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Redox Control on Arsenic and Molybdenum in an Acid Sulfate Soil from West Central Alberta.

by

Brooke Corrina Bennett ©

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

Department of Renewable Resources

Edmonton, Alberta

Fall 2002

0-612-81363-0

University of Alberta

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Degree:	Master of Science
Year this Degree Granted:	2002

Brooke Bennett
(Student's signature)

Permanent address:
9148-80 Avenue
Edmonton, Alberta, Canada
T6C 0T8

Date: Aug 14, 2002

University of Alberta

Faculty of Graduate Studies and Research

The undersigned certify that they have read, and recommended to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled Redox Control on Sorption of Arsenic and Molybdenum in an Acid Sulfate Soil from West Central Alberta submitted by Brooke Corrina Bennett in partial fulfillment of the requirements for the degree of Master of Science in Soil Science.

M.J. Dudas

M.J. Dudas (Supervisor)

Noorallah G. Juma

N. Juma

Y. Feng

Y. Feng

K. Devito

Aug 7, 2002

Date

ABSTRACT

Acid sulfate soils in Alberta have developed from weathered marine shales and are naturally enriched in arsenic. Adjacent soils have also developed from marine shales, mixed with calcareous till. The solubility of arsenic increases in anaerobic conditions, however little is known about the solubility of arsenic in acid sulfate soils. Reduction and oxidation experiments were designed to investigate the influence of redox potential on the sorption and dissolution of iron, arsenic, and molybdenum in an acid sulfate soil and in a mixture of acid soil and calcareous till. Elevated arsenic concentrations were consistently detected in reduced solutions of the soil/till mixture indicating arsenic levels in adjacent soils may be problematic. Aqueous arsenic and molybdenum was immobilized in oxidized solutions due to sorption onto newly precipitated iron oxides. Molybdenum may potentially be used as an indicator to distinguish between geogenic and anthropogenic sources of arsenic in reduced waters with high pH.

ACKNOWLEDGEMENTS

I would like to give my deepest and sincerest thanks to my supervisor, Dr. Marvin Dudas for all of his honest enthusiasm, support, and guidance throughout the course of my studies. Thank you for always keeping me focused on my project and for your sense of humor. It has been such a pleasure working with you.

I would like to thank the members of my supervisory committee, Drs. Kevin Devito, Yongsheng Feng, and Noorallah Juma for the contribution of their time and ideas. Their input to the project was much appreciated. Dr. Xinbang Feng of the Alberta Research Council performed the ICP-MS analyses and Dr. John Duke of the SLOWPOKE reactor performed the INAA analyses, and both were extremely helpful with any related questions. Patrick Steffes, Dr. Myrna Salloum, Monica Molina-Ayala and Chung Nguyen provided invaluable technical support and advice which contributed greatly to the completion of this project. Drs. Phil Fedorak and Bill McGill provided advice on designing the incubation experiment. I would also like to thank Dr. Salim Abboud for his patience, wealth of knowledge, and his love of science, which was inspiring. Thank you to Dr. Jim Robertson and his interest in the progress of the project.

Financial assistance was provided by the National Science and Engineering Research Council and the Province of Alberta.

The graduate students in the Department of Renewable Resources have been a great source of support over the past few years and have challenged me to do my best. In particular, I would like to gratefully thank Tracy Muloin for his constant support, encouragement, and most importantly his friendship.

I would also like to extend my thanks and gratitude to my family and friends, in particular to Benj Carson for his strong support and continual encouragement.

For my grandmother, Jennye Clearwater

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CHAPTER I
INTRODUCTION

Arsenic in soils and sediments will desorb from colloids when conditions become anaerobic, and enter groundwater systems and domestic drinking water sources. Arsenic in drinking water seriously impacts human health and is considered one of the prominent environmental causes of cancer mortality in the world (Welch et al., 2000). In many cases the arsenic is present naturally, the source originating from geological formations of marine shales, which contain pyrite (FeS_2). Pyrite is the principle carrier of arsenic in rocks and many types of mineral deposits (Boyle and Jonasson, 1973). When pyrite is exposed to the atmosphere it undergoes biogeochemical oxidation, leading to the formation of iron oxyhyroxides and sulfuric acid (Nordstrom, 1982). Pyrite oxidation also releases arsenic contained within the mineral structure. Released arsenic is subsequently immobilized by sorption principally to iron and also to aluminum oxides.

Acid sulfate soil conditions develop in soils where extensive pyrite oxidation occurs. These acid soils are enriched in arsenic and iron oxides, and also contain molybdenum sorbed to the iron oxides at near background concentrations (Dudas, 1984). In Alberta, acid sulfate soils have developed in outcrop areas underlain by marine shales, such as the Kaskapau formation in the Peace River region in west central Alberta. In outlying areas the shales may form outcrops through surficial glacial debris (Pawluk and Dudas, 1978). In low lying and slightly depressional areas on the landscape in this region soils have formed from poorly drained lacustrine materials combined with these fine textured shales (Pawluk, 1971). This thesis examines the trends in desorption/sorption behavior of arsenic and molybdenum from iron oxides in an inland acid sulfate soil and when the soil is admixed with calcareous glacial till under reduced and oxidized conditions.

Arsenic in solution readily forms oxyanions of arsenate [As(V)] and arsenite [As(III)] under oxidized and reduced conditions respectively (Sadiq, 1997). The arsenite species are the more mobile and toxic species. Molybdenum is also commonly found in solution as the oxyanion molybdate (MoO_4^{2-}), exhibiting similar behavior to arsenate. Iron oxides in soils play a very important role in sorption of trace elements due to high reactive surfaces and high adsorptive capacities. Fe-oxides are differentiated based on structure, ranging in crystallinity from amorphous to highly crystalline. Trace element oxyanions, such as arsenic and molybdenum, are free to diffuse throughout the loose structure of amorphous Fe-oxides and sorption is not restricted to external surface sites such as the case with more crystalline Fe-oxides (Pierce and Moore, 1982).

Iron oxide-arsenic biogeochemistry has been well documented in the literature. Dissolution, solubilization, and mobilization of both iron oxides and arsenic are primarily influenced by redox potential (Eh) and pH, with Fe-oxides undergoing dissolution at reduced conditions (less than +100 mV). Iron oxide dissolution releases sorbed arsenic and molybdenum into solution. A report issued by Alberta Health and Wellness (Health Surveillance, 2000) discovered a strong relationship between arsenic, molybdenum, and iron concentrations in ground waters.

Interactions between iron and arsenic have been studied in heavily contaminated soils and sediments, soils spiked with arsenic salts, sewage sludges, and arsenic sorption to various iron oxides under controlled conditions. However, specific examination of arsenic chemistry and arsenic biogeochemical cycling in acid sulfate soils is not reported, and it is for this purpose that the present study was undertaken. In addition, no studies to date have examined the co-solubilization of molybdenum and arsenic from iron oxides.

The objectives of this study are:

1. To elucidate variations in solution concentrations of naturally occurring arsenic under reduced and oxidized conditions in the subsurface (B) horizon from an acid sulfate soil enriched with Fe-oxides and native arsenic.
2. To examine the relationship between arsenic and molybdenum released into solution from dissolution of Fe-oxides under reduced conditions, and sorption to Fe-oxides under oxidized conditions in the soil.
3. To elucidate changes in solution concentrations of iron, arsenic, and molybdenum under reduced and oxidized conditions when the subsurface (B) horizon from an acid sulfate soil enriched with Fe-oxides is admixed with calcareous glacial till.

CHAPTER II
LITERATURE REVIEW

2.1. Redox potential

The redox potential (Eh) of an aqueous chemical system is a measure of the electron availability or potential, measured as a voltage (V) (Patrick et al., 1996). A great number of geochemical reactions such as the degradation of organic matter or the weathering of minerals (e.g. pyrite oxidation) are electron transfer reactions (Schüring et al., 2000). Redox reactions involve the transfer of electrons between an oxidized (electron donor) to a reduced (electron acceptor) species or compound. For example, the oxidation of realgar, a common arsenic sulfide, is described as (Sadiq, 1997):

$$AsS_{(s)} + 8H_2O \rightarrow HAsO_4{}^{2-} + 2SO_4{}^{2-} + 3OH^+ + 22e^- \qquad (2\text{-}1)$$

Redox potentials can be expressed in terms of pe, defined as the negative log of electron activity [-log(e$^-$)] in unites of mole L^{-1}, just as pH expresses the negative log of the proton activity [-log(H$^+$)]. pe is an intensity factor, measuring oxidizing intensity (Stumm and Morgan, 1970). The sum of pe + pH provides a convenient single-term expression for defining the redox status of aqueous systems. This redox parameter represents the sums of all redox equilibrium constants in an equilibrium system (pe + pH = log K) (Lindsay, 1979; Lindsay and Sadiq, 1983; Bartlett, 1986).

The Nernst equation expresses the relationship between the redox potential and the activities of the oxidized (Ox) and reduced (Red) species (Bohn, 1971):

$$Eh = Eh^0 - \frac{2.303RT}{nF} \log \frac{(Red)}{(Ox)(H^+)^a} \qquad (2\text{-}2)$$

Thus, a theoretical value for the redox potential of a system can be calculated from redox couples.

Where:

$$Eh^0 = \left(\frac{2.303RT}{nF}\right)(\log K) \qquad (2\text{-}3)$$

Eh = calculated redox value (V)

Eh^0 = redox potential at standard state (V)

R = universal gas constant ($8.31451 \text{ J K}^{-1} \text{ mol}^{-1}$)

T = absolute temperature in K

n = number of exchanged electrons

F = Faraday constant ($96\,485 \text{ C mol}^{-1}$)

H^+ = protons transferred

K = activity equilibrium constant for the reaction

$2.303RT/F = 0.059$ V at 25^0C

The Nernst equation can be simplified to:

$$Eh(mV) = 59.2 * pe \qquad (2\text{-}4)$$

allowing redox relationships to be expressed in terms of either pe or pH (Lindsay, 1979; Schüring et al., 2000).

Ranges of characteristic redox conditions for soils are listed in Table 1 at pH 7 (Bohn, 1971; Patrick et al., 1996). Soil is the unconsolidated material on the immediate surface of the earth that serves as a medium for plant growth. In natural aqueous environments redox conditions are imposed by the dissociation of water into $H_{2(g)}$ or $O_{2(g)}$. The most oxidized equilibrium conditions correspond to pe + pH = 20.78 when $O_{2(g)}$ at 1 atmosphere (atm). The most reduced equilibrium conditions are represented by pe + pH = 0, when $H_{2(g)}$ is at 1 atm (Lindsay, 1979).

Table 1. Suggested redox conditions for soils.

Soil condition	Redox potential (mV)
aerated[1]	+400 to +700
moderately aerated	+100 to +400
reduced	-100 to +100
highly reduced	-100 to -300

---

[1] due to poor poise and low sensitivity, Eh or pe is not a satisfactory measure of soil aeration (Ponnamperuma, 1972; Patrick et al., 1996)

Baas Becking et al. (1960) reported numerous redox measurements made in natural environments. Most soils were found to have a pH range between 3.5 to 9 and a pe range of –6 to +12. The pe + pH range for most soils lies between 2 and 18.

2.2. Acid sulfate soils

Acid sulfate soils form where extensive biogeochemcial oxidation of accumulated pyrite occurs (Doner and Lynn, 1989). Pyrite (cubic FeS_2) accumulates in marine sediments in coastal depositional environments (Pons et al., 1982). Pyrite weathering occurs once pyritic sediment and soil parent materials are exposed to an oxidizing environment through changes in sea level or drainage (Nordstrom, 1982; Bhumbla and Keefer, 1994), and is described by:

$$FeS_{2(aq)} + 15/4\ O_{2(aq)} + 7/2\ H_2O_{(l)} \rightarrow Fe(OH)_{3(s)} + 2\ H_2SO_{4(aq)} \qquad (2\text{-}5)$$

Pyrite oxidation leads to the formation of iron oxides and the release of sulfuric acid into the soil system (Pawluk, 1971; Mermut et al., 1985). Acid sulfate soils in Western Canada are common where soft pyritic shales outcrop through surficial glacial debris (Pawluk and Dudas, 1978; Dudas et al., 1988).

Pyrite is the principle carrier of arsenic in rocks and many types of mineral deposits. This mineral may contain up to 6 000 mg As kg^{-1} or more. Arsenic in arsenopyrite is apparently present in lattice sites due to substitution for sulfur and can accumulate in the mineral as a trace or minor constituent. As pyrite oxidation proceeds arsenic trapped in the lattice structure is released and subsequently binds to and concentrates onto the newly formed iron oxides (Welch et al. 2000). Due to the association of arsenic with pyrite, acid sulfate soils derived from the oxidation of pyritic material are considerably enriched in natural forms of arsenic (Boyle and Jonasson, 1973; Dudas, 1984; Gustafsson and Tin, 1994). The acid sulfate soil examined in this study is from in the Peace River region in Alberta, and has been shown to be considerably enriched in total arsenic with concentrations several orders of magnitude higher than other soils of the province (Dudas, 1987; Dudas et al., 1988).

Arsenic chemistry in acid sulfate soils from the Peace River region (Boundary soil series) has been previously examined, however, only preliminary analysis of arsenic partitioning in various soil particle fractions (sand, silt, and clay) and the association of arsenic and iron has been elucidated (Dudas, 1984; Dudas, 1987; Dudas et al., 1988). Gusstafson and Tin (1994) examined the solubility of arsenic with depth in soil profiles from Vietnamese acid sulfate soils. No studies to date have examined iron-arsenic biogeochemical interactions in acid sulfate soils when subjected to reduced or oxidized conditions.

2.3. Arsenic

Arsenic (As) is a ubiquitous, semi-metallic trace element found in the atmosphere, in aquatic environments, in soils and sediments, in atmospheric dust, and in organisms (Elkhatib et al., 1984b). Sources of arsenic are mainly from parent (or rock) materials and anthropogenic inputs (Yan-Chu, 1994; O'Neill, 1995). Anthropogenic additions of As into the environment include mining activities, agricultural practices, disposal of industrial wastes, smelters, coal-fired power plants, and erosion caused by intensive land use (Oscarson et al., 1980; Pearce, 1995; McGeehan et al., 1998). For a review of arsenic in atmospheric, aquatic systems, and interstitial waters see Cullen and Reimer (1989).

2.3.1. Arsenic in soils

Arsenic ranks fifty-two in crustal abundance, between tin and molybdenum. Average values for arsenic in terrestrial and aquatic environments are reported in Table 2. Soils in Alberta typically contain between 4.0 to 6.5 mg As kg^{-1} (Dudas and Pawluk, 1980). Actual concentrations can range from 0.1 to several hundred mg kg^{-1} depending on the types of rocks or soils being considered (Cullen and Reimer, 1989).

Arsenic in soils can undergo reactions of oxidation/reduction, precipitation/dissolution, adsorption/desorption, ligand exchange, and organic and biochemical methylation. All of these reactions control mobilization and bioaccumulation of arsenic in the environment (Bhumbla and Keefer 1994). Factors affecting the levels of arsenic in soils are redox potential, climate, organic and inorganic soils components (particularly iron oxyhydroxide content), parent material and clay content (Elkhatib et al., 1984a). Sedimentary rocks have been found to contain much higher concentrations of arsenic than igneous or metamorphic rocks (Boyle and Jonasson, 1973). Rainfall is an important factor affecting As levels in soils because in most climates arsenic sulfides are easily oxidized, become water-soluble, and are leached out of the soil by precipitation and transported with runoff (Yan-Chu, 1994).

Table 2. Average background concentrations of arsenic (As) in terrestrial and aquatic environments.

Environment	Average As content
Terrestrial	(mg kg^{-1})
crust[1]	1.8
shales[1]	4.1
granites[1]	1.29
soil[2]	2 to 5
Aquatic	(µg L^{-1})
rivers[3]	3.08

[1] Boyle and Jonasson (1973)

[2] Dudas and Pawluk (1980)

[3] Yan-Chu (1994)

2.3.2. Mineral forms of arsenic in soils

Arsenic is rarely present in soils as elemental arsenic [$As_{(s)}$] since $As_{(s)}$ forms only in very reduced and very acidic conditions (Elkhatib et al., 1984b). Direct precipitation of arsenic solid phases may not occur except in arsenic contaminated soils. Secondary precipitation of As compounds may occur on soil colloid surfaces subsequent to As adsorption (for full discussion see Sadiq, 1997).

Arsenic is found as a constituent of many minerals, most commonly combined with iron or nickel and sulfur (Bohn, 1976; Yan-Chu, 1994). Arsenic is most commonly associated with sulfur as insoluble As-sulfides, frequently as arsenopyrite (FeAsS), the form concentrated in coal. Arsenopyrite is the most common arsenic mineral (Boyle and Jonasson, 1973; Cullen and Reimer, 1989; Bhumbla and Keefer, 1994).

Arsenic will also form solids with Al, Ca, Cu, Fe, Mg, Pb, and Zn, and will form stable arseno-carbonate complexes (Boyle and Jonasson, 1973; Bhumbla and Keefer, 1994; Kim et al., 2000). Researchers have categorized soil arsenic into Fe-bound, Al-bound, Ca-bound, and occluded arsenate forms (Yan-Chu, 1994). Arsenic has also been found to easily substitute for Si, Al, or Fe in crystal lattices of silicate minerals (Bhumbla and Keefer, 1994).

For a review of the principal arsenic minerals, arsenic content of common minerals, and arsenic deposits see Boyle and Jonasson (1973).

2.3.3. Arsenic solution species

The valence states in which arsenic is usually encountered in nature include -3, 0, +3, and +5, with the states of +3 and +5 common in aqueous solutions. Both of these oxidation states can be subjected to chemically mediated oxidation and reduction reactions (Yan-Chu, 1994; Ehrlich, 1996). In solutions, rapid hydrolysis of the arsenite [As(III)] and arsenate [As(V)] ionic states occurs due to the high charges of these states. Arsenic in soil solutions transforms to multioxidation states as an oxyanion as a result of its affinity for oxygen. Thus, there is practically no cationic chemistry of arsenic except in extremely strong acid solutions (Boyle and Jonasson, 1973; Sadiq, 1997). Figure 1 depicts the differences in molecular configurations of arsenic oxyanions each with a net charge of zero. A net negative charge develops on the molecule upon dissociation of the protons.

Arsenic oxyanions are mobile under both acidic and alkaline conditions (Bolye and Jonasson, 1973). Arsenite is highly toxic and more mobile in solutions compared to arsenate. Arsenite can react with the sulfhydryl groups of amino acids such as cysteine, leading to a wide range of enzyme inactivation in intermediate metabolism (Webb, 1966).

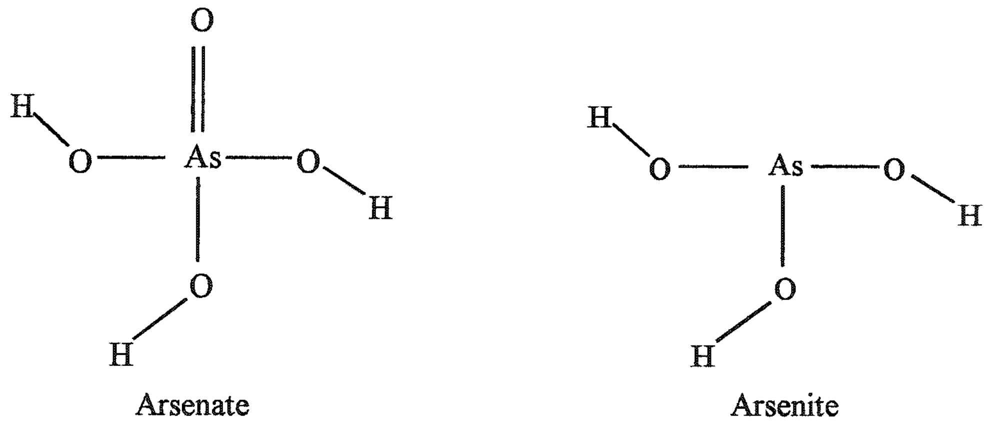


Figure 1. Configuration of arsenic oxyanion molecules, arsenate [As(V)] and arsenite [As(III)].

Arsenate [As(V)] species are found in oxidized soil solutions of $pe + pH > 9$ ($HAsO_4^{2-} > H_2AsO_4^- > AsO_4^{3-} > H_3AsO_4^0$ at pH 7). Arsenite [As(III)] species, including As(III) oxides and As sulfides, are found in relatively anoxic soil solutions of $pe + pH < 7$ ($HAsO_2^0 = H_3AsO_3^0 > AsO_2^- = H_2AsO_3^-$ at pH 7) (Ferguson and Gavis, 1972; Holm and Curtiss, 1989; McGeehan, 1996; Sadiq, 1997). Figure 2 shows the dependence of arsenic speciation on redox potential and pH.

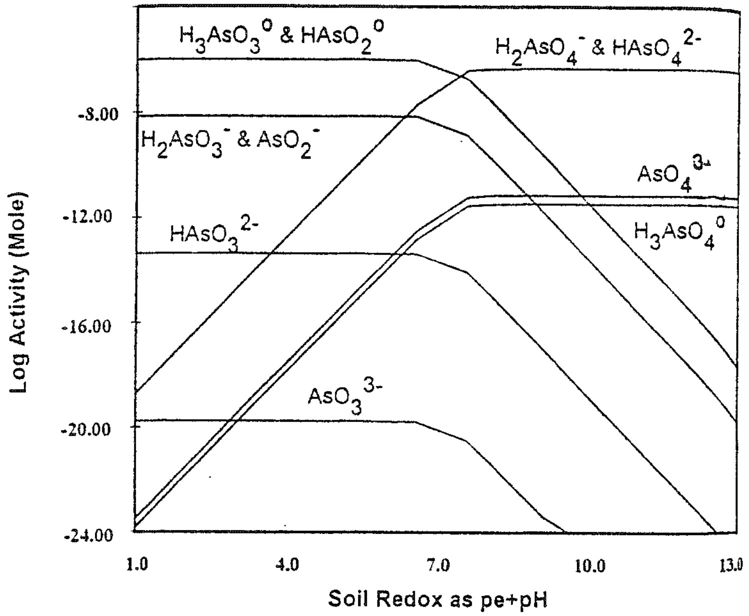


Figure 2. Chemical forms of inorganic arsenic species in soil solution (from Sadiq, 1997).

2.3.4. Organic and gaseous forms of arsenic in soils

Organoarsenical complexes and gaseous forms of arsenic constitute a minor fraction of the total dissolved As in soil solutions (Sadiq, 1997). Organoarsenical compounds (mono-, di-, and tri-methylated products) are formed by biomethylation of arsenite by soil microorganisms (Yan-Chu, 1994). Oxidative methylation of arsenic results in a decrease in toxicity, opposite to the increase in toxicity with methylation of mercury (Gupta and Chen, 1978; Cullen and Reimer, 1989). Biomethylation of arsenic is common in soils, however, methylated forms of As are thermodynamically stable only in reduced systems (Ferguson and Gavis, 1972; Cullen and Reimer, 1989; McGeehan and Naylor, 1994; Mok and Wai, 1994).

There is evidence that monomethylarsinic acid [$CH_3AsO_3^{2-}$] and dimethylarsinic acid [$(CH_3)_2AsO_2^-$] produced from oxidative methylation are reduced by soil microorganisms, including common fungi, yeasts, and bacteria, to toxic and highly volatile arsines {dimethylarsine [$(CH_3)_2AsH$] and trimethylarsine [$(CH_3)_3As$]} (Cullen and Reimer, 1989; Yan-Chu, 1994; Sadiq, 1997). Arsine gas forms only if the system is very acidic and very reduced, below the $H^+/H_{2(g)}$ boundary, and is quite unstable to light and heat (Webb, 1966; Ferguson and Gavis, 1972; Bohn, 1976; Sadiq et al., 1983). Inhaled arsine is much more toxic than arsenite (Webb, 1966).

For a review of organoarsenic compounds and known biomethylation products see Cullen and Reimer (1989). For review of biological effects on the distribution, biological accumulation, and microbial transformations of As species see Ferguson and Gavis (1972) and Sadiq (1997).

2.3.5. Influence of redox potential and pH

Arsenic speciation and mobility in solution is controlled by the pH and the redox conditions of the system (Deuel and Swoboda, 1972; Moore et al., 1988). The pH of a system influences the solubility and sorption of aqueous arsenic by controlling the speciation of As in aqueous solutions, the concentration of ionic species sorbed, and the surface charge of oxides (Frost and Griffin, 1977; Evans, 1989; Xu et al., 1988; Cullen and Reimer, 1989). At very low pH ions and metal hydroxides that immobilize As by coprecipitation are solubilized, releasing bound arsenic. At high pH amphoteric oxides develop a net negative charge and also release bound arsenic via a ligand exchange reaction with hydroxyl groups (Pierce and Moore, 1982; Xu et al., 1988; Mok and Wai, 1994). Adsorption of As(III) over the pH range 4 to 9 is not strongly dependent on pH, while pH has a stronger effect on adsorption of As(V) (Pierce and Moore, 1982; Wilkie and Hering, 1996). As(V) is stable at both high and low pH under oxidizing conditions (Bowell, 1994). Figure 3 depicts the changes in the distribution of mole fractions arsenate as a function of pH.

Using thermodynamic data, the theoretical oxidation-reduction potential for the reduction of arsenate to arsenite ($HAsO_4^{2-}$ to $H_3AsO_3^0$ at pH 7) can be calculated from the following reaction (Sadiq, 1997):

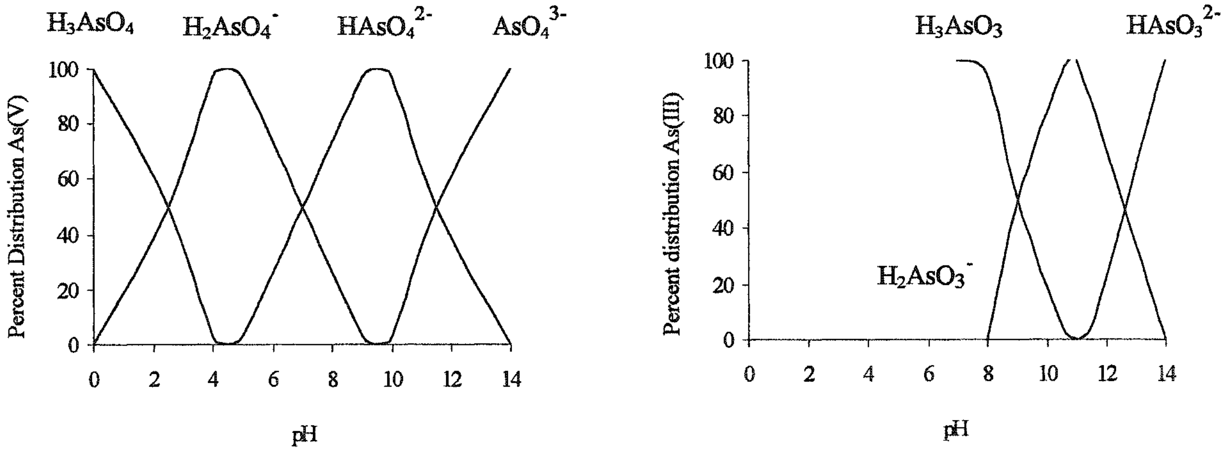


Figure 3. Predominance diagram for As(V) and As(III) as a function of pH (based on data from Gupta and Chen, 1978 and Sadiq, 1997).

$$HAsO_4^{-2} + 2e^- + 4H^+ \rightarrow H_3AsO_3^0 + H_2O \qquad \log K^0 = 28.63 \qquad (2\text{-}6)$$

The Gibb's free energy of reaction for Eq. 2-6 can be calculated by (Lindsay, 1979):

$$\Delta G_r^0 = -RT \ln K^0 \qquad (2\text{-}7)$$

Thus, the Gibb's free energy of the reaction from Eq. 2-6 is $\Delta G_r^0 = -163$ KJ mol^{-1}.

The Gibb's free energy is related to redox potential by (Bohn, 1971):

$$Eh = \frac{-\Delta G_r^0}{nF} \qquad (2\text{-}8)$$

From Eq. 2-8 the theoretical oxidation-reduction potential of the reduction of $HAsO_4^{2-}$ to $H_3AsO_3^0$ at pH 7 is at Eh 0.846 V. The theoretical redox potential for the reduction of $H_3AsO_4^0$ to $H_3AsO_3^0$ calculated by Yan-Chu (1994) is 0.557 V at 20°C. Arsenate in soil solutions has been measured to reduce to arsenite between Eh 0 and +100 mV (pH 7) (Patrick et al., 1996; Guo et al., 1997). The rate of As redox transformations are controlled by sorption/desorption kinetics (Reynolds et al., 1999).

