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# Trace metal remobilization following the resuspension of Saguenay Fjord sediments

by

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A thesis submitted to the
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in partial fulfillment of the requirements for the
Degree of Master of Science

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# ABSTRACT

Marine sediments represent the final repository of pollutants, but also play a key role in aquatic systems as potential sources and sinks of toxic substances. The fate of pollutants is related to the extent of biogeochemical transformations and their relative mobility or degradation under varying redox conditions. The Saguenay Fjord sediments are charactarized by high trace metal, organic matter and iron monosulphide (AVS) concentrations. The presence of important maritime activities, as well as dredging operations and natural slumpling events, contribute to the resuspension of the Fjord sediments and changes in their redox conditions.

The objective of this research was to determine the impact of sediment resuspension on the remobilization of trace metals (e.g. Hg, Cu, Ni, Pb, As, Fe and Mn) in the water column. Once dissolved in the water column, the trace metals are subjected to a suite of geochemical processes, while remaining available for the uptake by the biota, until they find their way out of the fjord or back into the sediments. The results of the resuspension experiments conducted in the laboratory reflect the reactivity of these anoxic sediments as well as the trace metal desorption and readsorption kinetics. By monitering the behaviour of different metals we were able to differentiate between the reactivity of those metals which are preferentially associated with the sulphides and organic matter.

Results of this study indicate that the amount of Fe and As remobilized is strongly correlated to the AVS concentration of the resuspended sediments. The release of Mn to the water phase,

however, appeared to be mainly controlled by the dissolution of a solid phase, other than the iron monosulphides, to which Mn (II) is associated. This phase could be a Mn carbonate or a mixed Mn and Ca carbonate. Following their release to solution, Fe, Mn and As were efficiently scavenged by the newly precipitated Fe and Mn oxyhydroxides. The As residence time in solution was very similar to that of Mn, implying that As (III) was oxidized to As (V) by the newly precpitated Mn oxyhydroxides prior to its readsorption onto Fe oxyhydroxides. Nevertheless, results of As speciation analysis also suggest that an important portion of dissolved As was rapidly oxidized following its release by newly precipitated Fe oxyhydroxides.

On the other hand, the observations made during this study highlighted the strong association of Hg, Cu, Pb and Ni with organic matter, as their behaviour throughout the experiments was strikingly different from that observed for Fe, Mn and As. These trace metals were probably readsorbed very rapidly onto particulate organic matter or Fe and Mn oxyhydroxides following their release to the slurry solution as a result of organic matter degradation or the dissolution of reduced sulphur minerals such as AVS.

# RÉSUMÉ

Les sédiments jouent un rôle primordial dans les systèmes aquatiques marins, pouvant servir à la fois de source et piège permanent auprès des substances polluantes. Le devenir de ces substances dépend à la fois de leurs comportements diagénétiques et des conditions chimiques et physiques à l'interface eau-sédiments. Les sédiments du Fjord du Saguenay sont caractérisés par de fortes concentrations en éléments traces, matière organique et monosulfures de fer (AVS). Une importante activité maritime, un dragage périodique de ses fonds aux alentours des installations portuaires et des glissements sous-marins sur ses pentes abruptes contribuent à la perturbation des sédiments du Fjord.

L'objectif de cette étude était de déterminer l'impact de la resuspension des sédiments sur le relargage de certains métaux traces (ex : Hg, Cu, Ni, Pb, As, Fe, Mn) dans la colonne d'eau. Ces métaux, une fois dissous dans la colonne d'eau, sont assujettis à de nombreux processus géochimiques, tout en restant disponibles à leur assimilation par la faune aquatique et ce jusqu'à ce qu'ils soient réadsorbés par la matière en suspension ou évacués du Fjord. Les résultats d'expériences de resuspensions effectuées en laboratoire reflètent à la fois la réactivité des sédiments anoxiques et la cinétique de la désorption et la réadsorption de différents métaux traces. L'analyse de différents métaux a permis de différencier la réactivité des éléments préférentiellement associés aux sulfures et à la matière organique.

Les résultats de cette étude indiquent que les quantités de Fe et As remobilisés lors des expériences de resuspensions sont fortement corrélées aux concentrations de monosulfures de fer (AVS) dans les sédiments. Le relargage du Mn en solution serait, par contre, contrôlé principalement par la dissolution d'une phase solide autre que les monosulfures de fer. Cette phase, extraite par une solution de HCl 1N, pourrait être un carbonate de Mn ou un carbonate mixte de Ca et Mn. Suite à leur relargage, le Fe, Mn ainsi que l'As furent efficacement réadsorbés par les oxyhydroxides de Fe et Mn nouvellement précipités. La similitude entre les temps de résidence en solution de l'As et du Mn suggère que l'As (III) aurait été oxydé par les oxyhydroxides de Mn nouvellement précipités avant d'être réadsorbé sur les oxyhydroxides de Fe. Cependant, des analyses de spéciation sur l'As en solution ont permis d'établir que la précipitation d'oxyhydroxides de fer aurait provoqué l'oxidation d'une fraction importante de l'As suite à son relargage.

Le comportement du Hg, Cu, Ni et Pb au cours des expériences de resuspensions se démarqua significativement de celui du Fe, Mn et As, reflétant la forte affinité de ces métaux traces envers la matière organique. Ces derniers furent probablement réadsorbés très rapidement sur la matière organique particulaire ou les oxyhydroxides de Fe et Mn, suite à leur relargage en solution occasionné par la dégradation de la matière organique ainsi que la dissolution de sulfures tels que les monosulfures de fer.

# 1.0 INTRODUCTION:

## 1.1 Problematic:

Sediments play a key role in marine aquatic systems representing the ultimate sink of anthropogenic contaminants. As a consequence of diagenetic and advective processes such as resuspension and bioturbation, sediments can also become a potential source of toxic substances. The fate of these substances depends on their diagenetic behaviour as well as the chemical and physical conditions that develop at and below the seawater-sediment interface.

The microbial degradation of organic matter during early diagenesis gives rise to various chemical transformations in the porewaters and solid phase of marine sediments. Recent studies have suggested that the geochemical behaviour of trace metals in marine environments is closely linked to the transport and degradation of organic matter (Bruland, 1980; Westerlund et al., 1986). As a result of oxic and suboxic organic matter mineralization, metabolites and metal soluble species are released directly to the porewaters and upon the reductive dissolution of inorganic solid phases, such as Fe and Mn oxyhydroxides (Klinkhammer, 1980; Klinkhammer et al., 1982; Westerlund et al., 1986; Gerringa, 1990; Shaw et al., 1990; Mucci and Edenborn, 1992; Lapp and Balzer, 1993). These species are then free to migrate along concentration gradients within the porewaters, reprecipitate in other regions of the sedimentary column, or escape to the overlying waters. Investigations carried out in coastal marine sediments have revealed surficial enrichment of a number of dissolved trace metals, whereas fluxes of trace metals across the sediment-water interface were measured in several marine environments displaying oxic surface conditions (Lu and Chen, 1977; Sawlan and Murray, 1983; Graybeal, 1984; Sundby et al., 1986;

Westerlund et al., 1986; Ridgway and Price, 1987). The sediment-water interface is, thus, considered to be the site of important interactions affecting the behaviour and release of trace metals to the overlying waters (Lu and Chen, 1977; Shaw et al., 1990; Sundby, 1994).

In coastal sediments, sulphate reduction also plays a significant role in the organic carbon oxidation and degradation (Jorgensen, 1982; Canfield, 1989). Trace metals solubilized under oxic and suboxic conditions near the sediment-water interface can migrate upward to escape to the overlying waters or adsorb onto Fe and Mn oxyhydroxides, or diffuse downwards where sulphides minerals act as a sink for many trace metals (Elderfield, 1981). Iron sulphides are the most abundant sulphides minerals in marine sediments and numerous studies have reported their strong affinity towards trace metals (Jean and Bancroft, 1986; Huerta-Diaz and Morse, 1992; Arakaki and Morse, 1993; Morse and Arakaki, 1993; Morse, 1994; Huerta-Diaz et al., 1997). Most metals do not form distinct sulphides thus, adsorption onto pyrite and metastable Fe monosulphides has proven to be an important process controlling the potential toxicity of several elements (Huerta-Diaz and Morse, 1992; Gagnon et al., 1997). However, the oxidation of these iron sulphide minerals upon exposure to oxygen, as a consequence of bioturbation or sediment resuspension, can lead to the liberation of associated trace metals to the water column (Gagnon et al., 1995; Huerta-Diaz et al., 1997).

The objective of this research is to determine the impact of sediment resuspension on the fate of a number of trace metals, Cu, Ni, Pb, As and Hg, as well as Fe and Mn in a contaminated coastal marine environment. The Saguenay Fjord sediments are characterized by a very thin oxic layer below which the rapid onset of sulphate reduction can be observed. They are also rich in organic matter, trace metals and Fe monosulphides (Gagnon et al., 1995). Resuspension of the Saguenay Fjord sediments occurs most frequently as a result of natural slumping events on the steep and narrow banks of the inner basin, bioturbation, dredging operations and dragging of ship anchors in and around the two main maritime harbors (i.e., Baie des Ha! Ha! and Grand-Anse). Because of their unique geochemical characteristics these sediments are likely to release part of their trace metals load to the overlying waters following exposure to an oxidizing environment.

## 1.2 The Saguenay Fjord :

The Saguenay Fjord, located on the north shore of the St. Lawrence estuary, is 170 km long and 1 to 6 km wide making it the largest fjord in eastern Canada. The fjord has one major tributary located at its head, the Saguenay river, and intersect the St. Lawrence estuary near Tadoussac (Figure1.1). The Saguenay Fjord possesses all the oceanographic and morphological characteristics of the classical fjords of northern Europe and the Canadian west coast. It is furthermore classified among the world's greatest fjord because of the beauty of the sites as well as its unique ecosystem. It is because of all these distinguishing characteristics that the federal government has decided to make the Saguenay Fjord the first marine park in Canada.

The Saguenay Fjord occupies an ancient tectonic depression embanked into the Greenville Precambrian rocks (Fortin and Pelletier, 1995). Its valley, carved into the crystalline rocks by the action of glaciers, is very deep and narrow and exhibits a typical U-shaped cross-section (Schafer et al., 1990; Fortin and Pelletier, 1995). The Saguenay Fjord branches into two shallow arms near its head at Bagotville and about 15 km east of Chicoutimi. Two shallow sills subdivide the fjord into two distinct basins. The first one, located at its mouth, is only 20 meters deep, whereas the second, 18 km upstream from Tadoussac is found at a depth of 80 meters. The eastern or outer basin is relatively small, but nearly 250 meters deep, whereas the western or inner basin, which extends westward over nearly 80 km to the Baie des Ha! Ha!, reaches a depth of 275 meters (Figure 1.1).

Deep water circulation and exchanges between the two basins, as well as between the St. Lawrence estuary and the outer basin are mainly controlled by the tides (Schafer et al., 1990; Fortin and Pelletier, 1995; Gratton, 1995). Flood tides are rapidly dissipated in the lower reaches of the fjord. Whereas the outer basin is affected by water intrusion from the estuary year round, only the winter influx appears to spread throughout the entire inner basin, the summer intrusion reaching only half way up. The deep waters of the Saguenay Fjord are saline (S~30), well oxygenated, and their temperatures vary between 0.5 and 2°C (Schafer et al., 1990). The surface currents are related to the annual discharge of more than $5.0 \times 10^9$ $m^3$ of freshwater from the Saguenay river, creating a thin surficial water layer (5–10 m) which carries the brackish water to the estuary. The freshwater discharge rates are strongest during the spring freshet, and the temperature and salinity variations are abrupt and well defined between the two water masses. The water column of the Saguenay Fjord is therefore characterized by a sharp and shallow thermohalocline, better delineated in the inner basin, which qualifies it as a stratified estuary. Vigorous mixing of the water column takes place year round in the outer basin, whereas limited mixing occurs in the inner basin, due in part to the surficial freshwater inputs and infrequent bottom water incursions (Schafer et al. 1990).

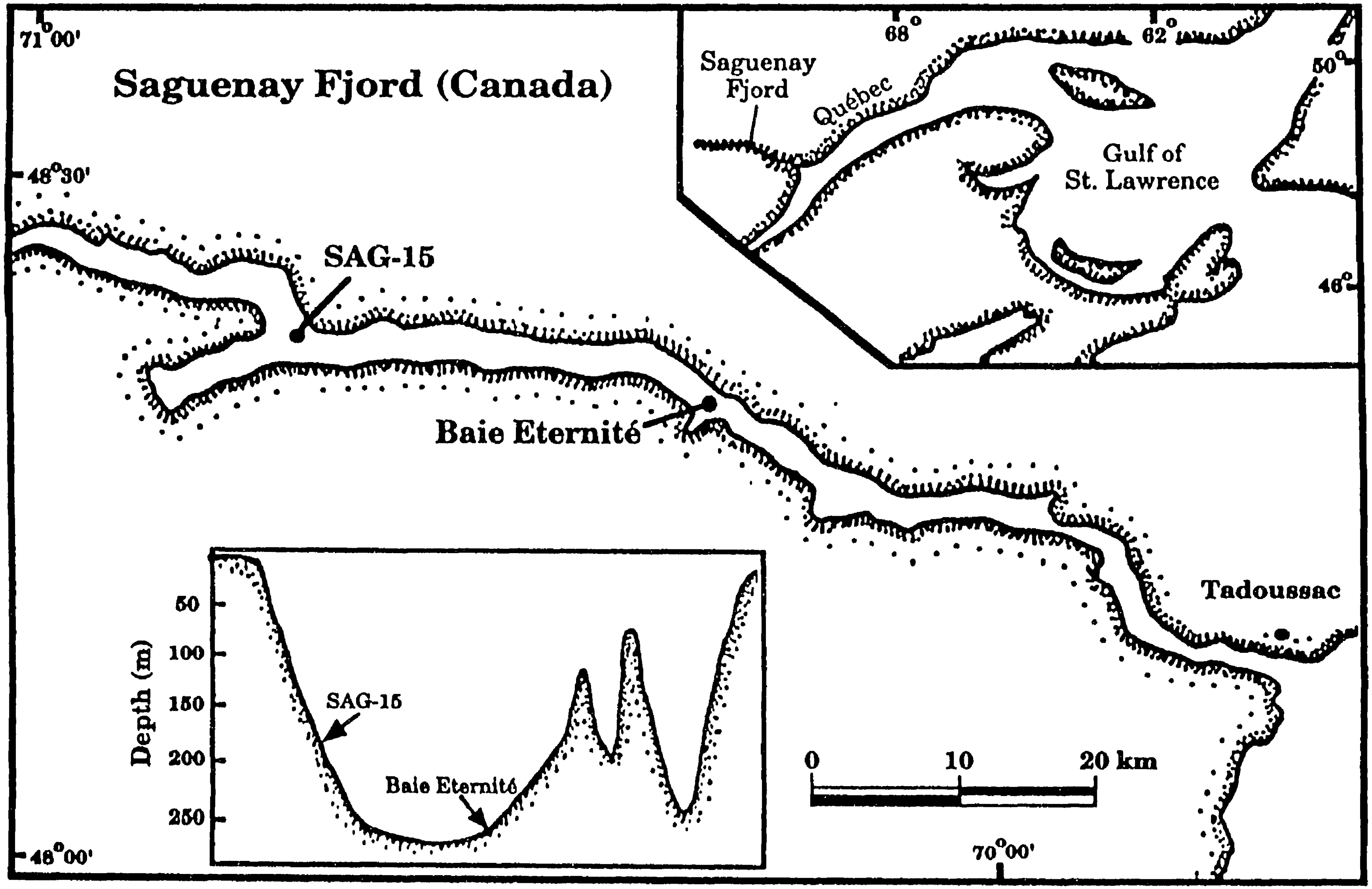

Figure 1.1. Geography and bathymetry of the Saguenay Fjord.

The watermass properties and circulation in the Saguenay Fjord are strongly reflected on the biological characteristics of its marine fauna, which is unique and extremely diversified. The Saguenay Fjord is not only the main habitat of a population of beluga whales, but over 238 species of invertebrates and 54 species of fish were inventoried in its environment (Schafer et al., 1990). If some, like the cod, mollusks, shrimps, crab and Groenland shark prefer the deep glacial, saline and well oxygenated waters, others like the eel prefer the more temperate and fresh surficial waters. The few species found in the surface waters are boreal, eurythermal and euryhaline, whereas the majority of the species observed in the deep layer are arctic, stenothermal and stenohaline. Many of these species found in the Saguenay Fjord are absent in the St.-Lawrence Estuary and in the Gulf of St.-Lawrence. The abundance of these endemic species in the deep waters of the fjord lead Drainville (1970) to suggest that the Saguenay could be a biogeographical arctic enclave in a boreal area.

Many aspects of the commercial activities of the Saguenay Fjord, like the fisheries, depend on this unique ecosystem. Over the past few years, a new and very flourishing industry was added to the economy of this region. Ecological tourism offers to visitors the possibility, for a number of privately-operated pleasure boats, to observe the beluga and rorqual whales, as well as the majestic sites of the Saguenay Fjord. The exceptional panoramic value of the Fjord is now the object of preparation plans in order to open new public beaches, nature interpretation centers, camping and yachting facilities in view of the creation of the Saguenay Park.

Unfortunately, the future park has been heavily impacted by human activities, and both inanimate and living components of its ecosystem were contaminated by toxic chemicals. This pollution has greatly affected the fisheries of the region, putting a stop to the shrimp and eel commercial fisheries, because of potential human health risks. It has also affected the natural equilibrium of this environment, causing a number of diseases and disorders among the marine fauna in some highly industrial areas, such as the Baie des Ha!Ha! (Cossa, 1990; Schafer et al., 1990) .

### 1.3 Pollution history and impact:

The industrialization of the Saguenay region during the 20th century, mainly related to the exploitation of forest and mining resources, led to the massive contamination of its ecosystem. The construction and operation of pulp and paper mills (e.g. Jonquiere and Kenogami), power dams along the main channel of the Saguenay river (e.g. Ilse Maligne, Chute-à-Caron and Shipshaw), and a chlor-alkali plant at Arvida, serving the aluminum ore smelting installations, added to the urban efflorescence and agricultural activity in the region. All contributed to the deterioration and contamination of the terrestrial and aquatic environment.

The pulp and paper industry is believed to be responsible for the development of strong sedimentary anoxic conditions in the Saguenay Fjord, with oxygen penetration depths reduced to only a few millimeters, as the result of the disposal of large volumes of organic waste (Cossa, 1990). This has lead to a reduction of both the population density and species diversity of benthic foraminifera (Cossa 1990). The scientific literature records the presence of several elements (e.g. Cd, Cu, Ni, Zn and Pb) of anthropogenic origin in the Saguenay Fjord sediments (e.g. Loring 1975 and 1976a ,b; Barbeau et al. 1981; Pelletier et al. 1989; Fortin and Pelletier, 1995) but the most widely-documented case is undoubtedly that of mercury. Fossil fuel combustion, mining operations, but mosty the former chlor-alkali factory are the three main sources of anthropogenic mercury (Cossa 1990).

The mercury contamination of the St. Lawrence Estuary and of the Saguenay Fjord caused a significant concern in the 70's, when high mercury concentrations were measured in organisms, whose habitat or diet is directly linked to the sediments (Loring, 1975; Loring and Bewers, 1978; Smith and Loring, 1981; Cossa and Desjardins, 1984). In 1972, the implementation of federal regulations and the closure in 1976 of the most important source of anthropogenic mercury to the fjord, the Arvida chlor-alkali plant, resulted in an important decrease of the contamination, allowing a partial rehabilitation of the fjord. Nevertheless, after nearly 20 years, the surface sediments still remain highly contaminated in mercury, with average concentrations well above pre-industrial level (Barbeau et al., 1981; Pelletier and Canuel, 1988 and Gagnon et al., 1997). This observation lead Pelletier and Canuel (1988) to suggest that diagenetic remobilization of Hg and active bioturbation down to a depth of 15 cm could be responsible for this phenomenon. The sediments, final repository of mercury and other trace metals, could therefore be responsible for a persistent and significant level of contamination of their benthic organisms.

## 1.4 Sediments :

The river systems that discharge into the Saguenay Fjord, at the western ends of its arms, drain a basin that covers more than 78 000 km$^2$. The drainage basin of the fjord belongs to the Greenville orogenic province. Its mineralogy consists mainly of granites, although the presence of pegmatite as well as biotite and hornblende gneiss can be observed (Fortin and Pelletier, 1995). The modern sedimentary processes observed in the Saguenay Fjord, over the past several centuries, could be classified into fluvial, hypopycnal (i.e. the transport and deposition of riverine suspended sediments into a basin containing stratified water) and mass transport ( terrestrial or submarine) categories (Schafer et al., 1990). The total suspended particulate matter concentrations measured near the head of the fjord reach values of up to 10 mg/L, and decrease exponentially to less than 0.3 mg/L in the deeper parts of the inner basin (Sundby and Loring, 1978). The relationship with the distance is due to particle settling enhanced by flocculation, agglomeration and pelletization, resulting from mixing of river water and seawater (Schafer et al., 1990; Perret et al., 1995).

The sediment accumulation rates in the Saguenay Fjord vary from 0.2-0.4 cm /yr in the inner basin to 7 cm/yr at the head of the fjord. The fjord has been divided into three lithotopes on the basis of sediment type: an upper estuarine, a transitional , and a deep fjord lithotope (Smith and Walton, 1980). The sediments found in the upper estuarine lithotope present alternating layers of mud and very sandy mud (> 30 %). The mud layer consists of both inorganic and organic material supplied in suspension to the fjord, and the organic matter content varies between 5 and 10 %. The transitional lithotope is characterized by black anoxic sandy (5-10%) muds accumulating in the upper arms of the fjord, with organic matter concentrations ranging from 0.5 to 3 % (Loring, 1975; Smith and Walton, 1980). These sediments merge seaward into dark greenish-grey muds, through the deep fjord lithotope located in the deep inner basin (Loring, 1975; Smith and Walton, 1980). East of the deep fjord lithotope, the sediments become coarser grained downstream with very sandy (>30%) muds in the western part of the outer basin, and muddy sands covering the sills between them. Sand, gravel and rocks can be found covering the floor at the mouth of the Saguenay Fjord which is adjacent to the St. Lawrence Estuary (Figure 1.2, Loring, 1976a). The occurrence of gravel and clean sand deposits in the outer basin of the

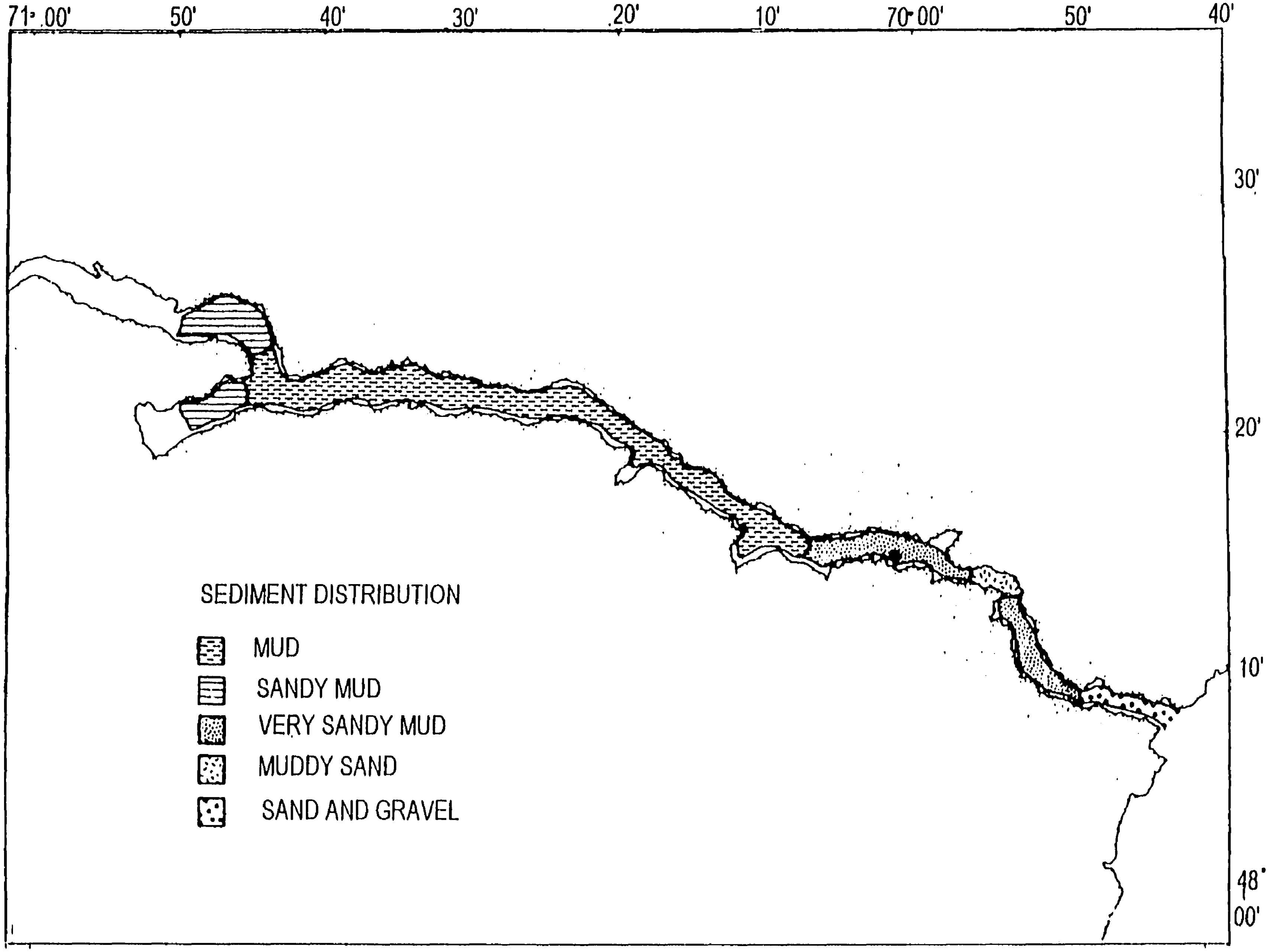

Figure 1.2 Surface sediment map of the Saguenay Fjord (from Loring, 1976).

fjord is a reflection of the high near bottom turbulence due to vigorous mixing, whereas the presence of bioturbated muddy sediments in the inner basin is suggestive of limited mixing.

The sand and silt size material found in the Saguenay Fjord sediments is mainly composed of rocks fragments, feldspar, quartz and accessory minerals, whereas the clay fraction is composed of quartz, feldspar, amphiboles and clay minerals such as illite and chlorite. This mineralogical assemblage is indicative of immature sediments, derived from the mechanical weathering of the crystalline rocks and the Quaternary deposits of the Canadian Shield (Loring, 1975 and Schafer et al., 1990). The Saguenay Fjord sediments also contain particulate organic matter (1.4 to 3.7%) of both natural and anthropogenic origin (Mucci and Edenborn, 1992; Gagnon et al., 1997; Louchouarn et al., 1997).

The Saguenay Fjord sediments are characterized by high trace metals, organic matter and metastable iron monosulphide (AVS: acid volatile sulphides) concentrations and become anoxic a few millimeters under the seawater-sediment interface (Edenborn et al., 1987). The elevated organic matter concentrations are mostly associated to pulp and paper industry solid-waste discharges. The organic matter, which exhibits a C/N ratio of about 20, reaching values as high as 40 at the head of the fjord, is predominantly of terrigenous origin and therefore more refractory to microbial degradation (Pocklington and Leonard, 1979; Gagnon et al., 1997; Louchouarn et al., 1997). Woody gymnosperm tissues constitute the main component of this sedimentary terrigenous organic matter (Louchouarn et al., 1997). Municipalities and industries located along the Saguenay Fjord are responsible for most of the trace metals contamination. Whereas Hg principally originated from the former chlor-alkali plant, other metals such as Cu and Zn are introduced by municipal effluents as well as by the pulp and paper industries (Fortin and Pelletier, 1995; Louchouarn et al, 1997). Lead, on the other hand, is believed to be mostly derived from atmospheric dustfall and precipitations (Barbeau et al., 1981; Fortin and Pelletier, 1995). The high availability of reactive Fe in the Saguenay Fjord sediments is believed to be responsible for the anomalously high AVS concentrations found in these sediments. Reactive Fe would restrict the accumulation of reduced sulphur in porewaters as well as the establishment of a strong $H_2S$ gradient, thereby limiting the formation of intermediate sulphur species and the conversion of AVS to pyrite (Mucci and Edenborn, 1992; Gagnon et al., 1995).

Due to the high reducing capacity of the sediments, the oxygen penetration depth in the fjord sediments is very shallow and similar to those observed in other coastal marine environments (1 to 5 mm) (Lefrançois, pers. comm.; Gerringa, 1990). The thickness of the zones where oxic, sub-oxic and anoxic processes occur are compressed, and the depth at which they appear are not always easily distinguishable (Mucci and Edenborn, 1992).

Oxygen concentrations in sediment porewaters are not only affected by the microbial catabolic processes and abiotic oxidation reactions but also by bioturbation processes. Benthic organisms such as polychaete worms constantly mix the sediments, to depths reaching 20 to 30 cm in the Saguenay Fjord (Schafer et al., 1990), promoting sediment resuspension and spatial heterogeneities. Sediment resuspension can also be induced by physical processes such as landslides and slumping as well as dredging operations near harbor installations. The Saguenay Fjord valley is characterized by very steep and polished walls resulting from the repeated advance of glaciers along its axis, making it a propicious site for terrestrial and submarine slide and slumping events. The sediments accumulating on its walls are mainly constituted of poorly consolated muds, enhancing furthermore the probabilities of such events (Locat and Leroueil, 1988; Schafer et al., 1990; Fortin and Pelletier, 1995). Over the past centuries a number of major landslides, involving the sensitive Champlain marine deposits, occurred in the Saguenay valley. These events, like the St.-Jean Vianney (May, 1971) and Kenogami (1924) slides, and the more recent floods in Chicoutimi, La Baie and Anse St.-Jean (July, 1996), have had a significant impact on sediment deposition and early diagenesis (Schafer et al., 1990; Mucci and Edenborn, 1992). The Saguenay Fjord is also the site of important maritime activity, mainly centered around the Baie des Ha !Ha ! and Grand-Anse harbors. Because of these physical and biological processes, as well as maritime activity, sediment resuspension is a recurring phenomenon, especially on the landward slope of the deep inner basin, where poorly consolidated sediments accumulate rapidly (Fortin and Pelletier, 1995). As suggested previously, these processes may be responsible for a persistent level of contamination of Hg in surficial sediments of the inner basin, as well as of organisms whose diet is linked to these sediments. (Pelletier et al., 1989; Schafer et al., 1990; Cossa, 1990). Toxic chemicals and heavy metals could therefore be recycled many times across the sediment-water interface, as a result of sediment resuspension, before being permanently buried (Santschi et al, 1990). A general review of early diagenesic processes as well as the diagenetic behaviour of the trace metals analyzed in this study is presented later.

### 1.5 Hypothesis :

Anoxic sediments are likely to release part of their trace metal load to solution following exposure to an oxidizing environment. This applies particularly to the AVS which will rapidly oxidize in the presence of oxygen. Once dissolved in the water column, the metals will be subjected to a suite of geochemical processes, while remaining available for ingestion and bioaccumulation by pelagic and benthic organisms, until they are carried out of the fjord or scavenged by particles and settle back to sediments. Due to their unique geochemical characteristics, the resuspension of the Saguenay Fjord sediments in oxygenated water could lead to the partial remobilization of the trace metals associated to their reactive solid phases. Sediment resuspension is frequent in the Saguenay Fjord, resulting from processes such as bioturbation, terrestrial and submarine slides, and dredging operations. Recents events such as the St-Jean-Vianney landslide of May, 1971, and the July, 1996 floods in the Saguenay region are very good examples of mass wasting events generating sediment resuspension.

## 1.6 Objectives :

The main objective of this study is to document the mobility and observe the geochemical behaviour of mercury, arsenic, copper, nickel, lead, as well as manganese and iron, following the resuspension of anoxic Saguenay Fjord sediments in oxygenated seawater. This will be achieved by monitoring the concentrations of these elements in natural seawater as a function of time in laboratory simulations. These resuspension experiments will enable us to evaluate the reactivity of some of the solid phases which are found in the Saguenay Fjord sediments, such as the organic matter, iron monosulphides (AVS), and manganese and iron oxides. Insight on the kinetics of desorption and adsorption reactions of trace metals on these phases will also be acquired. The choice of the different trace metals will allow us to differentiate between the reactivity of those metals, in anoxic sediments, which are preferentially associated with the sulphides (e.g. As, Ni), the organic matter (e.g. Hg, Cu) or both (e.g. Pb).

In order to identify the mechanisms responsible for the release of metals during the experiments, correlations to the sediments initial composition will be required. Therefore, characterization of the vertical distribution of several trace metals (Cu, Ni, Pb, Hg and As) as well as Fe and Mn, and their association with various solid phases in the sedimentary column, using common extraction methods, will be performed.

# 2.0 LITERATURE REVIEW :

## 2.1 Early diagenesis:

Diagenesis is the sum of the processes that bring about changes in a sediment subsequent to deposition in water (Berner 1980). These processes transform and degrade many components of the sedimentary deposit well before lithification occurs. Strong interactions between the biosphere, hydrosphere and lithosphere are observed in the early stage of diagenesis. Burrowing benthic organisms mix and ingest sediment particles, bacteria mineralize energy-rich organic matter, and inorganic components dissolve or precipitate in response to the changing chemical environment created by the organisms (Silverberg and Sundby, 1990).

The sediments accumulating in an oxic basin represent a mixture of both reducing (i.e. organic matter) and oxidizing (i.e. manganese and iron oxides, oxygen, nitrate and sulphate) compounds (Silverberg and Sundby, 1990). Early diagenetic processes are fueled by the microbial degradation of organic matter. The microorganisms oxidize the organic matter using a series of electron acceptors, creating a layered zonation of decreasing redox potential in the sediments. These electron acceptors are consumed, through reduction reactions, in a sequence determined by the free energy yield of the reaction (Froelich et al., 1979). The idealized sequence of reactions, starting at the surface of the sediments, corresponds to the reduction of oxygen, nitrate, manganese and iron oxides, sulphate and carbon dioxide (observed near the head of the Saguenay Fjord at Sag-5) (Froelich et al., 1979; Santschi et al., 1990). The redox zonation created by the microbial activity and the release of metabolites give rise to concentration gradients in the sediment porewaters that promote diffusion and the accumulation of diagnostic solid phases in distinct layers of the sediment column (Sundby, 1994). Particle mixing occurs between these layers through physical and biological processes such as bottom currents and bioturbation.

The oxygen penetration depth in the sediments is determined by the oxygen concentration of the overlying waters, the sediment porosity and accumulation rate, the amount and composition of the sedimentary particulate organic matter, as well as processes such as sediment resuspension and bioturbation. The oxygen penetration depth in the Saguenay Fjord sediments is very shallow, reaching only few millimeters, inspite of the presence of well oxygenated bottom waters, as a result of elevated organic matter concentrations in the sediments (Mucci and Edenborn, 1992; Lefrancois, pers. comm.).

Manganese and iron oxyhydroxides enrichment, at or near the oxic sediment-water interface, can be observed in the Saguenay Fjord (Mucci and Edenborn,1992; Gobeil and Cossa,1993; Gagnon et al., 1995). Upward diffusion of Fe(II) and Mn(II) released in the anoxic sediments below, followed by their reoxidation and precipitation as authigenic oxyhydroxides, at or near the redox boundary, is responsible for this phenomenon. According to free energy calculations, both manganese and iron oxyhydroxides should be reduced before the onset of sulphate reduction (Froelich et al., 1979). In the Saguenay Fjord sediments, however, the sequential use of electron acceptors is not clearly distinguishable because these reactions are compressed near the sediment-water interface (Mucci and Edenborn, 1992) and the reactivity of ferric phases is highly variable (Canfield et al., 1993; Gagnon et al., 1995). The onset of sulphate reduction occurs a few centimeters below the interface, leading to the formation of $H_2S$ and the precipitation of AVS in the presence of reduced iron (Mucci and Edenborn, 1992; Gagnon et al., 1995).

The diagenetic behaviour of many trace metals is intimately related to the organic matter degradation (Loring, 1976a and b; Klinkhammer, 1980; Sawlan and Murray, 1983; Mucci and Edenborn, 1992), their marine geochemistry being closely linked to the cycle of production, transport, and destruction of organic matter (Westerlund et al., 1986). Trace metal concentrations in sediment porewaters are controlled by several processes such as oxidation, reduction, dissolution and precipitation reactions, as well as adsorption and desorption onto sedimentary particle surfaces (Santschi et al., 1990; Sundby, 1994). These reactions depend directly or indirectly on the redox and pH conditions prevailing in the sediment porewaters (Sundby, 1986, 1994). Consequently, the geochemical behaviour of trace metals in the sediments, their bioavailability, and speciation are determined primarily by these two variables (Lapp and Balzer, 1993; Sundby, 1994).

