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Potential chemical remediation of mercury in recently impounded reservoirs.

by

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ABSTRACT

Abnormally high mercury concentrations are found in aquatic organisms from recently impounded hydroelectric reservoirs. The mercury has been shown to originate from the inundated soils. Hg emitted from anthropogenic and natural sources, finds its way to the soils following aeolian transport and wet and dry deposition. Mercury is either directly incorporated into the soil's humic horizon or is temporarily stored on vegetation. Upon flooding, the microbial degradation of organic soil material releases Hg to the pore waters and conditions develop which are conducive to methylmercury (MeHg) production. These compounds can either diffuse along their concentration gradients to the overlying waters or be adsorbed to the more refractory solid components of the flooded soil or newly accumulated sediments. Mercury and methylmercury may then be transferred to aquatic organisms through ingestion and respiration.

Several mitigation procedures have been proposed to limit the transfer of Hg and MeHg to aquatic organisms but most cannot be applied to large reservoirs such as those of northern Quebec for practical, economical, and environmental reasons. A better understanding of the diagenetic behaviour of Hg and methylmercury in aquatic environments has lead us to consider methods of enhancing natural processes which would either limit the mobility of Hg in flooded soils or its methylation. Different concentrations of iron oxide, iron shavings and ferrous ammonium sulphate were added to soil slurries in the presence or absence of calcite and gypsum. Mercury released to the supernatent solutions and methylmercury adsorbed to the slurry solids were monitored with time to determine the trapping efficiency of the different chemical additives under both reducing and oxygenated conditions. Whereas all three reagents limited the release of Hg(2+) to the supernatent solution when reducing conditions were allowed to develop in the slurries, ferrous ammonium sulphate appeared to be the most effective at limiting Hg methylation.

RÉSUMÉ

Suivant la mise en eau de réservoirs hydro-électriques, de fortes teneurs en mercure ont été observées dans les organismes aquatiques. Il a été démontré que ce mercure provient des sols inondés. Le mercure, émit de sources anthropiques et naturelles, est transporté via l'atmosphère et déposé à la surface des sols par précipitations sèches et humides où il est retenu par la matière organique. Suite à l'inondation des sols, une forte activité bactérienne libère une partie du mercure lié à la matière organique et contribue au developpement de conditions qui favorisent sa méthylation. Le mercure et le méthylmercure peuvent être relargués dans les eaux interstitielles où ils peuvent diffuser librement ou être réadsorbés à la fraction résiduelle du sol ou des sédiments nouvellement formés. Une fois dans la colonne d'eau, le mercure peut être respiré ou ingéré par les organismes aquatiques.

Plusieurs techniques d'atténuation ont été proposées pour limiter le transfert du mercure et du méthylmercure aux organismes aquatiques mais la plupart ne s'appliquent pas aux grands réservoirs du Nord québecois pour diverses raisons pratiques, économiques et environnementales. Une meilleure connaissance du comportement diagénétique du mercure et du méthylmercure dans les milieux aquatiques nous a permis de concevoir différentes façons de promouvoir les procédés naturels qui limitent la mobilité et la méthylation du mercure dans les sols inondés. Des ajouts d'oxide de fer, de limaille de fer et de sulfate d'ammonium ferreux, additionés de calcite, ainsi que de gypse à diverses concentrations ont été effectués dans des suspensions d'un sol organique. Les concentrations de mercure total dissous dans la solution surnageante et de méthylmercure absorbé aux solides ont été mesurées en fonction du temps afin de comparer l'efficacité de ces sels en milieu oxygéné ainsi qu'en milieu réducteur. Les trois composés ont limité le relargage du mercure dans les eaux surnageantes lorsque des conditions réductrices se sont developpées dans les suspensions. Le sulfate d'ammonium ferreux semble, néanmoins, avoir été le plus efficace des trois composés à inhiber la méthylation du mercure.

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1.0 Introduction

Although the toxic effects of mercury have been known for centuries, health risks caused by the ingestion of Hg-contaminated fish became evident in the 1950's after the poisoning outbreak in Minamata Bay, Kyushu Island, Japan. For several decades, a pharmaceutical company, the Chisso Corp. used mercury as a catalyst for acetaldehyde production and discharged large quantities of Hg compounds to the bay which was used as fishing grounds by the local population. Over several months, a neurological disease developed. There were symptoms of brain damage, and several hundred villagers died. Although the epidemic was immediately linked to fish consumption, it was only in 1958 that McAlpine and Araki (1958) identified methylmercury (MeHg) as the cause. In Canada, concerns over mercury contamination of aquatic environments have been raised over the past few decades with the discovery of high levels of mercury in the effluents of chlor-alkali plants on major tributaries such as the Saguenay Fjord (Loring, 1975; Smith and Loring, 1981) and the Wabigoon River system (Turner and Rudd, 1983a,b) but most strikingly, in the biota of newly impounded hydroelectric reservoirs situated far from any point source of contamination (Potter *et al.*, 1975; Bodaly and Hecky, 1979; Cox *et al.*, 1979; Waite *et al.*, 1980; Hecky *et al.*, 1987; Messier and Roy, 1987; Jackson, 1988a,b; Chaire de Recherche en Environnement HQ/CRSNG/UQAM, 1992). In the case of the hydro development carried out by Hydro-Québec in the James Bay Territories, the contamination impacts directly on the health of the local population for which fish is a staple source of protein.

The relationship between reservoir impoundment and the rise of MeHg concentrations in fish tissue was first mentioned in the United States in the late 1970's. Cox *et al.* (1979) showed that Hg enters the food chain from the inundated soil where it accumulates in the organic horizon, prior to impoundment, through wet and dry deposition from the atmosphere (Nriagu, 1979, 1989; Evans, 1986; McMurty *et al.*, 1989; Ouellet and Jones, 1982; Verta *et al.*, 1989). More recently, it has been demonstrated that bacterial activity associated with the decomposition of organic matter in the flooded soils of hydroelectric reservoirs promotes the methylation of inorganic mercury (Furutani and Rudd, 1980; Ramlal *et al.*, 1987; Lindqvist *et al.*, 1991). Several mechanisms have been proposed to explain the transfer of MeHg from the sediments to the biota: diffusion to the overlying water column (Morrison and Thérien, 1991); resuspension of organic-rich particles (Louchouarn *et al.*, 1993; Mucci *et al.*, 1995); emergence and ingestion of insect larvae (André *et al.*, 1991; Bloom, 1992; Parkman and Meili, 1993; Tremblay *et al.*, 1993). In fish, methylmercury is readily bioaccumulated through food ingestion and respiration.

1.1 Hg Cycling in the Environment

Mercury is released into the atmosphere by both anthropogenic and natural sources as elemental, organic and inorganic mercury. Mercury's characteristic physico-chemical properties (high vapour pressure and low solubility in water) renders most inorganic and organic mercury compounds, with the exception of mercury salts such as $HgCl_2$, strongly resistant to chemical, photochemical, and biochemical degradation (Siegel and Siegel, 1979; Landa, 1978; Ferrara *et al.*, 1982; Fitzgerald *et al.*, 1983). These mercury compounds may therefore persist and be transferred within the different reservoirs of the environment (biosphere, hydrosphere, atmosphere...).

The present emission budget of mercury to the atmosphere is difficult to estimate because of difficulties in assessing diffuse anthropogenic and natural emissions. This is compounded by measurement errors at point sources. The combustion of coal and peat, waste incineration, mining activities, and ore roasting account for most of the anthropogenic emissions of Hg to the atmosphere (Mitra, 1986; Nriagu and Pacyna, 1988; Shieh, 1992). Inorganic mercury is released to the atmosphere by industrial processes which produce chloride (electrolysis of NaCl), Hg vapour lamps, urethane plastics, and acetaldehydes (Lindberg and Turner, 1977; Fitzgerald, 1986; 1989; Nriagu and Pacyna, 1988; Ferrara *et al.*, 1992). Elemental Hg is used in chemical and physical laboratories, in thermometers and in barometers. Compounds such as calomel, Hg_2Cl_2, and mercury chloride, $HgCl_2$, are routinely employed as pesticides and bactericides. Organic mercurials (e.g. methylmercury and phenylmercury), which are generally more toxic than their inorganic counterparts, are used as pesticides in agriculture, and fungicides by the pulp and paper industry. Landfill deposits of municipal and industrial waste, slag from metal production, and fossil fuel combustion also release mercury to the atmosphere. Total anthropogenic emissions have been estimated at approximately 3.5×10^9 g Hg/yr (Nriagu and Pacyna, 1988).

Mercury is also released to the atmosphere through four main natural processes which include: 1) emission from soils and plants (Rodgers, 1979; Siegel *et al.*, 1981; Schroeder *et al.*, 1989; Xiao *et al.*, 1991); 2) degassing from geological mineral deposits (Andren and Nriagu, 1979); 3) emissions from volcanic activity (Anderson, 1975; Unni *et al.*, 1978; Nriagu, 1989); and 4) the photoreduction of Hg(2+) in natural waters (Lindqvist *et al.*, 1991; Xiao *et al.*, 1991). Lindqvist *et al.* (1991) proposed a mercury flux of 10 g Hg yr^{-1} km^{-2} for Scandinavian forest soils, which taken over a global scale gives a total mercury flux of 1.48×10^9 g yr^{-1}. Volatilization of Hg from a large variety of vascular plants (Siegel *et al.*, 1974, 1981), non-vascular plants such as lichens and mosses (Siegel *et al.*, 1980), and algae (Ben-Bassat and Mayer, 1975, 1977, 1978) also contribute to the Hg emission from soils but the amount of Hg released cannot be readily quantified. Using an inventory of mineralized and non-mineralized areas of the United States, Andren and Nriagu (1979) calculated an average degassing rate of 0.13 x 10^{-9}g Hg m^{-2} yr^{-1} for the United States. Similarly, Lindqvist *et al.* (1991) estimated that 0.25 x 10^{9} g Hg are globally emitted each year from mineral deposits if area-normalized global rates are taken to be half those encountered in Sweden. Globally, the sum of natural Hg emissions has been estimated at about 3 x 10^{9} g yr^{-1} (Nriagu and Pacyna, 1988). It is now generally accepted that the total global atmospheric Hg emission budget is about 6 to 7.5 x 10^{9} g yr^{-1} (Nriagu and Pacyna, 1988; Lindqvist *et al.*, 1991).

Almost all of the mercury found in the atmosphere (95%) is in the Hg(0) form. Elemental mercury has an atmospheric residence time of 0.5 to 2 years (Lindqvist and Rodhe, 1985; Slemr *et al.*, 1985; Fitzgerald, 1986; Lindqvist *et al.*, 1991; Slemr and Langer, 1992) and can therefore be dispersed over long distances. Once in the higher troposphere, a small fraction of Hg(0) within the cloud cover may be oxidized to Hg(2+) by ultraviolet radiation, or by reacting with free radicals (e.g., OH and OOH) and ozone (Lindqvist et al., 1991). Mercury may then be washed out of the atmosphere through its hydration in cloud droplets. The newly formed aqueous Hg(2+) may also associate with airborne particulates. If the cloud is evaporated, compounds bound to particulates may stay in the aerosol phase, whereas the reactive Hg(2+) compounds will be reduced to Hg(0) by photodissociation (Lindqvist *et al.*, 1991). In contrast to gaseous Hg(0) (Brosset, 1982; Fitzgerald *et al.*, 1991), particulate Hg finds its way to the ground through wet precipitation (rain and snow) and dry deposition (Bjorklund *et al.*, 1984; Fitzgerald *et al.*, 1986; Verta *et al.*, 1989; Slemr and Langer, 1992; Lucotte *et al.*, 1995) often showing a pattern of decreasing mercury concentrations with distance from the point of emission (Chaire de Recherche en Environnement, 1991, 1992; Nater and Grigal, 1992). Methylmercury concentrations which are very low in the atmosphere (~0 to 5%

of the total atmospheric inventory) (Bloom and Fitzgerald, 1988), appear to increase with altitude (Lindqvist *et al.*, 1991).

1.2 Effects of Impoundment

Once on the soil, Hg(2+) is readily taken up by organic matter and, if conditions remain oxidizing, will accumulate in the humic horizon of the soils (Lindqvist *et al.*, 1991; Bodaly *et al.*, 1994; Lucotte *et al.*, 1995) and to a lesser extent in the mineral accumulation zone (B-horizon) (Lindqvist *et al.*, 1991; Schuster, 1991; Dmytriw, 1993; Dmytriw *et al.*, 1995). Upon flooding, soils undergo important physical, chemical, and biological changes. Redox conditions vary as oxygen is consumed as a result of the microbial degradation of organic matter and the oxygen penetration depth migrates up toward the newly established sediment-water interface (Grondin *et al.*, 1995; Dmytriw *et al.*, 1995). As labile organic matter is degraded, part of the inorganic mercury is released to the soil waters whereas a fraction is methylated through bacterial activity (Abernathy and Cumbie, 1977; Bodaly and Hecky, 1979; Jackson, 1988a, 1988b). The rate of methylation of mercury is increased under suboxic and anoxic conditions as well as by the increase in pH of soil waters following impoundment. Remobilized mercury may be adsorbed to authigenic and detrital Fe and Mn oxihydroxides in the oxygen penetration zone (Jackson, 1988a, 1988b), precipitate with sulphides below the redox boundary (Huerta-Diaz *et al.*, 1993), be released to the water column (Gunnison *et al.*, 1985; Thérien and Morrison, 1985) but most likely be readsorbed by organic matter. The integrated total Hg burden of the O-horizon of flooded soils is generally unaffected by the impoundment (Grondin *et al.*, 1995). In contrast, methylmercury accumulates in the flooded soil where little if any is detectable before flooding (Chaire de Recherche en Environnement HQ/CRSNG/UQAM, 1993). Upon migration into the overlying waters, through diffusion or active transport (e.g. resuspension of methylmercury-laden particles, assimilation and emergence of insect larvae) methylmercury will be absorbed by phytoplankton and benthic organisms and bioaccumulated through the food chain. Bloom (1992) confirmed that more than 85% of the total mercury in fish is in the form of methylmercury.

Methylmercury is a powerful neurotoxin with ten times the toxicity of the inorganic mercury compounds (Magos and Webb, 1980). In fish, methylmercury is readily taken up by the liver, muscle and fatty tissues but is only excreted slowly (Ganther and Sunde, 1974). Canadian regulations state that the level of mercury in fish acceptable for human consumption should not exceed 0.5 µg/g. Thus, although mercury can only be found at low concentrations in the water column of inundated hydro-electric basins (Montgomery *et al.*, 1995), aquatic organisms may assimilate and concentrate enough methylmercury in their muscle tissues to render them hazardous for human consumption. The degree of Hg contamination in fish appears to be proportional to the flooded surface area (Abernathy and Cumbie, 1977; Bodaly *et al.*, 1984; Hecky *et al.*, 1987; Jackson, 1988a,b, 1989). The LG-2 Reservoir (53^0 N, 77^0W) which belongs to the hydroelectric complex of La Grande River in James Bay resulted in the inundation of 2630 km^2 of land (92% of the total surface area of the reservoir) (Louchouarn *et al.*, 1993). Verdon et al. (1991) and recent reports from the James Bay Mercury Committee (1993, 1994) have shown that, 9 years after impoundment, mercury levels in fish from the LG-2 reservoir were approximately four times their natural levels (around 6 µg Hg/g for Northern pike).

1.3 General Considerations

In order to reduce mercury accumulation in fish tissue, the methylation of mercury must be inhibited. This can be achieved by isolating Hg(2+) in the sediment, reducing its bioavailability or promoting demethylation. Because our research focuses on the sources and fate of mercury in large hydro-electric reservoirs, many of the potential mitigation procedures cited in the literature are inapplicable. Proposed deforestation, soil removal, and burning of the O-horizon could destroy mercury sources prior to impoundment. Liming of the waters may reduce methylation rates in acid lakes by increasing pH (Hakansson, 1990), whereas nutrient dumping increases productivity and overfishing dilutes mercury concentration in fish tissues (Hakansson, 1990; Verta, 1990). There is still much debate over the efficiency of these methods which, given the size of the reservoirs in Northern Quebec (13 672 km^2 of flooded soil for the La Grande complex), are either impractical or economically unrealistic. Furthermore, the use of some of the chemical additives proposed in past studies are not environmentally acceptable and, in fact, could add to the problem by substituting pollutants. A review of proposed and tested mitigation procedures appears in the next chapter.

In this study, I have investigated the ability of iron oxides, iron shavings and ferrous ammonium sulphate to sequester Hg(2+), to inhibit mercury methylation, and to promote demethylation. Gobeil and Cossa (1993) observed the strong affinity of Hg(2+) for Fe oxihydroxides in coastal marine sediments. Gagnon *et al.* (1996) reported that authigenic Fe oxihydroxides which accumulate in the oxic zone may serve as a geochemical barrier to the release of Hg and MeHg from a contaminated coastal marine sediment. They propose that MeHg is catalytically demethylated by the oxides whereas Hg(2+) is strongly adsorbed by the same phases. Consequently, the presence of iron oxide phases at or near the soil/sediment interface may act as a trap for mercury and methylmercury diffusing out of the inundated soil of a reservoir. If allowed to migrate with the sediment/water interface, Fe oxihydroxides will continually scavenge Hg diffusing from below. Upon burial in the suboxic zone, the oxides will be reduced and release their Hg load to the pore waters. The reduced iron may then migrate back to the redox boundary where it will precipitate as oxides and be recycled, complex with organic matter or precipitate as a sulphide.

1.4 Objectives of this study

The concern over mercury contamination of fish in hydro-electric reservoirs has created an impetus to develop suitable mitigation procedures. Although many different methods have been proposed, their viability, effectiveness, cost, and environmental impact may not be suitable.

There exist three approaches toward successfully resolving the problem of mercury contamination in aquatic systems: 1) reduce mercury emissions; 2) decrease mercury bioavailability and methylation; 3) decrease methylmercury bioaccumulation.

The present study attempts to find an economic and environmentally acceptable means of inhibiting or at least limiting the release of Hg from soils, as well as its methylation and bioaccumulation in aquatic organisms. We experimented with various combinations and concentrations of innocuous chemicals which could be added directly to a soil prior to impoundment or to the water column following impoundment. We sought reagents that would promote the sequestration of Hg within the soil, and thus render it unavailable for methylation. Iron oxide (Fe_2O_3) and iron shavings were selected because they are readily available at low cost from sources such as primary ore deposits, mine tailings and smelter waste. An iron salt, ferrous ammonium sulphate was also tested because it combines three compounds which should promote the sequestration of mercury: iron for which the properties of the oxides and sulphides have already been mentioned, ammonia which promotes bacterial activity and sulphate which, upon reduction to sulphide, may precipitate with

Hg or Fe. Our experiments were conducted with a naturally Hg-contaminated forest soil from the shores of the La Grande-2 reservoir in Northern Quebec. Because the availability of inorganic mercury for methylation is dependent upon the abundance and type of organic matter, only the humic horizon was used.

This study thus attempts to determine the effects of Fe oxides, elemental iron and ferrous ammonium sulphate additions on the release of Hg and methylmercury accumulation in a flooded Hg-contaminated forest soil. In addition, the influence of Eh and pH on the trapping efficiency of the reagents was investigated. Finally, since methylation and demethylation occur concurrently and are difficult to distinguish, known concentrations of methylmercury were added to soil-water slurries in order to determine the demethylating ability of the reagents. Total dissolved mercury, dissolved organic carbon (DOC), and methylmercury associated with the solid were measured over time on aerated and incubated soil slurries in order to determine which reagents and redox conditions are best suited for limiting Hg release and methylation after a soil is flooded.

2.0 Literature Review

2.1 Review of Attempted and Potential Remediation Procedures

As mentioned earlier, a number of remediation procedures have been cited in the literature which may or may not be applicable to the hydroelectric reservoirs of Northern Quebec. The following is a brief review of the proposed methods, the theory of their mechanism, and how they impact on the mobility and bioavailability of mercury in aquatic systems.

2.1.1 Chemical bonding of Hg

i. *Manganese and Iron Oxihydroxides*

Manganese and iron oxihydroxides are nearly ubiquitous in natural aquatic environments and are known to play an important role on the geochemical behaviour and mobility of heavy metals (Krauskopf, 1956; Goldberg, 1961; Jenne, 1968; Posselt *et al.*, 1968; Gadde and Laitinen, 1974; Lion *et al.*, 1982; Laxen, 1985; Young and Harvey, 1992). The discovery of marine manganese nodules enriched with heavy metals, including mercury, was the first evidence of mercury scavenging by manganese oxides (Goldberg, 1963). Gobeil and Cossa (1993) recently demonstrated that authigenic iron and manganese oxihydroxides which accumulate in oxic sediments of the Laurentian Trough can efficiently scavenge mercury. Very few studies have dealt with the addition of Mn and Fe oxihydroxides to natural freshwater environments but laboratory experiments suggest that these phases could play a significant role in controlling Hg contamination in hydro-electric reservoirs.

The adsorption of Hg by Mn and Fe oxihydroxides can remove mercury from fresh waters that are oxygenated and low in organic matter (Ponnamperuma, 1972; Lockwood and Chen, 1973; Tessier *et al*, 1985; Jackson, 1989). Colloidal manganese oxides produced through the oxidation of Mn(2+) and the reduction of Mn(7+) have a high affinity for Hg(2+) (Posselt *et al.*, 1968; Lockwood and Chen, 1973; Loganathan and Burau, 1973; Lia and Li, 1982). Crystalline forms of MnO_2 adsorb only small amounts of mercury but hydrous Mn(4+) oxide coatings strongly increase the scavenging capacity of other colloidal particles for Hg(2+) from natural waters (Thanalabasingam and Pickering, 1985). Hg can also be efficiently removed from contaminated waters through adsorption onto goethite (FeOOH) (Inoue and Munemori, 1979) Gunneriusson *et al.* (1995) observed an 80% removal of both methylmercury and inorganic mercury from solutions treated with goethite. Results, however, indicated that methylmercury adsorption onto iron oxides can only take place in iron-rich environments (Gunneriusson *et al.*, 1995). Following Hg scavenging, the Mn and Fe oxihydroxides must settle quickly and deposit as solid particulate matter in the sediment bed of the basin to avoid being ingested by aquatic organisms. If allowed to remain suspended these oxihydroxides may serve as the main source of trace metals to bottom dwelling organisms (Luoma and Jenne, 1977; Andrews and Fitchko, 1987).

The concentration of methylmercury present in solution results from the competition between methylation and demethylation rates. As such, catalysis or inhibition of methylation and/or demethylation reactions result in changes in CH_3Hg^+ concentrations. Studies by Jackson (1989) indicated that the addition of large amounts of hydrous manganese oxide (manganite, MnOOH) to a mercury contaminated basin reduced methylation considerably while small amounts of MnOOH, present as coatings on clay surfaces, actually stimulated methylation or had no appreciable effect. Jackson (1989) proposed that, in recently flooded forest soils, the effect of MnOOH on methylmercury production may be superseded by the availability of inorganic Hg and the increased microbial growth which result from the degradation of plant remains. In nutrient-poor environments, however, MnOOH coatings on clay particles appeared to enhance demethylation (Jackson, 1989). In the same study, the author found that goethite promoted demethylation in both nutrient-rich and nutrient-poor environments.

Mercury adsorbed to Mn and Fe oxihydroxides is not easily displaced unless the geochemical system is altered and the mineral substrate becomes unstable (Jarvis, 1984). Ferric and manganic ions are reduced under suboxic and anaerobic conditions. Upon inundation, changes in redox conditions promoted by microbial degradation of organic matter lead to a thinning of the oxygen penetration depth, the reduction of the oxihydroxides below it and the release of Hg(2+) associated to these phases to the pore waters (Stumm and Sulzberger, 1992; Sposito, 1989; Ponnamperuma, 1972). Gobeil and Cossa (1993) observed an increase in Hg concentrations in marine sediment pore waters following Mn and Fe oxihydroxide reduction. Once released, Hg(2+) may diffuse as soluble complexes both vertically and horizontally depending on concentration and hydraulic gradients (Davison *et al.*, 1982; Gunnison *et al.*, 1985). Molecular and eddy diffusion can transport soluble reduced Mn and Fe species to the sediment-water interface (Tessier *et al.*, 1985) where they can be reoxidized and precipitated if oxygen is present in the overlying waters. These authigenic oxides will undergo the same cycle of dissolution if buried below the redox boundary (Davison *et al.*, 1982; Davison, 1993). Consequently, the system should always be well oxygenated if Mn and Fe oxihydroxides are to be used to mitigate mercury contamination.

Adding Mn and/or Fe oxihydroxides to an inundated soil may be an efficient way to treat Hg contamination. Technically, this method which does not require an extensive deployment of equipment is suitable regardless of the size of the reservoir involved. Because mitigation calls for significant amounts of these scavenger phases, Fe oxihydroxides are favoured in the treatment of large areas such as Quebec's inundated soils because they are readily available as industrial wastes and can be bought at extremely low costs.

ii. Iron Sulphides

The use of iron sulphides in the treatment of mercury contaminated freshwater systems was considered when it was discovered that heavy metals readily associate with sulphides. It is now well documented that several heavy metals are strongly associated with the sulphide fraction of sediments (Luther *et al.*, 1980; Kitano *et al.*, 1980) or suspended particulates (Jacobs and Emerson, 1982). The adsorption of metal ions onto pre-existing sulphides (Phillips and Kraus, 1965; Brown *et al.*, 1979; Wu and Yang, 1976; Forssberg and Jonsson, 1981; Kislingskaya *et al.*, 1981) is known to play an important role on the geochemical behaviour of these metals particularly when their concentrations do not permit the formation of distinct insoluble sulphides (Jacobs and Emerson, 1982; Dryssen *et al.*, 1984).

Because of the abundance of Fe in natural systems and the low solubility of iron sulphides over a wide range of redox conditions, iron sulphides are ubiquitous in anoxic sediments. Naturally occurring iron sulphides such as pyrrhotite (FeS) and pyrite (FeS_2) are excellent adsorbers for Hg(2+) and Hg(0) from aqueous solutions (Brown *et al.*, 1979; Hyland *et al.*, 1990). Sulphide minerals may also limit methylmercury production by sequestering Hg(2+) (Craig and Morton, 1983) or by promoting the formation of volatile hydrophobic dimethylmercury which is lost to the atmosphere following migration through the water column. Studies by Huerta-Diaz *et al.* (1993) suggest that trace metals, including Hg, may also be associated with AVS (acid volatile sulphides: amorphous FeS + mackinawite). Iron monosulphides are metastable phases that form instead of the more stable pyrite in the presence of excess reactive iron (Gagnon *et al.*, 1996; Huerta-Diaz *et al.*, 1993). AVS concentrations as high as 312 μmol/g have been measured in freshwater sediments (Davison et al., 1985; Davison, 1988). Brown *et al.* (1979) indicated that pyrrhotite may sorb much larger amounts of Hg(2+) than pyrite, under equivalent mercury, sodium, and chloride concentrations. Pyrite, however, appears to be a superior adsorber for Hg(0).

