University of Alberta

The Form and Removal of Mercury From Co-Contaminated Soils

by

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Abstract

The past actions of the oil and gas industries in Alberta have resulted in areas that are contaminated with hydrocarbons and mercury. In order to remediate these sites more must be known about the form and behavior of mercury in co-contaminated soils. The primary objective of this study was to determine the distribution of mercury in nine co-contaminated soils. This objective was accomplished using a ten step sequential extraction. It was found that the majority of mercury is contained in the organic matter phase of soil.

A secondary objective was to determine how effective a calcium hypochlorite solution was in lowering the mercury and hydrocarbon content of the nine co-contaminated soils. The hypochlorite treatment reduced the hydrocarbon content of four of the nine soils. In no soil was the mercury concentration lowered to background concentrations.

For Robin, who was there through it all.

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1.0. Introduction

The past actions of the oil and gas industries in Alberta have resulted in areas that are contaminated with hydrocarbons and mercury. The sites that are contaminated with the metal tend to be localized but can have very high concentrations of mercury. The original contaminant in most cases was elemental mercury. Over time the elemental mercury has reacted with soil constituents and has been redistributed within the soil. In order to remediate these mercury-contaminated soils the distribution of mercury within them needs to be determined. The distribution and form of mercury will determine the availability of mercury, chemically and to biological receptors, and how the mercury will respond to remediation attempts. The purpose of the present study was to determine the form of mercury in nine contaminated soils and their response to treatment with calcium hypochlorite.

1.1. Soil Mercury Concentrations.

Mercury is found naturally, usually in low concentrations, in every phase of the environment. It is a minor element in several rocks, it is found in air, volcanic gases, fresh water, seawater, lake and river sediments, living organisms and soils (Gaudet et.al., 1995). Mercury concentrations in Alberta soils usually range between 0.01 to 0.071 mg kg^{-1} (Dudas and Pawluk, 1976). Soil mercury concentrations can become elevated naturally if the soils overlay or receive sediment from a cinnabar (HgS) deposit. Mercury in such soils can reach concentrations of up to 14 mg kg^{-1} (in the Liard series of the North West Territories; the Liard series is the taxonomic name of a specific Regosolic soil found at 61°42'N, 121°17'W) (McKeague and Kloosterman, 1974).

1.2. Mercury Contaminated Industrial Sites.

There are several industries whose activities can result in the elevation of the mercury content of soil. These industries include the mining and metallurgy, paints and dyes, pesticides, electrical and electronic, chemical manufacturing, explosives, rubber and plastic, batteries, pharmaceuticals, pulp and paper industries (Forstner, 1990). In Alberta a major cause of mercury contaminated soils are the oil and gas industries. In the past mercury filled gas flow manometers were used to monitor pressure at gas metering sites. Manometers contain 3-5 kg (8-10 lb.) of elemental mercury (Charlton et.al., 1992, Wilhelm and McArthur, 1995). This mercury can spill onto the soil surface during regular maintenance, from pressure surges, from vandalism, or from breakage of the manometer (Wilhelm and McArthur, 1995). As mercury is more dense than soil, the mercury will infiltrate the soil and cleanup may become necessary if soil or ambient air quality guidelines for mercury concentrations are exceeded. Guidelines for mercury in soil range from 0.2 mg kg $^{-1}$ for Alberta Tier I criteria to 10 mg kg $^{-1}$ for CCME guidelines for commercial sites (Alberta Environmental Protection 1994, CCME 1991).

Several authors have studied the distribution of mercury around and within industrial sites. Henke et.al. (1993) and Stepan et al. (1995, 1993) produced several reports on mercury contamination at natural gas industry sites and listed many possible techniques to remediate these sites. The sites they described were contaminated with elemental mecury released from broken manometers. The remediation techniques discussed included physical, electrolytic, thermal, biological, in situ vitrification, isolation, and chemical technologies. The chemical treatment technologies included soil washing with hypochlorite solutions.

Kohut et al. (1995) investigated the Turner Valley Gas Plant, the source of soil M19 used in the present study. The Turner Valley Gas Plant (located in L.S.D. 14, northwest quarter of section 6, township 20, range 2, west of the fifth meridian) operated for approximately 60 years until 1985 and plans exist to develop the area as an historic site. The concentration of mercury at this sites ranged between 0.08 and 213 mg kg^{-1}.

Although previous studies had concluded the mercury was deposited naturally, Kohut et al. presented evidence the elevated mercury concentration was due to elemental mercury released from manometers. A subsequent report prepared by Luther and Dudas (1996) listed many techniques they believed could be used to remediate the soil at the Turner Valley Gas Plant. Among these techniques was soil washing using calcium hypochlorite.

1.3. Mercury Toxicity.

Soils contaminated with mercury may pose environmental and health risks as a result of mercury's physical (Appendix 1) and toxicological properties. Elemental mercury is very volatile (14 mg m^{-3} at 20°C) (Nriagu et.al., 1979) and mercury vapours can accumulate in poorly ventilated buildings. Some mercury species are soluble (70 g L^{-1} at 20°C for $HgCl_2$) (Nriagu et.al., 1979) and can leach into groundwater. Soil mercury can become methylated, enter an aquatic environment and accumulate in aquatic fauna.

A person's response to mercury will vary with the form they are exposed to, concentration, and route of exposure. Acute exposure to mercury vapour can lead to hallucinations, delirium, and respiratory effects. Chronic exposure to mercury vapour can result in erythism, irritability, insomnia, gingivitis and tremors (EPA, 1999). Inorganic mercury attacks metalo-enzymes and may replace zinc in some enzymes (Forstner, 1995) and acute exposure to inorganic mercury can cause nausea and vomiting. Chronic exposure to inorganic forms of mercury may result in kidney damage. Some organic forms of mercury, such as methyl-mercury, can be more toxic than inorganic forms. Acute exposure to methyl-mercury can cause blindness, deafness, an impaired level of consciousness, and death. Chronic exposure to organic forms of mercury damages the central nervous system, can cause paresthesia, blurred vision, deafness, speech difficulties and constriction of visual fields (EPA, 1999).

Organisms can be exposed to mercury in soil through several routes. The first route is through inhalation of volatile forms of mercury, such as elemental mercury and $(CH_3)_2Hg$. Another route is through the ingestion of mercury contaminated soil. The final common route of exposure is the leaching of soluble mercury compounds or mercury bound to soluble organic matter, into groundwater and drinking water.

1.4. Mercury in Soil

The behavior of mercury in soil must be understood before attempting to remediate mercury contaminated soils. The form of mercury in the soil, which can be affected by various factors including the oxidation state of mercury, governs mercury's behavior in soil. Mercury can exist in three oxidation states, elemental mercury (Hg^0), mercurous mercury (Hg^+) and mercuric mercury (Hg^{2+}). Mercurous mercury is uncommon in soils, it exists as the unstable Hg_2^{2+}, and will break down forming Hg^0 and Hg^{2+} (Andersson, 1979; Steinnes, 1990). Mercury can form several different species in soil depending on existing ligands in the environment, the form of mercury released into the environment and the effect of chemical and/or biological reactions in the soil (Revis et. al., 1989). The various species that mercury can form include volatile compounds such as Hg^0, $(CH_3)_2Hg$, soluble species such as HgX_2, HgX_3^-, HgX_4^{2-} ($X = OH^-, Cl^-, Br^-$), HgO, CH_3Hg^+, CH_3HgCl, CH_3HgOH and unreactive species such as HgS (Alloway, 1990). Mercury is a soft Lewis acid and will bind with soft and borderline Lewis bases such as SO_32^-, S^{2-}, Cl^-, preferentially over ligands such as SO_4^{2-}, PO_4^{2-}, OH^-, which are hard Lewis bases (Sposito, 1981).

The Hg containing species that form are partially controlled by the pH and redox potential of the soil. Under acidic conditions the sulfur containing species dominate; HgS in reducing conditions and $HgSO_4$ in oxidizing conditions, if S^{2-} or SO_4^{2-} are present in solution. Around neutral pH Hg^0 dominates under reducing or mildly oxidizing conditions, $HgCl_2$ dominates under oxidizing conditions when Cl^- is present in solution. At higher pHs and oxidizing potentials the OH^- containing species dominate (Benes and Havlik, 1979) (Appendix 2).

When elemental mercury is first added to soil it's behavior is governed by adsorption-desorption reactions. Subsequently the mercury can undergo volatilization or biological or chemical transformations (Hogg et al., 1978). The results of these transformations will vary between soils with different organic matter qualities and quantities, clay content and mineralogy, and the chemistry of the soil solution. The main biotic transformation elemental mercury undergoes is methylation to CH_3Hg^+ or $(CH_3)_2Hg$ by bacteria such as *Clostridium* (Andersson, 1979). As already mentioned the pH, redox potential, and ligands present in the soil will govern the final form of mercury in the soil solution. Mercury can form complexes with Cl^-, OH^-, NH_3, F^-, SO_4^{2-}, and NO_3^- but the latter four ligands are only important under unnaturally high concentrations, thus Cl^- and OH^- species dominate mercury chemistry (Schuster, 1991). These mercury species can then either react with soil constituents, precipitate or be abiotically or biotically reduced to Hg^0 (Andersson, 1979).

Mercury can interact with the mineral phase of soil in various ways: nonspecifically adsorbed, binding mainly due to electrostatic forces; specifically adsorbed, bound through covalent or coordinative forces; precipitated as pure mercury containing minerals; coprecipitated as sulphides, carbonates, hydroxides etc. (Schuster, 1991). Being a positively charged ion and existing as positively charged species, mercury can form electrostatic bonds with negatively charged soil particles. Mercury is concentrated in the clay fraction of soils because of the high surface area and negative charge of the clays (Andersson, 1979). Some mercury species are negatively charged and form electrostatic bonds with positively charged sites within soil. Different types of clays can adsorb varying amounts of mercury, depending on their surface area and cation exchange capacity: montmorillonite>vermiculite-chlorite>kaolinite (Obukhovskaya, 1982). Mercury will be associated with hydrated ferric oxides in soil (Forstner, 1990). Hg^{2+} binds to the ferric hydroxides by forming two bridges with the hydroxyl groups (Obukhovskaya, 1982). During the interaction of mercury and clay minerals, mercury is sorbed mainly through surface sorption and practically does not penetrate into the interpacket spacing (Obukhovskaya, 1982). The interaction of mercury with hydroxides is not through electrostatic forces alone, rather the mercury will exchange with the H^+ of the oxide

(Obukhovskaya, 1982). Although mercury can exist as positively charged species the mercury species that tend to dominate in soils are either neutral or negatively charged, limiting ion exchange on clay surfaces. Schuster (1991) stated that the mechanism for sorption on the solid phase is not ion exchange but rather stable complex formation or strong binding due to covalent or coordinative forces. This suggests that mercury's interaction with the clay phase in soil is not dominated by physical adsorption but rather chemical adsorption, which is a much stronger form of interaction than physical adsorption. The presence of Cl^- in solution will decrease the absorption of mercury as mercury chloride species are poorly adsorbed by soil minerals (Yin et.al., 1996).

Mercury can also be found associated with soil organic matter. Mercury has a high tendency to build complexes with OH^-, S^{2-} and S^- containing functional groups of organic ligands (Schuster, 1991, Yin et.al., 1996). Also, processes such as chelation, inner and outer sphere complex formation, adsorption, and coprecipitation occur simultaneously (Schnitzer and Kerndorff, 1981). The quality of the organic matter is also important in determining how much mercury is associated within the organic phase. Schuster (1991) reported that organic matter originating from different types of plants, indicating organic matter of different qualities, held different amounts of mercury. The different forms of organic matter, humic and fulvic acids and humin, can hold different amounts of mercury because of different molecular masses, varying densities of functional groups and varying solubilities (D'Itri, 1990). Many researchers have studied the interaction of mercury and humic acids and have discovered that mercury will form stable complexes with humic materials quite readily (Forstner, 1990, Schuster, 1991, Wallschlager, 1998). Mercury will also form complexes with soluble fulvic acids. Even though fulvic acids can hold more mercury, fulvic acids are less important than humic acids in determining the fate of mercury in soil, as surface soils tend to have fewer fulvic acids than humic acids (D'Itri, 1990). The complexes that mercury forms with humic and fulvic acids can be either soluble or insoluble, enabling mercury to enter the water phase. Few researchers have studied the interaction of mercury and humin in soil. The interaction of mercury species with organic matter can also result in the abiotic reduction of Hg^{2+} to Hg^0, perhaps resulting in mercury losses by volatilization (Allard and Arsenie, 1991).

Of course, in soils both inorganic and organic materials are present and can react with the mercury present in solution. At low mercury concentrations the relative importance of organic matter and clays varies with the quality and quantity of organic matter and clay minerals. Soil or horizons with higher organic matter contents tend to have more mercury associated with the organic matter (McKeague and Kloosterman, 1974, Dudas and Pawluk, 1976, Steinnes, 1990). Inorganic colloids tend to absorb more organomercurials while inorganic mercury compounds are more strongly and to a greater amount bound to soil organic matter (Schuster, 1991). The studies mentioned here are all on pristine soils; few researchers have investigated the distribution of mercury in contaminated soils.

1.5. Mercury-Hydrocarbon Co-contaminated Soils.

In Alberta, as a result of the actions of the oil and gas industries, the sites that are contaminated with mercury also tend to be contaminated with hydrocarbons. These petroleum hydrocarbons contain thousands of individual compounds in varying proportions and are complex and highly reduced, and hence very reactive. Hydrocarbons are composed mostly of hydrogen and carbon, with minor amounts of nitrogen, sulphur and oxygen. (CCME, 1997). The introduction of hydrocarbons to a soil may alter the local soil chemistry producing changes in micro and macroscale biotic communities (Saterbak et.al., 1999).

In soil, petroleum hydrocarbons can form a phase separate from the solid particles, aqueous liquid, or the air. For this reason they are sometimes referred to as non-aqueous phase liquids (NAPL). The NAPLs can either be more or less dense than water (LNAPL or DNAPL). The hydrocarbon phase will react with the other phases in soil and there are several characteristics used to describe these interactions. The octanol-water partition coefficient (Kow) is a measure of the hydrophobicity of a compound, a larger Kow means a compound is more hydrophobic. The Kow can be used to indicate to what extent hydrocarbons will enter the soil solution, to perhaps move with the soil solution. The vapour pressure of a hydrocarbon is a measure of volatility and can be used to estimate to what extent a hydrocarbon will volatilize and maybe leave the soil.

When hydrocarbons are in a soil they will become partitioned in the soil. Some of the hydrocarbons will coat soil particles. If enough hydrocarbons are present a separate NAPL phase may form, filling micropores or macropores. If enough pores are filled with hydrocarbons the movement of soil water may be inhibited. Since the hydrocarbons can penetrate into so many places in the soil there will be variability in the availability of the hydrocarbons, the hydrocarbons in the micropores will be less available and harder to remove from the soil than hydrocarbons in the macropores.

Hydrocarbon contaminated soils may pose a problem due to the toxicity, volatility or mobility of some of the constituents of the hydrocarbons. The reduced nature of hydrocarbons and the volatility of some hydrocarbons pose a fire or explosion risk. Most petroleum hydrocarbons are toxic to some degree and some may be mobile. Many of the more complex hydrocarbons are persistent in soil and the presence of hydrocarbons in soil poses aesthetic problems. Hydrocarbon contaminated soils may also experience a degradation of soil quality, the hydrocarbons may interfere with water retention and transmission and with nutrient supplies. (CCME, 1997). The presence of hydrocarbons in a soil may result in the failure of common acute toxicity tests such as earthworm reproduction and survival, plant germination and plant root length (Saterbak, et.al., 1999). Although consistent soil quality guidelines are lacking one interim soil quality guideline for total non-chlorinated polycyclic aromatic hydrocarbons (PAH) at commercial sites is 10 mg kg^{-1} (CCME, 1991).

When soils are contaminated with both mercury and hydrocarbons the two contaminants can interact and result in a phase containing both contaminants. The interactions between mercury and hydrocarbons are similar to the interactions between mercury and soil organic matter. Hydrocarbons have S and O containing active sites, as does soil organic matter. If the hydrocarbons are present in the soil at high enough concentrations the hydrocarbons will coat soil particles or form droplets within the soil. The mercury can then partition into these non-aqueous liquid phases.

These co-contaminated soils present unique problems related to the interactions of the contaminants. Any risk analysis must account for any differences in transmission and toxicity due to the presence of both contaminants. Remediation protocols should be able to remove both contaminants from the soil.

1.6. Reclaiming Co-contaminated Soils.

1.6.1. Calcium Hypochlorite.

Oxidants can be used to solubilize mercury (Pedroso et.al., 1994), and will also attack hydrocarbon bonds (Wade, 1991). Fenton's reagent, hydrogen peroxide and sodium hypochlorite have all been studied by different researchers (Pedroso et.al., 1994, Wilhelm and McArthur, 1995) and have been found to be effective in removing mercury from different media, including sediments and soils.

Few researchers have studied calcium hypochlorite but the mechanism by which it reacts is similar to that of sodium hypochlorite. Calcium hypochlorite has several advantages over sodium hypochlorite. Sodium hypochlorite introduces sodium ions into the soil solution, possibly at high enough concentrations to deflocculate the soil particles, while calcium hypochlorite releases Ca^{2+} into solution which competes with Hg^{2+} for binding sites on clay particles (Forstner, 1995). This deflocculation of soil particles could potentially increase removal of soil mercury by exposing more soil surface area to the solution but would be detrimental after treatment due to a loss in soil structure. The placement of Hg^{2+} within the lyotropic series explains why Ca^{2+} will compete with Hg^{2+} for binding sites on clays better than Na^+: $Li \approx Na > K \approx NH_4 > Rb > Cs \approx Mg \approx Hg > Ca > Sr \approx Ba > La \approx Al > Th$ (ease of removal) (Bohn et al., 1979).

The basis for using hypochlorite is that it converts insoluble or slightly soluble forms of mercury into more soluble forms, as in the following reactions (Pedroso et.al., 1994):

1. $HgS(s) + 4\ OCl^- \rightarrow HgCl_2(aq) + 2Cl^- + SO_4^{2-}$

2. $Hg(l) + Cl^- + OCl^- + H_2O \rightarrow HgCl_2(aq) + 2OH^-$

The pH of the soil should be above 5 to prevent the production of chlorine gas. If the pH of the soil is too high (above 8) mercuric oxides or oxychlorides may precipitate (Pedroso et.al, 1994).

The addition of calcium hypochlorite to the soil will increase the concentration of chloride ions in the soil solution. An increase in chloride is expected to increase the solubility of mercury because mercury chloride compounds are more soluble than other mercury compounds (Nriagu et.al., 1979):

$Hg = 60 - 80\ \mu g / L$ @20°C

$HgS = \sim 10\ \mu g / L$

$HgO = 53\ 000\ \mu g / L$

$HgCl_2 = 70\ 000\ mg / L$

The extra chloride ions are also expected to aid in the formation of $HgCl_4^{2-}$, a very soluble form of mercury (Wilhelm and McArthur, 1995):

$Hg^{2+}(aq) + Cl^- \rightarrow HgCl^+$ $K_1 = 5.8*10^6$

$HgCl^+ + Cl^- \rightarrow HgCl_2$ $K_2 = 2.5*10^6$

$HgCl_2 + Cl^- \rightarrow HgCl_3^-$ $K_3 = 6.7$

$HgCl_3 + Cl^- \rightarrow HgCl_4^{2-}$ $K_4 = 13$

$Hg^{2+} + 4\ Cl^- \rightarrow HgCl_4^{2-}$ $\beta_4 = 1.3*10^{15}$

The presence of excess chloride is expected to drive these reactions forward and allow more $HgCl_x$ complexes to enter solution. The chloride ion has the ability to complex with the adsorbed mercury on the surfaces of the sediment components and subsequently enter into the solution phase (Wang, 1991). If the concentration of Cl^- becomes too high, mercuric chloride may precipitate. If the solubility product of free Hg^{2+} and Cl^- becomes greater than $6.3x10^{-5}$ $HgCl_{2\,(s)}$, may precipitate.