Detrital and authigenic Fe and Mn oxyhydroxides which accumulate in oxic surface sediments were reported in several studies to play an important role in determining the distribution of trace metals in the sedimentary column through adsorption processes (Inoue and Munemori, 1979; Klinkhammer, 1980; Luoma and Davis, 1983; Tessier et al., 1985; Peterson and Carpenter, 1986; Belzile, 1988; Gobeil, 1989; DeVitre et al., 1991; Matty and Long, 1995). In a study on trace metal adsorption in oxidized estuarine sediments, Luoma and Davis (1983) stated that amorphous Fe oxyhydroxides as well as extractable organic matter (extracted with a 0.5 N NaOH solution) possessed the largest binding capacities for trace metals. The authors also indicated that the contribution of Mn oxides to metal binding was generally less than that of Fe oxyhydroxides because of their lower abundance in oxic sediments. Iron oxyhydroxide surfaces are believed to comprise various binding sites which can adsorb different metals with minimal competitive interactions (Tessier et al., 1985). Adsorption and coprecipitation of many trace metals with iron monosulphides (Morse and Arakaki, 1993) and pyrite (Belzile and Lebel, 1986; Edenborn et al., 1986a; Huerta-Diaz and Morse, 1992) in anoxic sediments, are also important mechanisms controlling trace metal concentrations in interstitial waters. Adsorption and desorption processes of trace metals on solid phases, such as organic matter, Fe-Mn oxyhydroxides and iron sulphides, often determine the fate of trace metals in aquatic systems, and the role of sediments as the ultimate sink of contaminants discharged to the surface waters

(Benes and Havlik, 1979; Jean and Bancroft, 1986; Gobeil and Cossa, 1993; Gagnon et al., 1997).

## 2.2 Diagenetic behaviour of trace metals investigated in this study:

In the following section our current understanding of the early diagenetic behaviour of the trace metals investigated in this study will be presented in order to better elucidate the processes which are responsible for their release and uptake from the sediments, as well as the environmental factors which control these reactions. As the cycling of many trace metals is intimately related to that of Fe and Mn, the latter metals will be discussed first in this synthesis.

### 2.2.1 Iron :

The Fe accumulating in the Saguenay Fjord sediments originates mostly from the weathering of crystalline rocks belonging to the Greenville orogenic province and which constitute the essence of the Fjord drainage basin (Schafer et al., 1990; Silverberg and Sundby, 1990; Fortin and Pelletier, 1995). Iron oxyhydroxides are used in the sequence of organic matter degradation reactions as an electron acceptor, after $O_2$, $NO_3^-$ and Mn oxides, according to this reaction (Froelich et al., 1979):

$$\mathbf{(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 212\ Fe_2O_3\ (or\ 424\ FeOOH) + 848\ H^+}$$

$$\mathbf{\rightarrow 424\ Fe^{2+} + 106\ CO_2 + 16\ NH_3 + H_3P0_4 + 530\ H_2O\ (or\ 742\ H_2O)}$$

On the basis of thermodynamic considerations, Fe is present in oxygenated seawater under the oxidation state of $Fe^{3+}$, and can mainly be found in the particulate form as goethite (FeOOH), hematite ($Fe_2O_3$) or crystallographically amorphous ferrihydrite (Santschi et al., 1990; Stumm and Morgan, 1981). Colloidal hydrous Fe oxides settling through the water column are excellent scavengers for many trace metals, playing an important role in the regulation of their concentrations in natural waters (Loring, 1976a; Tessier et al., 1985; Peterson and Carpenter, 1986; Belzile, 1988; De Vitre et al., 1991).

Detrital and authigenic iron oxyhydroxides are stable and accumulate at the oxic sediment-water interface. Once they are buried below the $O_2$ penetration depth and following $NO_3^-$ and Mn oxyhydroxide reduction, Fe oxyhydroxides become unstable and dissolve, thereby releasing soluble Fe(II) to the porewaters (Klinkhammer, 1980; Santschi et al., 1990; Shaw et al., 1990; Mucci and Edenborn, 1992; Canfield et al., 1993). The dissolved Fe(II) released to the suboxic interstitial waters can migrate upwards to be oxidized and reprecipitate at the redox boundary as oxyhydroxides, or diffuse downwards in the anoxic zone and precipitate mainly as Fe sulphides (Klinkhammer, 1980; Shaw et al., 1990; Mucci and Edenborn, 1992; Canfield et al., 1993; Morse, 1994; Huerta-Diaz et al., 1997).

The redox-controlled cycle of Fe has a tremendous effect on the distribution and fate of many trace metals, such as As and Pb ( Luoma and Davis, 1983; Edenborn et al., 1986a; Belzile, 1988; Gobeil and Silverberg, 1989; Shaw et al., 1990). Trace metals adsorbed onto Fe oxyhydroxides are released to porewaters following the reductive dissolution of carrier phases. They are subsequently scavenged by the authigenic Fe oxyhydroxides precipitated near the redox boundary, and by sulphides minerals in the anoxic zone, following their migration in sediment porewaters (Klinkhammer, 1980; Edenborn et al., 1986a; Belzile ,1988; Gobeil and Cossa, 1993; Matty and Long, 1995; Richard, 1996; Gagnon et al., 1997).

In anoxic seawater, Fe occurs in the oxidation state of Fe(II), and can be found in the form of aqueous Fe(II), $FeOH^+$ and $FeCl^+$ (Pyzik and Sommer, 1981). Ferrous sulphide formation is considered to be the dominant factor controlling the solubility of Fe(II). The precipitation of a carbonate phase, siderite ($FeCO_3$), however, has also been observed (Stumm and Morgan, 1981;

Emerson et al.,1983; Kremling, 1983). The formation of authigenic iron sulphides is dependent upon the amount and quality of organic matter and the availability of reactive iron and sulphate in the sediments (Berner, 1970, 1984; Gagnon et al., 1995). Pyrite ($FeS_2$) and metastable acid volatile iron monosulphides (AVS : FeS) thus represent the two major end-products of reduced sulphur in marine sediments, iron being usually the most abundant sulphide-forming metal in marine sediments (Kremling, 1983; Arakaki and Morse, 1993; Gagnon et al., 1995).

Schoonen and Barnes (1991) examined the mechanisms of formation of pyrite at temperatures below 100°C and concluded that the nucleation and sulphidation of a precursor iron monosulphide phase was the dominant process. Thus, although pyrite is thermodynamically more stable than iron monosulphides, the latter phase, due to kinetic factors, may control the concentrations of sulphidic sulphur and ferrous iron in anoxic porewaters (Schoonen and Barnes, 1991). The conversion of iron monosulphides (AVS) to pyrite requires the presence of intermediate reduced sulphur species (elemental sulphur or polysulphides). The rate of the formation of these species is controlled by the availability and supply of oxidants, such as $O_2$, $NO_3$, $MnO_2$ and FeOOH to the anoxic sediments by diffusion or bioturbation (Middelburg, 1991; Gagnon et al., 1995).

Numerous studies conducted on the adsorption affinity of pyrite (Belzile and Lebel, 1986; Jean and Bancroft, 1986; Hyland et al., 1990; Huerta-Diaz and Morse, 1992; Morse, 1994) and iron monosulphides (Arakaki and Morse, 1993; Morse and Arakaki, 1993; Morse, 1994) towards divalent metals, revealed that iron sulphides are important sinks for many trace metals such as As, Hg, Pb, Cu and Ni, as well as many others. However, physical disturbance of the sedimentary environment (e.g. dredging, bioturbation, slumping, etc.) could lead to the oxidation of these iron sulphides, especially the metastable AVS, releasing to the porewaters and possibly to the overlying waters significant amounts of associated trace metals (Huerta-Diaz and Morse, 1992; Morse and Arakaki, 1993; Gagnon et al., 1995).

The Saguenay Fjord sediments exhibit high concentrations of particulate reactive Fe (e.g. 1N HCl, hydroxylamine/ acetic acid, and citrate-dithionite-bicarbonate extractable Fe) in the oxic surface sediment as a result of authigenic Fe oxyhydroxide precipitation following the upward diffusion of Fe(II), released to the porewaters in the suboxic and anoxic zone (Belzile et al., 1988; Gobeil and Silverberg, 1989; Mucci and Edenborn, 1992; Gagnon et al., 1995; Richard, 1996). The dissolved Fe concentrations in the fjord sediments display a minimum at the sediment-water interface, increasing steadily to reach maximum concentrations in the suboxic zone, below the Fe oxyhydroxide precipitation zone, whereas the concentrations decrease deeper in the sediments (Edenborn et al., 1986a; Belzile, 1988; Gobeil and Silverberg, 1989; Mucci and Edenborn, 1992; Gagnon et al., 1995; Richard, 1996).

The 1N HCl and hydroxylamine–extractable Fe profiles in the Saguenay Fjord, representing the sum of Fe associated with Fe oxyhydroxides as well as acid volatile sulphides (AVS), display relatively high concentrations in the anoxic zone. Iron monosulphides measurements in the Saguenay Fjord sediments show negligible concentrations in surficial sediments increasing slowly with depth (Gagnon et al., 1995; Bono ,1997). Precipitation of Fe monosulphides, thus, occurs in the anoxic region as a consequence of the downward migration of reduced Fe, released to the suboxic interstitial waters following the dissolution of Fe oxyhydroxides as well as direct reduction of ferric phases by $H_2S$ (Belzile, 1988; Mucci and Edenborn, 1992; Gagnon et al., 1995).

Gagnon et al. (1995) found abnormally high ratios of acid-volatile sulphides (AVS: amorphous FeS, $FeS_x$ $(0.9< X< 1.5)$) to pyrite in the Saguenay Fjord sediments. The AVS-S: FeS-S ratio observed by the authors throughout the anoxic sediments generally exceeded 1, reaching values as high as 7 near the head of the fjord. They proposed that the high availability of reactive iron suppressed the built-up of reduced sulphur in the porewaters, as well as the establishment of a strong $H_2S$ gradient, limiting the formation of intermediate reduced sulphur species and the conversion of AVS to pyrite in these anoxic sediments.

To summarize, reactive iron is present in the Saguenay Fjord surficial sediments as detrital and authigenic oxyhydroxides. Upon sediment burial and as a consequence of organic matter degradation, these Fe oxyhydroxides are reduced, releasing Fe(II) to the interstitial suboxic waters. Once in solution, Fe(II) can diffuse upwards and reprecipitate as oxyhydroxides upon oxidation at or near the redox boundary, or diffuse downwards in the anoxic zone to precipitate as iron monosulphides and pyrite. However, the exposure of these iron sulphides to oxygen, as a consequence of bioturbation or sediment resuspension, can cause their oxidation and the release of Fe(II) as well as adsorbed trace metals, to the porewaters, reinitiating the cycle. Iron can therefore be extensively recycled in the sediment column, greatly affecting the distribution and fate of many trace metals.

### 2.2.2 Manganese :

Manganese accumulating in the Fjord sediments also originates from the weathering of crystalline rocks of the Greenville orogenic province (Schafer et al., 1990; Silverberg and Sundby, 1990; Fortin and Pelletier, 1995). Manganese oxyhydroxides are used as electron acceptors, after $O_2$ and nitrate ($NO_3^-$), in the sequential oxidation of sedimentary organic matter (Froelich et al., 1979). Mn reduction occurs, in suboxic environments, according to the following reaction (Froelich et al., 1979):

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 236\ MnO_2 + 472\ H^+$$
$$\rightarrow 236\ Mn^{+2} + 106\ CO_2 + 8\ N_2 + H_3PO_4 + 366\ H_2O$$

In general, this reaction is mediated by the catabolic activity of microorganisms (Santschi et al., 1990).

According to thermodynamic data, Mn is present as Mn(III) and Mn(IV) in oxygenated seawater in the form of particulate Mn oxides. These phases exhibit strong scavenging capacities for many trace metals because of their large specific surface areas (Santschi et al., 1990).

Mn is released to the porewaters in the form of Mn(II), below the redox interface as the detrital and authigenic Mn oxyhydroxides are reduced and dissolved following their burial (Froelich et al., 1979; Klinkhammer, 1980; Sundby et al., 1981; Santschi et al., 1990; Shaw et al., 1990). Many studies have reported linear dissolved Mn(II) gradients in sediment porewaters, implying the existence of a diffusion zone between the onset of $MnO_2$ reduction and Mn(II) oxidation (Klinkhammer, 1980; Sawlan and Murray, 1983; Santschi et al., 1990). Thereby, Mn(II) would migrate upwards, following its solubilization in the Mn reduction zone, to be reoxidized and reprecipitated as Mn oxyhydroxides in the oxic zone (Froelich et al., 1979; Sundby et al., 1981; Shaw et al., 1990). Reduced Mn being metastable in the presence of oxygen, its oxidation and precipitation horizon in oxic sediments is often located above the Fe oxyhydroxide precipitation zone. Furthermore, manganese oxidation probably occurs on particle surfaces, as Mn(II) adsorbs preferentially onto pre-existing Mn oxyhydroxide phases within sediments (Santschi et al., 1990; Canfield et al., 1993). In the absence of such solid surfaces, dissolved Mn(II) can remain in solution over a decade (Sundby et al., 1986; Canfield et al., 1993). Alternatively, the position of the authigenic Mn oxyhydroxides has been explained by temporal oscillation of $O_2$ penetration depth (Gobeil et al., 1997).

A fraction of the dissolved Mn(II) can also diffuse downwards in the anoxic zone, where it can precipitate as solid sulphide or carbonate phases, thereby limiting its remobilization (Jacob and Emerson, 1982; Emerson et al., 1983; Kremling, 1983; Santschi et al., 1990). Rhodochrosite ($MnCO_3$), a manganese carbonate phase, has been reported to contribute to the solubility control of Mn in sulphidic waters (Kremling, 1983). Mixed Ca-Mn carbonate phases have also been shown to limit Mn(II) solubility in marine porewaters (Pederson and Price, 1982; Middelburg et al., 1987; Jakobson and Postma, 1989). Mn sulphides being more soluble than iron sulphides, dissolved Mn(II) is most likely adsorbed onto (or to some extent coprecipitated with) iron sulphides, the dominant sulphide phases in most marine sediments (Arakaki and Morse, 1993; Huerta-Diaz et al., 1997). Huerta-Diaz and Morse (1992), in their study on the pyritization of trace metals in anoxic marine sediments, proposed that sedimentary pyrite may represent a significant sink for Mn, whereas Arakaki and Morse (1993) suggested that adsorption of Mn(II) onto iron monosulphides could be much more important than coprecipitation processes. However, upon exposure to oxygen, as a consequence of bioturbation and resuspension of the anoxic sediments, the iron sulphides will dissolve and release their trace metal load, including Mn, to the porewaters or the overlying waters.

The Saguenay Fjord sediments display a minimum dissolved Mn concentration at the sediment-water interface, followed by a maximum value in the suboxic zone, at an approximate depth of 1.5 cm, whereas the concentrations decrease and stabilize deeper in the sediments (Sundby et al., 1981; Edenborn et al., 1986a; Belzile, 1988; Mucci and Edenborn, 1992; Richard, 1996). Accordingly, hydroxylamine and 1N HCl extractable Mn phases, as well as total Mn, show maximum concentrations at the sediment surface, sharply decreasing in the suboxic zone to maintain lower values deeper in the sediments (Mucci and Edenborn, 1992; Richard, 1996). The Saguenay Fjord sediments are therefore enriched in Mn oxyhydroxides at the surface as a result of the upward diffusion of reduced Mn, released to the porewaters in the suboxic zone, and their precipitation at or near the redox boundary.

In a recent study on the Saguenay Fjord sediments, Mucci and Edenborn (1992) observed that the anoxic porewaters were undersaturated with respect to solid manganese sulphide phases (MnS and $MnS_2$). The authors also determined that the saturation state of the interstitial waters with respect to rhodochrosite increased linearly with depth, while there was no evidence of $MnCO_3$ precipitation. The increased solubility of Mn (II) in these porewaters could be explained by its complexation by dissolved organic matter and reduced sulphur species (Jacobs and Emerson, 1982; Kremling, 1983; Mucci and Edenborn, 1992), or by a lack of $MnCO_3$ precipitation due to the presence of growth inhibitors and lack of appropriate substrate. The Saguenay Fjord sediments contain anomalously high iron monosulphide concentrations, the adsorption of Mn on this phase is likely to exert a strong influence on the porewater Mn(II) concentrations.

Many studies on metal fluxes across the sediment-water interface reported the uptake of Mn by oxic sediments and its release to the overlying waters upon the onset of anoxic conditions at the sediment-water interface (Lu and Chen, 1977; Westerlund et al., 1986; Shaw et al., 1990; Sundby, 1994). Oxidized sediments would therefore provide an efficient sink for Mn, through the formation of a Mn oxyhydroxide layer near the redox interface, whereas anoxic surficial sediments would act as a potential source of Mn to the overlying waters.

In summary, Mn is extensively remobilized within organic-rich marine sediments overlain by oxygenated bottom waters, like in the Saguenay Fjord. Both the dissolved and solid Mn profiles in the Fjord sediments reflect a reduction of the solid oxides accumulated in the oxic zone, upon burial, and release of Mn(II) to the suboxic interstitial waters. Following its release, Mn(II) mostly diffuses upwards to reprecipitate as authigenic Mn oxyhydroxides. The Mn oxyhydroxides are strong adsorbents for many trace metals (i.e. Ni, Cu), their cycling in subsurface sediments can greatly affect the diagenetic behaviour and geochemical cycle of these metals.

### 2.2.3 Mercury :

The major source of anthropogenic Hg in fresh and marine waters in Canada, prior to the implementation of government regulation in the 1970's, was the effluents of chlor-alkali factories (Gobeil and Cossa, 1993). The chlor-alkali plant located along the Saguenay river at Arvida was mainly responsible for the severe Hg contamination which led to the closure of commercial fisheries in the Saguenay Fjord (Loring, 1975; Loring and Bewers, 1978; Cossa and Desjardins, 1984; Cossa, 1990; Gobeil and Cossa, 1993; Gagnon et al., 1997). Other sources such as fossil fuel combustion as well as mining operations, also contributed to the contamination of natural aquatic environments following transport through the atmosphere and deposition by wet and dry precipitation (Cossa, 1990).

Mercury is preferentially associated with particulate matter in aquatic systems (Matty and Long, 1995). Terrigenous organic matter represents the main scavenging agent and carrier of Hg to the sediment (Loring and Bewers, 1978). In a recent study on the geochemical behaviour of anthropogenic Hg in the Saguenay Fjord sediments, it was observed that dissolved Hg accounts for less than 0.01% of the integrated bulk sediment Hg content, whereas solid inorganic Hg (II) represents nearly all (99.5%) of the Hg found in the sediments (Gagnon et al., 1997). Dissolved Hg can be found in oxygenated seawater in inorganic species such as elemental mercury and anionic chlorocomplexes, among which the main soluble form should be $HgCl_4^{2-}$ (Benes and Havlik, 1979; Stumm and Morgan, 1981). In sulphidic marine waters, Hg can form soluble complexes with sulphides and polysulphides species ($HgS_2^{2-}$, $HgHS_2^{-}$, $Hg(HS)_2$ etc.) which may be dominant under these conditions (Lindberg and Harris, 1974; Benes and Havlik, 1979; Stumm and Morgan, 1981; Gagnon et al., 1997).

Dissolved organic matter is known to contribute to the solubilization of Hg under both oxic (Benes and Havlik, 1979) and anoxic (Lindberg and Harris, 1974; Emerson et al., 1983; Gagnon et al., 1997) conditions. High porewater Hg concentrations, sometimes largely exceeding HgS thermodynamic solubility, have been measured in marine sulphidic sediments (Lindberg and Harris, 1974; Gobeil and Cossa, 1993; Gagnon et al., 1997). The formation of both polysulphides and organic complexes could explain the observed anoxic porewater enrichment of Hg, relative to the overlying oxic waters, as well as the apparent supersaturation with respect to HgS in organic-rich marine sediments (Lindberg and Harris, 1974; Gagnon et al., 1997).

The methylation of Hg can also increase its solubility in sediment porewaters (Gagnon et al., 1996b and 1997). Methylmercury ($CH_3Hg(II)$), an organomercurial, is undoubtedly the most toxic form of Hg in natural waters, and is readily bioaccumulated by aquatic organisms (Benes and Havlik, 1977; Gagnon et al.,1997). The formation of $CH_3Hg(II)$, which could involve sulphate-reducing bacteria, would be favored in anoxic sediments exhibiting sulphide-poor porewaters, enriched with biodegradable organic carbon and nutrients (Parks et al., 1989; Gagnon et al., 1996). The surficial oxidized sediment layer appears to serve as a geochemical barrier to the diffusion of dissolved $CH_3Hg(II)$ towards the overlying waters through bacterial or catalytical demethylation or extraction by burrowing organisms (Gagnon et al, 1996b, 1997).

As Hg is highly particle reactive in aquatic environments, it is rapidly scavenged from the water column (Benes and Havlik, 1979; Matty and Long, 1995). The association of Hg with particulate organic matter is well documented. A strong correlation between the distribution of particulate organic matter and Hg has been reported in numerous types of sediments (Ferguson and Gavis, 1972; Lindberg and Harris, 1974; Matty and Long, 1995) as well as in the Saguenay Fjord sediments (Loring, 1975; Loring and Bewers, 1978; Pelletier and Canuel, 1988; Mucci and Edenborn, 1992; Gobeil and Cossa, 1993 ; Gagnon et al., 1997; Bono, 1997). More recently, Louchouarn and Lucotte (1997) have demonstrated that despite its strong affinity for organic matter, there is no correlation between the distribution of lignin and Hg in the Saguenay Fjord sediments. The lignin is a residue of the pulp and paper industries operating in the region.

Gobeil and Cossa (1993) demonstrated that Hg is also strongly associated with the Fe and Mn hydroxylamine/acetic acid extractable phase (i.e. Mn and Fe oxyhydroxides), whereas Gagnon et al. (1997) observed the simultaneous extraction of high levels of Fe, Mn and Hg from the Saguenay Fjord sediments by a 1N HCl solution. Similar results were also reported by Matty and Long (1995) in their recent study on Hg early diagenesis in the Laurentian Great Lakes. Detrital and authigenic Fe-Mn oxyhydroxides concentrated in the oxidized layer of the sediments would, therefore, appear to be important scavengers of Hg. Upon burial of these phases and their reductive dissolution, Hg would be released back to the porewaters (Loring, 1975; Loring and Bewers, 1978; Froelich et al., 1979; Gobeil and Cossa, 1993; Matty and Long, 1995; Gagnon et al., 1997). The presence of an oxidized sediment surface layer thus plays an important role in inhibiting the diffusion of Hg to overlying waters, as the Fe and Mn oxyhydroxides present in this layer act as a sink for Hg (Gobeil and Cossa, 1993; Gagnon et al., 1997).

Sulphides minerals such as pyrite and iron monosulphides are also excellent scavengers for Hg in anoxic sediments (Jean and Bancroft, 1986; Hyland et al., 1990; Huerta-Diaz and Morse, 1992; Bono, 1997). The Saguenay Fjord sediments are relatively poor in pyrite but are anomalously rich in Fe monosulphides or acid volatile sulphides (FeS; AVS). These solids are metastable precursors to pyrite and very reactive in the presence of oxygen (Mucci and Edenborn, 1992;

Gagnon et al., 1995). They may serve as a temporary sink to Hg in the anoxic sediments (Hyland et al., 1990), releasing it back to the porewaters following their exposure to oxygen as a consequence of bioturbation and resuspension processes. Therefore, although Hg is not readily remobilized from the sediments because of its strong affinity to organic matter, a fraction adsorbed to or coprecipitated with the Fe and Mn oxyhydroxides and Fe sulphides may be released to porewaters following changes in redox conditions.

In résumé, Hg is mainly associated with particulate organic matter in the sediment. Inorganic Hg is released to the oxic and suboxic sediment porewaters by processes such as the degradation of Hg-laden labile organic matter and the dissolution of authigenic Mn and Fe oxyhydroxides. Once in solution, Hg can be readsorbed onto refractory organic matter. Moreover, it can also migrate up and adsorb onto Mn and Fe oxyhydroxides or fresh organic matter, as well as diffuse down to be scavenged by Fe sulphides, or precipitate as HgS. Formation of complexes with intermediate reduced sulphur species and dissolved organic matter, as well as Hg methylation can however enhance Hg solubility in anoxic sediments. The absence of dissolved or particulate $CH_3Hg(II)$ in the oxic surface sediments of the Saguenay Fjord may be interpreted as a catalytic demethylation of the mercury by the oxidized solid phases. The surficial oxic sediment layer appears to be an effective barrier to the diffusion of dissolved $CH_3Hg(II)$ and inorganic Hg(II) to the overlying waters.

The Hg adsorbed or coprecipitated with the Fe monosulphides and pyrite can be released back the overlying waters following their oxidation and dissolution, upon exposure to oxygen, as a result of bioturbation and sediment resuspension. The oxidative release of Hg associated with Fe sulphides may represent an important Hg source, enhancing its potential bioavailability.

### 2.2.4 Arsenic :

Arsenic is introduced in the marine environment mainly as a consequence of continental weathering and hydrothermal activity (Ferguson and Davis, 1972; Azcue, 1995). Substantial input of As from industrial (e.g mining, smelting) and agricultural (e.g. herbicides, pesticides) activities, as well as from fossil fuel combustion also appear to contribute significantly to the accumulation of As in natural environments (Ferguson and Davis, 1972; Edenborn et al., 1986a; Belzile, 1988; Azcue, 1995). The Saguenay Fjord sediments are enriched in As compared to the St-Lawrence Gulf sediments and other similar marine environments (Tremblay and Gobeil, 1990; Gobeil, 1996). Although As has been extensively used industrially (Ferguson and Gavis, 1972), no local source of As contamination has been found in the Saguenay Fjord area. The river water As concentrations are much lower than most industrialized or pristine rivers (Richard, 1996).

Arsenic is a very toxic element, although, unlike Hg, it is not strongly bioaccumulated through the food chain. Nevertheless, because of their similar chemical properties, arsenate is often mistaken for phosphate by marine organisms and taken up during metabolic processes (Planas and Healy, 1978; Andreae, 1979; Kuhn and Sigg, 1993; Aurillo et al., 1994; Richard, 1996). As a result, the distribution and speciation of As in aquatic environments is strongly affected by phytoplankton ingestion and excretion in its methylated form (Sanders, 1985; Belzile, 1988; Anderson and Bruland, 1991; Azcue, 1995). The potential human health hazard of arsenic would be mainly through the ingestion of drinking waters with high As concentrations rather than consuming As concentrated by organisms (Ferguson and Gavis, 1972). In natural aquatic systems, As is present under two stable oxidation states; As(V) (arsenate) and As(III) (arsenite). In oxygenated waters, As is found primarily in the form of arsenate, although lesser concentrations of As(III) as well as methylated arsenicals can also be found (Andreae, 1979; Sanders and Windom, 1980). The first study conducted on As speciation in marine porewaters indicated that arsenate was also the predominant species under anoxic conditions (Andreae, 1979). On the other hand, Peterson and Carpenter (1986) suggested that arsenite would be the dominant species of As in anoxic porewaters. Dissolved As therefore exist, in oxygenated seawater, mostly in the form of $HAsO_4^{2-}$( Stumm and Morgan, 1981), whereas in sulphidic porewaters, it may be found mainly as $H_3AsO_3$ and $AsS^{2-}$ (Ferguson and Gavis, 1972).

In oxic surface sediments, dissolved arsenate is removed from solution upon adsorption onto authigenic and detrital Fe oxyhydroxides, owing to their high adsorptive capacity and their positively charged surface (Ferguson and Gavis, 1972; Edenborn et al., 1986a; Peterson and Carpenter, 1986; Gobeil, 1996). Gobeil (1996) recently proposed that colloidal Fe oxyhydroxides, present in large quantities in the Saguenay River, could serve as a vector of authigenic As to the Saguenay Fjord sediments. The author suggested that colloidal iron oxyhydroxides present in the Saguenay River coagulate upon mixing with seawater in the Fjord. This mechanism would be responsible for the As enrichment observed in these sediments. Numerous studies conducted on the diagenetic cycling of Fe and As in both marine and lacustrine sediments reported that authigenic Fe oxyhydroxides play a very important role in determining the distribution of As in the sediment through adsorption and oxidation processes (Edenborn et al., 1986a; Peterson and Carpenter, 1986; Belzile, 1988; Belzile and Tessier, 1990; De Vitre et al., 1991; Richard, 1996). De Vitre et al. (1991) suggested that most of the As associated with Fe oxyhydroxides is in the form of arsenate.

Most investigations of As behaviour in sediments report very low concentrations of dissolved As at or near the oxic sediment-water interface, followed by a subsurface maximum near or at the base of the oxic zone, and rather constant values below (Peterson and Carpenter, 1986; Belzile, 1988). These observations as well as the surface enrichment of solid As observed in the Laurentian Trough sediments lead Belzile (1988) to infer that a mobile fraction of As is associated with Fe oxyhydroxides and therefore follows their redox cycle of dissolution in the suboxic zone, upward diffusion and reprecipitation near the sediment-water interface. The simultaneous release of As(III) and Fe(II) in the suboxic zone, as well as the As removal from porewaters following its adsorption onto Fe oxyhydroxides in the oxic zone and sulphides under anoxic conditions was demonstrated by Edenborn et al. (1986a). Recent studies, however, indicate that the As(III) diffusing towards the oxic zone would be oxidized by the Mn oxyhydroxides prior to the adsorption of As(V) onto the Fe oxyhydroxides (Peterson and Carpenter, 1983; Richard, 1996). Under surficial oxic conditions, the adsorption of As onto the Fe oxyhydroxides may efficiently prevent its release to the overlying waters.

Another process which strongly impacts on the mobility of As in the sediments is its adsorption (or coprecipitation) onto iron sulphides such as pyrite and iron monosulphides (Huerta-Diaz and Morse, 1992; Morse, 1994; Huerta-Diaz et al., 1997). According to Belzile (1988), the distribution of arsenic associated with pyrite in the Gulf of St-Lawrence sediments implied the capture and inclusion of As into the lattice sites of the mineral in a Fe/As ratio of 1000. Microprobe analysis of framboidal pyrite from the Saguenay Fjord sediments indicated that they contain up to 1000 ppm of As (Mucci, pers. comm.). Belzile (1988) suggested that dissolved As released upon the dissolution of Fe oxyhydroxides may be immediately scavenged by Fe sulphides, just below the surface sediments, in the St-Lawrence Gulf and Estuary sediments. The Saguenay Fjord sediments, as mentioned earlier, are characterized by relatively low pyrite and anomalously high iron monosulphides concentrations. Adsorption and coprecipitation with iron monosulphides may control the concentration of Fe and As in the porewaters following the reductive dissolution of Fe oxyhydroxide carrier phases in the anoxic zone (Belzile, 1988). On the other hand, upon sediment resuspension or bioturbation, As may be released back to the interstitial waters as a consequence of the rapid oxidation and dissolution of iron monosulphides. Arsenic can then be recycled by diffusing upward to the sediment-water (or redox) interface where it can be readsorbed with detrital or authigenic Fe oxyhydroxides, under oxic conditions.

To summarize, As is accumulated in oxidized surface sediments mainly in association with Fe oxyhydroxides. Upon burial these Fe oxyhydroxides are reduced and dissolved, releasing As(V) to the suboxic porewaters. Once in solution arsenate can be reduced to arsenite and migrate upwards to be reoxidized by the Mn oxyhydroxides and subsequently adsorbed onto newly precipitated Fe oxyhydroxides. On the other hand, dissolved As(III) can also diffuse downwards, to the anoxic zone where it can be adsorbed or coprecipitated with Fe sulphides. However, as a consequence of sediment resuspension and bioturbation processes, these Fe sulphides can be oxidized, releasing As to the interstitial and overlying waters. The fate of As is therefore strongly linked to the geochemistry of Fe in both oxidizing and reducing sedimentary environments. Arsenic is expected to be internally cycled in sediments maintaining an oxic surficial layer, whereas depletion of oxygen in bottom waters and the migration of the redox boundary to the water column would promote the release of As to the overlying waters.

### 2.2.5 Lead :

Lead distribution in marine and lacustrine sediments of the northern hemisphere display increasing concentrations since the beginning of the industrialization period, although a slight decrease can be observed over the last decade (Bruland et al., 1974; Barbeau et al., 1981; Gobeil and Silverberg, 1989). The ubiquitous use of Pb alkyls in automobile gasoline for many decades has been linked directly to the ascension of Pb concentrations in sediments (Bruland et al., 1974; Barbeau et al., 1981). On the other hand, the recent decline of Pb concentrations in sediments reflects the progressive substitution of unleaded for leaded automobile gasoline (Bruland et al., 1974; Barbeau et al., 1981; Gobeil and Silverberg, 1989). A number of studies have reported that the isotopic composition of Pb in surficial sediments is comparable to industrial Pb added to gasoline, whereas it differs from that of natural Pb isolated from ancient sediments (Shirahata et al., 1980; Ridgway and Price, 1987; Gobeil and Silverberg, 1989; Carignan and Gariépy, 1995; Gobeil et al, 1995).

The Saguenay Fjord sediments show an enrichment in Pb concentrations relative to those of the Gulf and St. Lawrence Estuary (Loring, 1976a). Most of the lead found in the Saguenay Fjord sediments is of anthropogenic origin (Gobeil and Silverberg, 1989). The increased consumption of leaded gasoline after the Second World War is clearly registered in the sedimentary record of this region (Barbeau et al., 1981). An important part of the lead found in recent sediments of the Saguenay Fjord most likely originates from atmospheric dustfall and precipitation (Barbeau et al., 1981; Gobeil et al., 1995). In a recent study on the sources of Pb in the St. Lawrence Estuary, Gobeil et al. (1995) stated that the weathering of the crystalline rocks of the Canadian Shield also represented a source of Pb to this environment, although its contribution was almost negligible in the first 30 cm of the sedimentary column.

Lead is introduced into the Saguenay Fjord in solution or in association with solid and colloidal inorganic and organic particles (Loring, 1976a). Dissolved inorganic Pb is present as a divalent ion in oxygenated seawater and predominantly in the form of $PbCO_3^{\circ}$ although $PbOH^+$ could also be present (Stumm and Morgan, 1981). Under sulphidic conditions dissolved Pb is also present as a divalent ion, and has the tendency to form strong complexes with reduced sulfur species as well as solid sulphides (Stumm and Morgan, 1981; Emerson et al., 1983).

Lead, like Hg, is a very particle reactive element and is rapidly scavenged by Fe oxyhydroxides and organic matter settling through the oxic water column (Loring, 1976a; Gobeil and Silverberg, 1989). Gobeil and Silverberg (1989) observed that dissolved Pb in the Laurentian Trough sediments displayed a concentration maxima near the sediment-water interface, whereas the concentrations were parallel to the dissolved Fe profile below this surficial layer. The authors suggested that Pb was released to the porewaters near the sediment surface during the aerobic degradation of organic matter. The strong correlation between Pb and Fe distributions below the surficial layer lead them to conclude that Pb was implicated in the redox-controlled cycle of Fe. In the same study, they also characterized the depth distribution of various solid phase fractions of Pb through sequential extractions. A pH5 sodium acetate buffer treatment was performed to extract Pb adsorbed to solids and associated with carbonates, whereas an hydroxylamine hydrochloride-acetic acid treatment was employed to extract Pb associated to Mn and Fe oxyhydroxides. The results of their analyses showed that the vertical distribution of Pb followed closely that of Fe for both extraction methods as it was the case for the dissolved phase. The extraction performed with hydroxylamine hydrochloride-acetic acid dissolved between 40 to 70 % of the total Pb present in the sediments, with maximal concentrations in the first few centimeters below the surface. On the other hand, the Pb fraction soluble in the pH 5 sodium acetate buffer extraction only reached maximal abundance at mid-depth in the cores, where it represented 21 to 31 % of the total Pb found in these sediments. Their observations confirmed the chemical association of Pb and Fe, implying that Pb may be entrained in the dissolution, diffusion and reprecipitation cycle of Fe in the sediments. Moreover, relative variations in the distribution of solid phase associated Pb prompted the authors to suggest that it might be subjected to remobilization and chemical transformation during early diagenesis. The implied diagenetic mobility of Pb would jeopardize the validity of the $^{210}$Pb dating method. In fact, Ridgway and Price (1987) found significant differences between the sediment accumulation rates estimated from the vertical distribution of $^{137}$Cs and $^{210}$Pb in the Loch Etive (Scotland) sediments and concluded that a portion of Pb was lost to the overlying waters during aerobic organic matter degradation. However, Westerlund et al. (1986) were unable to detect a flux of Pb out of the surficial oxic sediments of a Sweden Fjord during bell-jar experiments.

