



PII S0016-7037(02)00861-X

Early diagenetic processes in coastal marine sediments disturbed by a catastrophic sedimentation event

BRUNO DEFLANDRE,^{1,*†} ALFONSO MUCCI,² JEAN-PIERRE GAGNÉ,¹ CONSTANCE GUIGNARD,² and BJØRN SUNDBY^{1,2}¹ISMER, Université du Québec à Rimouski, 310 allée des Ursulines, Rimouski, QC G5L 3A1, Canada²Department of Earth and Planetary Sciences, McGill University, 3450 University St., Montreal, QC H3A 2A7, Canada

(Received June 19, 2001; accepted in revised form January 31, 2002)

Abstract—Following a catastrophic flash flood in July 1996, as much as 50 cm of post-glacial clays were deposited in less than 2 days in the upper reaches of the Saguenay Fjord (Quebec, Canada), disrupting the normal sedimentation and diagenetic regimes. We report detailed geochemical analyses of sediments (porosity, Eh, organic and inorganic carbon, Fe and Mn reactive solid phases, and acid volatile sulfide) and porewaters (salinity, dissolved organic carbon (DOC), Fe(II), Mn(II), nitrate, ammonium, and sulfate) for seven stations located in the Saguenay Fjord. Three of these (SAG-05, SAG-09, and SAG-30) were visited in 1996 and once per year thereafter to document the chemical evolution of the sediment toward a new steady state. The flood deposits contain less organic carbon and more inorganic carbon than the indigenous fjord sediments. The flood deposit modified the distribution patterns of reactive Mn and Fe as a result of the reduction of Mn and Fe oxides delivered with the deposit and those concentrated at the now buried former sediment-water interface. Most of the Mn(II) migrated to the new sediment-water interface, where a Mn-rich layer was formed. In contrast, much of the Fe(II) was precipitated as sulfides and remained trapped at or close to the old interface. A nitrate peak developed in the porewater at the old sediment-water interface, possibly because of the oxidation of ammonia by Mn oxides. The distributions of porewater DOC within the flood deposit correlate with the distributions of dissolved Mn(II) and Fe(II), suggesting that adsorbed DOC was released when metal oxides were reduced. Copyright © 2002 Elsevier Science Ltd

1. INTRODUCTION

Early diagenesis of marine sediments is often described as a steady state phenomenon (e.g., Froelich et al., 1979; Berner, 1980), whereas in reality, the sediment composition can vary temporally because of variations in organic carbon input, sedimentation rate, chemical composition of bottom waters, and biologic activity. Several studies have considered non-steady-state diagenesis of sediment (e.g., Lasaga and Holland, 1976). Most of these have dealt with long (e.g., geological) time scales, such as changes in sediment chemistry caused by the emplacement of relatively organic-rich turbidites at abyssal depths (Colley et al., 1984; Thomson et al., 1984; De Lange, 1986; Wilson et al., 1986; Kennedy and Elderfield, 1987; Buckley and Cranston, 1988; Wilson and Thomson, 1998). Non-steady state diagenesis on much shorter (e.g., annual and seasonal) time scales has been examined by Alongi et al. (1996), Gobeil et al. (1997), Luther et al. (1997), Mortimer et al. (1998), and Anschutz et al. (2000). Gobeil et al. (1997) showed that the offset distributions of solid-phase and dissolved Mn observed in continental margin sediments can be explained by a fluctuating redox boundary responding to seasonal sedimentation of organic matter, whereas Gehlen et al. (1997) observed that the porewater composition in sediments of the western Mediterranean responded rapidly to a pulse in organic matter deposition and evolved back to its initial composition within a few months.

Reports of non-steady state diagenesis on intermediate time scales are sparse. Mucci and Edenborn (1992) described the influence of an organic-poor landslide deposit on the differential mobility of iron and manganese in a coastal marine sediment, but their conclusions and the proposed conceptual model were inferred from a single sampling 12 yr after the depositional event. An opportunity to study non-steady state diagenesis on intermediate time scales arose in July 1996 when a catastrophic flood in the upper reaches of the Saguenay Fjord (Fig. 1) eroded an estimated 9 to 15 million tons of postglacial sediments and carried them into the fjord. Details of the event were reviewed by Lapointe et al. (1998). Some of the most dramatic results of the flood were recorded in the Baie des Ha! Ha! and the Bras Nord (Fig. 1), where several tens of centimeters of sandy clay were rapidly deposited over the indigenous sediments (Pelletier et al., 1999a). In this paper, we report on the evolution of sediment and porewater chemistry between 1996 and 1998 at seven locations in the fjord.

2. MATERIALS AND METHODS

2.1. Environmental Setting and Sampling

The Saguenay Fjord is a long (93 km) and narrow (1 to 6 km) submerged valley that joins the St. Lawrence Estuary at Tadoussac (Fig. 1). The fjord branches into two shallow arms near its head, one leading south into the Baie des Ha! Ha! and the other leading north toward Chicoutimi and its main tributary, the Saguenay River. Hydrographic, geological, and biologic features of the Saguenay Fjord were described by Schafer et al. (1990) and Fortin and Pelletier (1995). Erosion of raised glaciomarine clays in the drainage basin of the fjord supplies much of the suspended load to the Saguenay Fjord (Schafer et al., 1990). Sediment accumulation rates measured before the flood are regionally variable: 2 to 7 cm yr⁻¹ at the head of the fjord (SAG-SF), ~1 cm yr⁻¹ at SAG-05, and <0.2 cm yr⁻¹ in the Baie des Ha! Ha!

* Author to whom correspondence should be addressed (b.deflandre@qmul.ac.uk).

† Present address: School of Biological Sciences, Queen Mary, University of London, Mile End Road, London E1 4NS, United Kingdom.

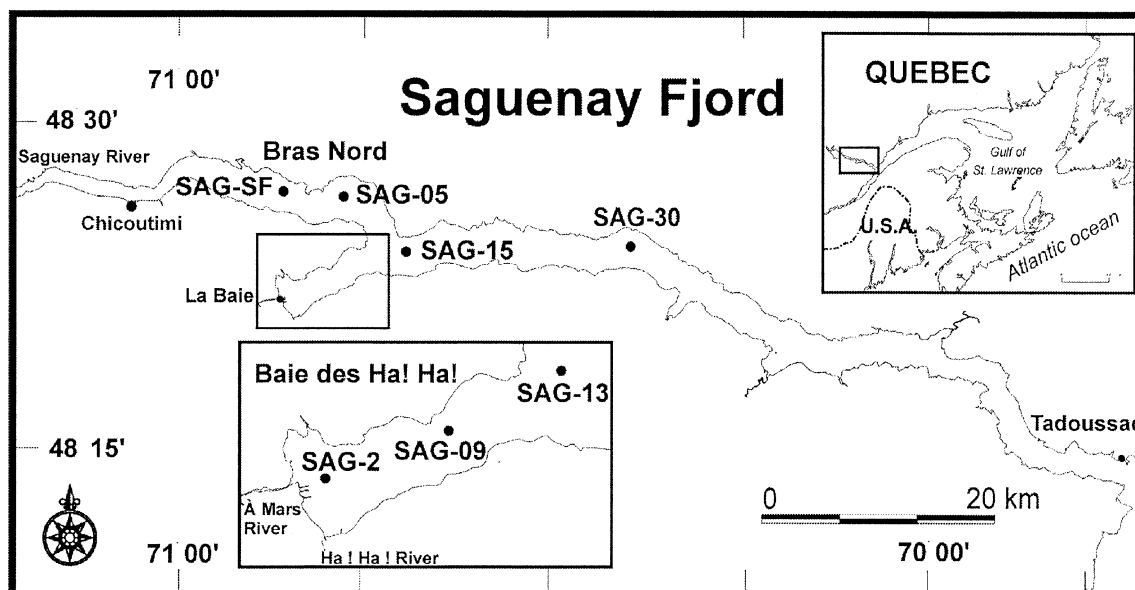


Fig. 1. Map of the Saguenay Fjord (Quebec, Canada) showing the seven sampling sites.

