The Differential Geochemical Behavior of Arsenic and Phosphorus in the Water Column and Sediments of the Saguenay Fjord Estuary, Canada

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Abstract. The distribution and partitioning of dissolved and particulate arsenic and phosphorus in the water column and sediments of the Saguenay Fjord in Quebec, Canada, are compared. In addition, selective and/or sequential extractions were carried out on the suspended particulate matter (SPM) and solid sediments to contrast their geochemical behaviors in this natural aquatic system. Results of our analyses show that both arsenic and soluble reactive phosphate are actively scavenged from the water column by settling particles. Upon their accumulation at the sediment-water interface some As and P may be released to porewaters following the degradation of organic matter to which they are associated. The porewater concentrations are, however, limited by their strong affinity for authigenic, amorphous iron oxyhydroxides which accumulate in the oxic sediments near the sediment-water interface. The geochemical behavior of arsenic and phosphorus diverge most strikingly upon the development of anoxic conditions in the sediments. Following their burial in the anoxic zone, amorphous iron oxyhydroxides are reduced and dissolved, releasing phosphate and arsenic to the porewaters. We observed, however, that porewater arsenic concentrations increase at shallower depths than phosphate in the sediments. The reduction of arsenate, As(V), to arsenite, As(III), and its desorption prior to the reductive dissolution of the carrier phase(s) may explain this observation. Driven by the strong concentration gradient established in the suboxic zone, phosphate diffuses up towards the oxic layer where it is readsorbed by authigenic iron oxyhydroxides. In the organic-rich and rapidly accumulating sediments at the head of the Fjord, porewater sulfate depletion and the resulting absence of a sulfide sink for Fe(II), may lead to the formation of vivianite in the fermentation zone, a potential sink for phosphate. Arsenite released to the porewaters in the suboxic and anoxic zones of the sediments diffuses either down, where it is adsorbed to or incorporated with authigenic iron sulfides, or up towards the oxic boundary. Arsenite appears to migrate well into the oxic zone where it may be oxidized by authigenic manganese oxides before being adsorbed by iron oxyhydroxides present at the same depth. Whereas, in the absence of authigenic carbonate fluorapatite precipitation, the ability of oxic sediments to retain mineralized phosphate is a function of their amorphous iron oxyhydroxide content, arsenic retention may depend on the availability of manganese oxides, the thickness of the oxic layer and, its co-precipitation with iron sulfides at depth.

1. Introduction

The geochemistry of phosphorus and arsenic is of broad interest to a range of disciplines, including biogeochemistry, elemental cycling, water quality, and metal-biota interactions. This interest is compounded by the fact that phosphorus and arsenic are both group V elements, they have similar chemical properties and display similar geochemical behaviors. However, whereas phosphorus is an essential nutrient, arsenic is toxic to most living organisms. Nevertheless, arsenic is readily taken up by phytoplankton (Sanders and Windom, 1980). Its uptake is dependent on the availability of dissolved phosphate and is subject to some discrimination (Planas and Healy, 1978; Sanders, 1980; Planas and Lamarche, 1983). Once inside the cell, arsenic inhibits oxidative phosphorylation and growth (Planas and Healy, 1978; Stryer, 1981). Despite the close similarities and important distinctions, few studies (e.g., Feely et al., 1991) have attempted to contrast the geochemistry of arsenic and phosphate in natural aquatic environments.

1.1. ARSENIC AND PHOSPHATE SPECIATION IN AQUATIC ENVIRONMENTS

Arsenic is present primarily as the inorganic ion arsenate, As(V), in oxygenated waters although lesser concentrations of reduced arsenite, As(III), and methylated arsenicals have also been reported (Andreae, 1978, 1979; Waslenchuk, 1978; Sanders, 1980, 1983; Seyler and Martin, 1990; Anderson and Bruland, 1991). Biotic methylation of As may be a strategy adopted by marine micro-organisms to deal with its toxicity. Consequently, organisms have a considerable impact upon arsenic speciation, and the highest concentrations of these lesser compounds in an oxic water column are often found in the photic zone (Andreae, 1979; Sanders, 1980, 1985; Michel et al., 1993; Howard et al., 1995). Arsenite, As(III), should be the predominant inorganic species under slightly reducing conditions (Andreae, 1978; Andreae and Froelich, 1984; Edenborn et al., 1986a; Riedel et al., 1987) whereas arsenic sulfides should form in the presence of sulfide (Ferguson and Gavis, 1972). It is most common, however, to find arsenic as a solid solution with authigenic iron sulfides in marine sediments (Belzile and Lebel, 1986; Huerta-Diaz and Morse, 1992; Morse, 1994). In contrast, phosphate is the only stable inorganic species in the field of stability of water. A complex mixture of organo-phosphorus compounds can also be found which originate from various metabolic and catabolic processes.

1.2. THE FATE OF ARSENIC AND PHOSPHATE IN ESTUARINE SEDIMENTS

Estuarine sediments play an important role in arsenic and phosphorus cycling (Pomeroy et al., 1965; Fisher et al., 1982; Maher, 1984, 1985; Fox et al., 1986; Holm, 1988; Maher and DeVries, 1994; Widerlund and Ingri, 1995). The fate of these elements is related to the extent of biogeochemical transformations and their relative mobility under varying redox conditions. Upon their accumulation at

the sediment-water interface, As and P are believed to be released to porewaters following the degradation of organic matter to which they are associated (Williams et al., 1971; Krom and Berner, 1981; Peterson and Carpenter, 1986). The porewater concentrations and fluxes of both elements to the overlying waters are, however, buffered by their strong affinity for authigenic, amorphous iron oxyhydroxides which accumulate in the oxic sediments near the sediment-water interface (e.g., Sundby et al., 1992; Maher and De Vries, 1994; Jensen et al., 1995; Slomp et al., 1996; Sullivan and Aller, 1996).

Remobilization of arsenic following the reduction and dissolution of Fe(III)- and/or Mn-oxides during early diagenesis is well documented (Farmer and Lovell, 1986; Belzile, 1988; Belzile and Tessier, 1990; Widerlund and Ingri, 1995; Sullivan and Aller, 1996) but, in general, the relative importance of these oxides as arsenic carriers remains unclear (Edenborn et al., 1986a; Peterson and Carpenter, 1986; Riedel et al., 1997). Similarly, the diagenetic phosphate cycle has been intimately linked to that of iron (Krom and Berner, 1981; Froelich, 1988; Chambers and Odum, 1990; Sundby et al., 1992; van Raaphorst and Kloosterhuis, 1994; Jensen et al., 1995; Filippelli and Delaney, 1996; Slomp et al., 1996; Anschutz et al., 1998). Consequently, the redox conditions at or near the sediment-water interface will often determine whether the sediments serve as a sink or a source for these elements (Klump and Martens, 1981; Watanabe and Tsunogai, 1984; Aggett and O'Brien, 1985; Edenborn et al., 1986a; Sundby et al., 1986; Holm, 1988; Ingall and Jahnke, 1994; Riedel et al., 1997). Biological and physical disturbances may also promote sedimentary cycling of iron and coupled elements (Lucotte and d'Anglejan, 1983; Riedel et al., 1988, 1997; Sullivan and Aller, 1996; Saulnier and Mucci, 2000).

As indicated above, in the presence of sulfide, arsenite coprecipitates with iron sulfides which may serve as temporary or permanent sinks for the arsenic (Belzile and Lebel, 1986; Huerta-Diaz and Morse, 1992; Morse, 1994). Similarly, the precipitation and burial of a carbonate fluorapatite (Jahnke et al., 1983; Froelich et al., 1988; Lucotte, 1993; Ruttenberg and Berner, 1993; Reimers et al., 1996; Louchouarn et al., 1997a) can permanently sequester phosphate in coastal and estuarine sediments.

In this paper we will describe and interpret how the geochemical behaviors of arsenic and phosphorus contrast in the water column and most strikingly during early diagenesis in the coastal marine sediments of the Saguenay Fjord. Results of this study will provide additional insights on the role of authigenic manganese oxides on the cycling and preservation of arsenic in marine coastal sediments.

2. Methods

2.1. STUDY SITE CHARACTERISTICS AND SAMPLING

The Saguenay Fjord, the largest fjord in eastern Canada, is a long and narrow glacially-scoured submerged valley which joins the St-Lawrence Estuary at Tadoussac (Figure 1). Typical of classical fjords, it has a U-shaped cross-section
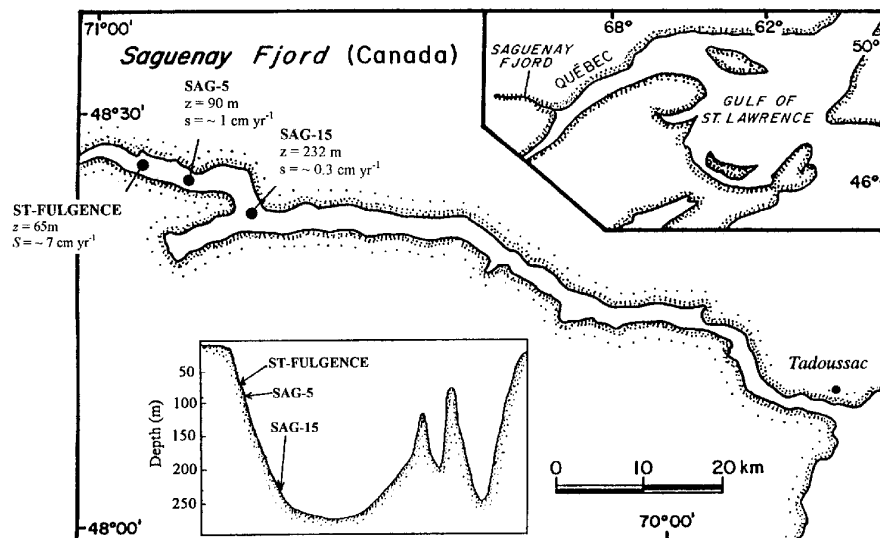
Figure 1. Map of the Saguenay Fjord showing coring and water column sampling sites (St-Fulgence, SAG-5, and SAG-15) and bottom topography of the fjord. "*Z*" corresponds to the depth of sampling and "*s*" to the estimated sedimentation rate at each sampling site.

and two shallow sills which subdivide it into two distinct basins. The largest of the two basins, the "interior" basin, extends from the sill westward to the Baie des Ha! Ha! reaching a maximum depth of 275 m. Steep and narrow banks promote the rapid accumulation of terrigenous organic-rich sediments (Pocklinton and Leonard, 1979; Louchouarn et al., 1997b).