Calcium hypochlorite will produce free radicals when exposed to UV light or heat. Free radicals are capable of breaking the carbon-carbon and carbon-hydrogen bonds of hydrocarbons. The hypochlorite free radical, chloride free radical and the hydroxyl free radical can degrade hydrocarbons, as in the following reactions (Venkatadri and Peters, 1993, Wade, 1991):

$$RH + X^{\circ} \rightarrow HX + R^{\circ}$$

(R=hydrocarbon, X°=free radical, R°=hydrocarbon with a free radical active site)

The reaction can proceed to polymerize, degrade, halogenate or hydrolyze the existing hydrocarbons.

Polymerization:

$$\begin{tikzcd} R_1 + X^{\circ} \rightarrow R_1^{\circ} + X \arrow[dr] & \\ & R_1R_2 + 2X \\ R_2 + X^{\circ} \rightarrow R_2^{\circ} + X \arrow[ur] & \end{tikzcd}$$

Degradation:

$$R_1\text{-}R_2 + X^0 \rightarrow R_1^0 + R_2^0 + X$$

Halogentation:

$$R_1{=}R_2 + X^0 \rightarrow R_1\text{-}R_2\text{-}X$$

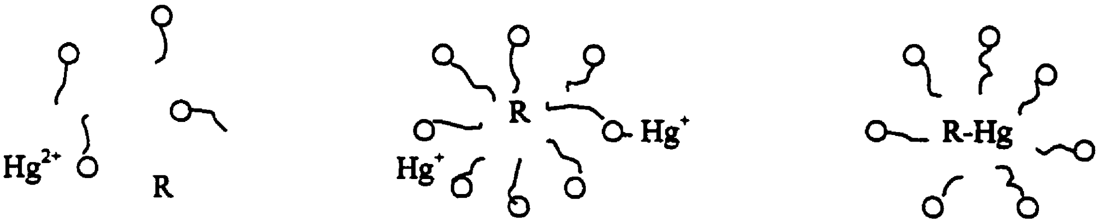
Hydrolysis:

$$R_1{=}R_2 + OH^0 \rightarrow R_1\text{-}R_2\text{-}OH$$

1.6.2. Surface Active Agents.

Treating contaminated soils with a surface active agent (surfactant) is meant to reduce the amount of hydrocarbons in the soil. If the soil is contaminated with mercury along with the hydrocarbons the presence of mercury may pose problems when disposing of the treatment waste water as the waste water may have elevated concentrations of mercury. Conversely, a dianionic surfactant such as Dowfax 8390 has the potential to reduce the concentration of mercury within the soil along with the hydrocarbon content.

The action by which surfactants work is detailed in Appendix 1 and is summarized in Figure 1. Below the critical micelle concentration (CMC) micelles will not form and hydrocarbons and mercury may be solubilized through lowering surface tension and electrostatic attraction respectively (a). Above the CMC micelles can form and hydrocarbons will be attracted to the center of the micelle and mercury can be attracted electrostatically to the micelle (b) or enter the micelle while bonded to a hydrocarbon (c).



a. Below CMC b. Above CMC c. Above CMC

Figure 1. Surfactant solubilization of hydrocarbons and mercury.

1.6. Purpose of Study.

Much is known about the chemistry and behavior of mercury in soils. It is known that mercury will bind to organic matter and form stable compounds with sulphides. Most of our knowledge on mercury in soil is from studies that have been performed on uncontaminated soils. To date there has been no study on the re-distribution of elemental mercury in soil following a spill. The primary objective of this study is to determine how mercury is distributed in co-contaminated soils. All of the soils used in this study were originally contaminated with elemental mercury and hydrocarbons. To achieve this first objective, a sequential extraction, similar to that proposed by Eganhouse et.al in 1978 and later incorporated into standard methods of soil analysis (Crock, 1996), was used. The sequential extraction was originally developed to determine the distribution of mercury at background levels within the soil and had only eight steps. Two additional steps were added to the eight originally proposed in order to analyze the contaminated soils used in this study. The ten extraction steps will identify the:

1. Mercury in the total extractable organic (TEO) phase
2. Elemental mercury
3. Water soluble mercury,
4. Ion exchangeable mercury,
5. Mercury associated with organic acids (two steps),
6. Mercury associated with organic bases,
7. Mercury associated with residual organic matter (two steps)
8. Mercury associated with the mineral fraction of soil.

The results of the sequential extraction will provide data on the distribution of mercury within soil.

A secondary objective of this study, beyond determining the distribution of mercury in co-contaminated soils, is to test whether two protocols have the potential to remediate co-contaminated soils. The ideal protocol would be one that could remove all contaminants in the same treatment. The two treatments investigated in this study, calcium hypochlorite and Dowfax 8390, have the potential, according to theory, to remove the two contaminants of concern, mercury and hydrocarbons, from the soils. The first method proposed to remediate mercury contaminated soils is to treat the soils with calcium hypochlorite. Nine co-contaminated soils were treated with a solution of hypochlorite, four soils were treated once and five soils were treated three times. Several soils that are contaminated with hydrocarbons and mercury will be treated with a solution of Dowfax 8390 in order to determine if the soil mercury and hydrocarbon concentrations will decrease and to determine if mercury becomes elevated in the waste water (Appendix 3).

The final objective of this study is to determine which forms of mercury the calcium hypochlorite treatment removes. The sequential extraction will be performed on untreated contaminated soils and contaminated soils treated with a solution of calcium hypochlorite. The forms of mercury oxidized by the calcium hypochlorite can then be determined.

2.0. Materials and Methods

2.1. Soil Samples

Soils M11-M18 were received from Komex International Ltd. in early July 1998 and were stored in glass containers at 4°C until the soils were used. In late July 1998 the soils were air dried, sieved to 2mm and then stored in nalgene containers at 4°C when not in use. These eight soils were all sampled from sites in central Alberta. The sites were all located in or next to agricultural fields at well metering sites. The source of contamination was elemental mercury released from manometers located at well heads. Soil M19 was sampled from the Turner Valley Gas Plant in October 1995 then stored at 4°C in a plastic container until the spring of 1996 when the soil was air-dried and then sieved. Following sieving soil M19 was stored in a glass Kerr jar at room temperature. The source of contamination for this soil was also elemental mercury released from manometers.

2.2 Routine Characterizations.

The particle size distribution was determined for each soil. Approximately 5g of air dry soil was deflocculated using a Cole Parmer Ultrasonic Homogenizer. The clay sized fraction was removed following sedimentation and the remaining particles were then separated into sand and silt size fractions through sieving, the fractions were allowed to dry and the weight of sand and silt was determined. The weight of the clay fraction was found by difference.

The concentrations of chloride (Cl^-), sulphate (SO_4^{2-}) and total carbonates were determined from a saturated paste extract (Rhoades, 1982). The saturated paste was prepared for each soil by equilibrating approximately 100g of saturated soil for 24 hours. The solution was then removed from the soil through vacuum filtration. Total carbonates were determined using a titration method, Cl^- using a colourimetric method and SO_4^{2-} was determined using a turbidimetric method (Adriano and Doner, 1982, Tabatabai, 1982).

Total soil carbon was determined for each soil using a Leco Carbon Auto-analyzer. Total inorganic carbon was determined using a titration method (Bundy and Bremner, 1972). The organic carbon fraction was calculated by subtracting the total inorganic C from the total C.

The pH of the soils were measured on a 1:2 soil:water mixture using a digital pH meter with a glass electrode. The electrical conductivities of the soils were measured on a saturated paste extract using a Model 31 Conductivity Bridge.

2.3. Mercury Analysis.

The mercury content of soil samples and solutions was determined using Cold Vapour Atomic Absorption (CVAA). Melton, Hoover and Howard (1971) developed the method used for digesting soil samples in order to determine soil mercury content. The same digestion protocol was followed for all types of samples used in this study. The sample was placed into a 100mL volumetric flask along with 5mL of $K_2S_2O_8$ and 15mL of concentrated nitric acid. The flask containing the sample was placed on a hot plate at a temperature of 83±2°C for approximately 3 hours. The flask was then removed from the hot plate, allowed to cool and then the solution was made up to volume. The solution was diluted to a concentration that falls within the range of the standard curve. Four standard mercury solutions, 0.05µg, 0.10µg, 0.20µg, 0.40µg; were analyzed so a standard curve could be created.

A sample of the solution was placed in a 125mL Erlenmeyer flask (no. 4980) and 40 mL of distilled deionized water was added. A stannous chloride solution (20mL) was added to the sample solution, reducing the mercuric mercury in the solution to elemental mercury vapour. The mercury vapour was forced out of the flask using a Perkin-Elmer Mercury Analysis System aerator and through a quartz detection cell. The concentration of mercury within the detection cell was determined using a Perkin-Elmer Atomic Absorption Spectrophotometer Model 2380 set up for cold vapour analysis for mercury content. A Perkin-Elmer recorder model R50 was used to record the output of the spectrophotometer.

2.4. Total Extractable Organics.

The total extractable organic (TEO) content for each soil was determined in triplicate using Soxhlet extraction with dichloromethane (MeCl) as an extractant. A 5g sample of air dry soil was mixed with 1g of anhydrous sodium sulphate in a cellulose extraction thimble (Whatman cellulose extraction thimble 30mm x 80mm). The soil was extracted with 100mL of MeCl for 16 hours. The extracted solution was concentrated to 50mL. The TEO content of each soil was determined by allowing 40mL of this solution to evaporate in an aluminum weighing dish; the weight of the evaporite remaining after evaporation was used to calculate the TEO content of the soil. The remaining 10mL of solution was stored in a 15mL amber glass vial at 4°C until used in determining the mercury content of the TEO fraction, the first step of the sequential extraction.

2.5. Calcium Hypochlorite Treatment.

Each soil was treated once with a 0.4M calcium hypochlorite solution in an effort to reduce the total mercury content of the soil. In a previous study on the Turner Valley soils a 0.4M solution of calcium hypochlorite was found to be effective in reducing the concentration of mercury in contaminated soils (Dowey, 1998). Each soil was mixed with the calcium hypochlorite solution at a ratio of 20g soil:100g solution in a 250mL nalgene centrifuge container. The container was placed on a flatbed shaker overnight. The soil and solution were separated by centrifugation and decanting of the supernatant. The supernatant was filtered through #40 ashless filter paper to remove the remaining particles. Both the soil and solution were then analyzed for mercury content.

Four soils were chosen to be treated two more times with the calcium hypochlorite solution (Figure 2). The four soils treated twice were M11, M14, M17 and M18. The same method described above was followed except only 12g of soil and 60g of solution were used for the second treatment, for the third treatment 8g of soil and 40g of solution were used, maintaining the 1:5 ratio.

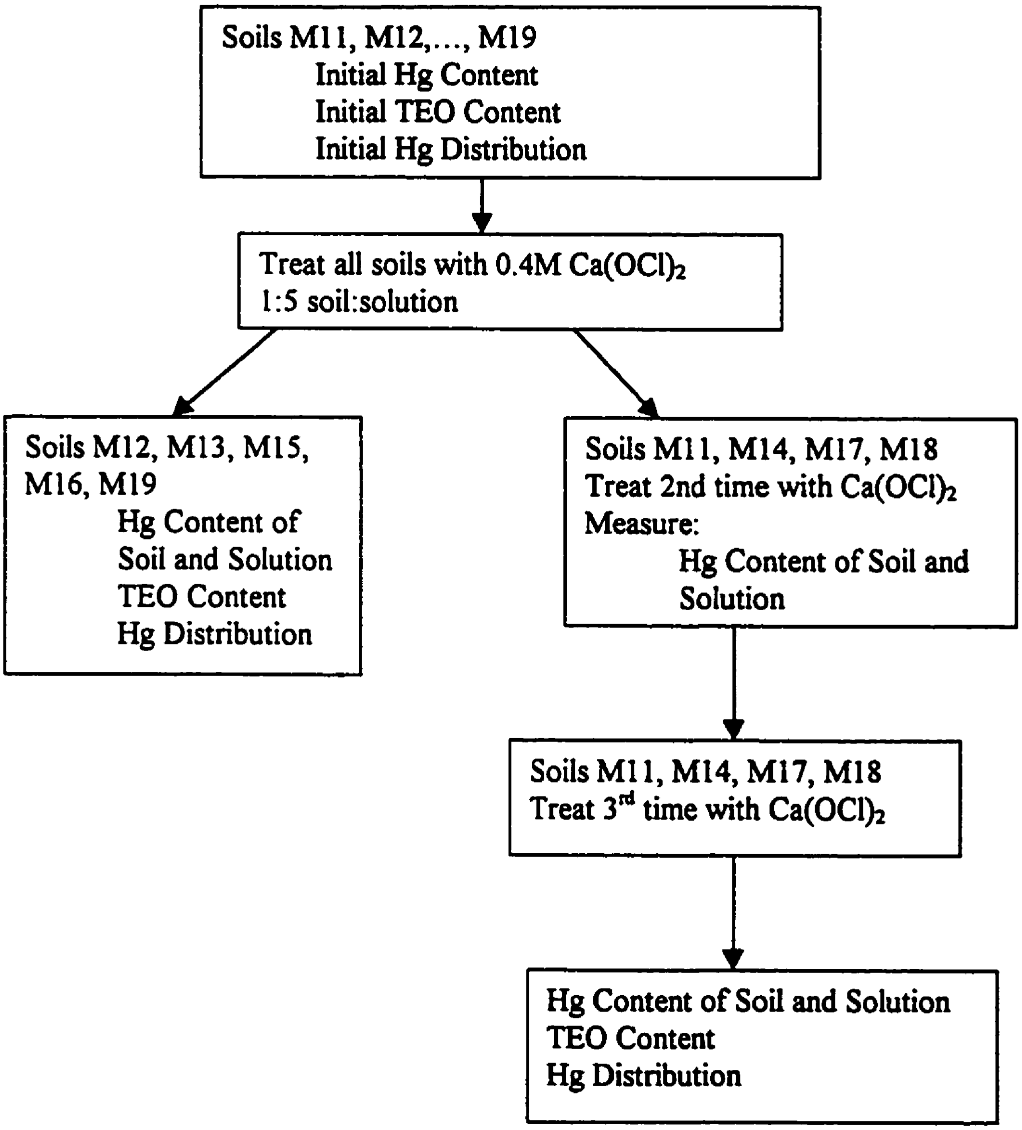


Figure 2. Treatment Protocol.

2.6. Sequential Extraction.

A ten step sequential extraction was used to determine the distribution of mercury in soil. The original sequential extraction proposed by Eganhouse et.al., (1978) and later adopted by the SSSA (Crock, 1996) was developed for uncontaminated soils and only had eight steps. The eight steps determined mercury in the water phase, ion exchangeable mercury, mercury associated with organic acids (2 steps), mercury associated with organic bases, residual organic matter bound mercury (2 steps) and mercury in the mineral phase. An additional two steps used in this study because of the high mercury and hydrocarbon content and were performed before the original eight. The additional steps are a measurement of TEO-extractable mercury and elemental mercury content. The TEO extractable mercury was determined first. The method described under section 2.4 was followed to extract the TEO content. The 10 mL of dichloromethane solution was analyzed for mercury content. Three 1 mL subsamples were analyzed for mercury.

The elemental mercury content was then measured. Elemental mercury content was measured by determining the total soil mercury content before and after thermal desorption. A 7g soil sample was taken, a 1g sub-sample was analyzed immediately for total mercury, the remaining soil was placed in a 250mL Erlenmeyer flask. The flask was placed on a hot plate, inside of a fume hood, at 85±2 °C for 16 hours. This will cause any elemental mercury to volatilize (Windmoller et al., 1996). A 1g sample of the thermally treated soil was then measured for total mercury content and elemental mercury content determined by difference between thermally treated soil and non-treated soil.

The remaining eight steps were performed in triplicate on 1.5g samples and were:

1. To soil sample, add 100mL distilled, de-ionized water, shake for 30 min., centrifuge, filter (Glass Fiber filter paper) and analyze extract using CVAA. This procedure extracts the mercury in the water phase (WP).

2. Residue extracted with 100mL of 1N $MgCl_2$, shake on flatbed shaker for 30min, centrifuge, decant and analyze extract. This extracts the ion exchangeable mercury (IE).

3. As in step 1 using 0.2N NaOH. This procedure extracts mercury associated with organic acids (OAI).

4. As in step 1 using 0.005N NaOH, extracting mercury associated with any remaining organic acids (OAII).

5. As in step 1 using 0.005N CH_3COOH. This extracts mercury associated with organic bases (OB).

6. Digest residue with 50mL of 3% H_2O_2 (pH=2) at 85°C for 2h. Dilute contents to 100mL using DDW, shake for 30min., centrifuge, filter, and analyze filtrate. This extracts mercury associated with residual organic matter (OMI).

7. Digest residue with 50mL of 30% H_2O_2 (pH=2) at 85°C for 5h. Dilute contents to 100mL using DDW, shake for 30 min., centrifuge, filter, and analyze filtrate. This extracts mercury associated with residual organic matter not oxidized by the 3% H_2O_2 (OMII).

8. Analyze residue following procedure of Melton et al. (1971) This extracts all remaining mercury and is assumed to represent mercury associated with the mineral phase (Min)

2.6.1. Using the Sequential Extraction.

The sequential extraction is designed to determine the forms of mercury in soil, or where in soil mercury is found. Each step will extract only a certain form of the mercury that occurs in soil. The forms are likely not discrete as one extractant may extract forms of mercury that are not included in the definition of that extractant. The form of mercury extracted is operationally defined and the mercury species cannot be determined without some ambiguity.

The sequential extraction was performed first on all nine of the untreated soils. This provided data on the distribution of anthropogenic mercury in soil. After treating all nine soils once with calcium hypochlorite, five soils were analyzed using the sequential extraction protocol. The five soils were M12, M13, M15, M16 and M19. This provided data on the distribution of mercury after treatment with calcium hypochlorite. The remaining four soil underwent the sequential extraction after being treated a total of three times with the calcium hypochlorite solution. By performing the extraction on hypochlorite treated and untreated soils, the forms of mercury that are removed by the $CaOCl_2$ treatment can be determined.

2.7. Water Phase Mercury.

Mercury in the water phase is the third step in the sequential extraction. This extract only provides the total mercury that is in solution with no information on the form of the soluble mercury. To learn more about the form of mercury in solution the extracted water phase mercury was analyzed in two ways. One half of the extracted solution was analyzed following the prescribed digestion method using nitric acid. The second half of the extracted solution was not digested before being analyzed for mercury content.