Hg sorption can occur through the co-precipitation of Hg species with iron sulphide minerals and their subsequent accumulation in these phases or through the formation of detrital Hg sulphides (Luther *et al.*, 1980; Huerta-Diaz and Morse, 1990; Huerta-Diaz *et al.*, 1993). Adsorption is dependent upon redox conditions. Trace metals associated with iron sulphides can potentially be released into the aquatic environment when reduced sediments are transported to oxic environments through bioturbation or dredging activities (Moore *et al.*, 1988; Huerta-Diaz *et al.*, 1993). The oxidation of pyrrhotite by oxygenated waters will release adsorbed/co-precipitated Hg(2+) rendering it available for methylation. FeS may also undergo non-oxidative dissolution when oxidation of dissolved sulphides in neighbouring sediments creates a concentration gradient within the sediment medium (i.e. during the fall overturn of stagnant lakes, dredging, bioturbation, or organic matter degradation at the sediment-water interface) (Pankow and Morgan, 1980). Fe(2+) may then diffuse toward an anoxic/oxic boundary within the sediments or water column. On the other hand, pyrite oxidation is very slow and thus, it is more suited for Hg-adsorption under varying Eh conditions. As mentioned previously, HgS is not readily precipitated when dissolved sulphides are found in natural waters. Because of the speciation of Hg in natural waters, iron sulphides will usually form preferentially when reducible Fe(3+) phases are abundant in the sediments. In the presence of Fe(3+), low solubility cinnabar (HgS, solubility 0.002 ng/g) will oxidize and release Hg to solution (Burkstaller *et al.*, 1975).

Quebec's hydroelectric reservoirs are dynamic systems characterized by frequent changes in chemical and physical conditions. During the summer, reservoirs become stratified as a thermocline develops in the water column. The hypolimnion may become depleted in oxygen and reduced components produced in-situ or accumulating in the sediments may be released to the overlying waters. Reservoirs lose their stratification in late summer or early fall when temperatures begin to decrease. Wind effectively mixes the surface waters and, with the dissipation of the thermocline, dissolved oxygen is again found throughout the water column. Thus, the direct addition of iron sulphides to the water column as a potential mitigation protocol would not be feasible nor effective in the treatment of northern Quebec's hydroelectric reservoirs. Iron sulphides are undoubtedly excellent Hg scavengers but an appropriate mitigation procedure for the treatment of hydroelectric reservoir should promote their authigenic formation in the sediments by the addition of suitable innocuous chemicals such as iron oxides and sulphate minerals like gypsum.

iii. Iron

Schultz (1989) proposed the addition of iron dust to reduce mercury contamination of harbour waters in Australia. The iron filing treatment successfully reduced Hg concentrations in the water column by 90% by fixing the metal at the sediment surface. Fe^0 was oxidized in the water column to iron oxides which scavenged mercury according to the mechanisms described previously. Upon burial in the sediments and the establishment of anoxic conditions, reduced iron was precipitated as iron sulphides which also contributed to the scavenging.

Electrochemical methods have also been proposed as a means to reduce mercury concentrations in waste water (Williams and Olson, 1976; Robertson et al., 1978; Oren and Soffer, 1983; Matlosz and Newman, 1986). Grau and Bisang (1995) used iron felt, instead of electrical energy, as a reducing agent to remove mercury from waste waters containing chloride ions. The waste waters containing mercuric and chloride ions in contact with the iron formed a battery:

$$HgCl_4^{2-} + 2\,e^- \rightarrow Hg^0 + 4\,Cl^-$$
$$Fe^0 \rightarrow Fe^{2+} + 2\,e^-$$

Iron felt loaded with mercury was subsequently dissolved with hydrochloric acid to recover the mercury. This method has industrial applications and is relatively inexpensive, but is not suited to the treatment of freshwater systems. Laying down of iron felt over Quebec's large reservoirs would require a great deployment of resources which are not technically practical. Furthermore, raising the chloride concentration of the systems is not economically nor environmentally viable.

2.1.2 Physical bonding of Hg

i. Suspended Particulate Matter

The suspension of particulate matter as a remedial strategy is questionable because findings on its effects have been contradictory and thus treatment could be ineffective, or even worse, aggravate the problem. The formation of inorganic compounds of low solubility (precipitation or co-precipitation) and adsorption onto particulate matter will generally decrease the mobility of mercury whereas complexation of mercury with dissolved organic and inorganic ligands may increase its mobility if these substances remain in solution (Xu and Allard, 1991). The affinity of dissolved Hg for suspended particulate matter in the water column is well documented (Jernelov, 1969, 1972; Cranston and Buckley, 1972; Reimers and Krenkel, 1974; So, 1980; Frenet, 1981; Airey and Jones, 1982; Jackson et al., 1982; Nishimura and Kumagai, 1983; Ferrara *et al.*, 1986, 1989). Sediment resuspension is a very efficient transport mechanism for Hg in a variety of natural aquatic environments including lakes (Hulscher *et al.*, 1992), rivers (Jackson *et al.*, 1982; Rudd and Turner, 1983), and marine estuaries (Lindberg and Harris, 1977; So, 1980). Ferrara *et al.* (1991) noted that suspended particulate matter was responsible for most of the transport of Hg in a naturally contaminated river. Cranston and Buckley (1972) observed higher concentrations of mercury associated with suspended particles than in the deposited sediments. Finally, Turner and Rudd (1983a) reported that the addition of particulate matter to an enclosure reduces the supply of Hg to fish and other organisms by an order of magnitude, whereas Jackson (1989) proposes that it inhibits methylation and fosters demethylation.

The extent of particulate adsorption in the water column is dependent upon the size, nature, and concentration of the particles that are held in suspension. Smaller particles will usually carry more Hg per unit weight than larger ones (Hakansson, 1972; Craig and Morton, 1976; Airey and Jones, 1982), given their greater relative surface area. Cranston and Buckley (1972) reported a positive correlation between the mercury content of size-fractionated river and estuarine sediments and the logarithm of the mean specific surface area of each fraction. Similarly, Garland and Wildung (1974) observed substantially higher concentrations of mercury in suspended matter than in the corresponding bed sediments, which they attributed, at least in part, to size effect. Organic-rich particles, because of their greater affinity for Hg, will generally have higher Hg concentrations than suspended clays or sands (Rae and Aston, 1982). The mechanisms responsible for Hg adsorption onto particulate organic matter will be discussed in the next chapter.

Adsorption of Hg on suspended solids is also dependent on the composition of the waters, in particular the pH and the redox conditions. A decrease in water column pH allows increased desorption of mercury from suspended particles and thereby increases the availability of mercury for methylation (Wood, 1980; McMurty *et al.*, 1989). Since the waters of northern Quebec's reservoirs are known to be slightly acidic (Morrison and Thérien, 1991), remediation by way of particulate matter addition may not be suitable. In addition, for particulate matter to successfully inhibit mercury availability to aquatic biota, the particles in suspension must flocculate and accumulate at the sediment-water interface quickly so that they do not become a potential food source for pelagic and benthic dwellers. Mucci *et al.* (1995) have shown, that upon the resuspension of the "O"-horizon of a soil, methylmercury released to the overlying waters remains in suspension with fine grained particles and thus may be an important vector of methylmercury to the biota. If contained in suspended or bed sediments Hg may still be remobilized by desorption due to changes in the chemistry of the pore waters or of the overlying waters. Thus, whereas this method may efficiently control mercury level in some aquatic systems, dredging activities and erosion processes along the exposed shores of impoundments through drawdown, wind-induced waves and ice scouring (Louchouarn *et al.*, 1993) make it inapplicable to hydroelectric reservoirs where periodically suspended Hg- and CH_3Hg-laden particulates will render Hg available for bioaccumulation.

ii. Clays

Similarly, the addition of clays as a remedial solution is not without controversy. Clay particles introduced to a contaminated reservoir have been shown to inhibit methylation and foster demethylation but, in some cases they also promote methylation (Jackson, 1988a,b, 1989; Kelso *et al.*, 1994). Reimers and Krenkel (1974) observed that, in the absence of chloride, illite sorbed twice as much inorganic mercury as montmorillonite, and kaolin sorbed 20% less than montmorillonite. Turner and Rudd (1983a) have shown that the addition of clays to an enclosure reduced the supply of Hg to fish and other organisms by an order of magnitude. Jackson (1989), however, established that the apparent role of clay in microbial Hg transformations was actually a function of the nature and concentration of associated oxides present as coatings on the clay surfaces. The binding of inorganic mercury and/or methylmercury to the clays renders it less available for methylation and/or bioaccumulation from both the water column and the surface sediments of the reservoir. As opposed to other proposed methods, there appears to be a very low reversibility of the adsorption of mercury on clays (Reimers and Krenkel, 1974). This suggests that chemisorption or surface co-precipitation are the mechanisms responsible for Hg fixation onto clays (Jenne, 1977). This method may help control Hg contamination in hydroelectric reservoirs, but the addition of clay may modify water quality by diluting and rapidly burying organic nutrients and suppressing primary productivity by blocking out sunlight (Jackson, 1989).

2.1.3 Hg Bioaccumulation and Depuration

i. Selenium

The addition of selenium to an aquatic environment seems to inhibit both Hg methylation and uptake by aquatic biota (Wren and Stokes, 1988; Kelso *et al.* 1994). The interactions between Se and Hg in aquatic organisms are well documented (Pelletier, 1985) but the true effect of selenium on mercury bioaccumulation has not yet been clearly shown. Many results are unrelated and sometimes contradictory (Pelletier, 1985; Micallef and Tyler, 1987). Modification of mercury toxicity in the presence of Se has been observed in a number of studies: adult fish and their developmental stages (Huckabee and Griffith, 1974; Kim *et al.*, 1977; Heisinger *et al.*, 1979; Bowers *et al.*, 1980; Sharma and Davis, 1980; Klaverkamp *et al.*, 1983a,b; Turner and Rudd, 1983b; Bjornberg *et al.*, 1988), crustaceans (Lucu and Skreblin, 1981) and phytoplankton (Gotsis, 1982). However, it has been shown that the presence of both Se and Hg had a synergistic interaction on fish eggs (Huckabee and Griffith, 1974).

Paulsson and Lundbergh (1991) reported that the application of 2 µg/L of Se to a contaminated water column over a two year period was effective in reducing the concentration of mercury in perch. In experiments undertaken in the English-Wabigoon River, the addition of sodium selenite to the sediments appeared to impede the rate of Hg bioaccumulation by fish, crayfish, and benthic organisms (Rudd *et al.*, 1980; Turner and Rudd, 1983b; Turner and

Swick, 1983). Similar results were obtained when sodium selenite was added directly to the water column (Parks, 1988; Lindqvist *et al.*, 1991). The modification of Hg toxicity by Se, however, seems to be concentration dependent. Klaverkamp *et al.* (1983b) found that whereas Hg bioaccumulation was decreased by low selenium concentrations (1 µg of Se/L), it was maintained by high Se concentrations (100 µg Se/L). Ganther and Sunde (1974) propose that in spite of high concentrations of mercury in tuna fish, its toxicity is significantly reduced by their high selenium content. On the other hand, Micallef and Tyler (1987) showed that the most effective treatment against acute lethal Hg toxicity in mussels was the addition of an equivalent amount of selenium so that Hg:Se =1 in the water column. The literature on the co-accumulation of Se and Hg in bivalves is also conflicting. Whereas field studies have shown that an inverse correlation exists between selenium and mercury levels in mussels (Karbe *et al.*, 1977), laboratory experiments found that selenium had no effect on the accumulation rate of Hg (Pelletier, 1985).

Like mercury, selenium is bioaccumulated through the food chain (Rudd *et al.*, 1980; Turner and Rudd, 1983 a,b; Turner and Swick, 1983; Leskinen *et al.*, 1986) and can be methylated by microbial processes (Burkes and Flemming, 1974; Chau *et al.*, 1976; Paulsson and Lundbergh, 1991). Se is an essential micronutrient for many animals (NAS, 1976) and it naturally occurs with mercury in a 1:1 molar ratio in many aquatic organisms (Koenam *et al.*, 1973; MacKay *et al.*, 1975; Pelletier, 1985; Leonzio *et al.*, 1986). Fish muscle have a finite number of receptor sites for mercury and selenium which increases with the age, length and weight of the specimen (Leonzio *et al.*, 1982). In the presence of both Hg and Se, these protein sites are occupied preferentially by Hg. When additional selenium is added to a water basin, it competes directly with Hg for the available sites (Pelletier, 1986). If Se concentrations exceed that of Hg in the water column, Se ions are preferentially taken up (Leonzio *et al.*,

1982) thereby reducing mercury concentrations in fish tissues proportionally to the amount of selenium absorbed (Turner and Rudd, 1983b). Chemical investigations have shown that, in aquatic environments, Se is present in various oxidation states (Measures and Burton, 1978, 1980; Takayanagi and Cossa, 1985), but the available evidence indicates that it is the selenide form of selenium which diverts the binding of Hg (Gasiewicz and Smith, 1978; Whanger *et al.,* 1980): H_2Se binds to a sulfhydryl group of proteins and subsequently binds to mercury (Ridlington and Whanger, 1981). In addition to competing with Hg for binding sites in live tissue, selenium present in the water column and/or sediments can also bind with Hg to form HgSe which is resistant to methylation (Ridlington and Whanger, 1981; Pelletier, 1985; Kelso *et al.,* 1994). The same process is responsible for the biochemical detoxication of mercury in mammals (Pelletier, 1985; Martoja and Viale, 1977). In fish, however, the antigonism of selenium for Hg uptake is mostly due to alterations in the biological activity or the distribution of mercury in fish tissue (Chen *et al.,* 1974, 1975; Endo *et al.,* 1977; Ridlington and Whanger, 1981; Micallef and Tyler, 1987) rather than its effect on Hg adsorption or elimination from fish or to its conversion to a less toxic form (Demayo *et al.,* 1979).

Although Se could be of interest in reducing mercury contamination, it too can be toxic in excessive amounts. Rudd *et al.* (1980) and Paulsson and Lundbergh (1991) noted the toxicity of Se to aquatic invertebrates at concentrations exceeding 10 µg Se/L. Magos and Webb (1980) reported that mammals may suffer growth retardation, loss of hair, renal failure, liver degeneration, and possibly death upon exposure to high levels of selenium. Current Canadian regulations state that Se levels in waters should not exceed 1 µg/L (IJC, 1981; CCREM Task Force on Water Quality Guidelines, 1987). To prevent toxic Se enrichment within fish tissue, only the lowest possible level of selenium should be used. This in turn, may prove insufficient for mercury remediation.

2.1.4 Other Methods

Other remediation methods have been proposed which are readily applicable to small lakes which have economic importance due to tourism or high land values. The size of northern Quebec's hydro-electric reservoirs, however, and their remoteness may not justify the use and expense of some of the proposed treatment methods.

i. Fertilization and over fishing

Verta (1990) proposed three different mechanisms for the decrease of mercury concentrations in fish tissue: an increase in primary productivity, a change of diet or a decrease in the methylmercury concentration of the water column. An increase in the primary productivity through the addition of nutrients was proposed as a means to dilute mercury concentrations in fish tissue (Beijer and Jernelov, 1979; Hakanson, 1980). Subsequent studies, however, have shown that an increase in primary productivity, is accompanied by an increase in fish mercury levels (Turner and Rudd, 1983a). Recent studies by Hakanson (1990) have shown similar results. Overfishing removes the older and most contaminated fish from the reservoir. This relatively quick remediation method has produced good results in Finland where the removal of 50% of the fish biomass of a small lake significantly reduced mercury concentrations in the remaining fish population (Verta, 1990). This method which has been carried out successfully in many small lakes (less than 5 km^2) has never been tried in reservoirs. For effective treatment of Quebec's large hydroelectric reservoirs, perhaps millions of tonnes of fish would have to be removed and buried, thus possibly creating additional environmental problems.

ii. Liming

Several authors have shown a direct relationship between the acidity of water and the Hg content in fish (Jones et al., 1986; Verta et al., 1986; Hakansson et al., 1988; Lindqvist et al., 1991). Consequently, the addition of limestone (calcium carbonate or dolomite), has been considered as a method to decrease methylation in acid lakes. Liming decreases acidity through the following mechanism:

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-$$

Studies on Swedish acid lakes have documented a 30% decrease in Hg contamination within two years following liming (Hakanson, 1990; Lindqvist et al., 1991; Andersson and Borg, 1994). Sloan and Schofield (1983), however, reported that liming had no appreciable effect on the level of mercury bioaccumulation in fish. Liming introduces large concentrations of dissolved Ca(2+) to the aquatic environment thereby altering water quality and modifying its ionic strength. Changes in the ionic strength of the overlying waters may trigger the desorption of mercury already trapped in the sediments (Duarte *et al.*, 1991). Liming is an expensive procedure which has only be used on relatively small reservoirs (i.e. a few km^2). The poor effectiveness of liming would render it unsuitable for the treatment of Quebec's hydroelectric reservoirs.

iii. Deforestation and soil removal

Deforestation and the removal of the soil's O-horizon could significantly reduce Hg contamination in hydroelectric reservoirs by eliminating the Hg source. Studies have shown, however, that trees do not contribute their mercury load to the system. Messier et al. (1985) suggested that deforestation would not have a significant effect on mercury accumulation by fish tissue because forest trees do not contribute significantly to the easily degradable organic horizon (Hydro-Quebec, 1992). Thérien (1992) indicated that, following impoundment, a tree will take an average of 100 years to decompose whereas twigs and cones will take 30 years, and leaves and needles, only 5 years. Leaves and needles, as well as the "O"-horizon which contribute most of the mercury to the reservoir should be the main targets for removal. Selective removal of these components is not technically nor economically feasible. Sbeghen (1994) estimated at $ 1 044 000 000 the cost of deforestation and removal of the organic horizon of a 450 km^2 reservoir. In light of the fact that most of Quebec's hydroelectric reservoirs span thousands of square kilometers, such an endeavour would certainly not be technically nor economically viable. Clear-cutting for commercial exploitation would no be justified either since the trees of the taiga have little commercial value, especially when transportation costs are considered (Morrison and Thérien, 1991). Burning of the area would release large amounts of CO_2, Hg, and soot to the atmosphere and would probably require a complete environmental impact assessment. Burning may remove trees but forest fires usually have minimal effects on ground-level vegetation (Morrison and Thérien, 1991). In addition, deforestation and soil removal may have a serious environmental impact on the water quality by increasing erosion and exposing to the water, components of the soil which would normally be buried (Sbeghen, 1994). Finally, the removal of the organic horizon could reduce nutrient availability for the fish community (Sbeghen, 1994) and worsen the ecological impact.

2.2 Mercury Speciation in Soils

The availability of mercury for methylation is dependent upon the abundance, surface area, and binding capacity of soil constituents prior to and after impoundment. Consequently, the characterization of these constituents and their associated mercury speciation is important to this study as they will regulate mercury remobilization, methylation, and accumulation in aquatic organisms.

Hg may occur in the soil in various forms:

1. dissolved (free ion or soluble complex),
2. non-specifically adsorbed (binding mainly due to electrostatic forces),
3. specifically adsorbed (binding due to covalent or coordinative forces),
4. chelated (bound to organic substances), and
5. precipitated (as sulphide, oxide, hydroxide, etc.) (Sposito, 1989).

The type of mercury associations formed will depend not only on the mercury speciation in solution but also on the physical and chemical properties of the binding substrates, and the strengths of the bonds formed. The geochemical behaviour of mercury in soils is mainly controlled by adsorption and desorption processes. Mercury adsorption on a substrate (oxide, organic matter, sulfide, clay) depends largely on that substrate's abundance and binding capacity relative to other soil components (Young and Harvey, 1992; Andersson, 1979). Mercury speciation is dependent on soil pH (MacNaughton and James, 1974; Forbes *et al.*, 1974), organic matter content (Semu et al., 1987), chloride concentration (Xu and Allard, 1991), and bacterial activity (Farrah and Pickering, 1978). Chloro complexes of mercury in soil are amongst the most mobile and stable Hg compounds (Schuster, 1991). Studies conducted by Andersson (1979) indicate that Hg is preferentially sorbed by organic matter in acidic soils such as podzols whereas in neutral soils, iron oxides and clay minerals dominate Hg sorption.

2.2.1 Complexation with organic matter

Since mercury is bound to organic matter in soils and remains associated with the humic horizon, the behaviour and distribution of Hg in soils is determined by the physical fractionation of organic matter. Both the quantity and the type of organic matter are key factors in the adsorption of Hg (Landa, 1978; Hurley *et al.*, 1991; Schuster, 1991; Lodenius *et al.*, 1987). Humic matter consists of a humic fraction (soluble in basic solutions only) and a fulvic fraction (soluble over the full pH range), both of which can form water-soluble and water-insoluble complexes with a variety of metal ions (Schnitzer and Kerndorff, 1981; Mierle and Ingram, 1991). Humic compounds (both humic and fulvic fractions) are complex three-dimensional macromolecules that consist of aromatic and aliphatic rings which are irregularly cross-linked by a variety of bonds. The structure of these humic molecules, linked primarily through hydrogen bonds, offers a number of voids, of varying size, in which organic and inorganic molecules can be contained (Rashid, 1985). Because the specific surface area and cation exchange capacity of humic matter is higher than any other soil substrate (Landa, 1978; Rashid, 1985), the humic and fulvic fractions of organic matter show the strongest affinity for Hg adsorption (Lag and Steinnes, 1978; Lodenius *et al.*, 1987). Studies by Dmytriw *et al.* (1995) indicate that, in a podzol, 60 to 80% of the total Hg in the O-horizon is extracted with partially degraded organic matter by a 1M NaOH solution. Sodium hydroxide extractions dissolve both the humic and fulvic fractions of organic matter (Rashid, 1985). Humic compounds in soils may also form low solubility solid gels. Mercury may incorporate these gels, accumulate within them and remain stable as long as the soil is well drained (Arakel and Hongjun, 1992) which is not the case of flooded soils.

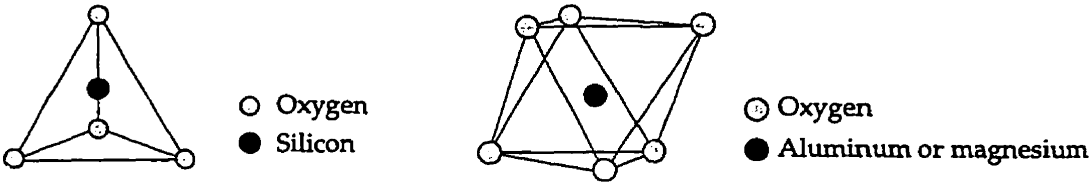
The strong affinity of mercury for humic matter is most likely related to the stability of the sulfhydryl-mercury complexes (Gavis and Ferguson, 1972). Hg adsorption by organic matter may also occur via oxygen-rich functional groups such as carboxylic -COOH, phenolic and alcoholic -OH, and ketonic and quinonoid -C=O (Lamar, 1968; Semu *et al.*, 1987; Allard and Arsenie, 1991). Hg will bind with these functional groups through metal chelation, ion exchange, coordination bonding, pi bonding, and Van der Waals bonding (Gjessing, 1976). The most common bond between Hg and organic matter is formed through chelation reactions. Approximately 1/3 of the total binding capacity of soil humus is used for cation exchange whereas 2/3 of the available binding sites serve for metal chelation (Lodenius *et al.*, 1987; Dmytriw, 1993). $Hg(OH)_2^0$ complexes with organic ligands possessing S^- (Schuster, 1991) and with carboxyl groups of humic acids (Allard and Arsenie, 1991). The adsorption of mercury on organic matter is pH dependent (Rashid, 1985). As soil pH increases, the surface charge on both organic and inorganic soil colloids becomes more negative. The increase in the cation exchange capacity of the complexes (Helling *et al.*, 1964) allows more Hg(2+) to be attracted and retained onto the colloids. Mercury complexation with humic compounds increases with increasing pH as a result of the ionization of the reactive functional groups (Duarte *et al.*, 1991; Schuster, 1991) whereas Hg availability increases upon acidification.

Although strong bonds form between humic matter and mercury, Miller (1975) has shown that Hg (2+) in soils and sediments can be reduced to Hg(0) in the presence of humic acid and released back to the water column. Similarly, Trost (1970) reported an increase in the solubility of cinnabar and mercuric oxide in the presence of humic acids. Allard and Arsenie (1991) noted that the abiotic reduction of Hg(2+) by humic matter may be insignificant in soils where microbial processes dominate because the presence of sulphidic groups in humic matter enhances the stability of Hg complexes. In contrast, the dissolved humic substances of aqueous systems, as opposed to particulate humics in the soil, may help promote the abiotic redox process (Allard and Arsenie, 1991).

2.2.2 Adsorption onto Clay Minerals

Studies conducted by Farrah and Pickering (1978) show that clay minerals are effective substrates for Hg adsorption. Because of their high specific surface area and significant surface charge, clay minerals are important sorbents of Hg(2+) as they expose large internal and external surfaces to the soil solution (Greenland and Hayes, 1981).

Clay minerals are primarily crystalline aluminum or magnesium silicates with stacked-layer structures of tetrahedral or octahedral sheets. In the *tetrahedral sheet*, each silicon atom is surrounded by four oxygen atoms in a tetrahedral arrangement; these tetrahedra are connected in an open hexagonal pattern in a continuous 2-dimensional array. The *octahedral sheet* consists of two layers of oxygen atoms (or hydroxyl groups) in a hexagonal closest-packed arrangement with Al or Mg atoms at the octahedral sites (Figure 1). The sheets are stacked into two- or three-layer units (T-O or T-O-T) through the sharing of their oxygen atoms. Clay mineral structures consist of various combinations of the T-O and T-O-T layers. Isomorphic substitution of the cations by ions in the soil solution may lead to negatively charged layers. Since Hg(2+) has a large ionic radius, it may possibly fit into the three-layer crystal assemblage of illite and similar clay minerals, where K(+) is usually found (Andersson, 1979). In addition, Andersson (1979) suggests that clay surfaces to which Hg is adsorbed may become covered by new precipitates. Following the growth of these precipitates, Hg may be trapped and fixed.



