the contaminated zone may be compared. A number of other concerns may also be addressed in the field study (Piontek, 1989):

- effects of low permeability zones;
- effects of in situ treatment on permeability;
- performance of specific equipment; and
- relation between amendment delivery rates and subsurface amendment concentrations. This relation will affect the sizing of delivery equipment.

3.2.2.2.5 In Situ Bioreclamation at Wood Preserving Sites

Contamination at wood preserving sites differs from that of other industries. Consequently, in situ bioreclamation of wood preserving sites involves some unique concerns, which are primarily associated with the forms of contamination present, and the means of providing amendments to the subsurface.

The environmental transport and fate of waste wood preserving fluids was considered in section 1.5. In general, creosote- and PCP-based mixtures are bulk hydrocarbon fluids which can exist in a number of forms in the environment (Figure 1.5-4):

- residual saturation hydrocarbon trapped by capillary forces in the vadose and saturated zones;
- non-aqueous phase liquid (NAPL), blob or emulsion in groundwater; and
- individual chemical constituents partitioned to the soil and aqueous phases.

While in situ bioreclamation can remediate distinct-phase liquids and the individual chemicals dissolved in groundwater, these materials are best remediated by pumping and above-ground treatment, for two reasons:

- these materials are easily recovered by wells, and should be treated above-ground, where oxygen, nutrients and acclimated microbes can be provided in abundance (U.S.EPA, 1989c).
- the distinct phase liquids (NAPL, emulsion, blobs) are highly concentrated and would require enormous amounts of amendments. Because amendment mobility is limited in the

> subsurface, these liquids would significantly increase the period of reclamation (Hurlburt, 1987; Thomas and Ward, 1988; Piontek, 1989). In addition, the large contaminant concentrations are likely toxic to subsurface microflora, further decreasing the rate of remediation (Thomas and Ward, 1988).

However, aquifer pumping cannot in most cases produce sufficient hydraulic gradients to dislodge and recover residual saturation hydrocarbon, or individual constituents adsorbed to soil. These contamination forms act as a source area for groundwater contamination, continuously partitioning chemical components to the aqueous phase, as predicted by partition equilibria. In situ bioreclamation can remediate both saturated and vadose zone residual saturation hydrocarbon, as well as adsorbed constituents. Treatment of these contamination forms is the best application of in situ bioremediation at wood preserving sites (Piontek, 1989; Thomas and Ward, 1988; U.S.EPA, 1989c).

Another concern of in situ biorestoration at wood preserving sites involves the means of delivering amendments to the contaminated zone. Much of the contamination at wood preserving sites originates at the ground surface (eg. drip pad) or shallow subsurface (eg. sludge lagoon). Consequently, both vadose and saturated soil zones are contaminated at most wood preserving sites, and in situ bioreclamation systems must provide amendments to both regions.

Three types of amendment delivery systems can be used: injection wells, pipelines, and infiltration galleries. Injection wells are simply groundwater wells where a positive hydraulic head is used to force amendments into the formation. Injection wells are best suited to use in the saturated zone, as they are less expensive than other systems for deeper contamination. Pipelines consist of a group of horizontal perforated pipes, which can supply amendments to the contaminated zone under a positive hydraulic head. The horizontal pipes are installed in the bottom of a trench, which is subsequently backfilled. Pipelines become more expensive than wells with increasing depths of installation. Horizontal pipelines offer a number of advantages over a more typical system of injection and withdrawal wells (Piontek, 1989):

- higher achievable flow rates;
- more linear flow paths; and
- lower installation and operating costs for shallow contamination.

Infiltration galleries are simply lagoons or trenches where amendments are stored and allowed to percolate through the contaminated zone. Obviously, unstable amendments such as ozone or hydrogen peroxide would be ineffective with this type of delivery system. Infiltration galleries are the least expensive delivery system for the shallow subsurface, and are best used in remediating the vadose zone (Thomas and Ward, 1988). Horizontal pipelines and wells possess one distinct advantage over infiltration galleries: wells and drainlines can be used initially to recover distinct-phase liquids. Once recovery of NAPL, blobs and emulsions is complete, the pumping system can be converted into an amendment injection system. At wood preserving sites, both injection wells and horizontal drainlines have been employed; monitoring wells were converted to injection wells at a site in Montana (Piotrowski, 1989), and horizontal drainlines were used to recover DNAPL and then provide amendments at a site in Wyoming (Piontek, 1989; Flechas, 1989). The use of wells, pipelines and an infiltration gallery for in situ bioreclamation at a wood preserving site is illustrated in Figure 3.2-4.

A number of wood preserving sites in the U.S. are currently in the process of implementing in situ bioreclamation, as shown in Table 3.2-4. Full-scale treatment is expected to begin late in 1990 at a wood preserving site in northwestern Montana. The climate at this site is likely similar to that of southern Alberta, implying that in situ bioreclamation has been judged to be feasible for northern areas.

3.2.2.2.6 Advantages and Disadvantages

The advantages and disadvantages associated with the use of in situ bioreclamation at wood preserving sites are summarized below.

- Advantages:
  - soil does not require excavation. This reduces costs and fugitive air emissions.
  - in situ bioreclamation can be less expensive than other alternatives. For example, 1500 m^3 of gasoline-contaminated soil will be remediated for about \$247 Cdn/m^3 (U.S.EPA, 1988a).
  - in some ways, in situ bioreclamation is a benign technology: treatment quickly ceases when nutrients, oxygen or substrate are no longer available.
  - in situ bioreclamation can remediate vadose and saturated zones, and residual saturation.

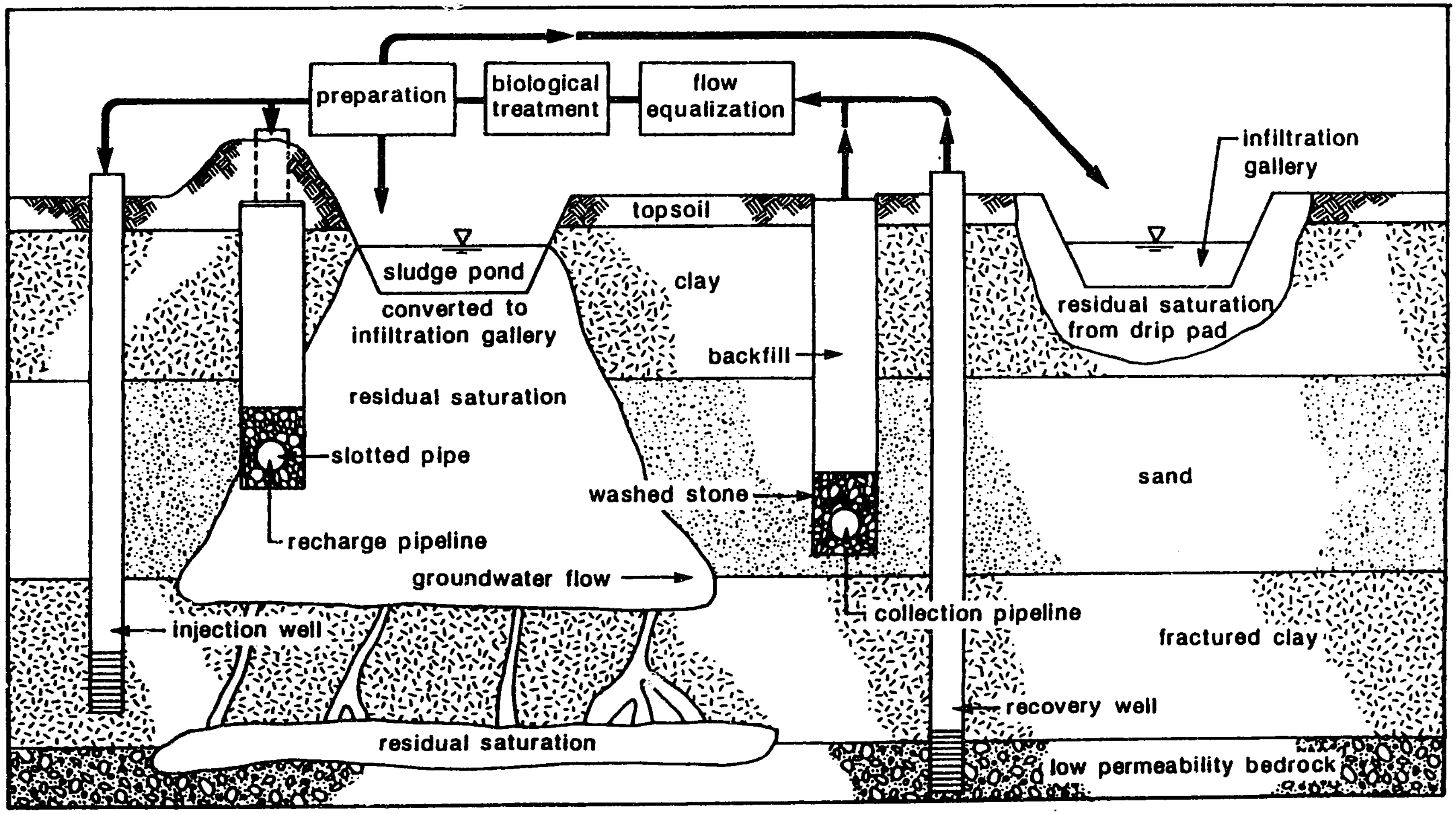


FIGURE 3.2-4 : TYPICAL IN SITU BIORECLAMATION SYSTEM AT A WOOD PRESERVING SITE, AFTER RECOVERY OF PURE-PHASE LIQUIDS

Table 3.2-4: Wood Preserving Sites in the U.S. Where In Situ Bioreclamation Has Been Proposed or Implemented

Site Name	State	Proposed Remediation	Stage in Remediation as of late 1989	Comments
L.A. Clark and Sons	Virginia	Pump DNAPL, flush soil, followed with in situ bioremediation	Have not begun treatability study	Estimated 5 years to complete remediation at a cost of $24,000,000 U.S.
North Cavalcade Street	Texas	In situ bioreclamation	Have not begun treatability study	Estimated 2 years to complete remediation of 99 000 cubic metres
Union Pacific Railroad	Wyoming	DNAPL recovery, soil flushing, in situ bioreclamation	Pilot-scale studies completed. Currently (1990) evaluating results	Approximately 22 000 000 litres of waste wood preserving oil are contained in 765 000 cubic metres of soil
Champion International	Montana	Land treatment for surficial soil, in situ bioreclamation for deeper soil and groundwater	Pilot-scale studies completed. Full-scale in situ bioreclamation will begin in late 1990	First Superfund Record of Decision mandating the use of in situ bioreclamation

Notes:

- Sources: Sims, 1988; Piontek (personal communication), 1990; Piontek, 1989; Flechas, 1989; Piotrowski, 1989; Dworkin et al., 1988.

- Disadvantages:
  - process efficiency is adversely affected by low temperatures which increase groundwater viscosity and reduce microbial activity. It is also hampered by low permeability formations which limit amendment transport. One or both of these conditions exists at the HELP sites.
  - degradation products are generally more water soluble than the parent compound, because microbes seek to detoxify, and also must excrete the transformation product (Utah State, 1989). Consequently, degradation products are typically more mobile than the parent compound, and may escape hydraulic containment in the treatment zone. Many degradation products are pollutants themselves.
  - large amounts of nutrients are required for in situ bioreclamation. Releases of these nutrients from the treatment zone may impact surface and ground waters. Excess nutrient levels can lead to eutrophication of water bodies and also adversely affect humans. For example, nitrate-N levels in water in excess of 10 mg/L have been responsible for 29 infant deaths by methemoglobinemia (Steel and McGhee, 1979). Nitrate is a common nitrogen additive for in situ bioreclamation.
  - in situ bioreclamation may take a long time and become quite expensive if distinct phase liquids remain in the subsurface.
  - this treatment approach may not be able to achieve extremely low cleanup levels without a complementary technology.

Consequently, limits of treatability must be assessed in the laboratory study.

3.3 Concentration Strategies

3.3.1 In Situ Vapour Extraction

In situ vapour extraction, in situ vacuum extraction, in situ air stripping, and induced soil venting are all terms that refer, with minor variations, to the same basic remediation process. These processes will all be referred to as in situ vapour extraction.

For this remediation technique, clean surface air is injected into the contaminated soil zone above the water table (vadose zone). Vapour extraction wells draw the clean air through the contaminated zone, where volatile contaminants partition to the vapour phase. Contaminated air is recovered by the extraction wells, stripped of contaminants and re-injected. In essence, vapour extraction is the vapour-phase equivalent of groundwater pump and treat:

- in pump and treat, groundwater is moved through the contaminated saturated zone along a hydraulic gradient. The replacement of existing pore water with fresh water disrupts chemical equilibrium between pore water, soil and residual saturation hydrocarbon (Figure 1.5-3). Chemical equilibrium is the minimum chemical energy state attainable by the aquifer, and molecular diffusion works to restore this level by partitioning chemical constituents from the soil and residual hydrocarbon phases to the pore water. This pore water is, in turn, replaced by fresh water, and the cycle continues until adsorbed constituents and residual saturation hydrocarbon are depleted.

- in vapour extraction, air is moved through the contaminated vadose zone along a vapour pressure gradient. The replacement of existing pore gases with clean air disrupts chemical equilibrium between pore air, soil, pore water and residual saturation hydrocarbon (Figure 1.5-3). Molecular diffusion attempts to re-establish equilibrium by partitioning chemical constituents from the various phases to the pore air. This pore air is, in turn, replaced by clean air, and the cycle continues until adsorbed and dissolved constituents, as well as residual hydrocarbon, are depleted.

The efficiency of vapour extraction is related to how fast pore gases can be replaced in the subsurface, how fast the contaminants partition to the vapour phase (kinetic concern), and the maximum contaminant vapour-phase concentrations achievable (equilibrium concern). Low permeability soils containing low volatility chemicals are not effectively remediated with this technology. The use of in situ vapour extraction is typically limited to permeable, unconsolidated soils containing volatile contaminants above the water table (Dupont, 1989; Johnson et al., 1990; U.S.EPA, 1988e; Anastos et al., 1987; U.S.EPA, 1990; U.S.EPA, 1988a).

Different variations of the basic vapour extraction approach exist, but likely only the variation using steam could enhance contaminant recovery at wood preserving sites. Injecting steam into the subsurface heats the soil being remediated, which increases the vapour pressure of the contaminants and the rate at which they can be stripped (U.S.EPA, 1990; Boikess and Edelson, 1981). Steam stripping is expected to enhance the rate and extent of remediation, and may be applicable to less volatile compounds as well (U.S.EPA, 1988e). In this process, steam is injected through two hollow blades, which simultaneously loosen and homogenize the contaminated soil to a depth as much as 9 metres (30 feet) (U.S.EPA, 1988e). The resulting mixture of steam, hot air and volatile organics is brought to the soil surface by a vacuum shroud, which conveys the mixture to a treatment process (U.S.EPA, 1988e; U.S.EPA, 1989a; U.S.EPA, 1990). As with other vapour extraction techniques, the efficacy of this process decreases in low permeability and low temperature soils, and for low volatility compounds. Benzene, chlorobenzene, dichloroethane, tetrachloroethene, octanol and butanol have all been effectively recovered from soil by this technology (U.S.EPA, 1989a; U.S.EPA, 1990). Wood preserving chemicals, which are significantly less volatile than the aforementioned compounds, have not been tested.

Both vapour extraction and steam stripping produce a gaseous waste stream containing small amounts of the contaminants. Typically, the waste is concentrated by direct carbon adsorption, though the gas may be condensed first. In any case, the ultimate emission from this process is exhausted activated carbon.

3.3.1.1 Important Parameters

Several factors affect the applicability of vapour extraction systems. These parameters can be grouped into three categories: chemical properties, site characteristics, and system operation.

3.3.1.1.1 Chemical Properties

Compounds amenable to vapour extraction must be volatile, and must be present in sufficient amounts in chemical mixtures. U.S.EPA (1988e) concluded that compounds require a Henry's Law Constant (k_H) greater than 3×10^{-3} atm·m^3/mol to be successfully recovered by vapour extraction, and that steam extraction should apply to less volatile compounds. This guideline value is an order of magnitude larger than that of U.S.EPA (1989c), which recommends a minimum k_H value of 0.24×10^{-3} atm·m^3/mol. In addition, Dupont (1989) suggests a minimum compound vapour pressure of 0.5 mm Hg at ambient temperatures. The compounds present in creosote- and PCP-based preservative fluids possess moderate to negligible volatilities (Appendix A). In comparison, waste CCA-based fluids contain inorganic chemicals, which are not volatile (Table 1.4-12). However, the biotransformation products of arsenic (methylarsines) are quite volatile (section 1.5.2.2.1). Consequently, vapour extraction is a possible remediation alternative at PCP, creosote, and CCA sites (for arsenic only).

Another important chemical property for in situ vapour extraction at wood preserving sites is compound volatility in mixtures. In single compound environments, a chemical will partition to the vapour phase from water according to its Henry's Law Constant. In chemical mixtures however, cosolvent effects and cohesive forces may affect vapourization rates. This is of concern at creosote and PCP sites, where a large number of chemicals exist as part of a bulk hydrocarbon phase. Studies on the vapour extraction of gasoline constituents have provided information on the volatilization of chemicals from hydrocarbon mixtures. In general, sequential volatilization of gasoline components is related to individual compound vapour pressure and the mole fraction at any time (Hoag et al., 1987; Johnson et al., 1990). It is reasonable to assume this conclusion extends to creosote and PCP mixtures utilizing diesel as the carrier fuel. Consequently, it is likely that the vapourization of chemicals in waste wood preserving mixtures is dependent on compound volatility and percentage in the mixture.

3.3.1.1.2 Site Properties

Site characteristics also influence the applicability of in situ vapour extraction, as discussed below.

- **vapour conductivity of soil:** the efficiency of vapour extraction depends on how fast pore gases can be replaced in the subsurface. The ability of soil to transmit air is measured by the soil vapour conductivity. This parameter is the gaseous-phase equivalent of hydraulic conductivity, and is usually expressed in terms of the latter because of the relative ease in determination. For example, Dupont (1989) postulated that vapour extraction would not be effective for soils of saturated hydraulic conductivity less than 10^{-4} cm/s. The relationship between vapour conductivity and contaminant removal rate is related to the different transport processes. In soils of low vapour conductivity (eg. clay), molecular diffusion is the predominant contaminant transport mechanism. Molecular diffusion occurs as a result of concentration gradients, and is an extremely slow process. In soils of high vapour conductivity (eg. sand), advection is the predominant transport mechanism. Advection occurs as a result of vapour pressure gradients, and is much more rapid than diffusion. Consequently, greater recovery rates are possible in more permeable soils (Anastos et al., 1987; U.S.EPA, 1989c; U.S.EPA, 1988e).

- **soil moisture content:** differing viewpoints exist as to the effect of soil moisture on vapour extraction efficacy. U.S.EPA (1988e) postulated that high moisture levels hinder air movement through soil, decreasing vapour removal rates. U.S.EPA (1989c) concluded that increasing moisture levels increases vapourization, as water may be preferentially adsorbed over the contaminant to soil surfaces, resulting in higher vapour phase chemical concentrations. Vapour extraction models developed by Johnson and coworkers (1990) indicate that soil moisture content does not influence recovery of gasoline constituents. As a result of these differing opinions, it appears that the effect of soil moisture on vapour recovery will be site- and contaminant-specific.
- **soil organic carbon:** U.S.EPA (1988e) concluded that a high soil humic content decreases volatilization, presumably because hydrophobic contaminants preferentially partition to organic rich soils over the vapour phase.
- **preferential flow paths:** air, like water, follows the path of least resistance. In soil, this path is comprised of fractures and other macropores. The existence of preferential flow paths in soil means the vapour in smaller pores will not be replaced as often as

that in larger pores, increasing the remediation period (Dupont, 1989). In essence, volatile contaminants located along preferential flow paths will be quickly transported by advection, while those in the smaller pores must rely upon diffusion for transport.

- **temperature**: compound vapour pressure decreases with diminishing temperature (U.S.EPA, 1990; Boikess and Edelson, 1981). Lowering soil temperature will therefore decrease the number of contaminant molecules in the vapour phase, reducing contaminant recovery. Partition kinetics, which describe the rate of vapourization, may also be adversely affected by declining temperatures. The temperature sensitivity of volatilization is a concern in Alberta, where soil temperatures seldom exceed 10°C. Johnson and coworkers (1990) concluded that decreasing the soil temperature from 27°C to 0°C would increase the remediation period of a gasoline spill by five times, using vapour extraction alone. Steam stripping may be a way of applying vapour extraction to cold climates.

Several conclusions have been made about the types of soil amenable to remediation by vapour extraction:

- the use of vapour extraction systems is typically limited to permeable unsaturated soils such as sands, gravels and coarse silts. Clay soils generally lack the conductivity necessary for effective vapour extraction (U.S.EPA, 1990).
- clay lenses significantly increase the remediation period (Anastos et al., 1987).

- in situ vapour extraction is effective for permeable, sand soils containing small amounts of moisture and organic carbon (Dupont, 1989).

3.3.1.1.3 System Properties

The design and operation of an in situ vapour extraction system can influence contaminant recovery, as discussed below.

- **well spacing and depth:** work done by Wilson (presented in U.S.EPA [1989c]) has shown that contaminant recovery by vapour extraction is greatest for closely spaced extraction wells installed near to the water table. Smaller well spacing is expected to improve contaminant recovery by increasing the vapour pressure gradient. Vapour extraction wells installed near the water table may enhance vapourization of aqueous-phase contaminants, thereby increasing the mass of contaminant recovered.
- **pumping cycle:** tailing is the slow, nearly asymptotic decrease in contaminant concentration in pore gases successively flushed through contaminated soil. This phenomena has been observed in vapour extraction systems (U.S.EPA, 1990; U.S.EPA, 1989c), and is likely due to the diffusion of contaminants from fine-grained materials. Pulsed pumping, where air injection and extraction is periodically stopped to allow time for chemical diffusion, can enhance recovery of the remaining fractions (Hutzler et al., 1989a; U.S.EPA, 1990; U.S.EPA, 1989c).

3.3.1.2 In Situ Vapour Extraction at Wood Preserving Sites

The success of vapour extraction in contaminant recovery primarily depends on compound volatility, soil permeability and temperature. Wood preserving mixtures contain two main components: the toxic agent and the carrier. In creosote- and PCP-based wood preservation, the toxic components are moderately to negligibly volatile, whereas the constituents of the diesel carrier are somewhat more volatile.

Table 3.3-1 lists the vapour pressures of many of the constituents in wood preserving mixtures. Comparing this data with the guideline vapour pressure value of 0.5 mm Hg (Dupont, 1989), it appears that none of the toxic components in PCP- or creosote-based wood preserving mixtures are amenable to recovery by vapour extraction. Some of the diesel components may be recoverable, but these compounds do not present the greatest risk to human health at wood preserving sites (section 1.4.1.3.1).

In section 3.3.1.1.2, desirable soil properties for vapour extraction were outlined. Favourable soils consist of sand, gravels or coarse silts. Hydraulic conductivities greater than 10^{-4} cm/s are required. Soils that are wet, rich in humic matter, or contain clay lenses are poorly remediated. Table 3.2-2 summarizes the hydrogeology and hydraulic conductivity of soil at the HELP sites. Comparing this data with the foregoing recommendations, only one or two of the sites possess suitable soil conditions for in situ vapour extraction. Most of Alberta is underlain by glacially-deposited clays, and it is unlikely that other wood preserving sites

Table 3.3-1: Vapour Pressures of Some Chemicals in PCP- and Creosote-Based Wood Preserving Solutions

Preserving Solution	Constituent	Vapour Pressure in mm Mercury at 20°C unless Otherwise Noted	Comments
Diesel fuel (carrier in all PCP and some creosote preserving solutions)	2-methylnaphthalene	0.045	at 25°C
	toluene	21.8	
PCP-based	Pentachlorophenol (PCP)	1.1×10^{-4}	
	2,4,6-trichlorophenol	8.4×10^{-3}	at 24°C
	4-chlorophenol	0.087	at 25°C
	Octachlorodibenzofuran	1.9×10^{-7}	at 25°C
Creosote-based	Naphthalene	0.0492	
	Acenaphthene	0.020	
	Fluorene	0.013	
	Acenaphthylene	0.029	
	Anthracene	1.96×10^{-4}	
	Phenanthrene	6.80×10^{-4}	
	Fluoranthene	6.0×10^{-6}	
	Pyrene	6.9×10^{-7}	
	Benzo[a]anthracene	5.0×10^{-9}	
	Chrysene	6.3×10^{-7}	
	Benzo[k]fluoranthene	5.0×10^{-7}	
	Benzo[a]pyrene	5.0×10^{-7}	
	Dibenzo[a,h]anthracene	1.0×10^{-10}	
	Benzo[g,h,i]perylene	1.0×10^{-10}	
	Indeno[1,2,3-c,d]pyrene	1.0×10^{-10}	

Notes:

- Sources: Battelle (1989), Environment Canada (1988a), Howard (1989), U.S.EPA (1986a), Sims et al. (1986), McGinnis (1984), McGinnis et al. (1988), Environment Canada (1984), Montgomery and Welkom (1990).

slated for decommissioning will possess adequate soil conditions for in situ vapour extraction.

Decreasing soil temperature decreases the equilibrium concentrations of contaminants in the vapour phase, as well as decreases the rates of volatilization. In Alberta, soil temperatures seldom exceed 10°C, and soil freezing is common in the winter. Consequently, at wood preserving sites in Alberta, volatilization rates and vapour-phase concentrations achievable will both be lower than in warmer regions. It should be noted that soil freezing provides a form of natural vapour extraction, because freezing soil liberates pore vapours when pore water freezes and expands.

In conclusion, wood preserving sites in Alberta are not amenable to remediation by in situ vapour extraction, because of unfavourable contaminant, soil and temperature conditions. The low volatility of the contaminants is likely the most important parameter. Vapour extraction is not being considered for remediation at a number of wood preserving sites in the U.S. which possess more favourable soil and temperature conditions (based on a compilation of remedial activities at ten sites by Sims, 1988). Dupont (1989) concluded that vapour extraction could best be used for two purposes at wood preserving sites:

- recovery of volatile components in the carrier, and
- enhancement of in situ bioreclamation through improvement of subsurface oxygen levels.

In situ vapour extraction will likely find its only use at wood preserving sites as the air transport/air recovery component of in situ bioremediation.

3.3.2 In Situ Soil Washing

Waste wood preserving mixtures percolating through soil may become immobilized by capillary forces arising from interfacial tension (section 1.5). In addition, the individual chemicals in the fluid may adsorb onto soil mineral or organic matter. These contamination forms are difficult to remediate, because they are unresponsive to gravitational or pressure forces. They also represent a long-term contamination source, because the constituents will gradually desorb when contacted with cleaner pore water.

Bioreclamation is not applicable to CCA (inorganic) contamination, and its efficacy is decreased for large pockets of residual saturation, which act as concentrated pools of toxic chemicals. In situ soil washing can overcome both of these limitations.

In situ soil washing involves the injection of a washing solution into the contaminated zone. This solution alters the characteristics of the soil pore water, so that the contaminants preferentially exist in the aqueous as opposed to solid or oil phases. The mobilization may occur through solubilization of adsorbed contaminants, emulsification of residual bulk hydrocarbon fluid, or by chemical reaction with the flushing solution (U.S.EPA, 1990; Amdurer et al., 1986). In any case, the elutriate solution (washing chemicals and mobilized contaminants) is mobile in groundwater and recoverable by wellpoints or subsurface drains. Recovered elutriate is treated to separate contaminants from the groundwater.

Soil washing uses physical and chemical processes, which are applicable to CCA (inorganic) contamination and are unaffected by high contaminant concentrations in residual saturation hydrocarbon. Consequently, soil washing is a more widely applicable technology than in situ bioreclamation.

Washing solutions may be comprised of one or more of acids, bases, surfactants, alkaline agents, polymers, solvents, or complexing (chelating) agents (Sale and Piontek, 1988; U.S.EPA, 1988e; Amdurer et al., 1986; U.S.EPA, 1989c; Roy and Griffin, 1988; U.S.EPA, 1990). Some of these washing chemicals may be pollutants themselves, so complete hydraulic control throughout the treatment zone is required to prevent releases of washing solution or elutriate to the surrounding groundwater regime. Water flushing is often used as the last step in soil washing to displace residual elutriate and unused washing solution (Sale et al., 1989), as well as to prepare the soil for any subsequent treatment such as bioreclamation.

In situ soil washing is most efficiently completed in a closed-loop system, because such a system minimizes reagent inputs and environmental impacts from fugitive chemical releases. A closed-loop treatment cycle involves the injection of washing solution upgradient of the contamination, circulation through the contaminated vadose and saturated zones, elutriate collection, treatment of recovered elutriate, addition of make-up chemicals, and re-injection. The formation of such a cycle depends largely on the groundwater injection and recovery system (section 3.3.3). Consequently, in situ soil washing can be viewed as another variation of pump and treat technology.

3.3.2.1 Parameters Affecting Process Efficacy

Several factors affect the applicability of in situ soil washing systems. These parameters can be grouped into three categories: chemical properties, site characteristics, and system properties.

3.3.2.1.1 Chemical Properties

The feasibility of soil washing at a site will depend on the number of different solution formulations required to mobilize all the adsorbed contaminants. Wood preserving plants, as well as most other industrial sites, are contaminated with a variety of chemicals, displaying differing environmental behaviours. Ideally, all of these contaminants could be mobilized with one washing solution. If not, a sequence of different solutions may be required, markedly increasing the time and cost of site remediation. The problem of multiple washing solution formulation only exists for individual constituents adsorbed to soil. The situation is simplified for residual saturation hydrocarbon, where the washing solution must simply mobilize the hydrocarbon to recover all the contaminants. The applicability of soil washing to wood preserving sites is discussed in section 3.3.2.2.

3.3.2.1.2 Site Characteristics

Site characteristics also influence the applicability of in situ soil washing, as discussed below.

- **soil permeability**: the success of soil washing depends on the ability to deliver the flushing solution to the contaminated zone, circulate it through this region, and recover the elutriate in downgradient wells. This transfer of washing solution and elutriate depends on the hydraulic conductivity (permeability) of the soil. Soil washing will be impractical in low permeability formations which only transmit water at a rate of 1 or 2 metres per year ($k = 10^{-5}$ cm/s). In general, in situ soil washing is best applied to permeable soils containing negligible amounts of silt, clay, and organic matter (U.S.EPA, 1990; Raghavan et al., 1989; U.S.EPA, 1988e). It has been generally held that low permeability soils such as clays and silts can be more efficiently flushed of contaminants in above-ground reactors, where mass transfer limitations can be overcome. However, a review of current approaches by Raghavan and coworkers (1989) concluded that above-ground recovery of contaminants and elutriate has not been successfully demonstrated for clay and organic-rich soils.
- **adsorption capacity of soil**: the movement of washing solution through soil is resisted by adsorption, capillary forces, and interfacial tension, which are the same processes responsible for contaminant immobilization. In general, free washing solution will only be available to mobilize contaminants when the background requirements of the soil have been satisfied. Consequently, the larger the immobilization capacity of the formation, the greater are the requirements for washing solution. Clay and organic-rich soils are particularly effective in

immobilizing flushing solutions, because of greater capillary forces and more available adsorption sites. For example, cationic surfactant adsorption is related to the cation exchange capacity of soil (Roy and Griffin, 1988), which is especially large for clay soils containing organic matter. In addition, anionic surfactants may precipitate with exchangeable cations adsorbed to clay and humic material (Roy and Griffin, 1988). The effect of background reagent demand was also noted by Vigon and Rubin (1989), who used surfactant-soil adsorption curves in predicting surfactant effectiveness for aquifer remediation. In addition, contaminants may be more tightly adsorbed to clay minerals and organic matter because of multiple adsorption sites, and therefore less likely to be desorbed (U.S.EPA, 1988e).

- **temperature:** the temperature of the soil environment at a site affects the solubility of contaminants in washing solutions, as well as groundwater viscosity. The aqueous solubility of most compounds decreases with diminishing temperature (Sale and Piontek, 1988). Consequently, lower contaminant concentrations are recovered by the washing solution at lower temperatures. In addition, groundwater viscosity increases with declining temperature. This viscosity increase can be represented as a permeability decrease, as hydraulic conductivity is dependent on both media and fluid properties (Freeze and Cherry, 1979). The overall effect of diminishing temperature would be to decrease the efficiency of soil washing, because of less groundwater movement and lower equilibrium contaminant concentrations in the elutriate. In situ soil washing is likely less sensitive to temperature than in situ bioreclamation, as microbial activity is generally more temperature dependent, over the range of interest, than aqueous solubility or viscosity.

3.3.2.1.3 System Properties

Characteristics of the soil washing system can also affect process efficacy.

- **recovery technique:** design and operation of the recovery system affects the amount of elutriate recovered, as well as the ease of subsequent treatment. For example, the use of surfactants can allow residual hydrocarbon to be miscible in water through a reduction in interfacial tension. Recovery well pumps that impart mechanical energy to this unstable mixture can create an emulsion, which is difficult to treat (Sale et al., 1989; Sale and Piontek, 1988; Roy and Griffin, 1988). It is also not yet possible to break surfactant-induced emulsions so that the surfactant may be reused (Roy and Griffin, 1988; Downey, 1989).
- **washing solution properties:** washing solutions should not reduce formation permeability, be pollutants themselves, adversely alter the soil for subsequent treatment, or be largely immobilized in the soil. Washing solutions often contain polymers such as xantham gum to increase washing fluid viscosity to that of the contaminant, ensuring similar migration patterns (Sale et al., 1989). These polymers may be easily biodegraded, and the resulting biomass may reduce formation permeability. In addition, some flushing chemicals, such as

alkaline agents, can lead to precipitation of inorganics (eg. calcium carbonate) (Sale and Piontek, 1988; Roy and Griffin, 1988; Downey, 1989). These precipitates may also reduce permeability. Some washing solutions, such as organic solvents, may be pollutants themselves, and their use should be avoided (Sale and Piontek, 1988). Washing solutions may alter soil properties to the point that a subsequent technology is no longer practical. For example, acidic or basic washing solutions may leave the soil at a pH unfavourable to microorganisms, thereby eliminating bioreclamation as a subsequent treatment alternative. Finally, washing solutions should be negligibly immobilized in soils, as free solution capable of treatment will only exist when the background demand of the soil has been satisfied.

3.3.2.2 In Situ Soil Washing at Wood Preserving Sites

Soil washing can be used to remediate two forms of contamination at wood preserving sites: individual constituents adsorbed to soil, and bulk hydrocarbon preservative trapped as residual saturation.

Wood preserving fluids contain a variety of chemicals with differing environmental behaviours (sections 1.4 and 1.5). Adsorbed CCA components are all metals. Because copper exists as a cation in soil whereas chromium and arsenic exist as oxo anions, a single washing solution may not be effective. For example, in laboratory studies, the complexing agent EDTA promoted the mobilization of adsorbed copper (Roy and Griffin, 1988). However, there are no reported successes on the use of chelation agents to extract anionic contaminants such as arsenate or chromate from soils (Roy and Griffin, 1988).

At PCP and creosote sites, the extreme diversity in contaminant properties implies that a number of different washing solutions will be required to recover all the contaminants adsorbed to site soils. For example, chlorophenols from PCP treatment may be solubilized by a basic washing solution (section 1.5.1.2.1), leaving dioxins, furans and diesel fuel components as a residual. These compounds may require several different formulations for complete remediation. Chemical diversity is larger for creosote, implying even a greater number of formulations would be required. Consequently, soil washing is not practical for adsorbed contaminants at creosote or PCP sites.

