Impact of salmon aquaculture on sediment chemistry and mercury loading

by

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Abstract

One of the main environmental impacts of salmon aquaculture activities in the Bay of Fundy is the alteration of sediment chemistry as a result of the large amount of organic waste that accumulates below fish pens. To investigate these impacts, vertical profiles of $\delta^{13}C$, $\delta^{15}N$, C_{org}, C_{org}:N_{tot}, Fe_{HCl}, Mn_{HCl}, P_{tot}, P_{HCl}, SO_4^{2-}, AVS, Hg_{tot}, and Hg_{pyrite} in sediment cores collected throughout the bay were acquired. These profiles were then used to identify tracers of aquaculture activities and their impact on the redox zonation of the sediment. In addition, representative samples of fish food as well as farmed and wild salmon were analyzed to determine their Hg_{tot} content as well as $\delta^{13}C$, $\delta^{15}N$, C_{org}, C_{org}:N_{tot}.

Our results show that, as by-products of salmon aquaculture (e.g., uneaten food, feces, antibiotics, and anti-fouling agents) accumulate in the sediments, their reactive organic carbon content increases and generate a greater oxygen demand. Subsequently, an upwards migration of the oxygen penetration depth and redox boundaries in the sediment column occurs, which is confirmed on the basis of the distribution of redox-sensitive phases (e.g., authigenic metal oxides and AVS) in the sediments. High resolution voltammetric microelectrode measurements show that the Fe_{HCl} and Mn_{HCl} distributions overestimate the oxygen penetration depth in the sediments. The total phosphorus distribution in the sediment record is shown to be a suitable tracer of marine aquaculture, reflecting the recent history of residual feed and fecal matter accumulation in the sediments.

Elevated mercury concentrations in sediments under fish pens are explained by its strong affinity for organic carbon. Although the source of additional Hg has yet to be resolved, as the organic carbon content of the sediments increases in response to the input from fish farming activities, so does the associated Hg. Mercury also partitions strongly to authigenic pyrite in the deeper sulfidic sediments. Of the few farmed Atlantic salmon analyzed, mercury levels were not elevated compared to the concentrations of mercury in the wild salmon captured in two rivers of the Canadian east coast.

Résumé

Une des incidences principales sur l'environnement des activités de mariculture du saumon dans la Baie de Passamaquoddy (Baie de Fundy, Nouveau Brunswick) est le changement de la chimie des sédiments en raison de la grande quantité de matière organique qui s'accumule sous les cages de poissons. Afin d'étudier ces impacts, des profils verticaux de $\delta^{13}C_{org}$, $\delta^{15}N$, C_{org}, C_{org}:N_{tot}, Fe_{HCl}, Mn_{HCl}, P_{tot}, P_{HCl}, SO_4^{2-}, AVS, Hg_{tot}, Hg_{pyrite} ont été déterminés sur des carottes de sédiments récoltées un peu partout dans la baie. Ces profils ont permis d'identifier des traceurs des activités de la mariculture et de la zonation redox du sédiment. De plus, des échantillons représentatifs de la nourriture de poissons ainsi que des saumons d'élevage et sauvages ont été analysés pour déterminer leur contenu en Hg_{tot} aussi bien que les $\delta^{13}C_{org}$, $\delta^{15}N$, C_{org}, C_{org}:N_{tot}. Les résultats démontrent qu'à mesure que les résidus de la pisciculture (par exemple, nourriture résiduelle, matière fécale, antibiotiques, et agents anti-encrassement) s'accumulent dans les sédiments, le contenu en carbone organique augmente et génère une plus grande demande en oxygène dissous. Ceci se reflète par une migration de la profondeur de pénétration de l'oxygène et des frontières redox dans la colonne sédimentaire vers l'interface eau-sédiment, et est confirmée sur la base de la distribution des espèces redox-sensibles comme les oxydes métalliques authigènes et les AVS dans le sédiment.

La distribution du phosphore total dans la colonne sédimentaire semble être un traceur approprié de la mariculture du saumon, reflétant la récente accumulation de nourriture résiduelle et de matière fécale dans les sédiments. Les concentrations élevées en mercure des sédiments sous les cages à poissons s'expliquent par la grande affinité de ce dernier pour le carbone organique. Bien que la source additionnelle de Hg demeure indéterminée, à mesure que la teneur en carbone organique des sédiments augmente, en réponse aux activités de pisciculture, il en est ainsi du Hg qui lui est associé.

Preface

This thesis consists of three chapters. The first chapter is a general introduction to the thesis. The second chapter is in manuscript form, and is intended for the submission to the refereed journal *Marine Ecology Progress Series*. This manuscript was integrated as a chapter formatted to the general layout of the thesis. The third chapter is the conclusion and includes the contributions to knowledge and suggestions for future work.

The following is excerpted from Guidelines for Thesis Preparation, Office of Graduate and Postgraduate Studies, McGill University:

"Candidates have the option of including, as part of the thesis, the text of one or more papers submitted for publication, or the clearly-duplicated text of one or more published papers. These texts must be bound as an integral part of the thesis.

If this option is chosen, connecting texts that provide logical bridges between the different papers are mandatory. The thesis must be written in such a way that is more than a mere collection of manuscripts; in other words, results of a series of papers must be integrated.

The thesis must still conform to all other requirements of the "guidelines for thesis preparation". The thesis must include: A Table of Contents, an abstract in English and French, an introduction which clearly states the rationale and objectives of the study, a review of literature, a final conclusion and summary, and a thorough bibliography or reference list.

Additional material must be provided where appropriate (e.g. in appendices) and in sufficient detail to allow clear and precise judgment to be made of the importance and originality of the research reported in the thesis.

In the case of manuscripts co-authored by the candidate and others, the candidate is required to make an explicit statement in the thesis as to who contributed such work and to what extent. Supervisors must attest to the accuracy of such statements at the doctoral defense. Since the task of the examiner is made more difficult in these cases, it is in the candidate's interest to make perfectly clear the responsibilities of all authors of the co-authored papers."

Contributions of Authors

The author performed most of the experimental and analytical work comprising the data of this thesis. The interpretation of the results was the sole responsibility of the author. Prof. Mucci gave advice through critical comments and suggestions of the data and of the logical development of the scientific concepts expressed in the thesis.

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CHAPTER 1
General Introduction

1.1 Salmon aquaculture in the Bay of Fundy

Salmon production from marine aquaculture in the Bay of Fundy has been the subject of recent environmental concern. Whereas this industry is the lifeblood of Maritime Canadians and spawns much economical benefit, salmon aquaculture also generates considerable amounts of anthropogenic waste in the area (Haya et al., 2001). One of the main environmental impacts of these activities is the alteration of sediment geochemistry as a result of the large amount of organic waste that accumulates below fish pens (i.e., uneaten feed and fish feces) as well as contaminants introduced through feed sources (e.g., antibiotics, Hg) and maintenance (e.g., anti-fouling agents) (Holby and Hall, 1991; Hargrave et al., 1997; Karakassis et al., 2000; Haya et al., 2001; Brooks and Mahnken, 2003). Waste accumulation in sediments beneath net-pens leads to greater oxygen demand, a thinning of the oxygen penetration depth and its eventual migration to the overlying waters, thus modifying the physical and chemical characteristics of the original sediment (Haya et al., 2001).

The majority of Maritime salmon production originates from New Brunswick marine aquaculture sites located in the Passamaquoddy Bay and Grand Manan sectors of the southwestern Bay of Fundy (Figure 1.0). The Bay of Fundy is the site of the world's largest tidal amplitude, reaching up to 16 m at the Bay's mouth (Gregory et al., 1993) and, thus, provides substantial water replenishment and efficient flushing for aquaculture activities. Passamaquoddy Bay, a well-mixed estuary influenced by river discharge, is separated from the rest of the Bay of Fundy by Deer Island and covers an area of about 98.5 km^2 at high water. The St. Croix River, which serves as the US/Canada border, is the main source of freshwater to Passamaquoddy Bay. Running parallel along the northern

coast of Deer Island is a bidirectional northeast-southwest water current vector with a north-south vector component that changes direction as the tide enters and leaves the Bay (Forrester, 1958). This Bay does not experience strong wave action and, thus, its inlets and bays provide shelter for the net-pen sites.

Passamaquoddy Bay has been host to Atlantic salmon farming within floating net-pens since 1979. The early years of southwestern New Brunswick's aquaculture industry developed from opportunities offered through studying the farming techniques of Europe, local trials, product demand and suitable site accessibility. As aquaculture became more expensive, challenges arose such as global competition, site availability, and environmental and economic sustainability (DELG, 2001). The response of the provincial government in the early 1990s to the environmental sustainability challenge was addressed by both industry and the Canadian government. As a result of environmental studies and published provincial guidelines, an industry-wide environmental monitoring program has been conducted annually since 1995. Shortly after, the monitoring program went through a critical review by the government, industry and public to become an Environmental Management Guideline (EMG). The ultimate goal of the EMG is to maintain long-term environmental sustainability of the marine finfish cage aquaculture industry in the context of a healthy marine environment (DELG, 2001). In order to achieve this goal, the following were elaborated: an outline of an environmental monitoring method on cage sites, monitoring protocols to comply with environmental quality objectives, and a guide for cage site remediation when environmental quality objectives are not met (DELG, 2001).

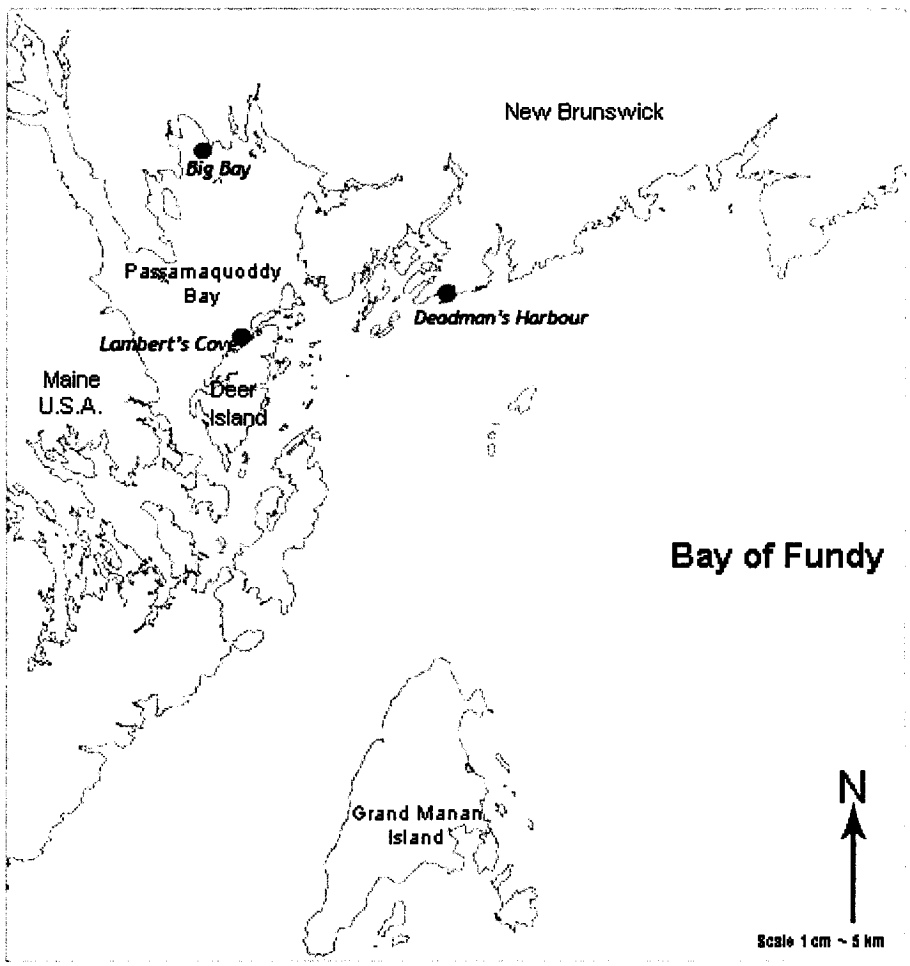

Figure 1.0. Map of Passamaquoddy Bay and Grand Manan Island, New Brunswick, Canada.

Salmon aquaculture marked its debut in Norway in 1969. The rapid growth of this industry and the farming of fish in floating net cages in open fresh and coastal waters is now practiced in many countries including Spain, Scandinavia, Chile, the Faroe Islands, USA, Australia, New Zealand, Japan, Scotland, France, the German Democratic Republic, Poland and Canada (Rosenthal 1988; Hall et al., 1990; Tovar et al., 2000). Maritime Canada produced 6 t of farmed salmon in 1979 but production had reached 20 310 t by 1997 (DFO Maritimes Regional Habitat Status Report, 1999). The first finfish farm was licensed in 1979 and located at Lambert's Cove (see Figure 1.0) (Bugden et al., 2001). By August 2003, there were 93 licensed marine finfish sites in the Passamaquoddy

Bay and Grand Manan area (I. Yuksel, pers. comm. 2004). Atlantic salmon farming in the southwestern Bay of Fundy accounts for more than 95 percent of the production in New Brunswick (DFO Maritimes Regional Habitat Status Report, 1999).

The increase of salmon farming activities has led to a greater awareness of the chemical and biological impact of aquaculture to the marine environment (Holby and Hall, 1991; Haya et al., 2001). Impact studies of salmon aquaculture on the North American west coast were carried out by Nash and Waknitz (2003), Brooks and Mahnken (2003), Waknitz et al. (2003), and Nash (2003) on bio-deposits, heavy metal accumulation and the effects of the escape of non-native species. Spatially confined regions like Passamaquoddy Bay may not have the capacity to maintain high salmon production. Salmon farming generates large amounts of organic and inorganic waste (i.e., uneaten food and fecal matter) that are delivered directly under the pens to the sediments. In 2000, the New Brunswick Department of Fisheries and Aquaculture established a fallowing (resting/restoring the local environment) strategy for licensed farmers that would require them to periodically abandon their farming sites for up to six months to combat disease and allow the sediments to fallow (McGhie et al., 2000; Haya et al., 2001).

Most of the research in Passamaquoddy Bay has focused on the near-field effect of organic enrichment of aquaculture. In addition, studies have highlighted the wide spread variations in dissolved nutrient and oxygen concentrations in the sediments as well as the impact of organic loading on the benthic biota (Pohle et al., 2001). Acoustic mapping, sediment traps, benthic grabs and core sampling were used to characterize sedimentation rates, substrate texture, sediment chemistry and benthic communities

within cage sites (Hargrave, 2002). Zinc from fish food and copper used in antifouling agents at cage sites have served as tracers to document far-field effects of aquaculture activity (Brooks and Mahnken, 2003). Chemicals used in the treatment of sea-lice infestations are lethal to shrimp and lobsters, and have been shown to decrease the reproductive success of lobsters at sub-lethal levels (Haya et al., 2001; Chou et al., 2002).

Hargrave (1997) observed that the most sensitive indicators of benthic organic enrichment are benthic O_2 uptake and CO_2 release as well as total sulfide concentrations and redox potential (Eh) in the first few centimeters of the surface sediment. Total macrofauna and deposit feeder biomass were used by Hargrave (1997) as sensitive indicators of organic enrichment. Currently, the Department of Environment and the Local Government of New Brunswick use redox potential, sulfide and ammonia concentrations, and the density of macrofauna/ microfauna populations to assess the quality of the sediment (see Wildish et al., 1999, for a further description of these conditions). Unacceptable impacts are considered to have been reached when sediments become anoxic (Eh $\leq$-100mV_{NHE} and/or Total Dissolved Sulfide $\geq$6000μM) within the top 3 cm (Heinig, 2001; DELG, 2000). Since 1994, Deadman's Harbour has been used as a reference site to evaluate the impact of aquaculture in the southwestern Bay of Fundy (Pohle et al., 2001). No aquaculture activities have taken place in Deadman's Harbour since 1992, and improvement of the quality of the ecosystem has been noted since 1999 (Pohle et al., 2001).

1.2 Impact on sediment chemistry and early diagenesis

Waste from salmon aquaculture is increasingly becoming a major source of organic and inorganic anthropogenic inputs (i.e., organic matter, nutrients, and

therapeutic agents such as antibiotics and pesticides) to Passamaquoddy Bay sediments (Hargrave, 1997; Haya et al., 2001; Chou et al., 2002). This waste is dispersed to the waters surrounding the net-pens and to the underlying sediment where it may affect indigenous fish stocks via genetic interference and disease transmission as well as the benthic communities which reside under net-pens (Hall et al., 1990; McGhie et al., 2000; Carroll et al., 2003). Increased input of labile organic matter will modify the physical and chemical properties of the sediment and can lead to the accumulation of metabolites such as methane and hydrogen sulfide that are potentially hazardous to the farmed fish (McGhie et al., 2000).

The extent of environmental impact depends on various factors such as the nature and amount of waste material delivered to the sediment, the time-scale over which deposition takes place, sediment composition, water current speed, tidal flushing, seasonal storm-related resuspension and the presence of benthic fauna. The distribution pattern of fish pen sediments is influenced by the current, the bottom topography and the position of the cages (Gowen and Bradbury, 1987; Kelly et al., 1993; Ackefors and Enell, 1994). To counter the accumulation of organic matter within the sediments, biochemical degradation and physical processes such as sediment mixing and fallowing may be effective, but only if the rate of removal by these means is greater than the rate of organic matter accumulation.

Waste feed and fish fecal matter are the main source of organic enrichment at salmon aquaculture sites with minor organic inputs from dead fish and fouling communities (Brooks and Mahnken, 2003). Unconsumed food pellets and feces under salmon fish pens contribute from 20% to 70% of the carbon, nitrogen and phosphorus

accumulating in the sediments (Holby and Hall, 1991; Hargrave, 1994). As more effective feeding technologies are employed, dry feed fed to salmon in net-pens will account for about 5% or less of the organic waste and, thus, most of it will originate from fecal matter (Haya et al., 2001; Brooks and Mahnken, 2003). Wild salmon stocks and other organisms can, however, reduce the amount of organic matter accumulating in the sediments under the pens by consuming excess food pellets, but these processes alone cannot mitigate the organic matter buildup. Organic loading to the sediments under salmon net-pens in Passamaquoddy Bay has increased both nitrogen and phosphorus loadings, leading to local eutrophication and the development of hypoxic and anoxic sediment conditions within the top 2 cm of the sediment (Hargrave, 1997; Chou et al., 2002).

1.2.1 Organic matter accumulation and sediment oxidant demand

Within the sediment, organic matter is remineralized microbially using a sequence of oxidants whose order is determined by the free energy yield per mol of organic carbon oxidized (Froelich et al., 1979). As the most efficient oxidant becomes depleted, oxidation proceeds using the next most efficient oxidant. This sequence continues until all oxidants are consumed or all oxidizable organic matter is depleted, leading to a redox zonation in the sedimentary column. The classical sequence of electron-acceptor (i.e., oxidants) use is: $O_2 > NO_3^- >$ Mn-oxides > Fe-oxides > SO_4^{2-}.

Dissolved oxygen is, therefore, used first for the microbial degradation of organic matter that settles and accumulates in the sediment.