2.8. Geochemical Modeling.

The mercury speciation was modeled using Solmineq.88 (ARC, 1988). The concentration of mercury found in the undigested extracted water samples was assumed to represent total mercury in solution. A representative mercury concentration was used in all modeling scenarios. Several scenarios were modeled to investigate how differing the concentrations of the ligands (OH^-, HCO_3^-, Cl^-, SO_4^{2-}) would change the final mercury speciation. The scenarios investigated were:

1. High pH, high carbonate, high Cl^-.

   Input parameters:

   $pH = 8.5$
   $SO_4^{2-} = 5.0\ mg\ L^{-1}$
   $Cl^- = 150\ mg\ L^{-1}$
   $CO_3^{2-} = 150\ mg\ L^{-1}$
   $HCO_3^- = 300\ mg\ L^{-1}$
   $Hg = 1.5\ mg\ L^{-1}$
   $Ca^{2+} = 100\ mg\ L^{-1}$
   $Na^+ = 115\ mg\ L^{-1}$
   $Mg^{2+} = 48\ mg\ L^{-1}$
   $K^+ = 117\ mg\ L^{-1}$

2. High pH, high carbonate, low Cl^-.

Input parameters:

pH = 8.5
SO_4^{2-} = 5.0 mg L^{-1}
Cl^- = 20 mg L^{-1}
CO_3^{2-} = 150 mg L^{-1}
HCO_3^- = 300 mg L^{-1}

Hg = 1.5 mg L^{-1}
Ca^{2+} = 100 mg L^{-1}
Na^+ = 46 mg L^{-1}
Mg^{2+} = 48 mg L^{-1}
K^+ = 117 mg L^{-1}

3. Neutral pH, HCO_3^- dominated.

Input parameters:

pH = 7.2
SO_4^{2-} = 5.0 mg L^{-1}
Cl^- = 20 mg L^{-1}
HCO_3^- = 300 mg L^{-1}

Hg = 1.5 mg L^{-1}
Ca^{2+} = 50 mg L^{-1}
Na^+ = 11.5 mg L^{-1}
Mg^{2+} = 18 mg L^{-1}
K^+ = 39 mg L^{-1}

4. Neutral pH, Cl^- dominated.

Input parameters:

pH = 7.2
SO_4^{2-} = 5.0 mg L^{-1}
Cl^- = 100 mg L^{-1}
HCO_3^- = 25 mg L^{-1}

Hg = 1.5 mg L^{-1}
Ca^{2+} = 80 mg L^{-1}
Na^+ = 184 mg L^{-1}
Mg^{2+} = 72 mg L^{-1}
K^+ = 117 mg L

5. Acidic pH, SO_4^{2-} dominated.

Input parameters:

pH = 6.3
SO_4^{2-} = 500 mg L^{-1}
Cl^- = 20 mg L^{-1}
HCO_3^- = 25 mg L^{-1}

Hg = 1.5 mg L^{-1}
Ca^{2+} = 240 mg L^{-1}
Na^+ = 46 mg L^{-1}
Mg^{2+} = 36 mg L^{-1}
K^+ = 39 mg L

The concentrations of metals were chosen to maintain an ion balanced solution.

3.0. Results

3.1. Soil Characteristics.

The morphological and mineralogical information presented on soils M11-M18 was gathered from soil survey maps (Bowser et al., 1962) using the legal land locations provided by Komex Int. The soils M11-M18 were all collected within a relatively small geographic area and have similar characteristics. They are all either Orthic Black Chernozems or Eluviated Black Chernozems, soil M16 is slightly saline. The parent geological material for these eight soils is lacustrine or alluvial-lacustrine. The dominant compounds that the soils evolved from would include limestone, dolomite, shale, and quartzitic sandstone, the dominant clay in these soils is montmorillonite. Soil M19 has a slightly different history. Soil M19 is an Orthic Regosol and developed over glacio-lacustrine terrain (Kohut et al., 1995). This soil would have a similar mineralogy to the other eight soils. The dominant clays of soil M19 include micas and kaolinite, with minor amounts of chlorite and vermiculite.

The various soil characteristics, including texture, pH, electrical conductivity, organic matter content and the concentrations of SO_4^{2-}, Cl^-, and HCO_3^- are summarized for each soil in tables 1 and 2.

Table 1. Whole Soil Characteristics.

Soil	Texture	% Clay	pH	% O.M.	% T.C.	% T.I.C.
M11	SiL	25	7.0	3.34	2.15	0.212
M12	SL	17	7.4	3.65	2.33	0.212
M13	L	23	7.4	3.73	2.44	0.274
M14	L	18	7.3	5.68	3.63	0.338
M15	SL	12	7.3	12.19	7.45	0.381
M16	SL	12	6.7	5.87	3.60	0.194
M17	SL	12	7.4	2.79	1.78	0.164
M18	SL	10	7.6	3.98	2.62	0.312
M19	L	14	7.0	5.08	3.19	0.243

%O.M. = % Organic Matter; %T.C.=% Total Carbon; % TIC= % Total Inorganic C

Table 2. Pore Water Chemistry.

Soil	E.C. ($dS\ m^{-1}$)	SO_4^{2-} ($mg\ L^{-1}$)	Cl^- ($mg\ L^{-1}$)	NO_3^- ($mg\ L^{-1}$)	HCO_3^- ($mg\ L^{-1}$)
M11	1.73	20	54	14	310
M12	0.80	24	20	15	120
M13	0.99	22	25	13	150
M14	1.39	22	38	12	310
M15	0.28	16	27	10	280
M16	2.32	26	77	13	250
M17	0.63	32	13	13	220
M18	0.63	21	12	10	280
M19	0.82	140	11	12	250

E.C. = Electrical Conductivity.

All nine soils are similar in their physical and chemical characteristics. They are all loam (L, SL, SiL) textured and have similar clay contents. Two soils (M11, M13) have a higher clay content than the other seven soils. The type of clay minerals found in each of the soils except M19 is also expected to be similar; the dominant clay will be montmorillonite. The dominant clays of soil M19 include micas and kaolinite, with minor amounts of chlorite and vermiculite. Other minerals expected to be present in all soils include dolomite, sesquioxides, and quartz. The dominance of montmorillonite in soils M11-M18 would allow for small amounts of mercury to be adsorbed on clay cation exchange sites. The dominance of kaolinite in soil M19 would preclude much mercury being adsorbed on clay cation exchange sites.

The organic matter content of the nine soils varies slightly. The organic matter content will determine, more than the clays, how much mercury is adsorbed on cation exchange sites. In these nine soils the cation exchange capacity will largely be determined by the organic matter content. The quality and quantity of organic matter will also determine how much mercury binds chemically to the organic matter active sites. The quality of organic matter in the soils is partially determined by the vegetation grown on the soil. Nothing is known about the vegetative history of the sites so there are no conclusions that can be drawn about the quality of organic matter in each soil.

The chemistry of each soil is dominated by bicarbonate. Chloride and sulfate are not present in large concentrations, except in soil M19, which has a high concentration of sulfate. All of the soils are well drained surface soils. All of the soils are aerobic and have near a neutral pH.

The geochemical environment presented by each soil will govern the mercury speciation and behavior within the soil. The species that can form with the ligands present include $HgCl_x$, $HgSO_4$, $HgNO_3$, HgOH, and $Hg(OH)_2$. $HgNO_3$ will not be an important species at the low concentrations of NO_3 that are present in the soils. Since the chemistry of each soil is dominated by HCO_3^- and the concentrations of sulfate and chloride are relatively low the mercury speciation should be dominated by mercury hydroxides.

3.2. Soil Mercury Distribution.

3.2.1. Initial Distribution.

The untreated contaminated soils used in this study can be separated into two groups based upon the distribution of mercury within them, primarily the relative amount of mercury found in the mineral phase (Figure 3 a, b). Soils M13, M14, M15, M19 have between 22-36% of their total mercury in the mineral phase while soils M11, M12, M16, M17, M18 have less than 10% of total mercury in the mineral phase. In all soils the majority of the mercury is found associated with organic matter, ranging between 62% and 87% of the total mercury. Of the mercury associated with organic matter, for all soils except M15, the fraction labeled Organic Matter II is the dominant fraction. For soil M15 the dominant fraction is the fraction labeled Organic Acids II.

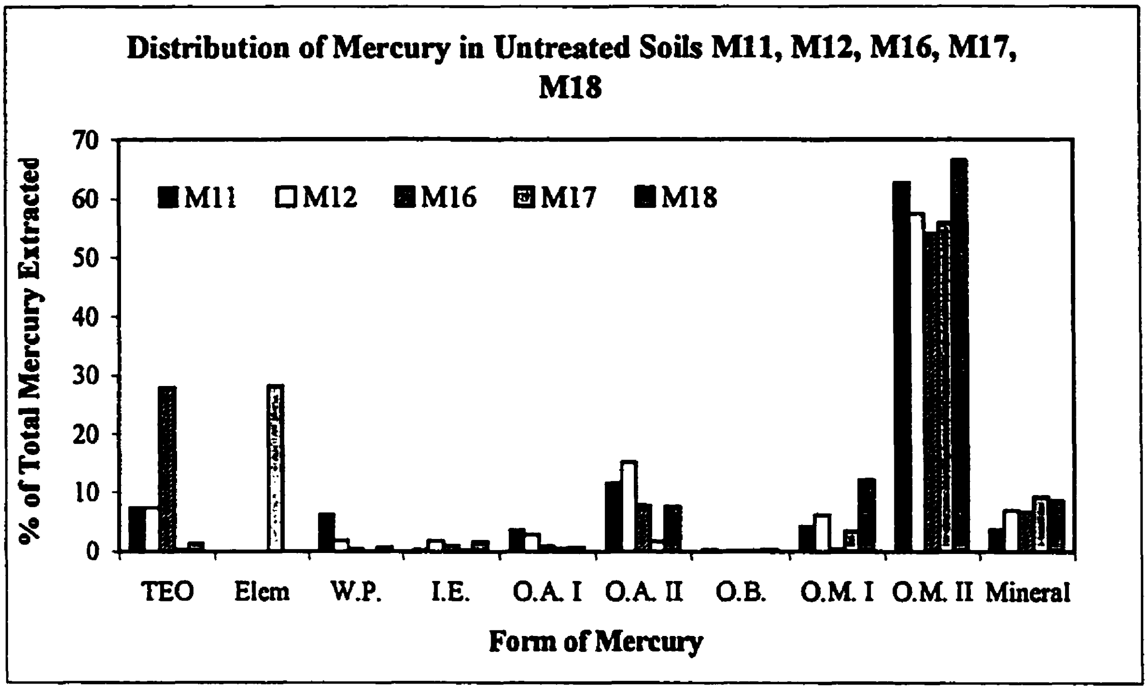


Figure 3a. Initial Mercury Distribution in Soils M11, M12, M16, M17, M18.

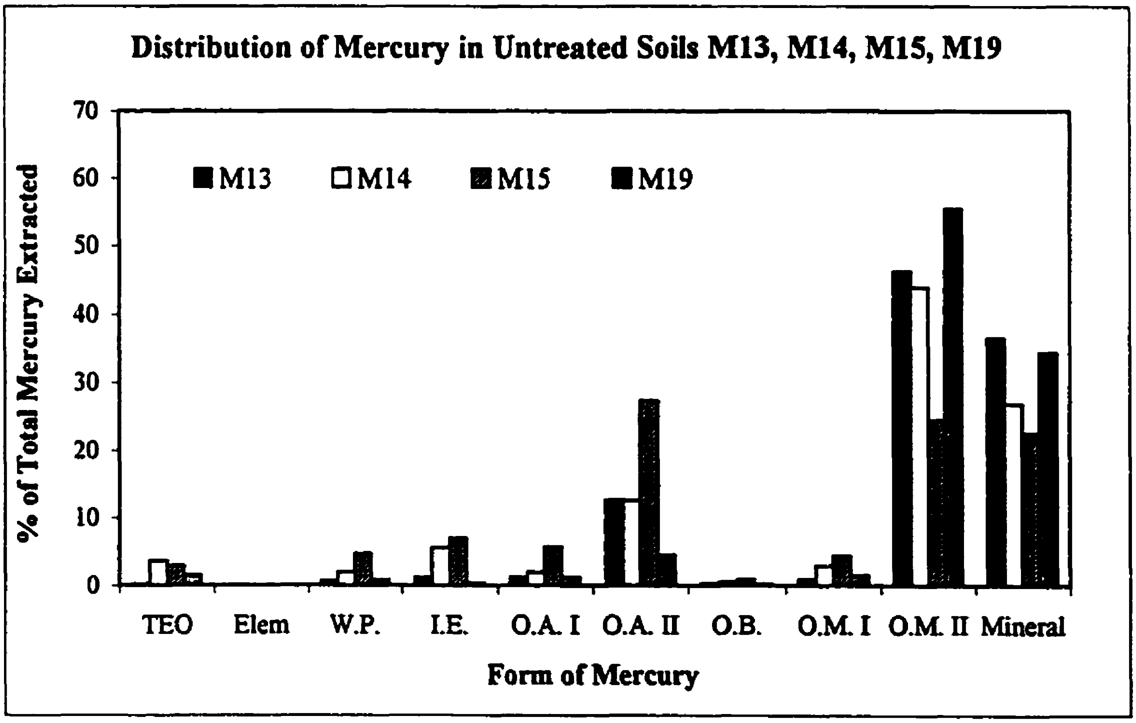


Figure 3b. Initial Mercury Distribution in Soils M13, M14, M15, M19.

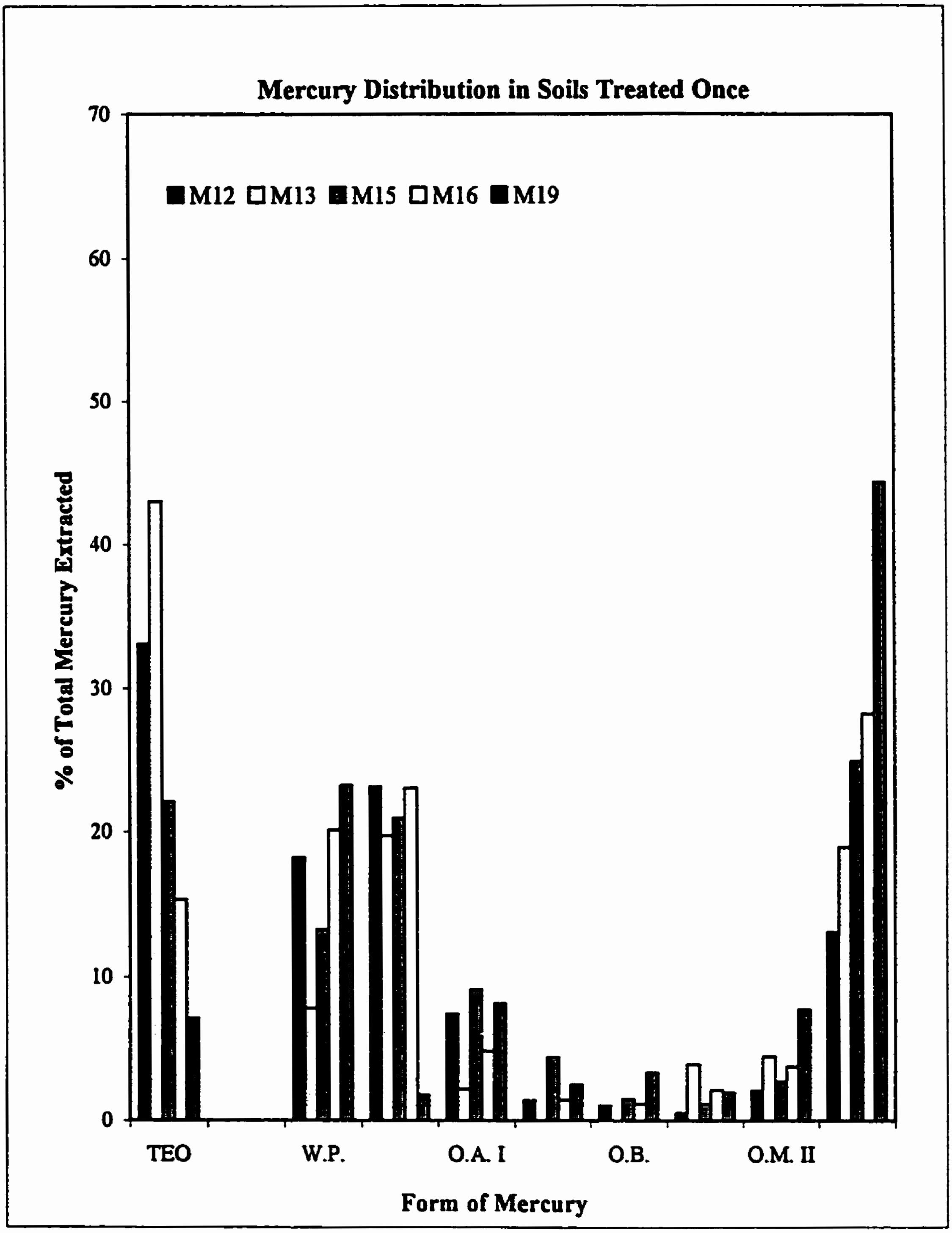


Figure 4. Distribution of Mercury in Soils After One Hypochlorite Treatment.

3.2.2. Distribution of Mercury in Soils Treated One Time.

After treating the soils once with calcium hypochlorite the mercury remaining in the soil is mainly associated with the TEO fraction, for soils M12 and M13, or with the mineral fraction, for soils M15, M16, M19 (Figure 4). For all soils, after one treatment, the relative amount of mercury found in the water phase and ion exchangeable extracts increased 7-22% and 2-22% respectively (Figures 5a-e). The relative amount of mercury associated with the TEO fraction also increased between 5-34% in all soils except soil M16, in which it decreased 13%. For each soil, except M13, the relative amount of mercury associated with the mineral phase also increased 6-21%, for soil M13 the relative amount decreased by 17%. The mercury associated with the OAII and OMII decreased 7-23% and 21-56% respectively relative to the other forms of mercury in each soil after treatment with calcium hypochlorite.

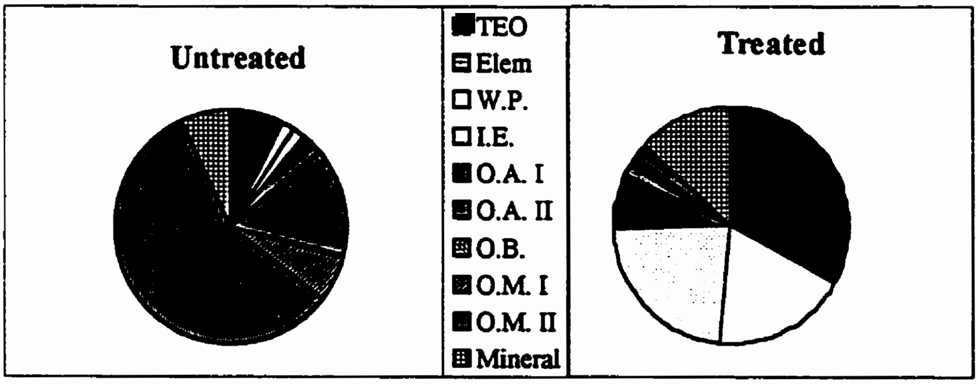


Figure 5a. Mercury Distribution in Soils – Pre- and Post-Treatment Soil M12.

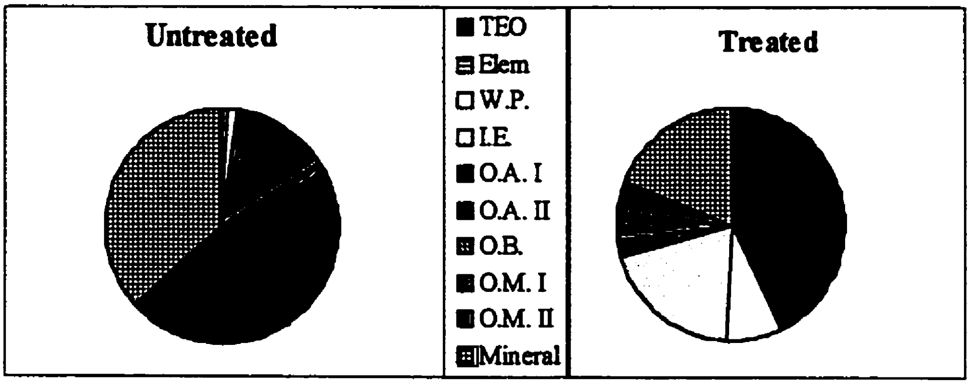


Figure 5b. Mercury Distribution in Soils – Pre- and Post-Treatment Soil M13.

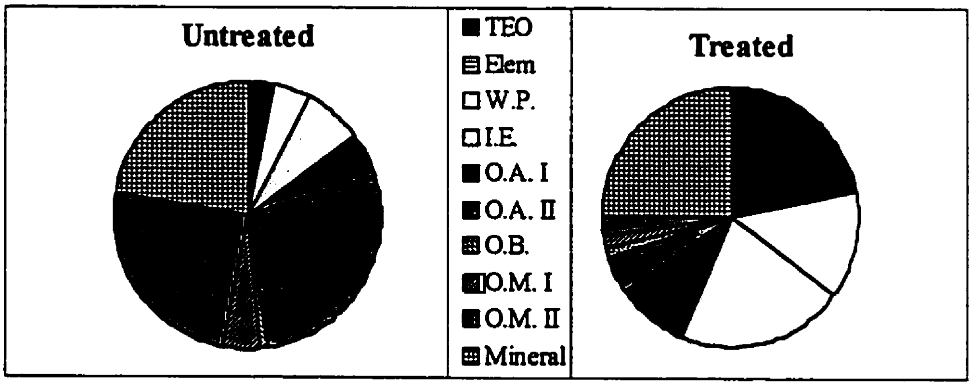


Figure 5c. Mercury Distribution in Soils – Pre- and Post-Treatment Soil M15.