Silicon tetrahedron

Aluminum or magnesium octahedron

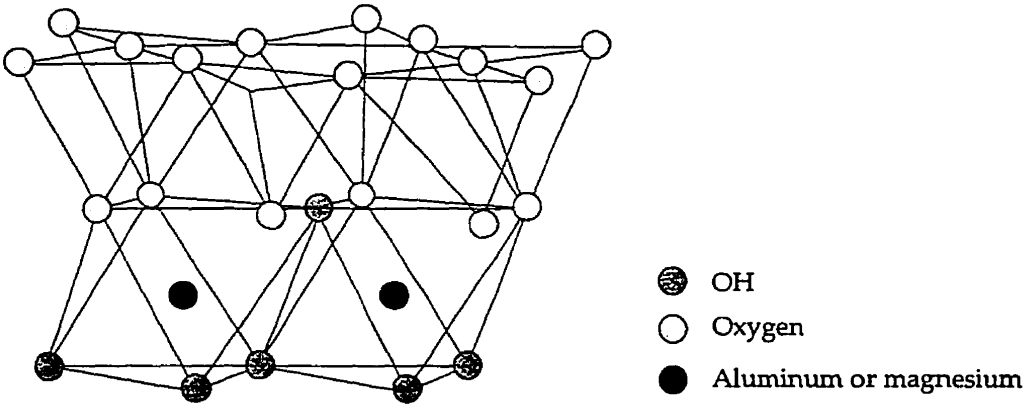


Figure 1 : Diagrammatic sketch of a two layer (T-O) clay mineral. The tetrahedral sheet is bonded on one side by an octahedral layer (from Grim, 1968)

Reimers and Krenkel (1974) observed that clays and sands adsorbed less Hg with increasing chloride ion concentrations. In the absence of ligands such as chloride or dissolved organic matter, the Hg sorption capacity of some clay minerals, such as illite and kaolinite is independent of pH except for montmorillonite for which Hg uptake decreases with increasing pH (Farrah and Pickering, 1978).

2.2.3 Adsorption onto Oxides

Iron and manganese oxides can serve as effective sinks for metal fixation by soils and sediments (Jenne, 1968). The adsorption capacity for Hg of amorphous and poorly crystalline Fe and Mn oxides in soils has been studied by numerous authors (Shimomura *et al.*, 1969; Forbes *et al.*, 1974; Lockwood and Chen, 1974; Inoue and Munemori, 1979; Barrow and Cox, 1992). In soils, iron oxides are present as Fe_2O_3, FeOOH and $Fe(OH)_3 . nH_2O$ (Ponnamperuma *et al.*, 1967) whereas the distribution of Mn is controlled by the precipitation of insoluble (Mn(3+) and Mn(4+)) hydrous oxides and the leaching of soluble Mn(2+) compounds (Jarvis, 1984). Manganese and iron oxihydroxides scavenge trace metals through adsorption and co-precipitation reactions (Jenne, 1968; Lockwood and Chen, 1973). The mechanisms of adsorption can be described according to :

$$S - OH_x + M \leftrightarrow S - OM + xH^+$$

where $S - OH_x$ are the free surface sites, S - OM is the complex surface, and x is the average number of H^+ ions released by the metal (M) sorbed (Posselt *et al.*, 1968; Tessier *et al.*, 1985).

Cation sorption by solid oxide surfaces is a pH-dependent process (McKenzie, 1980; Benjamin and Leckie, 1981). With increasing pH, the degree of ionization of the surficial -OH functional groups increases (Benjamin and Leckie, 1981; Young and Harvey, 1992). Consequently, Hg adsorption increases since adsorption occurs through the formation of two hydroxy bridges with the oxide surfaces (Figure 2) (Forbes *et al.*, 1974). Mercury is actively adsorbed by manganese oxides over a wide range of pH (3 to 11) in the absence of chloride and organic ligands (McNaughton and James, 1974), but mercury adsorption increases significantly between pH 6 and 8, where $Hg(OH)_2^0$ becomes the dominant species in solution (McNaughton and James, 1974; Jarvis, 1984; Tessier *et al.*, 1985; Thanalabasingam and Pickering, 1985) (Figure 3). This would indicate that Hg(2+) and $HgCl_2$ are either not adsorbed or only weakly adsorbed in comparison to $Hg(OH)_2^0$ (Lockwood and Chen, 1973; McNaughton and James, 1974; Evans, 1989):

$$S - OH \rightarrow SO^- + H^+$$

$$SO^- + Hg(OH)_2^0 \rightarrow S - O - HgOH + OH^-$$

The amount of Hg sorbed to Fe and Mn oxihydroxides is dependent on pH but also on the mercury ion concentration, chloride concentration, and the ratio of adsorbate to adsorbent (Slavek and Pickering, 1986). In addition to ligand exchange with surface hydroxyl groups, $Hg(OH)_2^0$ can be transformed into a solid hydroxy phase (Posselt *et al.*, 1968; Thanalabasingam and Pickering, 1985; Evans, 1989). With time, the agglomeration of the precipitate decreases the availability of adsorption sites and changes the rates of adsorption (Morgan and Stumm, 1964; Lockwood and Chen, 1973).

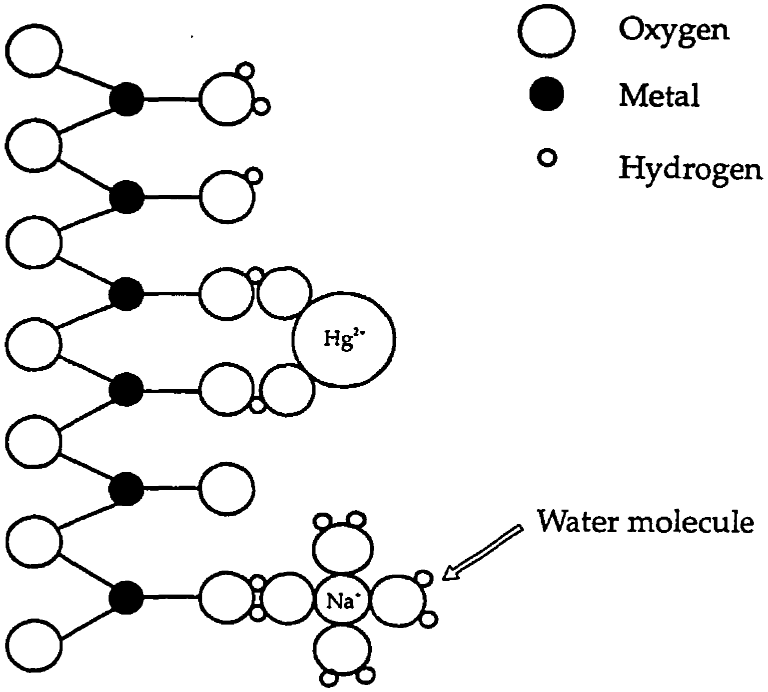


Figure 2: Schematic diagram of a Hg-hydroxy bridge to an inorganic hydroxyl surface (modified from Sposito, 1989).

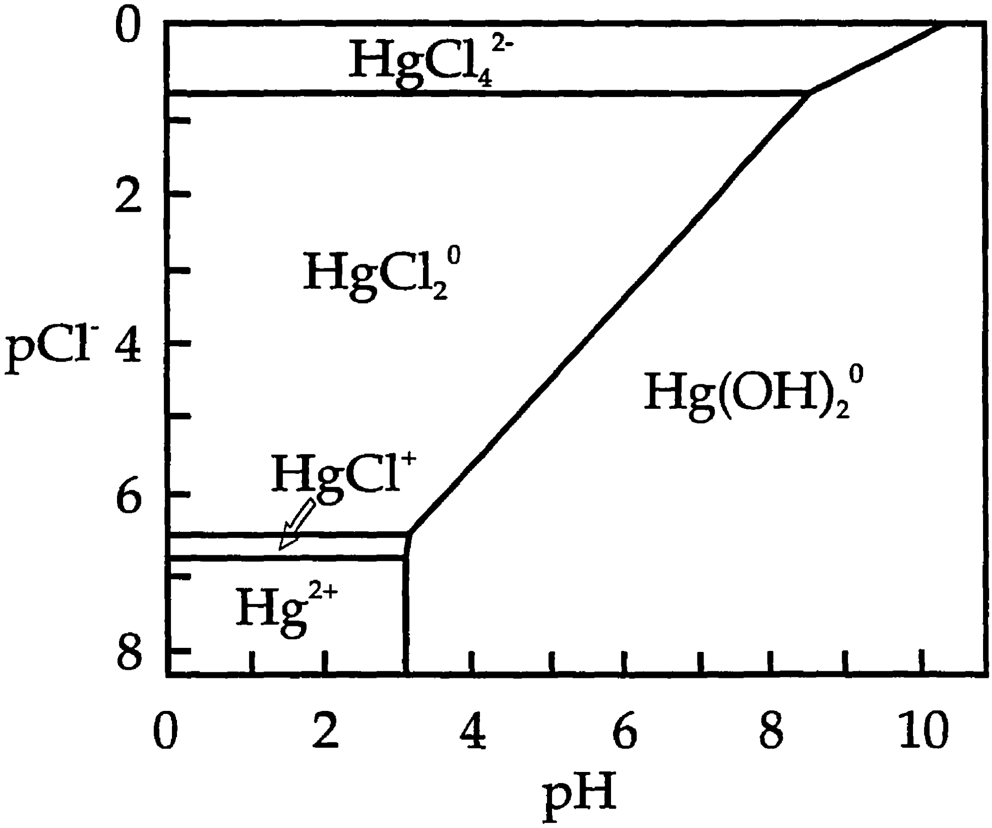


Figure 3 : Predominance diagram for chloride and hydroxy complexes of divalent mercury in aqueous solutions (from Lockwood and Chen, 1973).

2.2.4 Adsorption and Co-precipitation with Sulphides

Naturally occurring sulphides are efficient mercury scavengers. Desorption experiments using a variety of ligands suggest that more than one Hg species is involved in the sorption process and that the strength of the bonds formed vary (Hyland *et al.,* 1990). For example, on galena surfaces, strongly bound HgS is formed through the dissolution of PbS. Concurrent reactions, however, are responsible for the deposition of weakly bound Hg which renders galena inert and prevents the continued deposition of HgS. Similarly, $HgCl_2$ can be weakly bound to pyrite through both adsorption and surface precipitation processes but HgS is not formed to any significant extent. Hyland *et al.* (1990) demonstrated that the presence of crystallites on the surface of pyrite were indicative of both adsorption and surface precipitation of $HgCl_2$. Theoretical considerations also indicate that the formation of HgS from $HgCl_2$ at the expense of pyrite is thermodynamically favourable:

$$HgCl_2\,(aq) + FeS_2 \rightarrow HgS\,(s) + FeCl_2\,(aq) + S(0) \qquad (K = 1.6 \times 10^{10})$$

log K_s of HgS = -38.9 (Dyrssen and Kremling, 1990)
log Ks of FeS_2 = -21.58 (Sillén and Martell, 1964)).

Laboratory experiments, however, have revealed the existence of only very small amounts of strongly bound HgS on pyrite surfaces which cannot be removed by extraction (Hyland *et al.,* 1990). The fact that HgS is not formed to any significant extent and that the mineral structure of pyrite is not disturbed by the $HgCl_2$ reaction owes to the kinetic stability of pyrite (Hyland and Bancroft, 1990; Hyland *et al.,* 1990). Almost ten times more Hg is sorbed than Fe is lost in the reaction of $HgCl_2$ with pyrite.

HgS is not a major component in aerobic soils (Schuster, 1991). Under reducing conditions, iron associated with reducible minerals can be precipitated by dissolved H_2S and other sulfur compounds produced by sulphate-reducing bacteria. Hg released from soil metal oxides and organic matter can either co-precipitate with iron sulphides or form its own metal sulphide if present in sufficient amounts (Huerta-Diaz and Morse, 1990; Luther *et al.*, 1980).

2.3 Mercury Speciation in Freshwater

Mercury speciation in freshwaters must be characterized since it influences Hg uptake by benthic and other aquatic organisms in hydroelectric reservoirs. Mercury can form a wide variety of species in natural waters thanks to the comparable stability of Hg(0) and Hg(2+), and the ability of Hg(2+) to complex with both organic and inorganic ligands in solution. Divalent mercury will also form organomercuric compounds when linked to one or two organic radicals (R or R′) via their carbon atom: R-Hg-X (where X is an inorganic ligand) or R-Hg-R′ (Benes and Havlik, 1979). The radicals in these organomercuric compounds are usually methyl and phenyl groups whereas the most common inorganic ligands are chloride, hydroxide, nitrate, and sulphate ions (Benes and Havlik, 1979). In addition to the formation of dissolved mercury species in freshwaters, Hg adsorption on solid particles results in the formation of "particulate" or "insoluble" Hg species.

2.3.1 Dissolved forms of mercury

i. *Inorganic species*

The chemical speciation of inorganic mercury in natural waters is strongly dependent on the redox conditions and the pH of the system. Using chemical equilibrium constants and standard redox potentials published in the literature, Hem (1970) as well as Gavis and Ferguson (1972) determined which mercury species predominate in typical freshwater environments. The results are presented in the form of a Eh-pH diagram (Figure 4). Monovalent mercury is unstable and dismutates spontaneously into Hg(0) and Hg(2+) in aquatic environments (Moser and Voigt, 1957). In well oxygenated waters (Eh ~ 0.5 V), mercuric species will be the predominant form of inorganic soluble mercury. Under mildly oxidizing or reducing conditions, Hg(0) should prevail unless there is enough sulphide present in the system to precipitate HgS (log K= -38.9, solubility 0.002 ng/g) (Furutani and Rudd, 1980; Sillén and Martell, 1964). Although limited in freshwaters, sulphidic complexes may be abundant in sediment porewaters or in certain types of waste waters (Benes and Havlik, 1979).

In well oxygenated surface waters, the nature of Hg(2+) complexes will depend on the pH and the chloride concentration of the system as divalent mercury forms very stable chloride complexes. Lockwood and Chen (1973) constructed a diagram illustrating the predominance regions of different chloro- and hydroxomercury species as a function of pCl and pH (Figure 3). These results, in accordance with Anfalt et al. (1968), show that in the absence of organic ligands, $Hg(OH)_2^0$ or $HgCl_2^0$ will predominate in most freshwaters.

ii. *Complexes with organic ligands*

Mercury is known to form stable complexes with a number of organic ligands in solution (Sillén and Martell, 1964, 1971). Goulden and Afghan (1970) found that approximately 50% of the soluble mercury in streams is organically complexed. The formation of such complexes depends on the concentration and the type of organic species present (Lockwood and Chen, 1974; Sen and De, 1987), the pH, ionic strength (Lockwood and Chen, 1973), as well as the

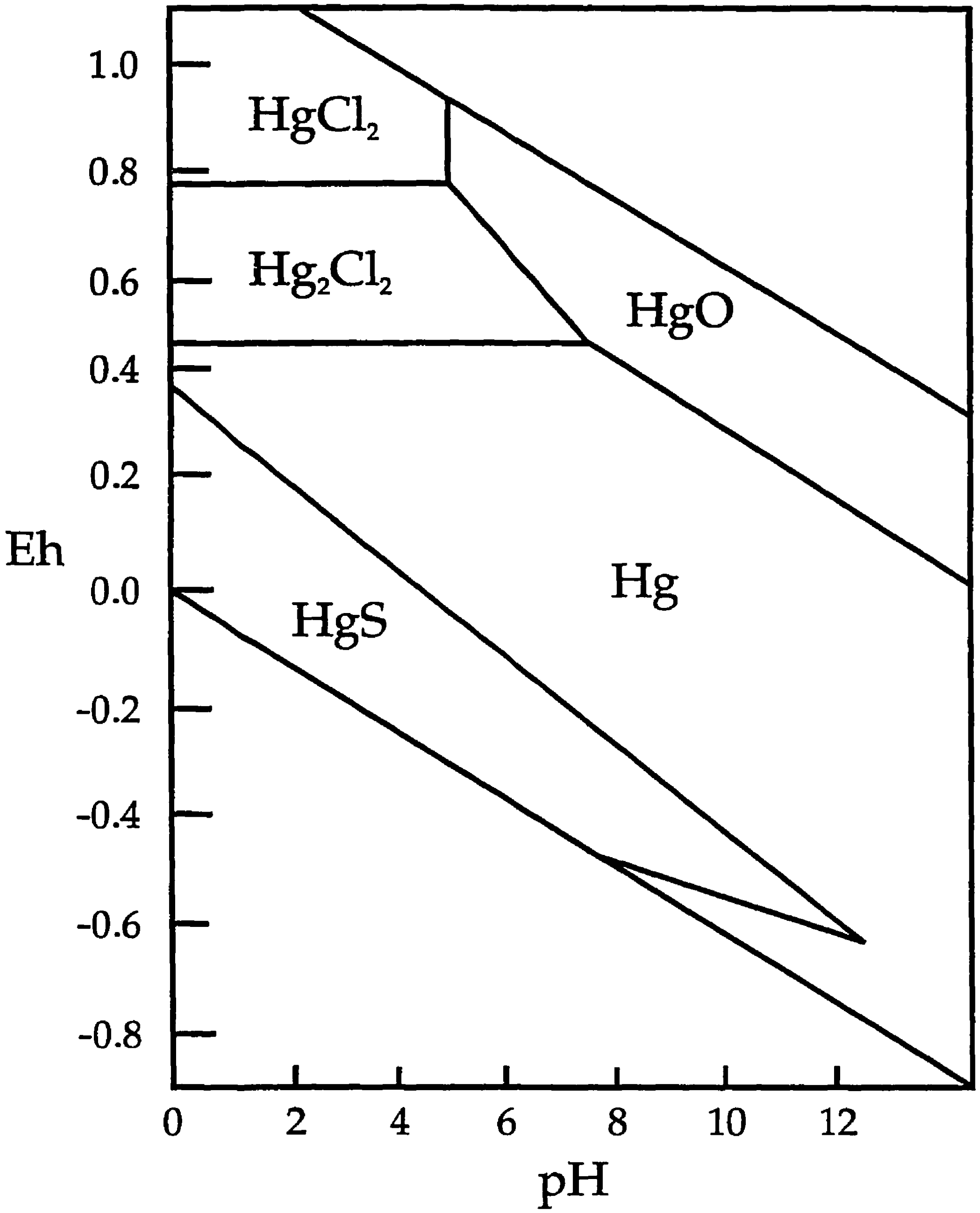


Figure 4: The Eh-pH diagram for Hg, showing solid phases in equilibrium with water and the atmosphere at 25°C with 10^{-3} mol/l each of chloride and total sulfur (from Gavis and Ferguson, 1972).

composition of the water (Benes and Havlik, 1979; Farrah and Pickering, 1978). Xu and Allard (1991) suggested that fulvic acids in solution could play an important role in the distribution and mobility of Hg in natural waters. Experiments have shown that dissolved humic substances can strongly bind mercury. Strohal and Huljev (1971) studied the interaction of mercury with humic acids and observed a slow but very strong binding of mercury in a humate complex. Cline et al. (1973) reported that humic substances may mobilize mercury more effectively than the formation of organomercurials.

iii. *Organomercurials*

This group of compounds represents the most toxic forms of mercury. Organomercurials may have their mercury atom linked to one or two organic radicals. The first type is fairly soluble in water where it can dissociate to give the $R\text{-}Hg^+$ cation and the X^- anion. Its properties and the extent of the dissociation depend on the nature of the organic radical and on the composition of the aqueous solution (Benes and Havlik, 1979). Calculations carried out by Reimers and Krenkel (1974) show that methylmercuric chloride (CH_3HgCl) or hydroxide should predominate in natural waters according to the pH and the chloride concentration of the water.

The second type of organomercurials includes compounds such as dimethylmercury and diphenylmercury. Because of their covalent bonds, these compounds are volatile, nonpolar, and poorly soluble in water. It is assumed that dimethylmercury escapes from solution by bubble entrainment when it is formed in an aquatic system. Below a pH of 7, however, little or no dimethylmercury is formed (Fagerstrom and Jernelov, 1972).

2.3.2 Particulate forms of mercury

As discussed previously, the geochemistry of inorganic mercury strongly favors association with particulate phases (Cranston and Buckley, 1972; Hannan and Thompson, 1977). The reported partitioning of total Hg between dissolved and particulate fractions indicates that particulate Hg is dominant in freshwaters (Fitzgerald and Gill, 1979). Mucci *et al.* (1995) calculated the partition coefficient, K_D ($K_D = [\mathrm{Hg}]_{\mathrm{SPM}}$ (ng/g)/ $[\mathrm{Hg}]_{\mathrm{diss}}$ (ng/ml)), for total mercury between the suspended particulate matter and the dissolved phase in a protected bay of the La Grande-2 reservoir. Values varied between $2.8\ (\pm 0.3) \times 10^4$ and $7.2\ (\pm 3.6) \times 10^4$. Similar values were reported by Hurley *et al.* (1993) in the waters of a seepage lake in northern Wisconsin. As noted by both research groups, K_D values decrease with increasing concentrations of the sorbate. Adsorption and desorption processes of mercury on particulate matter are of great importance in determining the fate of mercury in aquatic systems. Many studies have shown that Hg mobility and dispersion in aquatic systems is strongly dominated by the transport of particulates (Lindberg and Harris, 1977; So, 1980; Jackson *et al.*, 1982; Ferrara *et al.*, 1991; Hulsher *et al.*, 1992; Mucci *et al.*, 1995).

2.4 Mercury Methylation

Mercury can be methylated chemically and/or biologically. Organisms capable of mercury methylation have been found among anaerobes, facultative anaerobes, and aerobes (Beijer and Jernelov, 1979). The rate of anaerobic methylation, however, is greater than that of the aerobic reaction at equivalent mercury concentrations (Gavis and Ferguson, 1972). Under anaerobic conditions, sulphate-reducing bacteria produce sulphide ions which can lead to the precipitation of relatively insoluble HgS or FeS_x which are good Hg scavengers (Farrah and Pickering, 1978; Summers and Silver, 1978; Compeau and Bartha, 1985; Revis et al., 1989). Aerobic bacteria convert Hg(2+) to Hg(0) and CH_3Hg^+ (Compeau and Bartha, 1985; Barkay and Olson, 1986; Revis *et al.*, 1989). Methylmercury can be demethylated by the enzyme mercury lyase found in several aerobic bacterial species.

Chemical methylation of mercury will occur in the presence of suitable methyl donors. Methylation involves the transfer of methyl (CH_3) moieties from methylcobalamine (a derivative of vitamin B_{12}) under reducing conditions (Wood et al., 1968) :

$$CH_3Co[B_{12}] + Hg^{2+} + H_2O \rightarrow (H_2OCo[B_{12}])^+ + CH_3Hg^+$$

Hg can also be methylated by methylcobalamine under oxic conditions but the initial product is dimethylmercury ($(CH_3)_2Hg$) (Andersson, 1979). Another possible pathway for mercury methylation in freshwater involves a mixture of biotic and abiotic processes. Studies performed by Huey et al. (1974) indicate that a species of *Pseudomonas* in the presence of Hg(2+) and Sn(4+) can produce methylmercury through a chemical alkylation by methyl tin.

The rate of methylation is dependent on the metabolic activity of the methylating organisms, the total concentration of inorganic mercury, the redox potential, pH, temperature, and the presence of sulphides and other ligands. Production of methylmercury (CH_3Hg^+) increases with decreasing pH as mercuric Hg is made more available. Methylmercury formation, however, will not increase with increasing total mercury ad infinitum, due to the eventual toxic effects of mercury on the microbes. The pH will determine whether mono- or dimethylmercury will be the dominant species formed, and the competition between methylation and demethylation will determine the methylmercury level in the benthic environment. Acidic pHs favour the formation of monomethylmercury over dimethylmercury and favour methylation over demethylation (Fagerstrom and Jernelov, 1972; Wood, 1980). Since the pH is inversely related to the rate of freshwater methylation (Ramlal *et al.*, 1985; *Xun et al.*, 1987; Bloom *et al.*, 1991), it may regulate the bioavailability of CH_3Hg to the food chain (Rodgers and Beamish, 1983). Temperature is also a factor controlling mercury methylation (Winfrey and Rudd, 1990; Bodaly *et al.*, 1993; Mucci *et al.*, 1995). Methylation is inhibited by low temperatures (Wright and Hamilton, 1982) and has a temperature optimum of about 35^0C (Callister and Winfrey, 1986). In lakes, mercury methylation will often peak in late summer but remain low throughout the remainder of the year (Ramlal, 1983; Korthals and Winfrey, 1987; Ramsay and Ramlal, 1987).

3.0 Materials and Methods

3.1 Experimental procedures

Organic-rich forest soil was sampled manually from site 120 ($54^0\ 13'\ 01.6''$ N, $72^0\ 42'\ 19.9''$ W), at the south-west end of Lac Jobert in the LG-2 hydroelectric reservoir (Figure 5). This naturally Hg-contaminated soil was used to make up the various soil-water slurries in our experiments. The soil profile at the sampling site was characterized by a gold moss cover (0 to 2cm) overlying a brown fibrous horizon (2 to 6 cm) which lead into a pure non-decomposed brown moss horizon (6 to 18 cm). At a depth of 18 to 19 cm, a clear transition to a rich humic black horizon was observed. The organic soil contained small amounts of sand and gravel at a depth of 29 to 30 cm.

Although sieving of the soil was impossible, twigs and branches were removed by hand when observed. The remaining material was mixed manually

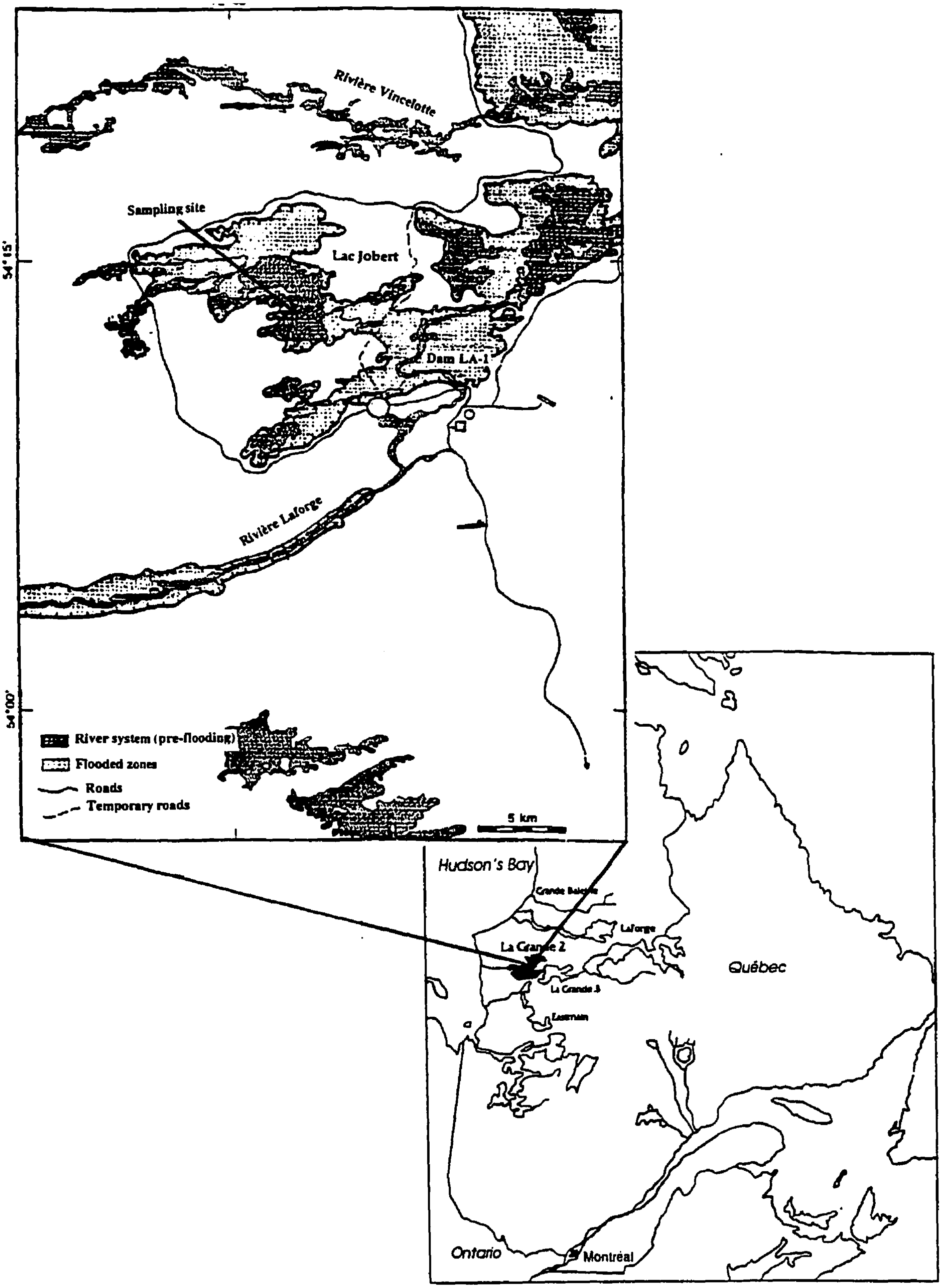


Figure 5: Map of the province of Québec showing the location of the La Grande-2 hydroelectric reservoir and sampling site off Lac Jobert.

to homogenize it. Part of the soil was transferred into a pre-cleaned glass beaker and placed into a freeze dryer for 48 hours at a temperature of - 50^0C. The water content of the soil was evaluated at 70%. Both wet and dry soils were then analyzed for total mercury content. All sampling equipment and containers were thoroughly cleaned in a cold 20% HNO_3 solution for at least 24 hours and rinsed several times with NANOpure® deionized distilled water.