2.3.6. Arsenic sorption/desorption reactions

Sorption/desorption reactions, rather than precipitation reactions, play a significant role in attenuating the migration of arsenic in groundwater and soil solutions (Livesey and Huang, 1981; McGeehan, 1996). Specific adsorption through the formation of inner-sphere complexes via ligand exchange (the formation of a covalent bond between the arsenic ion and a ligand) is the mechanism commonly considered to be involved in arsenic adsorption reactions in soils (Parfitt, 1978; Lumsdon et al., 1984; Evans, 1989; Sun and Doner, 1996; Sadiq, 1997). Non-specific adsorption via electrostatic attraction also occurs, but is limited to pH dependent charged surfaces below the zero point of charge (z.p.c) for a given adsorbent (McGeehan and Naylor, 1994). Once arsenicals are adsorbed they are not easily desorbed due to the formation of binuclear adsorption complexes (Elkhatib et al., 1984a, 1984b; Sun and Doner, 1996, 1998; Lombi et al., 1999; O'Reilly et al., 2001).

In oxidized systems solution concentration of arsenic species is controlled primarily by adsorption reactions most notably onto oxyhydroxides of Fe, Al, and Mn (Huang, 1975; Pierce and Moore, 1982; Oscarson et al., 1983; McGeehan and Naylor, 1994; McGeehan, 1996; Guo et al., 1997; Lombi et al., 1999). Sorption commonly increases with a decrease in soil pH (Galba, 1972; Anderson et al., 1976; Welch et al., 2000). The adsorption capacity and behaviour of adsorptive soil colloids [clay, (hydr)oxide surfaces of Al, Fe and Mn, calcium carbonates, and/or organic matter] is dependent on changing factors, such as hydration, soil pH, specific adsorption changes in cation coordination, isomorphous replacement, and crystallinity (Sadiq, 1997).

The literature is consistent in indicating As(V) is more strongly and quickly sorbed than As(III) at low surface coverages, but will rapidly desorb if the system becomes anaerobic due to reductive dissolution of oxides (Gulens et al., 1979; Cullen and Reimer, 1989; Pierce and Moore, 1982; Gruebel et al., 1988; Masscheleyn et al., 1991; Bowell, 1994; Wilkie and Hering, 1996; Manning and Goldberg, 1997; Lombi et al., 1999; Jones et al., 2000; Ladwig and McLearn, unpub.). Other studies have found at higher As surface coverages As(III) sorbs more strongly than As(V) (Sun and Doner 1998, Jones et al. 2000). Oscarson et al. (1980) found there were no changes in As oxidation states when As(V) and As(III) were sorbed onto colloids, and the amount of adsorbed arsenic is little affected by temperatures below about 50^0C (Yan-Chu 1994).

2.4. Iron oxides

Iron (Fe) oxides are the most abundant metallic oxides in soils. They are present in most soils of different climatic regions as very fine particles at variable concentrations (Schwertmann and Taylor, 1989). Iron oxides possess either a crystalline or amorphous structure, and can form partial coatings on clays, soils, and sediments, leading to high reactive surface areas and high adsorptive capacities (Ferguson and Gavis, 1972; Pierce and Moore, 1982; Schwertmann and Taylor, 1989). The charge density for goethite and hematite is one positive charge per 0.37 nm^2 and 0.2 nm^2 respectively (Parfitt, 1978). Principal forms of ferric oxyhydroxides are listed in order of decreasing solubility (i.e. increasing crystallinity) in Table 3. Sorption capacities of iron oxides variy with pH, crystallinity, and As:Fe ratios and are discussed in sections 2.5.1. and 4.2.12.

Table 3. Forms of ferric oxyhydroxides in soils in order of increasing crystallinity (Lindsay, 1988).

Ferric oxyhydroxides	Formula
amorphous hydrous ferric oxide	$Fe(OH)_3$(amorp)
ferrihydrite	$Fe_2O_3 \cdot 2H_2O$
maghemite	γ-Fe_2O_3
lepidocrocite	γ-FeOOH
hematite	α-Fe_2O_3
goethite	α-FeOOH

Goethite is common in oxidized soils and is generally considered to be the ultimate weathering product of Fe in soils. Iron solubility in well-oxidized soils is generally controlled by goethite (Lindsay, 1988; Schwertmann and Taylor, 1989; Matis et al., 1999). Ferrihydrite is considered to be one of the most important adsorbents of minor elements in surface and groundwater systems (Waychunas et al., 1993). Brennan and Lindsay (1998) determined that Fe solubility was controlled by amorphous iron hydroxide [$Fe(OH)_3$] and amorphous iron oxide (Fe_3O_4) in reduced and oxidized systems respectively.

Oxides in soils display amphoteric characteristics, with variable pH-dependent surface charge. Figure 4 depicts changes in surface charge distribution for specific oxides. Iron oxides display amphoteric characteristics with a zero point of charge (z.p.c) at pH 7.6 to 8.1 for goethite and at pH 6.5 to 8.6 for hematite, two of the most common forms of iron oxides in soils. Iron oxides develop a net positive charge below and a net negative charge above this pH range either due to protonation/deprotonation, hydration, specific adsorption, changes in cation coordination, isomorphous replacement, etc. (Parks and De Bruyn, 1962; Hingston et al., 1972; Evans, 1989; Sadiq, 1997). The pH of most soils is generally below the z.p.c, leaving iron oxides with excessive positively charged surfaces. This excess of positive charge easily attracts various oxyanions including arsenic species (Sadiq, 1997).

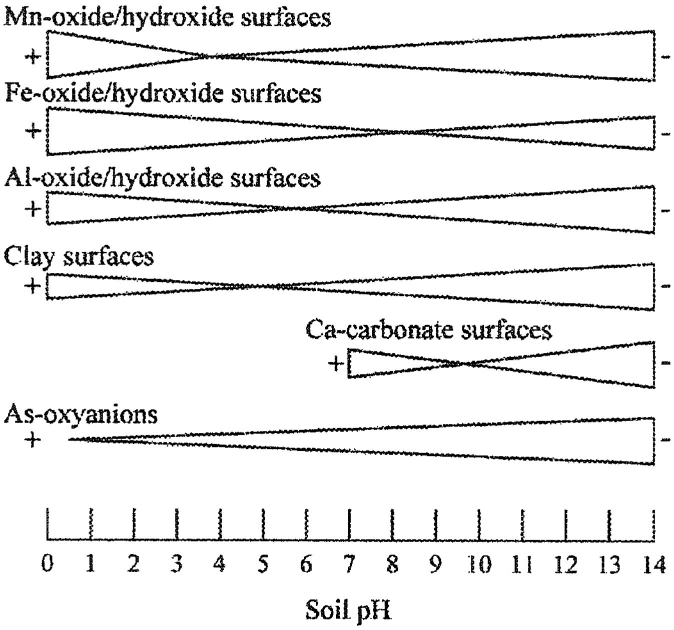


Figure 4. Generalized charge distribution on soil colloids (after Sadiq, 1997).

Iron oxides are only metastable in soils and are subjected to pronounced changes in structure depending on redox conditions. Fe oxyhydroxides undergo reductive dissolution under anaerobic conditions, beginning at Eh ~100mV (Ponnamperuma, 1972; Guo et al., 1997; MeGeehan et al., 1998). Prolonged reducing conditions result in the conversion of semicrystalline Fe minerals to amorphous hydroxides, magnetite (Fe_3O_4), ferrous and ferric hydroxides, siderite ($FeCO_3$) and various Fe sulfides (Lindsay, 1988). The redox potential at which Fe reduces depends on the iron phases present (Rochette et al., 1998). McGeehan et al. (1998) found during flooding short-range order (amorphous) Fe(III) solids increased as the length of flooding period increased. In turn, the crystalline Fe(hydr)oxide fraction decreased as the flooding period increased.

2.5. Iron-arsenic geochemistry

2.5.1. Arsenic sorption to iron oxides

All arsenicals form very insoluble complexes with hydrous oxides in soil systems (Jacobs et al., 1970; Fordham and Norrish, 1974, 1979; Pierce and Moore, 1980; Elkhatib et al., 1984a; Sakata, 1987; Cullen and Reimer, 1989; Fendorf et al., 1997; Guo et al., 1997; Manning and Goldberg, 1997; Welch et al., 2000). Arsenic adsorption onto and coprecipitation with iron oxyhydroxides is the most important mechanism for As accumulation in soils in both acidic and alkaline conditions (Ferguson and Gavis, 1972; Livesey and Huang, 1981; Masscheleyn et al., 1991; Fuller et al., 1993; Waychunas et al., 1993; McGeehan and Naylor, 1994; Mok and Wai, 1994; Sadiq, 1997). The quantity of As coprecipitated with Fe depends on the form of As and Fe, and competing ions (Reynolds et al., 1999). Coprecipitated As can be released from Fe-oxides as crystalline growth of the oxides proceeds (Fuller et al., 1993; Welch et al., 2000). Iron oxides are reported to contain up to 2 000 mg As kg^{-1} as a result of the strong adsorption capacity of hydrous iron oxides (Boyle and Jonasson, 1973). Ferric hydroxides in sediments are reported to potentially adsorb approximately 0.17 to 1.7 kg m^{-3} of aquifer matrix.

Pierce and Moore (1982) determined there was more than one type of surface site on amorphous Fe-hydroxides, and that an open, permeable, hydrated structure exists for these hydroxides. Ions, such as arsenic oxyanions, are free to diffuse throughout the structure and are not restricted to external surface sites such as the case with more crystalline Fe-oxides. This is also in agreement with the findings of Bowell (1994) who noted a higher proportion of arsenic was associated with amorphous iron oxyhydroxides than with crystalline iron oxyhydroxide and oxide minerals at a mine site in Ghana.

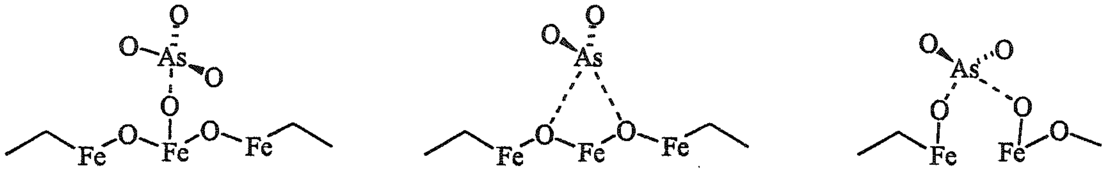
Pierce and Moore (1980, 1982), Fuller et al. (1993), and Lombi et al. (1999) found the adsorptive capacity of amorphous iron hydroxides to be very high and fast for both arsenate and arsenite, with As(V) being adsorbed more quickly than As(III). O'Reilly et al. (2001) determined that As(V) sorption on goethite was initially rapid at pH 4 and 6. Elkhatib et al. (1984b) also found As(III) sorption to be fast onto five West Virginia soils. Arsenate adsorption onto amorphous Fe-hydroxides was found to be maximum at approximately pH 4.0, while maximum adsorption for arsenite occurred closer to pH 7.0 (Pierce and Moore 1980, 1982).

Arsenic adsorption often follows the Langmuir model, which can be used to obtain estimates of sorption maxima and bonding energies for different soils or oxides (Hingston et al., 1972; Huang, 1975; Anderson et al., 1976; Gupta and Chen, 1978; Pierce and Moore, 1980, 1982; Livesey and Huang, 1981; Yan-Chu, 1994; Manning and Goldberg, 1997; Sun and Doner, 1998). The Langmuir model represents specific adsorption of anions on oxide and clay surfaces (Bowden et al. 1973). At higher As concentrations Pierce and Moore (1982) found that sorption followed a linear isotherm, as did As(III) sorption at lower concentrations ranges (Sakata, 1987). Elkhatib et al. (1984a, 1984b), Carbonell Barrachina et al. (1996), and Matis et al. (1999) described arsenite sorption data by the linearized form of the Freundlich isotherm equation.

2.5.2. Binding mechanism between arsenic and iron oxides

Arsenic oxyanions adsorb onto iron oxides by specific adsorption by forming strong, inner-sphere complexes via ligand exchange (Pierce and Moore, 1982; Waychunas et al., 1993; Grossl et al., 1997; Sadiq, 1997; O'Reilly et al., 2001). Inner-sphere complexes are defined as covalent linkages between the adsorbed ion and the reactive surface, with no water of hydration between the adsorbed ion and the surface functional group (Sposito, 1984). The effect of ligand exchange on oxides is to neutralize positive sites until the surface reaches a new z.p.c. where no further adsorption of the specifically adsorbed anion takes place (Hingston et al. 1972).

Waychunas et al. (1993) and Fendorf et al. (1997) examined the molecular structure of $HAsO_4^{2-}$ retained by ferrihydrite and goethite respectively and concluded three different types of surface complexes may form. At low surface coverages monodentate surface complexes dominate, at high surface coverages bidentate mononuclear complexes dominate, and bidentate binuclear complexes dominate at even higher surface coverages near monolayer capacity (Figure 5). Waychunas et al. (1993) determined the bidentate binuclear complex to be the dominant surface complex with ferrihydrite, as did Fendorf et al. (1997) and O'Reilly (2001) onto goethite. All authors found this bond to be stable for extended time periods.



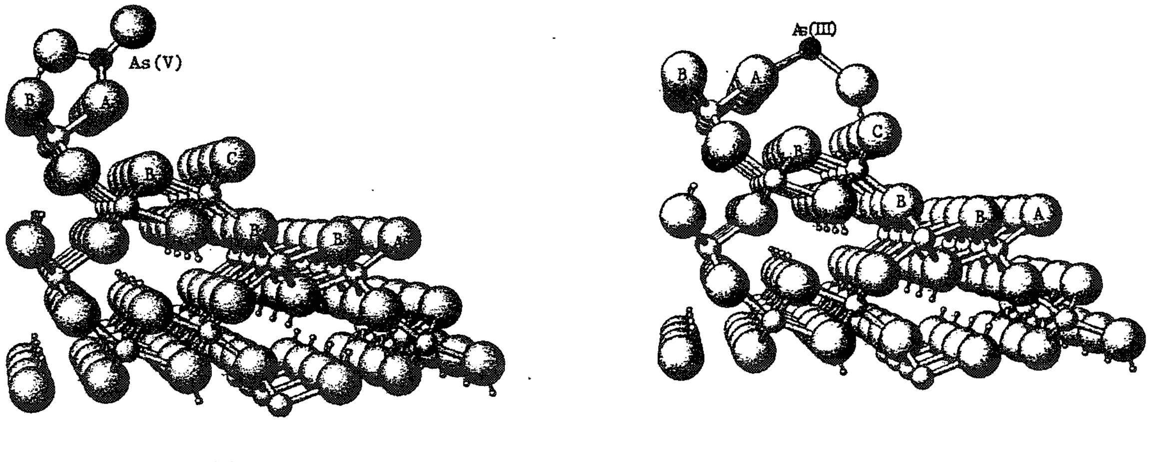
monodentate complex

bidentate complex
mononuclear

bidentate complex
binuclear

Figure 5. Arsenate complexes on oxide surfaces (after Schwertmann and Taylor 1989, Fendorf et al. 1997, O'Reilly et al. 2001).

Sun and Doner (1996) also determined that a binuclear bond formed most commonly between arsenate and arsenite atoms and goethite surfaces, replacing two singly coordinated surface OH groups (Figure 6).



(a)

(b)

Figure 6. (a). Possible bonding structure for As(V) onto goethite. (b). Possible bonding structure of As(III) (after Sun and Doner, 1996).

2.5.3. Reductive dissolution of iron oxides

Under reducing conditions (Eh approximately < 100 mV) arsenic mobilization is controlled by the dissolution of hydrous iron oxides (Deuel and Swoboda, 1972; Aggett and O'Brien, 1985; Cullen and Reimer, 1989 and references therein; Masscheleyn et al., 1991; Jones et al., 2000). Rates of iron oxide reduction in natural environments is influenced by the intrinsic reactivity of the oxides, the effectiveness of the reducing agent, and by microbial catalysis (Postma, 1993). Reductive dissolution of Fe-oxides, commonly referred to as dissimilatory iron reduction, is the redox process that occurs after microbial oxidation of organic matter (or petrochemicals) has consumed dissolved O_2 and NO_3 (Lovely, 1991; Nickson et al., 1998, 2000). Reductive dissolution of Fe-oxides can be described according to the following reaction (Nickson et al., 2000):

$$4FeOOH + CH_2O + 7H_2CO_3 \rightarrow 4Fe^{2+} + 8HCO_3^- + 6H_2O \qquad (2\text{-}9)$$

where CH_2O represents organic matter.

The concurrent increase in ferrous iron and arsenic in solution has been noted (Peterson and Carpenter, 1986; Moore et al., 1988; Bowell, 1994; Onken and Hossner, 1996). McGeehan and Naylor (1994) concluded that arsenate released under anaerobic conditions was due to the reduction of ferric ions to ferrous ions, liberating bound arsenic. The authors detected an increase in As(III) with the disappearance of dissolved As(V) suggesting rapid reduction, within days, of desorbed As(V) to As(III).

2.6. Arsenic association with other soil colloids

2.6.1. Aluminum oxyhydroxides

A number of crystalline aluminum (Al) hydroxides, oxyhydroxides, and oxides exist, with one of the crystalline $Al(OH)_3$ polymorphs, gibbsite, common in most soils. Aluminum oxides display amphoteric properties and are reported to have a zero point of charge at pH 8.0 to 9.2, similar but slightly higher than Fe-oxides (z.p.c. at pH 6.5-8.6) (Figure 4). Thus, Al-oxides posses a net positive charge under most natural soil conditions, attracting oxyanions. In all known Al hydroxides, oxyhydroxides, or oxides, a large portion of the surface OH^- or O^{2-} are linked between Al^{3+} ions and are therefore inactive. Only the OH^- at the broken edge is reactive and will sorb ions from solution (Hsu, 1989).

The surfaces of Al (hydr)oxides may play a role in arsenic adsorption, but only in acidic soils (Sadiq, 1997). Jacobs et al. (1970) determined the amount of As sorbed by untreated soils to be in the same order as the amount of amorphous Al_2O_3 and Fe_2O_3 extracted by oxalate or citrate dithionite bicarbonate. However, these authors did not determine the amount of As sorbed to each separate Al and Fe fraction. Lombi et al. (1999) determined that with sequential extractions sorbed arsenate was essentially associated with aluminum and iron fractions of the soil, with a greater proportion associated with the Fe fraction. Hydroxy-Al on the external surfaces of micaceous minerals was significantly correlated to arsenate retention (Huang, 1975). Electrostatic interactions and specific adsorption are important mechanisms for arsenic retention by soil aluminum (Anderson et al., 1976; Gupta and Chen, 1978).

Anderson et al. (1976) and Gupta and Chen (1978) found As(V) adsorption onto amorphous aluminum hydroxide and activated alumina (Al_2O_3) to be very fast, reaching equilibrium within 48 hrs. Arsenate adsorption maxima was determined to be near pH 5 for alumina and pH 6 for gibbsite, decreasing drastically above pH 6 (Gupta and Chen, 1978; Xu et al., 1988; Manning and Goldberg, 1996). Arsenite adsorption onto activated alumina varied only slightly over the pH range 4 to 7, and decreased above pH 9. Arsenite was found to sorb relatively poorly on alumina and Al-oxides compared to arsenate (Gupta and Chen, 1978; Oscarson et al., 1983; Manning and Goldberg, 1997). Arsenic sorption onto both aluminum hydroxides and alumina can be described by the Langmuir adsorption isotherm (Anderson et al., 1976; Gupta and Chen, 1978).

2.6.2. Manganese oxides

Manganese (Mn) oxides are very active components of natural environments. They occur as coatings on other soil/sediment particles and as nodules, and exist in close association with many other chemical species. Mn-oxides posses a pH-dependent charge. The zero point of charge (z.p.c) for the most common Mn-oxide, birnessite (δ-MnO_2) is pH 1.5 and for the hollandite group (α-MnO_2) is pH 4.6 (McKenzie, 1989) (Figure 4). Due to low z.p.cs, Mn-oxides possess a very high negative surface charge within the pH values of most soils (Galba, 1972; Xu et al., 1988). The surface charge of Mn-oxides can be changed by adsorption of other divalent cations, leading to a decrease in negative surface charge and finally to a positive surface charge. Anions of weak acids, such as arsenate and molybdate, are strongly adsorbed on Mn-oxide surfaces by specific adsorption, or may coprecipitate with the oxides (McKenzie, 1989; Mok and Wai, 1994).

Mn-oxides will undergo reductive dissolution at very moderately reduced redox potentials (Hess and Blanchar, 1977; Guo et al., 1997). Some arsenic is associated with manganese oxides, however, manganese oxides undergo reductive dissolution under moderately reduced conditions (Eh of approximately 550 mV) prior to iron oxides. Arsenate sorbed to Mn-oxides is released into solution upon reductive dissolution of the oxides (McGeehan, 1996). Thus, any arsenic released during dissolution of Mn-oxides will be reabsorbed by iron oxides (Oscarson et al., 1981; Cullen and Reimer, 1989; McGeehan and Naylor, 1994; McGeehan et al., 1998).

Manganese oxides, particularly birnessite, are found to rapidly oxidize As(III) to As(V) (Oscarson et al., 1981; Sun and Doner, 1998). Through oxidation of As(III) to As(V) Mn-oxides are able to catalyze the adsorption of arsenic by aluminum. Oscarson et al. (1983) found As adsorption to Mn-oxides greatly increased when coated with iron and aluminum since both have a greater sorption capacity for arsenic.

2.6.3. Clay minerals and organic matter

Various studies have examined arsenic sorption onto alluminosilicates, organic matter, and carbon with varying results. For example, Sakata (1987) determined distribution coefficient values (K_D) for As(III) were not related to clay percentage and total carbon content, while Elkhatib et al. (1984b) found As(III) Kd values to be significantly correlated to clay and organic carbon content. Other studies found no correlation between the amount of sorbed arsenic and alluminosilicates or soil organic matter (Jacobs et al., 1970; Fordham and Norrish, 1979; Yan-Chu, 1994).

Frost and Griffin (1977) determined adsorption isotherms for arsenate and arsenite adsorption onto montmorillonite and kaolinite. The authors found montmorillonite adsorbed more As(V) and As(III) anions than kaolinite, possibly attributed to a higher edge surface area and/or broken clay particle. Adsorption of As(V) onto kaolinte and montmorillonite reached a maximum at pH 5, and As(III) showed an increase in adsorption as pH increased from 3 to 9, reaching a maximum near pH 7. The pH of maximum adsorption of As(V) and As(III) onto montmorillonite and kaolinite is similar to the pH values for maximum As adsorption onto amorphous iron oxides found by Pierce and Moore (1982). Fordham and Norrish (1979) found anatase (TiO_2) to sorb arsenate to a significant degree against competition from iron oxides. Other components of the clay fraction examined, including kaolinite, illite, vermiculite, muscovite, potassium-felspar, and quartz, were comparatively inert towards arsenate.

Near the soil surface organic fractions typically dominate As adsorption. Humic acids are the most active component of organic fractions in soils and sediments and have a strong retention for arsenic. The adsorption of arsenic by humic acids is high in pH range 5 to 7. Humic acids can contribute more to the retention of arsenic in acidic environments than do clays and some metal oxides (Cullen and Reimer, 1989; Mok and Wai 1994). The humus content and the degree of humification were also found to influence As(V) adsorption by organic mineral soil colloids (Galba 1972). In the pH ranges of most soils As has a limited affinity for organic complexation due to similar and repulsive negative charges of oxyanions and organic matter (Sadiq 1997).

2.7. Molybdenum in soils

Molybdenum (Mo) is an essential nutrient for both plants and animals, utilized by plant enzymes responsible for nitrate reduction and required for fixation of molecular nitrogen by microorganisms. Geologic sources of Mo are primarily shales, sedimentary sulfides, and granitic conglomerates (Allaway, 1977; Doyle and Fletcher, 1977; Morse et al., 1987). The principle source of molybdenum in soils is sulfides (MoS_2), including iron sulfides, and Mo is released during the transformation of FeS to pyrite. Average Mo content of the lithosphere is estimated at 2.3 mg kg^{-1} and the content of shales is estimated at 2 mg kg^{-1}. The range of molybdenum in soils is < 0.1 to 5 mg kg^{-1} with an estimated average of 2 mg Mo kg^{-1} (Mitchell, 1964). Molybdenum in soils can be divided into four categories: (1) Mo in solution (estimated at 50 to 240 $\mu g\ L^{-1}$), (2) Mo occluded with oxides, (3) adsorbed Mo associated with solid phases, and (4) Mo associated with organic compounds (Barrow, 1977; Reddy et al., 1997).

Molybdenum exits in the lithosphere at oxidation states ranging from Mo^{3+} to Mo^{6+}, with Mo^{4+} and Mo^{6+} predominating under reducing and oxidizing conditions respectively (Lindsay, 1979; Edwards et al., 1995). In natural waters and soil solutions Mo becomes fully hydrolyzed and exists as the oxyanion molybdate (Evans, 1989). Molybdate, arsenate, and phosphate are all tetrahedral oxyanions and compete for adsorption sites on soil mineral surfaces (Roy et al., 1986; Ryden et al., 1987; Manning and Goldberg, 1996; Goldberg and Forster, 1998). The form of molybdate species in solutions is dependent on pH and aqueous Mo concentrations (Reisenauer et al., 1962). In general, above pH 4 MoO_4^{2-} is the major solution species, and below pH 4 Mo is present as $H_2MoO_4^0$ or $HMoO_4^-$ (Barrow, 1977; Barber, 1995).

Molybdenum in soils is associated principally with hydrous iron and aluminum oxides, where Mo^{4+} substitutes for Fe^{3+} in oxides (Schwertmann and Taylor, 1989). Molybdate may also be bound to organic-rich argillaceous sediments and complexed with organic fractions in soils (Allaway, 1977; Edwards et al., 1995). Mo will also form insoluble molybdates with iron, aluminum, and zinc (Misra et al., 1977).

In well aerated soils the solubility and sorption of molybdenum to soil colloids and oxides is strongly pH-dependent, and the solubility of exchangeable or adsorbed Mo increases as pH increases. Sorption is also dependent on Mo solution concentrations (Reisenauer et al., 1962; Vlek and Lindsay, 1977; Edwards et al., 1995). Sorption of Mo follows an adsorption envelope, increasing with increasing solution pH from 2 to 4, exhibiting a maximum near pH 4, and decreasing with increasing pH above 4 (Hingston et al., 1972; Barrow, 1977; Goldberg and Forster, 1998). Maximum adsorption of Mo by soil colloids and oxides is close to pH 4, coinciding with the pK_2 (dissociation constant) of molybdic acid ($H_2MoO_4^0$) (Hingston et al., 1972; Barrow, 1977).

Studies of soil surface reactions have shown that Mo is more strongly adsorbed to hydrous ferric oxides (e.g. goethite and hematite) than Al-oxides, but sorption reactions with both types of oxides show analogous patterns (Reisenauer et al., 1962; Barrow, 1977; Edwards et al., 1995). Maximum Mo retentive capacity on goethite was observed in the pH range of 4 to 5, with no adsorption above pH 10. Mo adsorption onto gibbsite was found to be similar to goethite, but with sharper dependence on pH (Misra et al., 1977; Manning and Goldberg, 1996). In acidic soils iron molybdates have been found to be the predominant form of inorganically combined Mo (Allaway, 1977; Evans, 1989). The minimum solubility of ferric molydate is at pH 2.7 in contrast with Al-molybdates having a minimum solubility at pH 4.8 (Reisenauer et al., 1962; Allaway, 1977). Under acidic conditions ($pH < 6$) molybdate is strongly sorbed by soil colloids and hydrous ferric oxides by ligand exchange. Molybdate, arsenate, and phosphate are all adsorbed by inner-sphere ligand exchange mechanisms (Parfitt and Russel, 1977; Waychunas et al., 1993; Manning and Goldberg, 1996).

Generally, Mo concentrations in solutions are low, less than 10 $\mu g\ L^{-1}$ (Barber, 1995). According to Ponnamperuma (1972), molybdenum is probably not involved in oxidation-reduction reactions, except as its solubility might be governed by the solubilization of sorbing phases, and Eh can influence the solubility of Mo minerals. Under wet soil conditions, the solubility of molybdenum is enhanced due to lowered redox potentials, higher pH, and high organic status of soils (Edwards et al., 1995). A change from ferric to ferrous iron, accompanied by increased dissolution of ferric molybdate compounds or complexes may be involved. Ferrous molybdate is substantially more soluble than ferric molybdate at the same pH (Allaway, 1977).