The fjord possesses one major tributary at its head, the Saguenay river, from which about 90% of its runoff is derived. The water column is characterised by a strong halocline near the surface (10–15 m) but is fairly well mixed below 50 m. The bottom waters, which originate from the St-Lawrence estuary (Thérriault and Lacroix, 1975; Siebert et al., 1979) have a salinity of about 30, they are always well oxygenated and display only small annual temperature variations (-1 to $+1$; Drainville, 1968; Sundby and Loring, 1978). Detailed hydrographic characteristics of the fjord can be found in Schafer et al. (1990).

Sediments were collected at three stations on the landward slope of the interior basin in the Saguenay Fjord (i.e., St-Fulgence, SAG-05, and SAG-15 at depths of, respectively, 65, 90, and 232 m) in September 1994. Undisturbed sediment cores were obtained using a 0.12 m^2 Ocean Instruments Mark II box corer. The cores were subsampled on deck at close intervals (i.e., 0.5 cm at the surface, and up to 5 cm interval at depth; see Table III) in a large glove box (Edenborn et al., 1986b) purged by a continuous flow of nitrogen to minimize sediment oxidation. As each sampling interval was sequentially exposed, solid samples were transferred to porewater squeezers and pre-weighed plastic scintillation vials. The latter samples were freeze-dried and the water content used for estimating the porosity.

The dried samples were then homogenized by grinding in an agate mortar and used for subsequent solid phase analyses.

Porewaters were extracted using Reeburgh-type squeezers (Reeburgh, 1967) modified to filter the water through a 0.45 μm Type HA (mixed cellulose acetate and nitrate) Millipore^R filter as it passed directly into a 50 cc syringe. The porewaters were partitioned among a number of plastic and glass vials and treated according to the type of analyses to be performed. The samples were stored untreated in pre-washed polyethylene bottles for chlorinity and sulfate or acidified with a 1% equivalent volume of Seastar^R concentrated HCl for dissolved As, Fe and Mn determinations. Soluble reactive phosphate (SRP) was measured on subsamples which were kept in glass bottles and acidified to a pH 2 with a 5M H_2SO_4 solution. All porewater samples were keep refrigerated until analysis.

Water column samples were collected at Station SAG-15 in May/June 1995 using 12-L PVC Niskin bottles mounted on a galvanised hydrowire. In addition, the Saguenay river waters were sampled along the navigation buoys between St-Fulgence and Chicoutimi. Waters were filtered on 0.45 μm Type HA Millipore^R filters. The filtered water column samples were stored and treated as the porewaters. The suspended particulate matter (SPM) was collected following filtration of 3 to 25 liters of water on pre-weighed Whatman^R EPM 2000 0.3 μm glass microfiber filters. The filter was then rinsed twice with 10 ml of de-ionized water and stored frozen. In the laboratory, the filters were dried at 65 °C in a clean oven before being re-weighed and analyzed.

2.2. PARTICULATE AND SEDIMENT EXTRACTION PROTOCOLS

Particulate matter collected on the glass microfibre filters and the freeze-dried sediments were subjected to a sequential extraction protocol in order to distinguish, operationally, the association of phosphorus and arsenic with different solid phases. The extraction sequence, associated protocols, and analytical procedures are described in Table I. The authors recognize the flaws inherent in any extraction procedure but even researchers critical of these techniques concede that they are useful tools which must be used and interpreted with caution. We are also aware that changes occur in solid phase speciation of metals upon oxidation and freeze-drying of the sediments (Rapin et al., 1986). The most significant change is the oxidation of acid volatile sulfides (AVS) to oxides which are readily extracted by the dithionate reagent (Raiswell et al., 1994; Kostka and Luther, 1994; Bono, 1997). The distribution of AVS was characterised independently on wet anoxic sediments (Gagnon et al., 1995) at SAG-05 and SAG-15. The H_2S generated following the acidification (9M HCl + 20% $SnCl_2$; Chanton and Martens, 1985) of the anoxic sediment in a sealed glass container for 3 hours at room temperature was trapped in an alkaline zinc chloride solution (Hsieh and Yang, 1989). The trapped sulfide was titrated iodometrically and the AVS was assumed to have a FeS stoichiometry.

Table I. Sequential extraction protocol applied to suspended particulate matter collected on filters and solid sediments. Unless specified, this protocol and procedures are similar to those described by Lucotte and d'Anglejan (1985) and Ruttenberg (1992).

Nominal fraction extracted		Nomenclature	Reagent and references
(A1)	Exchangeable fraction	P-ex and As-ex	1M Ammonium acetate at pH 8.5
(A2)	Oxyhydroxides	P-cdb and As-cdb	Citrate-dithionite-bicarbonate (CDB)
	(amorphous and crystalline,		For As, it was obtained from difference
	including the oxidation products		between a total digestion before and
	of AVS)		after extraction
(A3)	Carbonate fluorapatite	P-cfa	1N Sodium acetate at pH 4 + $MgCl_2$ wash
	(Authigenic/sedimentary apatite)		Not applied to arsenic
(A4)	Apatite	P-apa	1N HCl
	(Igneous/terrigenous apatite)		Not applied to arsenic
(A5)	Organic phosphorus/arsenic	P-org and As-org	Ash at 550 °C for 1 hour + 1N HCl extraction
(B1)	Pyritic arsenic	As-pyr	Step A2 at 75 °C + 10M HF/H_3BO_3 + 10M HNO_3
			Lord (1982), Belzile (1988), Huerta-Diaz and
			Morse (1992)
(C1)	Total arsenic	As-tot	Microwave digestion in 10 : 1 HNO_3 : HCl of
			the untreated freeze–dried sediment

2.3. ANALYTICAL METHODS

Water column and porewater chlorinities were determined by potentiometric titration using a standardized $AgNO_3$ solution. The reproducibility of these titrations was better than $\pm 0.5\%$. Salinities were calculated from the chlorinity determinations ($S = 1.80655$ Cl; Fofonoff, 1985). Sulfate was measured by ion chromatography with a reproducibility of $\pm 1\%$ (Dionex, 1986) after 100-fold dilution in distilled water.

Total carbon (C_{TOT}) and total nitrogen (N) concentrations of the freeze-dried sediments and dried SPM were measured using a Carlo-Erba elemental analyzer with a reproducibility of better than $\pm 5\%$. The inorganic carbon (C_{INORG}) content of the sediments was determined by coulometric titration of the CO_2 evolved following acidification with 2N HCl. The precision of the C_{INORG} analyses is better than $\pm 2\%$. 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 $\pm 7\%$. In general, C_{INORG} accounts for less than 10% of the C_{TOT}. The C_{INORG} content of the SPM is assumed to be negligible.

Soluble reactive phosphate (SRP) concentrations in the water, porewater and solid extracts were determined colorimetrically as the molybdenum blue complex, using a Traacs-800 auto-analyser. The reproducibility of this method is estimated to be 7%. Phosphate extracted by the citrate-dithionate-bicarbonate (CDB) reagent was analysed according to the method of Watanabe and Olsen (1962). Total arsenic concentrations in the water, porewater and solid extracts (with the exception of the CDB extraction) were determined by flameless atomic absorption spectrophotometry (AAS) following hydride generation (Aggett and Aspell, 1976; Andreae, 1977). The reproducibility of these measurements, as expressed by the coefficient of variation, was determined to be on the order of 10%. Arsenic extracted by the CDB reagent, As_{CDB}, cannot be determined directly by AAS since the borohydride solution is neutralised by the CDB reagent (Belzile, 1987). The amount of As_{CDB} was obtained by difference between the total As content of solids before and after CDB extraction. Total As was determined following a microwave acid digestion of the solid, freeze-dried sediments in a $10:1$ concentrated $HNO_3:HCl$ solution. Because of the limited amounts of SPM collected on filters, total As in this component was calculated from the sum of the selective extractions when the complete sequence was carried out.

