Seasonal Changes in the Phosphorus-Iron Geochemistry of the St. Lawrence Estuary

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ABSTRACT ■

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The phosphorus-iron partitioning is studied on suspended particulate matter, sampled from October 1983 to May 1985 in the St. Lawrence Upper Estuary. The ratios of the iron hydroxides (Fe_{CDB}) to the inorganic non detrital phosphorus (P_{CDB}) show four different mean values, grouped as "modes". Each mode characterizes a process involving either precipitation of iron with incorporation of P ("flocculation"), release of P during reductive destruction of iron oxides ("desorption"), stasis in the salinity gradient ("equilibrium"), stasis in the freshwater upstream ("fresh water"). Phosphate adsorption actively takes place in the low brackish water of the South Channel. On the other hand, phosphate desorption only occurs via exchange of particulate matter with surrounding marshes. The intense fall erosion of the Cap Tourmente flats by migrating geese represents the major annual input of phosphate-depleted suspended particulate matter to the estuarine mixing zone. The kinetics regulating the subsequent phosphate readsorption appear to be fairly slow.

ADDITIONAL INDEX WORDS: *Phosphorus, iron, geochemistry, St. Lawrence estuary, suspended particulate matter, marsh erosion.*

INTRODUCTION

The estuarine transition between fresh and salt water is commonly associated with a maximum turbidity zone (MTZ). In the St. Lawrence Upper Estuary, this zone is maintained by local sediment erosion or resuspension due to the prevailing highly energetic conditions (SILVERBERG and SUNDBY, 1979; d'ANGLEJAN, 1981; d'ANGLEJAN and INGRAM, 1984). Recently, LUCOTTE and d'ANGLEJAN (1986) showed that seasonal fluctuations in the intensity and the position of the MTZ are mainly determined by the suspended sediment exchanges between the estuary and the marshes of Cap Tourmente region (Figure 1). From May to September, fine sediments are advected over the flats by the tide, the deposition being enhanced by marsh plant growth. A period of intense erosion then coincides with

the destruction of the plant cover by migratory geese.

The uncertainties regarding the reactions of phosphorus adsorption on and desorption from suspended matter and sediment are partly responsible for the problems encountered in estimating the fluvial fluxes of reactive P to the oceans (FROELICH *et al.*, 1982). The "adsorption" of orthophosphates onto iron oxy-hydroxides is closely related to environmental parameters such as salinity, pH, organic matter content and levels of oxidations (STROM and BIGGS, 1982; FROELICH *et al.*, 1982; CARPENTER and SMITH, 1984; SALOMONS, 1985). In addition, the importance of the role played by tidal wetlands in modifying nutrients and heavy metal loading in estuaries needs further consideration (VALIELA *et al.*, 1978; SIMPSON *et al.*, 1983; BOWDEN, 1984).

In this paper, we use the partitioning of particulate phosphorus into several fractions and its association with iron to follow the transformations of the suspended particulate matter
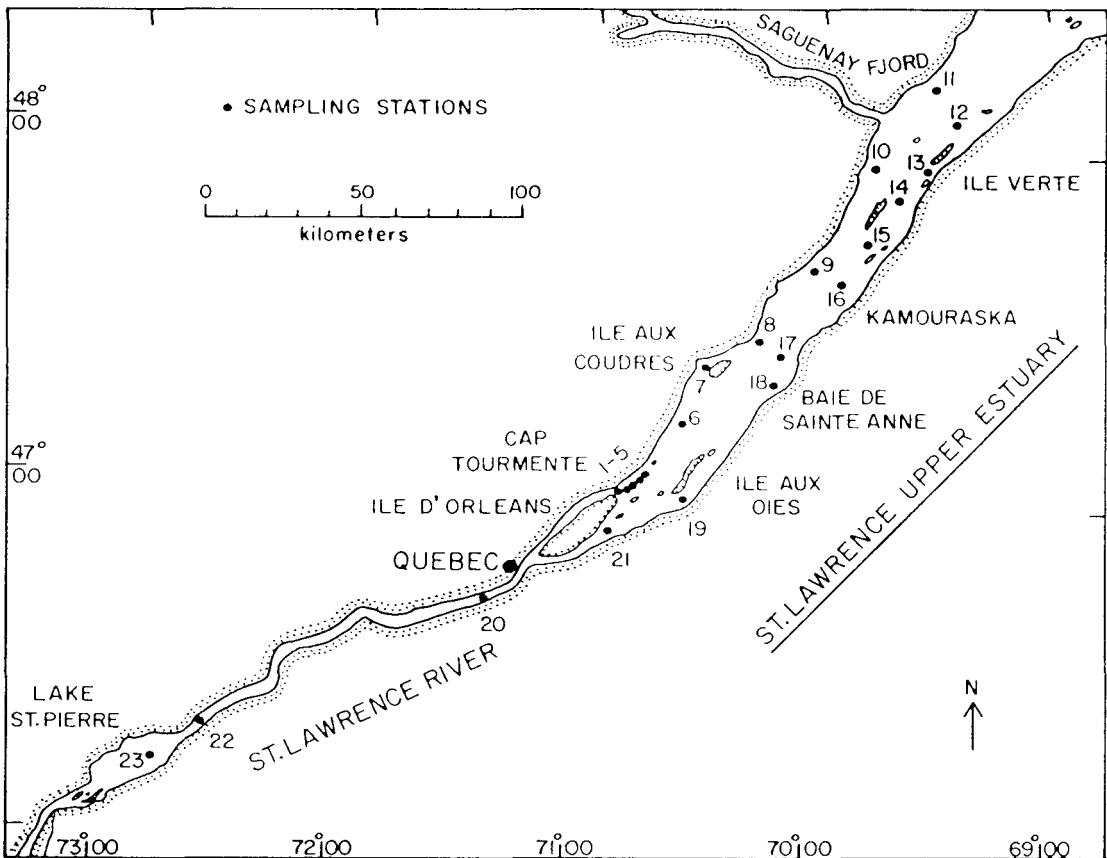
Figure 1.   The St. Lawrence River and its Upper Estuary: Location of the sampling stations.