(SAG-2, SAG-09, and SAG-13) and at SAG-15 and SAG-30 in the 275 m deep main basin (Smith and Walton, 1980; Barbeau et al., 1981; Mucci and Edenborn, 1992; Perret et al., 1995; St-Onge and Hillaire-Marcel, 2001). The sediments consist generally of gray-black anoxic sandy (5 to 10%) muds with organic carbon concentrations ranging from 0.5 to 3%, but more than 5% organic carbon can be found in the very sandy (>30%) muds of the Bras Nord (Smith and Walton, 1980). The reductive capacity of the sediment is such that oxygen is depleted within the first few millimeters below the sediment-water interface (Lefrançois, 1998; Deflandre et al., 2000), and sulfate reduction dominates organic matter remineralization at depth (Edenborn et al., 1987; Mucci and Edenborn, 1992; Mucci et al., 2000a).

Sediments were collected at up to seven stations along the main axis of the fjord and in the Baie des Ha! Ha! (Fig. 1), but at least three stations (SAG-05, SAG-09, and SAG-30) were sampled each year between 1996 and 1998. Time series from SAG-05 and SAG-30 are presented in this paper because data are available from before the flood event. Details of the sampling program pertinent to this study are summarized in Table 1. Sediment cores were taken using a 0.06m², Hessler-type box corer. Upon recovery, the box cores were placed upright in a large glove box (Edenborn et al., 1986) and subsampled in a nitrogen atmosphere to minimize sediment oxidation during the procedure. The sediments were subsampled according to a set grid,

typically every 0.5 cm over the 1st cm, every 1 cm over the next 5 to 10 cm, and at 2 to 5 cm intervals below, depending on visual observations. The redox potential, Eh (vs. saturated calomel electrode [SCE]), was measured by inserting a platinum electrode and a calomel reference electrode (Radiometer PHM-80 meter) directly in the sediment at each sampling depth. The electrode pair was calibrated against a ferricyanide-ferrocyanide buffer solution (+196 mV SCE at 25°C) and responded with a precision of ± 10 mV. As each sampling interval was sequentially exposed, sediments were transferred to porewater squeezers and preweighed glass or plastic vials for porosity and solid-phase composition analyses. Minicores (i.e., 13 mL polyethylene screw-cap test tubes with their distal ends cut off and a 10 mL syringe plunger) were taken at a rate of two per depth at the same intervals by inserting the test tube directly into the face of the exposed sediment as the front plate of the corer was lowered. The minicores were frozen immediately to maintain the anoxic character of the sediments. They were used for acid-volatile sulfides (AVS) determinations.

Sediment porewater samples were extracted using Reeburgh-style squeezers (Reeburgh, 1967) modified to filter the water through a 0.45 μ m HA Millipore filter as it passes directly into either a 60 mL BD plastic syringe or a 20 mL Potter & Sons glass syringe. The samples were partitioned among a number of plastic and glass vials and treated according to the type of analysis to be performed. The subsamples were

Table 1. Sampling dates and positions occupied in the Saguenay Fjord.

Stations	Date of sampling	Latitude	Longitude	Water depth (m)
	<i>1996</i>			
SAG-05	21 August	48°24.65'N	70°49.82'W	104
SAG-30	20 August	48°21.72'N	70°23.69'W	268
	<i>1997</i>			
SAG-05	4 June	48°24.566'N	70°49.988'W	97
SAG-30	2 June	48°21.83'N	70°23.7'W	266
	<i>1998</i>			
SAG-SF	23 August	48°25.31'N	70°51.52'W	63
SAG-05	13 May	48°24.660'N	70°49.945'W	90
SAG-13	24 August	48°21.83'N	70°44.62'W	188
SAG-09	14 May	48°21.26'N	70°47.47'W	155
SAG-2	16 May	48°20.4'N	70°51.4'W	109
SAG-15	14 May	48°21.508'N	70°42.267'W	230
SAG-30	17 May	48°21.75'N	70°23.8'W	266

stored untreated in prewashed polyethylene bottles for chlorinity and sulfate or acidified with a 1% equivalent volume of Seastar concentrated HCl for dissolved Fe and Mn determinations. These subsamples were kept refrigerated until analysis. Porewater samples for nutrient (nitrate + nitrite; ammonium) analysis were transferred to two 5 mL polyethylene vials and frozen immediately. The analysis of these samples was completed within a few months of sampling. One milliliter was set aside in a glass vial for dissolved organic carbon (DOC) analysis, which was carried out immediately in the field. DOC leaching from the components of the squeezer system (i.e., squeezer, filter holder, filter, and syringe) contributed an estimated $0.50 (\pm 0.47)$ mg/L^{-1} , on the basis of the analysis of 20 surface water samples filtered using both the squeezer components and an all-glass filtration apparatus with glass microfiber filters. This contamination can be considered to be systematic and is therefore not critical to the shape of the porewater profiles and their interpretation.

2.2. Porewater Analyses

Porewater chlorinity was determined by potentiometric titration using a AgNO_3 solution standardized with IAPSO (International Association for the Physical Sciences of the Oceans) Standard Seawater (P112) and converted to salinity ($S = 1.80655\text{Cl}$; Fofonoff, 1985). Dissolved Mn and Fe concentrations in acidified porewater samples were determined by flame atomic absorption spectrophotometry (AAS). Aqueous AAS standards were prepared in 0.6 mg L^{-1} NaCl and diluted with 1 N HCl to the ionic strength of the samples. Nitrate + nitrite (ΣNO_3) were analyzed on an Alpkem rapid flow analyzer following the procedure outlined in Grasshoff and Almgren (1983). Ammonium (NH_4) was analyzed using a flow-through conductivity method (Hall and Aller, 1992). Porewater DOC concentration was estimated immediately after sampling using a UV method (Deflandre and Gagné, 2001). Sulfate was measured by ion chromatography (Dionex Corporation, 1986) after 100-fold dilution in distilled water. The precision of the various analytical procedures described above was better than 5%.

2.3. Solid-Phase Analysis

Sediment porosity was calculated from percentage water loss after freeze drying using a porewater density of 1.03 g cm^{-3} and dry sediment density of 2.50 g cm^{-3} (Smith and Walton, 1980). Porosity (data not shown) and solid-phase analyses were corrected for the sea salt content using the measured salinities. All analyses of the solid sediment were carried out on freeze-dried samples finely ground and homogenized in an agate mortar. Total carbon and nitrogen in the sediment were determined by combustion in a PerkinElmer model 2400 elemental analyzer using acetanilide as standard. Inorganic carbon (C_{inorg}) was measured by coulometric titration, using a UIC Inc. instrument, of the CO_2 evolved upon acidification of a known weight of freeze-dried sediment. The reproducibility of these measurements was better than 2%. The organic carbon (C_{org}) content of the sediments was obtained from the difference between the total and inorganic carbon concentrations and thus carries a cumulative uncertainty of ~4%. The reactive (i.e., acid-soluble) particulate Mn and Fe were determined following the extraction at room temperature of 0.1 g of freeze-dried sediment in 5 mL of 1 N HCl for 24 h under continuous shaking. The reactive phases extracted by the 1 N HCl digestion represent an operationally defined fraction comprising amorphous and crystalline Fe and Mn oxyhydroxides, carbonates, and hydrous aluminosilicates but may not include the oxidation products of Fe monosulfides (Raiswell et al., 1994; Saulnier and Mucci, 2000). Mn_{HCl} and Fe_{HCl} were measured by flame AAS. The reproducibility of these analyses (including the extraction procedure) is estimated at better than 10%. AVS, including amorphous Fe monosulfides (FeS), mackinawite, and poorly crystallized greigite, were determined following the treatment of 5 to 10 mL of wet, fresh-frozen sediment with 15 mL of a 20% SnCl_2 solution in 9 N HCl under a nitrogen atmosphere in a closed container at room temperature. The evolved H_2S was trapped in an alkaline ZnCl_2 solution and measured by iodometric titration with a precision better than 10% (Gagnon et al., 1995).