In résumé, it appears that Pb could be solubilized near the sediment-water interface during the aerobic mineralization of organic matter and diffuse upward to the overlying waters or downward to be adsorbed onto Fe oxyhydroxides. As a consequence of sediment accumulation and migration of the redox interface, Pb may be released to the porewaters following the reductive dissolution of the Fe oxyhydroxides. Dissolved Pb can then diffuse upward to readsorb onto Fe oxyhydroxides, in the oxic layer or diffuse downward to adsorb (or coprecipitate) onto iron sulphides, such as iron monosulphides which are abundant in the Saguenay Fjord. Lead present in anoxic porewaters may also form complexes with reduced sulphur species, as well as with organic matter, or precipitate as insoluble PbS. A correlation between solid phase Pb and interstitial $SO_4^{2-}$ concentrations profiles was observed by Ridgway and Price (1987) in a Scottish sea loch, confirming the tendency of Pb to form sulphide complexes with increasing reduced sulfur species concentrations. Moreover, Huerta-Diaz and Morse (1992) stated that Pb adsorption onto pyrite was generally not important in anoxic marine sediments, whereas Huerta-Diaz et al. (1997) suggested that a remobilization of Pb occurred in anoxic sediments as a result of its complexation with sulphides. Upon bioturbation or sediment resuspension to an oxygenated environment, Pb present in sulphidic porewaters or associated to Fe sulphides would be released to the overlying waters.

### 2.2.6 Copper :

Cu concentrations found in the Saguenay Fjord sediments, unlike the Hg, Pb, and As concentrations, are comparable to those found in the Estuary and the Gulf of St-Lawrence and much lower than those reported for polluted sediments (Loring, 1976a ; Barbeau et al., 1981; Pelletier and Canuel, 1988; Fortin and Pelletier, 1995). The input of anthropogenic Cu in the Saguenay Fjord would appear to be much less important than other metals, even though a small increase in Cu concentrations has been observed since 1945 in the Fjord sediments (Loring, 1976a). This increase could, however, be derived from anthropogenic sources such as mining and pulp and paper mill industries, chlor-alkali factories as well as effluents from municipalities located along the Saguenay Fjord (Cossa, 1990; Fortin and Pelletier, 1995).

In oxygenated seawater, Cu is present under the oxidation state of Cu(II) (cupric). Inorganic dissolved Cu is present mainly in the form of $CuCO_3^{\circ}$, although $CuOH^+$ and $Cu(CO_3)_2$ should also be present based on thermodynamic calculations (Stumm and Morgan, 1981). Organic matter plays an important role in Cu solubilization, inhibiting its adsorption onto suspended particles (Sholkovitz and Copland, 1981). In a study on the relationship between naturally occurring organic matter and the solubility, adsorption and coagulation properties of metals, Sholkovitz and Copland (1981) observed that Cu solubilization by organic ligands in natural waters could be the dominant process and therefore be more important than adsorption onto suspended particles. Under anoxic conditions, Cu (II) (cupric) is reduced to Cu(I) (cuprous) at the $O_2$-$H_2S$ interface (Jacob and Emerson, 1982; Kremling, 1983). Under this oxidation state, Cu forms very strong complexes with reduced sulfur species and its solubility is primarily controlled by Cu polysulphide complexes (Jacob and Emerson, 1982; Emerson, 1983; Kremling, 1983). Most studies addressing the speciation and solubility of trace metals in anoxic waters do not include organic complexation in their treatment. However, their complexing ability with many metals such as Cu must not be ignored and could even explain the apparent supersaturation of trace metals (e.g., Cu, Hg and Pb) relative to their respective sulphides minerals in many environments (Lindberg and Harris, 1974; Sholkovitz and Copland, 1981; Kremling, 1983; Carignan and Nriagu, 1985).

The early diagenetic behaviour of Cu and organic matter appear to be intimately related. Pelletier and Canuel (1988), as well as Loring (1976a), observed a strong linear correlation between particulate Cu and organic matter concentrations in the Saguenay Fjord sediments. Furthermore, many studies have reported the presence of maximum dissolved Cu concentrations near the sediment-water interface in oxic sediments. This observation has been interpreted as the release of Cu resulting from aerobic oxidation of labile organic matter upon its aerobic oxidation (Klinkhammer, 1980; Klinkhammer et al., 1982; Sawlan and Murray, 1983; Ridgway and Price, 1987; Gerringa, 1990; Shaw et al., 1990; Lapp and Balzer, 1993). This surficial porewater enrichment is often reflected by a diffusive flux of Cu to the overlying waters, as observed by Sundby et al. (1986), Sundby (1994) and Westerlund et al. (1986) during their benthic chamber experiments in coastal sediments of Western Sweden.

Below the sediment surficial layer, a fraction of the total content of Cu may be adsorbed onto Mn oxyhydroxides (Klinkhammer, 1980) and be released to the interstitial waters following burial and reductive dissolution of the host Mn oxide carrier phase (Sawlan and Murray, 1983). In their studies on marine sediments, Klinkhammer (1980) as well as Sawlan and Murray (1983) observed that Cu was released to the porewaters in the Mn reduction zone. Moreover, the observation of a significant decrease of Cu concentrations in the porewaters of the Fe reducing zone lead these authors to conclude that sulphide minerals act as a sink for this metal; the sulphate reduction zone following closely the Fe reduction zone in organic-rich sediments (Froelich et al., 1979; Klinkhammer, 1980). Pyrite and iron monosulphides are believed to be significant sinks for Cu in anoxic sediments (Huerta-Diaz and Morse, 1992; Morse and Arakaki, 1993; Morse, 1994). In their recent study on the geochemistry of trace metals in lacustrine sulphidic sediments, Huerta-Diaz et al. (1997) observed supersaturated porewaters with respect to Cu sulphides. The authors also reported that the decrease of Cu and Fe concentrations in sulphidic porewaters did not occurred at the same depths. These observations lead the authors to conclude that Cu was probably removed from the porewaters as discrete Cu sulphide precipitates rather than through coprecipitation with $FeS_{(s)}$ (Huerta-Diaz et al., 1997). Sundby et al. (1994) and Westerlund et al. (1986) noted a diffusive flux of Cu as well as Ni to the sediments, during their benthic chambers experiments, as anoxic conditions developed in the water column, confirming the scavenging ability of sulphide minerals for these trace metals. Lu and Chen (1977) observed a diffusive flux of Cu to the sediments under anoxic conditions, in their laboratory experiments, which they also attributed to the formation of sulphide solids.

Briefly, Cu is rapidly liberated to the porewaters near the oxic sediment-water interface. Dissolved Cu profiles in oxidizing porewaters can be explained by remobilization at the interface and removal at depth. Copper released following the aerobic organic matter degradation near the interface can diffuse upwards to the overlying waters and adsorb onto Mn oxyhydroxides accumulating throughout the oxic layer. Copper associated with the Mn oxyhydroxides can be released back to the porewaters following their dissolution in the Mn reduction zone and diffuse back to the Mn oxidation zone. Under anoxic conditions, dissolved Cu will be scavenged by sulphide minerals such as pyrite and iron monosulphides or precipitate as discrete Cu sulphides. Nevertheless, the exposure of anoxic sediments to an oxidizing environment, as a consequence of bioturbation and resuspension processes, may lead to the dissolution of Cu-bearing sulphide phases (e.g. CuS, FeS) and release it back to the overlying waters.

### 2.2.7 Nickel :

As it is the case for Cu, the Saguenay fjord sediments are not enriched in Ni compared to the Estuary and Gulf of St-Lawrence, although their Ni concentrations are higher than the average content of the crystalline shield rocks (Loring, 1976b). The pulp and paper, mining and chlor-alkali industries as well as effluents from the municipalities located along the Fjord could be responsible for these slightly elevated concentrations in the sediments (Cossa, 1990; Fortin and Pelletier, 1995).

Nickel is a transitional metal and is present in oxygenated seawater as a divalent ion. Dissolved inorganic Ni can be found in oxic seawater mainly in the form of $Ni^{+2}$ and possibly $NiCl^{+}$ and $NiSO_4^{0}$. In sulphidic seawater Ni can form solid sulphides, as no change in Ni oxidation state occurs (Jacob and Emerson, 1982; Emerson, 1983; Kremling, 1983). The predominant dissolved inorganic species in anoxic porewaters, according to the thermodynamic predictions, should be $Ni(HS)_2^{\circ}$ (Kremling, 1983).

Nickel has been reported to be released to the surficial sediment porewaters during the degradation of organic matter (Gerringa, 1990; Shaw et al., 1990; Lapp and Balzer, 1993). Fluxes of Ni from surficial oxic sediments to the water column have been observed during experiments with benthic flux chambers (Westerlund et al., 1986; Sundby, 1994). On the other hand, Loring (1976b) suggested that in contrast to Hg, Cu and Pb, organic matter does not play a significant role in determining the distribution of Ni in sediments. The author observed that non-detrital Ni was primarily associated with soluble Mn oxides on suspended particulate matter in the water column and present as grain coatings in the sediments. Investigations of the geochemical behaviour of Ni in interstitial waters of coastal marine sediments have highlighted a strong association between Ni and Mn oxides and lead authors to conclude that Ni distribution was mostly dictated by the Mn sedimentary cycle (Klinkhammer, 1982; Sawlan and Murray, 1983; Shaw et al., 1990).

Ni released to the surficial porewaters following the organic matter degradation (Gerringa, 1990; Lapp and Balzer, 1993) can diffuse upwards to the overlying waters (Lu and Chen, 1977; Westerlund et al., 1986; Sundby, 1994) or be adsorbed onto Mn oxyhydroxides accumulating near the redox interface (Klinkhammer, 1980; Sawlan and Murray, 1983; Shaw et al., 1990). Nickel is released back to the porewaters in the Mn reduction zone, where maximum concentrations are usually observed (Klinkhammer, 1980; Shaw et al., 1990). Once again, Ni can diffuse upwards to readsorb onto authigenic Mn oxyhydroxides and downwards to the Fe and sulphate reduction zones to be adsorbed onto Fe sulphides or precipitate as a distinct NiS (Klinkhammer, 1980; Jacob and Emerson, 1982; Emerson et al., 1983; Kremling, 1983; Sawlan and Murray, 1983; Huerta-Diaz and Morse, 1992; Mucci and Edenborn, 1992; Morse and Arakaki, 1993; Morse, 1994; Huerta-Diaz et al., 1997).

A decrease of Ni concentrations in anoxic porewaters, attributed to the precipitation of sparingly soluble metal sulphides, has been observed in the sediments of stratified marine basins displaying seasonal bottom water anoxic conditions (Jacob and Emerson, 1982; Kremling, 1983; Shaw et al., 1990; Lapp and Balzer, 1993). On the other hand, Huerta-Diaz et al. (1997) proposed that iron monosulphides may be the major sink for Ni in anoxic sediments from two Canadian Shield Lakes, even though sedimentary pyrite is also an efficient metal scavenger (Huerta-Diaz and Morse, 1992). A diffusive flux of Ni to the sediments, under anoxic bottom water conditions has been observed and interpreted as resulting from sulphide precipitation in the sediments (Lu and Chen, 1977; Westerlund et al., 1986; Sundby, 1994).

Conversely, Kremling (1983) reported dissolved Ni concentrations in anoxic waters which are higher than those predicted from the calculated thermodynamic solubility of NiS. He concluded that these observations strongly supported assumptions that complexation by bisulphides and polysulphides ions play a major role in controlling the solubility of this metal, like most class B metals (Jacob and Emerson, 1982), such as Cu and Pb. Lapp and Balzer (1993) also proposed that the formation of sulphides, polysulphides, as well as organic metal complexes may explain the elevated porewater Ni concentrations measured in reducing sediments of the Western Baltic Sea.

To summarize, Ni accumulates in sediments in association with particulate matter settling through the water column. As a result of microbial organic matter degradation Ni is released to the surficial porewaters. Once in solution, Ni can diffuse upwards to the overlying waters adsorb onto authigenic Mn oxyhydroxides. Upon burial, these Mn oxyhydroxides are reduced and dissolved, releasing Ni back to the suboxic porewaters. Dissolved Ni can then migrate upwards to readsorb onto newly precipitated Mn oxyhydroxides or downwards to be adsorbed onto Fe sulphides or precipitate as a distinct NiS. Moreover, Ni can be complexed by sulphides or polysulphides, as well as organic matter. The oxidation of the solid sulphides, as a consequence of sediment mixing or resuspension in an oxygenated environment would release Ni back to the waters and allow its remobilization.

### 2.3 Sediment resuspension experiments:

Very few studies have been carried out on the remobilization of trace metals following the resuspension of contaminated sediments in the water column. Furthermore, most of the experiments performed were conducted over short periods of time and only considered a few trace metals.

Lindberg and Harris (1977) looked at the release of dissolved Hg and organics following the resuspension of near-shore sediments collected in Mobile Bay and the Shark River in the Everglades National Park. The authors observed two distinct dissolved Hg peaks within the first three hours of each experiment with Hg concentrations returning nearly to the original solution values between each. A steady-state Hg concentration in the overlying waters was reached within 4.5 hours in all cases, while the sediments were maintained in suspension for a total of 6 hours. As no consistent variation pattern for pH, redox potential, total dissolved sulphides and dissolved organic matter was observed throughout the experiments, it was proposed that the mechanisms controlling the release and redeposition of Hg were not simply related to these factors. The authors suggested that the initial Hg peak resulted from the release of exchangeable Hg and physical mixing between the surface water and porewaters which were enriched in dissolved Hg, Fe and organic complexes. The decrease in dissolved Hg concentration which followed was attributed to scavenging of Hg by freshly precipitated Fe oxyhydroxides resulting from the oxidation of reduced Fe released to the oxygenated surface water. The partial solubilization of sediment organomercury complexes or the slow oxidation of mercuric sulphide species were proposed to have promoted the second release of Hg to ambient waters. Finally, clay minerals in suspension as well as precipitated Fe oxyhydroxides are suspected to have scavenged Hg from solution until steady-state conditions were reached within few hours after the beginning of each experiments.

The results obtained by Lindberg and Harris (1977) indicated that the highest Hg concentrations observed in solution during their experiments could not be accounted for by the release of dissolved Hg from the porewaters alone, but also included the release of Hg originally present in the sediments as a solid phase. Therefore, Lindberg and Harris (1977) concluded that large-scale resuspension of estuarine sediments, by processes such as dredging operations, could cause a temporary release of Hg to the surrounding waters, followed by a decrease to levels close to those predicted by ideal dilution calculations. The authors, however, warned that the resuspension of previously undredged organic-rich sediments could lead to a much more important release of Hg than a resuspension of organic-poor sediments.

Gerringa (1990) investigated the effect of aerobic decomposition processes on the distribution of Cu, Cd, Ni, Pb, Fe and Mn, following the resuspension of coastal anoxic sediments collected in the Wadden Sea. The experiments were conducted using mixed slurries, subjected to continuous mixing over 3 months, at a fixed pH (7.8), oxygen concentration (100% air saturated) and temperature (14°C). Both sediment and porewater metal concentrations were measured in samples withdrawn from the slurries at set time intervals, while organic carbon degradation rates were determined from $O_2$ consumption as well as by $NO_3^-$ and $NH_4^+$ production. Dissolved metal concentrations were determined following a liquid-liquid extraction whereas the partitioning of the metals in the solids was evaluated using a sequential extraction procedure (Gerringa, 1990).

The behaviour of the individual metals observed by the author throughout her laboratory experiments can be summarized as follows. Copper, Pb and Cd were released to the dissolved phase as a result of the aerobic degradation of particulate organic matter (POM). Furthermore, the fraction of these trace metals that was extractable by sodium dodecyl sulphate (e.g. Cu and Pb) and acetic acid (e.g. Cd) increased throughout the experiments. The sodium dodecyl sulphate was employed to solubilize labile organic matter, whereas acetic acid was used for the removal of sorbed metals as well as the dissolution of most carbonates. Dissolved Cu concentrations seemed to be limited by the concentration of organic ligands in solution. The latter appeared to have no influence on the solubility of Cd, since it forms stable chloro-complexes in seawater. Finally, dissolved Pb concentrations were probably controlled by a precipitation equilibrium reaction. Gerringa (1990) observed that aerobic degradation of POM did not affect the distribution of Ni within the different fractions solubilized by the sequential extraction. However, Ni was readily released to solution upon an increase in dissolved organic ligand concentrations. Both the Fe and Mn dissolved concentrations remained constant throughout the experiments, although, like Cu, Cd and Pb, they became more easily extractable from the sediments with time.

Duarte et al. (1991) observed the effects of pH and ionic strength on Hg desorption from contaminated coastal sediments, during a series of laboratory experiments conducted in Erlenmeyer flasks mechanically shaken for 1 to 3 days. The results of their experiments indicated that an increase in ionic strength lead to a decrease in the amount of Hg released from the sediments. The author attributed this observation to a decrease in the stability of colloidal particles of organic matter and clay minerals, onto which Hg is preferentially bounded in the sediments. An increase in ionic strength leads to an increase of London-Van der Waals attractive forces as well as a decrease of repulsive electrostatic forces between colloidal particles, thereby promoting their aggregation and precipitation.

In addition, the authors observed that an increase in pH in the overlying waters, to values above 5, caused a decrease in the amount of Hg released from the sediments. This dependence appeared, however, much less pronounced for pH values beyond 7. On the basis of their findings, Duarte et al. (1991) proposed that an increase in pH results in the hydrolysis of Hg, leading to its precipitation and adsorption to the sediments, whereas a decrease in pH favours $H^+$ over other cations, such as $Hg^{2+}$, for the adsorption sites. This hypothesis is consitent with the observations of Forbes et al. (1974) which stated that the contribution of $Hg(OH)_2$ to Hg adsorption onto solid phases became very significant with increasing pH. Finally, Duarte et al. (1991) concluded that the higher the ionic strength (salinity) and the pH of the solution, the smaller the amount of Hg desorbed from the sediments to the overlying waters.

Gambrell et al. (1991) also conducted laboratory experiments with contaminated sediments to determine the effect of pH, redox conditions and salinity on the release of trace metals (Cd, Cu, Ni, Pd and Zn) to the soluble phase. The sediments were collected from a contaminated brackish marsh in New Jersey, which exhibited strongly anaerobic conditions. The experiments were conducted using stirred sediment slurries. The first observation made by the authors was the significant drop in pH, from neutral (7.0) to strongly acid (3.0) conditions following their exposure to an oxygenated environment. The laboratory experiments demonstrated that Cd, Cu, Ni and Zn solubility increased with increasing redox potential, as their highest concentrations in solution were measured under strongly oxidizing conditions. The solubilization of Pb, however, was little affected by redox potential variations. The authors attributed this behaviour to the fact that Pb is tightly bound to sulphide minerals and complexation with refractory organic matter under strongly reducing conditions, whereas it is efficiently immobilized by precipitated Fe oxyhydroxides under well-oxidized conditions. The concentrations of dissolved Cd and Cu increased with increasing salinity, although no consistent and significant salinity effect could be observed for Pb and Ni. The highest concentrations of Cd, Ni, Pb and Zn in solution were attained under moderately acidic conditions but a strong pH effect on the solubilization of Cu was not apparent.

Gambrell et al. (1991) stated that under the prevailing slightly basic and strongly anaerobic conditions of these marsh sediments, trace metals were being efficiently immobilized. They concluded, however, that the oxidation and ensuing acidification of the sediments, as a consequence of resuspension by dredging operations, would probably release significant amounts of trace metals, such as Zn and Cd, to the surrounding waters.

# 3.0 METHODOLOGIES :

## 3.1 Sediment sampling :

Sediments were collected at the station Sag-15 in the fall of 1994 and spring 1995. Sag-15 is located at the junction of the Baie des Ha !Ha ! and the north arm of the Saguenay Fjord, on the upstream slope of the landward basin (Figure 1.1). The exact locations and depths of the sampling sites were 48°22. 00 N/ 70°42.58 W at 198m for 1994 and 48°21.79 N/ 77°42.22 W at 231m for 1995. This station is known to be the site of sediment accumulation from episodic submarine slides and, consequently, displays heterogeneous metal distributions in the sedimentary column. Relatively undisturbed sediments cores were recovered using a 0.12 $m^2$ Ocean Instruments Mark II box corer (Hessler-type). The cores were subsampled onboard, at various depth intervals (Appendix 1), in a nitrogen filled glove-box (Edenborn et al. 1986b). Samples of 25 to 35g were collected, at each interval, in pre-weighed plastic scintillation vials. These samples were subsequently freeze-dried and reweighed for determination of water content. The sediments were then homogenized, by grinding in an agate mortar, for solid phase composition determinations. Mini-cores (13 cc polyethylene screw cap test tube with their distal end cut off and 10 cc syringe plunger) were taken at the rate of 3 to 4 per depth interval and frozen immediately in order to maintain the anoxic character of the sediments. The latter samples were used for AVS and pyrite content determinations as well as for the sediment resuspension experiments.

## 3.2 Sediment analysis :

The chemicals used for all the analysis were of ultrapure quality and Milli-Q deionized distilled water was always used for making solutions. Total and reactive phase associated metal concentrations were determined using homogenized freeze-dried sediments. Total Hg (1994 and 1995 samples) and As (1994 samples only) content of the sediments were obtained following a $HNO_3$- HCl digestion (10:1 ratio), at a solid/solution ratio of 1:16,5 (g/mL) (Agemian and Chau, 1976; Bono,1997). The digestions were carried out in Teflon® reactors held in a pressure cooker and heated in a microwave in the following sequence: 1 minute at low intensity (210 W), 4 minutes at medium (490 W) and 15 minutes at maximum power (700 W) (Agemian and Chau, 1976; Bono, 1997). Mercury and As concentrations in the digestate were analyzed by cold-vapor atomic absorption spectrophotometry (AAS), following hydride generation in the presence of a 2% sodium borohydride and 0.5 % sodium hydroxide solution (Agget and Aspell, 1976), on a Perkin Elmer 5100 AAS equipped with a flow injection system. Marine sediment standards (BEST-1 and PACS-1, NRC) were carried through the same procedure to ensure the extraction efficiency (95 to 100 %) and the accuracy of the analyses. Before the analysis, the As present in the digestates was reduced to As (III) with a 5% ascorbic acid and potassium iodide solution, and the samples were reacidified with concentrated HCl (3 mL of HCl and 1 mL of reductive solution for 10 mL of sample). On the other hand, samples for Hg determinations were treated with the addition of few drops of a 5% potassium permanganate solution, prior to their analysis. The detection limit was 0.25 ng/g for Hg and 0.08 ng/g for As. The analytical precision of the instrument was better than 10 % and external aqueous standards were used for the calibrations.

The total concentration of other metals (i.e As, Cu, Ni, Pb, Mn and Fe) in the samples collected in 1995 were determined by X-ray fluorescence (XRF) using a Philips PW2400 automated XRF spectrometer system with a Rhodium 60 kV end window x-ray tube. Iron, Mn, Cu and Ni present in the sediments were analyzed using 32 mm diameter fused beads prepared from sample powder and a lithium tetraborate mixture (1:5 ratio), whereas As and Pb were determined from 40 mm diameter pressed pellets prepared with a mixture of sample powder and Hoechst Wax C Micropowder (5:1 ratio). The instrument was calibrated using IS-40 Certified International Reference Materials. The detection limits, based on three times the background sigma values, were 15 μg/g for Cu, 2 μg/g for Ni, 1 μg/g for Pb and As, 23 μg/g for Mn and 21μg/g for Fe. The relative standard deviations of the analysis with this instrument were of 1% for the major elements and 0.65% for the trace metals. X-ray fluorescence analyses of the 1994 samples could not be carried out because insufficient freeze-dried sediments remained.

Reactive metals were determined following a 24 hours extraction in 1 N HCl at a solid/solution ratio of 1: 50 (Huerta-Diaz and Morse, 1990; Leventhal and Taylor, 1990). Extracts were filtered through 0.45 um Millipore filters prior to analysis. Copper and Ni were analyzed by graphite furnace atomic absorption spectrophotometry (GFAAS) with Zeeman background correction on the Perkin Elmer 5100. The detection limits were 0.4 ng/g for Cu and 0.6 ng/g for Ni whereas the analytical precision were better than 5%. Arsenic and Hg concentrations were determined, respectively, by hydride generation and cold-vapor AAS using the flow injection system. The analytical precision for both analyses was better than 10%. The detection limits were 0.25 ng/g for Hg and 0. 13 ng/g for As. Finally, Fe and Mn were measured directly by flame AAS with an analytical precision of 5%. The detection limits were 0.12 μg/g for Fe and 0.05 μg/g for Mn and external aqueous standards were used for the calibrations.

Reactive iron was defined by Canfiled (1989) as the fraction of Fe in marine sediments which readily reacts with sulphide to form various Fe sulphide minerals. The reactive phases extracted by the 1N HCl digestion represent an operationally-defined fraction that comprises iron monosulphides, amorphous and crystalline iron and manganese oxyhydroxides, carbonates and hydrous alumimosilicates (Huerta-Diaz and Morse, 1990, 1992). This method was selected over the citrate-bicarbonate-dithionite (CDB) procedure (Lucotte and d'Anglejan, 1985), which is most commonly used to leach amorphous and poorly crystalline iron oxide/hydroxides, for mainly two reasons. The first is that the CDB reagent, and specifically the dithionite, can reduce Hg (II) to Hg (0) resulting in its volatilization from the samples. Furthermore, the reagent interferes with the analysis of As by reacting with the borohydride (Belzile, 1987; Richard, 1996). Secondly, CDB extraction will lead to an under-estimation of reactive iron, because this reagent cannot dissolve the oxidation products of Fe monosulphides which form during the handling and storage of the samples (i.e. freeze-drying) (Raiswell et al., 1994; Gagnon et al., 1995). The AVS oxidation products, on the other hand, would appear to be solubilized by the 1N HCl digestion (Rapin et al., 1986; Huerta-Diaz and Morse, 1992). Reproducibility of the extraction procedure was better than 10% (Gagnon et al., 1995).

The acid volatile sulphide (AVS) concentrations, including amorphous iron monosulphides (FeS), mackinawite and poorly crystallized greigite, were determined following their conversion to $H_2S$ under nitrogen atmosphere, in a closed container at ambient temperature. A flat-bottomed vial, filled with 10 mL of a 3% zinc acetate and 2N sodium hydroxide solution, was inserted upright into a 250 mL flask in which 5 g of frozen sediments had already been introduced. Fifteen mL of a 9 N HCl solution containing 20% $SnCl_2$ were then added and were allowed to react for 18 hours in the sealed flask at room temperature. All the reagents used for this extraction were purged with nitrogen for about 2 hours, and all manipulations were carried out in a nitrogen filled glove-bag. The evolved $H_2S$ which quantitatively diffused into the alkaline zinc solution was determined by iodometric titration (Hsieh and Yang, 1989 ; Gagnon et al, 1995 ; Bono, 1997). The reproducibility of the method was better than 10%.

The pyrite content of the sediments was measured following the selective dissolution of pyrite and the quantitative analysis of the released iron (Lord III, 1982). This method was preferred to others which are based on the pyrite sulphur analysis (Chanton and Martens, 1985 ; Hsieh and Yan, 1989) due to the elimination of the ambiguity in the separation between the pyrite, elemental and organic sulphur species, as well as much better reproducibility (Lord III, 1982). Freeze-dried sediments (0.250 g) were pretreated with a citrate-bicarbonate-dithionite solution followed by a hydrofluoric-boric acid solution, removing all iron compounds other than pyrite, associated with oxides and clay minerals, from the samples. Concentrated nitric acid was then added to the samples to quantitatively dissolve the pyrite. The digestate was then filtered through a 0.45 μm Millipore filter, and the dissolved iron was analyzed by flame AAS (Lord III, 1982). A correction factor of 1.079 was applied to the results, the average recovery of pyrite with this method being of 92.7 % (Lord III, 1982). The mean relative standard deviation obtained was 1.6% whereas the detection limit was of 0.2 μg/g of pyrite (1.8 nmol/g) (Lord III. 1982).

Total carbon ($C_{tot}$) and total nitrogen ($N_{tot}$) were determined on freeze-dried sediments with a Carbo-Erba$^{TM}$ Elemental Analyzer. The detection limit for these procedures was approximatively 0.1% C and <0.05% N by weight. Inorganic carbon ($C_{inor}$) was obtained by coulometric titration of $CO_2$ evolved from the sediments following their acidification with a 2N

HCl solution. The analytical precision and reproducibility were better than 5%, whereas the detection limit was lower than 0.06% C per 50 mg sample (Bono, 1997). The organic carbon ($C_{org}$) was estimated from the difference between the $C_{tot}$ and the $C_{inor}$.

## 3.3 Remobilization experiments :

### 3.3.1 Experimental design :

One to three frozen sediment mini-cores were extruded into an Erlenmeyer containing 400 mL of filtered (0.45 and 0.1 μm) seawater (see Table 3.1). The seawater (S=30) was collected in 1995 near Cap Eternite (Figure 1.1) at a depth of 200 m using 12 l PVC Niskin bottles. The sediments were maintained in suspension by mounting the Erlenmeyers on an orbital shaker (VWR Scientific) set at 230 RPM. The experiments were monitored as a function of time for periods of at least 2 months. The pH of the slurries was measured regularly during the experiments with a glass electrode calibrated using NIST-traceable buffer solutions. The remobilization experiments were conducted at room temperature and atmospheric pressure. The Erlenmeyers were covered with Parafilm in which small holes were perforated in order to allow gas exchange with minimal evaporation.

| Experiment # | sediments depth interval (cm) | porosity $\Phi$ | wet sediment weight (g) | dry sediment weight (g) | total volume of solution (mL) |
|---|---|---|---|---|---|
| 11 | 0-0.5 | 0.806 | 38.0342 | 14.5861 | 422.88 |
| 9 | 0.5-1.0 | 0.821 | 37.2968 | 13.4380 | 423.39 |
| 10 | 3.0-4.0 | 0.738 | 32.6582 | 15.6102 | 416.63 |
| 7 | 13.0-15.0 | 0.762 | 32.4445 | 14.4800 | 417.53 |
| 8 | 19.0-21.0 | 0.764 | 29.3857 | 13.0678 | 415.92 |
| 12 | 34.0-37.0 | 0.754 | 30.5412 | 13.9573 | 416.18 |

Table 3.1. Characteristics and quantity of sediments used for the resuspension experiments.

### 3.3.2 Sampling :

Thirty mL aliquots of the slurry were withdrawn with clean syringes at close time intervals during the first hours of the experiments (0, 2, 5, 15 and 30 minutes followed by 1, 3, 5 and 24 hours) and episodically over the next days and weeks ( 48 h and 1, 2, 4, 6, and 8 weeks). During the first three samplings the volume of solution drawn from the slurry was not replaced. It was assumed that the samples were representative of the slurry and had the same solid:solution ratio. In subsequent sampling, the amount of solution withdrawn was replaced by an equivalent volume of the original filtered seawater. This allowed us multiple sampling of the slurry without significant depletion of the initial volume. In this case, the shaker was stopped for two to five minutes prior to sampling and solids allowed to settle. The samples were then taken from the supernatant solution in order to maintain invariant the sediment:water ratio of the slurry.

Samples were filtered through pre-weighed 0.45 μm Millipore filters. The filters were recovered and weighed to monitor changes of the sediment:water ratio throughout the experiments. The filtered samples were stored in acid-cleaned (20% HCl) glass bottles with aluminum-lined screw caps and refrigerated at 4°C. A fraction of the filtered samples (20 to 25 mL) was acidified with 1% equivalent volume of concentrated HCl for trace metals analyses, including Hg, As, Cu, Ni, Pb, Mn and Fe. The remainder of the solution (5 to 10 mL) was stored without acidification for dissolved organic carbon (DOC) and total nitrogen ($N_t$) analyses.

### 3.3.3 Experimental solution analysis :

Mercury concentrations in solution were determined using a gold amalgamation system combined with a Brooks Rand Ltd. Model-2 cold vapor atomic fluorescence spectrometry system

(CVAFS) (Bloom and Crecelius, 1983; Bloom and Fitzgerald, 1988). Five hundred µL of a 50 % $SnCl_2$ solution were added to 100 mL Milli-Q water in a Teflon® reactor and purged under an Ar flow for approximatively 2 hours. Five mL samples were allowed to react with 100 µL of a BrCl solution (0.556 g $KBrO_3$ + 0.750 g KBr dissolved in 10 mL Milli-Q water and 40 mL concentrated HCl) and 100 µL of an hydroxylamine hydrochloride solution (12 g of $NH_2OH$-HCl diluted in 100 mL of Milli-Q water). Samples were then transferred into the $SnCl_2$ Teflon® reactor and were allowed to react for 10 minutes. Mercury (II) was reduced to metallic mercury, volatilized, entrained in the Ar stream and trapped as an amalgam on gold-coated quartz. Elemental Hg was released from the amalgam upon heating (500 °C) and carried to the spectrophotometer by a pre-cleaned argon gas flow. The detection limit of this system was of 20 ng/L and the precision better than 10%.

The determination of dissolved As (III) and total As concentrations were carried out by atomic absorption spectrophotometry after hydride generation on a Perkin Elmer 5100 with a flow injection system. Total dissolved As was measured following the procedure detailed earlier for the sediment analysis, whereas dissolved As(III) was obtained by the addition of an acetate buffer to the samples in order to maintain their pH values between 3.5 and 5.5. The arsine (arsenic hydride) generation from As (V) is strongly pH dependent and practically negligible at $pH > 3.5$, but a quantitative conversion of the As(III) into arsine proceeds at these pH values (Aggett and Aspell, 1976). The detection limit of both procedures was 0.05 µg/L and the standard deviations of the analysis were lower than 10%. External aqueous standards were used for calibrations.

Manganese concentrations in solution were measured by GFASS following the 1:10 dilution of the samples with Milli-Q water. External aqueous standards were used for the calibration and the detection limit for this element was of 0.14 µg/L. The relative standard deviation of replicate analyses was lower than 5%. Iron in solution was determined by the colorimetric method described by Stookey (1970). Briefly, 5 to 10 mL samples were diluted with 50 mL of Milli-Q water and transferred into a 125 mL Erlenmeyer flasks. The flasks were placed on a hot plate and maintained at the boiling temperature for ten minutes, after the addition of 1 mL of a mixed acid reagent (0.5140 g of ferrozine + 10,0 g of hydroxylamine hydrochloride diluted in 40 mL of concentrated hydrochloric acid). The samples were then allowed to cool back to room temperature and were transferred quantitatively into 50 mL volumetric flasks. They were diluted to the mark following the addition of 1 mL of an ammonium acetate and ammonium hydroxide buffer solution (40 g of ammonium acetate + 35 mL of ammonium hydroxide dissolved in 100 mL of Milli-Q water), and color development was allowed to proceed over the next minute. Absorbance measurements were then performed on the samples, at a wavelength of 562 nm, with a Bausch and Lomb Spectronics 21 spectrophotometer. A calibration curve was established using standard solutions (1 to 300 ppb Fe(II)) that were carried through the same procedure. The reproducibility of the method determined by replicate analyses was better than 5 % whereas the detection limit was of 0.5 µg/L.

Dissolved Cu, Ni and Pb were determined following a liquid-liquid extraction with Freon (1,1,2-Trichloro-1,2,2 Trifluoroethane; $Cl_2FCCF_2Cl$) and a mixture of dissolved ammonium pyrrolidine dithiocarbamate with diethylammonium-diethyldithio-carbamate (APDC/DDDC), and the metals were back extracted into an acidified aqueous solution before analysis (Danielsson et al.. 1978, 1982). This extraction was necessary because of the low concentrations of the samples as well as the complexity of the seawater matrix which interferes with GFAAS analyses. This method was chosen over other recommended procedures because it presented a much higher sensitivity. The solvent is also less toxic than others commonly used (e.g. hexone, chloroform, carbon tetrachloride), non carcinogenic and inexpensive. Furthermore, the back extraction into an acidified aqueous solution permitted the conservation of the samples over a longer period of time, and it provided a well suited solution for GFAAS analyses (Danielsson et al., 1978, 1982).

Danielsson et al. (1978, 1982) originally developed this method for 500 mL samples, and simple scaling down of the procedure for samples of 5mL or less was not appropriate (Gerringa, 1990). Gerringa (1990), in concert with Danielsson, refined this extraction method so it could be performed successfully on smaller samples. She used 50 μL of a mixed solution ( made of a 0.5% solution of APDC/DDDC and an acetate buffer in a 1:1 ratio), 5 mL of Freon and 50 μL of concentrated $HNO_3$ for a 5 mL sample previously acidified to 0.1 % HCl. However, since it was decided in this study to acidify the water samples to 1% HCl, for a better preservation, further modifications were necessary. Best results were obtained when the extraction of a 2.5 mL sample was carried out using 275 μL of mix solution and 5 mL of Freon, whereas 25 μL of $HNO_3$ and 2.475 mL of Milli-Q water were added for the back extraction providing a final volume of 2.5 mL. This treatment resulted in an extraction efficiency between 90 and 100 %, as evaluated on standard solutions with matrices and concentrations similar to the samples. The metal concentrations were measured by GFAAS and the calibrations were performed with external aqueous standards. The detection limits were 0.23 μg/L for Cu, 0.36 μg/L for Ni and 0.18 mg/L for Pb and relative standard deviations of replicate analyses were better than 5%.

Dissolved organic carbon (DOC) concentrations were determined by thermal decomposition on a heated platinum catalyst (680 °C) with a Shimadzu TOC-5050 system. The samples were acidified to pH 2 and purged with $CO_2$–free air prior to analysis. The $CO_2$ evolved from the thermodecomposition of DOC was then detected by a non-dispersive infra-red analyzer. The reproducibility was generally better than 2% for concentrations higher than 1 mg/L. However, it varied between 5 and 7% for concentrations lower than 1 mg/L.