Porewater iron and manganese concentrations, as well as those of the solid extracts were determined by AAS with an air-acetylene flame. The reproducibility of measurements is better than 5% for the porewater samples and on the order of 10% for the extracts.
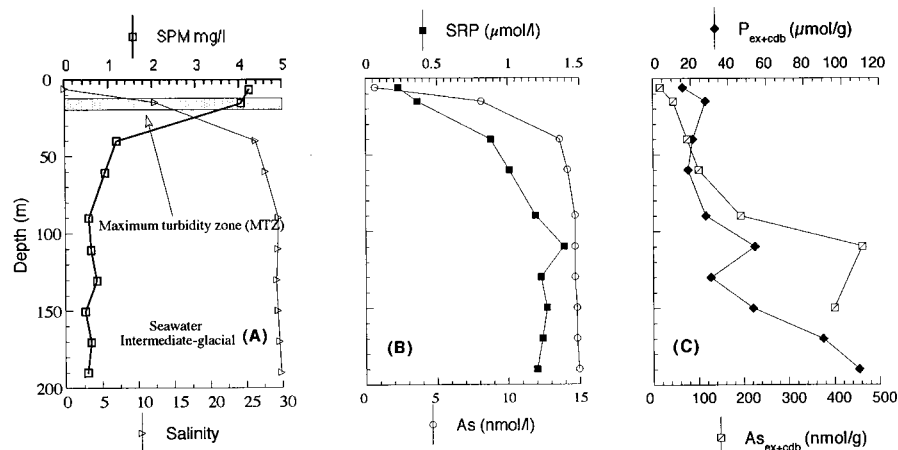
Figure 2. Vertical profiles of (a) salinity and suspended particulate (SPM) load, (b) dissolved reactive phosphate (SRP) and total dissolved arsenic and, (c) exchangeable + CDB-extractable SRP and arsenic on SPM in the water column at SAG-15. Error bars are not included for clarity: SPM see Table II, others see text.

3. Results

3.1. THE WATER COLUMN

A summary of the water column analytical results is presented in the form of vertical profiles (Figure 2) for the Station SAG-15. A more complete set of measurements appears in Table II. The SRP and total arsenic concentrations measured at the outlet of the river, upstream of the fjord, on the same cruise were, respectively, 0.23 μmol/l and 0.4 nmol/l.

The freshwater lens at Station SAG-15 is characterised by low salinities, SRP and total dissolved arsenic concentrations but high SPM concentrations (Figure 2a,b). The latter is also reflected in the *in-situ* light attenuation measurements (not shown) which are high throughout the freshwater lens (~30% transmittance), increase sharply at the pycnocline (~5% transmittance) and decrease even more rapidly as we enter the marine waters below (~95% transmittance). The SPM concentrations, however, do not appear to be highest at the halocline but this distribution may reflect either our inability to precisely sample the halocline or a difference in the size population and nature of the particles (see Figure 2a) (Baker and Lavelle, 1984).

3.2. SEDIMENTS

A summary of the solid sediment and porewater analytical results is presented in the form of vertical profiles (Figure 3) for each of the three sampled stations. A more complete set of measurements appears in Table III. The sediments of the Saguenay Fjord are rich in organic matter (Corg = 1–3%; Table III). The oxygen

Table II. Concentrations and partitioning of As and P in suspended particulate matter (SPM) recovered from the water column at Station SAG-15.

Depth (m)	SPM (mg/l)	C/N (molar)	P-ex (μmol/g)	P-org	P-cdb	P-cfa	P-apa	P-tot	As-ex (nmol/g)	As-org	As-cdb	As-tot
6	4.33 ± 0.17 (6)	16.2	4.0	8.0	12	23	4.7	52	0.7	68	16	85
15	4.03 ± 0.13 (6)	14.5	11	10	17	24	4.8	67	24	45	21	90
40	1.20 ± 0.08 (6)	16.4	9.1	7.8	12	19	5.6	54	38	64	38	140
60	0.96 ± 0.18 (5)	15.7	6.5	4.5	12	29	3.7	56	40	32	61	135
90	0.61 ± 0.09 (4)	14.4	10	7.2	18	19	4.3	59	114	26	80	230
110	0.63 ± 0.16 (4)	15.9	11	4.8	43	20	3.4	82	182	44	280	520
130	0.60 ± 0.15 (4)	21.6	7.5	4.1	23	8	1.9	45	IS	30	270	IS
150	0.48 ± 0.06 (3)	23.0	13	5.5	40	18	4.2	81	230	48	170	460
170	0.58 ± 0.06 (3)	22.6	11	4.7	79	19	3.0	117	220	38	IS	IS
190	0.47 ± 0.05 (3)	17.6	14	5.5	95	24	3.6	142	410	IS	IS	IS

SPM = Suspended particulate matter; number of replicates in parentheses.

C/N = Molar ratio of total carbon to total nitrogen, determined by Carlo-Erba. P-tot = Total phosphorus = P-ex +P-org + P-cdb + P-cfa + P-apa.

As-tot = Total arsenic = As-ex +As-org +As-cdb.
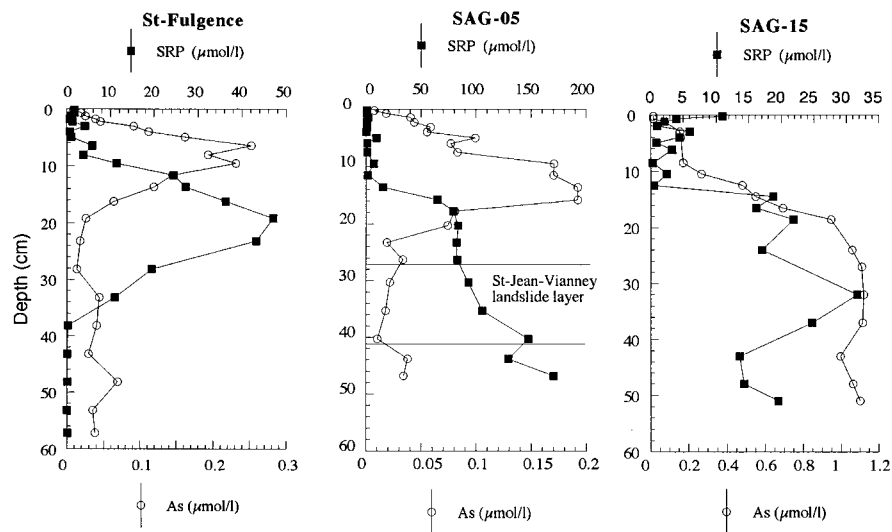
IS = Insufficient Sample.

Figure 3a. Vertical profiles of (a) SRP and total dissolved arsenic, (b) dissolved iron and manganese, (c) CDB-extractable phosphate and arsenic, (d) CDB-extractable iron and manganese, and (e) total solid phosphate and arsenic in porewaters and sediments at the three sampling sites. Error bars are not included for clarity, see text.

penetration depth is typically on the order of a few millimetres (LeFrancois, pers. comm.; voltammetric micro-electrode measurements). Sulfate reducing conditions are encountered within the first two centimetres as evidenced by porewater sulfate depletion (Figure 4) and/or the appearance of acid volatile sulfides (AVS) in the solid sediments (Gagnon et al., 1995; Saulnier, 1997; Figure 5). The shallow oxygen penetration depths and the rapid onset of sulfate reduction reflect the high oxidant demand of these sediments (i.e., the amount and accumulation rates of degradable organic matter at each station). Porewater sulfide concentrations were not measured during this study because they have been shown to be buffered at very low concentrations ($<5\ \mu$M) by the reactive iron-rich sediments in this region (Gagnon et al., 1996).

Sediment accumulation rates at the head of the fjord can reach 2–7 cm y^{-1} (i.e., St-Fulgence) but decrease rapidly to 0.2–0.4 cm y^{-1} in the interior basin (Smith and Walton, 1980; Perret et al., 1995). They are, however, highly variable over small horizontal scales because of the steep bottom topography and frequent submarine mass flow events (Pelletier and Locat, 1993). The sedimentation rate at SAG-5 was estimated at ~1 cm y^{-1} by Mucci and Edenborn (1992) based on the position of the upper boundary of the St-Jean-Vianney landslide layer deposited in May 1971. The sedimentation rate at SAG-15 was estimated at 0.3 cm y^{-1} based on the ^{137}Cs activity profiles of Barbeau et al. (1981).
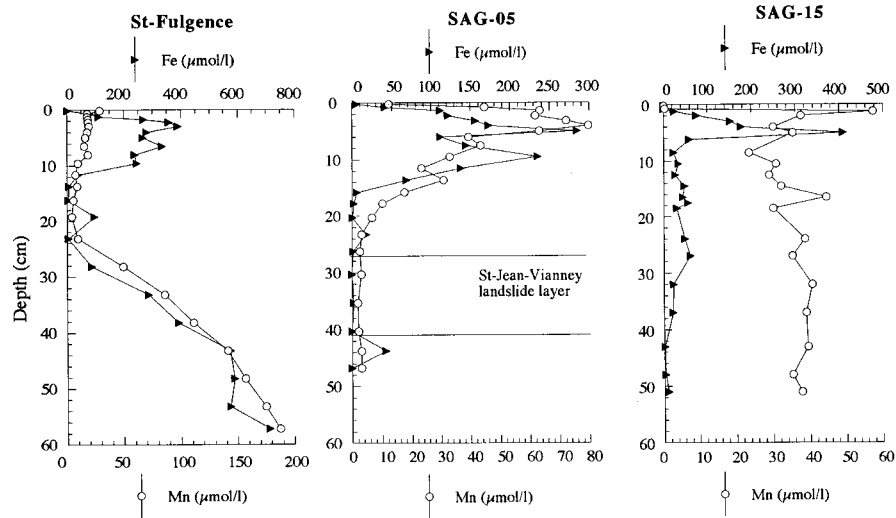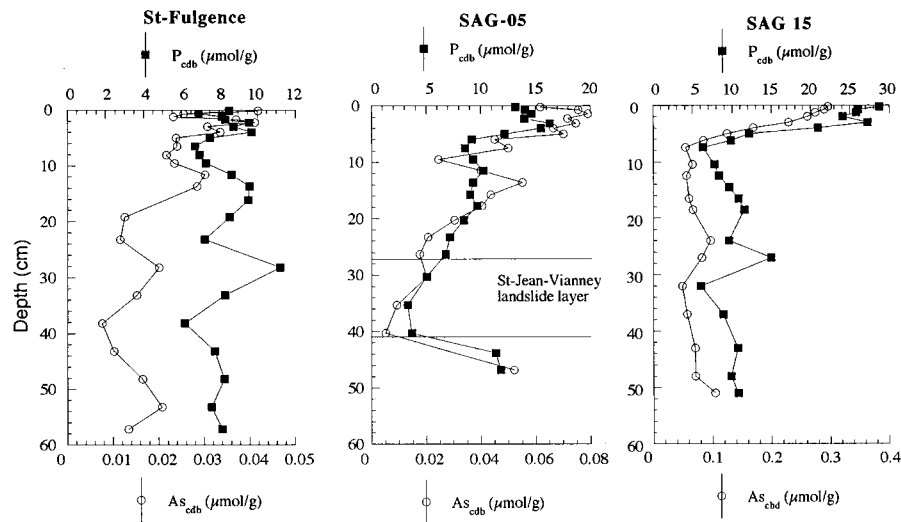
Figure 3b.