3. RESULTS AND DISCUSSION

The normal diagenetic regime of the fjord sediments, fueled by the comparatively slow sedimentation of material eroded from the drainage basin, was interrupted in July 1996 when the Baie des Ha! Ha! and the Bras Nord were the scene of a catastrophic influx of sediments. The sediment-water interface was rapidly covered by as much as 50 cm of postglacial marine clays. In the following discussion, we compare the composition of the indigenous fjord sediment and the flood deposit material and discuss the evolution of the composition of sediment and porewater toward their present state.

3.1. The Indigenous Sediment in the Saguenay Fjord

Station SAG-05, which is used in this paper to describe the evolution of the sediment and porewater compositions since the 1996 event, was visited before the flood. The near-surface sediment was then characterized by a thin, brown, oxidized layer approximately 5 mm thick (Mucci and Edenborn, 1992). With the exception of a gray-blue clay layer located between 17 and 36 cm deep, the sediment contained less than 0.1% inorganic carbon and as much as 2 to 3% organic carbon (Fig. 2a). This gray-blue clay layer was deposited following the catastrophic St-Jean-Vianney landslide in May 1971 (Tavenas et al., 1971). Mucci and Edenborn (1992) discussed the influence of this landslide deposit on the sediment chemistry. Despite the differential remobilization of authigenic Fe and Mn oxides that followed the emplacement of the landslide material (Mucci and Edenborn, 1992), porewater Mn(II) and Fe(II) profiles measured 20 yr after the event reflect the establishment of a new steady state. Dissolved Mn(II) concentrations increased rapidly with depth and reached $\sim 90 \mu\text{mol/L}$ within 1 cm of the sediment-water interface. Mn_{HCl} decreased from ~ 10 to $\sim 5 \mu\text{mol g}^{-1}$ dry wt over the same interval. Below 1 cm, both dissolved Mn(II) and Mn_{HCl} became nearly constant down-core, which may reflect an equilibrium with an authigenic mineral phase (e.g., mixed Mn-Ca carbonate; Middelburg et al., 1987; Mucci, 1988). Similarly, dissolved Fe(II) and Fe_{HCl} profiles reflect the sequestration of Fe with an authigenic mineral phase (e.g., authigenic AVS). Previous studies showed that sulfate reduction and the precipitation of AVS occur within the first 2 cm of these sediments (Mucci and Edenborn, 1992; Gagnon et al., 1995; Mucci et al., 2000a).

Station SAG-30 is sufficiently far from the head of the fjord (Fig. 1) that only a negligible amount of flood material was deposited at this site. Porewater Mn(II) profiles obtained between 1991 and 1998 are virtually identical (Fig. 3), as one would expect for steady state diagenesis under a relatively constant sedimentation regime ($\sim 0.3 \text{ cm yr}^{-1}$; Smith and Walton, 1980). The vertical distribution of geochemical parameters at SAG-30 is similar to that at SAG-05 before the flood (i.e., in 1991; see Figs. 2 to 4).

3.2. The Flood Deposit

The flood deposit was clearly visible in cores as a lighter colored, gray-brown layer on top of the dark gray to black indigenous sediment. Although its thickness was variable in the affected area of the fjord (10 to 50 cm), the flood sediments

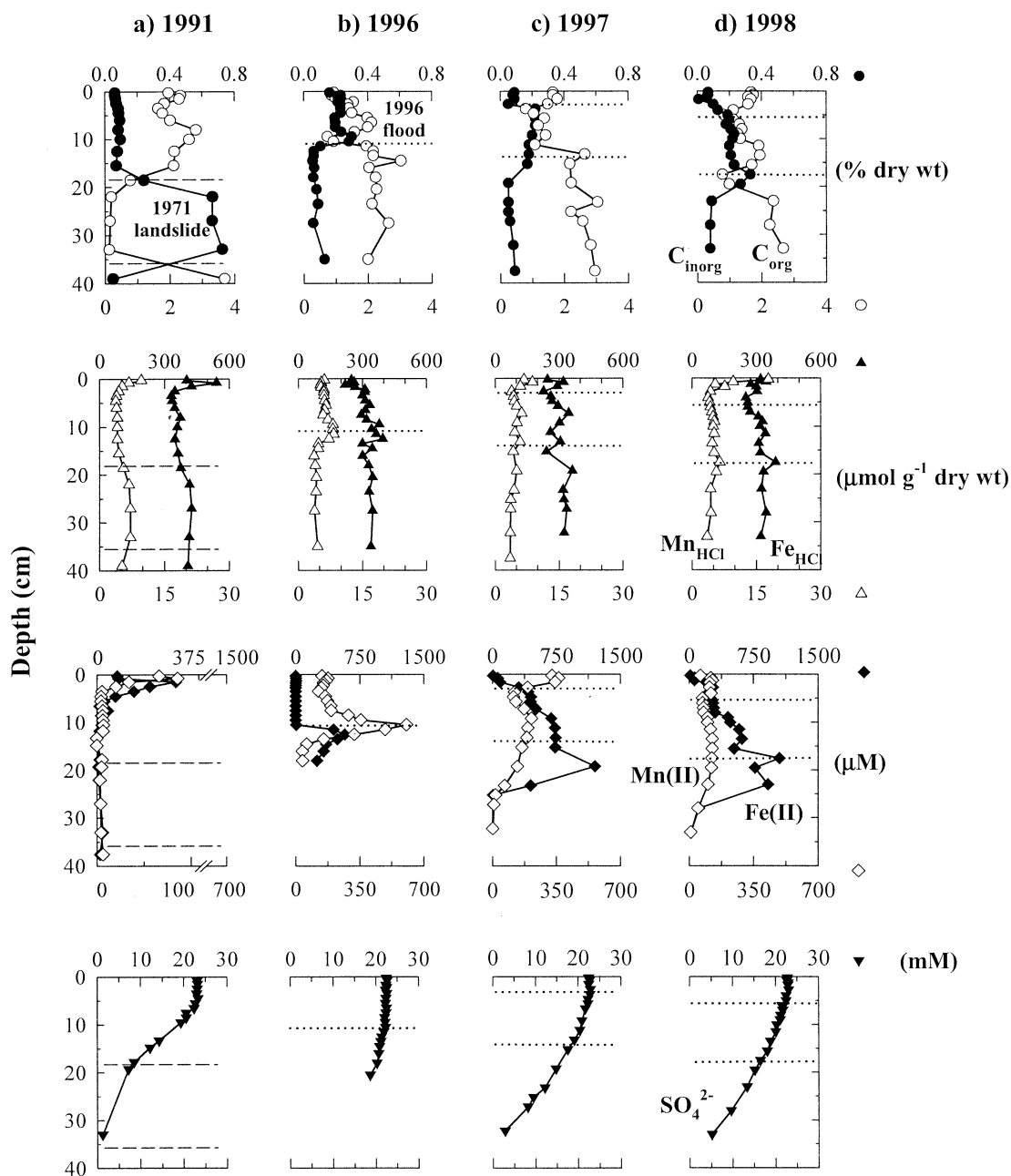


Fig. 2. Temporal evolution of sediment and porewater chemistry at SAG-05 in the Saguenay Fjord between 1991 and 1998. \circ = sedimentary organic carbon, \bullet = sedimentary inorganic carbon, \blacktriangle = extractable iron, \triangle = extractable manganese, \blacklozenge = dissolved iron, \diamond = dissolved manganese, \blacktriangledown = sulfates. All data before the flood event are from a core collected in 1991 (Gagnon et al., 1995). Dotted and dashed lines indicate, respectively, the approximate location of the 1971 landslide and of the 1996 flood layers. Note the progressive burial of the flood layer with time as the normal sedimentation regime resumed.