Creosote- and PCP-based preserving mixtures are bulk hydrocarbon fluids of low aqueous solubility, which often exist in soil as a distinct hydrocarbon phase immobilized by capillary forces (residual saturation) (section 1.5.1.1). A remediation approach which can mobilize and recover the trapped hydrocarbon will also be successful in recovering the contaminants which are constituents of the distinct phase. Consequently, one formulation of washing solution may be successful in recovering residual saturation hydrocarbon. The use of soil washing to remediate residual saturation is the only application of soil washing that has been proposed at wood preserving sites (Dworkin et al., 1988; Flechas, 1989; Kuhn and Piontek, 1988; Sale et al., 1989; Sale and Piontek, 1988).

In general, waterflooding or some other enhanced oil recovery process is typically used to recover the free (mobile) oil existing in the aquifer (section 3.3.3.2.1). These oil recovery processes generally leave a large amount of residual oil behind, which is trapped by capillary forces due to interfacial tension. This residual saturation is best recovered by soil washing, where one formulation can recover the trapped oil. After recovery of the residual saturation, contaminants still remain adsorbed to soil. This contamination is best remediated by in situ bioreclamation. The relationship between the different remediation techniques and optimum treatment ranges is illustrated in Figure 3.3-1. The applicability of this staged approach to wood preserving sites has been identified by Dworkin and coworkers (1988), Flechas (1989), as well as by Sale and Piontek (1988).

Soil washing is currently being evaluated at pilot-scale for two wood preserving sites in the U.S. (L.A. Clarke and Sons in Virginia [Daniel Dworkin, Roy F. Weston Inc.; personal communication, 1990] and at a Union Pacific Railroad site in Wyoming [Kuhn and Piontek, 1988; Flechas, 1989; Sale et al., 1989]).

Three factors are responsible for residual oil remaining after primary oil recovery, and make this residual difficult to flush from the subsurface (Sale and Piontek, 1988):

- low water solubility of wood preserving oils;
- large interfacial tension (IFT) between the oil, water and soil phases, which gives rise to capillary forces; and
- high relative permeability of oil and water.

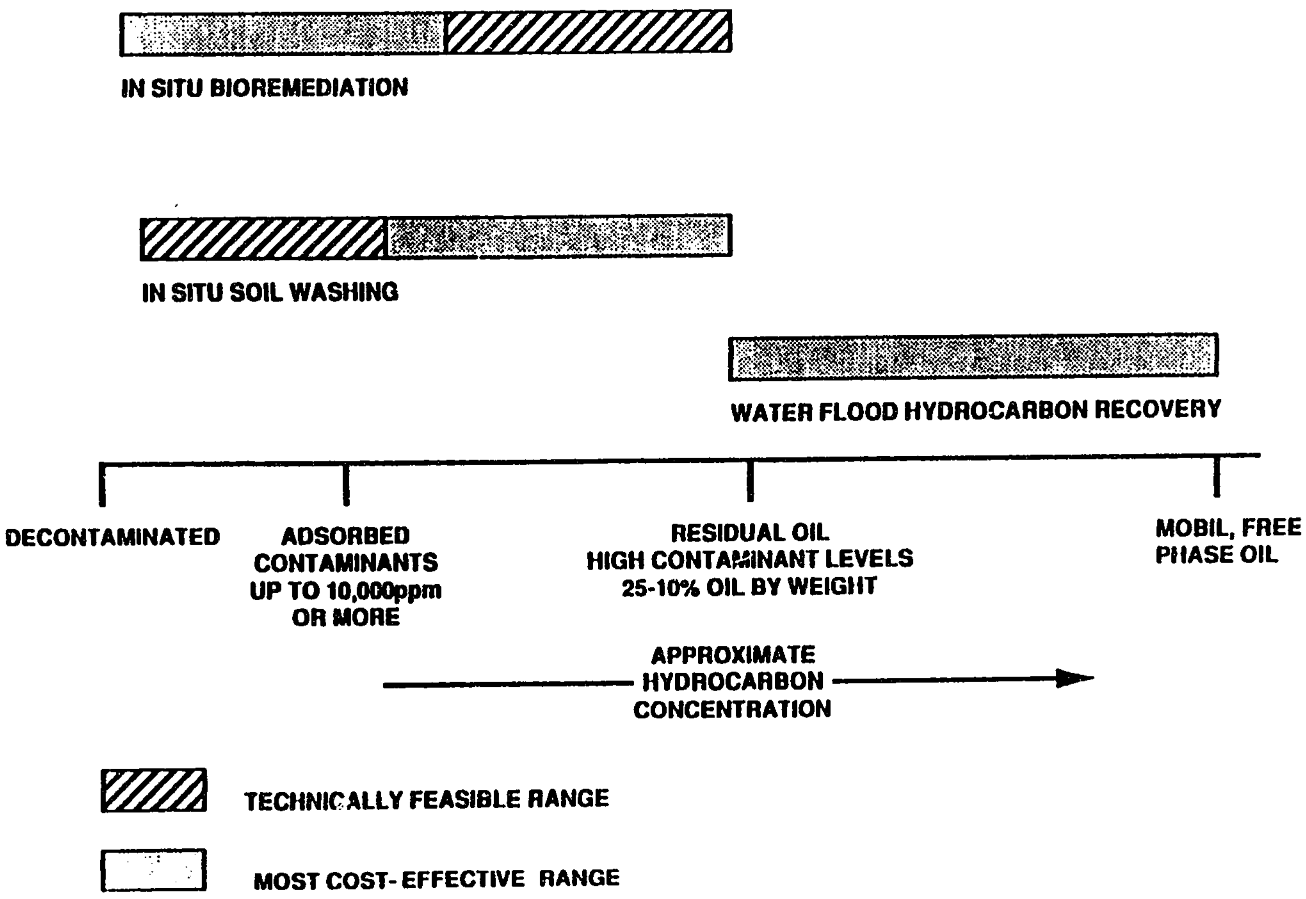


FIGURE 3.3-1 : PROBABLE RANGE OF EFFECTIVENESS FOR SELECTED IN SITU HYDROCARBON REMEDIATION TECHNIQUES (SALE AND PIONTEK, 1988)

The low aqueous solubility of PCP (diesel) and creosote oils limits the effectiveness of water-based flushing methods, because the amount of oil that dissolves in water and is flushed from the subsurface is small in comparison with the remaining residual (Sale and Piontek, 1988).

IFT can be described as the unbalanced forces acting on a droplet of hydrocarbon contamination (Kuhn and Piontek, 1988). The lower the IFT, the greater the tendency of the droplet to be miscible in groundwater. Large interfacial tension results in the retention of hydrocarbon on soil as opposed to its movement with groundwater (Sale and Piontek, 1988).

Relative permeability is a measure of the tendency of a porous medium to selectively conduct one fluid when two or more fluids are present (Kuhn and Piontek, 1988). The mobility ratio reflects the relative permeability of fluids in a two-fluid system, and is defined as (Sale et al., 1989):

$$(3.3\text{-}1) \qquad m = \frac{\text{mobility of displacing fluid (washing solution)}}{\text{mobility of displaced fluid (oil)}}$$

$$= \frac{K_{wro}\,\mu_o}{K_{orw}\,\mu_w}$$

where: K_{wro} = effective permeability of water (washing solution) at the residual oil concentration

K_{orw} = effective permeability of oil at the residual water concentration

μ_o = viscosity of oil

μ_w = viscosity of water (washing solution)

The higher the mobility ratio, the greater the tendency of the displacing fluid (water or washing solution) to flow around, rather than to wash out, the residual oil (Sale and Piontek, 1988). In situ soil washing aims to mobilize the residual oil by reducing the large interfacial tension and high mobility ratio existing between oil and pore water. This reduction can be accomplished at wood preserving sites using a mixture of alkaline agents, polymers, and surfactants (APS) (Dworkin et al., 1988; Kuhn and Piontek, 1988; Sale et al., 1989).

Alkaline agents such as sodium carbonate can react with hydrocarbon mixtures to form surfactants via a saponfication reaction (Flechas, 1989; Kuhn and Piontek, 1988; Sale and Piontek, 1988). Surfactant molecules possess both hydrophobic and hydrophilic regions, and consequently concentrate on interfaces between organic and aqueous phases (Amdurer et al., 1986; Roy and Griffin, 1988). Surfactants reduce the interfacial tension between the oil and aqueous phases, altering the shape of the globules trapped in the pore-throat restrictions, allowing the globules to move (Sale et al., 1989; Roy and Griffin, 1988; Sale and Piontek, 1988). Because the surfactants produced by alkaline-hydrocarbon reactions are formed at the aqueous-hydrocarbon interface, they can effectively reduce IFT, while being adsorbed to soils less than externally injected surfactants. Treatability studies at wood preserving sites have shown that both alkaline agents and proprietary surfactant mixtures are required for optimum hydrocarbon recovery (Kuhn and Piontek, 1988; Dworkin et al., 1988).

A polymer may be added to increase the viscosity of the washing solution, thereby decreasing the mobility ratio (equation 3.3-1) (Kuhn and Piontek, 1988; Sale and Piontek, 1988). In practical terms, increasing the viscosity of soil washing fluids almost to the viscosity of the hydrocarbon will ensure similar movement in the subsurface, and thus thorough contact between the substances. Large amounts of polymer may be required to obtain a favourable mobility ratio. For example, 1050 mg/L of xanthum gum were used during pilot tests at one wood preserving site (Sale et al., 1989). Large polymer concentrations increase the remediation period, because viscous washing solutions take longer to deliver and recover from contaminated zones.

In summary, washing solutions containing alkaline agents, polymers and surfactants (APS) have been demonstrated to recover residual hydrocarbon at wood preserving sites; the alkaline agent and surfactant reduce interfacial tension, while the polymer reduces the mobility ratio.

3.3.2.3 Monitoring

The following parameters can be used to monitor the progress of soil washing systems, or to detect adverse impacts arising from treatment.

- **soil contaminant concentrations**: to measure contaminant removal.
- **formation permeability**: to detect permeability decreases arising from biofouling or precipitation.

- **inorganic concentrations**: to ensure the washing solution is not mobilizing native inorganics, which may serve as nutrients for microbes or be pollutants themselves.
- **toxicity**: to detect adverse changes in the soil which may impact the feasibility of in situ bioreclamation.

Contaminant concentration monitoring is the only indicator of soil washing treatment performance. The other parameters simply indicate adverse side effects arising from treatment. Consequently, process observability is poor (Monenco, 1989).

3.3.2.4 Laboratory- and Pilot-Scale Tests

As with other in situ technologies, the feasibility of soil washing must first be assessed in the laboratory, using soil cores from the proposed site to determine (Sale and Piontek, 1988; Sale et al., 1989; U.S.EPA, 1990):

- optimum washing solution formulation, based on contaminant recovery rates;
- permeability decrease during treatment due to biofouling or inorganic precipitation;
- maximum and minimum limits of treatability;
- adsorption of washing solution by soil (background demand);
- treatability of recovered fluids. Recovered elutriate may contain stable emulsions or other chemical mixtures that are difficult to treat;
- toxicity of the washing solution to indigenous microbes; and

- effects of the washing agent on soil properties, to determine if mineral leaching is promoted, and if the soil would be amenable to subsequent treatment.

If the laboratory study demonstrates that contaminant recovery can occur at practical rates, and that no unacceptable impacts are associated with treatment, a pilot-scale study may be commissioned.

The object of the pilot-scale study is to identify operational concerns, and to generate data required for design of the full-scale system. Other concerns to be addressed during the pilot study include (Kuhn and Piontek, 1988; Sale et al., 1989):

- degree of contaminant removal achievable in the field;
- ability of injection and recovery systems to effectively deliver reagents to, and recover elutriate from, the contaminated zone;
- potential for releases of soil washing solution and elutriate to surrounding groundwater (degree of hydraulic control); and
- treatability of recovered fluids.

Data generated in the pilot-scale study can be used to assess the feasibility of full-scale treatment. A typical pilot soil washing test is illustrated in Figure 3.3-2.

3.3.2.5 Advantages and Disadvantages

The advantages and disadvantages of using in situ soil washing at wood preserving sites are summarized below.

- Advantages:

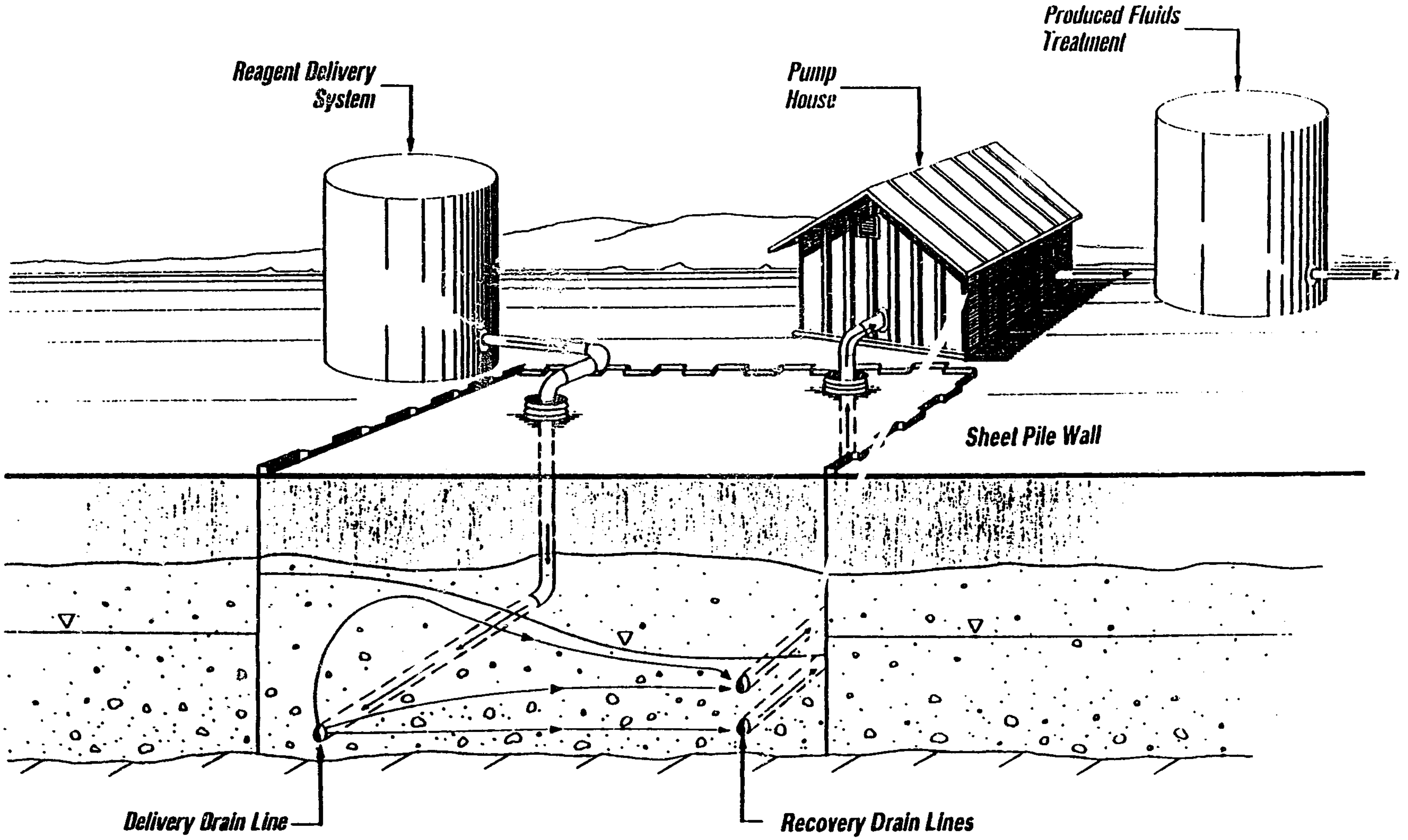


FIGURE 3.3-2 : PILOT-TEST OF IN SITU SOIL WASHING (SALE ET AL., 1989)

- soil does not require excavation. This reduces costs and fugitive air emissions.
- in situ soil washing can remediate both vadose and saturated zones.
- soil washing is more effective in remediating high levels of residual saturation hydrocarbon than in situ bioreclamation.

- Disadvantages:
  - in situ soil washing is only practical in permeable formations, and process efficiency is adversely affected by low temperatures.
  - treatment may produce an elutriate that is difficult to treat, and costly to dispose.
  - incomplete hydraulic control in the treatment zone may release washing solution and mobilized contaminants to surrounding groundwater.
  - treatment progression is difficult to observe because of few useful monitoring parameters.
  - in situ soil washing cannot effectively recover all adsorbed contaminants at most sites. Consequently, soil washing may require a complementary technology such as in situ bioreclamation to achieve cleanup goals.
  - washing solution properties may alter the soil environment, limiting the applicability of subsequent treatment processes.

3.3.3 Pump and Treat

Pump and treat remediation uses withdrawal wells to recover contaminated groundwater plus any mobile distinct-phase liquids from an aquifer. Groundwater withdrawal wells efficiently control aqueous-phase contaminants because they utilize pumps to create a suction potential. Removal wells therefore act as hydrologic sinks in an aquifer, and contaminated fluids will flow towards them along a gradient from the aquifer hydrologic potential to well hydrologic potential. Contaminants recovered in this manner are treated on-site.

Most pump and treat systems couple injection and withdrawal wells in a closed-loop arrangement. Injection wells installed upgradient of the contaminated zone inject treated water into the subsurface, creating a hydrologic mound, while downgradient recovery wells induce a drawdown in the phreatic surface. This combination of wells creates a steep hydraulic gradient within the aquifer, along which aqueous-phase contaminants are rapidly transported and collected (Quince and Gardner, 1982). Two additional benefits result from the use of such a system:

- hydrologic mounding can flush contaminants from the vadose zone towards the recovery system (Ohneck and Gardner, 1982; Unites et al., 1984); and
- treated water that is subsequently injected may contain agents that further enhance contaminant destruction or recovery (for example: acclimated microorganisms).

A closed-loop arrangement incorporating both types of wells is illustrated in Figure 3.3-3.

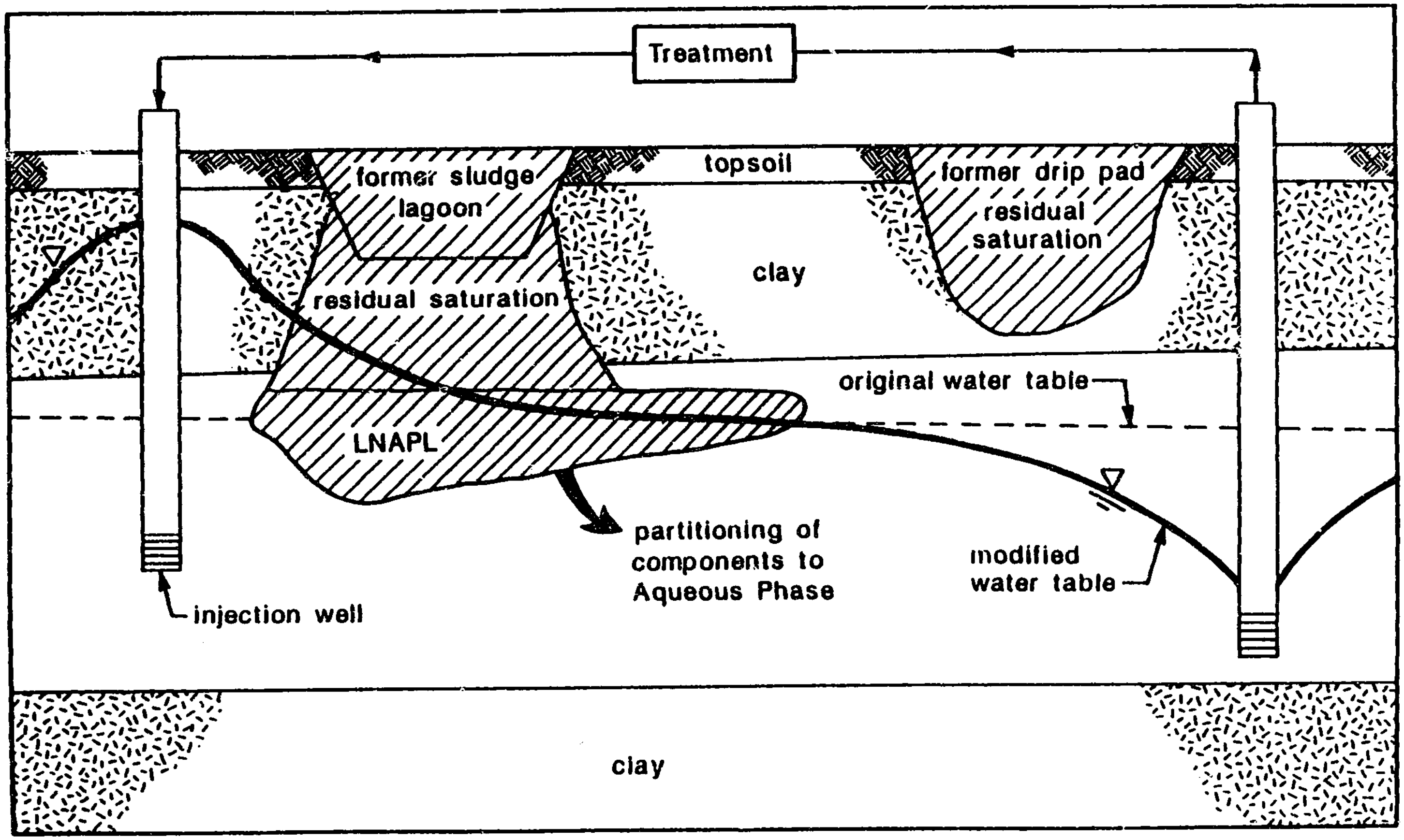


FIGURE 3.3-3 : TYPICAL PUMP AND TREAT SYSTEM

Pump and treat systems can effectively recover aqueous-phase contaminants in permeable formations. They also reverse existing flow gradients, preventing further plume migration. However, site remediation using pump and treat alone is generally a long-term treatment process, because of four limiting factors (Keely, 1988; Hall, 1989; Hall, 1987; Mackay and Cherry, 1989):

- slow diffusive releases of aqueous-phase contaminants from fine-grained sediments;
- hydrodynamic isolation because of induced groundwater flow patterns;
- strong sorption of contaminants; and
- low aqueous-phase partitioning of residual saturation components.

All of these factors may adversely affect the performance of pump and treat systems at wood preserving sites.

Aquifers located above the bedrock surface are generally comprised of sands and gravels. Almost all aquifers however, contain low-permeability lenses of fine-grained material, such as silt and clay (Mackay and Cherry, 1989). Although these fine-grained lenses may display a lower hydraulic conductivity than the surrounding materials, they generally contain larger amounts of dissolved and sorbed contaminants per volume, because of their higher porosity (Keely, 1989; Mackay and Cherry, 1989). During pump and treat remediation, dissolved contaminants in the more permeable aquifer material are rapidly transported to recovery wells with the bulk groundwater flow (advection). However, dissolved contaminants in the low-permeability lenses are not effectively recovered by the groundwater, which follows the most permeable path. These trapped contaminants gradually diffuse from the fine-grained materials to the less-contaminated water in the aquifer. The rate at which this diffusive release occurs is dependent on the difference in contaminant concentration between the low permeability sediments and adjacent aquifer materials (concentration gradient).

Molecular diffusion is generally much slower than advection, and consequently, bleeding of contaminants from fine lenses into the aquifer will continue long after contaminants in the larger pores have been recovered (Hall, 1987; Mackay and Cherry, 1989; Keely, 1988). Matrix diffusion from fine-grained lenses is partially responsible for the slow, nearly asymptotic decrease in contaminant concentrations observed in most pump and treat systems (Hall, 1987) (Figure 3.3-4a).

Hydrodynamic isolation occurs in the stagnation zone formed downgradient of an extraction wellfield and upgradient of an injection wellfield. The downgradient stagnation zone forms where the velocity of flow back to the extraction wellfield is offset by the velocity of flow away from the wellfield caused by the natural flow system (Keely, 1988). The upgradient stagnation zone forms where the upgradient velocity of injected water from the injection wellfield equals the natural downgradient velocity of the original system (Keely, 1988). Water in these stagnation zones is hydrodynamically isolated from the remaining aquifer, so contaminant transport into or out of the isolated water may occur only by molecular

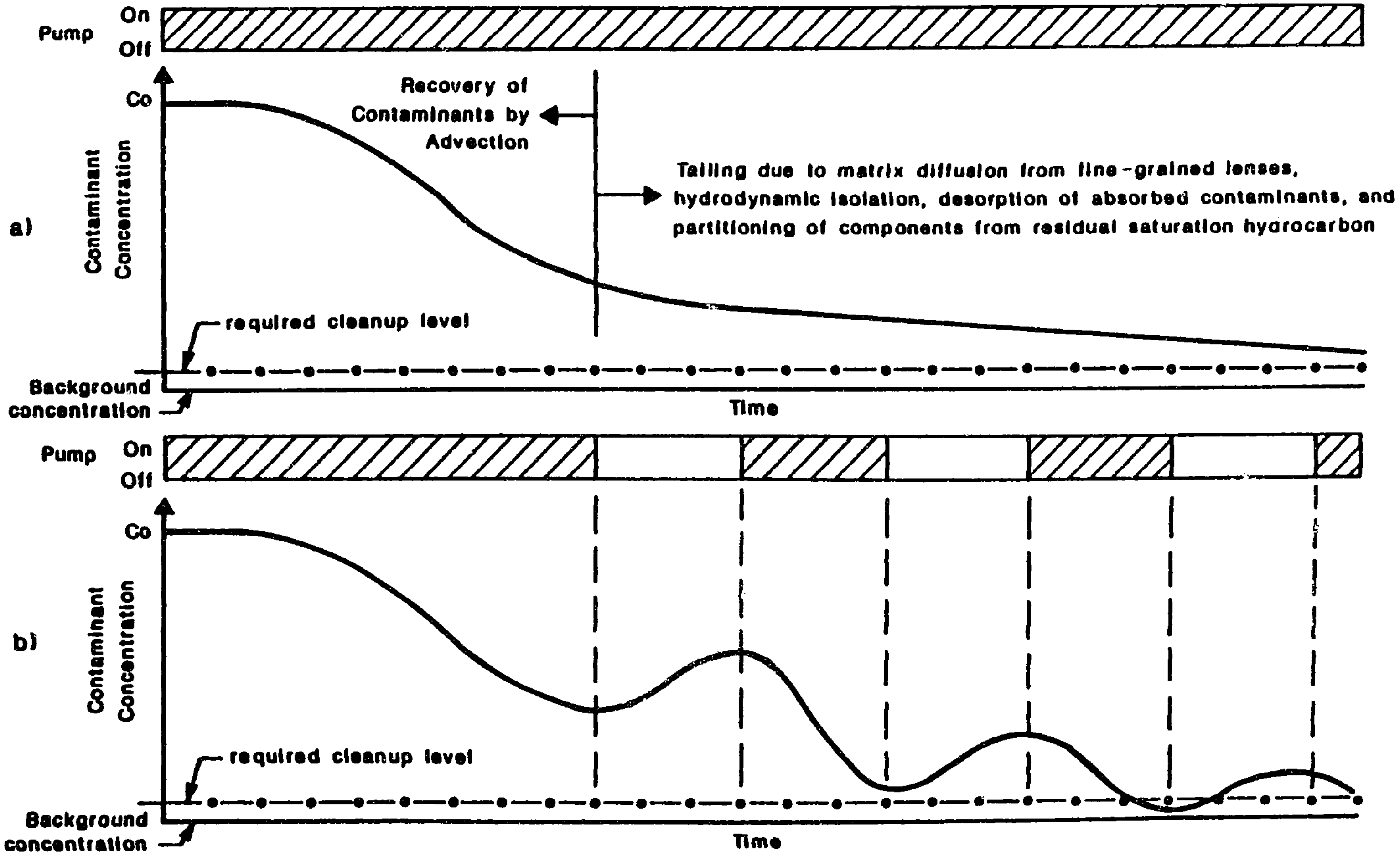


FIGURE 3.3-4 : A) TAILING OF CONTAMINANT CONCENTRATIONS WITH TIME
B) PULSED PUMPING USED TO REDUCE RESIDUAL (ADAPTED FROM KEELY [1988] AND KEELY [1989])

diffusion (Keely, 1989). Hydrodynamic isolation can be mitigated by adjusting flow rates, which alters the stagnation zone boundaries, allowing isolated plume constituents to be mobilized with the bulk groundwater flow. Consequently, hydrodynamic isolation is more easily remedied than matrix diffusion from low-permeability lenses.

Pumped removal of groundwater prevents the establishment of chemical equilibrium in an aquifer, because pore water is continually replaced with uncontaminated upgradient material. Chemical equilibrium is the lowest chemical potential attainable by a soil system, and adsorbed contaminants will solubilize in an attempt to re-establish this level. The rate and extent of this desorption is dependent on kinetic and equilibrium limitations. First, the maximum contaminant concentration achievable in the pore water is the compound's aqueous solubility. This is the equilibrium limitation. Secondly, desorption is a rate process, which depends on both the contaminant and its concentration in the pore water; desorption rate generally decreases as the equilibrium concentration is approached, because of a diminishing concentration gradient (Keely, 1988; Mackay and Cherry, 1989). The kinetic and equilibrium limitations of desorption act to increase both the time required for remediation and the total volume of water that must be used to flush the contaminated zone (Mackay and Cherry, 1989; Hall, 1987).

A final limitation of pump and treat technology exists for contaminants present as part of a distinct hydrocarbon phase. Portions of these non-aqueous liquids (NAPLs) may become trapped in the pores of subsurface soils by capillary forces arising from interfacial tension (section 1.5.1.1). Diffusive liquid-liquid partitioning controls dissolution of the residual hydrocarbon into groundwater (Mercer et al., 1990; Keely, 1988) (Figure 1.5-4). As with adsorbed constituents, kinetic and equilibrium constraints dictate partitioning to the groundwater phase. In addition, the mass of contaminant present in a given volume of residual saturation hydrocarbon may be many orders of magnitude greater than the mass present if the soil volume were contaminated only with dissolved and sorbed phases (Mackay and Cherry, 1989). Consequently, residual NAPL material will contaminate groundwater for longer periods than adsorbed or dissolved constituents.

The four limitations discussed imply that pump and treat remediation is ineffective for contaminants which preferentially adsorb to solids or exist as NAPLs, or to aquifers containing low permeability zones. However, process innovations such as pulsed pumping have been developed to overcome some of these limitations. Pulsed operation of a wellfield is the cycling of extraction and/or injection wells on and off in active and resting phases (Keely, 1988) (Figure 3.3-4b). The resting phase allows sufficient time for contaminants to diffuse from low to high permeability zones, as well as for sorbed contaminants and the constituents of residual hydrocarbon to reach equilibrium concentrations in local groundwater (Keely, 1989). Pumping during the active phase removes a smaller amount of more highly contaminated groundwater than is recovered by a continuous pumping system where large amounts of groundwater are required to produce small amounts of contaminants. Pulsed pumping possesses three distinct advantages over conventional systems:

- recovered groundwater is more highly concentrated, and thus easier to treat;
- power requirements are less for the phased operation; and
- cleanup levels can be achieved more quickly (U.S.EPA, 1989c; Keely, 1988).

However, pulsed operation of remediation wellfields also incurs additional costs and risks (Keely, 1988). Specifically, peripheral hydraulic gradient control is required to ensure adequate containment of the contaminant plume during resting cycles. A physical containment system such as a slurry wall may be required for this purpose.

3.3.3.1 Parameters Affecting Process Efficacy

Many of the parameters affecting pump and treat remediation are discussed for other technologies which incorporate injection and recovery wells, such as in situ bioreclamation and in situ soil washing. However, the importance of the most relevant parameters will be reviewed below. In general, the important parameters can be divided into three categories: chemical properties, site characteristics, and system operation.

Contaminants amenable to recovery by pumping wells have a large aqueous solubility, low soil adsorption potential, and rapid desorption rate. These properties minimize the potential for slow, diffusive contaminant releases from adsorbed or residual hydrocarbon fractions.

Desirable site properties for pump and treat remediation include permeable, homogeneous formations, and high groundwater temperatures. The subsurface transport rate of contaminants depends mainly on formation permeability; low permeability soils will not transmit aqueous-phase contaminants at practical rates, even under the gradients induced by pumping wells. The presence of low permeability lenses in heterogeneous aquifers adversely affects pumping remediation, because contaminants are only slowly released from such formations by diffusion (matrix diffusion). Low groundwater temperatures increase groundwater viscosity, which acts like a decrease in formation permeability. Equilibrium concentrations of dissolved contaminants also increase with increasing temperature. Consequently, high groundwater temperatures are desirable.

Finally, design and operation of a pump and treat system affects process efficacy. Well placement should ensure contaminant recovery in all portions of the aquifer, as well as prevent further plume migration. In addition, pumping rates can be altered or pulsed to ensure capture of contaminants in stagnation zones.

3.3.3.2 Pump and Treat Remediation at Wood Preserving Sites

3.3.3.2.1 Sites Which Used Oil-Based Preservatives

Creosote- and PCP-based wood preserving mixtures classify as bulk hydrocarbon (oil-based) fluids (section 1.5.1). Contaminants in these mixtures may exist in several forms in groundwater (sections 1.5.1.2.4 and 1.5.1.3.4):

- continuous distinct phase (NAPL);
- discontinuous distinct phase (blobs);
- emulsion;
- dissolved molecules;
- adsorbed molecules; and
- residual saturation.

It is likely that blobs of waste preserving fluid, emulsions, and dissolved molecules can all be adequately recovered with the bulk groundwater phase. Adsorbed molecules and residual saturation constituents cannot be recovered outright with the bulk groundwater flow, but will gradually be recovered as they diffuse into the aqueous phase.

NAPLs are not generally recovered with groundwater, but by a separate pump, for two reasons:

- the flow of viscous distinct-phase liquid to a single recovery pump may be truncated by flow of less viscous groundwater.
- single-pump systems may create an oil-and-water emulsion where two separate phases existed before. Emulsions of this form require considerable effort to break. There is also an economic incentive to recovering the distinct phase separately, as it may be of sufficient quality to be re-used (U.S.EPA, 1984e; Flechas, 1989).

Consequently, unique and separate groundwater systems are used for recovery of distinct-phase material. Differences also exist in the systems utilized for PCP and creosote distinct phases.

PCP-based preserving mixtures can exist as an LNAPL on the phreatic surface of an unconfined aquifer (section 1.5.1.1). LNAPLs migrate with the hydraulic gradient, though at a lesser rate than the underlying groundwater because of greater viscosity (Kuhn and Piontek, 1988). Consequently, a recovery well that draws down the phreatic surface will also collect LNAPL. Most LNAPL recovery wells contain two pumps. The lower pump recovers groundwater, creating a cone of depression and enhancing the existing flow gradient. The more viscous LNAPL material flows along this gradient into the well, where it is collected by a skimming pump (U.S.EPA, 1984a; U.S.EPA, 1989c). Unites and coworkers (1984) report that the water table depression pump should be located as close to the product recovery pump as possible to maximize flow at the phreatic surface and minimize the volume of water recovered. Sensors that differentiate a hydrocarbon phase and water are used with each pump to regulate pump elevation and cycling. Recovery of LNAPLs is well developed because of numerous oil and gasoline spills, and there have been successes in pumping a significant portion of the distinct phase to the surface (Mackay and Cherry, 1989; Hall, 1987).