(SPM) in the St. Lawrence MTZ, as the SPM is carried through the estuarine zone and is subject to exchanges with adjacent flats. This work brings into particular focus the role of the fall erosion of the Cap Tourmente intertidal flats as a major source of phosphate-depleted SPM in the estuarine mixing zone.

MATERIALS AND METHODS

Sampling

A series of 23 stations (Figure 1) in Lake Saint-Pierre and along the North and South Channels of the Upper Estuary were visited repeatedly during 5 cruises in October 1983; June, August and October 1984; and May 1985. The periods were chosen to coincide with the spring run-off, the lowest summer fresh water

discharge, and the presence of the migratory Greater Snow Geese (*Anser caerulescens atlantica*) on the marshes in the fall. The currents, turbidity distributions and sediment transports are described in a previous paper (LUCOTTE and d'ANGLEJAN, 1986). Special emphasis was placed on the sedimentary exchanges between the Cap Tourmente marshes and the adjacent estuarine water (stations 1 to 5, Figure 1). The exact sampling procedures of the turbidity, salinity and the bottom sediments are described in details in the earlier paper. For the study of the SPM, both the near-surface and near-bottom water were sampled by pumping through a polyethylene hose, followed by centrifugation through a continuous-flow de Laval Gyrotester. This process removes at least 95% of the material that can be retained on a 0.45 µm Millipore filter. Both the filtered water sam-

ples and the seston samples were immediately frozen at $-20°C$ and brought to the laboratory, where the seston samples were freeze-dried.

Laboratory Analyses

The dissolved orthophosphate was analysed with a Technicon II Autoanalyser. Some PO_4-P values were also obtained by a colorimetric method (LUCOTTE and d'ANGLEJAN, 1983) for comparison purposes. The precision for the determination of the dissolved P was found to be better than ± 5% at the 95% confidence level.

The partitioning of the various phases of phosphorus present in the suspended matter is to some extent dependent on the type of analytical procedure utilized. Several methods have been tested, and an extraction sequence chosen both for its specificity and reproducibility (LUCOTTE and d'ANGLEJAN, 1985). The citrate-dithionite-bicarbonate ("CDB") method makes it possible to distinguish between 4 phosphorus and 3 iron fractions. The iron-hydroxides extracted by this method and the orthophosphate associated with it will be referred to later as Fe_{CDB} and P_{CDB}. The precision of the method is ± 7% (95% confidence level).

RESULTS

Dissolved Phosphate

As reported earlier (LUCOTTE and d'ANGLEJAN, 1983), the dissolved orthophosphate has a positive linear correlation with salinity throughout the St. Lawrence Upper Estuary. This was interpreted as reflecting the dilution of the enriched waters, upwelled at the head of the Laurentian Channel, with the river inputs. Table 1 gives the regression equations for each sampling period. Very few systematic devia-

tions from the calculated dilution lines were detected among the large number of samples analyzed. The differences between the equations for the various seasons probably reflect only changes in end member values.

In contrast, at the head of the estuary, offshore of the Cap Tourmente marshes (Figure 1), half-hour interval sampling over semi-diurnal tidal cycles showed recurring deviations in orthophosphate values from dilution lines calculated for this area. Although the values during full ebb and flood fall on the regression lines, positive or negative departures greater than the analytical errors were noticed near low tide slack water. As shown on Table 2, these deviations were of two different types. In spring and summer (1984, 1985), a decrease by 0.2 µg-at.L^{-1} persisted at all stations for about two hours, whereas an excess was noticed in October 1983. Significant uptakes of dissolved P were also observed in the South Channel in May 85 and October 84 (Table 3). In contrast, in August 84, the average $PO_4 - P$ concentrations were about 25% higher than the theoretical dilution lines in the entire early mixing zone (Table 3).

