



Preliminary study of the heavy metal chemistry of schorre and slikke clay deposits in the Brouage region: concentration of Cd, Sn and As related to P

Bruce VELDE

*Laboratoire de Géologie, UMR 8538 CNRS Ecole Normale Supérieure
24 rue Lhomond, 75231 Paris, E-mail: velde@geologie.ens.fr*

Abstract : Mineralogical and chemical analysis (major and minor elements, such as heavy metals) of sediments in the Brouage area indicates that the clay-rich muds deposited were derived from the major coastal rivers, the Gironde and the Loire. Certain clays, high smectite content mixed layer minerals, are under-represented suggesting loss to the open ocean. Relatively important related concentrations of Cd, As, Zn and Sn, higher than those in river sediments of the area, suggest a concentration increasing with time in coastal material. It is of course possible that coastal contamination, independent of river input, has contributed to these concentrations. A second experiment involves destruction of organic matter in the clay fraction sediment samples which shows a greatly increased phosphorous concentration and a strong relation to Cd and As. This action could have implications for biological cycles in the mudflat environment.

Résumé : *Etude préliminaire des métaux lourds de la vase du schorre et de la slikke de la région de Brouage : concentration en Cd, Sn et As en relation avec le phosphore.* L'analyse minéralogique et chimique de quelques éléments en trace, notamment des métaux lourds, indique que les argiles déposés dans les vasières sont d'origine estuarienne de la Gironde et de la Loire, mais que les fractions fines contenant des smectites sont moins abondantes. Par contre, les relativement fortes concentrations des métaux lourds Cd, As, Zn et Sn sont évidentes. Une deuxième expérience par destruction de la matière organique met en évidence une forte teneur en phosphore indicatrice d'une affinité entre Cd et As.

Keywords: Heavy metals; Estuarine clay; Phosphorous; Mudflat.

Introduction

The objective of the study was to study the spatial distribution of sediments and certain heavy metal elements along the Atlantic Coast in the Brouage region and to compare these results with compositions and mineralogy in

the major source rivers of the Gironde and the Loire. The majority of the sites (6) were sampled between the Gironde and Charente rivers. Clay mineralogy was determined as well as major element and some minor elements with the aim of determining whether or not clays are carriers of the heavy metals. Comparisons are made with classical studies of elements in suspension or dissolved in river waters.

The question posed is how much heavy metal material is associated with sedimented clays transported along a tidal coastal deposition area? These materials are largely

ignored in studies of river and ocean contamination in that such studies concentrate on the dissolved or ultrafine material in suspension. Clays, omnipresent, can be carriers of material as adsorbed species. Such material is subject to sorption (concentration) and de-sorption effects depending upon the chemical environment that they encounter. Since clays are sorbers and constitute the substrate of organic-clay assemblages forming the food input for much animal life on littoral sites, such an approach might prove to be important.

Materials and Analytical Methods

The sites samples were as follows (Fig. 1):

- 1 site 2 (Université de La Rochelle) mudbank off of Brouage (slikke)
2. confluence of the Brouage river and the bay at the intersection of shore and slikke (Brou 1, 2, 3)
- 3 Port de Barques (mouth of the Charente river, shore)
- 4 Soubise (Charente river bank)
- 5 Saint Vaize, Charente river above the control dam at Saint Savenien (fresh water site)
- 6 Gironde river bank (Saint André de Cubzac)
- 7 Samples from the slikke in the baie de l'Aiguillon (north of La Rochelle)
- 8 River bank sediment at the mouth of the Loire river (Paimboeuf)

All sites except number 5 are influenced by salt water tidal deposition effects but sites 6 and 8 are dominated by river sediment inputs. Vertical sampling was effected by using a 50 cm long 10 cm diameter PCV tube pushed into the sediment and extracted.

Attention was centered on the clay fraction in that this the most sorptive part of sediments (containing the clays and organic matter). Several sites were sampled at multiple depth points. Numbers 1 = 1-5 cm depth, 2 = 5-10 cm, 3 = 10-15 cm, etc.

Certain samples were treated with 30% H_2O_2 solutions in the clay fraction ($<2\mu m$) to remove organic matter in the hopes of determining the elements fixed by the organic fraction of the clay samples.