were everywhere similar and noticeably different from the sediment accumulating in the Saguenay Fjord under the normal sedimentation regime (Figs. 2 and 4). The organic carbon (C_{org}) content of the flood deposit was on average $\sim 50\%$ lower than in the sediment it covered. The C_{org}/N molar ratio (~ 18 ; data not shown) was similar in the two types of sediment. The flood sediment contains $\sim 0.5\%$ inorganic carbon (C_{inorg}), which is almost undetectable in the normal fjord sediment. The C_{inorg} is most likely composed of detrital calcareous materials associ-

ated with post-Wisconsinian marine clays transported during the flood event. The low C_{inorg} content of the indigenous sediment may have resulted from the dissolution of detrital and biogenic calcium carbonate during oxic diagenesis (Wilson and Thomson, 1998; Mucci et al., 2000b). We suspect that the decrease in C_{inorg} observed at the upper boundary of the flood layer in 1998 (Figs. 2 and 4a) may result from the same process. In contrast, the anoxic conditions that prevail below will help preserve the carbonate (Mucci et al., 2000b), which,

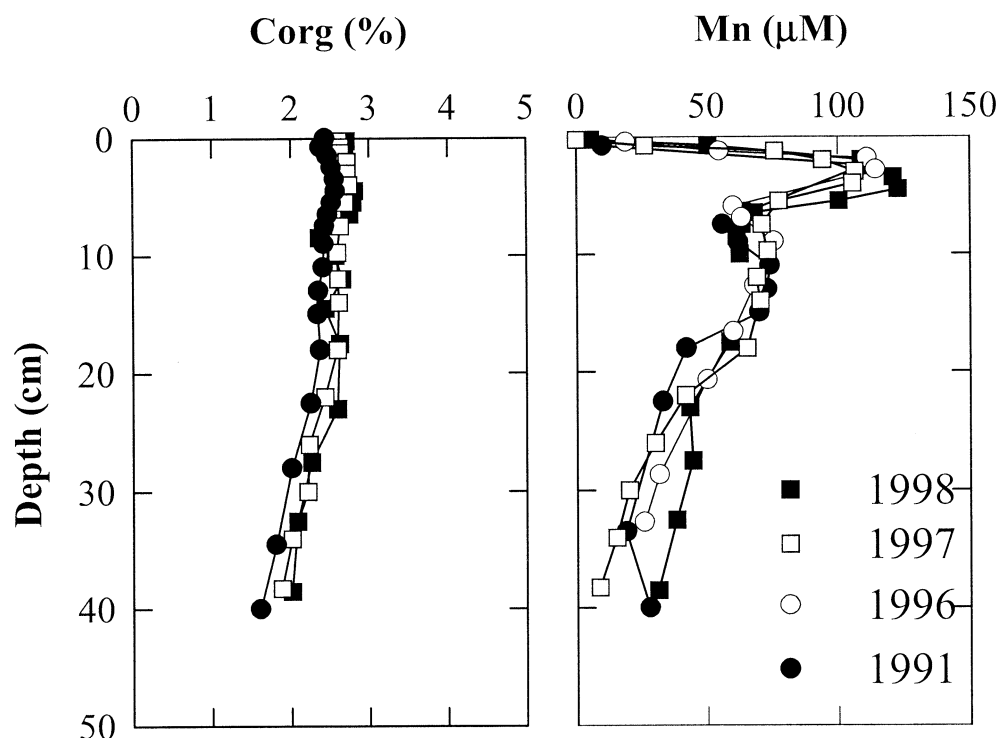


Fig. 3. Steady state distributions of sedimentary organic C and porewater manganese in sediment at SAG-30 in the Saguenay Fjord between 1991 and 1998. The 1991 data are from Gagnon et al. (1995).

in the future, may serve as a tracer of this event. In some cases, a small C_{org} peak was observed at and immediately below the original interface. It may originate from the sudden burial of organic matter that had not undergone extensive degradation. Remains of organisms and relict burrows at the original interface were observed both during sampling and later with Computerized Axial Tomography Scanner (CAT-Scan) imaging of the cores (Crémer et al., 2000), suggesting that benthic organisms living in the surface sediment may have been trapped during the flash deposition of a thick layer of new sediment.

3.3. Evolution of the Sediment Composition Between 1996 and 1998

3.3.1. Evolution of the porewater salinity

Salinity is a conservative tracer, and in Saguenay Fjord sediments, it normally reflects the salinity of the overlying bottom waters, which is approximately 30 and relatively constant (Schafer et al., 1990; Pelletier et al., 1999b). The porewater salinity in the flood deposit at SAG-2 shortly after the flood was anomalously low (Fig. 5). This reflects the mode of transport and deposition of the flood material. Sediments eroded on land were carried to the Baie des Ha! Ha! as a fluidized, high-density debris flow in at least two episodes and were deposited with little sorting (Crémer et al., 2000). Consequently, brackish waters were trapped within the deposit. The salinity anomaly coincided with porosity anomalies (Pelletier et al., 1999a) and with the presence of layers of sandy sediment observed during sampling and later by CAT-scan imaging

(Crémer et al., 2000). The salinity anomaly was still present 1 yr after the flood event but could no longer be detected in the spring of 1998. The anomaly was likely dissipated by diffusion, possibly augmented by advection as the flood layer compacted. According to the Einstein-Smolouchowski equation ($x^2 = 2tD_s$, with $D_s = D_0/\theta^2$, where θ^2 is assumed to be equal to $1 - \ln \phi^2$, and ϕ is the porosity; Boudreau, 1996), the period of time, t , required to dissipate the salinity gradient by molecular diffusion over the mean thickness, x , of the flood deposit (~ 30 cm with an average porosity of 0.61; Pelletier et al., 1999a) is on the order of 2 yr or less (using $D_0 = 1.99 \times 10^{-5}$ cm² s⁻¹ for NaCl; Applin and Lasaga, 1984).

3.3.2. Post-flooding diagenetic remobilization of iron and manganese

A significant difference between the flood deposit and the sediment accumulating in the Saguenay Fjord under normal conditions is seen in the distribution and concentration of dissolved metals. The porewater Mn(II) concentration, which was maximum immediately below the peak of solid-phase Mn in the pre-flood sediment (Fig. 2a), was up to 3 times higher and was spread as a broad peak over much of the flood layer (Figs. 2 and 4d). Similarly, the porewater Fe(II) concentration in the flood deposit was up to 6 times higher than in the unaffected fjord sediments. To facilitate the discussion of post-depositional reactions and their influence on metals, we now discuss briefly the redox conditions and the distribution of metals observed only 3 weeks after the flood event.