Particulate Phosphorus and Iron

The values of the $(Fe/P)_{CDB}$ clustered around four distinct means, each covering a specific location and season. Based on these means, four modes are identified as corresponding to stages of the sorption reaction of P on Fe hydroxides which are often referred to in the estuarine literature: mode 1 represents the P-adsorption on the flocculating Fe hydroxides, mode 2 and mode 3 are respectively taken as indicative of equilibrium and desorption, while mode 4 characterizes pre-mixing conditions existing in the river above the estuary. Table 4 gives the four modes based on the five sampling periods. The first three modes are significantly different

Table 1. *Linear regressions between dissolved $PO_4 - P$ ($\mu g - at.L^{-1}$, and Salinity (° /oo) in the St. Lawrence Estuary.*

Season	Equation	Number of Samples	Correlation Coefficient
05/85*	P = 0.028 S + 0.35	64	0.74
06/84	P = 0.032 S + 0.40	26	0.93
08/84*	P = 0.016 S + 0.57	28	0.79
10/83	P = 0.010 S + 0.45	8	0.62
10/84	P = 0.028 S + 0.36	6	0.99

*Cap Tourmente values not included.

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Table 2. *Systematic deviations of the dissolved $PO_4 - P$ ($\mu g - at.L^{-1}$) (differences between the measured values and those deduced from the regression lines) at Cap Tourmente around low tide, with their approximate duration over a tidal cycle.*

Type	Season	Station	Systematic Deviation	Duration (Hours)
1	05/85	2	− 0.2	6
		5A	− 0.2	6
1	06/84	2	− 0.2	2
		4	− 0.2	2
1	08/84	2	− 0.2	1
		5	− 0.2	2
2	10/83	2	+ 0.3	2
		4	+ 0.05	1

Table 3. *Significant $PO_4 - P$ deviations ($\mu g - at.L^{-1}$) with respect to the values deduced from the dilution line, for stations of the early mixing zone. (*) For $S°$ / oo $\leqslant 1°$ / oo only, average 4.5° / oo.*

Season	Station	Theoretical Value	Mean Value
05/85	19	0.35	0.08
	21		0.06
08/84	2/5(*)	0.57	0.76
	19	0.57	0.72
10/84	20	0.36	0.26
	19	0.36	0.21

Table 4. *SPM Modes of distribution according to the $(Fe/P)_{CDB}$ ratios.*

Mode	Mean $(Fe/P)_{CDB}$	Standard Deviation	Number of Samples	Suggested Process
1	10.1	2.1	15	Flocculation
2	14.1	1.6	65	Equilibrium
3	18.5	2.3	18	Desorption
4	17.9	4.2	5	Fresh water

from each other at the 95% confidence level (two sided level "α-test") applied to their respective means. Mode 4 is also significantly distinct from the three others and in particular from mode 3, as it groups exclusively samples collected above the limit of the salt intrusion. The interpretation given to the four modes is supported by results of laboratory experiments in which samples of SPM and water from the estuary were reacted with each other (LUCOTTE and d'ANGLEJAN, 1987). The geographical and temporal variation of the modes, along with the significant deviations of the dissolved PO_4 with respect to the dilution line, are recapitulated in Figure 2.

The detailed partitioning of particulate P and Fe into their various forms is shows for each mode of association and for the various months of sampling on Table 5. For each month, only the average values for the stations belonging to the same mode are listed, with the standard deviation in brackets. For all sampling months, mode 1 is characterized by the lowest recorded $(Fe/P)_{CDB}$ ratios (range: 6.9 to 11.6). This mode is called the "adsorption" mode as the low values of the ratios result from high concentrations of P_{CDB}. It occurs in the low brackish zone (salinity $\leqslant 1‰$) of the South Channel most of the year, and further upstream when the run-off is minimal (Figure 2). The same mode was never clearly identified in the North Channel, for reasons which are given below. The distribution of this mode coincides with the region of flocculation, the main process which affects the SPM as it reaches salt water (BEWERS and YEATS, 1979).