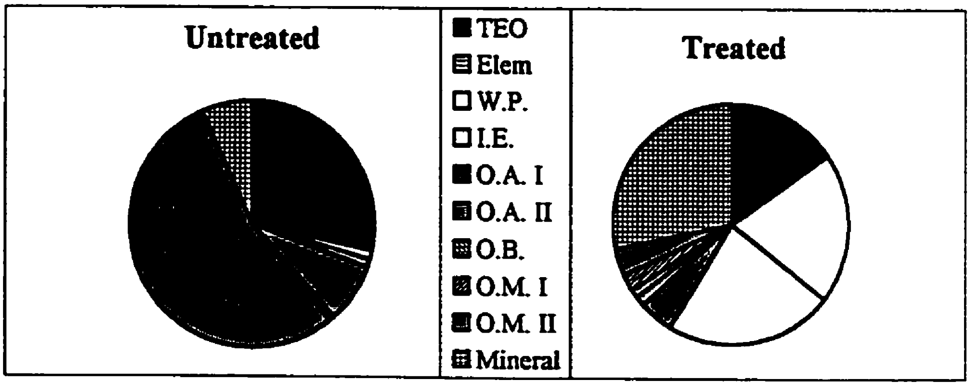


Figure 5d. Mercury Distribution in Soils – Pre- and Post-Treatment Soil M16.

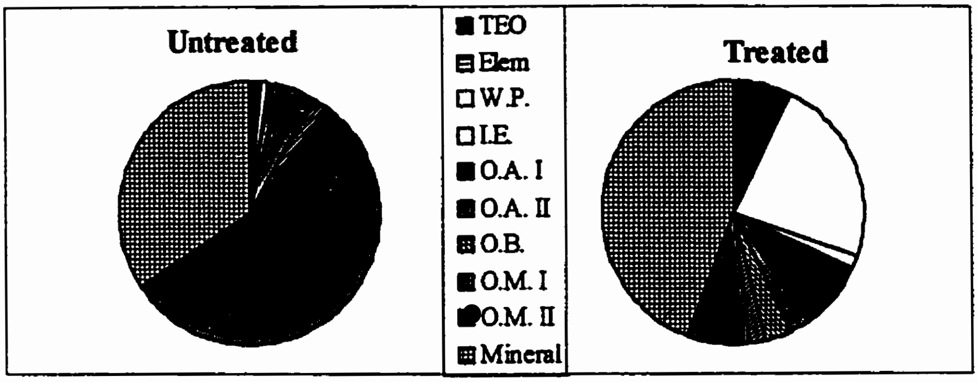


Figure 5e. Mercury Distribution in Soils – Pre- and Post-Treatment Soil M19.

When comparing the absolute concentrations of each form of mercury after treating the soils with calcium hypochlorite (Tables 3a-e) a different pattern emerges than when comparing the relative amounts of each form of mercury (Figure 5). The concentration of mercury associated with the TEO fraction increased in soils M13 and M15, decreased in M16 but did not change significantly in soils M12, M19. The concentration of mercury found in the water phase (mg Hg kg^{-1} soil) increased in all of the soils treated once with hypochlorite, except for soil M15 in which the concentration of mercury in the water phase did not change significantly. The amount of mercury in the ion exchangeable fraction also increased in soils M12, M13 and M16 but showed no significant change in soils M15 and M19. The concentration of mercury in the OAI phase decreased in soils M12, M13 and M15 but was not significantly different in soils M16 and M19. After treating the soils once the concentration of Hg in the OAII and OMII and mineral fractions decreased in each soil, except soil M16 which showed no change in the OMII and mineral fractions.

Table 3a. Change in mercury distribution in soil M12 after one $Ca(OCl)_2$ treatment.

Soil M12 Hg Form	Initial (mg Hg/kg soil)	Treated (mg Hg/kg soil)	% Changee	Significant (Y/N)*
TEO	5.8	5.1	+12	N
Elem.	0.0	0.0	0	N
W.P.	1.4	2.8	+100	Y
I.E.	1.4	3.5	+150	Y
O.A.I	2.2	1.1	-50	Y
O.A.II	12	0.2	-98	Y
O.B.	0.2	0.2	0	N
O.M.I	3.2	0.1	-97	Y
O.M.II	45	0.3	-99	Y
Mineral	5.4	0.2	-96	Y
Total Extracted	77	15	-81	Y
Total in Soil	120	32		
% Recovered	64	47		

* 0.01 level of significance.

Table 3b. Change in mercury distribution in soil M13 after one $Ca(OCl)_2$ treatment.

Soil M13 Hg Form	Initial (mg Hg/kg soil)	Treated (mg Hg/kg soil)	% Change	Significant (Y/N)*
TEO	0.3	4.4	+1200	Y
Elem.	0	0	0	N
W.P.	1.4	3.2	+129	Y
I.E.	2.6	8.0	+208	Y
O.A.I	2.5	0.8	-68	Y
O.A.II	26	0.0	-100	Y
O.B.	0.5	0.0	-100	Y
O.M.I	2.0	1.6	-20	N
O.M.II	96	2.0	-98	Y
Mineral	75	7.6	-90	Y
Total Extracted	210	28	-87	Y
Total in Soil	280	68		
% Recovered	75	41		

* 0.01 level of significance.

Table 3c. Change in mercury distribution in soil M15 after one $Ca(OCl)_2$ treatment.

Soil M15 Hg Form	Initial (mg Hg/kg soil)	Treated (mg Hg/kg soil)	% Change	Significant (Y/N)*
TEO	4.0	9.5	+139	Y
Elem.	0.0	0.0	0	N
W.P.	6.3	5.7	-9.6	N
I.E.	9.5	9.0	-4.9	N
O.A.I	7.7	3.9	-49	Y
O.A.II	37	1.9	-95	Y
O.B.	1.3	0.6	-51	Y
O.M.I	6.0	0.5	-92	Y
O.M.II	33	1.2	-97	Y
Mineral	30	11	-65	Y
Total Extracted	140	43	-68	Y
Total in Soil	260	51		
% Recovered	51	84		

* 0.01 level of significance.

Table 3d. Change in mercury distribution in soil M16 after one $Ca(OCl)_2$ treatment.

Soil M16 Hg Form	Initial (mg Hg/kg soil)	Treated (mg Hg/kg soil)	% Change	Significant (Y/N)*
TEO	120	14	-89	Y
Elem.	0	0	0	N
W.P.	2.5	18	+620	Y
I.E.	4.9	20	+320	Y
O.A.I	4.1	4.2	+2	N
O.A.II	34	1.2	-97	Y
O.B.	0.9	0.9	0	N
O.M.I	2.0	1.8	-10	N
O.M.II	240	3.3	-99	Y
Mineral	29	25	-14	N
Total Extracted	440	89	-80	Y
Total in Soil	540	130		
% Recovered	81	67		

* 0.01 level of significance.

Table 3e. Change in mercury distribution in soil M19 after one $Ca(OCl)_2$ treatment.

Soil M19 Hg Form	Initial (mg Hg/kg soil)	Treated (mg Hg/kg soil)	% Change	Significant (Y/N)*
TEO	0.8	0.7	-13	N
Elem.	0	0	0	N
W.P.	0.5	2.4	+393	Y
I.E.	0.2	0.2	-2.6	N
O.A.I	0.6	0.8	+29	N
O.A.II	2.4	0.3	-90	Y
O.B.	0.1	0.3	+180	N
O.M.I	0.8	0.2	-77	N
O.M.II	30	0.8	-97	Y
Mineral	19	4.5	-76	Y
Total Extracted	54	10	-81	Y
Total in Soil	56	16		
% Recovered	98	66		

* 0.01 level of significance.

3.2.3. Distribution of Mercury in Soils Treated Three Times.

The soils treated three times with calcium hypochlorite show a trend similar in the distribution of mercury within them to the soils treated one time (Figure 6). Two soils, M11 and M14, had the majority of mercury in them within the TEO fraction. In one soil, M17, the largest fraction of mercury was found in the mineral phase. The final soil, M18, had most of its mercury found within the ion exchangeable phase. In all soils the predominant forms of mercury were in the TEO, water phase, ion exchangeable and mineral fractions. In no soils were there detectable levels of mercury within the elemental, OAII or OB fractions.

The concentration of Hg decreased in the majority of fractions in each soil, with some soils showing no change in the TEO, water phase or ion exchangeable while the concentration of mercury in two fractions increased in one soil (Tables 4a-d). The concentration of Hg within the TEO fraction did not significantly change in soils M11, M17 or M18 but it decreased in soil M14. The elemental mercury in soil M17 was removed after three treatments. For soils M11 and M18 the concentration of mercury within the water phase did not significantly change while it increased in soil M17 and decreased in soil M14. Ion exchangeable mercury decreased in soil M14 and remained unchanged in soils M11, M17 and M18. In each soil treated three times with calcium hypochlorite the concentration of mercury within the OAI, OAII, OB, OMI, OMII and mineral fractions decreased, the one exception being soil M11 which did not show a decrease in the concentration of mercury within the OB or mineral phases.

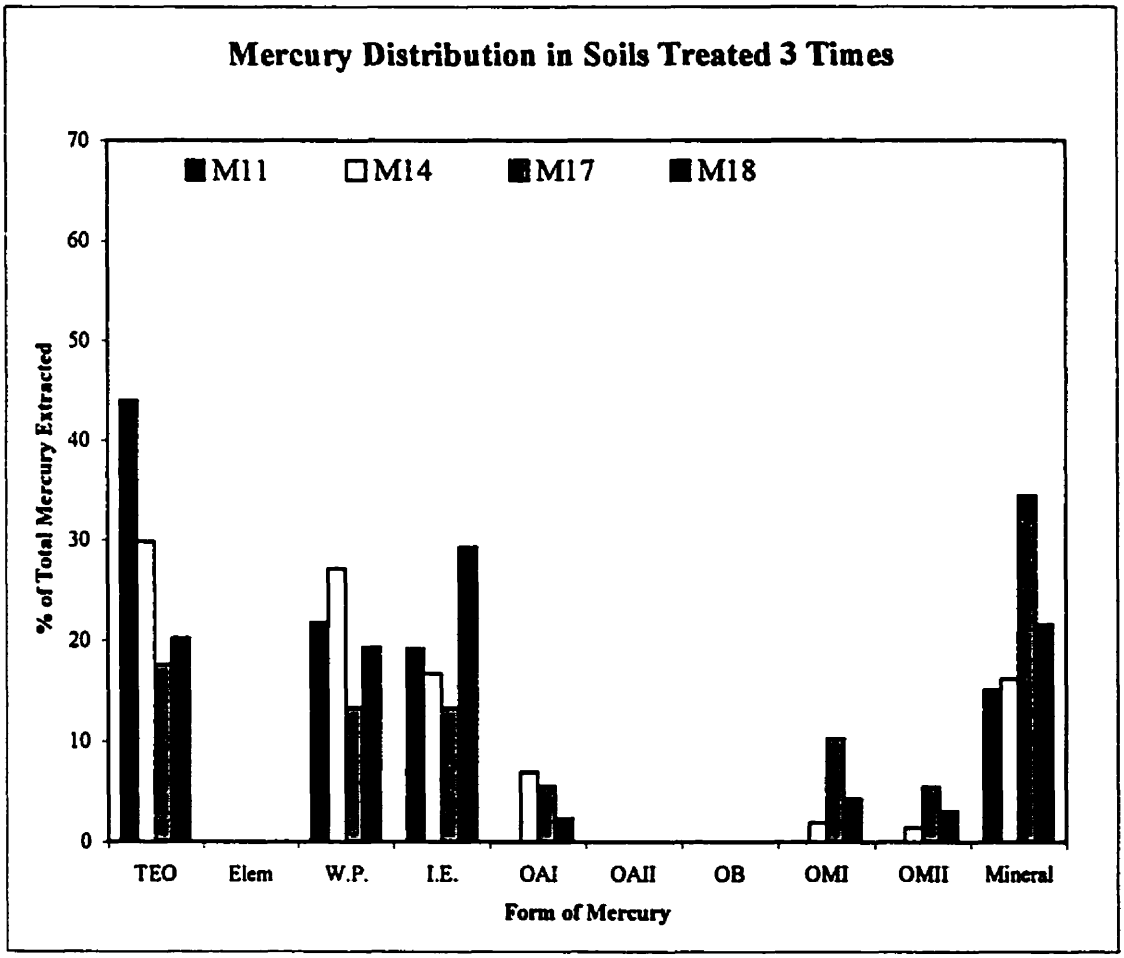


Figure 6. Distribution of Mercury in Soils Treated Three Times.

Table 4a. Change in mercury distribution in soil M11 after three treatments.

Soil M11 Hg Form	Untreated (mg Hg/kg soil)	Treated (mg Hg/kg soil)	% Change	Significant (Y/N)*
TEO	1.4	1.8	+28	N
Elem.	0.0	0.0	0.0	N
W.P.	1.2	0.9	-25	N
I.E.	0.1	0.8	+1300	N
O.A.I	0.7	0.0	-100	Y
O.A.II	2.2	0.0	-100	Y
O.B.	0.1	0.0	-100	N
O.M.I	0.8	0.0	-100	Y
O.M.II	12	0.0	-100	Y
Mineral	0.7	0.6	-13	N
Total Extracted	19	4.1	-79	Y
Total in Soil	30	4		
% Recovered	65	103		

* 0.01 level of significance.

Table 4b. Change in mercury distribution in soil M14 after three treatments.

Soil M14 Hg Form	Untreated (mg Hg/kg soil)	Treated (mg Hg/kg soil)	% Change	Significant (Y/N)*
TEO	10	3.5	-65	Y
Elem.	0.0	0.0	0	N
W.P.	5.4	3.2	-41	Y
I.E.	15	2.0	-87	Y
O.A.I	5.4	0.8	-85	Y
O.A.II	34	0.0	-100	Y
O.B.	1.4	0.0	-100	Y
O.M.I	7.8	0.2	-97	Y
O.M.II	120	0.2	-99	Y
Mineral	73	1.9	-97	Y
Total Extracted	270	12	-96	Y
Total in Soil	340	13		
% Recovered	79	92		

* 0.01 level of significance.

Table 4c. Change in mercury distribution in soil M17 after three treatments.

Soil M17 Hg Form	Untreated (mg Hg/kg soil)	Treated (mg Hg/kg soil)	% Change	Significant (Y/N)*
TEO	58	51	-12	N
Elem.	4500	0	-100	Y
W.P.	9.7	39	+300	Y
I.E.	46	39	-15	N
O.A.I	80	16	-80	Y
O.A.II	280	0	-100	Y
O.B.	43	0	-100	Y
O.M.I	550	30	-95	Y
O.M.II	9000	16	-99.8	Y
Mineral	1500	100	-93	Y
Total Extracted	16000	291	-98	Y
Total in Soil	16300	390		
% Recovered	99	75		

* 0.01 level of significance.

Table 4d. Change in mercury distribution in soil M18 after three treatments.

Soil M18 Hg Form	Untreated (mg Hg/kg soil)	Treated (mg Hg/kg soil)	% Change	Significant (Y/N)*
TEO	3.6	2.4	-33	
Elem.	0	0	0	N
W.P.	2.6	2.3	-12	N
I.E.	5.0	3.4	-32	N
O.A.I	2.2	0.3	-86	N
O.A.II	19	0	-100	Y
O.B.	0.8	0	-100	Y
O.M.I	25	0.5	-98	Y
O.M.II	150	0.4	-99	Y
Mineral	29	2.5	-91	Y
Total Extracted	240	12	-95	Y
Total in Soil	260	9		
% Recovered	90	133		

* 0.01 level of significance.

3.3. Results of Hypochlorite Treatment

3.3.1. Soil Mercury Concentrations – Pre- and Post-Treatment.

Every soil had a significant decrease in total Hg concentrations after treatment with calcium hypochlorite (Table 5). The largest total decrease occurred in soil M17, which decreased from 16000 mg Hg kg^{-1} before treatment to 2600 mg Hg kg^{-1} after treatment, a decrease of 13400 mg Hg kg^{-1}. One treatment with calcium hypochlorite removed between 70-88% of the mercury from the soils, with an average 78% decrease. The soils treated three times had an average cumulative decrease of 95%, ranging between 87-98%.

Table 5. Soil Mercury Concentrations – Pre- and Post- Treatment.

Soil	No. of Treatments	Hg Concentration (mg Hg kg^{-1} soil)				% Decrease	Significantly Different* (Y/N)
		Before Treatment		After Treatment			
		Average	St.Dev.	Average	St.Dev.		
M11	3	30	5.0	4	2.8	87	Y
M12	1	120	22	30	9.8	75	Y
M13	1	300	60	68	20	77	Y
M14	3	344	26	13	19	96	Y
M15	1	260	9.3	51	13	80	Y
M16	1	540	42	130	44	76	Y
M17	3	16000	970	390	830	98	Y
M18	3	260	3.8	9	5.4	97	Y
M19	1	56	2.4	16	0.71	71	Y

*0.01 level of significance.

The first hypochlorite treatment was the most effective in removing mercury from the soil. After one treatment the soil mercury content decreased 70-88%. A second treatment lowered the mercury content of the soil 40-78% and the third treatment resulted in a 0-46% decrease in soil mercury content (Table 6).

Table 6. Mercury Content of Soils after 1, 2 and 3 Treatments.

	Initial Conc.		1 Treatment		2 Treatments		3 Treatments	
Soil	Avg. (mg kg^{-1})	St.Dev	Avg. (mg kg^{-1})	St.Dev	Avg. (mg kg^{-1})	St.Dev	Avg. (mg kg^{-1})	St.Dev
M11	29	5	5	2	3	0.9	4	0.01
M14	344	26	103	22	24	5	13	0.45
M17	16300	970	2500	820	540	170	390	1.8
M18	260	4	30	5	12	1.5	9	0.76

All of the soils used in this study were originally contaminated with elemental mercury. Elemental mercury tends to form small droplets in the soil. This results in uneven distribution of mercury within the soil; there will be some hot spots and some areas with less mercury. The standard deviation associated with the mercury content of each soil can be used as an indication of the variability in mercury distribution in the whole soil sample. Some of the deviation will be due to analytical and sampling errors, the remainder of the deviation should be due to uneven distribution of the mercury within the soil. The error associated with the method can be estimated using the standard deviation of the results from soil standards. Theoretically, the only source of error for standard soils is analytical error. The standard deviation of the standard soil used during this study was approximately 5% of the average soil mercury content. The standard deviations of the experimental soils used in this study ranged between 1-20% of the average soil mercury content. All of the soils were homogenized prior to analysis to reduce variability. In three soils (M15, M18, and M19) the variability in analysis was less than the variability recorded from the standard soil. The remaining soils all had more variability in their results than did the standard soil, an indication of the variability in mercury distribution. The most surprising result from this is soil M17. Soil M17 had visible drops of mercury, which would indicate that there are hot spots and cold spots. The standard deviation of M17 is only 6% of the average soil mercury content, indicating little variation in soil mercury distribution.

To maintain mass balance with respect to Hg the amount of Hg contained in the hypochlorite solution was measured. The recovery of Hg in the treated soil and hypochlorite solution for all soils ranged between 56% for soil M14 to 99% for soil M19, with an average recovery of 71% after one treatment (Figure 7a-7b). The difference between the mercury initially in the soil and the mercury recovered in the hypochlorite solution plus the mercury in the treated soil was calculated and assumed to be volatile mercury. After three treatments the total amount of Hg recovered in the soil and OCl^- solution averaged between 41% for soil M14 to 88% for soil M11 of the total initial Hg content, with an average of 62% (Figures 8a-8d).