X-ray Diffraction

Mineralogical identification was effected using a numerical output of oriented material subjected to copper radiation. The composite curves were decomposed using the methods of Lanson (1997) as well as identification criteria proposed therein and by Righi et al. (1995). Peak positions and peak surface areas can be calculated using these methods in order to compare the phases present from one sampling point to another.

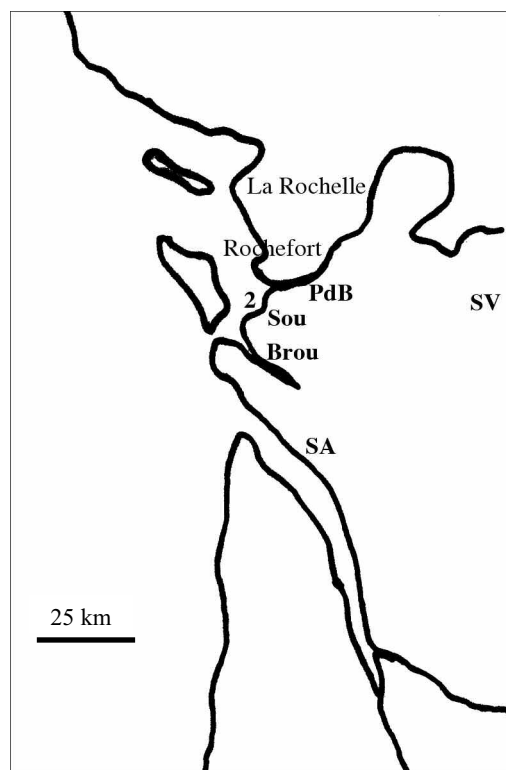


Figure 1. Sketch map of sampled sites. SV = SaintVaise, SA = Saint André de Cubzac, Brou = Brouage, Sou = Soubise, PfB = Port des Barques, 2 = Mud flat sampling site.

Figure 1. Carte des sites échantillonnés. SV = SaintVaise, SA = Saint André de Cubzac, Brou = Brouage, Sou = Soubise, PfB = Port des Barques, 2 = Mud flat sampling site.

Chemical analysis

24 sub-samples of clay fraction of the site 2 sample were compacted into 6 mm diameter and 2 mm thick disks mounted on glass slides are subjected to LA ICP-MS (laser ablation, induction coupled plasma excited mass spectrometer analysis) treatment for the minor elements and X-ray fluorescence analysis of major elements under SEM (scanning electron microscope, X-ray fluorescent analysis) treatment. Both methods used glass standards of known compositions. The SEM method was analyzed statistically comparing clay and glass sample analysis (Fig. 2). It is clear that the statistical variation for both methods is a function of elemental abundance (total events counted) for major elements with a slightly higher variation for the clay mineral preparations. Samples run for 50 and 200 second accumulation times are shown. Here one can note the interest in using a longer counting time. Basically the reliability of the determinations is related to the square root of the number of counts observed.

LA ICP-MS samples indicated that the more volatile elements such as Pb were un-reliable. Measurements were