The total nitrogen ($N_t$) content of the samples was calculated from the sum of the ammonia, nitrate and nitrite determinations. Ammonia concentrations were determined spectrophotometrically following reaction of the sample solution with an hypochlorite solution, and the formation of the indophenol blue complex (Koroleff, 1973) in presence of phenol and citrate. The samples were diluted tenfold to 15 mL with Milli-Q water to which 0.45 mL of each of the three reagents were added (citrate, hypochlorite and phenol), and color development was allowed to proceed overnight in the dark. Absorbance measurements were made with a Bausch and Lomb Spectronics 21 spectrophotometer in a 10 cm cell at 630 nm. A calibration curve was constructed using standard solutions made from dry ammonium chloride ( 0.5 to 50 μmol N/L), which were carried through the same procedure. The relative error of the method was of 5.5% and the detection limit of 0.7 μg N/L. The relative standard deviation of the analysis was of 5 %.

The most sensitive methods for the nitrate determination in seawater are based on the reduction of nitrate to nitrite which can be then determined spectrophotometrically following the addition of sulphanilamide and n- (1-naphthyl ethylene diamine) solutions and the formation of an azo dye (Grasshoff, 1976). For our samples, nitrite and nitrate were analyzed together following elution of the solution through a glass Pasteur pipette filled with copper-coated cadmium granules and the quantitative reduction of nitrate into nitrite. The cadmium column was activated with an ammonium chloride buffer and kept brimful with this solution during working pauses, to prevent air contact with the copperized cadmium granules. For the analysis, 15 mL of the ammonium chloride buffer were added to 5 mL of diluted samples (1:5) and thoroughly mixed. Samples were allowed to pass through the column at a rate of 5 mL per minute. The first 10 mL were discarded whereas 0.45 mL of each reagents were added to the following 10 mL collected. The azo dye color was allowed to develop completely (20 to 30 minutes) and the absorbance measurements were done with a Bausch and Lomb Spectronics 21 spectrophotometer at a wavelength of 540 nm in a 1 cm cell. Calibration were performed with a stock standard solution made with dry potassium nitrate (0,5 to 50 μmol N/L). The reduction column efficiency was better than 90 % and the relative standard deviation of the measurements was on the order of 5%. Finally, the detection limit of the instrument for this procedure was of 4.2 μg N/L.

# 4.0 RESULTS:

## 4.1 Sediment analysis:

The sediment cores collected at Sag-15'94 and 95 were characterized by the presence of black sediments below a thin (~3-4 mm) brown oxidized layer, reflecting the high biochemical oxygen demand and the rapid onset of bacterial sulphate reduction in these sediments. The presence of benthic organisms such as tubificid worms, at depths reaching 20 centimeters, attested to the importance of bioturbation processes at this station.

### 4.1.1 Organic Matter:

The organic carbon concentration and reactivity determine the metabolic activity taking place in the sediment column. The concentrations of total, inorganic and organic carbon ($C_{TOT}$, $C_{inorg.}$, $C_{org.}$) as well as total nitrogen ($N_{TOT}$) and C/N at Sag-15 are presented in Appendix 1. The organic carbon concentrations in the cores from Sag-15'94 and 95 vary between 1.43 and 2.67 wt% (Figure 4.1). The concentrations remain constant or increase slightly in the first two centimeters of the sediment surface, below which they decrease rapidly to reach minimum values at a depth of 4.5 cm at Sag-15'94 and 6 cm at Sag-15'95. This minima is followed by a linear increase at Sag-15'95 to a depth of 14 cm, whereas a subsequent decline can be observed at this site in the depth interval of 14 to 20 cm. The organic carbon concentrations at Sag-15'95 remain more less constant below this depth. On the other hand, the organic carbon concentrations at Sag-15'94 reincrease to a depth of 7 cm, decreasing afterwards to attain a second minima at a depth of 11 cm. Organic matter concentrations at this site remain relatively constant over the next 6 cm, rising significantly deeper in the core. The presence of these interlayerings of organic-poor

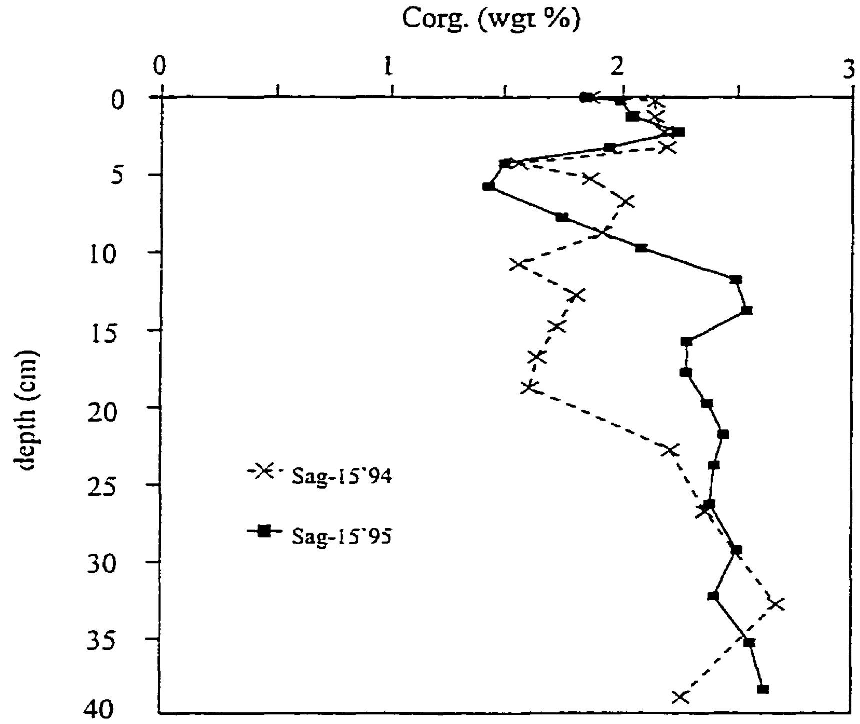

Figure 4.1. Vertical distribution of organic carbon in Saguenay Fjord sediments at Sag-15.

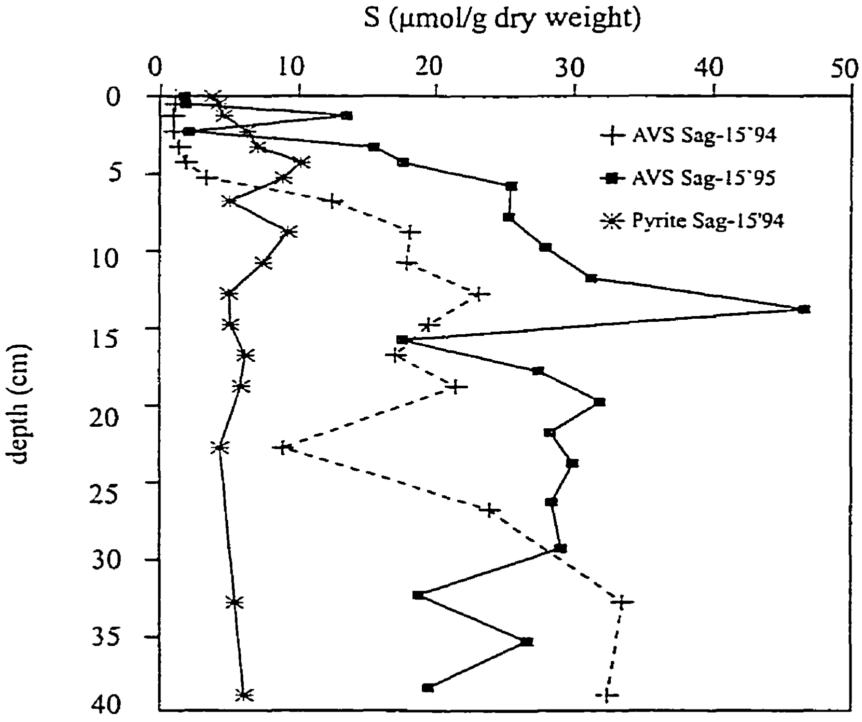

Figure 4.2. Vertical distribution of AVS and pyrite in Saguenay Fjord sediments at Sag-15.

sediments can be interpreted as the result of the deposition of organic-poor post-glacial marine clays from landslides and slumping events (Mucci and Edenborn, 1992). The Saguenay Fjord is characterized by very steep and polished walls resulting from the repeated advance of glaciers along its axix. As a consequence of its steep topography, slumping and submarine slides triggered by seismic or strong hydrologic events result in frequent reworking of the sediments, particularly on the landward slope of the interior basin where Sag-15 is located.

The C/N ratio of the organic matter in the sediments is elevated, with a minimum value of 21.9 and a maximum value reaching 30.4 (Appendix 1). These results are consistent with the conclusion of previous studies which highlight the predominant terrestrial origin of the organic matter accumulating in these sediments as well as the contribution from paper, pulp, and sawmill outfalls upstream (Schafer et al., 1990; Mucci and Edenborn, 1992; Louchouarn et al., 1997). The C/N ratio profiles at both stations are similar in the first 20 centimeters and display maxima near a depth of 5 cm as well as between 13 and 20 cm. This observation is consistent with the hypothesis of episodic deposition of highly refractory organic-poor marine clays during landslide or slumping events (Mucci and Edenborn, 1992). The material found in the depth interval of 13 to 20 cm probably originated from the St-Jean Vianney landslide deposit. This layer would have been, however, remobilized following its deposition, as the sedimentation rates at this station ($\cong$ 0.3 cm $y^{-1}$) (Smith and Walton, 1980; Barbeau et al., 1981; Silverberg et al., 1986) are not compatible with the emplacement of the organic-poor marine clay layer in the cores.

### 4.1.2 AVS and pyrite:

The AVS vertical distribution patterns at Sag-15'94 and 95 are very similar in the first 25 centimeters of the cores, although the concentrations at Sag-15'95 are larger throughout most of the core (Appendix 1, Figure 4.2 ). The iron monosulphide concentrations remain relatively low to a depth of 5 cm, increasing rapidly downcore to attain a peak near 13 cm. This first maxima is followed by a decrease, more pronounced at Sag-15'95, and a subsequent increase reaching a second peak in the depth intervals of 18-20 cm for Sag-15'94 and 19-21 cm at Sag-15'95 (Figure 4.2). Below this depth, the AVS profiles at Sag-15'94 and 95 exhibit different behaviours as the concentrations at Sag-15'94 tend to increase downcore, whereas the concentrations at Sag-15'95 decrease slightly to the bottom of the core (Figure 4.2). The two peaks observed at approximately 13 and 20 cm below the sediment-water interface represent the upper and lower boundaries of a clay layer, which may have originated from the St-Jean Vianney landslide. They reflect the rapid precipitation as AVS of, respectively, the Fe released from the landslide material which diffused up and of the Fe trapped as oxyhydroxides at the original sediment-water interface (Mucci and Edenborn, 1992).

The pyrite content of the sediments at Sag-15'94 are much lower than the AVS concentrations (Appendix 1, Figure 4.2). The AVS-S: $FeS_2$-S ratios at this station vary between 0.4 and 6.20. These observations confirm the results obtained by Gagnon et al. (1995) and the presence of anomalously high AVS concentrations in the Saguenay Fjord sediments. The formation of authigenic pyrite depends upon the amount and quality of the organic matter as well as the availability of reactive iron and sulphate in the sediments (Gagnon et al., 1995). As the Saguenay

Fjord sediments are rich in organic matter and reactive-Fe, these parameters do not limit pyrite formation in these sediments. On the other hand, the availability of reactive Fe and the rapid precipitation of AVS in the Fjord sediments may suppress the build up of reduced sulphur in the porewaters, as well as the establishment of a strong $H_2S$ gradient. This, in turn, would restrict the formation of soluble intermediate reduced sulphur species required for the formation of pyrite (Gagnon et al., 1995; Rickard, 1997). The lack of soluble reduced intermediate species would limit the conversion of AVS to pyrite in these sediments, explaining the observed high AVS:$FeS_2$ ratios (Gagnon et al., 1995; Rickard, 1997).

At Sag-15'94, the pyrite concentrations are nearly constant throughout the core, although the presence of small peaks near 5, 10 and 17 cm from the surface, coinciding with lower organic matter concentrations can be observed (Appendix 1, Figure 4.2). The pyrite maxima observed at 17 cm is also coincident with the minima displayed, at both stations, in AVS concentrations (Figure 4.2). This observation was also reported by Mucci and Edenborn (1992), as they detected maximum pyrite and minimum AVS concentrations in the St-Jean Vianney landslide layer. The authors stated that most of the pyrite present in the landslide layer could be of detrital origin and may have been deposited with the landslide material. The occurrence of landslides and slumping events, resulting in the deposition of organic-poor marine clays, could, therefore, explain the presence of increased pyrite concentrations, coinciding with lower organic carbon and AVS concentrations, in the sediments.

### 4.1.3 Total and 1N HCl–extractable metal distribution profiles:

Authigenic Fe oxyhydroxides and sulphides are important sinks for many trace metals (i.e. As, Hg, Pb, Cu , Ni etc.) (Inoue and Munemori, 1979; Klinkhammer, 1980; Luoma and Davis, 1983; Tessier et al., 1985; Belzile and Lebel, 1986; Jean and Bancroft, 1986; Peterson and Carpenter, 1986; Belzile, 1988; Gobeil and Silverberg, 1989; Hyland et al., 1990; DeVitre et al., 1991; Huerta-Diaz and Morse, 1992; Arakaki and Morse, 1993; Morse and Arakaki, 1993; Morse, 1994; Matty and Long ,1995). The 1N HCl extractable–Fe represents the fraction of Fe in marine sediments which readily reacts with dissolved sulphide to form various Fe sulphide minerals, including Fe monosulphides and pyrite (Rapin, 1986; Canfield, 1989; Huerta-Diaz and Morse, 1990, 1992). The 1N HCl extractable trace metal profiles therefore represent the reactive fraction of these trace metals which are available for participation in chemical reactions during early diagenesis (Huerta-Diaz and Morse, 1990). These trace metals would also be affected by redox-controlled reactions occurring as a result of sediment resuspension as well as bioturbation processes.

The vertical distributions of total and 1N HCl extractable trace metals in the solid phase of the Saguenay Fjord sediments at Sag-15'94 and 95 are noticeably different, reflecting the spatial heterogeneity of these sediments as well as the non steady-state sedimentation regime in this environment (Figures 4.3 and 4.4). The Saguenay Fjord, as mentioned previously, is characterized by very steep and polished walls, onto which poorly consolidated muds accumulate, making it a propicious site for slumping events. Transport of landslide material from

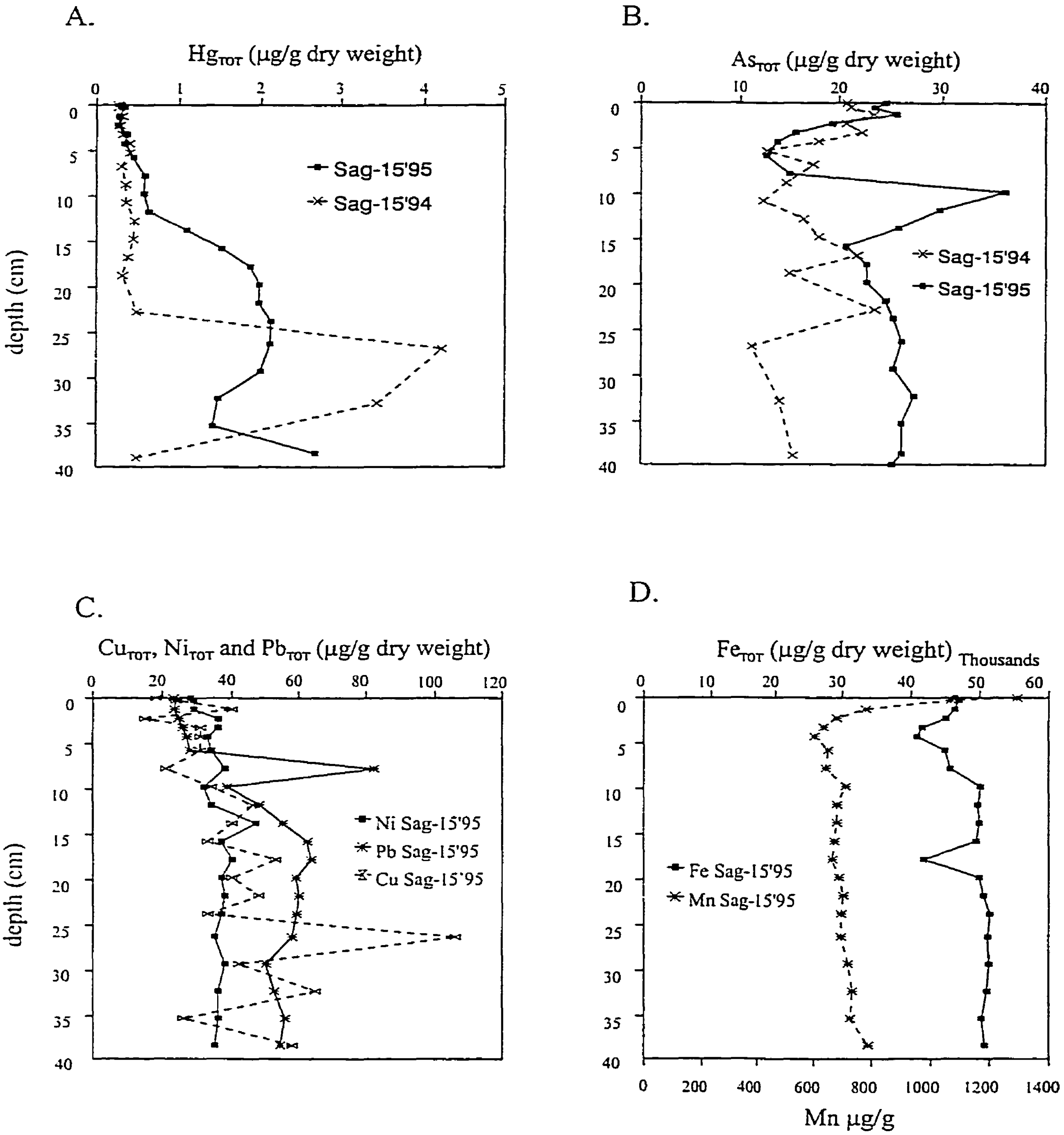

Figure 4.3. Distribution of total (A) Hg, (B) As, (C) Cu, Ni and Pb, (D) Fe and Mn in the sediments of the Saguenay Fjord at Sag-15.

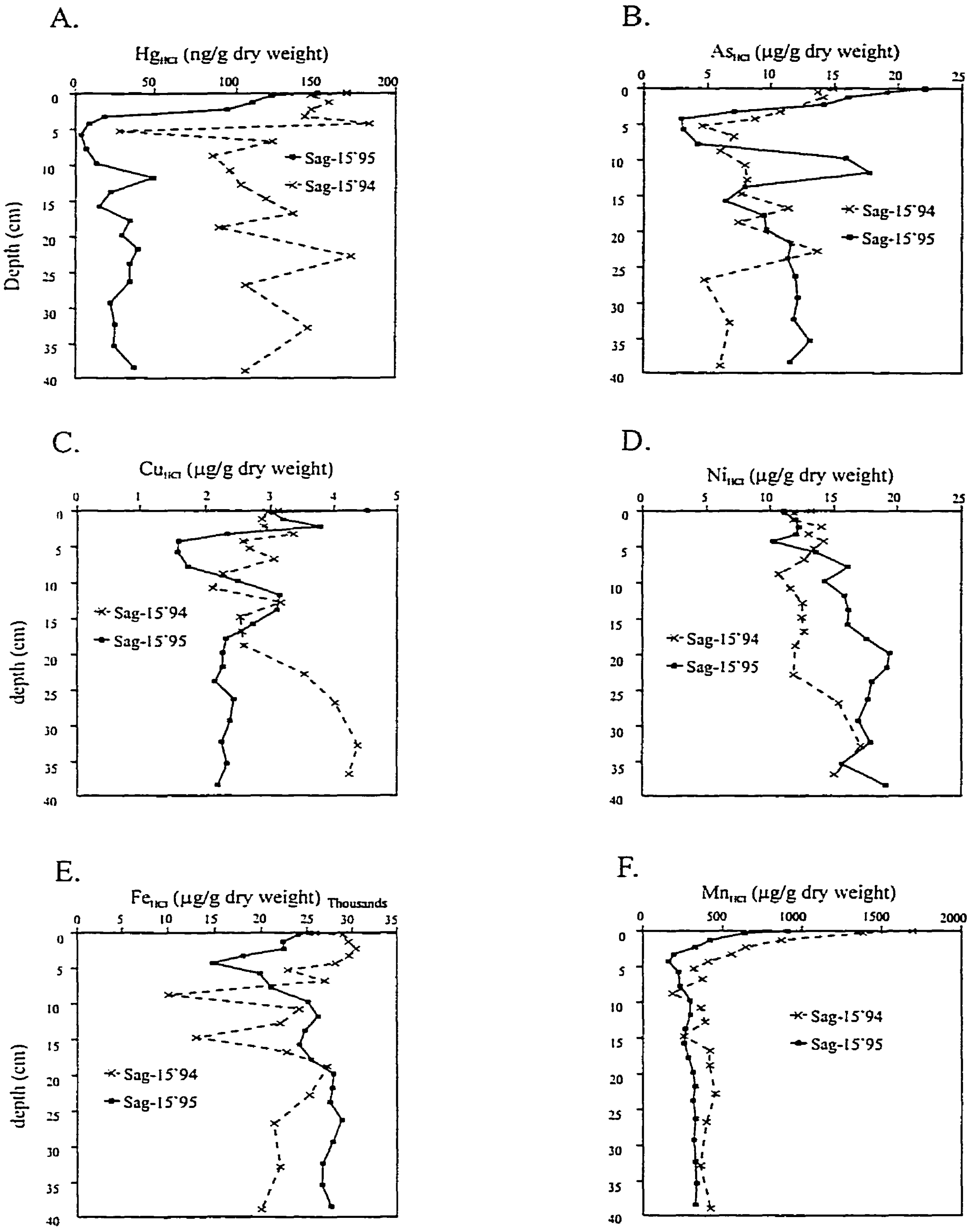

Figure 4.4. Distribution of 1N HCl-extractable (A) Hg, (B) As, (C) Cu, (D) Ni, (E) Fe and (F) Mn in the sediments of the Saguenay Fjord at Sag-15.

upstream as well as submarine slumping in this area of the fjord have led to this spatial heterogeneity and the non steady-state remobilization of redox-sensitive trace metals in the sediments (Mucci and Edenborn, 1992). Nevertheless, in spite of these episodic depositional events, some similarities in the vertical profiles of certain trace metals can still be observed and be related to their analogous diagenetic behaviours. Furthermore, in some cases, the vertical distribution of total trace metals in the sediments might even reflect their historic enrichment in this environment. The vertical profiles of total and 1N HCl-extractable trace metals at Sag-15'94 and 95 are reproduced, respectively, in Figures 4.3 and 4.4 and tabulated in Appendix 2.

### *4.1.3.1 Fe and Mn :*

The total Fe and Mn profiles clearly demonstrate a surficial enrichment, as a result of the accumulation of detrital and authigenic oxyhydroxides. Below the oxic surface layer, $Fe_{TOT}$ and $Mn_{TOT}$ concentrations decrease rapidly reaching minimum values at around 5 cm. They remain fairly constant or increase slightly deeper in the sediments, with the exception of a $Fe_{TOT}$ minima at 18 cm depth (Figure 4.3D).

As expected, the 1N HCl-extractable Fe and Mn profiles display a more pronounced surficial enrichment due to the precipitation of authigenic oxyhydroxides (Figure 4.4E,F). The authigenic phases are concentrated at or near the redox boundary following the upward diffusion of their reduced species released in the anoxic sediments. Beneath the sediment surface both 1N HCl-extractable Fe and Mn concentrations decrease abruptly to attain a minimum at a depth of approximatively 5 cm, following the reduction and dissolution of their oxyhydroxides as a consequence of suboxic diagenesis (Figure 4.4E,F).

The maximum surficial enrichment in $Fe_{HCl}$ at Sag-15'94 is observed slightly deeper (2-3 cm interval) than at Sag-15'95, where it is located very close to the sediment-water interface (Figure 4.4E). Moreover, the minimum concentration in $Mn_{HCl}$ is found one centimeter deeper at Sag-15'94 than at Sag-15'95 (Figure 4.4F). These observations indicate that the redox sequence at Sag-15'95 is more compressed than at Sag-15'94, suggesting a greater biological oxygen demand at Sag-15'95. This may result from higher sedimentation rates or an increase in the quantity as well as reactivity of the organic matter accumulating in the surface sediments at this site. Since the organic matter concentrations and C/N ratios of the surface sediments recovered at both sites are very similar, this phenomenon is most likely the consequence of higher sedimentation rates at Sag-15'95. The occurrence of greater AVS concentrations at this site throughout the core further supports this conclusion (Figure 4.2). On the other hand, these variations could also reflect seasonal changes in the accumulation rates, since the cores were collected during the fall at Sag-15'94 and the spring at Sag-15'95.

Whereas $Mn_{HCl}$ concentrations remain low and nearly constant below the first 5 centimeters and throughout the core, $Fe_{HCl}$ profiles display many excursions, but generally maintain fairly high concentrations downcore and within the anoxic zone (Figure 4.4E,F). $Fe_{HCl}$ minimum concentrations are found at 9 cm beneath the sediment-water interface at Sag-15'94, and near 16 cm at both stations (Figure 4.4E). On the other hand, $Fe_{HCl}$ concentration peaks can be observed at 7 cm from the sediment surface at Sag-15'94, and near 12 and 20 cm at both stations (Figure 4.4E). These excursions are correlated with the organic matter and AVS vertical distributions discussed earlier, supporting the hypothesis of the occurrence of several slumping events at this station (Figure 4.1 and 4.2). The $Fe_{HCl}$ maxima would correspond to the upper and lower boundaries of the landslide layers, reflecting the rapid precipitation of Fe (II) as AVS in these horizons. On the other hand, the $Fe_{HCl}$ minima which occur within the landslide layers would reflect the original composition of the source material or the remobilization of $Fe_{HCl}$ under anoxic but sulphide-poor conditions.

In a recent study on the influence of an organic-poor landslide deposit on the early diagenesis of Fe and Mn in the Saguenay Fjord sediments, Mucci and Edenborn (1992) stated that the diagenetic remobilization of Mn appeared to be unaffected by the deposition of the landslide material. The authors suggested that reduced Mn diffused freely to the newly established redox boundary and precipitated as oxyhydroxides. In contrast, the reduced Fe was rapidly precipitated as AVS at the landslide upper and lower boundaries. The $Mn_{HCl}$ profiles determined in this study at Sag-15'94 and 95, however, show evidence of the occurrence these slumping events, albeit to a lesser extent than other markers (i.e., organic matter, AVS, $Fe_{HCl}$, and pyrite) (Figures 4.1, 4.2 and 4.4E). $Mn_{HCl}$ minima can be observed at depths of 9 and 16 cm at Sag-15'94 which correspond to the $Fe_{HCl}$ minima described earlier. The latter could have resulted from the reductive dissolution of Mn oxyhydroxides and diffusion of Mn(II) out of the landslide material.

#### *4.1.3.2 Trace metals:*

The vertical distribution of Hg, as well as Pb, unlike most trace metals, were believed to be little affected by early diagenetic processes (Bruland et al., 1974; Loring, 1975; Loring and Bewers, 1978; Shirahata et al., 1980; Barbeau et al., 1981; Cossa and Desjardins, 1984; Gobeil and Cossa, 1994). Their total solid-phase profiles have, thus, often been used to reconstruct the historical record of the aquatic environment contamination (Bruland et al., 1974; Barbeau et al., 1981; Loring, 1981; Smith and Loring, 1981; Gobeil and Cossa, 1993). Recent studies, however, demonstrated that both Pb and Hg are susceptible to some diagenetic remobilization and that their total solid-phase profiles may not always be interpretable in an historical context (Pelletier and Canuel, 1988; Gobeil and Silverberg, 1989; Matty and Long, 1995; Gagnon et al., 1996, 1997).

Nevertheless, The vertical distribution of total Hg (Figure 4.3A) appears to provide an historical record of the Hg contamination in the Saguenay Fjord by a chlor-alkali plant which was operated between 1947 and 1976. Both Sag-15'94 and 95 display lower Hg concentrations in the first 12 centimeters, increasing dramatically below this depth to reach a maximum at around 25 cm. The Hg peak could correspond to the period of maximum discharge from the plant before the implementation of new government regulations in 1971 and would be located below the 1971 landslide deposit layer (Gagnon et al., 1996b, 1997). On the other hand, the lower concentrations in the upper cores would reflect the decrease in the amount of Hg released to the Fjord after this period. The sedimentation rate determined at this station (~ 0.3 cm $y^{-1}$), however, are not compatible with this hypothesis (Smith and Loring, 1980; Barbeau et al., 1981). According to the data reported in the literature, the Hg-contaminated sediments at Sag-15 should have been buried under 7 cm of recent sediments. This discordance may infer that the sedimentation rates prevailing at this station are higher than those reported in the literature, due in part to the complexity of its sedimentation regime (i.e., submarine slides and slumping events).

The vertical profile of total lead (Figure 4.3C) also seems to show a partial historical record of its enrichment in the Fjord sediments. Enrichment resulted from the increased utilization of leaded gasoline after the World War II. The profile of total Pb displays minimum concentrations in the first 5 centimeters of the core, which would reflect both the recent government regulations controlling the Pb content in gasoline and the rapid sedimentation rates at this station. Below this depth, Pb concentrations increase gradually reaching a maximum at the 19-21 cm interval and remaining relatively constant below. However, as it is the case for Hg, the sedimentation rates published in the literature for this station are not compatible with the $Pb_{TOT}$ profile determined in the current study.

Therefore, the total Pb and Hg profiles of the sediments collected at Sag-15'94 and 95 do not appear to have been significantly affected by early diagenetic remobilization despite their incompatibility with the accumulation rates reported for this station. These differences may, however, reflect the contribution of episodic depositional events, which are usually substracted from the sedimentation records in order to calculate the sedimentation rates. Our results instead suggest that the sedimentation rates prevailing at Sag-15, uncorrected for the episodic events, may be of 0.5 cm $y^{-1}$ .

In contrast, the other trace metals analyzed in this study, including Cu, Ni and As, are known to be strongly subjected to post-depositional remobilization during early diagenesis (Klinkhammer, 1980; Klinkhammer et al., 1982; Peterson and Carpenter, 1983; Sawlan and Murray, 1983; Carignan and Nriagu, 1985; Edenborn et al., 1986a; Westerlund et al., 1986; Belzile, 1988; Santschi et al., 1990; Shaw et al., 1990; Sundby, 1994; Lapp and Balzer, 1993). Thus, within the sampled depth interval, evidence of an anthropogenic enrichment cannot be distinguished from the solid-phase vertical distribution of these trace metals (Figure 4.3C). The total Cu concentrations in the solid sediments display a saw-toothed distribution throughout the cores, whereas total Ni concentrations remain more or less constant downcore (Figure 4.3C). The solid-phase distribution of these trace metals, however, do not show strong evidence of early diagenetic transformations. On the other hand, the total As profiles from Sag-15'94 and 95 clearly indicate the occurrence of post-depositional remobilization (Figure 4.3B).

Total As profiles at Sag-15'94 and 95 display a surficial enrichment with maximal concentrations at 1.5 cm below the sediment-water interface (Figure 4.3B). As concentrations, at both stations, decrease by a factor of 2 within the next 3 centimeters, reaching minimum concentrations at a depth of 4.5 cm from the sediment surface. Below this depth, $As_{TOT}$ concentrations at Sag-15'95 rise abruptly to attain maximum values at 10 cm depth. The origin of the latter peak, which can also be seen in the $As_{HCl}$ vertical distribution of Sag-15'95, will be discussed in the following paragraph. Following this peak, the concentrations at this site decrease almost linearly to a depth of 16 cm, after which they slowly increase downcore. On the other hand, $As_{TOT}$ distribution below 4.5 cm at Sag-15'94 display more fluctuations than at Sag-15'95 as peaks can be observed at depths of 7, 13, 17 and 23 cm, whereas minima are found at 11, 19 and 27 cm.

$As_{HCl}$ vertical distributions at Sag-15'94 and 95 parallel their respective $As_{TOT}$ profiles (Figure 4.4B). $As_{HCl}$ concentrations are greatest in the first centimeter of sediment at both stations, as a result of As remobilization and adsorption onto Fe oxyhydroxides. Their values decrease dramatically by a factor of 3 to 8, respectively, at Sag-14'95 and Sag-15'95 over the next 5 cm.

Below this depth, the $As_{HCl}$ concentrations at Sag-15'95 rise rapidly to form a peak around 10 to 12 cm depth. Following this peak, the concentrations at this site drop over the next 4 cm and gradually increase downcore afterwards. As it is the case for $As_{TOT}$ profiles, the $As_{HCl}$ distribution at Sag-15'94 exhibits more excursions that at Sag-15'95 beneath 5 cm. $As_{HCl}$ concentrations at Sag-15'94 display peaks at 7, 13, 17 and 23 cm, whereas troughs can be observed at 11, 19 and 27 cm depth.

The important peak which occurs at a depth of around 10 to 12 cm on the $As_{HCl}$ profile from Sag-15'95 could have resulted from the adsorption of As onto precipitated AVS at the upper boundary of the reworked St-Jean Vianney landslide material. Processes responsible for the accumulation of AVS at this depth have been discussed previously. The $As_{HCl}$ vertical distributions from Sag-15'94 and Sag-15'95 display notable similarities with the $Fe_{HCl}$ profiles (Figure 4.4B,E). These similarities emphasise the strong association between these metals since the fate of As in sediments is closely linked to the redox-controlled cycle of Fe (Edenborn et al., 1986a; Belzile, 1988; Gobeil, 1996).

The $As_{HCl}$ and $Hg_{HCl}$ profiles from each of the Sag-15'94 and 95 cores exhibit very similar features (Figure 4.4A,B). As it is the case for $As_{HCl}$, $Hg_{HCl}$ concentrations are highest close to the sediment-water interface, decreasing very rapidly within the first 5 centimeters of the cores by a factor of 6 at Sag-15'94, and 50 at Sag-15'95. With the exception of a peak at 12 cm, concentrations remain fairly stable below 5 cm at Sag-15'95, whereas they exhibit a more erratic behaviour downcore at Sag-15'94. Nevertheless, the $Hg_{HCl}$ profile at Sag-15'94 closely parallels the $As_{HCl}$ profile (Figure 4.4A,B).

The vertical distributions of $Cu_{HCl}$ from Sag-15'94 and 95 also present a surficial enrichment, as it was the case for Hg and As (Figure 4.4C). $Cu_{HCl}$ concentrations then decrease slightly before they increase sharply to a depth of 3 cm. Below this depth, $Cu_{HCl}$ concentrations decrease rapidly over the next few cm and rise again reaching a maxima between 12 and 14 cm as was observed in the $As_{HCl}$, $Hg_{HCl}$ profiles (Figure 4.4A to C). The latter peak, as mentioned earlier, could have resulted from the adsorption of these trace metals onto precipitated AVS at the upper boundary of the reworked St-Jean Vianney landslide material. Following this peak, $Cu_{HCl}$ concentrations remain stable throughout the core at Sag-15'95, whereas they increase steadily downcore at Sag-15'94 (Figure 4.4C).

Finally, in contrast to the $As_{HCl}$, $Hg_{HCl}$ and $Cu_{HCl}$ profiles, the $Ni_{HCl}$ (Figure 4.4D) distributions at Sag-15'94 and 95 do not show significant evidence of early diagenetic remobilization (Figure 4.4D). $Ni_{HCl}$ concentrations at Sag-15'94 exhibit several troughs in the first 20 centimeters (e.g., 2.5, 4.5 and 15), whereas they tend to increase downcore below this depth. On the other hand, $Ni_{HCl}$ concentrations at Sag-15'95 increase in the first 2 to 3 cm, after which they decrease to reach minimum values at a depth of 4.5 cm. Below this depth the concentrations rise gradually to 20 cm depth and decrease slowly in deeper sediments.

In résumé, the sediments collected at Sag-15'94 and 95 are very heterogeneous and early diagenetic processes remain difficult to describe and explain. The occurrence of episodic and catastrophic landslide events have led to a non-steady state diagenetic remobilization of redox-sensitive elements revealing the importance of sediment reworking in this environment.

Nevertheless, the profiles of $Hg_{TOT}$ and $Pb_{TOT}$ at Sag-15 appear to reflect the historical enrichment of these trace metals in the Fjord sediments. Our results, however, indicate that the sedimentation rates prevailing at this station are higher than that reported in the literature. This may be due to the non steady-state sedimentation regime of this environment. On the other hand, Cu, Ni and As concentration profiles show no evidence of anthropogenic enrichment. The total As profile exhibits strong indications of post-depositional remobilization, whereas Cu and Ni do not show significant signs of early diagenetic transformations.