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138\ O_2 \rightarrow 106\ HCO_3^- + 16\ NO_3^- + HPO_4^{2-} + 124\ H^+ + 16\ H_2O$$

The oxidative degradation of organic matter will proceed until sufficient oxygen is consumed to drive the redox potential low enough to favor the next most efficient oxidant. The balance between the diffusion rate of oxygen from the overlying waters and its consumption in the sediments is reflected by the oxygen penetration depth (Cai and Sayles, 1996). The oxygen penetration depth is dependent on temperature, the concentration of oxygen in the overlying waters, the porosity of the sediments and the rate of organic matter decay, itself a function of the amount and reactivity of the organic matter.

Following the consumption of O_2, NO_3^-, including that released through the preceding reaction, will be reduced. There is, however, very little nitrate in the porewaters and it is rapidly exhausted.

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 94.4\ NO_3^- \rightarrow 106\ HCO_3^- + 55.2\ N_2 + HPO_4^{2-} + 13.6\ H^+ + 71.2\ H_2O$$

After oxygen and nitrate have been consumed in the sediments, oxidation proceeds using the next most efficient oxidant, MnO_2, according to the following reaction:

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 236\ MnO_2 + 364\ H^+ \rightarrow 236\ Mn^{2+} + 106\ HCO_3^- + 8\ N_2 + HPO_4^{2-} + 636\ H_2O$$

Burial below the oxygen penetration depth of detrital or authigenic Mn-oxides (MnO_x) accumulating at the sediment surface will trigger their reductive dissolution to

Mn(II). MnO_x reduction will continue as long as easily metabolizable organic matter is present or until the reactive oxides are exhausted. Consequently, the porewater Mn(II) concentration will increase but should not, theoretically, exceed the solubility of rhodochrosite ($MnCO_3$) although its precipitation kinetics may be inhibited (Mucci, 2004). Adsorption to acid volatile sulfides (AVS; Arakaki and Morse, 1996) and calcite (Michard, 1971; McBride, 1979; Thomson et al., 1986; Wartel et al., 1990) and the precipitation of authigenic phases (e.g. carbonates: Calvert and Price, 1972; Manheim, 1982; Calvert and Pedersen, 1996; sulfides: Suess, 1979) may also limit the [Mn(II)] in the suboxic and anoxic porewaters. The accumulation of Mn(II) in the porewaters will generate a concentration gradient and drive its diffusion up to the oxic zone where it will be oxidized and precipitated as an oxide at or near the oxic-anoxic boundary and down in the presence of a suitable sink (Mucci, 2004). As sediments accumulate and are buried below the oxic zone, reactive manganese oxides are recycled across the redox boundary (i.e., oxic/suboxic boundary) and are concentrated into a distinct layer, a sedimentary manganese trap (Burdige, 1993). The position of the solid Mn accumulation layer is dependent on the balance between the downward O_2 and upward Mn(II) diffusion rates and the oxidation kinetics of Mn(II) (Froelich et al., 1979). A schematic representation of the distribution of dissolved and solid Mn at steady state is depicted in Figure 1.1.

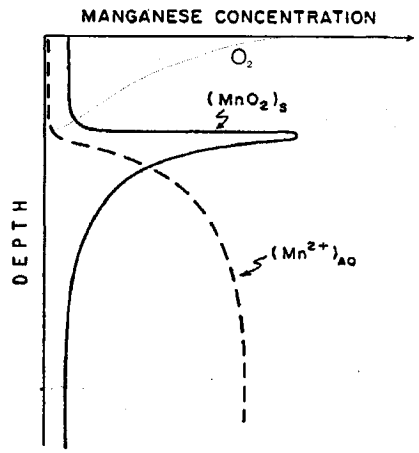

Figure 1.1. Schematic representation of dissolved and solid phase Mn profiles in a hypothetical steady - state system. The depth of the oxygen penetration depth is typically found just below the solid phase manganese peak. Modified from Froelich et al. (1979).

The presence of a gap between the solid MnO_2 peak and the Mn(II) profile has been ascribed to reactions of MnO_x with NH_4^+ and Mn(II) with IO_3^- (Anschutz et al., 2000). If the redox boundary moves up close to the sediment-water interface, dissolved manganese may escape to the overlying waters (Froelich et al., 1979). It must be noted, however, that the redox reactions are rarely at steady state in sediments and the relative positions of reducing and oxidizing sediment components can shift due to bioturbation or other bio-geo-physico-chemical disturbances, such as variations in the organic matter inputs (Froelich et al., 1979; Anschutz et al., 2000). The depth scales at which iron and manganese reduction occur are controlled in part by the organic carbon input to the sediment surface and its composition, the oxygen content of the bottom waters, the sedimentation rate, and the bioturbation rate (Froelich et al., 1979; Anschutz et al., 2000).

Upon the exhaustion of MnO_2 and according to the sequence of electron-acceptor use noted earlier, Fe(III) reduction will proceed as follows:

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 424\ Fe(OH)_3 + 756\ H^+ \rightarrow 424\ Fe^{2+} + 106\ HCO_3^- + 16\ NH_4^+ + HPO_4^{2-} + 1060\ H_2O$$

The Fe(III) pool of solids is composed of a range of minerals of varying reactivities (Raiswell et al., 1994). Unlike manganese, only a small portion of the total iron in sediments is readily reducible. A schematic representation of the Fe cycle, including settling of detrital Fe(III)-bearing solid phases, reduction of reactive phases to dissolved Fe(II) at depth, the diffusional transport of Fe(II), its oxidation to insoluble Fe $(OH)_3$ in the oxic layer and sulfide precipitation in sulfidic sediments at depth can be seen in Figure 1.2. In this figure, the dissolved and solid Fe profiles display patterns that are similar to the Mn profiles depicted in Figure 1.1, *except* that Mn(II) concentrations generally do not decrease rapidly with depth because there are typically no strong sinks for Mn(II) and FeO_x persist to greater depth because the Fe(II)/Fe(III) redox boundary generally occurs well below the manganese redox boundary in most sediments (Stumm et al., 1996). Finally, unlike dissolved Mn(II) which is metastable in the presence of oxygen, the oxidation of Fe(II) to FeO_x in the presence of oxygen is rapid (Stumm et al., 1996).

Whereas the position of the oxygen penetration depth under steady state conditions corresponds more closely to the depth of the FeO_x peak, oscillations of the oxygen penetration depth due to temporally variable inputs of organic matter to the sediment are best revealed through the migration of manganese oxide peaks (Gobeil et al., 1997). Episodic inputs of organic matter to the sediment shift the manganese redox boundary closer to the sediment-water interface. Iron oxides are less sensitive to variable organic matter inputs to the sediment because the upper boundary of the iron reduction

zone is located below the manganese reduction zone and, thus, FeO_x reduction will not be initiated until most of the reactive MnO_x is consumed (reduced).

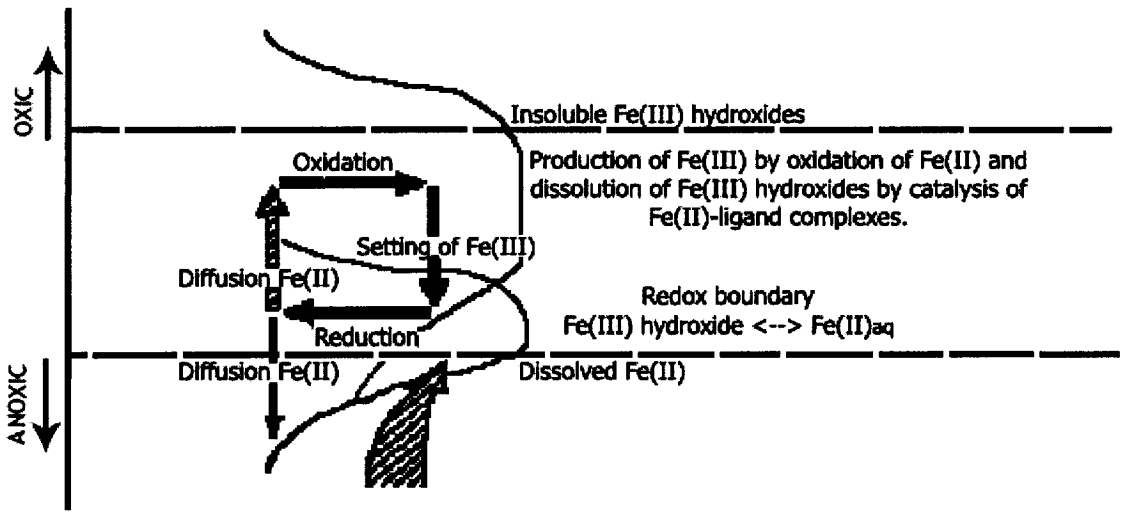

Figure 1.2. Transformation of Fe(III)/Fe(II) at an oxic-anoxic boundary in the sediment column. Modified from Stumm and Morgan (1996).

Just as fluctuating inputs of organic matter to the sediment cause the sedimentary MnO_x peak to migrate upward to the upper limit of the redox excursion (Gobeil et al., 2001), addition of organic matter to the sediment will drive the sulfate reduction zone upward.

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53\ SO_4^{2-} \rightarrow 106\ HCO_3^- + 16\ NH_4^+ + 53\ HS^- + HPO_4^{2-} + 39\ H^+$$

The iron and sulfur cycles are linked together through the formation of iron monosulfides (FeS_x) and pyrite (FeS_2) via the mineralization of particulate organic carbon (Schippers and Jorgensen, 2001, 2002). In organic-rich sediments, Fe^{2+} and some resistant Fe(III) phases are precipitated as pyrite and iron monosulfides in the presence of hydrogen sulfide resulting from the oxidation of organic matter by sulfate-reducing bacteria within the sediments (Schippers and Jorgensen, 2002). For example:

$$Fe^{2+} + HS^- \rightarrow FeS\ (s) + H^+$$

$$FeS\ (aq) + H_2S\ (aq) \rightarrow FeS_2 + H_2\ (g) \quad \text{or} \quad FeS + S^0 \rightarrow FeS_2$$

$$8\ Fe(OH)_3 + 9\ HS^- + 7\ H^+ \rightarrow 8\ FeS + SO_4^{2-} + 20\ H_2O$$

$$8\ Fe(OH)_3 + 15\ HS^- + SO_4^{2-} + 17\ H^+ \rightarrow 8\ FeS_2 + 28\ H_2O$$

The amount and nature (i.e., composition, mineralogy) of the iron sulfide will depend on the availability of reactive iron phases, time of burial, and the availability of oxidants (Middelburg, 1991; Gagnon et al., 1995). Iron monosulfides are most often referred to as acid volatile sulfides or AVS, and include amorphous iron monosulfide, mackinawite and poorly crystallized greigite. They are highly unstable in the presence of dissolved oxygen and other oxidants.

Iron sulfides can be transported up the sedimentary column to the oxic layer by bioturbation where they will be oxidized by dissolved oxygen through a number of intermediates, namely thiosulfate, polythionates and elemental sulfur that are then oxidized to sulfate by aerobic bacteria (Gagnon et al., 1995; Schippers and Jorgensen, 2002). In addition to dissolved oxygen, manganese oxides and nitrate can also oxidize pyrite and iron monosulfides. Mn-oxides, either physically mixed into or in close contact with sulfidic, anoxic marine sediment, can oxidize reduced sulfur to sulfate (Aller et al., 1988) in the absence of oxygen. The rate of oxidation is not instantaneous and is apparently proportional to the amount of oxides available (Aller et al., 1988).

The reactive (1N HCl extractable) iron and manganese profiles should be useful proxies of the oxygen penetration depth since their maximum concentrations are almost

coincident with the lower boundary of their authigenic oxide accumulation layer. In cases where the organic inputs fluctuate in time (e.g., seasonally), the location of the manganese oxide peak corresponds to the upper limit of excursion of the oxygen penetration depth (Gobeil et al., 2001). Conversely, the position of the acid volatile sulfide peaks in the sediment column corresponds to the lower limit of the excursion of the oxygen penetration depth (Gobeil et al., 2001).

1.2.2 Diagenetic behaviour of phosphorus and its use as a tracer of aquaculture

Phosphorus is supplied to the sediment as a mixture of labile and refractory organic and inorganic phosphorus compounds from the overlying water column and nearby land masses. The scales, bones and teeth of fish are also a major source of phosphorus to the sediment and can account for 60-70% of the hydroxyapatite found in sediment (Posner et al., 1984). A large fraction of fish debris may undergo dissolution in the water column and during early diagenesis since seawater is undersaturated with respect to apatite, but its preservation upon burial, particularly where there is a large input, should record its loading from the water column. For this reason, phosphorus was found to be a good indicator of the thickness of sediment originating from a fish farm (Holby and Hall, 1991). The phosphorus debris from fish-pens can be differentiated from the labile forms of phosphorus to reveal the fraction of phosphorus supplied by farms to sediments.

Within the sediments, solid phosphorus exists in three main chemical forms: detrital and authigenic minerals, organic compounds and adsorbed onto sediment particles. Upon accumulation at the sediment-water interface, phosphorus may be

released to the porewaters upon the microbial degradation (i.e., remineralization) of organic matter and the dissolution of detrital phosphate minerals (Sundby et al., 1992). Driven by the established concentration gradient, it may then diffuse out of the sediment, adsorb onto authigenic and detrital iron oxyhydroxides that accumulate in the oxic zone or precipitate out as authigenic mineral phases (Lucotte, 1993; Froelich et al., 1988). Authigenic phosphorus minerals are the ultimate sinks of phosphorus in marine sediments (Filippelli, 1997; Louchouarn et al., 1997; Sundby et al., 1992). The main authigenic phosphate containing minerals within marine sediments are calcium carbonate, smectite clays, biogenic apatite and carbonate fluorapatite (CFA) (Sasaki, 2001). The precipitation and burial of carbonate fluorapatite can permanently sequester phosphate within the sediment if the presence of $CaCO_3$ does not inhibit CFA formation (Lucotte, 1993; Froelich et al., 1988; Jahnke et al., 1983).

The only stable oxidation state of phosphorus in the aquatic environment is P(V) and the dominant species in seawater at pH=8 is HPO_4^{2-}. It has been estimated that 99.6% of the PO_4^{3-} species and 44% of the HPO_4^{2-} species are complexed with cations other than Na^+ in seawater (Stumm et al., 1996). Many organo-phosphorus compounds which originate from various metabolic and catabolic processes are also stable in the field of stability of water (Stumm and Morgan, 1996).

The strong affinity of inorganic phosphate for ferric oxyhydroxides is believed to control its porewater concentration in oxic sediments and, thus, the phosphorus cycle across the oxic-suboxic redox boundary (Schuffert, 1998) as well as its loss to the overlying waters (Sundby et al., 1992). Iron oxides that accumulate near the sediment-water interface can also extract P directly from the overlying seawater to maintain high

subsurface concentrations of dissolved P without a large reservoir of labile particulate P within the surficial sediment (Froelich et al., 1988). In other words, the phosphorus-rich surface layer is in dynamic equilibrium with the porewaters and as sediment accumulates, this layer moves upward with the redox boundary. The authigenic iron oxyhydroxides precipitated upon the oxidation of Fe (II) serve as a sink for the phosphate released to the porewaters during early diagenesis and prevents it from escaping to the overlying water column, see Figure 1.3. Whereas this mechanism is active when the overlying waters are well oxygenated, in oxygen-depleted bottom waters where the oxic layer is thin or the redox boundary is above or nearly coincident with the sediment-water interface, phosphate can escape to the overlying waters (Sundby et al., 1992). Bioturbation or other bio-geo-physico-chemical disturbances may also affect the P cycle in much the same way as the Fe and Mn cycles, as the phosphorus and iron cycles are intimately coupled.

Upon iron oxyhydroxide reduction and dissolution, phosphate as well as other adsorbed elements are released to the porewaters. The finest and least crystalline iron oxyhydroxide particles (e.g., ferrihydrite or nano-goethite) (van der Zee et al., 2003) are more readily dissolved and carry more surface-bound phosphate than the more crystalline fractions (e.g., goethite and hematite) (Raiswell et al., 1994). As sediments become sulfidic, more resistant ferric oxyhydroxides are reduced as well as ferric iron phases such as clays (Raiswell et al., 1994: Canfield, 1992). Ferrous iron is precipitated as sulfides such as FeS and FeS_2 in the presence of hydrogen sulfide produced as a result of sulfate reduction in organic-rich sediments. These sulfide phases do not absorb phosphate strongly (Krom and Berner, 1980).

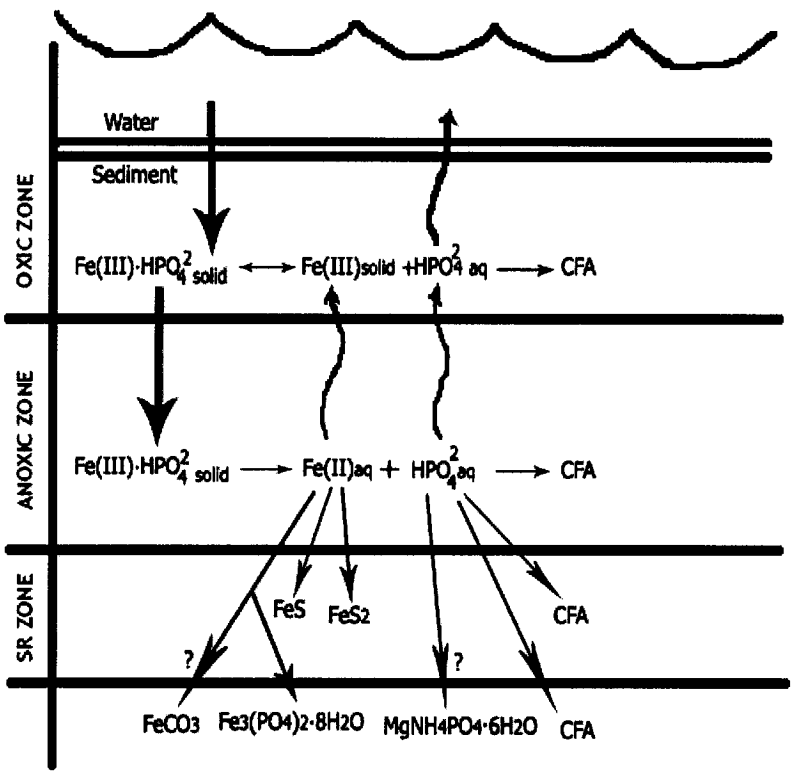

Figure 1.3. Schematic representation of the diagenetic cycle of phosphate in coastal marine sediments. Straight, single lines, double lines, and wiggly lines represent, respectively, reactions, burial, and diffusion (+ oxidation). SR and CFA stand for the sulfate reduction zone and carbonate fluorapatite, respectively. Modified from Mucci et al. (2000).

The flux of dissolved phosphate at the sediment-water interface is determined by the polarity (i.e., sign) and magnitude of the concentration gradient between the porewaters and the overlying waters, the diffusion coefficient, and the thickness of the diffusive boundary layer. The diffusive boundary layer (DBL), the <1mm sediment layer adjacent to the sediment-water interface, constrains the transport of solutes to molecular diffusion (Boudreau and Guinasso, 1982). The two-way flux can be calculated by the equation:

$$J = D_m(C_s - C_w)/Z$$

where J is the flux, D_m the molecular diffusion coefficient of phosphate in seawater, C_s the concentration of ΣPO_4 at the bottom of the DBL, C_w the concentration of ΣPO_4 in the bottom water at the top of the DBL, and Z the thickness of the DBL. Since the adsorption-desorption reaction at the surface of the iron oxyhydroxides fixes the porewater concentration, the gradient and the flux will depend on the overlying water phosphate concentration. If the total phosphorus flux to the sediment is seasonal, then the direction of the adsorption-desorption reactions in the oxic sediments is subject to a reversal. The kinetics of the reactions (i.e., sorption-desorption, mineralization of organic phosphorus) that release phosphate to the porewaters may also influence the flux of P at the sediment-water interface.