A total of 10 experiments were conducted as part of this study. In all experiments, approximately 6.5 g of wet soil were transferred to a pre-cleaned 50 ml Pyrex® centrifugation tube. Varying concentrations of iron oxide, iron shavings or ferrous ammonium sulphate were added to the soil in the presence and absence of calcium carbonate and/or gypsum. The following reagents, from American Chemicals Ltd., were used in the experiments: 1) iron oxide (Fe_2O_3) 99.9% assay, < 0.239% impurities; 2) iron reduced powder (Fe(0)) 96% assay, < 0.135% impurities; 3) ferrous ammonium sulphate ($Fe(NH_4)_2\ (SO_4)_2 \cdot 6H_2O$) 98.5 - 101.5% assay, < 0.089% impurities; 4) calcium carbonate ($CaCO_3$) 99% assay, < 0.267%; 5) gypsum ($CaSO_4 \cdot 2H_2O$) 98.0 - 102.0% assay, < 0.333% impurities. The exact amounts of solids added to the soil are listed in Appendix 1.1.

Forty ml of NANOpure® water were subsequently added to the tubes to create soil-water slurries which were then stirred to ensure homogeneity. Some of the tubes were covered with Parafilm® immediately after mixing and left undisturbed until sampled in order to achieve anoxic conditions below the thin oxic zone at the solution-slurry interface. In the remainder of the experiments, air from an aquarium pump was bubbled continuously through the slurries using Pasteur pipettes inserted at the bottom of the tubes. The experimental design was adopted to maintain the solids in suspension, promote adsorption of mercury onto the suspended particles, and maintain an oxygenated environment. The bubbling rate was adjusted to about 2 bubbles per second. Control experiments insured that the air bubbled through the solutions contained no Hg. In addition, a Parafilm® cover prevented the introduction of Hg from the atmosphere to the slurries.

The sampling procedures were the same for all slurries, except for the specific days of sampling. pH and Eh measurements were performed on the slurries immediately prior to sampling. pH measurements were carried out using a Radiometer Copenhagen® pH combination electrode (GK 2401C) with Ag/AgCl reference. Electrodes were calibrated using three NIST-traceable buffers with pH values of 4, 7, and 10 respectively. The redox potential, Eh, of the oxygen depleted slurries was determined using a platinum wire which was carefully inserted into the soil while an Ag/AgCl reference electrode rested in the overlying water. The platinum electrode was calibrated with a 0.1 M ferrocyanide/ 0.05 M ferricyanide buffer solution ($Eh_{(Ag/AgCl)}$= 242 mV at 25°C).

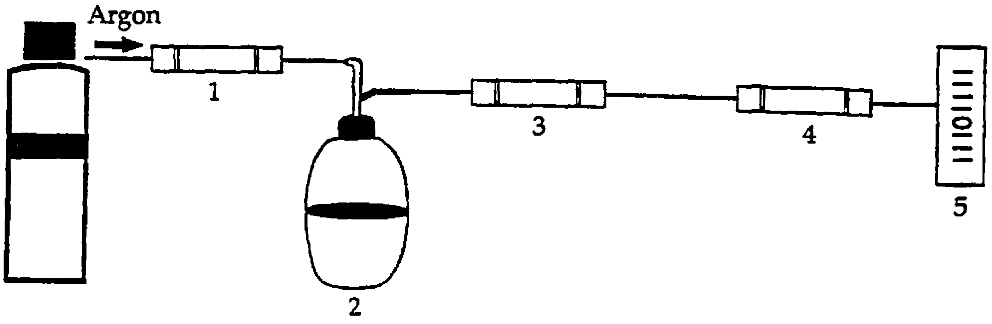
All bubbled solutions were centrifuged in order to recuperate the particles in suspension. The supernatent solution was carefully removed by decantation into a beaker and filtered through a .45 µm Millipore® filter. In the case of the quiescent soil-water slurries, the supernatent solution was recovered with disposable 10cc plastic syringes and Teflon canula and filtered through the above mentioned filters. All solutions were stored into separate glass bottles until analysis. Aliquots of the soil slurry were transferred to pre-washed glass bottles using a Teflon spatula which was thoroughly washed with a 10% HCl solution and with NANOpure® water after each sample. The bottles were weighed and immediately frozen until methylmercury analyses could be undertaken.

3.2 Analytical procedures

3.2.1 Solutions

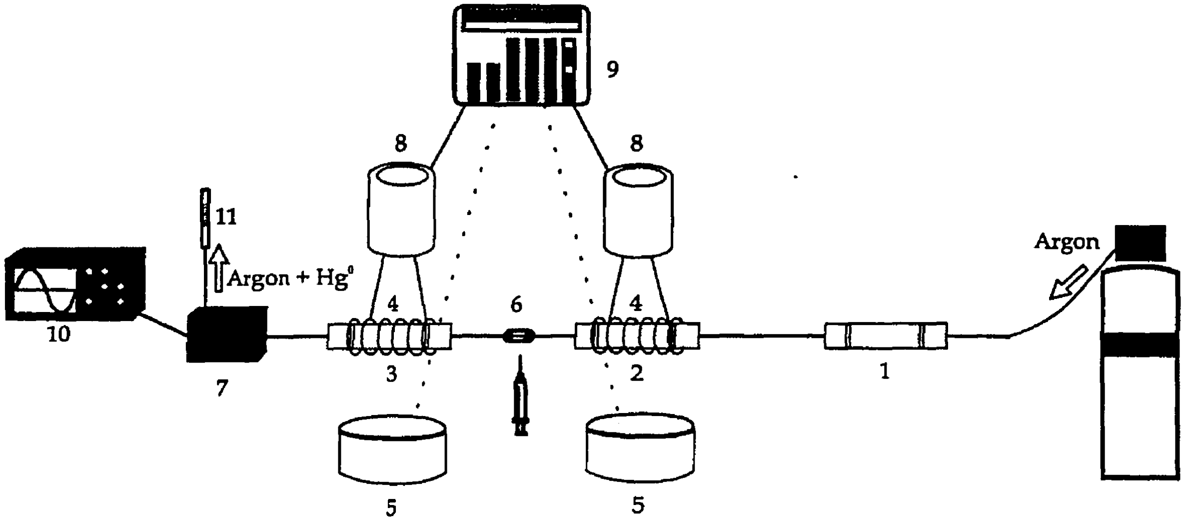
i. Total mercury analysis

The total mercury concentration in the supernatent solutions was determined using a two stage gold amalgamation system combined with a Brooks Rand Ltd. Model-2 CVAFS (cold vapour atomic fluorescence spectrometer). Seven ml aliquots of the solutions were allowed to react with 100 µl of BrCl for 20 minutes in order to release Hg(2+) bound to the organic matter (DOC) in the solution. Following this reaction, 100 µl of a 8% hydroxylamine hydrochloride solution (NH_2OH-HCl) were added to the mixture in order to counteract the corrosive effect of BrCl vapours on the gold-coated quartz column. Once neutralized, the solution was transferred into a Teflon reactor (125 ml bottle) containing a tin chloride ($SnCl_2$) solution where it was allowed to react and degas for 10 minutes. (Figure 6). The mercury, reduced to its elemental form ($Hg^{2+} + Sn^{2+} \leftrightarrow Hg^0 + Sn^{4+}$), was then swept out of the solution with a stream of pre-cleaned argon gas and trapped on a gold coated quartz beads column as an amalgam. The argon flow rate was set at 25 ml/min as recorded on the post-column flow meter. A Teflon column containing about 3 g of indicator-free soda-lime was placed between the purging vessel and the gold trap. It adsorbed and trapped acid fumes as well as aspirated droplets from the vessel which would otherwise poison the gold traps if allowed to enter in contact with them. After 10 minutes, the gold column was transferred to the atomic fluorescence analysis system (Figure 7). The sampling column was heated and the released elemental mercury vapour transferred to an analytical column, using pre-cleaned argon as the carrier gas. The Hg was eluted from the analytical column by controlled heating and carried to the spectrometer by the



1 gold coated quartz sand column
2 purging vessel
3 soda lime column
4 gold coated quartz sand column (Hg_{tot} trap) / Tenax® column (MeHg trap)
5 flowmeter

Figure 6: Schematic diagram of the purging system used for Hg_{tot} and MeHg analyses.



1 gold coated quartz sand column
2 gold coated quartz sand column containing the sample
3 analytical column
4 heating coils
5 cooling system
6 Hg vapour injection site
7 spectrometer
8 transformers
9 synchronizing apparatus
10 signal integrator and recorder
11 flowmeter

Figure 7: Schematic diagram of the atomic fluorescence analysis system used for Hg_{tot} analyses.

argon flow. Fluorescence was induced by means of a mercury lamp producing a 254 nm wavelength band. The radiation was passed trough a quartz U.V. cell with a 1 cm path length. The resultant fluorescence was detected at right angle to the excitation beam using a photomultiplier tube. A monochromating filter within the detector tube attenuated background radiation so that only the wavelength of interest was measured.

ii. Methylmercury analysis

The concentration of methylmercury in the supernatent solutions after treatment and incubation, was determined using a modification of the method proposed by Bloom (1989). First, the frozen samples were thawed in the microwave and transferred to pre-cleaned 125 ml Teflon bottles. To isolate methylmercury from chloride ions and dissolved organic matter, 4 ml of a 3% $CuSO_4$ solution were added to the bottles which were shaken before adding 2 ml of a 30% KBr solution at room temperature and 10 ml CH_2Cl_2. The bottles were then capped and put on a mechanical shaker for 20 minutes before being transferred to a Teflon decantation vial. An additional 10 ml of CH_2Cl_2 were added and the vial was shaken manually to extract the organic phase. This extraction was repeated three times with 10 ml CH_2Cl_2 and care was taken so that no gas escaped. The organic phase was transferred to a 125 ml Teflon bottle and washed repeatedly with NANOpure® water which was decanted in a beaker. Approximately 50 ml of NANOpure® water was then added to the bottle with 200 µl of a 10% sodium acetate buffer which brought the solution pH to 4.9. The methylmercury was extracted back into the water by solvent evaporation. Nitrogen was bubbled in the solution for approximately 30 minutes to eliminate all traces of the solvent. The solutions were diluted to 125 ml and transferred to a purging vessel. A 1% sodium tetraethylborate solution (100 µL) was added, and the mixture was allowed to react without purging for

10 minutes. Sodium tetraethylborate is a strong ethylating agent which converts non-volatile inorganic species and methylmercury into their ethylated, volatile forms, i.e. diethylmercury and methyl-ethylmercury, respectively. The Ar flow was then resumed at a rate of 25 ml/min for 20 minutes. The purge gas outflow was passed through a Tenax® column (Tenax-TA, 20/35 mesh) to collect the volatile organomercury compounds. After the sample was purged, the column was connected in-line with the GC column packed with 45 cm pre-conditioned 15% 0V-3 on Chromasorb® W-AW-DMCS, 60/80 mesh (Bloom and Fitzgerald, 1988). Argon gas at 55 ml/min was allowed to pass over the column for approximately 10 minutes in order to remove residual water condensation from the trap. The Tenax® column was then heated with a heating coil at a temperature of 300°C under a continuous Ar flow. The volatile organomercury compounds desorbed from the Tenax® column were separated on the GC column contained within a cylindrical oven held at 180°C, and decomposed to elemental mercury as they emerged into a quartz wool tube heated to 800°C.

External calibration and sensitivity of the CVFAS

For total mercury analysis, the sensitivity of the spectrometer was determined by the maximum voltage produced following the syringe injection of 30 μl of saturated elemental Hg vapour into the system. For methylmercury analysis, the sensitivity was determined by the peak area produced. The amount of mercury introduced into the system was calculated from the volume of injections, the temperature, and atmospheric pressure in the Hg vapour reservoir. The mercury vapour density was inferred by reading its temperature in the holding tank and using Table 1. In order to obtain accurate results, at least three replicate analyses were made for each sample. The accuracy of the system was verified every 10 samples by running aqueous Hg standards (1000 pg) and a fish tissue (NRC BEST) standard (0.092 mg/kg ± 0.009) during total

T °C	Vapour density ng.cm^{-3}	T °C	Vapour density ng.cm^{-3}	T °C	Vapour density ng.cm^{-3}	T °C	Vapour density ng.cm^{-3}	T °C	Vapour density ng.cm^{-3}
0.0	2.416	0.2	2.226	0.4	2.274	0.6	2.322	0.8	2.368
1.0	2.416	1.2	2.467	1.4	2.516	1.6	2.566	1.8	2.616
2.0	2.665	2.2	2.717	2.4	2.769	2.6	2.820	2.8	2.872
3.0	2.923	3.2	2.979	3.4	3.035	3.6	3.091	3.8	2.147
4.0	3.203	4.2	3.266	4.4	3.328	4.6	3.391	4.8	3.453
5.0	3.515	5.2	3.584	5.4	3.653	5.6	3.722	5.8	3.791
6.0	3.860	6.2	3.935	6.4	4.011	6.6	4.086	6.8	4.161
7.0	4.236	7.2	4.318	7.4	4.400	7.6	4.482	7.8	4.563
8.0	4.644	8.2	4.733	8.4	4.822	8.6	4.911	8.8	5.000
9.0	5.088	9.2	5.184	9.4	5.279	9.6	5.375	9.8	5.471
10.0	5.566	10.2	5.669	10.4	5.771	10.6	5.874	10.8	5.976
11.0	6.078	11.2	6.189	11.4	6.300	11.6	6.411	11.8	6.522
12.0	6.632	12.2	6.755	12.4	6.876	12.6	6.999	12.8	7.120
13.0	7.242	13.2	7.363	13.4	7.509	13.6	7.641	13.8	7.775
14.0	7.907	14.2	8.052	14.4	8.197	14.6	8.341	14.8	8.486
15.0	8.630	15.2	8.787	15.4	8.942	15.6	9.099	15.8	9.254
16.0	9.410	16.2	9.578	16.4	9.746	16.6	9.912	16.8	10.08
17.0	10.25	17.2	10.43	17.4	10.61	17.6	10.79	17.8	10.97
18.0	11.15	18.2	11.34	18.4	11.54	18.6	11.73	18.8	11.93
19.0	12.12	19.2	12.33	19.4	12.54	19.6	12.75	19.8	12.97
20.0	13.18	20.2	13.40	20.4	13.63	20.6	13.86	20.8	14.09
21.0	14.31	21.2	14.56	21.4	14.80	21.6	15.05	21.8	15.29
22.0	15.54	22.2	15.80	22.4	16.07	22.6	16.34	22.8	16.60
23.0	16.87	23.2	17.15	23.4	17.44	23.6	17.73	23.8	18.02
24.0	18.30	24.2	18.61	24.4	18.92	24.6	19.23	24.8	19.54
25.0	19.85	25.2	20.18	25.4	20.51	25.6	20.84	25.8	21.17
26.0	21.50	26.2	21.86	26.4	22.22	26.6	22.57	26.8	22.93
27.0	23.28	27.2	23.67	27.4	24.05	27.6	24.43	27.8	24.81
28.0	25.19	28.2	25.61	28.4	26.02	28.6	26.43	28.8	26.84
29.0	27.25	29.2	27.69	29.4	28.14	29.6	28.58	29.8	29.02
30.0	29.46	30.2	29.94	30.4	30.41	30.6	30.88	30.8	31.36
31.0	31.83	31.2	32.34	31.4	32.85	31.6	33.35	31.8	33.86
32.0	34.37	32.2	34.92	32.4	35.46	32.6	36.01	32.8	36.56
33.0	37.10	33.2	37.69	33.4	38.28	33.6	38.86	33.8	39.45
34.0	40.03	34.2	40.66	34.4	41.29	34.6	41.91	34.8	42.54
35.0	43.17	35.2	43.84	35.4	44.51	35.6	45.18	35.8	45.84

Table 1: Density of saturated elemental Hg vapour at 1 atm and from 0 to 35^{0}C.

mercury analyses and aqueous MeHg standards (5,40 ng/g) for methylmercury analyses. The detection limit, taken as three times the standard deviation of the blank solutions, was estimated at 11 pg/ml for total mercury and 51 pg/g for methylmercury analyses. The reproducibility of the measurements was always better than 10%.

iii. *DOC analyses*

Five ml of the filtered supernatent solutions were analyzed on a Shimadzu TOC-5050 thermal decomposition system with a platinum catalyst heated to 680^{0}C. The samples were acidified to pH 2 and sparged for 10 to 15 minutes with CO_2 free air. The total carbon content of the samples was oxidized to CO_2, detected by a non-dispersive infra-red analyzer (NDIR) and logged by a data processor. Reproducibility of the measurements was always better than 2%.

iv. Fe and Ca analyses

Iron and calcium concentrations in the supernatent solutions were measured in order to determine if precipitation or dissolution of Fe and Ca phases were taking place. Iron and calcium in the supernatent solutions were analyzed using the Perkin-Elmer Atomic Absorption Spectrophotometer 3100 using an air-acetylene flame coupled with a hollow- cathode lamp at the desired wavelength (Fe= 248.33 nm and Ca= 422.67 nm). The instrument was calibrated by preparing external standard solutions over the concentration range of interest and measuring their absorption under the same conditions as the samples. Three replicate analyses were made of each sample and reproducibility of the measurements was always better than 5%. Detection limit was estimated at 0.1 mg/l.

v. Sulphate analyses

Sulphate concentrations in the supernatent solutions were analyzed by ion chromatography using a Dionex 4500i system. Aliquots of the solutions were eluted and passed through a Dionex IonPac AS5 analytical column with suppressed conductivity detection. The accuracy of the system was verified by analyzing aqueous standards (1000 mg/l) periodically. The limit of detection was estimated at 0.25 mg/l. The reproducibility of the measurements was always better than 10%.

3.2.2 Solids

i. Total mercury Analysis

The total mercury content of the soil was determined by a procedure described by Van Delft and Vos (1988). Briefly, 0.4 g of humid soil was weighed and placed in Teflon reactors (Rantala and Loring, 1989) with 0.3 ml Ultrapure HCl and 3 ml Ultrapure HNO_3. HCl was used in the extractions to maintain Hg in solution through chloride complexation. The bombs were subsequently sealed and placed in a pressure cooker filled with approximately 2 cm of NANOpure® water. The pressure cooker was placed in a commercial microwave oven activated in the following sequence: 1 min at Low power (50 W), 4 min at Medium power (250 W) and 10 min at High power (500 W). The pressure cooker was then removed from the oven, placed in a sink and rinsed with cold water. Once the pressure dropped, the cooker was returned to the microwave and allowed to stand an additional 5 minutes at High power. Subsequently, the reactors were taken out of the pressure cooker and allowed to cool completely before opening. The samples were quantitatively transferred to 50 ml volumetric flasks using Pasteur pipettes and diluted with

NANOpure® water to the final volume. One ml of the solution was then placed into a purging vessel and underwent the same analytical procedure described previously for the solutions.

ii. Methylmercury analysis

The concentration of methylmercury present in solid soil samples was determined using the technique described by Bloom (1989). Briefly, the methylmercury in the soil is extracted with a KOH-methanol solution, ethylated, adsorbed onto a Tenax® column, thermally desorbed and separated by gas chromatography, thermally decomposed to elemental mercury which is detected by a highly sensitive cold vapor atomic fluorescence detector (CVAFS)(Bloom and Fitzgerald, 1988). First, approximately 0,5 g of each soil sample was placed in a clean Teflon bottle. Ten ml of a 25% KOH in methanol solution were added to the soil sample. Bottles were capped, shaken for approximately 25 minutes, and allowed to stand in an oven at 70°C for 3 hours to complete the digestion. Subsequently, 1 ml of the digestate was transferred into a 50 ml glass flask. Four ml of a 10% sodium acetate buffer were added to the aliquots in order to bring the pH of the solutions to 4.9. The solutions were diluted with NANOpure® water to a final volume of 50 ml. Ten ml of the diluted solutions were transferred to a 125 ml purging vessel filled to 2/3 of its capacity with NANOpure® water. The ionic mercury species were converted to their volatile ethyl analogs following the addition of a 1% sodium tetraethylborate solution. The volatile species were then purged from solution onto a Tenax® trap, and subsequently analyzed as described previously for the supernatent solutions.

4.0 Results and Discussion

Prior to treatment, the initial mercury concentration in the soil was determined to be 400 ± 80 ng Hg g^{-1} (dry weight). The relatively large uncertainty in the measurement may owe to the heterogeneity of soil aliquots. This in turn may also explain the high variability of results obtained for the different treatment experiments. Interestingly, the experiments behaved similarly under the same conditions. All control samples displayed a "saw-toothed" pattern. The initial increase in total Hg concentrations likely resulted from the suspension of colloidal material and changes in redox conditions following water addition. It was followed by a decrease in mercury levels as organic particles settled out of solution and Hg was scavenged by soil material. The degradation of organic matter depleted oxygen levels within the slurries and released mercury to the overlying waters. Under reducing conditions, iron and manganese oxihydroxides in the slurry soil likely dissolved, contributing their mercury load to the soil solution. Following the reduction of sulphate to sulphide and Fe(3+) to Fe(2+), the precipitation of iron sulphides scavenged Hg(2+) out of solution. Subsequent "saw-tooth" patterns may have been due to changes in microbial activity which impacted redox conditions thereby affecting mercury sorption and/or release.

4.1 Iron Oxide

i. Incubated slurries

Soil-slurries treated with Fe oxide were incubated and monitored over 84 days to study the release of mercury to solution and the evolution of methylmercury concentrations in the system. The additions of iron oxides at various concentrations did, as expected on the basis of previous literature reports, scavenge part of the Hg out of solution, at least for the first 70 days (Figure 8). All

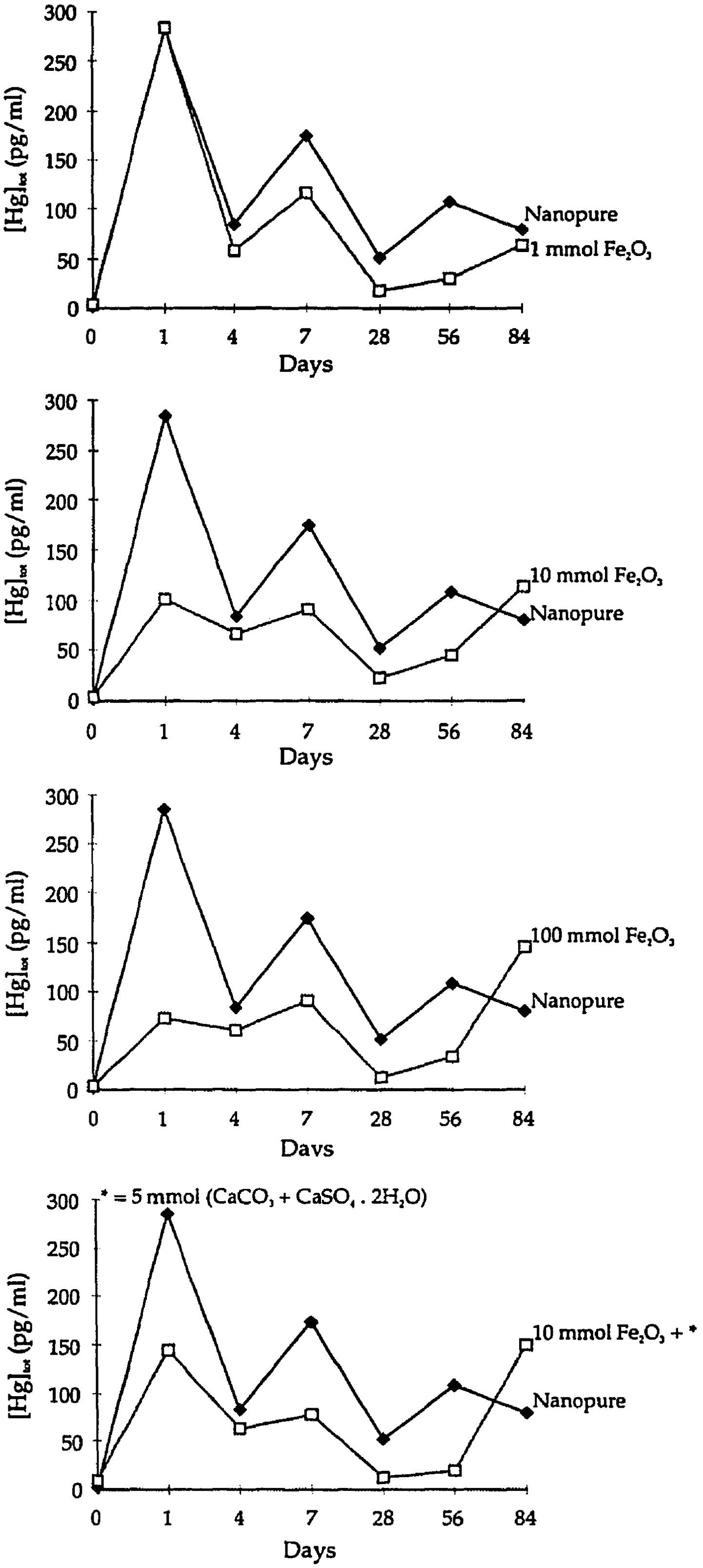


Figure 8: Total mercury concentrations in the supernatent solution as a function of time in incubated soil slurries treated with Fe_2O_3.

treated samples show lower total mercury concentrations in solution than the control in the first two months following the addition of water to the soil. There seems to be a turnover, however, in the behaviour of the treated slurries around Day 70 when mercury is apparently released to the supernatent solutions. After this time, the total Hg concentrations in the supernatent solution of the treated soil slurries exceed those in the control. Although it shows a trend similar to the other treated slurries, only the slurry treated with the lowest concentration of Fe_2O_3 (i.e. 1 mmol) showed an overall net decrease in total mercury concentrations in solution after 84 days. In all experiments, Fe_2O_3 was likely hydrated and converted to ferrihydrite ($Fe(OH)_3$) which would display a different adsorption behaviour than the oxide (Shimomura *et al.*, 1969; Forbes *et al.*, 1974; Innoue and Munemori, 1979). Hematite has been shown to bind metal ions less strongly than freshly precipitated hydrous oxide (Slaveck and Pickering, 1986). Consequently, the formation of hydrated phases during the treatment likely contributed to increased Hg scavenging. Iron oxide additions also successfully limited methylmercury formation in the slurries. Iron oxide in the presence of calcite and gypsum suppressed methylation most efficiently.