Reactive Hg, As and Cu are generally enriched in the upper part of the cores and are probably associated with detrital and authigenic Fe and Mn oxyhydroxides (Figure 4.4) (Inoue and Munemori, 1979; Klinkhammer, 1980; Luoma and Davis, 1983; Tessier et al., 1985; Edenborn et al., 1986a; Peterson and Carpenter, 1986; Belzile, 1988; Gobeil and Cossa, 1993; Gobeil, 1996; Gagnon et al, 1997). Cu and Hg may also be intimately associated with organic matter, with which they are delivered to the sediments (Loring, 1975; Lorin and Bewers, 1978; Klinkhammer et al., 1982; Sawlan and Murray, 1983; Pelletier and Canuel, 1988; Gerringa, 1990; Shaw et al., 1990; Gobeil and Cossa, 1993; Matty and Long, 1995; Gagnon et al., 1997; Bono, 1997). The nature of their specific associations to these solid phases remains, however, difficult to discern. The Fe and Mn 1N HCl extractable profiles indicate a very compressed redox reaction sequence and the rapid onset of sulphate reduction within the first few centimeters of the sediment column.

Below the sediment surface, trace metal HCl-extractable concentrations decrease, as a consequence of Fe and Mn oxyhydroxides dissolution as well as organic matter degradation, reaching minimum concentrations at 5 cm. This depth would represent the onset of sulphate reduction in the sediments and the rapid reduction of reactive Fe and Mn in the presence of reduced sulphur (Canfield, 1989). These low HCl-extractable trace metal concentrations, at this depth, could also be enhanced by the presence of an organic-poor sediment layer, which can be observed on the organic carbon vertical distribution of both stations (Mucci and Edenborn, 1992) (Figure 4.1).

Deeper in the cores HCl-extractable trace metals display peaks just above and below the organic-poor layers, as well as minimum values within these layers, appearing in some cases simultaneously with those observed in the $Fe_{HCl}$ and AVS vertical distributions (Figures 4.4E and 4.2). These observations are consistent with those reported by Mucci and Edenborn (1992) in a recent study on the influence of an organic-poor landslide deposit on the early diagenesis of Fe and Mn in the organic-rich sediments of the Saguenay Fjord. The authors proposed that Fe and trace metals were immobilized in Fe monosulphides, near the upper boundary of an organic-poor landslide layer, following the upward migration of the redox boundary near the newly established sediment-water interface. On the other hand, Mucci and Edenborn (1992) suggested that these metals were also trapped in Fe monosulphides, at the lower boundary of the landslide layer, as the Fe oxyhydroxides accumulated at the original sediment-water interface were reduced due to the rapid onset of sulphidic conditions following the depositional event.

### 4.2 Resuspension experiments:

The results of the resuspension experiments conducted in the laboratory are presented and described in the next pages (Appendix 4, Figures 4.5 to 4.10). The duration of the experiments is shown on the x axis of the figures, on a logarithmic scale, in order to completely display the behaviour of the metals through time. The same linear scales were used for all the experiments to report the concentrations of dissolved trace metals and organic carbon in the slurries in order to facilitate comparisons between each experiment. Only the scales of the dissolved Hg concentrations in experiments #9 and 12 (Figures 4.6 and 4.10) differ from the others, whereas the total nitrogen concentrations from experiments # 8, 9 and 10 (Figures 4.6, 4.7 and 4.9) could not be presented on the same scale due to large differences in the results. Furthermore, the Fe concentrations displayed in all the figures were divided by a factor of 5 to simplify the presentation of the results. The sediment:water ratio of the slurries varied between 1/25 and 1/30 (g/mL) in all the resuspensions, with the exception of #10 where the ratio was 1/22 (g/mL). The concentrations presented in the figures were not corrected to account for these sediment:water ratio variations. The trace metal and DOC concentrations of the original seawater varied from 0.5 to 5.8 µg/L for Fe, 0.14 to 49.4 µg/L for Mn, 0.3 to 0.99 µg/L for As, 0.23 to 2.85 µg/L for Cu, 0.36 to 7.89 µg/L for Ni, 0.18 to 3.72 µg/L for Pb, 45 to 88 ng/L for Hg, 1.9 to 3.2 mg/L for DOC, and 127 to 251 µg/L of N (see Appendix 4). Finally, results of the experiments are presented according to the depth at which the original sediments were collected (see Table 3.1).

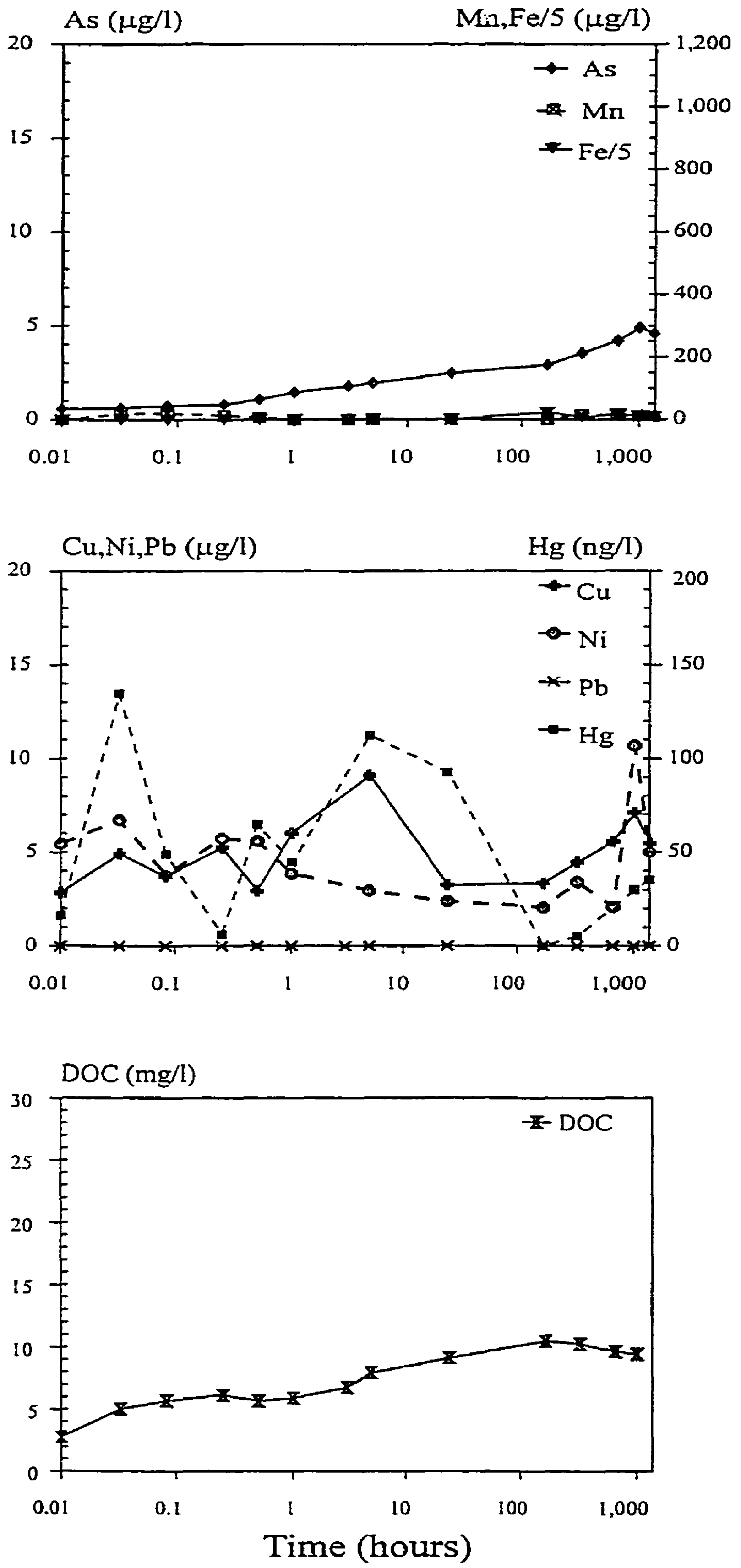

Figure 4.5. Dissolved metals and DOC concentrations remobilized from resuspension experiment #11, sediments taken from the depth interval of 0-0.5 cm at Sag-15'95.

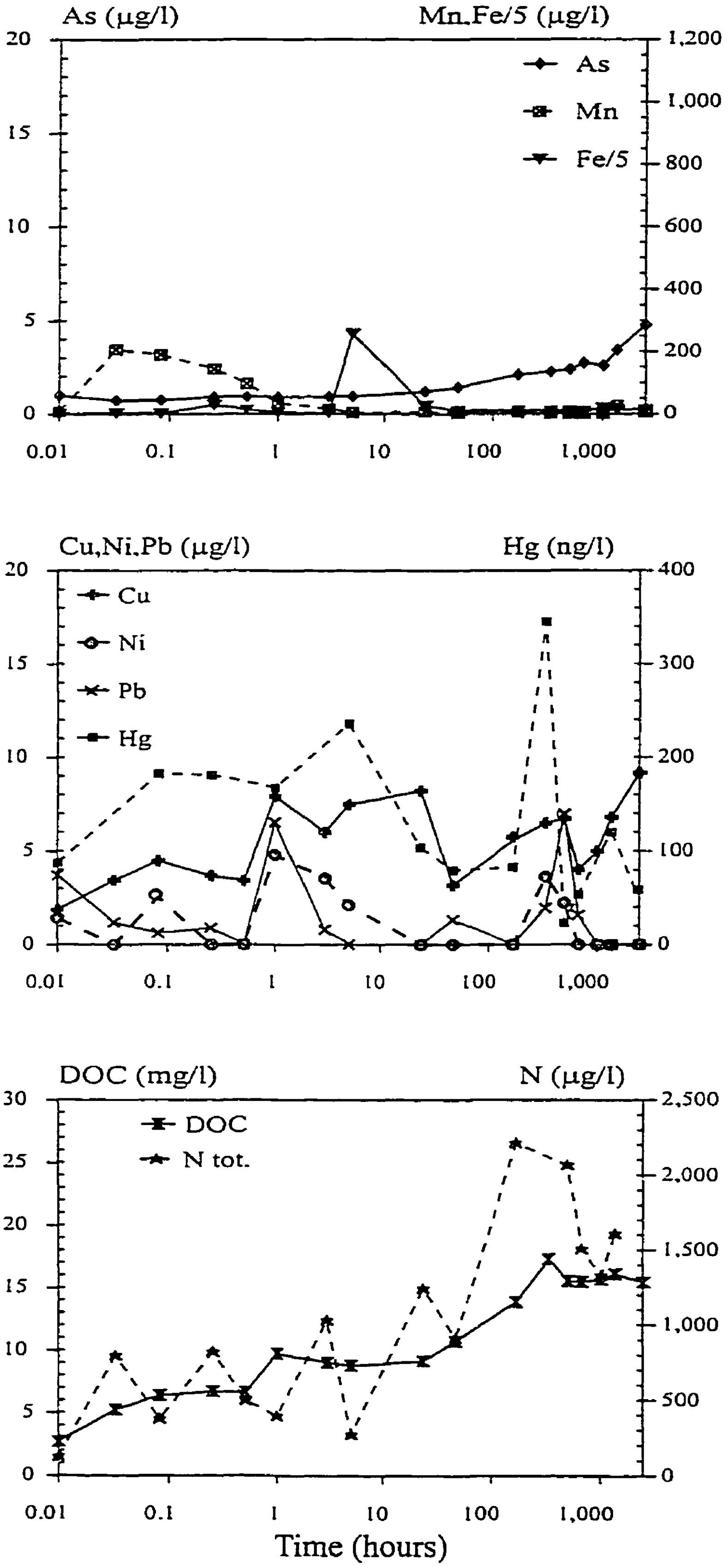

Figure 4.6. Dissolved metals, DOC and $N_{TOT}$ concentrations remobilized from resuspension experiment #9, sediments taken from the depth interval of 0.5 - 1.0 cm, at Sag-15'94.

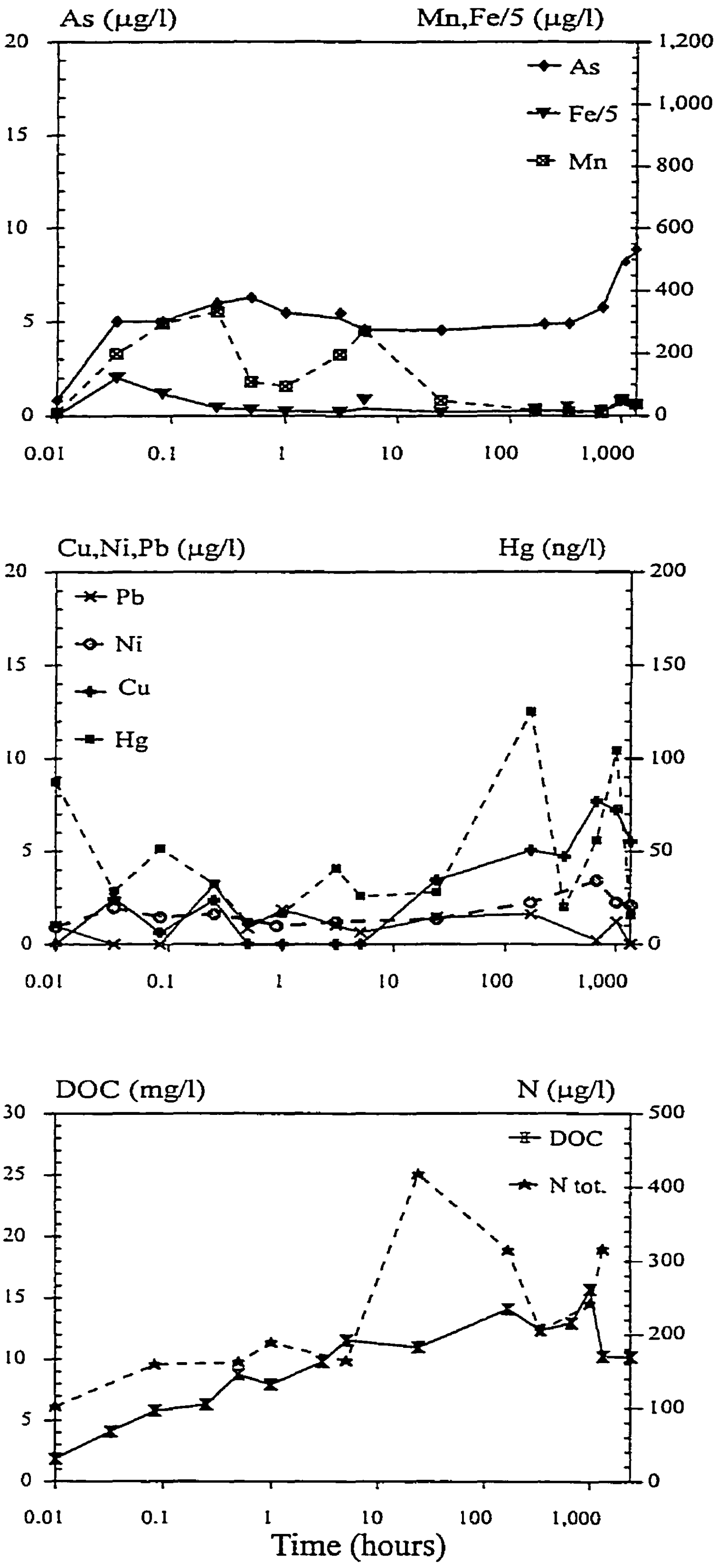

Figure 4.7. Dissolved metals, DOC and $N_{TOT}$ concentrations remobilized from the resuspension experiment #10, sediments taken from the depth interval of 3.0-4.0 cm at Sag-15'95.

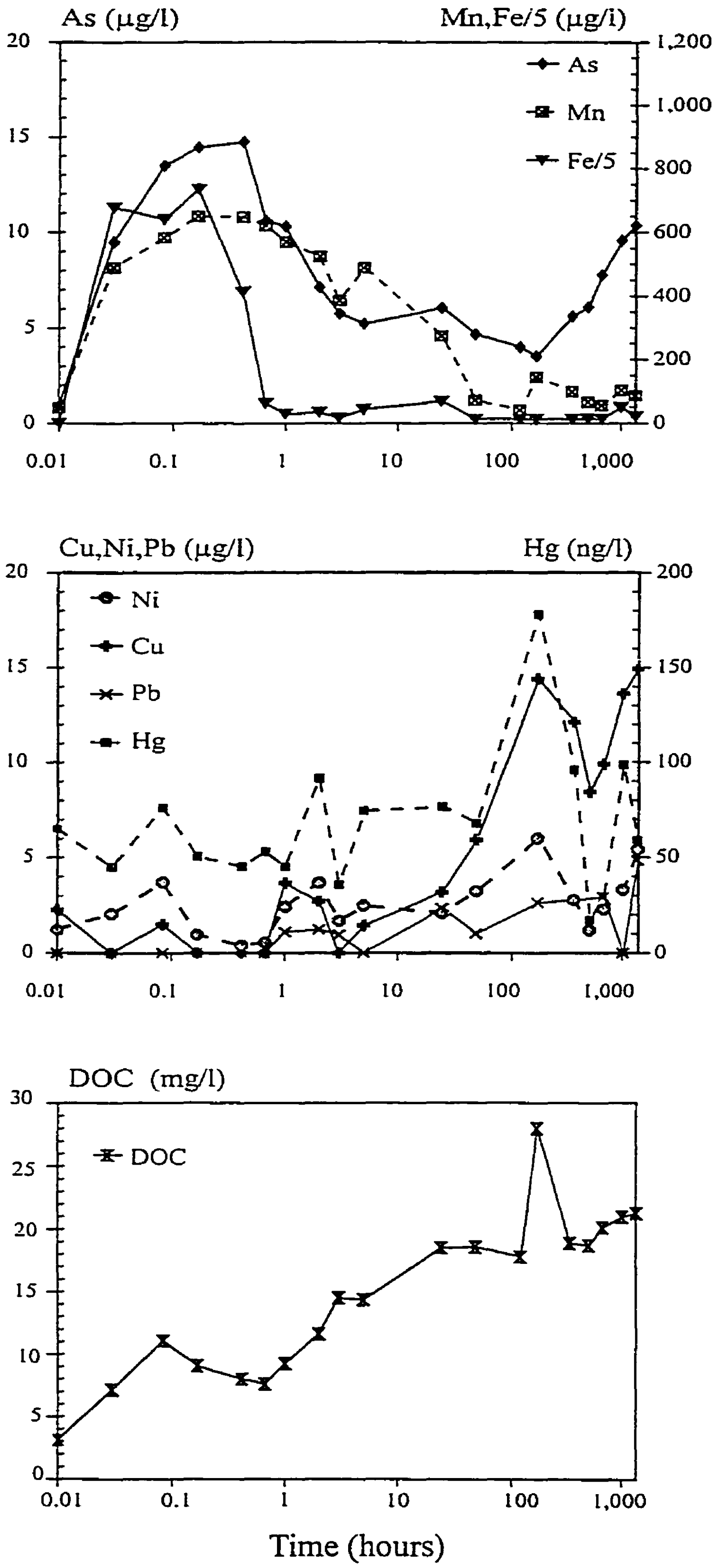

Figure 4.8. Dissolved metals and DOC concentrations remobilized from the resuspension experiment #7, sediments were taken from the depth interval of 13-15 cm at Sag-15'95.

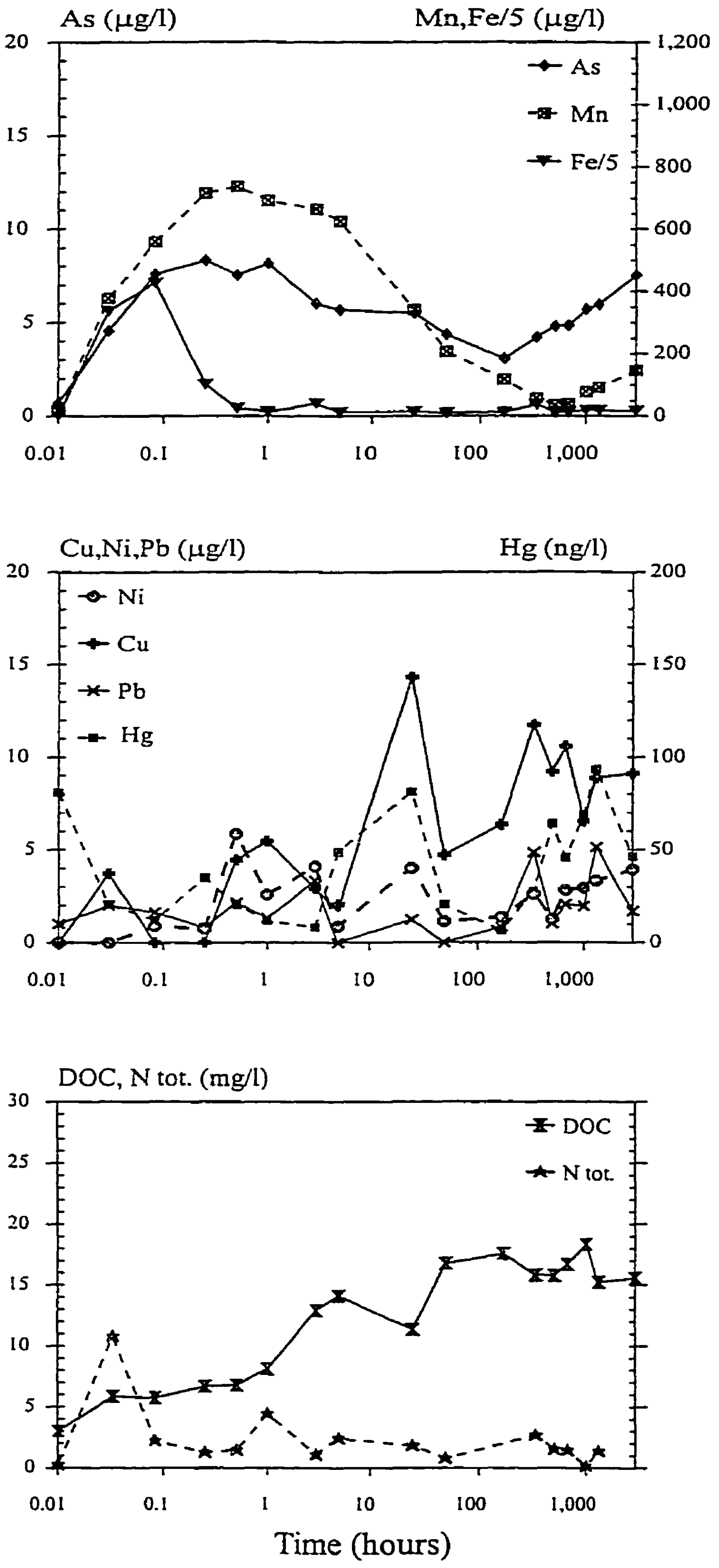

Figure 4.9. Dissolved metals, DOC and $N_{TOT}$ concentrations remobilized from the resuspension experiment #8, sediments taken from the depth interval of 19.0-20.0 cm at Sag-15'95.

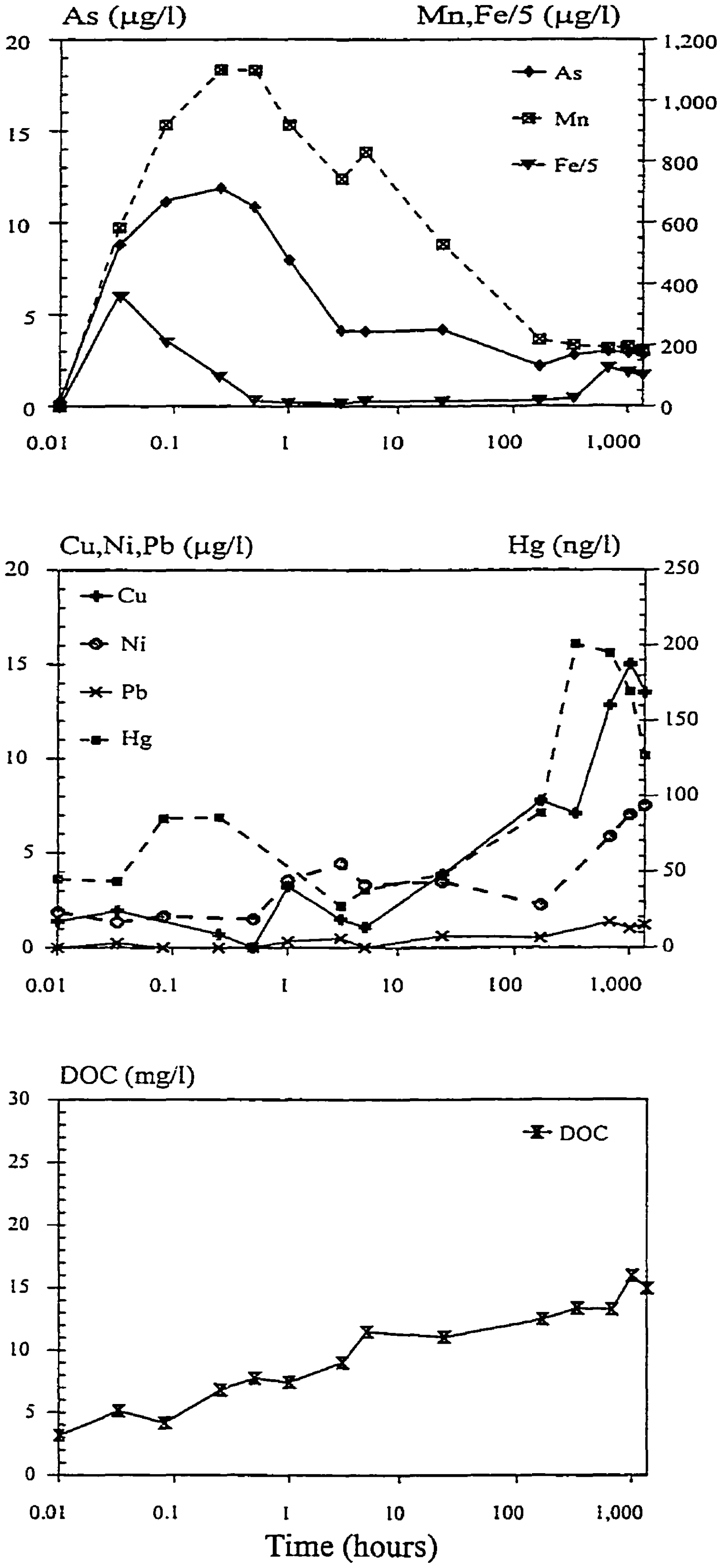

Figure 4.10. Dissolved metals and DOC concentrations remobilized from the resuspension experiment #12, sediments taken from the depth interval of 34.0-37.0 cm at Sag-15'95.

### 4.2.1 Mn and Fe:

The resuspension experiments performed with oxic and suboxic sediments did not give rise to any significant Fe and Mn remobilization (Figures 4.5 and 4.6). Resuspension # 11, conducted with oxic sediments (i.e., the 0-0.5 cm interval), revealed no Fe and Mn remobilization, as their concentrations in the dissolved phase remained at low levels throughout the experiment (Appendix 4, Figure 4.5). Similarly, no substantial remobilization of Fe occurred in experiment #9 carried out with sub-oxic sediments (i.e., the 0.5-1 cm interval), but a small amount of Mn was released to solution (Figure 4.6). Dissolved Mn concentrations attained maximum values at 0.03 hour (2 minutes) and declined to reach steady-state concentrations (~ 5 μg/L) within the first hour. These concentrations prevailed until the end of the experiment.

The results from the resuspension experiments performed with anoxic sediments (i.e. sediments recovered at depths >3 cm ) differ considerably from the ones described above, as they are charactarized by important Fe and Mn remobilizations (Figures 4.7 to 4.10). Dissolved Fe concentrations in these slurries increased very rapidly to attain maximum values between 0.03 and 0.25 hour (2 and 15 minutes) after the exposure of the sediment to the seawater solution. Following this release, concentrations decreased rapidly and remained at relatively low levels, between 45 to 60 μg/L, over the following 2 to 3 weeks (≅ 300 to 500 hours). These concentrations were, nevertheless, one order of magnitude higher than those measured in the original seawater. A small increase in dissolved Fe is observed towards the end of the experiments, after 3 to 6 weeks (≅ 500 to 1000 hours).

The release of Mn to solution during these experiments occurred over a longer period of time. Maximum concentrations were attained 0.25 to 0.5 hour (15 to 30 minutes) following resuspension of the sediment and decreased slowly subsequently to reach stable levels after nearly one week (≅ 170 hours) (Figures 4.7 to 4.10). In most cases, however, the slow decrease was ponctuated by a sharp negative gradient between 1 and 3 hours, after which concentrations partially rebounded and continued their progressive fall. This erratic behaviour was more pronounced in experiment #10 (Figure 4.7). Like Fe, dissolved Mn concentrations increased slightly by the end of these resuspension experiments.

### 4.2.2 Trace metals:

#### *4.2.2.1 Arsenic:*

As it was the case for Fe and Mn, the behaviour of As in resuspension experiments # 11 and 9, conducted with oxic and sub-oxic sediments (Figures 4.5 and 4.6), contrasts from those carried out with anoxic sediments (Figures 4.7 to 4.10). However, unlike Fe and Mn for which little or no remobilization occurred, in both the oxic and suboxic sediment resuspension experiments, dissolved As concentrations increased progressively with time.

Arsenic was strongly remobilized during the experiments performed with anoxic sediments (Figures 4.7 to 4.10), and its behaviour closely resembled that of Mn, as their concentrations evolved in parallel through time. As concentrations in solution reach maximum values between 0.25 and 0.5 hour (15 and 30 minutes) after resuspension and decreased afterwards to attain minimum values, around 3 µg/L, a week after (170 hours). During the following weeks, the concentrations increased gradually until the end of the experiments (≅ 335 to over 1000 hours).

This progressive release of As was particularly notable in resuspensions # 7 and 8 (Figures 4.8 and 4.9). Moreover, the dissolved As concentrations in the last two samples withdrawn from experiment # 10 were greater than the peak values observed early on in the experiment (Figure 4.7). The As remobilization appeared to be intimitaly related to that of Fe and Mn during the resuspension of anoxic sediments into oxygenated seawater.

#### *4.2.2.2 Copper, Ni, Pb and Hg:*

The behaviours displayed by Cu, Ni, Pb and Hg during all the resuspension experiments differed significantly from that of As, Mn and Fe (Figures. 4.5 to 4.10). The concentration of these trace metals in solution were much more variable and erratic throughout each experiment. In contrast to As, Mn and Fe, no systematic differences could be noted between results of the resuspension experiments carried out with oxic, suboxic, and anoxic sediments. Nevertheless, similarities in the behaviour of Cu, Ni, Pb and Hg could still be discerned.

Dissolved Cu, Ni and Hg concentrations peaks were observed in all the experiments between 0.03 and 0.25 hour (2 and 15 minutes) after the beginning of the resuspensions (Figures. 4.5 to 4.10). A lead concentration peak appeared 0.03 to 0.25 hour (2 to 15 minutes) following the resuspension of the sediment in experiments # 8, 9 and 10 (Figures 4.6, 4.7 and 4.9).

The experiments conducted with suboxic and anoxic sediments, with the exception of experiment # 10, exhibited a second maxima of Cu and Ni concentrations in solution between 0.5 and 2 hours (30 min. – 2 h.) after resuspension (Figures 4.6, 4.8–4.10). Lead concentrations also showed a second peak between 0.5 and 2 hours (30 min.– 2 h.) in these experiments as well as in resuspension #10 (Figure 4.7), whereas Hg concentrations only display a maxima in this time interval in the slurries of resuspension experiments # 7, 10 and 11 (Figures 4.5, 4.7 and 4.8).

Dissolved Cu and Hg concentration maxima could be seen in experiments # 11 and 9, conducted with oxic and suboxic sediments, 5 hours after resuspension of the sediments (Figures 4.5 and 4.6). Both Cu and Hg concentrations decreased significantly afterwards to reach minimum concentrations at 24 hours and 168 hours (1 week), respectively, from the beginning of these experiments.

During the resuspensions conducted with anoxic and suboxic sediments, Cu, Ni, Pb and Hg concentrations in the slurries began to rise approximatively 5 hours after exposure of the sediments to the seawater solution and systematically until the end of the experiments (Figures 4.6 to 4.10). With the exception of experiment #12 (Figure 4.10), the increase of dissolved trace metal concentrations was, however, ponctuated with significant drops in the second and third week (≅335 and 500 hours) of the resuspension. An increase in Cu, Ni and Hg concentrations was also observed one week after the beginning of the resuspension conducted with oxic sediments (i.e., experiment #11), which prevailed over the next five weeks (≅ 1000 hours) of the experiment.

In résumé, Cu, Ni, Pb and Hg exhibited highly variable concentrations in the slurries during the resuspension experiments. Copper and Hg were more substantially remobilized than Ni and Pb throughout the experiments, especially after the first week of resuspension. Lead was not significantly released to solution in most of the experiments. In experiment # 11 (Figure 4.5), undetectable (< 0.18 µg/L) amounts of Pb were released to the solution, whereas in resuspension # 12 (Figure 4.10) minor but steadily increasing concentrations of Pb were measured in solution. Finally, in contrast to As, the remobilization of Hg, Cu, Ni and Pb, immediately following the resuspension of either oxic, suboxic, and anoxic sediments into an oxygenated seawater solution, did not appear to be related to that of Fe and Mn. The progressive release of these trace metals and As to the solution, after the first week of sediment resuspension, however, probably resulted from the same process, and will be discussed in more details in the following chapter.

### 4.2.3 Dissolved Organic Carbon (DOC) and Total Nitrogen ($N_{TOT}$):

The total dissolved nitrogen content of the slurry solutions was determined for experiments # 8, 9 and 10. The results of experiment # 8 (Figures 4.9) indicate a possible loss of nitrogen to the atmosphere. $N_{TOT}$ concentrations in this experiment attained maximum values 0.03 hour (2 minutes) after resuspension of the sediments, and decreased progressively afterwards. Although they show a general positive trend in time, the concentrations of $N_{TOT}$ in experiments # 9 and 10 (Figures 4.6 and 4.7) display irregular variations, unlike the DOC time-series profiles of these experiments. Due to the ambiguities mentionned above, these results are not interpreted in the discussion.

All the DOC time-series display a continuous increase in concentrations, more pronounced in the first 24 hours of the resuspension experiments. The profiles are punctuated by a number of peaks but are otherwise smooth. The peaks occurred mainly towards the end of the experiments and often coincide with those of Hg, Cu and Pb. For example, the maximum Hg concentration registered during experiment #9 coincided with the strongest DOC peak observed on the second week (≅335 hours) of the resuspension (Figure 4.6). In experiment #10, simultaneous peaks of Hg and DOC also occurred at one and 8 weeks (≅170 and 1345 hours) (Figure 4.7). Similarly, coincident peaks of Hg, Cu, Ni and DOC were observed in resuspension experiment #7 at the one week mark (170 hours) (Figure 4.8). Finally, in resuspension experiment #8 (Figure 4.9), Hg, Pb and DOC concentrations peaks appeared at 6 weeks (≅1010 hours), whereas in experiment #12 (Figure 4.10) both Cu and DOC maximum concentrations occurred after the same period.

# 5.0 DISCUSSION:

## 5.1 The resuspension experiments:

### 5.1.1 DOC:

In all the resuspension experiments conducted in this study, the DOC concentrations increased rapidly within the first 24 hours of the resuspensions, and more slowly afterwards. This is reflected by a nearly linear increase in DOC concentrations when plotted as a function of the logarithm of time (Figures 4.5 to 4.10). This behavior is akin to the kinetics of production of DOC from a single or homogeneous pool of particulate organic matter (POM). This interpretation would assume that the release of DOC during the experiments resulted from the oxic degradation of POM. Furthermore, it could be inferred that the DOC itself was unreactive and therefore not consumed during the resuspension experiments, but rather accumulated in solution. Since the original porewater DOC concentrations were not measured, their exact contribution to the dissolved phase of the experimental slurries is unknown. This contribution can however be estimated from the DOC concentrations of the sample withdrawn from the slurries at 0.03 hour (2 minutes). According to these calculations, and with the exception of experiment #7, 1,95 to 2,85 mg/l of DOC would have originated from the initial porewaters (Figures 4.5 to 4.10). This value, however, increases to 4 mg/l in the latter resuspension (Figure 4.8), where DOC concentrations highly exceeded those recorded in the other experiments.

The results of our DOC measurements display striking differences with those reported by Gerringa (1990) in a similar study. In the latter study, in the presence of oxygen, and following the release of DOC to solution upon the resuspension of the anoxic sediments, the author observed a rapid consumption of DOC over the first five days. The DOC concentrations remained nearly constant or decreased slightly over the next 80 days. The author also monitored the oxygen consumption as well as the inorganic nitrogen production ($NH_4^+$, $NO_3$- and $NO_2$-) in the same experiment, in order to estimate the extent of organic matter degradation. The oxygen consumption increased sharply in the first two days of sediment resuspension and decreased almost as rapidly during the following two days. As it was the case for DOC concentrations, oxygen consumption remained nearly constant over the next days of the experiment. On the other hand, total nitrogen concentrations increased throughout the experiment, exhibiting a steeper rise in the first 35 days of sediment resuspension.