It does not appear that solubilization of molybdenum through formation of organic molybdenum compounds or complexes are major factors in enhancing solubility of Mo. Organic matter may have an indirect effect on Mo solubility through more rapid lowering of redox potentials in soils following establishment of wet conditions (Allaway, 1977). Removal of organic matter and halting additions of macronutrients to soils (mainly in the form of fertilizers) has also been found to decrease Mo retention in soils (Misra et al., 1977).

Under anaerobic conditions, iron oxides undergo reductive dissolution, releasing sorbed elements, such as molybdate and arsenate into soil solution. Only one report, issued by Alberta Health and Wellness (Health Surveillance, 2000), has examined the relationship between molybdenum, arsenic, and iron concentrations in ground waters. No studies to date have examined the co-release of molybdenum and arsenic from iron oxides.

2.8. Purpose of the study

From the above literature review it is clear a great deal is known about the basic reactions of arsenic as they may apply to soils. However, most of the studies used pure phase mineral components rather than whole soils in assessing sorption behavior. How the fundamental sorption chemistry of arsenic elucidated from these studies applies to real soils still requires examination.

This study was conducted to examine the sorption behavior of arsenic in relation to redox conditions for soil materials that contain elevated levels of native arsenic. While the fundamental geochemistry of arsenic and related oxyanions is well established, this study examines how the fundamental reactions express themselves with whole soils. To meet these objectives a reduction incubation and an oxidation experiment were designed to enhance arsenic and molybdenum desorption and sorption respectively from soil iron oxides. This study also examines the validity of using molybdenum as and indicator of naturally occurring arsenic. Using molybdenum as a indicator of geogenic vs. anthropogenic sources of arsenic would be extremely helpful, particularly since elevated concentrations of arsenic are being recorded in more domestic wells in northwestern and east-central Alberta (Fitzgerald et al., 1997; Health Surveillance, 2000; Stein et al., 2000).

CHAPTER III

MATERIALS AND METHODS

3.1. Sample collection

3.1.1. Acid sulfate soil

Soil samples for this study were collected from an outcrop area of weathered pyritic shale from the Kaskapau formation of Cretaceous age, in Sec8-Tp82-R8-W6. The area is located near the hamlet of Blueberry Mountain in northwestern Alberta, approximately 25 km south of the Peace River. The outcrops of acid shale are associated with rolling to hilly topography (Reeder and Odynsky, 1965). Acid sulfate soils belonging to the Boundary soil series (undifferentiated Podzolic) have formed on knoll top and side slope positions and Gleysolic soils belonging to the Josephine soil series have formed on lower slope and depressional areas. The acid sulfate soil used in these studies had two desirable characteristics that made it ideal for experimental purposes. The acid sulfate soil was naturally enriched in native arsenic (about 10X higher than other soils) and in secondary iron oxides (Dudas, 1984; Dudas, 1987; Dudas et al., 1988). The soil was collected from the Bftj horizon of the acid sulfate soil. Bulmer (1987) has provided a complete profile description of this soil and surrounding vegetation. Upon returning to the laboratory portions of the soil were placed in glass mason jars and plastic bags. All containers were refrigerated (2°C) for up to 8 months prior to analysis to slow microbiological activity and to preserve field redox conditions.

3.1.2. Glacial till

A large sample of calcareous glacial till was collected at a depth of 70 cm from the lower Cca horizon of an Orthic Black Chernozem approximately 35 km east of Edmonton. Glacial till is composed of unsorted, unstratified mixtures of clay, silt, sand, gravel, and boulders. The till was collected in order to prepare an acid soil/till mixture for the experiments. This mixture was designed as a surrogate of glacial debris that may have been deposited in the vicinity of shale outcrops when glacial ice overrode the topographic high spots. Till deposits surrounding the shale outcrops would consist of a mixture of the acid marine shale and till of continental origin. The soil/till mixture therefore represents the parent material of soils associated with the Josephine soil series (Pawluk and Dudas, 1978). The till was air-dried, homogenized using a mortar and pestle, and sieved using a 2 mm sieve (mesh no. 10), and stored at room temperature in large plastic Nalgene® bottles and glass mason jars for the duration of the experiments.

3.2. Characterization of Physical Properties

3.2.1. Particle size separation

Thirty grams of field moist soil (26.4% moisture content) was used to determine particle size fractions of sand (50 μm - 2 mm), silt (2 μm - 50 μm), and clay (< 2 μm). The ultrasonification technique was used to disperse the soil sample, and clay separation was achieved through successive dispersion and gravity sedimentation cycles. Dispersion of the soil was performed without pre-treatment for the removal of organic matter, calcium carbonates or iron oxides. Sand and silt fractions were separated by wet sieving, oven dried at 105^0C for 24 hours, and weighed. Clay content was calculated by difference (Dudas, 1992). Clays were further separated into coarse, medium, and fine fractions by centrifugation.

3.2.2. Elemental analysis of bulk soil and till

Six subsamples of the acid soil samples and five subsamples of the till were randomly chosen to assess the homogeneity of the soil and till collected for the experiments. All soil and till samples were air-dried and ground to pass through a 2 mm sieve using a mortar and pestle. Elemental analysis of the bulk soil and till was performed using instrumental neutron activation analysis (INAA) at the SLOWPOKE II (Safe Low Power Kritical Experiment) nuclear reactor at the University of Alberta. The procedure used was specifically developed to optimize arsenic determination (long-irradiation) (Duke, pers. comm.).

Total iron and arsenic concentrations in the particle size fractions (sand, silt, and the coarse, medium, and fine clay fractions) from the acid sulfate soil were also measured by INAA. The particle size fractions of the soil were analyzed separately to determine if arsenic was concentrated in one or more of the particle size fractions. Results obtained from the six bulk subsamples of soil and the five subsamples of till were used to report total arsenic and iron concentrations.

3.3. Characterization of Chemical Properties

3.3.1. Redox potential

There is no standard protocol for taking redox measurements, therefore, procedures outlined by Brown (1933), Patrick et al. (1996), and Salloum et al. (in press) were combined to create a reproducible method. Large pieces of organic matter were removed from the soil. Redox measurements were made on a field moist, unsieved acid soil sample and a dried, sieved (2 mm) sample of till. Sample preparations for the soil and till were identical. A 1:2 mixture (w:v) sample: deionized distilled water (DDW) [50 g sample: 100 mL (DDW)] were thoroughly mixed in 250 mL centrifuge bottles. The bottles were left uncovered at room temperature and equilibrated for 24 hours, and subsequently centrifuged at 1500 rpm for 10 minutes using an International Centrifuge (International Equipment Co., Boston, Mass.). A combination ORP electrode (Cole-Parmer, Chicago, IL) was placed immediately in contact with the sediment. The digital oxidation/reduction potential (ORP) reading was recorded (mV) from a Cole-Parmer Digi-Sense® after the probe stabilized for one hour. The redox potential (Eh) was calculated by adding 235 to the ORP reading (Jacob, 1970).

3.3.2. pH

The pH of the soil and the till were determined in 0.01 *M* $CaCl_2$ and DDW (Hendershot et al., 1993). A 1:2 mixture (w:v) sample: solution ratio was prepared using twenty five grams of field moist, unsieved soil and a dried and sieved (2 mm) sample of till. The pH was recorded after 24 hours using a Cole-Parmer pH meter (Cole-Parmer, Chicago, IL).

3.3.3. Sample preparation for additional analyses

Mixtures of 1:2 (w:v) soil: DDW using 50 g of field moist soil and sieved till were equilibrated for ten days for the following analyses: electrical conductivity, sulfate concentration, cation analysis, and ferrous iron determination (Kittrick, 1980). Soil and

DDW were mixed thoroughly in 250 mL centrifuge bottles and covered with parafilm® and equilibrated at room temperature. Bottles were centrifuged at 1500 rpm for 20 minutes prior to collecting supernatant for all analyses.

3.3.4. Electrical Conductivity

Electrical conductivity of the supernatant collected from the soil and the till were measured using a Model 31 Conductivity Bridge (Yellow Springs Instrument Inc., Yellow Springs, OH) (Salloum et al., in press).

3.3.5. Ion analyses

Sulfate concentrations in the supernatant collected from the soil and till were determined using a Dionex 4000i ion chromatograph (Dionex Corp., Sunnyvale, CA). Chromatograms and peak areas were obtained using Peaknet Software®. Solutions were prepared in triplicate in 10 m*M* D-mannitol to prevent oxidation of reduced sulfur species, specifically sulfite, to sulfate. This was done so that sulfate values were not artificially high (Wagner and McGarrity, 1991; Dionex Corporation, 1999).

Select ions (Al, As, Ca, K, Fe, Mg, Mo, Mn, Na, and Pb) in the supernatant collected from the soil and till were determined by inductively coupled plasma-mass spectrometry (ICP-MS) using a Perkin-Elmer SCIEX Elan Model 5000 ICP quadrupole mass spectrometer (Thronhill, ON) by the Alberta Research Council, Edmonton. Two to four drops of toluene were added as a microbial sterilant to inhibit shifting of the redox potential of the liquid by microbial activity (Alef and Nannipieri, 1995; McGill, pers. comm.). Toluene did not interfere with ion detection. Solutions were transported in 130 mL plastic bottles pre-washed with nitric acid and were refrigerated (2°C) prior to transportation. Complying with routine procedures, solutions were filtered (pore size 0.45 μm) and acidified with nitric acid prior to analysis (Feng, pers. comm.). Operational parameters are outlined by Wu et al. (1996).

Ferrous iron (Fe^{2+}) in the supernatant collected from the soil was determined by the spectrophotometric method outlined by Phillips and Lovley (1987). The oxalate extraction was not performed prior to analysis. Sample volumes of the supernatant (0.10 mL) were collected in triplicate using an automatic pipette (Pipetman) and injected into a

10 mL ferrozine solution. Absorbance at 562 nm was recorded using a Spectronic® 20 Series spectrophotometer (Milton Roy, Rochester, N.Y.).

Measurement of total carbonates and inorganic carbon in the till was performed using the titrimetric method as described by Dudas (1988). Duplicate blank samples weighing both 1.0 g and 0.50 g were prepared, since relative initial carbonate levels were unknown. n-Octanol was not added due to the low organic matter content of the till. The till was treated with HCl and equilibrated for 24 hours. The CO_2 generated was collected by KOH and the solution titrated with HCl to calculate carbon and carbonates.

3.4. Reduction experiment

3.4.1. Sample preparation

The protocol developed for the reduction experiment is based on studies by McGeehan and Nalyor (1994), McGeehan (1996), McGeehan et al. (1998), Reynolds et al. (1999), and Jones et al. (2000). The acid sulfate soil that was incubated was prepared as a 1:2 mixture (w:v) soil: 1 *M* C D-glucose. During preliminary experiments a 1 *M* C glucose solution (equivalent to 144 mg C $g \cdot soil^{-1}$) promoted iron reduction in the soil. Fifty grams of field moist soil was weighed into 250 mL centrifuge bottles. Large pieces of organic matter, including leaves and twigs, and stones were removed from the soil prior to weighing. The glucose solution was added to the centrifuge bottles and the solid and solution were mixed thoroughly. The bottles were then purged between 10-15 minutes with pre-purified nitrogen gas in a glove bag under nitrogen atmosphere. The bottles were capped tightly, sealed with Teflon® tape, and incubated in darkness at room temperature.

Acid soil/till mixtures that were incubated were prepared in a similar manner to soil samples using a 1 soil + till:2 1 *M* C D-glucose. Fifty grams of soil + 12.5 g till were mixed in 250 mL centrifuge bottles. Based on preliminary experiments a 25% addition by weight of till was sufficient to increase the pH of the soil to a minimum of 6.0. Glucose solution was added, the solid and liquid phases were thoroughly mixed, and the bottles purged with nitrogen gas in a glove bag. The bottles were capped tightly, sealed with Teflon® tape, and incubated in darkness at room temperature.

3.4.2. Incubation and analyses

All soil and soil/till mixture incubation vessels were harvested and analyzed using similar procedures unless otherwise noted.

Bottles were shaken daily by hand in an attempt to promote homogeneous reduction by mixing the solid and solutions phases. Periodically, the bottles became pressurized, and the pressure was released by loosening the caps in the glove bag under $N_{2(g)}$ atmostphere. Small quantities of soil material were lost when bottles under high pressure were opened in the glove bag. Three incubation vessels were removed from incubation at 3 day intervals. The bottles were centrifuged at 1860 rpm for a minimum of 10 minutes prior to all analyses and opened in a glove bag under nitrogen atmosphere. The redox potential of the *solid phase* and pH of the supernatant were measured immediately once the bottles were uncapped in the glove bag. Redox potential measurements were recorded after one hour, allowing the probe to stabilize. Aliquots of the supernatant were removed under $N_{2(g)}$ for the following analyses: electrical conductivity, sulfate concentration, select ion analysis (Al, As, Ca, K, Fe, Mg, Mo, Mn, Na, and Pb), and ferrous iron/total iron measurements. Solutions collected to measure electrical conductivity and sulfate were filtered using a 10 mL syringe and a 0.22 μm PTFE non-sterile filter. Electrical conductivity, sulfate concentrations, ion analysis, and ferrous iron measurements were determined as outlined in sections 3.3.4. and 3.3.5. respectively. Organic acids produced during fermentation were detected during sulfate measurements using ion chromatography (Steffes, pers. comm.), however the types and concentrations of the acids were not measured during analysis. Total iron was determined as described by Phillips and Lovley (1987) by adding hydroxylamine hydrochloride as a reducing agent to reduce amorphous iron oxides (Ross and Wang, 1993).

All bottles were moved from the side laboratory room to cupboards in the main laboratory near the end of the incubation because the side room was cooler than the main lab. At this time, remaining samples were bubbled with $N_{2(g)}$ for a minimum of 10 minutes in a glove bag in attempts to stimulate further reduction. Of the remaining bottles, eight vessels/day were put on a rotational shaker (Associated design & mfg. Co., Alexandria, VA) to also try to stimulate reduction by thoroughly mixing and homogenizing the solid and solutions phases.

3.5. Oxidation experiment

The geochemical behavior and interactions between arsenic, molybdenum, and iron during the oxidation experiment were only examined in the soil/till mixture. The mixture was first incubated to promote Fe-oxide reductive dissolution and desorption of As and Mo into solution. The solutions that were incubated contained high concentrations of As, Mo, and Fe and were then oxidized by purging with O_2 or by leaving solutions open to the atmosphere.

3.5.1. Sample preparation

Sample preparation for the incubation of soil/till mixtures followed the same procedure outlined for the reduction experiment (section 3.4.1), however a larger volume of soil was used and samples were incubated in larger containers. Samples were prepared using 400 g soil + 100 g till (25%): 1 *M* C D-glucose [1 soil: 2 solution mixture (w:v)]. Quantities of field moist soil and sieved till were weighed into large plastic Nalgene® bottles and the bottles purged with nitrogen in a glove bag for a minimum of 15 minutes. The bottles were sealed tightly and incubated in darkness for 5 weeks (based on observations from preliminary experiments) at room temperature (McGeehan and Nalyor, 1994; McGeehan, 1996; McGeehan et al., 1998; Reynolds et al., 1999).

3.5.2. Oxidation

Soil and solution from the plastic bottles was transferred into 250 mL centrifuge bottles under $N_{2(g)}$ in a glove bag. All bottles were centrifuged at 1,860 rpm for a minimum of 15 minutes. The supernatant from all of the centrifuge bottles was decanted into a 4 L Erlenmeyer flask in a glove bag and mixed thoroughly to homogenize the solutions. Initial measurements (Eh, pH, EC, ferrous/total iron, cations, sulfate) were performed on the homogenized liquid as outlined in sections 3.3. and 3.5.3. Using a 100 mL glass pipette, 200 mL of solution were transferred from the flask to 250 mL plastic bottles. The bottles were left open to the atmosphere at room temperature to allow oxidation of the solutions. Initially, the redox potential of the solutions did not increase as predicted. Thus, approximately one dozen bottles were continuously purged with pre-purified $O_{2(g)}$ from 30 minutes to 1 hour intervals to increase the redox potential. Deionized distilled water was added periodically when solution levels were observed to be lowering due to evaporation.

3.5.3. Analyses

All solutions, including those left open to the atmosphere (not purged) and those purged with oxygen were harvested periodically based on changes in aqueous concentrations of ferrous iron. Prior to analysis solutions were centrifuged at 26,891 g for 15 minutes using a Sorvall® RC-B5 Refrigerated Superspeed Centrifuge (DuPont Instruments, Norwalk, CT) and any precipitates were collected once they dried in the centrifuge tubes. The color of the dried plugs was determined using a Munsell color chart. All analyses were performed on the liquid once centrifuged and included: redox potential (of the *liquid phase*), pH, electrical conductivity, ferrous iron/total iron concentrations, sulfate concentrations, and a minimum of 20 mL of solution was collected for selected cation analysis (measurements performed as described in section 3.3.). The redox potential was measured when the probe stabilized, which was within 10 minutes. Once centrifuged, the liquid to be collected for analysis by ICP-MS was filtered using a 10 mL syringe and a 0.22 µm PTFE non-sterile filter. Toluene was added drop-wise to sterilize solutions collected for cation and anion analysis.

Bicarbonate concentrations were measured during sampling as described by Brundy and Bremner (1972). Bromocresol green was added to the solutions as an indicator, and the solutions were then tritrated with HCl. The volume of acid was recorded when the indicator changed from green to yellow. Due to the strong yellow color of the liquid of the initial solutions, initial carbonate values could not be determined. Carbonates were measured on all subsequent solutions. Bicarbonate concentration was calculated by:

$$[HCO_3^-] = \frac{(\text{final mL - initial mL})(\text{acid molality in moles/L})(62.0\text{ g mol}^{-1})}{(\text{sample volume in mL})(1\text{L}/1000\text{ mL})} \qquad (3\text{-}1)$$

CHAPTER IV

RESULTS AND DISCUSSION

4.1. Results of routine characterization

4.1.1. Sample homogeneity

The concentration of twenty elements in the acid soil and till were determined using short and long irradiation times by INAA. The INAA procedure developed for this study optimized arsenic analysis. Average concentrations for select elements chosen for testing sample homogeneity are listed in Table 4.

Table 4. Average concentration of elements in bulk soil (n = 6) and till (n = 5) with ± 1 standard deviation (σ) error as determined by INAA.

Element	Soil	Till
arsenic[2] (mg kg^{-1})	37.9 ± 0.3	10.3 ± 0.25
sodium[1] (g kg^{-1})	2.11 ± 0.002	10.3 ± 0.01
sodium[2] (g kg^{-1})	2.14 ± 0.008	9.97 ± 0.011
iron[2] (g kg^{-1})	48.1 ± 0.07	23.9 ± 0.08
aluminum[1] (g kg^{-1})	89.2 ± 0.06	53.7 ± 0.04
chromium[2] (mg kg^{-1})	111 ± 4	62 ± 4

[1]short-irradiation (4 minutes)

[2]long-irradiation (120 minutes)

Sodium was measured during both short- and long-irradiation with good agreement, demonstrating the reproducibility of the method. Arsenic concentrations in the soil ranged from 34.4 to 42.4 mg kg^{-1}, and in the till from 9.57 to 11.0 mg kg^{-1}. Molybdenum was not reported mainly because Mo does not activate well (Duke, pers. comm.). The variation within the soil and till samples was low, demonstrating acceptable sample homogeneity for the soil and till.

4.1.2. Particle size analysis

A textural class of silty clay was assigned to the acid sulfate soil using criteria outlined in the Canadian System of Soil Classification which was based on results from the particle size separation (Agriculture Canada, 1987). Total arsenic and iron concentrations measured by INAA were highest in the medium clay-size fraction and lowest in the sand fraction separated during particle analysis. These results support other studies by Dudas and Pawluk (1980), Dudas (1984; 1987), Elkhatib et al. (1984a), and Yan-Chu (1994) who reported the highest concentrations of arsenic in the clay-size fraction.

Soil arsenic concentrations are reported to be strongly influenced by and associated with iron (Ferguson and Gavis, 1972; Livesey and Huang, 1981; Masscheleyn et al., 1991; Waychunas et al., 1993; McGeehan and Naylor, 1994; Sadiq, 1997). The relationship between arsenic and iron determined by INAA in the various particle fractions separated during particle size analysis is shown in Figure 7. The asterisk denotes the data point representing the bulk soil sample. There is a strong linear relationship ($r^2 = 0.97$) between arsenic and iron concentrations in the soil fractions, demonstrating that similar arsenic-iron associations exist in acid sulfate soils as in other systems previously described in the literature.

4.1.3. Physical and chemical parameters

Results for all preliminary physical and chemical analysis are listed in Table 5. Both the soil and till were oxidized, and the soil was very acidic and the till neutral. After the ten day equilibration of the acid soil with DDW, very low aqueous concentrations of iron, arsenic, and molybdenum were detected in the soil solution. During equilibration the soil remained oxidized therefore solid phase (mineral) Mn- and Fe-oxides remained stable. Supernatant collected from the equilibration with the till contained high concentrations of soluble salts (Ca, K, Mg, Na, and SO_4^{2-}) contributing to the neutral pH of the till. The acid sulfate soil is enriched in arsenic (37.9 mg kg^{-1}) relative to the average value for shales (4.1 mg kg^{-1}), and is also enriched in iron (4.81%). The till is not enriched in arsenic (10.3 mg kg^{-1}) as this value is within the range of concentrations reported for non-enriched materials (McKeague et al., 1979).

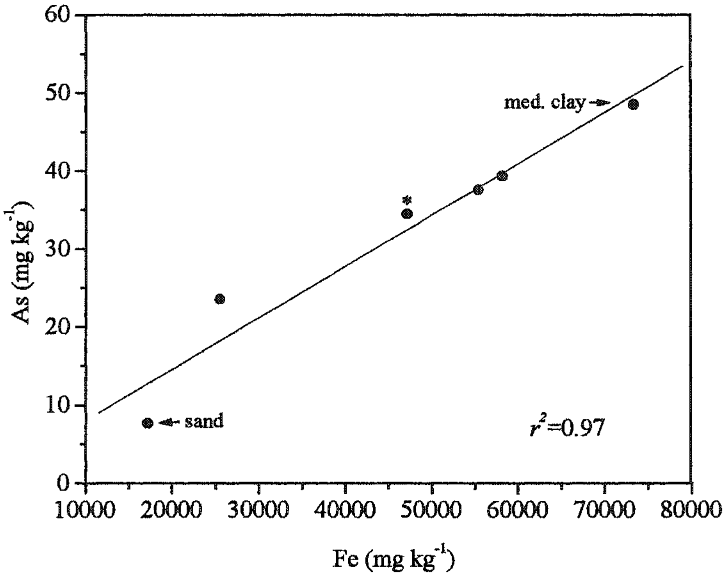


Figure 7. Concentrations of iron and arsenic in the coarse, medium, and light clay fractions (< 2 μm), silt (2 μm – 0.05 mm), and sand fractions (0.05 mm – 2 mm) and in one bulk soil sample (denoted by *) of the acid sulfate soil. Data was collected using instrumental neutron activation analysis (INAA).

4.1.4. Iron-, aluminum oxide characterization, and clay mineralogy

The various forms of iron oxides and the clay mineralogy of the acid sulfate soil have been reported by Pawluk and Dudas (1978), Bulmer (1987), and Dudas et al. (1988). The types of iron oxides in the B horizon as determined by X-ray diffraction (XRD), the use of microprobes, and ammonium oxalate extraction include: goethite, hematite, lepidocrocite (trace amounts), and amorphous Fe-oxides (possibly ferrihydrite). Bulmer (1987) and Pawluk and Dudas (1978) used XRD combined with seven pre-treatments as outlined by Dudas and Pawluk (1980) to determine the clay mineralogy of the soil. The types of clays include: kaolinite (dominant), mica (dominant), hydrous mica, muscovite, and vermiculite (trace amounts). Pawluk and Dudas (1978) and Bulmer (1987) found the major portion of extractable aluminum to be either organically combined or in exchangeable form. Bulmer (1987) also found Al to dominate on the exchange complex, reflecting the very low base saturation of these acid sulfate soils. Also, due to the low pH of the soil solution, the tendency for Al hydrolysis and polymerization may be retarded, with much of the aluminum existing as exchangeable and organically combined Al^{3+}.

Table 5. Physical and chemical characteristics of soil from the Bftj horizon of the Boundary soil series and glacial till. Symbol (-) denotes no analysis performed.

Physical or chemical parameter		Bftj horizon	Glacial till
Textural class		Silty clay	*Clay loam
Redox potential (mV)		686	483
pH	$CaCl_2$	3.43	7.56
	water	3.91	7.07
Electrical conductivity (dS m^{-1})		0.0750	0.501
Total elements	Al (μg L^{-1})	337	58.7
(solution)	As (μg L^{-1})	0.0231	0.700
	Ca (mg L^{-1})	1.76	50.9
	Fe (μg L^{-1})	9.83	20.7
	K (mg L^{-1})	1.01	1.21
	Mg (mg L^{-1})	0.362	12.4
	Mn (μg L^{-1})	9.57	1.71
	Mo (μg L^{-1})	0.149	3.10
	Na (mg L^{-1})	0.457	3.32
Ions (mg L^{-1})	Fe^{2+}	trace	-
	Cl^-	< 5	< 5
	SO_4^{2-}	14.8	111
Total elements	As (mg kg^{-1})	$\boxed{37.9 \pm 0.3}$	10.3 ± 0.25
(soil)	Fe (g kg^{-1})	48.1 ± 0.07	23.9 ± 0.08
Carbonates (mg g·soil^{-1})	% $CaCO_3$	-	6.50

*reported by M. Abder-Ruhman (1980)

4.2. Reduction experiment

The acid sulfate soil was incubated for 51 days and the soil/till mixture for 48 days. Uniform reduction of the acid sulfate soil did not occur during the incubation and only moderately reduced conditions were attained in many incubation vessels. All soil and soil/till samples were harvested in triplicate for analysis according to the design of the sampling procedure, however results were not averaged due to non-uniform reduction during the incubation.

The extreme acidity of the acid sulfate soil limited reduction of the soil. Microbial reduction of sequential electron acceptors is the main process responsible for creating anaerobic soil conditions, and microbial growth is extremely restricted at low pH ($pH < 4$) (Fedorak, pers. comm.). Soil samples that did reduce may have had some initial microbial activity prior to sample preparation. During sample collection the soil was at field moist condition, and even though homogeneous based on elemental analysis, the soil could have contained reduced aggregates with high microbial activity (Bartlett, 1986). During sample preparation, pockets of active microorganisms could have been added to some containers and not others, since microorganisms are not distributed evenly throughout a soil. With the addition of glucose and mixing of solids with solutions, microbial populations from these reduced microsites likely flourished, creating biologically reduced conditions.

The influence of pH on pe is described by (Bartlett, 1986):

$$pe = \log K - pH \qquad (4\text{-}1)$$

where log K is the stability constant for a chemical reaction, for example the oxidation of glucose during the reduction incubation. For one such reaction, or one value for log K, acidification results in an increase in pe (or Eh), while an increase in pH leads to a lower pe. Thus, a lower pe value was more easily attained during incubation of soil/till mixture since the initial pH was higher compared to the soil.

4.2.1. Redox potential

The redox potential of the *solid phase* was measured during the incubation as outlined in section 3.4.2. The redox potential of the acid sulfate soil dropped from around 600 mV to between 7 and -230 mV on day 12 (Figure 8). Eh values after this time were variable among replicates, but remained near this range with a minimum Eh of -349 mV measured after 42 days. The redox potential of the soil/till mixture dropped after only 3 days from around 300 mV to around -335 mV, and a minimum of -343 mV was measured after 21 days. The Eh increased slightly after 24 days and the variation among replicates increased after this time. The mean Eh calculated when the soil and soil/till mixture reduced was –152 mV and –266 mV respectively (Table 6).