In contrast, creosote may exist as a distinct phase on the bottom of an aquifer, as it is more dense than groundwater (section 1.5.1.1). Very little success has been achieved in even locating DNAPLs, let alone recovering them (Mackay and Cherry, 1989). For example, a large bedrock well was abandoned when it failed to recover significant amounts of creosote DNAPL from a highly permeable formation ($K = 10^{-1}$ to 10^{-3} cm/s) (Flechas, 1989;

Kuhn and Piontek, 1988). Dracos (1987) also postulated that extraction of DNAPLs from an aquifer by pumping wells would be less successful than recovery of an equivalent mass of LNAPL. However, a unique recovery approach for DNAPL creosote has been pilot-tested at a wood preserving site in Wyoming (documented by: Sale and Piontek, 1988; Flechas, 1989; Piontek, 1989; Kuhn and Piontek, 1988). The pilot system recovered 830 000 litres (220 000 U.S. gallons) of waste creosote oils from an area of 0.8 hectares (2 acres). The water content of the recovered oil was less than 0.1%, and the oil was of sufficient quality to be sent directly to another preserving facility for reuse. The innovative system contains a horizontal injection line and two horizontal recovery lines. The two recovery lines are located vertically one above the other, and the injection line is at the same elevation as the groundwater collection drain (Figure 3.3-5a). Horizontal injection and recovery lines were selected over vertical wells for three main reasons (Piontek, 1989):

- higher flow rates are achievable with the horizontal lines;
- more linear flow paths are attainable; and
- lower installation and operating costs are associated with the horizontal network.

By pumping water into the injection line and recovering it at the water recovery line, groundwater moves across the top of the oil body. This water induces a shear on the oil surface and imparts a flow gradient in the oil, causing it to mound at the oil recovery line, from which it can be collected (Figure 3.3-5b,c). Pumping rates at the respective drainlines must be optimized for adequate recovery; excessive pumping of the upper line will recover both oil and water, creating an emulsion, while excessive pumping

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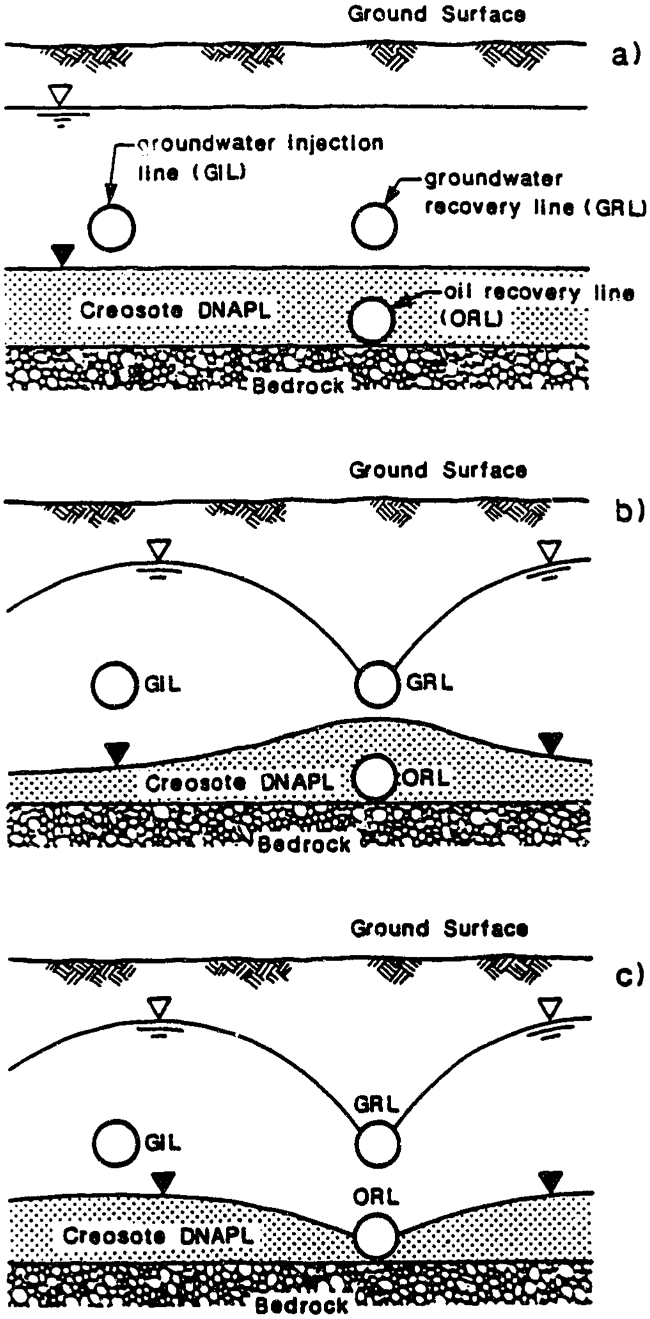

a) No pumping or injection.

b) Operation of GIL and GRL but not ORL. Movement of water across the oil surface from GIL to GRL imparts a gradient in the oil, and results in creosote mounding beneath the GRL.

c) Pumping from both the GRL and ORL collects oil in the ORL. Relative pumping rate for the GRL and ORL must be determined to prevent mixing of the phases or truncation of the oil flow.

FIGURE 3.3-5 : RECOVERY OF CREOSOTE DNAPL WITH HORIZONTAL INJECTION AND RECOVERY LINES (ADAPTED FROM FLECHAS, 1989)

of the oil recovery line will lead to a truncation in the oil flow by the less viscous groundwater. The pumping rate ratio of the two recovery lines was about 75 during the initial pilot test (2 900 000 litres of water pumped from the upper line to recover 39 000 litres of oil from the lower one). During optimization of the pumping rates, it was noted that at high pumping rate ratios, the oil-water interface between the drainlines became unstable, causing oil and water layers to mix.

Once recovered with groundwater, wood preserving contaminants in all forms will require treatment, which is the second half of pump and treat remediation. The treatment approach selected will be dependent on the contaminant form; recovered groundwater may initially require settling and separation to remove distinct-phase material such as NAPL and blobs from the water; physical and chemical treatment may be required to separate emulsion components; only flow equalization may be required prior to treatment of contaminants dissolved in groundwater. Regardless of the specific treatment approach adopted, several characteristics of contaminated groundwater treatment require strategies different from those employed in conventional wastewater treatment (Berger et al., 1987; Frick et al., 1987):

- nonconventional (industrial) contaminants may be involved;
- contaminant concentrations are low;
- contaminated groundwater flows fluctuate;
- contaminant concentrations are highly variable; and
- site conditions may impose operating limitations.

For most sites, these factors necessitate the use of treatability and pilot-scale studies, modular equipment, and consideration of low-maintenance processes (Berger et al., 1987). Several approaches that have been considered for treatment of groundwater contaminated with creosote- or PCP-based wastes are summarized in Table 3.3-2.

3.3.3.2.2 Sites Which Used Water-Based Preservatives

CCA-based wood preserving mixtures use water as the carrier, and contaminants in these fluids may exist in two forms in groundwater (section 1.5.2.2.4):

- dissolved ions; and
- ions adsorbed to aquifer materials.

Dissolved CCA ions will be recovered by single-pump extraction wells, because the constituents will be transported with the bulk groundwater flow. Consequently, no specialized recovery well equipment will be required. Adsorbed ions cannot be recovered outright with the bulk groundwater flow, but will gradually be recovered as they diffuse into the aqueous phase in an attempt to obtain chemical equilibrium.

All CCA components recovered with groundwater will be dissolved, simplifying treatment. Flow equalization will likely initially be required, followed by primary treatment and final polishing. Several different processes could comprise the treatment and polishing steps (Winandy, 1983; U.S.EPA, 1984a; Montgomery, 1985):

- adsorption on activated carbon;

Table 3.3-2: Treatment of Contaminated Groundwater at Creosote and PCP Sites

Contaminant Form Considered	Treatment Approach Evaluated/Considered	Results	Source
Dissolved PAHs	Adsorption on activated carbon	PAHs readily adsorbed	Berger et al. (1987)
Dissolved chlorophenols	Adsorption on activated carbon	Trichlorophenol, PCP readily adsorbed	Berger et al. (1987)
PCP-contaminated process water, and PCP-contaminated groundwater from beneath a wood preserving site	Immobilized (stationary) biofilm reactor	PCP was reduced to below 1 ppm in all wastes tested. Other chlorophenols and PAHs were also removed.	Frick et al. (1987)
Groundwater contaminated with creosote and PCP from wood preservation	Biological oxidation, Activated carbon treatment, Chemical oxidation (ozone)	PCP concentrations were not significantly reduced in the four-month biological oxidation test. Consequently, biological oxidation was not considered to be practical. Activated carbon displayed excellent removal of all major components, though large amounts of carbon would be consumed (0.3 cubic metres per day consumed in treating 100 000 litres of groundwater). Removal of contaminants with ozone was successful.	Thompson (1984)
PCP-contaminated groundwater	Proprietary fixed-film (stationary media) Aerobic biological reactor (MikIE)	Successfully used to treat PCP-contaminated groundwater at a wood preserving site in Mississippi.	MoTec (1984) Dr. Gary McGinnis (personal communication)
Dissolved chlorophenols in groundwater	Air stripping in a patented process	Several demonstrations showed that dissolved chlorophenols could be reduced to ppb levels with this process.	Robbins (1980)

Continued

Table 3.3-2: Continued

Contaminant Form Considered	Treatment Approach Evaluated/Considered	Results	Source
Pure-phase PCP	Patented reactor utilizing white-rot fungus (*P. chrysosporium*)	The reactor degraded 250 ppm PCP in water to 5 ppm in 8 hours (5 ppm is PCP's aqueous solubility at 0°C)	Glaser (1988)
Pure-phase PCP in groundwater from a wood preserving site	Packed bed bioreactor	The bioreactor effectively removed over 99% of the PCP from groundwater initially containing 60 to 80 ppm. The bioreactor also removed a number of non-target compounds.	Frick and Crawford (1986)
Dissolved chlorophenols	Activated carbon adsorption	2,4-dichlorophenol and PCP were recovered from groundwater by carbon adsorption.	U.S.EPA (1984e)

- precipitation induced by the addition of alum ($Al_2(SO_4)_3$), lime, ferric chloride, ferric hydroxide, sulfide, hydrogen peroxide (H_2O_2);
- ion exchange (cationic for copper and anionic for complexes of chromium and arsenic);
- reduction and precipitation (for Cr^{6+});
- electrolytic recovery; and
- reverse osmosis.

The different behaviour of each CCA component suggests that staged treatment will be required for complete treatment. Contaminant destruction is not possible for CCA, so a concentrated chemical residue requiring disposal will result from treatment.

3.3.3.3 Monitoring

Monitoring of pump and treat remediation requires wells or piezometers within, and downgradient of, the contaminant plume (Keely, 1988; Keely, 1989). Monitoring wells located inside the plume provide information on the relative rate of remediation of various plume locations. This information can be used to adjust pumping flowrates, ensuring uniform treatment throughout the aquifer (Keely, 1989).

Observation wells downgradient of the plume are primarily used to detect breaches in hydraulic containment, ensuring the safety of downgradient public supply wells. Observation wells are also used to ensure that minimum groundwater flows are maintained during treatment for downgradient users. In addition, data from these wells defines background contaminant concentrations in the aquifer, which may be used in the formulation of cleanup levels.

Data from both types of wells or piezometers is used to ensure maintenance of an inward hydraulic gradient at the plume boundary, and to evaluate horizontal and vertical gradients from which hydraulic contour maps can be constructed.

3.3.3.4 Advantages and Disadvantages

The advantages and disadvantages of pump and treat remediation are summarized below.

- Advantages:
    - the technology is well-understood because of extensive experience with wells used for potable water supplies (U.S.EPA, 1984a).
    - pumping contaminated groundwater can recover contaminants and prevent further plume migration (hydraulic containment).
    - previously installed monitoring wells can sometimes be employed as part of the well system (U.S.EPA, 1984a).
    - the process has high design flexibility and requires less above-ground area than other technologies such as land treatment. This minimal space requirement is advantageous at sites that have been redeveloped.
    - the treatment process can be automated, minimizing operational costs (Unites et al., 1984).

  - hydraulic containment is achieved with well systems at a much lower cost than is attainable with physical containment technologies such as slurry walls (U.S.EPA, 1984a; Unites et al., 1984).
- Disadvantages:
  - contaminants in recovered groundwater may be dilute and therefore expensive to treat if they are only negligibly soluble or sufficient time is not allowed for soil-pore water equilibrium to be established.
  - NAPL recovery wells may convert mobile oil into immobile residual saturation by drawing the NAPL into areas previously unwetted by oil (Sale and Piontek, 1988; Keely, 1989). For example, a PCP LNAPL floating on the phreatic surface may be drawn down to the well screen along the cone of depression, wetting areas previously unwetted by oil, converting much of the LNAPL into residual saturation.
  - single-pump wells may produce difficult-to-separate chemical mixtures when several contaminant forms exist in an aquifer.
  - this technology does not remediate contaminants in the vadose zone.
  - treated water may have to be re-injected downgradient of the plume to provide sufficient flows for subsequent users.
  - process efficacy is adversely affected by low-permeability aquifers and low groundwater temperatures.
  - hydrophobic contaminants, low permeability lenses and pollutants which exist as part of a hydrocarbon phase are

responsible for the slow, nearly asymptotic decrease in contaminant concentration with time (tailing) observed in most pump and treat remediations. These contaminant and site characteristics act to withhold the pollutant from the bulk groundwater flow. In such instances, contaminant migration only occurs by molecular diffusion, and pump and treat reclamation can be viewed as remediation in perpetuity (Mackay and Cherry, 1989).

- the operational and maintenance costs of long-term pump and treat remediation can be large (U.S.EPA, 1984a; Mackay and Cherry, 1989). In addition, a risk exists that sometime during remediation, hydraulic containment will be breached by well failure or extreme water table fluctuation. This risk increases in magnitude the longer remediation continues.

3.3.3.5 Conclusions

Pump and treat remediation can successively recover aqueous-phase contaminants at wood preserving sites, while preventing further plume migration. However sorbed contaminants, contaminants trapped in low permeability lenses, and residual hydrocarbon are not effectively recovered or treated with this technology. These contamination sources can best be remediated using enhanced pump and treat technologies such as soil washing or in situ bioreclamation.

3.4 Summary of Remediation Alternatives

As seen in the previous sections, not all remediation alternatives are equally applicable to each contamination form present at wood preserving sites. A summary of the relevance of each alternative for the different contamination forms is presented in Table 3.4-1. The classification scheme used in this table is somewhat arbitrary, as the actual applicability of a technology will depend on relevant site conditions, discussed in the respective sections.

In practical terms, this analysis implies no one technology can effectively remediate all contamination forms present at wood preserving sites; a treatment scheme, incorporating several technologies, will be required for complete remediation.

Table 3.4-1: Relative Applicability of Remediation Alternatives to Contamination Forms at Wood Preserving Sites

Classification	Alternative	Unsaturated Zone							Saturated Zone						
		Oil-Based Preservatives				Water-Based Preservatives			Oil-Based Preservatives					Water-Based Preservatives	
		Residual Saturation	Pore Air	Pore Water	Soil	Pore Air	Pore Water	Soil	LNAPL	DNAPL	Residual Saturation	Ground -water	Soil	Ground -water	Soil
Containment	Landfill Disposal	2	3	2	2	3	2	2	3	3	2	3	2	3	2
	Solidification /Stabilization	2	3	2	2	3	2	1	3	3	2	3	2	3	1
Destruction	Incineration	1	3	2	2	3	3	3	2	2	1	3	2	3	3
	Land Treatment	1	3	1	1	3	3	3	2	2	1	3	1	3	3
	In Situ Bioreclamation	1	3	1	1	3	3	3	2	2	1	1	1	3	3
Concentration	Vapour Extraction	2	2	2	2	2	3	3	3	3	3	3	3	3	3
	Soil Washing	1	3	2	2	3	2	2	2	2	1	2	2	2	2
	Pump and Treat	3	3	3	3	3	3	3	1	2	2	1	2	1	2

Notes:

- information presented in this table is derived from the report sections discussing these alternatives.
- pore air refers to gaseous contaminants in soil pores.
- pore water refers to dissolved contaminants in unsaturated zone soil water.
- soil refers to individual constituents adsorbed to soil.
- groundwater refers to dissolved contaminants for oil- and water-based preservatives, and also includes emulsified microdroplets and blobs for oil-based mixtures.
- ranking scale:
  1 = technology readily remediates contamination form;
  2 = technology remediates contamination form, but remediation is likely limited in rate and/or extent; and
  3 = technology cannot be applied, or does not significantly remediate contamination, due to technical or regulatory constraints.

4. Recommendations for HELP Site Remediation

A thorough assessment of contamination at the five HELP sites using the recommended methodology (section 2.5) is beyond the scope of this study. However, the remediation alternatives presented in section 3 can be evaluated for their applicability to conditions at the HELP sites, assuming a proper site assessment will reveal the need for remediation.

Each subsection in section 4 begins with a brief introduction of the particular HELP site, followed by a discussion of site concerns arising from field observations and the site characterization study. Background information such as site characterization data and a technical evaluation of this data are presented in Appendix E. The final result of each site discussion is a recommendation of one or more technologies with the greatest potential of remediating the contamination hazard existing at the site. A summary of these recommendations is presented along with those of the preliminary study consultants in Table 4-1. My recommendations differ considerably from those of some of the consultants. The differences may be the result of the broader perspective and more extensive terms of reference for my study. As well, the consultants would need to be concerned with minimizing their residual liability in the face of limited site characterization and access to remedial cleanup experience elsewhere. My recommendations attempt to achieve maximum overall risk reduction, and are based on engineering judgement.

Table 4-1: Recommendations for HELP site Remediation

Site Location	Preservative Used	Consultant for Preliminary Study	Consultant's Recommendations	Study Recommendations
Blackfalds	PCP	Stanley Associates (1989)	• Incineration of soil contaminated above 1000 ppm PCP. • Landfill disposal of less contaminated soil.	• Enhanced land treatment of contaminated soil. • Pump and treat remediation of groundwater.
Calgary	Creosote, PCP	O'Connor (1989b)	No options discussed.	• Impermeable barrier containment. • In situ vapour extraction. • Pump and treat, enhanced with bioreclamation or soil washing.
Cayley	PCP	Monenco (1989)	• Incineration, landfill disposal, and bioreclamation strategies were assessed to be the most applicable alternatives.	• Incineration of sludge pond material. • Enhanced land treatment of contaminated soil. • Pump and treat remediation of groundwater.
Elmworth	CCA	Thurber (1989)	• Landfill disposal of soil containing greater than 500 ppm arsenic and chromium at the Swan Hills Facility. • Secure landfill disposal of less contaminated soil.	• Solidification/stabilization of both contaminated soil and residual sludge, followed by landfill disposal.
Faust	PCP, CCA	Hardy BBT (1989)	• Incineration at Swan Hills for soil jointly contaminated with PCP and arsenic.	• Solidification/stabilization of arsenic contaminated soil. • Enhanced land treatment of PCP contaminated soil. • pump and treat groundwater.

4.1 Former Alberta Western Post - Blackfalds

4.1.1 Introduction

Alberta Western Post and Timber Treating Ltd. operated a wood preserving plant near Blackfalds, Alberta from 1961 to 1970. PCP was the primary preservative used, though creosote and CCA were initially suspected as additional treating agents. The total area of the site is 5 hectares. Site characterization data and an evaluation of this data are presented in Appendix E.1.

4.1.2 Site Concerns

The following list of concerns should be addressed at the Blackfalds site, based on the characterization study and site observations.

- The site is almost completely covered with thick, healthy prairie grasses roughly 1 m tall. Only 3 small, bare areas were observed at the site:
    - the former sludge lagoon;
    - a small part of the trench leading to the lagoon; and
    - a small section in the timber storage area.

- Assuming impact upon surface vegetation would reflect contamination of surface soils, the extent of contamination is likely limited. The results of the Stanley Associates Ltd. (1989) investigation also suggest limited site contamination, except for two anomalies:

- The soil sample with 5826 ppm PCP at 0.3 m depth at location 20T (treater building). This value is so high compared to other values that it either involves an inaccurate result or is an anomaly. The latter means an accurate value obtained from a sample, but the sample is not representative of site conditions. The next highest PCP soil concentration was 134 ppm in the sludge pond. If the 5826 ppm value is correct, it indicates a very small band of soil highly contaminated with PCP, as the 1.0 m and 2.0 m samples at location 20T contained 9.9 ppm PCP and 5.1 ppm PCP respectively. PCP was not detected at the 6.0 m level at this location. In addition, both shallow and deep piezometers (89-3S and 89-3D) near sampling hole 20T showed non-detectable PCP concentrations.
- The groundwater sample with 120.0 mg/L PCP at location 89-7D (sludge pond). This value, as described in section E.1.2, indicates significant distinct-phase material in the aquifer. The existence of free product will guarantee significant groundwater contamination. Two nearby piezometers in the sludge pond (89-4S and 89-4D), however, are screened to roughly the same level and contain PCP concentrations of 5.4 mg/L and 0.15 mg/L respectively. The 5.4 mg/L value could only be achieved by having free product nearby, and this sample must be regarded as confirming the existence of a distinct PCP-hydrocarbon phase in the aquifer.

- Before the feasibility of any remediation options can be considered, a consultant must address the following concerns:
  - verify that CCA and creosote were not used at this site by additional soil and groundwater sampling;
  - analyze soil and groundwater samples for dioxin and furan concentrations;
  - evaluate the two anomalies (contradict them or confirm them and delineate their extent); and
  - delineate the contamination to the point of generating a first estimate of contaminated soil volume requiring remediation. Stanley Associates arrived at a soil volume of 1600 m^3 for the sludge pit, but this value is not sufficiently accurate to use in comparing remediation options.

- The following general decommissioning procedures should be completed:
  - remove all remaining rubble, concrete pads, and scrap metal from the site. This waste should be tested for preservative contamination so that disposal may be directed to the proper landfill.
  - re-grade the site to contain site run-off and prevent run-on. The collected water should be diverted to a storage compartment (eg. lined lagoon) and analyzed for contamination. If the surface run-off water is contaminated, it should be treated with GAC to a level such that collected material could be discharged to the Blindman River from time

to time. Given the thick vegetation existing at this site, it is doubtful that surface run-off would be contaminated from sediment erosion. However, re-grading the site to prevent run-on from the neighbouring CN Rail Yard is probably a bigger advantage than preventing surface run-off from leaving the Blackfalds site. A visual inspection of the CN Rail Yard to the north of the site revealed the following possible sources of contamination:

- sulfur stained ground;
- oil puddles; and
- stockpiles of oily material.

It is apparent that the CN Rail Yard is used for cleaning railway cars, and that the residual material is stored there. The yard is also upslope of the Blackfalds site, and any surface or ground water contamination arising from practices at the CN Rail Yard would typically follow the topological gradient onto the Blackfalds site.

- In addition to the two aforementioned anomalies, there is some question as to the extent of groundwater contamination by PCP. Only 4 of the 10 groundwater samples showed detectable PCP concentrations, and three of these were obtained from piezometers in the sludge lagoon. The fourth value arose from the chemical storage area, and is quite small. These samples imply that groundwater contamination is limited to a distinct PCP-hydrocarbon phase beneath the sludge pond and groundwater directly in contact with it. The minimal contaminant movement implicated in these results agrees with the Stanley Associates Engineering Ltd. estimate of less than 3 m/year for groundwater movement. However, vertical cracking to depths of 6 metres was noted in the silt and clay deposits. The existence of any fractures in the water-bearing strata could mean groundwater movement at rates in excess of those predicted by localized soil permeability tests (slug tests). Any groundwater contamination at this site may thus have moved much further than expected. The placement of monitoring wells by Stanley Associates Ltd. seems generally sound, however, the existence of four domestic water wells within a 500 m radius of the site necessitates the delineation of any contaminant groundwater plume. The Blindman River also passes within 500 m of the site and may be a discharge point for nearby aquifers, further emphasizing the need for contaminant plume delineation.

- The one groundwater well on-site is covered by a "doghouse" structure. The people who reside in the house directly east of the site use the well water for domestic purposes, but they currently have their drinking water hauled in. The mechanic working in the shop on-site apparently uses the water occasionally for drinking. The well water should not be used for human consumption until it has been analyzed for contamination. This should be performed as soon as possible. Regardless if the well water is contaminated or not, the well may have been poorly constructed, and may be providing a pathway for downward migration of surficial contaminants. This well should thus be removed from the site during general site cleanup.

- Wood preservation processes ended at this site during 1970. It is thus possible that CCA was used at this site, because CCA has been used in Alberta since the early 1960s (for example, at the Alberta Osmose Plant in Faust).

- Alberta Transportation owns the portion of the property west of the AA' line in Figure E.1-1, and Mr. Grewal owns the portion to the east. It is believed that Alberta Transportation is selling their interest to CN Rail for construction of a spur or to expand CN Rail's car-servicing yard, and that Mr. Grewal wants to develop his portion for residential purposes. It should be noted that any on-site treatment of contaminated soils will prevent site development by either party for a period of at least 3 years, assuming stringent cleanup criteria compatible with subsequent residential land use will be used. If sufficient pressure is exerted by either owner to develop the land sooner than allowed with on-site methodologies, off-site alternatives may have to be considered.

4.1.3 Remediation Alternatives

Based on site observations and data presented in the Stanley Associates Ltd. report, the remediation alternatives outlined in section 3 can be evaluated for use at the Blackfalds site.

- **In situ technologies (bioreclamation, vapour extraction, soil washing, pump and treat) will be limited in effectiveness because of the low permeability (k = 10^{-5} cm/s) clay which underlays the site.**

- **Solidification/stabilization does not successfully remediate hydrocarbon-contaminated soils.**

- **Incineration, landfill disposal, and enhanced land treatment are applicable to this site, though the one "best" alternative cannot be determined without more precise information on costs and the volume of material to be treated. However, land treatment is likely to be less expensive than incineration, and because it is a treatment alternative, land treatment is more sound on the basis of long-term hazard mitigation than containment strategies such as landfill disposal.**

- **Consequently, the following recommendation for site remediation can be formulated:**
  - **enhanced land treatment of contaminated soils.**
  - **pump and treat hydrocarbon phase and contaminated groundwater, recovering contaminants and preventing plume migration.**

4.2 Former Canada Creosoting Ltd. - Calgary

4.2.1 Introduction

Canada Creosoting Limited operated a wood preserving facility on the banks of the Bow River in Calgary from 1932 to 1966. Creosote and PCP were the main preservatives used. A preliminary site investigation was performed by O'Connor Associates early in 1989 (O'Connor, 1989b). In general, the investigation revealed extensive contamination in soil and groundwater on the site. Information from the O'Connor report is supplemented by that of Golder Associates (1990), who conducted a preliminary risk assessment after creosote was found seeping into the Bow River in November, 1989 (O'Connor, 1989b). Site characterization data and an evaluation of this data are presented in Appendix E.2.

4.2.2 Site Concerns

The former Canada Creosoting Limited site is heavily contaminated with wood preserving chemicals and their degradation products. The following is a list of conclusions about this site and concerns which should be addressed in any subsequent study, based on the O'Connor and Golder studies as well as site observations.

- Based on soil analyses, it does not appear that CCA or any other inorganic wood preservative, such as zinc-based formulations, were used at this site.

- The DNAPL was only noted in BH3 and BH4. From Figure E.2-2, it is apparent that BH3 and BH4 are not located in areas expected to be highly contaminated, such as near the sludge lagoons, treater building or storage tanks. Following discussion with Mr. Alan Hingston of the HELP project, I suspect the DNAPL is likely originating from the sludge ponds and migrating along an old river channel, filled in during the 1920s to increase the area of the site. This conclusion was based on examination of a sequence of air photos (Alan Hingston, HELP Project Manager, personal communication).

- Indigenous microbes at the site are most likely relatively inactive because of nutrient-limiting conditions; excess substrate in the form of organic contamination exists at the site, but given the length of time the soil has been contaminated, microbial activity is likely limited by other factors such as oxygen transport and nutrient availability.

- Outside of the bicycle path, the small field behind G.S.L. Chev City, and a few grassed medians, this site is paved commercial property in downtown Calgary. Two car dealerships as well as a paved snow dump are situated on the site. The site is bounded on the West and East by the Pumphouse Theatre and Greyhound Terminal, respectively. The pavement may be acting as an asphalt cap, retaining any vapours generated in the vadose zone. The first concern of any subsequent study on this site is to confirm that the explosive hydrocarbon vapours do not present an unacceptably high risk, of either explosion or toxicological exposure, to the people working on or near this site. Upon receiving the O'Connor Associates report, Alberta Environment promptly measured vapours in the commercial buildings on-site and found the above-ground vapour concentrations to be low and acceptable (Alan Hingston, HELP Project Manager, personal communication). Future studies must continue to confirm this finding, as vapour emissions are sensitive to changes in temperature and groundwater chemistry. Given that the vapour concentrations in the buildings were measured while the ground was frozen, it is likely that the Alberta Environment study considered conditions conducive to high vapour concentrations, as freezing soil displaces soil vapours because of the increased volume occupied by pore water. If vapour concentrations exceed allowable levels at some future period, a vapour extraction system could be employed to recover vapours originating in the near subsurface.

- The principal exposure pathways by which site contamination can affect humans and/or the environment are summarized below:
  a) Discharge of LNAPL, DNAPL, and contaminated groundwater to the Bow River.
    - Although the site is downstream of Calgary's municipal water intake, it is upstream of other cities such as Medicine

Hat. Many components of wood preserving wastes such as the carcinogenic benzo[a]pyrene from creosote and various dioxins from PCP are dangerous to humans in extremely small concentrations (section 1.4.2.3). Thus any contaminated groundwater, LNAPL or DNAPL discharging to the Bow River may pose health risks to downstream communities.

- Creosote contains several compounds associated with tainting of fish flesh, such as naphthalene and benzothiophene.
- Bioconcentration of toxic constituents in fish may occur from contaminated water or through consumption of benthic organisms residing in contaminated sediment.

b) Combustible vapour reservoir in the soil. Such vapours may pose a danger during any excavations on-site or to people who work in the car dealerships.

c) There are no users of groundwater near the site, and surficial soils on the site are clean topsoils. Ingestion of contaminated groundwater or dermal contact with contaminated soils are thus insignificant exposure pathways.

(The Golder study concluded that consumption of contaminated water and fish were the two most significant exposure pathways at this site, and that naphthalene concentrations in some fish samples exceeded tainting thresholds.)

- A possible exposure pathway for the contamination at this site is the discharge of LNAPL, contaminated groundwater and DNAPL to the Bow River. No work was done in the O'Connor study to delineate if or how the aquifer beneath the site discharges to the Bow River. In November 1989, creosote blobs were observed in Bow River sediments near a stormwater outfall. Golder (1990) subsequently estimated that the creosote DNAPL encompasses an area of about 20 000 m^2, originating near the former treating building and extending a distance of over 300 m to beneath the Bow River.

- There are also additional concerns at this site which should be addressed in any subsequent study.
    - **Location of bedrock depressions**: the O'Connor Associates report noted that the bedrock beneath the site contains local undulations, most likely associated with closed depressions. It is quite possible that creosote pools are trapped in these closed depressions, hydrologically separated from the rest of the aquifer. Any creosote trapped in these depressions will not be recovered by a general pumping scheme, and will continue to partition PAHs to the aqueous phase. Pumping wells will have to be drilled directly into the depression to recover this residual product. In addition, O'Connor Associates observed DNAPL in bedrock fractures. It is thus possible that bedrock wells will have to be installed to recover this product.

- **Cleanup of contaminated river sediments**: if LNAPL, contaminated groundwater and DNAPL from this site have been discharging to the Bow River, it is likely that a large amount of river sediment has been contaminated with wood preserving chemicals. As indicated previously, sediment samples from the river should be analyzed, and if they are contaminated, they must be remediated to avoid a long-term source of contamination. Guidance in remediation of the contaminated sediments is provided by the U.S.EPA (1984d) and by Weston (1982). Both of these reports present cost effective methods of recovering and treating river sediments contaminated with creosote from wood preserving sites.

4.2.3 Remediation Alternatives

Based on site observations and data presented in the O'Connor and Golder reports, the remediation alternatives outlined in section 3 can be evaluated for use at the Calgary site. A more detailed remediation scenario is outlined for this site compared to the others because of the potential hazard magnitude and complex site conditions.

- The first objective of hazard mitigation is the prevention of further contaminant migration from source areas. Considering the principal exposure pathways from this site are associated with the discharge of distinct-phase hydrocarbon and contaminated groundwater to the Bow River, the most urgent containment requirement is the prevention of further discharges. An impermeable barrier, such as a slurry wall or plastic cut-off curtain, should be installed on the downgradient edge of the site to prevent continued contaminant migration into the river (Figure 4.2-1). The barrier should extend into the bedrock to prevent DNAPL migration, and the barrier material must be compatible with the wastes. For example, a polyethylene curtain could be dissolved by the hydrocarbon phase, whereas a grout curtain would be more chemically resistant. Pumping wells should be installed on the upgradient side of the barrier to prevent the formation of a hydrologic "mound" behind the curtain, as well as to recover LNAPL, contaminated groundwater and DNAPL. Pumping wells alone, without the hydrologic barrier, would not effectively recover contaminants at this site, as these wells would likely recover large volumes of uncontaminated river water, and may not be able to maintain hydraulic control in such a permeable formation. It may be possible to incorporate the four types of pumping wells shown in Figure 4.2-1 into one innovative design to minimize site disturbance. An alternate containment scenario incorporates both upgradient and downgradient barriers. Barriers installed upgradient of the site could prevent the influx of uncontaminated off-site groundwater. In this alternate scenario, the extraction wellfield near the downgradient barrier could be decreased in size, as site groundwater flows would be limited to barrier leakage and surface infiltration.

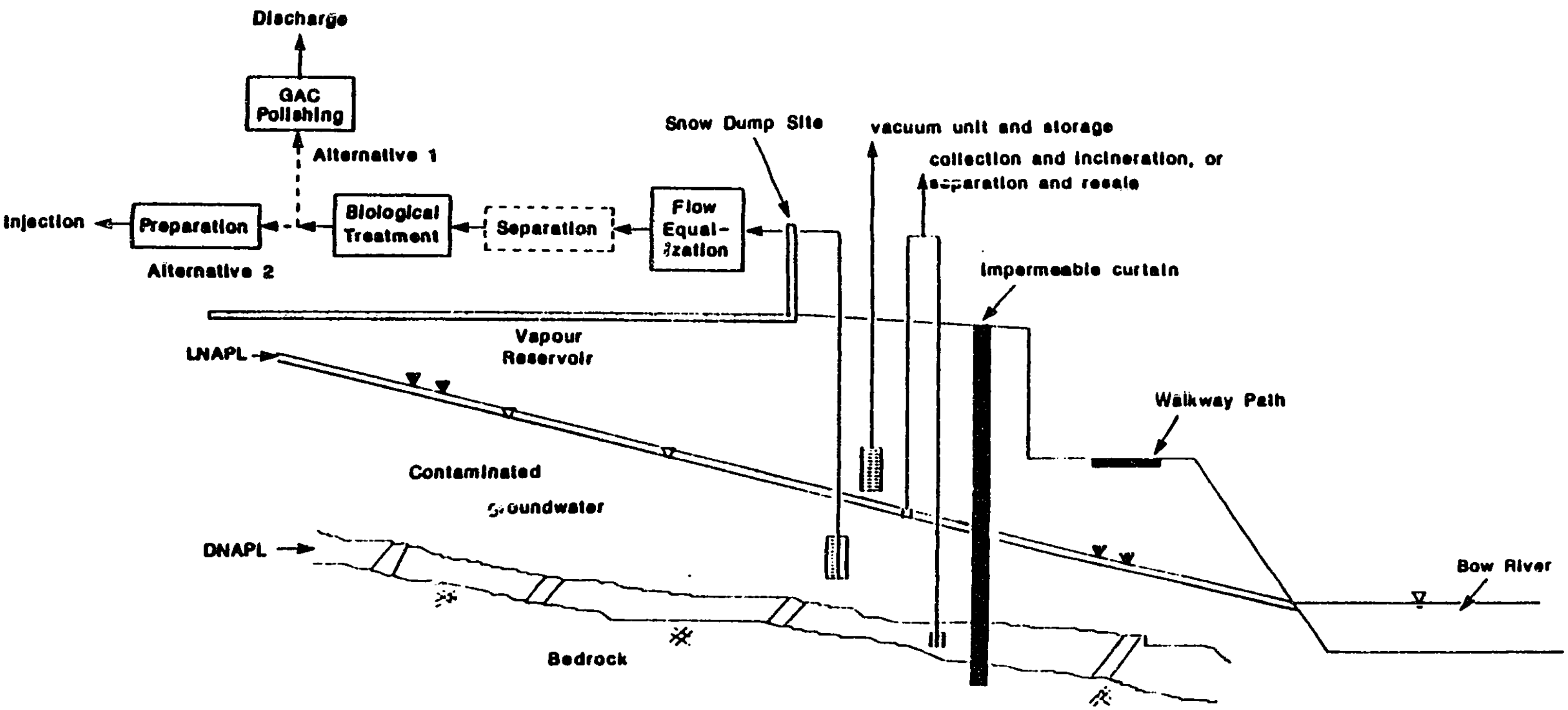

FIGURE 4.2-1 : PROPOSED RECLAMATION SCHEME, AND GROUNDWATER CONDITIONS PRIOR TO PUMPING AT THE FORMER CANADA CREOSOTING LIMITED SITE

- DNAPL ponded beneath the river is presently discharging to the river because the groundwater table and bedrock surface converge, resulting in a convergence of flow zones. Remediating the DNAPL beneath the river will be extremely difficult. The containment barrier(s) should be installed prior to addressing the DNAPL beneath the river, to prevent DNAPL recharge from the pool beneath the site.

