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University of Alberta

Co-contaminant Removal of Mercury and Hydrocarbons from Soil Using Oxidative Free Radical Reactions

by

Una Dowey ©

A thesis
submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Master of Science

in

Soil Science

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Date: March 23, 1998

For My Dad

ABSTRACT

Co-contamination of land with mercury and hydrocarbons pose unique problems from both a social and regulatory perspective. Few technologies address the remediation of co-contaminated sites. Oxidative reagents may be a promising remediation technology based on their ability to non-specifically oxidize both inorganic and organic compounds. Three oxidative reagents were applied to mercury (Hg) and hydrocarbon contaminated soils to evaluate their ability to remove co-contaminants. Total soil and solution Hg and total extractable organics (TEO) were analyzed before and after oxidative treatment. Sodium hypochlorite (NaOCl) and hydrogen peroxide (H_2O_2) significantly reduced TEO content in selected soils at both 20 and 40°C. Soil oxidation reduced total soil Hg content of selected soils below the Canadian Council of Ministers of the Environment (CCME) remediation criteria for specific land use classifications. Hydrogen peroxide oxidation resulted in the generation of volatile elemental Hg species and NaOCl and $Ca(ClO)_2$ oxidation primarily generated soluble Hg species.

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CHAPTER 1: INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction

Co-contamination of soils with hydrocarbons and heavy metals is an important environmental concern that is common to many industrial sites throughout Canada and the United States. Consequently, due to increasing regulatory and social pressures there is a demand for technologies that can potentially remediate sites that are co-contaminated. The use of chemical oxidative treatment technologies have been evaluated for the removal of metals and hydrocarbons separately from soil, sediment and solution phases, with no application to co-contaminated sites (Watts *et al.*, 1991; Tyre *et al.*, 1991; Stepan *et al.*, 1993 and Kohut *et al.*, 1995). However, oxidative reagents generate oxidative free radical reactions, which could be capable of nonspecific oxidation of both organic and inorganic compounds.

Hypochlorite and hydrogen peroxide-iron catalyzed mixtures (Fenton's reagent) are strong oxidants and may offer a potential mechanism for the degradation and removal of specific contaminants bound to soil and in soil solution. Therefore, oxidative free radical reactions possess a potential mechanism for the simultaneous removal of heavy metals, metal-organic complexes and hydrocarbons from soil.

1.2 Remediation

The pervasive occurrence of contaminated land has become a major issue facing society. After more than a decade of intense activity directed towards these problems, it is the underlying rationale that contaminated site remediation must achieve an overall reduction in both short and long term risk. Additional regulations associated with contaminated land has resulted in the development of a number of remediation technologies. However, regardless of the contaminant type all of the remediation technologies fall into three general categories: 1) containment or immobilization,

2) mobilization and 3) destruction (Hrudey and Pollard, 1993). However, few, if any, technologies have been used to evaluate the remediation of sites that are co-contaminated with a combination of organic and inorganic substances.

In response to a growing public concern over the potential environmental and human health effects associated with contaminated sites, the Canadian Council of Ministers of the Environment (CCME) has initiated the National Contaminated Sites Remediation Program (NCSRP) for the remediation of high priority sites in Canada (CCME, 1991). As a result of this program, there has been increasing pressure to remediate sites and, therefore, the need to find technologies to clean co-contaminated sites is evermore pressing.

Co-contamination of land with mercury and hydrocarbons poses unique problems that require innovative remediation approaches. As soil and groundwater contamination may take many forms, a large range of possible remedial solutions to a given contamination problem exist. At present, there are a number of technologies available: 1) biological, 2) chemical fixation and/or solidification, 3) chemical hydrometallurgical processes and 4) physical (Stepan *et al.*, 1993). Not all of the above technologies can be utilized to clean soil that is co-contaminated because it is essential to recognize that a single technology will rarely accomplish all remediation goals for all contaminants at a remediation site. Therefore, it is apparent that the selection of goals and the remedial options analysis process can be among the most important steps in the clean up procedure. There are fundamental challenges that are apparent with the remediation of land contaminated with a complex mixture of organic and inorganic chemicals, which not only relates to the complexity of the soil environment, but also to the type of wastes present. Consequently, the remediation technology that is chosen for a particular site must take the waste present into consideration in conjunction with the soil environment and the regulatory concerns associated with contamination.

1.3 Turner Valley Gas Plant

The Turner Valley gas plant is located 1.5 Km south of the town of Turner Valley and about 50 km southwest of Calgary, Alberta. The gas plant is in L.S.D 14, northwest quarter of section 6, township 20, range 2, west of 5th meridian (Kohut *et al.*, 1995). The Turner Valley gas plant has been used for petroleum production and refining since 1914. In 1985, the Turner Valley Gas Plant was decommissioned by Western Delcalta Petroleum Ltd. after 60 years of operation (Thompson, 1995). In 1986, ownership was passed to Alberta Community Development who planned to develop the area into an historic site commemorating the oil and gas industry (Monenco Consultants Ltd. 1988). However, concerns arouse with regard to elevated levels of mercury on the site.

The distribution of Hg within the plant area was evaluated by Kohut *et al.*, 1995. Hydrocarbon contamination was not quantified in their study, but subsequent studies have confirmed widespread contamination of hydrocarbons at the Turner Valley gas plant (Thompson, 1995). Soil mercury levels were documented to range from 0.2 to 232 mg kg^{-1}, with the highest levels of Hg being observed near doorways and entrances to the absorber building, gasoline plant, lean oil pump house and scrubbing plant. There was also evidence of elemental mercury within and surrounding the buildings in the surface soil. In the context of gas industry impacts to the environment, it has been recognized that mercury related problems result from the release of elemental mercury into the environment from manometers that have been used for decades to monitor pressures and flow rates at gas wellheads and along gas distribution lines. Mercury manometers are most commonly located inside metering houses, which often have dirt floors. Contamination has resulted from leaky fittings, pressure surges, equipment failures, vandalism and inadvertent spills during servicing. At the Turner Valley gas plant, most Hg was found highest within the top 15 cm, which was primarily associated with the clay fraction (up to > 2000mg kg^{-1}) and lowest within the sand fraction. It was also indicated that soil Hg concentrations dropped to less than 30mg kg^{-1} below 30 cm (Kohut *et al.*, 1995)

Selective thermal extraction of soil from the gas plant indicated that most of the Hg was liberated at 150 to 200°C while over 90% was released by heating to 250°C (Kohut *et al.*, 1995). These authors suggested that sorbed mercury was primarily associated with soil organic matter (Kohut *et al.*, 1995 and Dudas and Pawluk, 1976) and is retained as organomercurial species. Thermal extraction data, from the Turner Valley gas plant, indicated that there was limited elemental Hg, HgS, or HgO present in the soils used in this study. These findings, therefore, excluded the initial theory indicated by Monenco Inc. (1995) that Hg at the Turner Valley site was deposited naturally by the Sheep River (Kohut *et al.*, 1995).

A number of chemical extractants were evaluated for the removal of Hg from soil: H_20, 0.5M $CaCl_2$, 1M HCl, 1M NaOH, 1M sodium acetate, 1M hydroxylamine hydrochloride and 6% NaOCl (Kohut *et al.*, 1995). However, most of the extractants examined were not effective at removing Hg from the soil, with the exception of NaOCl, which was indicated to be effective in removing 29 to 93% of the total soil Hg with a single extraction using a 4:1 weight to weight ratio (solution : soil), reacting for only one hour (Kohut *et al.*, 1995). These findings were impetus for the research on the application of oxidative chemical extractants to remove Hg and hydrocarbon from co-contaminated soil reported in this thesis.

1.4 Mercury

Mercury (Hg) and its compounds are among the most toxic of environmental pollutants known. Mercury occurs naturally and its distribution with respect to the earth's crust, is approximately 0.05 mg kg^{-1} (Lindsay, 1979). Mercury occurs in both igneous and sedimentary rock. Some shales high in organic matter have been reported to contain up to 0.4 mg kg^{-1}(Kabata-Pendias and Pendias, 1992). High natural levels of Hg have been reported to range from 1-10 mg kg^{-1}, which are associated with cinnabar deposits (Adriano, 1986). Elevated natural levels of Hg are also associated with gold and molybdenum base metal deposits with values generally ranging from 0.025 to 0.25 mg kg^{-1} (Jonasson and Boyle, 1972). In soils, it is often noted that normal mercury levels are less than 0.10 mg kg^{-1} (Adriano, 1986). For Alberta soils Hg values are typically less than 0.08 mg kg^{-1} (Dudas and Pawluk, 1976).

Mercury possess the following chemical properties: 1) an atomic weight of 200.5, 3) boiling point of 356.6°C, 4) melting point $^-38.9$°C, 5) vapor pressure of 1.22×10^{-3} mm at 20°C, 6) specific gravity of 13.55 and 7) Hg^o solubility in water of 0.056 mg/L at 25°C

(Adriano, 1986). The wide distribution of Hg in nature results from both its unique chemical properties and the ability to form organic and inorganic complexes.

1.4.1 Fate of Mercury in the Soil Environment

Mercury occurs in various forms: 1) soluble, 2) nonspecifically adsorbed (electrostatic forces), 3) specifically adsorbed (covalent or coordinated forces), 4) chelated (bound to organic matter) and 5) precipitates (sulfide, carbonate, hydroxide and phosphate) (Schuster, 1991). The relative distribution of Hg between the solid, liquid and gases phases within soil will depend on its chemical form, which will ultimately influence the potential remediation of Hg contaminated soils.

There are three main oxidation states that predominantly exist in soil: 1) Hg^o(elemental), 2) Hg (I) (mercurous ion) and 3) Hg (II) (mercuric ion) (Schuster, 1991). Mercury (I) is usually not present in soil systems, due to its unstable nature. Mercury converts to mercuric ions or mercuric ion complexes. Mercury (II) compounds predominates under oxidative conditions ($Eh > 0.4V$). This is mainly a result of the strong tendency of Hg (II) to associate with hydroxyl- and chloride ions (Schuster, 1991). While Hg^o occurs under moderately oxidizing and reducing conditions (Schuster, 1991).

The release of Hg^o, may result in the chemical, physical and biological development of variable Hg species ranging from inorganic complexes, such as $HgCl_2$ and $Hg(OH)_2$, to organic complexes, such as CH_3Hg (Henke *et al.*, 1993). Organomercury compounds, such as dimethyl and monomethyl mercury, can also be present in the soil environment and can arise through biotic and abiotic mechanisms. Microbial transformations of mercury in soil can result in the following interconverting mechanisms (Silver, 1990):

$$Hg^o \leftrightarrow Hg^{2+} \leftrightarrow CH_3Hg^+ \leftrightarrow CH_3HgCH_3$$

Once Hg enters a soil system, adsorption is believed to be the dominant process initially and to a certain extent will determine how much mercury precipitates and/or remains in soil solution. In solution, Hg generally undergoes complexation with organic and inorganic ligands to form different Hg species of variable solubilites (Stein *et al.*, 1996). Where organic matter is present, organo-metallic complexes may occur in soluble or colloidal forms. Studies suggest that inorganic colloids contribute more to the adsorption of organomercurials whereas inorganic Hg is more strongly bound to soil organic matter (Adriano, 1986). Since mercury is a class B character chalcophile element, Hg has a strong affinity for sulfur and thioligand containing groups (Pearson, 1968). These groups are found extensively in soil organic matter, especially under acidic conditions (Anderson, 1963). Consequently, mercury accumulates in organic rich surface soil horizons (Kohut *et al.*, 1995; Dudas and Pawluk, 1976). Processes such as ionic exchange, inner and outer sphere complexes, adsorption and co-precipitation are likely to occur as Hg interacts with organic matter.

The adsorption of Hg to mineral surfaces is determined by hydroxo, sulfato and carbonato metal complexes, while the free metal form determines adsorption to organic matter (Schuster, 1991). Therefore, under low organic matter and neutral soil conditions, Hg complexation with iron oxides and clay minerals predominates (Stein *et al.*, 1996). Thus, retention of Hg by soil systems will be a function of both the soil solid and solution phases.

An additional chemical characteristic unique to Hg is the potential for volatilization. Volatilization of mercury is also influenced by abiotic and biotic mechanisms. Abiotic mechanisms include the loss of Hg through physico-chemical reactions (Revis *et al.*, 1991). Biotic mechanisms for volatile Hg generation includes microbial methylation or reduction of more oxidized Hg species to more reduced forms. (Silver, 1990 and Rogers, 1976). The potential for volatilization is influenced by a number of factors, such as pH, organic matter content and temperature. Soils high in organic matter content, exhibit limited volatile Hg losses due to surface adsorption reactions (Landa, 1978a). Further, Clever *et al.*, (1985) indicated that increasing temperature leads to an increase in Henry's constant for Hg, which translates into higher volatile losses of mercury at elevated soil temperatures.

Increases in soil pH results in corresponding increases in volatilization. Frear and Dill (1967) showed that the volatile loss of Hg from a series of limed silty loam soils, amended with $HgCl_2$, increased as the soil pH increased from 5.3 to 6.4. Therefore, the loss of mercury through volatilization appears to be related to the form of mercury species present in conjunction with soil environmental conditions. In the majority of work reported to date, the major species of Hg vapor emitted from soils appears to be Hg^o, although the mechanisms of volatilization is still not clear (Landa, 1978a; Lindberg *et al.*, 1979).

In general, Hg is unstable in the environment because it is subject to abiotic and biotic reactions and therefore, Hg can exist as a solid, liquid, vapor and/ or adsorbed phase. The equilibrium between these phase are dependent on a number of factors, including pH, redox, cation exchange capacity, ionic strength and temperature.

1.4.2 Environmental Concern

Mercury has wide applications in science, industry and agriculture. It has been estimated that 100 000 tons of mercury contaminate land and water sources annually (Stewart and Bettany, 1982). Industry is mainly responsible for many of the contaminant problems associated with Hg. The major sources of environmental Hg contamination are associated with: 1) burning of fossil fuels, 2) cholor-alkali industry, 3) mining and refining, 4) pulp and paper and 5) natural gas facilities (Mitra, 1986).

Exposure to elemental Hg vapors is a risk in a number of industries, including mining and the natural gas industry (Stopford, 1979). A considerable number of studies relating Hg exposure to human health effects have been published (Skerfving and Lindstedt, 1972 and Vostal, 1972; Rose, 1979; Kaiser and Tolg, 1980 and Mitra, 1986). Most data are from exposure to elemental Hg vapor, but often it is not possible to decide to what extent exposure to aerosols of other Hg forms have been involved.

The relation between exposure and effects can range from acute to chronic. Acute exposure entails high levels of Hg contact over short periods of time, primarily resulting in pulmonary manifestations. Chronic exposure, low levels of Hg contact over an extended period of time, produces mental disturbances and both hearing and vision impairment (Skerfving and Lindstedt, 1972 and Vostal, 1972). More specifically, organic Hg exposure can create variable responses depending on the chemical form. Most organomercurials are quickly excreted from the body, with the exception of short alkylmercury compounds. Short alkyl mercury compounds, such as methyl mercury are more lipid soluble than inorganic or elemental Hg forms. Thus, methyl mercury may accumulate in body lipid reserves in addition to breaching the blood brain barrier. Symptoms of alkyl mercury poisoning are usually neurological in nature, resulting in: 1) loss of vision, 2) loss of speech, 3) emotional instability and 4) motor disturbances to name a few (Kaiser and Tolg, 1980).

1.5 Hydrocarbon Chemistry

The fate of soil hydrocarbons is dependent on the chemical and physical properties of the individual constituents. These include: solubility, vapor pressure, specific gravity, structure and sorption coefficients. The principal properties of interest are: 1) vapor pressure, 2) water solubility, 3) organic carbon or octanol water partition coefficients and 4) volatilization, which is dependent on specific chemical properties, such as vapor pressure and Henry's Law constant. The above properties can dictate to some degree how persistent a particular organic compound may be within a particular phase, all of which can be excessively complicated when there is a mixture of organic compounds present.

Another chemical parameter that has an important role is chemical reactivity. There are five major reactions that an organic compound can participate in. These are: 1) oxidation, 2) reduction, 3) hydrolysis, 4) precipitation and 5) polymerization. Oxidation and reduction or redox processes can be mediated both biotically or abiotically. Hydrolysis reactions are those in which a hydroxide and the products are more polar and, therefore, more soluble than the starting molecule.

In general, a hydrocarbon will migrate through air and water if an appreciable fraction of it can partition into these phases. Also of importance are the biological and chemical degradation or reaction properties of a particular contaminant (Mackay, 1988). Organic compounds can fall into four major classes: acid, base, polar and non-polar and each class can vary widely in their chemical properties; hence, their behavior in soil will vary as well. For example a particular charge on an organic contaminant will determine the potential mobility and solubility. Soil constituents can further add to the complexity of organic contaminant movement, which can be compounded by varying soil pH. Polar and non-polar compounds behave differently in soil than charged organics. Non-ionic organics will tend to primarily associate with soil organic matter, which involves complex sorption mechanisms.

Organic contaminants are often complex, mulitcomponent mixtures that are present in the environment as separate organic liquid phases, commonly referred to as nonaqueous phase liquids (NAPLs). The presence of NAPLs can lead to limitations in remediation technologies based on constraints imposed by slow rates of mass transfer and uncertainties regarding both location and mobility of NAPLs (Peters et al., 1997). In addition, multicomponent organic mixtures derived from petroleum processing have some fraction of aromatic hydrocarbons, which may pose a risk to human health.

1.5.1 Hydrocarbon Contamination and Environmental Concern

Environmental contamination by petroleum products is a significant concern throughout Canada and the United States. It is estimated that there are over 2 million underground storage tanks subject to federal underground tank regulations, designed to minimize potential hydrocarbon release (Lord and Perwak, 1988). Other sources of petroleum contamination include, heating oil tanks, refineries and/or accidental crude oil spills and other sources. It is known that petroleum hydrocarbons are composed of numerous chemical constituents that contain complex mixtures of organic agents, some of which are considered suspect or known human carcinogens. Therefore, pollution from hazardous waste landfills and contaminated sites have been recognized as a potential public health hazard (Calabrese *et al.*, 1988). It is apparent we are faced with extensive environmental problems, not only with hydrocarbon contamination, but with the additive complexity of metal contamination, such as Hg. Further, most contaminated sites are often contaminated with a complex mixture of inorganic and organic pollutants. Therefore, the need to find applicable remediation technologies to clean co-contaminated sites becomes an important issue from both a social and financial perspective.

1.6 Oxidative Free Radical Generation

Chemical oxidants, such as peroxide (H_2O_2), chlorine, potassium permanganate, chlorine dioxide, ozone and ultraviolet light, have been used for many years for the disinfection and treatment of organic contaminants in ground water and wastewater (Venkatadri and Peters, 1993; Plant and Jeff, 1994). These chemical oxidants may have a potential influence on the removal of both inorganic and organic contaminants from soil and sediments. This assertion relies on the principal that all of the above oxidative reagents are capable of generating oxidative free radical reactions. Based on this theory, it is hypothesized that the application of oxidative reagents, such as sodium hypochlorite (NaOCl), calcium hypochlorite($Ca(ClO)_2$) and hydrogen peroxide (H_2O_2) will remove both Hg and hydrocarbons simultaneously from soil.

Sodium hypochlorite has been shown to remove mercury from both geologic material and soils as a soluble species (Parks and Baker, 1969; Parks and Fittinghoff, 1970; Pedroso et al., 1994; Stepan et al., 1993). In a recent study by Kohut et al (1995) it was shown that NaOCl was effective at reducing total soil Hg in industrially contaminated soil. The theory proposed for the basis of sodium hypochlorite mechanisms centers on the ability of ClO^- free radicals to convert less soluble mercury to water soluble compounds (Pedroso et al, 1994). Consequently, the form of mercury present will influence the degree of extraction and this is reflected in the wide range of recovery documented previously by Kohut et al. (1995). The following reactions of sodium hypochlorite have been proposed as the mechanisms underlying Hg removal (Pedroso et al, 1994, Wilhelm and McArthur, 1995):

$$HgS_{(s)} + 4\,ClO^- \longrightarrow HgCl_{2\,(aq)} + 2Cl^- + SO_4^{2-}$$

$$Hg_{(s)} + Cl^- + ClO^- + H_2O \longrightarrow HgCl_{2\,(aq)} + 2OH^-$$

$$Hg^o + ClO^- + 3Cl^- + H_2O \longrightarrow HgCl_4^{2-} + 2OH^-$$

$$Hg^{o} + ClO^{-} + 3Cl^{-} + H_2O \longrightarrow HgCl_4^{2-} + 2OH^{-}$$

$$Hg^{2+} + 4Cl^{-} \longrightarrow HgCl_4^{2-}$$

Work by Mountain States R&D International has examined the application of another oxidative reagent, calcium hypochlorite. Results indicated a significant reduction in total soil Hg and an increase in solution Hg phase concentrations with $Ca(ClO)_2$ treatment (Stepan et al., 1993).

Hypochlorite has also been utilized for the removal of organic matter prior to physical, chemical and mineralogical analysis. The application of hypochlorite to soil has been shown to remove organic matter in a rapid and efficient manner without causing dissolution of MnO_2, exfoliation of mica and/or the removal of carbonates from soil (Anderson, 1963 and Lavkulich and Weins, 1970). However, some limitations associated with hypochlorite application to contaminated soil may be: 1) the presence of organic matter will act to reduce the reaction efficiency of hypochlorite by competing for oxidative free radicals and 2) alter soil characteristics, such as decreasing soil organic matter content (Wilhelm and McArthur, 1995).

One alternative to sodium hypochlorite is hydrogen peroxide. Hydrogen peroxide is a strong oxidant which has been used to remove a variety of contaminants from waste water, soil and sediments (Watts *et al.*, 1991; Tyre *et al.*, 1993 and Venkatadri and Peters, 1993). A few examples of industrial application of H_2O_2 are: 1) purification of iron and manganese-containing ground water by conversion of the heavy metals to insoluble hydroxides/oxides, 2) removal of chlorite and hypochlorite in waste water, air or in bleached textiles and pulps by reaction with chloride salts and 3) treatment and eventual degradation of hydrocarbon contaminated soils, sediments and waste water (Venkatadri and Peter, 1993). Hydrogen peroxide is also used to destroy organic matter from soil prior to physical, chemical and mineralogical analysis. Destruction of organic matter and the degradation of organic contaminants is believed to be a result of hydroxyl free radical formation.

Previous studies (Barr and Aust, 1994) indicate that ferrous iron combined with hydrogen peroxide, better known as Fenton's reagent, chemically forms oxidative free radicals. Fenton's reagent has proven to be effective in the degradation and mineralization of organic contaminants. The degradation of contaminants is through hydroxyl free radical reactions, which follows first order kinetics (Watts *et al*, 1991). The formation of hydroxyl radicals plays the major role in the oxidation of organics (Walling, C. 1975):

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + OH^\cdot$$

There are a number of additional competing reactions that occur in association with Fenton's reagent. Carbonate and bicarbonate ions and organic matter can compete successfully for hydroxyl free radicals, which results in much lower reaction efficiencies (von Sonntag *et al.*, 1997). The generation of hydroperoxyl radicals ($OH_2^\cdot$) are also known to possess lower oxidation capabilities compared with hydroxyl radicals, therefore decreasing reaction efficiencies (Pignatello, 1992):

$$OH^\cdot + Fe^{2+} \longrightarrow OH^- + Fe^{3+}$$

$$Fe\text{-}OOH^{2+} \longrightarrow HO_2^\cdot + Fe^{2+}$$

$$HO_2^\cdot + Fe^{2+} \longrightarrow Fe^{3+} + HO_2^-$$

$$Fe^{3+} + HO_2^\cdot \longrightarrow Fe^{2+} + O_2 + H^+$$

$$OH^\cdot + H_2O_2 \longrightarrow H_2O + HO_2^\cdot$$

Chemical oxidative treatment methods, such as Fenton's reagent, which generate powerful oxidants ($OH^\cdot$) are known to remove contaminants ranging from inorganic to chlorinated aliphatic compounds and complex aromatic compounds (Venkatadri and Peters, 1993). Oxidative treatment has been proposed as a soil decontamination technology (O'Brien *et al.* 1995). Watts *et al.* (1991) indicated that aged sandy soils contaminated with a mixture of polyaromatic hydrocarbons were successfully treated with

Fenton's reagent, using 10% hydrogen peroxide, within 16 hours. Further work by Watts (1992) illustrated that controlled experiments conducted on silica sand with H_2O_2 and no iron additions, decreased organic contaminant concentrations. Therefore, naturally occurring iron in the form of amorphous or crystalline iron oxides may supply sufficient iron for Fenton's reactions in soil. The ability of minerals to promote Fenton-like reactions may occur by at least two mechanisms: 1) mineral dissolution with the release of soluble iron, resulting in the catalysis of peroxide decomposition and/or 2) heterogeneous catalysis on mineral surfaces (Watts, 1992). Fenton's reagent is also considered relatively benign to soil microenvironments, making it even more attractive for treating either aqueous or soil bound contaminants. Few studies have systematically investigated free radical reaction treatment of contaminated soil.

Based on the above considerations, it is postulated that oxidative free radicals should aid in the simultaneous removal of both metals and hydrocarbons from contaminated soils. Oxidative free radicals can be generated by NaOCl, $Ca(ClO)_2$ and H_2O_2 which are responsible for: 1) C-C bond cleavage, 2) H-abstraction, 3) demethylation, 4) hydroxylation, 5) benzylic alcohol oxidations and 6) dimerization of hydrocarbons (Venkatadri and peters, 1993). The general objective of the present research is to quantify the degree to which oxidative free radical reactions can facilitate the removal of both Hg and hydrocarbons bound to soil and to quantify the relative soil solid phase, solution and/or vapor distribution of Hg after oxidative treatment.

CHAPTER 2: MATERIALS AND METHODS

2.1. MATERIALS

2.1.1 Soil Sampling

Three bulk soil samples were obtained from the Turner Valley gas plant in October, 1995. Each soil sample contained various degrees of Hg and hydrocarbon contamination, based on initial site assessment (Table 2.1) (Kohut *et al.*, 1995). Samples were collected and then stored in sealed 10 gallon plastic buckets at 4°C to limit both microbial activity and Hg loss through volatilization prior to air drying and sieving.