The addition of organic carbon in the form of glucose stimulated microbial activity in both the soil and soil/till mixture. Glucose was oxidized first through aerobic respiration (glycolysis) as microbes metabolized the substrate. The initial drop in redox during the incubation of the soil and soil/till mixtures is associated with aerobic oxidation of glucose to carbon dioxide (Bartlett, 1986) combined with the release of electrons as described by (Lindsay, 1979):

$$C_6H_{12}O_6 + 6H_2O \leftrightarrow 6CO_2 + 24e^- + 24H^+ \qquad (4\text{-}2)$$

Once oxygen was depleted, anaerobic metabolism of glucose occurred through the process of fermentation. Fermentation likely proceeded for the remainder of the incubation, since high concentrations of organic carbon were available to the organisms along with a large source of reducible Fe^{3+}. Fermentative microbes can couple the oxidation of organic matter to Fe^{3+} reduction, using iron as an electron acceptor (Eq. 4-4, p. 42). Acetic acid is the main compound formed during fermentation. There is no net transfer of electrons when acetic acid is produced therefore redox does not influence this transformation. Other fermentation products such as lactic, butyric, and propionic acids could also have been produced through oxidation of glucose, but would have been produced in much smaller concentrations (Lindsay, 1979; Lovley, 1991). The initial rapid decrease of Eh is also due to the release of reducing substances accompanying oxygen depletion before Mn(IV) and Fe(III) oxides can mobilize their buffer capacity (Ponnamperuma, 1972).

The initial Eh was lower in the soil/till mixture compared to the soil because liming an acid soil (in this case the addition of calcareous glacial till to the acid soil) will result in a decrease in acidity and will lower its pe (Bartlett, 1986). Redox potential values remained uniformly low within replicates of the soil/till mixture. In flooded soils, greater concentrations of redox-active ions and the high exchange currents of hydrogen

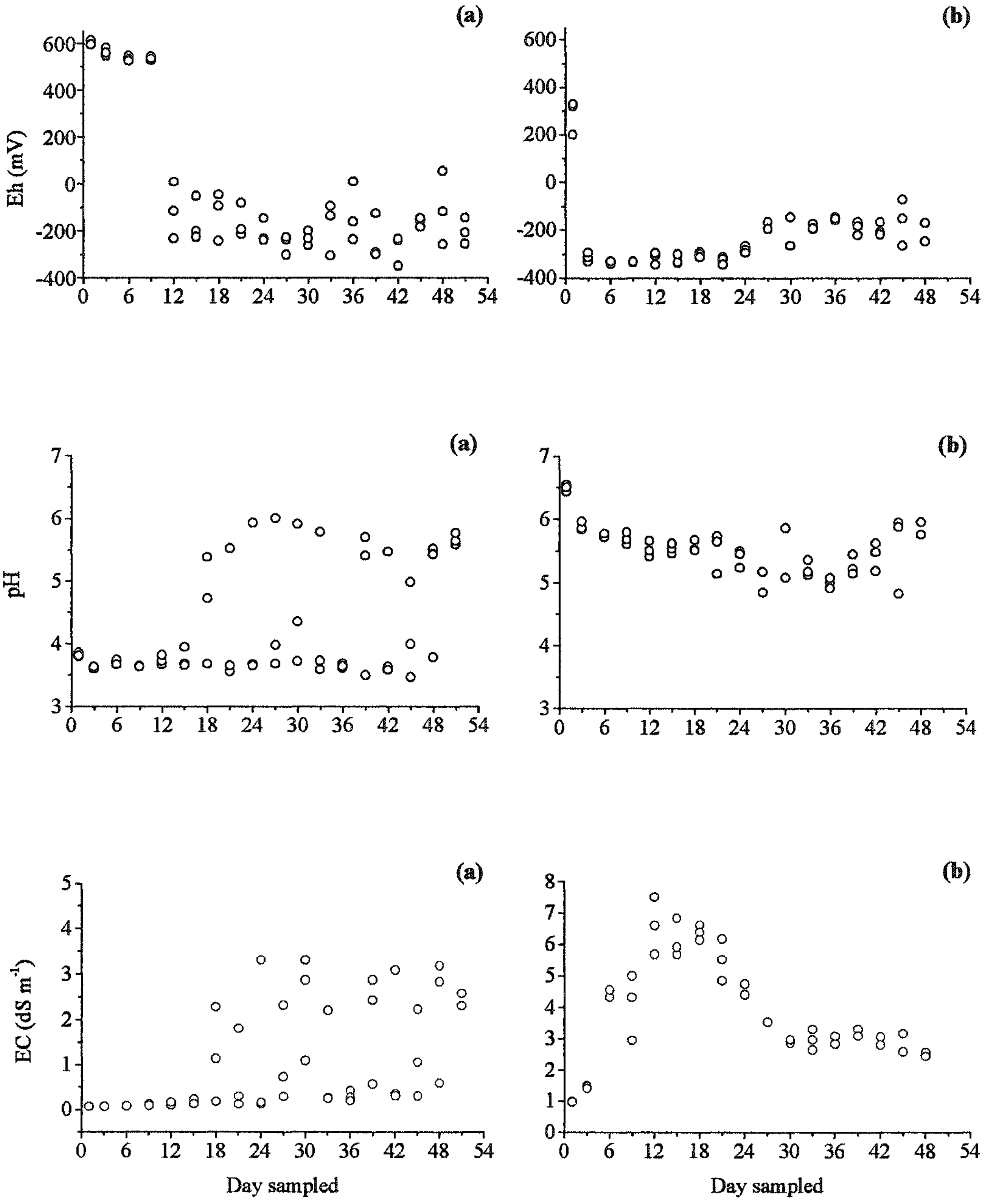


Figure 8. Changes in redox potential (Eh), pH, and electrical conductivity (EC) during the reduction incubation of the (a) acid sulfate soil and (b) the soil/till mixture.

Table 6. Mean values for chemical parameters and elemental analysis during the incubation of the acid sulfate soil and soil/till mixture.

Parameter	n	Acid sulfate soil	n	Soil/till mixture
Eh (mV)	54	-152	48	-266
pH	54	3.73	48	5.53
EC (dS m^{-1})	54	0.295	48	3.23
Ion				
Fe^{2+}	34	42.7 mg L^{-1}	44	3.08 g L^{-1}
As (μg L^{-1})	54	1.29	48	42.8
Mo (μg L^{-1})	45	0.0318	48	34.5
Al (mg L^{-1})	54	0.830	48	2.16
Mn	54	78.9 μg L^{-1}	48	22.4 mg L^{-1}
SO_4^{2-} (mg L^{-1})	49	145	38	730

lead to greater electromotive force, stability, and reproducibility of redox measurements (Bohn, 1971). High concentrations of ions were detected when the soil/till mixture reduced (electrical conductivities were high) compared to the soil, resulting in Eh readings that were more reproducible between triplicates from the soil/till mixture. After day 24 the Eh of the soil/till mixture increased and stabilized after day 30. This trend was also noted by Hess and Blanchar (1977), Ponnamperuma (1972), McGeehan and Naylor (1994), McGeehan (1996) and McGeehan et al. (1998) who found that submerging an aerobic soil resulted in a decrease in Eh during the fist few days and the Eh soon reached a minimum. In all studies, the Eh then increased slightly and became stable, as did the redox potential of the soil/till mixture.

4.2.2. pH

The initial pH of the acid sulfate soil was very low, near pH 3.82. During the incubation of the soil, the pH of some solutions remained low, close to initial values, and in others the pH increased to greater than 5.0 (Figure 8). The pH of the solutions of the submerged soil ranged from a minimum of 3.64 to a maximum of 6.00. The initial pH of the soil/till mixture was near pH 6.50, mainly due to the addition of till to the soil. The pH of the solutions of the soil/till mixture decreased slightly as the incubation progressed with some variability measured among replicates. The pH of the soil/till mixture ranged from a minimum of 4.83 to a maximum of 6.55 and the majority of solutions had pH of less than 6. The mean pH calculated for the soil was acidic, 3.73, and for the soil/till mixture was pH 5.53 (Table 6).

The overall effect of submergence on a soil is to increase the pH of acid soils and to decrease the pH of calcareous soils. These trends were observed in the soil and soil/till mixture. Since most soils contain more Fe(III) oxide hydrates than any other oxidant, the increase in pH of acid soils is largely due to the reduction of Fe (Ponnamperuma, 1972; Bartlett, 1986). The variations in pH observed in this experiment were similar to variations in pH in an acid sulfate soil subjected to oxidation/reduction cycles studied by Satawathananont et al. (1991). The pH of the soil/till mixture continued to decrease until day 30 and increased after day 39. Ponnamperuma (1972), Masscheleyn et al. (1991), McGeehan (1996), McGeehan et al. (1998), and Reynolds et al. (1999) also found this trend in flooded soils. The decrease in pH of the soil/till mixture shortly after submergence is likely due to accumulation of CO_2 produced by respiration of aerobic bacteria during glucose oxidation (Ponnamperuma, 1972).

4.2.3. Electrical conductivity

The variations in electrical conductivity (EC) of the soil during the incubation were similar to variations in pH. The EC of some solutions remained very low, close to initial values, and in other solutions the EC increased to greater than 2 dS m^{-1} (Figure 8). The initial EC of the soil was close to 0.0743 dS m^{-1}. EC of the soil increased sharply on day 18 and increased to a maximum of 3.31 dS m^{-1}. The EC of the soil/till mixture increased sharply from day 6 until day 18, decreased until day 30, and then stabilized until the end of the incubation. Initial EC of the soil/till mixture was close to 1.22 dS m^{-1}. The initial increase in EC corresponded to the decrease in the redox potential and the release of ions into solution during reduction. The mean EC calculated during reduction of the soil was 0.295 dS m^{-1} and of the soil/till mixture was 3.23 dS m^{-1} (Table 6).

Strongly acid soils have low initial conductances (Ponnamperuma, 1972). The initial conductance of the soil was much lower than the soil/till mixture, likely due to the presence of soluble salts in the till. EC values considerably in excess of 4 dS m^{-1} are possible in acid sulfate soils, although the maximum reached as the soil incubated was only 3.31 dS m^{-1}.

The specific conductance of most soil solutions increases after submergence, attains a maximum, and declines to a fairly stable value, which varies with the soil. This trend was most clearly observed during the reduction of the soil/till mixture. The increase in conductance during the first few weeks was due to the release of water-soluble Fe^{2+} and Mn^{2+} from reductive dissolution of insoluble Fe(III) and Mn(IV) minerals, the accumulation of ammonia, bicarbonates, organic acids, and the dissolution of $CaCO_3$ and $CO_{2(g)}$. An additional factor is the displacement of ions, especially cations, from soil colloids (Ponnamperuma, 1972). As the EC decreased in the soil/till mixture the Eh increased, possibly due to the attainment of a state of redox equilibrium.

4.2.4. Ferrous iron

Aqueous concentrations of ferrous iron increased during reduction of the soil and the soil/till mixture (Figure 9). Solutions with below detectable concentrations of ferrous iron are included in the figure because Fe^{2+} was detected in these solutions, however below detectable Fe^{2+} concentrations were not quantified during analysis. Insoluble Fe-oxides undergo reductive dissolution under moderately anaerobic conditions, when Eh decreases to ~100 mV (McGeehan et al., 1998). Chemical reductive dissolution of Fe-oxides is described by the chemical equation (Lindsay, 1979):

$$Fe(OH)_3 + 3H^+ + e^- \leftrightarrow Fe^{2+} + 3\ H_2O \qquad (4\text{-}3)$$

Fermentative microorganisms are also able to couple the oxidation of organic carbon to dissimilatory iron reduction. Fe^{3+} is used as a terminal electron acceptor during biological reduction of iron as described by (Lovley, 1991):

$$C_6H_{12}O_6 + 24Fe^{3+} + 12H_2O \leftrightarrow 6HCO_3^- + 24Fe^{2+} + 30H^+ \qquad (4\text{-}4)$$

The result of both reactions is the release of ferrous iron into solution. Under low redox conditions, soluble and exchangeable Fe^{2+} is released along with trace elements bound under oxidized conditions by Fe^{3+} (Bartlett, 1986). The initial increase in aqueous concentrations of Fe^{2+} in the soil and in the soil/till mixture coincided with the decrease in redox potential, which led to the reductive dissolution of Fe-oxides in the acid soil. Microorganisms in both the soil and soil/till mixture had an ample supply of organic carbon and iron therefore Fe reduction continued throughout the incubation and did not cease. The redox transformation line for iron reduction is often considered the boundary between aerobic and anaerobic soil, and the presence of ferrous iron in solution is considered a reliable indicator of the anaerobic status of a soil (Ponnamperuma et al., 1967; Bartlett, 1986).

Concentrations of ferrous iron in solution were below detection limit (BDL) in the soil until day 12 and increased sharply on day 18. Ferrous iron concentrations in the solution phase of the acid sulfate soil were variable among replicates and remained moderately high to high, ranging between 19.0 mg L^{-1} and 3.77 g L^{-1}. Aqueous concentrations of Fe^{2+} in the replicates of the soil/till mixture followed a uniform trend, increasing sharply on day 6 and remaining high, greater than around 2.50 g L^{-1} for the duration of the incubation. Fe^{2+} concentrations ranged from 0.760 g L^{-1} to 3.82 g L^{-1}. The mean concentration of Fe^{2+} in solution calculated for the acid soil was 42.7 mg L^{-1} and for the soil/till mixture was 3.08 g L^{-1} (Table 6). Maximum ferrous iron concentrations detected in the soil and soil/till mixture were similar. The large quantity of Fe in solution demonstrates that a large portion of the Fe-oxides in the soil were amorphous, easily breaking down, compared to more crystalline oxides (Lovely, 1991; Jones et al., 2000).

4.2.5. Arsenic

Aqueous arsenic concentrations in the acid sulfate soil increased gradually, and during the incubation only 3 samples contained arsenic concentrations above the Canadian drinking water quality guideline limit of 25 μg L^{-1} (Health Canada, 1996) (Figure 9). More than 5 weeks passed before As concentrations were detected in excess of the guideline limit. The highest concentration of As (44.2 μg L^{-1}) was measured on the last sampling period. Aqueous concentrations of As in the soil/till mixture increased steadily until day 21 and generally remained higher than 20 μg L^{-1} for the remainder of the incubation. Thirty-three of 48 soil/till mixture samples (almost 70%) exceeded the guideline limit for allowable As in drinking water. Concentrations of arsenic in solution in excess 25 μg L^{-1} were detected after 10 days in the soil/till mixture. The mean concentration of As in solution during the incubation was calculated to be 1.29 μg L^{-1} and

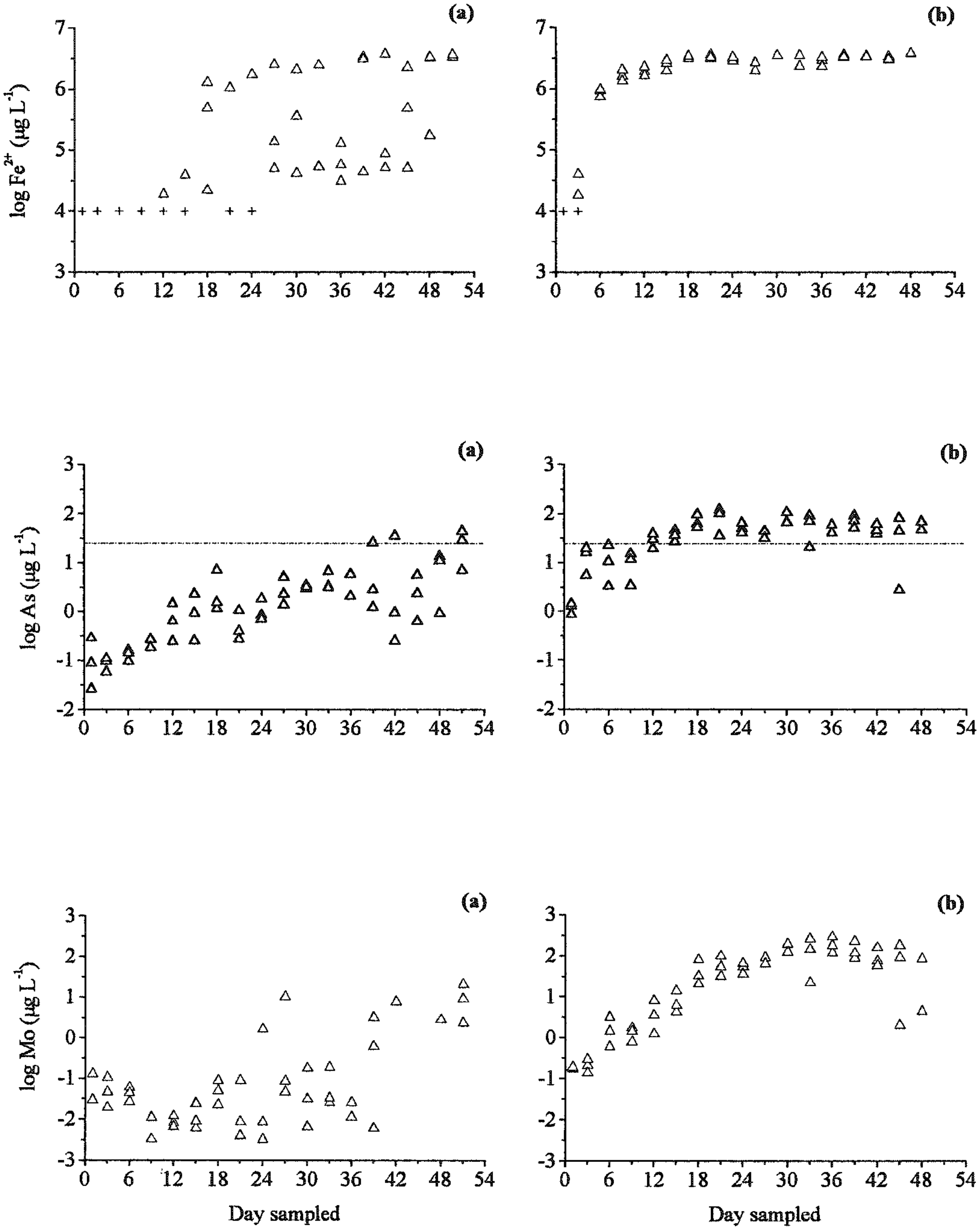


Figure 9. Changes in aqueous phase concentrations of ferrous iron (Fe^{2+}), arsenic (As), and molybdenum (Mo) during the reduction incubation of the (a) acid sulfate soil and (b) the soil/till mixture. Fe^{2+} concentrations below the detection limit are denoted by (+) and were not quantified during analysis. The dotted line in the figures showing changes in As concentrations denotes 25 µg L^{-1}, the Canadian limit for allowable As in drinking water.

42.8 μg L^{-1} for the acid sulfate soil and for the soil/till mixture respectively (Table 6).

Arsenic solubility is controlled by the dissolution of iron oxyhydroxides (Masscheleyn et al., 1991; Jones et al., 2000), thus the following discussion regarding As chemistry and geochemical behavior will focus on iron-arsenic interactions. A positive linear correlation between aqueous concentrations of arsenic and iron was observed during the reduction of the soil ($r^2 = 0.83$, n = 54, $p < 0.0001$) and of the soil/till mixture ($r^2 = 0.85$, n = 48, $p < 0.0001$) (Figure 10). An increase in aqueous concentrations of arsenic was related to an increase in reductive dissolution of Fe-oxides when the redox potential lowered in the acid soil and the soil/till mixture. A correlation between desorbed arsenic and reduced Fe-oxide phases has been reported extensively in the literature (Jacobs et al., 1970; Fordham and Norrish, 1974, 1979; Pierce and Moore, 1980; Gustafsson and Tin, 1994; McGeehan and Naylor, 1994; McGeehan, 1996; Reynolds et al., 1999; Welch et al., 2000, and references therein). Iron-arsenic geochemical relationships in the reduced acid sulfate soil and the soil admixed with till are similar to Fe-As interactions previously described in other systems.

Concentrations of arsenic in the acid soil solution remained low throughout the incubation, and less than 10 μg As L^{-1} was detected in most solutions. Arsenic concentrations ranged from 0.0264 μg L^{-1} to 44.2 μg L^{-1}, and As concentrations in the acid soil solutions increased steadily until day 18. Desorption of arsenic from iron oxides did not occur prior to reductive dissolution of the oxides during the early stages of reduction because increases in As concentrations coincided with increases in Fe^{2+} concentrations. Ferrous iron concentrations measured by the ferrozine method were below detectable limit before day 12, however total aqueous Fe concentrations were also measured by ICP-MS. Total Fe data was used to supplement Fe^{2+} data for the first 12 days of the incubation. Total Fe and As concentrations increased steadily before day 12, due to some initial reductive dissolution of amorphous Fe-oxides (Figure 11). Gleyed microsites were observed in the acid soil prior to sample preparation, and it was likely reduced Fe and desorbed As from these reduced microsites that was detected during porewater analysis. The variability in aqueous concentrations of As throughout the incubation were related to changes in concentrations of ferrous iron in solution. On 9 of

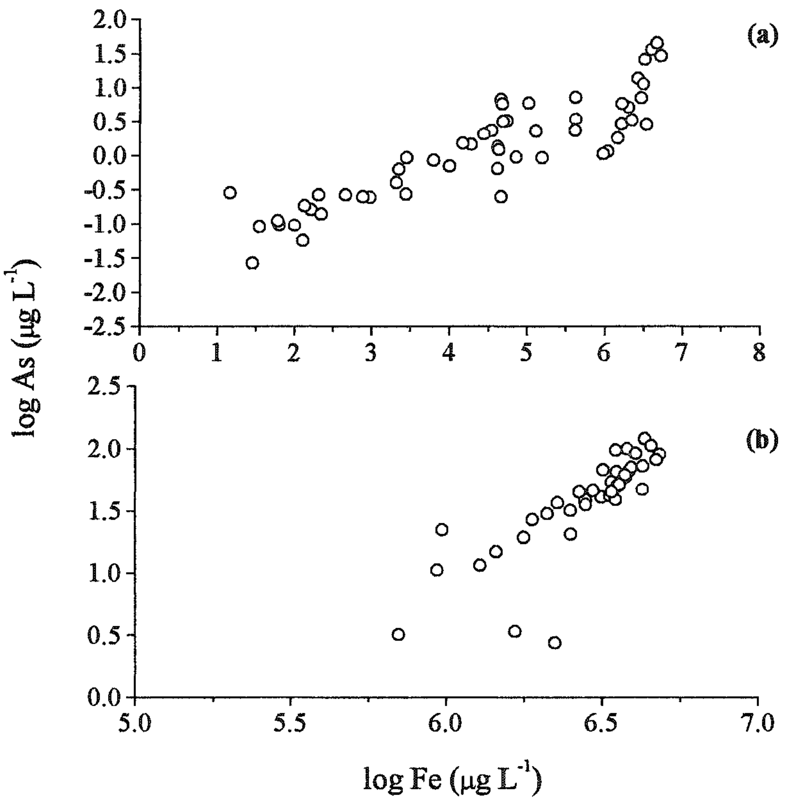


Figure 10. Relationship between aqueous phase concentrations of arsenic (As) and iron (Fe) during the reduction incubation of the (a) acid sulfate soil and (b) the soil/till mixture.

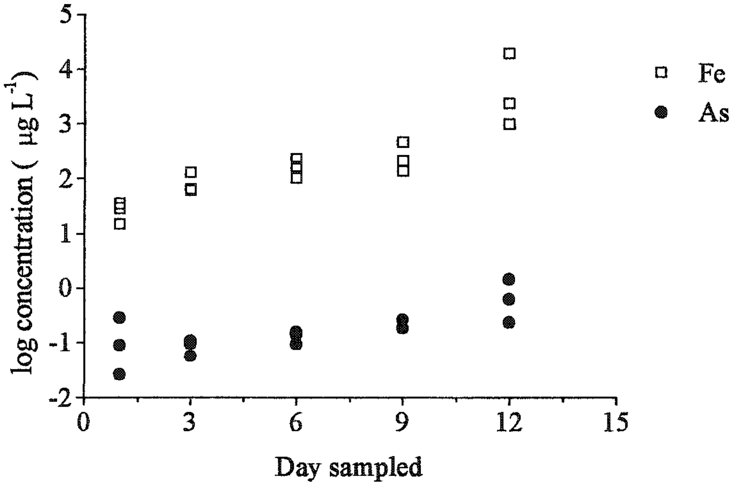


Figure 11. Changes in total iron and arsenic aqueous phase concentrations as measured by ICP-MS during the first 12 days of the incubation of the acid soil.

14 sampling periods (with detectable Fe^{2+}) the highest concentrations of aqueous As and Fe^{2+} were measured in the same solutions.

Aqueous concentrations of As in the reduced soil/till mixture ranged from 0.867 μg L^{-1} to 119 μg L^{-1}. Fe-oxide dissolution was extensive as the soil/till mixture reduced, resulting in high concentrations of desorbed aqueous As from the mixture. Concentrations of arsenic in the solution of the soil/till mixture increased until day 21 as did Fe^{2+} concentrations. Arsenic concentrations fluctuated after this time, but followed closely the variability in reduced iron released into solution, and arsenic concentrations continued to increase as Fe^{2+} increased over time. On nine of the 17 sampling periods the highest concentrations of aqueous As and Fe^{2+} were detected in the same solutions. On the other eight days maximum aqueous As concentrations corresponded to solutions with the second highest concentrations of Fe^{2+}, demonstrating the relationship between aqueous arsenic and iron. One sample on day 45 contained low As concentrations (2.75 μg L^{-1}). Ferrous iron concentrations in the solutions were slightly lower (2.98 g L^{-1}) compared to Fe^{2+} in other solutions at this period, possibly resulting in less As released into solution through desorption mechanisms.

The guideline limit for allowable arsenic in drinking water in Canada is 25 μg L^{-1} and 10 μg L^{-1} in the United States. The minimum concentration of aqueous Fe^{2+} measured in solution of the acid soil when As levels reached 10 μg L^{-1} and 25 μg L^{-1} was 3.39 and 3.32 g Fe L^{-1} respectively. Substantial and similar quantities of Fe-oxide reduction in the acid sulfate soil must occur before As concentrations will exceed international guideline limits. The minimum concentration of Fe^{2+} measured in solution of the soil/till mixture when concentrations of As reached 10 μg L^{-1} was 0.953 g Fe L^{-1}, and when As reached 25 μg L^{-1} was 1.9 g Fe L^{-1}. An increase in Fe-oxide reduction in soils derived from a mixture of marine shale and glacial till will correspond to an increase in As desorbed into soil solution.

Concentrations of arsenic in the solutions of the soil and the soil/till mixture increased as the redox potential decreased, demonstrating the typical redox sensitive behavior of As in solutions (Figure 12). Acid soil samples with low redox potentials and low aqueous As concentrations also contained low concentrations of reduced iron. Arsenic remained sorbed to Fe-oxides because little or no iron reduction occurred in

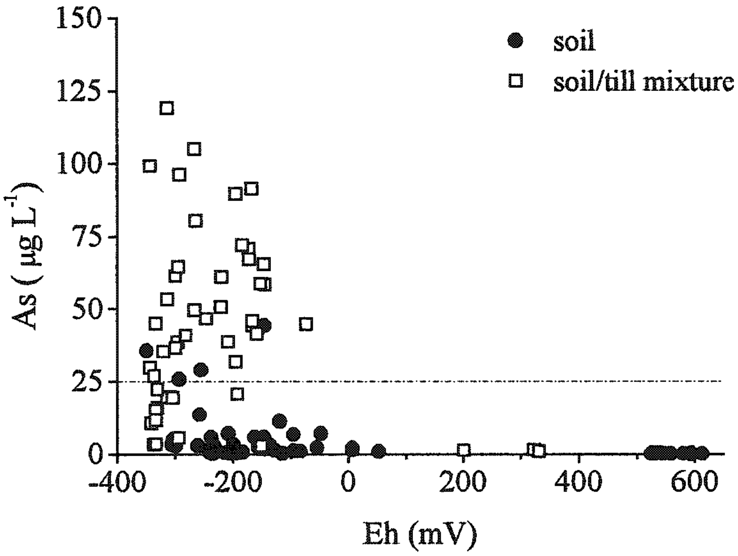


Figure 12. Changes in aqueous phase concentrations of arsenic as influenced by redox potential during the incubation with both the soil and soil/till mixture. The dotted line denotes the Canadian drinking water quality guideline limit of 25 μg L^{-1}.

these samples. Eh values between -100 mV and -150 mV were reached before aqueous As concentrations in excess of the Canadian guideline limit of 25 μg L^{-1} were detected in the soil and the soil/till mixture. High concentrations of arsenic in solution were also found at redox potentials less than -100 mV in aquifers in the Cold Lake region in eastern Alberta (Stein et al., 2000).