Gerringa (1990) concluded that two pools of organic matter of different reactivities were degraded during her resuspension experiment conducted in the presence of oxygen. The author stated that a relatively fast mineralization occurred in the first five days of sediment resuspension, during which DOC was actively degraded. A sharp decrease in DOC concentration and an intense $O_2$ consumption reflected this degradation. On the other hand, the author suggested that a slower organic matter degradation took place in the following days and weeks, illustrated by an increase in total nitrogen concentrations. The latter process would reflect the mineralization of a easily degradable POC.

The discrepancies in the DOC behaviour between both studies could be attributed to the nature of the organic material present in the resuspended sediments. The organic matter accumulating in the Saguenay Fjord sediment is mainly of terrigenous origin, reflecting the intense activity of the pulp and paper industry in this region. It is characterized by a high $C_{org.}$ /N ratio, with values varying between 21.8 and 30.4 at Sag-15'95 (Mucci and Edenborn, 1992; Gagnon et al., 1995; Richard, 1996; Louchouarn et al., 1997.). In a recent study on the organic matter in the Saguenay Fjord sediments, Louchouarn et al. (1997) demonstrated that lignin, one of the most abundant biopolymers in vascular plant and which is highly resistant to microbial degradation, represented 6 to 8 % of the total organic carbon in the sediments at Sag-15'95. The authors reported that this material was mainly comprised of gymnosperm wood tissues. In contrast, the organic material in the sediments collected by Gerringa (1990) in the Dutch Wadden Sea, had a much lower $C_{org.}/N$ ratio (11), indicating a greater marine contribution, and thus a greater reactivity towards aerobic degradation (Gagnon et al., 1995; Louchouarn et al., 1997). The more refractory nature of the organic matter (POC and DOC) present in the Saguenay Fjord sediments explains its slower degradation in our experiments, and the DOC build-up observed throughout the experiments.

### 5.1.2 Fe:

The experiments conducted with anoxic sediments led to an important release of Fe to the dissolved phase in the first hour of the resuspensions (Figures 4.7 to 4.10). In contrast, almost no Fe remobilization occurred during experiments # 11 and 9, performed with, respectively, oxic and suboxic sediments (Figures 4.5 and 4.6). In comparison, Gerringa (1990) observed no Fe remobilization in her experiment conducted with anoxic sediments. The dissolved Fe concentrations remained constant at about 615 mg/L throughout the 90 day experiment. The sediments used by Gerringa (1990) were collected in the depth interval of 2 to 4 cm below the sediment-water interface on the tidal flat in the Wadden Sea. According to her description, only the first centimeter of her sediment core was oxidized. The 2 to 4 cm interval used in her experiment most likely included the horizon separating the suboxic and anoxic zones and the sediments were more likely akin to those resuspended in our experiments # 9 and 10 (Figures 4.6 and 4.7). Given this assumption, the results reported by Gerringa (1990) would be consistent with those presented in this investigation. Furthermore, the author did not withdraw samples from her experiment in the first hour of the resuspension, therefore missing most of the Fe remobilization.

The amount of dissolved Fe contributed to the solution of our experiments by the original porewaters was evaluated from the porewater concentrations, the weight and porosity of the sediments, and the volume of seawater used in the resuspension experiments. Porewater Fe, Mn and As concentrations were measured by Richard (1996) on the same core from which sediments were collected for this study (Appendix 3). Porosity measurements were determined on sediments sampled from the same core and at the same depths following freeze-drying of the sediments collected in pre-wheighed plastic scintillation vials (Appendix 1).

The original porewater Fe concentrations accounted for less than 5 % of the maximum Fe released into solution during experiments # 7, 8 and 12 (Figures 4.8 to 4.10). Their contribution was nearly 70 % in experiment # 10 (Figure 4.7). The latter result is consistent with the $Fe_{HCl}$ (Figure 4.4E) and dissolved Fe (Richard, 1996) profiles at this station which indicate that these sediments originated from the Fe reduction zone. The sediments resuspended in experiment #10 (Figure 4.7) were therefore enriched in dissolved Fe but depleted in Fe oxyhydroxides and AVS (Figures 4.1 and 4.4E). Porewater contributions to slurry Fe, Mn and As concentrations were subtracted in order to correlate trace metal release during resuspension with the solid sediment composition.

A positive correlation was observed between the maximum amount of Fe remobilized during the resuspension experiments conducted in the present study and the amount of Fe associated to AVS in the resuspended sediments (Figure 5.1A, ($r^2$)= 0.9939). The latter parameter represents the concentration of Fe in the slurries available from the Fe monosulphides present in the resuspended sediments, and was expressed in terms of mg/L. It was calculated from the AVS concentrations in the sediments, the weight and porosity of the sediments, and the volume of seawater used in the resuspension experiments. The same procedure was used to evaluate the contribution of the reactive phases (e.g. AVS and HCl extractable phases) to Mn and As concentrations in the slurries.

This correlation suggests that the amount of Fe released to solution originated mainly from the oxidation of AVS. This is further supported by the intercept on the y-axis of this plot, which lies very close to zero. Experiment #10 did not abide to this linear relationship. The amount of Fe released to solution during this experiment was lower than predicted from this relationship. The sediments resuspended in this experiment were collected close to the maximum trace metal remobilization horizon, as indicated by the HCl extractable profile (Figure 4.4E). Furthermore, these sediments were probably also sampled near the upper boundary of a slump layer, as observed on the organic matter and AVS sediment profiles presented previously (Figures 4.1 and 4.2). Given these characteristics, sediment heterogeneity may be responsible for the poor correlation observed for the sediments collected at this depth interval (3-4 cm).

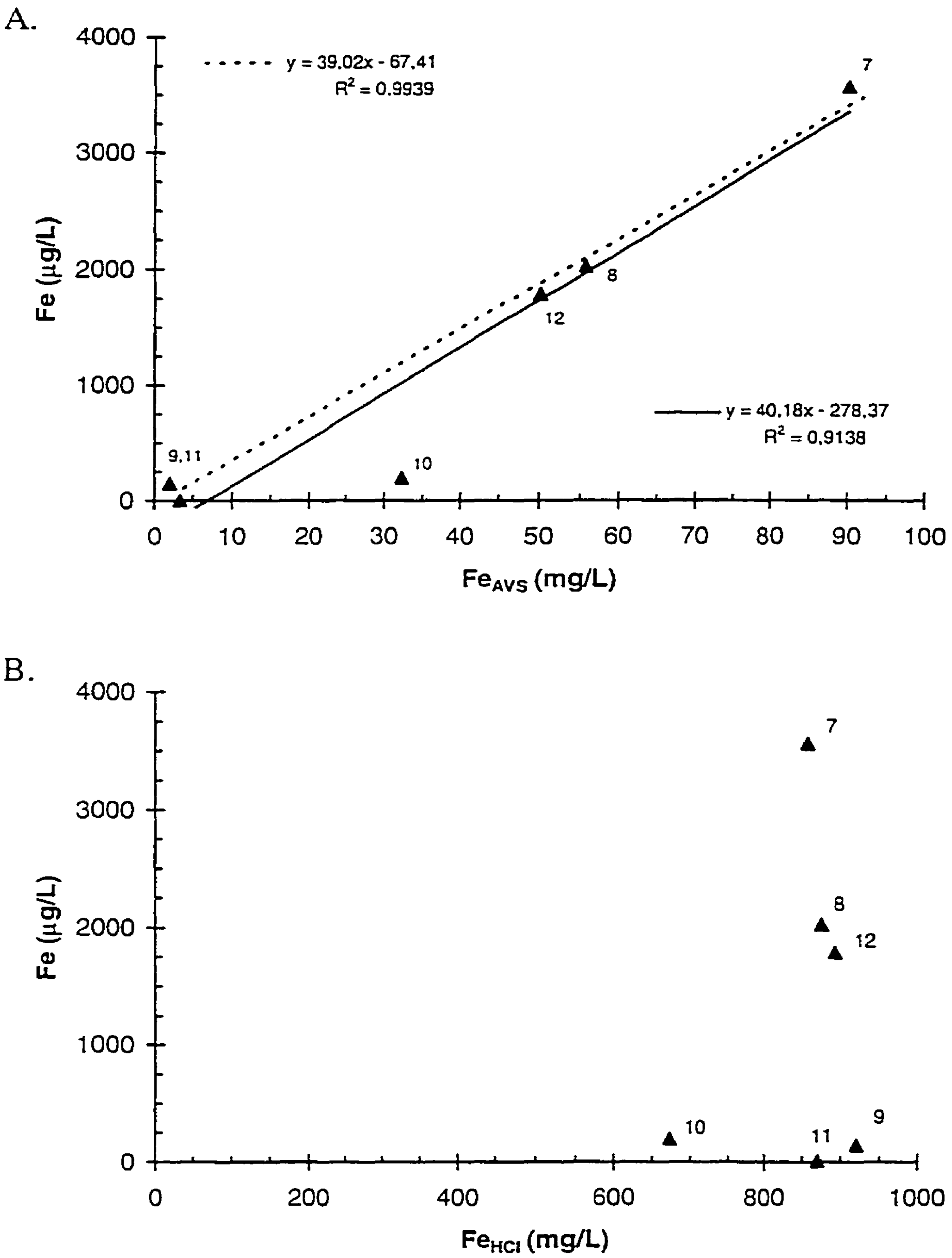

Figure 5.1. Relation between maximum (porewater corrected) dissolved Fe concentrations measured during the resuspension experiments and (A) $Fe_{AVS}$ and (B) $Fe_{HCl}$ contribution from the sediments. The dashed line is obtained by excluding experiment #10 from the correlation.

On the other hand, no correlation could be found between the maximum dissolved Fe measured during the resuspensions and the amount of HCl extractable iron in the resuspended sediments (Figure 5.1B). This lack of concordance suggests that no other reactive HCl extractable phases contributed significantly to the release of Fe to the solution during our experiments.

The rate at which the Fe was released to the dissolved phase in all experiments conducted with anoxic sediments ($\cong$ 2 minutes or 0.033 hour) indicates that the dissolution of a solid phase, highly reactive towards oxygen, was responsible for the liberation of Fe to the solution. The strong correlation between the amount of Fe associated to the AVS in the sediments and the magnitude of Fe released to the dissolved phase suggests that the Fe remobilization occurred mainly through the dissolution of Fe monosulphides (Figure 5.1A). The latter phase, as indicated previously, is very reactive towards oxygen and dissolves rapidly in its presence (Schoonen and Barnes, 1991; Arakaki and Morse, 1993; Morse and Arakaki, 1993; Morse, 1994). Given the low abundance of pyrite in these sediments and its slow oxidation kinetics in the presence of oxygen (Schoonen and Barnes, 1991), the dissolution of this phase did not contribute significantly to the Fe remobilization during our experiments. Based on this assumption and our calculations, 4 % ($3.5 \leq x \leq 3.95\%$) of the Fe associated to Fe monosulphides was released to the solution during our experiments conducted with anoxic sediments. However, all the Fe monosulphides present in the sediments were most likely rapidly dissolved upon exposure to oxygen, thereby releasing reduced Fe to the slurries. Accordingly, most of the Fe remobilization and removal in our experiments, would have taken place within the first two minutes of sediment resuspension. The results presented in this study, however, do not support this hypothesis. Iron concentrations in the slurries of our experiments reached maximum values between 2 to 5 minutes (0.033 to 0.083

hour) after the introduction of anoxic sediments into oxygenated seawater. Following its release to solution, reduced Fe was oxidized very rapidly and precipitated as Fe oxyhydroxides (Klinkhammer, 1980; Elderfield et al., 1981; Sundby et al., 1986; Mucci and Edenborn, 1992; Sundby, 1994), therefore remaining in solution over a very short period of time. The release of Fe most likely occurred according to the following reactions:

$$2\ \mathrm{FeS} + 4\ \mathrm{O_2} \rightarrow 2\ \mathrm{Fe\ (II)} + 2\ \mathrm{SO_4^{-2}}$$

$$2\ \mathrm{Fe\ (II)} + 1/2\ \mathrm{O_2} + 2\mathrm{H^+} \rightarrow 2\ \mathrm{Fe\ (III)} + \mathrm{H_2O}$$

$$2\ \mathrm{Fe\ (III)} + 6\ \mathrm{H_2O} \rightarrow 2\mathrm{Fe\ (OH)_3} + 6\mathrm{H^+}$$

The overall reaction is therefore:

$$2\ \mathrm{FeS} + 9/2\ \mathrm{O_2} + 5\ \mathrm{H_2O} \rightarrow 2\ \mathrm{Fe(OH)_3} + 2\ \mathrm{SO_4^{-2}} + 4\ \mathrm{H^+}$$

As predicted by this reaction, a decrease in pH was observed in the first hours of each experiments. These data are presented in appendix 5.

### 5.1.3 Mn:

The resuspension of anoxic sediments in oxygenated seawater resulted in a considerable release of Mn to the solution over the first week (168 hours) (Figures 4.7 to 4.10). The experiment conducted with suboxic sediments (#9) led to a minor liberation of Mn in the first few hours of the experiment, whereas in resuspension #11, performed with oxic sediments, no Mn remobilization occurred (Figures 4.5 and 4.6). The relative contribution of the original porewater Mn (Richard, 1996) was less than 10 % of the total Mn released to the solutions during the resuspension experiments, with the exception of experiment # 10, for which the contribution reached almost 30 %.

In contrast, Gerringa (1990) found no release of Mn to the dissolved phase following the exposure of her anoxic sediments to oxygenated seawater. Her observations, as stated earlier, could be explained by the provenance of the sediments, which might have been sampled near the transition between the suboxic and anoxic zone of the sedimentary column, as well as the lack of high resolution sampling at the beginning of the experiment. Given these considerations, her results may be entirely consistent with results of this study.

The affinity of Mn (II) for Fe monosulphides has been the subject of a recent study by Arakaki and Morse (1993). As a consequence of the anomalously high AVS concentrations found in the Saguenay Fjord sediments, this phase is likely to exert a significant influence on Mn distribution in these sediments. Nevertheless, the amount of porewater-corrected Mn released to solution during the resuspension experiments performed in the current study could not be entirely correlated to the amount of Fe associated to AVS in the resuspended sediments (Figure 5.2A, $(r^2)= 0.4463$). A poor correlation was also obtained between the maximum dissolved Mn concentrations measured during the experiments and the contribution of Mn adsorbed onto AVS in the resuspended sediments (Figure 5.2B, $(r^2)= 0.5946$). The amount of Mn adsorbed onto the AVS of the sediments used for this study was estimated using the Langmuir isotherm adsorption model developed by Arakaki and Morse (1993). In this model, Mn adsorption, which represents more than 90 % of Mn association with AVS (adsorption + coprecipitation), can be expressed as follows:

$$\frac{1}{Mn^{(X+2)-}} = \frac{K'}{TC\, a_{Mn^{+2}}} + \frac{1}{TC} \qquad \text{and} \qquad K' = \frac{\equiv x^{-}\, a_{Mn^{+2}}}{Mn^{(X+2)-}}$$

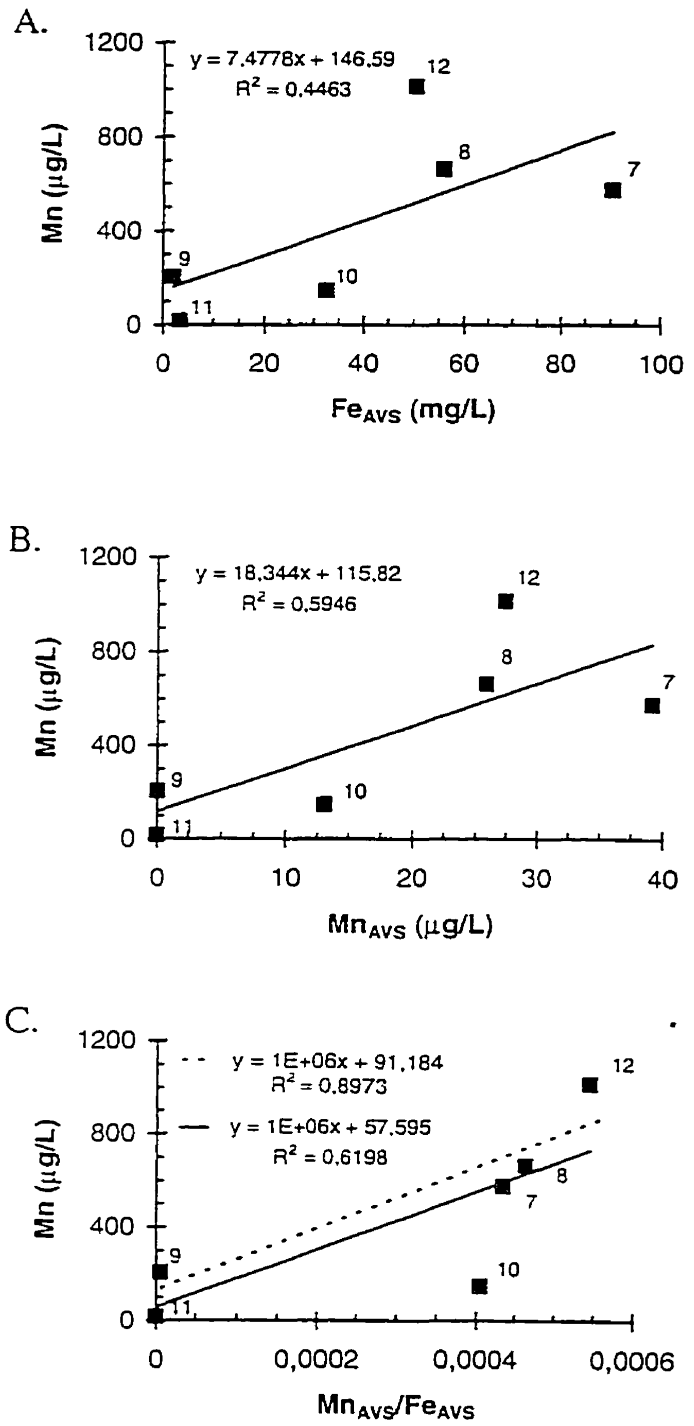

Figure 5.2. Relation between maximum (porewater-corrected) dissolved Mn concentrations measured during the resuspension experiments and (A) $Fe_{AVS}$ contribution from the sediments, (B) Mn adsorbed onto AVS and (C) $Mn_{AVS}$ (adsorbed)/ $Fe_{AVS}$. The dashed line is obtained by excluding experiment #10 from the correlation.

where Mn $^{(X+2)-}$ is the surface concentration of Mn adsorbed onto AVS in mole of Mn per mole of FeS, TC is the concentration of reactive sites on the surface of FeS (i.e. mackanawite) based on surface saturation ($\cong$ 0.08) , K' is the apparent equilibrium constant for the adsorption reaction, $\equiv x^-$ is the concentration of free surface sites (i.e., TC - Mn $^{(x+2)-}$), and $a_{Mn^{+2}}$ is the activity of $Mn^{+2}$ in the solution. The surface saturation evaluated by Arakaki and Morse (1993) was 0.08 for mackanawite (mole sites per mole of FeS). The apparent equlibrium constant of the adsorption reaction (K') was calculated for a seawater solution of 30 salinity with the linear regression derived from the salinity dependence of K' established by the authors at 25° C. The equation used was:

$$K' = (3{,}2696 * 10^{-5})\ S + 0.00095 \qquad r^2 = 0.7700$$

This constant was shown to be independent of pH between pH values of 6 and 7 (Arakaki and Morse, 1993). The $Mn^{2+}$ activity in solution was evaluated from the total porewater concentration and activity coefficient estimated using the Thrusdell-Jones equation:

$$\mathrm{Log}\gamma = \frac{-AZ^2 \bullet I}{1 + B\,\mathring{a} \bullet I} + bI = 0.3319$$

Where A= 0.50 (Stumm and Morgan, 1981)

B= 0.33 (Stumm and Morgan, 1981)

$\mathring{a} = 6$ (Stumm and Morgan, 1981)

b= 0.22 (Parkhurst, 1990)

$I \cong 0.62$ (ionic strength of the seawater)

Z= 2 (ion charge of $Mn^{+2}$)

These partial correlations suggest that the remobilization of Mn during the experiments was not solely related to the oxidation and dissolution of AVS, even though the association of this metal with Fe monosulphides, principally through adsorption, has been previously demonstrated (Arakaki and Morse, 1993). The positive intercept on the y-axis of these plots supports this hypothesis.

On the other hand, with the exclusion of experiment #10, a very good linear relationship was obtained between the maximum dissolved Mn concentrations released during the experiments and the ratio of Mn to Fe associated with the AVS in the resuspended sediments (Figure 5.2C, ($r^2$)= 0.8973). The latter parameter represents the amount of Mn, expressed in moles absorbed onto per of FeS, and was evaluated with the adsorption model described earlier (Arakaki and Morse, 1993). This correlation indicates that Mn was partially released to solution as result of the AVS oxidation and dissolution. This remobilization was, however, a function of the surface concentration of Mn on AVS (mole of Mn per mole of FeS), rather than the absolute concentrations of AVS and Mn associated to the latter phase in the sediments. Once again, experiment #10 did not abide to this linear relationship, supporting the hypothesis exposed earlier in section 5.1.2.

Nevertheless, assuming that the above calculations are valid and all the Mn adsorbed onto AVS was released to the solutions upon their oxidation, it would only account for less than 10 % of the maximum dissolved Mn concentrations measured in the resuspension experiments conducted in this study. This observation strongly suggests that the sediments contained other reactive phases which contributed Mn to the solution. The poor relationship between the magnitude Mn and Fe remobilization in the experiments indicates that the release of these two metals may have resulted from different processes (Figure 5.3A). A possible source for reduced Mn, other than AVS, may be a Mn carbonate ($MnCO_3$) or a mixed Ca Mn carbonate, which would be readily extracted by a 1N HCl solution. Exchangeable Mn, which is also solubilized by a 1N HCl digestion, could also have contributed to Mn remobilization during our experiments. The latter component would represent the fraction of this trace metal held to solid phases, such as clay minerals, by electrostatic attraction to non-specific ion adsorption sites.

Aller and Rude (1988) observed the direct precipitation of mixed Mn, Ca, and Mg carbonates during anoxic incubation experiments performed with marine sediments. Canfield et al., (1993) proposed that the precipitation of a Mn carbonate could explain the presence of constant Mn concentrations below the surface maximum in Skagerrak sediments. Meanwhile, Lapp and Balzer (1993) observed that the dissolved Mn concentrations in the sediments of the Western Baltic Sea decreased to low values as the carbonate levels in the solid phase increased. This observation led the authors to propose that the removal of dissolved Mn was probably linked to the high carbonate content of the sediments, most likely as a result of Mn adsorption onto calcite. Klinkhammer (1980) and Kremling (1983) determined that sediment porewaters recovered from the eastern equatorial Pacific and Atlantic, as well as the Baltic Sea, are undersaturated with respect to $MnCO_3(s)$. Nevertheless, the authors suggested that Mn solubility in these reducing sediments might be controlled by a mixed Mn and Ca carbonate. A mixed carbonate was identified in the Baltic Sea sediments (Kremling, 1983).

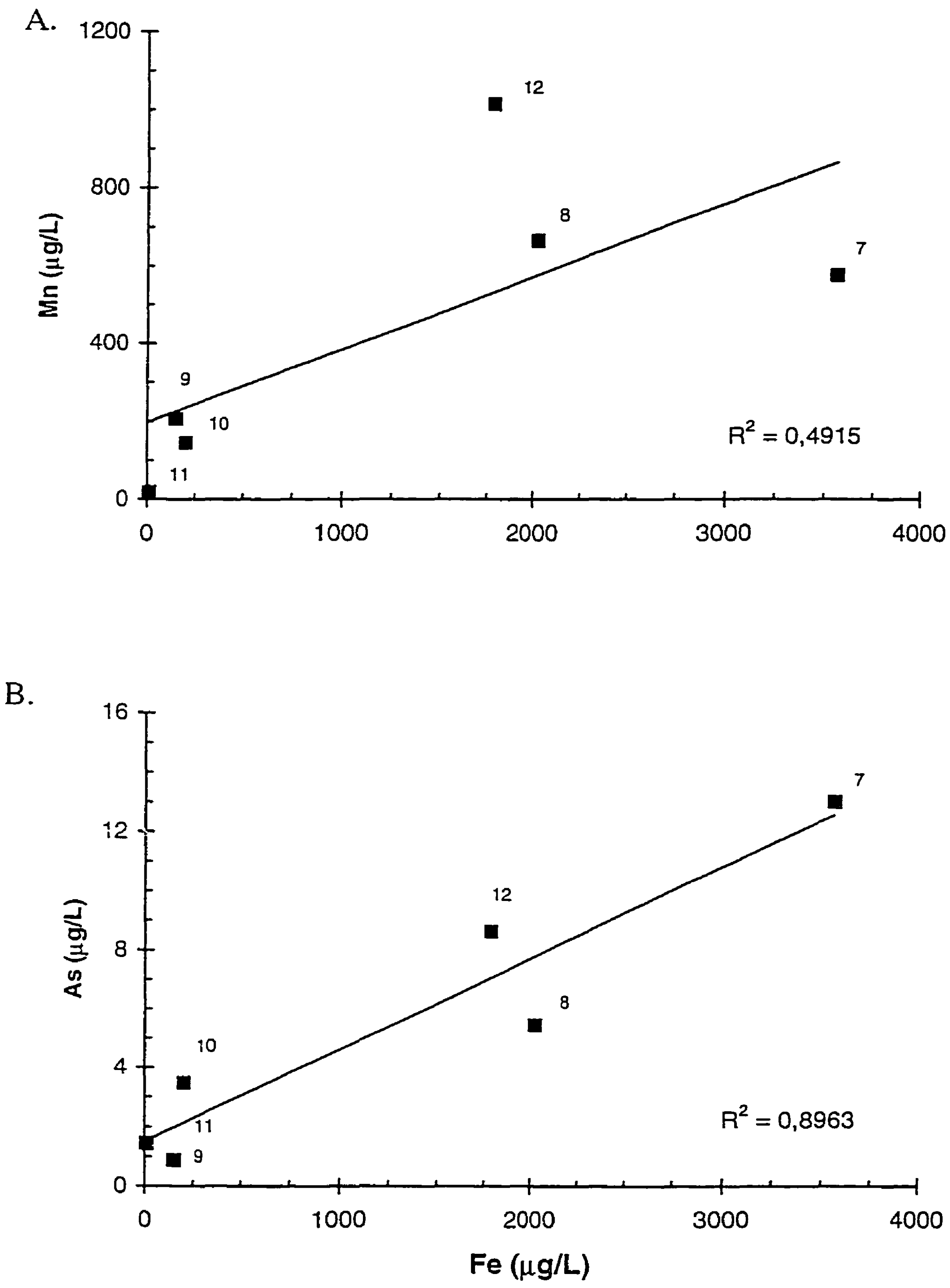

Figure 5.3. Relation between maximum (porewater-corrected) dissolved (A) Mn and Fe and (B) As and Fe concentrations released during the resuspension experiments.

Mucci and Edenborn (1992) calculated the saturation state of the Saguenay Fjord sediment porewaters with respect to rhodochrosite ($MnCO_3$) and calcite ($CaCO_3$). They determined that the saturation states increased almost linearly with depth becoming supersaturated with respect to $MnCO_3$ and $CaCO_3$ at a depth of 15 cm. The authors, however, reported no evidence of active Mn or Ca carbonate precipitation. Nevertheless, Mucci (1988) has demonstrated that Mn(II) strongly adsorbs to and forms a solid solution with calcite, even if the solution is undersaturated with respect to $MnCO_3$.

A linear relationship was observed between the extent of the Mn remobilization and the total amount of $Mn_{HCl}$ present in the anoxic resuspended sediments (Figure 5.4A, ($r^2$)= 0.9947). This correlation, however, does not extend to experiments #11 and 9, for which the sediments were characterized by the highest $Mn_{HCl}$ and lowest AVS concentrations. Accordingly, their resuspension into oxygenated seawater did not result in a substantial release of Mn to solution as most of the Mn present in these sediments was in the form of Mn (III, IV) oxyhydroxides (Mucci and Edenborn, 1992; Richard, 1996). These results suggest that the Mn remobilized during the sediment resuspensions conducted in this study may also have originated from the dissolution of a solid phase such as a mixed Mn-Ca carbonate, as well as exchangeable Mn. A fairly good correlation can be observed between the maximum dissolved Mn concentration measured in the slurries and the total amount of $C_{inog.}$ present in the anoxic and suboxic resuspended sediments (Figure 5.4B, ($r^2$)= 0.5460). This reasonable correlation seems to indicate that carbonates contributed to Mn remobilization during our resuspension experiments conducted with anoxic sediments. Again, experiment #10 does not abide to this correlation further supporting the hypothesis exposed earlier in section 5.1.2. On the other hand, experiment #11 which was

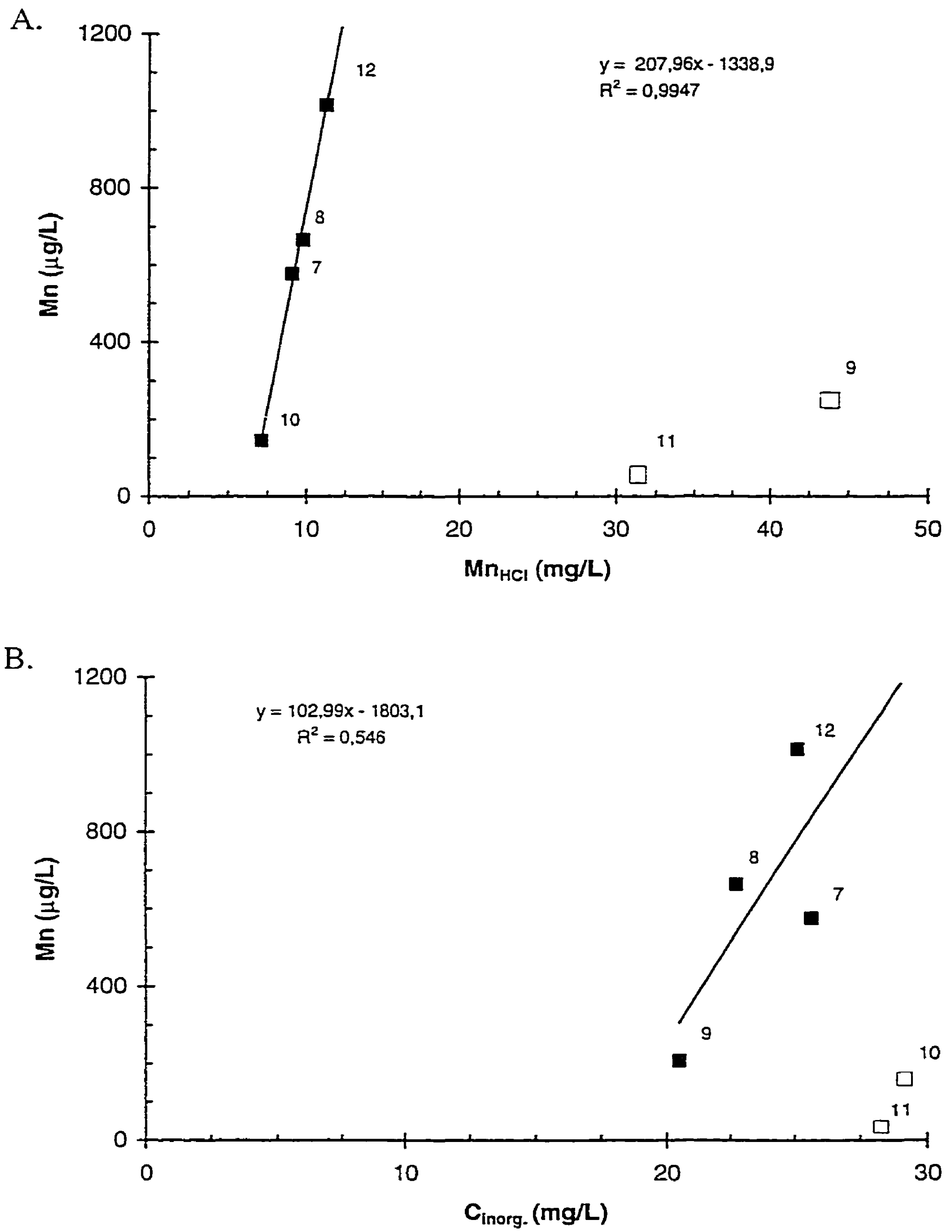

Figure 5.4. Relation between maximum (porewater-corrected) dissolved Mn concentrations measured during the resuspension experiments and (A) $Mn_{HCl}$ and (B) total $C_{inorg.}$ contributions from the sediments.

conducted with oxic sediments does not follow this linear relationship as most of the Mn present in these sediments is in the form of Mn(III, IV) oxyhydroxides.

Unfortunately, as no extraction procedures were performed on the sediments collected for this study in order to quantify the importance of exchangeable Mn, the relative contribution of these different components could not be established. However, assuming that all the Mn remobilized in our experiments conducted with anoxic sediments originated from Mn bearing HCl-extractable phases (i.e. exchangeable Mn, oxyhydroxides, carbonates, AVS), less than 11 % of the Mn associated to these phases would have been solubilized.

To summarize, Mn was released rapidly to the dissolved phase at the beginning of the experiments conducted with suboxic and anoxic sediments. The Mn originated from the oxidation and/or dissolution of a mineral phase or phases which are highly reactive towards oxygen and readily extracted from the sediments by a 1N HCl solution. Our results and calculations suggest that FeS oxidation and dissolution only accounted for a maximum of 5 % of Mn remobilization during the experiments. Most of the Mn remobilized would have therefore originated from the dissolution of a Mn carbonate or a mixed Mn Ca carbonate, as well as from the desorption of exchangeable Mn from surfaces such as clay minerals. Our extraction procedures did not, however, allow us to differentiate the relative contribution of these different phases. Following its remobilization, reduced Mn remained in solution over a longer period of time than Fe, since it is metastable in the presence of oxygen. It was ultimately oxidized and most likely reprecipitated as Mn oxyhydroxides after one week (168 hours) (Froelich et al., 1979; Klinkhammer, 1981; Sundby et al., 1986; Lapp and Balzer, 1993).

### 5.1.4 As:

Arsenic was also released to solution in the first week (168 hours) of resuspensions conducted with anoxic sediments, whereas the dissolved As concentrations remained fairly low throughout experiments carried out with oxic and suboxic sediments. The porewater As from the anoxic sediments resuspended in experiments #10 and 7 (Figures 4.7 and 4.8) accounted for approximately 10 % of the total As released to solution, whereas its contribution reached 30 % for experiments # 8 and 12 (Figures 4.9 and 4.10). The results observed during our resuspensions are analogous to those obtained with Fe and Mn. The residence time of dissolved As in the experimental slurries conducted with anoxic sediment was similar to that of Mn. Given that the As present in anoxic porewaters should be predominantly in the form of arsenite (Edenborn et al., 1986a; Peterson and Carpenter, 1986), it was assumed that the As remobilized during our resuspension experiments conducted with anoxic sediments was primarily released as As(III).