In May, 1996, contaminated soil samples were air dried and passed through a 2 mm plastic sieve. Kohut *et al.*, (1995) indicated that air drying and sieving of soil samples did not result in Hg losses. After sieving and air drying, soil samples were than stored in 500ml sealed glass kerr jars at room temperature, with no contact with metal kerr jar lids, until time for appropriate oxidative treatment.

Table 2.1. Content of Hg and estimated hydrocarbon contamination levels from soil samples obtained from the Turner Valley Gas plant (Kohut *et al.*, 1995)

Sample Number	Hg (mg kg^{-1})	Hydrocarbons (smell and color)	Soil Description
2	194	MODERATE	loam with no plants
4	2	NONE	loam with no plants
5	4	STRONG	loam with many rocks. Excessive hydrocarbon staining

2.1.2. Oxidative Reagents

Three oxidative reagents were used to evaluate the potential removal of Hg and hydrocarbons from soil. Sodium hypochlorite (NaOCl), calcium hypochlorite ($Ca(ClO)_2$) and hydrogen peroxide (H_2O_2) were the oxidative reagents utilized (VWR scientific, ACS grade). Oxidative reagents were free of positive or negative interferences in Hg analysis.

2.1.3. Complexing Reagents

Two complexing reagents were initially used to evaluate the speciation of the volatile generation of Hg after oxidative treatment (US EPA, 1980). Acidic potassium permanganate ($KMnO_4$) and iodide monochloride (ICl) were used to determine volatile Hg species released after oxidative treatment from soil (VWR scientific, ACS grade). Iodide monochloride and 4 % acidic potassium permanganate were synthesized according to EPA method 101A (US EPA, 1980). Mercury analysis was done on both complexing reagents prior to experimentation to evaluate potential interference with analysis. Serious negative interference from ICl complexing regent occurred in the Hg analysis. Consequently, acidic $KMnO_4$ was the only complexation solution used in the vapor characterization work.

2.2 METHODS

2.2.1 Physical Analysis

Approximately 30 g of oven dried contaminated and bulk soil samples, sieved to less than 2mm (plastic sieved), were washed repeatedly with deionized water until dispersed. Ultrasonification was used to disperse soil samples. Clay separation was achieved through successive dispersion and gravity sedimentation cycles (Jackson, 1979). Sand and silt fractions were separated by wet sieving, oven dried at 105°C for 24 hours and weighed. Clay content was then calculated by the difference.

2.2.2 Chemical Analysis

Soil pH was measured with glass electrode in deionized water using a 2:1 solution: soil ratio (McKeague, 1978). Inorganic carbon and total carbon in powdered (100 mesh) soil samples were measured by titrimetric (Bundy and Bremner, 1972) and Leco carbon determination (Tabatabai and Bremner, 1970) methods, respectively. Cation exchange capacity (CEC) of soil samples were measured using NH_4OAc and NH_4^+ index ion was measured by a continuous flow Technicon auto analyzer (McGill and Figueiredo,1993).

Aqueous phase characteristics of each soil samples were done in triplicate, using saturated paste extraction after 24 hours of equilibrium and extracting under vacuum (Richards, 1949). Electrical conductivity (E.C) was measured on the saturated paste extracts using a model 31 conductivity bridge. Soluble carbonates were measured immediately after extraction by H_2SO_4 titrimetric determination (Rhoades, 1982). Sulfate and chloride anions were determined using turbidimetric (Rhoades, 1982) and colorimetric methods (Adrian and Doner, 1982).

Analysis of total soil Hg content was determined prior to oxidative treatment by cold vapor atomic absorption spectrophotometry (CVAAS) using the method described by Melton *et al.*, (1971). Samples were digested with hot nitric acid in combination with potassium persulfate, a strong oxidizing agent, to convert all Hg to the divalent form (Figure 2.1). After cooling and connection of the sample flask to the air train connected to the AAS, a stannous chloride reducing solution was added to convert the divalent Hg to ground state Hg^o vapor. The concentration of Hg in the vapor phase was then measured using a flameless atomic absorption spectrophotometer (Perkin-Elmer model # 2380) with the absorbance recorded on a strip chart recorder (Perkin-Elmer model # R50) (Figure 2.2). Mercury concentrations in the unknown samples were calculated based on their peak heights compared to those of known Hg standards, which ranged from 0.05 to 0.20 *u*g Hg. Samples with high Hg concentrations were similarly treated, but with the digests diluted as necessary to achieve concentrations within the standard curve. Furthermore, all analyses followed QA/QC protocols, indicated by both EPA and Gas Research Institute guidelines for total Hg analysis by cold vapor atomic absorption spectrophotometry (Bloom *et al.*, 1994 and Mueller and Smith, 1991).

Total extractable organics (TEO) of each soil sample was determined prior to oxidative treatment. Approximately five grams of soil with 1 to 2 grams of anhydrous sodium sulfate was extracted in a soxhlet unit with 100 ml methylene chloride (CH_2Cl_2) at a heating temperature of 40°C (heating mantles # PL 312 minitrol Glas-Col) with approximately 3 cycles/hour for 16 hours. All soil samples were done in triplicate depending on experimental design, with one blank every 10 samples. After extraction, TEO solvent was concentrated to 5 ml with rotary evaporation, 15 to 20°C higher than the boiling point of CH_2Cl_2 (approximately 55°C) (VWR scientific, omnisolv grade). Concentrated TEO solvent was then removed and allowed to evaporate for one week. TEO percentage was then determined by the weight of the nonvolatile residues in grams, to the nearest 10th of a milligram, correcting for the moisture content of the initial sample (ASTM, 1996 and ESTAC, 1995).

2.2.3 Oxidative Treatment

2.2.3.1. PHASE I: Equilibrium Experiments

Initial apparent equilibrium experiments were conducted using 0.8M NaOCl, 1.69M H_2O_2 and 0.4M $Ca(ClO)_2$ concentrations with contaminated soil sample 2 (Table 2.1). Sodium hypochlorite and H_2O_2 concentrations were chosen based upon known literature values for Hg and hydrocarbon removal, respectively (Kohut et al., 1995; Watts et al., 1991; Tyre et al., 1993 and Lavkulich and Weins, 1970). Calcium hypochlorite concentration was based upon solubility limitations, due to $CaCO_3$ content of oxidative reagent. Batch equilibrium mixing times of 1, 3, 6, 9, 16 and 24 hours were utilized to determine optimal mixing times for the simultaneous removal of Hg and hydrocarbons from soil. Triplicates were run for each mixing time and a control sample in triplicate was also included, consisting of deionized water addition only. Mixing times were doubled from estimated literature values to compensate for an expected two fold decrease in reaction rates with the presence of native organic matter (Watts *et al.*, 1990). All soil samples were treated with a 5:1 weight ratio of oxidative reagent to soil. Approximately 12 g of 2 mm sieved soil was placed in a open 125 Erlenmeyer wide necked flask (#5100), with approximately 60 g of either oxidative reagent or deionized water. Samples were placed into a temperature controlled water bath set at 20°C and each sample was temperature monitored throughout the 16 hours of treatment (Fisher versa-water bath), within a flat bed shaker at 40rpm (New Brunswick Scientific) (Figure 2.3). Soil samples, after treatment, were removed from the water bath and transferred into 250ml Nalgene centrifuge containers. Soil pH after oxidative treatment were also measured for each sample. Samples were then centrifuged at 6250 x g for 30 minutes using a Sorvall ® RC-5B refrigerated superspeed centrifuge, with the temperature set to approximately 8 to

15°C. Following centrifugation the solution phase was decanted off and then filtered through two #1 whatman filter papers. Analysis of the filter paper indicated minimal loss of mercury (2% to 8%) and low density organic matter (e.g. roots and twigs) was prevented from contaminating solution phase. Solution phase was immediately digested (Figure 2.1) and then analyzed for total Hg (Figure 2.2). The remaining solution phase was then stored in 100 ml Nalgene bottles at 4°C. The soil phase was then left to air dry for one week. After the soil samples were air dried, soil samples were ground to 100 mesh with a stainless steel automatic grinder, digested (Figure 2.1) and analyzed for Hg (Figure 2.2). Optimal extraction time was determined by maximal removal of total Hg before and after oxidative treatment. Total extractable organics (TEO) was not determined on the soil in this experiment and, therefore, was not used as a criteria for choosing extraction time for subsequent experiments.

2.2.3.2. PHASE II: Mercury and Hydrocarbon Removal at 20°C

Chemical extraction was done using three concentrations each of NaOCl, $Ca(ClO)_2$ and H_2O_2. Concentrations chosen were variable between extractants due to limitations imposed by each oxidative reagent. Hydrogen peroxide and sodium hypochlorite concentrations were based upon maximum reagent grade and known literature values, plus a mid-value concentration (Watts *et al* 1991; Tyre *et al.*, 1991 and Lavkulich and Weins, 1970). Calcium hypochlorite concentrations were based upon its calcium carbonate content, which limited its utility due to low $CaCO_3$ solubilities (NIOSH, 1994). Similar to the Phase I experiment, soil samples were placed into a temperature controlled water bath set at 20°C within a flat bed shaker and mixed at 40 rpm. However, unlike Phase I, soils 4 and 5 were also included, in addition to soil 2, for total Hg and TEO changes with treatment. A total of 27 samples were set up for batch equilibrium experiments for each contaminated soil sample:

(2 oxidative reagents x 3 replicates x 3 concentrations
for NaOCl and H_2O_2 treated soil) +
(1 oxidative reagent x 3 replicates x 2 concentrations for $CaClO_2$) +
(1 deionized water x 3 replicates) = 27 samples

After treatment with oxidative reagents, soil samples were removed from the temperature controlled water bath. Soil and solution phases were separated by centrifugation and filtration as indicated previously in Phase I (Figure 2.3). Soil pH was monitored for each soil sample after oxidative treatment. Samples were then digested (Figure 2.1) and analyzed (Figure 2.2) for changes in total Hg concentration in both the soil and solution phases. Total extractable organics were analyzed before and after oxidative treatment for change in TEO with oxidative treatment using the same method as previously described with soxhlet extraction and gravimetric determination.

2.2.3.3. PHASE III: Mercury and Hydrocarbon Removal at 40°C

A subsequent experiment using co-contaminated soil 2, was designed to evaluate the removal of Hg and hydrocarbons at an elevated temperature. A total of 27 samples were prepared for oxidative treatment, as outlined in Phase II. However, unlike Phase II, temperature for treatment was set at 40°C.

After treatment, soil samples were removed and soil and solution phases separated as indicated previously. In addition, soil pH was again monitored for each soil sample after oxidative treatment. Samples were digested (Figure 2.1) and analyzed for total Hg content (Figure 2.2). Total extractable organics were also analyzed following oxidative treatment, following the same procedure as outlined earlier.

2.2.3.4. PHASE IV: Volatile Mercury Determination

The determination of total volatile portion of Hg released from soil after oxidative treatment was studied for contaminated soil 2. A total of 12 samples were analyzed for volatile Hg. Only the highest molar concentration of each oxidative extractant were examined, in order to minimize the total number of samples to be analyzed. Triplicates were run for each mixing time and a control sample in triplicate, consisting of deionized water, was also included in this study.

Two complexing agents were initially used to examine the species of Hg being generated after oxidative treatment: 1) 4% acidic potassium permanganate and 2) iodide monochloride. The 4% acidic permanganate complexing reagent was documented to complex inorganic mercury species only and the iodide monochloride complexing agent is documented to complex both inorganic and organic Hg species (US EPA, 1980; Pollution technology, 1977 and AIHA, 1969). However, it was established that the ICl complexing reagent created extensive interference with respect to Hg analysis and was subsequently not used. Consequently, only the $KMnO_4$ complexing method will be discussed in detail.

All samples were treated as indicated in Phases I and II, with a 5:1 weight to weight ratio of oxidative reagent to soil sample. Samples were placed in a temperature controlled water bath, maintained at approximately 20°C. However, due to experimental design limitations, mixing of the soil/solution complex was accomplished using a magnetic stir bar, rather than a flat bed shaker at 40 rpm. Approximately 12 g of contaminated soil was placed into a 250 ml Erlenmeyer flask. The flask was then closed with a rubber stopper, which was wrapped in parafilm and sealed tight with tape. Air flow was passed over the soil sample at a flow rate of 45 ml/min, determined by a flow meter rotometer. Oxidative extractant was then injected into the 250 Erlenmeyer flask reaction vessel. Samples were allowed to react for 16 hours. Air flow was used to strip Hg vapor form the surface of the soil/solution complex. Air was then allowed to flow through 3 (250 ml) sequential impingers, each containing $KnMO_4$ complexing reagent. The first impinger contained 50 ml of $KMnO_4$, while the second and third impinger contained 100 ml each of $KMnO_4$ (Figure 2.4). At the end of the reaction period, the air flow was turned off and allowed to settle for one hour, in order to drop the positive pressure within the bubblers and prevent backflow (Figure 2.4). The complexing reagent within each impinger was then combined and analyzed for total Hg (Figure 2.2). The remaining soil and solution phases were centrifuged and separated as indicated in Phases I through II and total Hg content was determined for each phase. No TEO analysis was done on any of the soil samples within this phase of experiments.

2.2.3.5. Phase V: Analysis of hydrocarbon transformed products

Qualitative analysis of selected TEO extracts were analyzed using GC-MS and electrospray MS techniques to examine any changes in TEO before and after oxidation which was not evident with gravimetric techniques. Selected TEO extracts of soil 2 treated at 20°C were evaluated: 1) before oxidative treatment, 2) 1.7 M NaOCl and 3) 7.1 M H_2O_2 using GC-MS with a DB-5 capillary column (Ultra 2, crossed linked 5% phenly methyl silicone, 30 m X 0.24 mm). Helium flow rate was set at 25 cm/sec and oven temperature was increased in 5°C increments from 50 to 275°C with elution time set for 50 minutes. Soil TEO extracts were prepared as discussed in section 2.2.3.2. An additional preparation step was included to purify the TEO extracts for analysis. Acid, neutral and base components of the TEO extract were separated with 5% HCl and 5% NaOH. The remaining neutral component was then filtered through normal solid phase extraction tubing and rinsed with $CHCl_2$ solvent and a secondary methanol solvent rinse (MeOH) . The $CHCl_2$ and MeOH rinses were concentrated and then injected (2 *u*l) into the GC-MS for analysis. Data acquisition and processing was achieved by using NIST software and library matching to determine potential hydrocarbon components of each TEO extract.

Soil 2 TEO extract before oxidative treatment was also analyzed using positive electrospray mass spectrometric analysis to determine polar components. Mass spectrometric analysis was performed by positive mode electrospray ionization on a Micromass ZabSpec Hybrid Sector-TOF. The liquid carrier (1:1 v / v methanol : water + 1% acetic acid) was infused into the electrospray source by means of a harvard syringe pump at a flow rate of 10 *u*l/minute. The sample solution was introduced via a 1 *u*l loop injector. Prepurified nitrogen was used as a spray pneumatic acid and filtered air as the bath gas, heated at 80°C. For low resolution, the mass spectra were acquired by magnet scan at a rate of 10 seconds/decade. Data acquisition and processing was achieved by using the OPUS software package on a Digital Alpha station with VMS operating system.

Figure 2.1. Total Hg Digestion Methodology:

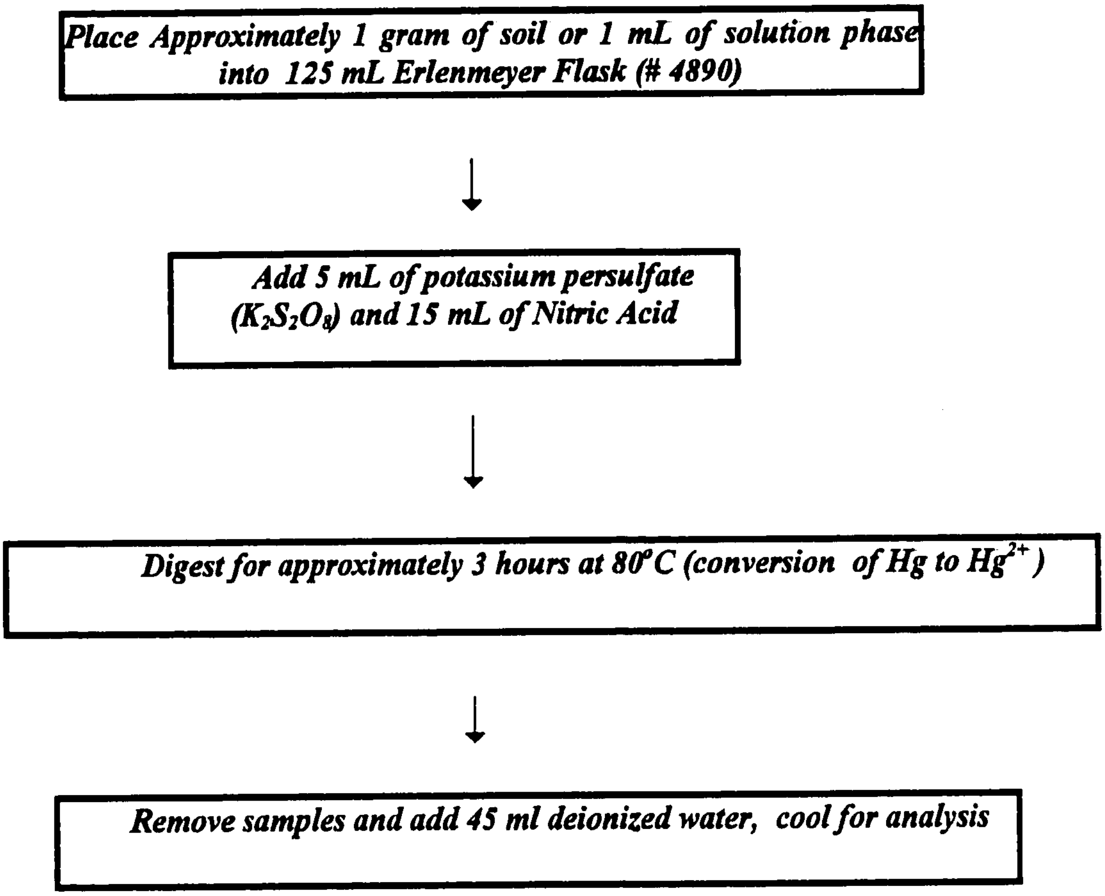


Figure 2.2. Total Hg Analysis Methodology After Digestion

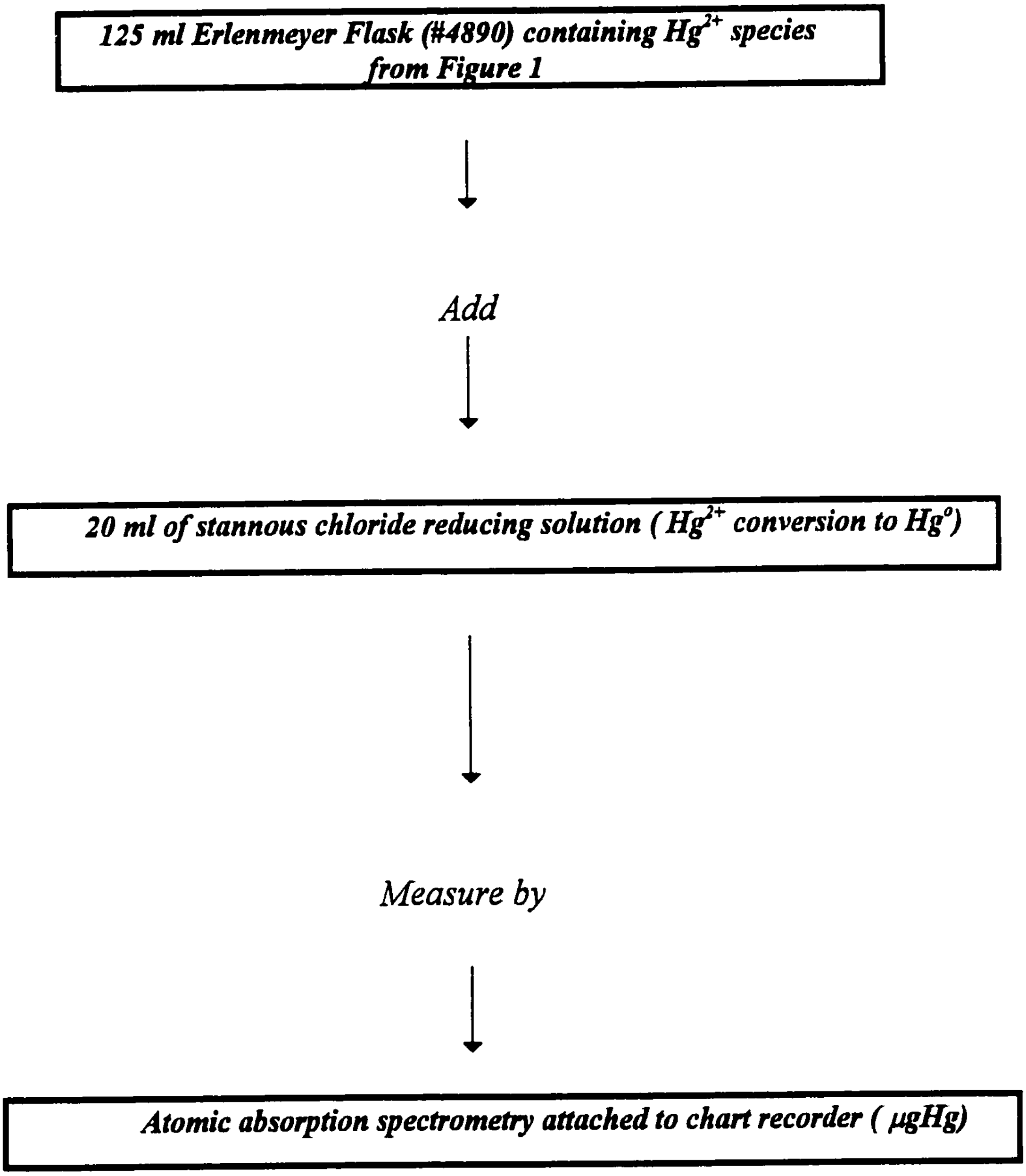


Figure 2.3. Experimental Design:

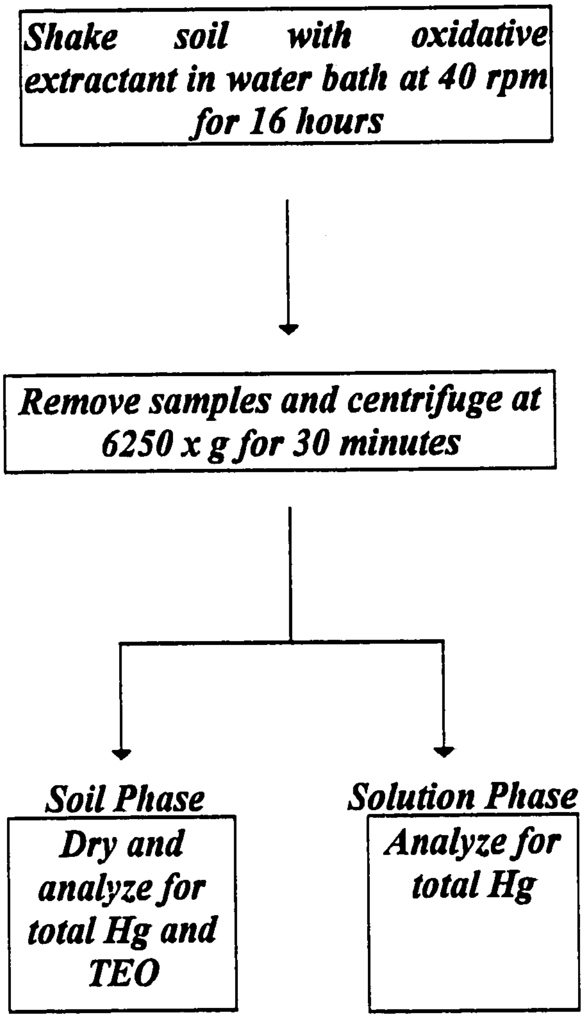
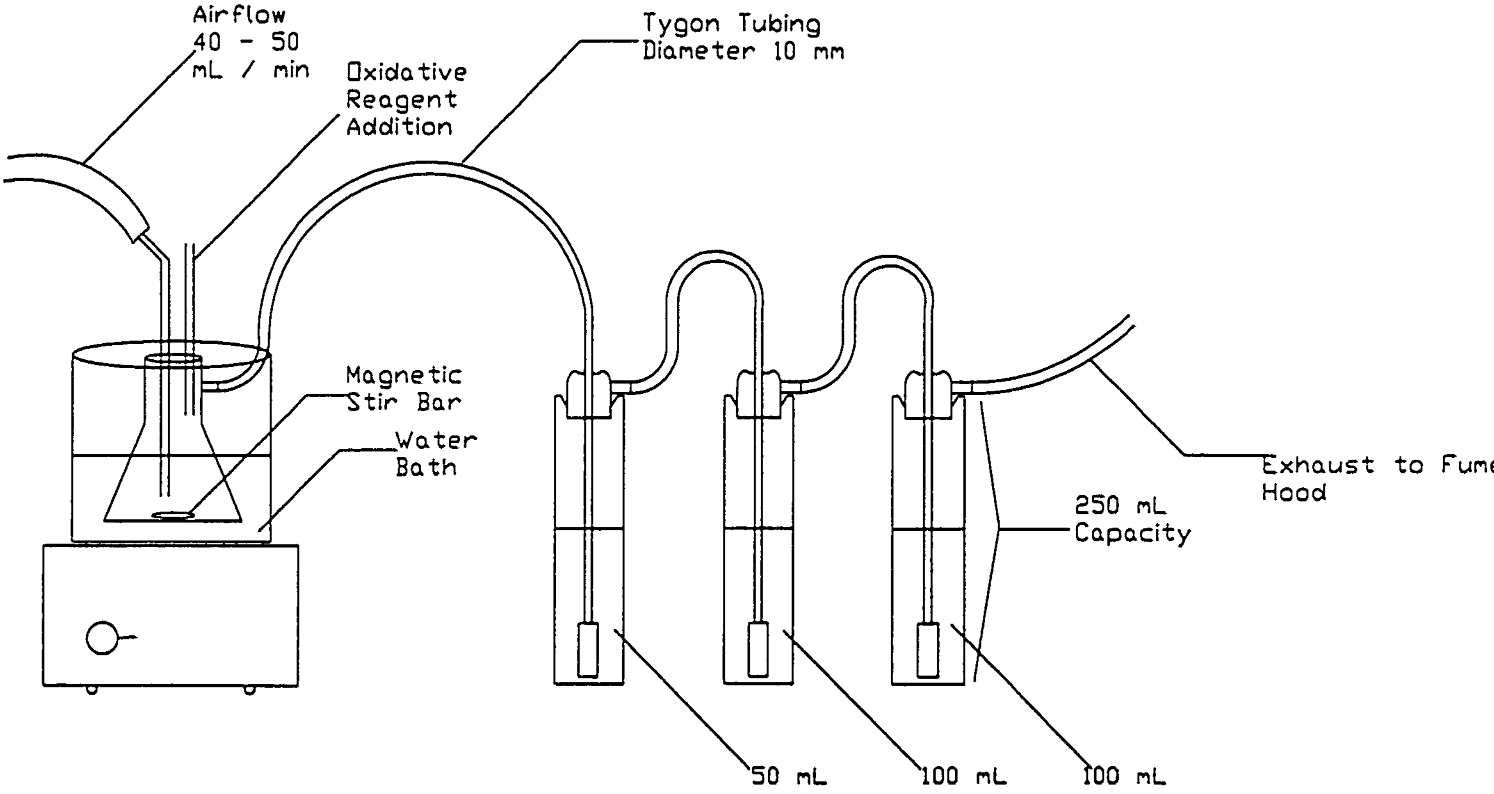


Figure 2.4. Volatile Determination Experimental Design:



CHAPTER 3: RESULTS AND DISCUSSION

3.1 Soil Physical and Chemical Properties

3.1.1. Soil Physical Properties

The textural classes (Table 3.1) of the contaminated soils, are consistent with a fluvial parent material (Kohut et al., 1995). Clay mineralogy of the soils from the Turner Valley area has been previously documented by Kohut et al., (1995). Their findings indicated that mica and kaolinite are the dominant clay minerals with minor amounts of chlorite and vermiculite.