1.2.3 Mercury

Mercury is a naturally occurring element but its concentration in natural ecosystems has increased significantly since the industrial revolution. The main anthropogenic sources of mercury to the environment are the burning of fossil fuels, municipal waste incineration, base metal mining and smelting, Hg use in gold mining, chlor-alkali production and biomedical waste (Health Canada and Ontario Ministry of Health, 1998). According to several studies, including Nriagu (1989), direct anthropogenic mercury emissions to the atmosphere are on average four times higher than the natural terrestrial Hg flux of 5 Mmol/yr (Lindqvist et al., 1991).

Elemental Hg^0 is highly volatile and is the most abundant form of mercury (98%) in the atmosphere (Jackson, 1997). Its residence time in the atmosphere varies from 10

days (under low air temperatures, sunlight conditions and the presence of deliquescent aerosol particles; Hedgecock and Pirrone, 2004) to one year (Slemr and Langer, 1992) and, thus, it can travel great distances before it is oxidized to Hg(II) and deposited on land or water by wet or dry deposition (Chan et al., 2003).

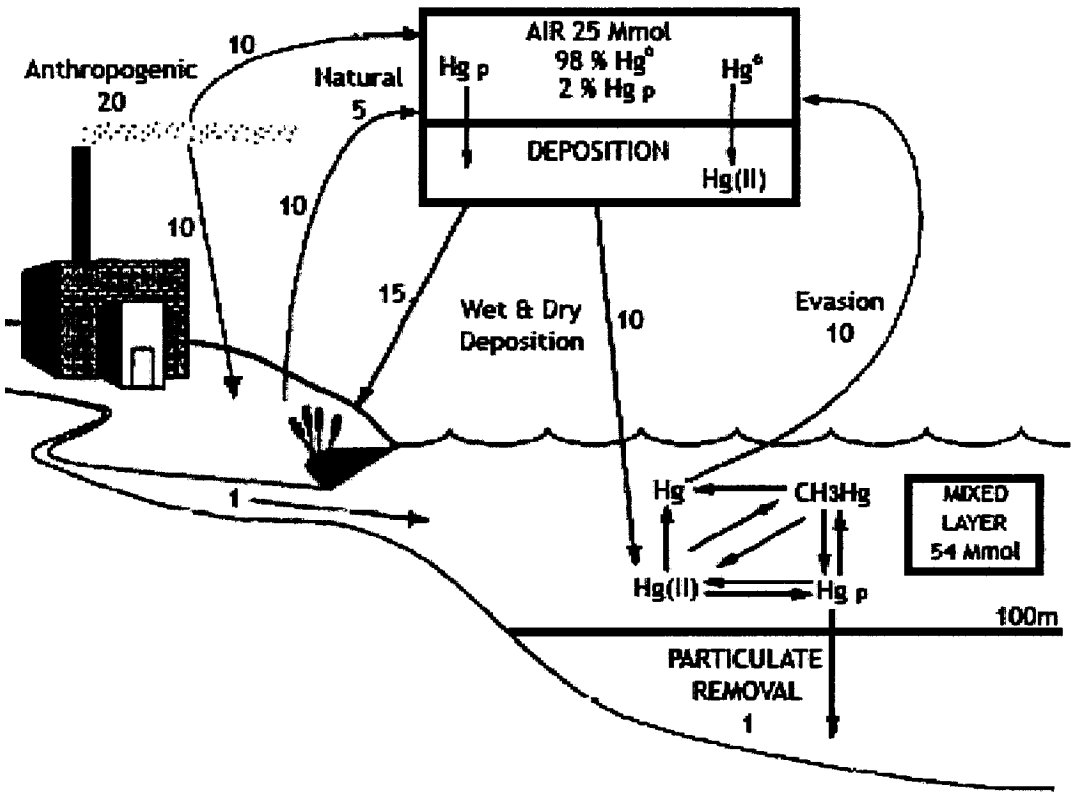

Figure 1.4. The Global Mercury Cycle. Modified from Mason et al. (1994).

Within the aquatic environment, Hg(II) may be reduced to Hg^0 (Figure 1.4). In aqueous environments, elemental Hg^0 is an important dissolved inorganic Hg species below the pε range 4-6 (Figure 1.5). Above this pε range, $Hg(OH)_2$ (aq) and $HgCl_4^{2-}$ predominate in freshwater and seawater respectively. The solubility of elemental Hg^0 in pure water is about $3x10^{-7}$ M or 0.06 mg $liter^{-1}$ (Stumm and Morgan, 1996). Inorganic Hg(II) is the most common form of mercury in soils and submerged sediments where it

can be biochemically transformed into methylmercury (MeHg), the most bioavailable and toxic form of mercury. In oxic/suboxic aqueous solutions, methylmercury ($MeHg^+$) exists as an aquo-complex CH_3-Hg-OH_2^+ or, in the presence of high chloride concentrations, such as in seawater, as a chloride complex (CH_3HgCl) (Stumm and Morgan, 1996). The combined accumulation of anthropogenic mercury and sulfate (i.e., acid rain) in natural freshwater environments stimulates the production of MeHg and its transfer to the aquatic biota (Scheuhammer and Graham, 1999). Methylmercury and inorganic mercuric ions may be reduced to volatile Hg^0 through biological and chemical reactions. Hg can also escape the sediments as gaseous elemental mercury.

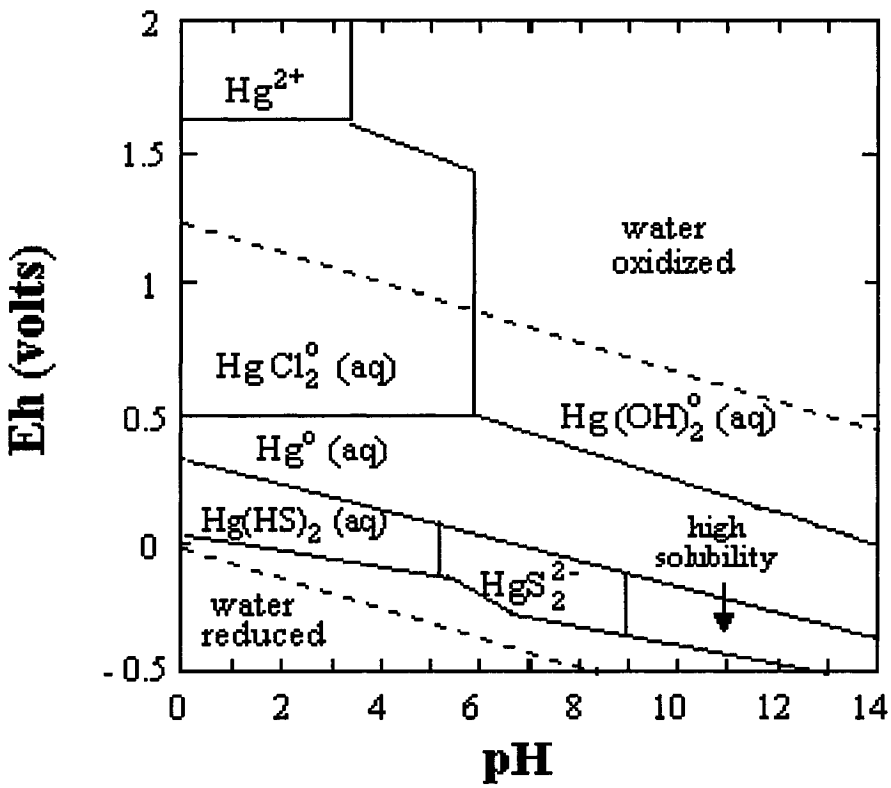

Figure 1.5. Eh-pH diagram for the main inorganic Hg species at [Hg]= 2 ppb, [Cl]= 3.5 ppm and [S]= 3.2 ppm. Adapted from Meech et al. (1997).

Methylmercury is a volatile alkyl compound that accumulates in living cells making it poisonous to the central nervous system of higher organisms (Chan et al.,

2003). MeHg can access the cells of many tissues through its high affinity for reduced sulfhydryl groups, including cysteine and glutathione (GSH) groups. The MeHg-l-cysteine molecule is structurally similar to the amino acid methionine and can act as a substitute substrate for active transport systems that carry the amino acid across cell membranes (Ballatori, 2002). Methylmercury is the only Hg species to undergo biomagnification. Hg^0 and Me_2Hg diffuse out of the cellular environment just as freely as they enter it and, thus, are unable to biomagnify (Ballatori, 2002). $MeHg^+$ behaves as a soft acid and has a strong preference for soft ligands containing I^-, SCN^- or $S_3O_3^{2-}$ donor atoms. Methylmercury compounds once formed, usually by biologically mediated methylation, can be biologically demethylated unless they have accumulated in the fatty tissues of higher organisms. If MeHg levels within the sediment are high, a bacterial mercury detoxification is triggered whereby MeHg is enzymatically demethylated to Hg^0. In sulfide-rich environments such as organic-rich sediments, the speciation of Hg is dominated by the charged species $HgHS_2^-$ and HgS_2^{2-} rather than the neutral HgS^0. The charged species cannot readily diffuse across microbial cell membranes to be methylated (Benoit et al., 1999). Charge neutral methylmercury species are hydrophilic, lipophilic and volatile.

Studies of the mercury levels of marine birds, fish and shellfish in the North Atlantic have shown that mercury concentrations in marine food chains are increasing at an exponential rate (Monteiro and Furness, 1995). The growing concern over mercury contamination of the environment is due to its high toxicity to both humans and animals (Myers and Davidson, 1998; Marsh, 1987). Methylmercury is cytotoxic and highly genotoxic, causing mutations in nuclear DNA. Extended exposure to low MeHg

concentrations can cause autoimmune disease and weakened immune system function which can result in chronic or repeated illness (Shenker et al., 1993; 1998). Given that mercury accumulation in the human population is omnipresent with fish as a common dietary source, Health Canada recently reduced its guideline from 0.47 to 0.2 μg/kg Hg bw/day for fish consumption by women of child-bearing age and children under the age of 12 (Easton et al., 2002).

Within oxic sediments, most of the mercury is bound to particulate organic matter and/or is adsorbed to Fe-Mn oxyhydroxides (Gagnon et al., 1997). Upon the reductive dissolution of iron and manganese oxyhydroxides during early diagenesis, Hg is released to the porewaters. In anoxic sediments, Hg (II) may be scavenged from porewaters, along with other heavy metals, by adsorption to several components of the solid sediment, including co-precipitation with authigenic sulfide minerals such as AVS and pyrite (Gagnon et al., 1997). The efficiency with which mercury is sequestered by the authigenic pyrite phase is dependent upon the degree of pyritization, a function of the concentration of reactive iron and the extent of sulfate reduction. In turn, the latter is dependent on the sedimentation rate, the quantity and reactivity of the organic matter and the availability of dissolved sulfate (Huerta-Diaz and Morse, 1992).

The solubility of Hg in anoxic sediments may be enhanced by the formation of complexes with intermediate reduced sulfur species (organic sulfides, polysulfides, and thiosulfates) as well as dissolved organic matter (e.g., humic compounds) (Gagnon et al., 1997). Remobilization of mercury associated with iron sulfide minerals can occur within anoxic sediment layers due to bioturbation because iron sulfide minerals can decompose upon their exposure to oxygen (Morse, 1994). Whereas pyrite oxidation is relatively

slow, AVS are metastable and very reactive in the presence of oxygen and, thus, are a less refractory sink for Hg than pyrite. Any Hg that is released in reducing sediments will likely re-adsorb to other solid phases such as organic matter unless it can diffuse to the oxic layer where it will become scavenged and adsorbed onto the detrital and authigenic Fe-Mn oxides and fresh organic matter as it diffuses through the oxic sediment layer where they appear to demethylate or adsorb onto solid components of the sediment (Gagnon et al., 1997; Bernier, 2005). Inorganic mercury is converted to methylmercury through biologically-mediated reactions carried out mostly by sulfate-reducing bacteria (Benoit al., 1999). Sulfate reducing bacteria (SRB) are a component of the bacterial population in estuarine and marine sediments where there is abundant sulfate in organic-rich sediments (Gilmore and Henry, 1991). In well-mixed sediments, sulfate, carbon and inorganic mercury are more bioavailable to the SRB and can potentially stimulate more methylating activity from these bacteria (Benoit et al., 1999). In coastal organic-rich marine sediments, methylmercury production is limited by the presence of high dissolved sulfide concentrations rather than by the availability of Hg or organic carbon (Gilmore and Henry, 1991). Conditions most conducive to mercury methylation are found in anoxic sediments enriched with biodegradable organic carbon and nutrients but sulfide-poor porewaters (Gagnon et al., 1996).

A higher level of methylmercury will be produced in the sediment with increasing level of mercury contamination only if the methylation potential of the sediment is not exhausted or overwhelmed by the contamination, the methylation potential being determined by the biogeochemical conditions of the sediment environment (Ikingura and

Akagi, 1999). Oxidized sediments appear to act as an efficient barrier to the diffusion of methylmercury and prevent its escape to the overlying waters.

1.3 Objectives

Given the input of organic matter and metals to the sediments under fish pens as a result of salmon aquaculture activities, we evaluated their impact on sediment chemistry, the oxygen penetration depth (OPD) and the migration of the oxic/suboxic as well as suboxic/anoxic boundaries within the sediments. In the absence of direct oxygen measurements, the distribution of reactive manganese (Mn_{HCl}) and iron (Fe_{HCl}) were used as proxies to estimate the position of the OPD within the sediments. Porewater sulfate depletion and the distribution of solid phase sulfides (i.e., acid volatile sulfides and pyrite) were used to evaluate the extent and position of the sulfate reduction zone.

The amount and nature (i.e., elemental C:N ratio, isotopic carbon and nitrogen signatures $\delta^{13}C$, $\delta^{15}N$) of the organic matter accumulating in the sediments near or at the edge of fish pens was examined to determine its source (i.e., marine, terrestrial, farming activities). Accordingly, the elemental (i.e., C:N ratio) and isotopic composition (i.e., $\delta^{13}C$, $\delta^{15}N$) of fish food samples were determined to estimate their contribution to the sediment organic matter burden. The vertical distribution of total and reactive phosphate in sediment cores recovered near (i.e., within 100 m) or at the edge of cages was determined to reveal the presence of excess particulate phosphate supplied via salmon food and feces, and to confirm that phosphate is a suitable indicator of salmon aquaculture activities.

Total mercury (Hg_{tot}) analyses of the fish feed, farmed salmon and sediments recovered near (i.e., within 100 m) or at the edge of the fish pens were carried out to

determine if farming activities are responsible for a higher Hg content of surface sediments (i.e., top 5 to 50 cm) observed in the southwestern Bay of Fundy. Hg_{tot} concentrations and the distribution of Hg_{tot} in pyrite (Hg_{pyrite}) were used to evaluate the extent and partitioning of Hg in the solid sediments. We also analyzed the Hg_{tot} levels in both cultured and wild Atlantic salmon flesh samples to determine if there are significant differences in their levels of contamination.

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CHAPTER 2
The influence of salmon aquaculture on sediment chemistry and mercury loading

Forward

Chapter 1 consisted of a general introduction embracing the scope of the thesis as a whole and included background information critical to this work, which may not be directly referenced in the following manuscript. Chapter 2 focuses on the impact of salmon aquaculture on sediment chemistry and mercury loading. Particular attention was paid to the oxygen penetration depth, its proxies, the geochemical tracers of salmon aquaculture and mercury geochemistry.

The influence of salmon aquaculture on sediment chemistry and mercury loading

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2.1 Abstract

The impact of salmon aquaculture activities on the chemistry of sediments in Passamaquoddy Bay, New Brunswick, Canada, was investigated. Vertical profiles of $\delta^{13}C_{org}$, $\delta^{15}N$, C_{org}, C_{org}:N_{tot}, Fe_{HCl}, Mn_{HCl}, P_{tot}, P_{HCl}, SO_4^{2-}, AVS, Hg_{tot}, Hg_{pyrite}, from sediment cores collected throughout the Bay were acquired to identify tracers of aquaculture activities and their redox zonation. In addition, representative samples of fish food as well as farmed and wild salmon were analyzed to determine their Hg_{tot} content as well as $\delta^{13}C_{org}$, $\delta^{15}N$, C_{org}, C_{org}:N_{tot}. The results show that as by-products of salmon aquaculture (i.e., residual fish feed and feces) accumulate in the sediments, their reactive organic carbon content increases and generates a greater oxygen demand. This, in turn, is reflected by an upwards migration of the oxygen penetration depth and redox boundaries in the sediment column, which is confirmed on the basis of the distribution of redox-sensitive phases (e.g., AVS) in the sediments.

The distribution of total phosphorus in the sediment record is shown to be a suitable tracer of marine aquaculture, reflecting the recent history of residual feed and fecal matter accumulation in the sediments. Elevated mercury concentrations in sediments under fish pens are explained by its strong affinity for organic carbon. Although the source of additional Hg has yet to be resolved, as the organic carbon content of the sediments increases in response to the input from fish farming activities, so does the associated Hg.

2.2 Introduction

In recent decades, marine aquaculture has become an increasingly important source of protein to the world population, providing the human populace with more than 36% of its daily protein intake (Jia, 2003). With the decline of wild salmon stocks, salmon farming has thrived in response to the demands of this popular commodity and replaced struggling, local fishing economies. One of the main environmental impacts of these activities is the alteration of the physical, chemical and biological properties of the sediment in the immediate vicinity of the fish pens as a result of the large amount of organic waste that accumulates below (i.e., uneaten feed and fish feces) as well as contaminants introduced through feed sources (e.g., antibiotics, Hg) and maintenance (e.g., anti-fouling agents) (Brooks and Mahnken, 2003; Haya et al., 2001; Karakassis et al., 2000; Hargrave et al., 1997; Holby and Hall, 1991).

As salmon farming activities within Passamaquoddy Bay, Bay of Fundy, NB increase, there is an increased awareness of the chemical and biological impact of aquaculture to this marine environment. Whereas this industry is an important source of income to Maritime Canadians and spawns much economical benefit for the Province, salmon aquaculture also contributes considerable amounts of anthropogenic waste to the area (Haya et al., 2001). In addition to modification of the physical (i.e., porosity, cohesiveness) and chemical (i.e., contaminant concentrations) properties of the original sediment, the accumulation of organic waste in the sediments below net-pens leads to a greater oxygen demand, a thinning of the oxygen penetration depth and its eventual migration to the overlying waters (Haya et al., 2001). This, in turn, impacts the benthic and pelagic biotic assemblages, production of H_2S and bubbling of methane as well as on

the remobilization of redox sensitive compounds accumulated in the sediments (Hall et al., 1991).