Figure 3c.

4. Discussion

4.1. WATER COLUMN

Results of our analyses indicate that phosphate displays a non-conservative behaviour during mixing of freshwater and seawater in the Saguenay Fjord (Figure 6a). In addition to being taken up by organisms in the surface waters, we believe that it is actively scavenged from the water column by settling particles. A significant part of these particles may form, flocculate or coagulate as a result of mixing and
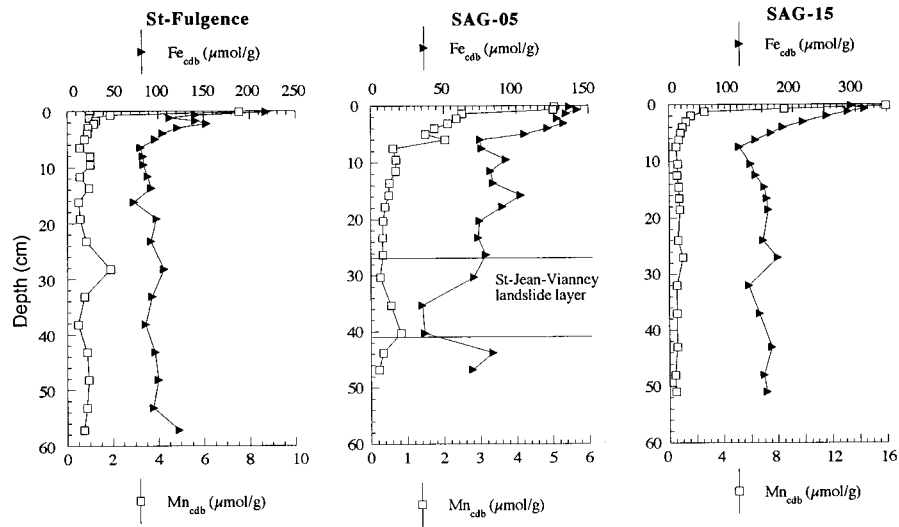
Figure 3d.
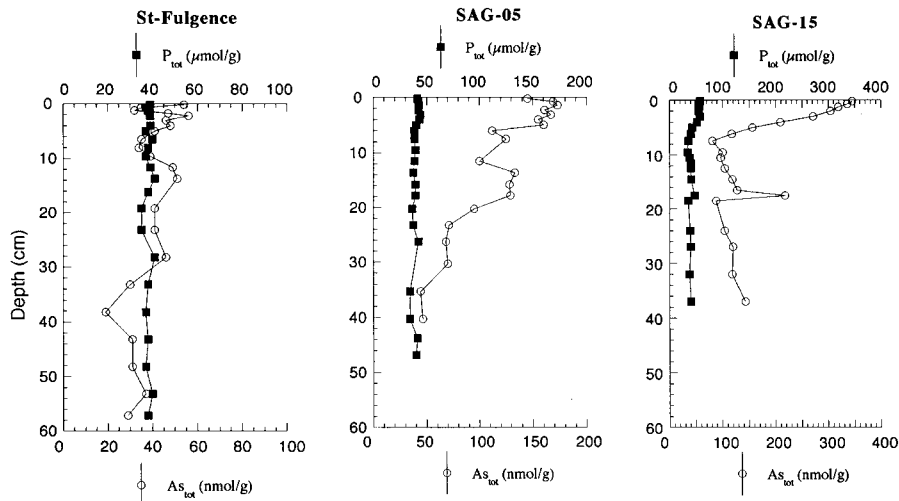
Figure 3e.

the change in ionic strength at the halocline (e.g., Sholkovitz, 1976, 1978; Farley and Morel, 1986; Yan et al., 1992; Dai et al., 1995; Kraepiel et al., 1997).

The data and theoretical mixing curve (Figure 6b) indicate that As behaves nearly conservatively upon mixing of freshwater and seawater in the Saguenay Fjord. This observation is consistent with the results of Tremblay and Gobeil (1990) in the Upper St-Lawrence Estuary and the Saguenay Fjord, as well as for most estuaries receiving little anthropogenic inputs (e.g., Waslenchuk and Windom, 1978; Froelich et al., 1985). In contrast, considerable deviation from

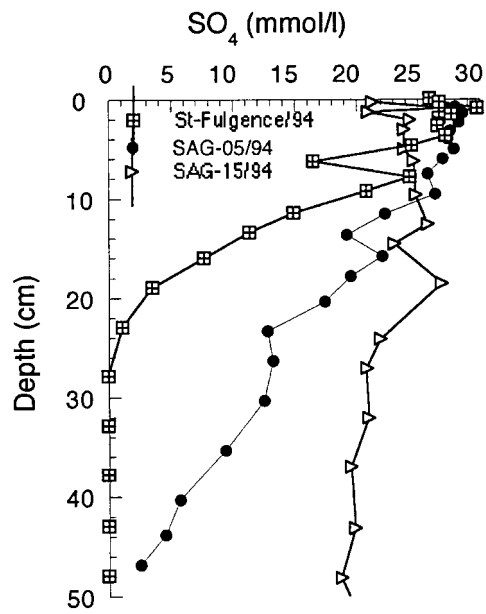*Figure 4.* Vertical distribution of sulfate in the porewaters at the three sampling sites. Error bars are smaller than symbols, see text.
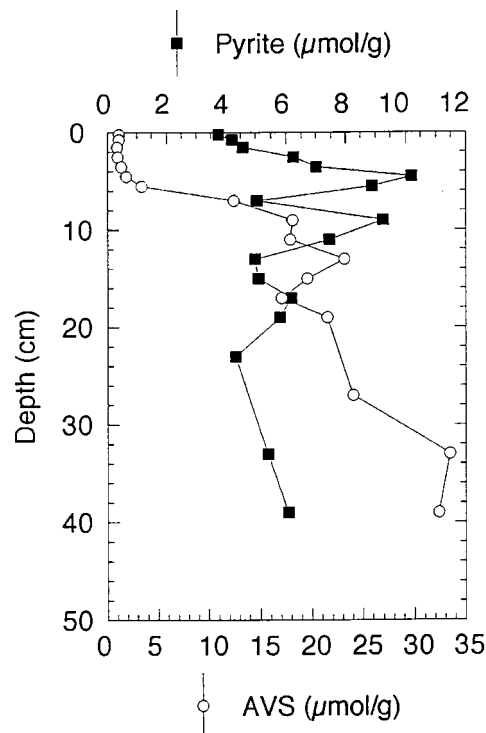

Figure 5. Vertical distribution of acid volatile sulfides (AVS) and pyrite at SAG-15 (from Saulnier, 1997).

Table IIIa. Porewater and solid sediment compositions from a core recovered at Station St-Fulgence

Depth (cm)	ø	[Ca] (mmol/kg)	At (meq/kg)	C-tot (% dw)	C-inorg (% dw)	C-org/N (molar)	P-org (μmol/g)	P-cfa	P-apa	P-tot	As-pyr (nmol/g)	As-tot (nmol/g)
0–0.4	0.84	10.8	2.50	3.59	0.055	19.8	3.0	14	14	39	12	54
0.4–1.0	0.75	10.1	2.51	3.04	0.056	21.5	2.4	13	14	37	9.2	35
1.0–1.5	0.71	11.3	3.14	2.52	0.057	23.8	2.3	13	14	38	8.6	32
1.5–2.0	0.72	11.3	3.31	2.46	0.074	22.1	2.0	14	15	39	10	47
2.0–2.5	0.73	10.7	3.82	2.62	0.058	24.8	2.2	13	15	39	15	56
2.5–3.4	0.76	11.7	4.36	2.66	0.064	23.0	2.2	12	IS	IS	15	46
3.4–4.5	0.70	10.9	5.53	2.52	0.065	22.7	2.4	13	14	39	14	48
4.5–5.5	0.72	10.4	5.72	2.42	0.062	23.2	2.1	12	15	37	17	41
5.5–7.5	0.70	10.3	7.86	1.90	0.072	23.2	2.1	14	17	40	11	35
7.5–8.6	0.67	10.1	8.18	1.91	0.079	22.7	2.1	14	16	38	12	34
8.6–10.6	0.70	ND	11.6	2.37	0.058	22.1	2.3	12	15	37	16	39
10.6–12.7	0.69	9.9	16.4	2.29	0.061	21.8	2.3	13	15	39	19	49
12.7–14.7	0.74	9.7	24.1	2.51	0.059	22.0	2.5	14	15	41	23	51
14.7–17.7	0.74	9.7	35.0	2.49	0.061	21.6	2.4	13	13	38	IS	IS
17.7–20.7	0.76	9.6	40.2	2.94	0.070	22.9	2.6	12	12	35	29	41
20.7–25.7	0.80	ND	45.5	3.05	0.066	24.5	2.6	12	13	35	29	41
25.7–30.7	0.76	9.8	48.4	3.23	0.069	23.6	2.7	14	13	41	26	46
30.7–35.7	0.74	6.9	ND	2.41	0.051	23.4	2.2	13	15	38	15	30
35.7–40.7	0.73	7.4	45.6	2.54	0.069	30.6	1.8	13	16	37	11	19
40.7–45.7	0.76	7.5	46.6	3.40	0.073	30.7	2.2	13	15	38	21	31
45.7–50.7	0.73	ND	49.9	3.63	0.055	33.0	2.3	14	13	37	15	31
50.7–55.7	0.71	ND	ND	2.39	0.052	26.7	2.1	14	16	40	16	37
55.7–58.7	0.76	6.6	46.5	4.69	0.073	35.6	2.5	14	13	38	16	29

ND = not determined.