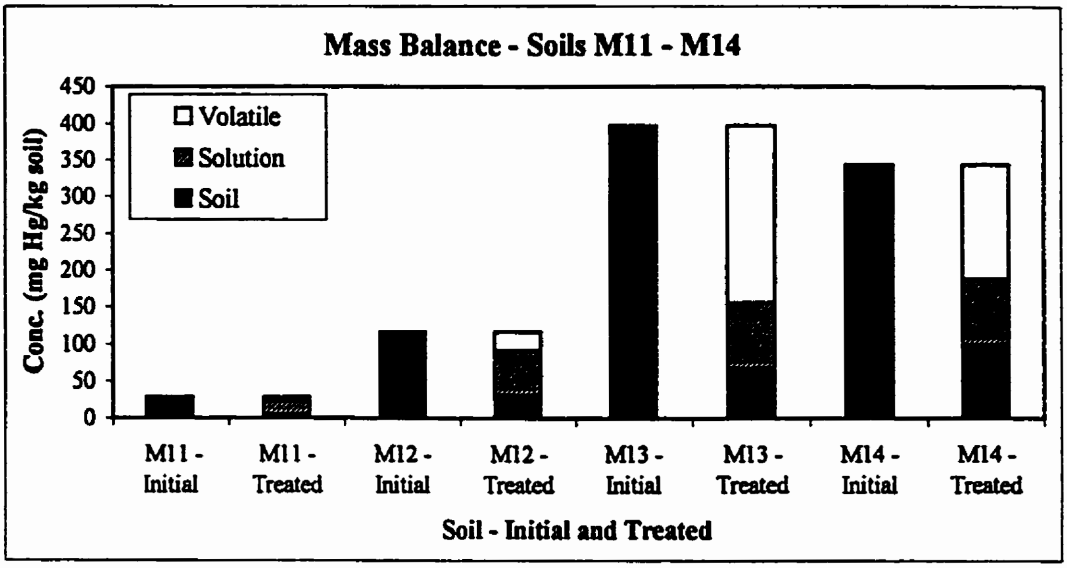


Figure 7a. Mercury in the Soil, Solution and Volatile Phases Pre- and Post Treatment of Soils M11-M14.

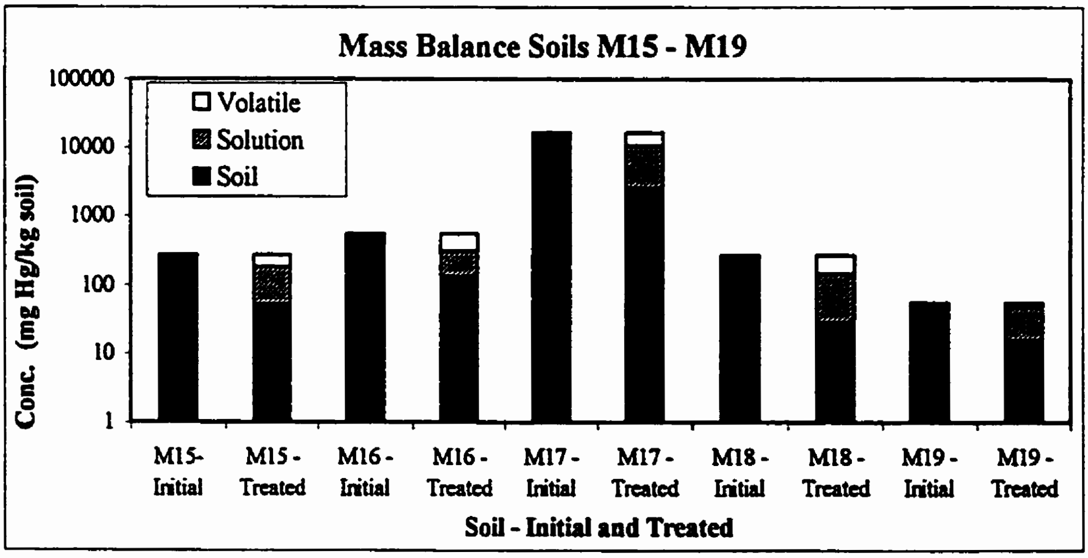


Figure 7b. Mercury in the Soil, Solution and Volatile Phases Pre- and Post Treatment of Soils M15-M19.

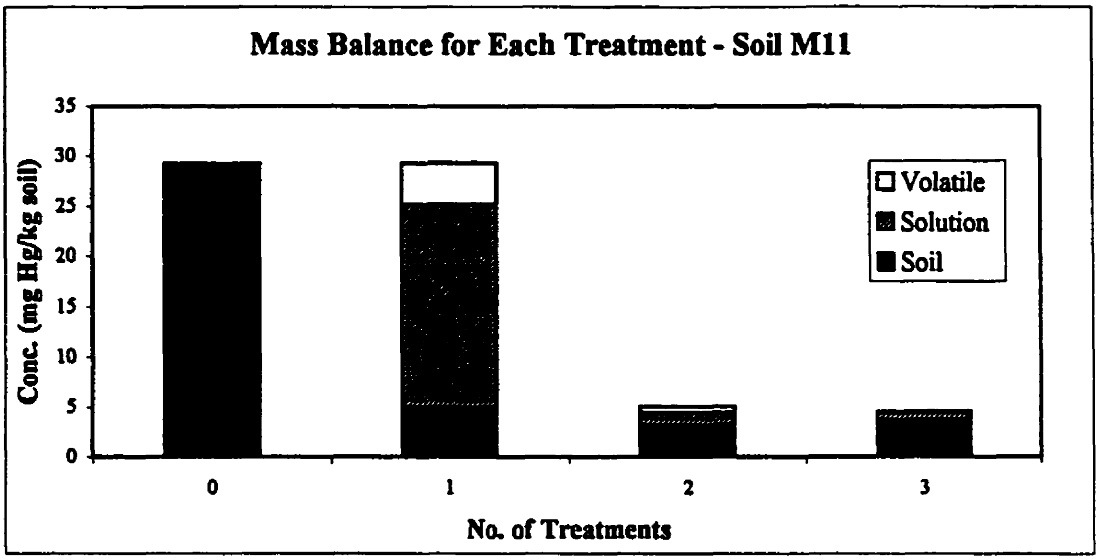


Figure 8a. Soil, Solution and Volatile Mercury Concentrations of Soil M11 After OCl⁻ Treatments.

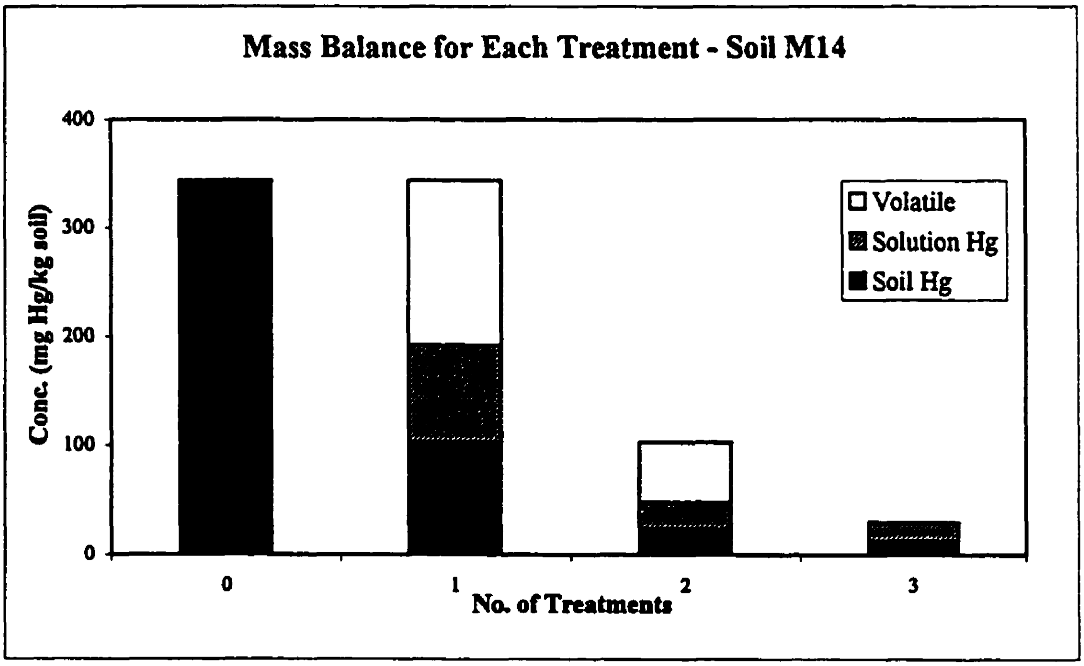


Figure 8b. Soil, Solution and Volatile Mercury Concentrations of Soil M14 After OCl⁻ Treatments.

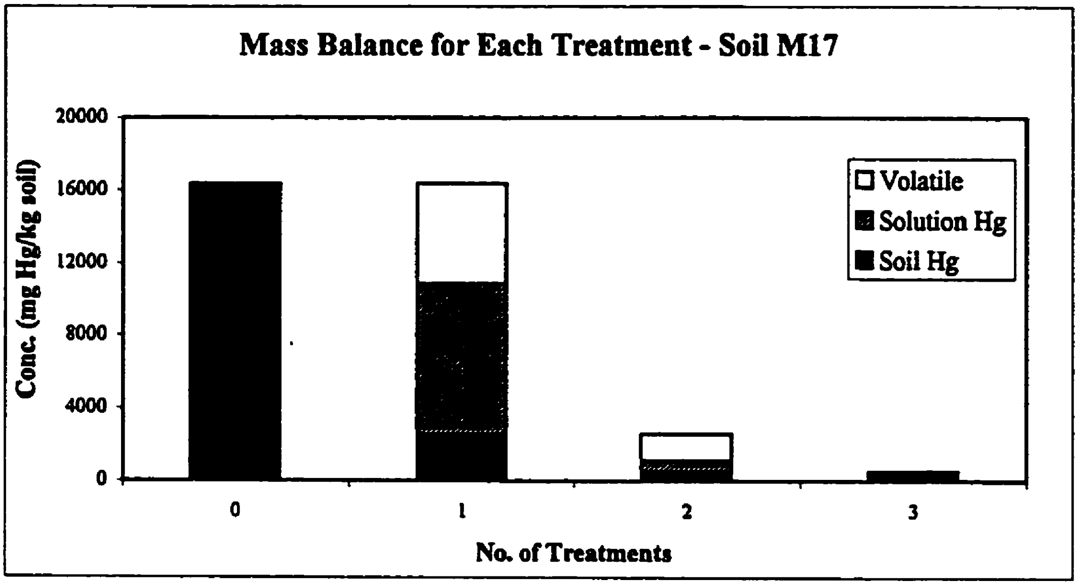


Figure 8c. Soil, Solution and Volatile Mercury Concentrations of Soil M17 After OCl⁻ Treatments.

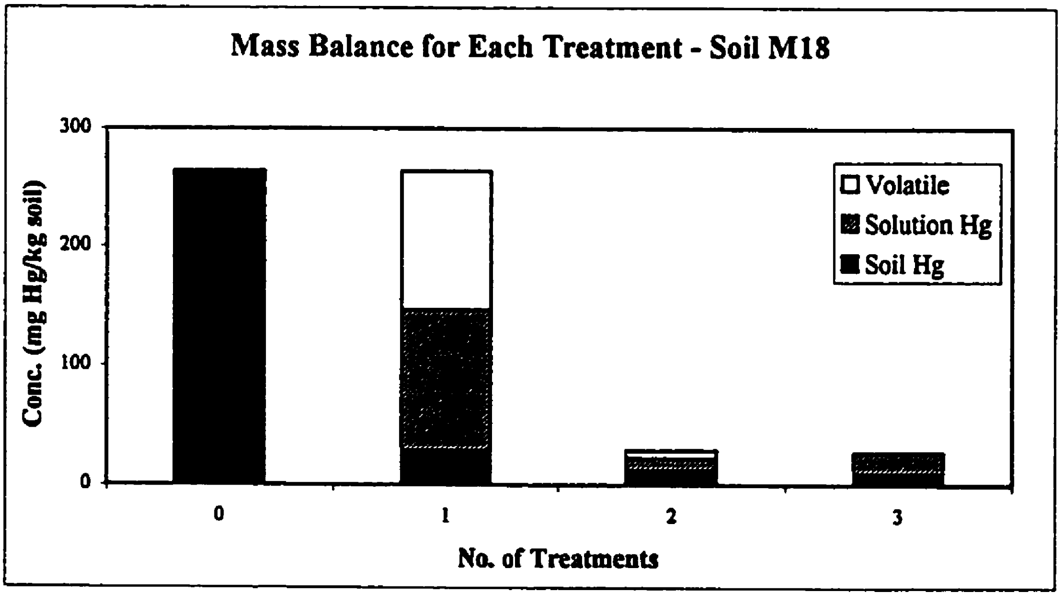


Figure 8d. Soil, Solution and Volatile Mercury Concentrations of Soil M18 After OCl⁻ Treatments.

3.3.2. Soil Carbon Content – Pre- and Post-Treatment.

All soils experienced a loss of total C after treatment with calcium hypochlorite (Table 7). For each soil the total organic C decreased, indicating a loss of soil organic matter. Total inorganic C increased in all soils after treatment with hypochlorite, likely the result of the calcium carbonate included with the calcium hypochlorite. Calcium carbonate is added to the calcium hypochlorite powder to increase stability. On average the soils lost 49% of their initial organic matter content, an average loss of 2.14% of total organic matter.

Table 7. C Content of Untreated and Treated Soils.

	Untreated Soil				Treated Soil			
Soil	% TC	%TIC	%TOC	%OM	%TC	%TIC	%TOC	%OM
M11	2.15	0.212	1.94	3.34	1.38	0.59	0.79	1.37
M12	2.33	0.212	2.12	3.65	1.37	0.52	0.85	1.46
M13	2.44	0.274	2.17	3.73	1.42	0.51	0.90	1.55
M14	3.63	0.338	3.29	5.68	2.14	0.65	1.49	2.57
M15	7.45	0.381	7.07	12.19	6.65	0.62	6.02	10.39
M16	3.60	0.194	3.41	5.87	2.48	0.48	2.00	3.44
M17	1.78	0.164	1.62	2.79	1.04	0.72	0.32	0.55
M18	2.62	0.312	2.31	3.98	2.02	0.66	1.36	2.34
M19	3.19	0.243	2.95	5.08	2.75	0.79	1.95	3.37

TC = Total C, TIC = Total Inorganic C, TOC=Total Organic C, OM=Organic Matter

3.3.3. Soil TEO Concentrations – Pre- and Post-Treatment.

Of the nine soils only four (M11, M14, M15, and M16) showed a significant decrease in TEO content after treating the soils with calcium hypochlorite (Table 8). There is no apparent relationship between the number of treatments and reduction in TEO. Of the four soils that had a significant decrease only one, M11, was treated three times. For the soils M11, M14 and M18 the TEO content was measured after one and three treatments. After the first treatment two soils, M11 and M18, showed no change in TEO content, while M14 had a significant decrease (Figure 9). After three treatments both M11 and M14 showed a significant decrease in TEO content while soil M18 experienced no change in TEO content.

Table 8. Soil TEO Concentrations – Pre- and Post- Treatment.

Soil	No. of Treatments	Total Extractable Organic Content				Significant Decrease* (Y/N)
		Before Treatment(%)		After Treatment		
		Average	St. Dev.	Average	St.Dev.	
M11	3	0.09	0.02	0.04	0.01	Y
M12	1	0.13	0.01	0.17	0.04	N
M13	1	0.21	0.01	0.17	0.02	N
M14	3	0.68	0.01	0.28	0.01	Y
M15	1	0.71	0.02	0.60	0.07	Y
M16	1	6.9	0.6	5.3	0.4	Y
M17	3	0.90	0.73	0.17	0.14	N
M18	3	0.58	0.001	0.46	0.01	N
M19	1	1.14	0.39	1.05	0.08	N

*0.05 Level of significance.

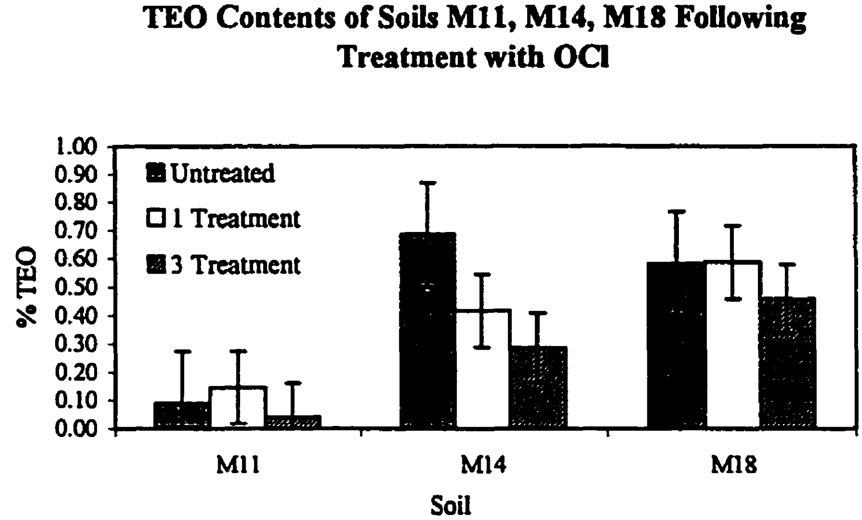


Figure 9. TEO Content of Soils M11, M14, M18 Following Sequential Treatment with OCl⁻

3.4. Water Phase Mercury.

3.4.1. Comparing Digested and Non-Digested Solutions.

When the water extractable Hg solution was not digested there was significantly less Hg detected compared to the nitric acid-digested sample (Table 9), the concentration of Hg detected in the undigested solution decreased between 67% (for soil M17) to 99% (for soil M19), an average decrease of 89%. These results indicate a sample should always be digested prior to analysis for mercury content.

Table 9. Water Phase Mercury – Digested vs. Non-Digested.

Soil	Digested		Non-Digested		Significantly Different* (Y/N)
	Average (mg Hg L^{-1})	St.Dev.	Average (mg Hg L^{-1})	St.Dev.	
M11	0.34	0.001	0.01	0.001	Y
M12	2.70	0.47	0.13	0.05	Y
M13	2.52	0.84	0.13	0.05	Y
M14	10.72	1.29	1.77	0.46	Y
M15	11.58	0.84	1.40	0.16	Y
M16	2.60	0.001	0.58	0.10	Y
M17	91.35	1.63	29.91	0.94	Y
M18	10.09	0.27	0.45	0.16	Y
M19	11.25	0.26	0.10	0.06	Y

*0.001 Level of significance.

3.5. Results of Geochemical Modeling

The results of the five simulations modeled using Solmineq.88 are presented in Table 10.

Table 10. Results from Geochemical Modeling.*

	Activity of Species (mol L^{-1})				
Species	Run 1	Run 2	Run 3	Run 4	Run 5
Hg^{2+}	9.6×10^{-17}	9.7×10^{-17}	3.7×10^{-14}	1.0×10^{-15}	1.0×10^{-12}
$HgCl^{+}$	6.3×10^{-13}	8.5×10^{-14}	3.4×10^{-11}	2.2×10^{-11}	8.5×10^{-10}
$HgCl_2$	2.4×10^{-8}	4.3×10^{-10}	1.8×10^{-7}	2.7×10^{-6}	4.1×10^{-5}
$HgCl_3^{-}$	1.1×10^{-8}	2.6×10^{-11}	1.1×10^{-8}	4.0×10^{-6}	2.4×10^{-7}
$HgCl_4^{2-}$	1.4×10^{-11}	4.8×10^{-15}	2.2×10^{-11}	1.8×10^{-8}	4.3×10^{-11}
$HgSO_4^{0}$	5.4×10^{-20}	5.7×10^{-20}	2.8×10^{-17}	5.0×10^{-19}	5.1×10^{-13}
$HgOH^{+}$	1.5×10^{-6}	9.0×10^{-12}	1.8×10^{-10}	4.7×10^{-12}	5.9×10^{-10}
$Hg(OH)_2^{0}$	9.0×10^{-12}	7.5×10^{-6}	7.3×10^{-6}	2.0×10^{-7}	3.1×10^{-6}

*Refer to section 2.8 for input parameters.