Table 3.1. Particle size distribution of contaminated (soils 2, 4 and 5)

sample	% sand	% silt	% clay	texture
soil 2	43	36	21	silt loam
soil 4	61	24	14	sandy loam
soil 5	55	28	17	loam

3.1.2. Soil Chemical Properties

The pH in deionized water, cation exchange capacity (CEC), total Hg concentration, total extractable organics (TEO), inorganic (TIC), organic (TOC) and total carbon (TC) content are all given in Table 3.2. The Turner Valley soils (2, 4 and 5) are characterized by a calcareous, humus rich Ahk horizon, approximately 15 cm deep and overlying a calcareous light colored gravely alluvial parent material (Ck horizon) (Kohut et al., 1995). Analyses indicated that soil sample 4 contained the highest amount of TIC compared to soil samples 2 and 5. Soil sample 5 contained the highest content of hydrocarbon contamination measured as TC, TOC and TEO content. It is evident that as hydrocarbon contamination increases there is a corresponding increase in TOC content. The CEC for the contaminated soils were consistent with the relative amount of organic carbon and clay minerals present with soils 2 and 4 (Hausenbuiller, 1985) (Table 3.2).

However, the CEC for contaminated soil 5 may be underestimated due to hydrocarbon interfernce with CEC analysis.

Table 3.2. Soil chemical properties

Sample	pH	TIC %	TOC %	TC %	Hg mgkg^{-1}	TEO %	CEC cmol(+)/kg
soil 2	7.60	1.45	1.63	3.08	67.0	1.64	12.7
soil 4	8.00	3.89	0.240	4.13	5.20	0.170	12.9
soil 5	7.80	2.82	3.61	6.43	5.82	5.33	14.3

The concentrations of major soluble components in saturated paste extracts of the contaminated soils are shown in Table 3.3.

Table 3.3. Major soluble components of contaminated soil saturated paste extracts

sample	E.C[1]	Ca	Mg	K	Na	SO_4^{2-}	Cl^-	HCO_3^-
	dS/m				mgL^{-1}			
soil 2	1.30	305	39.5	15.2	11.5	1.22×10^3	132	253
soil 4	0.780	206	22.0	11.5	9.75	155	111	365
soil 5	0.810	104	16.3	17.1	17.1	76.3	121	279

1. electrical conductivity

Elevated levels of calcium and sulfate, in addition to soil pH values (Table 3.2), for the contaminated soils indicate the likely presence of calcium sulfate (gypsum) and/or calcium carbonate (calcite). Geochemical modeling would be required to determine what the solubility controlling solid is for each contaminated soil. Electrical conductivities are low and typical of non-saline soil conditions for all co-contaminated soil samples.

Soil samples containing various levels of Hg and hydrocarbon contamination were chosen from the original Hg distribution information and maps of the Turner Valley Gas Plant (Kohut et al., 1995). Soil 2 had the highest level of Hg contamination and the largest variability in Hg content of the three soils (Table 3.4). Explanation for the variability observed in the contaminated soils may be a result of heterogeneous distribution of Hg in the soil samples.

Table 3.4. Total soil Hg concentration in contaminated soils

Sample	Total Soil Hg Concentration (mgkg^{-1})	[1] Number of Samples analyzed	C.V. [1] (%)
2	67.0	120	65.0
4	5.20	150	52.0
5	5.82	150	50.0

1. Coefficient of variance = (one standard deviation/mean) * 100

3.2. Oxidative Treatment

Extraction procedures with various chemical reagents have been commonly used in the investigation of the different forms of Hg. A variety of reagents have been used including: water, various soluble salts, inorganic solvents and strong acids and bases. The efficiency of these extraction procedures vary with experimental parameters, Hg speciation, soil properties and desired end-points. In addition, the application of some of the above extractants to hydrocarbon contaminated soils is promising. Despite potential limitations that could arise, situations may exist where useful information may be obtained using extraction systems for co-contaminated removal of Hg and hydrocarbon from soil. Sodium hypochlorite (NaOCl), hydrogen peroxide (H_2O_2) and calcium hypochlorite ($Ca(ClO)_2$) oxidative reagents were utilized to provide information on the potential effectiveness of Hg and hydrocarbon removal from soil.

3.2.1. *Phase I: Equilibrium Experiments*

Initial evaluation of NaOCl, H_2O_2 and $Ca(ClO)_2$ for removing Hg and hydrocarbons from soil was done in order to determine optimal extraction times for each extractant type. As indicated previously in section 2.2.3.1, only the lower molar concentrations of each oxidative reagent were used. Batch equilibrium mixing times of 1, 3, 6 ,9 ,16 and 24 hours were chosen to determine optimal treatment times. Soil 2 treated with H_2O_2 had an additional treatment period of 30 minutes added. This time was included to evaluate the trend in total soil Hg removal more accurately as initial experiments indicated that a large amount of total soil Hg was removed within the first hour of treatment.

3.2.1.1. Hg Removal

Results for NaOCl treated soil 2 indicated that increased mixing time produced an increase in Hg removal. Total soil Hg removal plateaued at or after 5 hours (Figure 3.1).

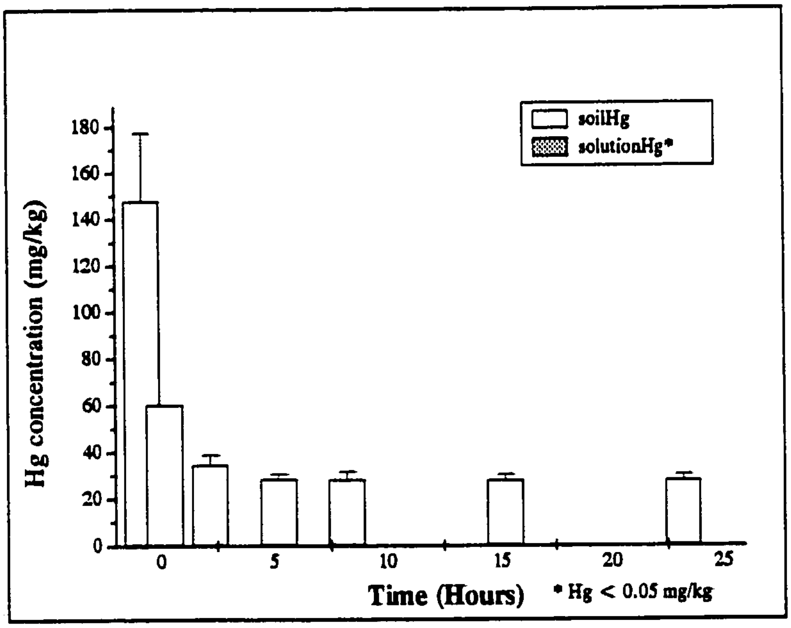


Figure 3.1. Changes in soil and solution Hg concentrations of soil 2 after addition of NaOCl

One way ANOVA (SPSS, version 4.1) indicated that total soil Hg content did not significantly decrease after 9 hours of extraction ($P > 0.05$). With respect to the solution phase, only a minor amount (< 10 %) of the initial total soil Hg removed was recovered following oxidation.

Hydrogen peroxide treated soil 2 illustrated that increased mixing time produced an increase in total soil Hg removal. Total soil Hg removal plateaued at or after 5 hours

(Figure 3.2).

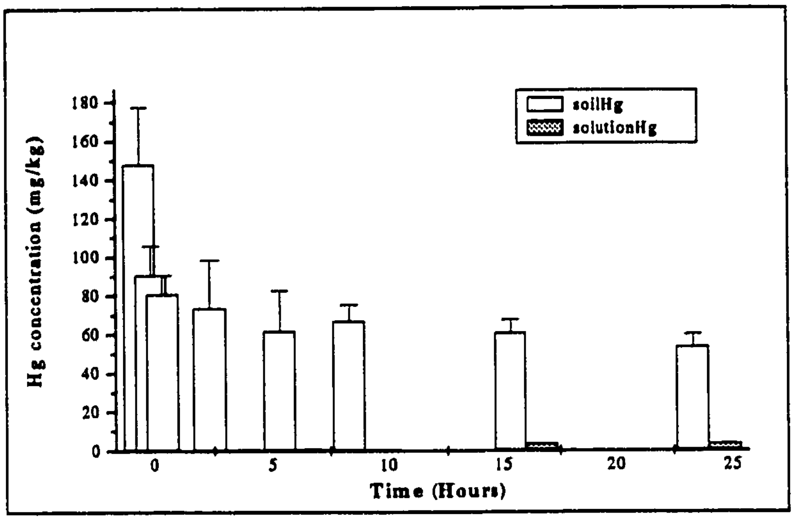


Figure 3.2. Changes in soil and solution Hg concentrations of soil 2 after addition of H_2O_2

One-way ANOVA analysis (SPSS, version 4.1) indicated that after 16 hours of extraction there was not a significant reduction in total soil Hg ($P > 0.05$). Only a small portion of the original soil Hg was recovered within the solution phase.

Calcium hypochlorite treatment of soil 2 indicated that increased mixing time produced a decrease in total soil Hg content. Total soil Hg removal plateaued at or after 5 hours (Figure 3.3). Again, one way ANOVA analysis (SPSS, version 4.1) indicated that total soil Hg was not significantly reduced after 9 hours of extraction ($P > 0.05$). Total solution Hg concentrations did not increase parallel to total soil Hg decreases.

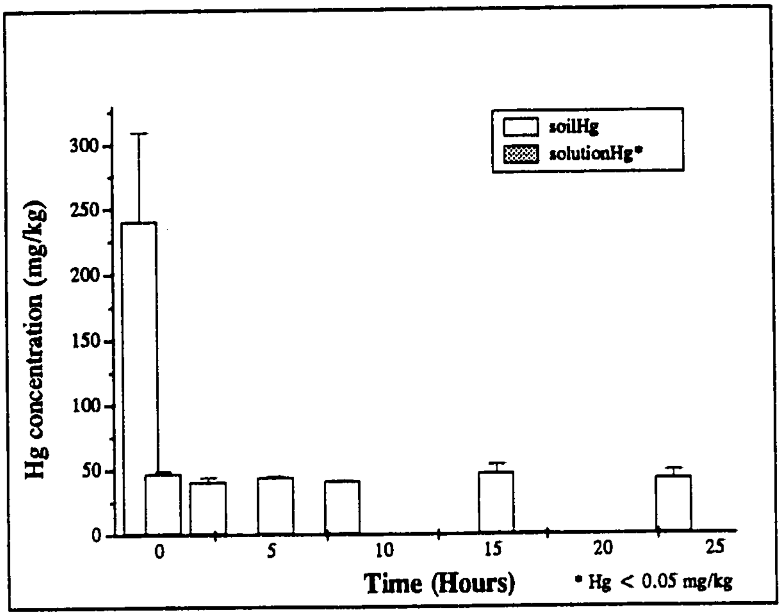


Figure 3.3. Changes in soil and solution Hg concentrations of soil 2 after addition of $Ca(ClO)_2$

3.2.1.2. Hydrocarbon Removal

Total extractable organics (TEO) were also evaluated for selecting extraction times that may be useful in subsequent experiments. However, H_2O_2 treated soil was not analyzed for TEO content, due to complications in experimental design. Hydrogen peroxide treated soil samples were lost through improper initial selection of speed, time and temperature of centrifugation. These problems were overcome for phase II experimental analysis. ANOVA analysis was not performed on TEO data due to limitations associated with sample treatments and data trends. Multiple linear regression analysis (SPSS, version 4.1) was used to indicate if extractant type and time had a significant influence on TEO removal. Multiple linear regression analysis of results from NaOCl and $Ca(ClO)_2$ treated soil indicated that there was no significant difference in TEO removal with respect to either extractant type or time of extraction ($P > 0.05$) (Figures 3.4 and 3.5).

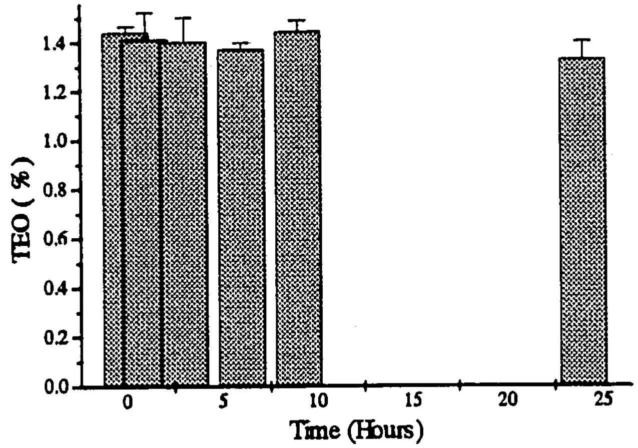


Figure 3.4. Changes in TEO of soil 2 after addition of NaOCl

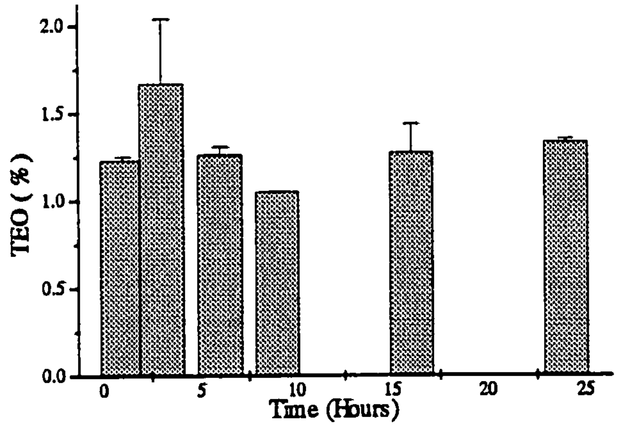


Figure 3.5. Changes in TEO of soil 2 after addition of $Ca(ClO)_2$

3.2.1.3. Significance

Although there was no decrease in TEO with respect to oxidative treatment experimental evidence suggests a significant difference with respect to both time and extractant type in removing total soil Hg. Two factorial analysis of total soil Hg removal and extractant type indicated that the type of extractant used was significant and does influence soil Hg removal. Time of extraction also had a significant influence on Hg extraction from soil and is variable depending on extractant type. Since each of the extractants possesses different chemical properties it is expected that each would have variable capabilities for facilitating soil Hg removal, producing different treatment times.

Evidence suggests a mass imbalance in total soil Hg content prior to oxidative treatment and Hg remaining in both the soil and solution phases after oxidation. It was hypothesized at this point that the oxidative treatment was yielding a volatile Hg species that was lost. An additional explanation for this mass imbalance results from the production of an insoluble co-precipitate that was not quantified by the chosen method of analysis. Based upon the results obtained from Hg removal in Phase I, extraction time of 16 hours was chosen for all extractant types to maintain experimental consistency.

3.2.2 Phase II: Removal of Hg and hydrocarbon at 20°C

As indicated in section 2.2.3.2, 3 oxidative reagent concentrations were examined for NaOCl and H_2O_2 and 2 oxidative reagent concentrations for $Ca(ClO)_2$, to evaluate Hg and hydrocarbon removal from soil. It was initially hypothesized that the higher oxidative reagent concentrations would aid in enhancing Hg removal and also facilitate some quantitative reductions in TEO. This trend was not evident in Phase I as only one reagent concentration was evaluated. Additional soils were examined in this phase, each possessing different levels of Hg and hydrocarbon contamination (Table 3.3). These soils were chosen in order to provide some understanding of co-contaminant removal of Hg and hydrocarbon with oxidation.

3.2.2.1. Hg Removal

Oxidative treatment of Hg and hydrocarbon co-contaminated soils 2, 4, and 5 indicated a significant drop in total soil Hg. Increasing molar concentration of oxidative reagents did not result in enhanced Hg removal for each oxidative reagent.

Statistical analysis for determining both the best extractant for each soil and optimal extractant concentration was not possible. The data fits a non-linear format and no linear type statistical analysis was applicable. Non-linear least square comparisons were initially examined, but were ruled out due to the data possessing a large numerical gap between water and the first oxidative extractant concentration (SAS, version 7.1) (Figure 1, Appendix I). Curve fitting was eventually used to provide some idea of the maximum amount of total soil Hg removal occurring with oxidative extraction (Figures 1 through 12, appendix I). Maximum Hg removal for each extractant within each soil based on curve fitting methods are shown in Tables 3.5, 3.6, 3.7.

Table 3.5. Curve fitting parameters for oxidative treatment of soil 2 at 20°C

Extractants	*Equation*	*ExC*
NaOCl	Y= 103 *(3.6X / 1 + 3.6X)	1.2
H_2O_2	Y = 83 * (1.5X / 1 + 1.5X)	3.5
$Ca(ClO)_2$	Y = 83 * (12 X/ 1 + 12X)	0.6

Y = Total Hg Removed (%)
X = Concentration of Oxidative Extractant (M)
ExC = Observed extractant concentration (M) for maximum Hg removal

Table 3.6. Curve fitting parameters for oxidative treatment of soil 5 at 20°C

Extractants	*Equation*	*ExC*
NaOCl	Y= 120 *(1.7 X / 1 + 1.7X)	1.7
H_2O_2	Y= 87 * (8.0X / 1 + 8.0X)	7.1
$Ca(ClO)_2$	Y = 98 * (7.5 X / 1 + 7.5X)	0.6

Y = Total Hg Removed (%)
X = Concentration of Oxidative Extractant (M)
ExC = Observed extractant concentration (M) for maximum Hg removal

Table 3.7. Curve fitting parameters for oxidative treatment of soil 4 at 20°C

Extractants	*Equation*	*ExC*
NaOCl	$Y = 56X + -4.6$	1.7
H_2O_2	$Y = 60 * (0.4X / 1 + 0.4X)$	3.5
$Ca(ClO)_2$	$Y = 46 * (90.8 X / 1 + 90.8X)$	0.4

Y = Total Hg Removed (%)
X = Concentration of Oxidative Extractant (M)
ExC = Observed extractant concentration (M) for maximum Hg removal

3.2.2.1.1. *NaOCl Treated Soil*

Sodium hypochlorite treatment of soil 2 at different molar concentrations of extractant indicated that increasing molar concentrations enhanced both total soil Hg removal and total solution Hg concentrations (Figure 3.6). For example, total soil Hg was reduced from 68 $mgkg^{-1}$ to 31 $mgkg^{-1}$ and 13 $mgkg^{-1}$ after addition of 0.8 M and 1.2 M NaOCl, respectively. Maximum soil Hg removal occurred at a 1.2 M of NaOCl and did not significantly change with increasing concentrations, based on curve fitting methods (Table 3.5).

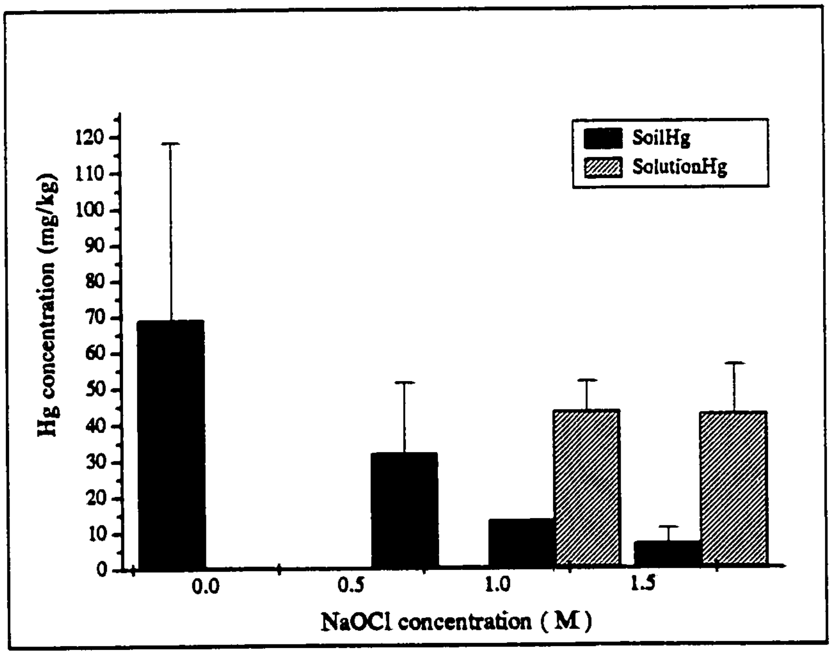


Figure 3.6. Changes in soil and solution Hg concentration of soil 2 after addition of NaOCl at 20°C

Sodium hypochlorite treatment of soil 5 showed a decrease in total soil Hg with increasing molar concentration of extractant and a corresponding increase in solution phase Hg concentrations (Figure 3.7). Maximum total soil Hg removal occurred at the highest molar concentration of NaOCl (0.76 mgkg^{-1} total soil Hg after oxidation), based on curve fitting methods (Table 3.6).

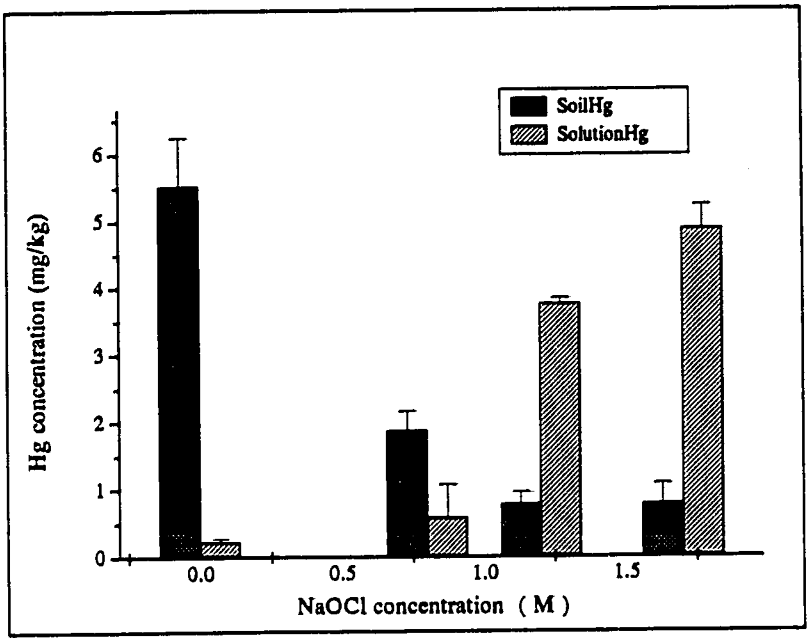


Figure 3.7. Changes in soil and solution Hg concentration of soil 5 after addition of NaOCl at 20°C

Oxidative treatment of soil 4 showed the same trend as soil 5 (Figure 3.8). Maximum removal of total soil Hg occurred at the highest molar concentration of NaOCl (0.52 mgkg^{-1} total soil Hg after oxidation) (Table 3.7). Solution phase Hg concentrations were also observed to increase with increasing molar concentrations of NaOCl (Figure 3.8).