ø = porosity.

[Ca] = porewater calcium.

At = Titration alkalinity.

C-tot = Total carbon determined by Carlo-Erba

C-inorg = Inorganic carbon determined by coulometry

C-org/N = Molar ratio of organic carbon (C-tot–C-inorg) to total nitrogen.

a conservative behavior has been observed in estuaries receiving anthropogenic inputs of arsenic (e.g., Langston, 1983; Howard et al., 1984; Sanders, 1985; Seyler and Martin, 1990). In spite of the apparent conservative behavior of As in the Saguenay Fjord, results of the SPM analyses reveal that arsenic is actively scavenged from the water column. In surface waters, particulate As is dominated by an organic component whereas sorption (i.e., $As_{ex} + As_{cdb}$) to settling particles generally increases with depth (Table II and Figure 2c).

Dissolved arsenic, like SRP, is characterised by very low concentrations in the freshwaters of the Saguenay River ($\sim$0.4 nM). This concentration is among the lowest values reported for world rivers (Waslenchuk, 1979). On the other hand, arsenic concentrations in the marine waters of the fjord ($\sim$14.8 nM at S = 30)

Table IIIb. Porewater and solid sediment compositions from a core recovered at Station SAG-05

Depth (cm)	ø	Ca-diss (mmol/kg)	At (meq/kg)	C-tot (% dw)	C-inorg (% dw)	C-org/N (molar)	P-org (μmol/g)	P-cfa (nmol/g)	P-apa (nmol/g)	P-tot	As-pyr	As-tot
00.5	0.84	10.9	2.12	2.43	0.064	22.8	2.6	13	13	41	83	145
0.5–1.0	0.82	13.4	2.21	2.1	0.059	22.7	2.1	14	12	42	93	169
1.0–1.8	0.79	10.1	2.12	2.29	0.062	24.3	2.4	13	13	43	94	173
1.8–2.8	0.76	11.8	2.28	2.41	0.063	23.8	2.7	13	12	42	89	161
2.8–3.5	0.75	12.3	2.39	2.37	0.066	23.8	2.6	14	11	44	92	167
3.5–4.5	0.74	11.2	2.31	2.29	0.066	23.2	2.3	14	11	43	88	155
4.5–5.5	0.73	10.9	2.32	1.98	0.067	24.2	2.4	14	12	40	90	160
5.5–6.5	0.71	11.2	2.46	2.08	0.082	26.7	2.2	15	12	38	67	112
6.5–8.5	0.66	10.7	2.68	2.06	0.074	25.6	2.2	14	14	38	75	125
8.5–10.5	0.70	10.9	2.78	2.64	0.062	25.2	2.4	13	14	39	49	74
10.5–12.5	0.71	11.2	3.29	2.60	0.061	25.2	2.4	13	13	38	60	100
12.5–14.8	0.70	11.0	5.74	2.39	0.063	25.4	2.3	14	12	37	78	133
14.8–16.8	0.73	10.6	8.29	2.57	0.065	30.0	2.9	13	14	39	84	128
16.8–18.8	0.75	10.5	10.9	2.98	0.060	29.0	3.1	15	11	39	89	129
18.8–21.8	0.72	ND	ND	3.09	0.064	31.0	2.6	13	12	36	65	95
21.8–24.8	0.71	10.3	15.2	2.97	0.067	33.8	2.8	14	13	37	50	71
24.8–27.8	0.71	ND	16.1	2.58	0.074	34.7	2.7	20	13	42	50	68
27.8–32.8	0.69	9.94	19.7	1.76	0.064	32.2	2.3	6.7	IS	IS	50	70
32.8–37.8	0.64	9.94	23.7	1.16	0.287	40.4	1.5	17	13	34	35	44
37.8–42.8	0.72	ND	23.7	1.29	0.620	54.2	1.4	21	7.7	34	41	46
42.8–44.8	0.77	9.44	30.3	3.60	0.064	36.6	2.6	13	14	41	IS	IS
44.8–48.8	0.72	ND	32.1	3.86	0.075	31.0	2.9	13	12	40	IS	IS

are nearly 40 times larger than the freshwaters but identical to those of the waters which spill over into the Fjord from the Estuary (Tremblay and Gobeil, 1990). Once normalized to salinity, the latter are also typical of the deep waters of the North Atlantic (Middelburg et al., 1988; Cutter and Cutter, 1995). Although the marine water column As concentrations are nearly identical, surface sediments in the Fjord contain 3 to 4 times more As than sediments of the Lower St-Lawrence Estuary (Gobeil, 1996, Richard, 1997). The anomalous sediment As concentrations most likely originate from progressive scavenging by particles as they settle through the marine waters of the Fjord (Figure 2c). Nevertheless, there are two potential sources of anthropogenic particulate As to the Fjord: mining and milling at a niobium mine along a tributary of the Saguenay river as well as off-loading of bauxite in the Baie des Ha! Ha!. The distribution of As concentrations (Fitzpatrick, 1998) in surface sediments of the North Arm of the Fjord and the Baie des Ha! Ha! indicates that the former is a minor, if not insignificant, source of particulate arsenic whereas the latter is likely important. On the other hand, the SPM in the surface waters contain about 30 times less As_{TOT} than the SPM found at depth. Nevertheless, we cannot discount the possibility that As-rich particles are carried

Table IIIc. Porewater and solid sediment compositions from a core recovered at Station SAG-15.

Depth (cm)	ø	Ca-diss (mmol/kg)	At (meq/kg)	C-tot (% dw)	C-inorg (% dw)	C-org/N (molar)	P-org	P-cfa	P-apa	P-tot (μmol/g)	As-pyr (nmol/g)	As-tot (nmol/g)
0–0.5	0.82	10.4	2.15	2.5	0.086	25.9	2.3	19	8.6	58	47	345
0.5–1.0	0.82	11.4	2.36	2.34	0.091	24.6	2.2	19	7.7	55	46	336
1.0–1.5	0.81	ND	ND	2.57	0.088	24.4	2.3	20	8.3	56	43	319
1.5–2.5	0.81	ND	ND	2.41	0.000	24.7	2.2	20	8.4	55	42	304
2.5–3.5	0.79	11.3	2.26	2.39	0.101	24.7	2.0	21	7.3	57	41	271
3.5–4.5	0.79	10.9	2.21	2.22	0.092	24.9	2.2	21	7.9	52	39	209
4.5–5.5	0.76	10.5	2.17	2.03	0.107	25.3	2.2	22	7.3	43	30	156
5.5–6.9	0.76	11.2	2.43	1.87	0.101	26.2	2.1	20	8.8	40	31	117
6.9–8.0	0.63	ND	2.91	1.18	0.114	29.0	1.6	14	13	35	26	81
10.0–11.0	0.69	ND	3.17	1.55	0.106	27.2	1.5	17	7.4	34	33	100
12.0–13.0	0.71	10.3	3.15	1.36	0.119	28.9	1.5	19	9.0	38	38	96
14.0-15.0	0.7	10.9	4.40	1.53	0.120	28.4	1.6	20	9.0	40	48	100
16.0–17.0	0.69	11.0	4.97	1.61	0.107	26.1	1.6	20	7.4	40	42	104
18.0–19.0	0.69	10.6	5.64	2.04	0.095	28.9	1.6	20	7.6	41	50	118
23.5–24.5	0.7	10.9	6.92	1.59	0.118	25.5	1.5	ND	ND	ND	30	127
26.5–27.5	0.67	10.3	7.30	1.31	0.136	26.5	1.4	22	7.8	47	ND	218
31.5–32.5	0.68	ND	ND	1.15	0.138	29.0	1.3	21	6.6	35	38	88
36.5–37.5	0.72	10.5	10.5	1.47	0.123	26.2	1.4	21	7.1	39	46	104
42.5–43.5	0.73	10.9	11.3	1.85	0.096	28.7	1.8	20	7.5	40	48	119
47.5–48.5	0.72	ND	11.7	1.62	0.108	26.7	1.3	19	7.3	38	45	118
50.5–51.5	0.72	10.2	12.5	1.88	0.100	25.6	1.5	20	8.1	41	38	143

to SAG-15 with bottom waters spilling over into the main arm of the fjord from the Baie des Ha! Ha! (see further discussion below).