The mercury hydroxyl species are important in each run, which is expected due to the near neutral or high pH used in the simulations. Mercuric chloride species dominate in two runs (4 and 5), simulations that have either high chloride concentrations and a neutral pH or a slightly acidic pH. Under these conditions the concentrations of HCO_3^- and OH^- are minimized and chloride begins to dominate the chemistry. $HgSO_4^0$ never dominates, even at high concentrations of SO_4^{2-}, because the pH does was not acidic enough. Solmineq.88 does not include the species HgOHCl, which is the species that dominates when chloride and OH activities are equal. One of the results is that in none of the five simulations did any mercury containing minerals precipitate. This is important because it indicates that the conditions found in the nine soils considered in this study are not suitable for precipitation of mercury containing minerals.

4.0. Discussion

4.1. Initial Distribution.

The distribution of mercury within the nine soils shows some general patterns but there is some minor variability. This variability could arise from several sources including: differences in quantity and quality of organic matter, differing mineralogies, quantity and type of contaminant hydrocarbon and the length of time since the original spill, and quantity of mercury released. However, the soil mineralogies should not differ. There is no information on the hydrocarbons, other than present amount. The length of time since the original spill and the quantity of mercury released are not known nor are there any data on the quality of the organic matter present. The only measured differences among the soils are the quantity of organic matter, minor differences in solution chemistry and total amount of mercury present.

The amount of mercury contained within the TEO fraction varies with the total amount of mercury within the soil and the amount of hydrocarbons ($r^2 = 0.78$). Soil M16, the only soil in which TEO-Hg accounts for more than 10% of the total Hg is the soil that has a TEO content of almost 7%. The hydrocarbon fraction itself can contain high levels of mercury. In soil M17 the TEO extract has a concentration of 18 000 mg Hg kg^{-1} TEO. The reason the TEO fraction is not a more dominant fraction is the low hydrocarbon content in most of the soils. Mercury will interact with the hydrocarbons in ways similar to mercury's interaction with soil organic matter. The mercury associated with the hydrocarbons is probably bound covalently to O- and S- containing active sites. Some mercury may be bound electrostatically to charged sites within the hydrocarbon and other mercury may be chelated by the hydrocarbon. Species of mercury can form electrostatic bonds with either positively or negatively charged sites within the hydrocarbon, positively charged species such as Hg^{2+}, $HgOH^+$, and $HgCl^+$ will bind with negative sites and negatively charged species such as $HgCl_3^-$ and $HgCl_4^{2-}$ will bind with positively charged sites.

It appears that in this study elemental mercury is not found in these soils with the relatively low mercury concentrations of 600 mg kg^{-1} and below. Elemental mercury is found in the soil with a mercury concentration of 16 000 mg kg^{-1} and will probably be found in soils with lower concentrations, as indicated by Winmoller et.al. (1996) and Biester and Scholz (1997) who found elemental mercury in soils with concentrations between 800 and 1500 mg kg^{-1}. It has been suggested (Allard and Arsenie, 1991) that elemental mercury can be formed from Hg^{2+} abiotically in soil by organic matter. If this abiotic reduction was occurring in these soils it was not detected.

The high concentration of mercury that was found within the water phase was surprising, as this would suggest that mercury would be mobile in soil. However, studies of sites contaminated with mercury found that little mercury has leached out of the surface soil (Kohut et al., 1995). The unexpectedly high concentrations of mercury within the water phase are most likely an artifact of the method and not indicative of in situ conditions. Shaking 1.5g of soil in 100mL of water for 30 minutes will extract more mercury than will rain falling on a soil in the field. The mercury extracted in the water phase could be considered mercury with the potential to be leached by rainwater.

For the nine soils considered in this study mercury associated with organic matter is the most dominant form. The five fractions of organic matter (OAI, OAII, OB, OMI, and OMII) account for up to 85% of the mercury extracted from the soil. The concentration of mercury within organic matter can be as high as 350 g Hg kg^{-1} O.M. (for soil M17) and ranges between 470 and 350 000 mg Hg kg^{-1} O.M. These are very high concentrations and cannot be explained by mercury bound to the cation exchange sites of organic matter. Some of the mercury must also be bound covalently to O-, S- and SO_4-containing active sites, particularly SO_4^{2-} containing sites as mercury is a soft acid and SO_4 is a soft base. Even if mercury occupied all of the cation exchange sites and all of the active sites within the organic matter there is still excess mercury. The organic matter in soil M17 is 35% mercury, higher than can be explained by cation exchange and active site binding. Another mechanism must be responsible for the high mercury concentrations found in the organic matter. One possible explanation is that the H_2O_2 solution used to oxidize the organic matter and extract the associated mercury is also oxidizing available mercury containing minerals.

One unexpected result of the extraction is the difference in the amount of mercury in OAI and OAII. The fraction extracted with the lower concentration of NaOH (OAII) had a higher amount of mercury within that fraction than the fraction extracted with a more concentrated NaOH solution (OAI). One possible explanation is that the higher pH of OAII solution causes more mercury hydroxides to precipitate compared to the OAI solution. As mercury hydroxide minerals are very soluble either the pH or the concentration of mercury within the solution would have to be very high. As this is not the case for these soils it is unlikely that mercury hydroxide minerals are precipitating. Another possibility relates to flocculation, dispersion and physical accessibility. The lower OH solution would favour dispersion of soil aggregates while the higher concentration of Na^+ in OAI would cause the soil aggregates to flocculate. By dispersing the soil aggregates the lower OH solution would be able to extract more mercury than the higher OH solution.

The OB fraction in all soil is insignificant, which is not unexpected due to the small amount of organic bases in most soils.

For all soils but M15, the fraction labeled OMII contains the most mercury. The OMII fraction in not removed until the soil is oxidized by a 30% H_2O_2 solution at 82°C for 5 hours, indicating that this is a recalcitrant organic matter fraction most likely consisting of humin. The two OA fractions are extracted using solutions of NaOH, which removes humic and fulvic acids, further supporting the idea that OMII consists of humin. In surface soils humin tends to be the most abundant organic matter fraction by weight. It is not surprising therefore that OMII is the organic matter fraction containing the most mercury.

The amount of mercury found in the mineral phase varies between the two groups of soils. One group (M11, M12, M16, M17, M18) has less than 10% of their total mercury found in the mineral phase while the other four soils have between 25-40% of their mercury in the mineral phase. Some of the mercury considered mineral mercury is likely mercury associated with organic matter not oxidized by the H_2O_2 and found on the surface of minerals. This does not explain the differences between the two groups; presumably there would not be significant differences between soils in the amount of organic matter remaining after oxidation. One explanation is the length of time since the original mercury spill. In older spills mercury may have had the chance to transform from elemental mercury and enter the mineral phase. This implies that more mercury will enter the mineral phase over time. This implication is not unreasonable as all the mercury was initially introduced as elemental mercury. Little if any elemental mercury remains. Since there is no information on the length of time passed since the original spill this hypothesis cannot be verified. As the mineralogies of the soils are not expected to vary widely differences in mineralogy are not a likely explanation for the differences in the amount of mercury in the mineral fractions observed in the two groups.

4.2. Hypochlorite Treatment

Treating co-contaminated soils with calcium hypochlorite is only partially effective in reducing the mercury and hydrocarbon content of the soils. The hypochlorite treatment was effective in reducing the mercury concentration in all nine soils. However, the final mercury concentration of the nine treated soils was not within the range of background mercury concentration of soils from Alberta. There was only one soil, M11, in which the mercury concentration was lowered below CCME guidelines for commercial sites. Four soils had their TEO contents reduced, after either one or three treatments. The TEO contents of all the soils, even after treatment with calcium hypochlorite, remained above CCME interim guidelines for total hydrocarbons.

The first treatment with hypochlorite was the most effective in removing mercury from soil. The mercury removed in this first step is the most available mercury, mercury that is relatively easy to oxidize and bring into solution. The majority of the organic matter also appears to be lost during the first treatment as the amount of organic matter lost in the soils treated once is not significantly different than the organic matter lost in the soils treated three times. This suggests that the loss of mercury may be related to the loss of organic matter, once the majority of the organic matter is lost the rate of mercury removal slows.

There are three possible reasons why a hypochlorite solution will react with and remove some mercury from soil and not react with the remaining mercury. The remaining mercury may be less physically available than the mercury that was removed. The mercury may be held between clay platelets and be unavailable in the short term. Obukhovskaya (1983) suggested that Hg^{2+} "practically does not penetrate into the interpacket spacing of minerals" but is sorbed mainly via surface adsorption. However Obukhovskaya also stated that phenylmercuryacetate becomes fixed in the interpacket spacing of montmorillonite but suggested mercury is not. Since metals such as Mg^{2+} can penetrate into the interpacket spacing of minerals such as montmorrilonite and vermiculite the minerals present would determine if Hg^{2+} could penetrate. Depending upon the mineralogy of the soils mercury may not be held physically unavailable through binding to soil minerals but mercury may still be held physically unavailable through chelation in the remaining organic matter or chemically unavailable due to the strength of the bonds holding mercury. The remaining mercury may also be more stable in a hypochlorite solution than the mercury removed. If true, this would indicate that the bonds holding the mercury are very strong. Mercury would have been removed from exchange sites on organic matter and soil minerals, as electrostatic bonds would not be strong enough to retain this mercury. Mercury bonded to hydroxide minerals by two hydroxyl bridges may be stable enough not to be removed by the hypochlorite solution. The bonds least likely to be broken by the hypochlorite solution are covalent bonds, particularly Hg-S bonds found in certain minerals and organic matter. The hypochlorite solution is highly oxidizing, has a high concentration of chloride and a high pH, conditions that would dissolve the known mercury containing compounds (HgS, $HgCl_2$, HgO, $HgSO_4$) as the concentrations in the hypochlorite solution do not approach saturation. This suggests that the mercury remaining in the soil is not in a crystalline precipitate form. The mercury may still be bound to Cl^-, OH^-S^{2-} and S containing functional groups of minerals and organic matter (Schuster, 1991). Mercury bonded to these functional groups would be very stable as "chemical sorption is practically irreversible" (Obukhovskaya, 1982). The third possible explanation for incomplete removal of mercury from soil is that the kinetics of any reaction are too slow for the reaction to occur overnight. Yin et.al. (1997) found that after an initial rapid desorption of mercury from soil the rate of desorption decreased rapidly until an equilibrium was reached at which point mercury desorption ceased. They speculated that mercury bonds preferentially to high energy sites, primarily in organic matter, and was only slowly released from these sites. This slow release of mercury is related to the stability of the bonds holding the remaining mercury, more stable bonds would require a longer reaction time to break than less stable bonds. The possibility exists that longer reaction times might remove more mercury from the soil.

The poor removal of hydrocarbons from the soil suggests that a 0.4M solution of $Ca(OCl)_2$ is not able to oxidize the hydrocarbons completely overnight. The loss of organic matter shows that calcium hypochlorite can oxidize complex carbon molecules to some degree. However, in all but one soil the organic matter content of the treated soils is still above 1%. The organic matter that was lost must be relatively easy to oxidize and is available to react with the hypochlorite in solution. The remaining organic matter and hydrocarbons must either be more recalcitrant or less available than the organic matter that was removed.

4.3. Distribution of Mercury in Treated Soils.

Although treating the soils once with hypochlorite caused a decrease in the total amount of mercury in each soil, mercury was not lost from every phase, some phases even increased their mercury content. The mercury associated with organic fractions in the soil decreased, as did mercury associated with the mineral fraction. However, in four soils the concentration of mercury found in the water phase increased after treatment with hypochlorite and for three soils the mercury in the ion exchangeable phase also increased. Several soils showed a relative increase of mercury in fractions such as TEO-Hg and WP-Hg. Some of these relative increases are from actual increases in the amount of mercury in the fractions. Most of the apparent increases are from negative enrichment, the other fractions lost more mercury, creating an apparent increase.

The water phase was the most consistent of the fractions that had an increase in their mercury content. In all soils but one the mercury content in the water phase increased between 1.4 to 15.5 mg Hg kg^{-1} soil after one hypochlorite treatment. The purpose of the hypochlorite treatment is to bring mercury out of the solid phase and into solution by oxidizing the available mercury. Some of the resulting soluble mercury remained in the soil because, after treating the soils with hypochlorite, there was no step to wash the remaining pore water out of the soil. The increase in water phase mercury is expected after one treatment with calcium hypochlorite because of the increase in soluble Cl^- and the increase in pH. The increased concentration of Cl^- would favour the formation of soluble mercuric chloride species (Figure 10) ($HgCl^+$, $HgCl_2$, $HgCl_3^-$ and $HgCl_4^{2-}$). The high pH of the soil solution after treatment would favour the formation of soluble mercury hydroxide species. The species that would dominate depends upon the pH of the solution and the concentration of chloride. At approximately pH 9 the $Hg(OH)_2$ species begins to dominate (Figure 11).

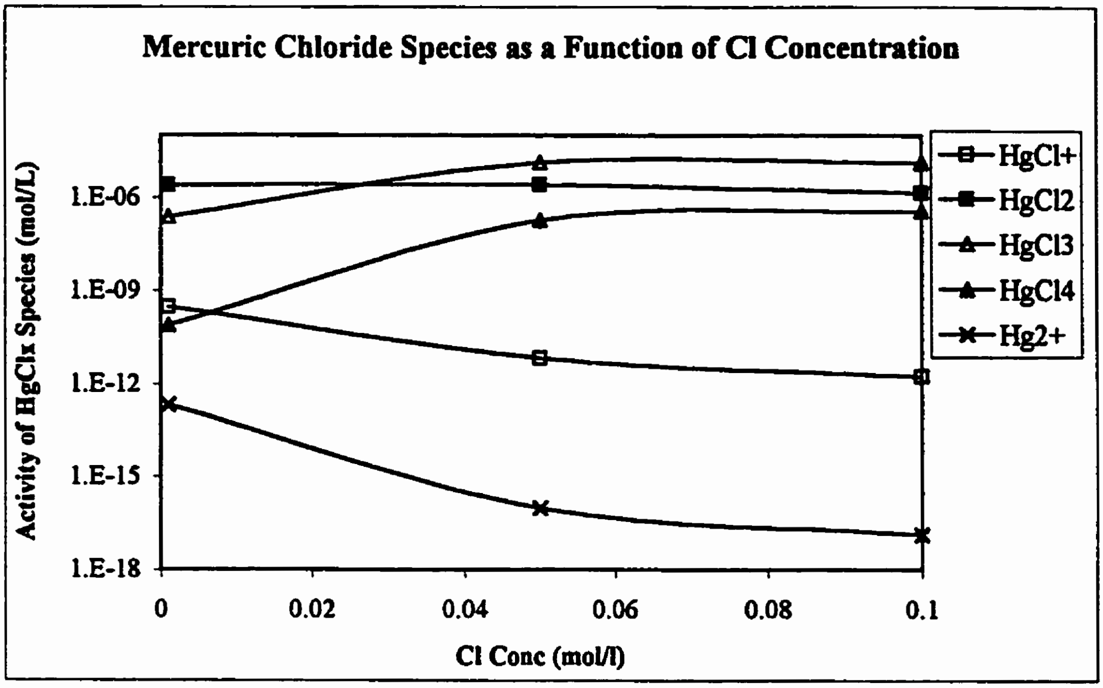


Figure 10. Mercuric Chloride Species as a Function of Cl^- Concentration

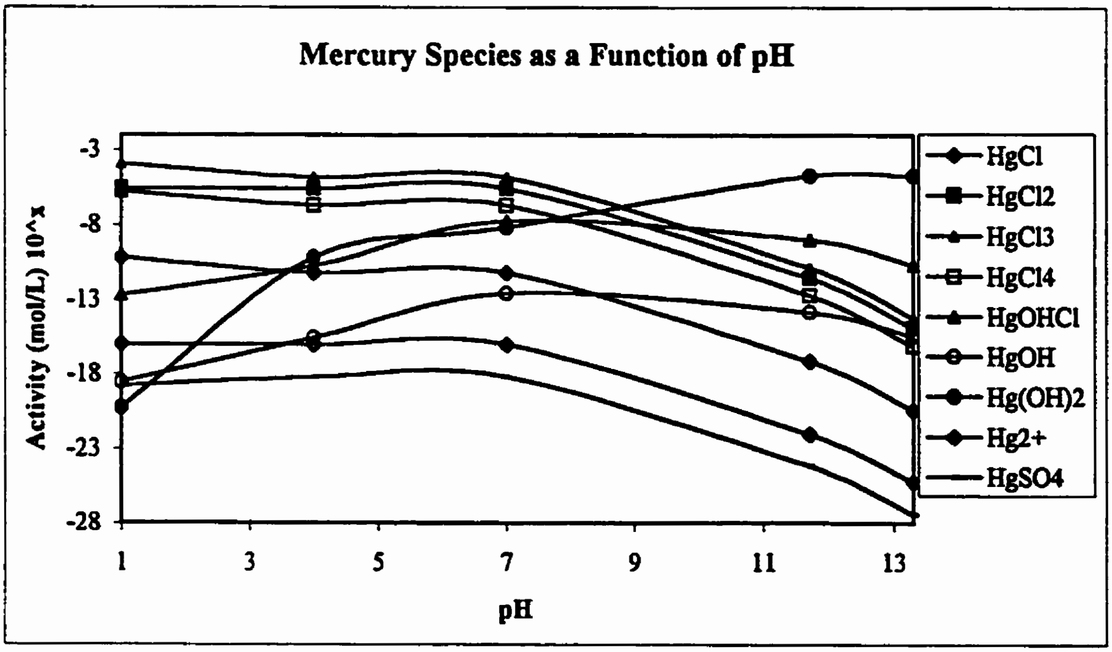


Figure 11. Mercury Species as a Function of pH.

In all but two soils the hypochlorite treatment also caused an increase in the ion exchangeable mercury. There are several facts that conflict when attempting to explain this increase in ion exchangeable mercury. An obvious explanation for this trend is the increase in the soluble mercury. A higher concentration of mercury and mercury species in solution would result in more mercury on the exchange sites within the soil. However two other results of the hypochlorite treatment conflict with this. The increased chloride in solution would cause the equilibrium of the mercuric chloride species to shift towards the negatively charged $HgCl_3^-$ and $HgCl_4^{2-}$ species while the increased pH would cause a shift towards $Hg(OH)_2^0$. These species would not be attracted to the cation exchange sites. The third result of the hypochlorite treatment is the loss of organic matter in each soil. This loss of organic matter would reduce the number of cation exchange sites in the soil. This loss of cation exchange sites and the dominance of negatively charged mercury chloride species would seem to suggest that the amount of ion exchangeable mercury would decrease rather than the observed increase. However, although the hypochlorite treatment results in a loss of total organic matter the higher pH resulting from the treatment would cause an increase in the cation exchange capacity of the remaining organic matter. Another result of the hypochlorite treatment is also a possible explanation for the increase in ion exchangeable mercury. The presence of $Hg(OH)_2^0$ may be a cause of the observed increase in ion exchangeable mercury. $Hg(OH)_2^0$ forms weak H-bonds with soils minerals (Obushkovskaya, 1983), bonds that are easily broken and could mimic cation exchange. While the pH of the hypochlorite solution is 11.8, which would cause $Hg(OH)_2$ to dominate the mercury speciation, the high concentration of Cl along with the high pH would cause the concentration of HgOHCl to increase. This mercury species is the species that is most attracted to soil minerals (Yin et al., 1996, Hogg et al., 1978). Mercury adsorption is maximized when HgOHCl dominates. The increase in HgOHCl concentration would increase mercury adsorption. The shift towards hydroxyl dominated species, the pH dependent cation exchange capacity of the organic matter, the increase in

HgOHCl and the rise in water phase mercury would be enough to cause the observed rise in ion exchangeable mercury.