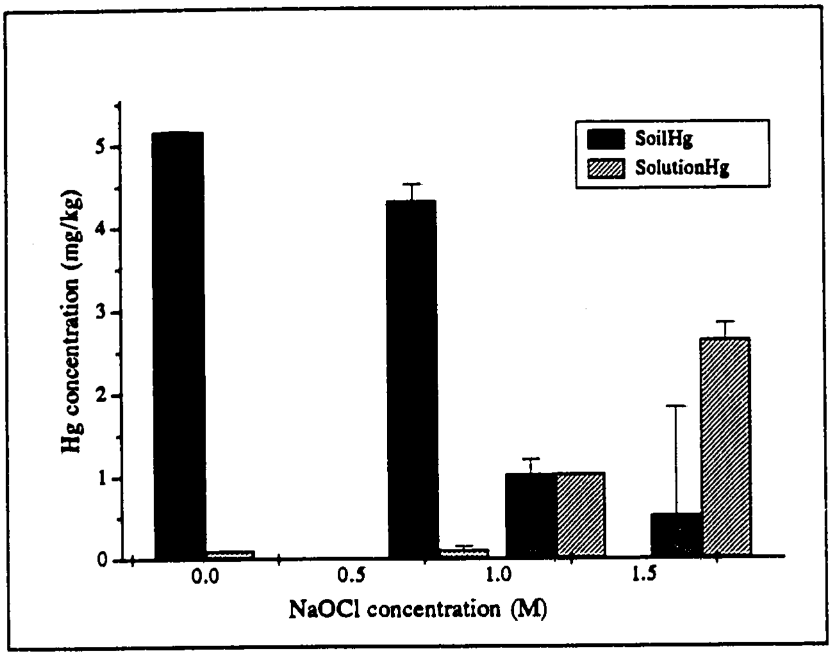


Figure 3.8. Changes in soil and solution Hg concentration of soil 4 after addition of NaOCl at 20°C

3.2.2.1.2. *H_2O_2 Treated Soils*

Hydrogen peroxide treatment of soil 2 reduced the total soil Hg content by approximately half of its original amount (30 mgkg^{-1} total soil Hg after oxidation). Extraction of total soil Hg with H_2O_2 produced a plateau for concentrations exceeding 3.5 M based on curve fitting methods (Table 3.5). However, H_2O_2 treated soil 2 showed no evidence of enhanced total soil Hg removal with increasing concentration of extractant (Figure 3.9). Hydrogen peroxide oxidation of soil 2 did not result in an increase in solution phase concentrations (Figure 3.9).

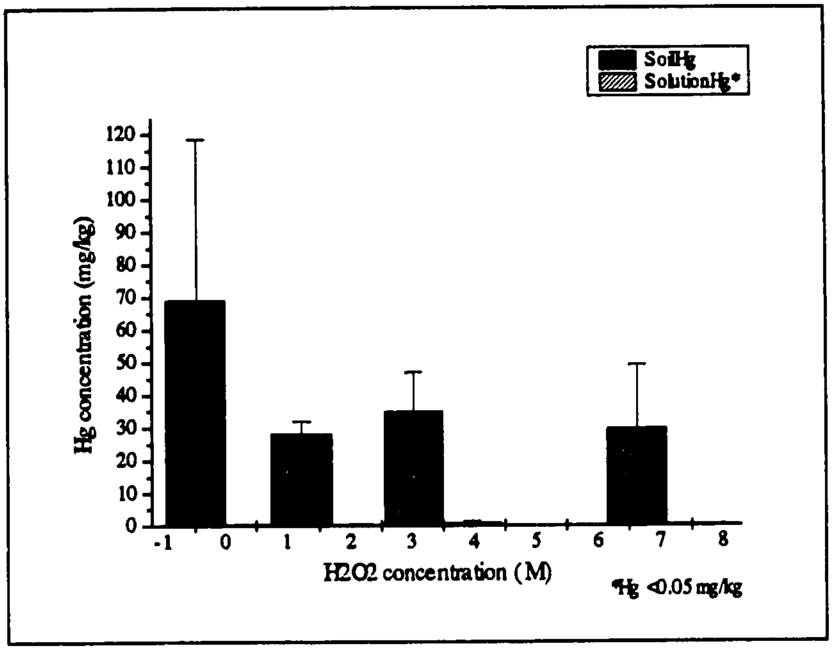


Figure 3.9. Changes in soil and solution Hg concentration of soil 2 after addition of H_2O_2 at 20°C

Hydrogen peroxide treatment of soil 5 indicated that increasing molar concentrations of extractant enhanced soil Hg removal, but did not significantly increase Hg solution phase concentrations (Figure 3.10). Maximum extraction of total soil Hg occurred at the highest molar concentration of H_2O_2 (0.76 $mgkg^{-1}$ total soil Hg after oxidation) (Table 3.6)

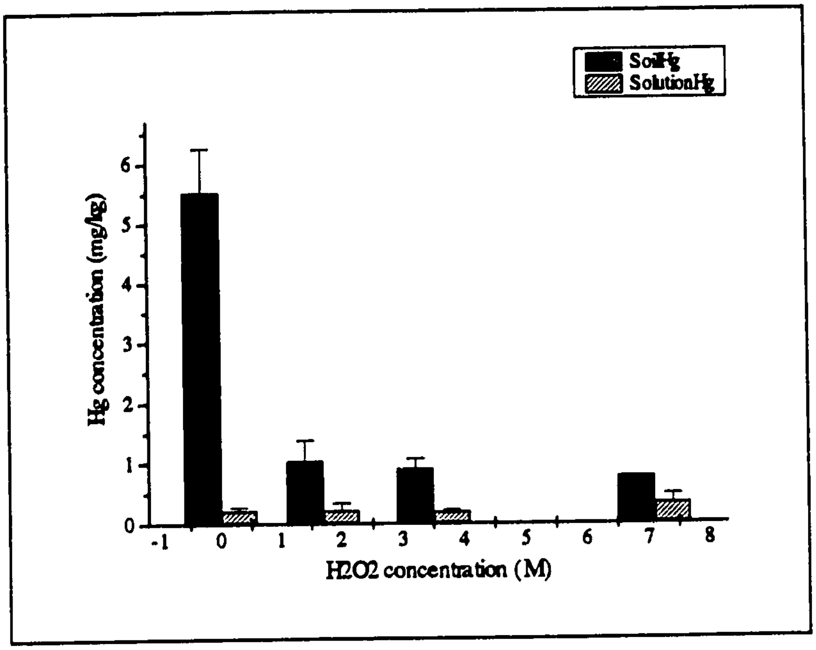


Figure 3.10. Changes in soil and solution Hg concentration of soil 5 after addition of H_2O_2 at 20°C

Hydrogen peroxide treatment of soil 4 illustrated that although H_2O_2 application decreases total soil Hg content, increasing molar concentrations of H_2O_2 neither significantly enhances total soil Hg removal nor increases the Hg solution phase concentrations (Figure 3.11). Maximum soil Hg removal, based on curve fitting methods occurred at 3.5 M H_2O_2 (3.16 mgkg^{-1} total soil Hg after oxidation) (Table 3.7). Both soil 2 and 4 had maximum total soil Hg losses at concentrations of 3.5 M. However, soil 5 required higher molar concentration of extractant to produce maximum total soil Hg removal. This latter trend may be related to elevated levels of hydrocarbon contamination associated with soil 5 (Tables 3.5, 3.6 and 3.7).

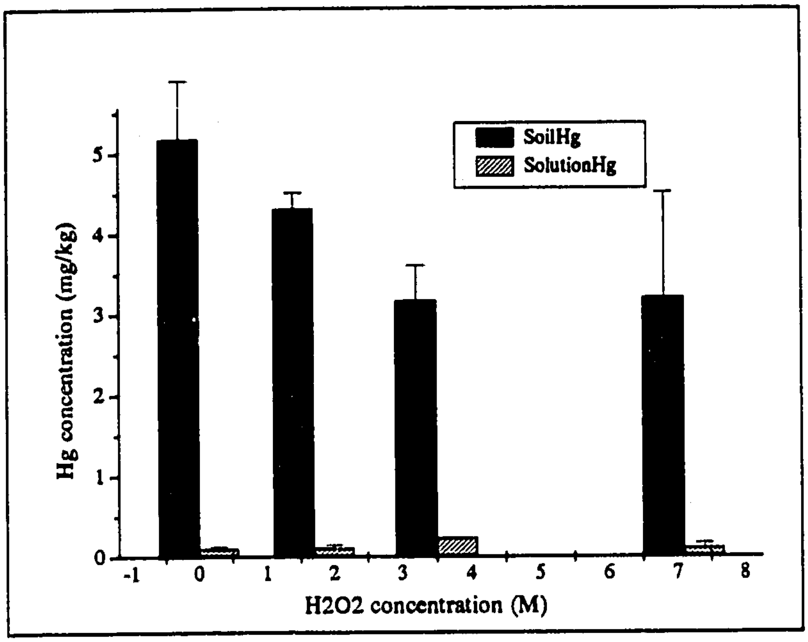


Figure 3.11. Changes in soil and solution Hg concentration of soil 4 after addition of H_2O_2 at 20°C

3.2.2.1.3. $Ca(ClO)_2$ Treated Soils

Calcium hypochlorite treatment of soil 2 produced a decrease in total soil Hg with increasing molar concentration of extractant and a corresponding increase in solution phase Hg concentrations (Figure 3.12). Total soil Hg was reduced from 68 $mgkg^{-1}$ to 21 $mgkg^{-1}$ and 18 $mgkg^{-1}$ after treatment with 0.4 M and 0.6 M $Ca(ClO)_2$, respectively. Calcium hypochlorite treatment of soil 2 did not produce a plateau in Hg removals for the concentrations used in this experiment. This is also evident with respect to the highest molar concentration being most effective at total soil Hg removal (Table 3.5). The lack of a plateau with respect to total soil Hg removal after treatment with $Ca(ClO)_2$ may be a result of the restricted molar range used for $Ca(ClO)_2$. Total soil Hg was reduced by more than half of the original Hg content.

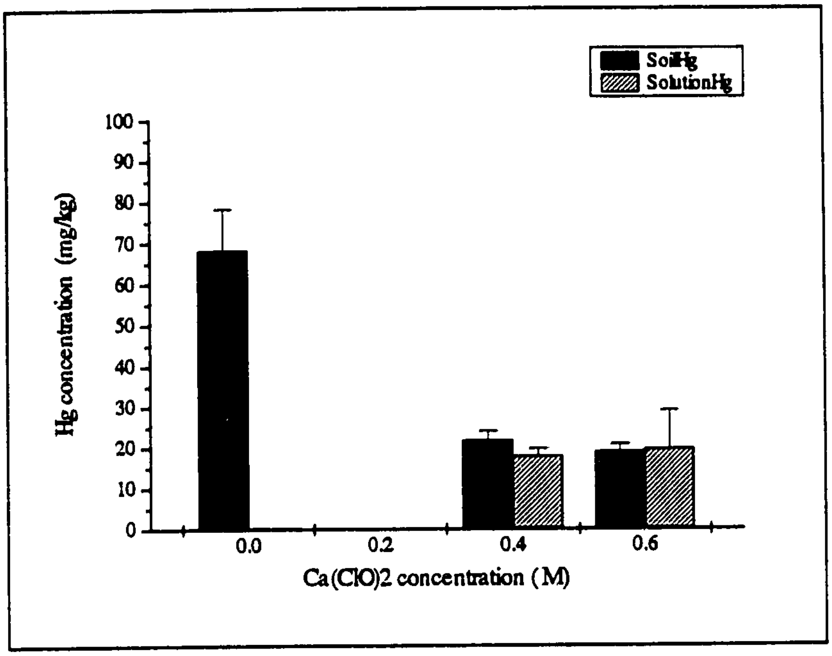


Figure 3.12. Changes in soil and solution Hg concentration of soil 2 after addition of $Ca(ClO)_2$ at 20°C

Oxidative treatment of soil 5 with $Ca(ClO)_2$ indicated the same trend as soil 4. As molar concentration of extractant increased there was an observed decrease in total soil Hg and a corresponding increase in the total solution phase Hg levels (Figure 3.13). The highest molar concentration of $Ca(ClO)_2$ used in this experiment achieved the greatest release of soil Hg based on curve fitting methods (0.98 $mgkg^{-1}$ total soil Hg after oxidation) (Table 3.6).

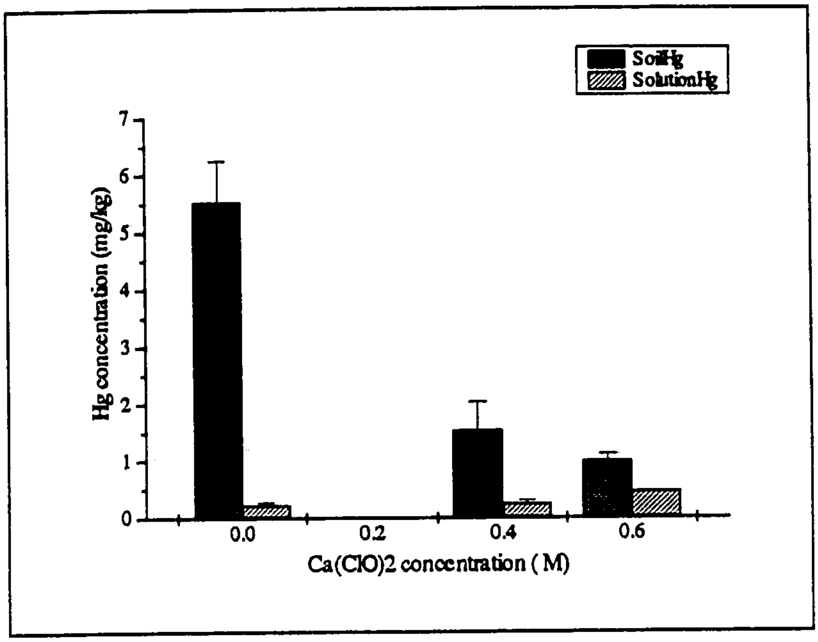


Figure 3.13. Changes in total Hg of soil 5 after addition of $Ca(ClO)_2$ at 20°C

Oxidative treatment of soil 4 with $Ca(ClO)_2$ resulted in a decrease in total soil Hg content and an increase in solution phase Hg concentrations (Figure 3.14). Total soil Hg was reduced from 5.16 mgkg^{-1} to 2.84 mgkg^{-1} after treatment with both 0.4 M and 0.6 M $Ca(ClO)_2$.

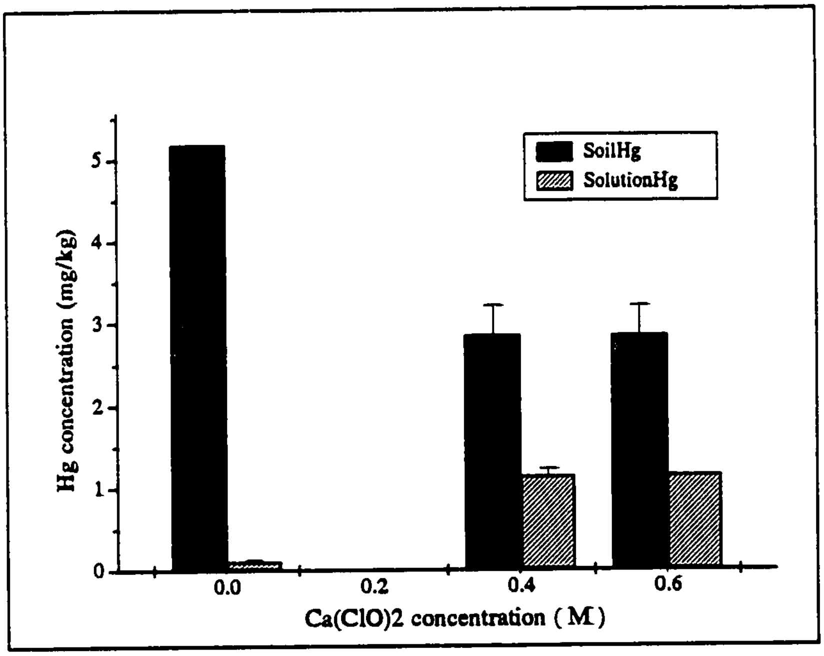


Figure 3.14. Changes in soil and solution Hg concentration of soil 4 after addition of $Ca(ClO)_2$ at 20°C

3.2.2.1.4. Significance

In contaminated soils 2, 4 and 5 oxidative treatment resulted in variable changes in both soil Hg concentrations and solution Hg concentrations. Reductions in total soil Hg were variable based on initial Hg concentrations, form of Hg present within each soil sample, chemical oxidant type and concentration applied. The molar concentration most effective for maximal removal of total soil Hg varied amongst soils, with the moderate to high molar concentrations being most effective.

Results obtained from this experiment indicated that some of the soils treated with one or more of the oxidants fell into one or more categories of the CCME land use remediation criteria for Hg contaminated soils (Table 3.8) (CCME, 1991).

Table 3.8. CCME Remediation Criteria land use classification for Hg (CCME, 1991)

CCME Land Use Remediation Classification	*Total soil Hg ($mgkg^{-1}$)*
Commercial/Industrial	< 10 $mgkg^{-1}$
Parkland/ Residential	< 2 $mgkg^{-1}$
Agricultural	< 0. 8 $mgkg^{-1}$

However, the purpose of this thesis was to elucidate some of the fundamental principles behind the potential application of hypochlorite and hydrogen peroxide oxidants to remove both Hg and hydrocarbons from soil. The results in this study only provide a frame work for future research directions at a practical scale. Further research is required to determine appropriate optimization based experimental protocols useful for field based applications to co-contaminated industrial sites.

Differences in molar concentrations required for maximum soil Hg removal are based on the presence of interfering compounds, such as carbonates, organic matter and hydrocarbons. In many oxidation reactions, the generation of a OH or OCl radical is just one step in a series of additional reactions. The presence of carbonates can lead to the generation of carbonate radicals ($CO_3^{\cdot -}$) that have lower reaction efficiencies and are known to be ineffective at degrading organic matter (Von Sonntag *et al.*, 1997).

Furthermore, the application of H_2O_2 and NaOCl to soils is commonly used to remove organic matter indicating that native organic matter can decrease reaction efficiencies of hydrocarbon removal (Anderson, 1963 and Lavkulich and Weins, 1970). It is believed that the level of hydrocarbon contamination, carbonate content and amount of native organic carbon will influence the required molar concentration for maximal removal of Hg, especially if the Hg is present as an organomercurial species associated with organic matter. Experimental evidence demonstrates this trend as evident from the higher molar concentration of oxidative reagents required for soil 5, which possesses the highest TEO and TOC content (Table 3.2). Soils 2 and 4 are similar, with respect to the molar concentration required for maximum total soil Hg removal, therefore both soils would likely possess similar levels of free radical consumption.

It was evident that treatment with NaOCl and $Ca(ClO)_2$ produced similar soil Hg removal mechanisms. Sodium and calcium hypochlorite removed soil Hg primarily as a soluble fraction, which has also been observed in a number of other studies (Stepan et al., 1995; Wilhem and McArthur, 1995; Pederoso et al., 1994; Schroeder *et al.*, 1991; Parks and Baker 1969 and Parks and Fittinghoff, 1970).

The initial application of hypochlorite oxidative extractants was developed by the hydrometallurgical industry because it was a more economical and safe way of removing Hg from cinnabar deposits than the original pyrometallurgical methods (Wilhelm and McArthur, 1995 and Pederoso et al., 1994; Parks and Baker, 1969). The principal behind the application of hypochlorite salts to remove Hg from cinnabar and Hg contaminated sludges and soil systems is based on the proposed generation of hypochlorite free radicals ($OCl^{\cdot}$) (Stepan et al., 1993; Wilhem and McArthur, 1995; Pederoso et al., 1994; Parks and Baker, 1969 and Parks and Fittinghoff, 1970). Hypochlorite free radicals remove Hg by converting elemental and less soluble Hg compounds to water soluble mercuric ions, primarily mercuric chloride ($HgCl_2$) species (Pedroso et al., 1994 and Wilhelm and McArthur, 1995).

The highly effective nature of hypochlorite can be related to the fact that the most important ligands in solution for Hg are hydroxide, chloride and organic anions. Since mercuric chloride ($HgCl_2$) and mercuric hydroxide ($Hg(OH)_2$) solids have high stability constants the affinity of Hg to these ligands leads to an increase in solubility and enhanced mobility (Shuster, 1991). The Hg complex that dominates is dependent on the systems' pH and complexation concentration of either the chloride or hydroxide anion. The importance of Cl^- to the formation of soluble $HgCl_2$ species relates to hard and soft acid-base chemistry (HSAB). Since Hg is a soft Lewis acid and chloride behaves as a soft Lewis base, an increase in Cl^- would result in increased solution phase concentrations of mercuric chloride species. Mercury and chloride interactions result in the development of inner sphere complexes of greater covalent binding creating larger stability constants. In contrast, the hydroxyl ligand is a hard base and complexation with Hg results in outer sphere complexations with the resulting mercuric hydroxide complexes possessing lower stability constants (Pearson, 1968). Consequently, the effectiveness of OH^- complexes to promote Hg (II) mobilization is more restricted due to the lower intrinsic solubility of $Hg(OH)_2$ as compared to the high solubility of $Hg(Cl)_2$ (Hahne and Krootje, 1973). Chloride also has the unique capacity to enhance Hg removal from soil by reducing Hg adsorption. Experimental evidence has shown that increasing chloride concentrations results in decreased Hg adsorption (Schuster, 1991).

Adsorption inhibition in the presence of chloride results primarily from complex formation with the resulting halide possessing lower adsorption affinity. For example, the inability of $HgCl_2$ to adsorb and for chloride to act as a poor bridging ligand is consistent with the absence of measurable specific adsorption of free chloride ions on geothite (Schuster, 1991). Newton et al., (1976) also demonstrated that the formation of $HgCl_2$ complexes reduced Hg(II) adsorption to inorganic colloids at chloride concentrations greater than 10^{-3} M or higher, especially in soil systems with pH values exceeding 8. The soils used in this study all fell within this pH range prior to oxidative treatment. Once treated with either NaOCl or $Ca(ClO)_2$ the soils had an observed increase in the soil pH ($pH > 8.0$) and Cl^- concentrations far exceeded 10^{-3} M (Figure 3.15 and 3.16).

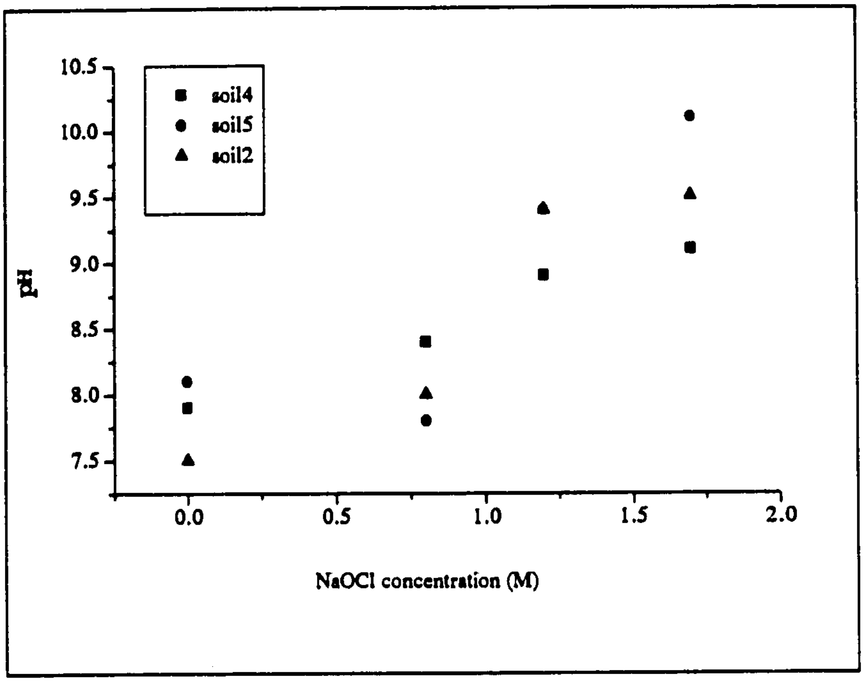


Figure 3.15. Soil pH after addition of with NaOCl at 20°C

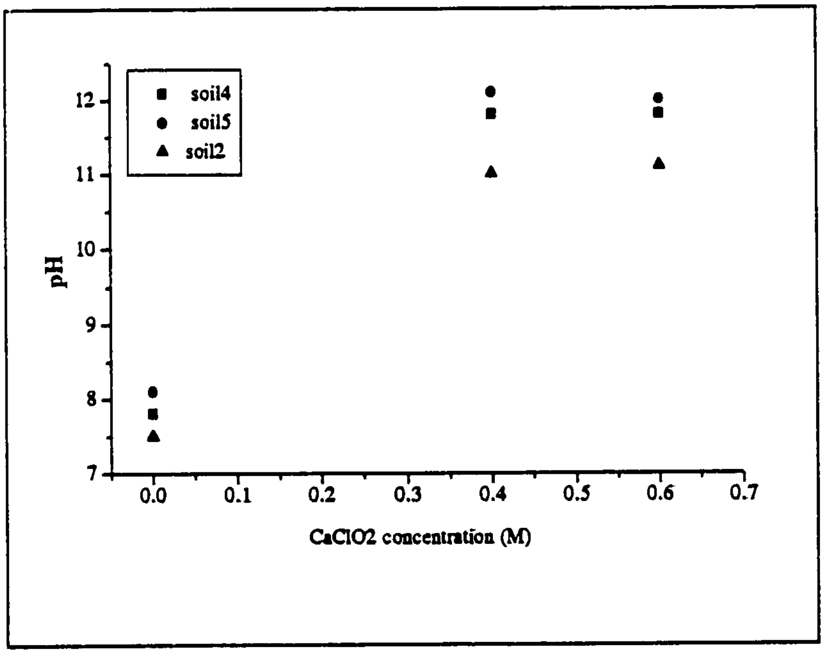


Figure 3.16. Soil pH after addition of $Ca(ClO)_2$ at 20°C

This pH range indicates that the dominant soluble species would likely be a $Hg(OH)_2$ species. However, based on the elevated concentrations of available Cl^- associated with the addition of NaOCl and $Ca(ClO)_2$ the dominant soluble Hg species would be: 1) $HgCl^+$, $HgCl_2$, $HgOH_2$ and HgOHCl at 0.4M $Ca(ClO)_2$ and 0.8 M NaOCl and 2) $HgCl_3^-$ and $HgCl_4^{2-}$ at 0.6 M $Ca(ClO)_2$, 1.2 M NaOCl and 1.7 M NaOCl. This is based on evidence from Hahne and Kroonjie (1973) who illustrated that at pH ranges from 8 to 9, $Hg(OH)_2$ species would normally dominate in solution. However, OH^- and Cl^- competition for Hg complexation in this pH range is also important. At pH values of 8.5 or greater, $Hg(OH)_2$ species are non-existent when the Cl^- concentrations exceed 5000 $mgkg^{-1}$ but become increasingly important at Cl^- concentrations less than 5000 $mgkg^{-1}$ (Hahne and Kroonjie, 1973). In this study only the lower molar concentrations of NaOCl and $Ca(ClO)_2$ falls below the 5000 ppm Cl^- limit. Therefore, at 0.4 M $Ca(ClO)_2$ and 0.8 M NaOCl $Hg(OH)_2$ species would play a greater role in dictating soluble Hg species. This translates into lower solution Hg concentrations after oxidation with 0.4 M $Ca(ClO)_2$ and 0.8 M NaOCl due to the lower intrinsic solubility of $Hg(OH)_2$ species, which was observed in this study. This further substantiates the importance of Cl^- and its ability to generate soluble mercuric chloride complexes even at highly alkaline pH values. The ability of anions to hydrolyze sparingly soluble Hg compounds has long been realized as an important factor in determining solubilites (Hahne and Kroontje, 1973). Consequently, it is not surprising that the application of hypochlorite extractants would promote the removal of soil Hg into a soluble form.