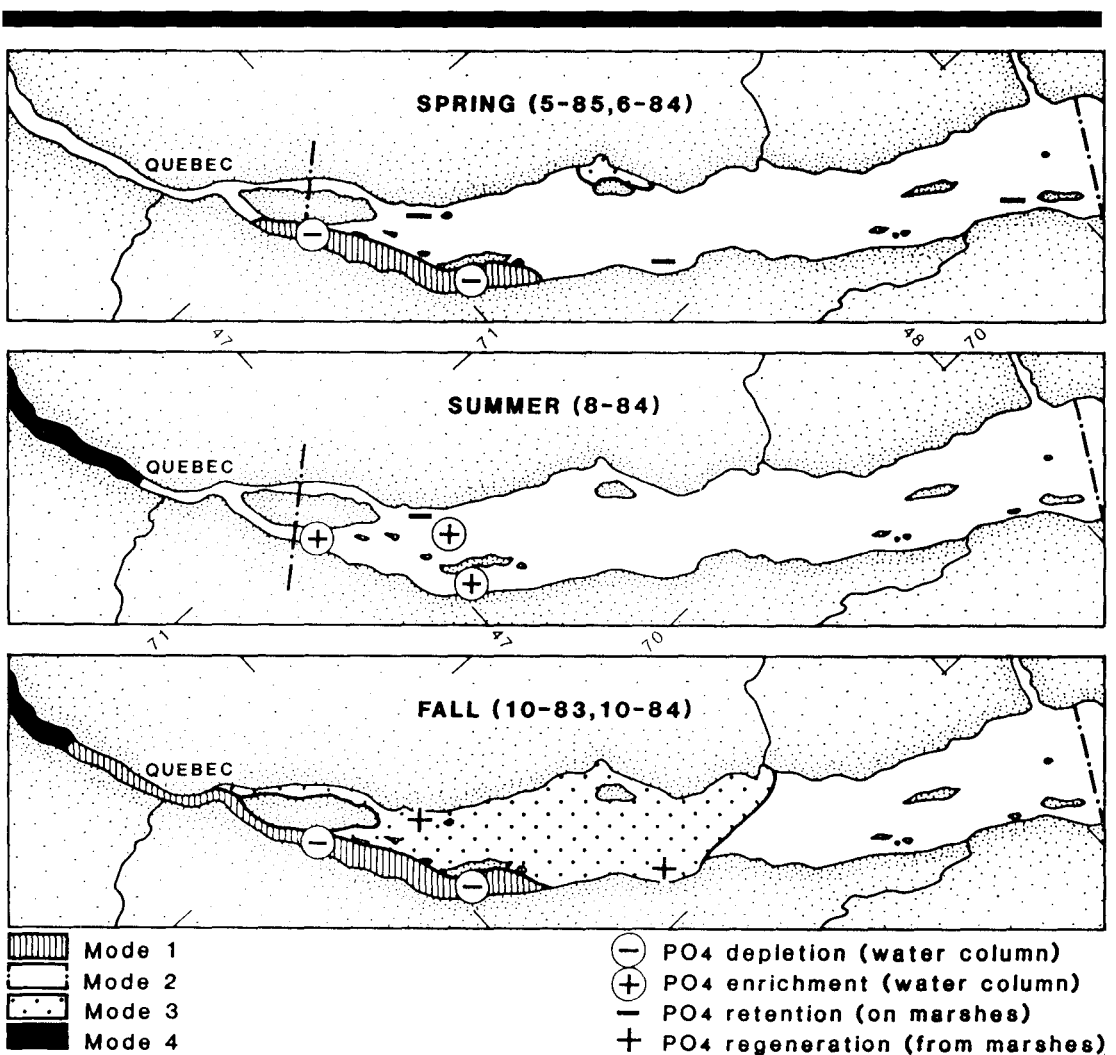Mode 2 prevails most of the time throughout the estuary (Figure 2). Only in the fall, it

Figure 2. Approximative geological and temporal variation of the $(Fe/P)_{CDB}$ modes, including the significant deviations of the dissolved PO_4 with respect to the dilution line.

appears much further seaward. The $(Fe/P)_{CDB}$ ratio fluctuations are minimal (13.3 to 14.3) and the P_{CDB} fraction remains quite constant (13.6 $\mu g\text{-}at.g^{-1}$, s = 1.3), suggesting that sorption of P on Fe has reached an equilibrium value. Only once (May 1985) was a slight significant increase in the $(Fe/P)_{CDB}$ ratio with the salinity observed ($(Fe/P)_{CDB}$ = 0.082 S + 13.83, r = 0.81, n = 6). It is interesting to note that this "equilibrium" ratio corresponds to values reported for marine SPM and sediments (DE LANGE, 1986).

Mode 3 suggests "desorption", being characterized by very high $(Fe/P)_{CDB}$ ratios (16.2 to 19.8) caused by a significant drop in the P_{CDB} fration (10.8 $\mu g\text{-}at.g^{-1}$, s = 1.0). It is centered offshore of the Cap Tourmente marshes in the fall, its relative importance decreasing downstream (Figures 1 and 2). SPM with similar $(Fe/P)_{CDB}$ values was also found locally at the bottom of the Ile aux Coudres Passage in May 85 (Figures 1 and 2).

Mode 4 is typical of the SPM found in the fresh water zone of the St. Lawrence. Both the

Table 5. *Seasonal partition of suspended particulate matter classified under the four modes: the P and Fe values* ($\mu g - at.g^{-1}$)
are followed by their standard deviations in brackets. "n" is the number of samples analysed for each season.
(*) P_{Ex}, P_{Org}, and P_{CDB} respectively represent the particulate exchangeable P, organic P, apatite P and orthophosphate, whereas Fe_{CDB} and Fe_{Lith} stand for iron hydroxides and lithogenous iron (Lucotte and d'Anglejan, 1985).