Looking closely at the trends, some observations may be drawn which may help us understand the mechanisms controlling the behaviour of mercury in our experimental setup. Twenty-four hours after water addition, total mercury concentrations in the waters of the control experiment were 285 pg Hg/ml. When taken over the entire volume of the supernatent solution, this translates into 11 400 pg Hg. The total mercury content of the slurry soils was 2600 ng Hg. This indicates that approximately 0.5% of the mercury trapped in the soil was released to the overlying waters soon after slurry preparation. I propose that suspension of the soil during slurry preparation (Mucci *et al.*, 1995), desorption and rapid degradation of labile organic matter likely allowed the transfer of Hg to the overlying solution. Colloidal particles, not retained by filtration or centrifugation during sampling are likely responsible for the observed increase in Hg concentrations in the supernatent solutions at the onset of the study. Hg has a high affinity for particulate matter in suspension (Jernelov, 1969; Cranston and Buckley, 1972; Jackson *et al.*, 1982; Ferrara *et al.*, 1986, 1989; Mucci *et al.*, 1995) and the smaller particles with their greater relative surface area carry more Hg per unit weight than larger ones (Airey and Jones, 1982). With time, the organic particles flocculated and settled out of solution, accumulating at the soil-water interface. Dissolved Hg released to the supernatent solution may also have been scavenged by soil components and iron oxides when present. However, Hg release from the slurry solids seemed to surpass scavenging after Day 4 (Figure 8). A net increase in total mercury concentration was observed for all experiments, 7 days after water addition. This release of mercury may have resulted from a change in redox conditions within the settled slurries. Because of the strong oxygen demand from degrading organic matter and the limited availability of oxygen to Parafilm® covered centrifuge tubes, reducing conditions (i.e. Eh < 0) developed within a few days (Figure 9). This decline in Eh values likely caused the reactive iron and manganese oxihydroxides in the soil to become unstable and dissolve (Ponnamperuma, 1972; Sposito, 1989; Stumm and Sulzberger, 1992; Young and Harvey, 1992), releasing adsorbed Hg to the soil solution (Figure 10). In all cases, Fe concentrations in solution increased with time showing that a ferric phase, most likely pre-existing oxihydroxides, was being reduced and released to solution. Only the slurries to which calcite and gypsum were added, yielded higher iron concentrations in the supernatent solution than the control. The dissolution of Fe oxides was likely accelerated by the presence of sulphide (Canfield, 1989; Canfield *et al.*, 1992). The onset of organic matter degradation under these reducing conditions also contributed additional mercury to the overlying waters.

With developing anoxic conditions, Hg concentrations in the supernatent solutions of all slurries, including the control, decreased as Hg(2+) was scavenged by authigenic sulphides (Figure 8). The reduction of sulphate to sulphide in

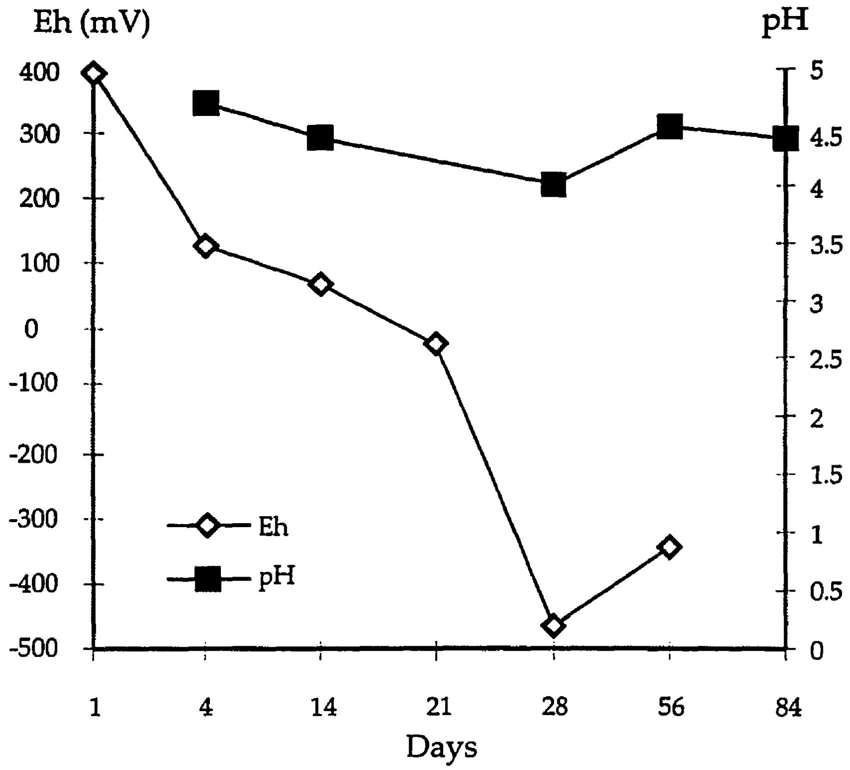


Figure 9 : Eh and pH data from incubated control slurries. Eh measurements were taken at a depth of approximately 2 cm below the soil-water interface and were corrected to the hydrogen scale. pH was measured in the supernatent solution.

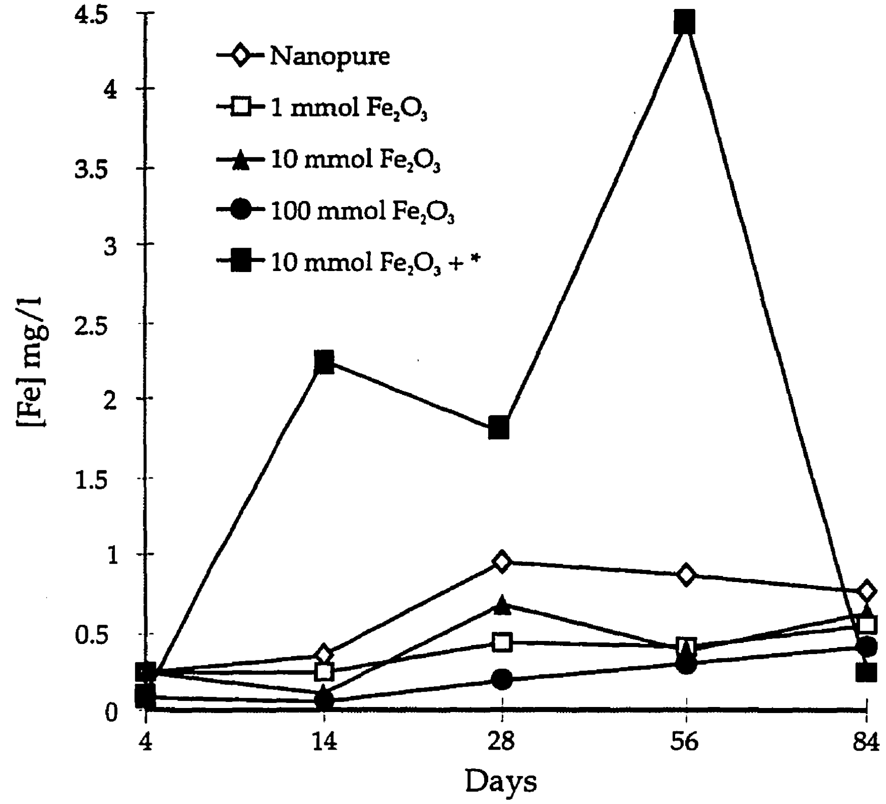


Figure 10 : Iron concentrations as a function of time in the supernatent solution of incubated soil slurries treated with Fe_2O_3.

slurries treated with gypsum probably allowed the formation of iron sulphides (FeS_x) which contributed further to Hg scavenging. In the first 7 days following water addition, sulphate concentrations in supernatent solutions increased steadily suggesting that gypsum dissolution was taking place (Table 2). Sulphate concentration in the sample's supernatent solution reached 575 mg/l (≅ 5.9 mmol) on Day 7. Complete dissolution of the added gypsum could have contributed 480 mg/l. Additional sulphate, although minimal, was likely supplied by the degradation of the soil organic matter (Cutter and Krahforst, 1988). Evaporation of the supernatent solution may also have resulted in a concentration increase. Increasing calcium concentration in the supernatent solution with time is also indicative of gypsum and calcite dissolution taking place (Table 3). The hypothesis of sulphide formation, especially when gypsum was added, is supported by the steady decrease of sulphate concentrations and its concordance with iron concentrations in the supernatent solutions with time (Figure 11). Fe(3+) in various solid phases was reduced to Fe(2+) by H_2S and released to the supernatent solution. Upon further sulphate reduction and H_2S buildup, saturation with respect to an iron sulphide phase was reached and precipitated out of solution. Following Day 28, all supernatent solutions show a steady increase in Hg concentrations. This may reflect increased microbial activity which superseded the scavenging ability of iron oxides and authigenic sulphides. The trend could also be explained by the stabilization of mercury in solution through complexation by the observed increase in dissolved organic carbon (DOC) which was promoted by the onset of anaerobic conditions (Figure 12).

Acidification of the system may have further contributed to Hg-desorption from the soil, especially from the oxides (McKenzie, 1980; Benjamin and Leckie, 1981; Duarte et al., 1991; Schuster, 1991; Young and Harvey, 1992). pH generally dropped significantly in the first 28 days following water addition to the soil and rose slightly afterwards (Figure 9). The initial decrease in pH resulted most likely

Treatment	Day 4	Day 7	Day 28	Day 56	Day 84
Nanopure®	1.29	1.41	2.83	2.72	0.86
1 mmol Fe_2O_3	1.64	1.87	2.55	4.90	3.94
10 mmol Fe_2O_3	1.45	2.59	3.36	2.65	1.48
100 mmol Fe_2O_3	3.33	4.49	8.76	6.02	2.65
10 mmol Fe_2O_3 + *	407	575	441	456	503

* = 5 mmol ($CaCO_3$ + $CaSO_4 . 2H_20$)

Table 2: Sulphate concentrations in mg/l in supernatent solutions of incubated soil slurries treated with Fe_2O_3. Initial sulphate concentrations (i.e. Day 0) are assumed to be 0 mg/l. The reproducibility of these measurements was always better than 2%.

Treatment	Day 0	Day 7	Day 14	Day 28	Day 56	Day 84
Nanopure®	0	0.3	0	0.1	0.1	0.1
1 mmol Fe_2O_3	0	0.2	0.1	0.1	0.1	0.2
10 mmol Fe_2O_3	0	0.1	0.1	0.1	0.1	0.1
100 mmol Fe_2O_3	0	0.4	0.2	0.1	0.1	0
10 mmol Fe_2O_3 + *	0	151	160	180	270	290

* = 5 mmol ($CaCO_3 + CaSO_4 . 2H_20$)

Table 3: Calcium concentrations in mg/l in supernatent solutions of incubated soil slurries treated with Fe_2O_3. The reproducibility of these measurements was always better than 5%.

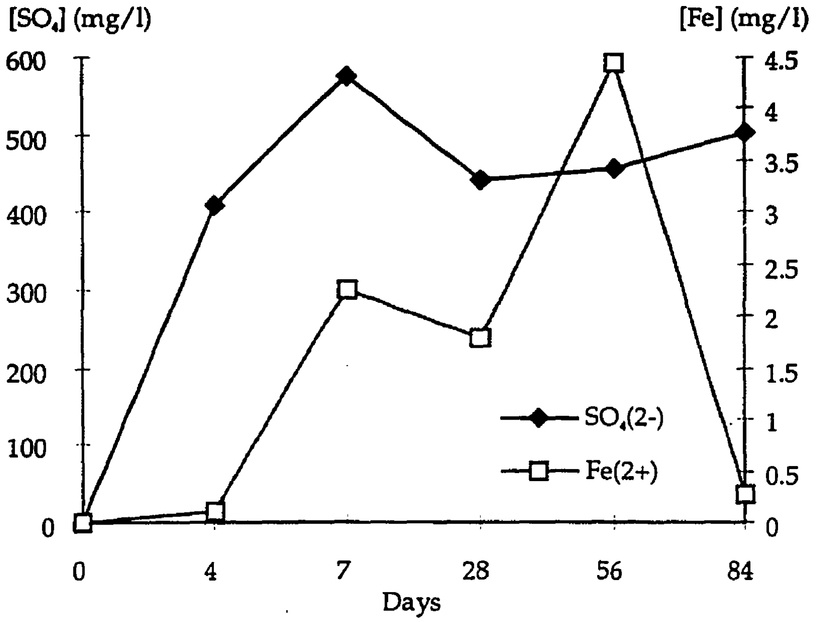


Figure 11: Comparison of sulphate and iron concentrations in the supernatent solution as a function of time in incubated soil slurries treated with 10 mmol Fe_2O_3 + 5 mmol ($CaCO_3$ + $CaSO_4 . 2H_2O$).

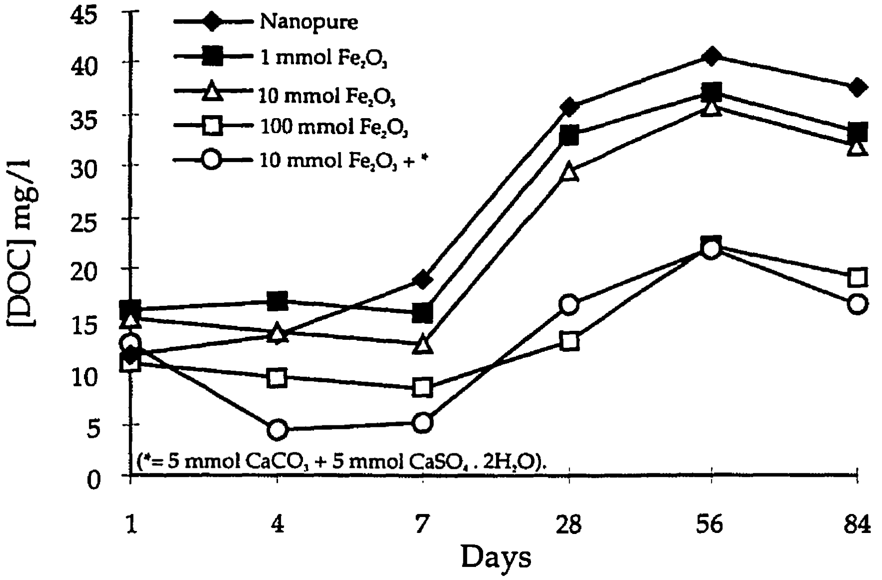


Figure 12: DOC concentrations in the supernatent solutions of incubated soil slurries treated with Fe_2O_3 as a function of time. (*= 5 mmol $CaCO_3$ + 5 mmol $CaSO_4 . 2H_2O$).

from the production and accumulation of metabolic CO_2 from the respiration of aerobic bacteria (Ponnamperuma, 1972) and the release of organic acids from the soil. The subsequent rise in pH can be explained from the reduction of iron (Stumm and Morgan, 1970):

$$\text{"}CH_2O\text{"} + 8\,H^+ + 2\,Fe_2O_3 \rightarrow 4\,Fe^{2+} + 5\,H_2O + CO_2$$

where "CH_2O" is a simplified representation of the degrading organic matter in the soil.

Low pH may have also favoured the activity of certain microbial species, or biochemical pathways that were effective at methylating mercury (Miskimmin *et al.*, 1992). Very little if any methylmercury is ever detected in a dry soil (Chaire de Recherche en Environnement, 1993). Methylmercury production is promoted by the microbial degradation of labile organic matter upon flooding (Abernathy and Cumbie, 1977; Bodaly and Heckie, 1979; Jackson, 1988a, 1988b). In our study, methylmercury concentrations increased rapidly soon after slurry preparation when anoxic and low pH conditions were established (Figure 13). Both conditions have been shown to promote Hg methylation (Fagerstrom and Jernelov, 1972; Wood, 1980). It is interesting to note, however, that the greater the amount of Fe_2O_3 added, the smaller the initial methylmercury peak. For the rest of the study period, methylmercury concentrations remained relatively stable. Lower methylmercury values were observed in slurries treated with gypsum since methylation was likely limited by the reduced availability of Hg(2+) sequestered by the formation of sulphides (Farrah and Pickering, 1972; Summers and Silver, 1978; Compeau and Bartha, 1985; Revis *et al.*, 1989).

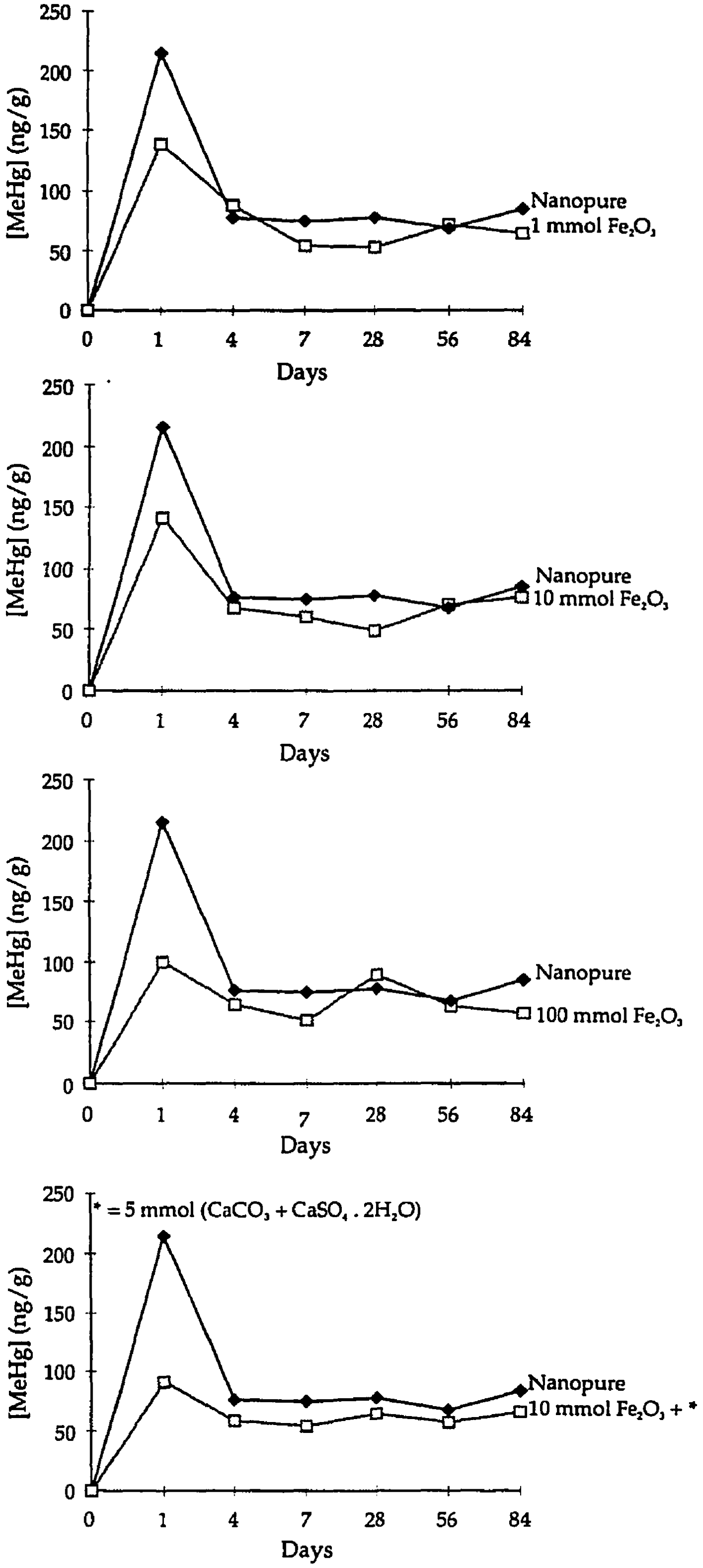


Figure 13: Methylmercury concentrations associated with the solids as a function of time in incubated soil slurries treated with Fe_2O_3.

ii. Oxygenated slurries

Only one experiment was conducted with slurries exposed to a continuous stream of air. The addition of iron oxide to the slurries had a positive influence on the evolution of both total and methylmercury concentrations in the experiments. It is interesting to note, however, that the control samples behaved similarly despite the high initial mercury concentrations of the supernatent solution. One possible interpretation would be that Hg sequestration was dominated by adsorption on soil components. After 84 days, all samples showed much lower concentrations of total Hg in solution than their incubated counterparts (Figure 14). Methylmercury concentrations, however, were similar. Because bubbling allowed oxygenated conditions to be maintained, the slurries behaved more coherently. As in the incubated experiments (described in the previous section), the sudden increase in total mercury concentration in solution soon after the addition of water may have resulted from the suspension of fine grained organic matter. After Day 7, mercury concentrations dropped steadily probably as a result of organic matter scavenging and iron oxide adsorption in the case of the treated slurries. Analyses of iron in solution were not undertaken for this set of experiments since it was assumed that Fe reduction would be minimal under oxygenated conditions. A spike in total mercury concentration was observed for the slurry treated with iron oxide in the presence of calcite and gypsum (Figure 14) but it most likely originated from contamination during the sampling procedure. The DOC behaviour for oxygenated slurries is quite different from the incubated experiments since aerobic conditions limited its formation. DOC concentrations in the supernatent solutions, while increasing slightly with time (Figure 15), did not appear to correlate with total dissolved Hg concentrations. This observation may be explained by the limited availability of Hg(2+) adsorbed onto the oxides or the nature and Hg-affinity of the DOC produced under anoxic conditions.

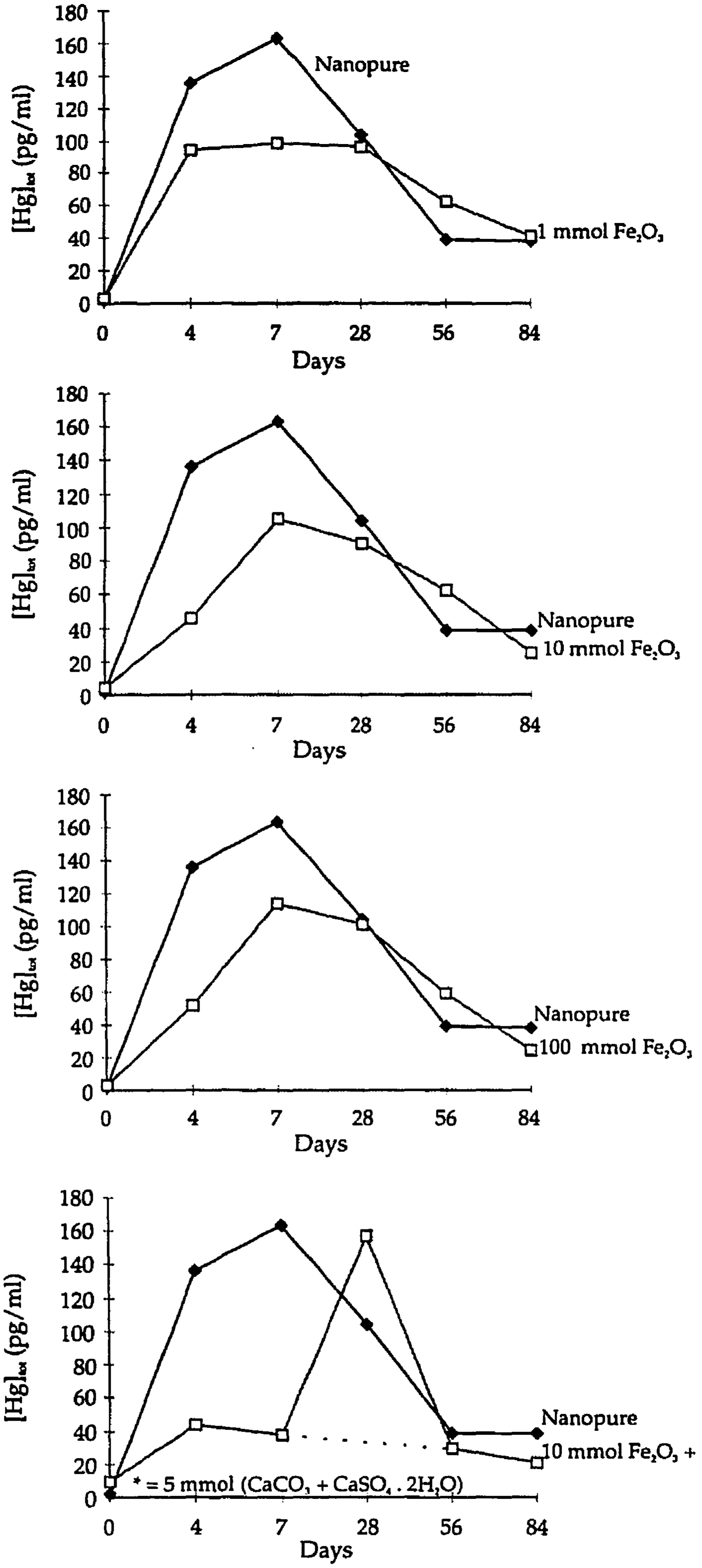


Figure 14: Total mercury concentrations in the supernatent solution as a function of time in oxygenated soil slurries treated with Fe_2O_3.