Whereas the distribution of the P_{ex} fraction of the SPM remains nearly constant throughout the water column, As_{ex} increases progressively with depth (Table II). However, this fraction represents the easily-exchangeable, electrostatically-bound component of the two elements to the SPM and both elements are known to form strong inner-sphere complexes on metal oxide particles (Waychunas et al., 1993; Persson et al., 1996). Consequently, a more accurate representation of the scavenging by settling particles should include the CDB-extractable fraction. The vertical distribution of the sum of the exchangeable and CDB-extractable fractions (i.e., SRP_{ex+cdb} and As_{ex+cdb}; Figure 2c) clearly shows that both elements are actively and progressively scavenged as particles settle through the water column. The subsurface peak which appears at 110 m is also visible on the SRP and SPM profiles as well as measurements of dissolved and CDB-extractable Fe and Mn (not shown). This could be interpreted as the presence of an older water mass which intercepts the reduced sediments on the slope of the basin or the spill-over of bottom waters from the Baie des Ha! Ha!.
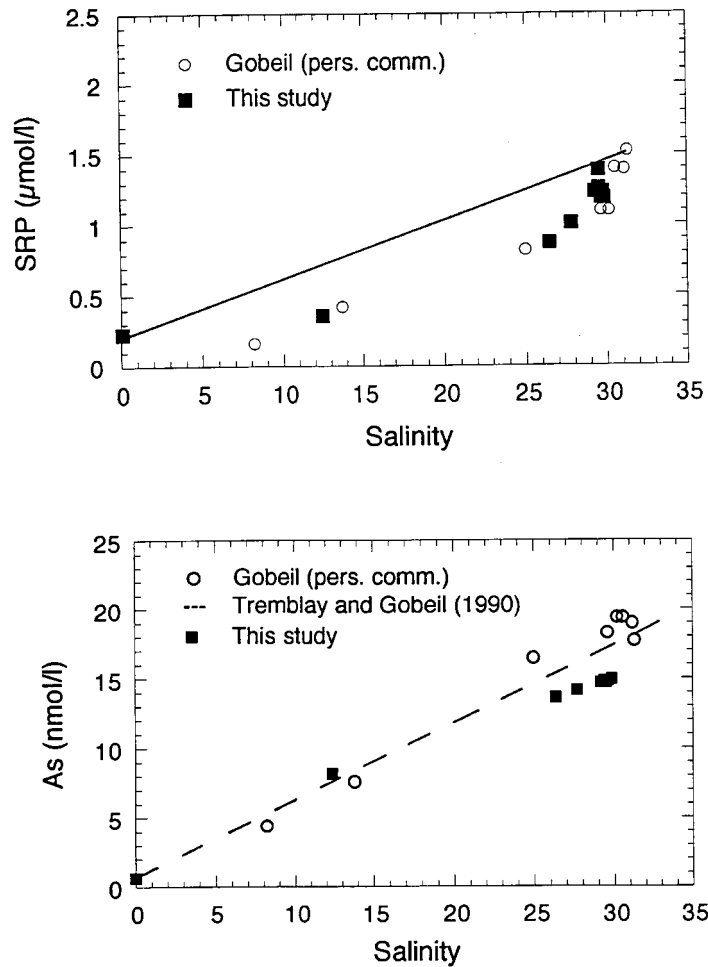
Figure 6. Saguenay Fjord water column (a) SRP and, (b) total dissolved As. Full and dashed lines represent theoretical mixing lines to, respectively, data in this study and by Tremblay and Gobeil (1990). Data provided by Dr. Charles Gobeil were obtained in July 1986.

Laboratory experiments have shown that oxic sediments collected in the interior basin of the Fjord display a "zero equilibrium concentration" (see Froelich, 1988 and Sundby et al., 1992 for a detailed explanation of the concept) of 1.3 μmol/l for phosphate and 7 nmol/l for arsenate at 4°C (Harris, 1996). Briefly, the "zero equilibrium concentration" corresponds to the concentration of maximum buffer capacity of the sediment or the concentration below which the solid will release the adsorbed species to the dissolved phase and above which they will be adsorbed by the solid. At SAG-15, surface sediments will be in equilibrium with the ambient SRP concentration (i.e., $\sim$1.25 μmol/l) when resuspended in the bottom marine waters but strongly adsorb arsenate ($\sim$15 nmol/l in the water column). Despite the progressive adsorption of As onto settling particles but, perhaps, because of their

low abundance in the marine waters (Figure 6b) and the frequent renewal of these waters (> once/year; Thérriault and Lacroix, 1975; Siebert et al., 1979), the dissolved [As] in the water column does not appear to be affected by this scavenging and displays an apparent conservative mixing behavior.

4.2. SEDIMENTS

The geochemical behaviors of arsenic and phosphorus diverge most strikingly within the sediments and upon the development of suboxic and anoxic conditions during early diagenesis. Before a discussion of their behavior can be entertained it should be confirmed that, in light of the high sedimentation rate at the landward station, their distribution in the porewaters is controlled by diffusive rather than advective processes. This can be ascertained by calculating the Peclet number or by comparing the sedimentation rate to the characteristic length scale for diffusion (Berner, 1980). Using a tortuosity-corrected solute diffusion coefficient of 2×10^{-6} cm^2 s^{-1} (63 cm^2 y^{-1}; Riedel et al., 1987), we calculated a characteristic length scale for diffusion, $(D_s/t)^{1/2}$, of $\sim$8 cm, which is slightly larger than the estimated sedimentation rate at the landward station (i.e., 2–7 cm y^{-1} at St-Fulgence). In other words, diagenetic redistribution of arsenic and phosphate can be treated solely in terms of molecular or biologically-enhanced diffusion while ignoring advective flow of porewaters induced by sediment compaction.

4.2.1. *The Behavior of SRP and Arsenic in Oxic and Suboxic Sediments*

Upon their accumulation at the sediment-water interface some of the As and P is released to porewaters following the degradation of organic matter to which they are associated. As indicated in Table II, however, the amount of organic As and P reaching to the sediment-water interface is small relative to other phase associations (e.g., CDB-extractable, exchangeable) and, with the exception of SAG-15, organic matter degradation does not contribute significantly to establishing a strong concentration gradient across the sediment-water interface.

Both arsenate and phosphate have a strong affinity for CDB-extractable detrital and authigenic iron oxyhydroxides which accumulate in the oxic sediments near the sediment-water interface (see Figures 3c,d). Upon burial in the suboxic/anoxic zone, amorphous iron oxyhydroxides are reduced and dissolved, releasing the associated SRP and As to the porewaters (Figures 3a,b). Arsenic is released to the porewaters at the same depth or shallower than SRP, and its release to the porewaters is nearly coincident with the distribution of dissolved Fe at St-Fulgence and SAG-05 (Figure 3a,b). At SAG-15, both SRP and As accumulate in the porewaters well after the most reactive iron oxyhydroxides are dissolved. Whereas porewater SRP and As may be derived from the dissolution of amorphous iron oxyhydroxides (Edenborn et al., 1986a; Anschutz et al., 1998), a complex interplay between re-adsorption onto more resistant iron oxyhydroxides (e.g., goethite, hematite), the relative reactivity of these oxides towards sulfide (Canfield et al., 1992), and the

redox behavior of arsenic may be responsible for the observed porewater distributions. In other words, release of SRP and As to the porewaters may occur only following the reductive dissolution of more resistant carrier phases in the presence of sulfide. Alternatively, in the case of As, the reduction of arsenate, As(V), to arsenite, As(III), and its desorption may occur prior to dissolution of the carrier phase(s) in the presence (Kuhn and Sigg, 1993) or absence of sulfide. The latter scenario would explain why As is released to the porewaters before SRP.

Because of volume constraints, we did not measure the speciation of the porewater As in the samples taken during this study. It was recently determined on samples recovered in the spring of 1999 at three sites in the Fjord, including SAG-05. Total dissolved As concentrations were determined as described in the methodology section. Porewater As(III) analyses were carried out after an acetate buffer was added to the samples in order to maintain their pH between 3.5 and 5.5. The arsine generation from As(V) is strongly pH dependent and practically negligible at pH > 3.5, but a quantitative conversion of the As(III) into arsine proceeds at these pH (Aggett and Aspell, 1976). At all three sites, the As(III)/As$_{tot}$ ratio increased from 30–40% in the first sampling interval (0–0.5 cm) to 80–100% within the first 2–3 cm below the sediment-water interface. Thus, reduced As(III) is the predominant species in the suboxic/anoxic porewaters and could well have been released in this form before the reductive dissolution of the authigenic iron oxyhydroxides. Nevertheless, the proper sequence of events requires further elucidation, although all processes may occur over a narrow depth interval (i.e., they cannot be resolvable by our sampling protocol) in organic-rich sediments where the sequence of reactions is compressed.