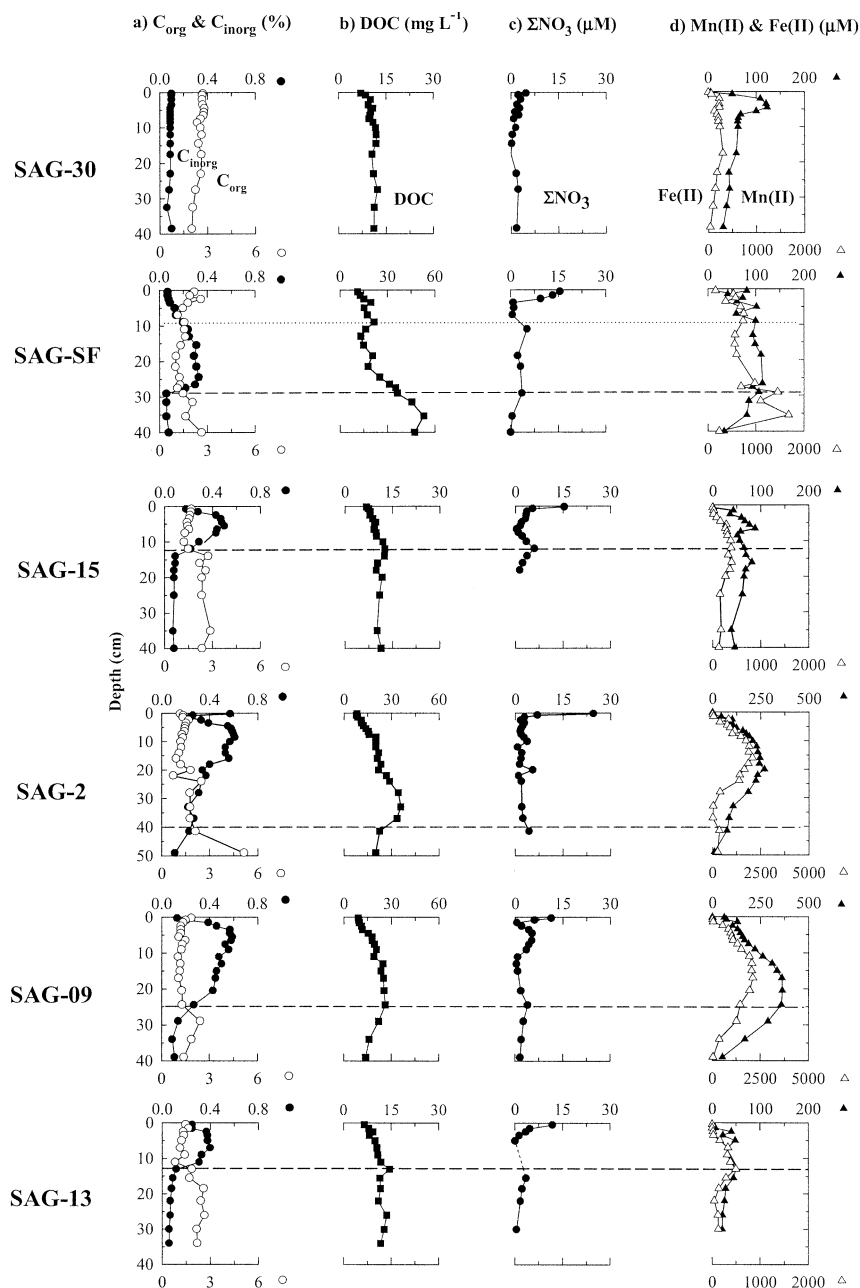


Fig. 4. Vertical profiles of (a) organic (\circ) and inorganic (\bullet) C content, (b) dissolved organic carbon (\blacksquare), (c) nitrate + nitrite (ΣNO_3) (\bullet), and (d) dissolved iron (\triangle) and manganese (\blacktriangle) in porewater and sediment collected in 1998 in the Saguenay Fjord. Also see Fig. 2d, which reports data from SAG-05. Note the different depth scale for SAG-2. Dashed and dotted lines indicate, respectively, the approximate locations of the former sediment-water interface and the interface between the flood and post-flood sediments.

The thickness of the flood material deposited at SAG-05 (Fig. 1) was ~ 10 cm, on the basis of the vertical distribution of solid-phase inorganic carbon (Fig. 2b). Although there are practical difficulties with its interpretation, Eh can provide qualitative information about redox changes in sediments. In 1996, Eh was nearly constant (~ -50 mV SCE; Fig. 6) in the 0.5 to 10 cm depth interval, indicating that suboxic conditions may have extended through the flood layer less than 3 weeks after its deposition. Dissolved oxygen may initially have been

present throughout much of the deposit, but is likely to have been consumed rapidly. Microelectrode measurements made 3 weeks after the event (L. Lefrançois, personal communication) revealed that oxygen was depleted to within a few millimeters of the new sediment-water interface. Most of the reactive Fe and Mn (i.e., oxides: ~ 300 and $\sim 6 \mu\text{mol g}^{-1}$ dry wt, respectively) carried with the flood material were preserved in the first 10 cm (Fig. 2b), but the presence of dissolved Mn(II) in excess of $\sim 300 \mu\text{mol/L}^{-1}$ throughout the flood deposit in 1996 indi-

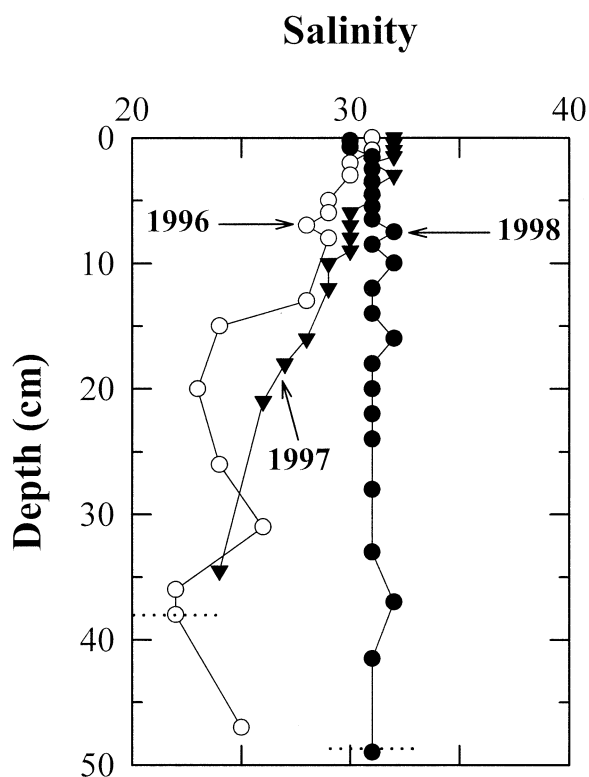


Fig. 5. Temporal evolution of salinity in sediment at SAG-2 in the Saguenay Fjord between 1996 and 1998. Dashed lines indicate the approximate location of the original sediment-water interface. The sampling in 1997 was not deep enough to observe the position of the original sediment-water interface.

icates that Mn oxide dissolution had already been initiated (Fig. 2b). It is likely that the sediment was not sufficiently reducing in 1996 (Fig. 6) to maintain Fe(II) in solution (Fig. 2b). Alternatively, the reaction between dissolved Fe(II) and Mn oxides (Postma, 1985) may explain the very low concentrations of dissolved Fe(II) and the high levels of dissolved Mn(II) in the sediment porewater (Fig. 2b).

The Fe and Mn oxide concentrations (~ 400 and $\sim 8 \mu\text{mol g}^{-1}$ dry wt, respectively) at the lower boundary of the flood deposit, which corresponds to the original sediment-water interface in 1991 (Figs. 2a and 2b). The presence of porewater Fe(II) and Mn(II) peaks and the strong Eh gradient ($\sim 90 \text{ mV SCE cm}^{-1}$) at or near this interface in 1996 (Figs. 2b and 6) implies reduction of authigenic oxides under the sulfate-reducing conditions ($< -200 \text{ mV SCE}$; Fig. 6) that set in soon after the flood layer was deposited.