4.2.6. Molybdenum

Concentrations of molybdenum in the soil solution phase of the acid sulfate soil remained extremely low, less than 0.0894 μg L^{-1}, for the first 24 days of the incubation (Figure 9). After this time Mo concentrations were variable among replicates and Mo concentrations in some solutions remained low, close to initial levels. Aqueous concentrations of Mo in the soil/till mixture gradually increased until day 36. After this time concentrations fluctuated, but Mo concentrations followed very closely changes in aqueous concentrations of arsenic. The mean concentration of Mo in solution during reduction of the soil was calculated to be 0.0318 μg L^{-1} and of the soil/till mixture was 34.5 μg L^{-1} (Table 6).

Molybdenum in the acid sulfate soil is associated principally with hydrous iron hydroxides. Bulmer (1987) determined that 11.0 mg Mo kg^{-1} was associated with Fe-oxide veinlets in the Boundary soil compared to 6.30 mg Mo kg^{-1} present in the parent geological material. Molybdate and arsenate are both tetrahedral oxyanions and will sorb onto similar adsorption sites on oxide surfaces. Molybdenum (and As) desorbed from reduced Fe-oxides in the acid soil when the redox potential lowered and iron oxide dissolution progressed in both the soil and the acid soil/till mixture.

Maximum sorption of molybdenum in soil systems occurs at pH 4 (Hingston et al., 1972; Barrow, 1977; Goldberg and Forster, 1998), and the concentrations of Mo detected in the soil solution phase of the soil and soil/till mixture were found to be pH dependent (Figure 13). Aqueous concentrations of Mo in the soil ranged from 0.00327 $\mu g\ L^{-1}$ to 21.4 $\mu g\ L^{-1}$. The pH of many acid soil solutions remained below pH 4 and aqueous concentrations of Mo in these solutions were less than 0.150 $\mu g\ L^{-1}$. Average aqueous concentrations of Mo for soils under normal conditions range from 1.92 $\mu g\ L^{-1}$ to less than 10 $\mu g\ L^{-1}$ and in solutions are estimated at 50 $\mu g\ L^{-1}$ to 240 $\mu g\ L^{-1}$ (Lavy and Barber, 1964; Barrow, 1977; Barber, 1995; Reddy et al., 1997). The average Mo concentration reported by Fitzgerald et al. (1997) from well water samples collected throughout Alberta was 5 $\mu g\ L^{-1}$. Concentrations of Mo in the solution phase of the soil increased as the pH increased above pH 4.50. In some cases when the soil reduced low concentrations of Mo in solution were detected along with high concentration of Fe^{2+}. The pH of these solutions was low and Mo that desorbed during Fe-oxide dissolution likely resorbed to other soil colloids. Aqueous concentrations of Mo during the incubation of the soil/till mixture ranged from 0.414 $\mu g\ L^{-1}$ to 296 $\mu g\ L^{-1}$. High concentrations of Mo were detected in the soil/till mixture because the pH of the solution phase remained greater than pH 4. In several different studies, increasing the pH by liming was found to double the amount of Mo released into solution from acid soils (Barber, 1995).

A positive linear correlation between aqueous concentrations of molybdenum and arsenic in solution was observed during reduction of the soil ($r^2 = 0.84$, n = 45, $p < 0.0001$) and the soil/till mixture ($r^2 = 0.63$, n = 48, $p < 0.0001$) (Figure 14). When the acid soil and the acid soil/till mixture reduced an increase in aqueous concentrations of

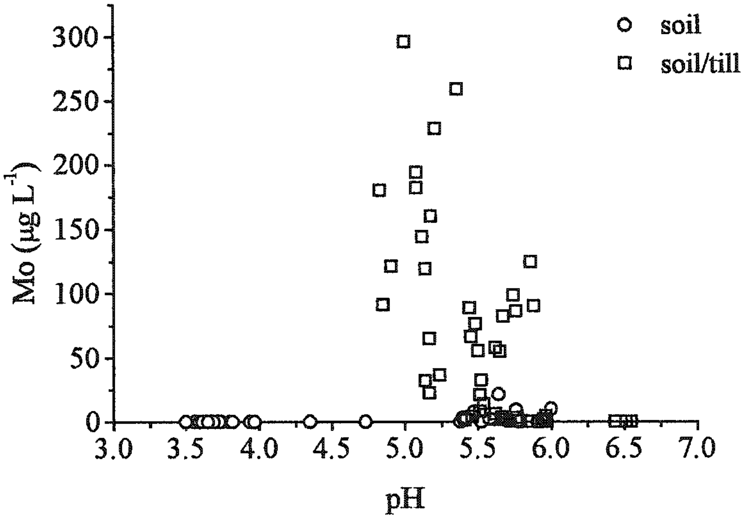


Figure 13. Changes in aqueous phase concentrations of molybdenum (Mo) as influenced by pH during the incubation of the soil and the soil/till mixture. Maximum sorption of Mo to soil colloids typically occurs near pH 4. Solutions with high pH and low concentrations of Mo had little Fe reduction, therefore Mo remained sorbed to Fe-oxides.

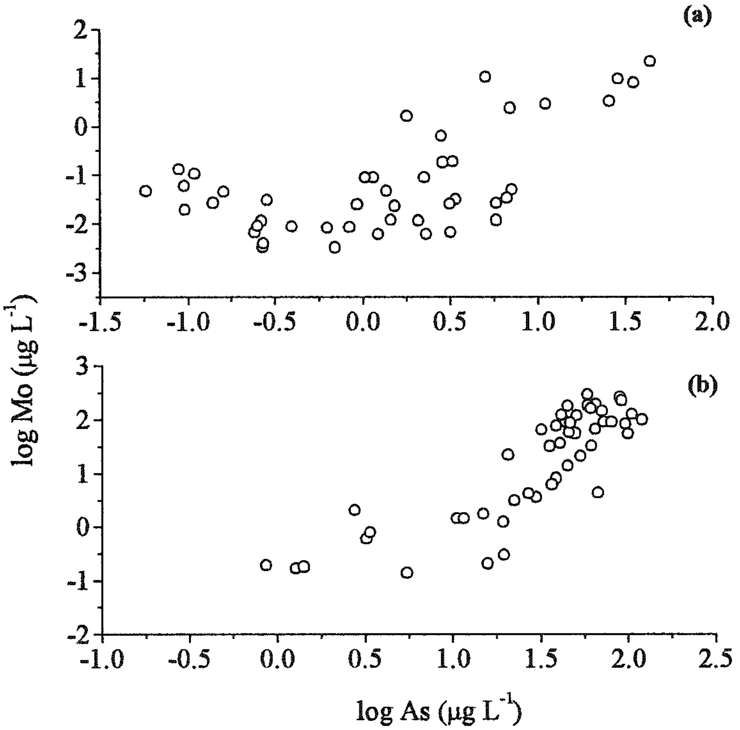


Figure 14. Relationship between aqueous phase concentrations of arsenic (As) and molybdenum (Mo) during the reduction incubation of the (a) acid sulfate soil and (b) the soil/till mixture.

molybdenum were related to an increase in desorbed arsenic from iron oxides. A positive linear correlation was also observed between aqueous concentrations of molybdenum and iron during the incubation of the soil ($r^2 = 0.75$, n = 45, $p < 0.0001$) and the soil/till mixture ($r^2 = 0.69$, n = 48, $p < 0.0001$).

On five sampling periods the highest concentrations of aqueous Mo and arsenic were detected in the same acid soil solutions. On 13 of 17 sampling periods solutions from the soil/till mixture with the highest aqueous concentrations of Mo contained the highest concentrations of As (Table 7). Approximately 20 times more Mo was measured in the solution phase when the soil/till mixture reduced compared to the acid soil, and near the end of the incubation of the mixtures concentrations of Mo in solution exceeded As concentrations. Iron oxide reductive dissolution that occurred in the soil and soil/till mixture resulted in desorption of Mo and As.

Table 7. Concentrations of aqueous phase arsenic and molybdenum during the reduction incubation of the soil/till mixture for 13 of the 17 sampling periods. On these sampling periods the highest concentrations of arsenic were detected in conjunction with the highest concentrations of molybdenum. Mo exceeded As concentrations after the 9th sampling period (day 24).

Day	As	Mo
soil/till mixture	(µg L^{-1})	(µg L^{-1})
3	19.6	0.300
6	22.3	3.15
9	15.0	1.77
12	38.5	8.16
15	44.9	14.1
18	96.1	82.4
21	99.1	55.1
24	64.5	66.3
27	44.1	91.1
33	89.5	259
36	58.3	296
39	91.4	228
42	60.9	159

From the results of this study a maximum of 44.2 µg As L^{-1} and 21.4 µg Mo L^{-1} will desorb from reduced iron oxides if acid sulfate soil from the Boundary series is subjected to prolonged reducing conditions (Table 8). In outlying areas on the landscape in the Peace River region where soils derived from the marine shale mixed with glacial debris (the Josephine soils) a maximum of 119 µg As L^{-1} and 296 µg Mo L^{-1} will desorb if conditions become anaerobic. The pH of the soil solutions of the acid soil and soils derived from a marine shale/calcareous till mixture must increase to greater than approximately pH 4.5 to achieve substantial desorption of As and Mo during reductive dissolution of Fe-oxides.

Table 8. Maximum aqueous concentrations of arsenic (As) and molybdenum (Mo) during the incubation of the acid sulfate soil and the soil/till mixture (italicised values). Maximum As and Mo concentrations were detected in the same solution of the acid sulfate soil and in two different solutions during the incubation of the soil/till mixture. Redox potential (Eh), pH, and electrical conductivity (EC) of the solutions are also included for reference.

	As µg L^{-1}	Mo µg L^{-1}	Fe^{2+} g L^{-1}	Eh mV	pH	EC dS m^{-1}
Acid sulfate soil	*44.2*	*21.4*	3.33	-146	5.64	2.31
Soil/till mixture	*119*	99.0	3.35	-313	5.74	6.18
Soil/till mixture	58.3	*296*	2.91	-145	5.00	2.85

4.2.7. Aluminum

Concentrations of aluminum in the solution phase of the acid sulfate soil increased until day 18 (Figure 15). After this time Al concentrations were variable among replicates and concentrations in some solutions were lower than initial values. Aqueous concentrations of Al in the soil/till mixture increased until day 36 attaining a maximum of 59.1 mg L^{-1}, and after this time Al concentrations were variable among replicates. The mean concentration of Al in solution during the incubation of the acid soil was calculated to be 0.830 mg L^{-1} and with the soil/till mixture to be 2.16 mg L^{-1} (Table 6). There was no correlation between aqueous concentrations of aluminum and arsenic in either the soil or the soil/till mixture.

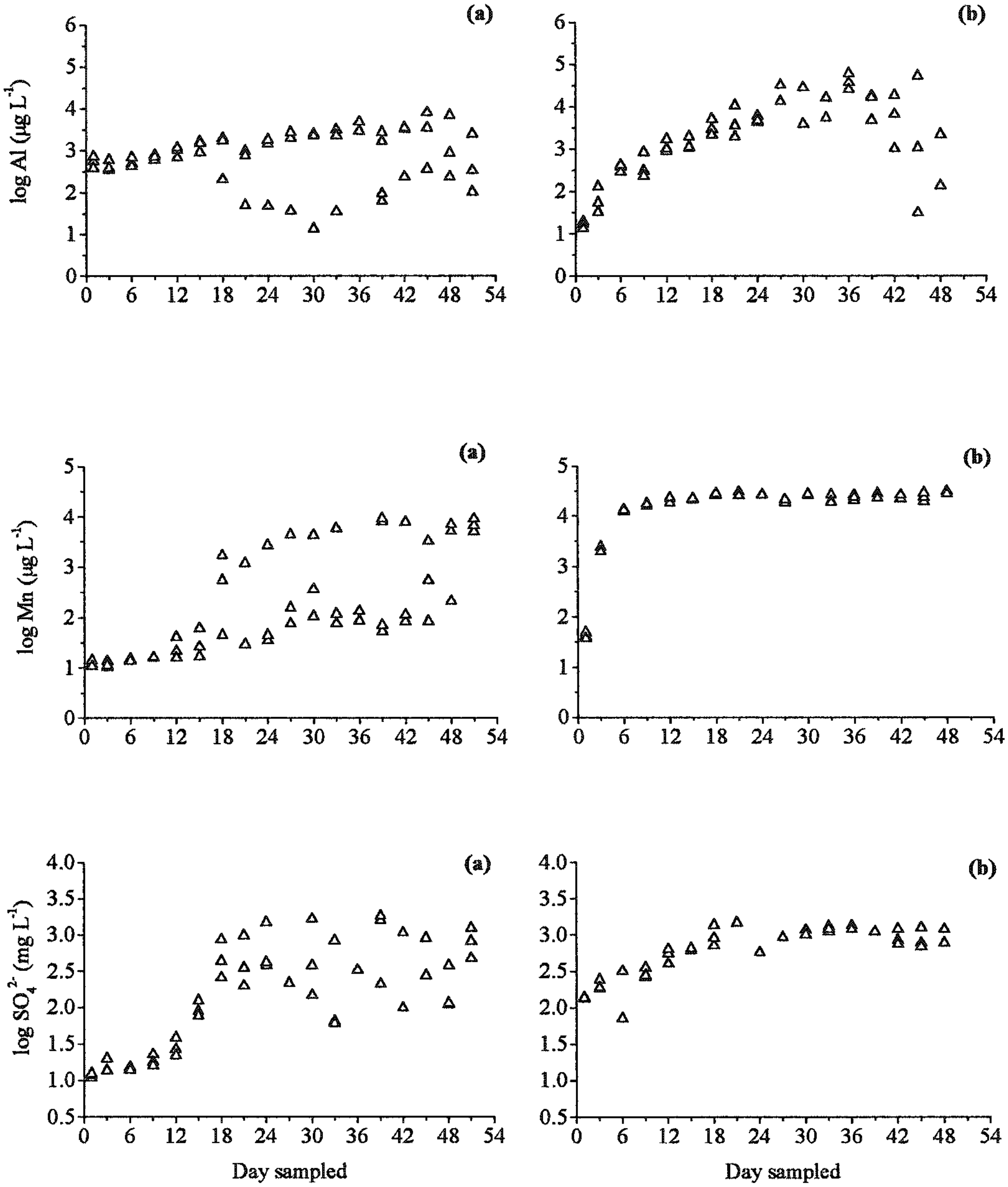


Figure 15. Variations in aqueous phase concentrations of aluminum (Al), manganese (Mn), and sulfate (SO_4^{2-}) during the reduction incubation of the (a) acid sulfate soil and (b) the soil/till mixture.

Aluminum is mobilized upon formation of acid sulfate soils when the soil becomes acidic, and subsequently Al satisfies a large proportion of the exchange capacity (Doner and Lynn, 1989). Aqueous aluminum concentrations in the soil and the soil/till mixture were found to be pH dependent, similar to aqueous concentrations of molybdenum. Concentrations of aluminum in solution during the incubation of the acid soil ranged from 13.7 μg L^{-1} to 8.02 mg L^{-1}. A pH of 5.5 or less is required before Al^{3+} from clays or Al-oxides becomes soluble. The pH of the majority of the soil solutions was less than 4, and aqueous concentrations of Al increased because the pH of these solutions remained low. The pH in the other acid soil solutions increased during the incubation resulting in a decrease in aqueous Al concentrations because increased OH^- concentrations resulted in the formation of insoluble $Al(OH)_3$ (Ponnamperuma, 1972). Concentrations of aluminum in the solution of the soil/till mixture increased throughout the incubation because the pH decreased from initial values, and in most solutions the pH was less than 6. After day 36 the pH increased slightly for the remainder of the incubation, leading to the formation of insoluble Al precipitates and a decrease in aqueous concentrations of aluminum. Aluminum organic complexes may also have formed in the soil and soil/till mixture, resulting in a decrease in aqueous Al concentrations in reduced solutions (Hsu, 1989).

4.2.8. Manganese

Concentrations of manganese in the solution phase of the acid soil and the soil/till mixture followed closely the variability of reduced iron released into solution (Figure 15). Aqueous concentrations of Mn in the soil increased until day 18. After this time Mn concentrations were variable among replicates and remained moderately high to high, ranging between 29.0 μg L^{-1} to 9.08 mg L^{-1}. Increases in aqueous concentrations of Mn in the soil/till mixture followed a uniform trend, and Mn concentrations increased steadily until day 21 and ranged between 41.1 μg L^{-1} and 31.4 mg L^{-1}. After this time Mn concentrations generally stabilized and remained high at greater than 18 mg Mn L^{-1}. The mean concentration of Mn in solution calculated for the soil was 78.9 μg L^{-1} and for the soil/till mixture was 22.4 mg L^{-1} (Table 6).

Manganese is a redox sensitive species and the presence of reduced Mn (Mn^{2+}) denotes moderately reduced conditions. Mn-oxides are the principle source of Mn in soils and will undergo reductive dissolution at Eh values lower than ~ 530 mV at pH 5 (Lindsay, 1979; Lindsay and Sadiq, 1983; Bartlett, 1986). Aqueous concentrations of Mn in the acid soil and the soil/till mixture increased sharply on day 12 and 3 respectively due to a drop in the redox potential, and Mn concentrations continued to increase throughout the incubation when the Eh remained low. Less variation in aqueous concentrations of Mn among replicates in the soil/till mixture was observed because reduction was more uniform in the mixture compared to the soil.

4.2.9. Sulfate

Concentrations of sulfate in the solution phase of the soil increased steadily until day 18 (Figure 15). After this time SO_4^{2-} concentrations continued to increase and remained moderately high to high, ranging between 11.0 mg L^{-1} to 1.82 g L^{-1}, but concentrations were variable among replicates. Aqueous concentrations of sulfate in the soil/till mixture increased steadily until day 36, and the maximum concentration measured was 1.47 g L^{-1} on day 21. Sulfate concentrations after this time remained uniform near 1.10 g L^{-1}. The mean concentration of SO_4^{2-} in solution calculated during the reduction of the soil was 145 mg L^{-1} and of the soil/till mixture was 730 mg L^{-1} (Table 6).

The principle source of sulfate in the acid sulfate soil is natrojarosite [$NaFe_3(OH)_6(SO_4)_2$], one of the most common sulfate minerals produced during pyrite oxidation (Doner and Lynn, 1989). Natrojarosite in acid sulfate soils is stable at lower depths (in B and C horizons) where the pH is less than 3.5, and will hydrolyze to form goethite as the pH increases closer to the soil surface (van Breeman, 1982; Dudas, 1984). When soil conditions become less acidic natrojarosite hydrolyzes and releases sulfate, which becomes strongly sorbed to hydrous iron and aluminum oxides. Sulfate is the major exchangeable anion in the acid sulfate soil, and it was released into solution upon iron oxide reduction in the soil and the soil/till mixture. In addition, SO_4^{2-} likely became soluble as iron present in natrojarosite reduced under low redox conditions.

The initial increase in aqueous concentrations of SO_4^{2-} in the acid sulfate soil corresponded to the increase in pH of the system upon reduction. In acid soils, sulfate is strongly sorbed to oxides and becomes soluble with an increase in pH. Submerged acid soils typically show an increase in water-soluble sulfate, which was observed during the incubation of the soil, and then a slow decrease spread over several months (Ponnamperuma, 1972). Initial sulfate concentrations during the reduction of the soil/till mixture were higher than in the soil, near 136 mg L^{-1} compared to 11.0 mg L^{-1}, and this was likely due to the presence of high concentrations of soluble sulfate salts present in the till (Table 5).

Sulfate is a redox sensitive species and the presence of reduced sulfate in the form of sulfide (S^{2-}) denotes strongly reduced conditions. Sulfate reduction to sulfide occurs subsequently to manganese and iron reduction at low pH. Sulfate reduction was not directly detected during the incubation of the soil and the soil/till mixture since aqueous concentrations of sulfate continued to increase in both systems. However, sulfate reduction likely occurred in reduced microsites with substantial iron reduction so that sulfate became the following electron acceptor. Sulfate reduction will occur at around -100 mV at pH 5 (Lindsay, 1979) and the mean Eh calculated for the solid phases of the soil and the soil/till mixture were below this level. The reduction of sulfate could have occurred without a net decrease in aqueous sulfate concentrations because any decrease during sulfate reduction could have been countered by the continued dissolution of iron oxides and/or natrojarosite. The dissolution of either iron oxides or natrojarosite would have re-established sulfate solution equilibrium concentrations or increased sulfate concentrations in the soil and the soil/till mixture.

4.2.10. Arsenic speciation diagrams

pe-pH diagrams are useful thermodynamic tools for estimating ion speciation and precipitate stability ranges in natural systems, where outlined fields are areas where the designated species make up more than 50% of the total concentration. Figures 16 (a) and (b) are basic pe-pH diagrams constructed for arsenic species, including arsenic sulfide minerals, based on thermodynamic data from Cherry et al. (1979), Lindsay (1979), and Sadiq (1997). Total dissolved As was set at 5 $\mu g\ L^{-1}$ to construct the stability field for

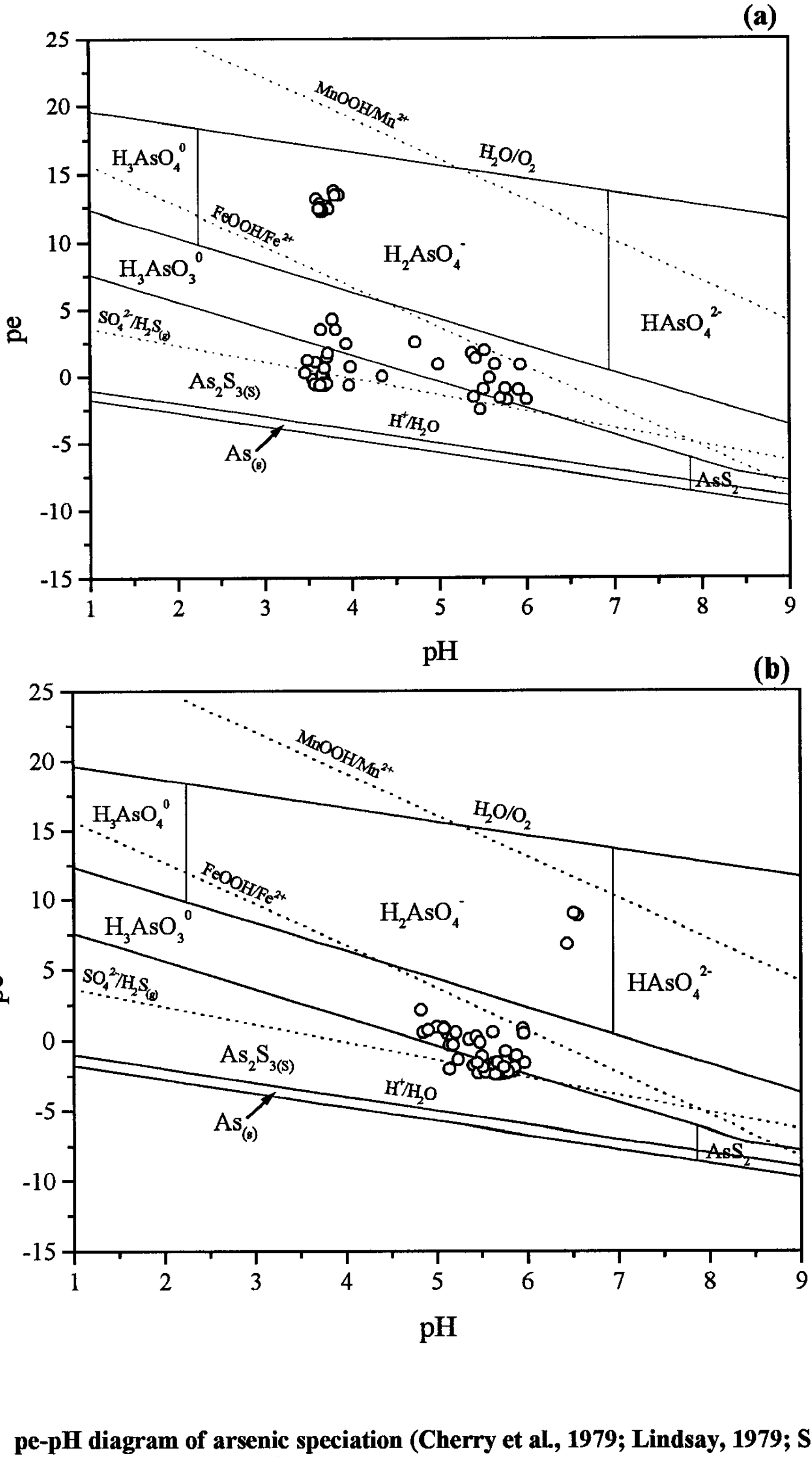


Figure 16. pe-pH diagram of arsenic speciation (Cherry et al., 1979; Lindsay, 1979; Sadiq, 1997). Total dissolved As was set at 5 μg L^{-1} to construct the stability fields for solid arsenic compounds. Mn was set at 78.9 μg L^{-1}, Fe^{2+} at 42.7 mg L^{-1}, and SO_4^{2-} species at 145 mg L^{-1} to position the redox transformation lines of Mn-, Fe-oxides and sulfate. Solution pe was estimated by adding 200 mV to soil Eh measurements from the (a) acid sulfate soil and (b) the soil/till mixture.

solid arsenic compounds, and is a reasonable estimate of aqueous arsenic under moderately reduced conditions. The redox transformation lines for Mn-, Fe-oxides, and sulfate are also included on the diagram. These lines are derived from thermodynamic data but can be shifted depending on ion concentrations of a specific system. In these pe-pH diagrams, the mean concentrations of aqueous Mn, Fe^{2+}, and SO_4^{2} calculated for the incubation of the acid sulfate soil were used to set the redox transformation lines for Mn-, Fe-oxides, and sulfate. All calculated values used in construction of the pe-pH diagrams are within concentration ranges described by Cherry et al. (1979).

The redox potential and pH of the solution phase of a system must be known in order to use pe-pH diagrams to prediction ion speciation. The pH of the supernatant of the soil and soil/till mixtures were measured, however, the Eh of the *solid phase* was measured during the incubation. Redox potentials measured in solutions are commonly higher and reflect the changes in activities of the ions participating in redox equilibria, compared to redox potentials measured in the solid phase (Ponnamperuma et al., 1967). Therefore, 200 mV was added to the Eh reported for the solid fractions of all of the samples as a reasonable estimate of the difference in redox potentials between soils and solutions (Salloum et al., in press). Based on the measured pH and the estimated Eh of the supernatant (i.e. measured Eh of the solid phase + 200 mV for each sample) samples were plotted onto the pe-pH diagram to predict arsenic speciation during the incubation.

Arsenate ($H_2AsO_4^-$), the prevalent form of As(V) present below pH 7, was the species of arsenic predicted to be present at high redox potentials (pe greater than 7.50) during the incubation of the acid soil (Figure 16). Arsenite ($H_3AsO_3^0$) was predicted to be present when the redox potential lowered, and amorphous arsenic sulfide precipitates ($As_2S_{3(s)}$) were predicted to form in the majority of solutions when the pe continued to decrease (pH less than 5). Arsenite was also predicted to be the dominant species of arsenic as the pH increased during the incubation of the soil. Arsenate ($H_2AsO_4^-$) was predicted to be the dominant species in the three oxidized solutions during the incubation of the soil/till mixture. Arsenite ($H_3AsO_3^0$) was predicted to be dominant in about 3/4 of the solutions when the pe lowered and amorphous arsenic sulfides ($As_2S_{3(s)}$) were predicted to form in the remaining solutions. Arsenite was predicted to form in a greater number of solutions during the incubation of the soil/till mixture compared to the soil and arsenic sulfide precipitates were predicted to form in a greater number of acid soil solutions compared to the mixture.

The solubility and toxicity of aqueous arsenic is known to increase when As(V) is reduced to As(III) (Webb, 1966; Ferguson and Gavis, 1972; Sadiq, 1997). Arsenic solubility in the soil solution of acid sulfate soils and in soils derived from mixtures of marine shales and glacial till is predicted to increase if the redox potential lowers and As(III) forms. Arsenic sulfide was predicted to form in both the soil and the soil/till mixture, however decreases in concentrations of As or SO_4^{2-} were not observed during the incubations. A detectable decrease in arsenic and sulfate concentrations could have been offset by the continued release of As and SO_4^{2-} from the dissolution of either Fe-oxides or natrojarosite. Iron sulfides, in addition to arsenic sulfide, will readily form as black precipitates in very reduced conditions. The formation of a black precipitate was only observed in the solid phase of one acid soil sample. Sulfate concentrations in the solution of this sample were below the mean SO_4^{2-} concentration possibly due to sulfate reduction, however Fe^{2+} concentrations were greater than the mean Fe^{2+} concentration. Iron sulfides could have formed in the solid phase of other samples but might not have been visible because samples were stirred frequently.