(*) P_{Ex}	P_{Org}	P_{Ap}	P_{CDB}	Fe_{CDB}	Fe_{Lith}	$(Fe/P)_{CDB}$
MODE 1, FLOCCULATION						
05/85; Stations 19, 21; n = 4.						
3.6 (0.5) 8.5 (0.1)		20.5 (0.4)	22.5 (0.4)	173 (4)	550 (16)	7.7 (0.2)
06/84; Station 19; n = 2.						
4.4 1.3		22.2	20.1	139	616	6.9
10/84, Stations 19, 20, 21; n = 6.						
1.6 (0.3) 6.0 (0.7)		23.0 (2.0)	14.3 (1.5)	161 (18)	660 (24)	11.6 (1.1)
MODE 2, EQUILIBRIUM						
05/85; Stations 2, 5, 6, 12, 13, 15, 17; n = 26.						
0.9 (0.4) 6.0 (0.7)		24.0 (2.6)	14.0 (1.2)	196 (24)	724 (75)	14.3 (1.4)
06/84; Stations 2, 4, 6, 9, 14, 15, 16, 17; n = 18.						
0.9 (0.5) 2.8 (2.2)		23.3 (1.9)	13.3 (2.0)	172 (22)	617 (99)	13.3 (1.5)
08/84; Stations 2, 5, 6, 7, 9, 11, 12, 13, 15, 17, 19; n = 23.						
0.8 (0.3) 4.9 (1.2)		24.7 (1.7)	14.4 (1.8)	190 (21)	706 (59)	13.4 (1.4)
10/84; Stations 9, 12, 13, 15, 17; n = 13.						
0.6 (0.1) 4.7 (1.0)		22.9 (1.6)	13.0 (1.2)	188 (10)	738 (25)	14.3 (0.8)
MODE 3, DESORPTION						
05/85; Stations 7 (surface), 7 (bottom), 9; n = 8.						
0.6 (0.2) 5.8 (1.1)		23.1 (2.2)	13.0 (2.4)	229 (23)	790 (79)	17.0 (1.2)
10/84; Stations 2, 5, 6, 7; n = 17.						
0.8 (0.3) 4.6 (0.9)		24.2 (1.5)	10.4 (1.1)	176 (10)	687 (43)	17.2 (1.6)
10/83; Stations 2, 4, 6, 7; n = 11.						
0.2 (0.1) 5.9 (0.9)		23.7 (1.6)	11.1 (0.8)	218 (22)	684 (45)	19.8 (2.1)
12/84; Station 21 n = 4.						
0.5 (0.1) 5.7 (1.1)		22.6 (2.5)	12.1 (2.2)	196 (32)	698 (65)	16.2 (0.5)
MODE 4, FRESH WATER						
08/84; Station 20; n = 2.						
1.5 5.9		24.9	9.9	159	734	16.2
10/83; Stations 22, 23; n = 3.						
0.3 (0.2) 5.2 (2.1)		23.8 (0.9)	7.8 (2.7)	140 (18)	593 (80)	19.2 (5.4)

Fe_{CDB} and P_{CDB} are low (140 to 159 μg-at.g^{-1}; and 7.8 to 9.9 μg-at.g^{-1} respectively). Its downstream limit fluctuates with the seasonal intensity of the fresh water run-off of the St. Lawrence River.

The partitioning between the particulate P and Fe is fairly uniform within each of the four modes. In all four, the "apatite" P fraction (P_{Ap}) which represents the inorganic detrital component of the total P (LUCOTTE and d'ANGLEJAN, 1985) occurs in a narrow range of concentrations (20.5 to 24.9 μg-at.g^{-1}), and this independently of the season.

In contrast, the organic phosphorous fraction, P_{Org}, presents the largest fluctuations within as well as between each month of observation and shows no significant correlation with salinity. From June to October, the average particulate P_{Org} fraction in the estuary doubles from 2.8 μg-at.g^{-1} (s = 2.2) to 4.7 μg-at.g^{-1} (s = 1.0). Very large differences also exist between the mean spring values of 1984 and 1985: the May 1985 concentrations, 6.0 μg-at.g^{-1} (s = 0.7) are about triple of those of June 84. Primary production in the upper estuary being low (BAH and LEGENDRE, 1985), the P_{Org} fraction is highly dependent on the spring and summer supply of plant detritus from the river as well as from local marshes (TAN and STRAIN, 1979). This supply is expected to increase in the

course of the summer, and to fluctuate from year to year.

In both modes 2 ("equilibrium") and 3 ("desorption"), the Fe_{CDB} fraction is linearly correlated with the P_{Org} fraction in all months of sampling except June (Fe_{CDB} = 27.04 P_{Org} + 54.36, r = 0.824, n = 31). Thus, the Fe_{CDB} levels reach their maximum, 230 μg-at.g^{-1}, in May 1985, the peak period for the P_{Org} fraction. In June, low values occur for both Fe_{CDB} and P_{CDB}; the ratio still falls within mode 2, but does not correlate with P_{Org}.

The mean value for the detrital iron in the SPM, Fe_{Lith}, is always near 79% (s = 1.76) of the particulate total iron content, $Fe_{CDB} + Fe_{Lith}$, whatever the season or the salinity, in both the surface and bottom layers. The values of the P_{CDB} fraction are quite constant within each of the four modes for a given season. Small fluctuations might be undetected because of analytical error.

Finally, the levels of exchangeable phosphorus, P_{Ex}, are always smaller than 1 μg-at.g^{-1}, that is to say negligible, except in the low brackish zone in the spring where they reach 3 to 4 μg-at.g^{-1}.