The relative affinity and rates of adsorption of As(V) and As(III) onto iron oxide surfaces may be critical in describing the diagenetic behavior of arsenic but laboratory results are often difficult to reconcile because iron oxides of various mineralogies (i.e., ferrihydrite, lepidocrocite, goethite, and hematite) and a wide range of arsenic concentrations have been used. Furthermore, most of these studies have been carried out in dilute solutions ($I < 0.1$ m) and may not be directly applicable to seawater. All studies agree that arsenic adsorption onto iron oxides is highly pH dependent with maximum adsorption occurring between pH 4 and 7 (Yoshida et al., 1976; Pierce and Moore, 1982; Bowell, 1994; Raven et al., 1998; Manning et al., 1998). Most of these studies show that, at circum-neutral to alkaline pH and high arsenic concentrations ([As] > 10^{-5} M), arsenite adsorbs more strongly to iron oxides than does arsenate. Both species have been shown to form inner-sphere bidentate, binuclear complexes on the surface of iron oxides (Waychunas et al., 1993; Manning et al., 1998) and it has been proposed that ferrihydrite may be transformed to a ferric arsenite phase (Raven et al., 1998). However, as concentrations of dissolved arsenic are reduced, the trend is reversed (Pierce and Moore, 1982; Raven et al., 1998). At concentrations more representative of natural aquatic environments and of this study ([As] < 10^{-6} M), As(V) was observed to show a greater affinity for iron oxide surfaces than As(III), even under

alkaline conditions (Yoshida et al., 1976; Pierce and Moore, 1982; Bowell, 1994). Similarly, it is interesting to note that all the arsenic adsorbed onto authigenic iron oxyhydroxides in lacustrine sediments has been found to be As(V) (Belzile and Tessier, 1990; De Vitre et al., 1991).

Yoshida et al. (1976) and Raven et al. (1998) report that more than 90% of both dissolved As(III) and As(V) are adsorbed onto iron oxides within a one hour whereas Pierce and Moore (1982) claim that the rate of adsorption of As(V) onto amorphous iron hydroxide was much faster than that of arsenite. Fuller et al. (1993) proposed that the adsorption kinetics of As(V) onto ferrihydrite could be described by a two step process with rapid adsorption occurring within 5 minutes. A recent laboratory study (Yan Gao, pers. comm.), however, suggests that adsorption onto goethite from seawater is much slower and may take as much as one week. Finally, it would also appear that, like phosphate (Lijklema, 1980; Slomp et al., 1996; Anschutz et al., 1998), arsenate is preferentially bound to an amorphous iron oxyhydroxide which would be extractable selectively by a citrate-ascorbic acid-bicarbonate (Ferdelman, 1988; Kostka and Luther, 1994) reagent. The greater affinity of arsenate for amorphous iron oxyhydroxides is supported by the work of Fuller et al. (1993) who reported that arsenate adsorption on ferrihydrite decreases with time as a result of crystallite growth.

4.2.2. *The Behavior of SRP and Arsenic in Anoxic Sediments*

Arsenite released to the porewaters can diffuse either down, where it will be adsorbed to or incorporated with authigenic iron sulfides (Belzile and Lebel, 1986; Huerta-Diaz and Morse, 1992; Morse, 1994; Huerta-Diaz et al., 1998) or up towards the oxic boundary. Unfortunately, the distribution of pyrite or As associated with pyrite in these sediments (see As_{pyr} in Table III) is of little use to support this mechanism since it comprises a significant detrital component. We have, however, carried out microprobe analyses of framboidal pyrite in thin section grain mounts of Saguenay Fjord sediments. These authigenic pyrite grains contained 800 to 1000 ppm As. Belzile and Lebel (1986) found similar arsenic concentrations in authigenic pyrite isolated from anoxic sediments of the lower St-Lawrence Estuary. The amount of pyrite in the Saguenay Fjord sediments, however, is small (5–60 μmol-S g^{-1}) relative to acid volatile sulfides (AVS = amorphous FeS + mackinawite + poorly crystallised greigite) which are up to 7 times more abundant (Mucci and Edenborn, 1992; Gagnon et al, 1995). The AVS content of these sediments increases sharply 3 to 5 cm below the sediment-water interface (Figure 5). These oxygen sensitive phases are, however, difficult to isolate from the sediment for compositional characterisation. Huerta-Diaz et al. (1998) reported that as much as 50% of the arsenic in a freshwater sediment may be sulphidized with AVS. Saulnier and Mucci (2000) described the remobilization of Fe, Mn and As following the resuspension of anoxic Saguenay Fjord sediments in oxygenated seawater. They observed that the amount of Fe and As released to the dissolved phase during the first hour of the resuspension is proportional to the AVS content of the sediments.

The importance of the AVS as a sink for arsenic is clearly demonstrated but remains unexplored for phosphate.

    In contrast to arsenate, phosphate is the only stable species under the field of stability of water. As indicated above, SRP is also released to the porewaters upon the reductive dissolution of iron oxyhydroxides. Under the strong concentration gradient, phosphate diffuses up towards the oxic layer where it can be re-adsorbed by freshly precipitated amorphous iron oxyhydroxides. With the exception of the St-Fulgence station, there is no strong sink for phosphate at depth in these sediments and SRP concentrations increase slightly or remain nearly constant (Figure 3a). Our extraction protocol indicates that an authigenic phase such as apatite or carbonate fluorapatite is not being formed at depth (see P_{CFA} in Tables IIIa,b,c). The rapid decrease in SRP concentrations at depth at the St-Fulgence station may reflect the adsorption of phosphate onto authigenic calcite (de Kanel and Morse, 1978) which precipitates from the highly supersaturated porewaters generated in the sulfate reduction zone (Mucci and Edenborn, 1992). The calcite precipitation hypothesis in this zone is supported by the progressive decrease in dissolved calcium concentration below 10 cm (see Table IIIa). Alternatively, the rapid decrease in SRP at depth may be explained by the precipitation of vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$) or struvite ($MgNH_4PO_4 \cdot 6H_2O$). Once sulfate becomes depleted, there is no longer a sulfide sink for Fe(II) and its concentration builds up progressively in the porewaters (Figure 3b). Under these conditions, vivianite is likely to form (Martens et al., 1978). The ion activity product of the porewaters with respect to vivianite ($IAP_{vivianite}$) was calculated according to:

$$IAP_{vivianite} = a(Fe^{2+})^3 a(PO_4^{3-})^2 = ([Fe^{2+}]\gamma(Fe^{2+}))^3([PO_4^{3-}]\gamma(PO_4^{3-}))^2, \quad (1)$$

where $a(i)$, $[i]$ and $\gamma(i)$ are, respectively, the ion activities, the total ion concentrations, and total ion activity coefficients. The phosphate ion concentration was calculated from the SRP concentration:

$$[PO_4^{3-}] = [SRP]/(1 + a(H^+)/K_3^* + a(H^+)^2/K_2^* K_3^* + a(H^+)^3/K_1^* K_2^* K_3^*, \quad (2)$$

where K_1^*, K_2, and K_3^* are the first, second, and third stoichiometric dissociation constants of phosphoric acid in seawater (Millero, 1995). The total activity coefficient of the Fe^{2+} under the *in-situ* conditions ($T = 1$ °C, $S = 30$) was assumed to be equal to that of Mg^{2+}. The Mg^{2+} and PO_4^{3-} total ion activity coefficients were taken from Millero and Pierrot (1998) and are assigned values of 0.22 and 3.3 $\times 10^{-5}$, respectively. Unfortunately, the pH of the porewaters was not measured but a realistic range (i.e., 7.0–8.0) was used for the calculations. Results of these calculations are presented in Table IV. The thermodynamic solubility constant of vivianite is 10^{-36} at 25°C and 1 atm. (Nriagu, 1972). Solubility data at lower temperatures and enthalpies for the reaction are not available. Nevertheless, comparing this value with the IAP data in Table IV shows that the sediment porewaters become saturated with respect to vivianite between 26 and 41 cm. In addition, below 27 cm,

Table IV. Calculated IAP for vivianite and porewater ammonium concentration required for saturation with respect to struvite at Station St-Fulgence.

Depth	SRP	[PO$_4$]	[Fe]	log a(Fe)$^3 a$(PO$_4$)^2			[NH$_4$]
(cm)	(μmol/l)	(μmol/l)	(μmol/l)	(pH = 7.0)	(pH = 7.5)	(pH = 8.0)	(mol/l)
20.7–25.7	43.2	0.59	5.4	−40.3	−39.2	−38.2	0.62
25.7–30.7	19.4	0.27	88	−37.3	−36.2	−35.3	1.4
30.7–35.7	10.9	0.15	290	−36.3	−35.2	−34.2	2.5
35.7–40.7	0.2	0.003	390	−39.4	−38.2	−37.3	125
40.7–45.7	0.06	0.0008	575	−39.9	−38.9	−37.8	450
45.7–50.7	0.05	0.0007	590	−40.0	−38.9	−37.9	540
55.7–58.7	0.03	0.0004	715	−40.2	−39.2	−38.1	890

SRP concentrations decrease as iron concentrations increase. Below 41 cm, the porewaters appear to be undersaturated with respect to vivianite but the IAP is nearly constant.

Porewater NH_4^+ data are unavailable at the St-Fulgence station but given a K_{sp} of $10^{-13.15}$ for struvite at 25 °C and 1 atm. (Taylor et al., 1963), equilibrium NH_4^+ concentrations can be calculated:

$$[NH_4^+]_{eq} = K_{sp}/[Mg^{2+}]\gamma(Mg^{2+})\ [PO_4^{3-}]\ \gamma(PO_4^{3-})\gamma(NH_4^+), \quad (3)$$

where $[Mg^{2+}]$ is assumed to be conservative and calculated from porewater salinity $(4.53 \times 10^{-2}$ mol/kg) and $\gamma(NH_4^+) = 0.59$ (Millero and Pierrot, 1998). Results of these calculations are presented in Table IV and show that saturation with respect to struvite would require NH_4^+ concentrations in excess of 0.6 M. This concentration is about three orders of magnitude larger than one would expect for this environment, it is clearly unreasonable and, thus, struvite is not likely to serve as a sink for phosphate in these sediments.