The high alkaline conditions observed after NaOCl and $Ca(ClO)_2$ treatment may have enhanced soil organic matter solubilization. This would translate into potentially higher rates of Hg solubilization observed with treatment due to soil pH changes rather than the concentration of chloride. The enhanced solution Hg concentration with increasing chloride concentrations implicates that chloride is playing a greater role in Hg solubilization rather than soil organic matter solubilization. However, this does not completely exclude the importance of soil pH on Hg transformations.

The addition of hypochlorite salts to Hg contaminated soils also indicated that NaOCl was more effective at total soil Hg removal compared to $Ca(ClO)_2$. The presence of sodium with the NaOCl oxidant results in the dispersion of aggregates, allowing for greater surface area exposure for Hg removal. However, at concentrations above 1.7M

NaOCl conditions are conducive for flocculation of clays because the high NaCl concentration (NaCl > 10%) suppresses the electric double layer of clays (McBride, 1994).

Hydrogen peroxide treatment of soils 2, 4 and 5, resulted in much different results compared to NaOCl and $Ca(ClO)_2$ treated soils. Hydrogen peroxide treatment of contaminated soils 2, 4 and 5 all indicated: 1) treatment decreased soil Hg content, 2) increasing molar concentrations of extractant did not enhance soil Hg removal and 3) solution Hg concentrations did not increase significantly with treatment. One of the few mechanisms believed responsible for total soil Hg removal with H_2O_2 treatment is based on the conversion of organic mercury to inorganic forms. Atmospheric dimethyl mercury ($(CH_3)_2Hg$) is photolysed by UV light, whereby radicals generated might result in the following reaction and potential by-products (Kaiser and Tolg, 1980) :

$$(CH_3)_2Hg \longrightarrow CH_3^{\cdot} + CH_3Hg^{o} \longrightarrow Hg^{o} + C_2H_6$$

In the above reaction $(CH_3)_2Hg$ is decomposed to CH_3Hg via demethylation, H-abstraction or C-C bond cleavage mechanisms yielding another methyl radical. This methyl radical can then further react to cause additional demethylation, C-C bond cleavage or hydrogen abstraction to give rise potentially to methane, ethane or additional by-products, including Hg^{o}. Furthermore, the presence of Hg as both organic and inorganic compounds in the atmosphere has been documented to yield Hg^{o} in the presence of sunlight based on oxidation reactions. These findings suggest that this mechanism could be occurring with the co-contaminated soils treated with H_2O_2 (Kasier and Tolg, 1980).

The limited concentration of total solution Hg witnessed with H_2O_2 treatment is consistent with Hg^{o} as the final product. Elemental Hg possesses an inherently low water solubility (6×10^{-5} g/ L at 25°C). Furthermore, the pH drop that occurred with H_2O_2 treatment of soils in this study would indicate that $Hg(OH)_2$ would be the dominant soluble species since the distribution of Hg in solution at pH 6 to 7 is determined by $Hg(OH)_2$ solubility (Hahne and Kroontje, 1973 and Schuster, 1990) (Figure 3.17). However, the effectiveness of OH^- complexes to promote Hg(II) mobilization is more restricted due to lower intrinsic solubility of $Hg(OH)_2$ compared to the high solubility of $HgCl_2$ (Hahne and Kroontje, 1973). Therefore, limiting the ability to remove total soil Hg as primarily a soluble species with H_2O_2 treatment.

Consequently, the application of H_2O_2 to the Turner Valley contaminated soils may potentially result in the generation of an inorganic volatile Hg species. This assumption is based upon the fact that the Turner Valley soils have been previously documented to contain primarily organomercurial species associated with organo-clay complexes. The addition of H_2O_2 results in the generation of $OH^{\cdot}$ radicals that cause C-C bond cleavage, H- abstraction or demethylation of organomercurial species from organic matter clay complexes, ultimately giving rise to the release of elemental Hg. This concept would also explain why Hg losses (initial total soil Hg before oxidation minus soil Hg + solution Hg after oxidation) would vary between soils possessing variable organic matter content and compositions and levels of Hg and hydrocarbon contamination.

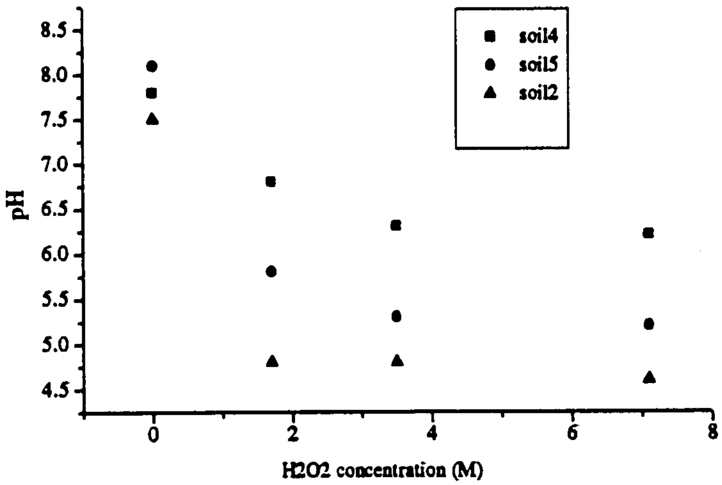


Figure 3.17. Soil pH after addition of H_2O_2 at 20°C

It is evident that oxidative treatment of contaminated soils 2, 4 and 5 resulted in different total Hg losses depending on the type of extractant. Differences in the relative levels of Hg loss between soils were also observed after oxidative treatment with the same oxidants (Table 3.9). This indicates that the contaminated soils may have had competing secondary oxidative intermediates present, which would decrease reagent efficiency.

Table 3.9. Hg loss after oxidative treatment for soils 2,4 and 5 at 20°C

Extractant Type	Extractant Concentration (M)	average Hg loss (%) soil 2	S.D.[1]	average Hg loss (%) soil 4	S.D.[1]	average Hg loss (%) soil 5	S.D.[1]
NaOCl	0.8	50	28	13	2.5	60	11
NaOCl	1.2	32	23	68	3.8	24	53
NaOCl	1.7	25	6.4	42	37	23	52
H_2O_2	1.7	63	11	15	0.54	79	3.8
H_2O_2	3.5	49	36	41	13	81	3.1
H_2O_2	7.1	57	28	40	11	82	2.6
$Ca(ClO)_2$	0.4	46	1.2	28	8.5	66	5.7
$Ca(ClO)_2$	0.6	41	5.9	29	6.3	79	91

1. Standard deviation

The difference in Hg loss (inital soil Hg before oxidation minus soil Hg + solution Hg after oxidation) between soils is believed to result from different Hg species present in conjunction with differences in soil carbonate, organic matter and hydrocarbon contents. For example, comparing Hg loss between soil 2 and 5 following H_2O_2 treatment, it is apparent that the soil with greater hydrocarbon contamination had the higher degree of Hg loss. Soil 5, which possesses the highest level of hydrocarbon contamination had greater Hg loss than soil 2 with H_2O_2 and $Ca(ClO)_2$ treatment, which is believed to be a result of hydrocarbon contamination. The content and composition of hydrocarbons present not only will decrease the reaction efficiency of H_2O_2, but may also influence the mechanism of Hg removal. To date there has been no literature published examining the effect of hydrocarbons on Hg removal because this method has only been recently examined.

However, since NaOCl and H_2O_2 have been used previously for organic matter destruction, it would seem reasonable that the composition and content of hydrocarbon contamination could compete for free radicals as organic matter does and could alter or reduce Hg removal. Furthermore, it is difficult to determine what types of Hg species were present within each soil. Work by Kohut et al., (1995) have indicated that most of the soil mercury is present as organomercurial species, but the specific nature of these compounds remains to be clarified. Therefore, it is likely that different organic species of Hg are present within each soil sample and that could translate into different removal efficiencies.

The generation of either $OH^{\cdot}$ or $OCl^{\cdot}$ free radicals through oxidative treatments is just one step in a series of further oxidations, with subsequent secondary oxidation species expected. The generation of these unknown secondary oxidants may influence the species of Hg formed during treatment of contaminated soils (Hoign, 1997). Watts et al., (1990) have indicated that the addition of hydrogen peroxide to soil results in non-specific oxidation with organic compounds ranging from native organic matter to hydrocarbons, ultimately resulting in variable intermediate organic radicals. These intermediate organic radicals can vary in reaction efficiencies, resulting in a variety of side reactions that could influence both hydrocarbon and Hg removal from soil. Kaiser and Tolg (1980) illustrate that organic mercury forms are converted to inorganic forms based on the generation of secondary organic radicals, such as methyl radicals, throughout the oxidative free radical reaction caused by photolyses. Carbonates react similarly to organic matter because they compete successfully for oxidative free radicals. The generation of secondary intermediates, such as $CO_3^{\cdot -}$ radicals, are often lower in reactivity than the original $OH^{\cdot}$ and have also been noted to be particularly ineffective in the degradation of organic matter. This trend could further translate into decreased hydrocarbon degradation and variable Hg removal (von Sonntag, 1997). These competing reactions would also explain why soil 5 would require greater molar concentration of extractant than other soils for total soil Hg removal. Soil 2 and 4 behaved similarly, with respect to oxidative reagent addition and Hg changes, which implicates that soils 2 and 4 possess similar competing constituents resulting in reduced reaction efficiencies. The degree to which secondary oxidants may influence Hg removal is not clearly understood and further work in this area may provide insight into optimizing Hg removal from hydrocarbon contaminated soils.

3.2.2.2. Hydrocarbon Removal

The application of NaOCl, H_2O_2 and $Ca(ClO)_2$ to soils 2, 4 and 5 resulted in variable reductions in TEO content. Two factorial ANOVA analysis was done on contaminated soils 2 and 5 (SAS, version 7.1). Contaminated soil 4 was not analyzed by two factorial analysis because the TEO content was observed to be < 0.01 % before and after oxidative treatment. Soil 4 was chosen as a control based on its lack of hydrocarbon contamination.

3.2.2.2.1. NaOCl Treated Soils

Treatment of soil 2 with NaOCl significantly reduced TEO content ($P < 0.05$). Increasing molar concentration of NaOCl significantly reduced TEO content and each extractant concentration was significantly different with respect to TEO removal ($P < 0.05$) (Figure 3.18). This indicates that each increasing molar concentration of NaOCl resulted in a significant reduction in TEO.

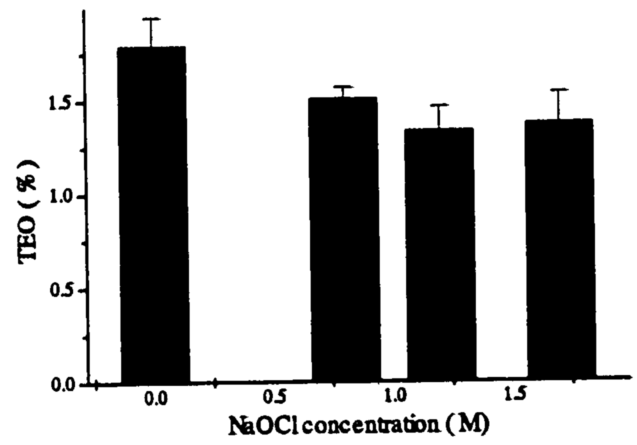


Figure 3.18. Changes in TEO of soil 2 after addition of NaOCl at 20°C

Sodium hypochlorite treatment of soil 5 did not significantly reduce TEO content at 0.8 M NaOCl ($P > 0.05$). However, TEO content was significantly reduced at 1.2M and 1.7M NaOCl ($P < 0.05$). The addition of 1.2 M and 1.7 M NaOCl were not significantly different with respect to TEO removal ($P > 0.05$) (Figure 3.19).

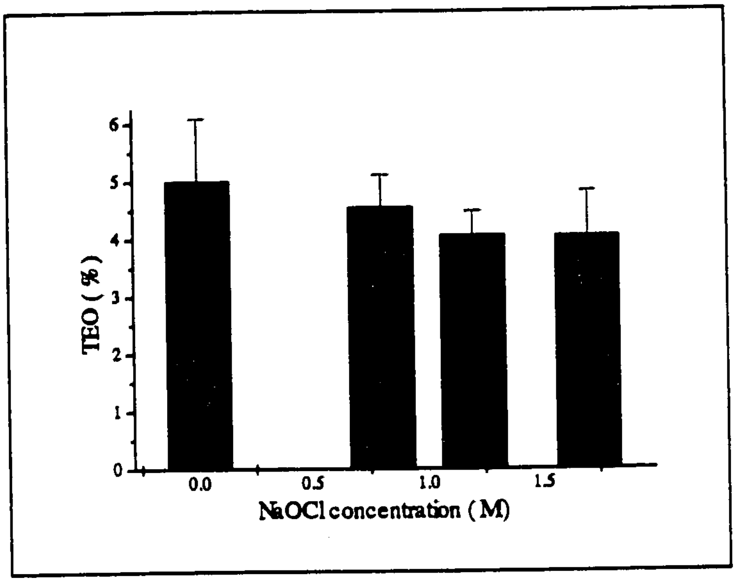


Figure 3.19. Changes in TEO of soil 5 after addition of NaOCl at 20°C

Oxidative treatment of soil 4 with NaOCl did not decrease TEO content significantly. Increasing molar concentration did not enhance the removal of TEO from soil. Soil 4 TEO content before and after oxidative treatment with NaOCl was observed to remain less than 0.01 %.

3.2.2.2.2. H_2O_2 Treated Soils

Hydrogen peroxide application to soils 2, 4, and 5 did not significantly reduce TEO content ($P > 0.05$). Increasing molar concentrations of H_2O_2 did not significantly enhance TEO removal ($P > 0.05$) (Figures 3.20 and 3.21). However, further examination of the trend in TEO content after oxidative treatment of soil 2 would indicate a reduction in TEO that is not considered statistically significant. Based on the method of statistical analysis the large variability associated with soil 5 may have skewed the statistical significance of H_2O_2 treatment on soil 2.

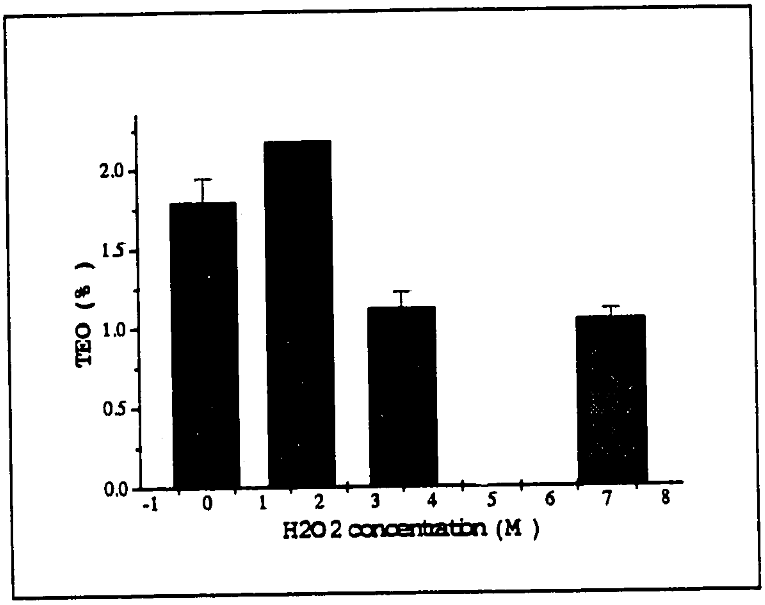


Figure 3.20. Changes in TEO of soil 2 after addition of H_2O_2 at 20°C

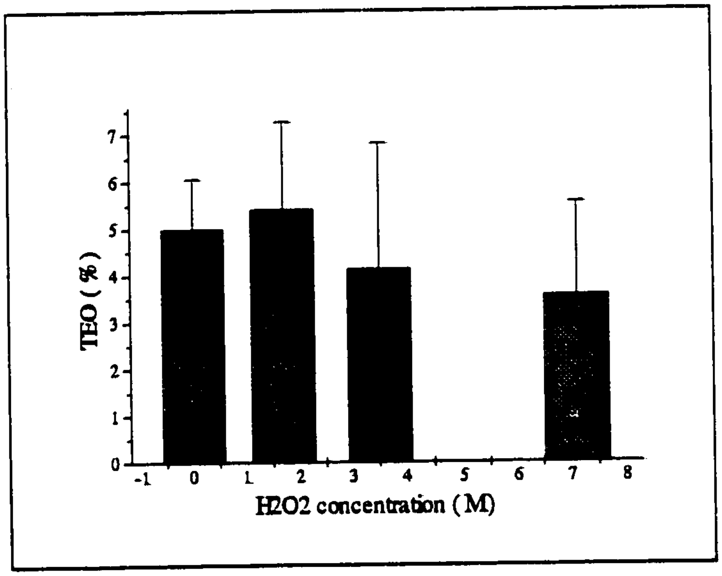


Figure 3.21. Changes in TEO of soil 5 after addition of H_2O_2 at 20°C

Soil 4 TEO content before and after oxidative treatment with H_2O_2 was observed to remain less than 0.01 %. There was no significant difference in extractant concentration and TEO removal with this soil.

3.2.2.2.3. *$Ca(ClO)_2$ Treated Soils*

Calcium hypochlorite treatment of soils 2, 4, and 5 indicated mixed results with respect to TEO removal after oxidation. Calcium hypochlorite addition to soil 2 resulted in a significant reduction in TEO content ($P < 0.05$). Furthermore, each extractant concentration was significantly different with respect to TEO removal ($P< 0.05$) (Figures 3.22 and 3.23). Calcium hypochlorite treatment of soil 5 indicated that there was not a significant reduction in TEO content ($P > 0.05$). Increasing molar concentration of $Ca(ClO)_2$ did not enhance TEO removal, which is evident by the increase in TEO content with increasing molar concentration of $CaClO_2$ (Figures 3.22 and 3.23). The observed increase in TEO content may be due to matrix variability with respect to hydrocarbon contamination and sample size.

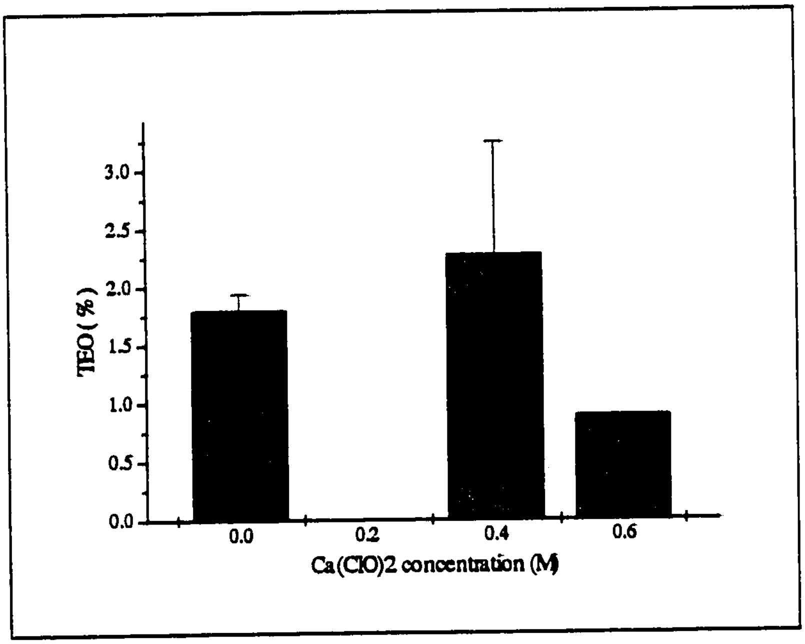


Figure 3.22. Changes in % TEO of soil 2 after addition of $Ca(ClO)_2$ at 20°C

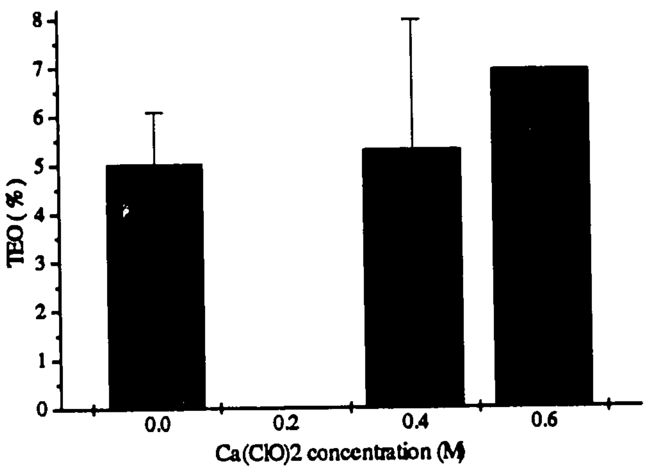


Figure 3.23. Changes in TEO of soil 5 after addition of $Ca(ClO)_2$ at 20°C

TEO content of soil 4 before and after oxidative treatment with $Ca(ClO)_2$ was observed to remain less than 0.01 %. There was no significant difference in extractant concentration and TEO removal.

3.2.2.2.4 Significance

The dominant form of Hg present within the Turner Valley soil is an organomercurial species, which has been documented by Kohut et al., (1995) to be associated primarily with the clay fraction. Since free radicals are responsible for C-C bond cleavage, H-abstraction, hydroxylation and demethylation, the addition of NaOCl, H_2O_2 and $Ca(ClO)_2$ possibly acted upon the organomercurial species causing their removal from the organo-clay complexes as either a soluble form with NaOCl and $Ca(ClO)_2$ treatment or a volatile inorganic species with H_2O_2 treatment. Oxidative treatment should then produce a reduction in both Hg and hydrocarbons because the generation of oxidative free radicals has been proposed to act non-selectively in that they react with most organic and inorganic compounds with very high rate constants which was not observed to be the case for all 3 oxidative reagents (Hoigne, 1997).

The variability observed between soils and oxidative reagents may be related to free radical consumption by natural organic materials, carbonates, and bicarbonates. Interference by the generation of intermediate radicals often complicates the use of oxidative reagents in removing organic contaminants as discussed in section 3.2.2.1. Further, most of the research to date has focused on H_2O_2 (Fenton type) remediation technologies using: 1) acidic conditions with an optimal pH range of 2-3, and 2) sandy textured soils with low soil organic matter < 0.4 % (Ravikumar and Gurol, 1994). The successes claimed with Fenton's reagent appear to be limited to soils that do not have high contents of carbonates and/or soil organic matter. In this study, carbonate rich surface soils possessing large buffering capacities were used for oxidative treatment. This high intrinsic buffering translates into potentially lower TEO removal efficiencies as was observed with H_2O_2 addition in this study.

The significant reduction in TEO observed with NaOCl and $Ca(ClO)_2$ addition, compared to H_2O_2, are believed to result from the elevated pH conditions produced with treatment. The alkaline pH range observed after oxidative treatment with NaOCl and $Ca(ClO)_2$ may have resulted in enhanced soil organic matter solubilization. Humic and Fulvic acids are soluble in alkali conditions present in this study following hypochlorite addition (Kononova, 1961). Consequently, the significant reduction in TEO may be an artifact of the soil solution pH following hypochlorite addition and not a result of free radical mechanisms. The observed increase in TEO after $Ca(ClO)_2$ treatment of soil 5 may be a result of soil matrix hydrocarbon variability and/or experimental error inherent to soxhlet extraction methods.

Soil Hg removal, without a corresponding removal of TEO following H_2O_2 addition can be further explained by the relative difference in: 1) level of contamination and 2) degree of precision and accuracy associated with TEO analysis and 3) sample variability. Total soil Hg content changes are of the order of mg/kg, while changes in TEO were evaluated on a percent TEO basis only. Therefore, the concentration of oxidative reagent required to cause a significant reduction in TEO would have to far exceed the amount used in this study. The accuracy associated with TEO gravimetric analysis may also mask changes in TEO content. Soxhlet extraction and evaluation of

TEO changes with gravimetric comparisons between non-treated and treated samples is limited in determining changes in hydrocarbon composition. The significant changes in total Hg observed with oxidation would have to translate into changes in TEO content based on the non-selective nature of free radical reactions. Consequently, oxidative treatment may have resulted in the transformation of hydrocarbons present in the soils, but not an observed significant decrease in TEO content. Burns (1993) observed that hydrocarbon content after photo-chemical oxidation tends to be measured by the reduction of total hydrocarbon loads rather than by oxygenated intermediates in the degradation process. Burns (1993) has also indicated that surface seawater contaminated with high petroleum inputs have higher amounts of oxidation products present after photo-chemical oxidation than the original parent hydrocarbons even though the total load does not significantly change. Furthermore, the oxidation by-products tend to be more polar and are often not subject to analysis. Visual observation of TEO extracts after oxidation showed a change in color with treatment. It was observed that increasing molar concentration of oxidant lightened the TEO extract color from light brown to clear, which would indicate compositional transformations or degradation of hydrocarbons occurring. The limited information provided from gravimetric TEO analysis before and after oxidative treatment and the evaluation of intermediate oxidation by-products will be discussed further in section 3.2.5.