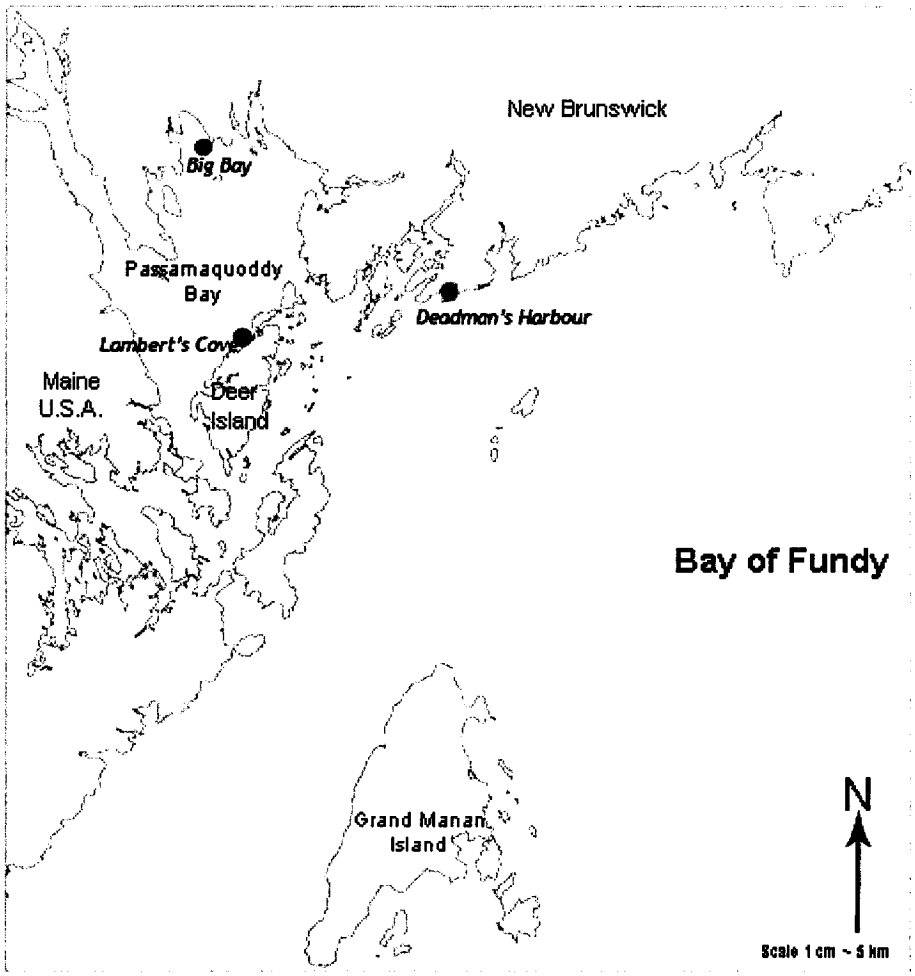


Figure 2.2.0. Map of Passamaquoddy Bay and Grand Manan Island, New Brunswick, Canada.

The majority of Canadian Maritime salmon production originates from the New Brunswick marine aquaculture sites located in the Passamaquoddy Bay and Grand Manan sectors of the southwestern Bay of Fundy (Figure 2.2.0). The Bay of Fundy experiences the world's largest tidal amplitude, Passamaquoddy Bay, and its many inlets and bays provides adequate shelter for salmon cages from strong waves while benefiting from tidal water replenishment. Since 1979, Passamaquoddy Bay has been host to the farming of Atlantic salmon within floating net-pens. The early years of southwestern New

Brunswick's aquaculture industry developed from opportunities offered through studying the culture techniques of Europe, local trials, product demand and suitable site accessibility. As aquaculture became more expensive, challenges arose such as global competition, site availability, and environmental and economic sustainability (DELG, 2001). The response of the provincial government in the early 1990s to the environmental sustainability challenge was also addressed by both industry and the Canadian government. As a result of environmental studies and published provincial guidelines, an industry-wide environmental monitoring program has been conducted annually since 1995. Among environmentalists and fish growers is the growing concern that the impact of fish farming on the quality of the aquatic environment could threaten fish health and thus, the economy of the farms. Currently, the federal Department of Environment and the local Government of New Brunswick use redox potential, sulfide and ammonia concentrations, and the density of macrofauna/microfauna populations to assess the quality of the sediment (see Wildish et al., 1999, for a further description of these conditions). Unacceptable impacts are considered to have been reached when sediments become anoxic (Eh $\leq$-100 mV_{NHE} and/or total dissolved sulfide $\geq$6000 μM) within the top 3 cm of the surface (Heinig, 2001; DELG, 2000).

The aim of this study is to identify tracers that can be used to estimate the history and quantity of fish food and waste delivered to the sediment and its impact on the geochemistry of the sediment, including the oxygen demand, the position of the redox boundaries, and mercury loading and partitioning within the sediment.

Reactive manganese (Mn_{HCl}) and iron (Fe_{HCl}) distribution were used as proxies to estimate the position of the oxygen penetration depth (OPD) within the sediments. The

extent and position of the sulfate reduction zone was evaluated via porewater sulfate depletion and the distribution of solid phase sulfides (i.e., AVS and pyrite).

Organic matter in the fish food and the organic matter accumulating in the sediments under fish pens were examined to correlate their source. The suitability of phosphate as an indicator of marine aquaculture activities was confirmed through the examination of the distribution of total and reactive phosphate in sediment cores recovered under cages and the presence of excess particulate phosphate supplied via salmon food and feces. Total mercury analyses of the fish feed, farmed and wild salmon and sediments recovered under the fish pens were undertaken to determine if farming activities are responsible for the higher Hg content of surface sediments observed in the southwestern Bay of Fundy. Sediments taken from areas of Passamaquoddy Bay distant from fish farms were used to characterize sediments that accumulate under the normal sedimentation regime.

2.3 Materials and Methods

2.3.1 Study site and sampling

Passamaquoddy Bay, a marine embayment subject to the world's largest tidal amplitude, is located in the southwestern Bay of Fundy in eastern Canada. This bay covers an area of about 98.5 km^2 at high water and is separated from the rest of the Bay of Fundy by Deer Island. It is a well-mixed system influenced by river discharge, of which the St. Croix River, which serves as the US/Canada border, is the main source of freshwater to the bay. It has intense currents and counter-currents, but does not experience strong wave action so that the inlets and bays provide good sites for the net-pen farming sites. Sediments were collected from sites within the Passamaquoddy Bay

region (i.e., around Deer Island, Big Bay and Deadman's Harbour; Figure 2.2.0) in 16 to 35 m of water. The sediments collected were comprised of sand, fine silt and clay-sized particles.

In early June 2002, short sediment cores were collected along three transects within 50 m of a salmon aquaculture site at Lambert's Cove (Deer Island; Figure 2.3.1) whereas a long sediment core was taken at the intersection of two of the transects. Long sediment cores were taken from Big Bay, where several fish pens were located, to confirm geochemical observations at our main study site (i.e., Lambert's Cove) as well as from Deadman's Harbour, a site that had not been farmed since the early 1990s and which served as a reference or baseline location for this study. Despite the absence of populated fish pens, surface sediments (i.e., top 15 cm) were also sampled in August 2003, with the assistance of divers, along a transect across the Lambert's Cove aquaculture site.

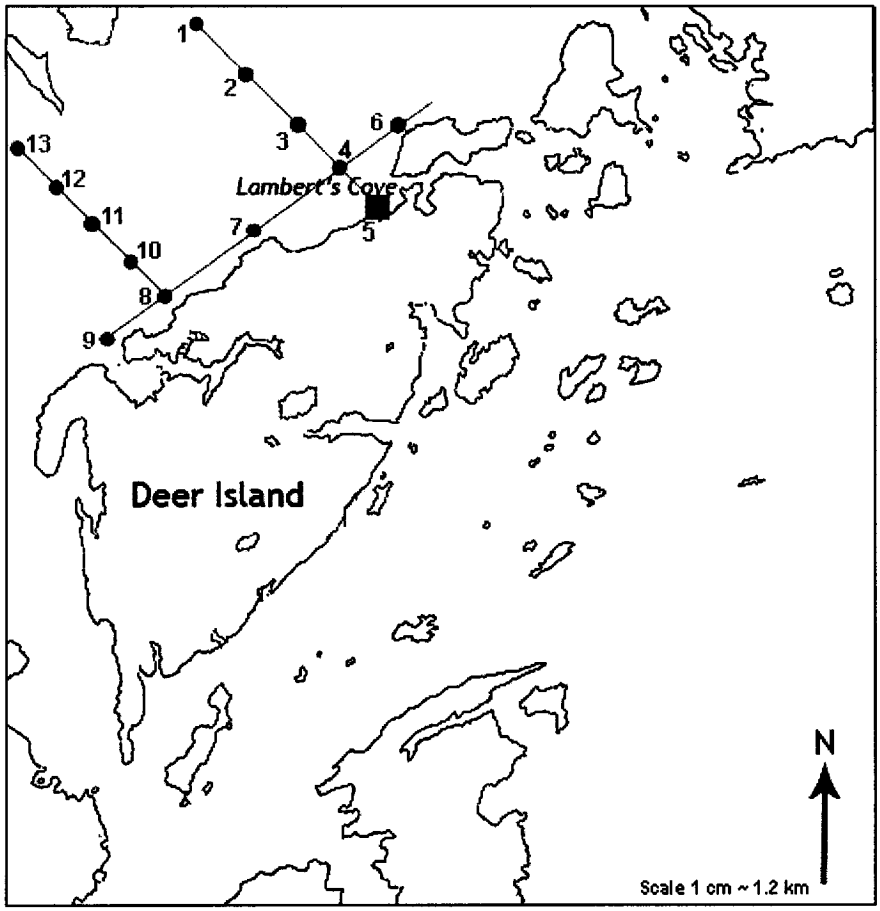


Figure 2.3.1. Three orthogonal transects along which sediments were collected in 2002 in the vicinity of Deer Island, NB.

Surface sediments (i.e., top 10 cm) were obtained with a small, hand-operated box corer (0.023 m^2 x 20 cm length), whereas the long sediment cores (i.e up to 45 cm) were recovered using an Ocean Instruments Mark II Box Corer (0.12m^2 x 60cm length) on board the CCGS J.L. Hart, a 23 m coastal research vessel/trawler. A mostly undisturbed interface was recovered in both cases but a bottom nepheloid or surface flock layer was not always captured since the water often drained out of the corers during recovery. The short cores were sub-sampled at 1 cm intervals after being fully extruded into a plastic container. The long cores were mounted on a custom holding table (Edenborn et al., 1986) and the sediment was sampled at set intervals, typically every 0.5 cm over the first

centimeter, every cm over the next 5 to 10 cm, and at 2-5 cm intervals below depending on visual observations, as the front plate of the core was lowered. The redox potential (Eh) of the sediment was measured during sub-sampling by punching electrodes (i.e., a platinum and Ag/AgCl reference electrode) directly into the sediment at each sampling interval. The electrodes (Radiometer P1312-K4112) were calibrated using a ferri/ferro cyanide buffer solution (+242 mV with respect to the standard Ag/AgCl electrode at 25°C; precision ± 10mV). As each sampling interval was sequentially exposed, solid samples were transferred to pre-weighed plastic vials. The latter were re-weighed, freeze-dried, and the water content and bottom-water salinity (i.e., salt content) were used to estimate the porosity. The dried samples were then homogenized by grinding with an agate mortar and pestle and used for subsequent solid phase analyses. Additional sub-samples were taken with re-sealable mini-corers (i.e., screwcap plastic test tube with 10-ml syringe plunger inserted through the cut off round bottom) and frozen until acid-volatile sulfide (AVS) analyses were performed on the solids and porewater sulfate was determined.

2.3.2 Analyses and analytical methods

The chemical reagents used for all experiments and analytical procedures were of reagent grade quality or better. Specific grades were used as required by some techniques and are described in the respective sections. All glassware and reusable plasticware were rinsed with Nanopure™ water after soaking in a 10% HNO_3 (glassware) or 10% HCl (plasticware) acid bath for at least 24 hours. Millipore Nanopure™ water was used for preparation of all solutions.

Total carbon (C_{TOT}) and total nitrogen (N) concentrations of the freeze-dried sediments and fish feeds were measured using a Carlo-Erba elemental analyzer with a reproducibility of better than ±3%. The inorganic carbon (C_{INORG}) content of the sediments was determined by coulometric titration of the CO_2 evolved following their acidification with 2N HCl. The precision of C_{INORG} analyses is better that ±2%. Organic carbon (C_{ORG}) content was calculated from the difference between the C_{TOT} and C_{INORG} and thus carries a cumulative uncertainty of about ±4%. Aliquots for isotopic analysis were acidified twice with 1 N HCl to remove carbonates before being combusted in a quartz tube for 1 h at 850°C in the presence of purified cupric oxide wire and high quality granular copper. The gases were analyzed on a VG-PRISM™ mass spectrometer. Isotope measurements of C_{org} ($\delta^{13}C$) and N ($\delta^{15}N$) are reported in δ‰ values (Craig, 1965), after usual corrections, and with reference to V-PDB (Coplen-Tyler, 1995) and atmospheric N, respectively. Uncertainties are lower than ±0.1%, as determined from routine replicate measurements of standards (Muzaka and Hillaire-Marcel, 1999).

The total mercury content of the sediments as well as the farmed and wild salmon was determined after microwave acid digestion of the freeze-dried material (0.1g) with a 10:1 mixture (total volume 6.6 ml) of analytical grade HNO_3 and HCl in sealed, Teflon reactors (CEM Microwave Accelerated Reactor System: MARS) for 15 min. The mercury released from the sediments was analyzed by cold-vapor atomic fluorescence (CVAF) following its reduction to Hg^0 with stannous chloride, pre-concentration on a gold-coated quartz sand column, and thermal desorption (Gill and Fitzgerald, 1987; Gagnon et al., 1996). The accuracy of the analyses was verified using PCSS and BEST (NRC Canada) sediment standards for which a ±7% reproducibility was obtained. Total

mercury bound to the pyrite fraction of the sediments was determined by the same method following the dissolution of the isolated pyrite (see below) in concentrated HNO_3. Total mercury levels in fish flesh were determined by analysis of the acid extracts using a Perkin Elmer Flameless Mercury Analyzer (FIMS) following the reduction of Hg (II) to Hg (0) with sodium borohydride in a closed reactor and its transfer to the quartz analytical cell by a stream of argon gas. Potassium permanganate was added to the fish flesh digestions as a preservative and to eliminate possible interferences from sulfide. Analyses were carried out within 36 hours of the flesh digestions. The detection limit for the instrument used is 0.0002 mg l^{-1} and the results were verified using both DORM-2 and TORT-2 standards (NRC Canada). The correlation coefficient, r^2, of the calibration curve was always above 0.999.

In the absence of direct oxygen measurements, the vertical sediment distribution of reactive manganese and iron was characterized to localize the oxygen penetration depth under the salmon cages. The amount of reactive Fe and Mn was determined following reaction of freeze-dried sediments with 1 N HCl for 24 hr at room temperature (1:50 solid/solution) according to the method described by Leventhal and Taylor (1990). Whereas the vertical distributions of solid Mn_{HCl} and Fe_{HCl} provide a broad representation of the redox zonation in the sediment column, an ascorbate extraction (e.g., Anschutz et al., 1998) of the solid sediment would have better emphasized the accumulation of easily remobilizable authigenic metal oxides at and above the oxygen penetration depth (OPD). The ascorbate extraction, however, is not compatible with the analytical procedures of mercury and, thus, we elected to use the 1N HCl extraction protocol to determine the distribution of reactive Mn and Fe. The Fe and Mn concentrations in the 1 N HCl-extracts

were determined by atomic absorption spectrophotometry (AAS) using an air-acetylene flame (Perkin Elmer, Analyst 100, FIAS 400). The reproducibility of measurements was better than 10%. The detection limits were 610 and 55 ppb for Fe_{HCl} and Mn_{HCl}, respectively. Extractions were performed on samples recovered from stations that were sampled on at least two distinct depth intervals.

Acid-volatile sulfides were determined after conversion to H_2S following acidification (5 ml of sediment in 15 ml of a 9 N HCl solution + 20% $SnCl_2$) for 3 hours at room temperature (25±3°C) of fresh-frozen, wet sediments in screw-cap jars purged with nitrogen (Gagnon et al., 1995). The resulting H_2S was trapped into an alkaline zinc chloride solution. The trapped sulfide was titrated iodometrically according to the method of Hsieh and Tang (1989). Reproducibility of this method was better than ±5%. Pyrite (FeS_2) was isolated from the freeze-dried sediments by the sequential extraction method of Lord (1982), i.e., quantitatively dissolved in quartz-distilled nitric acid and the liberated iron determined by atomic absorption spectrophotometry (AAS) using an air-acetylene flame (Perkin Elmer, Analyst 100, FIAS 400).

Porewater sulfate was isolated from the sediment by centrifugation within a few hours of thawing the fresh-frozen samples (sealed mini-corers, see above) and analyzed using a DIONEX DX-120 ion chromatograph equipped with an IonPac-CG5 column after 100-fold dilution in distilled water. Measurements were calibrated using diluted IAPSO standard seawater (28.24 mM SO_4^{2-}) and the reproducibility was better than ± 1%.

Total phosphate content of the sediments was determined by analysis of the acid digestions used for the Hg analyses. Reactive phosphate was characterized by analysis of the 1 N HCl extracts described previously. Phosphate was determined by the

heptamolybdate spectrophotometric method of Koroleff (1976) using a Hewlett-Packard 8453 UV-visible spectrophotometer and 10 mm quartz cuvette. The detection limit and linear range of this method is reported as 0.01 μmol l^{-1} and 0.01 to 28 μmol l^{-1} respectively. Calibrations were conducted for each analytical session using dilute KH_2PO_4 stock solutions prepared on the day of the analyses and matrix-matched with those of the experimental solutions. The correlation coefficient, r^2, of the calibration curve was always above 0.999. Standards were measured in triplicate and correction for blanks was made. Samples were analyzed in triplicate and the RSD% values were better than 5%.

In the first few months after salt-water introduction in the spring, most fish are fed a juvenile-fish moist food, and in the fall of that year are fed dry feed. Moist feed supplied from M.G. Fisheries was sampled from Nantucket Seafarm Inc., Grand Manan, NB. The dry feed samples were obtained from various farmers and suppliers around St. Andrews, NB. The fish food samples were weighed and homogenized by grinding with an agate mortar and pestle. Water content of the samples was obtained following desiccation in a clean oven at 104°C. Total carbon, total nitrogen and their respective isotopic signatures were determined as described above. Mercury in the fish food samples was analyzed with an automatic SP-3D Mercury Analyzer at the University of Ottawa. Briefly, samples were set into a ceramic holder and introduced into a sample heating furnace. Upon combustion and mercury atomization, the mercury was trapped (as a gold-amalgam) and separated from the combusted gaseous products. The mercury was then thermally desorbed and transferred by argon gas to be detected via Cold Vapor Atomic Absorption at 253.7 nm. The precision of this method was 0.1 ppb.

Three Atlantic farmed salmon samples were obtained from a local grocer and a farm located in Chocolate Cove in the Passamaquoddy Bay region. Wild Atlantic salmon samples were procured through the Department of Fisheries and Oceans Canada and were captured in the Restigouche and Miramichi Rivers of New Brunswick in June 2004. All fish samples were kept frozen until freeze-dried, and later homogenized for total mercury (Hg) analysis.