- Following containment, source areas of contamination must be remediated. The most desirable site reclamation alternatives would be ones that would not interfere with the continued operation of on-site businesses. Consequently, strategies involving excavation of contaminated soil (incineration, landfill disposal, solidification/stabilization, land treatment) should not be pursued.

- The alluvial sands and gravels beneath the site are extremely permeable ($k = 4 \times 10^{-2}$ cm/s), and therefore amenable to in situ treatment:
  - vapour extraction wells should be used to recover gaseous contaminants from the vadose zone, reducing the toxicological and explosive threat of the vapour reservoir to on-site workers.
  - product recovered from the pumping wells should be treated on-site, possibly on the snow dump area, as it is paved and fenced. A possible treatment process is illustrated in Figure 4.2-1. The biological component of treatment could be

comprised of a number of processes, as discussed in section 3.3.3.2.1.

- contaminant removal by pumping could be enhanced by implementing in situ bioreclamation or soil washing. After treatment of recovered water, the required amendments could be added, and the solution injected. Groundwater beneath the site flows north and northeast from the snow dump towards the Bow River (Figure 4.2-2), and the formation is permeable enough for adequate movement and contact in the contaminated zone. Recovery wells located near the barrier could recover any elutriate or unused solution, completing the treatment cycle.

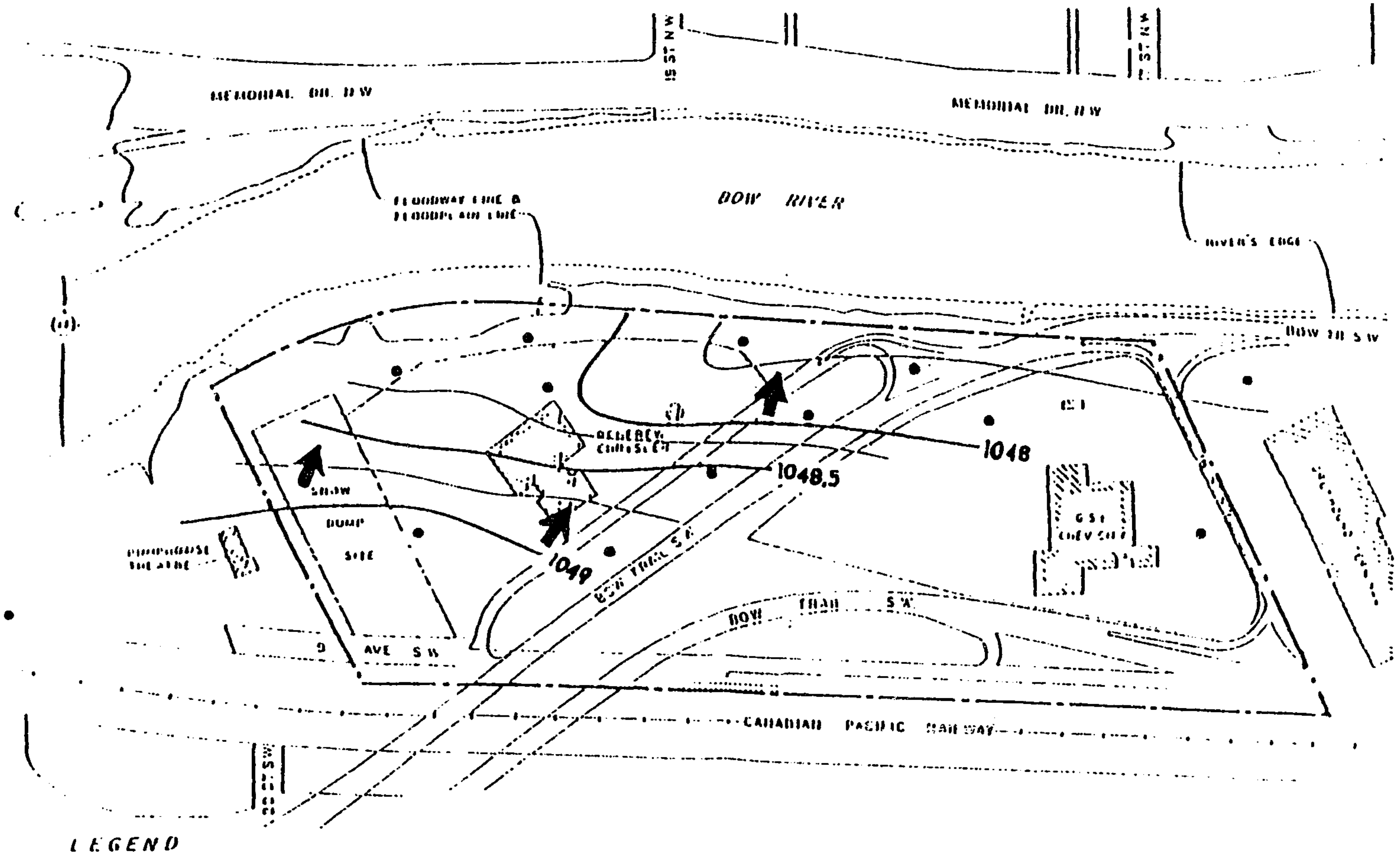

FIGURE 4.2-2 : ELEVATION OF THE PIEZOMETRIC SURFACE (m), AND PREDOMINANT GROUNDWATER FLOW DIRECTIONS (O'CONNOR ASSOCIATES, 1989B)

4.3 Former Peerless Wood Preservers - Cayley

4.3.1 Introduction

Peerless Wood Preservers Limited operated a wood preserving facility near Cayley, Alberta from 1958 to 1982. PCP was the only preservative used. Monenco Consultants Limited performed a preliminary investigation on the Cayley site early in 1989. In general, the investigation revealed significant contamination of surface soils in the process and sludge pond areas. PCP-contaminated groundwater also exists at this site, but the amount and its migration has been minimized by a tight clay till beneath the site. Site characterization data and an evaluation of this data are presented in Appendix E.3.

4.3.2 Site Concerns

The former Peerless Wood Preservers Limited site is moderately contaminated with wood preserving chemicals and associated wastes. Because the site is underlain by a glacial till of low permeability, contamination in soils from the process area has not migrated to any great extent to surrounding soils or groundwater. The following is a list of conclusions about this site and concerns which should be addressed in any subsequent study, based on site observations and the Monenco report.

- On page 3-29 of their report, Monenco Consultants Limited commented that the elevated PCP concentrations in groundwater samples from wells 89-2, 89-3 and 89-6 were possibly the result of cross-contamination in the field, as these wells are sufficiently far from the process area that contamination should not have migrated such a distance in site soils. Although PCP concentrations in 89-2 and 89-3 are very close to the detection limit, the value of 0.012 mg/L PCP in 89-6 is above the Quebec C limit of 0.005 mg/L PCP. The concentration in 89-6 is thus a concern, and the piezometer should be re-sampled to confirm or disprove this result.

- Former staff at the Peerless plant should be questioned for the existence of any well on-site, as there is a possibility, as noted by Monenco Consultants Limited, that PCP could migrate to subsurface soils and bedrock through a poorly constructed well. The presence of the large steam boiler on-site would seem to indicate that some stable water source must have been present.

- Well 89-6 should be re-sampled, and the sample analyzed for PCP content. As mentioned previously, the well is in the southeastern-most corner of the site, and a sample from this well showed a PCP concentration in excess of Quebec level C criteria. If groundwater from this perimeter well is highly contaminated, PCP migration from this site is significant, and the two nearby domestic wells may be in danger. In any case, these two domestic wells should be sampled for PCP, dioxin and PAH content to ensure the safety of the well users.

- The site contains large areas devoid of vegetation, implying extensive surface contamination. The contamination in soils near the process area is understandable, given the practices at this site, but the source of contamination in the remaining bare areas is not as clear. Most likely, these areas were timber drying and storage areas (section 1.2.4.1).

- Although slug test data of the wells and piezometers showed fairly consistent hydraulic conductivities for the clayey till, the permeability determined from well 89-2 is at least three orders-of-magnitude higher than the permeability determined from any other well. This value of 2.5×10^{-4} cm/s was not included in calculation of the geometric mean for this site, and was attributed to a silty fine sand lense. High permeability lenses thus exist within the clayey silt till at this site. This means that contaminated groundwater may have migrated further than expected at this site, and may also be responsible for the LNAPL found in well 89-4-1. The groundwater sample from well 89-4-1 contained 33 mg/L PCP, several times PCP's aqueous solubility. It is thus likely that PCP and diesel fuel may exist as a distinct phase on the water table. The three groundwater samples containing PCP in concentrations above 1 mg/L also likely arose from contact with an LNAPL. Future soil sampling should also confirm that the clayey silt till and bedrock are unfractured; fractures in soil and bedrock result in groundwater (and contaminant) movement in excess of that predicted by localized hydraulic conductivity tests (slug tests). Bulk hydrocarbon fluids such as PCP preserving fluids have been associated with increased fracturing in clays, as discussed in section 1.5.1.1. Calculations using Darcy's law have shown that contaminants most likely have migrated to the bedrock; any bedrock fractures could thus result in contamination, and this is a concern as nearby dwellings obtain their water from bedrock wells.

- Of the 81 soil samples analyzed, only 10 samples had a pH less than 8.0, and only 2 samples had a pH less than 7.5. For these pH values, chlorophenols largely exist in their ionic forms (section 1.4.1.1). This has two practical consequences:
  - The low permeability soils at this site may be offset by increased PCP mobility; PCP, as the soluble pentachlorophenate ion, may have migrated much further than expected. The PCP value at well 89-6 may thus not be an error.
  - Any land treatment unit must be lined to prevent pentachlorophenate migration from PCP-contaminated soils.

4.3.3 Remediation Alternatives

Based on site observations and data presented in the Monenco report, the remediation alternatives evaluated in section 3 can be assessed for their applicability to conditions at the Cayley site.

- Contaminants beneath the Cayley site are trapped in a low permeability ($k = 7.5 \times 10^{-8}$ cm/s) clay till. In situ remediation alternatives such as bioreclamation, soil washing, vapour extraction, and pump and treat cannot effectively remediate contamination in such soils, because of mass transfer limitations.

- Solidification/stabilization does not effectively remediate PCP-contaminated soils.

- Incineration, landfill disposal and enhanced land treatment could be used at this site. Incineration alone would be prohibitively expensive (total cost would be about $15 000 000 using the estimates presented in Table 3.2-1). Landfill disposal may not be a technically-sound alternative, given the high soil pH and potential chlorophenol mobility in such conditions.

- Land treatment could be used at this site because a large, uncontaminated area is available for construction of the land treatment unit (LTU). Amendments such as sawdust, wood chips, and manure also exist on-site. Consequently, the recommended remediation alternative incorporates land treatment of contaminated soil. (A more in-depth description of land treatment is presented in section 3.2.2.1).
  - Remove all residual process equipment, concrete pads, storage tanks and other rubble from the site. All equipment should be

examined for residual PCP prior to disposal/re-sale, and cleaned if necessary.

- Excavate and drum the sludge pond liquids, as well as the soil/sludge layer on the bottom of the pond. This material, as determined by the Monenco study, is highly contaminated with PCP. Samples 62 and C collected from the sludge pond contained the highest PCP concentrations of any soil samples collected (4000 and 6900 ppm respectively). The contaminated material should be sent to Swan Hills for incineration. Barrels full of liquid remaining at the site could also be hauled for incineration at this time. This sludge material is too highly contaminated with PCP to be land treatable as is, and would require significant amounts of clean soil to be "diluted" down to treatable levels.
- Excavate all the contaminated soil on the site to the specified cleanup level, mix this soil with amendments such as manure, straw, sand, nutrients and wood chips, and store in a covered, lined stockpile on an uncontaminated corner of the site. The exact amendment quantities would be determined in laboratory and pilot-scale studies.
- Cap the site with a clean clay, filling in the sludge pond and blowdown lagoon.
- Construct the LTU near the stockpile.
- Install pumping wells, or use existing monitors to provide hydraulic containment and recover the contaminated groundwater beneath the site. The recovered groundwater may

section.

- **When all the contaminated soil and groundwater is treated, the LTU can be decommissioned, and the site can be used for a purpose consistent with the cleanup criteria.**

4.4 Former Deep Basin Wood Preservers - Elmworth

4.4.1 Introduction

Deep Basin Wood Preservers Ltd. operated a wood preserving plant near Elmworth, Alberta from 1977 to 1982. The plant pressure treated fence posts with a CCA mixture called Osmose. Site characterization data and an evaluation of this data are presented in Appendix E.4.

4.4.2 Site Concerns

The following is a list of conclusions about the Elmworth site and concerns which should be addressed in any subsequent study, based on site observations and the Thurber report.

- When I visited the site in October 1989, the soil surrounding the sludge pit was bare of vegetation, as was a small area in the swamp northwest of the sludge pit. However, the remainder of the site contained a thick, healthy crop of prairie grasses. This finding is consistent with the Thurber data which showed the most contaminated surficial soil samples originated from TP89-1, TP89-2, TP89-6 and S15 (Figure E.4-1). The absence of large non-vegetated areas supports the premise that treated posts were transported off the property directly from the drying platform adjacent to the pressure vessel. Otherwise any soil drip pad on the site would likely still be bare of vegetation.

- As noted in section E.4.1, CCA sludge was periodically removed from the sludge pit in drums and disposed in a sawdust and chip fill area northeast of the Quonset hut. This disposal area was not located in the Thurber study. The fill area was possibly cut into the earth and may thus be close to the water table. Sludge deposited into this pit would presumably contain high concentrations of Cu, Cr and As. It is thus possible that the soil and groundwater near this disposal area are grossly contaminated with these metals. A greater emphasis should have been placed on locating this landfill. A geophysical survey using an electromagnetic device (EM) would likely work well in locating this landfill, as gross metals contamination markedly increases the specific conductivity of the soil/water matrix due to increasing ionic strength. This EM survey would work especially well if scrap metal such as the drums used were also deposited into the landfill.

- Data from the Thurber report conclusively show high adsorption of Cu, Cr and As to surface soils, as illustrated in Table 4.4-1. The behaviour of CCA in soils is discussed in section 1.5.2.2.1. Observations at the Elmworth site are consistent with predictions of high adsorption in the organic-rich clay present. An additional point of interest regarding mobility of Cu, Cr and As is apparent when comparing Figures E.4-3, -4, and -5, which map the surficial contamination:
    - Cu has migrated much less than either Cr or As.

Table 4.4-1 Adsorption of Cu, Cr and As to Soil

Parameter	Condition at Ground Surface	Condition at 0.15 m depth
Cu	4 soil samples exceed the Quebec C value (500 ppm)	1 sample exceeds the Quebec B value (100 ppm)
Cr	4 soil samples exceed the Quebec C value (800 ppm)	all samples are less than the Quebec B value (250 ppm)
As	14 soil samples exceed the Quebec C value (50 ppm)	2 samples exceed the Quebec C value (50 ppm)

Notes:

- The Quebec assessment criteria are included in Appendix B.

  - Cr and As have migrated virtually the same distance.

The observed relative mobilities are consistent with theory which predicts that anionic complexes of Cr and As should migrate further than cationic Cu in clay soils, which have a bulk negative charge arising from isomorphous substitution.

- Any subsequent study must locate and evaluate the landfill used for disposal of sludge from the lagoon. As discussed previously, Cu, Cr and As are likely being leached from the concentrated CCA sludge in this landfill. Excessive metals contamination may exceed the adsorption capacity of the soil, and CCA may consequently travel unhindered through the vadose zone to the groundwater table (section 1.5.2.1). This problem would be compounded if the fill area was cut into the earth. When this landfill is discovered, it is likely that an additional volume of soil will require remediation. At present it is difficult to evaluate reclamation alternatives without knowledge of this additional volume.

- As noted frequently in this section, CCA sludge was periodically removed from the sludge pit for disposal in an on-site landfill. The sludge pit is lined with a thin plastic sheet, perhaps 5 mm thick. When I visited the site, this liner appeared brittle in places, and missing or submerged in others. Considering that removal of dge likely tore the liner, and also my observations, it is able to assume that the residual material in the lagoon is leaking out into the soil and possibly affecting groundwater. This problem has two practical consequences:

- the sludge pond source material should be quickly removed to prevent further contamination of soil and possibly groundwater. Disposal of this material at Swan Hills is likely the only practical option.
- considerably more than a 0.5 m depth of soil as quoted in the Thurber report will require remediation.

- Thurber Consultants Ltd. stated on page 10 of their report that the sludge pit was overtopped every spring and during heavy rainfall events. This is confirmed by the high levels of surficial contamination apparent in TP89-1, TP89-2 and S15. It is also apparent from the results of TP89-6 as well as Figures E.4-3, -4, and -5 that the overflow material must have run towards the slough 45 m northwest of the sludge pit. During his visit to the site, I noted and photographed an electrical box adjacent to the sludge pit as well as some 4 cm diameter polyethylene tubing leading away from the pit. It is thus possible that a pump is or was at the bottom of the sludge pit, and that liquid was periodically pumped from the lagoon, likely to the nearby swamp.

- Thurber Consultants Ltd. also note on pages 9 and 10 of their report that dust and material in the chemical preparation shed and drying platform contain extremely high concentrations of arsenic, chromium and copper. The drying platform in the

Quonset hut is periodically used by two of the tenants to service farm vehicles. In addition, one of the tenants (Mr. Lee Headon) obtains his water from a well in the Quonset hut. Consequently, the chemical preparation shed and Quonset hut must be thoroughly cleaned or removed to a landfill to prevent further exposure of the tenants to particulate matter contaminated with CCA. Considering the contamination in these process buildings and in surficial soil near the sludge lagoon, inhalation of dust containing CCA must be emphasized as an exposure pathway during any risk assessment study on this site.

- As discussed in section E.4.1, all 5 groundwater samples analyzed by Thurber Consultants Ltd. satisfied the specified levels for arsenic, copper and chromium in the Guidelines for Canadian Drinking Water Quality (included in Appendix B). However, before assuming that this conclusion extends to all groundwater beneath this site, three issues must be considered.
    - only three of the samples were obtained from piezometers actually on the former plant site; the other two samples were background samples obtained from off-site monitoring wells.
    - 3 productive wells are located on the same quarter section of land as the former plant site, and one of these wells is located in the heavily contaminated Quonset hut. None of these wells have been sampled although all three are currently being used for potable water, as outlined below:

  - Mr. Lee Headon uses the well in the Quonset hut for all of his needs.
  - Mr. Bill Douglas uses a second well near the horse corral for his needs and also for livestock.
  - Mr. Ken Erickson, who owns the land and is a seasonal resident, uses a third well located on the farm building site.

- arsenic criteria for drinking water are under review with likelihood of substantial reduction in allowable levels. If these levels are lowered, groundwater at this site may become classified as contaminated with arsenic.

For these reasons I recommend that the domestic wells and the site piezometers be tested for As, Cr and Cu. It would also be desirable to install more piezometers at this site to provide additional groundwater quality data. Particular attention should be devoted to the As concentrations in the three domestic wells and anticipated new regulatory levels for arsenic in potable water. Mr. Headon's well should also be examined for any surficial cracks which may be transmitting CCA-contaminated water from the floor of the hut down to the groundwater.

- Because of the distance to neighbouring farms, the findings of the Thurber study and the prevailing site geology, it is reasonable to assume that groundwater beneath neighbouring farms is safe for human consumption. However, any subsequent finding of high Cr or As levels in the siltstone units beneath the Deep Basin site would justify testing of neighbouring wells, as these siltstone units form the aquifer used for groundwater in this area.

4.4.3 Remediation Alternatives

Based on site observations and data presented in the Thurber report, the remediation alternatives evaluated in section 3 can be assessed for their applicability to conditions at Elmworth site.

- Exposure pathways associated with groundwater do not appear to be significant for this site, considering all groundwater samples satisfied drinking water criteria. Consequently, remediation efforts should focus on the metal ions adsorbed to soil. However, subsequent observation of unacceptable CCA concentrations in on-site wells would dictate a change in emphasis.
- Only landfill disposal, solidification/stabilization, and soil washing are applicable to remediation of CCA-contaminated soil.
- Soil beneath this site is highly-plastic, organic-rich clay. Transport of washing solution and contact with adsorbed constituents would be difficult to achieve in such a formation, limiting the effectiveness of in situ soil washing.
- Solidification/stabilization has been used for CCA contaminated soils, though some forms of arsenic and chromium may not be sufficiently immobilized. In addition, high organic concentrations present in the clay may interfere with matrix setting.

- Landfill disposal could be used for site soils, though adsorption of Cu, Cr, As is pH-dependent, and these constituents may be leached in a municipal landfill environment.
- As a result of the inadequacies of individual strategies, a combined approach using both solidification/stabilization and landfill disposal is recommended:
  - the chemical preparation shed and Quonset hut should be thoroughly cleaned of residual CCA or demolished and landfilled. Other rubbish such as derelict vehicles, old drums, batteries and scrap metal should be tested for Cu, Cr and As if contamination is suspected and cleaned if necessary. All of this material should then be removed from the site.
  - in conjunction with this general cleanup, the sludge pit and adjacent soil should be drummed and transferred to the Special Waste Management Facility in Swan Hills, where it will be dewatered, stabilized and landfilled. Stabilization will likely be required prior to landfill disposal because of regulatory limitations on the disposal of liquid arsenic and chromium wastes (section 3.1.1.2).
  - from a regulatory standpoint, CCA-contaminated soil can be disposed "as is" in an approved industrial landfill (sections 3.1.1.2 and E.4.2). However, the objective of site remediation is hazard mitigation, and this objective may not effectively be achieved through landfill disposal of CCA-contaminated soil, because of the potential for contaminant leaching.

Consequently, this soil should be stabilized prior to disposal, to further immobilize adsorbed contaminants.

4.5 Former Alberta Osmose Pressure Preserving Ltd. - Faust

4.5.1 Introduction

Alberta Osmose Pressure Preserving Ltd. operated a wood preserving plant on property adjacent to Lesser Slave Lake just outside the hamlet of Faust, Alberta from 1961 to about 1970. A commercial mixture of copper, chromium and arsenic called Osmose or CCA was used to treat timber at the site from 1961 to 1967. In 1967 pentachlorophenol (PCP) replaced CCA as the preservative used. A fire originating in the treater building destroyed the plant in about 1970. Sawing of poles continued on the site until about 1973 under the Northern Pole Company. Site characterization data and an evaluation of this data are presented in Appendix E.5.

4.5.2 Site Concerns

The following is a list of conclusions about the Faust site and concerns which should be addressed in any subsequent study, based on site observations, discussions with former employees, and the Hardy BBT report.

- The following list of points was compiled from discussions between myself and Mr. Clarence Bittmann, who managed the plant site from 1961 until the fire in 1969.
  - the plant was owned by Mr. Howard McRae, who died in the 1980s.
  - Osmose (CCA) was used at the plant from 1961 until 1967. The Osmose salts used water as a carrier, and as a result the

operation was very clean. Treated timber was normally allowed to drip in the cylinder for a long time in order to reclaim treating fluid, which was filtered and reused. However, when the plant was very busy poles were allowed to drip on-site. The treated lumber was stored west of the loading track and south of the retort. No timber was ever stored north of the garage (Figure E.5-1).

- the considerable water requirements for the treating fluid and boiler which generated the retort vacuum were supplied by the creek northeast of the site. The creek was dammed and a pipeline to the site constructed. When the creek froze in winter, water was stored in a 500 or 1000 gallon cistern which was dug into the ground. Mr. Bittmann did not recall whether this storage area was cribbed with wood, and was adamant that there was never any well located on the Faust site. The significance of this point will be discussed later.
- the Osmose operation was very clean, and little, if any, sludge was generated. Mr. Bittmann did not recall the production or disposal of CCA sludge, but believed that any sludge produced would have been disposed in the lagoon north of the garage.
- this lagoon was constructed to be a holding pond for water in case of a fire at the site. However, the dugout held no water because of the sandy soil, and it became a landfill for refuse and eventually for PCP sludge.
- in about 1967 the operation switched to the use of PCP as the treating agent in an attempt to secure a contract from C.N.

Rail. Diesel fuel was then correspondingly substituted for water as the carrier fluid.

- the use of PCP caused a lot of difficulties not present with CCA. Some of these problems are outlined below:
    - the diesel fuel had to be heated to 125°C in the retort. This is near the flashpoint for some diesel fuel constituents, and a number of small spills and fires occurred.
    - a significant amount of sludge was produced with the PCP process. This sludge had the consistency of "chocolate pudding" (suggesting an emulsion) and was dumped into the unlined lagoon and burned immediately.
- Mr. Bittmann believed that there was no mixing of PCP and CCA wastes at this site because the CCA process was clean, and because he did not recall any production of CCA sludge.
- the site is located in a swampy area, and many truckloads of gravel were hauled to the plant to increase the elevation and footing. Unfortunately, this gravel just sunk into the ground. Because of the wet conditions, the site often had to shut down during heavy rainfalls or snowmelt. Mr. Bittmann holds however, that the site was never flooded, and that wastes were never washed west towards the swamp.
- coal sparks from the boiler in the treater building started a fire which destroyed the plant in 1969 or 1970. Sawing operations continued on the site until about 1973.

- When I visited the site, I noted an area south and east of the fence covered with wood chips to a maximum depth of 0.3 m. This area was completely bare of vegetation in many spots, and the vegetation that did exist was sparse and noticeably less healthy than surrounding grasses. Samples 24 and 25 of the Hardy BBT study were taken from this area, and they exceeded the Quebec C criteria for both PCP and arsenic. These observations and data agree with Mr. Bittmann who stated that treated lumber was stored and sometimes left to drip in this area. A subsequent study should delineate soil and groundwater contamination at this location.

- A second bare area was noted in the swamp west of the site. As mentioned in section E.5.2, the site topography suggests that surface runoff from the plant drains into the swamp. In addition, a long-time resident 100 m east of the site holds that the creek periodically overtopped and flooded the site, washing material to the swamp west of the site. This point is disputed by Mr. Bittmann. In any case, I suspect the pond area is contaminated and recommend that it be tested. The slough was not considered in the Hardy BBT study.

- When I visited the site, I noted a number of darkly-stained bare areas inside the fence, and a strong PCP odour all over the site. This is of some concern considering preserving operations ceased over 20 years ago. I also noted and photographed what appeared to be a crib-well adjacent to Hardy BBT's piezometer 9. The suspected well was filled in with soil which had subsequently slumped. In one small area the fill had sloughed to reveal groundwater and wooden cribbing. The groundwater was approximately 1 m below ground level, smelled of PCP and had a distinctly oily sheen. The suspected well appears to be about 2 m square. Conflicting reports exist as to what this structure actually is:

- Mr. Clarence Bittmann, the former plant manager, was adamant that no well ever existed on the property. He believed that the structure is an old storage bin, used to hold coal for the boiler, or the underground compartment where the water cistern was housed.
- Mr. Ian Terry, of Stanley Associates Engineering Ltd. (who performed some Phase II testing) is equally convinced that this structure is a crib-well, used to provide process water before the pipeline to the creek was constructed.

Regardless of what this structure is, it is likely transmitting contamination from the heavily contaminated process area directly to groundwater. The proximity of domestic groundwater wells and Lesser Slave Lake demands that this structure be expediently removed and replaced with a low permeability fill material.

- I consider this site to have a significant potential for causing environmental harm. Some possible exposure pathways by which contamination from this property can harm humans or the environment are discussed below.

- **contaminated groundwater.** The aquifer beneath this site is contaminated with PCP. There is a concern that contaminated groundwater may be discharging to the nearby creek or Lesser Slave Lake. More importantly, contaminated groundwater may be affecting nearby domestic wells. It is difficult to obtain an accurate number of wells in use near the site because many households are switching to municipal water from the nearby Faust-Kinuso force main. However Mr. Frank Madsen, who lives on the farm 100 m east of the site estimates that there are 4 active domestic water wells within 1 mile (1.6 km) of the site. Samples taken from perimeter piezometers, a nearby farm, and the creek during the Hardy BBT study imply that groundwater off the site is slightly contaminated with PCP, but not yet to a dangerous level. However, the sample from the one piezometer on the site indicates grossly contaminated groundwater not safe for human consumption. This sample also implies the presence of a distinct PCP-hydrocarbon phase in the groundwater. Such a separate phase was observed in the suspected crib well. Current data thus suggests that groundwater beneath the site is heavily contaminated with PCP but that this contamination has not yet migrated off-site to any significant extent. Considering the extensive sand zones beneath this site, continued sampling of nearby domestic water wells should occur. It should be noted that only background levels of Cu, Cr and As were found in all groundwater samples.

- **contaminated sediment**. Surface soil at this site is highly contaminated with PCP and As. The site is also located in a groundwater discharge zone, and is about 3 m higher than the average water level in Lesser Slave Lake. There is a corresponding potential for surface runoff to wash contaminated sediment into nearby areas or the lake. Inhalation of contaminated sediment as dust is expected to be an insignificant exposure pathway because surface conditions appear to be moist. The site is also fenced, so dermal contact with contaminated sediment is expected to be insignificant.

Considering the significance of the potential environmental hazards outlined above, present knowledge about the site is inadequate to reliably assess these hazards. Another study is required to better quantify site hydrogeology and the contaminant distribution, as well as to obtain the parameters necessary to perform a risk assessment. An on-going sampling program should be established for nearby residents with domestic wells. Connecting these residents with the nearby Faust-Kinuso force main may be more economical and provide better safety than initiating such a sampling program.

- Before reclamation alternatives are evaluated, a brief review of current site knowledge will be presented.
  - summary for soil:

  - the soil is heavily contaminated with PCP to depths as much as 3.5 m.
  - some minor surficial contamination with As exists.
  - the soil is not contaminated with Cu or Cr.
- summary for groundwater:
  - the groundwater beneath the site is heavily contaminated with PCP.
  - the groundwater is not contaminated with Cu, Cr or As. Measured arsenic concentrations were so low that even a substantial reduction in allowable levels would not result in this water becoming classified as contaminated.

The minimal CCA contamination at this site is consistent with Mr. Bittmann's comments that the process was extremely clean, generating little or no sludge, and that no spills or fires occurred prior to switching to PCP. Any CCA releases which did occur appear to have been immobilized in the clay which overlies the site.

4.5.3 Remediation Alternatives

Based on site observations and data presented in the Hardy BBT report, the remediation alternatives evaluated in section 3 can be assessed for their applicability to conditions at the Faust site.

- Less useful information was obtained during characterization of the Faust site compared with that obtained from investigations at other sites. Consequently, remediation alternatives are more difficult to evaluate for this site. However, the following recommended approach can be formulated.

- No estimation of hydraulic conductivity was made in the Hardy BBT study, though from the hydrogeologic description and Mr. Bittman's comments, it appears the underlying formation is quite permeable. Consequently, in situ technologies may be applicable.

- Assuming site contamination poses an unacceptable hazard, the first objective of remediation is to prevent further contaminant migration. A pump and treat system should be able to achieve this containment.

- From the Hardy BBT report, arsenic contamination of soil appears limited to the surficial soil at a few locations. The data implies this soil volume is probably small, and it could likely best be remediated through solidification/stabilization and landfill disposal.

- For the remaining PCP-contaminated soil, in situ technologies such as soil washing or bioreclamation could work, assuming formation permeability is sufficient. However, the site is located near several residences with domestic wells, as well as near Lesser Slave Lake. Consequently, inadequate hydraulic control or breaches in hydraulic containment could result in contamination of domestic water supplies or the lake with amended groundwater. Therefore treatment of PCP-contaminated soil should occur above ground in a land treatment unit.

5. Conclusions

Several conclusions arising from this study are summarized below.

- wood preserving chemicals pose a variety of serious health risks:
  - chloracne (technical-grade PCP);
  - embryo- and fetotoxicity (PCP, 2,3,4,6-tetrachlorophenol, octachlorodibenzo[p]dioxin, hexachlorodibenzo[p]dioxin); and
  - possibly cancer (2,4,6-trichlorophenol, hexachlorodibenzodioxin, quinoline, aniline, benzo[a]pyrene, chrysene). Arsenic compounds and chromium [VI] compounds are accepted as human carcinogens.

- oil-based wood preserving mixtures released to the environment as wastes may eventually exist in several forms:
  - continuous distinct phase (NAPL);
  - mobile discontinuous distinct phase (droplets, emulsion);
  - immobile discontinuous distinct phase (residual saturation);
  - dissolved molecules; and
  - adsorbed molecules.

- water-based wood preserving mixtures released to the environment will subsequently exist as ions dissolved in groundwater, and as ions or precipitates affixed to soil.

- humans may be exposed to wood preserving chemicals in the environment through several routes:

- water-based (ingestion of contaminated water or topical contact with it through showering or swimming);
- soil-based (consumption of contaminated soil on hands or plants, inhalation of contaminated dust, or topical contact with contaminated soil);
- air-based (inhalation of contaminant vapours); and
- bioaccumulation-based (consumption of contaminated plants and animals).

These pathways are not equally relevant for all wood preserving contaminants, because of the wide variation in partitioning behaviours.

- assessing site contamination and developing cleanup guidelines is difficult for several reasons:
  - both technical and non-technical concerns must be addressed;
  - the approach must be simple enough to be quickly implemented so that near-term exposures may be minimized, yet sufficient in depth to provide a comprehensive scientific evaluation of potential adverse human or environmental effects; and
  - the cleanup standards developed must be practically achievable with existing remediation technologies.

No single approach or simple combination of approaches appears to achieve all of these objectives, though risk assessment/risk management, statutory guidelines, and an expert system exposure assessment model appear to have the widest range of capabilities.

- no one technology can effectively remediate all contamination forms present at wood preserving sites; a treatment scheme, incorporating several technologies, will be required for complete remediation.

- most remediation strategies utilize chemical additives or physical processes to enhance contaminant recovery/transformation. In some cases, chemical amendments may be pollutants themselves, or physical treatment methods may inadvertently facilitate contaminant migration. In such instances, the risks associated with site contamination are increased through remediation efforts.