One year after the flood, the flood deposit was buried under a layer of new material settling under the normal sedimentation regime ($\sim 1 \text{ cm yr}^{-1}$; Barbeau et al., 1981; Mucci and Edenborn, 1992; Fig. 2c). High concentrations of dissolved Fe(II) and Mn(II) were observed below the sediment-water interface (Fig. 2c) as a result of the progressive, reductive dissolution of the Fe and Mn oxides present at the former sediment-water interface and in the flood deposit. Both elements were remobilized, but their fates were different (Fig. 2). At the sediment surface, both dissolved Fe(II) and Mn(II) were oxidized and

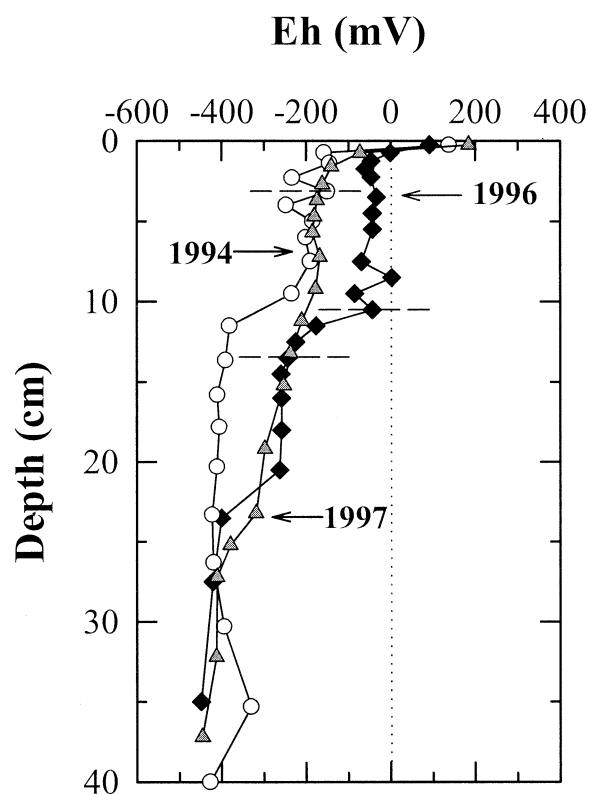


Fig. 6. Redox potential (vs. saturated calomel electrode) in sediment at SAG-05 in the Saguenay Fjord between 1994 and 1998. Dashed lines indicate the approximate location of the original sediment-water interface.

reprecipitated as oxides. At depth, Fe(II) was precipitated as AVS under the prevailing sulfidic conditions (Fig. 7). However, it is difficult to confirm the fate of porewater Mn(II). Mucci and Edenborn (1992) showed through saturation calculations that porewaters in the sulfate-reducing zone of the Saguenay Fjord are supersaturated with respect to calcite, and theoretical as well as experimental studies (e.g., Middelburg et al., 1987; Mucci, 1988) indicate that Mn(II) will coprecipitate with calcite. Alternatively, dissolved Mn(II) has also been shown to adsorb on AVS (Arakaki and Morse, 1993).

To estimate the relative importance of these reactions and the differential migration of reduced iron and manganese, we calculated vertical fluxes of dissolved Fe and Mn at SAG-05 between 1996 and 1998 (Table 2). The fluxes were computed according to Fick's law of diffusion (i.e., $J = -\phi D_s dC/dX$, where ϕ is the porosity and dC/dX is the concentration gradient; Berner, 1980). The bulk sediment molecular diffusion coefficient (D_s) was assumed to be equal to $D_s = D_0/\theta^2$, where θ is the tortuosity and D_0 is the diffusion coefficient in water (Berner, 1980). D_0 values were obtained from Li and Gregory (1974), and the value of θ^2 is assumed to be equal to $1 - \ln(\phi^2)$ (Boudreau, 1996). Positive values indicate upward fluxes; negative values indicate downward fluxes.

The highest fluxes of Fe(II) and Mn(II) were observed in 1996 at the former sediment-water interface (Table 2; Fig. 2b). These fluxes, both upward and downward, decreased sharply between 1996 and 1998 (Table 2) as the source of reducible Mn

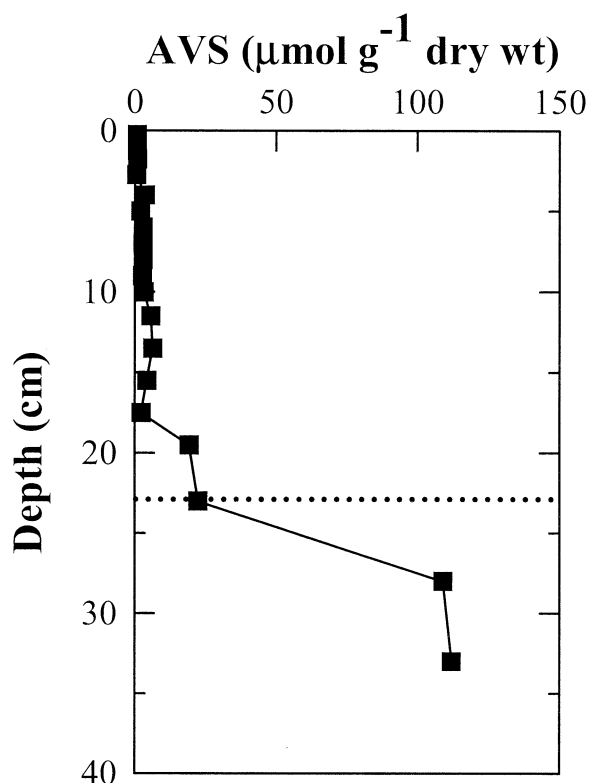


Fig. 7. Vertical profile of acid-volatile sulfides (AVS) in SAG-05 sediments in 1998. Dashed line indicates the approximate location of the original sediment-water interface.

and Fe was being progressively depleted. The reactive Mn content at the former sediment-water interface decreased from ~ 8.2 to $\sim 5.8 \mu\text{mol g}^{-1}$ dry wt between 1996 and 1998 (Figs. 2b to 2d), indicating that up to 30% of the reactive Mn inventory in 1996 had been remobilized by the spring of 1998. We estimate that $\sim 60\%$ of the Mn(II) released to the porewaters between August 1996 and May 1998 had diffused to the new sediment-water interface. Most of the Mn(II) diffusing up was precipitated near the new sediment-water interface (Figs. 2c

Table 2. Vertical fluxes, estimated from porewater gradients of dissolved iron and manganese (Fig. 2), at the original and the new sediment-water interfaces at SAG-05 since the 1996 flood event. All fluxes are expressed in $\mu\text{mol cm}^{-2} \text{yr}^{-1}$. D_0 values (at 0°C) used for flux calculation were 3.41×10^{-6} and $3.05 \times 10^{-6} \text{cm}^2$ for Fe(II) and Mn(II), respectively (Li and Gregory, 1974).

		Benthic fluxes at the sediment-water interfaces		
		Original		New
		Up	Down	Up
Mn(II)	1996	9.9	-7.9	2.7
	1997	0.8	-0.8	4.0
	1998	0.5	-0.4	5.5
	1996	22.4	-7.1	—
Fe(II)	1997	6.2	-9.5	9.0
	1998	5.3	-6.2	12.3

and 2d). The manganese inventory that accumulated near the new sediment-water interface (i.e., 0 to 0.5 cm) in 1998 exceeded by about a factor of 2 the inventory at the original interface in 1991. Very similar values (i.e., 14 to $16 \mu\text{mol g}^{-1}$ dry wt in the 0 to 0.5 cm sampling interval) were obtained in subsequent years. This excess manganese could only have originated from the reductive dissolution of reactive manganese supplied by the flood deposit.