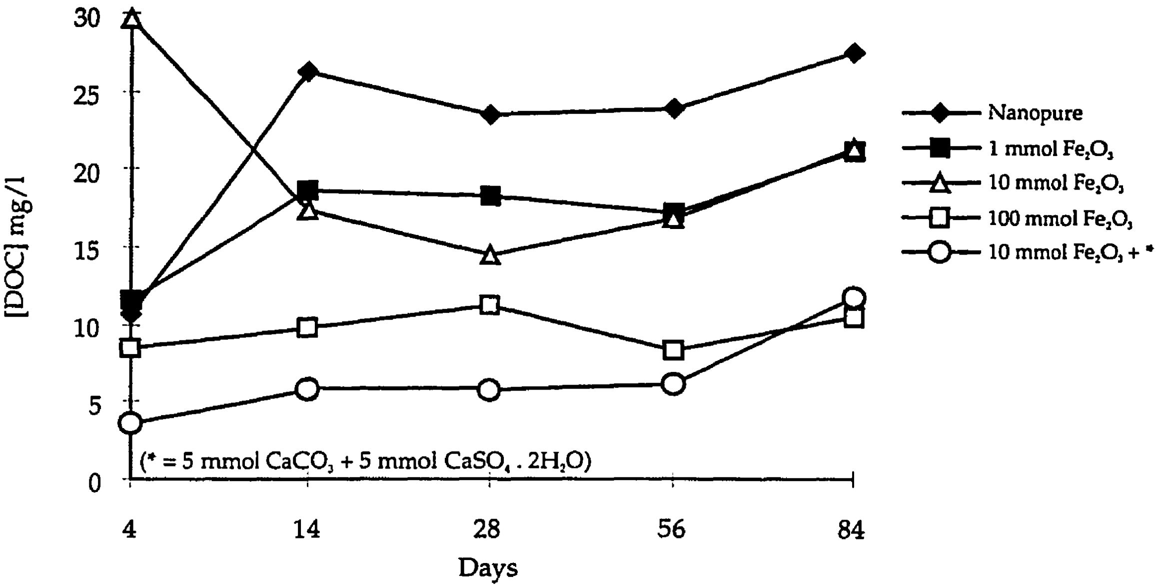


Figure 15 : DOC concentrations in the supernatent solution as a function of time in oxygenated soil slurries treated with Fe_2O_3.

Methylmercury concentrations in oxygenated slurries show an evolution that is quite similar to that of the incubated soils (Figure 16). The sharp initial increase, observed in the first 4 days likely resulted from the onset of microbial activity following water addition. Although they do not vary much in time after the initial increase, methylmercury concentrations were always lower in the treated slurries than in the control over most of the experimental period. Iron oxides may have inhibited methylation by limiting the availability of Hg(2+) through adsorption (Lockwood and Chen, 1974; Tessier *et al.*, 1985; Jackson, 1989) or catalyzing demethylation (Gagnon *et al.*, 1996).

iii. Conclusions

Although no definite conclusions could be drawn on which amount of reagent was better suited to limit inorganic mercury and methylmercury levels in the slurries, some general trends can be inferred. Iron oxide reduced the release of mercury in solution more efficiently under oxygenated conditions (45% vs 0-15% under reduced conditions) whereas it had a similar effect on methylmercury formation under both incubated and oxygenated conditions. Methylmercury concentrations reached higher values in the early stages of the experiments but settled at slightly lower or similar levels than in the oxygenated slurries by the end of the incubation period. Incubated soil slurries spiked with 50 ng/g (dry weight) methylmercury chloride and treated with the different reagents (Figure 17) failed to provide new insights. Methylmercury concentrations in the supernatent solutions of the treated slurries are lower than the control after 84 days, but in most cases, the addition of iron oxides stimulated methylation during most of the study period. The observed decrease in methylmercury concentrations towards the end of the study may have resulted from sulphide scavenging of Hg(2+) released following demethylation. Methylmercury concentrations are determined by a steady state equilibrium between the kinetics of microbial methylation and

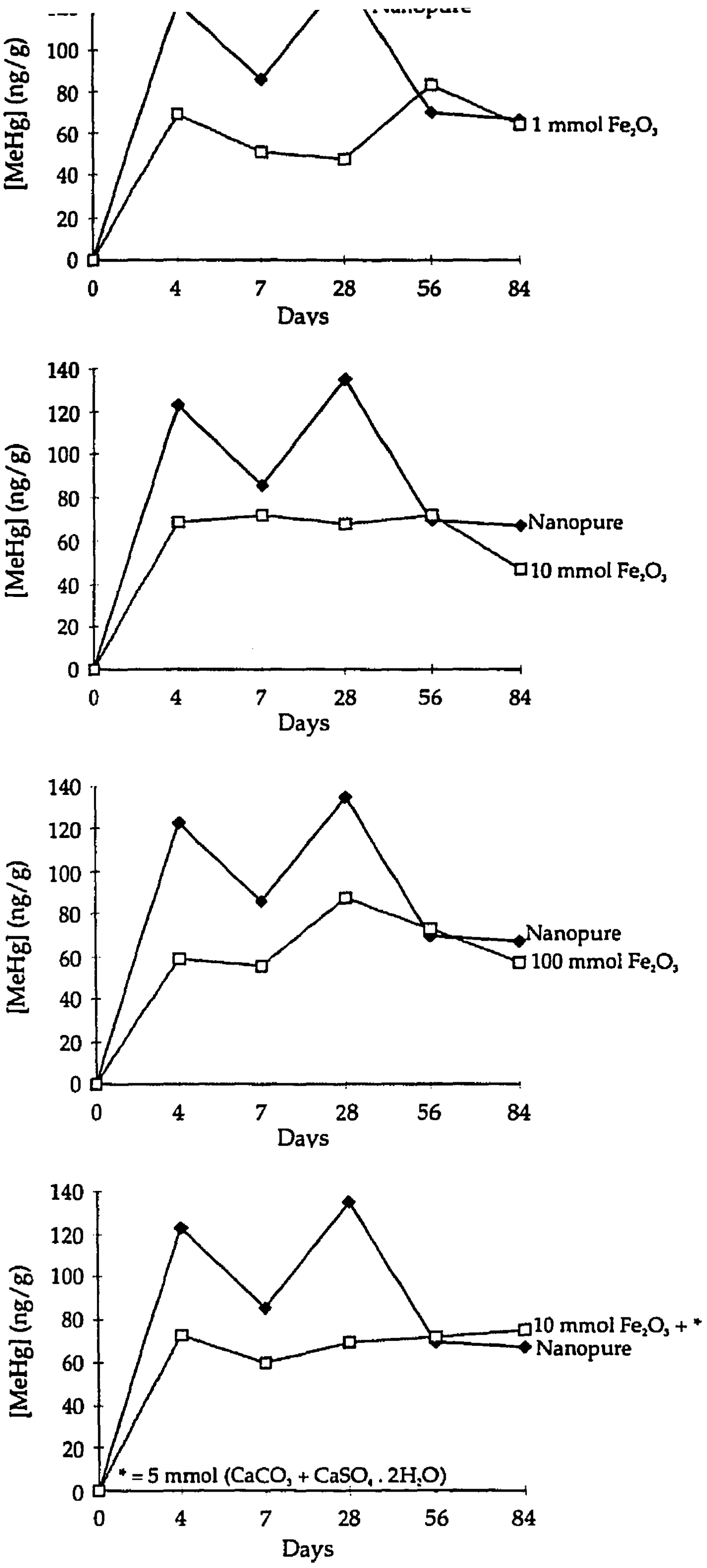


Figure 16 : Methylmercury concentrations associated with the solids as a function of time in oxygenated soil slurries treated with Fe_2O_3.

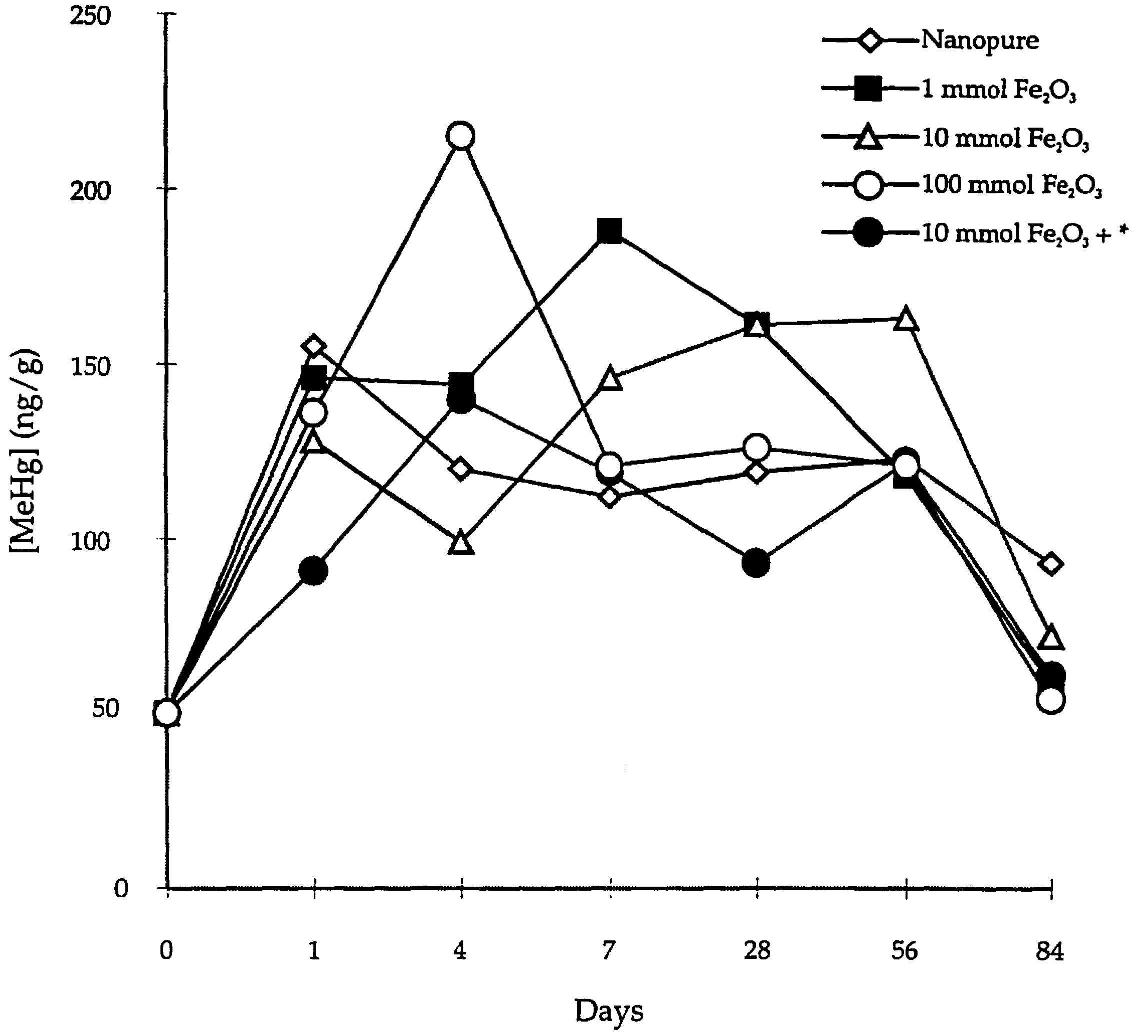


Figure 17: Methylmercury concentrations associated with the solids as a function of time in incubated methylmercury-spiked soil slurries treated with Fe_2O_3.

demethylation. If Hg(2+) released from demethylation is removed from the system, the steady state is shifted.

4.2 Iron Shavings

i. Incubated slurries

The addition of elemental iron, in the form of shavings, appeared to be very effective in controlling total dissolved mercury concentrations in supernatent solutions but had little influence on the production of methylmercury. In all but the slurry treated with the lowest concentration of Fe^0 (i.e. 1 mmol), total mercury concentrations in solution increased over the first 14 days following addition of water and steadily decreased thereafter often reaching minimal values by Day 84 (Figure 18). As proposed previously, the high mercury concentrations on Day 4 probably resulted from the suspension of fine-grained organic matter following sample preparation. The behaviour of the control experiment suggests that Hg was then successfully scavenged by the soil components and settling organic matter. Again, as in the treatment with iron oxide, scavenging by iron sulphides likely proceeded when reduced conditions were established. No Eh measurements were taken initially, but measurements on Day 4 suggest that anoxic conditions were established within the first few days following water addition (Table 4). With the exception of what appear to be erroneous measurements on Days 28 and 56 (-34 and -305 respectively), the variation of Eh with time in the slurries can be easily explained. Eh is most negative when H_2S is present in solution. After it is precipitated or after sulphate is consumed, its value may rise. The formation of sulphides was clearly evidenced in the slurry treated with gypsum where sulphate, provided by the dissolution of the salt, was progressively removed from solution by its reduction to S(2-) (Table 5). By Day 14 of the experiment, gypsum had undergone complete dissolution since sulphate and calcium concentrations in

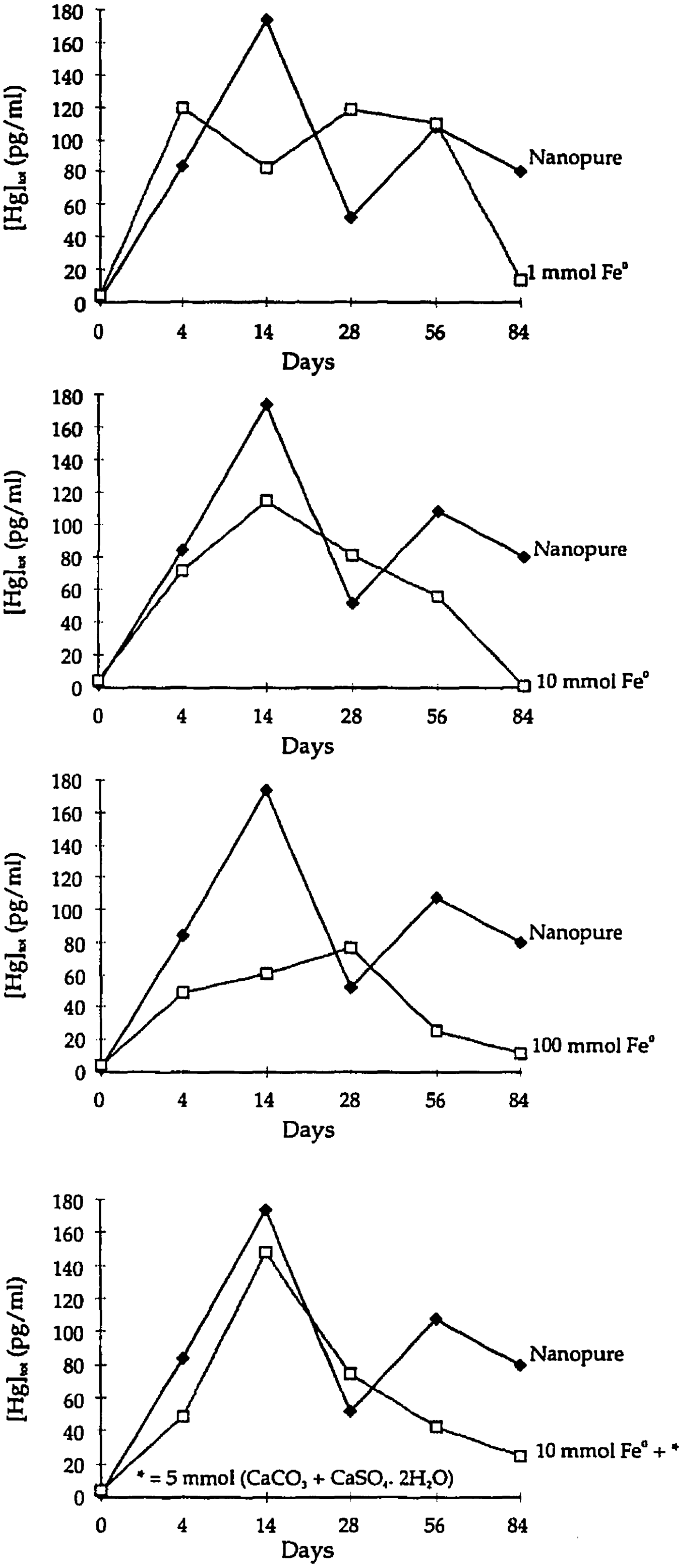


Figure 18: Total mercury concentrations in the supernatent solution as a function of time in incubated soil slurries treated with Fe^0.

Treatment	Day 4	Day 14	Day 28	Day 56	Day 84
1 mmol Fe^0	-164	-20	-51	-54	-86
10 mmol Fe^0	-239	-4	-68	-75	-98
100 mmol Fe^0	-249	-207	-147	-305	-115
10 mmol Fe^0 + *	-216	-204	-34	-232	-87

* = 5 mmol ($CaCO_3 + CaSO_4 . 2H_20$)

Table 4 : Redox potential in mV in pore fluids of incubated soil slurries treated with Fe^0. Measurements were corrected to the hydrogen scale.

Treatment	**Concentration (mg/l)**	**Day 4**	**Day 14**	**Day 28**	**Day 56**	**Day 84**
Nanopure®	[SO_4]		1.3	1.3	0.6	0.4
	[Ca]	0.2	0.1	0.1	0.4	0.2
1 mmol Fe^0	[SO_4]		1.2	1.3	0.7	0.3
	[Ca]	0.1	0.1	0.1	0.1	0.1
10 mmol Fe^0	[SO_4]		2.6	0.8	0.7	0.6
	[Ca]	0.1	0.1	0.1	0.2	0.1
100 mmol Fe^0	[SO_4]		0.3	0.3	0.4	0.5
	[Ca]	0.1	0.2	0.8	0.1	n/a
10 mmol Fe^0 + *	[SO_4]		584	450	419	134
	[Ca]	15	178	n/a	79	n/a

* = 5 mmol ($CaCO_3 + CaSO_4 . 2H_20$)

Table 5: Sulphate and calcium concentrations in mg/l in supernatent solutions of incubated soil slurries treated with Fe^0. The reproducibility of these measurements was always better than 2% for sulphate and 5% for calcium.

the supernatent solution reached 584 mg/l (≅ 6.0 mmol) and 187 mg/l (≅ 4.7 mmol) respectively (Table 5). The Ca : SO_4 does not match that of the salt because Ca(2+) was also provided to the solution from the dissolution of the added calcite. Additional sulphate would have been provided by the degradation of organic matter (Cutter and Krahforst, 1988). The covariance between sulphate and iron concentration in the supernatent solution (Figure 19) resulted from the reduction of Fe(3+), associated with oxides produced by the oxidation of Fe(0) under oxygenated conditions, or oxidation to Fe(2+) upon the onset of sulphate reduction and H_2S formation:

$$2\,Fe^0 + O_2 + 3\,H_2O \rightarrow Fe(OH)_3$$

$$4\,Fe(OH)_3 + \text{"}CH_2O\text{"} + 8\,H_2O \rightarrow 4\,Fe^{2+} + CO_2 + 11\,H_2O$$

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^-$$

$$Fe^{2+} + H_2S \rightarrow FeS + 2H^+$$

Figure 19 clearly illustrates the temporal variation between sulphate and iron concentrations. As reducing conditions developed in the slurries, sulphate concentrations decreased steadily. Concommitently, Fe(2+) concentrations increased as Fe(3+) was reduced until they reached a maximum on Day 56. Upon reaching saturation with respect to an iron sulphide phase, precipitation of pyrite or a monosulphide occurred following Day 56. Although DOC concentrations in some supernatent solutions increased with time (Figure 20), the complexation and solubilization of Hg would have been limited by the reduced availability of inorganic mercury adsorbed on the sulphides.

Iron shavings seemed to only slightly inhibit methylation and/or foster demethylation in the slurry solids since methylmercury concentrations are only 10 to 40% lower than the control by the end of the study (Figure 21). After four days, methylmercury concentrations in the treated slurries exceeded those of the control.

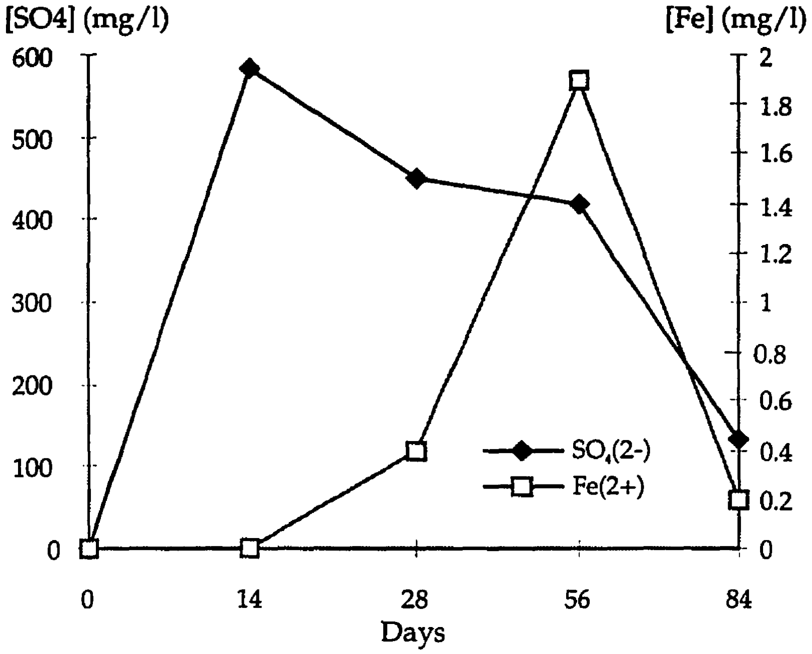


Figure 19: Comparison of sulphate and iron concentrations in the supernatent solution as a function of time in incubated soil slurries treated with 10 mmol Fe^0 + 5 mmol ($CaCO_3$ + $CaSO_4$. $2H_2O$).

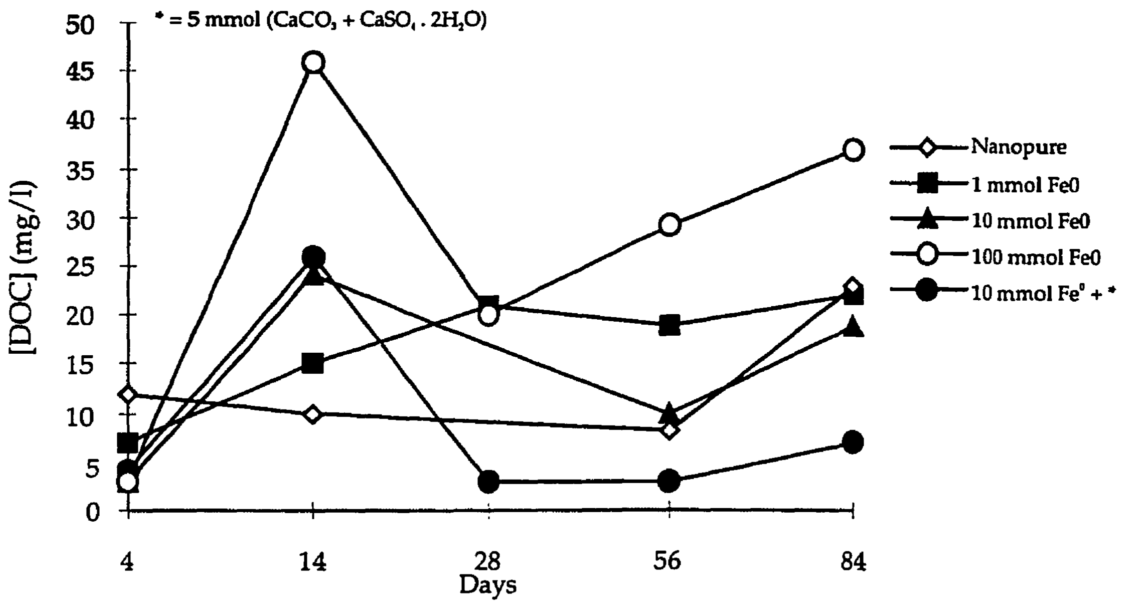


Figure 20: DOC concentrations in the supernatent solution as a function of time in incubated soil slurries treated with Fe^0.

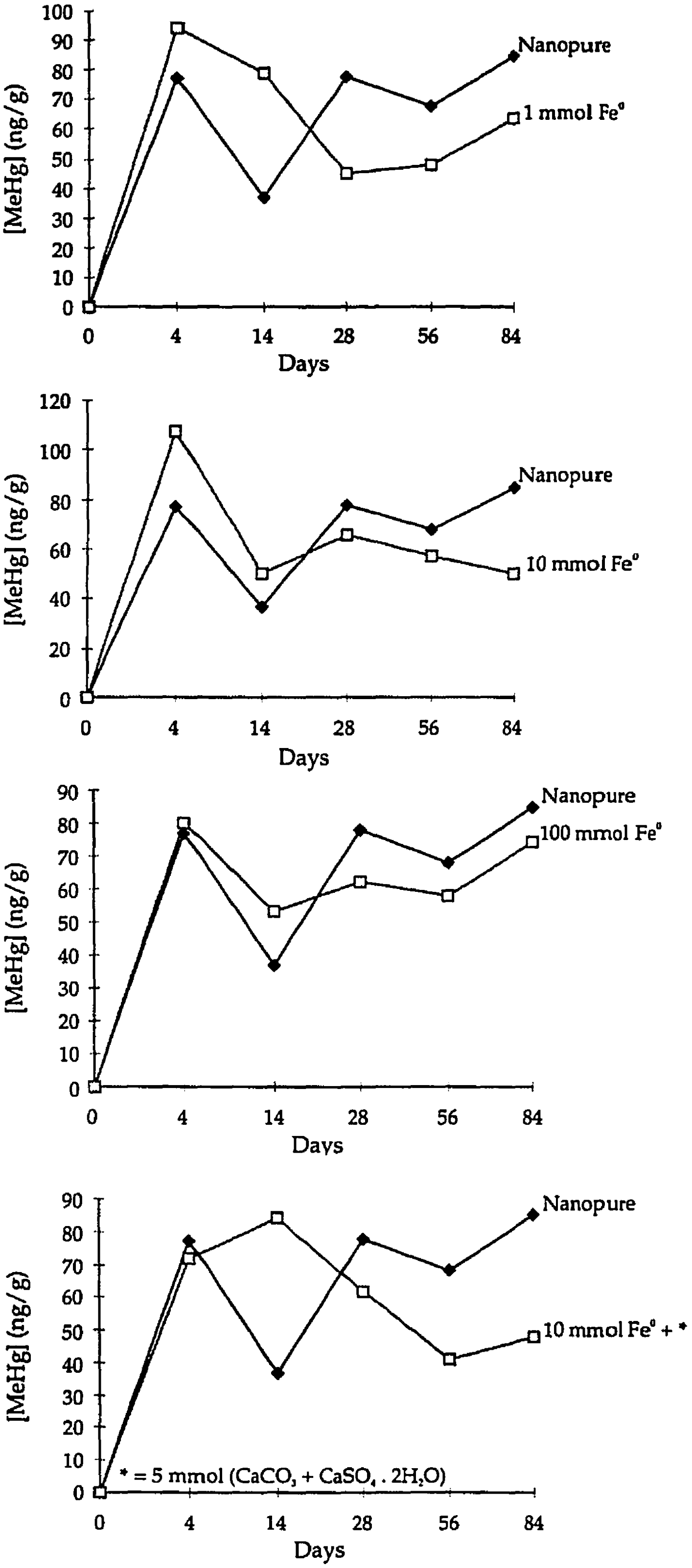


Figure 21: Methylmercury concentrations associated with the solids as a function of time in incubated soil slurries treated with Fe^0.