In summary, it is believed that the $OCl^{\cdot}$ free radicals caused the oxidation of reduced Hg species and less soluble Hg complexes to remove Hg as a soluble $HgCl_2$ form as indicated in a number of previous studies (Stepan et al., 1995; Pedroso et al., 1994; Parks and Baker, 1969 and Parks and Fittinghoff, 1970). This is based on: 1) chloride being a poor bridging ligand, 2) chloride acting as a soft base and having a strong association to Hg(II) species, 3) high ionic strength of the hypochlorite solutions enhances Hg desorption, 4) the high pH of the soil systems treated with NaOCl and $Ca(ClO)_2$ (> pH 8) increases Hg desorption and ultimately allowing for increased $HgCl_2$ complexation and 5) soil Hg present in the Turner Valley soils are likely weakly adsorbed. The alkaline pH values associated with hypochlorite addition may also have played a role in the enhanced Hg solution phase concentrations observed with all three contaminated soils. However, the degree to which Fulvic-Hg and humic-Hg complexes add to total solution Hg concentrations after hypochlorite addition is not clear due to the lack of soluble carbon data.

The application of hydrogen peroxide to the Turner Valley soils resulted in a change in soil Hg content, but limited changes in TEO content. In this case, the $OH^{\cdot}$ free radicals generated would again act on organic matter, inorganic carbon and hydrocarbons present. The presence of these competing naturally occurring compounds would result in variable secondary oxidants that could possibly alter the mechanisms by which soil Hg is removed after oxidation. In addition, these secondary oxidants may have transformed the existing hydrocarbon chemical composition to more polar constituents but not altered the TEO content significantly.

3.2.3. Phase III: Removal of Hg and hydrocarbon at 40°C

The generation of $OH^{\cdot}$ and $OCl^{\cdot}$ free radicals is a function of temperature. Therefore, at higher temperatures, free radicals are generated at much higher reaction rates. This translates into greater removal efficiencies and a reduction in contact time required for soil contaminant removal (von Sonntang, 1997). Consequently, it is assumed that an increase in temperature would result in both a reduction in TEO and enhanced total soil Hg removal at the same extraction time in contrast to treatment at ambient temperatures (20°C).

3.2.3.1 Hg removal

Oxidative treatment of soil 2 indicated that an increase in temperature enhanced total soil Hg removal in contaminated soil 2. Solution phase Hg concentrations increased with increasing NaOCl and $Ca(ClO)_2$ concentrations, but not H_2O_2. An increase in temperature to 40°C, did not significantly enhance solution phase concentrations of any of the oxidative reagents used in this study because the increase in temperature was removing soil Hg as another form.

Determination of optimal extractant and molar concentration for Hg extraction was not possible by either statistical linear comparisons or non-linear least square comparisons. Curve fitting (Origin, version 4.1) was used to provide some idea of the concentration of oxidative reagent required for maximum total soil Hg removal. Maximum removal for each extractant was also determined and results are provided in Table 3.10.

Table 3.10. Curve fitting parameters for oxidative treatment of soil 2 at 40°C

Extractants	*Equation*	*ExC*
NaOCl	$Y= 72\pm 8.4 *(2.4 \pm 0.6\ X/ 1 + 2.4 X)$	1.7
H_2O_2	$Y = 74.8\pm 2.1 *(90 X/ 1 + 90 X)$	1.7
$Ca(ClO)_2$	$Y = 91.7\pm 1.8 *(95.9 X/ 1 + 95.9 X)$	0.4

Y = Total Hg Removed (%)
X = Concentration of Oxidative Extractant (M)
ExC = Observed extractant concentration (M) for maximum Hg removal

3.2.3.1.1 NaOCl Treated Soil

Sodium hypochlorite treatment of soil 2 indicated that increasing molar concentrations of NaOCl enhanced total soil Hg removal and solution Hg phase concentrations (Figure 3.24). Maximum total soil Hg removal occurred at 1.7 M concentration of NaOCl (3.62 mgkg^{-1} total soil Hg after oxidation) (Table 3.10).

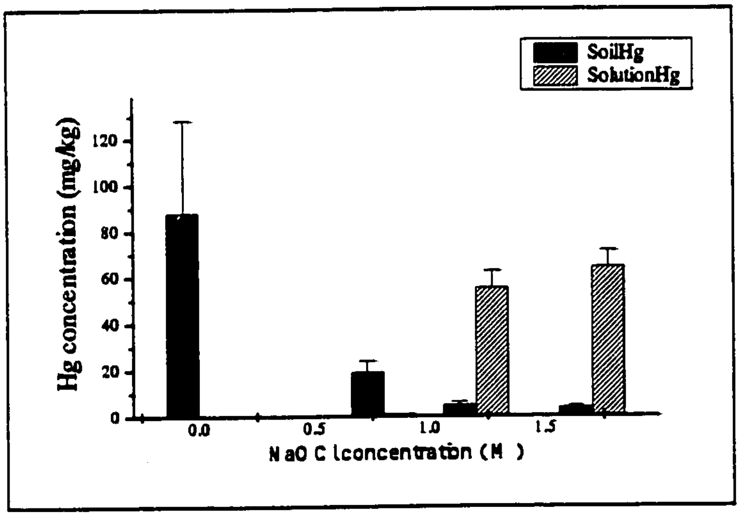


Figure 3.24. Changes in soil and solution Hg concentration of soil 2 after addition of NaOCl at 40°C

3.2.3.1.2. H_2O_2 Treated Soil

Hydrogen peroxide treatment of soil 2 indicates that total soil Hg decreased compared to controls. Increasing molar concentrations of H_2O_2 beyond 1.7 M did not enhance total soil Hg removal, nor did it increase solution phase concentrations (Figure 3.25). Maximum removal of total soil Hg occurred at 1.7 M H_2O_2 (22 $mgkg^{-1}$ total soil Hg after oxidation) (Table 3.10).

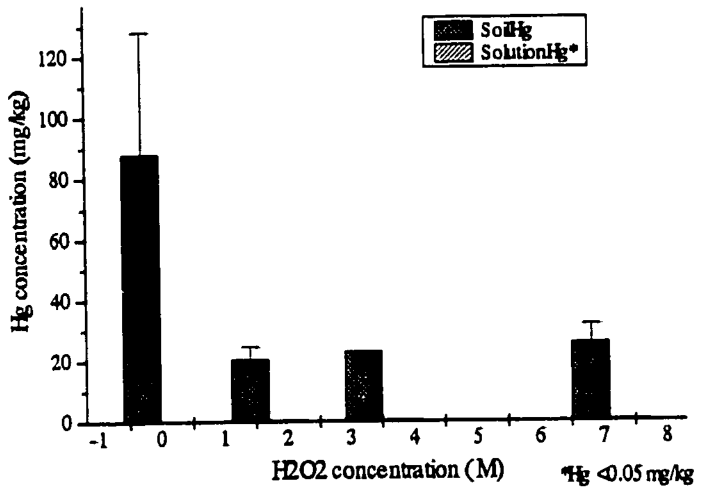


Figure 3.25. Changes in soil and solution Hg concentration of soil 2 after addition of H_2O_2 at 40°C

3.2.3.1.3 $Ca(ClO)_2$ Treated Soil

Calcium hypochlorite treatment of soil 2 produced a decrease in total soil Hg. Increasing molar concentrations of $Ca(ClO)_2$ enhanced total soil Hg removal and increased total solution Hg concentrations (Figure 3.26). Based on curve fitting methods, 0.4 M $Ca(ClO)_2$ is most effective at removing total soil Hg (10 $mgkg^{-1}$ total soil Hg after oxidation) (Table 3.10).

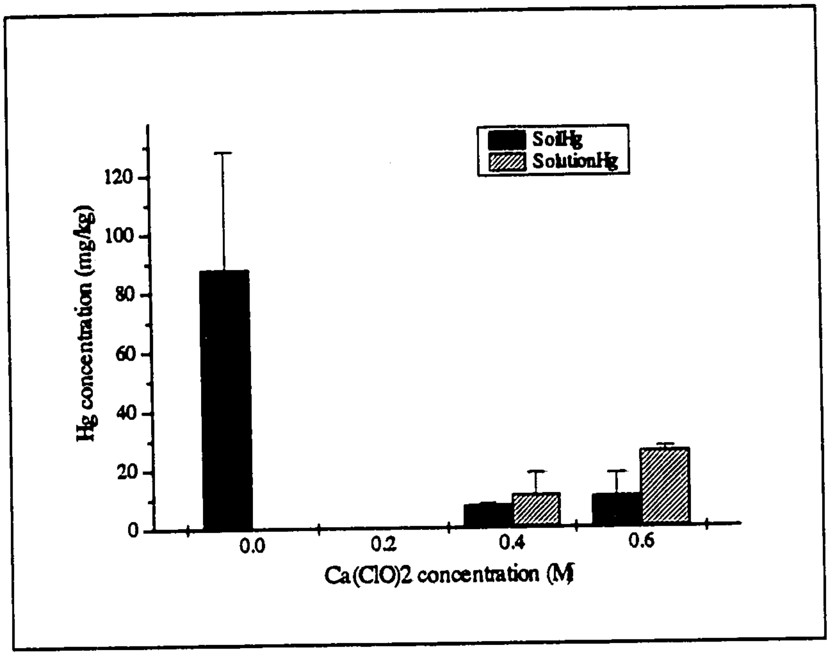


Figure 3.26. Changes in soil and solution Hg concentration of soil 2 after addition of Ca(ClO)$_2$ at 40°C

3.2.3.1.4 Significance

Oxidative treatment of soil 2 at 40°C resulted in a decrease in total soil Hg content that was greater than those observed at 20°C (section 3.2.2.1). Sodium hypochlorite treatment of soil 2 resulted in enhanced removal of total soil Hg at a lower molar concentration than at 20°C (Table 3.4 and Table3.9). Similar to treatment at 20°C total soil Hg content was reduced to one or more CCME remediation land use criteria and is provided to give a frame work of the reduction in total soil Hg after oxidative treatment, which may help with future research of Hg removal at a field application level (Table 3.9). The further reduction of total soil Hg at elevated temperatures did not result in a corresponding increase in total solution Hg concentrations. This translates into higher total Hg loss (not found in the soil and solution after oxidation) at 40°C (Table 3.11), compared to 20°C treatment (Table 3.9).

Table 3.11. Hg loss after oxidative treatment for soil 2 at 40°C

Extractant Type	Extractant Concentration (M)	average Hg loss (%)	S.D.[1]
NaOCl	0.8	74	1.4
NaOCl	1.2	40	5.4
NaOCl	1.7	26	12
H_2O_2	1.7	77	4.9
H_2O_2	3.5	75	1.8
H_2O_2	7.1	70	11
$Ca(ClO)_2$	0.4	80	8.1
$Ca(ClO)_2$	0.6	62	9.5

1. Standard deviation

For example, treatment of soil 2 at 40°C with $Ca(ClO)_2$ and H_2O_2, resulted in a significant decrease in total soil Hg content, but higher total Hg losses (initial soil Hg before oxidation minus soil Hg + solution Hg after oxidation). Total Hg loss increased by almost 40 % and 25 % with respect to $Ca(ClO)_2$ and H_2O_2 treatment and approximately 10% with NaOCl treatment (Table 3.9 and 3. 11).

The increase in total Hg loss, with respect to oxidative treatment at elevated temperatures, relates back to reaction rates and mercury's unique chemical properties. Since Hg possesses a high vapor pressure (0.0012 mm Hg @ 20°C), which increases rapidly with relatively small increase in temperature, it is expected that at elevated temperatures there would be an increase in volatile Hg losses (Stepan et al., 1993). Clever et al., (1985), indicated that as temperature increases there is a corresponding increase in Henry's law constant values, implying higher losses of Hg through volatilization. This is supported by Landa (1978) who observed increased Hg volatilization at 35°C compared to 10°C after the application of Hg salts to silty calcareous soils.

Increasing temperature not only increases the vapor pressure of Hg and additional Hg complexes, but also enhances Hg solubility (Pedroso et al., 1994 and Clever et al., 1985). Pedroso et al., (1994), applied hypochlorite salts to cinnabar deposits at temperatures ranging from 10 to 35°C and found that the 35°C temperature was more effective then lower temperatures in removal of Hg from mineral deposits. Clever et al., (1985) also indicated that mercuric chloride and mercuric chlorite solubility increases with increasing temperature.

Soil pH also will influence the potential loss of total soil Hg at elevated temperatures. For instance, Frear and Dill (1967) demonstrated that the volatile losses of Hg would increase from pH 5.3 to 6.4, through the redistribution of Hg salts to Hg^{o}. This process may be especially important with NaOCl and $Ca(ClO)_2$ oxidative treatment, where the soil pH increased in soil 2. These pH changes were from 7.6 to 9.5 and 7.6 to 11 with NaOCl and $Ca(ClO)_2$ treatments, respectively. This assumes that the process observed by Frear and Dill (1967) is applicable to the higher pH ranges observed in this study (Figures 3.27 and 3.28).

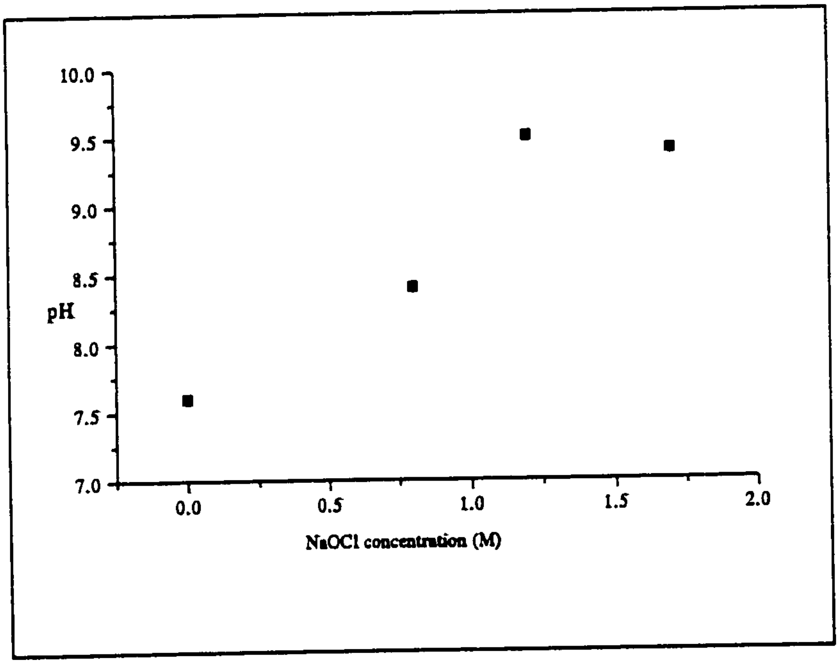


Figure 3.27. Soil pH (sample 2) after addition of NaOCl at 40°C

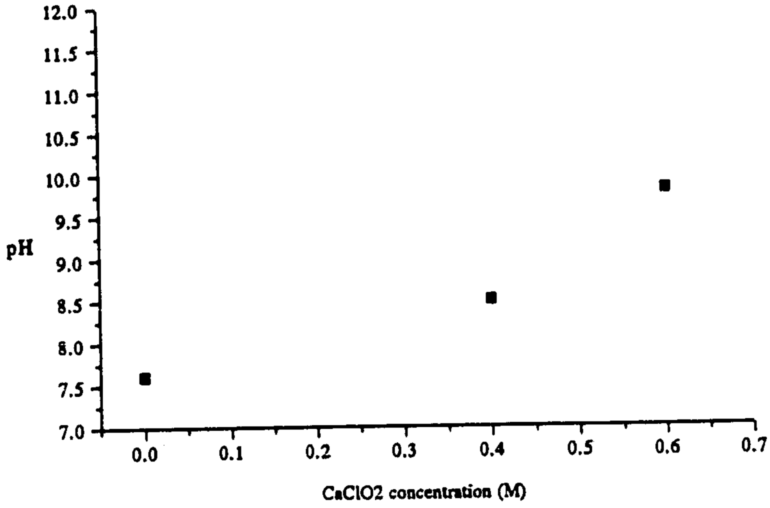


Figure 3.28. Soil pH (sample 2) after addition of $Ca(ClO)_2$ at 40°C

Therefore, based on the soil pH after oxidative treatment and the elevated temperature used for NaOCl and $Ca(ClO)_2$ treated soils, it is expected that total soil Hg removal would increase, which was observed in this experiment. However, the elevated temperature would also suggest greater $HgCl_2$ solubility, which was not observed after treatment with NaOCl and $Ca(ClO)_2$ oxidants. This might translate into Hg losses through volatilization greater than enhanced solubility which can not be verified by the data obtained in this study. The lower recovery efficiencies observed with 40°C treatment implicates that the elevated temperature primarily enhanced total soil Hg removal through the generation of volatile Hg species. In addition, the increase in soil pH with oxidative treatment, would further enhance volatile losses, due to the redistribution of Hg salts to Hg^o as has been observed previously by Landa (1978a).

Hydrogen peroxide treatment of soil sample 2 at 40°C also resulted in an increase in total Hg loss, compared to treatment at 20°C. Based on the elevated temperature of treatment and the proposed mechanism of removal as indicated previously in section 3.2.2.1.4, the reaction kinetics associated with H_2O_2 treatment appears more rapid than reaction rates for the other 2 oxidants. This translates into higher reaction efficiencies for

H-abstraction, demethylation, C-C bond cleavage, resulting in increased generation of inorganic (Hg^0) species from organic forms (Kaiser and Tolg, 1980). Elevated temperatures lead to the additive effect of enhanced generation of oxidative free radicals and an increase in the volatilization of Hg species. Elemental Hg vapor pressure is high even at normal temperatures (1.2×10^{-3} mm Hg at 20°C) and rapidly increases with rising temperatures (Vostal, 1972). Furthermore, the vaporization rate of Hg approximately doubles for every 10°C increase in temperature (Mintra, 1986 and Stahl, 1969). However, unlike NaOCl and $Ca(ClO)_2$ treatment, the soil pH does not increase with H_2O_2, but decreases, suggesting lower volatile losses (Landa 1978b) (Figure 3.29).

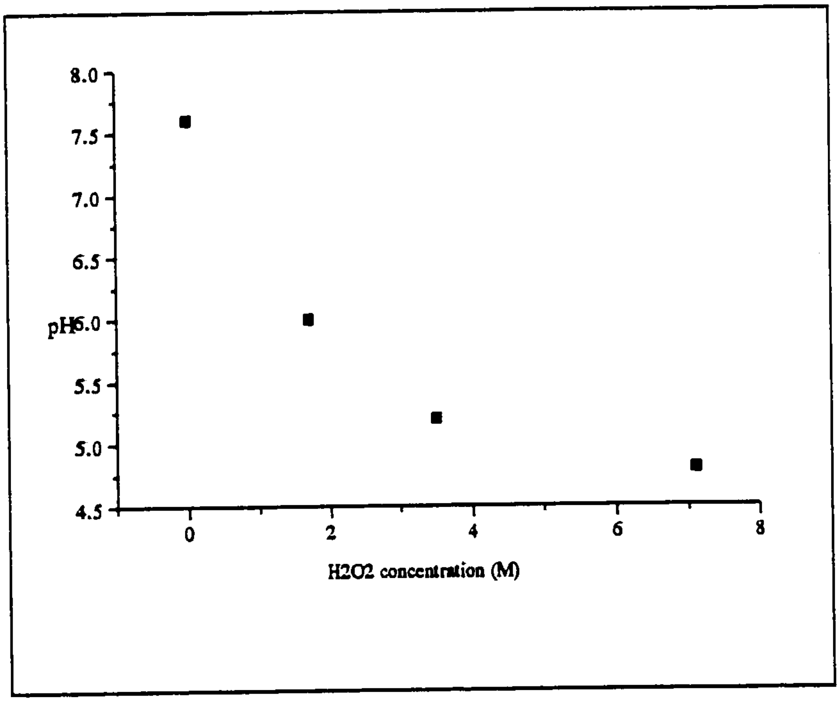


Figure 3.29. Soil pH (sample 2) after addition of H_2O_2 at 40°C

Based on the proposed mechanism of removal discussed in section 3.2.2.1, the combined influence of higher reaction efficiencies and larger vapor pressures for Hg with increasing temperatures, translates into an increase in total Hg loss at higher treatment temperatures observed with H_2O_2 treatment.

3.2.3.2. Hydrocarbon Removal at 40°C

The application of NaOCl, H_2O_2 and $Ca(ClO)_2$ to co-contaminated soils 2 resulted in variable TEO removal. Soil 2 changes in TEO content was evaluated using one-way ANOVA analysis (SAS, version 7.1).

3.2.3.2.1 NaOCl Treated Soil

Treatment of soil 2 with NaOCl significantly reduced TEO content (Figure 3.30). Application of NaOCl significantly reduced TEO content at 1.2M and 1.7M concentrations only. 1.2M and 1.7M NaOCl extractant were not significantly different with respect to TEO removal.

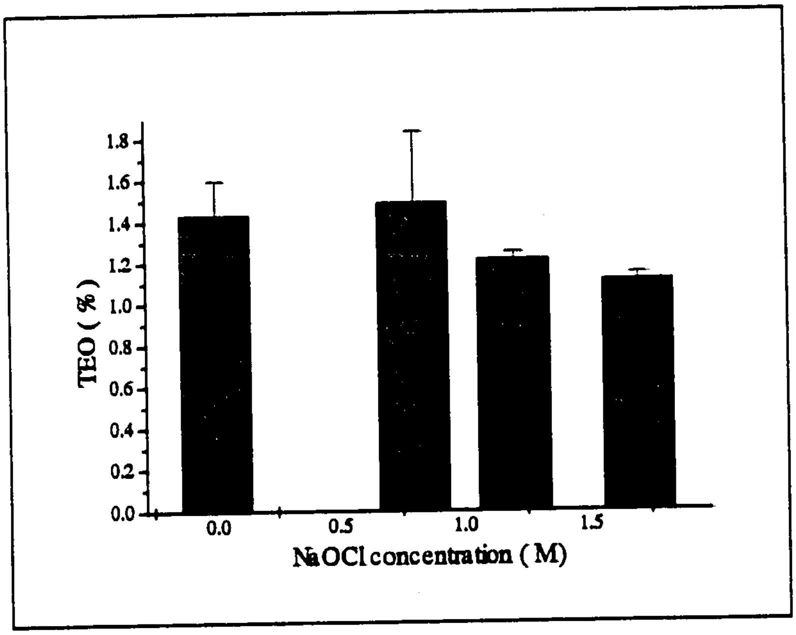


Figure 3.30. Changes in TEO of soil 2 after addition of NaOCl at 40°C

3.2.3.2.2 H_2O_2 Treated Soil

Hydrogen peroxide application to contaminated soil sample 2 indicated that TEO content was significantly reduced with 3.5M and 7.1M H_2O_2 treatment (Figure 3.31). 3.5M and 7.1M H_2O_2 were not significantly different with respect to TEO reduction.

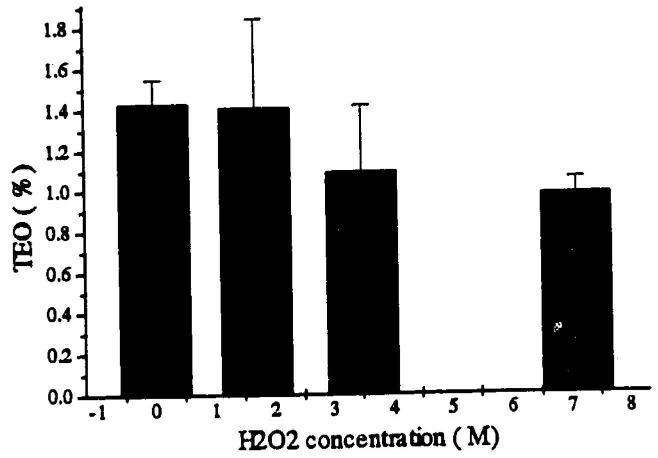


Figure 3.31. Changes in TEO of soil 2 after addition of H_2O_2 at 40°C

3.2.3.2.3. *$Ca(ClO)_2$ Treated Soil*

Calcium hypochlorite treatment of soil 2 illustrated that there was minimal change in TEO content (Figure 3.32). ANOVA analysis indicated that $Ca(ClO)_2$ addition did not significantly reduce TEO content. The observed increase in TEO content after oxidative treatment with $Ca(ClO)_2$ may be due to soil matrix variability with respect to soil hydrocarbon contamination.

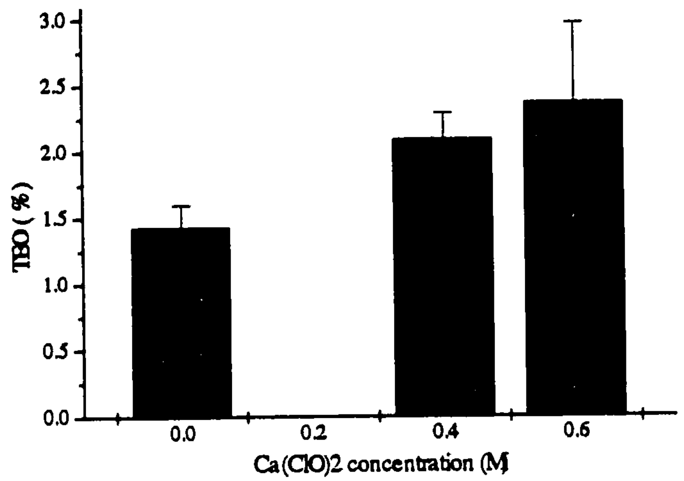


Figure 3.32. Changes in TEO of soil 2 after addition of $Ca(ClO)_2$ at 40°C

3.2.3.2.4 Significance

Oxidative treatment of soil 2 at 40°C significantly reduced TEO content for NaOCl and H_2O_2 treated soil. Calcium hypochlorite treatment of soil 2 at 40°C did not significantly reduce TEO, in contrast to the results at 20°C. As indicated in section 3.2.2.2, oxidative free radicals has been proposed to react non-selectively with most organic and inorganic compounds with very high reaction rates (Hoigne, 1997). Increasing reaction temperatures should translate into higher reaction rates and greater extractant efficiencies as was observed in this study for NaOCl and H_2O_2.