6. Identification of Research Needs

In completing this study, several knowledge gaps became apparent. The most significant areas of inadequate understanding are summarized below.

- **The composition and environmental properties of waste wood preserving mixtures.** The composition and environmental properties of the active agents in preserving mixtures are reasonably well quantified (i.e. technical-grade PCP, creosote, CCA). However, less is known about the composition and properties of the preserving mixture (active agent and carrier), and waste streams. Considerable changes in mixture properties and composition are likely to occur in the retort, as some preservative constituents will preferentially be absorbed by the wood, other chemicals may be leached from the wood, and water and sap from wood cells will contaminate the mixture. The waste streams arising from treatment, particularly those released as drips and sludges, are responsible for site contamination. Consequently, the composition and environmental properties (eg. viscosity, miscibility) of these wastes must be known to accurately assess the potential contaminants and probable environmental behaviour.

- **Constituent partitioning from waste wood preserving mixtures.** Partition coefficients are typically derived from single compound studies. These coefficients may poorly predict environmental partitioning from chemical mixtures, where cohesive and competitive effects modify compound behaviour. Consequently, constituent partitioning from waste wood preserving mixtures should be quantified.

- **Interim site prioritization scheme.** In developing an assessment methodology (section 2.5) and recommending remediation alternatives for the five HELP sites, it became apparent that some approach must be used to minimize receptor exposures in the period between site discovery and the completion of a full health risk assessment. Such a scheme must utilize the limited information available to prioritize contaminated sites, and to guide the need and selection of interim remedial measures (eg. containment) in the absence of a full risk assessment.

- **Uptake of soil-phase organic wood preserving chemicals by plants.** In the exposure quantification stage of risk assessment, contaminant concentrations in plants are calculated to estimate intakes via the produce consumption pathway. A general soil-plant partition coefficient (uptake ratio) is used in such calculations, based on correlations with k_{ow} values for organic chemicals. Such correlations are used because the mechanics of organic chemical uptake by plants are poorly understood (SENES, 1988). Relations derived based on k_{ow} values are generally specific to the chemical class and plant species tested; uptake of different groups of organic compounds or by different plants is generally poorly predicted by such relations. In the absence of a more thorough mechanistic understanding, specific uptake relations based on k_{ow} values should be developed for organic wood preserving chemicals.

- **Effect of decreased temperatures on in situ technologies.** Much of the literature used in this study implicitly considers conditions in the U.S., where soil and groundwater temperatures are typically higher than those prevailing in Canada. Soil/groundwater temperature influences the viscosity of groundwater, partitioning kinetics, equilibrium concentrations, as well as microbial activity. These factors affect the feasibility of in situ technologies at Canadian sites, and their dependence on temperature should be assessed.

These areas of inadequate understanding should be addressed in future research.

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APPENDIX A

Table A-1: Physico-Chemical Properties of Wood Preserving Chemicals

Preserving Mixture	Compound	CAS Registry Number	Aqueous Solubility (mg/L)	log k_{oc}	k_H (atm·m^3/mol)	log k_{ow}	Vapour Pressure (atm)
Diesel Carrier (used for both creosote and PCP processes)	2-methylnaphthalene	91-57-6	25	3.9	2.9×10^{-4}	3.9 - 4.1	5.9×10^{-5}
	benzene	71-43-2	1800	1.7 - 2.0	5.5×10^{-3}	1.6 - 2.2	1.0×10^{-1}
	toluene	108-88-3	515	2.1 - 2.2	6.7×10^{-3}	2.2 - 2.8	2.9×10^{-2}
PCP-based	pentachlorophenol (PCP)	87-86-5	14	2.9 - 4.7	2.8×10^{-7} - 3.4×10^{-6}	3.3 - 5.9	1.4×10^{-7}
	2,3,4,6-tetrachlorophenol	58-90-2	1000	-	3.1×10^{-7}	4.1	1.2×10^{-6}
	2.4.5-trichlorophenol	95-95-4	1190	2.9 - 3.5	1.8×10^{-7}	3.7 - 4.2	2.9×10^{-5}
	2,4,6-trichlorophenol	88-06-2	800	3.0	9.1×10^{-8}	2.8 - 3.7	1.1×10^{-5}
	hexachlorodibenzo[p]dioxin	344-654-68	0.00013	-	5.6×10^{-5}	7.8	1.9×10^{-11}
Creosote-based	naphthalene	91-20-3	30	2.7 - 3.5	3.6×10^{-4} - 1.2×10^{-3}	3.0 - 4.7	6.5×10^{-5}
	acenaphthene	83-32-9	3	1.3	7.9×10^{-5} - 2.4×10^{-4}	3.9 - 4.3	2.6×10^{-5}
	carbazole	-	1	-	1.5×10^{-4}	3.5	9.2×10^{-7}
	fluorene	86-73-7	0.8 - 2.0	3.7	2.1×10^{-4}	4.1 - 4.4	1.7×10^{-5}
	phenanthrene	85-01-8	0.9	3.7 - 4.6	2.6×10^{-5} - 1.3×10^{-4}	4.2 - 4.6	8.9×10^{-7}
	anthracene	120-12-7	0.03 - 0.08	4.2 - 4.4	1.8×10^{-5} - 1.4×10^{-3}	4.3 - 4.5	2.6×10^{-7}
	fluoranthene	206-44-0	0.2	4.6	1.7×10^{-2}	5.2	7.9×10^{-9}
	pyrene	129-00-0	0.01 - 0.2	4.7 - 5.1	1.1×10^{-5} - 1.9×10^{-5}	4.9 - 5.3	9.1×10^{-10}
	chrysene	218-01-9	0.002-0.02	5.4	7.3×10^{-20}	5.6 - 5.9	8.3×10^{-10}
	benzo[a]pyrene	50-32-8	0.004	5.6 - 6.7	2.4×10^{-6}	6.0 - 6.5	6.6×10^{-10}
	benzo[a]anthracene	56-55-3	0.01	6.1	6.6×10^{-7} - 8.0×10^{-6}	5.6 - 5.9	6.6×10^{-12}

continued

Table A-1: Continued

Preserving Mixture	Compound	CAS Registry Number	Aqueous Solubility (mg/L)	log k_{oc}	k_H (atm·m^3/mol)	log k_{ow}	Vapour Pressure (atm)
Creosote-based	benzo[b]fluoranthene	205-99-2	0.001 - 0.01	5.7	1.2×10^{-5}	6.6	6.6×10^{-10}
	benzo[k]fluoranthene	207-08-9	0.0006	6.6	-	6.9	6.6×10^{-12}
	benzo[g,h,i]perylene	191-24-2	0.0003	6.9	1.4×10^{-7}	7.1	1.0×10^{-10} - 1.3×10^{-13}
	dibenzo[a,h]anthracene	53-70-3	0.0005 - 0.005	6.2	7.33×10^{-9}	6.0 - 6.5	1.3×10^{-13}
	indeno[1,2,3-c,d]pyrene	193-39-5	0.06	7.5	3.0×10^{-20}	6.0 - 7.7	1.3×10^{-13}
	phenol	108-95-2	[illegible]00	1.2 - 1.4	1.7×10^{-7} - 4.0×10^{-7}	1.5	2.6×10^{-4}
	2,4,6-trimethylphenol	52-76-06	[illegible]	-	3.3×10^{-5}	3.4	2.1×10^{-5}
	quinoline	-	[illegible]000	-	2.8×10^{-6}	2.0	6.6×10^{-4}
	aniline	62-53-3	34 000	-	1.1×10^{-6}	0.9 - 1.0	3.9×10^{-4}
	benzo[b]thiophene	-	-	-	2.3×10^{-4}	3.1	-
	dibenzothiophene	-	-	-	4.4×10^{-4}	4.4	-

Notes:

- Sources: Montgomery and Welkom (1990), Battelle (1989), Golder (1990), Jardine (1988), Howard (1989), Sims et al. (1986).
- CAS = Chemical Abstracts Service. The CAS Registry Number is a unique identifier assigned by the American Chemical Society, which can assist in a database search.
- aqueous solubility = the maximum concentration of a compound dissolved in water. It is a measure of the affinity of a compound for the aqueous phase when the pure-phase (solid or liquid) compound is present.
- k_{oc} = organic carbon partition coefficient. The k_{oc} value provides a measure of the extent of chemical partitioning between solid-phase organic carbon and water at equilibrium. The larger the k_{oc}, the more likely a chemical is to bind to soil or sediment than to remain in water.

Table A-1: Continued

- k_H = Henry's Law Constant. The k_H value is a measure of the extent of chemical partitioning between air and water at equilibrium. The larger the k_H, the more likely a chemical is to volatilize than to remain in water. At values above about 10^{-5} atm·m^3/mol, compound volatilization from the aqueous phase is significant (Thomas, 1982). Below values of about 3 x 10^{-7} atm·m^3/mol, the compound is essentially nonvolatile (Thomas, 1982).
- k_{ow} = octanol-water partition coefficient. The k_{ow} value provides a measure of the extent of chemical partitioning between water and octanol at equilibrium. The larger the k_{ow}, the more likely a chemical is to partition to octanol than to remain in water. Octanol is used as a surrogate for lipids (fat), and k_{ow} can be used to predict bioconcentration in aquatic organisms (U.S.EPA, 1989b). It can also be used to qualitatively predict partitioning between a hydrocarbon mixture (eg. creosote) and water.
- vapour pressure = pressure exerted by the vapour (gas) of a compound in equilibrium with a pure phase of the compound. Vapour pressure provides an indication of the volatility of a chemical from soil or from a distinct chemical phase (Montgomery and Welkom, 1990).
- properties are for T = 20°C, pH = 7 where available.
- ranges are given when several different values have been cited.

APPENDIX B

Table B-1: Drinking Water Guidelines for Chemicals Used in Wood Preservation

Parameter	Maximum Acceptable Concentration (MAC) (mg/L)	Aesthetic Objectives (less than or equal to value) (mg/L)
Arsenic (As)	0.05	-
Chromium (Cr)	0.05	-
Copper (Cu)	1.00	-
Pentachlorophenol (PCP)	0.06	0.03
2,3,4,6-Tetrachlorophenol	0.1	0.001
2,4,6-Trichlorophenol	0.005	0.002
2,4-Dichlorophenol	0.9	0.0003
Benzo[a]pyrene	0.000 01	-

Notes:

- source: Guidelines for Canadian Drinking Water Quality (1989).
  Published by Health and Welfare Canada.
- MAC values apply to the sum of all forms of each substance present.
- MAC for arsenic is presently under review.

Table B-2: Soil and Groundwater Assessment Criteria Used by the Government of Quebec for Chemicals Used in Wood Preservation

Parameter	SOIL mg/kg of dry soil (ppm)			GROUNDWATER ug/L (ppb)		
	A	B	C	A	B	C
Arsenic (As)	10	30	50	5	50	100
Chromium (Cr)	75	250	800	15	40	500
Copper (Cu)	50	100	500	25	500	1000
Chlorophenols (each)	0.1	0.5	5	1	2	5
Chlorophenols (summation)	0.1	1	10	1	4	10
Phenanthrene	0.1	5	50	0.1	1	5
Naphthalene	0.1	5	50	0.2	10	30
Fluorene	0.1	10	100	0.1	2	10
Acenaphthene	0.1	10	100	0.5	20	30
Acenaphthylene	0.1	10	100	0.5	10	20
Benzo[a]anthracene	0.1	1	10	0.1	0.5	2
Dibenzo[a,h]anthracene	0.1	1	10	0.1	0.2	1
Chrysene	0.1	1	10	0.1	1	5
Benzo[b]fluoranthene	0.1	1	10	0.1	0.2	1
Benzo[j]fluoranthene	0.1	1	10	0.1	0.2	1
Benzo[k]fluoranthene	0.1	1	10	0.1	0.2	1
Benzo[g,h,i]perylene	0.1	1	10	0.1	0.2	1
Pyrene	0.1	10	100	0.2	7	30
Benzo[a]pyrene	0.1	1	10	0.1	0.2	1
Indeno[1,2,3-c,d]pyrene	0.1	1	10	0.1	1	5
Anthracene	0.1	10	100	0.2	7	20
Flouranthene	0.1	10	100	0.1	2	10
PAHs (summation)	1	20	200	0.2	10	50

Notes:

- source: Contaminated Sites Rehabilitation Policy (1988). Published by the Ministére de l'Environnement du Québec.
- material presented in this appendix is discussed in section 2.2.2.
- level A-B: the soil or groundwater is slightly contaminated. At this level, groundwater does satisfy drinking quality standards. Level A is meant to represent background concentrations for naturally-occurring contaminants and the detection limit for man-made organic chemicals.
- level B-C: the soil or groundwater is contaminated. At this level, contamination of groundwater exceeds quality standards for human consumption.
- level C: the soil or groundwater is contaminated. Groundwater cannot be used for drinking. Concentrations of many contaminants exceed standards governing storm sewer runoff.

APPENDIX C

APPENDIX C: AERIS Sensitivity Analysis

Statistical sensitivity analysis, using factorial design, is based on partial regression techniques, where the computer model is evaluated at a number of points in the input space, and a linear model is generated from the resulting output (Battelle, 1990). A detailed description of the theory and approach behind this experimental technique is presented in Box et al. (1978), Battelle (1990), and McKay et al. (1979).

If the true relation between total dose and the independent variables can be described by equation C-1, then the relation can be approximated by equation C-2:

$$\underline{Y} = \underline{x}\underline{\beta} + \underline{\varepsilon} \qquad \text{(C-1)}$$

$$\underline{Y}^* = \underline{x}\underline{\beta}^* \qquad \text{(C-2)}$$

where: Y = total receptor dose from the AERIS model (mg/kg-d)
x = standardized independent variables used to generate total dose
β = equation parameters (constants) (mg/kg-d)
ε = random error
Y^* = predicted total dose from fitted model (mg/kg-d)
β^* = partial regression coefficients (mg/kg-d)

underscores denote matrices. Matrices must be used as several tests are required to quantify the response surface and determine regression coefficients.

Equations C-1 and C-2 apply to a reparametrized model, where the input variables (x values) have been transformed to unitless parameters (Table C-1). This standardization also facilitates computation of the β^* values (orthogonal design).

In a 2^5 factorial design, 5 parameters are tested at 2 levels (+1 and -1) in 32 runs ($2^5 = 32$), generating 32 partial regression coefficients:

$$\begin{aligned} Y^* = {} & \beta_0^* + \beta_1^* x_1 + \beta_2^* x_2 + \beta_3^* x_3 + \beta_4^* x_4 + \beta_5^* x_5 + \beta_{12}^* x_1 x_2 + \\ & \beta_{13}^* x_1 x_3 + \beta_{14}^* x_1 x_4 + \beta_{15}^* x_1 x_5 + \beta_{23}^* x_2 x_3 + \beta_{24}^* x_2 x_4 + \\ & \beta_{25}^* x_2 x_5 + \beta_{34}^* x_3 x_4 + \beta_{35}^* x_3 x_5 + \beta_{45}^* x_4 x_5 + \beta_{123}^* x_1 x_2 x_3 + \\ & \beta_{124}^* x_1 x_2 x_4 + \beta_{125}^* x_1 x_2 x_5 + \beta_{234}^* x_2 x_3 x_4 + \beta_{235}^* x_2 x_3 x_5 + \\ & \beta_{345}^* x_3 x_4 x_5 + \beta_{134}^* x_1 x_3 x_4 + \beta_{135}^* x_1 x_3 x_5 + \beta_{145}^* x_1 x_4 x_5 + \\ & \beta_{245}^* x_2 x_4 x_5 + \beta_{1234}^* x_1 x_2 x_3 x_4 + \beta_{1235}^* x_1 x_2 x_3 x_5 + \\ & \beta_{2345}^* x_2 x_3 x_4 x_5 + \beta_{1345}^* x_1 x_3 x_4 x_5 + \beta_{1245}^* x_1 x_2 x_4 x_5 + \\ & \beta_{12345}^* x_1 x_2 x_3 x_4 x_5 \end{aligned} \tag{C-3}$$

where: β_i^* = partial regression coefficient representing the effect of parameter i on the response Y.

β_{ijk}^* = partial regression coefficient representing the effect of the interaction of parameters i,j,k on the response Y.

In a 2^5 AERIS sensitivity analysis, every possible combination of the x_i values at +1 and -1 levels is used, producing 32 "Y" values. The ancillary data for the AERIS runs is listed in Table C-2. The design matrix for this test, including the standardized independent variables, their actual

Table C-1: Transformation of Independent Variables to Unitless Parameters

Independent Variable	Description	Upper Value	Transformed Value	Lower Value	Transformed Value
x_1	Soil Ingestion Rate	477.75 mg/d	+1	100 mg/d	-1
x_2	Vegetative Productivity	4090 g/m^2	+1	280 g/m^2	-1
x_3	Representative Depth of Contamination	3.3 m	+1	1.1 m	-1
x_4	Representative Magnitude of Contamination	5794 ppm	+1	1190 ppm	-1
x_5	Groundwater Concentration	7.0 mg/L	+1	0.0004 mg/L	-1

<u>Notes</u>:

- Transformation equation:

  transformed x = (Variable level - Center level)/(Range/2)

  eg. transformed $x_1 = [(477.75) - 1/2(477.75 + 100)]/[1/2\ (477.75 - 100)]$
  $= +1$

Table C-2: Ancillary Data for AERIS Sensitivity Runs

Parameter Type	Parameter	AERIS Default	Value Used	Source	Comments
Chemical	chemical	-	Pentachlorophenol	-	-
	molecular weight (g/mol)	266.35	266.74	Table 1.4-3	-
	vapour pressure - summer (Pa)	0.231	0.231	-	-
	vapour pressure - winter (Pa)	0.231	0.231	-	-
	solubility - summer (mg/L)	14	10	-	10 mg/L at 10°C
	solubility - winter (mg/L)	5	5	-	-
	Log K_{oc}	4.72	4.72	-	-
	Log K_{ow}	5.05	5.0	Battelle (1989)	-
	$t_{1/2}$ (d)	50	1000	McGinnis (1988)	-
	Diffusivity - air (m^2/h)	0.018	0.018	-	-
	Diffusivity - water (m^2/h)	0.18×10^{-5}	0.18×10^{-5}	-	-
	RSD (mg/kg-d)	0.03	-	-	PCP is not a carcinogen (see text)
	RfD (mg/kg-d)	-	0.003	World Health Organication (1987)	-
	All bioavailability factors	1.00	1.00	-	-
	endpoint	Human Health Criteria	Human Health Criteria	-	-
	% acceptable dose	1.00	1.00	-	no effect on total dose
	degradation factor	1.00	1.00	-	no effect on total dose
	duration factor	1.00	1.00	-	no effect on total dose
Land Use	land use	Residential	Agricultural	-	agricultural area
Receptor	receptor	Adult	Child	-	more crucial than adult as higher soil ingestion rates per unit mass
	receptor weight (kg)	10.00	10.00	-	-
	air intake (m^3/h)	0.21	0.21	-	-
	soil ingestion rate - summer, outdoors (mg/d)	477.75	-	-	varied in sensitivity analysis
	soil ingestion rate - indoors, active (mg/d)	55.00	55.00	-	-

Table C-2: Continued

Parameter Type	Parameter	AERIS Default	Value Used	Source	Comments
Receptor	soil ingestion rate - indoors, passive (mg/d)	110.00	110.00	-	-
	soil ingestion rate - winter, indoors (mg/d)	110.00	110.00	-	-
	breathing zone height (m)	0.75	0.75	-	-
	drinking rate (L)	1.00	1.00	-	-
	fruit and vegetable consumption (kg/d)	0.30	0.30	-	-
	time in summer spent outdoors (h/d,d/w)	12,6	12,6	-	-
	time spent indoors - active (h/d,d/w)	12,6	12,6	-	-
	time spent indoors - passive (h/d,d/w)	24,1	24,1	-	-
	time in winter spent indoors (h/d,d/w)	18,7	18,7	-	-
	time in winter spent outdoors (h/d,d/w)	6,7	6,7	-	-
	groundwater resources used for drinking?	No	Yes	-	Nearby house with well
Site	representative city	-	Edmonton	-	used for climatological data (Edmonton is city in data base closest to site)
	summer/winter irrigation (mm/month)	-	0/0	-	known
	site length (m)	-	290	-	length of site in direction of predominant air/groundwater movement (easterly)
	aquifer thickness (m)	-	3.5	-	saturated thickness of clayey silt till
	soil type (unsaturated zone)	-	mixed grained glacial till	-	closest to actual soil type (lacustrine silts and clays)

Table C-2: Continued

Parameter Type	Parameter	AERIS Default	Value Used	Source	Comments
Site	organic carbon content in unsaturated zone (%)	1	5	-	-
	soil pH	6.0	8.0	-	arithmetic mean of all soil samples
	saturated zone soil type	-	glacial till	-	-
	horizontal hydraulic gradient (m/m)	0.01	0.00001	-	predominant flow gradient is vertically downwards
	water table depth (m)	-	3.5	-	arithmetic mean of values from site piezometers
	unsaturated soil porosity (m^3/m^3)	0.20	0.20	-	-
	particle density (mg/m^3)	2320	2320	-	-
	water content (m^3/m^3)	0.09	0.09	-	-
	saturated soil hydraulic conductivity (m/d)	$3.0x10^{-6}$	$2.0x10^{-4}$	-	geometric mean of values from all site piezometers ($2.4x10^{-7}$ cm/s)
	saturated soil porosity (%)	30	30	-	-
	bulk density (g/cm^3)	1.6	1.6	-	-
	longitudinal dispersivity (m)	3.0	1.0	-	used in Monenco (1989)
	percent of receptor's produce grown on site	5	5	-	-
	vegetative productivity (g/cm^2)	280	-	-	varied in sensitivity analysis
	fraction of dust intercepted by plants	0.40	0.40	-	-
	weathering constant (1/d)	0.033	0.033	-	-
	length of growing season (d)	180	180	-	-
	annual average dustfall rate ($mg/m^2 \cdot d$)	250	250	-	-
	representative depth of contamination (m)	-	-	-	varied in sensitivity analysis
	soil PCP concentration (ppm)	1	-	-	varied in sensitivity analysis

Table C-2: Continued

Parameter Type	Parameter	AERIS Default	Value Used	Source	Comments
Site	want to enter site specific media concentrations?	No	Yes	-	-
	groundwater PCP concentration (mg/L)	-	-	-	varied in sensitivity analysis

Notes:

- site specific data were inferred from Monenco (1989), and site observations.
- dashed (-) values in the AERIS Default column indicate parameters for which no default values exist (input required).

settings, and the model output, is included in Table C-3. The soil cleanup levels produced in the test runs are also included in this table, though they are not utilized in calculations.

The result of this experimentation is 32 output values associated with 32 different settings of the independent variables. The partial regression coefficients can be calculated from this data using equation C-4:

$$\text{(C-4)} \qquad \underline{\beta}^* = (\underline{x}'\underline{x})^{-1}\,\underline{x}'\underline{Y}$$

where: the prime (') represents a transposed matrix; and
the underscore represents matrices.

However, because of the orthogonal design resulting from transformation of the independent variables, the individual β_i^* values can be computed using a simpler equation:

$$\text{(C-5)} \qquad \beta_i^* = (\Sigma\, x_i Y)/(\Sigma\, x_i^2)$$

The β_i^* values computed for this experiment are listed in Table C-4. In this analysis, β_i^* means the estimated effect on Y of changing x_i from 0 to 1, where 0 represents the midpoint value. Therefore $2\beta_i^*$ represents the estimated effect on Y when x_i is varied from -1 to +1.

A partial regression coefficient (β_i^*) is a relative measure of the importance of the input variable on the output value (Battelle, 1990). Consequently, x_i values associated with larger β_i^* values have a greater effect on the output

Table C-3: Design Matrix

Test #	x_1	x_2	x_3	x_4	x_5	x_1 Soil Ingestion Rate (mg/d)	x_2 Productivity (g/m^2)	x_3 Depth (m)	x_4 Soil Concentration (ppm)	x_5 Groundwater Concentration (mg/L)	Y (mg/kg-d)	Soil Cleanup Level (ppm)
1	-1	-1	-1	-1	-1	100	280	1.1	1190	0.0004	0.02520	142
2	+1	-1	-1	-1	-1	477.75	280	1.1	1190	0.0004	0.04441	80
3	-1	+1	-1	-1	-1	100	4090	1.1	1190	0.0004	0.02359	151
4	+1	+1	-1	-1	-1	477.75	4090	1.1	1190	0.0004	0.04280	83
5	-1	-1	+1	-1	-1	100	280	3.3	1190	0.0004	0.02520	142
6	+1	-1	+1	-1	-1	477.75	280	3.3	1190	0.0004	0.04441	80
7	-1	+1	+1	-1	-1	100	4090	3.3	1190	0.0004	0.02359	151
8	+1	+1	+1	-1	-1	477.75	4090	3.3	1190	0.0004	0.04280	83
9	-1	-1	-1	+1	-1	100	280	1.1	5790	0.0004	0.1225	142
10	+1	-1	-1	+1	-1	477.75	280	1.1	5790	0.0004	0.2159	80
11	-1	+1	-1	+1	-1	100	4090	1.1	5790	0.0004	0.1146	152
12	+1	+1	-1	+1	-1	477.75	4090	1.1	5790	0.0004	0.2081	83
13	-1	-1	+1	+1	-1	100	280	3.3	5790	0.0004	0.1225	142
14	+1	-1	+1	+1	-1	477.75	280	3.3	5790	0.0004	0.2159	80
15	-1	+1	+1	+1	-1	100	4090	3.3	5790	0.0004	0.1146	152
16	+1	+1	+1	+1	-1	477.75	4090	3.3	5790	0.0004	0.2081	83
17	-1	-1	-1	-1	+1	100	280	1.1	1190	7.0	0.7232	5
18	+1	-1	-1	-1	+1	477.75	280	1.1	1190	7.0	0.7425	5
19	-1	+1	-1	-1	+1	100	4090	1.1	1190	7.0	0.7216	5
20	+1	+1	-1	-1	+1	477.75	4090	1.1	1190	7.0	0.7408	5
21	-1	-1	+1	-1	+1	100	280	3.3	1190	7.0	0.7232	5
22	+1	-1	+1	-1	+1	477.75	280	3.3	1190	7.0	0.7425	5
23	-1	+1	+1	-1	+1	100	4090	3.3	1190	7.0	0.7216	5
24	+1	+1	+1	-1	+1	477.75	4090	3.3	1190	7.0	0.7408	5
25	-1	-1	-1	+1	+1	100	280	1.1	5790	7.0	0.8205	21
26	+1	-1	-1	+1	+1	477.75	280	1.1	5790	7.0	0.9140	19
27	-1	+1	-1	+1	+1	100	4090	1.1	5790	7.0	0.8127	21
28	+1	+1	-1	+1	+1	477.75	4090	1.1	5790	7.0	0.9062	19
29	-1	-1	+1	+1	+1	100	280	3.3	5790	7.0	0.8205	21
30	+1	-1	+1	+1	+1	477.75	280	3.3	5790	7.0	0.9140	19
31	-1	+1	+1	+1	+1	100	4090	3.3	5790	7.0	0.8127	21
32	+1	+1	+1	+1	+1	477.75	4090	3.3	5790	7.0	0.9062	19

Table C-4: Calculated β_i^* Values

x_i	β_i^*	Significance of β_i^*	β_i^* (mg/kg-d)
1	β_0^*	estimated effect of other (not considered) variables on total dose	0.4487
x_1	β_1^*	estimated effect of summer soil ingestion rate (outdoors) on total dose	0.0282
x_2	β_2^*	estimated effect of vegetative (garden) productivity on total dose	–0.0024
x_3	β_3^*	estimated effect of depth of soil contamination on total dose	0.0
x_4	β_4^*	estimated effect of magnitude of soil contamination on total dose	0.0656
x_5	β_5^*	estimated effect of groundwater concentration on total dose	0.3490
x_1x_4	β_{14}^*	estimated effect of the interaction of soil ingestion rate and level of soil contamination on total dose	0.0186
x_2x_4	β_{24}^*	estimated effect of the interaction of vegetative productivity and level of soil contamination on total dose	–0.0016
all others	all others	-	0.0

Notes:

- Using these values of the partial regression coefficients, equation C-3 reverts to:

$$Y^* = 0.4487 + 0.0282x_1 - 0.0024x_2 + 0.0656x_4 + 0.3490x_5 + 0.0186x_1x_4 - 0.0016x_2x_4$$

Y than variables associated with smaller β_i^* values. However, for these regression coefficients to be accepted as measures of the importance of individual variables, the fitted model approximation of the original model must be adequate. A model multiple correlation coefficient (r^2) is used to assess the adequacy of fit (Battelle, 1990):

(C-6) $$r^2 = 1 - [\Sigma(Y - Y^*)^2/\Sigma(Y - Y_m)^2]$$

where: Y_m = arithmetic mean of Y.

Y^* values calculated using the computed β_i^* values are presented in Table C-5, along with the model multiple correlation coefficient. The value of r^2 is essentially equal to 1, implying the fitted model adequately represents the response surface. Consequently, the calculated β_i^* values can be accepted as measures of the relative importance of the respective independent variables.

Table C-5: Computation of the Model Multiple Correlation Coefficient (r^2)

Run	Y (mg/kg-d)	Y^* (mg/kg-d)	$(Y - Y^*)^2$	$(Y - Y_m)^2$
1	0.02520	0.02517	7.29×10^{-10}	0.1793
2	0.04441	0.04441	2.50×10^{-11}	0.1634
3	0.02359	0.02356	1.23×10^{-9}	0.1807
4	0.04280	0.04279	1.69×10^{-10}	0.1647
5	0.02520	0.02517	7.29×10^{-10}	0.1793
6	0.04441	0.04441	2.50×10^{-11}	0.1634
7	0.02359	0.02356	1.23×10^{-9}	0.1807
8	0.04280	0.04279	1.69×10^{-10}	0.1647
9	0.1225	0.1225	2.40×10^{-9}	0.1063
10	0.2159	0.2159	5.29×10^{-10}	0.0542
11	0.1146	0.1146	1.69×10^{-10}	0.1116
12	0.2081	0.2081	2.25×10^{-10}	0.0579
13	0.1225	0.1225	2.40×10^{-9}	0.1064
14	0.2159	0.2159	5.29×10^{-10}	0.0542
15	0.1146	0.1146	1.69×10^{-10}	0.1116
16	0.2081	0.2081	2.25×10^{-10}	0.0579
17	0.7232	0.7232	1.37×10^{-9}	0.0754
18	0.7425	0.7425	9.61×10^{-10}	0.0863
19	0.7216	0.7216	3.61×10^{-10}	0.0745
20	0.7408	0.7409	2.60×10^{-9}	0.0853
21	0.7232	0.7232	1.37×10^{-9}	0.0754
22	0.7425	0.7425	9.61×10^{-10}	0.0863
23	0.7216	0.7216	3.61×10^{-10}	0.0745
24	0.7408	0.7409	2.60×10^{-9}	0.0853
25	0.8205	0.8205	2.25×10^{-10}	0.1383
26	0.9140	0.9140	1.69×10^{-10}	0.2165
27	0.8127	0.8127	5.29×10^{-10}	0.1325
28	0.9062	0.9061	2.60×10^{-9}	0.2093
29	0.8205	0.8205	2.25×10^{-10}	0.1383
30	0.9140	0.9140	1.69×10^{-10}	0.2165
31	0.8127	0.8127	5.29×10^{-10}	0.1325
32	0.9062	0.9061	2.60×10^{-9}	0.2093
	$\Sigma = 14.3572$		$\Sigma = 2.8582 \times 10^{-8}$	$\Sigma = 4.0725$

Notes:

- independent variable settings for the respective runs as well as Y values are shown in Table C-3.
- Y^* values were computed using the relation shown in Table C-4.
- calculation of the model multiple correlation coefficient:

$r^2 = 1 - [\Sigma(Y - Y^*)^2/\Sigma(Y - Y_m)^2]$ where $Y_m = \Sigma Y/n = 14.3572/32 = 0.4487$

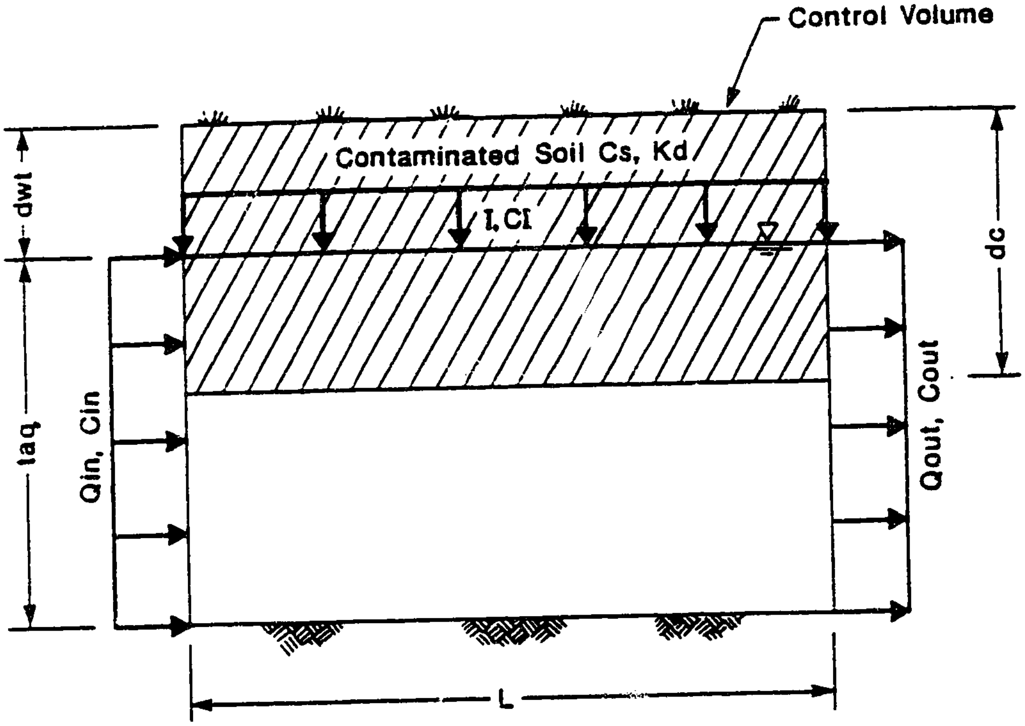
$r^2 = 1 - (2.8582 \times 10^{-8}/4.0725)$

$r^2 = 0.999999993 = 1.0$

APPENDIX D

APPENDIX D: Solution of AERIS Saturated Zone Equations

Case 1: Alternative B - Contaminant Source Present in Saturated Zone But Does Not Extend Full Aquifer Thickness (Not Considered in AERIS)



- where:

- d_{wt} = depth to water table (m)
- t_{aq} = aquifer thickness (m)
- Q_{in} = hydraulic flowrate entering control volume per unit width (m^2/h)
- C_{in} = contaminant concentration in water entering control volume (mol/L)
- I = infiltration rate (m/h)

- C_I = contaminant concentration in infiltrating water (mol/L)
- Q_{out} = hydraulic flowrate leaving control volume per unit width (m^2/h)
- C_{out} = groundwater concentration leaving control volume (used in exposure calculations) (mol/L)
- d_c = depth of contamination (m)
- L = length of site (m)
- C_s = contaminant concentration in soil (ppm)
- K_d = soil partition coefficient

- contaminant mass balance:
  - contaminant flux leaving control volume = contaminant flux entering control volume + contaminant flux generated in control volume

(D-1) $Q_{out}C_{out} = Q_{in}C_{in}$ + contaminant flux from contaminated unsaturated zone + contaminant flux from contaminated saturated zone

- where:
  - contaminant flux from contaminated unsaturated zone = ILC_I, where $C_I = C_s/K_d$, so
  - contaminant flux from contaminated unsaturated zone = $[C_s/K_d]IL$, and
  - contaminant flux from contaminated saturated zone = $[(d_c - d_{wt})/t_{aq}]Q_{in}\ (C_s/K_d)$, where
    - $(d_c - d_{wt})/t_{aq}$ = the fraction of Q_{in} that passes through the contaminated saturated zone, assuming Q_{in} is constant with

depth.