In order to compare the estuarine SPM with its immediate geochemical sources and sinks, we analysed by the same methods samples taken from outcrops of Champlain Sea clay submerged in the estuary as well as recent sediments (Table 6). We also examined rock fragments extracted from residual sands in the estuary, which are derived from Appalachian rocks to the South (d'ANGLEJAN and LUCOTTE, in preparation). Sediments from Lake Saint-Pierre (0–86 cm depth in sediment) and Champlain Sea clays from near Ile aux Oies (Figure 1) have $(Fe/P)_{CDB}$ ratios characteristic of mode 4 (fresh water). Ratios typical of mode 3 (desorption) are found in marsh sediments at depths between 9 and 17 cm below the surface in July, but occur up to the surface in October. Similar ratios were found along the entire length of a sediment core (75 cm long) made up of recently deposited brown silt collected off Ile aux Oies in June 1984. On the other hand, summer deposits from the Cap Tourmente marshes collected at 3 to 7 cm below the marsh surface belonged to mode 2 ("equilibrium"). The same mode was also found in the sand size rock fragments of the Kamouraska platform (Figure 1).

An interpretation of these differences in relation with the SPM fluctuations is given below.

DISCUSSION

The distributions of the dissolved phosphate and of the various fractions of particulate P and Fe in the SPM enable us to point out seasonal patterns (spring, summer and fall) existing between these two elements. These distributions can then be used to interpret the controlling reactions associated with the passage of the SPM through the maximum turbidity zone and its transport downstream.

Seasonal Patterns: Spring

The SPM as well as the surface sediments above the salt intrusion are characterized by low iron hydroxide (Fe_{CDB}) concentrations (mode 4 in both Tables 5 and 6). In the estuary brackish zone, the Fe_{CDB} in the SPM increases above values of 140 μg-at.g^{-1}; this change is suggestive of iron hydroxide precipitation during early estuarine mixing (SHOLKOVITZ et al., 1977; SHOLKOVITZ, 1978; BOYLE et al., 1977; LI et al., 1984). The reaction must reach completion before the salinity reaches 5 ‰ as no systematic additional increase of Fe_{CDB} occurs at higher salinities.

In May 1985 as well as June 1984, extreme values (20.1 to 22.5 μg-at.g^{-1}) of P_{CDB} are recorded in the South Channel at both stations 19 and 21. This 40% to 50% P_{CDB} increase above the concentrations observed in the fresh water zone, causes a sharp drop of the $(Fe/P)_{CDB}$ ratios down to 6.9 and 7.7, values typical of mode 1 (adsorption). In May 85, at the same stations, the orthophosphate concentrations reached only 20% of the theoretical dilution values for these South Channel stations. This suggests phosphorus adsorption on the freshly precipitated iron hydroxides (KROM and BERNER, 1980; STROM and BIGGS, 1982). No similar drop in orthophosphate was observed in June 1984.

By contrast, in similarly low brackish zones of the North Channel off Cap Tourmente (stations 2, 4 and 5), no significant increase in the P_{CDB} of the SPM was found during either May 1985 or June 1984. Fairly constant $(Fe/P)_{CDB}$ ratios (13.0, s = 0.8) throughout this region suggest that some equilibrium (mode 2) has

Table 6. *P and Fe partitions ($\mu g - at.g^{-1}$) in solid matter other than SPM, with their standard deviations; (1) 07/83; Marshes of Cap Tourmente, average of the 3-5-7 cm deep subsamples of a 17 cm − long core; (2) Crushed rocks of Kamouraska, magnetic separation; (3) 07/83; Marshes of Cap Tourmente, average of the 9-13-15-17 cm deep subsamples of a 17 cm-long core; (4) 10/83; Cap Tourmente, station 1, average of 4 subsamples from a 75 cm-long core; (5) 06/84; Station 19, average of 5 subsamples from a 40 cm-long brown clay core; (6) 10/83; Lac St-Pierre, average of 7 subsamples from a 86 cm-long core; (7) 06/84; Station 19, Top 5 cm of a compacted Champlain sea clay core.*

MODE 2							
Samples	P_{Ex}	P_{Org}	P_{Ap}	P_{CDB}	Fe_{CDB}	Fe_{Lith}	$(Fe/P)_{CDB}$
(1)	0.1 (0.1)	3.1 (0.1)	28.7 (1.6)	10.2 (1.2)	139 (10)	587 (6)	13.3 (2.5)
(2a)	1.8	1.7	8.7	73.5	946	645	12.9
(2b)	3.4	1.4	6.9	45.8	574	576	12.5

MODE 3							
Samples	P_{Ex}	P_{Org}	P_{Ap}	P_{CDB}	Fe_{CDB}	Fe_{Lith}	$(Fe/P)_{CDB}$
(3)	0.3 (0.1)	1.7 (0.7)	25.0 (2.7)	5.0 (1.6)	93 (28)	527 (122)	18.7 (0.6)
(4)	0.8 (0.1)	3.3 (0.2)	28.4 (0.7)	10.2 (0.8)	207	656	18.7
(5)	0	3.3 (0.3)	26.0 (0.6)	10.0 (0.6)	162 (6)	694	16.3 (0.5)