This observation could be interpreted as though the addition of Fe(0) promoted methylation. Following Day 14, this trend is reversed and methylmercury concentrations become smaller in treated slurries than in the control experiment. The addition of iron shavings, calcite, and gypsum, was most efficient at limiting the buildup of methylmercury. This observation can be explained by the greater availability of sulphate for the formation of sulphides or the lower rate of methylation at higher pH. All treated slurries had lower concentrations of methylmercury in the slurry solid than the control, but they all showed an increase in MeHg with time. Through iron oxidation and organic matter degradation, pH decreased in the supernatent solutions (Table 6) thereby favouring methylation. Methylmercury concentrations in slurries treated with iron shavings were comparable to previous experiments. As mentioned earlier, methylation is favoured by low pH conditions (Fagerstrom and Jernelov, 1972; Wood, 1980) but, by the end of the study, pH data for slurries treated with Fe(0) were only slightly lower than those treated with Fe_2O_3. Nevertheless, enhanced methylmercury production in Fe(0) treated slurries was likely limited by the formation of iron sulphide phases early in the incubation period.

ii. Oxygenated slurries

Under oxygenated conditions, Fe(0) would have been oxidized and formed FeOOH which should have scavenged Hg out of solution. The addition of iron shavings in oxygenated slurries, however, did not seem to have any influence on Hg scavenging (Figure 22). Again, supernatent solutions of control samples show a steady decrease in total mercury concentrations following the initial increase attributed to organic matter suspension as proposed earlier. Mercury scavenging in the controls was likely dominated by the soil organic matter which would have effectively trapped Hg(2+) at the sediment-water interface. The addition of gypsum did not influence Hg uptake either. When gypsum was added, sulphate

Treatment	Day 4	Day 14	Day 28	Day 56	Day 84
1 mmol Fe^0	5.1	5.5	4.9	4.3	4.4
10 mmol Fe^0	5.0	5.3	4.9	4.3	4.1
100 mmol Fe^0	4.3	3.9	4.4	4.3	3.2
10 mmol Fe^0 + *	6.1	6.6	6.7	6.5	5.9

Treatment	Day 4	Day 14	Day 28	Day 56	Day 84
1 mmol Fe_2O_3	4.8	4.5	4.1	4.6	4.6
10 mmol Fe_2O_3	4.7	4.4	4.0	4.5	4.5
100 mmol Fe_2O_3	4.5	4.2	3.9	4.3	4.3
10 mmol Fe_2O_3 + *	7.4	5.9	6.8	6.4	6.9

* = 5 mmol ($CaCO_3 + CaSO_4 . 2H_20$)

Table 6: pH in supernatent solutions of incubated soil slurries treated with Fe^0 and Fe_2O_3 .

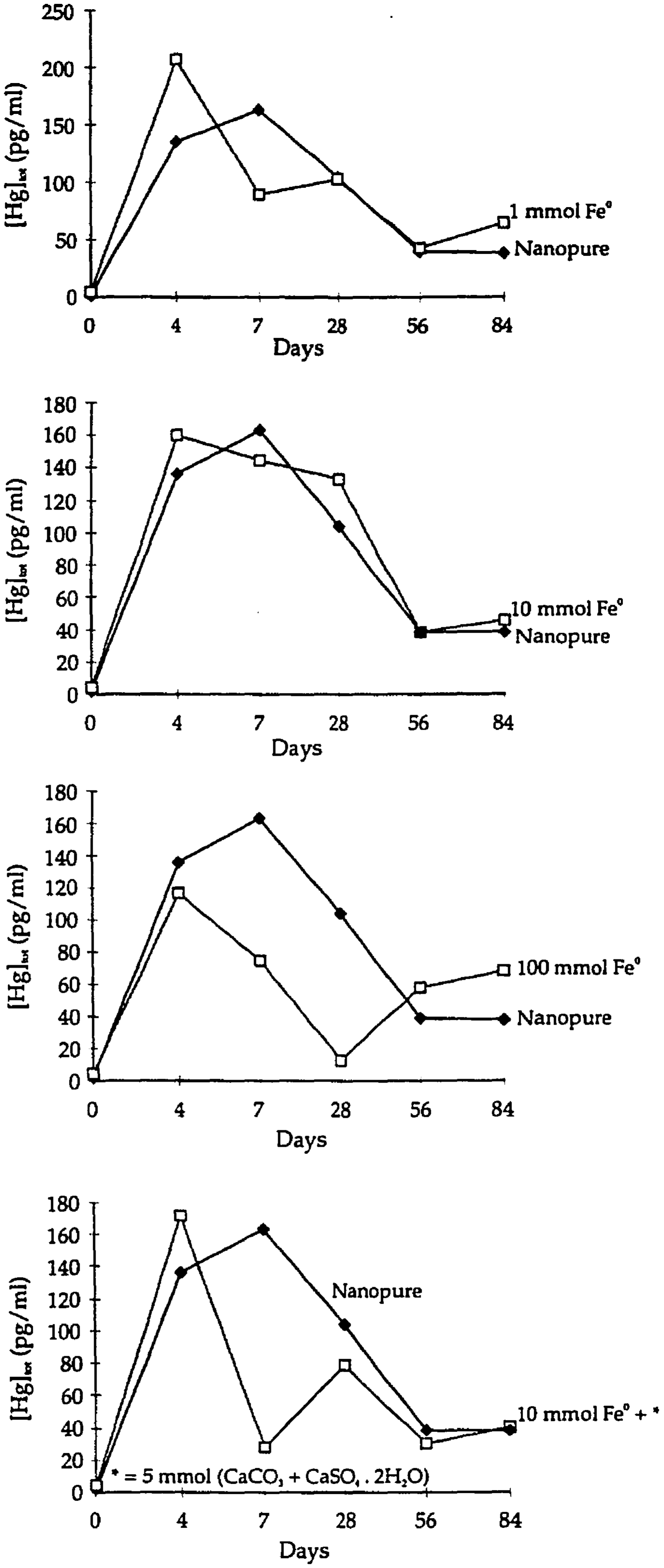


Figure 22 : Total mercury concentrations in the supernatent solution as a function of time in oxygenated soil slurries treated with Fe^0.

concentrations in the supernatent solution reached a maximum (480 mg/l ≡ 4.95 mmol) on Day 14 (Table 7), thereby indicating complete dissolution. The subsequent decrease in sulphate concentrations resulted from the activity of sulphate reducing bacteria within the slurry soils (Kelly *et al.,* 1982; Kelly and Rudd, 1984; Rudd *et al.,* 1986). DOC concentrations (Figure 23) in the supernatent solutions also failed to correlate with total dissolved mercury concentrations.

Iron shavings under oxygenated conditions did not successfully inhibit methylation either (Figure 24). Only the slurry treated with 1 mmol Fe^0 contained lower concentrations of methylmercury than the control by the end of the study period. In all cases, methylmercury concentrations seemed to increase with time. The presence of iron shavings successfully inhibited methylation in the first four weeks, but it seemed to promote methylation thereafter. By the end of the study, however, all the different combinations of reagents gave values which were comparable to the control thereby suggesting no long-term influence by the reagents. Methylmercury-spiked solutions showed that, in accordance with previous treatments, the most efficient methylmercury inhibitor was elemental iron in the presence of calcite and gypsum (Figure 25).

iii. Conclusions

Based on the compiled data, it appears that iron shavings could only effectively scavenge Hg out of solution and somewhat inhibit methylation when anoxic conditions prevailed. It would have been informative to pursue these experiments longer to find out if the behaviour is long term. Even at low concentrations, Fe(0) was able to limit total mercury concentrations in the supernatent solutions but, unfortunately this was not the case for methylmercury. This would suggest that the formation of iron sulphide phases was essential to mercury sequestration. Elemental iron in the presence of calcite and gypsum

Treatment	Day 14	Day 84
Nanopure®	1.14	1.77
1 mmol Fe^0	1.19	n/a
10 mmol Fe^0	1.02	2.07
100 mmol Fe^0	1.17	n/a
10 mmol Fe^0 + *	480	179

* = 5 mmol ($CaCO_3$ + $CaSO_4 . 2H_2O$)

Table 7 : Sulphate concentrations in mg/l in supernatent solutions of oxygenated soil slurries treated with Fe^0. Initial sulphate concentrations (i.e. Day 0) are assumed to be 0 mg/l. The reproducibility of these measurements was always better than 2%.

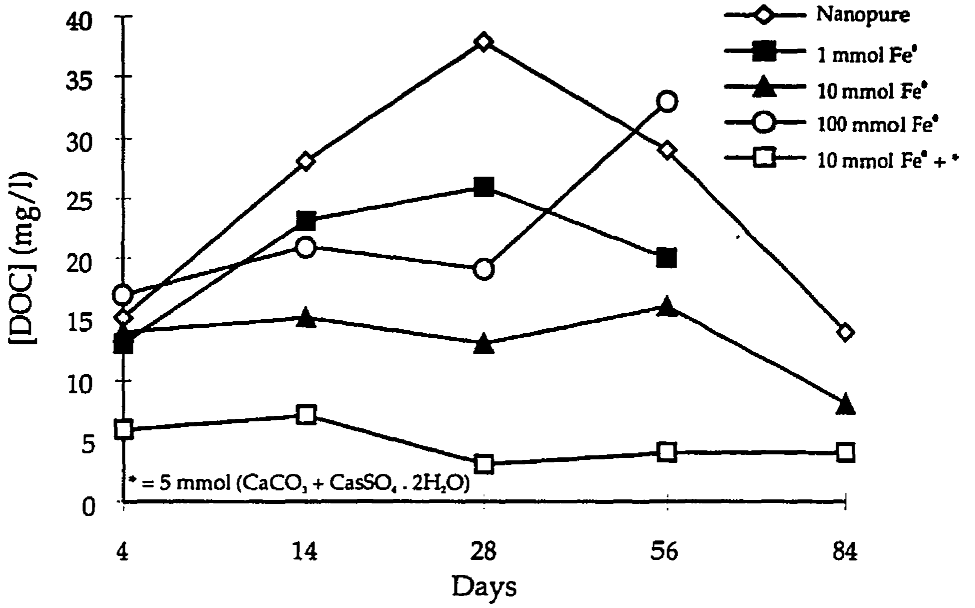


Figure 23 : DOC concentrations in the supernatent solution as a function of time in oxygenated soil slurries treated with Fe^0.

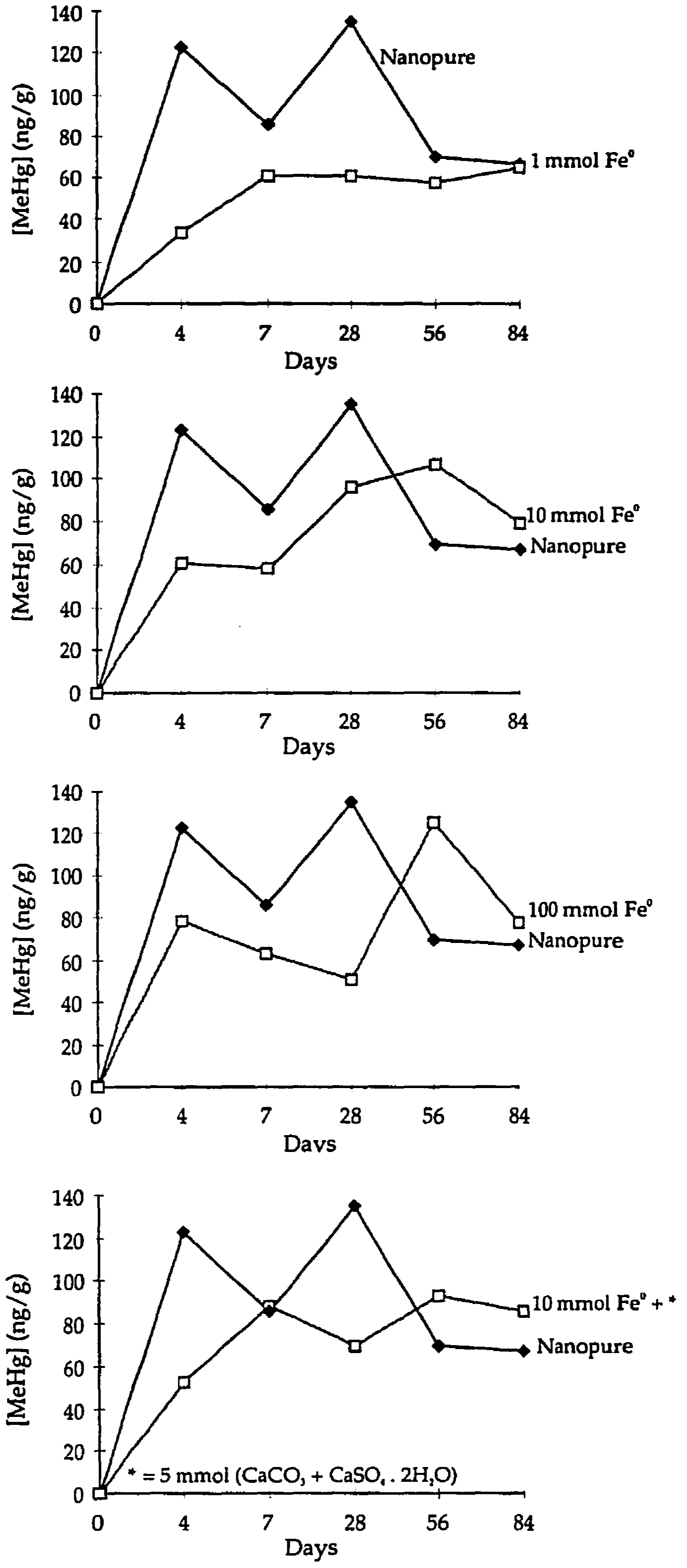


Figure 24 : Methylmercury concentrations associated with the solids as a function of time in oxygenated soil slurries treated with Fe^0.

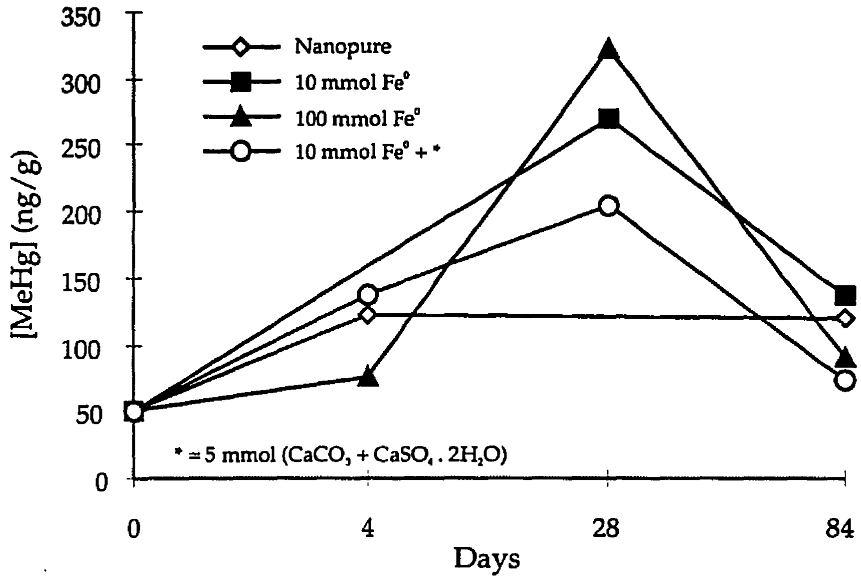


Figure 25 : Methylmercury concentrations associated with the solids as a function of time in oxygenated methylmercury-spiked soil slurries treated with Fe^0.

presented the most efficient treatment as the reduction of sulphate allowed the formation of iron sulphides which were able to scavenge Hg(2+) out of solution, sequester it within the slurry solids and thus prevent its methylation.

4.3 **Ferrous Ammonium Sulphate**

A separate study was conducted using ferrous ammonium sulphate on Hg-contaminated soil from a different locality (St-Hippolyte, Quebec). The total mercury concentration in the soil was determined to be 89 ± 4 ng/g Hg (dry weight) after analysis of four replicates. In this set of experiments, slurries were incubated over a period of 28 days. As in the studies described previously, total mercury concentrations in the supernatent solutions, methylmercury concentration in the solids, pH and DOC were monitored throughout the incubation period.

Ferrous ammonium sulphate successfully limited the release of Hg to the solution throughout the study period when concentrations exceeding 10 mmol were added (Figure 26). In these cases, total mercury concentrations in the supernatent solution were well below those of the control. Remarkably, all the treated slurries parallel the behaviour of the control. When 100 mmol of the salt were added, total Hg release to the supernatent solution only reached 14 pg/ml by the end of the study period. Again, the behaviour of the slurries was consistent with previous experiments. The collected data suggest that Hg remobilization through the suspension of the soil organic matter following sample preparation was hindered by the addition of ferrous ammonium sulphate. Indeed, only the control and the slurry treated with the lowest amount of salt (i.e. 1 mmol), show any significant increase in Hg concentrations on Day 1. As mentioned previously, redox conditions in the soil slurries changed following water addition. Despite the lack of Eh data, the establishment of anoxic conditions could be inferred from the consistent behaviour of control slurries in previous experiments. In all cases,

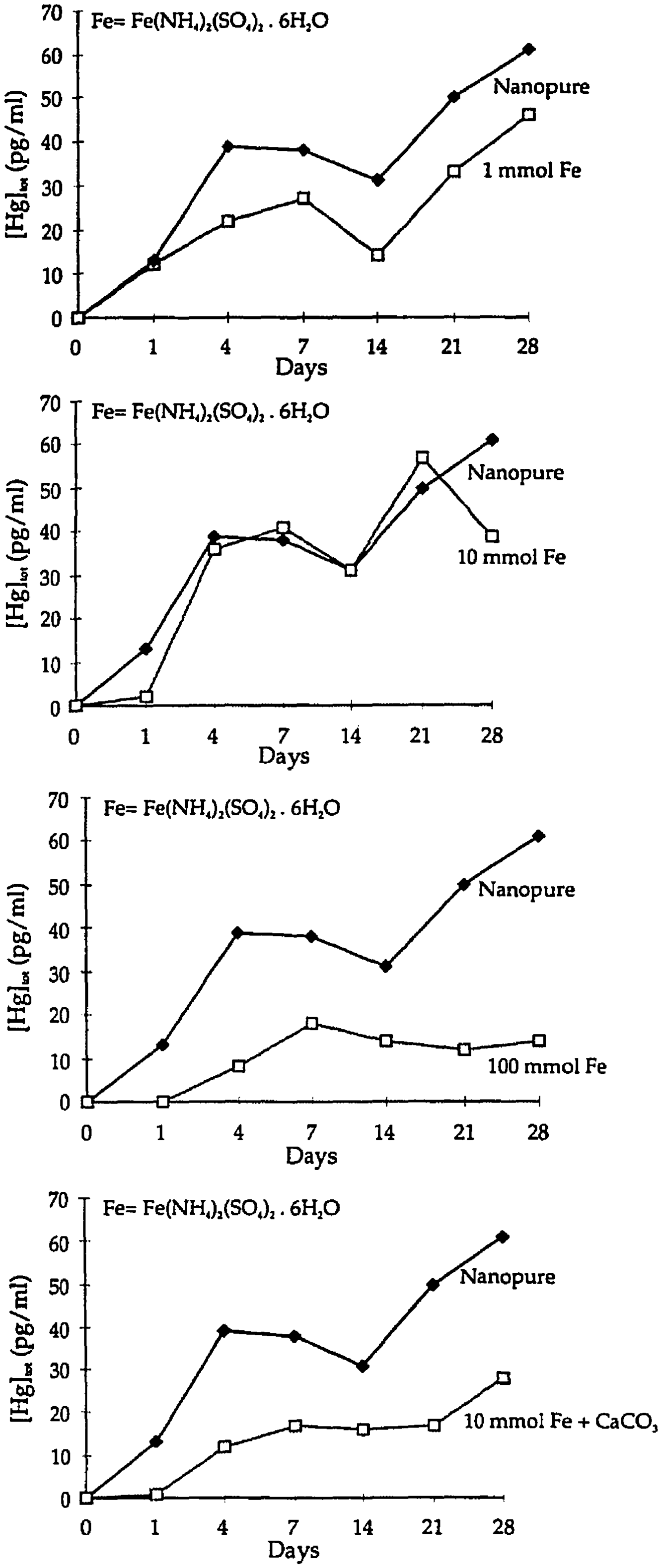


Figure 26 : Total mercury concentrations in the supernatent solution as a function of time in incubated soil slurries treated with ferrous ammonium sulphate.

mercury concentrations in the supernatent solution decreased following Day 7. Under anaerobic conditions, sulphate-reducing bacteria likely produced sulphide ions. These, supplied by the reduction of dissolved sulphate from the reagent, formed iron sulphide phases which proceeded with Hg scavenging (Farrah and Pickering, 1972; Summers and Silver, 1978; Campeau and Bartha, 1985; Revis *et al.*, 1989). DOC concentrations in the supernatent solutions increased with time, especially in slurries treated with the highest concentration of ferrous ammonium sulphate (Figure 27). Interestingly, this would indicate that the presence of high concentrations of Fe promotes the formation of DOC. The same trend was observed in slurries treated with iron shavings but not Fe_2O_3. In this case, however, the increase was not accompanied by increased Hg concentrations in the supernatent solution. This would suggest that the addition of 100 mmol of ferrous ammonium sulphate, lead to the formation of enough iron sulphides (FeS_x) to efficiently trap inorganic mercury within the solids thereby limiting its complexation with DOC which often serves as a vector for Hg to the dissolved phase.

Ferrous ammonium only successfully inhibited methylation after 28 days when present in large quantities (i.e. >10 mmol) (Figure 28). Here again, there seems to be a shift in reagent behaviour following the establishment of reducing conditions. Under reducing conditions, biological methylation of Hg within the solids may have superseded the oxides' (FeOOH) ability to suppress methylation. It is important to note, however, that the controls behaved similarly and failed to show any methylmercury concentrations within the first 7 days following water addition. This trend which differs from previous experiments may be explained by differences in the nature and organic matter content of this soil which consisted of leaves and twigs as opposed to mosses. In addition, the initial mercury content of this soil was much lower and may have been more strongly bound than in previous experiments. For ferrous ammonium sulphate concentrations greater

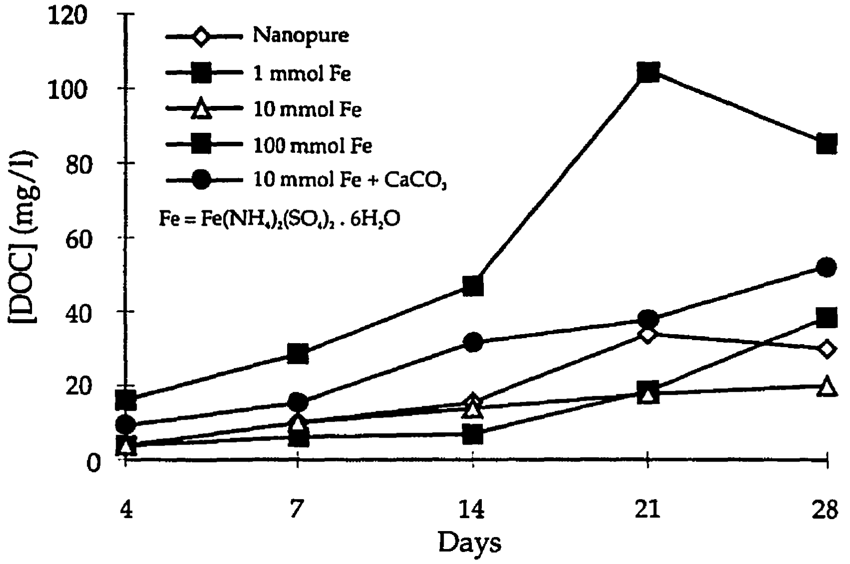


Figure 27: DOC concentrations in the supernatent solution as a function of time in incubated soil slurries treated with ferrous ammonium sulphate.

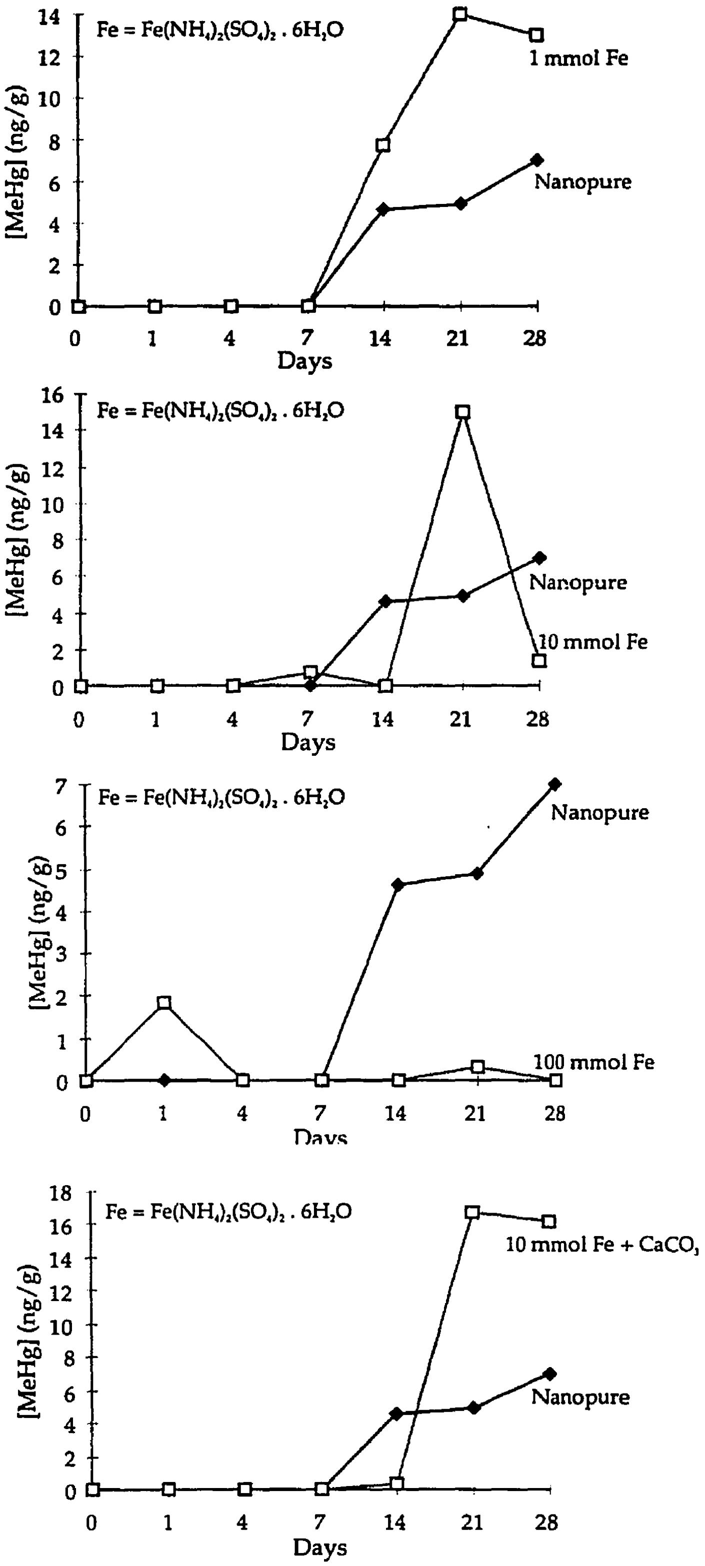


Figure 28 : Methylmercury concentrations associated with the solids as a function of time in incubated soil slurries treated with ferrous ammonium sulaphate.

than 10 mmol, the active precipitation of FeS_x was most likely responsible for methylmercury inhibition. As seen on the pH profile (Figure 29), the greater the amount of salt added, the greater the pH decrease. The evolution of pH can be explained by a number of reactions which occurred in sequence as redox conditions changed: pH initially decreased as Fe(2+) was oxidized to Fe(3+) and metabolic CO_2 was produced, then increased as SO_4^{2-} was reduced and Fe(3+) was reduced back to Fe(2+), and finally decreased as a result of sulphide precipitation:

$$Fe^{2+} + 1/2\,O_2 + H_2O \leftrightarrow FeOOH + H^+$$

$$\text{"}CH_2O\text{"} + O_2 \leftrightarrow CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$

$$2\,\text{"}CH_2O\text{"} + SO_4^{2-} \leftrightarrow H_2S + 2HCO_3^-$$

$$Fe^{2+} + xH_2S \leftrightarrow FeS_x + 2xH^+$$

When present in large quantities ferrous ammonium sulphate was able to suppress methylation completely since no methylmercury could be detected in the solids on Day 28.