- equation D-1 becomes:

(D-2) $$Q_{out}C_{out} = Q_{in}C_{in} + (C_s/K_d)\ \{IL + Q_{in}\ [(d_c - d_{wt})/t_{aq}]\}$$

- where:
  - $Q_{out} = Q_{in} + IL$, and
  - $C_{in} = 0$, assuming the background contaminant concentration is zero.

- equation D-2 becomes:

(D-3) $$C_{out} = \{(C_s/K_d)\ [IL + Q_{in}\ [(d_c - d_{wt})/t_{aq}]]\} / (IL + Q_{in})$$

Case 1: Alternative A - Contaminant Source Extends the Full Aquifer Thickness (Included in AERIS)

- for this alternative, $d_c = t_{aq} + d_{wt}$, which can be substituted into equation D-3:
  - $C_{out} = (C_s/K_d)\ [IL + \{Q_{in}\ (t_{aq} + d_{wt} - d_{wt})/t_{aq}\}] / (IL + Q_{in})$, which reduces to

(D-4) $$C_{out} = C_s/K_d$$

- equation D-4 is also given as equation 2.3-11 in text.

Case 2: Contaminant Source Not Present in

(Included in AERIS)

- for this scenario, equation D-1 can be rewritten as:

(D-5) $Q_{out}C_{out} = Q_{in}C_{in}$ + contaminant flux from contaminated unsaturated zone

- where:
    - contaminant flux from contaminated unsaturated zone = ILC_I,

      where
        - C_I = calculated in layer 2 of the unsaturated zone module (mol/L)
        - $C_{in} = 0$
        - $Q_{out} = Q_{in} + IL$

- equation D-5 becomes:

(D-6) $C_{out} = (ILC_I)/(Q_{in} + IL)$

- equation D-6 is also given as equation 2.3-12 in text.

APPENDIX E

E.1 Former Alberta Western Post - Blackfalds

E.1.1 Site Characterization

The following is a brief summary of the testing performed at the Blackfalds site by Stanley Associates Engineering Ltd. (1989), and their conclusions based on test results. Interested readers desiring further information are referred to the Stanley Associates Engineering Ltd. report, to which the page numbers in parentheses refer. Pertinent site features as well as suspected areas of contamination are shown in Figure E.1-1.

- 223 soil samples collected (p. 4.3)
  70 of these samples analyzed for PCP (p. 4.4)
  5 soil samples were analyzed for copper, chromium and arsenic (p. 4.4)

- In the soil samples analyzed, PCP content ranged from non-detectable levels to 5826 ppm. However, only three test holes produced PCP concentrations in excess of 100 ppm (p. 5.2), as shown in Table E.1-1.

- Cu, Cr and As levels in the five soil samples analyzed are comparable to background values (p. 5.3).

- 11 piezometers were installed at seven sites (p. 4.2), and 10 groundwater samples were collected and analyzed for PCP (p.

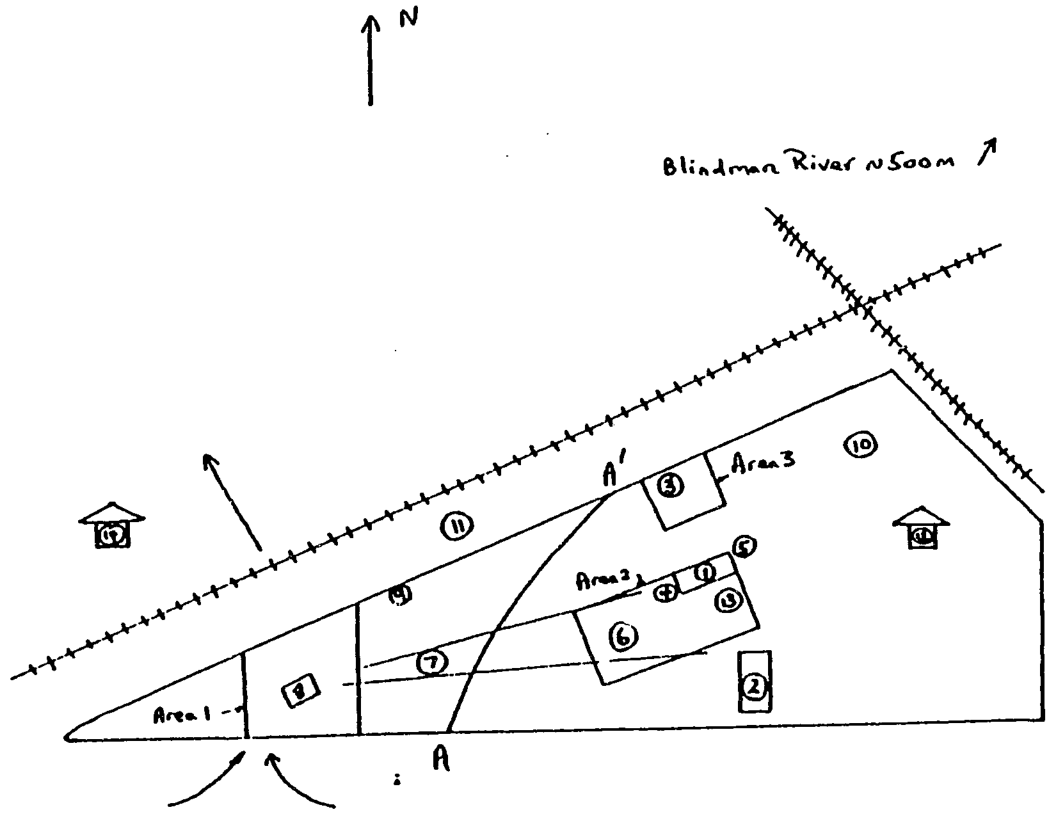


FIGURE E.1-1 : BLACKFALDS SITE FEATURES (STANLEY ASSOCIATES, 1989)

1 - Treater Building
2 - Operations Building
3 - Chemical Storage Location
4 - Concrete slab
5 - Concrete slab
6 - Piping, conduit, wiring evident
7 - Drainage Channels
8 - Sludge Disposal Pit
9 - Ridge
10 - Treated wood stockpile area
11 - CN Maintenance Area
12 - House on site
13 - Water Well
14 - House north of railway
Area1 - Sludge Pit Area
Area2 - Treater Building Area
Area 3 - Chemical Storage Location

Table E.1-1 Soil Sample Summary for Blackfalds Site

Test Hole	Location	Maximum PCP Concentration in Soils (ppm)
8T	Sludge Pond (Area 1)	134
30T	Treater Building (Area 2)	100
20T	Treater Building (Area 2)	5826
	Quebec C Level Criteria	5

(Quebec assessment criteria are included in Appendix B)

4.4). "Additional" groundwater samples were analyzed for Cu, Cr, As (p. 4.4).

- Only four of the ten samples showed detectable PCP concentrations. These are summarized in Table E.1-2. Cu, Cr and As values in the groundwater samples were extremely low, and comparable to background levels (p. 5.4).

- Two small areas bare of vegetation were located on-site where the treated lumber was stockpiled (p. 2.2)

- The site is underlain by a glaciolacustrine sequence of clay and silt deposits overlying a sandy clay till deposit. Vertical cracking to approximately 6 m was noted in the silt and clay (p. 5.6). The horizontal soil conductivity in the zone of piezometer completion is roughly 10^{-5} cm/s.

- Four domestic groundwater wells are within a 500 m radius of the site (p. 2.3).

- The Blindman River is about 500 m to the Northeast of the site (p. 2.3).

E.1.2 Technical Commentary

Technical commentary on the Stanley Associates Engineering Ltd. report is summarized below.

Table E.1-2 Groundwater Sample Summary for Blackfalds Site

Piezometer	Location	PCP concentrations (mg/L)
89-4 shallow	Sludge Pond (Area 1)	5.42
89-4 deep	Sludge Pond (Area 1)	0.153
89-6 shallow	Chemical Storage (Area 3)	0.012
89-7 deep	Sludge Pond (Area 1)	120
	Quebec C Level Criteria	0.005

- Stanley Associates Engineering Ltd. did not analyze any soil or groundwater samples for the polynuclear aromatic hydrocarbons (PAHs) comprising creosote. Though the preliminary inspection by Alberta Environment personnel in July 1988 did not indicate any creosote use (p. 2.3), that study was not sufficiently comprehensive to be confident that no creosote was used at this site. Other reasons for analyzing soil and groundwater for creosote include the following.
    - Creosote contains a number of carcinogenic PAHs (polynuclear aromatic hydrocarbons) (section 1.4.2.3), and these chemicals may present the most significant environmental and human health risks at this site.
    - PCP comprises roughly 5% of any PCP-based wood preserving fluid. The remaining portion is diesel fuel, used as a carrier solution (section 1.4.1). In addition to aliphatic hydrocarbons, diesel fuel contains PAHs as impurities. Thus PAH contamination at a site can result from either creosote or PCP processes.
    - It is quite rare to find a wood preserving plant from the 1960s which did not utilize both creosote and PCP based treatment fluids, because of the similarities of the processes involved (John E. Matthews, EPA Project Officer, personal communication).
    - Creosote wood preserving mixtures are more dense than water, and therefore sink to the bottom in any aquifer as a

DNAPL (dense non-aqueous phase liquid) (section
Such pools are difficult to locate, and may pose the most significant cleanup challenge and long-term environmental threat at any site.

- Stanley Associates Engineering Ltd. did not analyze any of the soil or groundwater samples for dioxins and furans. Dioxins and furans, especially those containing six to eight chlorines, are present as impurities in significant amounts in technical-grade PCP (section 1.4.1). These dioxins and furans are quite toxic and understandably recalcitrant to biological processes. Dioxins and furans remaining on-site from PCP wood preservation may thus exist in harmful concentrations.

- Only 5 soil samples were analyzed for Cu, Cr and As (p. 4.4). This is an insufficient number of samples to determine if CCA was used as a preservative at this site, particularly because Alberta Environment had suspected that CCA was used. The number of groundwater samples analyzed for Cu, Cr and As was not specified (p. 4.4).

- The detection limit for PCP using a methylene chloride extraction for both soil and groundwater samples analyzed by gas chromatography (GC) was given as 0.001 mg/L (p. 4.4, 4.5) The soil detection limit is significantly different from that quoted by other labs (eg. Enviro-Test Laboratories quotes detection limits of

0.1 ppm PCP for soil and 0.002 mg/L PCP for groundwater samples [Dr. Dieb Birkholz, personal communication]).

- I strongly disagree with Stanley Associates Engineering Ltd. suggestion that soil contaminated with 100 ppm PCP or less could be left on-site (p. 6.4), because the future use of Mr. Grewal's portion of the site is likely to be residential. The Quebec "C" criteria for PCP in soils is 5 ppm (Ministére de l'Environnement du Québec, 1988). This "C" standard implies that prompt remedial action may be required, and that land use restrictions apply unless remediation occurs. Without any further rationale to the contrary, the recommendation by Stanley Associates Engineering Ltd. is unacceptable.

- Stanley Associates Engineering Ltd. reported that the value of 120 mg/L PCP from piezometer 89-7D was due to:

  > "PCP extracted from suspended solids collected in the groundwater." (p. 5.4).

  PCP-based wood preserving mixtures are only slightly soluble in water (section 1.4.1.1). A reasonable estimate of PCP's aqueous solubility as part of the preserving mixture is its solubility as a pure compound (5 mg/L at 0°C), in the absence of information to the contrary. The Stanley Associates Engineering Ltd. explanation is not tenable considering the suspended solids concentration of most groundwaters and the amount of PCP these solids would have to carry to make up the difference between the solubility and reported sample value. The 120 mg/L PCP value is most likely not groundwater but rather LNAPL, a PCP/water emulsion, or water sample containing a blob of preserving fluid. All three of these phases can exist in aquifers contaminated with waste PCP preserving fluids (section 1.5.1.2.4).

E.1.3 General Discussion

In general terms, contamination at the Blackfalds site appears limited to small pockets of soil near the treater building and sludge lagoon, and to groundwater beneath the sludge pond. Concern for the environment was not demonstrated by the operators of Alberta Western Post and Timber Treating Ltd., as evidenced by the open, unlined trench which transported spent PCP treating fluid over half the length of the site from the treater building to the sludge lagoon. However, the low permeability of underlying soils (approximately 10^{-5} cm/s) likely prevented significant contaminant migration.

Because of the low permeability of the clay underneath the site, PCP and associated contaminants released on the ground surface migrated slowly down through the unsaturated zone. In this zone, PCP movement probably was further retarded by the processes of degradation and by sorption onto organic material and clay minerals. This slow downward contaminant migration means that the majority of contaminant released on the the ground surface is likely still contained in the unsaturated zone above the water table. This zone is the primary source of long-term contamination at this site, as contaminants and their degradation products will continue percolating downwards towards the groundwater table. Any remediation strategy must therefore concentrate on this zone. In situ processes such as enhanced degradation, pumping wells, and soil flushing/hydrodynamic control are not practical because the low permeability of the clay soils limits mass transfer and hinders contact. For example, Thomas et al. (1987a) concluded that permeabilities greater than 10^{-4} cm/s are required for successful in-situ biorestoration. Above-ground engineered land treatment and associated pumping of contaminated groundwater is a feasible option, as discussed in section 4.1.3.

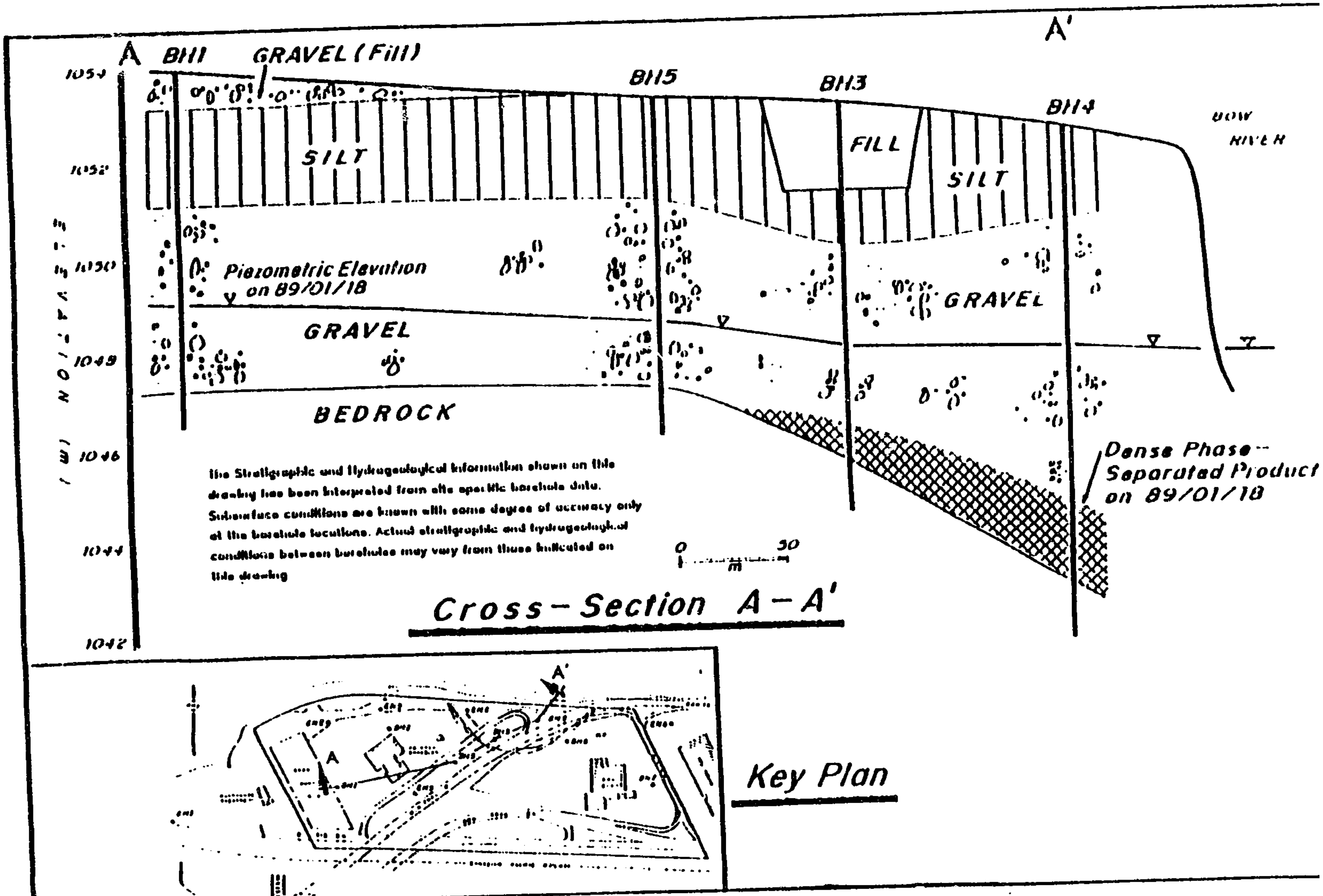
E.2.1 Site Characterization

The following is a brief summary of the testing performed at the Calgary site by O'Connor, and their conclusions based on test results. Interested readers desiring further information are referred to the draft copy of the O'Connor Associates report (1989b), to which the page numbers and table numbers in parentheses refer. Some information is supplemented by that obtained in the preliminary risk assessment, conducted by Golder Associates (1990).

- The site is comprised of silts and/or fill materials overlying alluvial gravels. These gravels overlay siltstone and sandstone bedrock (p. 6). A stratigraphic cross-section of the site is presented in Figure E.2-1, and a plan view of the site is shown in Figure E.2-2.

- The bedrock beneath the site contains local undulations which may be associated with closed depressions (p. 28).

- Seven boreholes (BH1 - BH7) were drilled to bedrock at this site, and piezometers were installed in each (p. 5). From these seven boreholes (Table 3. 1):
    - 9 soil samples were selected for creosote and PCP analysis.
    - 3 groundwater samples were selected for creosote and PCP analysis.



The Stratigraphic and Hydrogeological information shown on this drawing has been interpreted from site specific borehole data. Subsurface conditions are known with some degree of accuracy only at the borehole locations. Actual stratigraphic and hydrogeological conditions between boreholes may vary from those indicated on this drawing

Cross-Section A-A'

Key Plan

FIGURE E.2-1 : STRATIGRAPHIC CROSS-SECTION OF THE CALGARY SITE (O'CONNOR ASSOCIATES, 1989B)

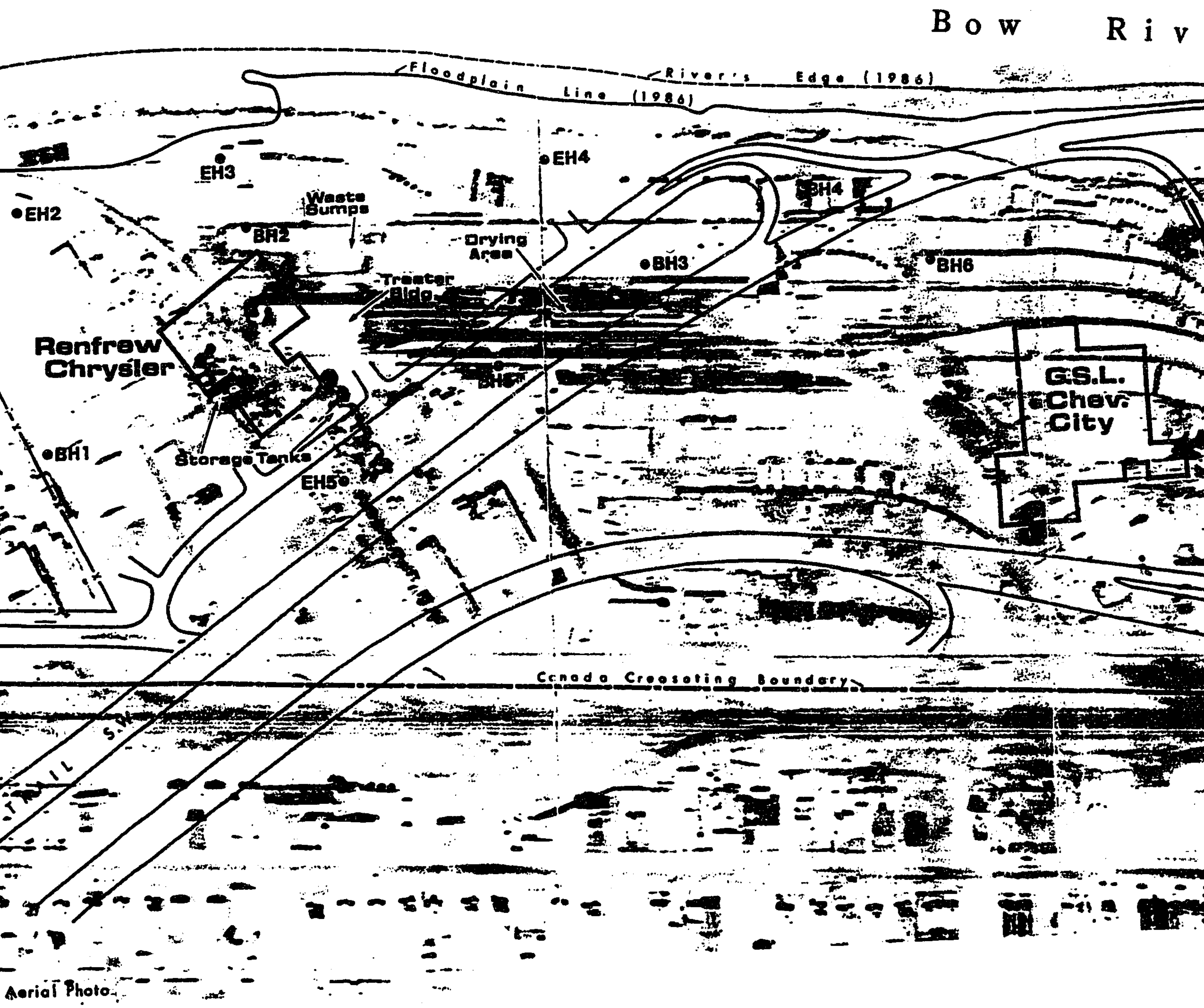


FIGURE E.2-2 : SITE FACILITIES IN 1951 AND A
PRESENT FACILITIES AT THE CA
ASSOCIATES, 1989B)

  - 2 soil vapour samples were selected for hydrocarbon characterization.

- Laboratory analysis of the soil samples indicated:
  - all 9 soil samples contained creosote concentrations above the Quebec Level C value of 200 ppm for total polynuclear aromatic hydrocarbons (PAHs) (Table 4.4). Five samples contained creosote in excess of 10 000 ppm. These 5 samples were recovered from former processing, product storage and waste disposal areas (p. 15, Table 4.4, Table 4.6).
  - 7 soil samples contained PCP concentrations in excess of the Quebec Level C value, which is 5 ppm (the Quebec assessment criteria are included in Appendix B of this report). Six of these values were in excess of 100 ppm, and 2 of these samples from the DNAPL (BH3 and BH4) contained PCP in excess of 1,000 ppm (Table 4.4, Table 4.6).
  - the 2 soil samples recovered from the DNAPL area (BH3 and BH4) contain large concentrations of dibenzofurans and dibenzodioxins. Unfortunately, these concentrations are not further categorized into the various chlorinated isomers of these compounds (Table 4.6).
  - the most contaminated soil is near BH2, which is situated near the former sludge lagoons (p. 28-29).

- Laboratory analysis of the groundwater samples indicated:

- all 3 samples analyzed contained creosote in excess of the Quebec Level C value of 0.050 mg/L for total PAHs (Table 4.7). The highest concentration was 23 mg/L from BH5, which is located in the former timber drying area (Table 4.7). This sample likely contained some distinct-phase preserving fluid such as DNAPL, an emulsion, or a blob, because the PAH concentrations exceed compound solubility (section 1.4.2.1).
- all 3 samples analyzed contained PCP in excess of the Quebec C value of 0.005 mg/L (Ministére de l'Environnement du Québec, 1988). The highest concentration was 38 mg/L, again recovered from BH5 (Table 4.7). This value strongly indicates the presence of free product, because it is several times the aqueous solubility of PCP (section 1.4.1.1).
- the most contaminated groundwater exists near BH5, which is located in the former timber drying area (p.30).

- Laboratory analysis of the two vapour samples revealed that 85.75% of the BH1 sample and 99.98% of the BH7 sample was comprised of methane (by mass) (p. 24).

- Although only two soil vapour samples were characterized (BH1 and BH7), bulk combustible vapour concentrations were measured in numerous borehole soil samples. This analysis revealed that combustible vapour concentrations in the seven boreholes frequently exceeded 100% of the lower explosive limit (LEL) (Table 4.2). These vapour concentrations may pose a threat to occupants on the site, as well as to any persons performing future excavations (p. 31).

- A dense non-aqueous phase liquid (DNAPL) on the bottom of the aquifer was noted in BH3 and BH4 as shown in Figure E.2-1. This dense product extends down to the bedrock in BH3 and BH4, and there was some evidence that the DNAPL had migrated along bedrock fractures. The DNAPL may be over 1.5 m thick, and was chemically characterized (p. 13, Table 4.3, Table 4.6).

- A 4 mm thick light non-aqueous phase liquid (LNAPL) was observed on the water table in BH3. This LNAPL was not chemically characterized (p. 15, Table 4.3).

- Principal groundwater flow directions are north and northeast towards the Bow River (p. 27). There are no known users of groundwater near the site (p. 24).

- The O'Connor Associates report concluded that five different types of contamination exist at the former Canada Creosoting Ltd. site (p. 26):
  - contaminated soil;
  - combustible vapours in the soil;
  - LNAPL on the water table;
  - contaminated groundwater; and
  - DNAPL on the bedrock.

E.2.2 Technical Commentary

Technical commentary on the O'Connor Associates report is summarized below.

- No detection limits or QA/QC procedures used during sample analysis were described in the report.

- No remediation options for the site were discussed.

- Analysis for dibenzodioxins and dibenzofurans was performed on the soil samples containing dense product from BH3 and BH4. However, the various isomers and congeners of polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) were not identified specifically, and no dioxin or furan analysis was performed on any other soil samples. Dioxins and furans, particularly those containing 8 chlorines, exist as impurities in technical-grade PCP. The toxicity of dioxins and furans varies widely between the different congeners and isomers (section 1.4.1.3.2), and a breakdown of the various forms is required for adequate hazard assessment.

- Only 7 boreholes were drilled, and only 9 soil samples and 3 groundwater samples from these boreholes were analyzed for PCP and creosote content. This number is inadequate to provide sufficient characterization of soil and groundwater contamination at a site occupying about 18 hectares. Additionally, only two soil vapour samples were characterized.

- No analysis was performed on the LNAPL encountered in BH3. This LNAPL could arise from some off-site contamination, such as from leaking underground gasoline storage tanks, common in most cities. However, it is most likely that the LNAPL arises from on-site contamination, because a groundwater sample from BH5 contained 38 mg/L PCP, several times PCP's aqueous solubility. Without LNAPL characterization, the source and composition of this non-aqueous phase liquid cannot be determined. (Golder Associates sampled the LNAPL, and its composition suggests that it is a mixed creosote-PCP hydrocarbon phase.)

- The method of sampling vapour concentrations was not identified, nor confidence intervals given. This information is needed to evaluate the accuracy of test results.

- From the description on page 5 of the O'Connor Associates report, it appears as if monitoring wells and not piezometers were installed at this site. Monitoring wells are screened over large intervals, whereas piezometers are screened over small intervals. Piezometer clusters are usually used at a site to determine the vertical distribution of contaminants within an aquifer, which is particularly desirable at sites involving multiphase

contamination (i.e., LNAPL, contaminated groundwater, DNAPL).

E.3 Former Peerless Wood Preservers - Cayley

E.3.1 Site Characterization

The following is a brief summary of the testing performed at the Cayley site by Monenco Consultants Limited (1989), and their conclusions based on data collected. Interested readers desiring further information are referred to the Monenco report, to which the page numbers and table numbers in parentheses refer.

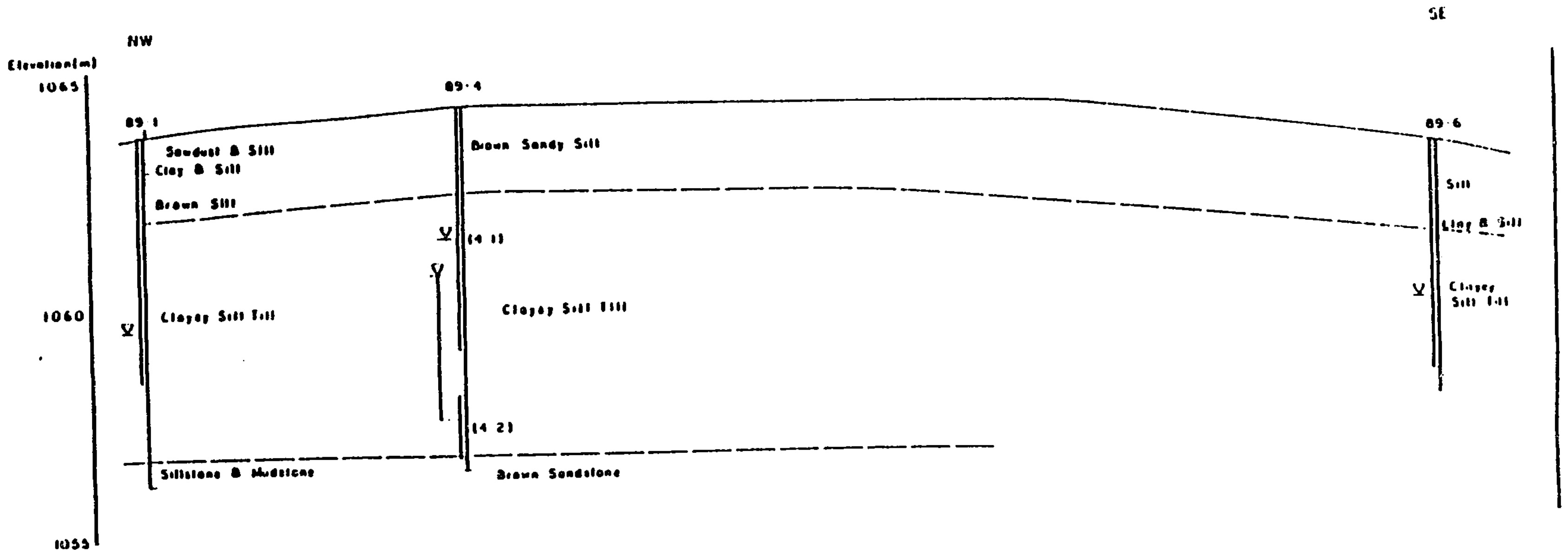
- The Cayley site is underlain by a thin layer of lacustrine silt and clay to a maximum depth of 2 metres. The lacustrine layer is underlain by a dense clayey silt till to a depth of 7 or 8 metres. This till is underlain by mudstone, siltstone and sandstone bedrock (p. vi-vii). A stratigraphic cross-section of the site is presented in Figure E.3-1.

- The water table occurs at a depth of about 3 metres below the ground surface (p. vii).

  The clayey silt till is essentially <u>unfractured</u>, and exhibits an extremely low hydraulic conductivity of 7.5×10^{-8}cm/s (p. vii).

- PCP was the only preservative ever used at this site (p. 2-6).

- Spent PCP treating fluid was conveyed to a sludge pond via unlined ditches. This pond was lined with a 6 to 10 mm



HORIZONTAL SCALE · 1 1000
VERTICAL SCALE · 1 100

NOTE Water Levels Measured
@ March 13, 1989

FIGURE E.3-1 : STRATIGRAPHIC CROSS-SECTION OF THE CAYLEY SITE (MONENCO CONSULTANTS LIMITED, 1989) construction grade plastic (p. 2-2). This liner is now in a poor state of repair (p. 2-8) (when visiting the site, I observed that the liner was torn in places and brittle). A schematic of the operating plant is presented in Figure E.3-2.

Numerous spills and leaks in the tank area occurred over the years (p. 2-7).

- The soil sampling program is summarized below:
  - 228 soil samples were collected from 67 sites (p. 3-1).
  - 81 of these samples were submitted for analysis (p. 3-4).
  - 26 of these samples were analyzed directly for PCP content (Table 3-2)
  - All 81 samples were analyzed for a parameter described as oil and grease content (p. 3-4). The analytical method used a dichloromethane extraction that also extracted any PCP in the sample (p. 3-6). This analysis would be more correctly described as "dichloromethane extractable organics".

- Laboratory analysis of the soil samples indicated the following:
  - Of the 26 samples analyzed for PCP (Table 3-2):
  - 16 had non-detectable concentrations (the detection limit was quoted as 0.1 ppm for a toluene/sodium hydroxide/hexane extraction [Table 3-1]).
  - 3 samples indicated PCP levels below 100 ppm.
  - 5 samples had concentrations between 100 and 1 000 ppm.

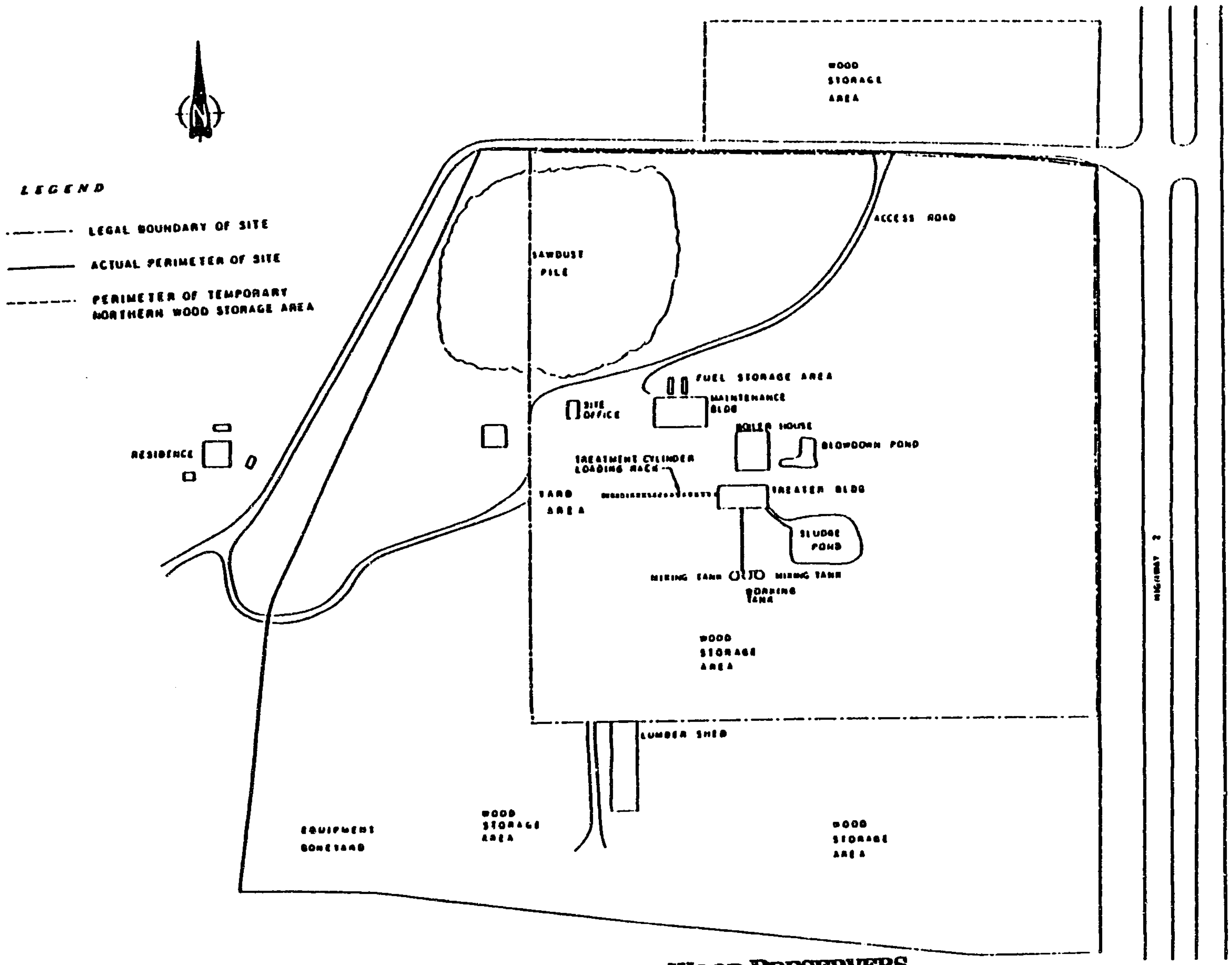


FIGURE E.3-2 : SCHEMATIC DIAGRAM OF THE PEERLESS WOOD PRESERVERS LIMITED SITE (MONENCO CONSULTANTS LIMITED, 1989)

  - 2 samples contained PCP above 1 000 ppm. The highest concentration was 6 900 ppm.