2.4 Results

2.4.1 Sediment chemistry and early diagenesis

2.4.1.1 Organic carbon loading and tracers of salmon aquaculture

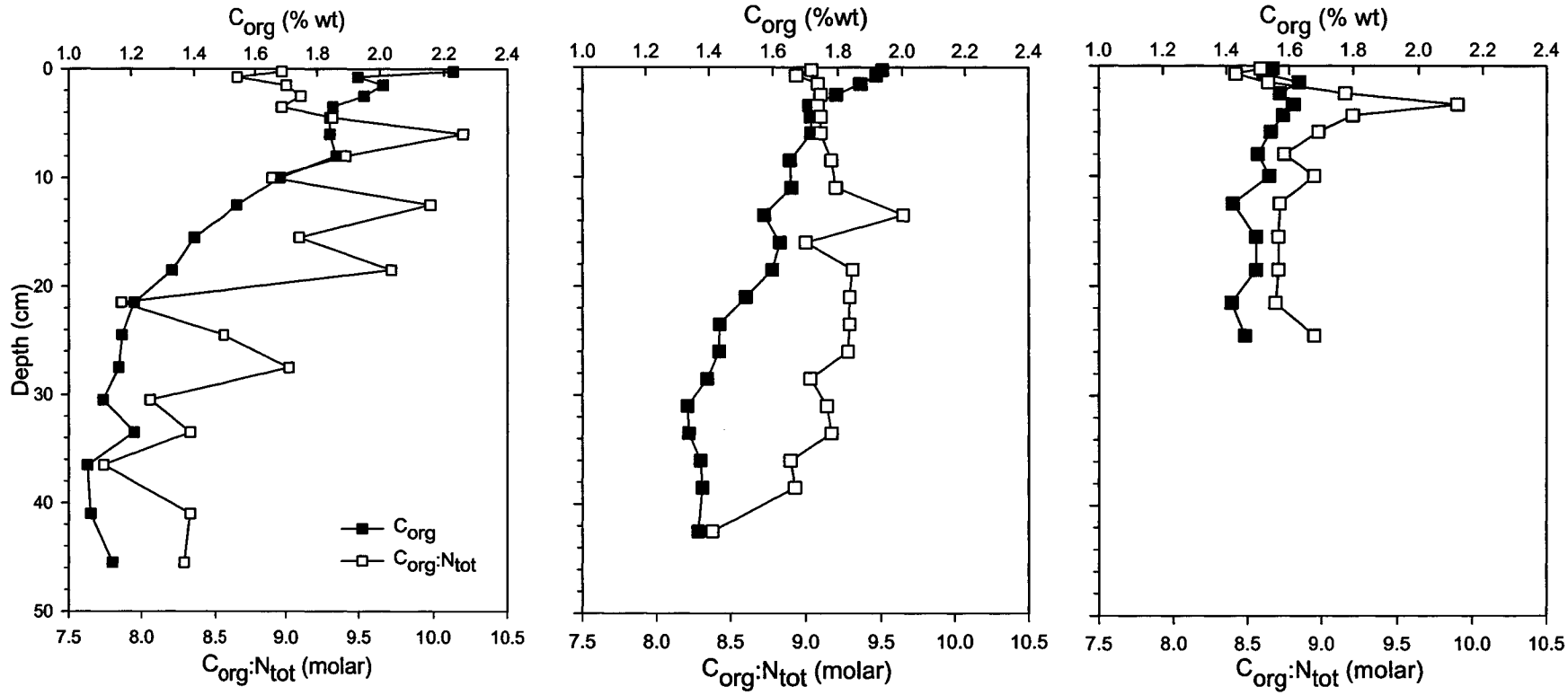
It is expected that higher organic carbon (C_{org}) content will be observed in sediments below fish pens, compared to sediments in unaffected areas of Passamaquoddy Bay, due to the settling of excess fish food and feces. The amount, composition, and isotopic signatures of the organic matter accumulating at the sediment surface should reflect the supply of fish food (salmon feed consists of fish meal, fish oil, soybean meal, wheat, maize gluten meal, vitamins, minerals and pigments) and feces to the sediment under the cages. A summary of the sediment analyses is presented in the form of vertical profiles for each of the three stations at which long box-cores were taken (Figures 2.4.1 and 2.4.2) as well as for the sites where short cores were collected in Lambert's Cove in 2003 (Figure 2.4.4). The Lambert's Cove 2002 transect data as well as a more detailed dataset from a long box-core can be found in the appendices.

The organic carbon content (C_{org}) of surface sediments recovered from the cage sites (1.79-2.23 %wt) are elevated compared to those of the control site, Deadman's Harbour (1.51-1.62 %wt), and the sediments recovered at depth at the same sites (1.16-1.39 %wt) (Figures 2.4.1; 2.4.2). The 2002 sediment core transect shows the aerial extent of the impact zone around the salmon cages, with the higher C_{org} concentrations in the sediments nearest the cages and a gradual decrease away from the cages (Figure 2.4.3). The C_{org}: N molar ratios of the organic matter in the sediments at the cage sites are within the same range (8.42-9.16) in the upper sediments compared to the control site. These values are slightly higher (8.42 to 9.16) than those found in the fish feed (5.0 to 7.7). The observed $\delta^{13}C$ and $\delta^{15}N$ enrichment of the organic matter accumulating in the surface sediments under the cage sites [$\delta^{13}C$: -22.15‰ to -21.5‰; $\delta^{15}N$: 5.42‰ to 6.0‰] is compatible with the addition of carbon of marine origin ($\delta^{13}C$-enriched), potentially from the fish food whose isotopic signatures varied between -23.4 and -21.4‰ for $\delta^{13}C$ and 4.9 to 6.0‰ for $\delta^{15}N$.

Phosphorus-containing organic and inorganic particulate matter is delivered to the sediment below fish pens in the form of settled food (i.e., ground fish muscle, oils and bones) and feces. This should be reflected by an increase of the total phosphorus content of the sediments. Total phosphorus (P_{tot}) and reactive phosphorus (1N HCl extractable, P_{HCl}) analyses were performed on the solid sediment. The reactive phosphorus concentrations (P_{Ref}), a measure of the diagenetically remobilizable fraction, were subtracted from the total phosphorus values to determine the fraction of refractory phosphorus supplied to the sediments via fish farming activities (see Figure 2.4.5a). The accumulation of P_{HCl} in the first centimeter of the sediment is consistent with the

presence of a thin oxic, metal oxide rich layer (Figure 2.4.5b) to which labile phosphate is strongly adsorbed. Conversely, there is a concentration of P_{tot} in the top 5 cm of the sediment which far exceeds the P_{HCl} signal and, thus, may reflect the historical accumulation of residual feed from the farming activities.

Figure 2.4.1 C_{org} and C_{org}: N_{tot} vertical sediment profiles for the three long core stations taken in 2002.

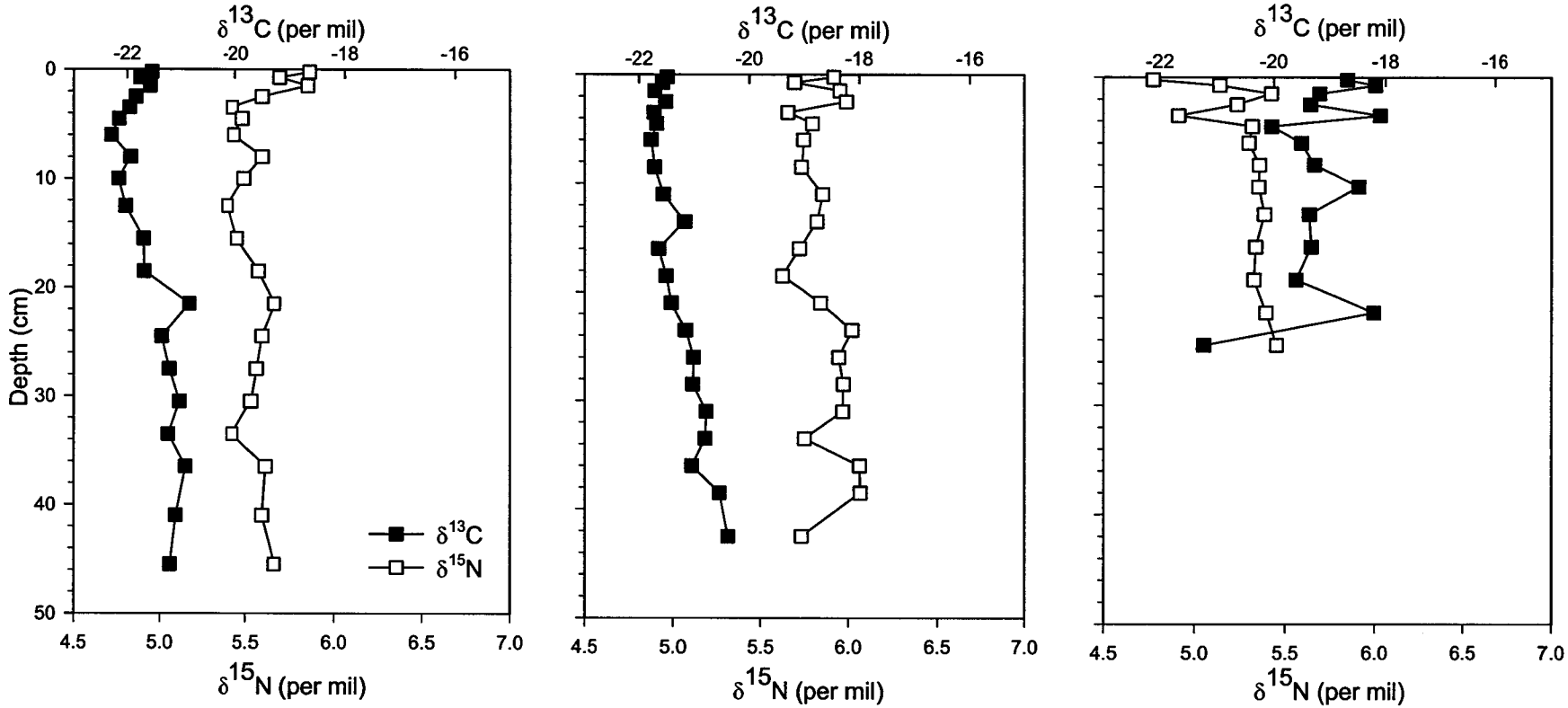


Lambert's Cove

Big Bay

Deadman's Harbour

Figure 2.4.2 $\delta^{13}C$ and $\delta^{15}N$ vertical sediment profiles for the three long cores taken in 2002.



Lambert's Cove

Big Bay

Deadman's Harbour

Figure 2.4.3 Vertical sediment profiles of porosity, C_{org}, C_{org}: N_{tot}, Hg_{tot}, as well as Mn_{HCl} and Fe_{HCl} for 6 short cores taken in the 2002 transects from Lambert's Cove.

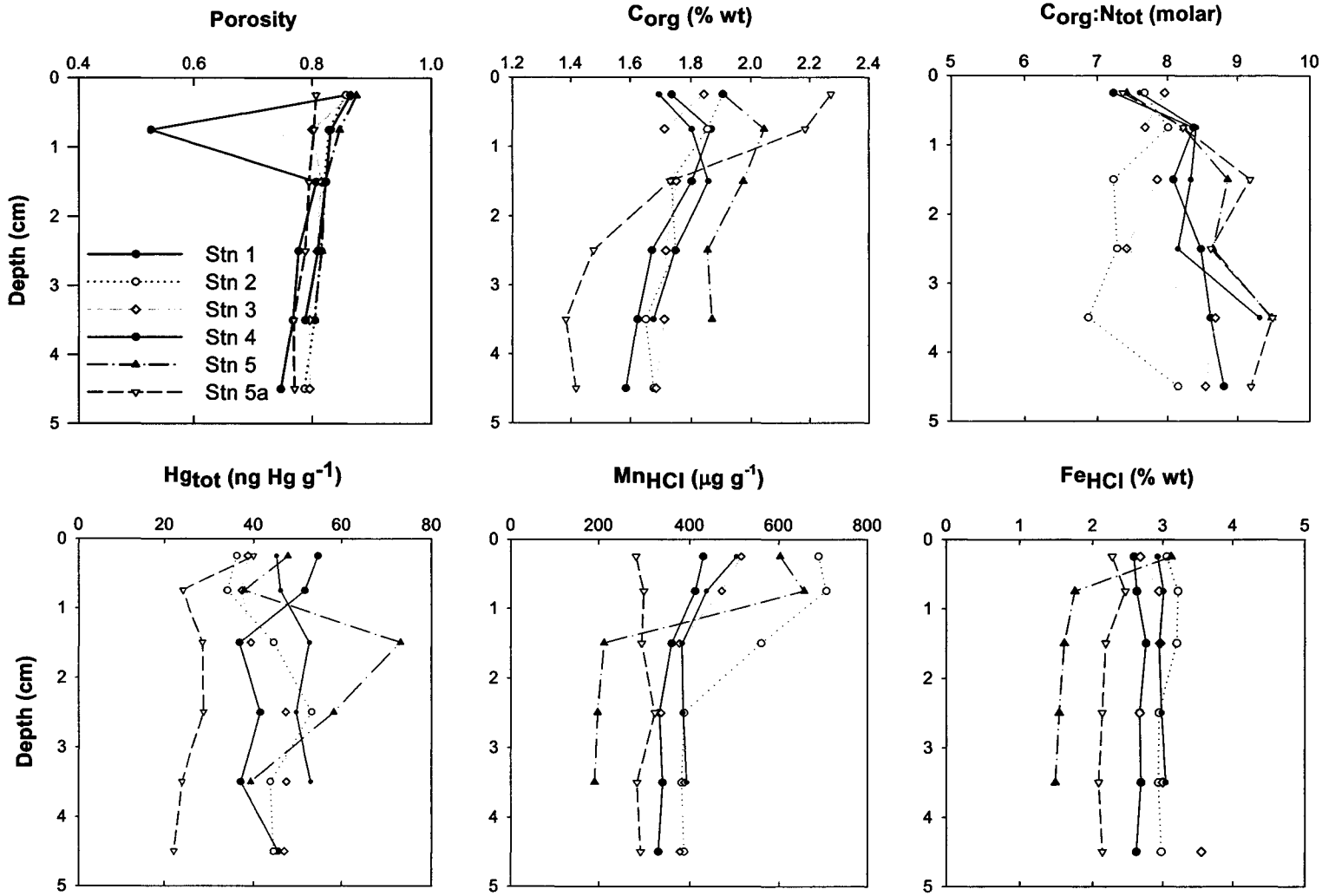


Figure 2.4.4 Vertical sediment profiles for the Lambert's Cove 2003 surface cores.

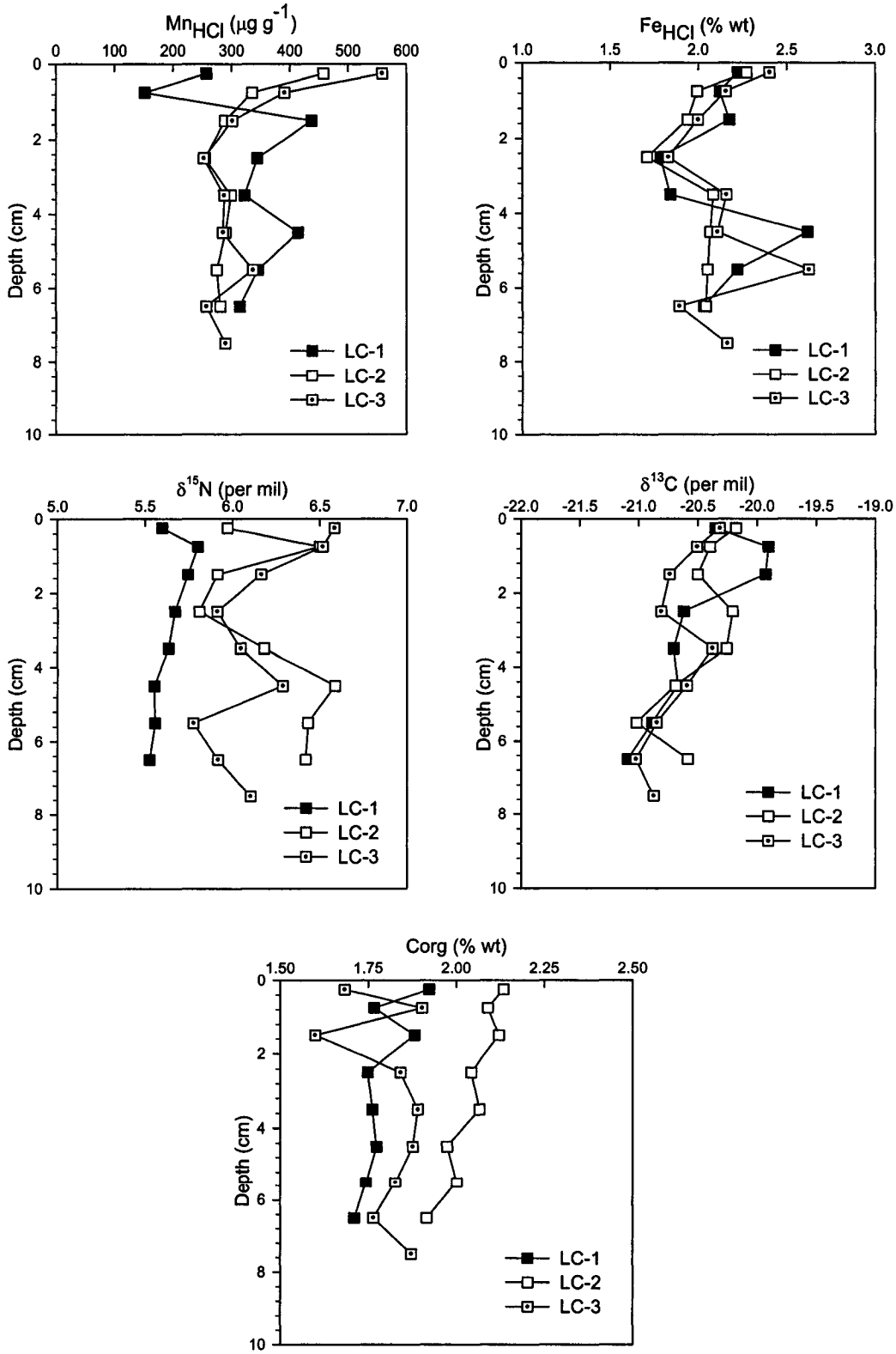
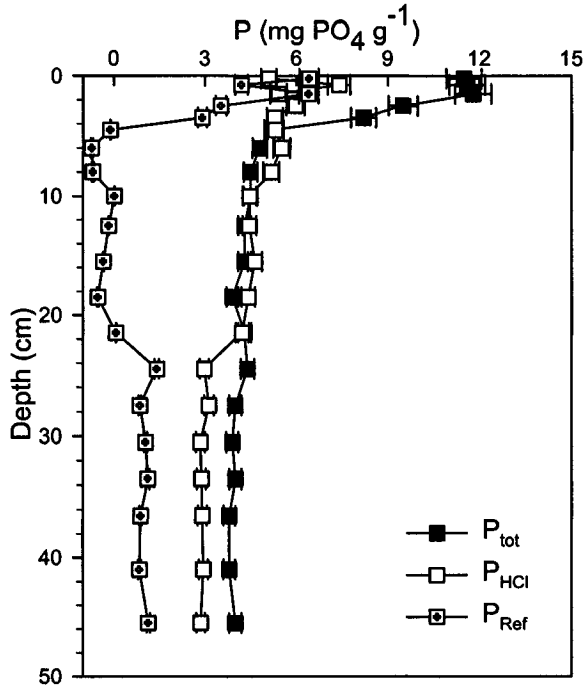
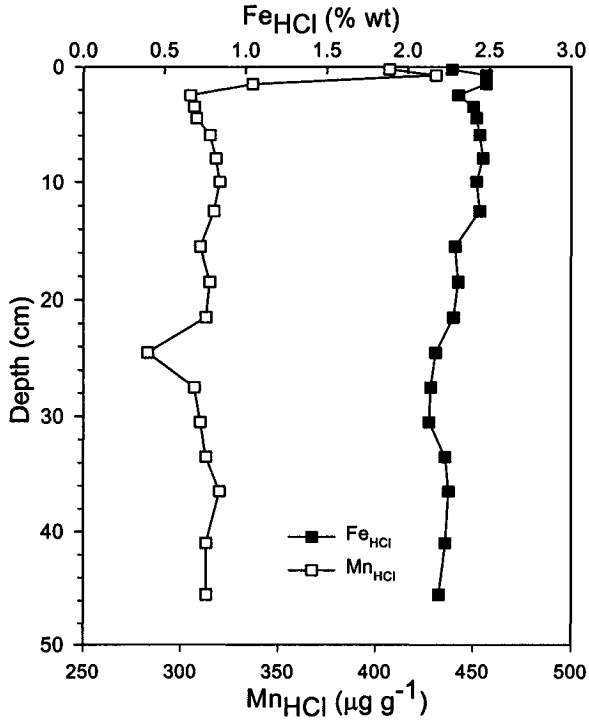


Figure 2.4.5



a) P_{tot}, P_{Ref} and P_{HCl} vertical sediment profiles for the 2002 Lambert's Cove long core station.



b) Fe_{HCl} and Mn_{HCl} vertical sediment profiles for the 2002 Lambert's Cove long core station.