4.2.3. *Fate of Arsenite Released to the Porewaters*

Arsenite which diffuses up towards the sediment-water interface is not quantitatively oxidised by authigenic iron oxyhydroxides and migrates further up where it may be adsorbed and oxidized by/or in the presence of authigenic manganese oxides or lost to the overlying waters. The authigenic manganese oxides generally accumulate above the depth of iron oxyhydroxide concentration (see Figure 3d), in part because Mn(II), released to the porewaters following reductive dissolution of the manganese oxides at depth, is metastable in the presence of oxygen (Stumm and Giovanoli, 1976; Emerson et al., 1982) and diffuses further into the oxic layer before being oxidized and precipitated. Furthermore, it has been shown that authigenic manganese oxides are swept closer to the sediment-water interface by

oscillations of the oxygen penetration depth in response to temporal variations in the flux of organic matter (Gobeil et al., 1997). In low-oxygen bottom waters (Johnson et al., 1992) or in organic-rich sediments where the oxygen penetration depth is close to the sediment-water interface (Sundby and Silverberg, 1985), some of the porewater Mn(II) may be lost to the overlying waters, limiting the accumulation of authigenic oxides in the oxic layer.

Although both iron and manganese oxides can oxidise As(III) to As(V) (Andreae, 1979; Oscarson et al. 1981a; Peterson and Carpenter, 1986; DeVitre et al., 1991) it is thought that manganese oxides are primarily responsible for the oxidation (Oscarson et al., 1981a,b; Moore et al., 1990; Peterson and Carpenter, 1986; Kuhn and Sigg, 1993). Oscarson et al. (1983) also observed that the kinetics of As(III) oxidation is faster on poorly-crystalline, high specific surface manganese oxides, such as those which are encountered as authigenic coatings on sediment grains in the oxic sediments. Furthermore, some laboratory and field studies have shown that As(III) is metastable in the presence of oxygen (Johnson and Pilson, 1975; Gulens et al., 1979; Oscarson et al., 1981a) and will not be oxidised to As(V) for days to months, even in the presence of iron oxides (Cherry et al., 1979). In contrast, the oxidation is rapid in the presence of MnO_2 (Oscarson et al., 1981a,b; Kuhn and Sigg, 1993) to which it will readily adsorb (Scott, 1991). It remains to be resolved whether the manganese oxide is the oxidant or if it serves as a catalytic electron transfer medium in the presence of oxygen. Upon oxidation to arsenate, this species will preferentially be re-adsorbed by iron oxyhydroxides present at the same depth. The adsorption of As(V) to iron oxyhydroxides is favoured relative to manganese oxides because the surface charge of the latter is negative at circum-neutral pH (Kuhn and Sigg, 1993). Therefore, the arsenic associated with authigenic manganese oxides may constitute a small fraction of the particulate or CDB-extractable arsenic inventory in marine sediments.

4.2.4. *Fate of SRP and Arsenic Delivered to the Sediment*

Whereas, in the absence of authigenic carbonate fluorapatite formation, the ability of oxic sediments to retain phosphate is a function of the amorphous iron oxyhydroxide content, arsenic retention and concentration depends on the availability of manganese oxides which in turn depends on the thickness of the oxic layer (Figure 3d,e). This should be reflected both in the flux of As and SRP to the overlying waters as well as in the retention capacity of the sediments. The thinner the oxic layer, the less Mn/Fe oxyhydroxides will accumulate at the sediment-water interface and intercept SRP and As diffusing up from below. This is even more critical in the case of As which appears to require the oxidation of As(III) to As(V) on the surface of Mn-oxides before being adsorbed by Fe-oxides. Similarly, it was observed that the flux of phosphate and arsenic out of sediments increases as the dissolved oxygen concentration of the overlying waters decreases (Sundby et al., 1986; Riedel et al., 1997) resulting in a decoupling of the iron and phosphate cycle (McManus et al., 1997).
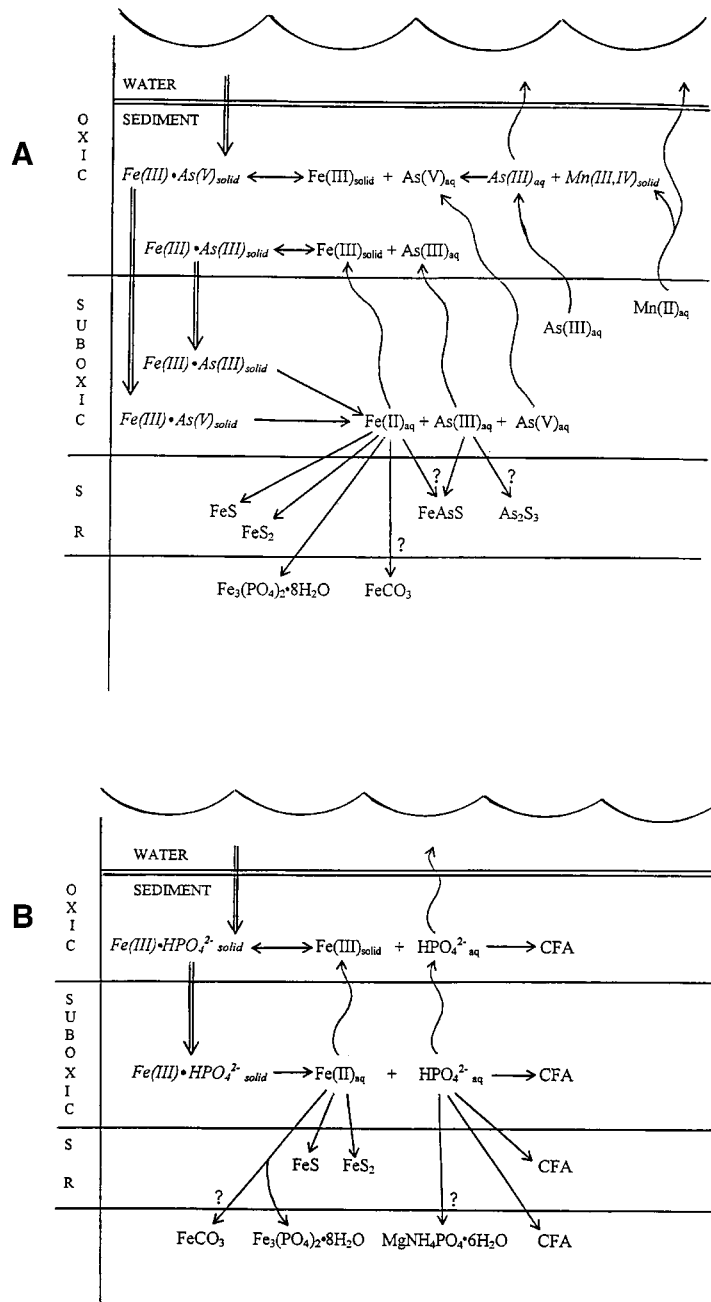
Figure 7. Schematic representations of the diagenetic cycles of (a) arsenic and, (b) phosphate in coastal marine sediments. Straight, single lines, double lines, and wiggly lines represent, respectively, reactions, burial, and diffusion (+ oxidation). SR and CFA stand for the sulfate reduction zone and carbonate fluorapatite, respectively. Note that the relative thickness of the various redox zones does not reflect the conditions encountered in this study (see text). Inspired from various sources, including Aggett and O'Brien (1985); Sullivan and Aller (1996).

The closer the redox boundary is to the sediment-water interface the less likely the sediment is to concentrate authigenic Mn-oxides and trap As(III) diffusing from deeper in the sediment. This is reflected by a progressive decrease in the total and CDB-extractable As, P, Fe, and Mn concentrations in the surface sediments of the Saguenay Fjord interior basin stations as we move landward and sedimentation rates increase (or oxygen penetration depths decrease) (Figures 3c,d,e).

5. Conclusions

On the basis of our observations, it appears that both As and SRP are scavenged by settling particles in the marine waters of the Saguenay Fjord. Under the suboxic conditions which are found a few centimeters below the sediment-water interface in the Saguenay Fjord, As and SRP are released to porewaters upon the reductive dissolution of iron oxyhydroxides. Unlike phosphate, arsenate can also be reduced to arsenite. This may explain why we observe arsenic being released to the porewaters before phosphate. In the presence of dissolved sulfide, arsenite coprecipitates with iron sulfides which may serve as temporary or permanent sinks for the arsenic. Under sulfidic conditions, authigenic carbonate fluorapatite may also serve as a sink for phosphate but it usually forms at much slower rates and under more restricted conditions. Once porewater sulfate is exhausted and dissolved iron concentrations are no longer buffered by sulfide, vivianite may precipitate but this would only be observed where organic-rich marine sediments accumulate rapidly, such as at the head of the Saguenay Fjord.

Phosphate and arsenite released to the porewaters under suboxic and anoxic conditions will both diffuse to the sediment-water interface under the established concentration gradients where phosphate will be intercepted, in most part, by iron oxyhydroxides. Arsenic will also be adsorbed to iron oxyhydroxides but it must first be adsorbed and oxidised to As(V) on the surface of manganese oxides which accumulate closer to the sediment-water interface. The efficiency of this trapping mechanism will depend on the thickness of the oxic sediment layer and the accumulation of authigenic Mn/Fe oxyhydroxides. These scenarios, the diagenetic cycles of phosphate and arsenic in coastal marine sediments, are summarised schematically in Figure 7a,b.

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