- The most contaminated soil samples originated from the sludge pond area (samples 62 and C) (p. 3-19), as shown in Figure E.3-3.

- A good correlation between "dichloromethane extractable organics" concentrations and PCP levels was determined to exist in the data from this study (p. 3-17).

- The groundwater sampling program is summarized below:
  - 6 monitoring wells and 1 piezometer were installed on the site (p. 3-6). The monitoring wells are screened for a 3 metre long interval (p. 3-9), and the piezometer is screened for 1 metre (p. 3-10).
  - 5 of the monitoring wells and the 1 piezometer were sampled. Well 89-1 was not sampled as it was recovering too slowly (p. 3-10).
  - All 6 samples were analyzed for routine potability parameters, trace metals and organic indicator parameters (total organic carbon, total hydrocarbons and PCP content) (p.3-11).

- Laboratory analysis of the groundwater samples revealed the following:
  - 4 of the 6 samples contained PCP concentrations in excess of 0.005 mg/L, which is the Quebec C level (the Quebec

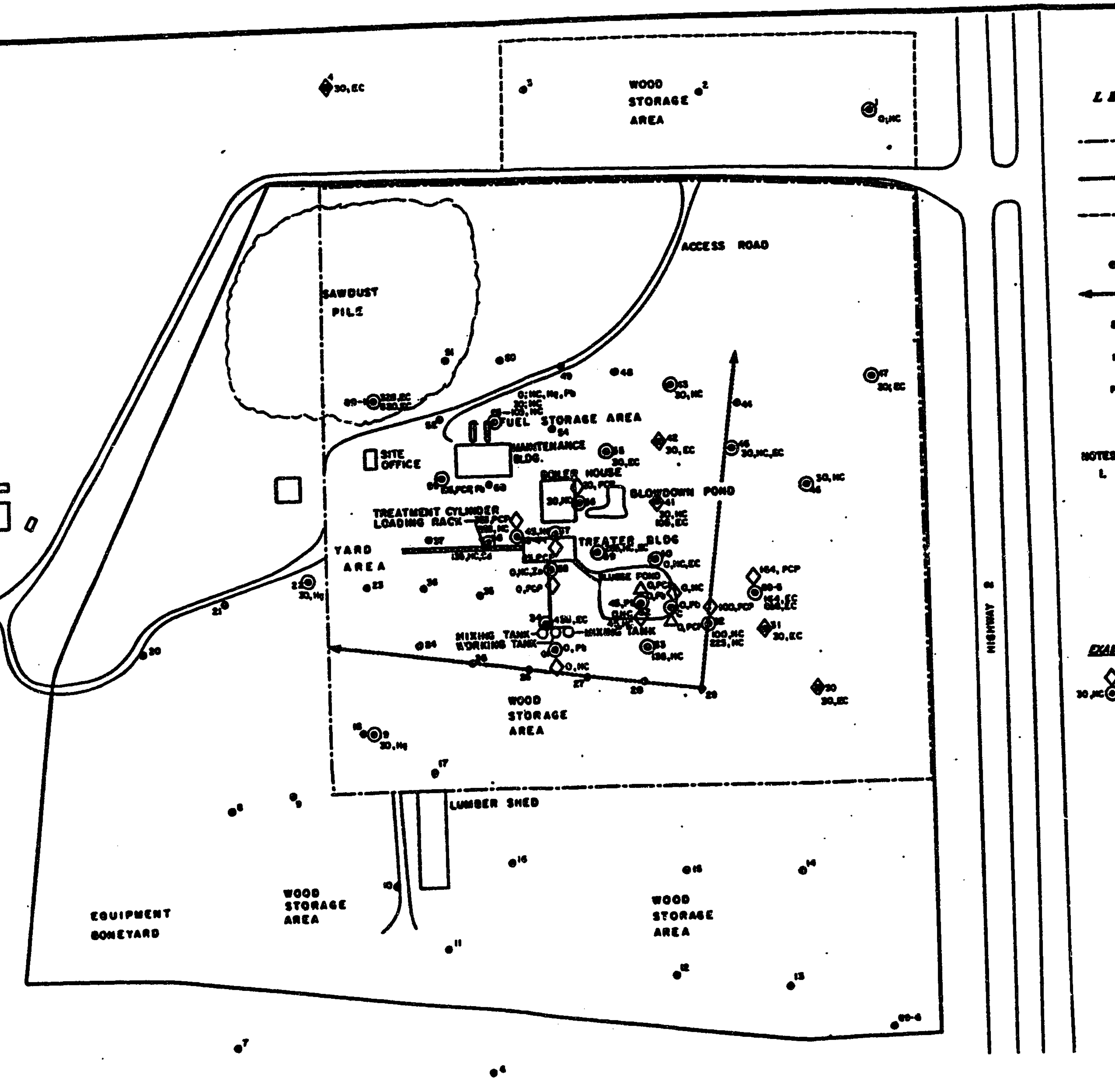


FIGURE E.3-3 : SAMPLING LOCATIONS AND PA
THE CAYLEY SITE (MONENCO

assessment criteria are included in Appendix B of this thesis). Three of these values were above 1 mg/L (Table 3-6):

  - Two values were less than 5 mg/L PCP (5 mg/L is PCP's aqueous solubility).
  - The third concentration was 33 mg/L PCP, several times PCP's aqueous solubility.
- The groundwater is highly mineralized; total dissolved solids, sulfate and fluoride concentrations exceeded Canadian Drinking Water Guidelines in many of the samples (p. 3-29).
- The detection limit for PCP analysis of the groundwater samples was listed as 0.2 μg/L (p. 3-30).

- The most contaminated groundwater samples were recovered from wells near the sludge pond (Figure E.3-3).

- Two farms are located within 0.5 km of the Cayley site (p.3-31), but domestic wells in the general area are cased to below 23 m to avoid the "hard" water in the upper bedrock zones (p. ix).

- The study failed to locate any well on-site, which may have supplied makeup water to the steam boiler (p.3-31).

- On page vii of their report, Monenco Consultants Limited concluded that the low permeability of the till underlying the Cayley site is expected to restrict the horizontal movement of contaminants to the vicinity of the process area. However, they also commented that PCP may have migrated vertically through the till and into the bedrock which underlies the site.

E.3.2 Technical Commentary

Technical commentary on the Monenco Consultants Limited report is summarized below.

- No analysis for polynuclear aromatic hydrocarbons (PAHs) was performed on any soil or groundwater samples. PAHs are present as impurities in the diesel fuel carrier used in PCP mixtures, and PAH analysis could also conclusively show whether creosote was ever used at this site.

- No analysis for dioxins or furans, present as impurities in technical-grade PCP, was performed on any soil or groundwater samples.

- The Monenco laboratory procedure for PCP extraction from soil samples had to be modified because of order-of-magnitude differences between PCP concentration results from Enviro-Test and Monenco (p. 3-19). After modification of Monenco's analytical procedure, approximately one-half of the initial PCP analyses were rerun (p. 3-20). The soil contamination data in Figure E.3-3 thus arises from two different analysis procedures, one of which leads to significantly lower results.

- Although the number of soil samples analyzed was sufficient, the number of groundwater monitoring wells installed on-site was not. Six monitoring wells and one piezometer were installed on-site, but three of the wells are perimeter wells (89-2, 89-3, 89-6), installed to determine if contaminated groundwater had migrated off-site (Figure E.3-3). Thus only three wells and one piezometer are actually located within the operating site boundaries. In addition, only one piezometer was installed on this site. This one piezometer may not be sufficient to accurately determine the vertical hydraulic gradient, the most significant gradient in such impermeable soils.

E.4 Former Deep Basin Wood Preservers - Elmworth

E.4.1 Site Characterization

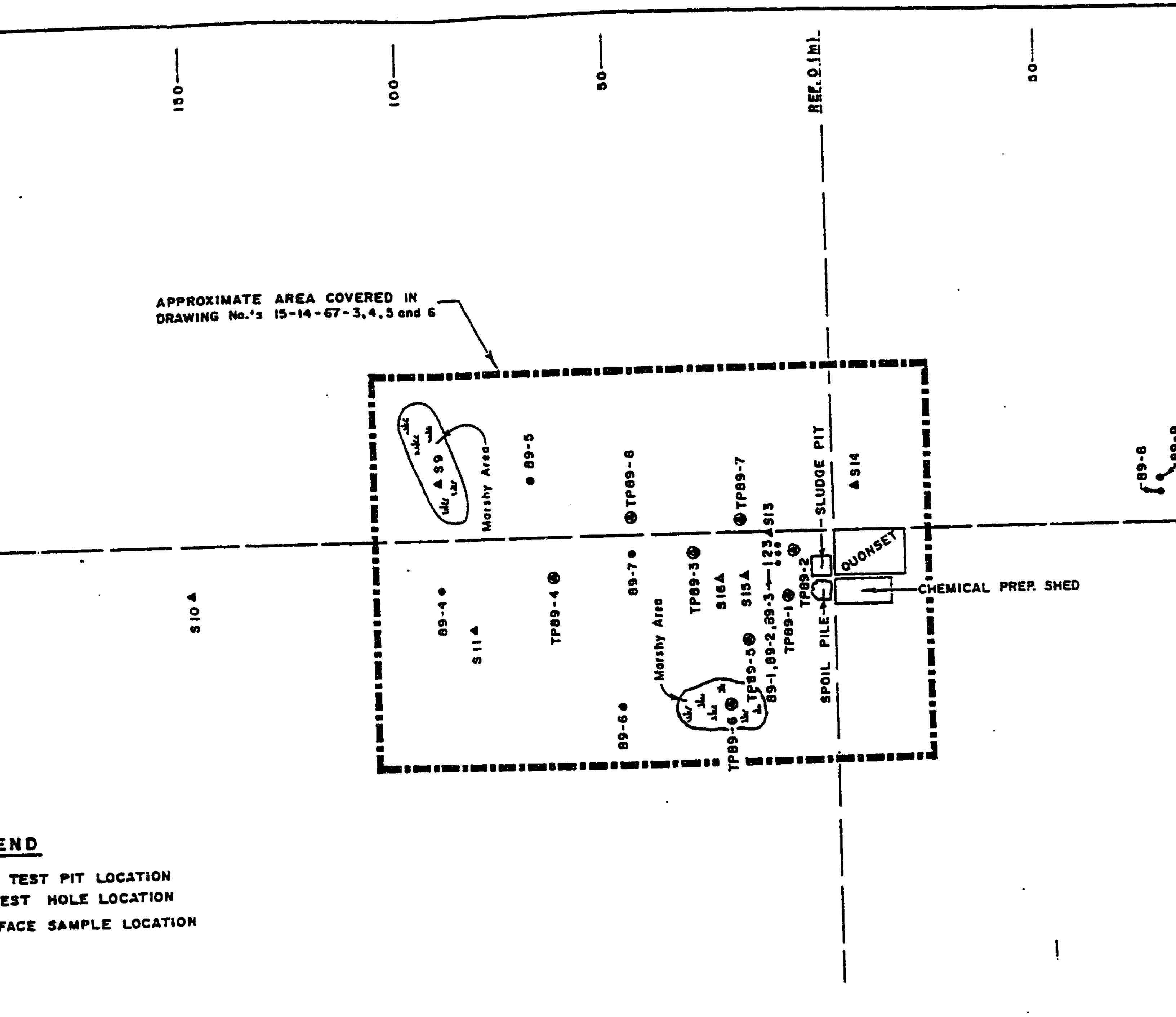
The following is a brief summary of the testing performed at the Elmworth site by Thurber Consultants Ltd. (1989), and their conclusions based on test results. Interested readers desiring further information are referred to the Thurber report, to which the page numbers, table numbers and appendices in parentheses refer. Pertinent site features and sample locations are illustrated in Figure E.4.1.

- The sludge lagoon is synthetically lined and is located directly below the pressure vessel outlet (p.2) (there was thus no transmission of any sludge through ditches or trenches, as seen in Figure E.4-1).

- Treated posts were normally transported off the property directly from the drying platform which was adjacent to the pressure vessel (p.2).

- The Osmose fluid was reused, and any sludge was deposited in the sludge pit (p.2).

- The CCA sludge was periodically removed from the sludge pit, placed in open barrels and transported to a sawdust and chip fill area approximately 100-120 m northeast of the Quonset hut. The



No. 15-14-67-1 FOR SITE LOCATION.
PITS SURVEYED BY THURBER CONSULTANTS LTD. AND ARE APPROXIMATE ONLY.

FIGURE E.4-1 : ELMWORTH SITE AND
(THURBER CONSULTA

location of this landfill was not discovered by Thurber personnel (p.2, 12).

- The sludge pit was frequently overtopped during snowmelt and heavy rainfall events (p.10).

- Soil sampling (p.3):
    - 8 test pits were excavated with a backhoe (TP89-1 through TP89-8).
    - 9 test holes were drilled using a truck mounted auger rig (89-1 through 89-9).
    - 8 additional surficial samples were also collected (S9 through S16).

- Soil drilling revealed that the site is underlain by a sequence of <u>highly plastic</u> lacustrine clay and silt overlying transitional lacustro-till deposits over medium plastic clay till. Weathered siltstone and claystone underlay the clay till at depths of about 14 m below ground surface (p.17). The clay till was also observed to contain fractures and localized sand zones (p.6). Variable fill and/or organic rich topsoil were encountered in the near surface beneath the site (p.5). A stratigraphic cross-section through the site is presented in Figure E.4-2.

- Soil testing (Table 3, p.9):
    - 32 samples were analyzed for Cu, Cr and As.

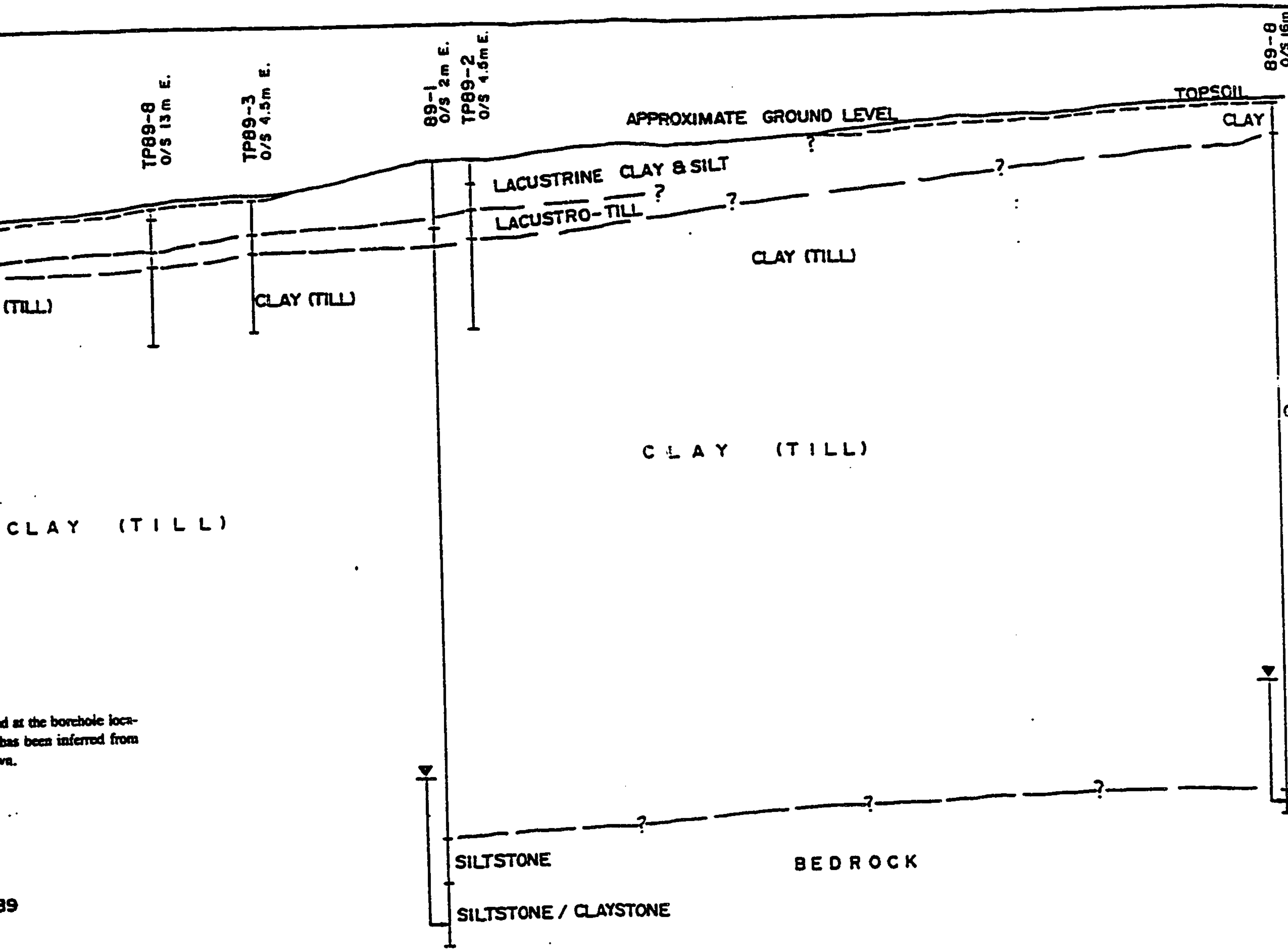


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FIGURE E.4-2 : CROSS-SECTION OF THE ELM
(THURBER CONSULTANTS LT

- 6 samples contained Cu concentrations exceeding the Quebec level C value (500 ppm).
- 5 samples indicated Cr concentrations greater that the Quebec level C value (800 ppm).
- 17 samples contained As concentrations exceeding the Quebec level C value (50 ppm).
- Below 0.5 m depth, all values of Cu, Cr and As were below the Quebec level A guidelines of 50, 75 and 10 ppm respectively.
- dust and material in the chemical preparation shed contains extremely high concentrations of As, Cr and Cu (i.e. greater than 10 000 ppm).
- several of the surface soil samples also indicate considerable CCA contamination.
- the approximate limits of contamination of the surface soil are presented in Figures E.4-3, -4, -5.

- In terms of soil remediation, two zones of significantly different levels of contamination exist at this site, as shown in Figure E.4-6 (p.10, 16):
  - zone 1 is comprised of the heavily contaminated areas, and includes the chemical preparation shed, drying platform, sludge pit and adjacent areas, as well as the slough 45 m northwest of the sludge pit. The two zone 1 areas contain roughly 300 m^3 of highly contaminated soil about 0.5 m deep. This material is prohibited from landfill disposal by the

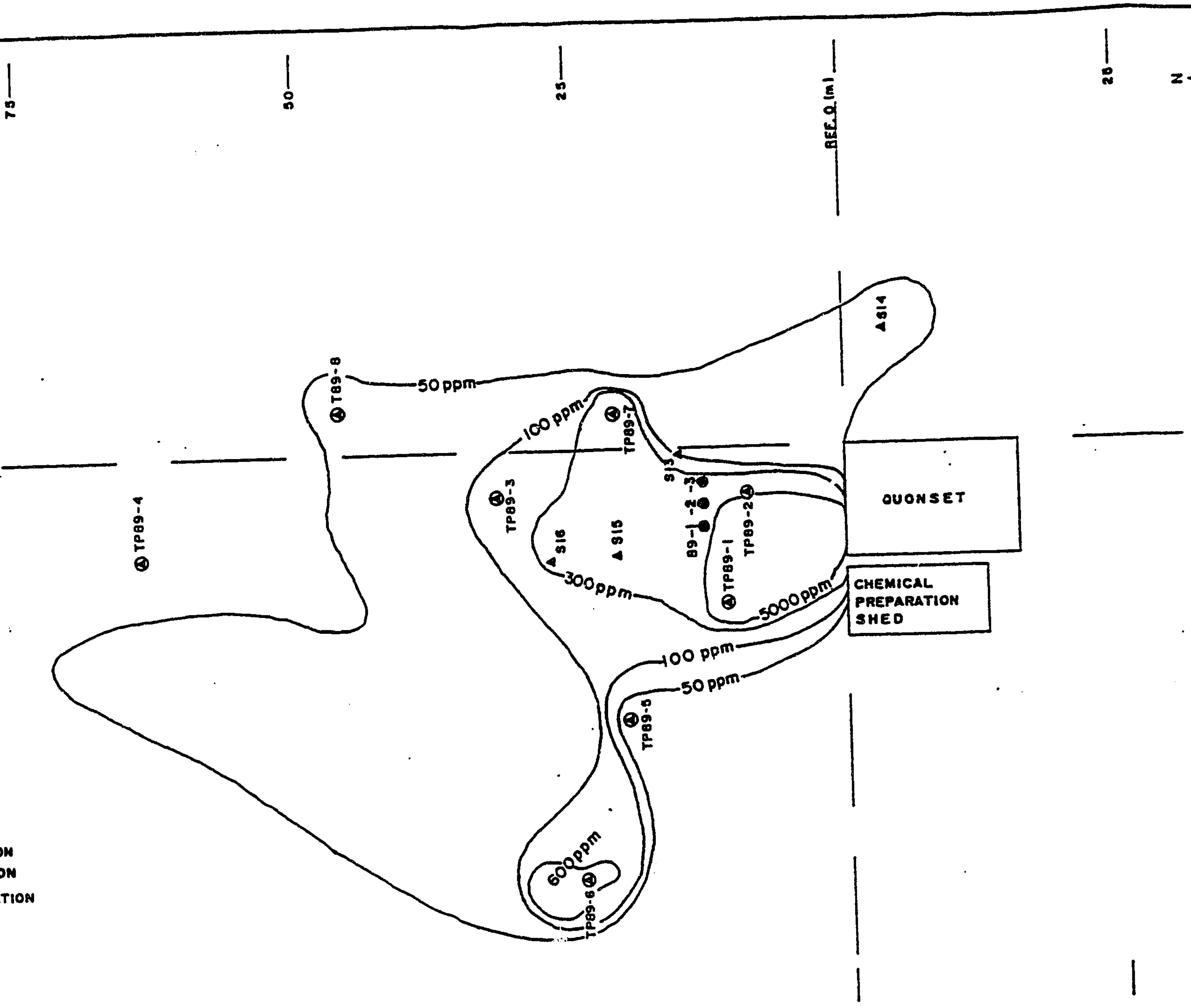

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FIGURE E.4-3 : SURFACE SOIL AREA CONTA
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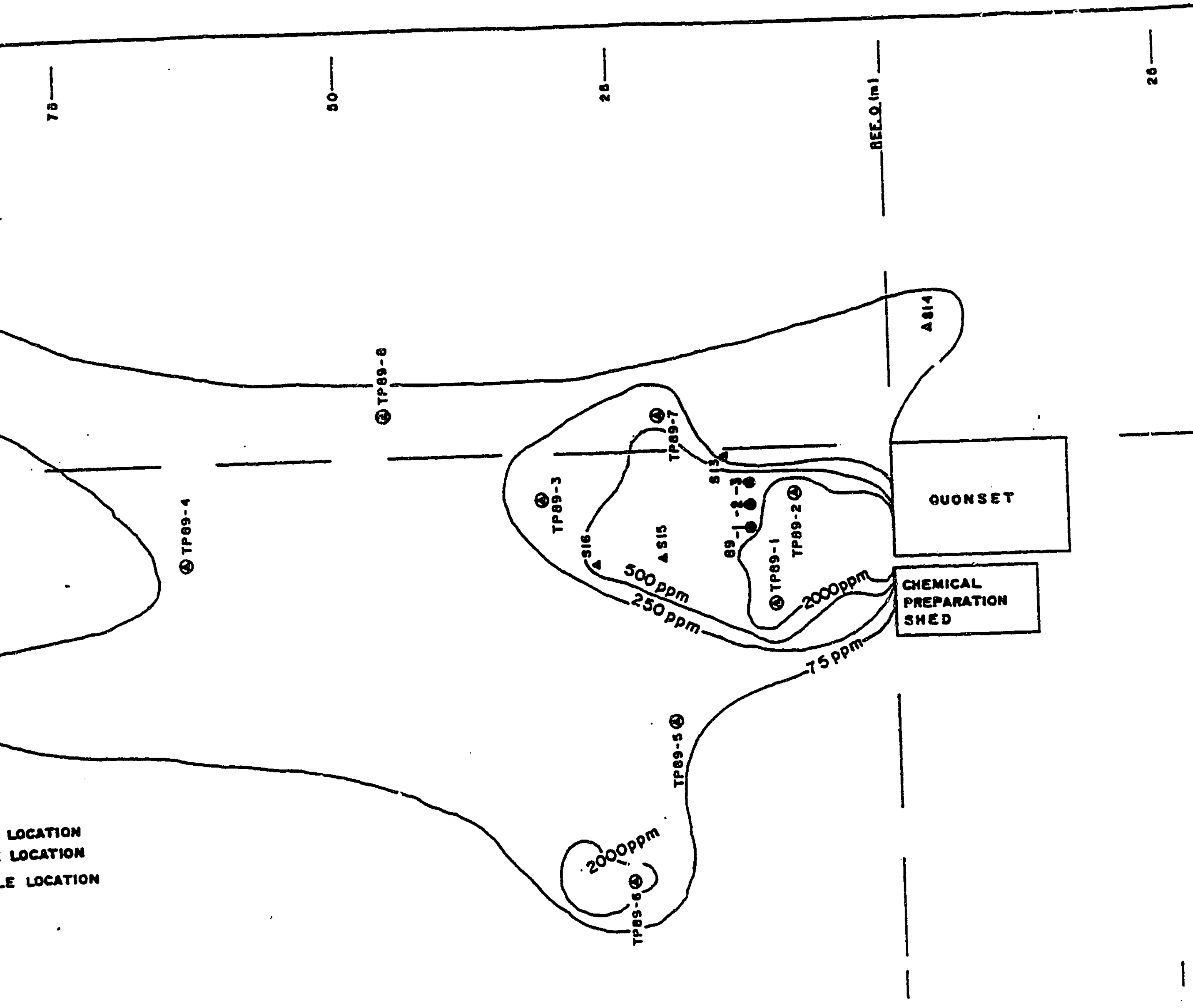

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FIGURE E.4-4 : SURFACE SOIL AREA CONTA
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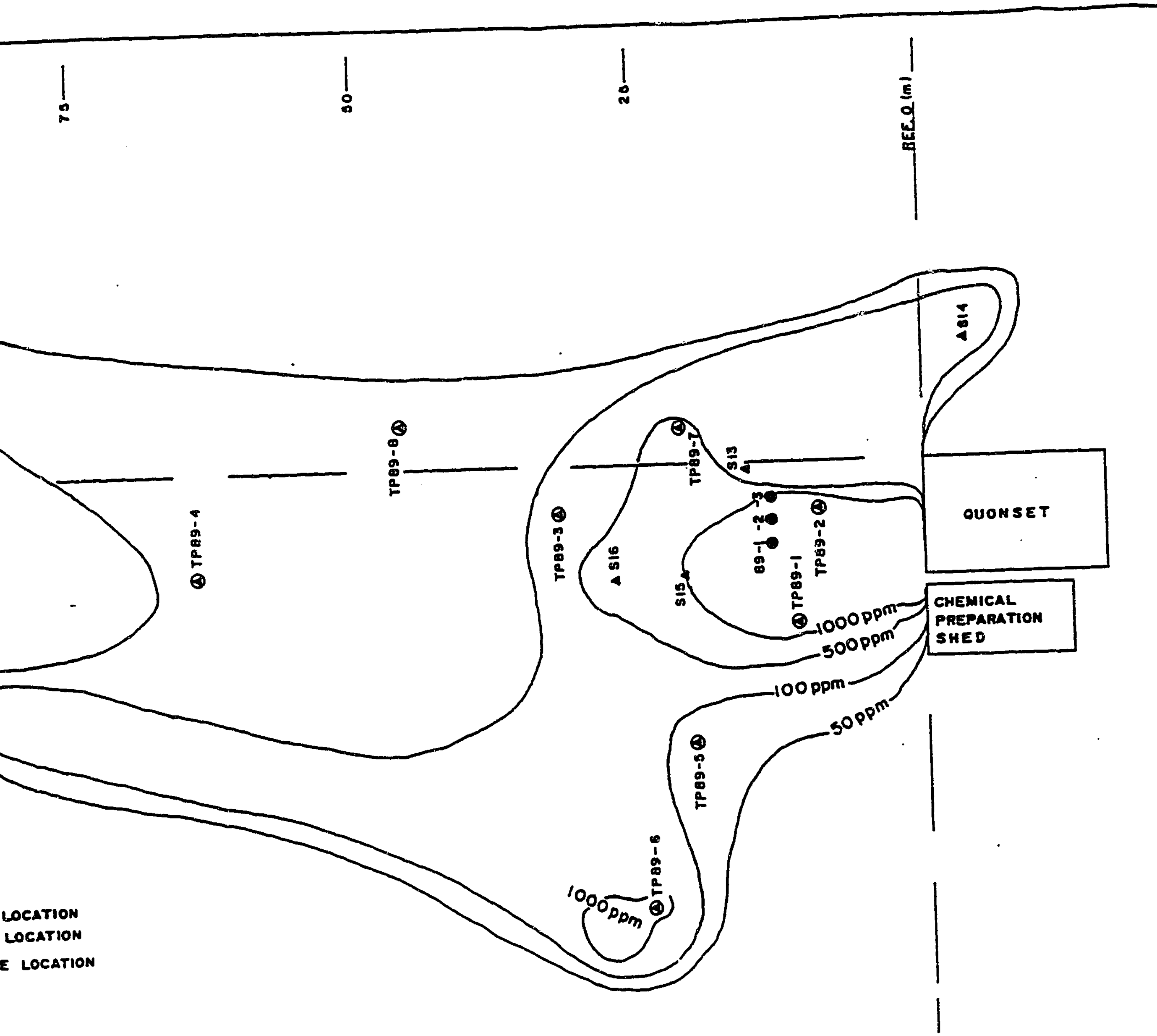

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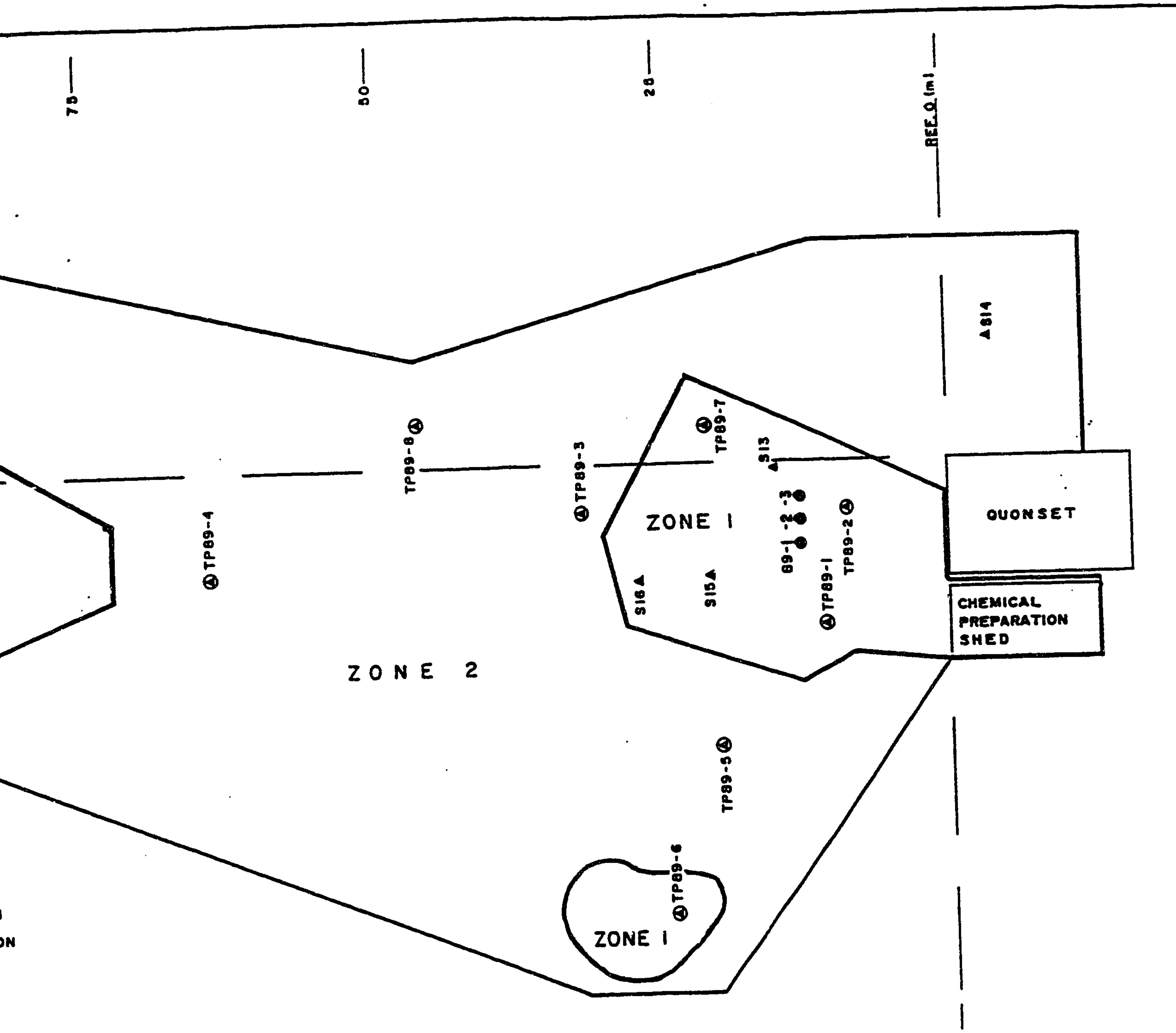
FIGURE E.4-5 : SURFACE SOIL AREA
ARSENIC (THURBER



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HEMICAL ANALYSES FROM THE TEST SITES.

FIGURE E.4-6 : ESTIMATED ZONES OF SU
BY CCA (THURBER CONSU

Province of Alberta's Hazardous Waste Regulations (this last conclusion is in error, as will be discussed in section E.4.2).

- zone 2 represents a larger, less contaminated area, which became contaminated from the operational activities and effluent overflow from the sludge pit during heavy rainfall events. Zone 2 contains roughly 900 m^3 of soil about 0.15 m deep with a lower level of contamination. This material should be disposed at an approved municipal landfill nearby.