MODE 4							
Samples	P_{Ex}	P_{Org}	P_{Ap}	P_{CDB}	Fe_{CDB}	Fe_{Lith}	$(Fe/P)_{CDB}$
(6)	0.8 (0.1)	2.1 (0.5)	25.0 (3.6)	4.3 (1.1)	138	667	25.1
(7)	0.2	2.8	17.5	5.3	142	1268	26.9

been reached in the SPM between P and Fe. LUCOTTE and d'ANGLEJAN (1986) have shown that SPM seasonal exchanges between the North Channel and the tidal flats and marshes of the Cap Tourmente platform are the dominant process in the area. These active exchanges of older SPM temporarily stored on the flats mask the reaction products of new suspended material introduced to the region from the river. On the other hand, the recurrent decrease in orthophosphate noted for two hours or more around low tide at stations 2, 4 and 5 near the edge of marshes can likely be interpreted as phosphate retention by macrophytes or benthic diatoms. This drop in orthophosphate below the expected dilution line is only detectable before the ebbing waters have been mixed with offshore water by the early flood tide. Similar indications of phosphate retention were also observed during the spring at low tide off the flats of Baie de Sainte-Anne and those of Ile Verte (Figure 1).

An exception to the downstream equilibrium in phosphate exchange between the SPM and the water is found in a turbid layer located below 25 m depth in the Ile aux Coudres passage in May 85 (Figures 1 and 2). Turbidity levels at the bottom of station 7 are at least 5 times what they are in the surface water, with (Fe/P)$_{CDB}$ ratios systematically higher by 2 to 5 units. Because of the low P_{CDB} concentrations

(under 10 μg-at.g^{-1}; 30% less than in the mode 2 SPM), these ratios reach values of 17.2 which fall into mode 3 ("desorption"). The origin of this layer is uncertain.

Summer

Most of the SPM found in the estuary in August 1984 shows evidence of equilibrium (mode 2). The "flocculation" mode (1) is absent or undetectable in the early mixing zone of either the South or the North Channels. There is also no indication of orthophosphate uptake from the dissolved P dilution line for station 19 in the South Channel. Off the Cap Tourmente marshes, in the North Channel, a systematic decrease in dissolved P at the end of the ebb, as it was in the spring, indicates that P retention on the marshes is still active.

Evidence of mode 3 SPM ("desorption") neither could be found in the MTZ. This is to be expected since massive erosion of the seasonal marsh deposits on Cap Tourmente has not yet started. However, below an "equilibrium" zone 9 cm deep, these deposits were sharply depleted in P_{CDB} (5.0 μg-at.g^{-1}, s = 1.6; Table 6), while the interstitial water was highly enriched in dissolved PO$_4$ (3 to 4 μg-at.L^{-1}, about 10 times the average concentrations of the overlying water). This is suggestive of phosphate liberation under slightly reducing conditions

(LYONS et al., 1980; CARIGNAN and FLETT, 1981; SALOMONS, 1985). The rate of upward diffusion of this desorbed P, enhanced by plant irrigation (CARIGNAN and KALFF, 1982), is unknown, but may be at the origin of the marked dissolved P increase, 15 to 25% above the theoretical dilution value (Table 3), at stations 19, 2 and 5.

Fall

In the fall, the SPM shows instances of the four $(Fe/P)_{CDB}$ modes (Figure 2). The iron flocculation (transition from mode 4 to mode 1) is clearly observed in the South Channel at stations 20, 21 and 19 as the concentrations of Fe_{CDB} reach about 160 μg-at.g^{-1}. The simultaneous phosphate adsorption is reflected by the highest P_{CDB} values in the estuary (14.3 μg-at.g^{-1} as compared to 13.0 μg-at.g^{-1} on average). As a result, the fall $(Fe/P)_{CDB}$ ratios (11.6) are the lowest in this region. Phosphorus uptake on the SPM is confirmed by a drop of the ambient orthophosphate below the theoretical dilution value at station 19.

The origin of the high turbidity levels in the MTZ off Cap Tourmente can be linked to the sudden and massive erosion of the marshes in October (LUCOTTE and d'ANGLEJAN, 1986). The distribution of the mode 3 (desorption) SPM coincides with the core of the turbid zone. The surface sediments on the flats and the SPM in the estuary immediately offshore of the flats are similar, being characterized by very high $(Fe/P)_{CDB}$ ratios due to very low P_{CDB} concentrations. The influence of this phosphate-poor SPM is felt quite far downstream of the marshes, as the high ratios found at stations 6 and 7 indicate. The marked increase in the dissolved phosphate concentrations at low tide directly offshore of the marshes suggests the possible release of phosphate-rich interstitial water from eroding marsh sediments. This effect disappears due to mixing when currents are stronger. Similar observations were made at low tide at station 17 in Baie de Sainte-Anne (Figures 1 and 2), possibly as a result of erosion on the nearby flats.

Controlling Reactions

After the iron oxy-hydroxide precipitation has reached completion in the low salinity zone,

Fe_{CDB} is found to be positively correlated with the seasonal levels of the particulate organic phosphorus, P_{Org}, everywhere in the estuary. Furthermore, evidence of adsorption coincides with a noticeable drop in dissolved phosphate only under conditions of marked increase in P_{Org} levels (May 1985 and October 1984). This is in agreement with the role which is known to be played by organic matter, particularly humic substances in iron colloid precipitation (RASHID, 1974; BOYLE et al., 1977; MANTOURA et al., 1978; POUTANEN, 1985).