The reduction in TEO content after NaOCl and H_2O_2 addition at 40°C to soil 2 can be further substantiated by additional soil studies. Work by Mohanty and Wei (1993) indicated that treatment of soils contaminated with 2,4-Dinitrotoluene caused greater TOC removal when the temperature of extraction with Fenton's reagent was increased from 10 to 35°C. This increase in TOC removal from soil organic matter has also been observed at higher temperatures with hypochlorite additions (Lavkulich and Weins 1970) The increase in TOC removal is based on the proposed elevation in reaction rates for free radical reactions. Mohanty and Wei (1993), have proposed that the enhanced removal of TOC is associated with the following reaction:

$$2\ OH^{\cdot} \longrightarrow H_2O_2$$

The above reaction is believed to dominate under elevated temperature regimes and could be responsible for greater reaction efficiencies.

The observed increase in extraction of total soil Hg at 40°C relates to the presence of organomercurial species within the contaminated soil (Kohut et al., 1995). These organomercrial species are associated primarily with the clay fraction, likely organo-clay complexes. Since free radicals are responsible for C-C bond cleavage, H-abstraction, hydroxylation and demethylation, the addition of oxidants promoted reactions with organomercurial species causing their removal as either a soluble or volatile species. This explanation implies that the TOC content of the soil samples must decrease with oxidative treatment which was observed in this study with the exclusion of $Ca(ClO)_2$ treated soil 2.

The fact that TEO removal was enhanced at 40°C indicates that organic matter solubilization with elevated pH values cannot be the sole mechanism for TEO and Hg removal. The limited reduction of TEO compared to Hg relates to: 1) competing reactions in the soil for free radicals, 2) variable levels of contamination, and 3) precision of TEO gravimetric analysis. As discussed in section 3.2.2.2.4, TEO changes with gravimetric comparisons between non-treated and treated samples is limited at determining subtle changes in hydrocarbon composition after oxidation. Oxidative treatment may have resulted in the generation of intermediate transformation by-products. The importance of evaluating hydrocarbon intermediates in oxidative degradation processes will be discussed further in section 3.2.5. Furthermore, similar to oxidative treatment at 20°C, TEO extract color changed from a light brown to clear with increasing molar concentrations of oxidant. This would suggest that hydrocarbon compositional transformations may have occurred with oxidation, but was not determined by TEO gravimetric techniques.

3.2.4. Phase IV: Volatilization Experiment

The imbalance in total Hg recovered after oxidative treatment at both 20°C and 40°C indicated an additional mechanism of Hg removal must have occurred beyond release to the aqueous phase. Initially it was anticipated that either a co-precipitate formed with oxidative treatment, which was not subsequently dissolved by the chosen method of analysis, or a volatile species was generated and then lost from the reaction vessels. Upon evaluation of the results obtained from phase II and phase III experiments, it was hypothesized that a volatile inorganic species was most likely being generated with oxidation.

Based on the proposed mechanisms of Hg removal discussed in sections 3.2.2.1 and 3.2.3.1, an experiment was designed to determine the extent of volatilization and the form of volatile species that was generated by the oxidation treatments. In this experiment, only the highest molar concentration of each oxidative reagent was applied to soil 2. Soil 2 was chosen as it contained the highest level of Hg contamination making it more amenable to evaluate small volatile Hg losses more accurately.

Oxidative treatment of soil 2 at 20°C indicated that inorganic volatile Hg was being generated after oxidation. The degree of volatilization was observed to be dependent on the oxidative reagent used.

Sodium hypochlorite treatment of soil 2 at 20°C revealed that less than 3% of total soil Hg removed from the solid phase was as an inorganic volatile species. Nearly all of the extracted Hg was released and remained as a soluble Hg species (Figure 3.33). The loss of Hg in the form of a volatile species with respect to NaOCl treatment, was similar to losses found with water.

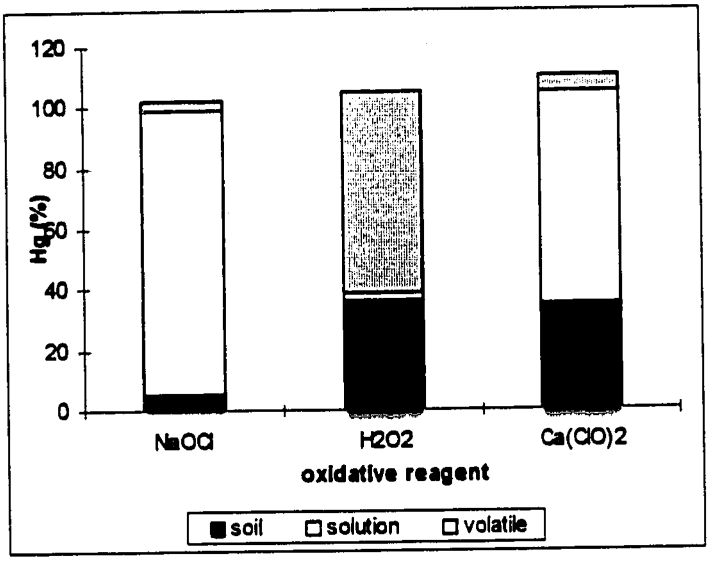


Figure 3.33. Distribution of total soil Hg (sample 2) after addition of NaOCl, H_2O_2 and $Ca(ClO)_2$ at 20°C

Hydrogen peroxide treatment of soil 2 at 20°C indicated that approximately 50 to 60% of the total soil Hg was released as an inorganic volatile Hg species based on volatile capture experiments (Figure 3.33). The loss of inorganic Hg vapor, with respect to the control soil treated with water, was observed to be less than 1%. Calcium hypochlorite treatment of soil 2 at 20°C indicated that approximately 3 to 5% of the total soil Hg removed through oxidation was as an inorganic volatile Hg species (Figure 3.33). Oxidative treatment of soil 2 illustrated that NaOCl and $Ca(ClO)_2$ primarily removed soil Hg as a soluble species, most likely a mercuric chloride complex as discussed previously in section 3.2.2.1 and 3.2.3.1. Calcium hypochlorite treatment was observed to have slightly higher volatile losses of Hg through the development of an inorganic Hg species. The enhanced volatile losses associated with $Ca(ClO)_2$ treatment may be a result of unknown constituents added to the reagent to stabilize the hypochlorite.

Hydrogen peroxide treatment illustrated that soil Hg was primarily removed as a volatile inorganic Hg species, with only a small portion retained as a soluble species. Consequently, it is apparent that the mechanism outlined in sections 3.2.2.1 and 3.2.3.1 with respect to H_2O_2 treatment is substantiated by the volatile capture experiment. The results support a mechanism involving the release of elemental Hg vapor.

The addition of NaOCl and $Ca(ClO)_2$ to soil 2 indicated minimal loss of Hg as an inorganic volatile Hg species. Losses observed with the volatile capture experiment indicated that an inorganic Hg vapor produced via NaOCl and $Ca(ClO)_2$ treatment would be as a mercuric chloride species. The assumption of $HgCl_2$ generation is based on the following volatility series, which indicates Hg^{o} to be the most volatile and HgO the least (Vostal, 1972):

$$Hg^{o} > Hg_2Cl_2 > HgCl_2 > HgS > HgO$$

Thus, based on the aforementioned results from the volatile capture experiments in conjunction with the predicted volatile Hg species formed by free radical reactions, it seems that Hg^{o}, Hg_2Cl_2 and/or $HgCl_2$ volatile species are generated with oxidative treatment.

3.2.5. Phase V: Hydrocarbon Analysis After Oxidation:

Total extractable organic content was observed to decrease significantly with NaOCl and $Ca(ClO)_2$ treatment with certain contaminated soils but H_2O_2 addition did not significantly decrease TEO content. Free radical reactions are non-selective and because all three extractants are assumed to generate oxidative free radicals it was anticipated that all soils would demonstrate a decrease in TEO content regardless of extractant type. The statistical analysis used for the TEO data would also suggest that the large variability within the soil samples skew the results because upon examination of Figure 3.20 it is evident that the TEO content decreases with increasing molar concentration of H_2O_2. Consequently, GC-MS and electrospray MS analyses were performed on a number of samples to evaluate changes in hydrocarbon composition.

GC-MS analysis of soil 2 before oxidative treatment and soil 2 treated with 1.7 M NaOCl and 7.1 M H_2O_2 indicated that all samples contained: Butyl hexadecanoate and octadecanoic acid (Appendix II, Figures 1 and 2). The H_2O_2 treated soil also contained additional constituents: 1) Butylated hydroxotoluene, 2) Bis-(2-methoxyethyl) phthalate, and 3) Benzendicarboxylic acid (Appendix II, Figures 3, 4, and 5). All of these compounds are known oxidative intermediates (Ehrhardt and Douabul, 1989, Ehrhardt and Petrick, 1985). The hydrocarbon constituents that were eluted from GC-MS analysis indicate the presence of oxygenated hydrocarbons. The presence of these compounds may be a result of oxidation from reagent addition, but upon comparison with the non-treated soil 2 it is evident there are no significant differences before and after treatment. This may be an artifact of sample aging and storage as the TEO extracts were processed approximately 10-11 months earlier and were exposed to photo-oxidative conditions. Based on these inconclusive results, electrospray MS analysis was used to try and discern additional polar hydrocarbon intermediates that were not observed with the GC-MS. Electrospray MS was only examined with soil 2 before oxidative treatment. The results indicate that there is an envelope of peaks that correspond to a variety of polar compounds, very similar to the distribution for napthenic acids (Appendix II, Figure 6). Napthenic acids are a complex mixture of mono and polycyclic alkanes often found naturally within crude oils. The potential presence of napthenic acids may pose additional problems at a number of levels: 1) napthenic acids interfere with a wide variety of analytical techniques, 2) removing napthenic acids from soil extracts is difficult and 3) napthenic acids are acutely toxic (Herman et al., 1994). Based on these results, future work will need to focus on the analysis of oxidative intermediates following chemical treatment of hydrocarbons, particularly polar compounds.

It is evident that TEO content was reduced to a greater extent by NaOCl and $CaClO_2$ addition and limited with H_2O_2. This may implicate that pH may play a greater role in TEO removal than the generation of oxidative free radicals and subsequent hydrocarbon oxidation. Based upon GC-MS analysis it is evident that there were no significant changes in hydrocarbon composition. However, the age and storage of the TEO extracts may have resulted in the deterioration of the samples through additional oxidation. This deterioration would make it difficult to distinguish quantitative changes that may have occurred with treatment. Furthermore, photo-oxidation works by the same free radical mechanisms suggested for hypochlorite and hydrogen peroxide, ultimately generating lower molecular weight hydrocarbons not observable with more traditional soxhlet $CHCl_2$ extractable gravimetric techniques (Ehrhardt and Petric, 1985).

The results obtained from this study have elucidated the importance and need for future analysis to include hydrocarbon oxidation products in evaluating the potential use of oxidative reagents as a remediation technology for hydrocarbon contaminated soils. These oxidation products pose even a greater issue when the presence of napthenic acids are included based on their acute toxicity.

CHAPTER 4: CONCLUSIONS

The present study was intended to determine if oxidative treatment could simultaneous remove Hg and hydrocarbons from soil. Co-contaminated soils containing variable levels of Hg and hydrocarbons were treated with various concentrations of these extractants. Soil and solution analysis after oxidative treatment provided information on Hg and hydrocarbon removal. Optimization and volatile experiments were also conducted to evaluate how temperature influences removal efficiencies of Hg and TEO and to evaluate Hg recoveries after oxidation, respectively.

4.1 Hg Removal:

Sodium and calcium hypochlorite treatment of co-contaminated soils indicated that soil Hg was removed primarily as a soluble mercuric chloride species. Hydrogen peroxide treatment of co-contaminated soils reduced total soil Hg content, but did not enhance soil solution Hg concentrations. Based on volatile capture analysis H_2O_2 treatment removed soil Hg as an elemental volatile Hg species. Increasing molar concentrations of H_2O_2 neither enhanced total soil Hg removal nor enhanced solution phase concentrations of Hg. Treatment with NaOCl, H_2O_2 and $Ca(ClO)_2$ was also observed to reduce total soil Hg content of co-contaminated soils to a level adequate to meet the CCME remediation criteria for one or more of the following land use classification: 1) commercial and industrial (Hg < 10 mgkg^{-1}), 2) residential and parkland (Hg < 2 mgkg^{-1}) and 3) agricultural (Hg < 0.8 mgkg^{-1}). The reduction in total soil Hg observed may be correlated with: 1) soil Hg concentration, 2) extractant type, 3) molar concentration of extractant and 4) hypothesized competing constituents present within each soil sample.

Oxidative treatment generates free radicals that are assumed to facilitate Hg removal from soil, however the resultant Hg species produced is dependent on the presence or absence of complexing ligands. Hydrogen peroxide addition results in the transformation of organic mercury species to inorganic volatile mercury species due to OH radical and secondary organic radical activity and the lack of a complexing ligand. Conversely, the generation of a soluble Hg species is due to the presence of chloride ligands. Hypochlorites ability to enhance Hg removal is based on: 1) chloride is a soft base and has a strong association for Hg (II), 2) chloride is a poor bridging ligand, 3) the high soil pH and Cl^- concentration resulted in mercuric chloride complexes dominating, 4) mercuric chloride complexes possess large stability constants and 5) the presence of sodium in the NaOCl reagent creates chemical conditions conducive to soil dispersion, translating into greater surface area contact for oxidation and greater overall soil Hg removal.

Enhancement of soil Hg extraction was evaluated by increasing the treatment temperature to 40°C. Treatment at 40°C indicated that total soil Hg removal was enhanced, but solution phase concentrations were not. The reduction in the total soil Hg content implicates that at higher temperatures total soil Hg is being lost as a volatile Hg species. Enhanced volatile losses of Hg at higher temperatures is substantiated by the observed decreases in solution Hg concentrations due to higher reaction efficiencies and increased vapor pressure of Hg.

4.2 Hydrocarbon Removal:

Oxidative treatment of co-contaminated soils with NaOCl and H_2O_2 significantly reduced TEO content in selected soils and treatments at both 20 or 40°C. Calcium hypochlorite was observed to have an increase in TEO in selected soils at both 20 and 40°C that may be a result of inherent soil variability in hydrocarbon contamination. As oxidative treatment was anticipated to reduce the hydrocarbon levels found in soil. The lower efficiency observed with TEO removal compared to total soil Hg removal is based on: 1) hypothesized free radical consumption by carbonates and soil organic matter constituents and 2) precision and accuracy of TEO gravimetric analysis can often mask changes occurring in hydrocarbon content.

4.3 Future Research Directions

This study was intended to elucidate some fundamental principles behind co-contaminant removal of both Hg and hydrocarbons from soil using oxidative free radical reactions. It is apparent from this study that the application of oxidants is effective at total soil Hg removal from soil. The results from this study have also provided a framework for future research focusing on some potential practical applications.

The effectiveness of hydrocarbon oxidation based on TEO analysis was variable. The application of hypochlorite and hydrogen peroxide oxidants to hydrocarbon contaminated soils have indicated that evaluating changes in hydrocarbon content with gravimetric techniques is insufficient. The results from this hydrocarbon study have underlined that future analysis should focus on hydrocarbon oxidation by-products. Quantitative and qualitative analysis of these oxidation products need to be thoroughly addressed in evaluating the potential use of oxidative remediation technologies. The presence of napthenic acids within hydrocarbon contaminated systems may complicate these analyses. Co-contaminant removal of both Hg and hydrocarbons using oxidative free radical reactions is a promising remediation technology, but further research is required to determine field scale viability.

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APPENDIX 1 Curve fitting for co-contaminated soils 2, 4 and 5 treated with oxidative reagents at 20°C and 40°C