In contrast to Mn, the extractable Fe concentration at the new sediment-water interface changed little between 1996 and 1998 (Figs. 2b to 2d). Much of the porewater iron originating from the reductive dissolution of authigenic oxides concentrated at the former sediment-water interface was trapped as sulfides and immobilized (Fig. 7). On the basis of a calculation of the degree of sulfidization (Boesen and Postma, 1988; Gagnon et al., 1995), we estimate that as much as 40% of the reactive iron (i.e., Fe_{HCl}) was converted to AVS. Although not as steep as before the flood, a sulfate gradient developed across the flood layer between July 1996 and May 1998 (Figs. 2b to 2d), and the presence of AVS within this layer attests to the development of sulfidic conditions over this time (Fig. 7). However, the abundance and reactivity of reducible iron phases within the flood material allowed the buildup of relatively high dissolved Fe(II) concentrations, which nearly doubled between 1996 and 1998 (up to 1mmol/L^{-1} in 1998; Fig. 2d). As a result, the upward and downward Fe(II) fluxes from the former sediment-water interface remained relatively high ($>5 \mu\text{mol cm}^{-2} \text{yr}^{-1}$; Table 2). Thus, the flood layer seems to be a reservoir of soluble Fe, supplying Fe(II) to the layers above and below it.

3.4. Evidence of Secondary Diagenetic Reactions

As our understanding of early diagenetic processes improves, it becomes apparent that metal oxides play a more complex and important role in biogeochemical cycles than previously thought, especially in the cycles of nitrogen (Luther et al., 1997; Aller et al., 1998; Hulth et al., 1999; Anschutz et al., 2000) and DOC (Krom and Sholkovitz, 1978; Hamilton-Taylor et al., 1996; Chin et al., 1998; Jakobsen and Postma, 1999). Many of these secondary diagenetic reactions are not readily observed when the system is at steady state. The non-steady state conditions induced by the rapid deposition of the flood material in the Saguenay Fjord and the evolution of the sediment chemistry toward a new steady state revealed some of these reactions.

3.4.1. Anaerobic nitrate production

Dissolved oxygen was absent below ~ 5 mm in the sediment of the core collected at SAG-15 in 1998 (Fig. 8a). Oxic respiration and nitrification should therefore be restricted to the upper 5 mm, in agreement with the high porewater ΣNO_3 concentration in the top of the core (Fig. 8b). Below the oxic layer, nitrate is consumed by bacterial denitrification or by oxidation of dissolved Mn(II) (Sørensen and Jørgensen, 1987; Aller, 1990; Schultz et al., 1994; Luther et al., 1997). Consequently, as is commonly observed in organic-rich coastal marine sediments, nitrate concentrations decrease with depth below the oxic layer and reach a steady state, near-null value depending on the amount of reactive carbon being deposited

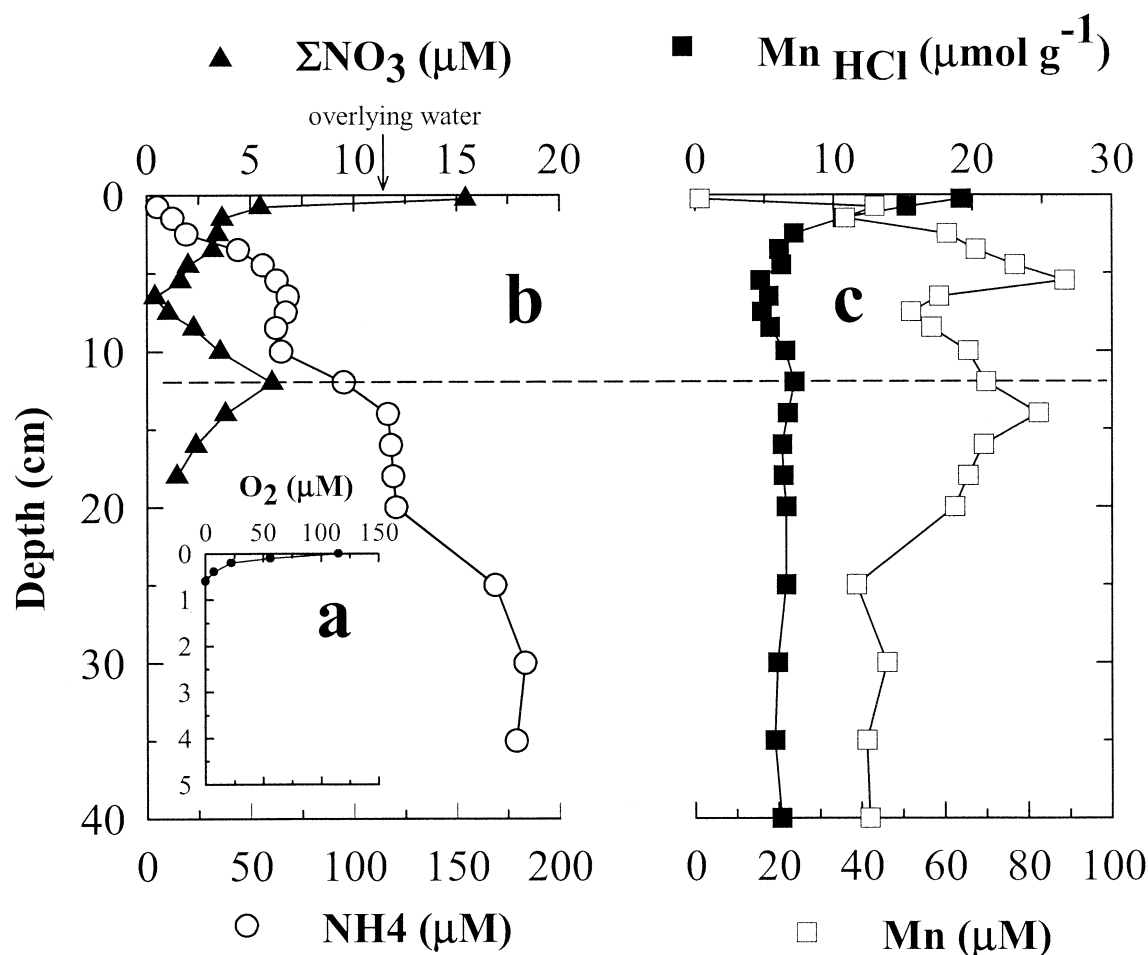


Fig. 8. Vertical profiles of (a) dissolved O_2 , (b) nitrate + nitrite (ΣNO_3) and ammonium concentrations, and (c) dissolved and extractable manganese concentrations at SAG-15 in 1998. The arrow indicates the nitrate concentration in the overlying water, and dashed lines indicate the approximate location of the original sediment-water interface. The microelectrode O_2 profile is from Deflandre et al. (2000).

and the rate of nitrate diffusion (Froelich et al., 1979; de Lange, 1986). However, in our core, the ΣNO_3 concentration gradient turned around at ~ 7 cm depth and a peak ($\sim 6 \mu\text{mol/L}^{-1}$) was observed near the old sediment-water interface (~ 12 cm depth in this core; Fig. 8b). A nitrate peak near the old sediment-water interface was also observed at other stations where flood material was deposited (Fig. 4c). Considering that bioirrigation in this area of the fjord is weak and limited to the first 5 cm of the flood deposit (Pelletier et al., 1999a; de Montety et al., 2000), it is unlikely that the ΣNO_3 peak was created by infiltration of bottom water through animal burrows, nor can this peak be a remnant from pre-flood conditions, since such a nitrate peak should have dissipated by diffusion in less than 80 d. The occurrence of a ΣNO_3 peak 2 years after the flood event thus requires that the rate of local nitrate production exceed the nitrate consumption due to denitrification.