4.2.11. Nernst equation

The thermodynamic relation of the potential Eh to the composition of the solution phase is expressed by the Nernst equation (Stumm and Morgan, 1970). The Nernst equation shows the relationship between the redox potential and the activities of the oxidized (Ox) and reduced (Red) species (Bohn, 1971):

$$\mathrm{Eh} = \mathrm{Eh}^0 - \frac{2.303\mathrm{RT}}{\mathrm{nF}} \log \frac{(\mathrm{Red})}{(\mathrm{Ox})(\mathrm{H}^+)^a} \qquad (4\text{-}5)$$

By definition, the Nernst equation relates the electrode potential (Eh) to the distribution of ion oxidation states of a specific redox couple, and the electrode potential is defined as the electron availability, or the electrochemical potential of the electron, at equilibrium (Bohn, 1971).

Equilibrium conditions are attained when the mixture of redox couples in a system has reacted until the net transfer of electrons is zero. Natural systems rarely reach oxidation-reduction equilibrium because of the continuous addition of electron donors. Equilibrium conditions must be attained before the potential of a specific redox couple calculated using the Nernst equation has any relevance to measured values. The acid soil and the soil/till mixture did not reach a state of redox equilibrium mainly because microbial decomposition of glucose or other electron donor did not cease. The Nernst equation can only be used to *estimate* the equilibrium potential of the reductive dissolution of Fe-oxides in the acid soil and the soil/till mixture because these systems were not in equilibrium.

The following redox reaction describes the reductive dissolution of Fe-oxides in the acid soil and the soil/till mixture (Stumm and Morgan, 1970):

$$Fe(OH)_3 + 3H^+ + e^- \leftrightarrow Fe^{2+} + 3H_2O \qquad Eh^0 = +\ 1.06\ V \qquad (4\text{-}6)$$

This redox reaction was chosen to calculate the electrode potential (Eh) of the supernatant of the soil and the soil/till mixture using the Nernst equation. This reaction was the dominant redox reaction during the reduction incubation and is the redox couple that governs the anaerobic status of a soil. The Eh values of the supernatant calculated using the Nernst equation were compared to the measured Eh of the solid phases of the soil and soil/till mixture to determine if equilibrium conditions had been reached in any of the incubation vessels.

To obtain the Nernst equation for the reduction of Fe-oxides to ferrous iron the value for Eh^0, and oxidized [$Fe(OH)_3$] and reduced (Fe^{2+}) species from Eq. 4-6 were substituted into Eq. 4-5. Once values and ions were substituted, Eq. 4-5 was simplified to:

$$Eh = 1.06\ V - 0.0591 \log Fe^{2+} - 0.177\ pH \qquad (4\text{-}7)$$

The equilibrium redox potential of the Fe-oxide/Fe^{2+} redox couple for the supernatant of each incubation vessel with detectable Fe^{2+} was calculated using the Nernst equation, using the activity of Fe^{2+} and the pH and solving Eq. 4-7. Equilibrium Eh values calculated using the Nernst equation and the measured redox potentials of the solid phases of the soil and the soil/till mixture are shown in Table 9. The mean Eh of the Nernst equation values calculated for the acid soil was calculated to be +1.20 V and for the mixture was +1.14 V. The mean Eh of the solid phases of the acid sulfate soil

Table 9. Equilibrium Eh potentials for the reductive dissolution of Fe-oxides estimated using the Nernst equation and measured Eh potentials of the solid phases during the incubation of the soil and the soil/till mixture. Ferrous iron activities and the pH were used to estimate the equilibrium Eh potentials in solutions with detectable Fe^{2+}. The table continues onto the next page.

Acid sulfate soil

Day sampled	Fe^{2+} ($g L^{-1}$)	Eh (mV) Nernst	Eh (mV) Soil
12	0.0190	1265	7
15	0.0390	1246	-54
18	1.30	1157	-95
18	0.0260	1257	-242
18	0.495	1181	-47
21	1.06	1162	-83
24	1.74	1149	-148
27	0.138	1214	-239
27	2.54	1139	-303
27	0.0500	1240	-228
30	2.10	1144	-261
30	0.361	1189	-200
30	0.0420	1245	-233
33	0.0544	1238	-137
33	0.0538	1238	-95
33	2.46	1140	-305
36	0.0584	1236	-238
36	0.130	1216	-163
36	0.0311	1252	7
39	3.39	1132	-293
39	3.12	1134	-299
39	0.0443	1243	-127
42	0.0518	1239	-235
42	3.77	1129	-349
42	0.0881	1226	-240
45	0.0510	1240	-184
45	0.492	1181	-156
45	0.228	1201	-147
48	3.26	1133	-258
48	3.32	1132	-119
48	0.176	1208	53
51	3.37	1132	-208
51	3.33	1132	-146
51	3.67	1130	-255
	Mean	1195 mV	-192 mV

Soil/till mixture

Day sampled	Fe^{2+} ($g L^{-1}$)	Eh (mV) Nersnt	Eh (mV) soil
3	0.0404	1246	-313
3	0.0184	1266	-294
6	0.760	1170	-337
6	0.953	1164	-341
6	0.978	1164	-330
9	1.62	1151	-333
9	1.36	1155	-333
9	2.02	1145	-332
12	1.94	1146	-343
12	1.65	1150	-304
12	2.28	1142	-295
15	1.98	1146	-336
15	2.63	1138	-333
15	2.94	1136	-299
18	3.25	1133	-292
18	3.15	1134	-299
18	3.40	1132	-313
21	3.58	1131	-313
21	3.12	1134	-320
21	3.32	1132	-343
24	3.07	1134	-266
24	2.86	1136	-281
24	3.28	1133	-294
27	2.69	1138	-166
27	2.48	1140	-195
30	3.50	1131	-146
30	3.54	1131	-266
33	0.350	1190	-195
33	3.49	1131	-173
33	2.33	1142	-192
36	2.91	1136	-145
36	2.31	1142	-158
36	3.31	1132	-152
39	3.31	1133	-167
39	3.60	1130	-184
39	3.35	1132	-220
42	3.41	1132	-208
42	3.45	1131	-166
42	3.35	1132	-219
45	3.37	1132	-73
45	2.98	1135	-151

Day sampled	Fe^{2+} (g L^{-1})	Eh (mV) Nersnt	Eh (mV) soil
45	3.09	1134	-264
48	3.72	1130	-246
48	3.82	1129	-171
	Mean	1135 mV	-274 mV

measured during the incubation with supernatant containing detectable Fe^{2+} was calculated to be -192 mV and for the mixture was -274 mV.

In practice, platinum electrodes are commonly used to measure the potentials of natural systems, and these electrodes measure the combined potential of all redox couples together. These potentials are at non-equilibrium and are referred to as mixed potentials (Stumm, 1966; Bohn, 1971; Patrick et al., 1996). Even in the simplest system, the relation of mixed potentials to equilibrium potentials is not well defined and Bohn (1971) and Patrick et al. (1996) have concluded that mixed potentials are quantitatively unrelated to the distribution of oxidation states expressed by the Nernst equation. Other authors (Jefferey, 1961; Gotoh and Yamashita, 1966; Ponnamperuma et al., 1967; Cullen and Reimer, 1989) have successfully reported quantitative application of redox potentials in flooded soils, and in certain natural aquatic systems and acidic mine drainage waters the Eh has been found to approximately obey the Nernst equation (Holm and Curtiss, 1989).

There was no agreement found between the redox potentials of the supernatant of the soil and soil/till mixture calculated using the Nernst equation and redox potentials of the solid phases measured during the incubation because the incubation vessels were not in equilibrium and redox reactions were continuously occurring during the incubation. A Pt-electrode was used to measure the redox potential of the solid phases of the soil and soil/till mixtures and the measured Eh includes the potential of the dissolution of Fe-oxides described by the Nernst equation, but it also includes the potential of all of the other redox reactions taking place. Also, the formation of iron organic complexes might have decreased the activity of ferrous iron, leading to an increase in the Eh values calculated using the Nernst equation (see also section 4.3.). These findings support the conclusions made by Bohn (1971) and Patrick et al. (1996), and a relevant comparison cannot be made between the equilibrium potential of the dissolution of Fe-oxides from the Nernst equation and measured potentials in the soil and the soil/till mixture. The mixed potential measured by the Pt-electrode is a more accurate measurement of the oxidation-reduction potentials of the solid phases of the soil and soil/till mixture during the reduction incubations.

4.2.12. Estimate of linear distribution coefficients (K_D) for the acid sulfate soil

The soil solid/liquid linear distribution coefficient (K_D) is a measure of the chemical mass that partitions to both the solid and liquid phases and is used to predict chemical partitioning and to estimate the retardation of elements in fate/transport models. K_D is expressed in units of L kg^{-1}. Distribution coefficients can either be determined from the slope of nonlinear relationships such as the Freundlich or Langmuir isotherms, or from the sorbed concentration of an element in the solid phase/aqueous concentration. The distribution coefficients of As(V) and As(III) onto various soils and soil colloids have been described in the literature and the sorption of arsenic species (i.e. sorption K_D) varies with pH and As:Fe ratios. Distribution coefficients for arsenate to soils and soil colloids range between 1.7 to 100,000 L kg^{-1} and for arsenite range between 0 and 1,000 L kg^{-1} (Ladwig and McLearn, unpub.)

Desorption K_D for arsenic in the acid sulfate soil was estimated for each harvested vessel during the reduction incubation. The total concentration of arsenic in the acid sulfate soil measured by INAA (37,900 $\mu g\ kg^{-1}$) was used as a value for the concentration of arsenic sorbed to the solid phase. Aqueous concentrations of arsenic measured in each vessel were used to estimate distribution coefficients throughout the incubation. The desorption K_D of the acid sulfate soil decreased with an increase in pH (Figure 17). The maximum K_D (log K_D 5.60) was several orders of magnitude greater than values reported in the literature and was estimated to occur at minimum pH (3.72). Desorption distribution coefficients were high when the pH was low because sorption of arsenate to soil colloids is reported to be maximum near pH 4.0 and greatest for soils with high concentrations of citrate-dithionate extractable iron (Pierce and Moore, 1982; Bowell, 1994, Wilkie and Hering, 1996; Manning and Goldberg, 1997). The minimum desorption K_D of 857 L kg^{-1} was estimated when the pH was 5.64. Microbial activity lowered the redox potential which in turn resulted in an increase in pH during the incubation of the acid sulfate soil. Iron oxides dissolved as the redox potential lowered, releasing arsenic into solution. The decrease in Eh and subsequent increase in pH and Fe-oxide dissolution lowered the desorption distribution coefficients of arsenic the acid sulfate soil. Once the pH increased to greater than 3.95 estimated desorption K_D values for the acid sulfate soil fell within ranges of sorption K_D values reported in the literature.

The regression equation for the relationship between log K_D of arsenic in the acid sulfate soil and pH is $\log K_D = -0.468\text{pH} + 6.37$. In 1990 the USEPA prepared a report containing statistics of aquifer material properties. In the report regression equations were derived for the relationship between sorption K_D and arsenate and arsenite in aquifer materials in six different states (in Ladwig and McLearn, unpub.) The statistical relationship between desorption K_D and pH from the reduction experiment yields distribution coefficients that are at least twice as high compared to distribution coefficients calculated using equations from the USEPA for specific pH values.

Distribution coefficients estimated for the desorption of arsenic from the acid sulfate soil during the reduction incubation are falsely high. The total concentration of arsenic was used to calculate desorption K_D, however arsenic will not completely desorb from Fe-oxides in the acid soil. Aqueous arsenic concentrations during the reduction incubation of the soil and soil/till mixture were only in the range of $\mu g\ L^{-1}$ whereas As concentrations in the bulk acid soil are in the range of $mg\ L^{-1}$. Large quantities of arsenic are incorporated into the structure of iron oxides in the acid soil and will not desorb, even under strongly reducing conditions.

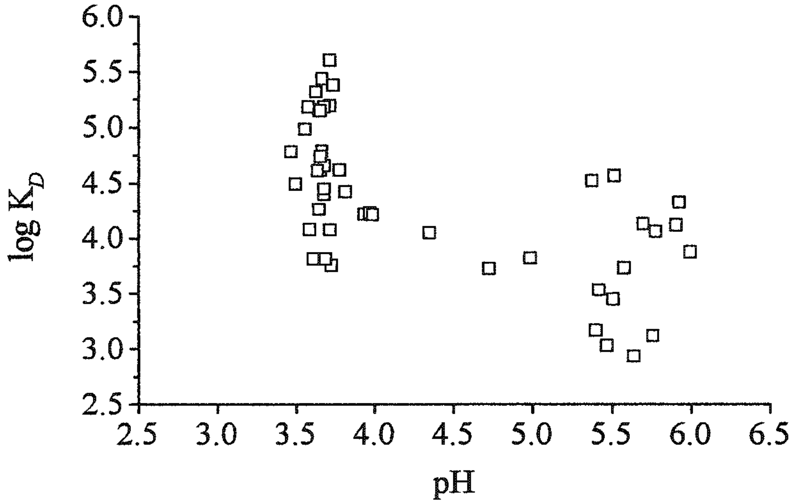


Figure 17. Distribution coefficients (log K_D) for the desorption of arsenic (arsenite was predicted to be the dominant ion) from the acid sulfate soil in relation to pH during the reduction incubation.

4.3. Oxidation experiment

Three types of precipitates formed upon re-oxidation of the reduced supernatant from the soil/till mixture. Only one type of precipitate (Fe-oxides) was predicted to form during oxidation based on fundamental iron chemistry and redox reactions. The precipitates were differentiated based on color, changes in aqueous phase concentrations of Fe/Fe^{2+} (because incubation vessels were harvested based on changes in soluble Fe^{2+}), and x-ray diffraction (XRD) analysis. The precipitates that formed were (*i*) dark reddish-brown gel precipitates (from solution A), (*ii*) light reddish-brown gel precipitates (from solution B), and (*iii*) reddish yellow crystalline precipitates (from solution C). The dark reddish-brown gel precipitates formed when solutions were continuously purged with $O_{2(g)}$, and the light reddish brown precipitates formed when solutions were partially purged and then left open to the atmosphere. The crystalline precipitates of solution C formed quickly and only in a few vessels. Only samples from solution A and samples from the first and last sampling periods from solution B were harvested in triplicate.

Precipitates were collected, centrifuged (26,891 g for 15 minutes), dried, and the Munsell color was recorded as part of the characterization procedure of the solution phases. Once dried the color of the precipitates from the solutions purged with oxygen was black (from solution A). Two precipitates formed in the solutions that were partially aerated with oxygen and left open to the atmosphere (solution B). Once dried, the less dense precipitate was black and the more dense precipitate was red to yellowish red. The dried color of the crystalline precipitates was reddish yellow.

Total aqueous iron concentrations remained relatively unchanged when solutions were purged with oxygen, however aqueous Fe^{2+} concentrations decreased during oxidation (solution A) (Figure 18). Total iron concentrations were predicted to decrease along with ferrous iron concentrations during oxidation, however total Fe concentrations remained constant between 3.12 g Fe L^{-1} and 3.58 g Fe L^{-1}. This discrepancy between the predicted decrease and actual Fe concentrations lead to the conclusion that iron organic complexes, rather than Fe-oxides, had formed when solutions were purged with oxygen. Iron organic complexes commonly form in environments containing high concentrations of decomposed organic matter even when activities of iron are low (Figure 19).

Low molecular weight organic acids (fulvic acids) produced during fermentation, such as ligands with COOH groups or carboxylates (COO^-), are the most active complexing substances in soils (McKeague et al., 1986; Schwertmann et al., 1986; Stevenson and Fitch, 1986). The ability of fulvic acids to form stable, soluble, complexes with metal ions such as Fe is attributed to their high content of O-containing groups, including COOH. Organic acids were detected in all solutions during sulfate analysis by ion chromatography (Steffes, pers. comm.) and were produced during glucose fermentation during the initial sample preparation. The formation of Fe-organic complexes resulted in a decrease in soluble Fe^{2+} concentrations. The complexes that formed were either ferric or ferrous-organic complexes, depending on the Eh of the solutions (Olomu et al., 1973).

Total Fe was determined using ICP-MS and solutions are ionized during analysis. Iron organic complexes would not have been filtered out during sample preparation and would have remained in solution. Upon analysis, iron complexed by organic ligands, in addition to soluble iron would have been ionized by the ICP-MS.

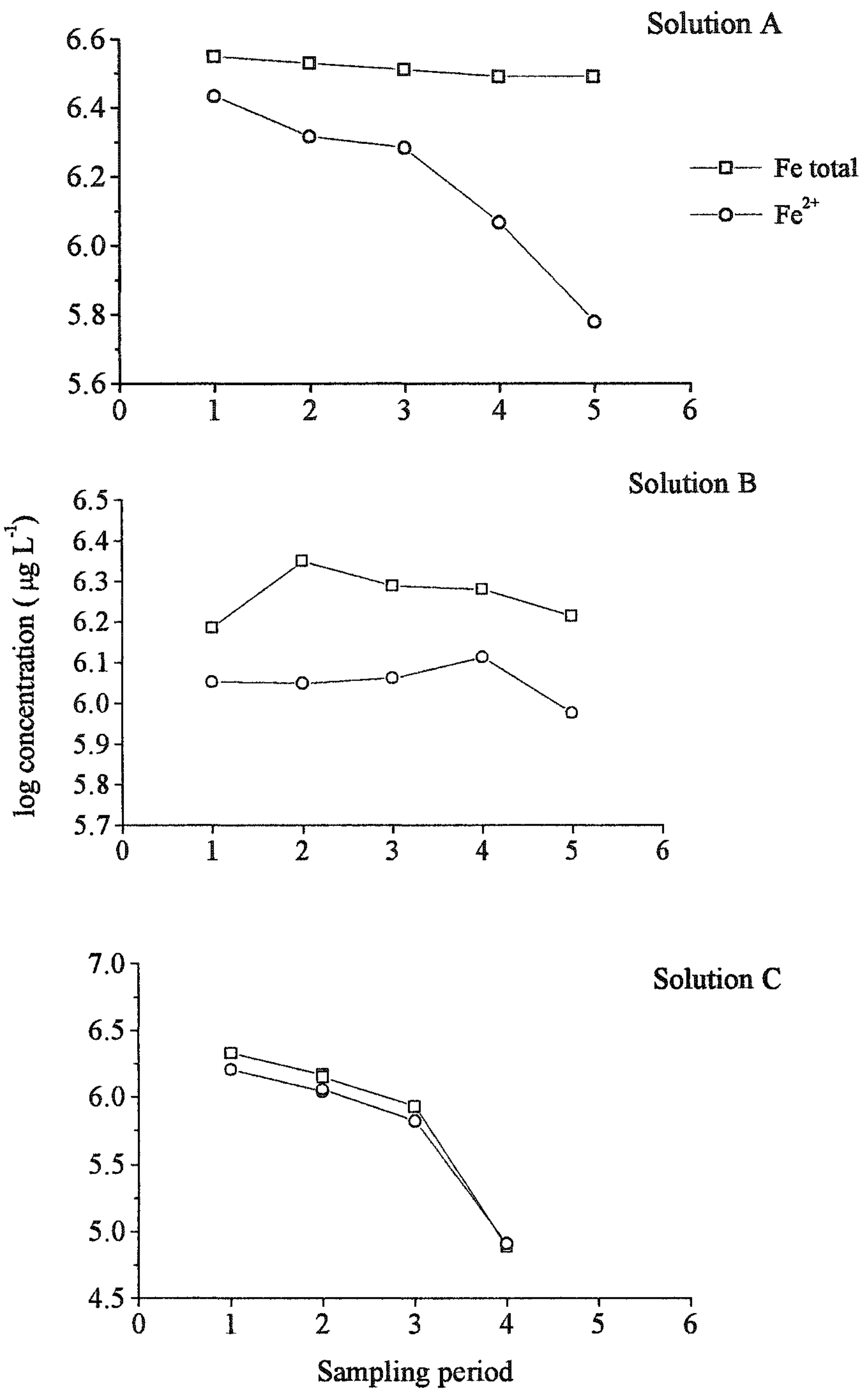


Figure 18. Aqueous concentrations of total iron (Fe) and ferrous iron (Fe^{2+}) when solutions A, B, and C collected from the soil/till mixture oxidized during the experiment. Iron organic complexes likely formed in solution A, both Fe-organic complexes and Fe-oxides likely formed in solution B, and Fe-oxides formed in solution C.

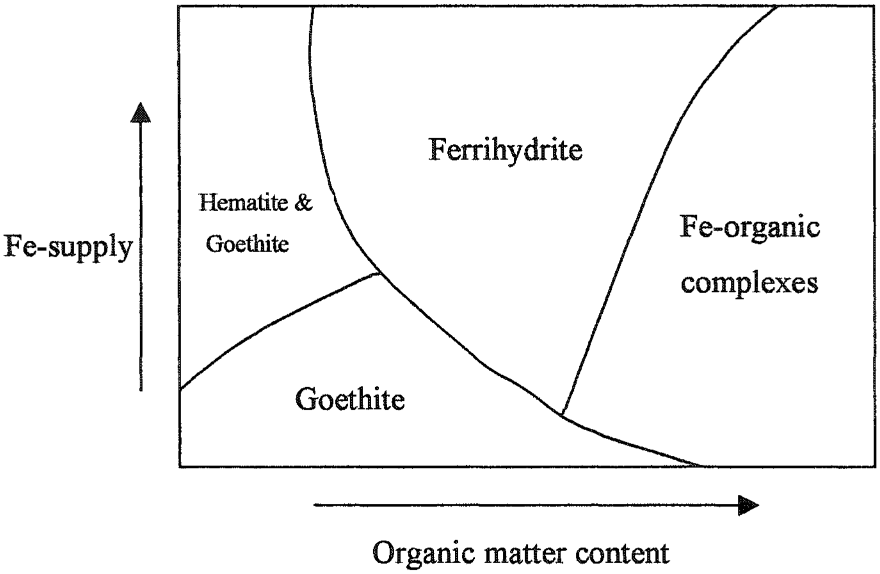


Figure 19. Schematic representation of the influence of organic matter content and the rate of soluble Fe supply on the formation of various Fe forms in soils (reproduced from Schwertmann et al., 1986).

Total iron concentrations remained unchanged when solutions were purged with oxygen because both complexed and soluble iron was detected at once.

Reddish-brown gelatinous precipitates formed when solutions were continuously purged with oxygen (solution A). Kononova (1966) and Ponnamperuma et al. (1967) have also described the formation of gelatinous precipitates during oxidation of solutions from acid sulfate soils. These authors confirmed the formation of Fe-organic complexes during oxidation. The dried precipitates were examined using a microscope and appeared to be tar-like (organic based) and had an amorphous structure as determined by XRD.

Organic complexes can strongly interfere with Fe-oxide formation, and may completely inhibit oxide formation by binding Fe as iron organic complexes (Schwertmann et al., 1986). Complexed ions typically react more slowly than uncomplexed ions, and this would have impacted the behavior of ferrous iron in the solutions purged with oxygen. Fe^{2+} normally can be oxidized to ferric iron or ferric iron oxides in minutes, however complexed Fe^{2+} may take months to complete the same reaction, as was observed in the solutions in this experiment. The formation of Fe-organic complexes removes iron from the system that could potentially form Fe-oxides, in turn decreasing the potential to immobilize arsenic.

Two types of precipitates formed when solutions were partially purged with oxygen (solution B). The low density, black precipitates that formed had identical characteristics to the precipitates from solution A, therefore it was concluded that iron organic complexes had formed when these solutions were partially aerated. Soluble Fe^{2+} concentrations were less than total Fe concentrations because Fe^{2+} was again complexed by organic ligands.

The high density precipitate was different in color from the Fe-organic precipitate and was amorphous in structure when analyzed using XRD. To help determine the composition of the precipitate a portion of it was heated at 550°C for 1 hour to determine if any portion of the precipitate was organic in nature. The magnetic properties of the heated precipitate were tested and confirmed using a small hand magnet. The conclusion was drawn that the heated precipitate was maghemite based on the magnetic properties of the precipitate. Maghemite in soils is commonly formed when ferrihydrite (amorphous Fe-oxides) is heated to 250-400°C in the presence of organic matter, for example when a forest fire heats soil (Schwertmann and Taylor, 1989). Pawluk (1971) noted the presence of maghemite in the Josephine soil series.

The conclusion was reached that ferrihydrite ($Fe_2O_3{\cdot}2H_2O$) was the form of the high density precipitate from solution B based on the identification of maghemite once the precipitate was heated to 550°C. Ferrihydrite commonly forms by microbial oxidation and hydrolysis of Fe^{2+}, is a characteristic component of young Fe-oxide accumulations, and will form in low-temperature environments including well waters or lake bottom sediments (Schwertmann et al., 1986). Organic complexes sorbed to the surface of the precipitate were the source of organic matter required for the transformation of ferrihydrite to maghemite.

The crystalline precipitate from solution C was positively identified as goethite (α-FeOOH) using x-ray diffraction analysis (Figure 20). Total aqueous iron and ferrous iron concentrations decreased as insoluble goethite formed during oxidation of solution C (Figure 17). Fe^{2+} oxidized to Fe^{3+}, and Fe^{3+} hydrolyzed to form goethite, resulting in a decrease in total iron and ferrous concentrations in solution. The oxides were removed from solution by filtration prior to solution analysis by ICP-MS.

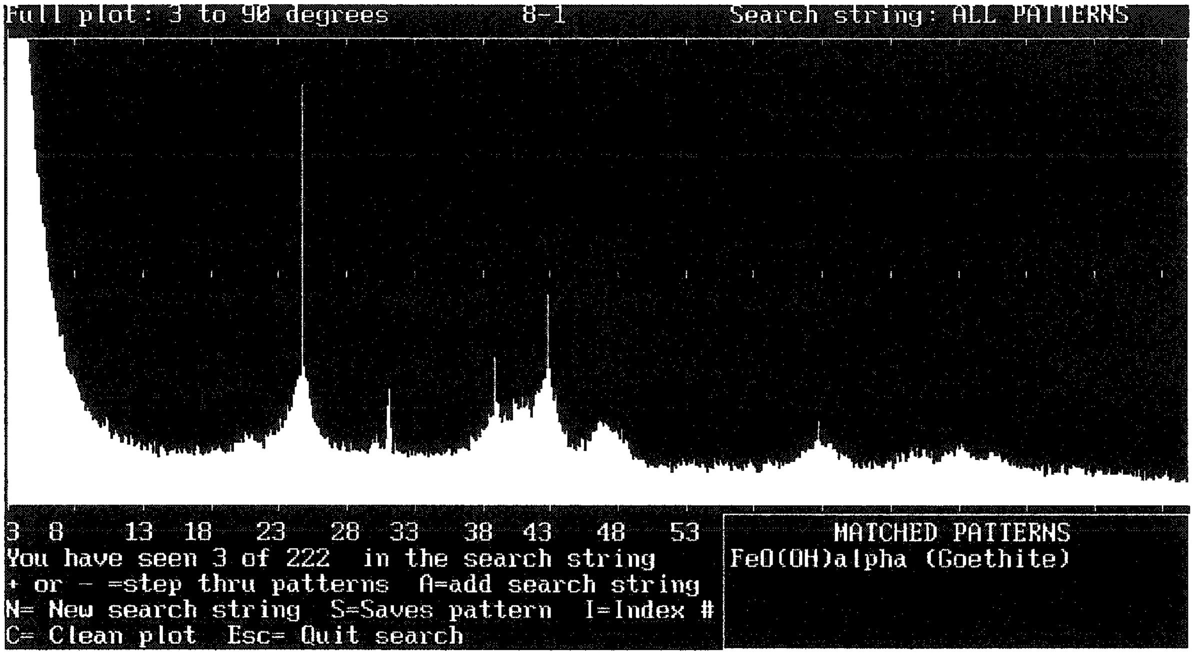


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Figure 20. X-ray diffraction pattern of the iron precipitate from solution C. Goethite was positively identified as the crystalline form of iron in this precipitate. The vertical index lines illustrate the documented diffraction behavior of goethite.