The magnitude of As remobilized during the experiments, corrected for the original porewater contribution, was positively correlated to the amount of Fe associated to the AVS in the resuspended sediment (see 5.1.2) (Figure 5.5A, ($r^2$)=0.9051). Moreover, the linear regression shown on this plot gave an intercept very close to zero on the y-axis. These observations strongly suggest that As was primarily released to solution following the oxidation and dissolution of the Fe monosulphides. Given the occurrence of abnormally high AVS and relatively low pyrite

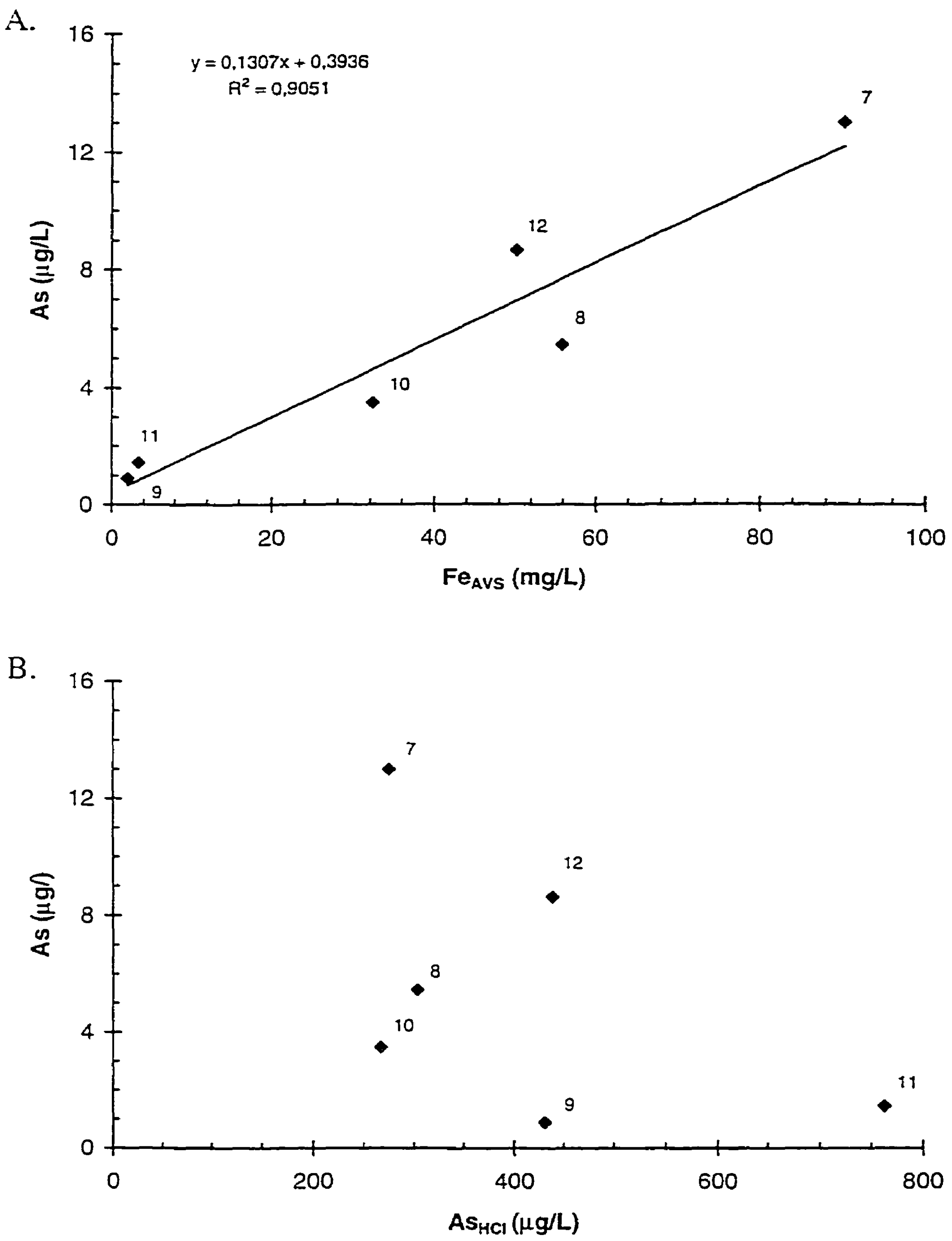

Figure 5.5. Relation between maximum (porewater corrected) dissolved As concentrations measured during the resuspension experiments and (A) $Fe_{AVS}$ and (B) $As_{HCl}$ contributions from the sediments.

concentrations in the Saguenay Fjord sediments (Gagnon et al., 1995), more As is probably adsorbed or coprecipitated with the Fe monosulphides, despite its strong affinity for pyrite (Belzile and Lebel, 1986; Belzile, 1988; Edenborn et al., 1986a; Huerta-Diaz and Morse, 1992; Morse, 1994; Bono, pers. comm. ). A microprobe analysis of framboidal authigenic pyrite grains from the Saguenay Fjord sediments showed that they contained 800 to 1000 ppm of As (Mucci, pers. comm.). Nevertheless, Belzile (1988) and more recently Huerta-Diaz et al. (1997) suggested that adsorption onto or coprecipitation with Fe monosulphides may control the solubility of As in anoxic porewaters, and play an important role in its cycling in sediments. The exact contribution of AVS to As remobilization in the resuspensions conducted in this study could not be determined, however, due to a lack of relevant thermodynamic data.

The maximum dissolved As concentrations measured during our experiments and the amount of As available from HCl-extractable phases in the sediments could not be successfully related (Figure 5.5B). This lack of correlation suggests that no other reactive phase contributed significantly to the release of As to the solutions of our resuspensions. The linear relationship between the maximum dissolved As and Fe concentrations observed in all the experiments conducted in this study further supports this hypothesis (Figure 5.3B, $(r^2)= 0.8963$). The latter results would suggest that As and Fe remobilization were related through a common source, which appear to be the Fe monosulphides.

On the other hand, the similarity between the residence times of dissolved As and Mn in the slurries of experiments # 7, 8 and 12 suggests that the oxidation and consequent removal of these two metals from the solution was intimately related (Figure 5.6). Results of recent diagenetic

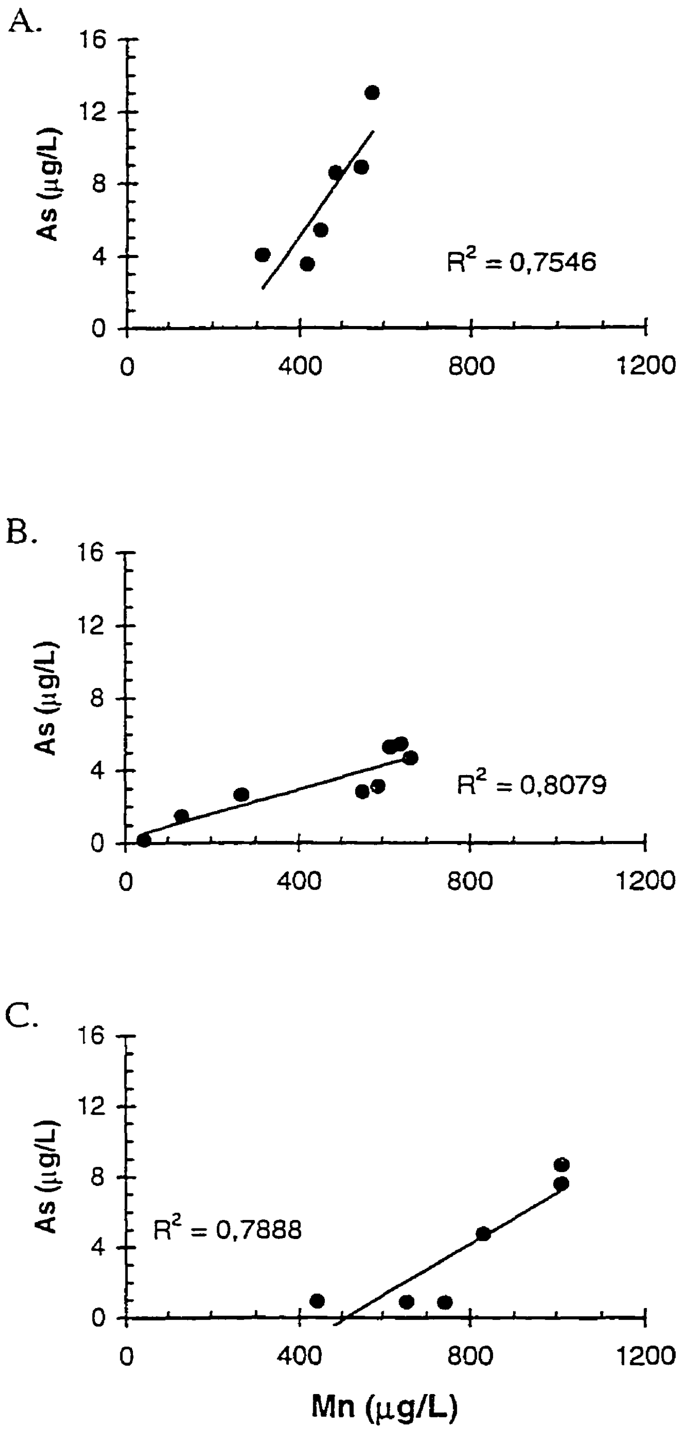

Figure 5.6. Relation between dissolved As and Mn concentrations (porewater corrected) during their removal from solution experiments (A) #7 (0.5-5 h.), (B) #8 (0.25-168 h.) and (C) #12 (0.25-24 h.).

studies conducted by Peterson and Carpenter (1983) and Richard (1996) suggest that arsenite released in anoxic sediments and diffusing towards the oxic zone is oxidized by Mn oxides prior to the adsorption of As(V) onto Fe oxyhydroxides. Oscarson et al. (1980) have demonstrated that Mn oxides are very efficient oxidants of As(III). Given these observations, it is reasonable to assume that the oxidation of the dissolved arsenite and its removal from solution would have been triggered in part by the precipitation of Mn oxyhydroxides from the oxygenated slurries. Accordingly, As (III) would have been oxidized to As(V) following its adsorption onto precipitating Mn oxyhydroxides, and subsequently readsorbed onto Fe oxyhydroxides, owing the strong affinity of this trace metals for the latter phase (Peterson and Carpenter, 1983; Maher, 1984; Edenborn et al., 1986a; Belzile, 1988; DeVitre et al., 1991; Gobeil, 1996; Richard, 1996). Arsenic speciation analysis performed on samples withdrawn from experiment #12, however, revealed that dissolved As(III) concentrations represented only 37% of total dissolved As concentrations at 0.083 hour (5 minutes), reaching 43 % at 0.25 hour (15 minutes). Arsenite concentrations represented 39 % of total dissolved As concentrations measured in the slurry at one hour. This result could imply that another oxidant was involved in the oxidation of arsenite at the beginning of the resuspension experiments.

Whereas arsenite oxidation by oxygen is unlikely to be important due to the slow kinetics of the reaction (Cherry et al., 1979), freshly precipitated Fe oxyhydroxides may also serve to oxidize As(III) to As(V). DeVitre et al. (1991) demonstrated that natural as well as synthetic Fe oxyhydroxides can rapidly oxidize As (III) to As (V) in 0.01 M $NaClO_4$ solutions. These results, however, contrast with those reported by Oscarson et al. (1980) from an investigation of As oxidation by aquatic sediments. DeVitre et al. (1991) suggested that this discrepancy may be explained in part by the much higher Fe : As molar ratio of the diagenetic material collected for their laboratory experiments compared to those reported by Oscarson et al. (1980) (i.e. 3400 vs. 10). According to this hypothesis and given the very high reactive Fe concentrations ($Fe_{HCl}$) of the Saguenay Fjord sediments, the oxidation of arsenite by newly precipitated Fe oxyhydroxides, was likely at the beginning of our resuspension experiments.

Arsenic oxidation and removal from the solutions could, thus, have been the result of two distinct processes. The Fe oxyhydroxides precipitation taking place in the first moments of the resuspensions could have triggered the oxidation of a significant portion (60 %) of dissolved As(III). Subsequently, the precipitation of Mn oxyhydroxides would have catalyzed the oxidation of the remaining arsenite in solution.

The gradual increase in dissolved As concentrations observed from the first week (170 hours) until the end of all the resuspension experiments conducted in this study could have resulted from various processes. Arsenic released to solution may have originated from the dissolution of mineral phases, less reactive than AVS in presence of oxygen, to which the trace metal was associated through adsorption or coprecipitation (e.g. orpiment). On the other hand, Gerringa (1990) observed that resuspension of anoxic sediment in the presence of oxygen altered the sediment matrix, thereby facilitating trace metal (i.e. Cd, Cu, Pb, Zn, Fe and Mn) release to solution. Moreover, the occurrence of a bacterial bloom, intensifying the microbial organic matter degradation at room temperatures (25°C) and the release of its associated trace metals may also have contributed to the solubilization of As after a week of sediment resuspension.

Arsenic desorption from Fe oxyhydroxides surfaces is unlikely to have triggered the As remobilization observed towards the end of all the resuspension experiments. Numerous studies reported that amorphous and crystalline Fe oxyhydroxides represent the main sorbents for As in oxic sediments (Pierce and Moore, 1982; Luoma and Davis, 1983; Edenborn et al., 1986a; Peterson and Carpenter, 1986; Belzile, 1988; DeVitre et al., 1991; Harris, 1996; Gobeil, 1996). Luoma and Davis (1983) stated that amorphous Fe oxyhydroxides possessed the largest binding capacity for trace metals in oxidized estuarine sediments. Moreover, in a recent study on the adsorption of As and $PO_4$ on oxic sediments of the Saguenay Fjord, Harris (1996) proposed that the behaviour of these elements under oxic conditions was dominated by adsorption onto Fe oxyhydroxides.

Finally, the formation of colloidal Fe oxide particles in the slurries of the resuspension experiments might have prevented As from returning to the sediments upon its release. Dissolved Fe concentration increases were observed 4 and 6 weeks (670 to 1010 hours) after the exposure of the sediments to the seawater solution, indicating the possible formation of Fe oxides colloidal particles in the slurries. The continuous agitation of the slurries during our experiment could have lead to the deflocculation of newly precipitated Fe oxyhydroxides and the formation of Fe colloidal particles. In a recent study on the accumulation of As in the Saguenay Fjord sediments, Gobeil (1996) stated that dissolved As has strong affinities towards colloidal Fe oxides particles present in the Saguenay water column. Nevertheless, As may also have remained in solution as a consequence of its complexation with DOC and the formation of organoarsenials (Ferguson and Gavis, 1972). Sanders and Windom (1980) reported that methylted forms of As comprised a significant proportion of the dissolved As in biollogically active waters. Moreover, Apte and

Howard (1986) suggested that microbial methylation of dissolved As may also occur in marine waters.

### 5.1.5 Hg, Cu, Ni and Pb:

The erratic behaviour of Hg, Cu, Ni and Pb during the resuspension experiments conducted in this study contrasted strongly with the results obtained for Fe, Mn and As (Figures 4.5 to 4.10). Whereas Fe, Mn and As were rapidly remobilized in the first hours of each experiment, Hg, Cu, Ni and Pb release to solution occurred after the first 24 hours of the resuspension and was punctuated by many variations. Assuming that Hg, Cu, Ni and Pb were remobilized at the beginning of our resuspension experiments, this difference would suggest that the affinity of these trace metals towards POM (Particulate Organic Matter) and precipitating Fe oxyhydroxides resulted in their immediate uptake from the dissolved phase following their release. On the other hand, the accentuated remobilization of these trace metals after 24 hours of sediment resuspension may have resulted from their association to DOM (Dissolved Organic Matter), competing for readsorption onto Fe oxyhydroxides and POM.

These results differ from those described by Gerringa (1990) and Lindberg and Harris (1977). In her experiment, Gerringa (1990) observed that both Cu and Ni were released to the solution in the first two days of resuspension and removed in the next two days as the DOC concentrations decreased. This observation led the author to propose that the trace metals were maintained in solution by complexation with DOC. This hypothesis, however, is consistent with the results of this study as high dissolved Cu, Ni and Hg concentrations in our resuspension experiments were associated with maximal DOC concentrations. Gerringa (1990) also suggested that Cu and Pb were released to solution during the degradation of POM as both metals and dissolved inorganic N concentrations increased in the following 25 days of her experiment.

Lindberg and Harris (1977), in their study of resuspended sediments collected in the Everglades National Park, observed a persistent pattern of Hg release to the water phase. Their results clearly contrast with those of the present study since no consistent Hg release to solution was observed from any of our resuspension experiments. Lindberg and Harris (1977) noted two distinct dissolved Hg peaks occurring within the first three hours of each experiment, with Hg concentrations returning to initial values between each. The author attributed the first Hg peak to the release of exchangeable Hg and the physical mixing between the surface waters and the Hg-enriched porewaters. The second peak was interpreted as resulting from the partial solubilization of sediment organomercury complexes as well as the slow oxidation of mercuric sulphide species, whereas newly precipitated Fe oxyhydroxides were thought to have scavenged Hg from solution between the two peaks. Steady-state conditions were established within a few hours after the beginning of each experiment, which, however, only lasted 6 hours. Lindberg and Harris (1977) concluded that the patterns of Hg release and redeposition are not simply related to variations in pH, redox potential, total dissolved sulphides or DOC concentrations, as no consistent co-variations of these measured variables were found. Although maximal DOC concentrations appeared to be associated with elevated dissolved Hg, Cu and Ni concentrations in our experimental slurries, results of this study, nevertheless, tend to agree with their observation .

The relatively fast POM degradation taking place within the first 24 hours of all resuspension experiments probably played a significant role in the initial release of Hg, Cu, Ni and Pb to the dissolved phase. The solubilization of Hg, Cu and Pb as a result of aerobic organic matter degradation in surface sediments has been widely documented (Klinkhammer, 1980; Klinkhammer et al., 1982; Sawlan and Murray, 1983; Gobeil and Silverberg, 1989; Ridgway and Price, 1987; Shaw et al., 1990; Gobeil and Cossa, 1993; Gagnon et al., 1997). Furthermore, Gerringa (1990) proposed that Ni, along with Cu and Pb, were released to solution during aerobic POM degradation.

On the other hand, Aller (1994) demonstrated that recycling organic matter between oxic and anoxic conditions increased its reactivity. The author suggested that the anoxic organic matter degradation products were more reactive when exposed to oxygen. Nevertheless, no systematic differences in the remobilization of Hg, Cu, Ni and Pb were observed between results of our resuspension experiments conducted with oxic, suboxic and anoxic sediments.

Some of the Cu, Ni, Hg and Pb released to the solution in the first moments of the resuspensions performed with oxic and suboxic sediments were derived, not only from the labile POM degradation, but also from the sediment porewaters. Many studies have reported the presence of maximum dissolved trace metals concentrations ( i.e. Cd, Cu, Cr, Hg, Ni, Pb, V, Zn ) near the sediment-water interface (Klinkhammer, 1980; Klinkhammer et al., 1982; Sawlan and Murray, 1983; Gobeil and Silverberg, 1989; Ridgway and Price, 1987; Shaw et al., 1990; Gobeil and Cossa, 1993; Lapp and Balzer, 1993; Gagnon et al., 1997). These enrichments were interpreted by the authors as resulting from the remobilization of these trace metals to the interstitial waters following the aerobic degradation of labile organic matter. The exact contribution of the original porewaters in our experiments could not, however, be established since no analysis of Hg, Cu, Ni and Pb porewater concentrations were performed on the sediments collected for this study. Nevertheless, their contribution could be estimated in the case of Hg from the dissolved Hg profiles measured by Gagnon et al. (1996b, 1997) on Saguenay Fjord sediments collected at Sag-15 in 1992 (Appendix 3). According to these data, the release of Hg upon mixing of the oxic and suboxic sediment with the oxygenated seawater would have lead to an increase of its concentration by approximately 2 ng/l in the slurries. This contribution, however, only represents 2% of the increase in dissolved Hg concentrations observed during the first two minutes of these experiments. This result would imply that the original sediment porewaters were not influential on Hg remobilization in the resuspensions conducted with oxic and suboxic sediments. On the other hand, porewater Hg could have been underestimated due to the extraction method (i.e squeezing), as colloidal organomercury complexes may not have been expelled from the sediments during their manipulations.

The remobilization of Hg, Cu, Ni and Pb at the beginning of the resuspension experiments conducted with anoxic sediments could have originated from the oxidation and dissolution of Fe sulphides, namely AVS, as well as from the sulphidic porewaters of the resuspended sediments. The association of Cu, Ni, Hg and Pb with Fe sulphides in reducing sediments as been demonstrated in several studies (Jean and Bancroft, 1986; Hyland at al., 1990; Huerta-Diaz and Morse, 1992; Morse and Arakaki, 1993; Morse, 1994; Huerta-Diaz et al., 1997). On the other hand, the contribution from the original anoxic porewaters must not be ignored. Copper, Hg and Pb, class B metals, form strong complexes with dissolved organic matter and reduced sulphur species, whereas Ni, a transition metal, displays a greater tendency to form solid sulphides (Lindberg and Harris, 1974; Sholkovitz and Copland, 1981; Jacob and Emerson, 1982; Emerson et al., 1983; Kremling, 1983; Ridgway and Price, 1987; Gagnon et al., 1997). Gagnon et al. (1997) reported that HgS precipitation was not limiting Hg solubility in the Saguenay Fjord sediments, despite the presence of relatively high Hg porewater concentrations. The authors suggested that Hg complexation with dissolved sulphides, polysulphides and dissolved organic matter strongly contributed to its solubilization. The presence of these trace metal sulphide minerals in the Saguenay Fjord sediments is probably very limited, although NiS may form. Once again, Fe monosulphides and original porewater contributions to Hg, Cu, Ni and Pb remobilization could not be established since sediment porewater concentrations were not measured on the sediments sampled for this investigation. Nevertheless, using the sediment porewater Hg profiles measured by Gagnon et al. (1996b, 1997) we estimated that the resuspension of anoxic sediments into oxygenated seawater would only account for an increase in dissolved Hg concentrations of about 1 ng/L.

Following their release to solution, Cu, Ni, Hg and Pb were most likely readsorbed rapidly onto POM and newly precipitated Fe oxyhydroxides, as no substantial remobilization of these trace metals was observed in the beginning of any of the experiments. Their strong affinity towards organic matter is well known (Lindberg and Harris, 1974; Loring, 1976a,b; Loring and Bewers, 1978; Klinkhammer, 1980; Sawlan and Murray, 1983; Gobeil and Silverberg, 1989; Ridgway and Price, 1987; Pelletier and Canuel, 1988; Gerringa, 1990; Shaw et al., 1990; Lapp and Balzer, 1993), whereas the ability of Fe oxyhydroxides to scavenge many trace metals in oxic sediments is profusely documented (Klinkhammer, 1980; Klinkhammer et al., 1982; Tessier et al., 1985;

Gobeil and Cossa, 1993). Lindberg and Harris (1977) suggested that newly precipitated Fe oxyhydroxides scavenged Hg from solution during their resuspension experiments conducted with riverine and estuarine sediments from the Everglades National Park. The uptake of Hg by the sediments observed in the first two minutes (0.03 hour) of the resuspensions conducted with anoxic sediments (Figure 4.7 to 4.10) may reflect its strong affinity towards POM as well as Fe oxyhydroxides. This uptake is reflected by the decrease of dissolved Hg concentrations between the original seawater solution and the first aliquot sample withdrawn from the slurries at 2 minutes (0.03 hour) (see Appendix 4).

The general increase of dissolved trace metals concentrations occurring after 5 to 24 hours of sediment resuspension, and which continued until the end of the experiments, most likely originated from the same processes described earlier in the case of As (see 5.1.4). The occurrence of a bacterial bloom at room temperatures (~25° C) may have intensified the microbial organic matter degradation and, thus, enhanced the release of these trace metals to solution. Since the Saguenay Fjord bottom water temperatures vary between 0 to 2°C annually, a 25°C increase in temperature is likely to accelerate the proliferation of bacteria (Aller, 1980; Jensen et al., 1992). A lack of nutrients in the slurries of our experiments may, however, have inhibited this process due to the highly refractory nature of the organic matter present in the sediments.

On the other hand, according to Gerringa (1990), an alteration of the sediment matrix could have occurred during sediment resuspension promoting the release of trace metals to solution with time. Gerringa (1990) reported that the extractability of Cu and Cd from the sediments increased considerably during her resuspension experiments, as a higher fraction of these trace metals in sediments were extracted by non-aggressive reagents. The author also observed the same phenomenon for Pb and Zn, although, to a lesser extent. No determination of the 1N HCl extractable metal concentrations of the solids in the resuspended sediments were carried out throughout the experiments. Consequently, the relevance of this hypothesis cannot be verified.

The remobilization of Cu and Hg observed a week after the beginning of the experiments (170 hours) was more important than that of Pb and Ni and coincided with maximum DOC concentrations. The strong affinity of Cu and Hg for dissolved organic matter maintained these trace metals in solution. Lindberg and Harris (1974) reported significant association between interstitial Hg and dissolved organic matter in the Everglades and Mobile Bay estuary sediments. Matty and Long (1995) proposed that Hg released by the decay of labile particulate organic matter was complexed by DOC. Similarly, Sholkovitz and Copland (1981) demonstrated that Cu adsorption onto suspended particles was considerably inhibited by the formation of dissolved Cu-organic complexes. On the other hand, Matty and Long (1995) also proposed that the Hg complexes with DOC may be transferred to the solid sediment through processes such as flocculation, coagulation and aggregation of colloids. The occurrence of such processes during our resuspension experiments may explain the high variability of these trace metal concentrations in the slurries.

Lead also exhibits a strong affinity towards dissolved and colloidal organic matter (Loring, 1976a; Emerson et al., 1983; Kremling, 1983). On the other hand, Gobeil and Silverberg (1989) suggested that an important fraction of Pb in sediments was implicated in the cycle of Fe diagenesis. The authors observed that 70 % of the total Pb in the Laurentian Through oxic sediments was solubilized by a hydroxylamine-acetic acid solution, releasing trace metals associated with Fe and Mn oxides. Moreover, Gerringa (1990) stated that dissolved Pb concentrations remained constant throughout her experiments. This observation is consistent with the results of the investigation conducted by Gambrell et al. (1991). The authors suggested that Pb was little affected by redox potential variations. Gambrell et al. (1991) concluded that Pb was very efficiently immobilized by sulphide precipitation and complexation with insoluble organic matter under reducing conditions and by Fe oxyhydroxides under well-oxidized conditions. Lead released to solution in our resuspension experiments as a result of organic matter degradation, therefore, was most likely readsorbed rapidly onto newly precipitated Fe oxyhydroxides. The relevance of this hypothesis may have been revealed by a 1N HCl extraction of the resuspended sediments.

Ni can also be released to solution as a consequence of microbial organic matter mineralization, but the distribution of this trace metal in sediments is not regulated by organic matter (Loring, 1976b; Westerlund, 1986; Gerringa, 1990; Shaw et al., 1990; Lapp and Balzer, 1993). Loring (1975) stated that Ni was primarily associated with Mn oxyhydroxides formed on particulate matter in the water column and present as grain coatings in sediments. Other authors also proposed that Ni distribution in sediments is mostly determined by the redox-controlled cycle of Mn (Klinkhammer, 1982; Sawlan and Murray, 1983; Shaw et al., 1990). Our results suggests that Ni concentrations in the slurries were mostly controlled by adsorption onto phases such as Mn oxyhydroxides during the first week of sediment resuspension. Nevertheless, Ni appears to have been associated to DOC during the following weeks, as its dissolved concentration increased similarly to those of Cu and Hg. Gerringa (1990) also observed that dissolved Ni was associated to DOC during her resuspension experiment.

### 5.1.6 Summary:

The DOC production during our experiments probably originated from a single and homogeneous pool of POM, as reflected by the nearly logarithmic linear increase in DOC concentrations observed throughout the resuspensions. The progressive accumulation of DOC observed in the slurries of our experiments reflects the refractory nature of the organic matter found in the Saguenay Fjord sediments as well as that of the DOC produced as a result of its degradation.

Iron remobilization at the beginning of our experiments was rapid, reaching concentrations as high as 3.7 ppm in experiment #7, and occurred mainly as a result of AVS dissolution. Given the relatively low pyrite concentrations in the Fjord sediments, and its slow kinetics of oxidation and dissolution, the contribution of this phase to trace metals remobilization during our experiments was not considered significant. Assuming that Fe monosulphides were the only important source of Fe in the slurries, less than 4 % of the Fe originating from the oxidation of this phase remained in solution 2 minutes (0.03 hour) after its resuspension. Dissolved Fe was rapidly oxidized following its release and presumably precipitated as Fe oxyhydroxides within the first hour of sediment resuspension.

Mn remobilization originated from the dissolution of different mineral phases. Based on the Langmuir isotherm adsorption model developed by Arakaki and Morse (1993), a small fraction of the Mn released to solution (<5%) originated from AVS oxidation and dissolution. This release was a function of the surface concentration of Mn on AVS (mole of Mn per mole of FeS). Most of the Mn remobilized, thus, took place following the dissolution of HCl-extractable phases, other than AVS, such as Mn carbonates or mixed Mn Ca carbonates, as well as from the desorption of exchangeable Mn from solid surfaces such as clay minerals. Our extraction procedures did not, however, allow us to evaluate the relative contribution of these different phases. Assuming that Mn remobilization during our experiments originated from Mn bearing HCl-extractable phases (i.e. exchangeable Mn, oxyhydroxides, carbonates, AVS), less than 12 % of the Mn associated to these phases would have been solubilized. Following its release, reduced Mn remained in solution over a longer period of time than Fe, due to its metastability in the presence of oxygen. It was ultimately oxidized and most likely reprecipitated as Mn oxyhydroxides after a week (168 hours).

Arsenic remobilization, as was the case for Fe, was mainly caused by the AVS oxidation and dissolution. A lack of relevant thermodynamic data, however, did not allow us to quantify the extent of As association to the Fe monosulphides. Once again, given the occurrence of abnormally high AVS and relatively low pyrite concentrations in the Saguenay Fjord sediments, As release from pyrite dissolution was assumed negligible, despite its strong affinity for pyrite. The As residence time in the slurries was very similar to that of Mn reflecting the possible implication of Mn oxyhydroxides precipitation in As (III) oxidation and removal from the solutions. On the other hand, our results also suggest that an important portion of dissolved arsenic (60%) was very rapidly oxidized following its release. Newly precipitated Fe oxyhydroxides may have triggered part of the arsenite oxidation in the first few minutes ( 0.083 hour) of sediment resuspension.

Mercury, Cu, Ni and Pb remobilization would have been predominantly induced by the relatively fast POM degradation, which occurred during the first 24 hours of sediment resuspension. However, the contribution of porewaters and other solid phases such as Fe monosulphides could not be determined due to a lack of relevant data. The strong affinity of these trace metals for POM as well as Fe and Mn oxyhydroxides most likely caused their immediate removal from solution following their release in the first hours of the resuspension experiments.

On the other hand, the general increase of these trace metals and As in the slurry solutions observed after a week of sediment resuspension, may have resulted from several processes. A bacterial bloom may have intensified microbial organic matter degradation at room temperature, and generated this progressive release of trace metal to solution. Moreover, the bacteria present in the experimental slurries may have produced strong metal ligands, resulting in an increase of dissolved trace metals concentrations. Many studies have reported that extracellular polymers of bacterial origin, occurring naturally in aquatic environments as dissolved macromolecules (McCarthy et al., 1993), were effective metal binding agents (Brown and Lester, 1982a, b; Lion et al., 1988; Chen et al., 1995). A bacterial bloom would, however, have required the presence of nutrients which may have been limited by the refractory nature of the organic matter available from the Saguenay Fjord sediments.

Additionally, sediment mixing may have modified trace metal partitioning within solid sediments over time, leading to an increase in their fraction associated to reactive phases and thereby promoting their remobilization (Gerringa, 1990). Upon their release, Hg, Cu and Ni, to some extent, were maintained in solution due to their strong affinity for DOC, as DOC concentrations in the slurries were maximal. On the other hand, Pb was mostly readsorbed onto the newly precipitated Fe oxyhydroxides, despite its strong affinity for DOC. Finally, colloidal Fe oxyhydroxides particles as well as the formation of organoarsenic complexes could have prevented As from returning to the sediments in the last weeks of our resuspension experiments. The formation of colloidal Fe oxyhydroxides would have originated from the deflocculation of newly precipitated Fe oxyhydroxides due to a continuous sediment mixing.

# 6.0 CONCLUSION:

Results of this investigation clearly highlight the spatial heterogeneity of the Saguenay Fjord sediments and the non steady-state sedimentation regime of this environment. The Saguenay Fjord, particularly the landward slope of the inner basin, is the site of slumping events due to its very steep and narrow banks, onto which poorly consolidated mud is accumulated. Moreover, dredging operations in and around harbor installations in the Saguenay Fjord further enhance these processes. The organic matter and AVS vertical distributions at Sag-15'94 and Sag-15'95, as well as other geochemical indicators, reflect the presence of these episodic depositional events.

Over the past century, a number of landslides events in the Saguenay valley have had a significant impact on sediment deposition in the north arm and inner basin of the Fjord. The most imporant ones are the St. Jean Vianney and Kenogami slides which took place, respectively, in 1971 and 1924. Additionally, geophysical surveys conducted in the northern arm of the Fjord revealed the presence of numerous types of topographic features which were attributed to the occurrence of submarine slides triggered by earth quakes in the region (Fortin and Pelletier, 1995). The recent flood of July 1996 is also a very good example of a mass wasting event generating sediment resuspension. Due to the thinness of the oxic layer in the Saguenay Fjord sediments, which varies between 1 to 5 mm, these events induce the resuspension of both oxic and anoxic sediments to the water column.

The results of our resuspension experiments show that the resuspension of oxic sediments should not lead to important trace metal release to the water column. On the other hand, the resuspension of anoxic sediments into an oxygenated water column should induce a significant release of Fe, Mn and more importantly, As to the environment. The contribution of the anoxic porewaters to trace metals remobilization in the Saguenay Fjord sediments is not substantial for Fe and Mn ( 10 %), but can be more important in the case of As (10 to 30 %). However, Fe and Mn porewater contribution can increase significantly in sediments sampled near past landslide layer boundaries (Mucci and Edenborn, 1992).

Iron and As remobilization is directly related to the AVS concentration in the sediments. The release of Mn to solution, however, appears to be mainly controlled by the dissolution of a solid phase, other than AVS, to which reduced Mn is associated. This phase, which is extracted by a cold 1N HCl solution may be a Mn carbonate, a Ca Mn carbonate or exchangeable Mn. The release of Mn to solution from AVS oxidation and dissolution would represent less than 5% of the total (porewater-corrected) remobilized Mn, and is a function of the surface Mn concentration on AVS. Assuming that Fe monosulphides were the only solid phase contributing to Fe remobilization, less than 4 % of the Fe originating from the oxidation of this phase remained in solution 2 minutes (0.03 hour) after its resuspension. Similarly, assuming that Mn and As in the slurries originated only from the dissolution of HCl-extractable phases, between 6 to 12% of $Mn_{HCl}$ and 2 to 5 % of $As_{HCl}$ were remobilized following the exposure of the fjord's anoxic sediments to oxygenated seawater.

Following their remobilization, these trace metals are efficiently scavenged by newly precipitated Fe and Mn oxyhydroxides. Our experiments showed that Fe released upon the resuspension of anoxic sediments into oxygenated seawater is removed very rapidly, within less than one hour, whereas Mn and As remain in solution for more than one week. The similarity of the Mn and As residence times suggests that a significant fraction of dissolved As(III) is oxidized to As(V) by the newly precipitated Mn oxyhydroxides prior to its adsorption onto Fe oxyhydroxides. Nevertheless, our results indicate that up to 60 % of dissolved As(III) may have been oxidized directly by precipitating Fe oxyhydroxides immediately after its release. The very high concentrations of reactive Fe found in the Saguenay Fjord sediments most likely enhance the importance of this process in our experiments.

On the other hand, Hg, Cu, Ni and Pb remobilization following the resuspension of Saguenay Fjord sediments does not appear to be significant. The contribution of the potential sources (i.e. porewater, POM degradation, AVS dissolution, etc.) to the remobilization of these trace metals remains unknown due to a lack of relevant data. Mercury, Cu, Ni and Pb were apparently removed from the solutions of our experiments immediately upon their release. The strong affinity of these trace metals towards POM and Fe and Mn oxyhydroxides is most likely responsible for their relatively low solubilization.

Finally, sediment reworking in the Saguenay Fjord environment, induced by dredging operations or natural slumping events, is most likely to release significant amounts of Fe, Mn and As to the water column. The relatively long residence time of As in solution certainly represents a threat to the biosphere of the Saguenay system. This toxic element is often mistaken for phosphate by marine organisms and taken up during metabolic processes (Planas and Healy, 1978; Andreae 1979; Richard, 1996). Moreover, As may also be bioconcentrated by marine organisms, although to a less extent than Hg (Ferguson and Gavis, 1972, Lunde, 1977). Finally trace metals exhibiting strong affinities for POM, like Hg, Cu and Pb, should not be strongly remobilized following the resuspension of organic-rich sediments.

# 7.0 FUTURE WORK AND RECOMMENDATIONS:

Despite the growing concern about trace metal contamination in coastal sediments, very few investigations have been conducted on the impact of sediment resuspension on aquatic systems. The objective of this research was to look at the reactivity of the Saguenay Fjord sediments and the potential hazard to the environment that would result from their resuspension into an oxygenated water column.

Whereas the results of this study were very conclusive for Fe, Mn and As remobilization upon sediment resuspension, our investigation demonstrated that the processes governing Hg, Cu, Ni and Pb remobilization are far more complex. The mechanisms controlling the remobilization of these trace metals following sediment reworking remain poorly understood. In order to obtain a better understanding of the processes, many unexplored aspects in this study should be reconsidered.

Analysis of solid sediments at various stages of the resuspension experiments may reveal more information on the different processes occurring during sediment reworking. The use of sequential extraction procedures, although plagued by operational definitions, can yield valuable information on the chemical behaviour of elements in the sediments. On the other hand, electron microprobe and x-ray diffractrometry can also provide important informations on the nature and evolution of solids in the resuspended sediments as well as their associated trace metals. These instrumental techniques, however, have high detection limits and would not detect amorphous phases. Alternatively, speciation analysis of dissolved trace metals may also provide insights on the nature of trace metal complexation in solution as well as the reactions resulting in their release to and removal from solution.

Moreover, futur resuspension experiments should be conducted using larger volumes of seawater solution to allow multiple sampling without replacing the sampled volume. This in turn would simplify sampling procedures and maintain the sediment:water ratio constant throughout the experiments. Sampling intervals should also be reduced in the first moments of the experiments (<2minutes) in order to obtain a better resolution on kinetically fast reactions such as the oxidation of FeS. Additionally, laboratory experiments should be performed at temperatures reflecting the natural environment where sediment reworking is most likely to take place.

Alternatively, the study of competitive and non-competitive trace metal adsorption on specific surfaces, naturally occurring in sediments, may further enlarge our knowledge on the reactions controlling trace metals remobilization as a result of sediment resuspension. Such substrate should include amorphous and crystalline Fe and Mn oxyhydroxides, organic matter, clays as well as pyrite and Fe monosulphides.