There are also some interesting trends in what occurred to the mercury in the TEO fractions. The two soils that showed no significant change in TEO-Hg (soils M12 and M19) also had no change in their TEO contents. This would suggest that the hypochlorite treatment is unable to remove mercury from the hydrocarbons in the soil; either because the mercury is bonded too strongly to remove, the mercury bonded to the hydrocarbon is physically or chemically unavailable, or the reaction rate was too slow to remove substantial mercury overnight. The bonds holding mercury to soil hydrocarbons would be similar to the bonds holding mercury to soil organic matter. Mercury will form complexes with Cl, OH^-, S^{2-} and S-containing functional groups of organic ligands (Schuster, 1991). Soil M16 showed a large decrease in the TEO-Hg, from 122 to 14 mg Hg kg^{-1}. The hydrocarbon content of soil M16 also decreased, from 6.9% to 5.3% TEO. If we accept that mercury is not removed from the hydrocarbons the loss of TEO-Hg must be due to the loss of hydrocarbon. However, the loss of hydrocarbons is not equivalent to the loss of TEO-Hg. The hydrocarbons that were removed by the hypochlorite treatment must have had higher concentrations of mercury than the hydrocarbons not removed. This suggests that some hydrocarbons are more accessible to mercury. The other two soils actually had more mercury in their TEO fractions after hypochlorite treatment than before treatment. This result suggests that during the hypochlorite treatment some mercury entered solution and was bound by the hydrocarbons in the soil.

In all soils the mercury found in the various organic fractions either decreased or did not change significantly after treatment with calcium hypochlorite. The concentration of mercury did not increase in any organic phase. The total organic matter in each soil also decreased after treatment with calcium hypochlorite. The loss of mercury from the organic matter fractions is related to the loss of organic matter (r^2=0.64). The loss of organic matter alone does not explain the decrease in the mercury found in the organic matter fraction. This result may be explained in two ways. The first explanation is that hypochlorite can remove some mercury preferentially from organic matter without oxidizing and thus losing the organic matter. However free radicals do not preferentially attack C-metal bonds or C-active site-metal bonds over C-C bonds, if the bonds are equally available. If the bonds holding mercury were more available to hypochlorite than the C-C bonds of organic matter, mercury could be preferentially removed, without losing organic matter. The second explanation is that mercury is concentrated in the organic matter fractions that are physically more available. This more available organic matter fraction is then preferentially oxidized by the hypochlorite solution, releasing the mercury. There are fractions of organic matter that are physically removed and thus unavailable to react with other soil components. The mercury in the soil would react with and bond to the more available fractions of organic matter before reacting with the less available fractions and would thus be concentrated in the available fractions. Similarly, the hypochlorite solution would react with the available organic matter fraction before the unavailable fraction. This is supported by the fact that organic matter does remain, even after three treatments with hypochlorite, which shows that the hypochlorite is unable to oxidize this remaining organic matter in the time allowed.

The concentration of mercury within the mineral phase decreased in all soils treated once with hypochlorite except for soil M16. This indicates that the hypochlorite is able to oxidize the mercury containing minerals or break the bonds of the mercury bound to soil minerals. Any pure mercury containing minerals would be oxidized by the hypochlorite solution, if they were available to the solution. The concentration of mercury in the hypochlorite solution was too low for any mercury containing minerals to precipitate. It is likely that the hypochlorite solution could remove mercury bound to hydroxide minerals as the bridges holding mercury to the hydroxyl groups are relatively weak. Either the hypochlorite solution is unable to break all of the bonds holding mercury to soil minerals or some mercury is unavailable to the solution. The bonds holding mercury to phosphate, carbonate and sulphate containing minerals are very strong, and suggested to be practically irreversible (Obukhovskaya, 1983).

The removal of mercury from the soils treated three times with calcium hypochlorite followed trends similar to the soils treated only one time. The mercury content of almost every fraction decreased in each soil. Only one soil had an increase of mercury in any fraction.

The water phase mercury increased in soil M17. Soil M17 initially had over 16 000 mg Hg/kg soil of total mercury. By the third treatment there was still a significant decrease in total mercury in the soil and still large amounts of mercury in the hypochlorite solution after treatment. The high concentrations of mercury in the hypochlorite solution, which was not removed from the soil, resulted in an increase in water phase mercury.

Of the four soils treated three times with hypochlorite only one (M14) had significantly less mercury in the TEO fraction after treatment. The hypochlorite treatment did not remove significant amounts of mercury from the TEO fractions in three soils (M11, M17 and M18). This is further evidence that a 0.4M calcium hypochlorite solution is unable to remove mercury from the hydrocarbon fraction in soil. Two of the three-times treated soils (M11 and M14) had significant decreases in their soil TEO content, however M11 only decreased 0.05%, which was not enough to cause a significant decrease in TEO-Hg. The TEO content of soil M14 decreased 0.40%, a decrease large enough to cause a significant decrease in the TEO-Hg fraction. The only way that the TEO-Hg fraction decreases is through a decrease in the soil TEO content.

As in the soils treated one time, the mercury found in the organic matter and mineral fractions of the soils treated three times showed consistent significant decreases. These decreases in organic matter associated mercury occurred with significant decreases in total soil organic matter.

4.4. Water Phase Mercury.

The concentration of mercury in a non-digested solution gives an idea of the amount of soluble mercury species in solution. Some of the mercury detected in a non-digested solution will be mercury released from suspended clays and dissolved and particulate organic matter when the stannous chloride reducing solution is added. The $SnCl_2$ solution does not reduce all of the mercury in the solution if some occurs as suspended mercury, as evidenced by the increase in mercury detected when the solution was digested. Assuming that the concentrations of mercury detected in the non-digested samples are largely due to soluble mercury allows for some conclusions about the mercury species in solution. Using the pH and the concentration of chloride in solution (pCl) along with stability diagrams the expected mercury species in solution can be determined (Figure 12). For all soils the dominant species in solution is either $HgOHCl^0$, $Hg(OH)_2^0$ or $HgCl_2$. In no soil does the concentration of the dominant mercury species approach saturation so it is not expected that the increase in mercury detected when the solution was digested is from suspended particulate mercury minerals.

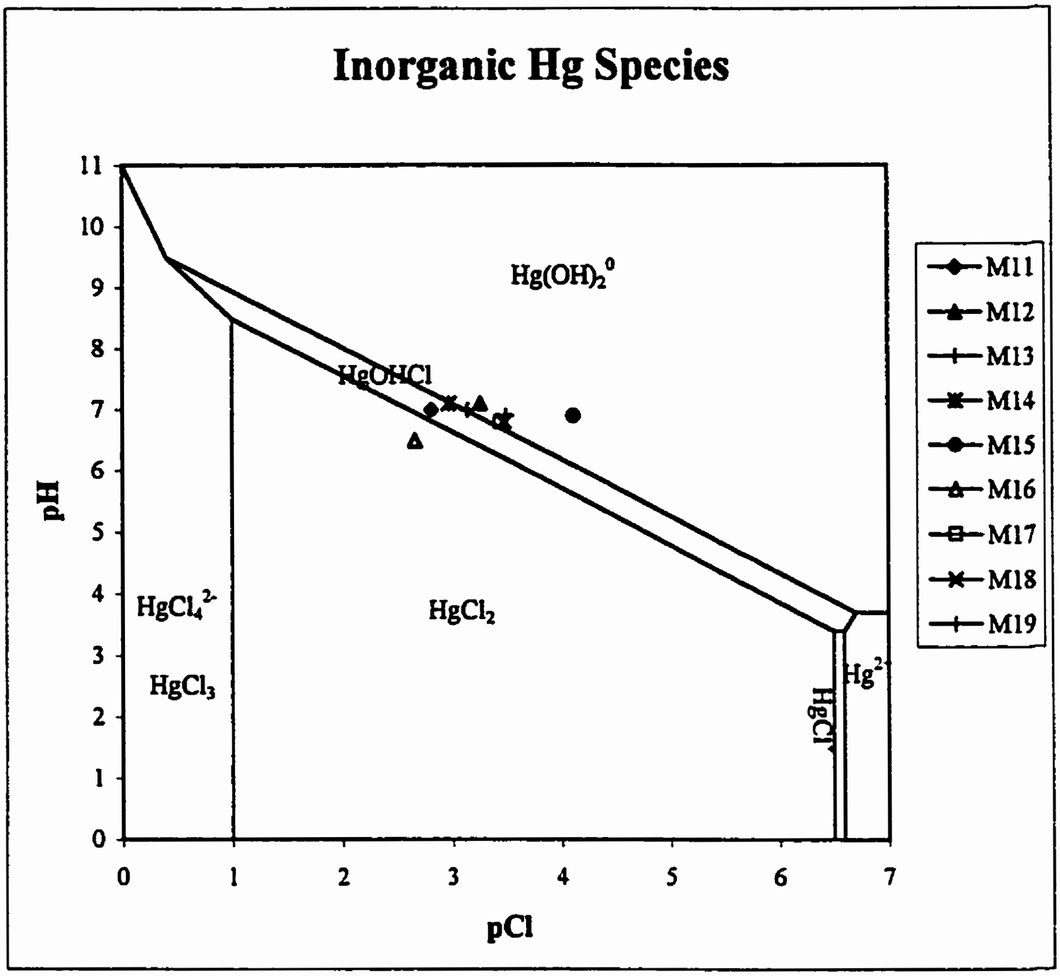


Figure 12. Inorganic Mercury Species.
From Andersson, 1979

Up to 99% of the total mercury in the water phase is released only after digestion with concentrated nitric acid and is not released by a strongly reducing solution of stannous chloride. This indicates that the mercury is bonded strongly to something in the solution, likely either suspended clays or dissolved or particulate organic matter. The filters used (#40 Whatman) will only remove particles larger than 8 μm, they do not remove clay sized particles. Mercury can bind strongly to certain minerals, including iron hydroxides. The strength of the bonds mercury forms with iron hydroxides are due to two hydroxyl bridges that form between the surface of the iron hydroxide and the adsorbed Hg^{2+} (Obukhovskaya, 1983). If present in high enough amounts, iron hydroxide can absorb as much as 99.5% of Hg^{2+} from solution (Obukhovskaya, 1983) in the absence of organic matter. This requires the mercury to be present as Hg^{2+}, as other forms of mercury, particularly $HgCl^+$, $HgCl_2^0$, $HgCl_3^-$, and $HgCl_4^{2-}$ are weakly sorbed by iron hydroxides. Geochemical modeling of mercury species using Solmineq.88 (ARC, 1989) indicated there is little free Hg^{2+} in solution. The majority of the mercury is bound as either HgOHCl or mercuric hydroxide species.

Mercury can also be bound to clays through ion exchange or chemisorption. The presence of chloride in solution inhibits the adsorption of Hg^{2+} by clays (Hogg et al., 1978, Schuster 1991, Yin et.al, 1996). Since, for the soils in this study, the mercury in solution exists as neutrally charged species (Figure 12), ion exchange with the negatively charged clays would be minimal. Mercury can also form strong bonds with organic matter, including soluble humic and fulvic acids. Several authors have suggested that most mercury in a water phase is bonded to humic acids, (Mierle and Ingram, 1991, Wallschlager et.al., 1996, Wallschlager et.al., 1998). The fact that the solutions have concentrations of dissolved organic carbon ranging between 5.6 and 16.8 mg L^{-1} suggests that there is organic matter in solution to which mercury can bind. The presence of soluble organic matter would inhibit the adsorption of Hg^{2+} on mineral surfaces (Schuster, 1991). It is likely that most of the mercury in the water phase is bound to soluble organic matter and not suspended clays. Wallschlager et.al (1996) found that mercury in the water phase "is transported entirely in the form of a complex bound to humic acids", most likely by sulphur-containing ligands. It is not clear whether the mercury in the water phase is associated with dissolved organic matter or particulate organic matter. Kolka et.al (1999) found that total mercury in a water phase is positively correlated with dissolved organic C but suggested that particulate organic C is the "dominant vector of transport". For the soils in this study it is likely that the mercury in the water phase is associated with organic matter rather than suspended clays or minerals. Whether the organic matter is dissolved or as particulate matter is not clear.

4.5. Synthesis.

It is important to know the distribution of mercury in soil and whether the behavior of mercury is dominated by precipitation-dissolution or adsorption-desorption reactions. The reactions that dominate will determine the concentration of mercury within the water phase and hence the mobility and availability of mercury. By determining the distribution of mercury certain conclusions can be drawn as to which type of reaction is controlling mercury's behavior in soil.

It is obvious from this study that the majority of soil mercury is associated with some form of organic matter. In most soils it was the fraction not released until the samples were digested with 30% H_2O_2. This indicates that the majority of mercury is dominated by an adsorption-desorption reaction with organic matter, unless mercury and organic matter are co-precipitating or the organic matter is chelating large amounts of mercury. Although some mercury is held in the cation exchange sites of the organic matter and some mercury is likely chelated by the organic the majority of the mercury is held by stable convalent bonds to O- and S- containing sites.

A second large mercury fraction is the mercury associated with the mineral phase. Except at microsites where mercury concentrates may become elevated it is unlikely that pure mercury minerals are precipitating in large amounts. Except for HgS the minerals are too soluble. D'Itri (1990) stated that it is possible for HgS to form in aerobic soils as the precipitate of a reaction between Hg^{2+} and S^{2-}. S^{2-} ions may be appropriated from other sulphides or via an interaction with the equilibria of organometallic compounds. HgS could also form in anaerobic microsites within the soil and, since the oxidation of HgS is very slow, persist within the mineral phase. Other mercury minerals may precipitate as impurities within other minerals or as pure, non-crystalline minerals whose activities would not be unity and thus would behave differently from the pure crystalline minerals assumed in this study. It is likely however that the majority of the behavior of the mercury found in the mineral phase is dominated by adsorption-desorption reactions. While mercury will sorb physically to the cation exchange sites of soil minerals the majority of the mercury in the mineral phase is bonded chemically (chemisorption). Mercury will form strong, stable bonds with sulphate, phosphate, and carbonate containing minerals

The results of this study lead to some questions that need to be answered. What is the rate of the adsorption-desorption and at equilibrium, what is the concentration of mercury within the water phase? The rate of adsorption-desorption and the equilibrium concentration would be one factor in determining the mobility and availability of mercury in soil. What is the maximum amount of mercury that can be adsorbed by the organic phase in soil? By determining the maximum adsorption of mercury in soil and the stability of mercury in the organic matter phase the risk associated with mercury in soil can be estimated. The concentration of mercury in organic matter and the availability of that mercury will determine how much mercury can reach potential receptors. What is the exact nature of the mercury within the mineral phase? Are pure minerals being formed? Is mercury co-precipitating? What is the maximum adsorption amount? It is important to determine if pure crystalline minerals are present, using x-ray diffraction, or if pure, amorphous mercury minerals are present, perhaps using thermal desorption or chemical extraction techniques. If mercury containing minerals are present in large amounts the expected equilibrium of the soil solution would be different than if adsorption-desorption processes dominate.

This study has also shown that a 0.4M solution of $Ca(OCl)_2$ can remove mercury from soil. The treatment does not remove all of the mercury from the soil and it will remove mercury from some fractions (O.M.II-Hg) easier than other fractions (e.g. TEO-Hg, mineral Hg). The treatment can also, in some soils, lower the TEO content of the soils. This partial removal of mercury and hydrocarbons is accompanied by a loss of organic matter. These results, the incomplete removal of mercury and hydrocarbons and the loss of organic matter, suggest that treating a co-contaminated soil with a 0.4M solution of $Ca(OCl)_2$ is not an effective treatment method. It is not likely that a chemical oxidant such as calcium hypochlorite could ever totally remove mercury and hydrocarbons from a contaminated soil without causing losses in organic matter. This does not mean that chemical oxidation of co-contaminated soils is not a valid treatment method, it only means that the endpoints must be reconsidered. This study did not consider the toxicity present in mercury and hydrocarbon contaminated soil. If mercury is held unavailable in either the organic matter or mineral fractions, would it still pose a toxicity risk? Undoubtedly some mercury fractions, such mercury in the water phase and organic acids phases are more available and pose a risk of moving into the groundwater or adjacent bodies of water. It is for these phases that chemical oxidation may be effective. If a weak hypochlorite solution was used to oxidize the easily available mercury and the resulting solution washed out of the soil it may be possible to lower the toxicity associated with a contaminated soil while removing less organic matter from the soil.

Another important result from knowing the distribution of mercury within soil is the ability to model where mercury will move. By knowing how mercury will distribute among the various soil phases and knowing how those phases will move would enable us to model how mercury will act in the environment. Before we can model accurately we must determine how the differences in mineralogies and organic matter between soils affect the distribution of mercury in soil.

5.0. Conclusions

The majority of mercury in these nine contaminated soils is found associated with a form of organic matter. For all but one soil the dominant fraction is the organic matter II fraction, the fraction released when treated with 30% H_2O_2. Even in the water phase the majority of the mercury is found associated with dissolved or suspended particulate organic matter.

Treating the co-contaminated soils with a 0.4M solution of $Ca(OCl)_2$ does not reduced the concentration of mercury to within the range of background concentrations. The mercury concentration of only one treated soil was below CCME guidelines for commercial sites. The hypochlorite treatment reduced the TEO content of four of the nine soils. Treating a soil with hypochlorite results in a loss of organic matter.

6.0. References

Adriano, D.C. and Doner, H.E. 1982. Bromine, Chlorine and Fluorine. in: Methods of Soil Analysis Part 2. Chemical and Microbiological Properties. Second Edition. Soil Science Society of America, Wisconsin.

Alberta Research Council. 1988. Solmineq.88 PC/Shell Manual.

Allard, B., and Arsenie, I. 1991. Abiotic reduction of mercury by humic substances in aquatic systems – an important process for the mercury cycle. Water, Air, and Soil Pollution. 56:457-464.

Alloway, B.J. 1990. Heavy Metals in Soils. Halsted Press, New York.

Andersson, A. 1979. Chapter 4. Mercury in Soils. In: The Biogeochemistry of Mercury in the Environment. Nriagu J.O. ed. Elsevier/North Holland Biomedical Press, New York.

Benes, P. and Havlik, B. 1979. Speciation of mercury in natural waters. In: The Biogeochemistry of Mercury in the Environment. Nriagu ed. Elsevier/North-Holland Biomedical Press. New York.

Beveridge, A., and Pickering, W.F. 1983. The influence of surfactants on the adsorption of heavy metal ions by clay. Water Research. 17: 215-225.

Biester, H., and Scholz, C. 1996. Determination of mercury binding forms in contaminated soils: Mercury pyrolysis verus sequential extractions. Environmental Science & Technology. 31(1): 233-239.

Bohn, H.L., McNeal, B.L. and O'Connor, G.A. 1979. Soil Chemistry. John Wiley & Sons, Toronto.

Bundy, L.G. and Bremner, J.M. 1972. A simple titrimetric method for determination of inorganic carbon in soils. Soil Science Society of America Proceedings. 36: 273-275.

CCME, 1991. Interim Canadian Environmental Quality Criteria for Contaminated Sites. Subcommittee on Environmental Quality Criteria for Contaminated Sites.

CCME, 1997. Report from the Canadian Council of Ministers of the Environment Workshop on Petroleum Hydrocarbons in Soil. October 15-17, 1997.

Charlton, D.S., Schmit, C.R., Stepan, D.J., and Beaver, F.W. 1992. Research program for dealing with mercury in soil at natural gas industry sites. pp 3-5 in: Mercury and Arsenic Wastes. Removal, Recovery, Treatment and Disposal. US Environmental Protection Agency.

Crock, J.G. 1996. Mercury. in: SSSA Book Series 5. Methods of Soils Analysis Part 3 – Chemical Methods. 769-791.

D'Itri, F.M. 1990. The Biomethylation and Cycling of Selected Metals and Metalloids in Aquatic Sediment. in: Sediments: Chemistry and Toxicity of In-Place Pollutants. Baudo, R., Giesy, J. and Muntau H. eds. Lewis Publishers Inc.