4.3.1. Chemical parameters - Eh, pH, and EC

Oxidized *solutions* were moderately to well aerated based on the redox potentials of the solutions. The redox potential of all solutions, except for two, ranged between 242 mV and 422 mV (Figure 21). The solution collected initially for the oxidation trial had the lowest Eh (-230 mV) because the solutions were reduced prior to the oxidation trial. The redox potentials of the solutions on the last sampling period were similar (average 395 mV) regardless of whether they were purged with oxygen or left open to the atmosphere to oxidize. The pH of the oxidized solutions decreased from around 5.02 (average) to 4.43 (average) over the sampling period (Figure 21) in response to the increase in solution Eh, similar to the inverse trend between Eh and pH observed in the

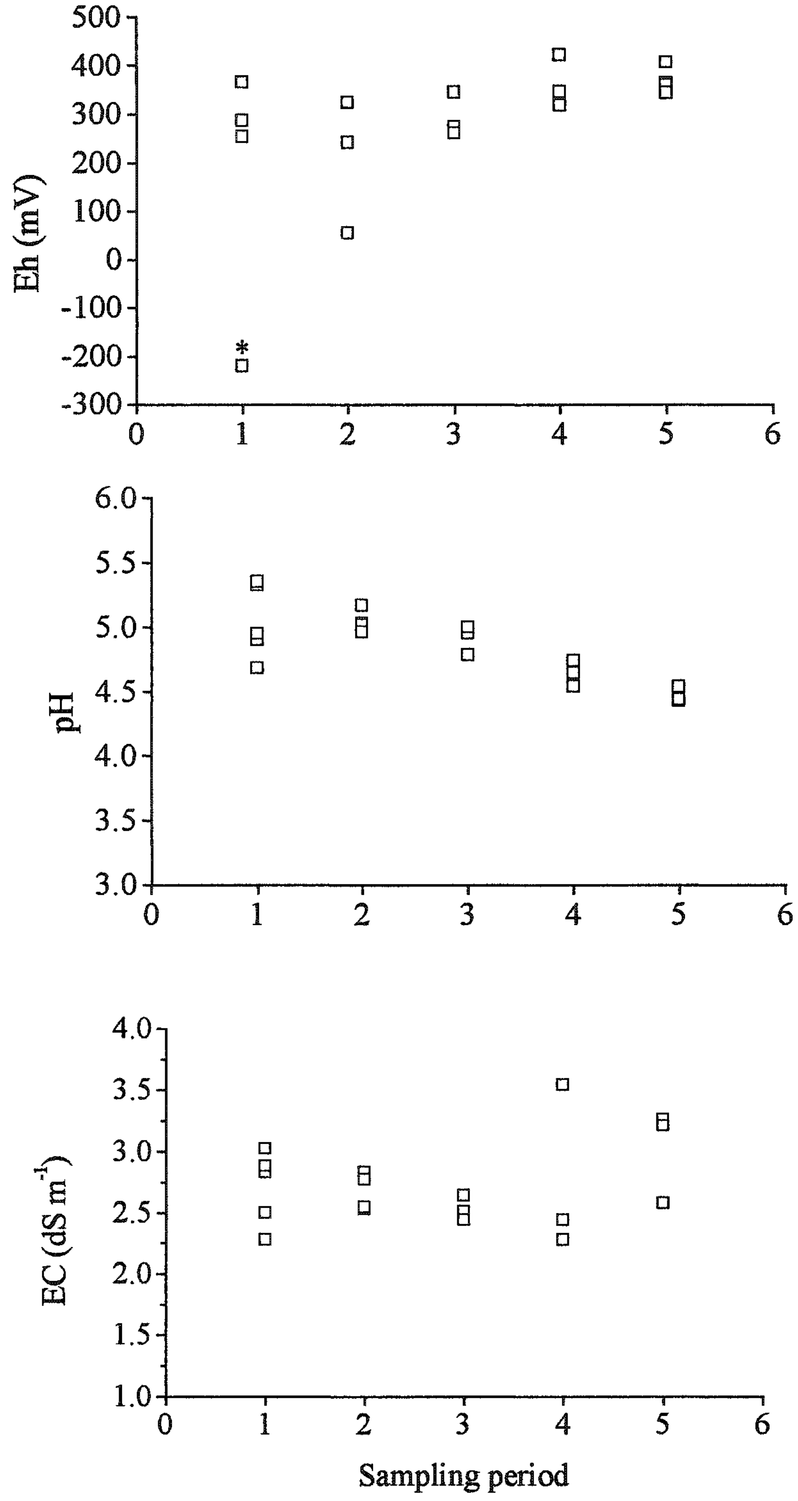

Figure 21. Changes in redox potential (Eh), pH, and electrical conductivity (EC) upon oxidation of solutions A, B, and C. The lowest redox potential was measured on the first sampling period and is denoted by (*) and was the initial Eh of the solution collected from the soil/till mixture.

reduction experiment. The pH of the solutions on the last sampling period were also similar between samples (average pH 4.46)

The variability in electrical conductivity decreased among solutions from the first to the third sampling period and then increased on the last two sampling periods (Figure 21). One solution on the fourth sampling period (from solution C) showed a large increase in EC to 3.54 dS m^{-1} compared to the other solutions. The EC of solutions in which iron organic complexes formed (solution A) remained stable at around 2.53 dS m^{-1} because ions remained in solution during oxidation. The EC of solutions in which Fe-oxides formed (solutions B and C) decreased because ion concentrations decreased when precipitates formed and ions were removed from solution. The increase in EC on the final sampling period relates to increases in ion concentrations, including increases in Al, Mn, and SO_4^{2-} concentrations. A clear trend in changes in electrical conductivity was not observed because different amounts of precipitates formed in all oxidized solutions.

4.3.2. Arsenic and molybdenum

Aqueous concentrations of arsenic and molybdenum remained low (below 19.0 µg As L^{-1} and below 73.0 µg Mo L^{-1}) in solutions with low initial concentrations of As and Mo. Concentrations remained high (between 78.0-03 µg As L^{-1} and between 247-308 µg Mo L^{-1}) in solutions with initially high concentrations of As and Mo during oxidation (Figure 22). Concentrations of molybdenum closely paralleled concentrations of As in all solutions.

Ferrihydrite or goethite formed in solutions containing low concentrations of both As and Mo (solutions B and C). Solutions in which goethite formed contained the lowest concentrations of As and Mo and solutions in which ferrihydrite formed contained As and Mo concentrations in the mid-range. Concentrations of arsenic and molybdenum in these solutions were low because As and Mo sorbed to the Fe-oxide when the oxides formed during oxidation. Arsenic ions likely bound to the oxides by the formation of monodentate surface complexes due to the low initial concentrations of aqueous As (1.0 x 10^{-6} *M*). Iron organic complexes formed in the solutions containing high concentrations of both As and Mo (solution A), and As and Mo remained in solution because there were no reactive surfaces onto which to sorb.

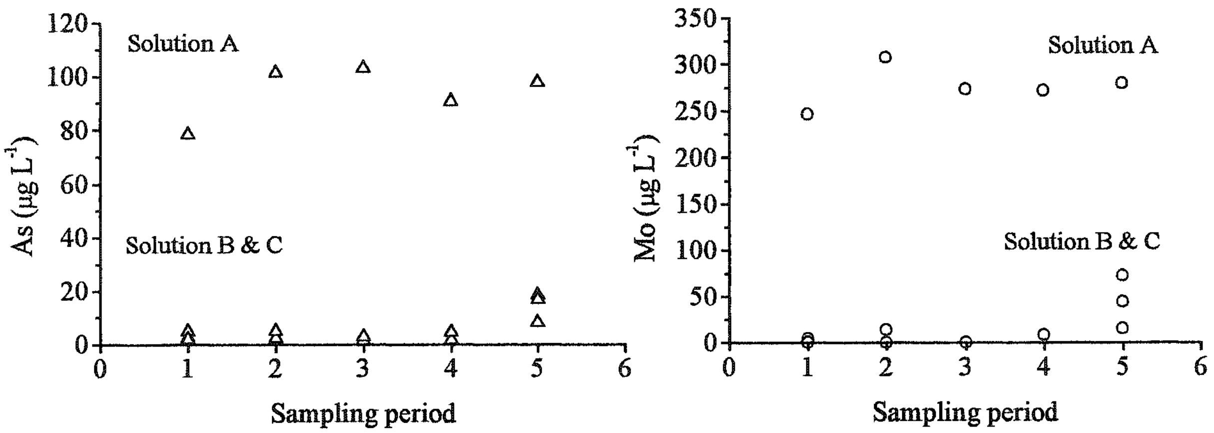

Figure 22. Changes in aqueous phase concentrations of arsenic and molybdenum during the oxidation of solutions A, B, and C.

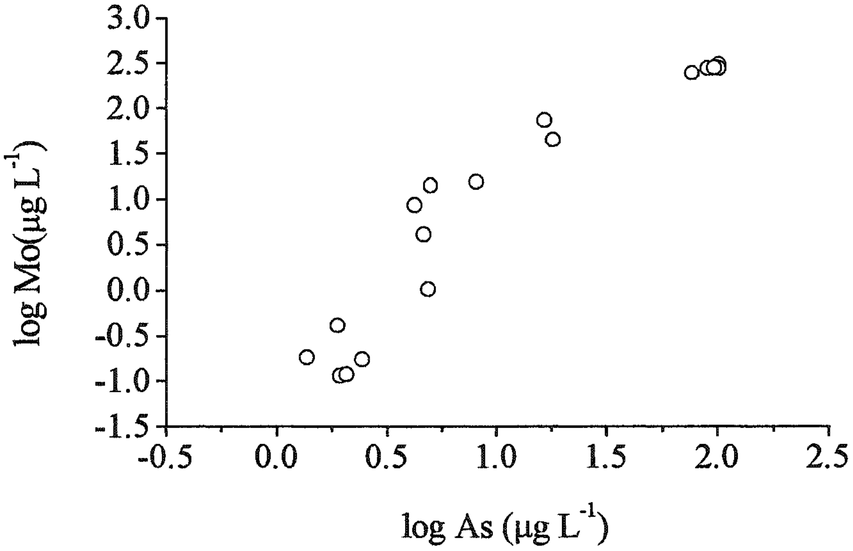

Figure 23. Relationship between aqueous phase concentrations of molybdenum and arsenic for oxidized solutions.

A positive linear correlation between aqueous concentrations of arsenic and molybdenum was observed for oxidized solutions from the soil/till mixture ($r^2 = 0.99$, $n = 25$, $p < 0.0001$) (Figure 23). This kind of correlation was also observed in the reduction experiment. A correlation between As and Mo in soil solutions has not been previously described in related literature.

4.3.3. Arsenic and iron

A positive linear correlation between aqueous concentrations of arsenic and iron was observed for oxidized solutions ($r^2 = 0.89$, $n = 27$, $p < 0.0001$) (Figure 24). This kind of correlation as was also observed in the reduction experiment. The solutions in which both Fe-organic complexes and Fe-oxides and only Fe-oxides formed contained the lowest concentrations of Fe and As (solutions B and C). The solution with the lowest concentration of iron had the second lowest concentration of As measured during oxidation (from solution C). Comparable oxidation studies have been reported elsewhere. Masscheleyn et al. (1991), Gustafsson and Tin (1994), McGeehan and Naylor (1994), McGeehan (1996), Reynolds et al. (1999), Jones et al. (2000) also show this relationship between As and Fe remaining in solution.

4.3.4. Aluminum, manganese, and sulfate

Aqueous aluminum concentrations remained high (between 43.0-58.0 mg L^{-1}) in solutions with high initial concentrations of Al and remained low (below 11.1 mg L^{-1}) in solutions with low initial concentrations of Al during oxidation (Figure 25). Aluminum organic complexes likely formed in solutions containing high concentrations of aqueous Al (solution A) (Hsu, 1989). Aqueous concentrations of Al increased slightly throughout the incubation in solutions with Fe-organic complexes, likely due to the dissolution of fine colloidal material, including Al-oxides, present in solutions during sample preparation. Concentrations of aluminum in solution were low in solutions where Fe-oxides formed or crystallized (solutions B and C) because Al ions were likely incorporated into oxides during goethite formation. Aluminum substitution for Fe in soil goethites is quite common, and the degree of Al substitution is pH dependent (Schwertmann and Taylor, 1989). Changes in aqueous aluminum concentrations were

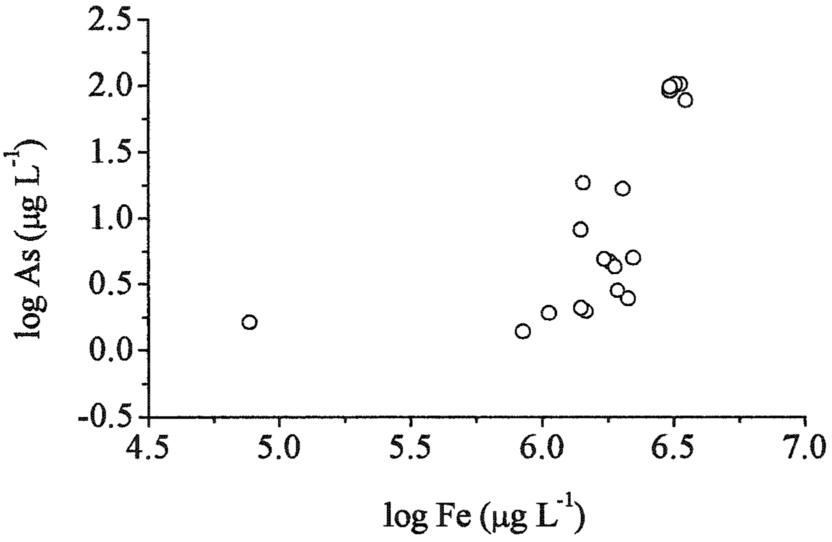

Figure 24. Relationship between aqueous phase concentration of arsenic and iron for oxidized solutions.

very similar to variations in arsenic and molybdenum concentrations in solution. Similar chemical behavior of Al, As, and Mo was likely due to sorption/incorporation of all three ions to oxide phases present in the solutions.

Aqueous Mn concentrations ranged between 14.1 mg L^{-1} and 35.4 mg L^{-1}, and the highest concentration of manganese was detected on the final sampling period (Figure 25). The increase in concentrations of Mn throughout the incubation could have been also due to the dissolution of fine colloidal material in the solutions. When solutions oxidized, the redox potential remained below the redox transformation line for Mn-oxides, therefore Mn species remained in solution as the manganous (Mn^{2+}) ion.

Aqueous phase concentrations of sulfate remained relatively unchanged on the first three sampling periods and then increased on the last two sampling periods (Figure 25). Sulfate concentrations ranged between 1.11 g L^{-1} and 2.52 g L^{-1}, and sulfate concentrations were the highest on the final sampling period, similar to concentrations of

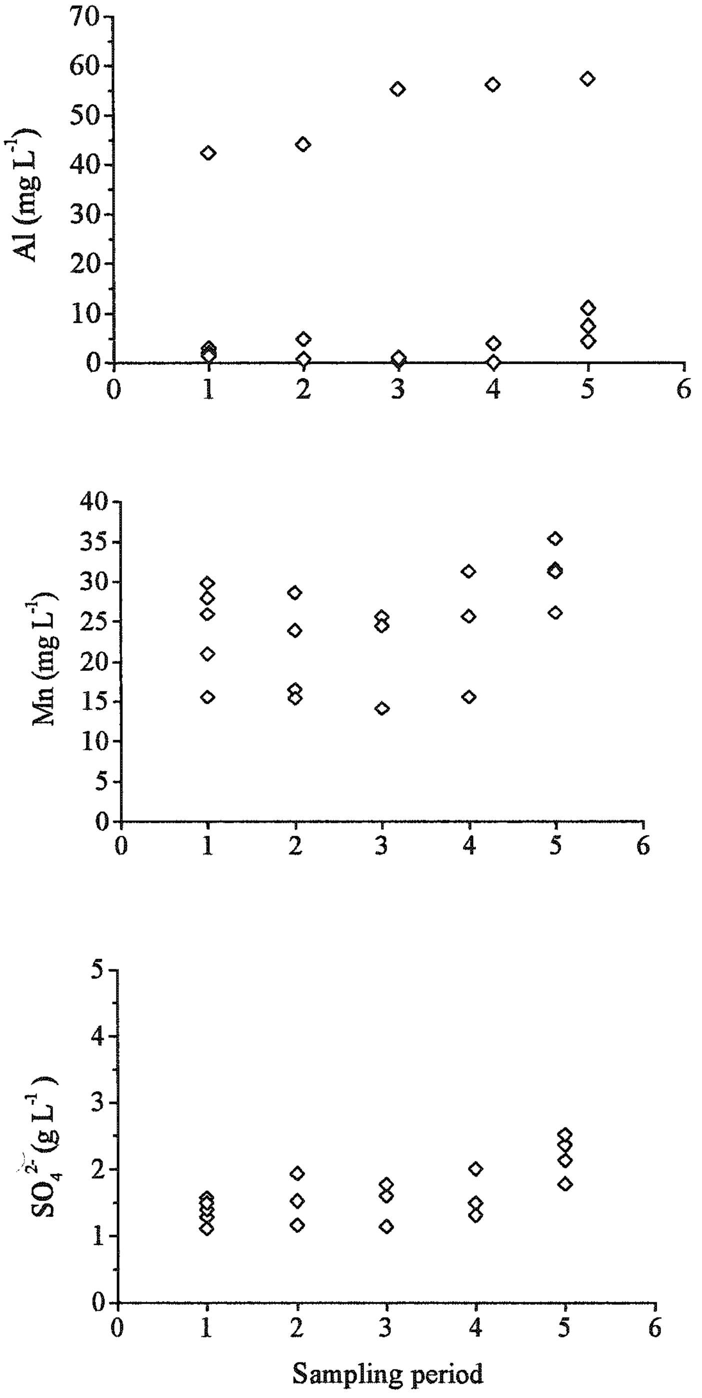

Figure 25. Changes in aqueous phase concentrations of aluminum (Al), manganese (Mn), and sulfate (SO_4^{2-}) during oxidation of solutions collected from the soil/till mixture. Concentrations of Al and Mn are shown in units of mg L^{-1} and sulfate in g L^{-1}.

Mn in solution and likely due to changes in the stability of colloidal material in the solutions. Redox potentials remained well above the redox transformation line for sulfate reduction, therefore SO_4^{2-} species remained in solution.

4.3.5. Arsenic speciation

A pe/pH diagram (Figure 26) of arsenic speciation, including arsenic sulfides, was constructed using the same thermodynamic data in section 4.2.10. The pe of all oxidized solutions was calculated (pe = Eh/59.2) and values were plotted on the diagram to determine arsenic speciation in solutions. Amorphous arsenic sulfides ($As_2S_{3(s)}$) were predicted to be the dominant form of arsenic to be present initially and in one other solution from the second sampling period. Arsenite ($H_3AsO_3^0$) was predicted to be the dominant species of arsenic present when the redox potential began to increase during oxidation. Arsenate ($H_2AsO_4^-$) was predicted to be present in approximately two thirds (2/3) of the oxidized solutions when the redox potential continued to increase to greater than pe 5.

Arsenic solubility in soil solutions of soils derived from mixtures of marine shales and glacial till is predicted to decrease when reduced solutions become oxidized and iron oxides form. The dominant form of arsenic in oxidized solutions is predicted to be As(V). Arsenate would easily and quickly sorb to newly formed oxides and become immobilized, decreasing the toxicity of aqueous arsenic (Webb, 1966; Ferguson and Gavis, 1972; Sadiq, 1997). Iron oxides were predicted to form in all oxidized solutions, however the high concentrations of organic ligands produced during fermentation resulted in the formation of Fe-organic complexes, which inhibited the formation of Fe-oxides. Arsenic sulfide was predicted to form in the most reduced solutions. An increase in aqueous concentrations of arsenic was observed between the first and second sampling period, which may have resulted from the oxidation of arsenic sulfides to arsenite [As(III)] as oxygen was introduced into the solutions.

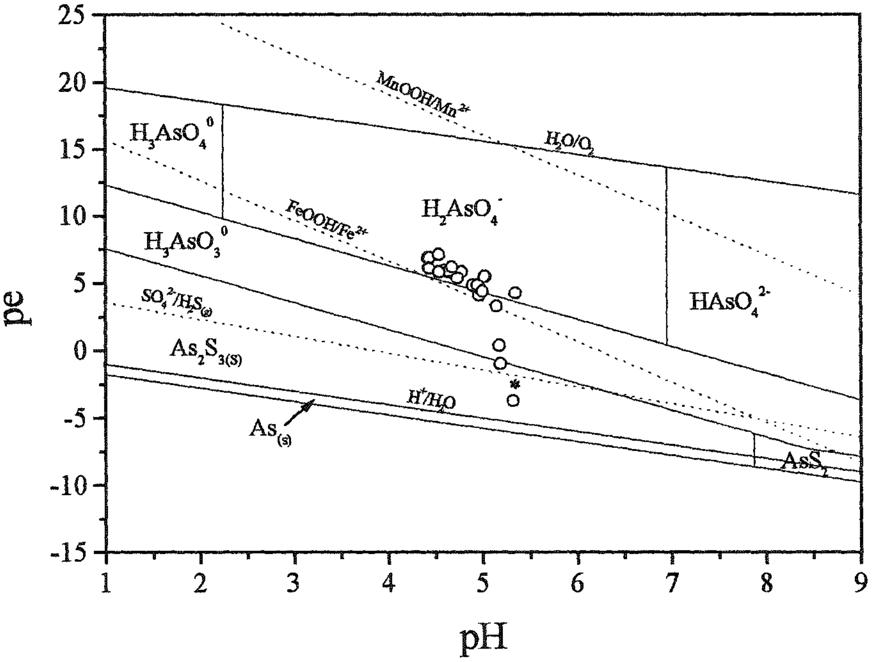

Figure 26. pe-pH diagram of arsenic speciation (Cherry et al., 1979; Lindsay, 1979; Sadiq, 1997). Total dissolved As was set at 5 µg L^{-1} to construct the stability fields for the solid arsenic compounds. Mn was set at 78.9 µg L^{-1}, Fe^{2+} at 42.7 mg L^{-1}, and SO_4^{2-} species at 145 mg L^{-1} to set the redox transformation lines of Mn-, Fe-oxides and sulfate. Eh values are superimposed onto the diagram. The initial measurement for the soil/till mixture is denoted by (*).

CHAPTER V

CONCLUSIONS

The present study was conducted to examine arsenic-iron-molybdenum biogeochemical interactions and the sorption behavior of As and Mo during reduction and oxidation of an acid sulfate soil and the acid soil admixed with calcareous glacial till. Low redox conditions were biologically mediated in both the soil and the soil/till mixtures to promote reductive dissolution of iron oxides and subsequent desorption of bound As and Mo in the reduction incubation experiment. Soil solution from a reduced soil/till mixture was collected and aerated with oxygen to promote iron oxide formation and subsequent adsorption of As and Mo in the oxidation experiment. Elucidating the chemical interactions between iron, arsenic, and molybdenum in these acid sulfate soils and soils derived from mixtures of marine shale and till adds insight to how environmental factors, such as redox potential and pH, influence the solubility of these elements.

Strongly reduced conditions were not achieved during the incubation of the acid sulfate soil due to the strong acidity of the soil. Acidic conditions suppress most microbial growth and acidic systems tend to remain oxidized as a result of the inverse relationship between pe and pH. Highly reduced conditions were easily sustained during the incubation of the soil/till mixture.

Aqueous phase concentrations of arsenic and iron, and arsenic and molybdenum were significantly correlated during the reduction of the soil and soil/till mixture and during the oxidation of the soil solution collected from the soil/till mixture. Arsenic and molybdenum desorbed from iron oxides in the acid sulfate soil and in the soil/till mixture when the oxides underwent reductive dissolution under low redox conditions. Arsenic and molybdenum sorbed to oxide phases that formed during oxidation of solutions from the soil/till mixture. Reduced conditions increased the solubility of As and Mo (and Fe) in solutions while these species were immobilized under oxidized conditions.

Aqueous extracts of the 2:1 mixtures used in the reduction incubation are not directly equivalent to groundwater samples, however a comparison between measured and guideline values are valid. Ion concentrations in aquifer materials subjected to similar reducing conditions are expected to be higher than concentrations measured in the saturated soil and soil/till mixtures based on differences in porosity and typical ratios of solid: solution phases in the aquifer materials and the incubated mixtures. The mixtures do not overestimate arsenic concentrations that may be detected in aquifer materials, therefore conclusions based on comparisons to guideline values are not excessively cautious.

Concentrations of arsenic in solution in excess of the Canadian drinking water quality guideline limit 25 μg As L^{-1} occurred when redox potentials in the soil and soil/till mixture fell between -100 mV to -150 mV similar to field results of Stein et al. (2000). Aqueous As concentrations in the soil/till mixture exceeded 25 μg L^{-1} in almost 70% of samples during the reduction experiment. The main As species predicted to be prevalent under moderately reduced conditions was $H_3AsO_3^0$ (arsenite), under strongly reduced conditions was amorphous $As_2S_{3(s)}$, and under oxidized conditions was $H_2AsO_4^-$ (arsenate). Aqueous molybdenum concentrations during incubation of the soil/till mixture exceed the mean concentration of 5 μg L^{-1} measured in Alberta well waters reported by Fitzgerald et al. (1997). In reduced waters with high pH Mo could potentially be used to indicate geogenic sources of arsenic.

There were no correlations between arsenic and aluminum in either the reduction or the oxidation experiment. Manganese and sulfate were used as redox indicators along with iron to assess levels of reduction and oxidation in the soil and soil/till mixture. Manganese oxides reduced and SO_4^{2-} concentrations continued to increase during the reduction experiment. Sulfate reduction may have occurred in reduced microsites, but a decrease in sulfate concentrations was likely offset by continued dissolution of natrojarosite. Manganese (Mn^{2+}) and SO_4^{2-} remained in solution during the oxidation experiment.

Based on observations and results of the present study, arsenic-iron biogeochemical interactions in acid sulfate soils are similar to interactions previously described in related literature. Reduced conditions in acid sulfate soils found in upper slope positions are likely difficult to achieve mainly due to the acidity of the soil, therefore elevated concentrations of arsenite in soil solutions are not likely to be problematic. In low lying or depressional areas of the landscape where soils are derived from a mixture of marine shales and calcareous glacial till, or nearby agricultural areas where farmers add lime to increase crop productivity, prolonged flooding could easily result in reduced conditions. Anaerobic conditions induced by the microbial degradation of organic materials during seasonally wet periods in these low lying areas will lead to the reduction of oxide phases and the desorption of arsenic and molybdenum. Lower concentrations of iron organic complexes are predicted to form in these depressional areas because there is less organic substrate in the field compared to concentrations added in either experiment.

The results of this study show that (1) high concentrations of arsenic in soil solutions are more likely to be detected in areas on the landscape where soils are derived from acid marine shales mixed with calcareous glacial till; (2) molybdenum can be used as an indicator of geogenic arsenic in reduced soil solutions in areas where soils have developed from mixtures of marines shales and glacial till, and; (3) aqueous concentrations of arsenic and molybdenum will decrease if reduced soil solutions from soils derived from these acid shale/till mixtures become sufficiently oxidized as ions sorb onto newly formed Fe-oxides. The results of this study indicate arsenic levels in the Josephine soils may be problematic since these soils have mineralogy and chemistry similar to the experimental soil/till mixture.

REFERENCES

Abder-Ruhman, M. 1980. Mineralogical characteristics of soils from east central Alberta. MSc. thesis. Department of Soil Science, University of Alberta. Edmonton, AB.

Aggett, J. and G.A. O'Brien. 1985. Detailed model for the mobility of arsenic in lacustrine sediments based on measurements in Lake Ohakuri. Environ. Sci. Tehcnol. 19:231-238.

Agriculture Canada Expert Committee on Soil Survey. 1987. The Canadian system of soil classification 2nd edition. Agric. Can. Publ. 1646.Pp. 164.

Alef, K. and P. Nannipieri. 1995. Methods in Applied Soil Microbiology and Biochemistry. Academic Press. New York, N.Y.

Allaway, W.H. 1977. Perspectives on molybdenum in soils and plants. *In* Molybdenum in the environment. Vol 2: The geochemistry, cycling, and industrial uses of molybdenum. Ed. W.R. Chappell and K.K. Petersen. Marcel Dekker, Inc. New York, N.Y. Pp. 317-339.

Anderson, M.A., Ferguson, J.F. and J. Gavis. 1976. Arsenate adsorption on amorphous aluminum hydroxide. J. Colloid Interface Sci. 54:391-399.

Baas Becking, L.G.M., Kaplan, I.R., and D. Moore. 1960. Limits of the natural environment in terms of pH and oxidation-reduction potentials. J. Geol. 3:243-284.