5.0 Conclusions

Hg contamination of aquatic environments has been a topic of major concern over the past few decades. Although several studies have been undertaken, no definite solution has been found to prevent the release of Hg trapped in soil or its methylation following impoundment of a hydro-electric reservoir. An attempt has been made here to find a suitable innocuous chemical reagent that could be added directly to a soil prior to impoundment or to the water column after impoundment that could sequester Hg(2+) within the soil and inhibit its biological methylation. We focused our attention on three different reagents: iron oxide (Fe_2O_3), iron shavings (Fe(0)), and ferrous ammonium sulphate ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$) since oxides and sulphides could adsorb Hg(2+) that would

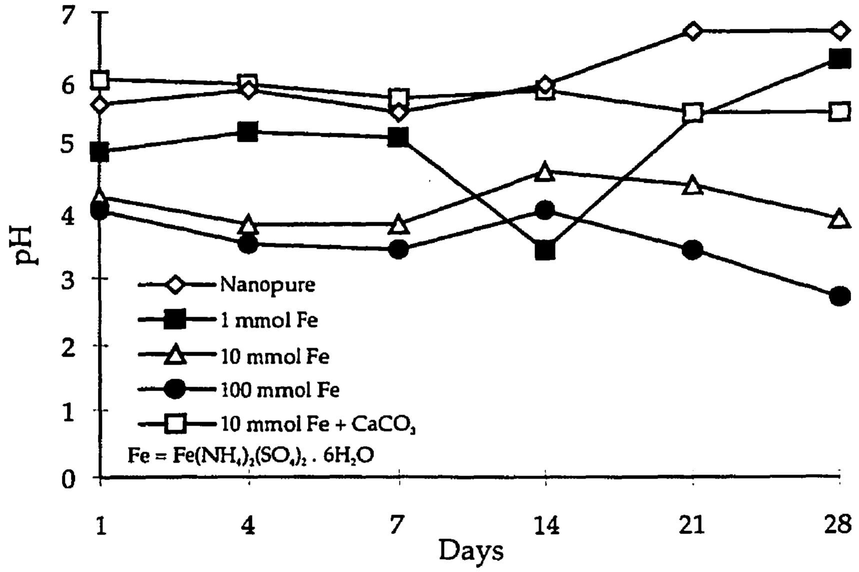


Figure 29 : pH in supernatent solutions of incubated soil slurries treated with ferrous ammonium sulphate.

be diffusing out of the inundated soils and oxides may demethylate mercury. The impetus for using iron oxide and iron shavings in treating northern Quebec's large hydro-electric reservoirs was also economical. These two reagents, readily available as mining waste products, can be obtained at relatively low costs. The synthetic salt, ferrous ammonium sulphate, although more expensive, was also considered since it provided iron for the precipitation of oxides or sulphides which would help trap Hg(2+), ammonia, a nutrient which would promote bacterial activity, and sulphate which would, upon reduction, provide additional sulphide. In addition to investigating the effect of various concentrations of these salts, some experiments were carried out in the presence and absence of calcite and gypsum. Gypsum was added to stimulate the production of iron sulphides in the anaerobic soil pore waters below the sediment-water interface whereas calcite was used to buffer the pH of the supernatent solutions.

All three reagents limited the release of Hg(2+) to the supernatent solution when reducing conditions were allowed to develop in the slurries but they differed significantly in efficiency and rate of uptake. Although not all the experiments were carried out with the same material, results suggest that efficiency increased in the order iron oxide (0 -15%) < elemental iron (15 - 75%) ≤ ferrous ammonium sulphate (80 - 90%). Iron oxide was better able to limit Hg(2+) release to the supernatent solution (up to 45%) when oxygenated conditions were maintained in the slurries. The adsorption of Hg onto the added or authigenic solid phases appeared to have little or no influence on the microbial methylation of Hg when iron oxide and iron shavings were used. Ferrous ammonium sulphate was the most effective of the three reagents tested in controlling Hg methylation. Ten mmol additions successfully suppressed methylation, whereas it was totally inhibited with 100 mmol $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$. This, and the fact that Hg scavenging was less effective under oxygenating conditions would suggest that the formation of sulphides was instrumental in scavenging Hg out of solution and preventing its methylation.

To what extent do the experimental results apply to natural environments? A natural environment is much more complex than a simple, controlled experimental system. Hydro-electric reservoirs are submitted to a number of site-dependent and seasonally fluctuating environmental factors such as pH, Eh, temperature, salinity, as well as nutrient, free oxygen, sulphides and pollutant concentrations (Fagerstrom and Jernelov, 1972; Gavis and Ferguson, 1972; Beijer and Jernelov, 1979; Benes and Havlik, 1979; Furutani and Rudd, 1980; Rudd and Turner, 1983; Bodaly *et al.*, 1984; Hecky et al., 1987; Jackson, 1988a,b, 1989). The effects of these environmental factors on methylmercury formation and breakdown may be extremely variable and not altogether predictable. Methylation and demethylation of Hg are natural processes mediated by many different microbial communities. Consequently, variations in the physico-chemical properties of their habitat (apart from changes in Hg supply and availability) may result in an increase or a decrease in methylmercury levels. Also, depending on the nature, quantity, and surface chemistry of innocuous reagents used, the source of the sediment (and therefore the nature of the microbial community), and environmental factors stated previously, the added phases may greatly suppress or promote Hg methylation or demethylation or else may have little effect. As shown in our study, the effects are not altogether consistent and predictable, although it is possible to formulate certain broad generalizations:

1) Variations in total mercury release to the supernatent solutions and methylmercury concentrations in slurry solids typically did not show a smooth simple trend which suggests shifts in reagent and microbial behaviour as a function of time.

2) Changes in total mercury and methylmercury concentrations were accompanied by distinctive changes in other parameters indicative of microbial activity (Eh, pH) which suggest that the reagents caused changes in the character and activities of microbes. Decreases in Eh were accompanied by increases in methylmercury concentrations while decreases in pH were associated, amongst other things, to H_2S production by micro organisms.

3) Except for ferrous ammonium sulphate (100 mmol), the reagents were not able to totally suppress microbial activity nor were they able to completely bind and immobilize Hg(2+) or impede methylation and/or promote demethylation. The long induction period to the formation of methylmercury in the solids of the slurries treated with ferrous ammonium sulphate may suggest a site-related difference in the microbial species or the nature and reactivity of the organic matter. Perhaps, the soil of St-Hippolyte was enriched in demethylating microbes. The low initial mercury content of the soil and its strong adsorption by soil material could also explain the observed trend.

As mentioned previously, the addition of ferrous ammonium sulphate to the soil of a hydro-electric reservoir, prior to impoundment, may help limit Hg methylation and release to the overlying waters through the formation of oxide and sulphide phases in the soil horizon. The trapped mercury may become mobile, however, if prevailing geochemical conditions (Eh and pH) change drastically. Engler and Patrick (1975) have noted that insoluble Fe and Hg sulphides may be converted to soluble oxidized salts upon oxidation of a flooded soil or sediment. With average water level variations in the LG-2 reservoir on the order of 4-5 meters as a result of drawdown, oxidation of sulphides may occur along reservoir margins. The oxidation of pyrite, however, is relatively slow and Hg released from sulphides may be captured once again by the newly formed oxide minerals within the oxygen penetration zone.

In light of our experimental results, we estimated the cost of treating a 1000 km^2 reservoir with ferrous ammonium sulphate. This is an average size for the hydroelectric reservoirs of northern Quebec. The La Forge reservoir, impounded in the summer of 1993, spans 1288 km^2. Our 10 mmol experimental equivalent per unit area (1.23×10^{-2} m^2) extrapolated over 1000 km^2 would necessitate the addition of 1.27×10^{12} g of the salt. Since 10^3 g of ferrous ammonium sulphate costs $38 (American Chemicals, pers. comm.), treatment of a 1000 km^2 reservoir would cost an estimated $ 4 850 000 000. It is obvious that treatment with the synthetic salt, although much more effective than other proposed methods, may not be economically viable. Furthermore, the addition of such a large quantity of salt would have an impact on water quality and would have to be carefully monitored to limit its effects on the aquatic biota. The depth of the water column of a hydro-electric reservoir is typically 3 m which represents a volume of 3×10^{12} l for a 1000 km^2 reservoir. Given the solubility of the salt (26.9g/10 ml cold water, Handbook of Chemistry and Physics, 1982), the added 1.27×10^{12} g of salt would totally dissolve releasing 39 mg/l NH_4 and 208 mg/l SO_4 to the overlying waters. The increased nutrient supply may promote microbial activity and fish productivity, The large supply of sulphate, above that found in most pristine and acid lakes (0.9 to 19 mg/l; Winfrey and Rudd, 1990; Wren *et al.*, 1991), would certainly have an impact on water quality. Sulphate would likely diffuse rapidly into the sediment, be reduced and precipitate as sulphides. Furthermore, the oxidation of Fe(2+) to Fe(3+) would decrease pH and liming would have to be undertaken to raise pH levels. Although this would tag on additional costs, hard water seems to impede methylmercury uptake in fish as Ca^{2+} induces changes in gill permeability (Rodgers and Beamish, 1983).

In conclusion, further work combining controlled experiments with field studies is needed to better understand the effects of iron oxide, iron shavings, and ferrous ammonium sulphate on the methylation and demethylation of Hg in nature. Experimental results presented here, however, suggest that these reagents, particularly ferrous ammonium sulphate, may offer a suitable remediation technique to mercury contamination in hydro-electric reservoirs. Since Hg(2+) adsorption is dominated by the formation of sulphides, the direct addition of sulphides to the contaminated environment may be a suitable alternate remediation procedure and should be investigated further. Of course, acidification of the water through sulphide oxidation would have to be controlled.

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Appendix 1

Weight of salts added to the slurries with 40 ml Nanopure® water.

Salts	1 mmol	5 mmol	10 mmol	100 mmol
Fe_2O_3	0.0064		0.0639	0.6388
Fe^0	0.0022		0.0223	0.2234
$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	0.0157			1.5686
$CaCO_3$		0.0200		
$CaSO_4 \cdot 2H_2O$		0.0345		

Appendix 2.1

Total mercury (Hg_{tot}) in pg/ml in the supernatent solution of incubated soil slurries treated with Fe_2O_3.

	Day 1	Day 4	Day 7	Day 28	Day 56	Day 84
Nanopure	285	84	174	52	108	80
1 mmol Fe_2O_3	285	59	116	17	30	63
10 mmol Fe_2O_3	102	66	91	22	45	114
100 mmol Fe_2O_3	72	61	91	13	33	45
10 mmol Fe_2O_3 + *	145	63	78	12	20	150

* = 5 mmol $CaCO_3$ + 5 mmol $CaSO_4 \cdot 2H_2O$

Appendix 2.2

Total mercury (Hg_{tot}) in pg/ml in the supernatent solution of oxygenated soil slurries treated with Fe_2O_3.

	Day 4	Day 7	Day 28	Day 56	Day 84
Nanopure	136	163	104	39	38
1 mmol Fe_2O_3	94	98	96	62	41
10 mmol Fe_2O_3	46	105	91	62	25
100 mmol Fe_2O_3	52	114	101	59	24
10 mmol Fe_2O_3 + *	44	37	157	29	21

* = 5 mmol $CaCO_3$ + 5 mmol $CaSO_4 \cdot 2H_2O$

Appendix 2.3

Methylmercury (MeHg) in ng/g (dry) associated with solids of incubated methylmercury-spiked soil slurries treated with Fe_2O_3.

	Day 1	Day 4	Day 7	Day 28	Day 56	Day 84
Nanopure	155	120	112	119	123	93
1 mmol Fe_2O_3	146	144	188	161	118	59
10 mmol Fe_2O_3	128	99	146	161	163	72
100 mmol Fe_2O_3	136	215	121	126	121	54
10 mmol Fe_2O_3 + *	91	140	119	93	122	61

* = 5 mmol $CaCO_3$ + 5 mmol $CaSO_4 \cdot 2H_2O$

Appendix 2.4

DOC in mg/l in the supernatent solution of incubated soil slurries treated with Fe_2O_3.

	Day 1	Day 4	Day 7	Day 28	Day 56	Day 84
Nanopure	12	14	19	36	40	38
1 mmol Fe_2O_3	16	17	16	33	37	33
10 mmol Fe_2O_3	15	13	13	30	36	32
100 mmol Fe_2O_3	11	9.4	8.2	13	22	19
10 mmol Fe_2O_3 + *	13	4.3	5.2	16	22	16

* = 5 mmol $CaCO_3$ + 5 mmol $CaSO_4 \cdot 2H_2O$

Appendix 2.5

DOC in mg/l in the supernatent solution of oxygenated soil slurries treated with Fe_2O_3 .

	Day 4	Day 14	Day 28	Day 56	Day 84
Nanopure	11	26	24	24	28
1 mmol Fe_2O_3	12	19	18	17	21
10 mmol Fe_2O_3	30	17	14	17	21
100 mmol Fe_2O_3	8.6	9.8	11	8.4	11
10 mmol Fe_2O_3 + *	3.6	5.7	5.8	6.1	12

* = 5 mmol $CaCO_3$ + 5 mmol $CaSO_4 \cdot 2H_2O$

Appendix 2.6

[Fe] in mg/l in the supernatent solution of incubated soil slurries treated with Fe_2O_3.

	Day 4	Day 14	Day 28	Day 56	Day 84
Nanopure	0.2	0.3	0.9	n/a	0.8
1 mmol Fe_2O_3	0.2	0.2	0.4	0.4	0.5
10 mmol Fe_2O_3	0.2	0.1	0.7	0.4	0.6
100 mmol Fe_2O_3	0.1	0.1	0.2	n/a	0.4
10 mmol Fe_2O_3 + *	0.1	2.2	1.8	4.4	0.3

* = 5 mmol $CaCO_3$ + 5 mmol $CaSO_4 \cdot 2H_2O$

Appendix 2.7

Methylmercury (MeHg) in ng/g (dry) associated with solids of oxygenated soil slurries treated with Fe_2O_3.

	Day 4	Day 7	Day 28	Day 56	Day 84
Nanopure	123	86	135	70	67
1 mmol Fe_2O_3	69	51	48	83	64
10 mmol Fe_2O_3	69	72	68	72	47
100 mmol Fe_2O_3	59	56	88	73	57
10 mmol Fe_2O_3 + *	73	60	70	72	75

* = 5 mmol $CaCO_3$ + 5 mmol $CaSO_4 \cdot 2H_2O$

Appendix 2.8

Methylmercury (MeHg) in ng/g (dry) associated with solids of incubated soil slurries treated with Fe_2O_3.

	Day 1	Day 4	Day 7	Day 28	Day 56	Day 84
Nanopure	215	77	75	78	68	85
1 mmol Fe_2O_3	139	88	54	52	72	64
10 mmol Fe_2O_3	142	68	60	49	71	76
100 mmol Fe_2O_3	99	65	52	89	64	58
10 mmol Fe_2O_3 + *	91	59	55	65	58	66

* = 5 mmol $CaCO_3$ + 5 mmol $CaSO_4 \cdot 2H_2O$

Appendix 3.1

Total mercury (Hg_{tot}) in pg/ml in the supernatent solution of incubated soil slurries treated with Fe^0.

	Day 4	Day 14	Day 28	Day 56	Day 84
Nanopure	84	174	52	108	80
1 mmol Fe^0	120	83	119	110	14
10 mmol Fe^0	72	115	81	56	1
100 mmol Fe^0	49	61	77	26	12
10 mmol Fe^0 + *	49	148	74	42	25

*= 5 mmol $CaCO_3$ + 5 mmol $CaSO_4 \cdot 2H_2O$

Appendix 3.2

Total mercury (Hg_{tot}) inpg/ml in the supernatent solution of oxygenated soil slurries treated with Fe^0.

	Day 4	Day 7	Day 28	Day 56	Day 84
Nanopure	136	163	104	39	38
1 mmol Fe^0	207	90	103	42	65
10 mmol Fe^0	160	145	133	39	46
100 mmol Fe^0	117	75	13	58	68
10 mmol Fe^0 + *	172	28	79	30	41

*= 5 mmol $CaCO_3$ + 5 mmol $CaSO_4 \cdot 2H_2O$

Appendix 3.3

Methylmercury (MeHg) in ng/g (dry) associated with the solids of incubated soil slurries treated with Fe^0.

	Day 4	Day 14	Day 28	Day 56	Day 84
Nanopure	77	37	78	68	85
1 mmol Fe^0	94	79	45	48	64
10 mmol Fe^0	107	50	66	57	50
100 mmol Fe^0	80	53	62	58	74
10 mmol Fe^0 + *	72	84	62	41	48

*= 5 mmol $CaCO_3$ + 5 mmol $CaSO_4 \cdot 2H_2O$

Appendix 3.4

Methylmercury (MeHg) in ng/g (dry)associated with the solids of of oxygenated soil slurries treated with Fe^0.

	Day 4	Day 14	Day 28	Day 56	Day 84
Nanopure	123	86	135	70	67
1 mmol Fe^0	34	61	61	58	65
10 mmol Fe^0	61	58	96	107	79
100 mmol Fe^0	79	63	51	125	78
10 mmol Fe^0 + *	53	88	70	93	86

*= 5 mmol $CaCO_3$ + 5 mmol $CaSO_4 \cdot 2H_2O$

Appendix 3.5

Methylmercury (MeHg) in ng/g (dry) associated with the solids of oxygenated methylmercury-spiked soil slurries treated with Fe^0.

	Day 4	Day 28	Day 84
Nanopure	123	–	121
10 mmol Fe^0	–	270	136
100 mmol Fe^0	75	322	90
10 mmol Fe^0 + *	136	204	73

*= 5 mmol $CaCO_3$ + 5 mmol $CaSO_4 \cdot 2H_2O$

Appendix 3.6

[Fe] in mg/l in the supernatent solution of incubated soil slurries treated with Fe^0.

	Day 4	Day 14	Day 28	Day 56	Day 84
Nanopure	0	0.2	0.1	0.2	0.1
1 mmol Fe^0	0	0.6	0.1	0.2	0.1
10 mmol Fe^0	0	3.7	0.1	0.5	0.2
100 mmol Fe^0	0	3.9	0.8	0.9	0
10 mmol Fe^0 + *	0	0	0.4	0.9	0.2

*= 5 mmol $CaCO_3$ + 5 mmol $CaSO_4 \cdot 2H_2O$

Appendix 3.7

DOC in mg/l in the supernatent solution of incubated soil slurries treated with Fe^0.

	Day 4	Day 14	Day 28	Day 56	Day 84
Nanopure	12	10	–	8	23
1 mmol Fe^0	7	15	22	19	22
10 mmol Fe^0	2.9	24	–	10	19
100 mmol Fe^0	3.5	46	20	30	37
10 mmol Fe^0 + *	4.2	26	3.4	3.1	6.9

*= 5 mmol $CaCO_3$ + 5 mmol $CaSO_4 \cdot 2H_2O$

Appendix 3.8

DOC in mg/l in the supernatent solution of oxygenated soil slurries treated with Fe^0.

	Day 4	Day 14	Day 28	Day 56	Day 84
Nanopure	15	28	38	29	14
1 mmol Fe^0	13	23	26	20	–
10 mmol Fe^0	14	15	13	16	8.5
100 mmol Fe^0	17	21	19	33	–
10 mmol Fe^0 + *	6.0	7.6	3.6	4.5	4.1

*= 5 mmol $CaCO_3$ + 5 mmol $CaSO_4 \cdot 2H_2O$

Appendix 4.1

Total mercury (Hg-tot) in pg/ml in the supernatent solution of incubated soil slurries treated with ferrous ammonium sulphate.

	Day 1	Day 4	Day 7	Day 28	Day 56	Day 84
Nanopure	13	39	38	31	50	61
1 mmol Fe	12	22	27	14	33	46
10 mmol Fe	2	36	41	31	57	39
100 mmol Fe	0	8	18	14	12	14
10 mmol Fe+ *	1	12	17	16	17	28

* = 10 mmol $CaCO_3$

Appendix 4.2

Methylmercury (MeHg) in ng/g (dry) associated with solids of incubated soil slurries treated with ferrous ammonium sulphate.

	Day 0	Day 1	Day 4	Day 7	Day 14	Day 21	Day 28
Nanopure	0	0	0	0	4.6	4.9	6.7
1 mmol Fe	0	0	0	0	7	14	13
10 mmol Fe	0	0	0	0.7	0	15	1.3
100 mmol Fe	0	1.9	0	0	0	0.3	0
10 mmol Fe + *	0	0	0	0	0.5	17	16

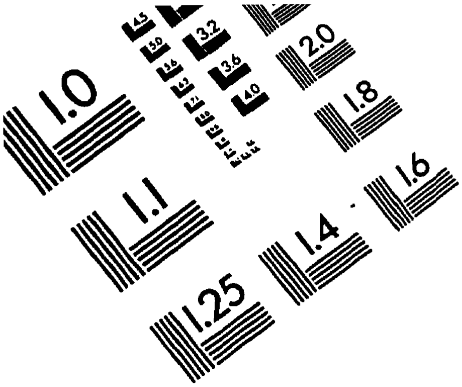
* = 10 mmol $CaCO_3$

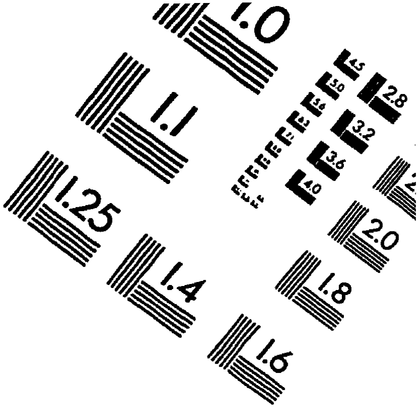
Appendix 4.2

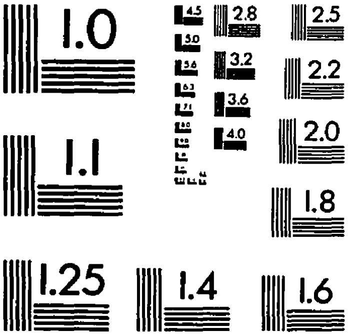
DOC in mg/l in the supernatent solution of incubated soil slurries treated with ferrous ammonium sulphate.

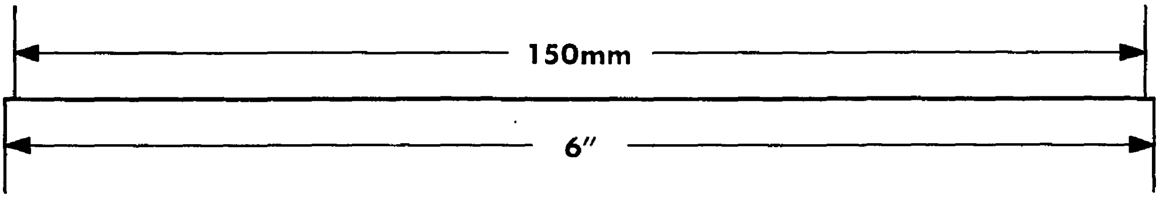
	Day 4	Day 7	Day 14	Day 21	Day 28
Nanopure	5.3	10	15	34	30
1 mmol Fe	4.1	6.3	6.6	19	38
10 mmol Fe	3.6	9.8	14	18	20
100 mmol Fe	15	29	47	105	85
10 mmol Fe+ *	9.4	16	32	38	52

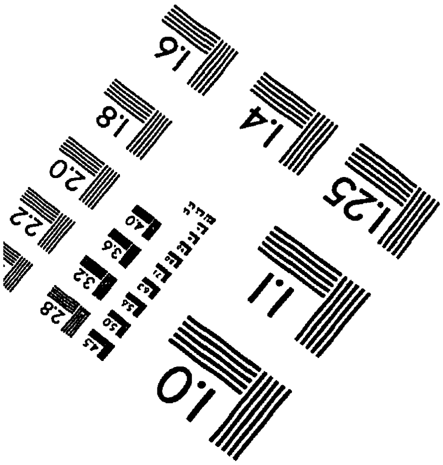
* = 10 mmol $CaCO_3$

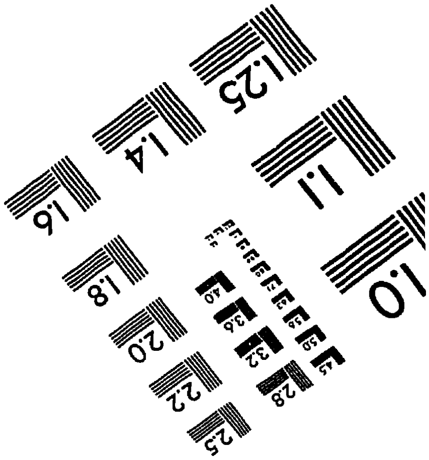












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