Dowey, U. 1998. Removal of Mercury and Hydrocarbons From Soil. Master's Thesis, University of Alberta.

Dudas, M.J., and Pawluk, S. 1976. The nature of mercury in Chernozemic and Luvisolic soils in Alberta. Canadian Journal of Soil Science. 56:413-423.

Dwarakanath, V., Kostarelos, K., Pope, G.A., Shotts, D., and Wade, W.H. 1999. Anionic surfactant remediation of soil columns contaminated by nonaqueous phase liquids. Journal of Contaminant Hydrology. 38: 465-488.

Eganhouse, R.P., Young, D.R., and Johnson, J.N. 1978. Geochemistry of mercury in Palos Verdes sediments. Environmental Science and Technology, 12(10): 1151-1157.

Environmental Protection Agency, 1999. www.epa.gov/ngispgm3/iris/subst/0692.html.

Farrah, H., and Pickering, W.F. 1978. The sorption of mercury species by clay minerals. Water, Air, and Soil Pollution. 9: 23-31.

Floyd, M. and Sommers, L.E. 1975. Determination of total mercury in soils and sediments. Journal of Environmental Quality. 4(3): 323-325.

Forstner, U., Salomons, W., and Mader, P. 1995. Heavy Metals: Problems and Solutions. Springer-Verlag, New York.

Fountain, J.C., Klimek, A., and Middleton, T.M. 1991. The use of surfactant for *in situ* extraction of organic pollutants from a contaminated aquifer. Journal of Hazardous Materials. 28: 295-311.

Gaudet, C., Lingard, S., Cureton, P., Keenleyside, K., Smith, S., and Raju, G. 1995. Canadian environmental quality guidelines for mercury. Water, Air, and Soil Pollution. 80: 1149-1159.

Hagemoen, S.N., Condemine, A., and Rockandel, M.A. 1994. The 'remerc' process for treatment of K106 mercury mud. Chlorine Institue Inc. Annual Meeting.

Hahne, H.C.H., and Kroontje, W. 1973. The simultaneous effect of pH and chloride concentration upon Mercury(II) as a pollutant. Soil Science Society of America Proceedings. 37: 838-843.

Henke, K.R., Kuhnel, V., Stepan, D.J., Fraley, R.H., Robinson, C.M. Charlton, D.S., Gust, H.M., and Bloom, N.S. 1993. Critical review of mercury contamination issues relevant to manometers at natural gas industry sites. Gas Research Institute, Environment and Safety Research Development.

Herman, D.C., Artiola, J.F., and Miller, R.M. 1995. Removal of cadmium, lead, and zinc from soil by a rhamnolipid biosurfactant. Environmental Science & Technology. 29: 2280-2285.

Hogg, T.J., Stewart, J.W.B., and Bettany, J.R. 1978. Influence of the chemical form of mercury on its adsorption and ability to leach through soils. Journal of Environmental Quality. 7(3): 440-445.

Kan, A.T., Fu, G., Hunter, M., Chen, W., Ward, C.H., and Tomson, M.B. 1998. Irreversible sorption of neutral hydrocarbons to sediments: Experimental observations and model predictions. Environmental Science & Technology. 32(7): 892-902.

Kohut, C., Dudas, M.J., and Luther, S.M. 1995. Investigation of Soil Mercury and Distribution at the Turner Valley Gas Plant. Alberta Environmental Protection, Alberta Community Development Report #HG003-95.

Kolka, R.K., Grigal, D.F., Verry, E.S., and Nater, E.A. 1999. Mercury and organic carbon relationships in streams draining forested upland/peatland watersheds. Journal of Environmental Quality. 28:766-775.

Lindsay, W.L. 1979. Chemical Equilibria in Soils. Wiley, New York.

Luther, S.M. and Dudas, M.J. 1996. Remediation options for mercury contaminated soil at the Turner Valley Gas Plant. Draft Report.

McKeague, J.A., and Kloosterman, B. 1974. Mercury in horizons of some soil profiles in Canada. Canadian Journal of Soil Science. 54: 503-507 Notes.

Melton, J.R., Hoover, W.L., and Howard, P.A. 1971. The determination of mercury in soils by flameless atomic absorption. Soil Science Society of America Proceedings. 35:850-852.

Nriagu, J.O. ed. 1979. The biogeochemistry of mercury in the environment." In: Topics in Environmental Health, Volume 3. Elsevier/North-Holland Biomedical Press, New York.

Obukhovskaya, T.D. 1983. Mercury sorption by soil minerals. Soviet Soil Science. 14(3): 49-55.

Pedroso A.C.S., Gomes, L.E.R., and De Carvalho, J.M.R. 1994. Mercury removal from process sludge via hypochlorite leaching. Environmental Technology. 15:657-667.

Revis, N.W., Osborne, T.R., Holdsworth, G. and Hadden, C. 1989. Distribution of mercury species in soil from a mercury-contaminated site. Water, Air and Soil Pollution. 45:105-113.

Revis, N.W., Elmore, J., Edenborn, H., Osborne, T., Holdsworth, G., Hodden, G., and King, A. 1991. Immobilization of mercury and other heavy metals in soil, sediment, sludge and water by sulfate-reducing bacteria. Biological Processes, Vol. 3. Innovative Hazardous Waste Treatment Technology Series. Technomic Publishing Co. Inc.

Sabatini, D.A., Knox, R.C., and Harwell, J.H. eds. 1995. Emerging technologies in surfactantant-enhanced subsurface remediation. in: Surfactant-Enhanced Subsurface Remediation. ACS Symposium Series 594.

Saterbak, A., Toy, R.J., Wong, D.C.L., McMain, B.J., Williams, M.P., Dorn, P.M., Brzuzy, L.P., Chai, E.Y., and Salnitro, J.P. 1999. Ecotoxicological and analytical assessment of hydrocarbon contaminated soils and application to ecological risk assessment. Environmental Toxicology and Chemistry. 18(7): 1591-1607.

Schuster, E. 1991. The behaviour of mercury in the soil with special emphasis on complexation and adsorption processes – a review of the literature. Water, Air, and Soil Pollution. 56:667-680.

Sposito, G. 1981. The Thermodynamics of Soil Solutions. Clarendon Press, New York.

Stepan, D.J., Fraley, R.H., and Charlton, D.S. 1995. Remediation of Mercury-Contaminated Soils: Development and Testing of Technologies. Gas Research Institure, Environment and Safety Research Group.

Stepan, D.J., Fraley, R.H., Henke, K.R., Gust, H.M., Hasset, D.J., Charlton, D.S., and Schmit, C.R. 1993. A Review of Remediation Technologies Applicable to Mercury Contamination at Natural Gas Industry Sites. Gas Research Institute, Environment and Safety Research Group.

Tabatabai, M.A. 1982. Sulfur. in: Methods of Soil Analysis Part 2. Chemical and Microbiological Properties. Second Edition. Soil Science Society of America, Wisconsin.

Venkatadri, R. and Peters, R.W. 1993. Chemical oxidation technologies: Ultraviolet light/hydrogen peroxide, Fenton's Reagent, and titanium dioxide-assisted photocatalysis. Hazardous Wastes & Hazardous Materials: 10(2): 107-149.

Wade, L.G. 1991. Organic Chemistry, Second Edition. Prentice-Hall Inc. United States.

Wallschlager, D., Desai, M.V.M, and Wilken R-D. 1996. The role of humic substances in the aqueous mobilization of mercury from contaminated floodplain soils. Water, Air, and Soil Pollution 90:507-520.

Wang, J.S., Huang, P.M., Liaw, W.K. and Hammer, U.T. 1991. Kinetics of the desorption of mercury from selected freshwater sediments as influenced by chloride. Water, Air, and Soil Pollution. 56: 533-542.

Wilhelm, S.M., and McArthur, A. 1995. Removal and treatment of mercury contamination at gas processing facilities. SPE/EPA Exploration and Production Environmental Conference, Houston.

Windmoller, C.C., Wilken, R-D., Jardin, W.D.F. 1996. Mercury speciation in contaminated soils by thermal release analysis. Water, Air, and Soil Pollution. 89: 399-416.

Yin, Y., Allen, H.E., Li, Y., Huang, C.P., and Sanders, P.F. 1996. Adsorption of Mercury(II) by soil: Effects of pH, chloride, and organic matter. Journal of Environmental Quality. 25:837-844.

Yin, Y., Allen, H.E., and Huang, C.P. 1997. Kinetics of Mercury(II) adsorption and desorption on soil. Environmental Science & Technology. 31(2): 496-503.

Zumdahl, S.S. 1992, Chemical Principles. D.C. Heath and Company, Toronto.

Appendix 1. Physical and Chemical Characteristics of Mercury

Melting Point = -38.87°C *

Boiling Point = 356.9°C *

Saturated Vapour Pressure = 14 mg m^{-3} (20°C) *

Density = 13.546 g cm^{-3} (20°C) *

Surface Tension = 480 dynes cm^{-1} (20°C) *

Solubility:

Hg = < 4 µg L^{-1} ***

$HgCl_2$ = 69 g L^{-1} **

HgO = 53 mg L^{-1} ***

$Hg(OH)_2$ = 145 mg L^{-1} **

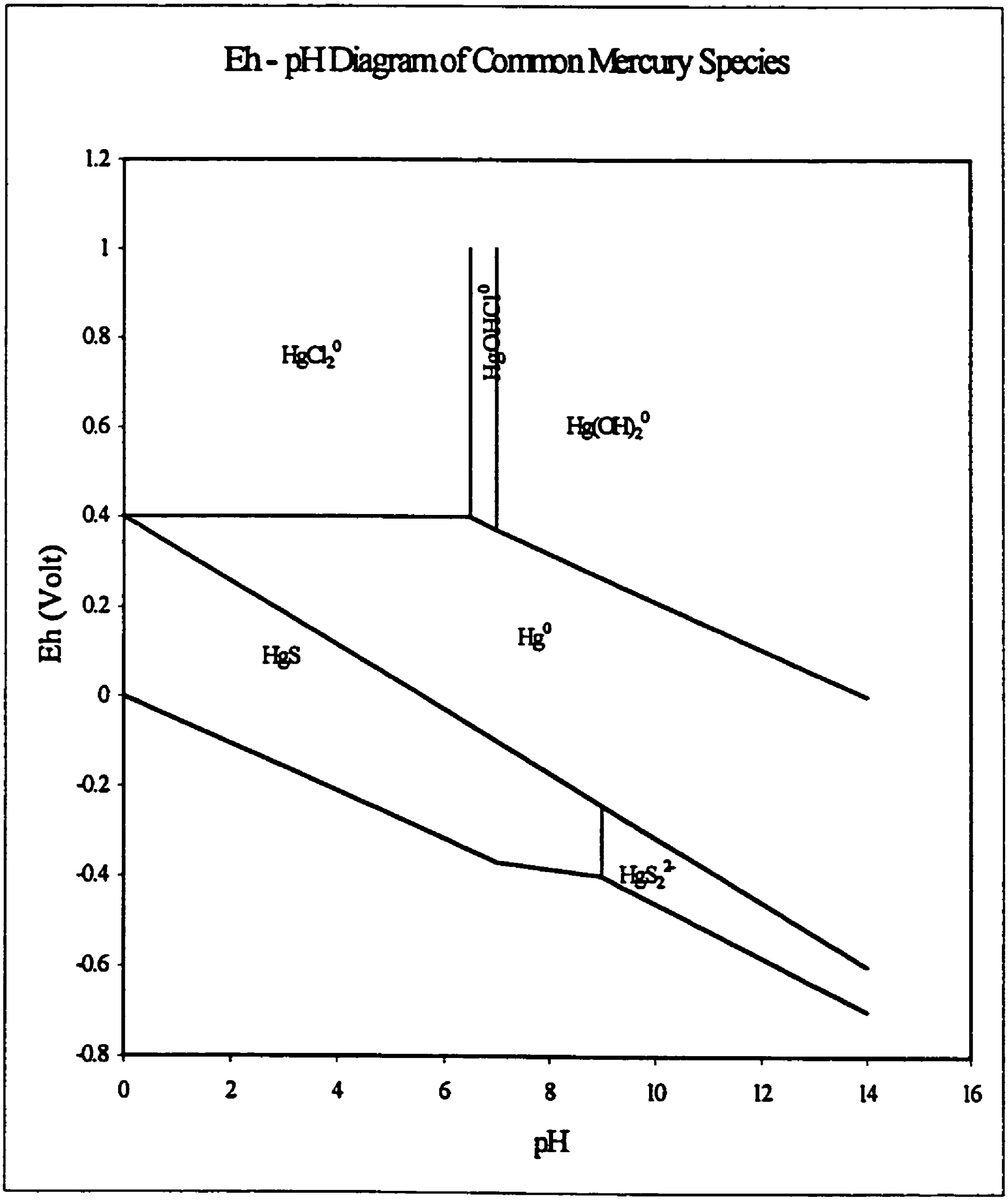
HgS = approx. 10 µg L^{-1} ***

* from Andren and Nriagu (1979).

** from Hahne and Krootje (1973).

*** from Nriagu (1979).

Appendix 2. Eh – pH Diagram of Common Mercury Species. (from Andersson, 1979)



Appendix 3. Surfactant Treatment of Co-contaminated Soils.

Introduction.

Surface active agents (surfactants) were developed to overcome the deficiencies of conventional pump and treat technologies. Pump and treat technologies are limited by parameters such as flow rates, non-aqueous phase liquid (NAPL) composition, mass transfer rates and the surface area available for mass transfer from NAPL to the water phase (Dwarakanath, et.al., 1999). Surfactants were studied to determine if the use of them could overcome some of these deficiencies. These early studies into the use of surfactants led to expanding their use from treating primarily sub-surface to surface soils. Many researchers have studied surfactants potential to remediate hydrocarbon contaminated soils (Sabatini et.al., 1995, Fountain et.al., 1991). Other researchers have investigated surfactant's ability to treat soils contaminated with heavy metals (Beveridge and Pickering, 1983, Herman et.al., 1995). Few researchers have attempted to use surfactants to remediate soils contaminated with hydrocarbons and heavy metals.

Surfactants have several properties that make them suitable to remediate hydrocarbon contaminated soils. Surfactants are amphiphilic, they have both hydrophilic and lipophilic moieties. This property allows surfactants to accumulate at interfaces between different phases, such as the water-oil interface. They will also self-assemble into dynamic aggregates called micelles, with a hydrophilic exterior and lipophilic interior. This allows for hydrocarbons to be suspended in water within the micelles, enabling the hydrocarbons to be washed from soil. These micelles only form when the concentration of surfactant is above the critical micelle concentration (CMC). The CMC varies between surfactants and can be raised or lowered in different system conditions. Surfactants can be anionic, cationic, nonionic or zwitterionic. The surface activity of surfactants can cause them to adsorb to soil particles, though for anionic surfactants the absorption is minimized. Another advantage of anionic surfactants is they experience minimal precipitation.

The ability of surfactants to treat either organic or inorganic contaminated soils means there is potential for surfactants to treat co-contaminated soils. Anionic surfactants have the most potential since they can attract positively charged heavy metals, they can partition hydrocarbons into the interior of micelles and anionic surfactants tend to have the least amount of interaction with the surfaces of soil particles.

The purpose of this experiment was to investigate to potential of an dianionic surfactant, Dowfax 8390, to remediate soils contaminated with hydrocarbons and mercury. A second goal was to determine the concentration of mercury within the treatment wastewater, as mercury within the wastewater may pose problems when disposing of the wastewater. The US EPA guidelines for the maximum permissible concentration of mercury in drinking water is 2 $\mu g\ L^{-1}$ (Forstner, 1990).

Method.

Dowfax Treatment

Five soils contaminated with hydrocarbons and mercury were chosen to determine if a surfactant wash would be effective in reducing levels of contamination. An 8.0×10^{-3} M solution of Dowfax 8390, an anionic surfactant, was added at a 10:1 solution:soil ratio. The solution was made by adding 13.67 g of a 35% Dowfax 8390 solution to 1 L of 0.01M K2SO4 and lowering the pH to 6.5. This results in a solution that is approximately 8.0×10^{-3}M, which is 10x the molarity of the critical micelle concentration (Sabatini et al., 1995). This concentration was chosen because previous studies have shown this to be an effective concentration to reduce the hydrocarbon content of soil.

The TEO and Hg contents of each soil were measured in triplicate before and after treatment with the surfactant solution. The soils were treated by shaking 12g of soil with 120g of solution in a Nalgene centrifuge container for 16 hours on a flatbed shaker. The mixture was then centrifuged and the supernatant solution removed and filtered. The Hg content of the soil and solution was measured using CVAA.

Results.

In all soils except M19 the concentration of Hg in soil decreased following treatment with the surfactant solution (Table 1.0.). The decreases ranged between 9%-29% of the total Hg in soil, averaging a 21% decrease. The TEO content decreased in all soils, though in two soils the decrease was not significant (Table 2.0.). The amount of Hg retained in the surfactant solution after treating the soils ranged between 12 – 125 μg per 120g of solution (10-1040 μg kg^{-1}) (Table 3.0.).

Table 1.0.

	Soil Hg Content (mg Hg kg^{-1} soil)				
	Initial		Treated		
Soil	Average	St.Dev.	Average	St.Dev.	P-Value*
M19	51	5.8	49	2.1	0.21
M20	2200	480	1760	40	0.02
M21	28	1.2	22	2.1	1.57×10^{-3}
M22	17	3.4	13	1.0	0.02
M23	183	16	133	3.6	1.73×10^{-5}

*One-tailed T-Test.

Table 2.0.

	%TEO				
	Initial		Treated		
Soil	Average	St.Dev.	Average	St.Dev.	P-Value*
M19	1.45	0.14	1.17	0.03	0.01
M20	0.39	0.01	0.23	0.20	0.12
M21	0.76	0.03	0.54	0.41	0.20
M22	0.36	0.02	0.08	0.01	1.61×10^{-5}
M23	0.33	0.006	0.05	0.03	7.37×10^{-5}

*One-tailed T-Test.

Table 3.0.

	Solution Hg Content			
	Total Hg in Solution (µg)		mg Hg kg^{-1} soil	
Soil	Average	St.Dev.	Average	St.Dev.
M19	25	2.1	3.5	0.3
M20	125	40	10.3	3.2
M21	20	2.2	5.9	0.3
M22	12	1.0	1.4	0.1
M23	44	3.6	4.2	0.08

Discussion.

Treating co-contaminated soils with Dowfax 8390 is partially successful in reducing the mercury and hydrocarbon contents of the soils. The reduction in soil mercury content, while it is statistically significant in all but one soil, is not a large decrease, averaging only 21% of the initial mercury content. The final mercury content of any of the treated soils does not meet CCME guidelines for commercial sites. The reduction in TEO content of the soils was more effective, averaging a decrease of 51%. It appears that a 10x CMC Dowfax 8390 solution is unable to remove mercury from soil, the solution likely can remove mercury from the water and ion exchangeable phases and remove mercury associated with removed hydrocarbons. The dianionic nature of Dowfax 8390 would attract positively charged mercury species. It does not appear that the Dowfax 8390 is able to remove mercury associated with the organic matter and mineral fractions. Large reductions in soil mercury content would not be possible without the ability to extract mercury from the less available organic matter and mineral fractions. The reductions in the TEO content of the soils shows that a Dowfax 8390 solution is able to remove hydrocarbons from soils, longer reaction times, higher temperatures or a stronger solution may be able to produce larger reductions in the TEO content.

Conclusions.

Treating co-contaminated soils with a 10x CMC solution of Dowfax 8390 for 16 hours is only partially successful in reducing the mercury and hydrocarbon contents of the soils. Longer reaction times, a stronger solution or higher temperatures may be effective in extracting more hydrocarbons from the soil but it is doubtful that much more mercury would be extracted.

The presence of mercury in the solution post-treatment must be considered when considering disposal or reuse of the wastewater. The solution of each soil post-treatment exceeded US EPA guidelines for mercury content of drinking water.