Recent laboratory and field studies (Aller et al., 1998; Hulth et al., 1999; Anschutz et al., 2000) indicate that ammonia can be oxidized to nitrate by Mn oxides in anaerobic sediments. In the experiments of Hulth et al. (1999), the rate of anoxic nitrate production was directly proportional to the amount of Mn oxide

added. The ΣNO_3 peak observed at SAG-15 was located at the old sediment-water interface (i.e., ~ 12 cm in this core), precisely where authigenic Mn oxides were buried by the flood material (Fig. 8c). It would thus seem that the nitrate peak is created by the oxidation of ammonia by Mn oxides.

3.4.2. Metal oxide reduction: an alternative source for porewater DOC

The progressive buildup of DOC with depth in marine sediments is generally interpreted as the accumulation of by-products of organic matter degradation (Fig. 4b, SAG-30). We observed DOC concentrations within the flood layer at stations in the Baie des Ha! Ha! and the Bras Nord that were up to 3 times higher than at SAG-30 (Fig. 4b). Within the flood layer, the porewater Fe(II) and Mn(II) concentrations were likewise high, up to 6 times greater than at SAG-30 (Fig. 4d), and were strongly correlated with DOC (Fig. 9). These correlations may reflect the partial oxidation of particulate organic matter delivered with the flood material by the Fe and Mn oxides present in the flood material. Another possible interpretation of these

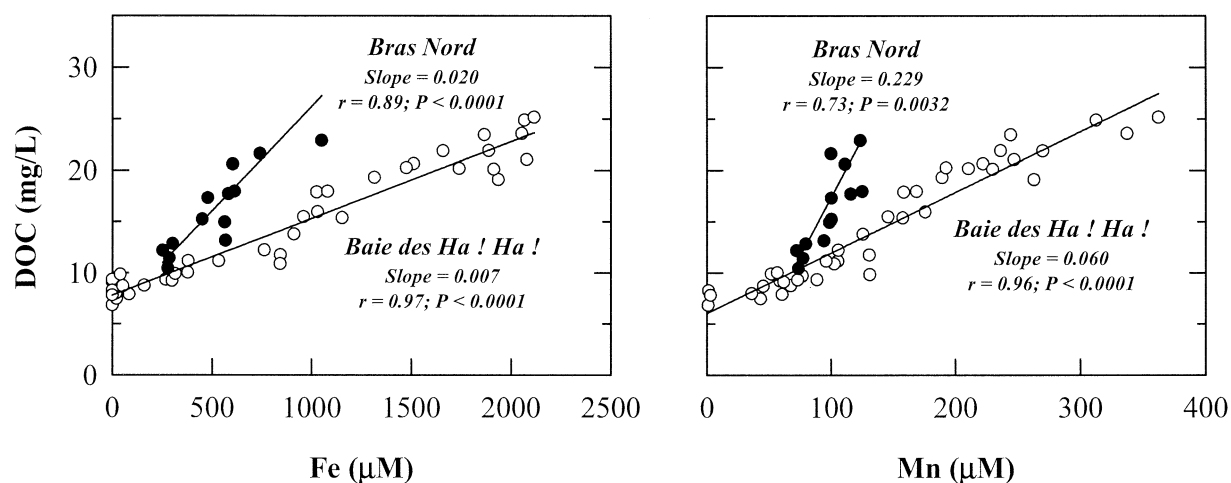


Fig. 9. Relationship between dissolved organic carbon (DOC) and dissolved Fe(II) and Mn(II) in the porewaters of the flood sediments in the areas of the Baie des Ha! Ha! and the Bras Nord in the Saguenay Fjord in 1998.

correlations is that the DOC originates from the same source as the dissolved Fe and Mn, the dissolution of authigenic and detrital metal oxides.

There have been many reports of correlations between the concentrations of metals such as Fe(II) and Mn(II) and DOC in porewaters (Krom and Sholkovitz, 1978; Elderfield, 1981; White et al., 1989; Alongi et al., 1996; Hamilton-Taylor et al., 1996; Chin et al., 1998; Jakobsen and Postma, 1999), and it has been shown that dissolved organic matter can be strongly adsorbed on hydrous metal oxides (Tipping, 1981; Davis, 1982; Gu et al., 1994, 1995; Filius et al., 2000). Tipping and Woof (1983) proposed that the co-accumulation of ferrous iron and DOC in anoxic bottom waters of lakes results from the release of organic matter upon the reductive dissolution of Fe oxides.

The Fe(II)-DOC relationship (Fig. 9) is similar to those reported by White et al. (1989) and Hamilton-Taylor et al. (1996) for lake sediment porewaters. The Fe(II)-DOC and Mn(II)-DOC relationships we observe are different, however, at the stations in the Baie de Ha! Ha! and the Bras Nord (Fig. 9). This could reflect differences in the nature and abundance of organic matter as well as differences in the composition and reactivity of the metal oxides in different areas of the fjord. Gu et al. (1995) showed that variations in mineralogy and solution composition affect both the extent of adsorption of DOC onto metal oxides and the sorption mechanism. At this stage, our results provide only circumstantial evidence for a relationship between metals and DOC.

5. SUMMARY AND CONCLUSIONS

Transport of large amounts of organic-poor post-glacial clays to the fjord by the flash flood in July 1996 created a non-uniform distribution of organic matter and changed the redox conditions in the sediment, perturbing the preflood steady state diagenesis. In a previous study, Mucci and Edenborn (1992) described the influence of a similar depositional event on the diagenetic remobilization of Fe and Mn in Saguenay Fjord sediments. Although their conclusions were inferred from a single sampling 12 years after the event, our results confirm

the validity of their conceptual model. Upon the establishment of suboxic-anoxic conditions in the flood layer, Fe(II) and Mn(II) were liberated upon the reduction of authigenic and detrital oxides. Most of the reduced Fe was sequestered locally as sulfides, whereas reduced Mn diffused toward the new sediment-water interface, where it was reprecipitated and created an oxide-rich layer. Further observations will be necessary to determine the time scales associated with the evolution of the present perturbed diagenetic system toward a new steady state and to develop a conceptual model for other metals.

The rapid deposition of the flood material revealed diagenetic reactions that tend to be imperceptible under steady state conditions. The persistence of authigenic Mn oxides at the former sediment-water interface appears to be responsible for the anaerobic oxidation of ammonia to nitrate. Tight correlations between DOC and both dissolved Fe(II) and Mn(II) in the flood sediments may reflect the release of adsorbed DOC to the porewaters as metal oxides are reduced.

Acknowledgments—We thank the captain and crew of the RV Alcide C. Horth for their assistance at sea; L. Lefrançois, M.-È. Parent, S. Ringuet, and B. Gouteux for help in the field; and D. Bérubé for analytical assistance. Financial support was provided by Strategic Grants (20198-97) to Alfonso Mucci and Jean-Pierre Gagné and Research Grants from the Natural Sciences and Engineering Research Council of Canada (to Alfonso Mucci, Bjørn Sundby, and Jean-Pierre Gagné). Bruno Deflandre thanks Jean-Pierre Villeneuve, INRS-Eau, for his hospitality during the writing of this paper. This work is in partial fulfillment of Bruno Deflandre's Ph.D. requirements of the oceanography program at the Université du Québec à Rimouski. We thank David J. Burdige and three anonymous reviewers for their valuable comments on the manuscript.

Associate editor: D. J. Burdige

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