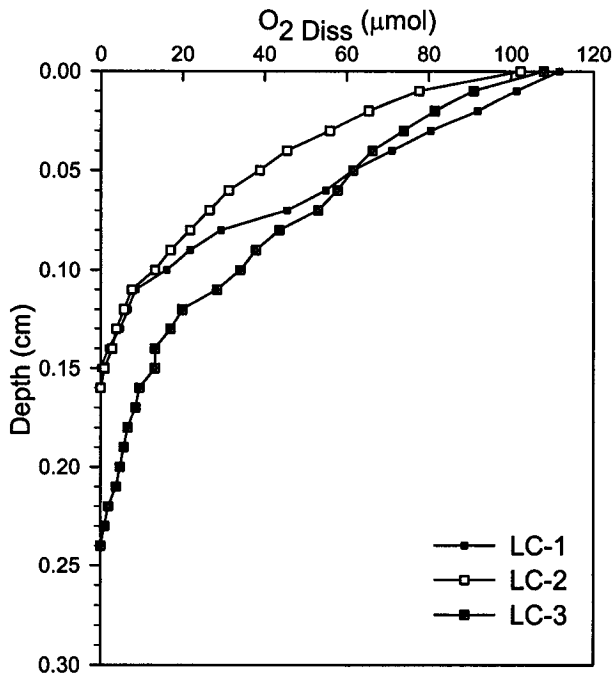
2.4.1.2 Migration of the oxygen penetration depth and suboxic-anoxic redox boundary

An increase in the organic carbon (C_{org}) content of the sediments below fish pens should lead to an increase of the reducing capacity of the sediments and a concomitant upward migration of the redox boundaries (i.e., oxic-suboxic boundary or oxygen penetration depth, oxic-anoxic boundary or sulfate-reduction zone).

In the absence of direct oxygen measurements, the distributions of reactive manganese (Mn_{HCl}) and iron (Fe_{HCl}) can serve as proxies of the oxygen penetration depth of the sediments. The vertical profiles of Mn_{HCl} and Fe_{HCl} are presented in Figure 2.4.5b for the long box-core taken from Lambert's Cove in 2002. The reactive manganese (Mn_{HCl}) depth profile reveals enrichment within the topmost 3 cm, as does the reactive iron (Fe_{HCl}) profile, suggesting that the combined oxic and nitrate-reducing zones may be as deep as 3 cm. Voltammetric microelectrode data provided by C. Magen (pers. comm.) show that the position of the Mn_{HCl} and Fe_{HCl} peaks overestimate the depth of oxygen penetration (Figures 2.4.6 and 2.4.4).

Dissolved sulfate as well as acid volatile sulfides (AVS) and pyrite in the sediments were determined in order to evaluate the reducing capacity of the sediments, the position of the suboxic/anoxic boundary, and the extent of sulfate reduction. The vertical profiles in Figure 2.4.8 present the summary of these analyses. Although there is no discernable porewater sulfate gradient in the sediments, evidence of sulfate reduction is confirmed by the presence of authigenic AVS and pyrite. The absence of a porewater sulfate gradient within the sampled depth interval reveals that sulfate reduction rates are small and compensated by the diffusion of sulfate from the overlying waters.

Figure 2.4.6 Vertical sediment profiles of O_{2Diss} for the Lambert's Cove 2003 short cores.



2.4.2 Mercury geochemistry

2.4.2.1 Sources of mercury to the sediment

Total mercury analyses were carried out on the fish food to determine if it is a significant source to the sediments under the fish pens. Four samples were analyzed and found to contain between 7 and 19 ng Hg per gram of feed (wet weight) (Appendix 2.8.8). Even the top layers of indigenous sediment from the control site, Deadman's Harbour, contain higher amounts of Hg (23.7-31.6 ng Hg g^{-1}) than the fish feed, thus demonstrating that the latter is likely a contributing source. The Hg_{tot} concentrations at and below 30 cm depth under the fish pens at Lambert's Cove and Big Bay display lower and less variable Hg concentrations of ~15 to 20 ng Hg g^{-1}. The vertical sediment profile at Deadman's Harbour displayed a rather smooth profile (Figure 2.4.7) at ~31 ng Hg g^{-1}, and began to decrease at 20 cm depth to concentrations similar to the background concentrations observed in the sediments at the aquaculture sites.

2.4.2.2 Partitioning of Mercury in the sediment

The relationships between C_{org} concentrations and Hg_{tot} concentrations in the sediments of the long cores were examined for each site. Lambert's Cove showed the strongest positive correlation between accumulated organic carbon and mercury (r^2=0.8534) (Appendix 2.8.2), Big Bay also showed a positive correlation (r^2=0.7117) (Appendix 2.8.3). The reference site, Deadman's Harbour, showed no significant correlation between C_{org} and Hg_{tot} (r^2=0.0153). This weak correlation is probably explained by a lower accumulation rate and the more refractory nature (i.e., higher C_{org}:N ratio and lower $\delta^{13}C$) of the organic matter in the sediments in the absence of aquaculture

activities coupled with a lower affinity or availability of mercury in this more open environment.

Given its chalcophile nature, Hg should be strongly partitioned with authigenic sulfides (Dyrssen et al., 1991). As more organic carbon is supplied to the sediment under the fish pens and the reducing capacity of the sediment is increased, more authigenic sulfides (i.e., AVS and pyrite) are precipitated (see section 2.4.1.2). Analyses of the mercury associated with the pyrite phase (Hg_{pyrite}) reveal that a large fraction (i.e., 13.63 to 92.73%) of the total sedimentary Hg is bound to pyrite (Fig. 2.4.7).

Figure 2.4.7 Hg_{tot} and Hg_{pyrite} vertical sediment profiles for the three long core stations taken in 2002.

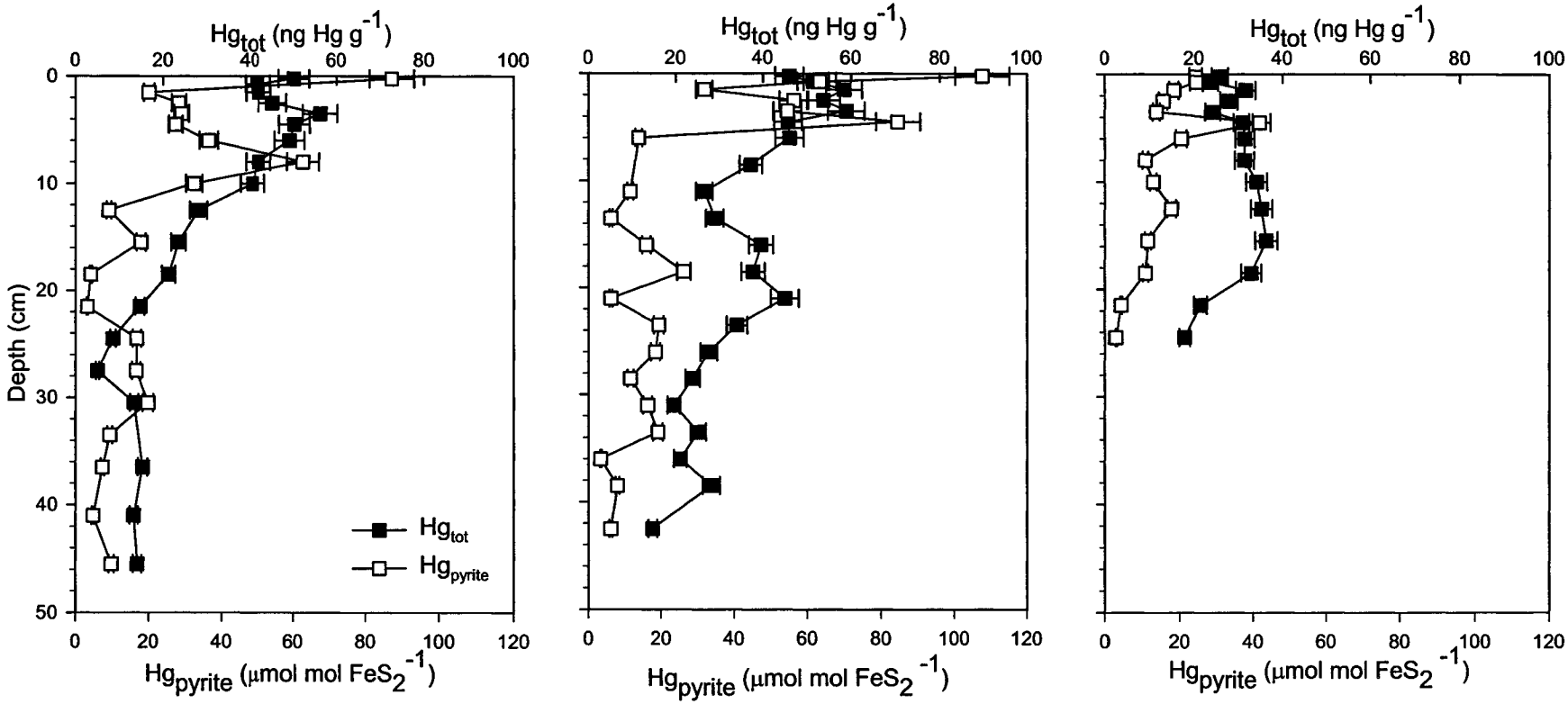
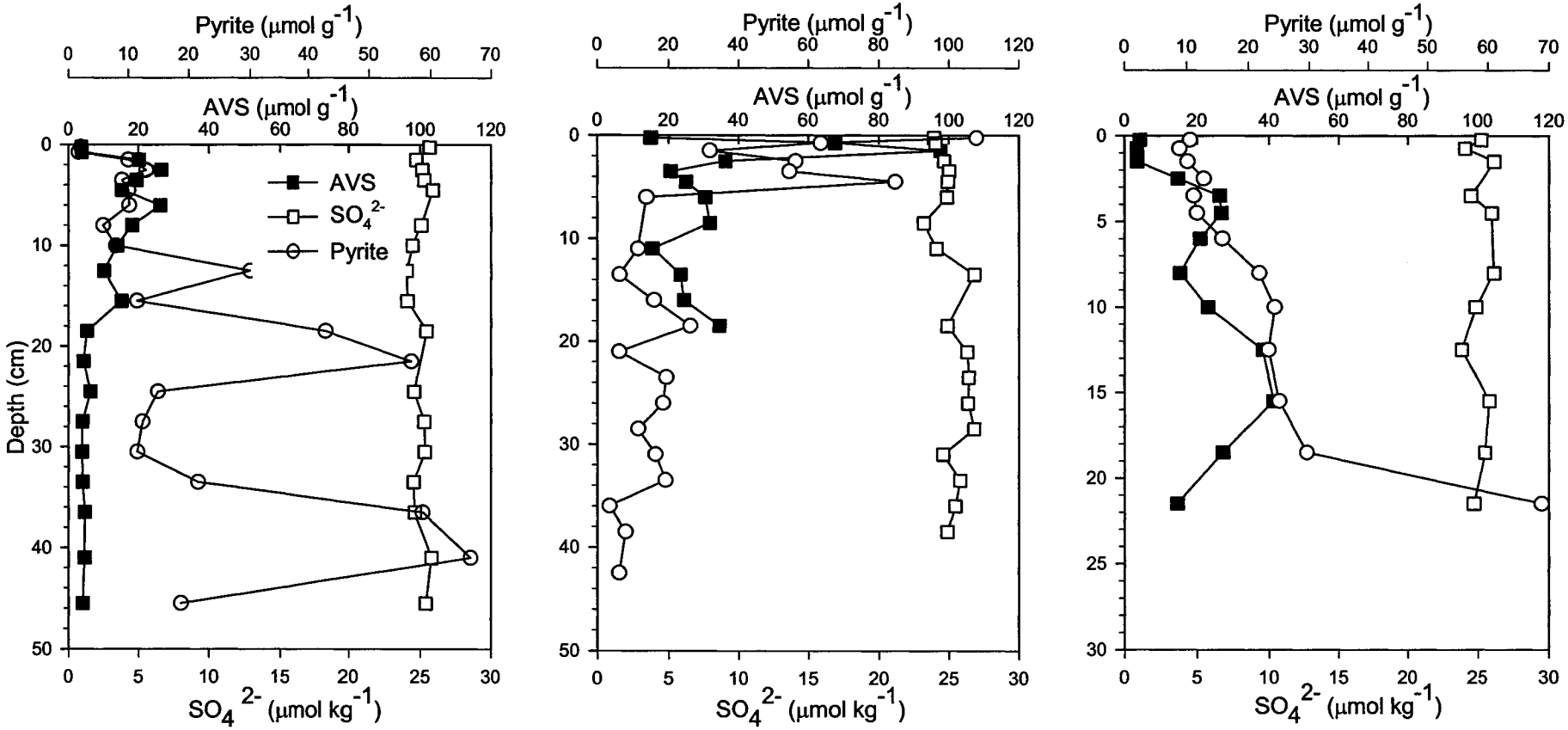


Figure 2.4.8 AVS and SO_4^{2-} and pyrite vertical sediment profiles for the three long cores taken in 2002.



2.4.2.3 Mercury in farmed and wild salmon

It is expected that the uptake of mercury in the fish food by the farmed salmon should be revealed through the mercury analysis of the fish muscle. As wild salmon feed on a diet of plankton, crustaceans and smaller fish (such as herring with an average Hg content of 0.04 ppm; NMFS Report, 1978), it is anticipated that wild salmon would have lower mercury concentrations in their flesh. According to the results of our analyses (Appendix 2.8.9), the mercury levels in the wild and farmed salmon were not statistically different (*wild*: range: 0.27-0.67 ppm wet weight; mean: 0.39; std dev: 0.10; n: 16 *farmed*: range: 0.30-0.40 ppm wet weight; mean: 0.34; std dev: 0.05; n: 3). Some of the wild salmon had higher total mercury values than the farmed salmon.

Table 2.4.1 Results of total mercury content in the tissues of farmed and wild salmon.

Sample	Length	Sex	Hg_{tot} (wet wt) $\mu g\ Hg\ g^{-1}$
Miramichi DFO 072	59.4	M	0.34
Miramichi DFO 092	57	M	0.32
Miramichi DFO 534	73.2	F	0.33
Miramichi DFO 539	58.5	n/a	0.28
Miramichi DFO 540	83.5	F	0.42
Miramichi DFO 541	65	M	0.34
Miramichi DFO 542	79	F	0.67
Miramichi DFO 543	58.7	M	0.40
Miramichi DFO 547	54.7	F	0.27
Miramichi DFO 548	85.5	F	0.39
Miramichi DFO 640	66.5	F	0.38
Restigouche 1	n/a	n/a	0.61
Restigouche 2	n/a	n/a	0.39
Restigouche 3	n/a	n/a	0.46
Restigouche 4	n/a	n/a	0.34
Restigouche 5	n/a	n/a	0.34
visited farm 2003	87.5	F	0.34
Conors bros 2004	n/a	n/a	0.40
Heritage 2004	85.3	n/a	0.30

2.5 Discussion

2.5.1 Sediment Chemistry

In addition to the material accumulating under the normal sedimentation regime, organic matter, in the form of either fish feces or unconsumed fish food derived from aquaculture activities, is delivered to the sediment under the fish pens. The additional input of organic matter to the sediments under salmon net-pens in Passamaquoddy Bay has been accompanied by higher nitrogen and phosphorus loadings, leading to local eutrophication and the development of hypoxic and anoxic sediment conditions within the top 2 cm of the sediment (Hargrave, 1997; Chou et al., 2002).

Carbon isotope ratios are typically used to determine whether the source of organic matter is marine or continental. This is based on the isotopically lighter $\delta^{13}C$ of terrestrial plants, -27 ‰, and the heavier values of marine organic material, which in mid-latitude environments lies between -20 ‰ to -22 ‰ (Meyers, 1994).

C_{org}:N ratios are also used to distinguish between algal and terrigenous sources of sedimentary organic matter (OM). C_{org}:N atomic ratios for algae are between 4 and 10, whereas the C_{org}:N ratios of terrigenous vascular land plants are ≥20 (Meyers, 1994). The C_{org}:N ratio of sedimentary organic matter increases as a result of selective degradation during early diagenesis (Meyers, 1994). Nevertheless, by combining the elemental (i.e., C_{org}:N ratio) and isotopic (i.e., $\delta^{13}C$ and $\delta^{15}N$) composition of the organic matter, it is possible to estimate the relative contribution of each source (Muzaka et al., 1999; Lucotte et al., 1991). The elevated OM $\delta^{13}C$ and $\delta^{15}N$ values observed in the sediment near or adjacent to cage sites indicate that a large proportion of the organic matter derived from fish farming activities is preserved in the sediment to a depth of ~10 cm.

Remineralization of the organic matter and mixing with the surface sediments smooth out the source signal over the bioturbation depth (Muzaka et al., 1999). A similar observation was reported by Hall et al. (1991) who note that between 20 to 70% of the organic carbon settling to the sediment surface under fish cages is buried whereas the remainder is remineralized and returned to the water column.

Within the surface sediments at Lambert's Cove, there is a sharp increase of the C_{org}:N ratio with depth (i.e., to ~8.3). This may reflect a recent input of more reactive organic matter to the sediments. The C_{org}:N ratio of fresh marine organic matter is typically given by the Redfield ratio and is equal to 6.6 (Redfield, 1934). The C_{org}:N ratios of the OM in surface sediments at the cage sites fluctuate between 7.1 and 9.1 whereas those of the fish feed vary between 5.0 and 7.7 (Appendix 2.8.8), indicating that the nature of the organic matter in the sediments was likely altered by the accumulation and mixing of fish feed or feces within the surface sediments. In surface sediments collected away from the pens, the C_{org}:N ratios of the OM fluctuate between 7.1 and 9.9; the C_{org}:N ratios of older (i.e., at depth) sedimentary organic matter, that was unaffected by the inputs from fish pens, fluctuate between 8.7 and 8.9. As expected, the $\delta^{13}C$ of the organic matter in surface sediments recovered at Lambert's Cove and Big Bay are more depleted and the $\delta^{15}N$-values enriched than values observed at Deadman's Harbour (Fig. 2.4.2), our fallowed reference site ($\delta^{13}C$= -18.1 to -20.0‰; $\delta^{15}N$= 4.8 to 5.4‰; C_{org}:N = 8.4 to 9.9).