Barber, S.A. 1995. Soil nutrient bioavailability: a mechanistic approach. 2nd edition. John Wiley & Sons, Inc. New York, NY.

Barrow, N.J. 1977. Factors affecting the molybdenum status of soils. *In* Molybdenum in the environment. Vol 2: The geochemistry, cycling, and industrial uses of molybdenum. Ed. W.R. Chappell and K.K. Petersen. Marcel Dekker, Inc. New York, N.Y. Pp. 583-595.

Bartlett, R. 1986. Soil redox behavior. *In* Soil physical chemistry. Ed. D.L. Sparks. CRC Press. Boca Raton, FL. Pp. 179-207.

Bhumbla, D.K. and R.F. Keefer. 1994. Arsenic mobility and bioavailability in soils. *In* Arsenic in the environment. Part 1: Cycling and characterization. Ed. J.O. Nriagu. John Wiley & Sons, Inc. Pp. 51-82.

Bohn, H.L. 1971. Redox potentials. Soil Sci. 112:39-45.

Bohn, H.L. 1976. Arsenic Eh-pH diagram and comparisons to the soil chemistry of phosphorus. Soil Sci. 121:125-127.

Bowden, J.W., Bolland, M.D.A., Posner, A.M. and J.P. Quirk. 1973. Generalized model for anion and cation adsorption at oxide surfaces. Nature: Phys. Sci. 245:81-83.

Bowell, R.J. 1994. Sorption of arsenic by iron oxides and oxyhydroxides in soils. Applied Geochem. 9:279-286.

Boyle, W. and I.R. Jonasson. 1973. The geochemistry of arsenic and its use as an indicator element in geochemical prospecting. J. Geochem. Explor. 2:251-296.

Brennan, E.W. and W.L. Lindsay. 1998. Reduction and oxidation effect on the solubility and transformation of iron oxides. Soil Sci. Soc. Am. J. 62:930-937.

Brown, L.A. 1933. Oxidation reduction potentials in soils: I. Principles and electrometric determination. Soil Sci. 37:65-76.

Bulmer, C. 1987. Nutrient imbalances of aspen poplar in acid sulfate soils in northwestern Alberta. MSc. thesis. Department of Soil Science, University of Alberta. Edmonton, AB. Pp.121.

Bundy, L.G. and J.M. Bremner. 1972. A simple titrimetric method for determination of inorganic carbon in soils. Soil Sci. Soc. Am. Proc. 36:273-275.

Carbonell Barrachinca, A.A., Burlo Carbonell, F.M and J.J. Mataix Beneyto. 1996. Arsenite adsorption and desorption by a calcareous soil. II. Equilibrium data: isotherms. Agrochim. 40:79-84.

Cherry, J.A., Shaikh, A.U., Tallman, D.E. and R.V. Nicholson. 1979. Arsenic species as an indicator of redox conditions in groundwater. J. Hydrology. 43:373-392.

Cullen, W.R. and K.J. Reimer. 1989. Arsenic speciation in the environment. Chem. Rev. 89:713-764.

Deuel, L.E. and A.R. Swoboda. 1972. Arsenic solubility in a reduced environment. Soil Sci. Soc. Am. Proc. 36:276-278.

Dionex Corporation. 1999. Determination of sulfite in food and beverages by ion exclusion chromatography with pulsed amperometric detection. Dionex Application Note no. 54. Sunnyvale, CA.

Doner, H.E. and W.C Lynn. 1989. Carbonate, halide, sulfate, and sulfide minerals. *In* Minerals in soil environments. Eds. J.B. Dixon and S.B. Weed. Soil Sci. Soc. Am. Madison, WI. Pp:279-330.

Doyle, P.J. and K. Fletcher. 1977. Molybdenum content of bedrock, soils, and vegetation and the incidence of copper deficiency in cattle in western Manitoba. *In* Molybdenum in the environment. Vol 2: The geochemistry, cycling, and industrial uses of molybdenum. Ed. W.R. Chappell and K.K. Petersen. Marcel Dekker, Inc. New York, N.Y. Pp. 371-386.

Dudas, M.J. 1984. Enriched levels of arsenic in post-active acid sulfate soils in Alberta. Soil Sci. Soc. Am. J. 48:1451-1452.

Dudas, M.J. 1987. Accumulation of native arsenic in acid sulphate soils in Alberta. Can. J. Soil Sci. 67:317-331.

Dudas, M.J. 1988. Soil Chemistry - Laboratory Manual Soil Science 450. University of Alberta. Edmonton, AB. Pp. 52.

Dudas, M.J. 1992. Soil mineral analysis - theory and methods. Laboratory Manual. Soils 415. Department of Soil Science, University of Alberta. Edmonton, AB.

Dudas, M.J. and S. Pawluk. 1980. Natural abundances and mineralogical partitioning of trace elements in selected Alberta soils. Can. J. Soil Sci. 60:763-771.

Dudas, M.J., Warren, C.J. and G.A. Spiers. 1988. Chemistry of arsenic in acid sulphate soils of northern Alberta. Commun. Soil Sci. Plant Anal. 19:887-895.

Edwards, R., Jones, K.C., and N.W. Lepp. 1995. Concentrations of heavy metals in soils and plants. *In* Heavy Metals in soils. 2nd edition. Ed. B.J. Alloway. Balckie Academic & Professional. New York, N.Y.

Ehrlich, H.L. 1996. Geomicrobiology. Third edition. Marcel Dekker, Inc. New York, NY.

Elkhatib, E.A., Bennett, O.L. and R.J. Wright. 1984a. Kinetics of arsenite sorption in soils. Soil Sci. Soc. Am. J. 48:758-762.

Elkhatib, E.A., Bennett, O.L, and R.J. Wright. 1984b. Arsenite sorption and desorption in soils. Soil Sci. Soc. Am. J. 48:1025-1030.

Evans, L.J. 1989. Chemistry of metal retention by soils. Environ. Sci. Technol. 23:1046-1055.

Fendorf, S., Eick, M.J., Grossl, P. and D.L. Sparks. 1997. Arsenate and chromate retention on goethite: I. Surface structure. Environ. Sci. Technol. 31:315-320.

Ferguson, J.F. and J. Gavis. 1972. A review of the arsenic cycle in natural waters. Water Res. 6:125-1274.

Fitzgerald, D.A., Kiely, D.A., Neilson, R.D., Shaw, S., Audette, R.J., Prior, M., Ashton, E., and E. Allison. 1997. Alberta Farmstead Water Quality Survey Report, Canada-Alberta Environmentally Sustainable Agriculture (CAESA) Agreement. Edmonton, AB.

Fordham, A.W. and K. Norrish. 1974. Direct measurement of the composition of soil components which retain added arsenate. Aust. J. Soil Res. 12:165-172.

Fordham, A.W. and K. Norrish. 1979. Arsenate-73 uptake by components of several acidic soils and its implications for phosphate retention. Aust. J. Soil. Res. 17:307-316.

Frost, R.R. and R.A. Griffin. 1977. Effect of pH on adsorption of arsenic and selenium from landfill leachate by clay minerals. Soil Sci. Soc. Am. J. 41:53-57.

Fuller, C.C., Davis, J.A., and G.A. Waychunas. 1993. Surface chemistry of ferrihydrite: Part 2. Kinetics of arsenate adsorption and coprecipitation. Geoch. Cosmochim. Acta. 57:2271-2282.

Galba, J. 1972. Arsenate sorption in soils. III. Effect of soil solution pH on arsenate sorption. Pol'nohospodarstvo. 18:1055-1061. Chem. Abs. 158234z.

Goldberg, S. and H.S. Forster. 1998. Factors affecting molybdenum adsorption by soils and minerals. Soil Sci. 163:109-114.

Gotoh, S. and K. Yamashita. 1966. Oxidation-reduction potential of a paddy soil *in situ* with special reference to the production of ferrous iron, manganous manganese, and sulfide. Soil Sci. Pl. Nutr. 12:230-238.

Grossl, P.R., Eick, M., Sparks, D.L., Goldberg, S., and C.C. Ainsworth. 1997. Arsenate and chromate retention mechanisms on goethite. 2. Kinetic evaluation using a pressure-jump relaxation technique. Env. Sci. Tech. 31:321-326.

Gruebel, K.A., Davis, J.A. and J.O. Leckie. 1988. The feasibility of using sequential extraction techniques for arsenic and selenium in soils and sediments. Soil Sci. Soc. Am. J. 52:390-397.

Gulens, J., Champ, D.R. and R.E. Jackson. 1979. Influence of redox environments on the mobility of arsenic in ground water. ACS Symposium Series. 93:81-95.

Guo, T., DeLaune, R.D., and W.H. Patrick, Jr. 1997. The influence of sediment redox chemistry on chemically active forms of arsenic, cadmium, chromium, and zinc in estuarine sediment. Environ. Int. 23:305-316.

Gupta, S.K. and K.Y. Chen. 1978. Arsenic removal by adsorption. Water Pollu. Control Fed. J. 50:493-506.

Gustafsson, J.P. and N.T. Tin. 1994. Arsenic and selenium in some Vietnamese acid sulphate soils. Sci. Total Env. 151:153-158.

Health Canada. 1996. Guidelines for Canadian drinking water quality. 6th edition. Ottawa, ON.

Health Surveillance. 2000. Arsenic in Groundwater from Domestic Wells in Three Areas of Northern Alberta. Alberta Health and Wellness report. Edmonton, AB. Pp.40.

Hendershot, W.H., Lalande, H., and M. Duquette. 1993. Soil reaction and exchangeable acidity. *In* Soil Sampling and Methods of Analysis. Ed. M.R. Carter. Lewis Publishers. Boca Raton, FL. Pp. 141-145.

Hess, R.E. and R.W. Blanchar. 1977. Dissolution of arsenic from waterlogged and aerated soil. Soil Sci. Soc. Am. J. 41:861-865.

Hingston, F.J., Posner, A.M. and J.P. Quirk. 1972. Anion adsorption by goethite and gibbsite. I. The role of the proton in determining adsorption envelopes. J. Soil Sci. 23:177-192.

Holm, T.R. and C.D. Curtiss. 1989. A comparison of oxidation-reduction potentials calculated from the As(V)/As(III) and Fe(III)/Fe(II) couples with measured platinum-electrode potentials in groundwater. J. Contam. Hydrol. 5:67-81.

Huang, P.M. 1975. Retention of arsenic by hydroxy-aluminum on surfaces of micaceous mineral colloids. Soil Sci. Soc. Amer. Proc. 39:271-275.

Hsu, P.H. 1989. Aluminum hydroxides and oxyhydroxides. *In* Minerals in soil environments. Eds. J.B. Dixon and S.B. Weed. Soil Sci. Soc. Am. Madison, WI. Pp:331-378.

Jacob, H.E. 1970. Redox potential. *In* Methods in microbiology. Vol 2. p 91-123.

Jacobs, L.W., Syers, J.K. and D.R. Kenney. 1970. Arsenic sorption by soils. Soil Sci. Soc. Amer. Proc. 34:750-754.

Jefferey, J.W.O. 1961. Measuring the state of reduction of a water logged soil. J. Soil Sci. 12:317-325.

Jones, C.A., Langner, H.W., Anderson, K., McDermott, T.R. and W.P. Inskeep. 2000. Rates of microbially mediated arsenate reduction and solubilization. Soil Sci. Soc. Am. J. 64:600-608.

Kim, M-J., Nriagu, J. and S. Haack. 2000. Carbonate ions and arsenic dissolution by groundwater. Environ. Sci. Technol. 34:3094-3100.

Kittrick, J.A. 1980. Gibbsite and kaolinite solubilities by immiscible displacement of equilibrium solutions. Soil Sci. Soc. Am. J. 44:139-142.

Kononova, M.M. 1966. Soil organic matter: its nature, its role in soil formation and in soil fertility. Pergamon Press. Oxford, UK.

Ladwig, K.J. and M. McLearn. Unpublished. Environmental chemistry of arsenic: a literature review. EPRI. Palo Alto, CA.

Lavy, T.L. and S.A. Barber. 1964. Movement of molybdenum in the soil and its effects on availability to the plant. Soil Sci. Soc. Am. Proc. 28:93-97.

Lindsay, W.L. 1979. Chemical equlibria in soils. John Wiley & Sons, Inc. N.Y.

Lindsay, W.L. 1988. Solubility and redox equlibria of iron compounds in soils. *In* Iron in soils and clay minerals. Eds. J.W. Stucki et al. D.Reidel Publishing Company. Pp. 37-60.

Lindsay, W.L. and M. Sadiq. 1983. Use of pe + pH to predict and interpret metal solubility relationships in soils. Sci. Total Env. 28:169-178.

Livesey, N.T. and P.M. Huang. 1981. Adsorption of arsenate by soils and its relation to selected chemical properties and anions. Soil Sci. 131:88-94.

Lombi, E., Wenzel, W.W. and R.S. Sletten. 1999. Arsenic adsorption by soils and iron-oxide-coated sand: kinetics and reversibility. J. Plant Nutr. Soil Sci. 162:451-456.

Lovley, D.R. 1991. Dissimilatory Fe(III) and Mn(IV) reduction. Microbiol. Rev. 55:259-287.

Lumsdon, D.G, Fraser, A.R., Russell, J.D. and N.T. Livesey. 1984. New infrared band assignments for the arsenate ion adsorbed on synthetic goethite (α-FeOOH). J. Soil Sci. 35:381-386.

Manning, B.A. and S. Goldberg. 1996. Modeling competitive adsorption of arsenate with phosphate and molybdate on oxide minerals. Soil Sci. Soc. Am. J. 60:121-131.

Manning, B.A. and S. Goldberg. 1997. Arsenic(III) and arsenic(V) adsorption on three California soils. Soil Sci. 162:886-895.

Masscheleyn, P.H., Delaune, R.D. and W.H. Patrick, Jr. 1991. Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil. Environ. Sci. Technol. 25:1414-1419.

Matis, K.A., Zouboulis, A.I., Zamboulis, D. and A.V. Valtadorou. 1999. Sorption of As(V) by goethite particles and study of their flocculation. Water Air Soil Pollut. 111:297-316.

McGeehan, S.L. 1996. Arsenic sorption and redox reactions: relevance to transport and remediation. J. Environ. Sci. Health. A31(9):2319-2336.

McGeehan, S.L. and D.V. Naylor. 1994. Sorption and redox transformation of arsenite and arsenate in two flooded soils. Soil Sci. Soc. Am. J. 58:337-342.

McGeehan, S.L., Fendorf, S. and D.V. Naylor. 1998. Alteration of arsenic sorption in flooded-dried soils. Soil Sci. Soc. Am. J. 62:828-833.

McKeague, J.A., Desjardins, J. G. and M.S. Wolynetz. 1979. Minor elements in Canadian soils. Land Resource Research Institute Contribution No. 27. Agriculture Canada. Ottawa, ON. Pp. 75.

McKeague, J.A., Cheshire, M.V., Andreux and J. Berthelin. 1986. Organo-mineral complexes n relation to pedogenesis. *In* Interactions of soil minerals with natural organics and microbes. Ed. P.M. Huang and M. Schonitzer. SSSA Special Pub. 17. SSSA, Inc. Madison, WI. Pp. 549-592.

McKenzie, R.M. 1989. Manganese oxides and hydroxides. *In* Minerals in soil environments. Eds. J.B. Dixon and S.B. Weed. Soil Sci. Soc. Am. Madison, WI. Pp:439-465.

Mermut, A.R., Curtin, D. and H.P.W. Rostad. 1985. Micromorphological and submicroscopical features related to pyrite oxidation an inland marine shale from east central Saskatchewan. Soil Sci. Soc. Am. J. 49:256-261.

Misra, S.G., Mishra, K.C., and P.C. Mishra. 1977. Retention and release of molybdenum by soils. *In* Molybdenum in the environment. Vol 2: The geochemistry, cycling, and industrial uses of molybdenum. Ed. W.R. Chappell and K.K. Petersen. Marcel Dekker, Inc. New York, N.Y. Pp. 317-339.

Mitchell, R.L. 1964. Trace elements in soil. *In* Chemistry of the soil. Ed. F.E. Bear. American Chemical Society Monograph Series. Reinhold Publishing Corporation. New York, N.Y. Pp. 320-368.

Mok, W.M. and C.M. Wai. 1994. Mobilization of arsenic in contaminated river waters. *In* Arsenic in the environment. Part 1: Cycling and characterization. Ed. J.O. Nriagu. John Wiley & Sons, Inc. Pp. 99-118.

Moore, J.N., Ficklin, and C. Johns. 1988. Partitioning of arsenic and metals in reducing sulfidic sediments. Environ. Sci. Technol. 22:432-437.

Morse, J.W., Millero, F.J., Cornwell, J.C., and D. Rickard. 1987. The chemistry of the hydrogen sulfide andiron sulfide systems in natural waters. Earth-Sci. Rev. 24: 1-42.

Nickson, R.T., McArthur, J.M., Burgess, W.G., Ahmed, K.M., Ravenscroft, P., and M. Rahman. 1998. Arsenic poisoning of Bangladesh groundwater. Nature. 395:338.

Nickson, R.T., McArthur, J.M., Ravenscroft, P., Burgess, W.G. and K.M. Ahmed. 2000. Mechanism of arsenic release to groundwater, Bangladesh and West Bengal. Applied Geochemistry. 15:403-413.

Nordstrom, D.K. 1982. Aqueous pyrite oxidation and the consequent formation of secondary iron minerals. *In* Acid sulfate weathering. Eds. J.A. Kittrick, D.S. Fanning, and L. R. Hossner. SSSA Special Pub. 10. Madison, WI. Pp. 37-56.

O'Neill, P. 1995. Arsenic. *In* Heavy metals in soils. Ed. B.J. Alloway. Blackie Academic & Professional. London, UK. Pp. 105-121.

O'Reilly, S.E., Strawn, D.G. and D.L. Sparks. 2001. Residence time effects on arsenate adsorption/desorption mechanisms on goethite. Soil Sci. Soc. Am. J. 65:67-77.

Olomu, M.O., Racz, G.J. and C.M. Chuo. 1973. Effect of flooding on the Eh, pH, and concentrations of Fe and Mn in several Manitoba soils. Soil Sci. Soc. Am. Pro. 37:220-224

Onken, B.M. and L.R. Hossner. 1996. Determination of arsenic species in soil solution under flooded conditions. Soil Sci. Soc. Am. J. 60:1385-1392.

Oscarson, D.W., Huang, P.M., and W.K. Liaw. 1980 The oxidation of arsenite by aquatic sediments. J. Environ. Qual. 9:700-703.

Oscarson, D.W., Huang, P.M., Defosse, C. and A. Herbillon. 1981 Oxidative power of Mn(IV) and Fe(III) oxides with respect to As(III) in terrestrial and aquatic environments. Nature 291:50-51.

Oscarson, D.W., Huang, P.M. and U.T. Hammer. 1983. Oxidation and sorption of arsenite by manganese dioxide as influenced by surface coatings of iron and aluminum oxides and calcium carbonate. Water Air Soil Pollut. 20:233-244.

Parfitt, R.L. 1978. Anion adsorption by soils and soil materials. *In* Advances in Agronomy. Vol 30. Ed. N.C. Bradly. Academic Press, Inc. New York, NY. Pp.1-42.

Parfitt, R.L. and J.D. Russell. 1977. Adsorption on hydrous oxides. IV. Mechanisms of adsorption of various ions on goethite. J. Soil Sci. 28:297-305.

Parks, G.A. and P.L. deBruyn. 1962. The zero point of charge of oxides. J. Phys. Chem. 66:967-973.

Patrick, W.H., Gambrell, R.P. and S.P. Faulkner. 1996. Redox measurements of soils. *In* Methods of soil analysis Pt 3 - Chemical Methods. Ed. D.L. Sparks. Soil Sci. Soc. Am. Madison, WI. Pp. 1255-1273.

Pawluk, S. 1971. Characteristics of fera eluviated Gleysols developed from acid shales in northwestern Alberta. Can. J. Soil Sci. 51:113-124.

Pawluk, S. and M. Dudas. 1978. Reorganization of soil materials in the genesis of an acid Luvisolic soil of the Peace River region, Alberta. Can. J. Soil Sci. 58:209-220.
Pearce, F. 1995. Death and the devil's water. New Sci. 147:14-15.

Peterson, M.L. and R. Carpenter. 1986. Arsenic distributions in porewaters and sediments of Puget Sound, Lake Washington, the Washington coast and Saanich Inlet, B.C. Geochim. Cosmochim. Acta 50:353-369.

Phillips and Lovely. 1987. Determination of Fe(III) and Fe(II) in oxalate extracts of sediment. Soil Sci. Soc. Am. J. 51: 938-941.

Pierce, M.L. and C.B. Moore. 1980. Adsorption of arsenite on amorphous iron hydroxide from dilute aqueous solution. Environ. Sci. Technol. 14:214-216.

Pierce, M.L. and C.B. Moore. 1982. Adsorption of arsenite and arsenate on amorphous iron hydroxide. Water Res. 16:1247-1253.

Ponnamperuma, F.N. 1972. The chemistry of submerged soils. *In* Advances in agronomy. Vol 24. Ed. N.C. Brady. Academic Press. New York, NY. Pp.29-96.

Ponnamperuma, F.N., Tianco, E.M. and T. Loy. 1967. Redox equilibria in flooded soils: I. The iron hydroxide system. Soil Sci. 103:374-382.

Pons, L.J., Van Breemen, N. and P.M. Driessen. 1982. Physiography of coastal sediments and development of potential soil acidity. *In* Acid sulfate weathering. SSSA Special publication no. 10. Eds. J.A. Kittrick, D.S. Fanning, L.R. Hossner. Madison, WI. Pp.1-18.

Postma, D. 1993. The reactivity of iron oxides in sediments: a kinetic approach. Geochim. Cosmochim. Acta. 57:5027-5034.

Reddy, K.J., Munn, L.C. and L. Wang. 1997. Chemistry and mineralogy of molybdenum in soils. *In* Molybdenum in agriculture. Ed. U.C. Gupta. Cambridge University Press. Cambridge, U.K. Pp. 4-22.

Reeder, S.W. and W.M. Odynsky. 1965. Soil survey of the Cherry Point and Hines Creek area. No. 23 – Alberta Soil Survey. University of Alberta. Edmonton, AB.

Reisenauer, H.M., Tabikh, A.A., and P.R. Stout. 1962. Molybdenum reactions with soils and the hydrous oxides of iron, aluminum, and titanium. Soil Sci. Soc. Am. Proc. 26:23-27.

Reynolds, J.G., Naylor, D.V. and S.E. Fendorf. 1999. Arsenic sorption in phosphate-amended soils during flooding and subsequent aeration. Soil Sci. Soc. Am. J. 63:1149-1156.

Rochette, E.A., Li, G.C. and S.E. Fendorf. 1998. Stability of arsenate minerals in soil under biotically generated reducing conditions. Soil Sci. Soc. Am. J. 62:1530-1537.

Ross, G.J. and C. Wang. 1993. Extractable Al, Fe, Mn, and Si. *In* Soil Sampling and Methods of Analysis. Ed. M.R. Carter. Lewis Publishers. Boca Raton, FL. Pp. 239-245.

Roy, W.R., Hassett, J.J. and R.A. Griffin. 1986. Competitive interactions of phosphate and molybdate on arsenate adsorption. Soil Sci. 142: 203-210.

Ryden, J.C., Syers, J.K., and R.W. Tillman. 1987. Inorganic anion sorption and interactions with phosphate sorption by hydrous ferric oxide gel. J. Soil Sci. 38:211-217.

Sadiq, M. 1997. Arsenic chemistry in soils: an overview of thermodynamic predictions and field observations. Water Air Soil Pollut. 93:117-136.

Sadiq, M., Zaidi, T.H. and A.A. Mian. 1983. Environmental behavior of arsenic in soils: theoretical. Water Air Soil Pollut. 20:369-377.

Sakata, M. 1987. Relationship between adsorption of arsenic (III) and boron by soil and soil properties. Environ. Sci. Technol. 21:1126-1130.

Salloum, M.J, Dudas, M.J, and P.M. Fedorak. In press. Microbial reduction of amended sulfate in anaerobic mature oil sand fine tailings. Waste Manage. Res.

Satawathananont, S., Patrick, W.H. and P.A. Moore. 1991. Effect of controlled redox conditions on metal solubility in acid sulfate soils. Plant Soil. 133:281-290.

Schüring, J., Schulz, H.D., Fisher, W.R., Böttcher, J., and W.H.M. Duijnisveld. 2000. Redox: fundamentals, processes, and applications. Springer-Verlag. Berlin, Germany.

Schwertmann, U. Kodama, H and W.R. Fischer. 1986. Mutual interactions between organics and iron oxides. *In* Interactions of soil minerals with natural organics and microbes. Ed. P.M. Huang and M. Schonitzer. SSSA Special Pub. 17. SSSA, Inc. Madison, WI. Pp. 223-250.

Schwertmann, U. and R.M. Taylor. 1989. Iron oxides. *In* Minerals in soil environments. Eds. J.B. Dixon and S.B. Weed. Soil Sci. Soc. Am. Madison, WI. Pp:379-438.

Sposito, G. 1984. The chemistry of soils. Oxford University Press. New York, NY.

Stein, R., Dudas, M.J. and M. Klebek. 2000. Occurrence of arsenic in groundwater near Cold Lake, Alberta. Alberta Environment report. Edmonton, AB. Pp. 41.

Stevenson, F.J. and A. Fitch. 1986. Chemistry of complexation of metals ions with soil solution organics. *In* Interactions of soil minerals with natural organics and microbes. Ed. P.M. Huang and M. Schonitzer. SSSA Special Pub. 17. Soil Sci. Soc. Am, Inc. Madison, WI. Pp. 29-58.

Stumm, W. 1966. Redox potential as an environmental parameter: conceptual significance and operational limitation. *In* Advances in water pollution research. Vol 1. Water Pollution Control Federation. Washington, D.C. Pp. 283-308.

Stumm, W. and J.J. Morgan. 1970. Aquatic chemistry. Wiley-Interscience. New York, N.Y.

Sun, X. and H.E. Doner. 1996. An investigation of arsenate and arsenite bonding structures on goethite by FTIR. Soil Sci. 161:865-872.

Sun, X. and H.E. Doner. 1998. Adsorption and oxidation of arsenite on goethite. Soil Sci. 163:278-287.

van Breeman, N. 1982. Genesis, morphology and classification of acid sulfate soils in coastal plains. Eds. J.A. Kittrick, D.S. Fanning, and L. R. Hossner. SSSA Special Pub. 10. Madison, WI. Pp. 95-108.

Vlek, P.L.G. and W.L. Lindsay. 1977. Thermodynamic stability and solubility of molybdenum minerals in soils. Soil Sci. Soc. Am. J. 41:42-46.

Wagner, H.P. and M.J. McGarrity. 1991. The use of pulsed amperometry combined with ion-exclusion chromatography for the simultaneous analysis of ascorbic acid and sulfite. J. of Chrom. 546: 119-124.

Waychunas, G.A., Rea, B.A., Fuller, C.C., and J.A. Davis. 1993. Surface chemistry of ferrihydrite: Part 1. EXAFS studies of the geometry of coprecipitated and adsorbed arsenate. Geochim. Cosmochim. Acta 57:2251-2269.

Webb, J.L. 1966. Arsenicals. *In* Enzyme and metabolic inhibitors. Vol III. Academic Press. New York, NY. Pp. 595-793.

Welch, A.H., Westjohn, D.B., Helsel, D.R., and R.B. Wanty. 2000. Arsenic in ground water of the United States: Occurrence and geochemistry. Ground Water. 38:589-604.

Wilkie, J.A. and J.G. Hering. 1996. Adsorption of arsenic onto hydrous ferric oxide: effects of adsorbate/adsorbent rations and co-occurring solutes. Coll. Surfaces A: Physicochemical and Engineering Aspects. 107:97-110.

Wu, S., Zhao, Y., Feng, X., and A. Whittmeier. 1996. Application of inductively coupled plasma mass spectrometry for total metal determination in silicon-containing solid samples using the microwave-assisted nitric acid-hydrofluoric acid-hydrogen peroxide-boric acid digestion system. J. Anal. At. Spectrom. 11:287-296.

Xu, H, Allard, B. and A. Grimvall. 1988. Influence of pH and organic substance on the adsorption of As(V) on geologic materials. Water Air Soil Pollut. 40:293-305.

Yan-Chu, H. 1994. Arsenic distribution in soils. *In* Arsenic in the environment. Part 1: Cycling and characterization. Ed. J.O. Nriagu. John Wiley & Sons, Inc. Pp. 17-49.