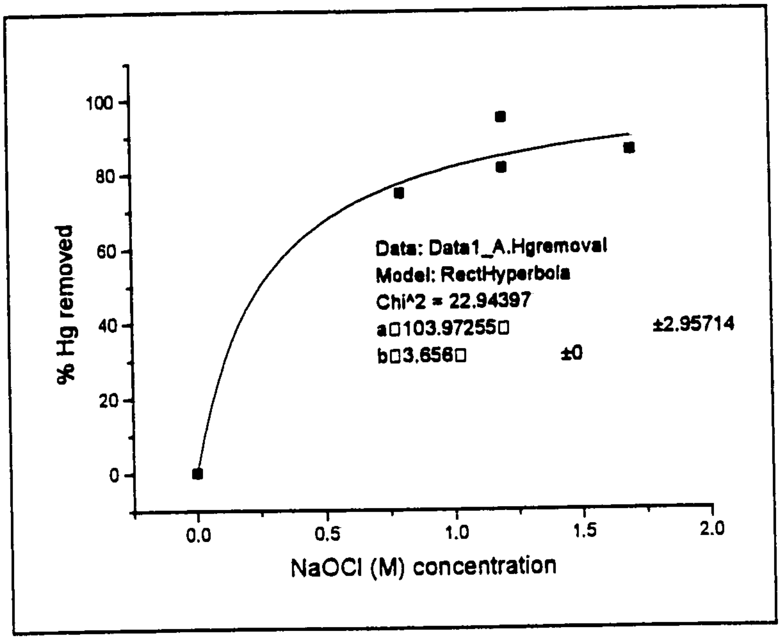


Figure 1. Curve fitting of soil 2 after addition of NaOCl at 20°C

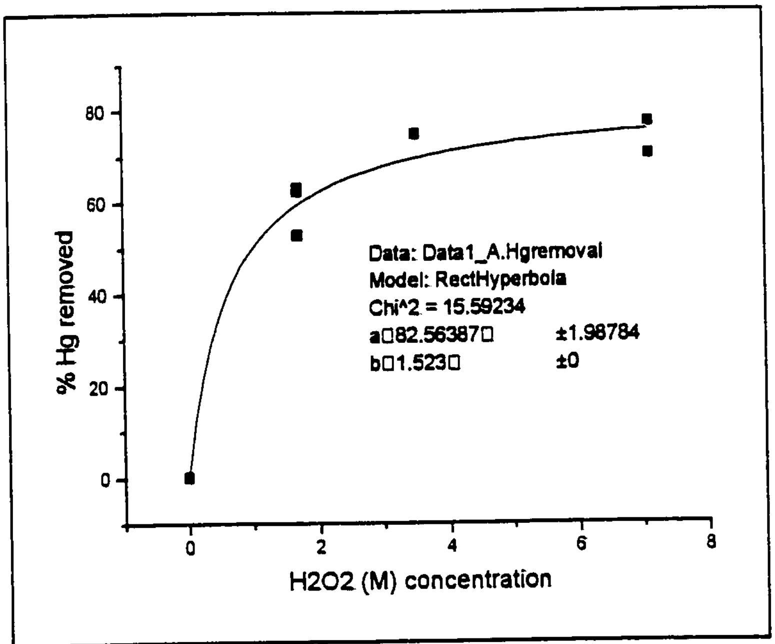


Figure 2. Curve fitting of soil 2 after addition of H_2O_2 at 20°C

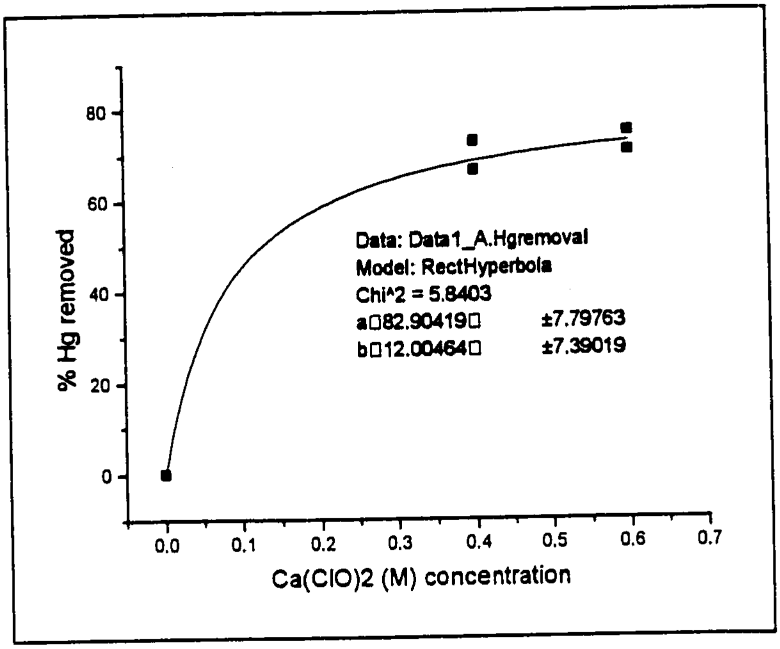


Figure 3. Curve fitting of soil 2 after addition of $Ca(ClO)_2$ at 20°C

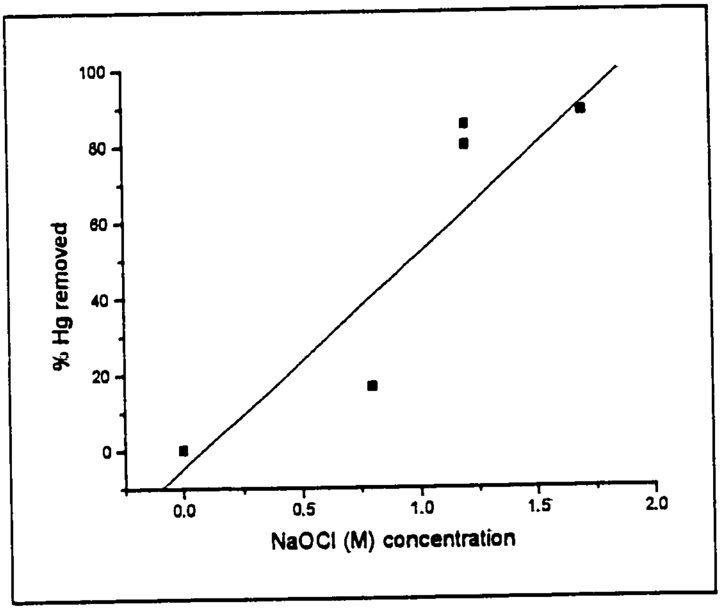


Figure 4. Curve fitting of soil 4 after addition of NaOCl at 20°C

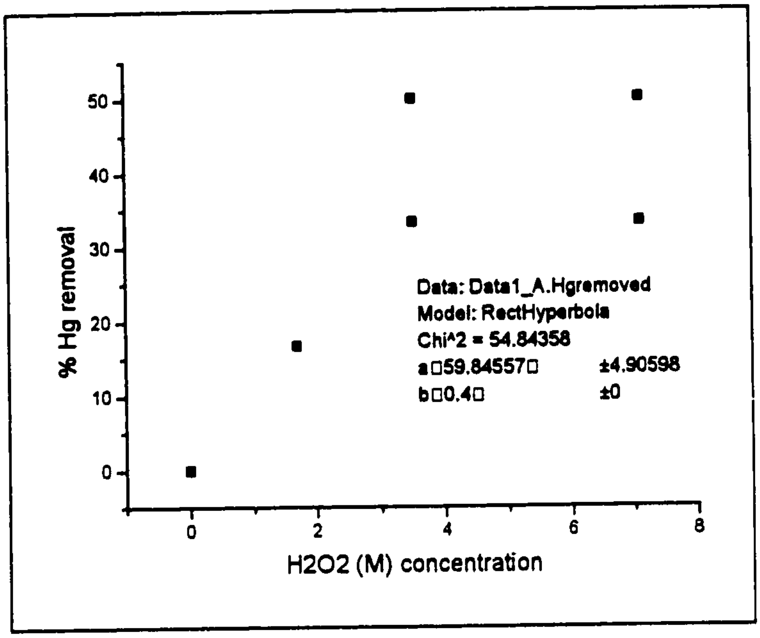


Figure 5. Curve fitting soil 4 after addition of H_2O_2 at 20°C

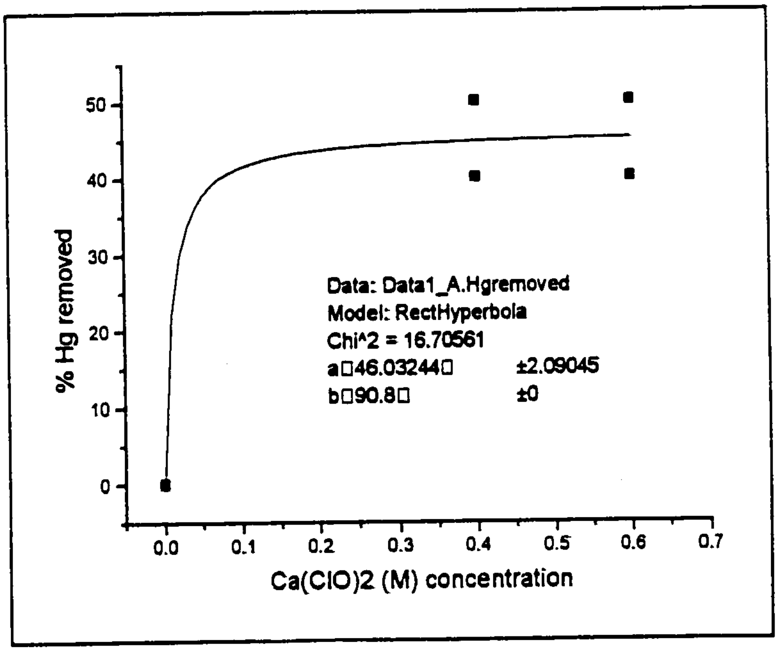


Figure 6. Curve fitting of soil 4 after addition of $Ca(ClO)_2$ at 20°C

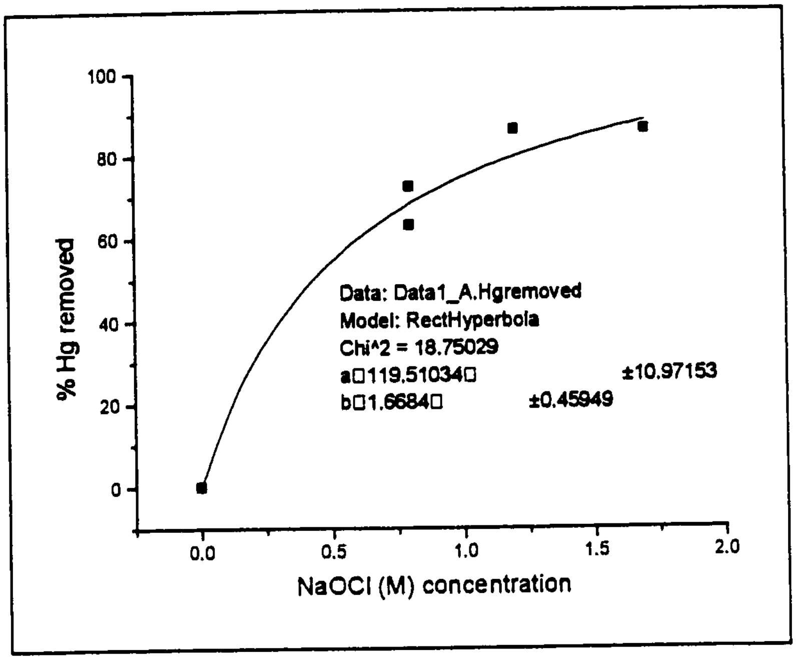


Figure 7. Curve fitting of soil 5 after addition of NaOCl at 20°C

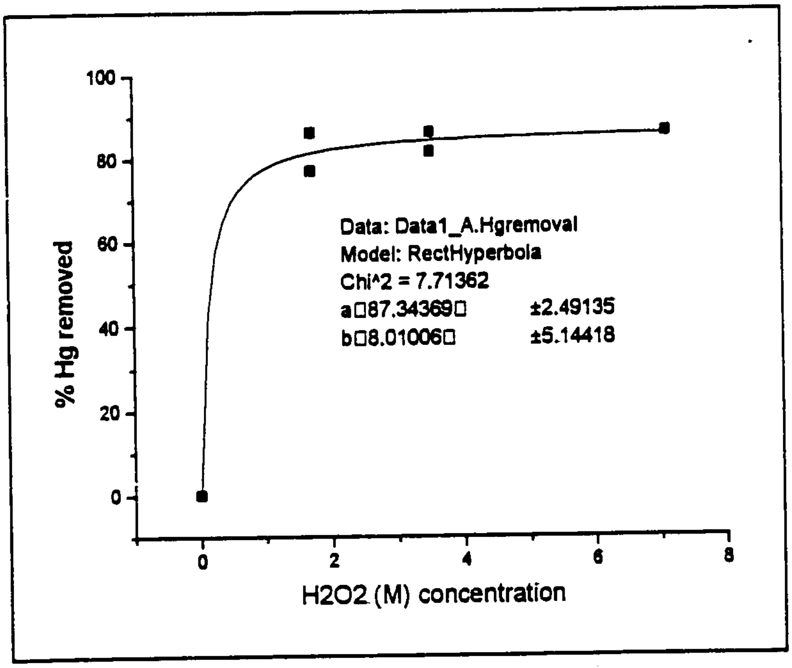


Figure 8. Curve fitting of soil 5 after addition of H_2O_2 at 20°C

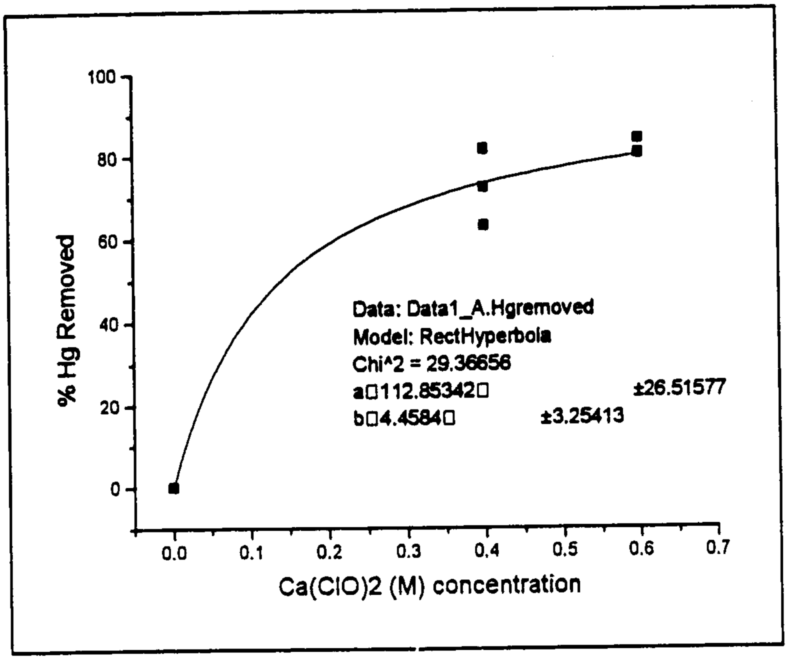


Figure 9. curve fitting of soil 5 after addition of $Ca(ClO)_2$ at 20°C

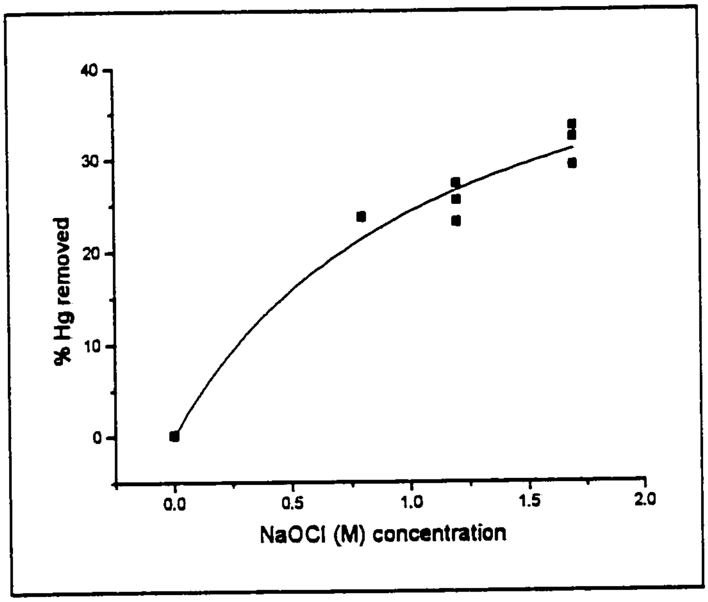


Figure 10. Curve fitting of soil 2 after addition of NaOCl at 40°C

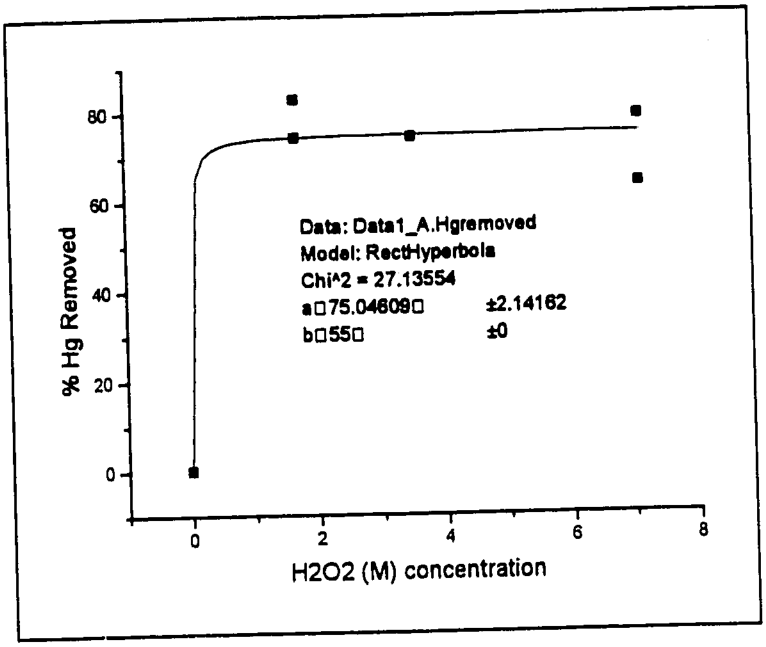


Figure 11. Curve fitting of soil 2 after addition of H_2O_2 at 40°C

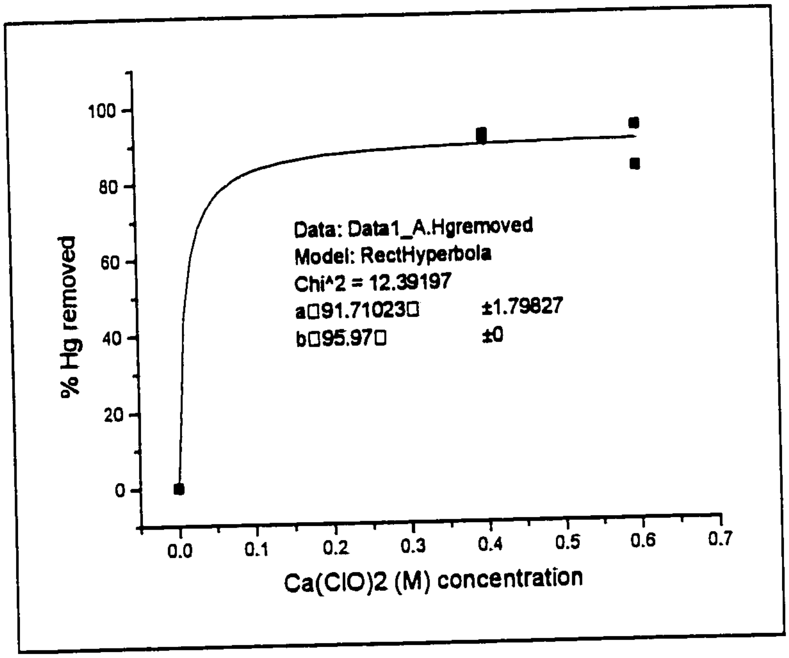


Figure 12. Curve fitting of soil 2 after addition of $Ca(ClO)_2$ at 40°C

APPENDIX 2 GC-MS and Electrospray MS results:

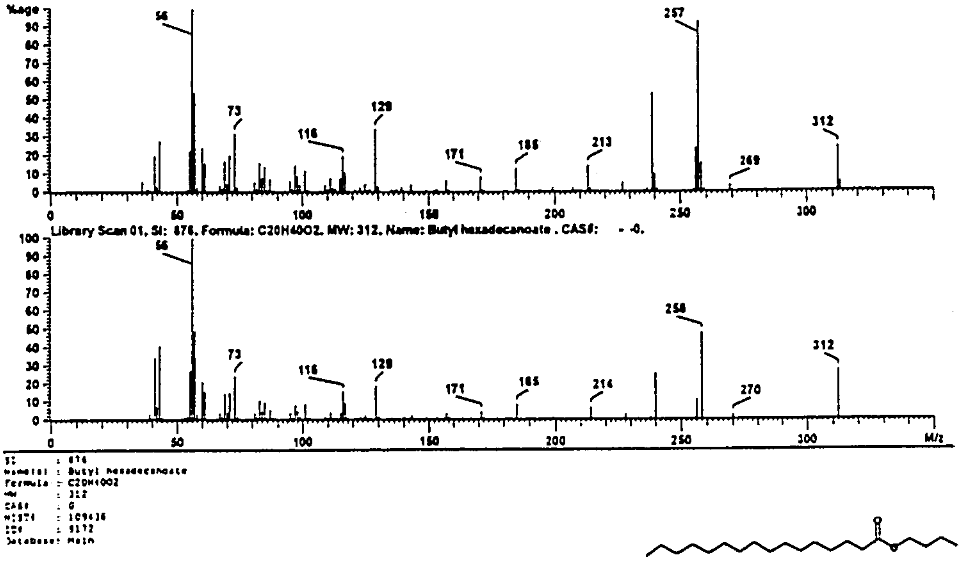


Figure 1. GC-MS determination of Butyl hexadecanoate using NIST library match for soil 2 TEO extracts before and after oxidative treatment with H_2O_2 and NaOCl

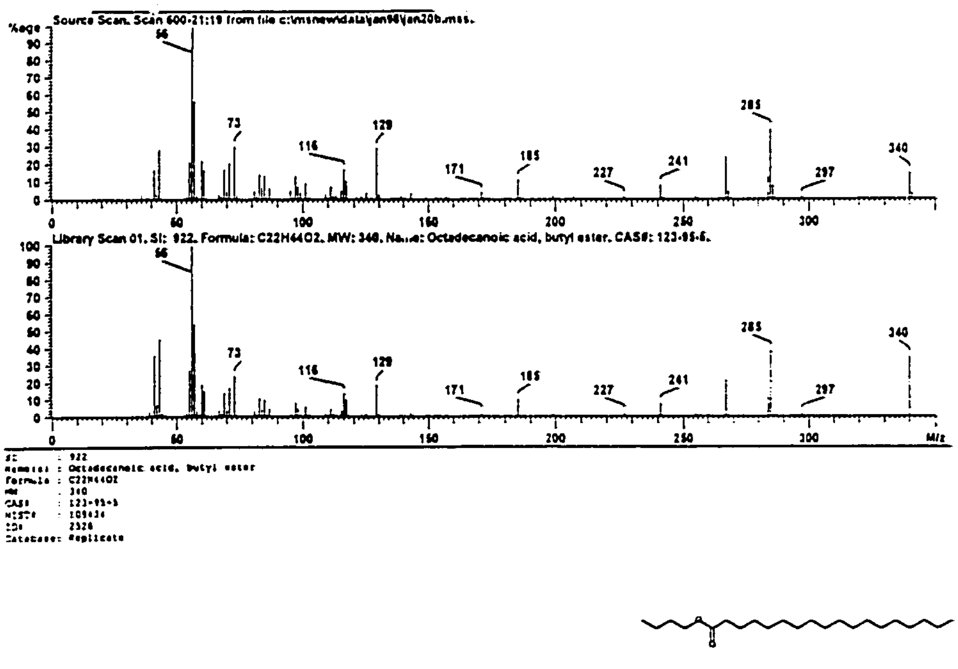


Figure 2. GC-MS determination of octadecanoic acid using NIST library match for soil 2 TEO extracts before and after oxidative treatment with H_2O_2 and NaOCl

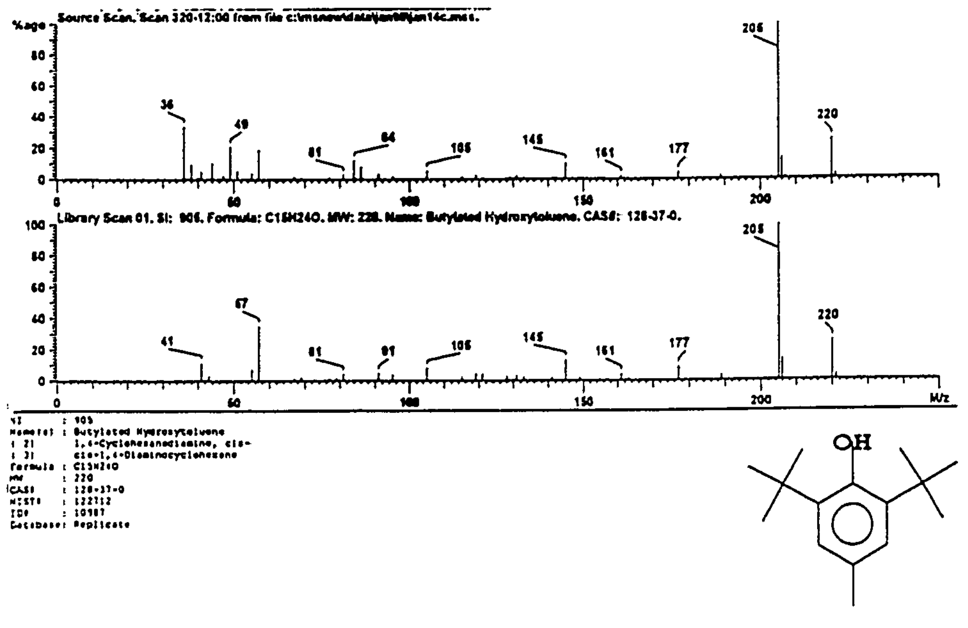


Figure 3. GC-MS Butylated hydroxotoluene using NIST library match for soil 2 TEO extracts before and after oxidative treatment with H_2O_2

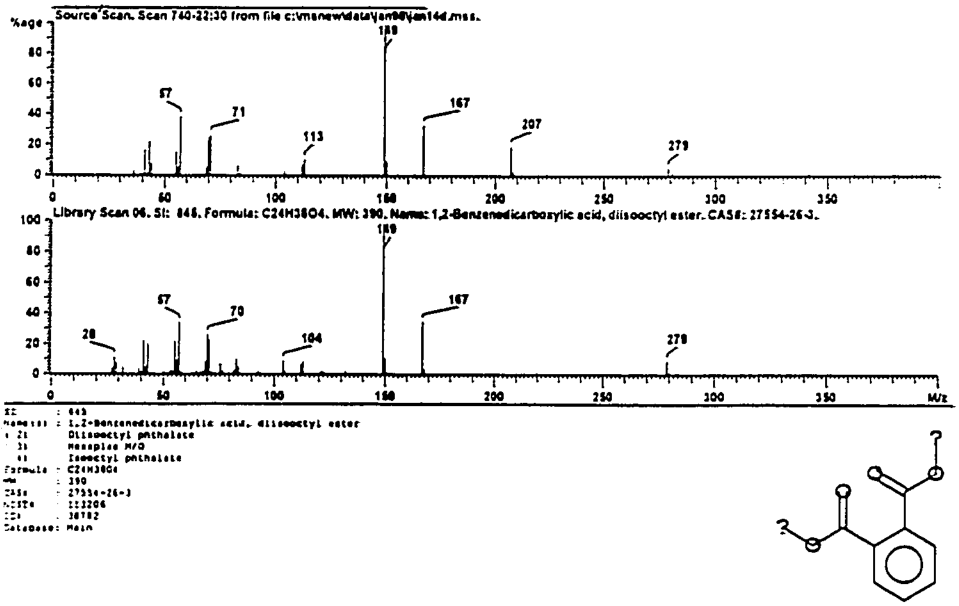
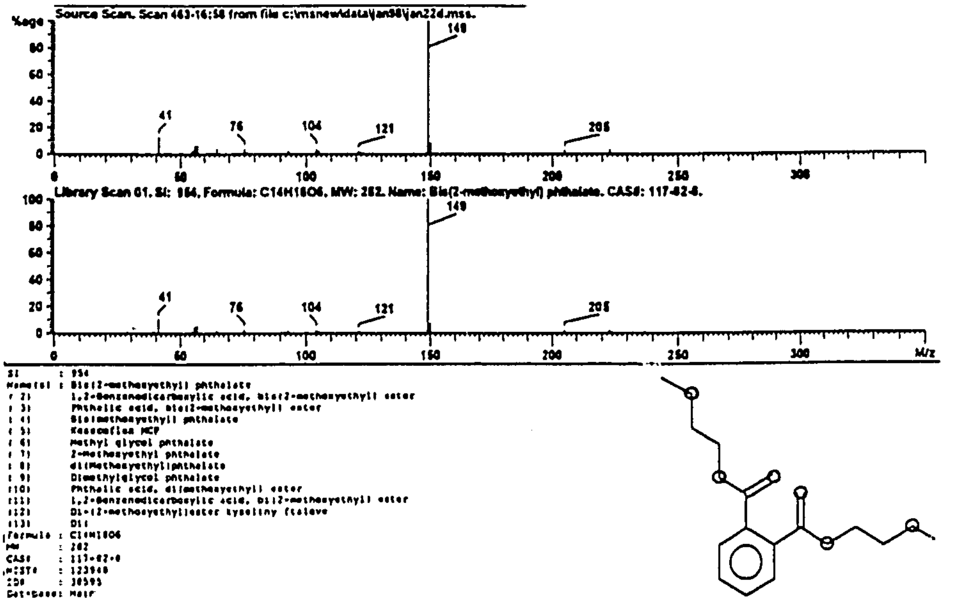


Figure 4. GC-MS Bis-(2-methoxyethyl) phthalate using NIST library match for soil 2 TEO extracts before and after oxidative treatment with H_2O_2



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SI        : 954
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( 2)        1,2-Benzenedicarboxylic acid, bis(2-methoxyethyl) ester
( 3)        Phthalic acid, bis(2-methoxyethyl) ester
( 4)        Bis(methoxyethyl) phthalate
( 5)        Kesscoflex MCP
( 6)        Methyl glycol phthalate
( 7)        2-Methoxyethyl phthalate
( 8)        di(Methoxyethyl)phthalate
( 9)        Dimethylglycol phthalate
(10)        Phthalic acid, di(methoxyethyl) ester
(11)        1,2-Benzenedicarboxylic acid, bis(2-methoxyethyl) ester
(12)        Di-(2-methoxyethyl)ester kyseliny ftalove
(13)        DI[illegible]
Formula : C14H18O6
MW        : 282
CAS#      : 117-82-8
NIST#     : 123948
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DataBase: Main
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Figure 5. GC-MS Benzendicarboxylic acid using NIST library match for soil 2 TEO extracts before and after oxidative treatment with H_2O_2

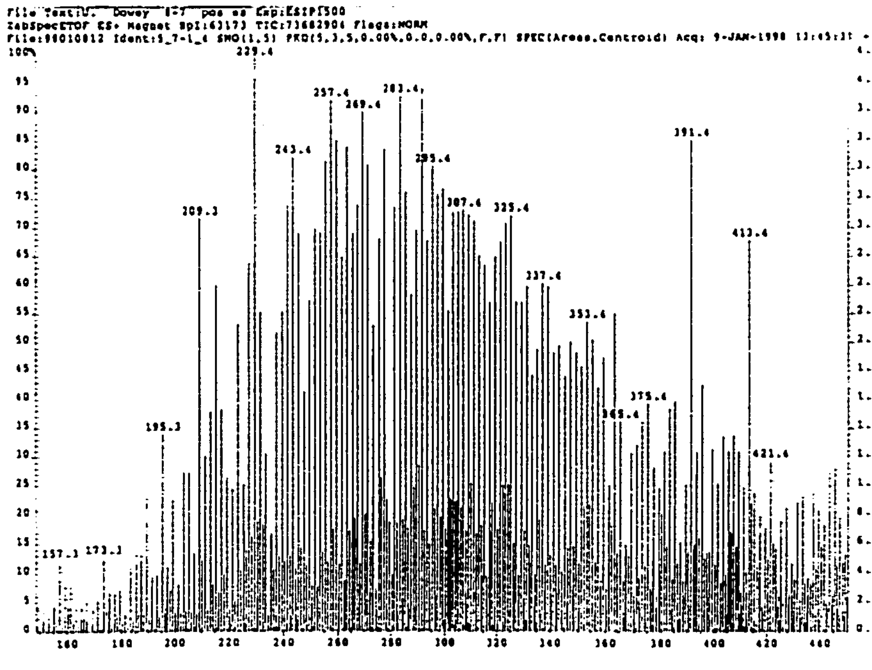

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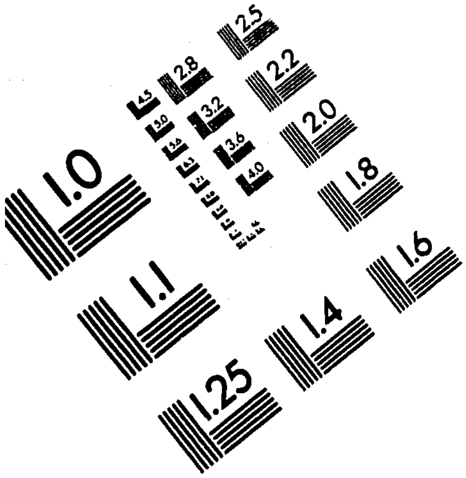
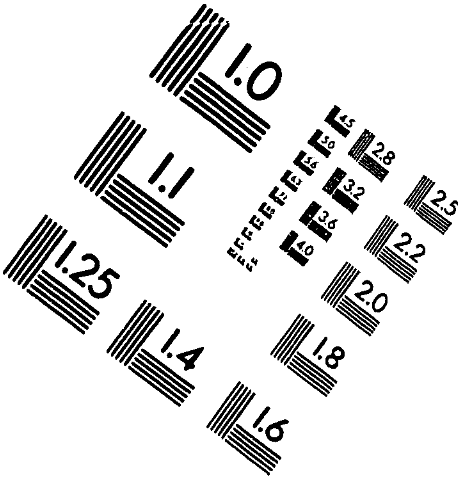
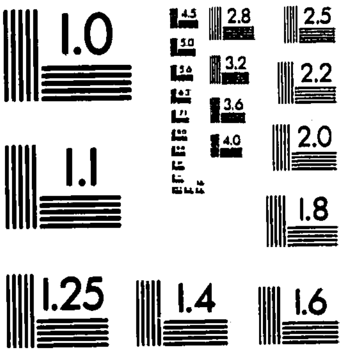
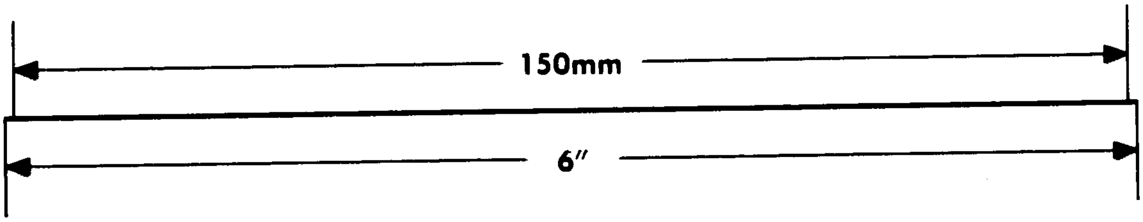
Figure 6. GC electrospray analysis of soil 2 TEO extract before oxidative treatment.

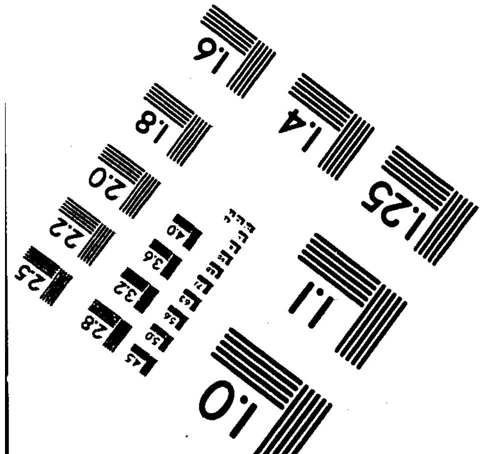
IMAGE EVALUATION
TEST TARGET (QA-3)











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