The early "flocculation" of Fe_{CDB} rich colloids coincides with high P_{CDB} levels in the South Channel, around Ile aux Oies. This process, described as phosphorus "adsorption", is only detected in this region because it is not directly influenced by sediment exchanges with intertidal marshes. Also, the South Channel is the main route for the St Lawrence River outflow.

The transition between the early mixing zone and the core of the MTZ is sudden and results in the rapid dilution of actively reacting particles by older more inert SPM. This latter material (mode 2) is deficient in P_{CDB} with respect to the "flocculation" mode. Mode 2 SPM is extensively found throughout the Upper Estuary, irrespective of the season and appears to be quite stable. It is interesting to note that rock fragments in the extensive sand deposits of the Kamouraska platform, a potential additional source of SPM, (d'ANGLEJAN & LUCOTTE, in preparation) have already $(Fe/P)_{CDB}$ ratios characteristic of mode 2 (equilibrium) (Table 6).

No evidence for a rapid buffer reaction keeping the dissolved orthophosphate concentrations constant by desorption from or adsorption on the SPM is found, unlike that reported for other estuaries (POMEROY et al., 1965). Also, no indication of definite P desorption with salinity increase is detected, as observed by LISS (1976), STIRLING and WORMALD (1977), STROM and BIGGS (1982), in spite of the minor desorption found in May 1985 (see above). On the other hand, the downstream pH increase in the St. Lawrence Upper Estuary (from 7.2 to 7.6) is too small to induce a noticeable phosphate desorption as in other estuaries (CARPENTER and SMITH, 1984).

The "equilibrium" mode is the result of the relatively long mean residence time (about one year) of the suspended particles in the MTZ. Internal adjustments in the P_{CDB} concentra-

tions are made seasonally since the $(Fe/P)_{CDB}$ ratios remain constant in spite of changes in Fe_{CDB} levels, which fluctuate with the abundance of P_{Org}.

The physico-chemical factors and the kinetics regulating the phosphate readsorption on the phosphate depleted SPM from the marsh are still unknown. After their return to the MTZ in October, the marsh sediments do not reequilibrate readily: high $(Fe/P)_{CDB}$ ratios were found in the SPM as far as 100 kilometers downstream of the marshes. These high ratios persisted offshore of Ile d'Orléans (station 21) in December 1984, two months after the massive erosion of the marshes. In the spring, they could still be found in the deep SPM of the Ile aux Coudres Passage (Table 5) and within fine muddy deposits of the South Channel near Ile aux Oies (Table 6). These two sites probably represent major areas of winter storage for sediments eroded from the marshes in October. The reactions leading towards a state of equilibrium seem therefore to be fairly slow.

CONCLUSIONS

This study has shown how the reactions between Fe and P in the SPM of the St. Lawrence Estuary are controlled by the dynamics of sediment exchanges between the MTZ and marginal tidal flats.

In the spring, the MTZ extends throughout most of the Upper Estuary, being entrained downstream by the peak freshwater run-off. At this time of the year, the marshes such as those of Cap Tourmente, start storing suspended sediments which have reached adsorption equilibrium with respect to dissolved phosphate. Evidence of dissolved orthophosphate consumption on the marsh is found only near low slack tide, when mixing of ebbing water with the estuary is minimal.

As the year goes by, the extent of the MTZ decreases, while the turbidity levels sharply increase around Cap Tourmente. Below 5 cm sub-bottom depth, the freshly deposited sediments are losing P_{CDB} through desorption in slightly reducing environments. These P_{CDB} depleted solids are returned to the core of the MTZ by tidal currents during October when the marsh vegetation and the summer deposits are destroyed by the migrating snow geese. P-read-

sorption appears to be fairly slow, and is not completed until the following spring.

In addition, the SPM in the MTZ is also subject to changes in P-Fe partitioning when river derived solids enter the low brackish zone of the South Channel. Precipitation of iron oxyhydroxides is observed in this zone and appears to be related to the seasonal abundance of particulate organic P. Orthophosphate "adsorption" on these precipitates also takes place preferentially at times when particulate organic matter is high.

No buffer reaction keeping constant the dissolved P in the estuary by adsorption/desorption process on/to the MTZ was evidenced.

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□ RÉSUMÉ □

Les rapports des hydroxydes de fer et des phosphates associés de la matière en suspension de l'estuaire moyen du Saint-Laurent ont permis de caractériser 4 processus: soit la précipitation du fer avec incorporation de P, soit la libération de P lors de la réduction des oxydes de fer, soit un mode d'équilibre dans la zone de transition saline, ou soit enfin un mode caractéristique des eaux douces. Alors que l'adsorption des phosphates n'est mesurable que dans les très faibles salinités du Chenal sud, leur désorption est uniquement associée aux dépôts sédimentaires saisonniers sur les marais avoisinants. L'érosion des battures du Cap Tourmente en automne par les oies représente le principal apport de particules appauvries en phosphate à la zone de turbidité de l'estuaire.