Analysis of the sediments recovered around the salmon cages at Lambert's Cove in 2002 reveal that C_{org} concentrations and C_{org}:N ratios vary little over a wide area (Figure 2.4.3). Surface sediment (< 1 cm) organic carbon concentrations as high as

2.27% were found at the cage site 5a and they slowly decrease (from 2.27 to 1.15%) with distance away from this fish farm site. The surface sediment C_{org} concentrations at site 5a are 50% higher than those collected at sites 1 through 4. The high C_{org} content of surface sediments throughout the Lambert's Cove transect, compared to the Deadman's Harbour reference site, may be explained by a widespread dispersion of fish pen waste by strong currents in the area. Strong currents, both parallel (sites 6 to 8; see Figure 2.3.1) and perpendicular to Deer Island (sites 1-5 on Figure 2.3.1), have been reported (Forrester, 1958). Although sediments from Deadman's Harbour may serve as a basis of comparison with Lambert's Cove sediments, it must be noted that Deadman's Harbour is not in Passamaquoddy Bay (Figure 1.0) and, thus, the sources of organic matter to this site may differ from those in Passamaquoddy Bay. It would be best to compare values with a station from within Passamaquoddy Bay, yet away from the aquaculture sites, but as fish farms are widely distributed within the Bay, it was difficult to find suitable sites within the same depth range. According to Hargrave (pers. comm.), the wastes derived from salmon aquaculture is widely distributed within the Bay because of its fine particle size and due to resuspension by storms.

High resolution (i.e., sub-mm), micro-electrode O_2 profiles measured on short cores recovered from the Lambert's Cove site in 2003 (Figure 2.4.6) reveal a sharp decrease of the porewater oxygen in the top 2.4 mm of the sediment. Results show that *in-situ* O_2 consumption from organic matter degradation exceeds the supply of O_2 from the overlying waters which results in the development of suboxic and anoxic conditions close to the sediment-water interface. The vertical Mn_{HCl} and Fe_{HCl} profiles in the Lambert's Cove long core (Figure 2.4.5b) indicate that Mn and Fe-oxides accumulate

within the top 2.5 cm of sediments, beneath which they undergo reductive dissolution under suboxic conditions. Unlike Mn_{HCl}, a sizable fraction of the Fe_{HCl} persists once it is buried within the suboxic and anoxic sediments (Kostka and Luther, 1994; Mucci et al., 2003).

Vertical reactive iron and manganese (i.e., Fe_{HCl} and Mn_{HCl}) profiles from short cores taken along the 2002 Deer Island transects (Figure 2.4.3) revealed that the oxygen penetration depth was within the first 2 cm of the sediments. The vertical distribution of reactive iron (Fe_{HCl}) at site 5 (i.e., directly under a fish pen) clearly reflects the presence of an iron oxide precipitation zone within the top 0-1 cm interval. The Mn_{HCl} of the sediment peaked at 660 $\mu g\ g^{-1}$ within the first cm at sites 5 (i.e., directly under a fish pen) and 2 (away from fish pens), decreased quickly within the next 1 cm depth interval, and remained almost constant within the next 3 cm. The vertical distribution of reactive manganese (Mn_{HCl}) at all sites reveals that the oxygen penetration depth is found within the top 0-1 cm interval of the sediments.

A comparison of the distributions of Mn_{HCl} in the sediments recovered from Lambert's Cove in 2002 and 2003 (see Figures 2.4.3; 2.4.4) illustrates that in 2002, when aquaculture activities were underway, the Mn_{HCl} peak was weaker and was distributed over a thinner sediment interval than in sediments collected in 2003 when no salmon farming was taking place in the same area. This observation may reflect a downward migration of the oxygen penetration depth and oxic-suboxic boundary following a decrease of organic carbon input to the sediments in the absence of aquaculture activities and a more efficient sequestration (i.e., oxidative precipitation) of porewater Mn(II) diffusing up from the suboxic to the oxic zone. The migration of redox boundaries in the

sediments is not as easily discernable from the distribution of Fe_{HCl} as iron oxides are composed of a suite of solids of varying reactivities (Canfield, 1989; Raiswell et al., 1994; Poulton et al., 2004) and they are less sensitive to variations of the organic matter inputs to the sediment (Gobeil et al., 2001) since iron reduction is suppressed until the majority of MnO_x are reduced.

The sulfate concentrations of porewaters extracted from the long box cores do not show depletion with depth. Although there is no sulfate gradient in the sediments over the sampled interval, detectable amounts of H_2S (i.e., by smell) and the presence of iron sulfides (i.e., AVS and pyrite) in these sediments confirm the presence of active sulfate reduction. In the presence of H_2S and ferrous iron or reducible ferric iron phases, authigenic pyrite (FeS_2) and acid-volatile sulfides (AVS) can be precipitated (Schippers and Jorgensen, 2002). Our results (i.e., [Fe_{HCl}]) confirmed the abundance of reactive iron phases in these sediments. The presence of FeS_2 and AVS was observed at all stations sampled by the short and long box cores (Figure 2.4.8). AVS are unstable in the presence of oxygen and, thus, the occurrence of AVS within the upper 2 cm of sediment at both the Lambert's Cove and Big Bay stations is indicative of the maximum excursion of the oxygen penetration depth. This is shallower than the depth at which AVS appear at the reference site (i.e., ~3 cm). The pyrite concentration profiles at the sites of aquaculture activities (i.e., Lambert's Cove and Big Bay) are discontinuous and more variable than those at the reference site, possibly indicating the influence of episodic, reactive organic matter inputs to as well as biological and physical mixing of the sediments over time.

2.5.2 Tracers of salmon farming activity

Proxies were used to estimate the depth of organic waste accumulation in the sediments under the fish cages. To verify the reliability of these proxies we compared the C:N ratios and stable isotopic signatures of the organic matter in the surface sediment and fish food. There was little difference in the stable isotope composition of the sedimentary organic matter ($\delta^{13}C$= -22.3 to -18.1‰, $\delta^{15}N$= 4.8 to 6.0‰) and the feed ($\delta^{13}C$= -21.4 to -23.4‰, $\delta^{15}N$= 4.9 to 6.0‰) whereas the C_{org}:N ratio was larger in the sediments (8.4 to 10.2) than the fish feed (5.0 to 7.7). Nevertheless, both tracers reveal that fish feed and/or feces contribute to the sediment organic matter load.

The 1N HCl extractible phosphate (P_{HCl}) accumulated in the top centimeter of the sediment coincides with the presence of a thin oxic, iron oxide-rich layer (Figure 2.4.5b) to which labile phosphate is strongly adsorbed. The reductive dissolution of the metal oxides under suboxic and anoxic conditions at depth leads to the release of the associated phosphate to the porewaters and its diffusion back to the oxic layer where it is re-adsorbed onto freshly precipitated authigenic iron oxides. Conversely, there is a concentration of P_{tot} in the top 5 cm of the sediment which far exceeds the P_{HCl} signal. The total phosphorus content of the sediment in the Lambert's Cove long core decreases from ~11.5 mg PO_4 g^{-1} (dry wt) at the surface to ~5.2 mg PO_4 g^{-1} at 4-5 cm depth below which it varies little (Figure 2.4.5a). The distribution of P_{tot} is believed to reflect the history of residual feed (1% P or 30 mg PO_4 g^{-1} dw in Shurgain feeds) and fecal matter accumulation in the sediments resulting from recent farming activities. Similar observations and conclusions were reported by Holby and Hall (1991) following a study of the chemistry of sediments recovered under a marine fish cage farm in the Gullmar Fjord of western Sweden.

2.5.3 Distribution of mercury in fish and sediments

Due to the complex sediment transport processes (e.g., cross-currents, resuspension, mixing) in Passamaquoddy Bay, a historical reconstruction of Hg_{tot} loading to the Bay from the sediment record is unrealistic and the use of traditional dating methods such as ^{210}Pb and ^{137}Cs is impractical, as is the case in other embayments (Smith, 2001). Sunderland et al. (2004) estimated, using the Cranston method (i.e., measurements of sulfate gradients in sediments and their correlation to the organic carbon content in the sediments (Cranston 1991, 1997), the present-day sediment burial rates at approximately 1-2 mm $year^{-1}$. On the basis of this estimate, they proposed that only the sediments below depths of 40 cm record reliable pre-anthropogenic Hg_{tot} concentrations.

There is much documented evidence of the affinity of mercury for sedimentary particulate organic matter (e.g., Benoit et al., 1999; 2001) and strong correlations have been reported between C_{org} and Hg in many sediment types (Lindberg and Harriss, 1974; Baldi and Bargagli, 1984). The vertical distribution of mercury in the sediments of our study area is strongly correlated to their organic carbon content and surface sediments are typically enriched in C_{org} and Hg_{tot}. The strongest correlations are found in Lambert's Cove (r^2=0.85) and Big Bay (r^2=0.71), the two farmed sites. In contrast, at Deadman's Harbour, our reference site, no significant correlation between C_{org} and Hg_{tot} (r^2=0.01) was observed, possibly due to the dilution effect of the lithogenic components in the sediment.

The Hg_{tot} content of the fish food samples we analyzed was lower than the concentrations found in the top 20 cm of all the sediment cores recovered in Passamaquoddy Bay, including sediments collected away from pens. Whereas the Hg_{tot}

from the fish food may contribute to the sediment load below the cage sites, it cannot explain the higher Hg_{tot} sediment concentrations observed at these sites compared to the reference site. On the other hand, the residual food and other organic waste that settle below the fish pens clearly increase the amount of organic matter that accumulates in these sediments and, in turn, the associated Hg load. The origin of the additional mercury has yet to be resolved but its strong affinity for organic matter is clearly responsible for its increased concentration in surface sediments (Lindberg and Harriss, 1974; Baldi and Bargagli, 1984). Our observations may possibly reflect the concentration of Hg delivered to the sediments with highly reactive organic matter (e.g., proteinaceous material) that is rapidly remineralized, leading to an increase in Hg concentrations in the sediments over time. Hg also displays a strong affinity for authigenic pyrite, a potential long-term sink in the sediments (Jean and Bancroft, 1986; Dyrssen et al., 1991). Analyses of mercury associated with the pyrite phase show that up to 93% of the mercury in the Passamaquoddy Bay sediments is bound to pyrite.

Despite the limited number of samples, results of the analyses of fish muscle reveal that the mercury levels in farmed salmon (n = 3; mean = 0.72 (± 0.11) μg Hg/kg ww) are not significantly different than those of wild salmon taken from the Miramichi (n = 11; mean = 0.78 (± 0.22) μg Hg/kg ww) and Restigouche (n = 5; mean = 0.89 (± 0.23) μg Hg/kg ww) rivers. As the age (or length) of the fish was not available for all samples, and the lengths of the fish studied were not identical, it is unclear if the Hg concentrations in the salmon flesh reflect the age and, thus, the residency time of the fish or the food chain preference of the wild salmon diet, or perhaps a combination of both factors. The wild salmon samples from the Miramichi River show a correlation between sex, length

and mercury levels whereby the females are larger and contain higher levels of Hg_{tot} than the wild male samples. The average Hg_{tot} levels of the wild salmon are not statistically different than the farmed salmon. In contrast, a different trend has been reported for the methylmercury levels of wild (mean = 49 (± 17) μg Hg/kg ww) and farmed salmon (mean= 29 (± 12) μg Hg/kg ww) of Pacific Coast salmon species (Easton et al., 2002).

Health Canada has reduced its guideline from 0.47 to 0.2 μg Hg/kg body weight/day for mercury intake by child-bearing aged women and children less than 12 years of age (Easton et al., 2002). Given the concentrations of mercury found in the Passamaquoddy Bay-farmed and wild salmon of the Miramichi and Restigouche rivers, a 70 kg adult may consume 0.25kg/week of wild salmon or 0.28kg/week of farmed salmon. All of the farmed and wild fish samples we analyzed appear to be of little concern for human consumption under these current safety guidelines. A greater sampling of wild and farmed salmon is recommended in future studies.

2.6 Conclusions

The primary objective of this study was to determine the impact of salmon aquaculture activities on the chemistry of sediments under fish cages in Passamaquoddy Bay, New Brunswick and identify tracers that could be used to reconstruct the history of these activities from the sediment record.

The vertical distributions of reactive iron (Fe_{HCl}) in the sediment specify that the oxygen penetration depth (OPD) is within the 2.5 cm of the sediment-water interface at all sites sampled in Passamaquoddy Bay. The vertical distribution of Mn_{HCl}, a more sensitive tracer of the OPD and its migration, reveals that the OPD is within the top 0-1

cm interval of the sediments at all sites. These latter observations are more consistent with high resolution, voltammetric micro-electrode profiles of dissolved oxygen distributions within the sediment. The Mn_{HCl} distribution also shows that, as a result of farming activities, there is an upward migration of the OPD and oxic-suboxic boundary with higher organic carbon inputs to the sediments.

The presence of active sulfate reduction in the sediments recovered under the salmon aquaculture cages (depth ~2 cm), as well as other stations in the Bay (depth ~3 cm), was confirmed by the presence of H_2S and iron sulfides (i.e., AVS and pyrite). The depth at which AVS first appears in the sediments is shallower under fish pens and in all cores, no porewater sulfate depletion was detected within the sampled depth (i.e., up to 45 cm). In contrast to fallowed sites or sites far from aquaculture activities, episodic inputs of reactive organic matter to and/or biological and physical mixing of the sediment at the sites of aquaculture activities was evidenced by the discontinuous vertical distribution of pyrite.

Organic carbon concentrations in surface sediments of cores taken underneath salmon aquaculture pens in Passamaquoddy Bay are higher than those in the surface sediments of the reference site (i.e., Deadman's Harbour). Lighter OM $\delta^{13}C$ and $\delta^{15}N$ values of the sedimentary organic matter under fish cages, compared to sediments recovered from the reference sites, indicate that fresh organic matter was added or mixed into the top 10 cm at cage sites. This is further substantiated by the lower C_{org}:N ratios of the surface sediments at cage sites

The use of total phosphorus as a suitable tracer of marine aquaculture activities in the sediment record was confirmed through the use of the distribution of total and

reactive phosphorus in a sediment core recovered under salmon cages. The presence of excess particulate phosphorus supplied via salmon food and feces clearly reflects the accumulation of farming waste in the sediments.

Strong correlations were observed between organic carbon content and the vertical distribution of mercury in the sediments of Passamaquoddy Bay. Sediments collected below or in the vicinity of aquaculture sites contained higher reactive organic matter content and, thus, total mercury. Our results show that sedimentary Hg displays a strong affinity for authigenic pyrite in the sediments in Passamaquoddy Bay and represent a potentially long-term sink of Hg in these sediments.

There is no striking difference in the total Hg concentrations of fish flesh sampled from the few wild and farmed salmons analyzed. The concentrations of Hg within the flesh of the farmed and wild salmon should be considered when establishing dietary intake guidelines of Atlantic salmon by humans.

Salmon aquaculture activities are prevalent in Passamaquoddy Bay and have triggered increased awareness of the chemical and biological impact of aquaculture to the marine environment. As the aquaculture industry matures, ongoing efforts from salmon producers, scientists and the local government are being made to better understand the impacts of the farming practices in Passamaquoddy Bay, and to reduce those impacts to maintain the excellent conditions that the Bay offers for farmed and wild native species. From this study it can be gathered that the impacts of salmon aquaculture on the sediment geochemistry near and at the edge of the cages are mostly subtle and, exclusive of the biota which was not surveyed, have not lead to a major degradation of the benthic environment, particularly when farm sites were allowed to fallow.

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2.8 Appendix

Appendix 2.8.1 Depth distribution of some chemical properties of the sediments from the three 2003 Deer Island short cores.

Station	Depth	$\delta^{13}C$	$\delta^{15}N$	C_{org}	$C_{org}:N_{tot}$	Mn_{HCl}	Fe_{HCl}
	cm	per mil	per mil	% wt	molar	$\mu g\ g^{-1}$	% wt
LC-1	0.25	-20.4	5.6	1.92	9.42	257	2.22
N 45 01..391	0.75	-19.9	5.8	1.77	9.64	152	2.12
W 66 58.842	1.5	-19.9	5.7	1.88	9.11	437	2.18
	2.5	-20.6	5.7	1.75	9.78	344	1.79
	3.5	-20.7	5.6	1.76	9.54	322	1.84
	4.5	-20.7	5.6	1.77	9.88	414	2.62
	5.5	-20.9	5.6	1.74	10.20	345	2.22
	6.5	-21.1	5.5	1.71	10.16	314	2.03
LC-2	0.25	-20.2	6.0	2.13	9.87	458	2.27
N 45 01.053	0.75	-20.4	6.5	2.09	10.12	335	1.99
W 66 58.317	1.5	-20.5	5.9	2.12	9.95	289	1.94
	2.5	-20.2	5.8	2.04	10.19	255	1.71
	3.5	-20.3	6.2	2.07	9.95	299	2.08
	4.5	-20.7	6.6	1.97	10.00	290	2.07
	5.5	-21.0	6.4	2.00	9.99	275	2.05
	6.5	-20.6	6.4	1.92	10.11	281	2.04
LC-3	0.25	-20.3	6.6	1.68	9.51	558	2.40
N 45 01.254	0.75	-20.5	6.5	1.90	9.23	390	2.15
W 66 58.627	1.5	-20.7	6.2	1.60	9.45	301	2.00
	2.5	-20.8	5.9	1.84	9.69	253	1.83
	3.5	-20.4	6.0	1.89	9.75	287	2.16
	4.5	-20.6	6.3	1.88	9.67	285	2.11
	5.5	-20.8	5.8	1.83	9.86	336	2.62
	6.5	-21.0	5.9	1.76	10.09	257	1.89
	7.5	-20.9	6.1	1.87	9.88	289	2.16

Appendix 2.8.2 Depth distribution of some chemical properties of the sediments from the Lambert's Cove long core taken in 2002.