- The end use of this property is expected to be agricultural and the soil should thus be decontaminated to a standard at or below the C level of the Quebec guidelines (p.15, 16).

- To sample the groundwater beneath the site, standpipe piezometers were installed in the 9 test holes to different depths, and were slotted for 0.9 m (p.3).

- Groundwater in the general area is derived from siltstone/ sandstone/claystone units near the bedrock surface. Perched localized water bearing zones were also present within the clay till. The two zones do not appear to be hydraulically connected (p.12, 17, Appendix C).

- Free water was not encountered during the investigation at any of the test sites. Additionally, water level measurements undertaken 28 to 29 days after piezometer installation indicated the presence of water in only 5 of the 9 piezometers (p.6).

- The groundwater levels in the five productive piezometers indicated a slight hydraulic gradient from the south to north, which parallels the topographical gradient (p.7, 17).

- Groundwater testing (Table 1, Table 4):
  - one sample was collected from each of the five productive piezometers.
  - As, Cr and Cu concentrations from the 5 samples were all <u>less than</u> values set out in the Guidelines for Canadian Drinking Water Quality (included in Appendix B of this thesis) (the Cr concentration in piezometer 89-5 was equal to the maximum acceptable value of 50 ppb).
  - the sample with the highest Cu, Cr and As concentrations was obtained from piezometer 89-5, which is located approximately 70 m north of the sludge pit. The water level in this piezometer is roughly 5.5 m below ground level (bgl).
  - the sample obtained from piezometer 89-1 near the sludge pit contained only background concentrations of Cu, Cr and As. The water level is about 12.8 m bgl at this location.

- 16 producing water wells exist with in a 1 km radius of the former plant. The shallowest completion interval for these wells begins around 12 m bgl (p.1, Appendix C) (these 16 wells are actually located within a 2 mile radius of the Deep Basin site).

- Some shallow migration of CCA to groundwater has occurred at this site. However, all groundwater sampled was at or within acceptable limits. In terms of remediation, the groundwater contamination at this site is not thought to be significant, and it is expected that it can be remedied by removal of contaminated soils and cleanup of the sludge pit (p.14, 18).

- The site contains a number of 45 gallon drums, some of which are full of an unknown liquid, as well as derelict vehicles, metal debris and household wastes. This material should be tested for contamination, cleaned if necessary, and classified for disposal (p. 15, 17).

E.4.2 Technical Commentary

Technical commentary of the Thurber Consultants Ltd. report is summarized below.

- No hydrogeological parameters were determined for this site. Parameters such as hydraulic conductivity and soil cation exchange capacity would be useful in assessing the hazard posed by this site and evaluating remediation alternatives.

- 3 productive wells are located on the same quarter of land as the former plant site (SW 1/4, 8-70-12-W6M). All three of these wells are currently being used for potable water, as will be discussed in tsection 4.4.2. The water from these wells should have been analyzed, considering their proximity to the site and the known human health effects of excess chromium and arsenic.

- Only 5 groundwater samples were analyzed, and only 3 of these samples originated from piezometers located on the actual plant site. More samples should have been analyzed, though it is understood that 4 of the piezometers on-site were dry.

- pH and redox values for soil and groundwater were not collected. These parameters are of fundamental importance to the mobility of metals in soil/ water systems.

- On page 16 of their report, Thurber stated:

  > "Based on the Province of Alberta's Hazardous Waste Regulation 505/87, as a minimum, contaminated soil containing arsenic and chromium levels greater than 500 ppm, should be directed to Swan Hills Special Waste Disposal Facility. Soil with a lower level of contamination may be directed to an approved secure landfill."

  The Hazardous Waste Regulation specifies in section 17(3)(f) that <u>liquid</u> wastes containing arsenic and chromium (+6 valence) in concentrations equal to or greater than 500 mg/kg could not be disposed of into any may refer to the residual sludge pond materials, soils are not logically included in this classification. In addition, not all of the chromium in the sludge pit and adsorbed to soil will exist in the +6 valence; the amount of chromium existing in the various valence states will depend on the redox potential of the soil/water matrix (section 1.5.2.2.1). There is apparently no specific regulatory limit in Alberta on landfill disposal of CCA contaminated soils. The scientific reasons for this discrepancy are not obvious because metals present in contaminated soils can be mobilized by leachate in a landfill. Approval of hazardous waste disposal to a landfill is at the discretion of the Director of Standards and Approvals provided the wastes are not listed in section 17(3) of the regulations. This situation does not seem to preclude the disposal of soils contaminated with arsenic and chromium into a landfill which may receive other liquid wastes. The net effect of such a situation on mobility of the arsenic and/or chromium adsorbed to soil could be the same as if liquid wastes containing arsenic and chromium were deposited. The latter is not allowed where concentrations exceed 500 mg/kg.

E.5.1 Site Characterization

The following is a brief summary of the testing performed at the Faust site by Hardy BBT Ltd. (1989), and their conclusions based on the test results. Interested readers desiring further information are referred to the Hardy BBT report, to which the page numbers and appendices in parentheses refer. Pertinent site features and sample locations are illustrated in Figure E.5-1.

- The plant operated from 1961 to 1973. Raw timber was sawed, peeled and treated at this site. Site facilities included a teepee burner, peeler, bark piles and wood treating buildings (p.1).

- Elevation of the site is approximately 580 m above sea level (asl) and the surrounding landscape slopes very gently northwest towards Lesser Slave Lake where the water level averages an elevation of 577 m asl (p.6).

- The site overlies a thick sequence of interbedded deltaic and outwash sands, silts and clays. Several till units containing coarse glaciofluvial or preglacial gravels also occur at depth. The site is located in a discharge zone with hydraulic heads in the bedrock and gravels underlying the site often exceeding ground elevations. Consequently, flowing wells are common in this area. This hydrogeological description of the site was taken mainly

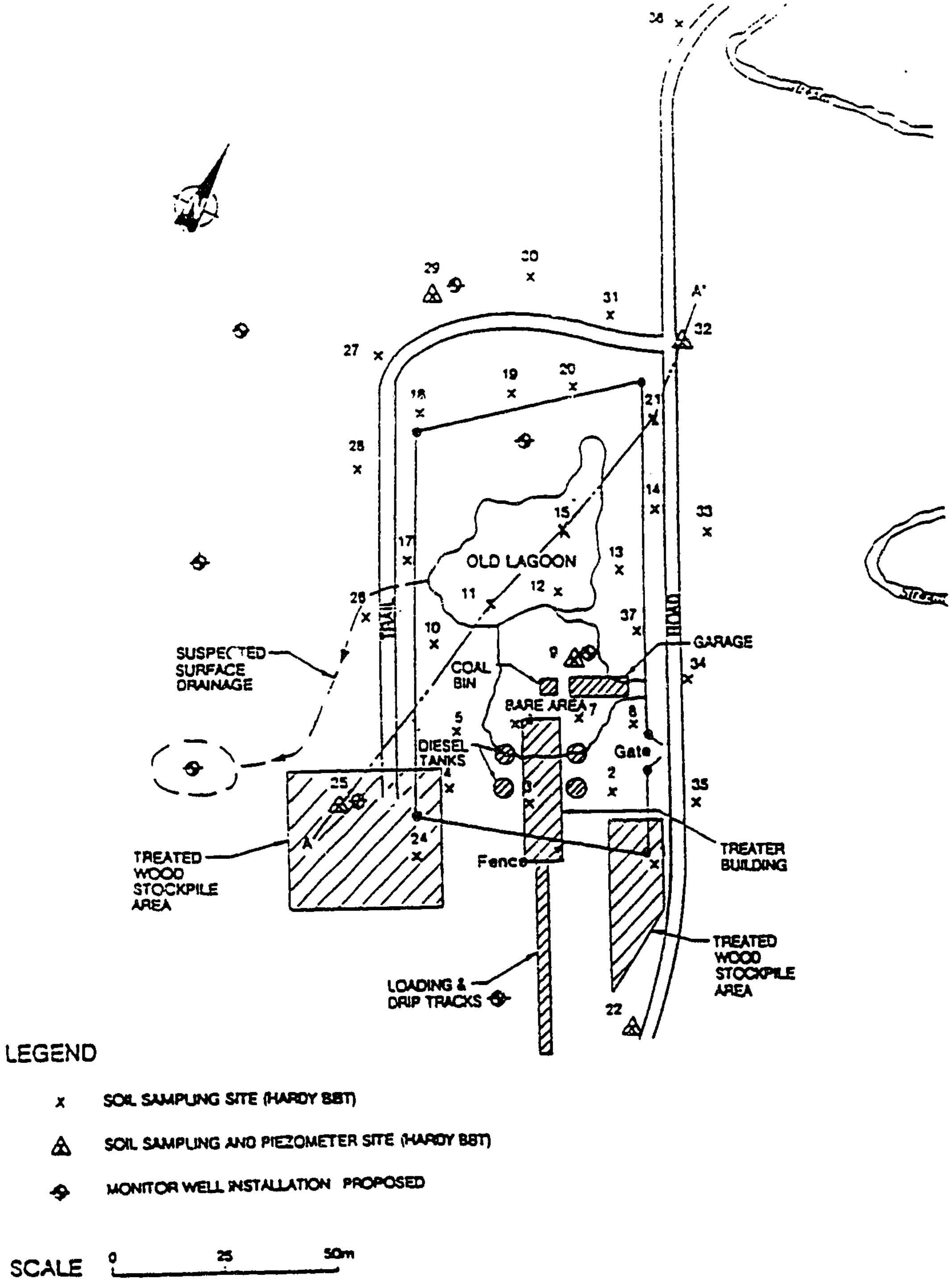

FIGURE E.5-1 : FACILITY LAYOUT AND SAMPLING LOCATIONS (STANLEY ASSOCIATES ENGINEERING LTD., 1990)

from an Alberta Research Council report on the Lesser Slave Lake area. A stratigraphic cross-section through the site is presented in Figure E.5-2 (p.6, 7).

- Local groundwater accumulation and flow appears to concentrate in sand units with a number of shallow wells (within 500 m to the south) deriving domestic water supplies from these sand units. There is some indication these sand units are discontinuous (p.11).

- Soil at this site was sampled at 35 locations, shown in Figure E.5-1. Standpipe piezometers consisting of four 5-foot PVC sections with a slotted lower section were installed at 5 such locations (p.3, 4) (from this report it appears as if the piezometers were slotted for 5 feet).

- Sampling and analysis (p.4, Appendix A):
  - one sample was obtained from each of the five piezometers the day after installation.
  - 106 soil samples were collected from the 35 sample locations.
  - the 5 groundwater and 106 soil samples were analyzed for PCP by gas chromatography, arsenic by hydride generation and for a suite of other metal including Cu and Cr using an ICP scan.

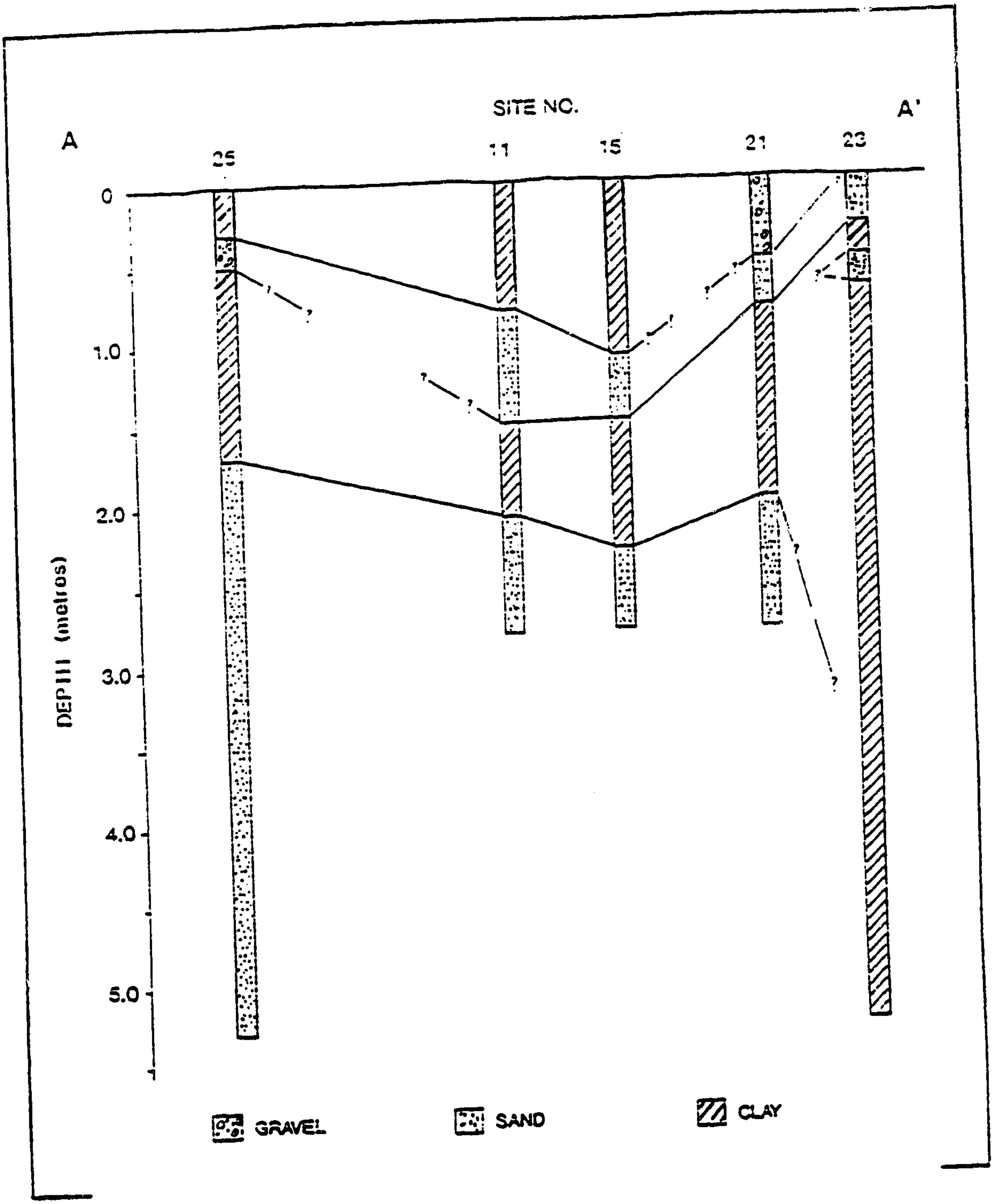

FIGURE E.5-2 : STRATIGRAPHIC CROSS-SECTION THROUGH FAUST SITE (HARDY BBT LTD., 1989)

- **Results of the soil analyses (p.7-10):**
  - elevated PCP concentrations were found at most sites within the fenced area. Highest concentrations occur in the surface soil of the bare area, where values ranged from 380 to 5000 ppm PCP. PCP concentrations decreased with depth.
  - elevated PCP concentrations were detected at site 24 and 36 outside the fenced area.
  - the highest arsenic value was 1500 ppm in a sample from site 6 in the bare area. The other two sites in the bare area contained arsenic below the Quebec level C value. Arsenic concentration decreases sharply with depth (the Quebec assessment criteria are included in Appendix B of this thesis).
  - high concentrations of arsenic occur within the surface 30 cm at selected locations outside the fenced area, such as at sites 24 and 25.
  - elevated chromium concentrations were only detected at a few sites, which correspond with those sites displaying elevated arsenic concentrations. These higher chromium concentrations do not exceed the Quebec level C value of 800 ppm.
  - copper concentrations are indicative of background values and are well below the Quebec level C limit.
  - all other metals tested for were well below their respective Quebec guideline level C limit.

- Results of the groundwater analyses (p.10-11):
  - the groundwater at site 9 in the bare area is heavily contaminated with PCP (1800 ppb), corresponding with the elevated PCP levels throughout the soil profile at this location.
  - PCP is below detection (less than 0.1 ppb) at site 32.
  - the other three piezometers contain PCP above the Quebec level C value of 5 ppb for phenolics.
  - a slightly elevated arsenic concentration was apparent at site 9. However, concentrations of As, Cr, Cu and other heavy metals are well below their respective Quebec level C limit.

- The affinity of PCP for organic sediments likely resulted in the soil retaining a large proportion of contaminants immediately below the site. This assumption is supported by the soil data at this site. In addition, further dispersion of any aqueous phase contamination is likely limited because the permeable sand units beneath the site appear to be discontinuous (p.11, 12).

- Local groundwater flow is generally along the local topographic gradient towards Lesser Slave Lake. Groundwater flow gradients are inferred to be relatively low through this site. Mechanical mixing and diffusion can therefore be expected to be a more significant factor in controlling the movement of any dissolved PCPs than transport by groundwater flow (p.11).

- Site conclusions (p.13):
    - PCP contamination of soil is widespread within the fenced area to a depth of at least 2.5 m. PCP also appears to have migrated in the groundwater as indicated by low, but significant (i.e. above Quebec Guidelines level C) PCP residue in three of the other four piezometers outside the fenced area. Two sites outside the fenced area also contain PCP in the surface soil, an indication that localized surface contamination may be widespread in the area.
    - contamination by As, Cr and Cu is much less pronounced than contamination by PCP. Of these inorganic constituents, arsenic is the only one in which selected sites had concentrations exceeding the Quebec level C limit. The inorganic contamination appears to be restricted to the near surface soil, and very low (near background) concentrations of the elements appear in groundwater.

- Site reclamation (p.8, 9, 15, 16):
    - reclamation of the site will likely entail treating approximately 10 000 m^3 of soil material (80 m x 50 m x 2.5 m) contaminated with PCP, 600 m^3 of soil (65 m x 30 m x 0.3 m) contaminated with both PCP and arsenic, and an unknown quantity of PCP-contaminated groundwater. Volume estimates are based on contamination in excess of the Quebec C level. Included in these amounts are approximately 200 m^3 of soil with more than 1000 ppm PCP content, a concentration which cannot be

disposed in a landfill according to the Alberta Hazardous Waste Regulations.

- the 600 m^3 of soil jointly contaminated with PCP and arsenic is likely best dealt with by excavation and transport to the Swan Hills Facility. At current prices this disposal would cost approximately $2 000 000.
- no remediation options are presented for the 10 000 m^3 of PCP-contaminated soil, though on-site treatment methods such as mobile thermal destruction, steam stripping and biodegradation are discussed as possibilities.

E.5.2 Technical Commentary

A number of deficiencies exist in the Hardy BBT report. Some of these are discussed in the following technical commentary.

- A large number of soil samples were analyzed, and a more thorough interpretation of the resulting data is warranted:
  - 38 samples exceeded the Quebec C value for PCP which is 5 ppm. PCP contamination was noted in samples as deep as 3.5 m below ground level. Recall that this "C" standard implies that prompt remedial action may be required, and that land use restrictions apply unless remediation occurs. Hardy BBT mistakenly quotes the Quebec C value as 10 ppm, which is the limit for the <u>sum</u> of all chlorophenol concentrations, and not the value for individual chlorophenols. Contour maps of PCP contamination are presented in Figures E.5-3 and -4.

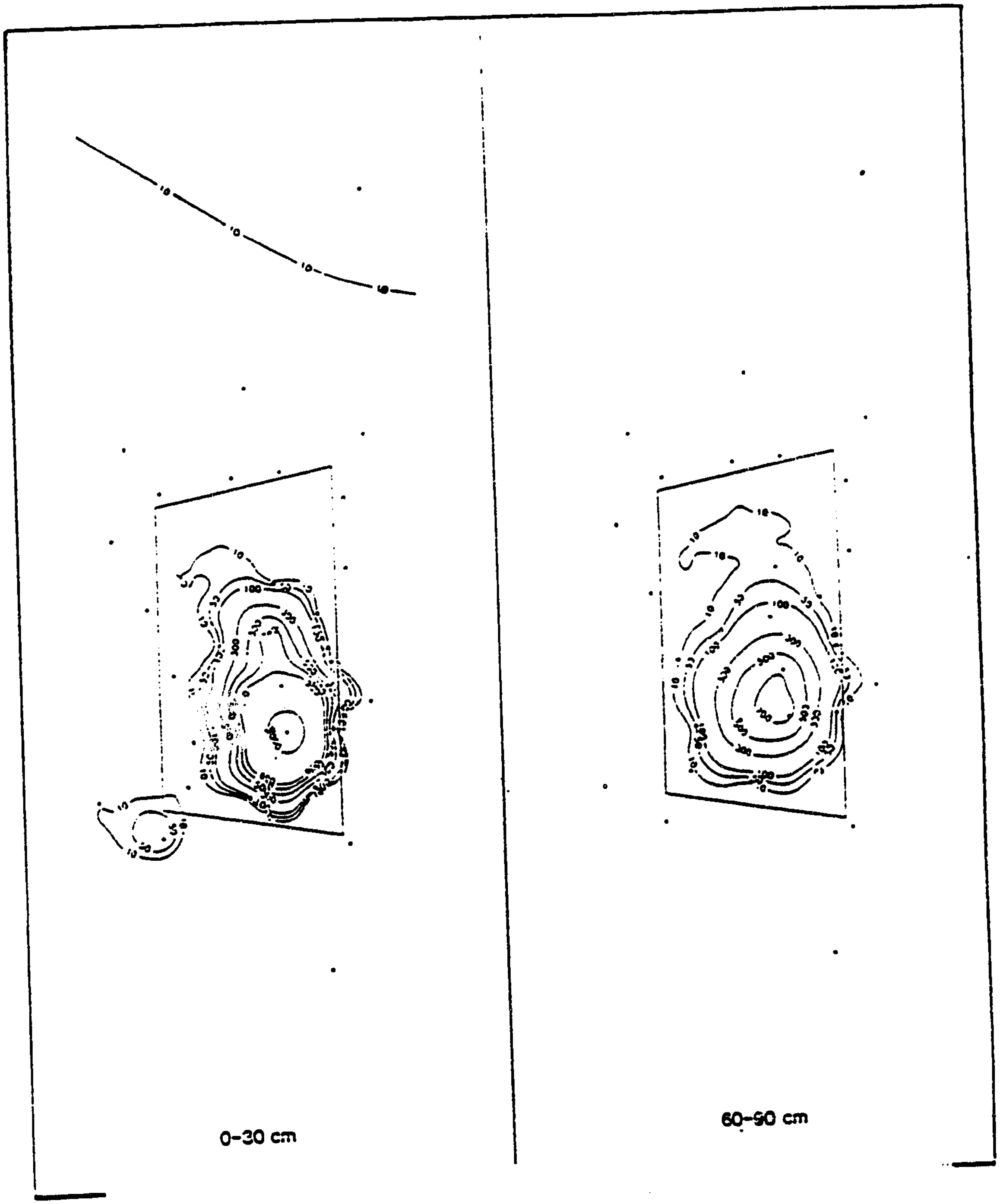

FIGURE E.5-3 : PCP CONTENT WITHIN 1 m OF THE SURFACE (ppm)
(HARDY BBT LTD., 1989)

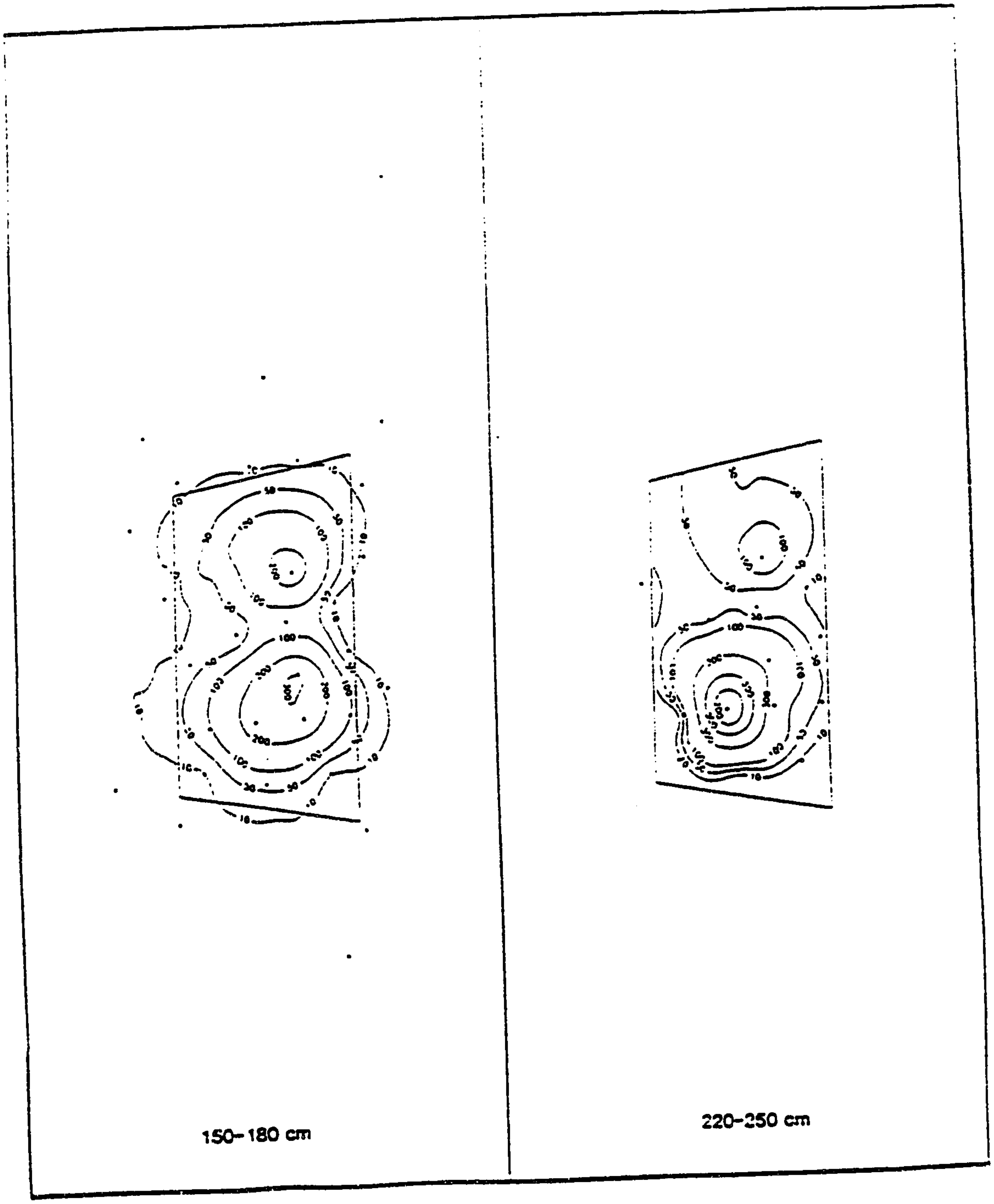

Figure E.5-4 : PCP Content Below 1 m of the Surface (ppm)
(Hardy BBT Ltd., 1989)

- all samples obtained from all depths from the bare area inside the fence exceeded the Quebec C value for PCP. Only 4 samples from outside of the fence exceeded this value.
- 7 samples contained arsenic in excess of the Quebec C value (50 ppm). 6 of these samples originated in the top 0.3 m of soil, and 5 were obtained from the area inside the fence. The other 2 contaminated samples were obtained from the treated wood storage area just outside the fence. The distribution of As at this site is presented in Figure E.5-5.
- a much more rapid decrease of arsenic concentration with depth is noted compared to PCP. This may occur for two reasons:
  - arsenic is more strongly adsorbed to site soils than PCP, or
  - larger PCP releases exhausted the adsorption capacity of the upper soil, resulting is deeper migration.
- all soil samples analyzed were below the Quebec C value for Cr (800 ppm). However, 3 samples exceeded the B value of 250 ppm. All 3 of these samples were obtained from the bare area inside the fence, and correspond with those sites containing elevated As concentrations.
- all 106 soil samples analyzed were below the Quebec level A guideline value for Cu (50 ppm). This "A" standard implies background levels of the contaminant in the environment.
- Cr and Cu also display a much steeper adsorption gradient with depth than PCP.

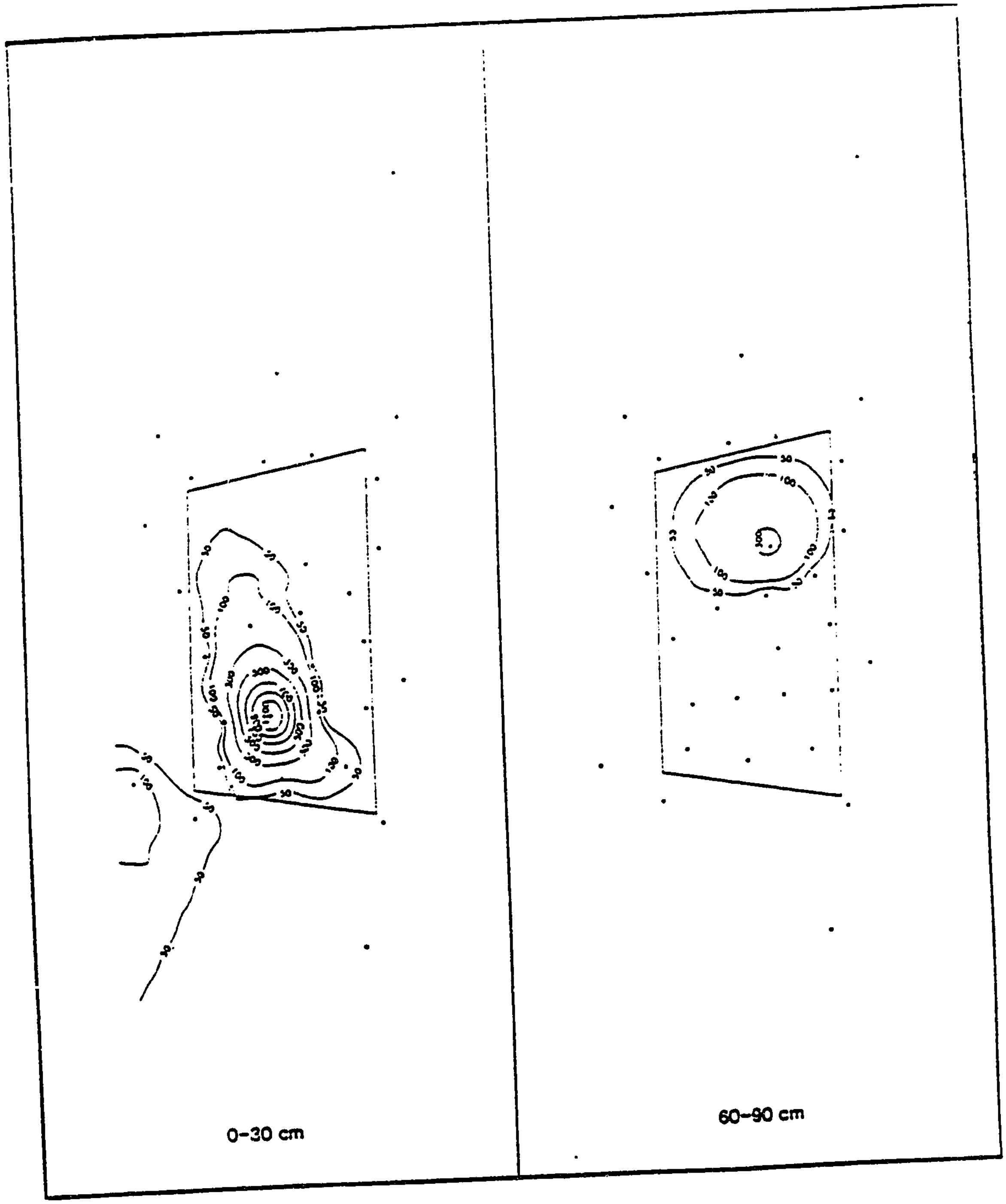

Figure E.5-5 : Arsenic Content Within 1 m of the Surface (ppm) (Hardy BBT Ltd., 1989)

- PCP concentrations in 4 of the 5 piezometers exceeded the Quebec level C value of 5 ppb. The sample from piezometer 9 contained 1800 ppb PCP, and is the only sample collected which exceeded the value of 60 ppb used as a limit by the Guidelines for Canadian Drinking Water Quality (1989). These guidelines are included in Appendix B of this thesis. Consequently, groundwater beneath this site is not safe for human consumption. Piezometer 9, which yielded the most contaminated sample, is located in the bare area where the soil is heavily contaminated with PCP. The groundwater from piezometer 9 should be considered as grossly contaminated with PCP. The proximity of the measured value to the 5000 ppb solubility limit for PCP strongly implies that this sample originated from contact with a distinct PCP-hydrocarbon phase.
- samples from all 5 piezometers were well below drinking water guidelines as well as the Quebec A criteria for Cu, Cr and As. This means that only background levels of these metals exist in groundwater beneath this site.
- in 1988 Alberta Environment sampled a 4.3 m deep well at the nearest residence approximately 200 m south of the site, as well as the stream 50 m northeast of the site. This data was included in Table 2 of the Hardy BBT report. PCP, As, Cr and Cu concentrations from the two locations were all far below

  the Quebec A level at the residence and stream. concentration at the residence exceeded the Quebec A value but was well below the guideline value for potable water. This value likely arose from the use of copper tubing in the household. The Cu value for the stream was below the A level. This very limited sampling suggested that surface and groundwater near the site were not being contaminated by groundwater or runoff from the site.
  - groundwater beneath the site as well as the nearby residence and creek do not indicate contamination by any of the other metals tested.
  - average depth to groundwater at this site is approximately 3.5 m.

- As seen in Figure E.5-1, only 14 sampling locations and 1 piezometer are located within the fenced area. Greater emphasis should have been placed on delineating the contamination in soil and groundwater in this area, as this is where the treating operation and sludge lagoon were located.

- Groundwater samples were obtained from the piezometers the day after installation. This is a poor practice because drilling fluid residues remaining in the borehole will affect the chemistry of the water samples. For example, the presence of bentonite has was sampled. The well should have been developed to remove sediment and residual drilling mud, allowed to recover for more than 90 days and then purged of stagnant water prior to sampling.

- No hydrogeological parameters were determined for this site. Parameters such as hydraulic conductivity and soil cation exchange capacity would be useful in assessing the hazard posed by this site and evaluating remediation alternatives.

- pH and redox values for soil and groundwater were not collected. These parameters are of fundamental importance to the mobility of metals in soil/ water systems.

- Soil and groundwater were not analyzed for dioxins or furans, which are present as impurities in significant amounts in technical-grade PCP.

- The hydrogeological description of the site was taken mainly from an Alberta Research Council report. A greater emphasis should have been placed on the local hydrogeology as it relates to contaminant migration at the Faust site.

- An inventory should have been taken of groundwater wells near the site, as this information is needed to assess the risks posed by any groundwater contamination.

- Soil and groundwater in the swamp west of the site should have been analyzed. Surface topography and a number of bare patches strongly suggest that wastes from the site periodically washed into the slough.

- 5 groundwater and 106 soil samples were analyzed from this site. The resulting data provides vital information regarding the extent and magnitude of contamination. However, the Hardy BBT study just interpreted this data with respect to the Quebec C criteria. Emphasis should have been placed on the relation between groundwater data and potable water limits, and on hazards posed by the highly contaminated soil. The proximity of domestic water wells and Lesser Slave Lake (less than 1 km from the site) emphasizes the need to assess the hazards posed by contamination at the former plant.

- From the report it does not appear as if Hardy BBT discussed the site with former employees or nearby residents. As a result, the report made no attempt to link former site activities with the observed contaminant distribution. For example, Figure E.5-1 which shows both the plant and present site conditions had to be extracted from a proposal for the Phase II study by Stanley

Associates Ltd., as no comparable figure was included in the Hardy BBT report. As seen in section 4.5.2, discussion with residents and former employees has yielded valuable information relating to additional exposure pathways as well as suspected patterns and magnitude of contamination.

APPENDIX F

APPENDIX F: STUDY BIBLIOGRAPHY

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