Finally, a better understanding of the implications of sediment reworking in contaminated environments is necessary to evaluate the potential risks for the biosphere of aquatic systems such as the Saguenay Fjord. Implications of this research may, thus, find applications in future management of aquatic systems punctuated by an important industrialization and maritime activity.

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# APPENDIX 1

## Characteristics and composition of the sediments

| Sag-15'94 | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Depth (cm) | Porosity $\phi$ | $C_{TOT}$ Wgt % | $C_{org.}$ Wgt % | $C_{inorg.}$ Wgt % | $N_{TOT}$ Wgt % | C/N Molar Ratio | AVS-S (umol/g) | Pyrite-S (umol/g) |
| 0-0.5 | 0.819 | 1.93 | 1.86 | 0.067 | 0.09 | 24.3 | 1.16 | 3.76 |
| 0.5-1.0 | 0.821 | 2.20 | 2.14 | 0.064 | 0.11 | 23.3 | 1.12 | 4.22 |
| 1.0-2.0 | 0.815 | 2.20 | 2.14 | 0.059 | 0.11 | 22.7 | 0.96 | 4.58 |
| 2.0-3.0 | 0.817 | 2.24 | 2.18 | 0.063 | 0.12 | 22.6 | 0.99 | 6.24 |
| 3.0-4.0 | 0.813 | 2.25 | 2.19 | 0.065 | 0.12 | 23.0 | 1.38 | 7.02 |
| 4.0-5.0 | 0.792 | 1.62 | 1.56 | 0.063 | 0.08 | 23.4 | 1.88 | 10.18 |
| 5.0-6.0 | 0.723 | 1.93 | 1.86 | 0.072 | 0.09 | 26.2 | 3.37 | 8.88 |
| 6.0-8.0 | 0.760 | 2.08 | 2.01 | 0.067 | 0.10 | 24.4 | 12.46 | 5.04 |
| 8.0-10.0 | 0.701 | 1.99 | 1.91 | 0.083 | 0.10 | 22.5 | 18.13 | 9.24 |
| 10.0-12.0 | 0.717 | 1.61 | 1.56 | 0.051 | 0.08 | 22.7 | 17.90 | 7.44 |
| 12.0-14.0 | 0.736 | 1.87 | 1.80 | 0.070 | 0.09 | 24.3 | 23.22 | 4.98 |
| 14.0-16.0 | 0.730 | 1.79 | 1.72 | 0.066 | 0.09 | 23.9 | 19.56 | 5.08 |
| 16.0-18.0 | 0.730 | 1.70 | 1.64 | 0.064 | 0.08 | 24.8 | 17.05 | 6.16 |
| 18.0-20.0 | 0.729 | 1.68 | 1.61 | 0.072 | 0.09 | 22.9 | 21.54 | 5.80 |
| 22.0-24.0 | 0.741 | 2.28 | 2.21 | 0.067 | 0.11 | 24.0 | 8.89 | 4.34 |
| 26.0-28.0 | 0.745 | 2.42 | 2.36 | 0.057 | 0.11 | 26.2 | 24.03 | - |
| 32.0-34.0 | 0.747 | 2.73 | 2.67 | 0.063 | 0.13 | 24.9 | 33.44 | 5.40 |
| 38.0-40.0 | 0.750 | 2.33 | 2.26 | 0.067 | 0.11 | 25.1 | 32.35 | 6.06 |

| Sag-15'95 | | | | | | | |
|---|---|---|---|---|---|---|---|
| Depth (cm) | Porosity $\phi$ | $C_{TOT}$ Wgt % | $C_{org.}$ Wgt % | $C_{inorg.}$ Wgt % | $N_{TOT}$ Wgt % | C/N Molar Ratio | AVS-S (umol/g) |
| 0-0.5 | 0.806 | 1.92 | 1.84 | 0.081 | 0.09 | 24.1 | 1.73 |
| 0.5-1.0 | 0.814 | 2.06 | 1.99 | 0.074 | 0.10 | 23.3 | 1.87 |
| 1.0-2.0 | 0.807 | 2.12 | 2.04 | 0.076 | 0.11 | 22.8 | - |
| 2.0-3.0 | 0.808 | 2.31 | 2.24 | 0.072 | 0.12 | 21.9 | 2.09 |
| 3.0-4.0 | 0.738 | 2.02 | 1.94 | 0.077 | 0.10 | 23.2 | 15.45 |
| 4.0-5.0 | 0.685 | 1.57 | 1.50 | 0.069 | 0.08 | 24.2 | 17.59 |
| 5.0-7.0 | 0.722 | 1.52 | 1.43 | 0.089 | 0.08 | 23.8 | 25.62 |
| 7.0-9.0 | 0.749 | 1.83 | 1.74 | 0.087 | 0.09 | 22.8 | 25.44 |
| 9.0-11.0 | 0.766 | 2.15 | 2.08 | 0.072 | 0.11 | 22.8 | 28.05 |
| 11.0-13.0 | 0.782 | 2.56 | 2.49 | 0.069 | 0.14 | 22.1 | 31.23 |
| 13.0-15.0 | 0.762 | 2.61 | 2.54 | 0.074 | 0.13 | 24.2 | 46.59 |
| 15.0-17.0 | 0.760 | 2.36 | 2.28 | 0.078 | 0.11 | 24.1 | 17.55 |
| 17.0-19.0 | 0.764 | 2.35 | 2.28 | 0.075 | 0.11 | 24.9 | 27.55 |
| 19.0-21.0 | 0.764 | 2.44 | 2.37 | 0.072 | 0.11 | 25.4 | 31.81 |
| 21.0-23.0 | 0.764 | 2.50 | 2.44 | 0.063 | 0.11 | 26.3 | 28.38 |
| 23.0-25.0 | 0.758 | 2.47 | 2.40 | 0.070 | 0.10 | 29.5 | 29.94 |
| 25.0-28.0 | 0.757 | 2.46 | 2.38 | 0.077 | 0.11 | 25.2 | 28.48 |
| 28.0-31.0 | 0.757 | 2.57 | 2.50 | 0.070 | 0.13 | 23.1 | 29.14 |
| 31.0-34.0 | 0.755 | 2.47 | 2.40 | 0.073 | 0.12 | 24.9 | 18.77 |
| 34.0-37.0 | 0.754 | 2.63 | 2.56 | 0.075 | 0.13 | 23.9 | 26.77 |
| 37.0-40.0 | 0.759 | 2.68 | 2.62 | 0.063 | 0.10 | 30.4 | 19.52 |

# APPENDIX 2

Distribution and concentrations of trace metals in the sediments

| Sag-15'94 | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Depth (cm) | $Fe_{HCl}$ (µg/g) | $Mn_{HCl}$ (µg/g) | $As_{TOT}$ (µg/g) | $As_{HCl}$ (µg/g) | $Hg_{TOT}$ (ng/g) | $Hg_{HCl}$ (µg/g) | $Cu_{HCl}$ (µg/g) | $Ni_{HCl}$ (µg/g) |
| 0-0.5 | 25959 | 1694 | 20.8 | 14.9 | 270 | 169 | 3.1 | 13.2 |
| 0.5-1.0 | 29019 | 1383 | 21.2 | 13.7 | 273 | 146 | 2.9 | 11.8 |
| 1.0-2.0 | 29554 | 872 | 23.4 | 14.1 | 312 | 158 | 2.9 | 11.8 |
| 2.0-3.0 | 30398 | 643 | 20.7 | - | 282 | 147 | 2.9 | 14.0 |
| 3.0-4.0 | 29635 | 553 | 22.2 | 10.7 | 317 | 143 | 3.4 | 13.0 |
| 4.0-5.0 | 28108 | 407 | 17.9 | 8.7 | 399 | 184 | 2.6 | 14.2 |
| 5.0-6.0 | 22867 | 318 | 12.7 | 4.6 | 402 | 28 | 2.7 | 13.4 |
| 6.0-8.0 | 26913 | 368 | 17.4 | 7.0 | 308 | 122 | 3.0 | 12.6 |
| 8.0-10.0 | 10039 | 182 | 14.7 | 6.0 | 349 | 85 | 2.3 | 10.7 |
| 10.0-12.0 | 24140 | 361 | 12.4 | 7.9 | 358 | 96 | 2.1 | 11.6 |
| 12.0-14.0 | 22033 | 384 | 16.4 | 8.1 | 461 | 103 | 3.2 | 12.5 |
| 14.0-16.0 | 12977 | 254 | 17.9 | 7.7 | 445 | 118 | 2.5 | 12.5 |
| 16.0-18.0 | 22731 | 419 | 21.8 | 11.4 | 379 | 135 | 2.6 | 12.7 |
| 18.0-20.0 | 27196 | 415 | 15.0 | 7.4 | 315 | 89 | 2.6 | 12.0 |
| 22.0-24.0 | 25259 | 451 | 23.5 | 13.7 | 488 | 172 | 3.5 | 11.8 |
| 26.0-28.0 | 21335 | 395 | 11.2 | 4.7 | 4217 | 106 | 4.0 | 15.4 |
| 32.0-34.0 | 21985 | 358 | 14.0 | 6.7 | 3434 | 145 | 4.4 | 17.1 |
| 38.0-40.0 | 19978 | 420 | 15.4 | 6.0 | 487 | 106 | 4.2 | 15.0 |

| Sag-15'95 | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Depth (cm) | $Fe_{TOT}$ (µg/g) | $Fe_{HCl}$ (µg/g) | $Mn_{TOT}$ (µg/g) | $Mn_{HCl}$ (µg/g) | $As_{TOT}$ (µg/g) | $As_{HCl}$ (µg/g) | $Hg_{TOT}$ (ng/g) | $Hg_{HCl}$ (ng/g) | $Cu_{TOT}$ (µg/g) | $Cu_{HCl}$ (µg/g) | $Ni_{TOT}$ (µg/g) | $Ni_{HCl}$ (µg/g) | $Pb_{TOT}$ (µg/g) |
| 0-0.5 | 46377 | 25223 | 1293 | 908 | 24.5 | 22.1 | 305 | 150 | 18 | 4.5 | 28 | 11.0 | 23.3 |
| 0.5-1.0 | 47006 | 24052 | 1069 | 636 | 23.5 | 19.1 | 341 | 122 | 24 | 3.0 | 29 | 11.1 | 23.9 |
| 1.0-2.0 | 45048 | 22334 | 782 | 418 | 25.5 | 16.1 | 285 | 110 | 40 | 3.2 | 29 | 12.0 | 23.5 |
| 2.0-3.0 | 41620 | 22434 | 682 | 325 | 19.3 | 14.2 | 268 | 94 | 15 | 3.8 | 36 | 12.2 | 24.7 |
| 3.0-4.0 | 40921 | 17990 | 635 | 191 | 15.6 | 7.1 | 363 | 18.2 | 31 | 2.3 | 36 | 12.0 | 25.8 |
| 4.0-5.0 | 44908 | 14774 | 604 | 160 | 13.8 | 2.9 | 342 | 8.4 | 31 | 1.6 | 33 | 10.2 | 27.0 |
| 5.0-7.0 | 45747 | 19835 | 651 | 221 | 12.7 | 3.1 | 451 | 3.3 | 31 | 1.6 | 34 | 13.6 | 27.9 |
| 7.0-9.0 | 50154 | 21017 | 643 | 230 | 15.0 | 4.2 | 586 | 6.6 | 21 | 1.7 | 38 | 16.1 | 82.2 |
| 9.0-11.0 | 49734 | 25105 | 713 | 294 | 36.1 | 15.9 | 577 | 13.2 | 34 | 2.5 | 32 | 14.3 | 38.7 |
| 11.0-13.0 | 49944 | 26219 | 682 | 296 | 29.7 | 17.7 | 635 | 49.0 | 46 | 3.1 | 34 | 15.8 | 48.1 |
| 13.0-15.0 | 49525 | 24742 | 682 | 262 | 25.7 | 7.9 | 1084 | 22.4 | 40 | 3.1 | 47 | 16.2 | 55.2 |
| 15.0-17.0 | 41845 | 24144 | 674 | 256 | 20.7 | 6.4 | 1509 | 15.1 | 33 | 2.7 | 37 | 16.1 | 62.6 |
| 17.0-19.0 | 49944 | 25437 | 666 | 284 | 22.7 | 9.4 | 1860 | 34.6 | 53 | 2.3 | 40 | 17.6 | 63.7 |
| 19.0-21.0 | 50574 | 27875 | 689 | 312 | 22.7 | 9.7 | 1974 | 29.7 | 40 | 2.3 | 37 | 19.4 | 59.2 |
| 21.0-23.0 | 51483 | 27775 | 705 | 327 | 24.5 | 11.6 | 1967 | 39.9 | 48 | 2.3 | 38 | 19.2 | 60.1 |
| 23.0-25.0 | 51203 | 27491 | 697 | 314 | 25.2 | 11.3 | 2118 | 34.6 | 33 | 2.1 | 37 | 18.0 | 59.3 |
| 25.0-28.0 | 51343 | 28827 | 720 | 329 | 26.0 | 11.9 | 2105 | 34.7 | 106 | 2.4 | 35 | 17.7 | 58.0 |
| 28.0-31.0 | 51064 | 27829 | 736 | 319 | 25.2 | 12.1 | 1991 | 22.2 | 42 | 2.4 | 38 | 16.9 | 50.1 |
| 31.0-34.0 | 50224 | 26698 | 728 | 328 | 27.2 | 11.8 | 1466 | 25.3 | 65 | 2.2 | 36 | 17.9 | 52.6 |
| 34.0-37.0 | 50714 | 26655 | 790 | 336 | 26.0 | 13.1 | 1404 | 24.8 | 26 | 2.3 | 36 | 15.6 | 55.8 |
| 37.0-40.0 | 50084 | 27607 | 720 | 327 | 26.0 | 11.5 | 2677 | 37.3 | 58 | 2.2 | 35 | 19.1 | 54.4 |

# APPENDIX 3

## Depth distribution of dissolved Fe, Mn and As [a]

| Sag-15'95 | | | |
|---|---|---|---|
| Depth (cm) | Fe (mg/L) | Mn (mg/L) | As (µg/L) |
| 0-0.5 | 0 | 0 | 1.14 |
| 0.5-1.0 | 0 | 0 | 1.11 |
| 1.0-1.5 | 1.35 | 3.15 | 5.63 |
| 1.5-2.5 | 4.27 | 2.06 | - |
| 2.5-3.5 | 8.56 | - | 11.60 |
| 3.5-4.5 | 9.95 | 1.65 | 11.93 |
| 4.5-5.5 | 22.84 | 1.94 | - |
| 5.5-6.9 | 3.31 | - | - |
| 6.9-8.0 | - | - | - |
| 8.0-9.0 | 1.26 | 1.29 | 12.86 |
| 9.0-10.0 | - | - | - |
| 10.0-11.0 | 1.86 | 1.69 | 19.95 |
| 11.0-12.0 | - | - | - |
| 12.0-13.0 | 1.47 | 1.59 | 35.95 |
| 14.0-15.0 | 2.7 | 1.77 | 41.25 |
| 16.0-17.0 | 23.34 | 2.45 | 51.95 |
| 17.0-18.0 | 3.14 | - | - |
| 18.0-19.0 | - | 1.65 | 71.00 |
| 23.5-24.5 | 2.74 | 2.13 | 79.50 |
| 26.5-27.5 | 3.44 | 1.94 | 83.30 |
| 31.5-32.5 | 1.23 | 2.23 | 84.10 |
| 36.5-37.5 | 1.17 | 2.14 | 83.65 |
| 42.5-43.5 | 0.13 | 2.17 | 74.80 |

[a] Richard (1996)

## Depth distribution of dissolved Hg [b]

| Sag-15-92 | |
|---|---|
| Depth (cm) | Hg (ng/L) |
| 0-0.5 | 55 |
| 0.5-1.0 | 51 |
| 1.0-2.0 | 47 |
| 2.0-3.0 | 42 |
| 3.0-4.0 | 64 |
| 4.0-5.0 | 62 |
| 5.0-6.0 | 60 |
| 6.0-7.0 | 35 |
| 8.0-9.0 | 29 |
| 9.0-10.0 | 37 |
| 10.0-12.0 | 43 |
| 12.0-14.0 | 35 |
| 14.0-16.0 | 30 |
| 18.0-20.0 | 32 |
| 20.0-22.0 | 82 |
| 24.0-27.0 | 59 |
| 27.0-29.0 | 63 |
| 29.0-33.0 | 105 |
| 33.0-36.0 | 78 |
| 36.0-40.0 | 49 |

[b] Gagnon et al. (1996b)

# APPENDIX 4

## Dissolved trace metal, DOC and N concentrations in the resuspension experiments

Resuspension experiments #11

| Sampling times (hour) | Fe (µg/L) | Mn (µg/L) | As (µg/L) | Cu (µg/L) | Ni (µg/L) | Pb (µg/L) | Hg (ng/L) | DOC (mg/L) |
|---|---|---|---|---|---|---|---|---|
| 0 | ≤0.5 | ≤0.14 | 0.57 | 2.85 | 5.45 | ≤0.18 | ≤20 | 2.8 |
| 0.033 | 2.5 | 18.4 | 0.62 | 4.93 | 6.73 | ≤0.18 | 135 | 5.0 |
| 0.083 | 1.8 | 19.6 | 0.72 | 3.71 | 3.80 | ≤0.18 | 49 | 5.7 |
| 0.25 | 2.3 | 12.0 | 0.80 | 5.25 | 5.72 | ≤0.18 | ≤20 | 6.1 |
| 0.50 | 3.8 | 7.1 | 1.08 | 2.94 | 5.59 | ≤0.18 | 65 | 5.7 |
| 1 | 7.6 | ≤0.14 | 1.45 | 6.02 | 3.85 | ≤0.18 | 45 | 5.9 |
| 3 | 2.3 | ≤0.14 | 1.78 | - | - | - | - | 6.8 |
| 5 | 15.3 | ≤0.14 | 1.95 | 9.11 | 2.94 | ≤0.18 | 113 | 7.9 |
| 24 | 2.8 | ≤0.14 | 2.47 | 3.23 | 2.37 | ≤0.18 | 92 | 9.1 |
| 168 | 112.5 | ≤0.14 | 2.91 | 3.35 | 2.06 | ≤0.18 | ≤20 | 10.5 |
| 336 | 33.7 | 15.5 | 3.54 | 4.47 | 3.40 | ≤0.18 | ≤20 | 10.3 |
| 672 | 83.1 | 11.6 | 4.20 | 5.56 | 2.06 | ≤0.18 | - | 9.7 |
| 1008 | 46.3 | 11.1 | 4.88 | 7.11 | 10.68 | ≤0.18 | 30 | 9.5 |
| 1344 | 45.1 | - | 4.58 | 5.47 | - | - | - | - |

Resuspension experiment #9

| Sampling times (hour) | Fe (µg/L) | Mn (µg/L) | As (µg/L) | Cu (µg/L) | Ni (µg/L) | Pb (µg/L) | Hg (ng/L) | DOC (mg/L) | N (µg/L) |
|---|---|---|---|---|---|---|---|---|---|
| 0 | ≤0.5 | 7.6 | 0.99 | 1.87 | 1.43 | 3.72 | 87 | 2.7 | 126.7 |
| 0.033 | 17.2 | 207.5 | 0.72 | 3.46 | 0.59 | 1.19 | - | 5.3 | 798.3 |
| 0.083 | 8.6 | 190.1 | 0.74 | 4.48 | 2.55 | 0.61 | 182 | 6.4 | 377.2 |
| 0.25 | 145.9 | 144.6 | 0.91 | 3.68 | - | 0.89 | 181 | 6.7 | 821.7 |
| 0.50 | 64.6 | 96.2 | 0.93 | 3.41 | 0.62 | 0.28 | - | 6.6 | 496.9 |
| 1 | 30.7 | 34.8 | 0.91 | 7.92 | 4.80 | 6.53 | 167 | 9.7 | 394.7 |
| 3 | 9.8 | 16.3 | 0.93 | 6.00 | 3.55 | 0.80 | - | 9.1 | 1033.5 |
| 5 | 145.9 | 4.4 | 0.95 | 7.48 | 2.11 | ≤0.18 | 236 | 8.8 | 272.2 |
| 24 | 132.6 | 6.2 | 1.19 | 8.21 | 0.52 | 0.50 | 104 | 9.2 | 1245.4 |
| 48 | 55.7 | 5.3 | 1.43 | 3.19 | 0.64 | 1.33 | 80 | 10.8 | 914.9 |
| 168 | 57.7 | 4.4 | 2.10 | 5.57 | - | - | 83 | 13.9 | 2214.2 |
| 336 | 51.9 | 25.5 | 2.26 | 6.48 | 3.65 | 1.97 | 345 | 17.3 | - |
| 504 | 46.2 | 19.5 | 2.34 | 6.71 | 2.24 | 6.98 | 23 | 15.6 | 2067.4 |
| 672 | 47.6 | 16.3 | 2.73 | 4.01 | 0.50 | 1.58 | 54 | 15.5 | 1507.8 |
| 1008 | 97.9 | 15.1 | 2.58 | 5.00 | ≤0.36 | ≤0.18 | - | 15.7 | 1330.0 |
| 1344 | 71.5 | 27.5 | 3.42 | 6.81 | ≤0.36 | ≤0.18 | 120 | 16.1 | 1610.0 |
| 2424 | 69.7 | 7.2 | 4.75 | 9.16 | 2.99 | 0.54 | 49 | 15.4 | - |

Resuspension experiment #10

| Sampling times (hour) | Fe (µg/L) | Mn (µg/L) | As (µg/L) | Cu (µg/L) | Ni (µg/L) | Pb (µg/L) | Hg (ng/L) | DOC (mg/L) | N (µg/L) |
|---|---|---|---|---|---|---|---|---|---|
| 0 | 5.8 | 9.8 | 0.82 | ≤0.23 | 0.92 | 0.99 | 88 | 1.9 | 102.2 |
| 0.033 | 607.3 | 197.1 | 5.01 | 2.45 | 1.94 | ≤0.18 | 29 | 4.1 | - |
| 0.083 | 359.9 | 295.0 | 6.00 | 0.63 | 1.45 | ≤0.18 | 51 | 5.8 | 159.5 |
| 0.25 | 127.3 | 331.8 | 6.29 | 2.36 | 1.61 | 3.17 | 33 | 6.3 | - |
| 0.50 | 95.2 | 108.5 | 5.47 | ≤0.23 | - | 0.86 | 11 | 8.7 | 162.3 |
| 1 | 70.5 | 94.6 | 5.17 | ≤0.23 | 0.98 | 1.85 | 16 | 7.9 | 188.9 |
| 3 | 61.6 | 194.8 | 4.56 | ≤0.23 | 1.19 | 1.03 | 41 | 9.8 | 164.6 |
| 5 | 119.2 | 270.1 | 4.55 | ≤0.23 | - | 0.64 | 26 | 11.6 | 417.6 |
| 24 | 55.8 | 48.4 | 4.83 | 3.45 | 1.35 | 1.44 | 28 | 10.9 | 314.4 |
| 168 | 75.1 | 16.0 | 4.91 | 5.05 | 2.23 | 1.61 | 125 | 14.1 | 204.8 |
| 336 | 75.6 | 16.1 | 5.17 | 4.71 | 7.48 | - | 20 | 12.4 | - |
| 672 | 56.1 | 11.2 | 5.74 | 7.71 | 3.43 | 0.21 | 56 | 13.0 | - |
| 1008 | 104.4 | 51.3 | 8.22 | 7.23 | 2.24 | 1.21 | 104 | 10.2 | 241.8 |
| 1344 | 15.5 | 37.6 | 8.75 | 5.53 | 2.08 | 0.19 | 15 | 10.2 | 315.8 |

Resuspension experiment #7

| Sampling times (hour) | Fe (µg/L) | Mn (µg/L) | As (µg/L) | Cu (µg/L) | Ni (µg/L) | Pb (µg/L) | Hg (ng/L) | DOC (mg/L) |
|---|---|---|---|---|---|---|---|---|
| 0 | 0.5 | 49.4 | 0.92 | 2.27 | 1.24 | ≤0.18 | 65 | 3.1 |
| 0.033 | 3392.2 | 490.5 | 9.50 | ≤0.23 | 2.04 | ≤0.18 | 45 | 7.1 |
| 0.083 | 3203.6 | 583.2 | 13.50 | ≤0.23 | 3.71 | ≤0.18 | 76 | 11.1 |
| 0.167 | 3677.7 | 650.7 | 14.46 | ≤0.23 | 0.96 | ≤0.18 | 51 | 9.1 |
| 0.417 | 2069.4 | 648.3 | 14.74 | ≤0.23 | 0.38 | ≤0.18 | 45 | 8.0 |
| 0.667 | 311.0 | 621.6 | 10.60 | ≤0.23 | 0.54 | ≤0.18 | 53 | 7.6 |
| 1 | 142.2 | 569.5 | 10.30 | 3.65 | 2.42 | 1.09 | 45 | 9.2 |
| 2 | 170.6 | 524.3 | 7.13 | 2.69 | 3.68 | 1.23 | 92 | 11.6 |
| 3 | 85.1 | 386.3 | 5.76 | ≤0.23 | 1.86 | 0.95 | 36 | 14.5 |
| 5 | 217.4 | 490.2 | 5.22 | 1.43 | 2.46 | 0.64 | 74 | 14.4 |
| 24 | 345.3 | 274.2 | 6.05 | 3.18 | 2.08 | 2.33 | 77 | 18.5 |
| 48 | 62.8 | 71.9 | 4.66 | 5.91 | 3.23 | 1.01 | 68 | 18.6 |
| 168 | 67.3 | 144.5 | 3.51 | 14.39 | 5.98 | 2.63 | 57 | 28.0 |
| 336 | 61.5 | 98.4 | 5.62 | 12.11 | 2.77 | 2.75 | 96 | 18.9 |
| 504 | 71.3 | 66.2 | 6.10 | 8.44 | 1.20 | ≤0.18 | 17 | 18.7 |
| 672 | 68.4 | 55.1 | 7.78 | 9.89 | 2.29 | 2.92 | 30 | 20.1 |
| 1008 | 247.5 | 103.4 | 9.58 | 14.91 | 3.32 | 0.43 | 99 | 21.0 |
| 1344 | 106.1 | 83.7 | 10.36 | 11.72 | 5.41 | 4.36 | 59 | 21.3 |

Resuspension experiment #8

| Sampling times (hour) | Fe (µg/L) | Mn (µg/L) | As (µg/L) | Cu (µg/L) | Ni (µg/L) | Pb (µg/L) | Hg (ng/L) | DOC (mg/L) | N (µg/L) |
|---|---|---|---|---|---|---|---|---|---|
| 0 | 4.27 | 16.6 | 0.67 | ≤0.23 | ≤0.36 | 1.01 | 81 | 3.0 | 251.4 |
| 0.033 | 1690.9 | 376.9 | 4.56 | 3.72 | ≤0.36 | 2.01 | 21 | 5.9 | 10794.0 |
| 0.083 | 2128.6 | 559.7 | 7.59 | ≤0.23 | 0.89 | 1.63 | 12 | 5.7 | 2231.9 |
| 0.25 | 513.3 | 715.6 | 8.32 | ≤0.23 | 0.74 | 0.83 | 35 | 6.7 | 1245.6 |
| 0.50 | 128.3 | 737.3 | 7.53 | 4.44 | 5.85 | 2.16 | 20 | 6.8 | 1458.8 |
| 1 | 65.6 | 691.3 | 8.13 | 5.45 | 2.57 | 1.31 | 12 | 8.1 | 4417.4 |
| 3 | 202.5 | 663.8 | 6.00 | 2.92 | 4.09 | 3.33 | 8 | 12.9 | 1082.9 |
| 5 | 61.3 | 625.5 | 5.67 | 1.73 | 0.88 | ≤0.18 | 49 | 14.1 | 2432.2 |
| 24 | 72.7 | 341.4 | 5.50 | 14.31 | 4.02 | 1.25 | 81 | 11.4 | 1834.4 |
| 48 | 48.5 | 205.8 | 4.34 | 4.71 | 1.14 | 0.54 | 21 | 16.8 | 776.9 |
| 168 | 61.3 | 117.0 | 3.05 | 6.35 | 1.38 | 0.83 | 6 | 17.6 | - |
| 336 | 184.6 | 56.8 | 4.19 | 11.72 | 2.61 | 4.84 | 28 | 15.8 | 2668.0 |
| 504 | 49.8 | 34.4 | 4.79 | 9.19 | 1.25 | 1.03 | 64 | 15.8 | 1502.1 |
| 672 | 63.2 | 38.8 | 4.83 | 10.57 | 2.82 | 2.06 | 46 | 16.7 | 1427.2 |
| 1008 | 92.6 | 76.9 | 5.71 | 6.53 | 2.94 | 1.96 | 69 | 18.3 | 136.1 |
| 1344 | 188.2 | 91.5 | 5.95 | 8.85 | 3.32 | 5.12 | 93 | 15.2 | 1371.4 |
| 3126 | 81.1 | 146.2 | 7.53 | 9.11 | 3.94 | 1.70 | 46 | 15.6 | - |

Resuspension experiment #12

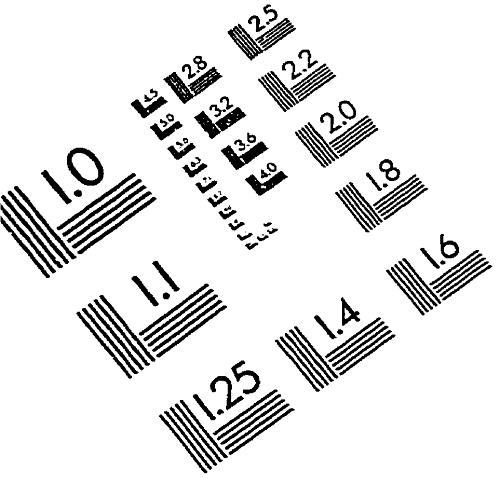
| Sampling times (hour) | Fe (µg/L) | Mn (µg/L) | As (µg/L) | Cu (µg/L) | Ni (µg/L) | Pb (µg/L) | Hg (ng/L) | DOC (mg/L) |
|---|---|---|---|---|---|---|---|---|
| 0 | ≤0.5 | ≤0.14 | 0.30 | 1.96 | 7.89 | ≤0.18 | 45 | 3.2 |
| 0.033 | 1829.7 | 582.7 | 8.80 | 1.95 | 1.34 | 0.24 | 44 | 5.1 |
| 0.083 | 1093.6 | 918.8 | 11.19 | - | 1.66 | ≤0.18 | 84 | 4.2 |
| 0.25 | 491.6 | 1100.8 | 11.88 | 0.70 | 10.92 | ≤0.18 | 86 | 6.9 |
| 0.50 | 94.6 | 1098.4 | 10.83 | <0.23 | 1.50 | ≤0.18 | - | 7.8 |
| 1 | 53.9 | 918.8 | 7.97 | 3.21 | 3.54 | 0.32 | - | 7.5 |
| 3 | 46.0 | 743.5 | 4.13 | 1.50 | 4.43 | 0.49 | 28 | 9.0 |
| 5 | 42.1 | 830.4 | 4.08 | 1.08 | 3.29 | ≤0.18 | 38 | 11.5 |
| 24 | 78.9 | 529.6 | 4.17 | 3.87 | 3.47 | 0.61 | 48 | 11.1 |
| 168 | 90.1 | 217.1 | 2.18 | 7.73 | 2.23 | 0.51 | 89 | 12.5 |
| 336 | 123.2 | 201.3 | 2.81 | 7.07 | - | ≤0.18 | 201 | 13.4 |
| 672 | 125.0 | 190.2 | 3.03 | 12.8 | 5.83 | 1.34 | 195 | 13.3 |
| 1008 | 110.2 | 195.4 | 3.14 | 15.1 | 7.0 | 1.03 | 169 | 16.0 |
| 1344 | 99.7 | 181.6 | 3.26 | 13.5 | 7.5 | 1.24 | 127 | 15.0 |

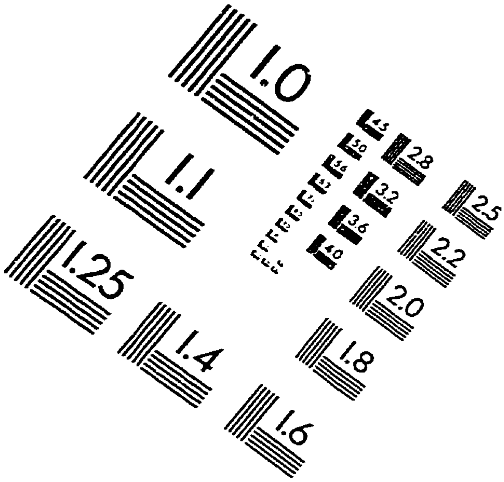
# APPENDIX 5

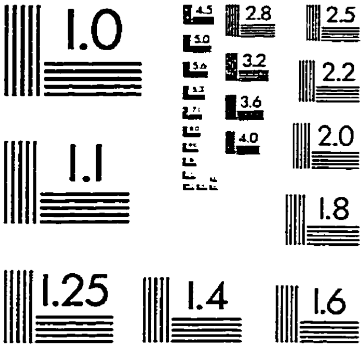
pH evolution during the resuspension experiments

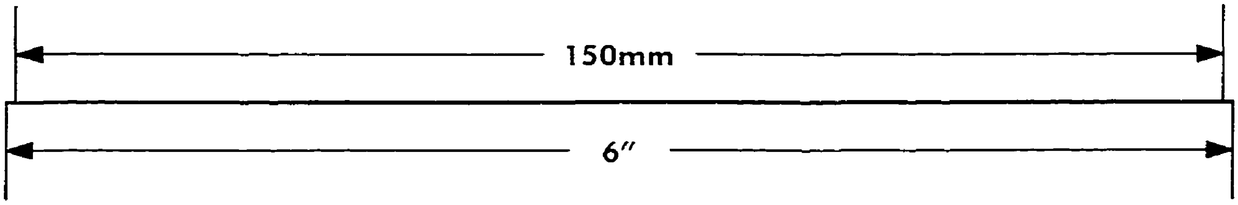
| | Resuspension Experiments | | | | | |
|---|---|---|---|---|---|---|
| Sampling times (hour) | #11 | #9 | #10 | #7 | #8 | #12 |
| 0 | 7.8 | 7.7 | 8.0 | 7.7 | 7.8 | 7.8 |
| 0.03 | 7.5 | 7.4 | 7.6 | 7.6 | 7.6 | 7.5 |
| 0.083 | 7.3 | 7.3 | 7.5 | 7.5 | 7.5 | 7.3 |
| 0.167 | - | | - | - | - | - |
| 0.25 | 7.3 | 7.2 | 7.4 | 7.3 | 7.3 | 7.3 |
| 0.417 | - | - | - | 7.3 | - | - |
| 0.50 | 7.3 | 7.2 | 7.4 | - | 7.4 | 7.3 |
| 0.667 | - | - | - | 7.3 | - | - |
| 1 | 7.4 | 7.3 | 7.5 | 7.3 | 7.4 | 7.4 |
| 2 | - | - | - | 7.4 | - | - |
| 3 | 7.4 | 7.3 | 7.4 | 7.4 | 7.4 | 7.4 |
| 5 | 7.4 | 7.3 | 7.5 | 7.6 | 7.5 | 7.4 |
| 24 | 7.4 | 7.4 | 7.4 | 7.6 | 7.6 | 7.2 |
| 48 | - | 7.5 | - | 7.5 | 7.3 | - |
| 168 | 7.6 | 7.5 | 7.5 | 7.3 | 7.1 | 7.1 |
| 336 | 7.6 | 7.6 | 7.4 | 7.5 | 7.2 | 7.2 |
| 504 | - | 7.5 | - | 7.5 | 7.3 | - |
| 672 | 7.6 | 7.5 | 7.5 | 7.5 | 7.3 | 7.3 |
| 1008 | 7.6 | 7.5 | 7.6 | 7.5 | 7.4 | 7.3 |
| 1344 | 7.6 | 7.6 | 7.6 | 7.5 | 7.4 | 7.3 |
| 2424 | - | 7.6 | - | - | - | - |
| 3126 | - | - | - | - | 7.4 | - |

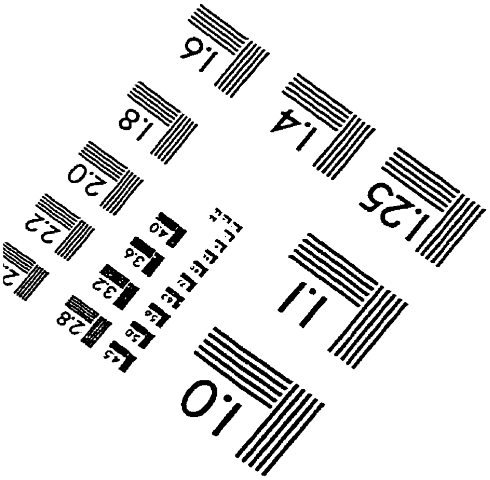
# IMAGE EVALUATION
# TEST TARGET (QA-3)











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