Depth	Porosity	$\delta^{13}C$	$\delta^{15}N$	C_{org}	$C_{org}:N_{tot}$	Fe_{HCl}	Mn_{HCl}	P_{tot}	P_{HCl}	SO_4^{2-}	AVS	Hg_{tot}	Hg_{pyrite}
cm		per mil	per mil	% wt	molar	% wt	$\mu g\ g^{-1}$	mg $PO_4\ g^{-1}$	mg $PO_4\ g^{-1}$	mmol kg^{-1}	$\mu mol\ g^{-1}$	ng Hg g^{-1}	$\mu mol\ mol\ FeS_2^{-1}$
0.25	0.85	-21.55	5.86	2.23	8.97	2.27	407	11.5	5.09	25.7	3.77	50.2	87.2
0.75	0.839	-21.76	5.69	1.93	8.66	2.48	431	11.6	7.4	n/a	3.92	41.7	n/a
1.5	0.818	-21.58	5.85	2.01	9	2.48	337	11.8	5.41	24.7	20.1	41.8	20.1
2.5	0.809	-21.84	5.59	1.95	9.1	2.31	305	9.5	5.97	25.1	26.5	45.2	28.2
3.5	0.803	-21.96	5.42	1.85	8.97	2.4	307	8.2	5.29	25.3	19.4	56.2	29.0
4.5	0.801	-22.15	5.48	1.84	9.32	2.42	308	5.2	5.31	25.9	15.3	50.3	27.4
6	0.789	-22.29	5.43	1.84	10.2	2.44	315	4.8	5.52	n/a	26.2	49.2	36.4
8	0.775	-21.94	5.59	1.86	9.41	2.46	318	4.5	5.18	25.1	18.2	41.8	62.7
10	0.759	-22.16	5.49	1.68	8.9	2.42	320	4.5	4.47	24.4	14.0	40.5	32.4
12.5	0.746	-22.03	5.39	1.54	9.98	2.44	317	4.3	4.46	24.0	10.2	28.0	9.2
15.5	0.746	-21.7	5.45	1.4	9.09	2.29	310	4.3	4.64	24.1	15.2	23.4	17.9
18.5	0.753	-21.69	5.57	1.33	9.72	2.31	315	3.9	4.42	25.4	5.37	21.2	4.3
21.5	0.726	-20.86	5.66	1.21	7.86	2.28	313	4.3	4.22	n/a	4.32	14.7	3.3
24.5	0.717	-21.37	5.59	1.17	8.56	2.17	283	4.4	2.98	24.6	6.39	8.6	16.8
27.5	0.733	-21.23	5.56	1.16	9.02	2.14	307	4.0	3.13	25.3	4.07	5.1	16.7
30.5	0.734	-21.04	5.53	1.11	8.06	2.13	310	3.9	2.85	25.3	3.92	13.4	19.8
33.5	0.733	-21.25	5.42	1.21	8.33	2.23	313	4.0	2.88	24.5	4.11	n/a	9.5
36.5	0.733	-20.93	5.61	1.06	7.74	2.25	320	3.8	2.91	24.6	4.70	15.3	7.5
41	0.723	-21.11	5.59	1.07	8.33	2.23	313	3.8	2.95	25.8	4.59	13.3	4.9
45.5	0.738	-21.22	5.66	1.14	8.29	2.19	313	4.0	2.86	25.4	4.09	14.1	9.9

Appendix 2.8.3 Depth distribution of some chemical properties of the sediments from the Big Bay long core taken in 2002.

Depth	Porosity	$\delta^{13}C$	$\delta^{15}N$	C_{org}	$C_{org}:N_{tot}$	P_{tot}	SO_4^{2-}	AVS	Hg_{tot}	Hg_{pyrite}
cm		per mil	per mil	% wt	molar	mg PO_4 g^{-1}	mmol kg^{-1}	μmol g^{-1}	ng Hg g^{-1}	μmol mol FeS_2^{-1}
0.25	0.895	-21.5	5.9	1.93	9.04	4.7	23.9	15.0	46	107.8
0.75	0.886	-21.6	5.7	1.91	8.94	3.82	24.1	67.5	51.4	63.5
1.5	0.872	-21.7	6.0	1.86	9.08	4.1	n/a	97.6	58.4	31.8
2.5	0.841	-21.5	6.0	1.79	9.10	3.38	24.6	36.3	53.7	56.4
3.5	0.816	-21.7	5.7	1.71	9.08	3.42	25.0	20.5	58.9	54.6
4.5	0.818	-21.7	5.8	1.71	9.10	3.4	24.9	24.9	45.7	84.6
6	0.812	-21.8	5.7	1.71	9.10	3.3	24.9	30.5	46.0	13.8
8.5	0.805	-21.7	5.7	1.65	9.17	3.2	23.2	31.8	37.2	n/a
11	0.795	-21.6	5.9	1.65	9.2	3.07	24.1	15.5	26.5	11.5
13.5	0.8	-21.2	5.8	1.57	9.65	3.17	26.8	23.4	28.9	6.2
16	0.799	-21.7	5.7	1.62	9.00	2.98	n/a	24.4	39.5	15.9
18.5	0.789	-21.5	5.6	1.59	9.31	2.9	24.9	34.5	37.7	26.2
21	0.762	-21.4	5.8	1.51	9.29	2.94	26.3	n/a	44.9	6.1
23.5	0.749	-21.2	6.0	1.43	9.29	2.61	26.4	n/a	34.0	19.3
26	0.753	-21.0	5.9	1.43	9.28	2.75	26.4	n/a	27.5	18.4
28.5	0.737	-21.0	6.0	1.39	9.03	2.79	26.8	n/a	23.8	11.5
31	0.737	-20.8	6.0	1.33	9.14	2.77	24.6	n/a	19.5	16.3
33.5	0.741	-20.8	5.8	1.33	9.17	2.67	25.8	n/a	25.1	19.1
36	0.746	-21.1	6.1	1.37	8.90	2.7	25.4	n/a	21.0	3.3
38.5	0.756	-20.6	6.1	1.37	8.93	2.72	24.9	n/a	28.1	7.9
42.5	0.758	-20.4	5.7	1.36	8.38	n/a	29.3	n/a	14.7	6.1

Appendix 2.8.4 Depth distribution of some chemical properties of the sediments from the Deadman's Harbour long core taken in 2002.

Depth	Porosity	$\delta^{13}C$	$\delta^{15}N$	C_{org}	$C_{org}:N_{tot}$	P_{tot}	SO_4^{2-}	AVS	Hg_{tot}	Hg_{pyrite}
cm		per mil	per mil	% wt	molar	mg PO_4 g^{-1}	mmol kg^{-1}	μmol g^{-1}	ng Hg g^{-1}	μmol mol FeS_2^{-1}
0.25	0.795	-18.7	4.8	1.54	8.59	3.48	25.3	4.3	25.8	24.4
0.75	0.773	-18.2	5.1	1.51	8.42	3.46	24.1	3.5	23.7	24.6
1.5	0.758	-19.2	5.4	1.62	8.64	3.53	26.2	3.5	31.6	18.4
2.5	0.774	-19.3	5.2	1.57	9.16	3.16	20.3	14.7	27.8	15.6
3.5	0.757	-18.1	4.9	1.61	9.9	2.83	24.5	26.3	24.2	13.7
4.5	0.749	-20.0	5.3	1.57	9.21	3.18	26.0	26.7	31.0	41.7
6	0.738	-19.5	5.3	1.54	8.98	2.98	24.1	20.9	31.4	20.5
8	0.73	-19.3	5.4	1.5	8.75	3.08	26.1	15.3	31.3	10.7
10	0.716	-18.5	5.4	1.53	8.95	3.00	24.9	23.0	34.1	12.9
12.5	0.708	-19.4	5.4	1.42	8.72	2.99	23.9	38.2	35.2	17.8
15.5	0.69	-19.3	5.3	1.49	8.71	3.00	25.8	41.2	36.3	11.5
18.5	0.694	-19.6	5.3	1.49	8.71	3.02	25.5	27.2	32.9	10.8
21.5	0.677	-18.2	5.4	1.41	8.69	2.73	24.7	14.5	21.4	4.2
24.5	0.679	-21.2	5.5	1.45	8.95	2.75	n/a	n/a	17.8	2.8

Appendix 2.8.5 Depth distribution of some chemical properties of the sediments from the 2002 Deer Island transects.

Station	Depth cm	Porosity	C_{org} % wt	C_{org}: N_{tot} molar	P_{tot} mg PO_4 g^{-1}	Hg_{tot} ng Hg g^{-1}	Mn_{HCl} μg g^{-1}	Fe_{HCl} % wt
1	0.25	0.858	1.74	7.23	3.31	54.7	430	2.59
	0.75	0.526	1.87	8.37	3.24	51.7	412	2.63
	1.5	0.807	1.80	8.08	2.57	36.8	360	2.76
	2.5	0.777	1.67	8.47	2.39	41.5	333	2.67
	3.5	0.767	1.62	8.61	2.28	37.1	340	2.69
	4.5	0.746	1.59	8.80	n/a	45.5	330	2.62
2	0.25	0.857	1.91	7.67	3.44	36.2	690	3.06
	0.75	0.829	1.85	8.01	3.56	34.2	708	3.22
	1.5	0.821	1.74	7.24	3.84	44.6	560	3.20
	2.5	0.816	1.75	7.28	3.11	53.3	387	2.95
	3.5	0.805	1.65	6.87	3.09	43.9	382	2.94
	4.5	0.788	1.68	8.15	3.13	44.5	387	2.98
3	0.25	0.866	1.84	7.96	3.96	38.7	515	2.68
	0.75	0.801	1.71	7.68	3.82	37.5	472	2.95
	1.5	0.816	1.75	7.86	3.34	39.4	377	2.96
	2.5	0.809	1.72	7.42	3.24	47.3	337	2.67
	3.5	0.796	1.71	8.68	2.95	47.5	388	3.00
	4.5	0.796	1.68	8.54	2.40	46.9	378	3.55

Appendix 2.8.6 Depth distribution of some chemical properties of the sediments from the 2002 Deer Island transects.

Station	Depth cm	Porosity	C_{org} % wt	C_{org}: N_{tot} molar	P_{tot} mg PO_4 g-1	P_{HCl} mg PO_4 g-1	Hg_{tot} ng Hg g^{-1}	Mn_{HCl} $\mu g\ g^{-1}$	Fe_{HCl} % wt
4	0.25	0.865	1.70	7.60	3.19	n/a	45.2	505	2.93
	0.75	0.831	1.80	8.41	3.33	n/a	46.1	437	3.01
	1.5	0.823	1.86	8.33	2.82	n/a	52.7	383	2.95
	2.5	0.81	1.75	8.15	2.46	n/a	49.7	385	2.98
	3.5	0.788	1.68	9.31	2.58	n/a	53.0	393	3.04
5	0.25	0.876	1.91	7.42	12.24	2.14	47.8	603	3.12
	0.75	0.847	2.05	8.23	12.41	1.9	38.0	658	1.76
	1.5	0.822	1.98	8.86	8.57	1.57	73.2	212	1.61
	2.5	0.817	1.86	8.65	2.47	1.29	58.3	198	1.54
	3.5	0.805	1.87	9.48	2.32	1.23	39.4	191	1.49
5a	0.25	0.807	2.27	7.36	5.90	n/a	40.0	283	2.28
	0.75	0.804	2.19	8.22	4.17	n/a	24.2	300	2.47
	1.5	0.795	1.73	9.18	5.68	n/a	28.6	295	2.19
	2.5	0.789	1.48	8.62	3.43	n/a	28.9	323	2.14
	3.5	0.768	1.38	9.49	2.5	n/a	24.0	285	2.09
	4.5	0.77	1.42	9.19	2.78	n/a	22.2	292	2.14
6	0.5	0.76	1.15	7.47	4.94	n/a	36.8	n/a	n/a
7	0.5	0.838	1.95	8.73	4.86	n/a	35.9	n/a	n/a
8	0.5	0.751	1.48	8.66	3.33	n/a	32.2	n/a	n/a

Appendix 2.8.7 Chemical properties of the sediments from the 2002 Deer Island transects.

Station	Depth cm	Porosity	C_{org} % wt	C_{org}: N_{tot} molar	P_{tot} mg $PO_4 g^{-1}$	Hg_{tot} ng Hg g^{-1}	Mn_{HCl} $\mu g\ g^{-1}$	Fe_{HCl} % wt
9	0.5	0.791	1.99	8.29	2.66	37.6	n/a	n/a
10	0.5	0.826	1.90	8.54	2.80	34.1	n/a	n/a
11	0.5	0.803	1.78	9.04	4.79	42.9	n/a	n/a
12	0.5	0.768	1.22	7.93	4.79	46.7	n/a	n/a

Appendix 2.8.8 Analytical results of fish food analyses.

Fish Food Sample	$\delta^{13}C$ per mil	$\delta^{15}N$ per mil	C_{org} % wt	N_{tot} % wt	C_{org}: N_{tot} molar	Hg_{tot} ng Hg g^{-1}
Shurgain 10.5MM Heritage Fall 2003	-21.4	4.9	51.1	6.3	5.2	7.0 $\pm$0.62
Shurgain 8MM Heritage Fall 2003	-21.7	5.0	52.4	5.1	5.0	19.0 $\pm$0.06
Nantucket Seafarm Wet Feed Aug 2002	-22.6	6.0	33.4	5.1	7.7	11.4 $\pm$0.30
Moore Clarke July 2002	-23.4	5.6	44.6	7.4	7.4	16.5 $\pm$1.29

CHAPTER 3
Conclusion

3.1 Contribution to Knowledge

This is one of few detailed studies that describe the impact of salmon aquaculture on the sediment chemistry of the Bay of Fundy, NB, Canada, as most focused on the biotic contamination and ecology. The impact of organic loading due to aquaculture is observed by comparing the chemistry of sediments recovered under salmon net cages and at reference sites away from salmon farms. The impact of farming activities is revealed by differences between the vertical distributions and signatures of $\delta^{13}C$, $\delta^{15}N$, C_{org}, $C_{org}:N_{tot}$, Fe_{HCl}, Mn_{HCl}, P_{tot}, P_{HCl}, SO_4^{2-}, AVS, Hg_{tot}, and Hg_{pyrite} found within the sediment.

The amount, composition and isotopic signatures of the reactive organic carbon in the surface sediment indicate that residual fish food and feces contribute a fraction of the organic carbon being delivered to the sediment under the fish pens. The additional input of reactive organic carbon to these sediments is accompanied by an increase in the mercury levels in the surface sediments. Our analyses show that the fish feed is not a significant source of Hg to the sediments and, thus, the identification of its source(s) deserves further investigation. The original packaging and labels of the Shurgain 10.5 MM Heritage Fall 2003 was obtained with the fish food sample. Lower Hg_{tot} values (7 ng Hg g^{-1}) were detected in this sample than in the other feed samples analyzed (~11 to 19 ng Hg g^{-1}). It is interesting to note that the package label indicates that selenium was added to the feed. Selenium may is an essential nutrient and is known to inhibit the bioaccumulation of methylmercury in living tissue (e.g., Turner and Swick, 1983). Results of our analyses reveal that mercury shows a strong affinity for organic matter in

sediments below the fish pens and partitions strongly to authigenic pyrite in the deeper sulfidic sediments.

In response to the addition of organic carbon to the sediments under the fish pens, the reducing capacity of the sediment increases. This leads to a migration of the redox boundaries (i.e., oxic-suboxic and suboxic-anoxic/sulfidic) towards the sediment-water interface (SWI) and authigenic sulfides (i.e., AVS and pyrite) to precipitate closer to the SWI.

We chose to use the vertical distribution of Fe_{HCl} and Mn_{HCl} as proxies of the oxygen penetration depth (or thickness of the oxic layer) in the sediments. On the basis of these results we concluded that the combined oxic and nitrate-reduction zones may extend to 4 cm below the SWI based on the Fe_{HCl} distribution whereas the Mn_{HCl} distribution shows that it is much shallower. High resolution voltammetric microelectrode measurements reveal that the Fe_{HCl} and Mn_{HCl} distributions overestimate the oxygen penetration depth in the sediments. With increased amounts of organic carbon to the sediments, the oxygen penetration depth migrates upward towards the sediment-water interface, as shown by the Mn_{HCl} profiles.

Whereas we could not detect a porewater sulfate gradient within the sampled depths, the presence of acid volatile sulfides (AVS) and pyrite in the sediments confirm the presence of active sulfate reduction in the sediments of Passamaquoddy Bay. The relative position of the sulfidic zone (i.e., appearance of AVS) in the sediments below pens is closer to the sediment-water interface than in sediments away from the fish pens.

The use of phosphate as a tracer of aquaculture was further documented in Passamaquoddy Bay. Total phosphorus concentrations in the surface sediments below

fish cages far exceed the diagenetically remobilizable phosphate concentrations, thus revealing refractory phosphorus supplied to the sediments through salmon aquaculture activities.

Analysis of a few farmed Atlantic salmon did not show increased levels of mercury compared to wild salmon captured in two rivers of the Canadian east coast. In fact, the mercury levels in the wild salmon were slightly but not significantly higher than those of the farmed salmon. Following proposed dietary guidelines by Health Canada, the amount of mercury uptake from farmed salmon does not outweigh the other health benefits of eating fish. The mercury concentrations detected within the flesh of the wild salmon is intriguing in itself. We hypothesized that the farmed salmon would have higher mercury concentrations in their muscle tissue than the wild salmon. Unknown to us is the source of the mercury that is bioaccumulating in the muscle tissues of the wild Atlantic salmon.

3.2 Suggestions for Future Research

This thesis reports the impact of salmon aquaculture on the chemistry of sediments under fish cages in Passamaquoddy Bay, New Brunswick. To fully explore the relationship between aquaculture and sediment chemistry, an integrated sampling/monitoring plan should be created. The provincial government of New Brunswick has already devised an industry-wide environmental monitoring program with the goal of maintaining long-term environmental sustainability of the marine finfish cage aquaculture industry in the context of a healthy marine environment. It was elaborated along the following strategy: an outline of an environmental monitoring method on cage sites, monitoring protocols to comply with environmental quality objectives, and a guide for cage site remediation when environmental quality objectives are not met (DELG, 2001).

To begin with, collaboration of cooperatives or fish farmers (and their association) should be well established before carrying out any studies to allow easy access to the farming sites, data collection (e.g., statistical data on feed use and production) and knowledge of farming history. Despite many attempts, we were denied access to this information and were not welcomed when approaching farm sites with the ship or Zodiac. Farm operators and their cooperatives are very defensive and will not share information unless compelled to do so by government regulations, in which case the information and samples (i.e., farmed fish) are only released to the agencies. Professional divers should be employed to visually characterize the extent of detritus accumulation under aquaculture pens since visibility is strongly impaired and the bottom is littered with cables, nets and sunken gear, major safety hazards to amateur or scientific

divers. Sediment cores should also be recovered with the assistance of professional divers in order to minimize disturbance and to obtain representative sampling of the SWI. In-situ benthic chambers could be employed to determine the flux of oxygen (i.e., oxygen demand), nutrients, and other metabolites across the sediment-water interface below fish pens. High resolution voltammetric electrodes could also be utilized to determine the vertical distribution of electro-active elements (e.g., O_2, Mn(II), Fe(II), H_2S) across the sediment-water interface. With access to a larger oceanographic platform (i.e., research vessel), more thorough sampling, processing (e.g., pore water extraction) and characterization (e.g., onboard incubations and voltammetric micro-electrode profiling) could be carried out on site.

Salmon and fish food sampling should be carried out simultaneously, to ensure that the elements detected in the fish are a more accurate measure of the food fed to them. For a more realistic view of mercury accumulation in the fish flesh, a larger sampling of both wild and farmed species should be undertaken. Ideally, reference sites with similar hydro-geographic conditions as the salmon cage sites should be selected for more dependable comparisons of the environmental impacts.

In terms of our experimental protocols, modifications or the application of other methods may provide a more complete set of data. A greater compilation of extraction methods to accurately characterize the porewater chemistry, the redox zonation, and the elemental fluxes estimated from the measured concentration gradients (which were limited in this study to sulfate on mini-cores preserved by freezing). The mercury concentrations in the fish could be more specific, to determine the exact concentration of methylmercury in the flesh. As well, methylmercury concentrations in the sediment

could be measured to better quantify the speciation of mercury in the sediment. As stated before, the application of more sensitive extraction methods (e.g., ascorbate; Anschutz et al., 1998) to characterize the distribution of reactive iron and manganese oxides in the solid sediment would have been better to resolve the thickness of the oxic layer and the oxygen penetration depth (OPD).