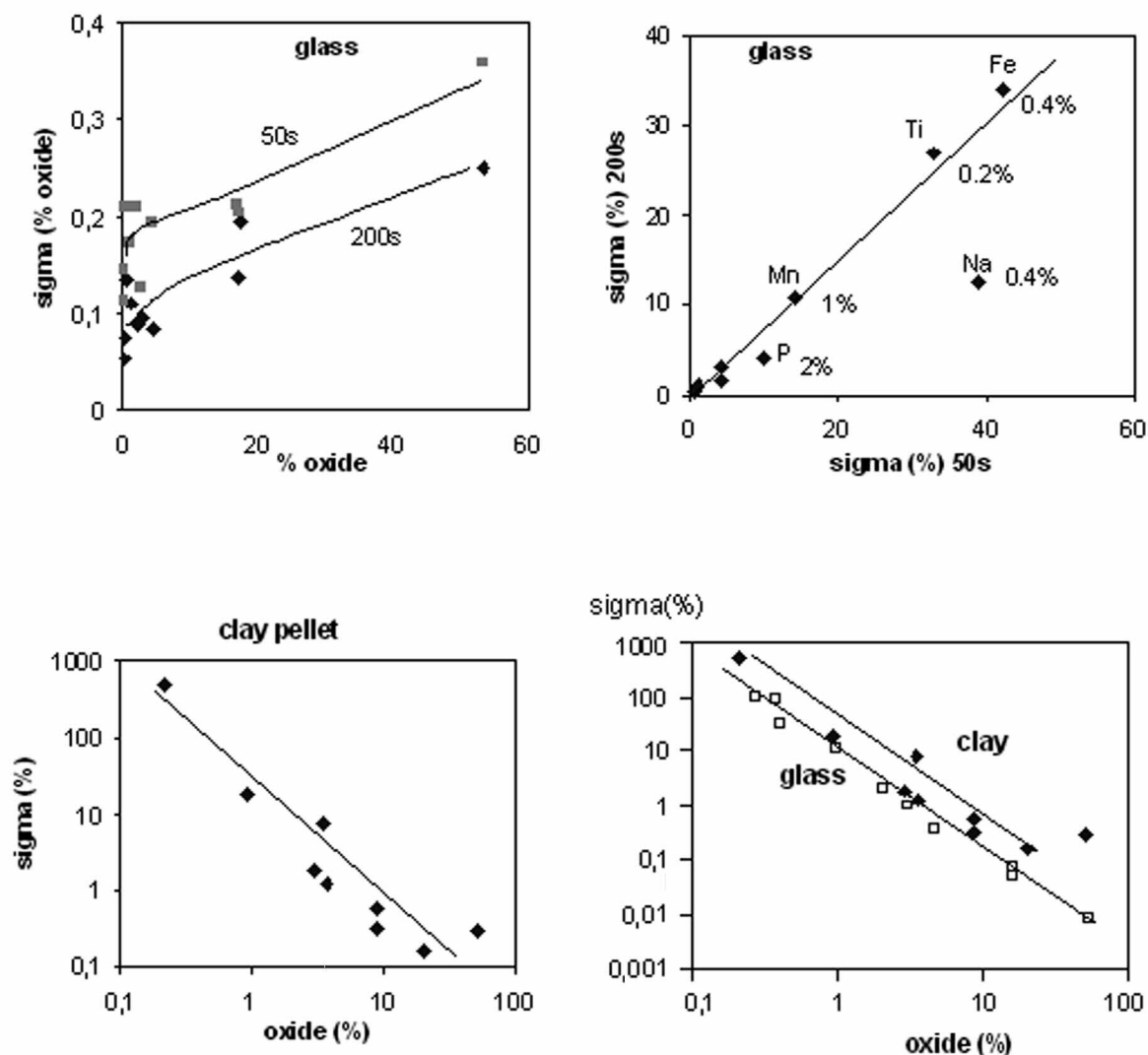


Figure 2. Results of tests on microprobe determinations of major elements in clay assemblages. Comparison is made between a standard glass sample and a clay sample from the Brouage site (10 measurements made on each sample, sigma values calculated from these measurements). Note the clear shift to less precision for the clays which remain within an acceptable range.

Figure 2. Test des microanalyses des éléments majeurs des argiles (10 replicats par échantillon, sigma calculé sur ces 10 mesures). Notez la perte de précision pour les argiles, les déterminations restant raisonnables.

made using a scan mode of near 2 mm length moving at $20 \mu\text{m.s}^{-1}$ on the compacted sample. Multiple runs on a Brouage sample (site 2-1) indicated that the minor element concentrations were reliable to 60 ppm for P, 30 for Mn, 7 for Cu, 22 for Ni, 1 for Co, 20 for Sr, 12 for Sn, 60 for Zn, 15 for Cd, 2 for As, 2 for Cs, 30 for Ba, 300 for Pb, 2 for Th and 0.3 for U. In general the abundances of the elements observed in the samples reported were well above the reliability threshold. A notable exception is Pb which is not reported.

Results

X-ray diffraction (mineralogy of clays)

The clays contained generally four phases; kaolinite, vermiculite-chlorite, illite and two mixed layer minerals. Our interest here lies in the minerals susceptible to be affected by chemical variations in their environment such as the illite (PCI and WCI components), and mixed layer

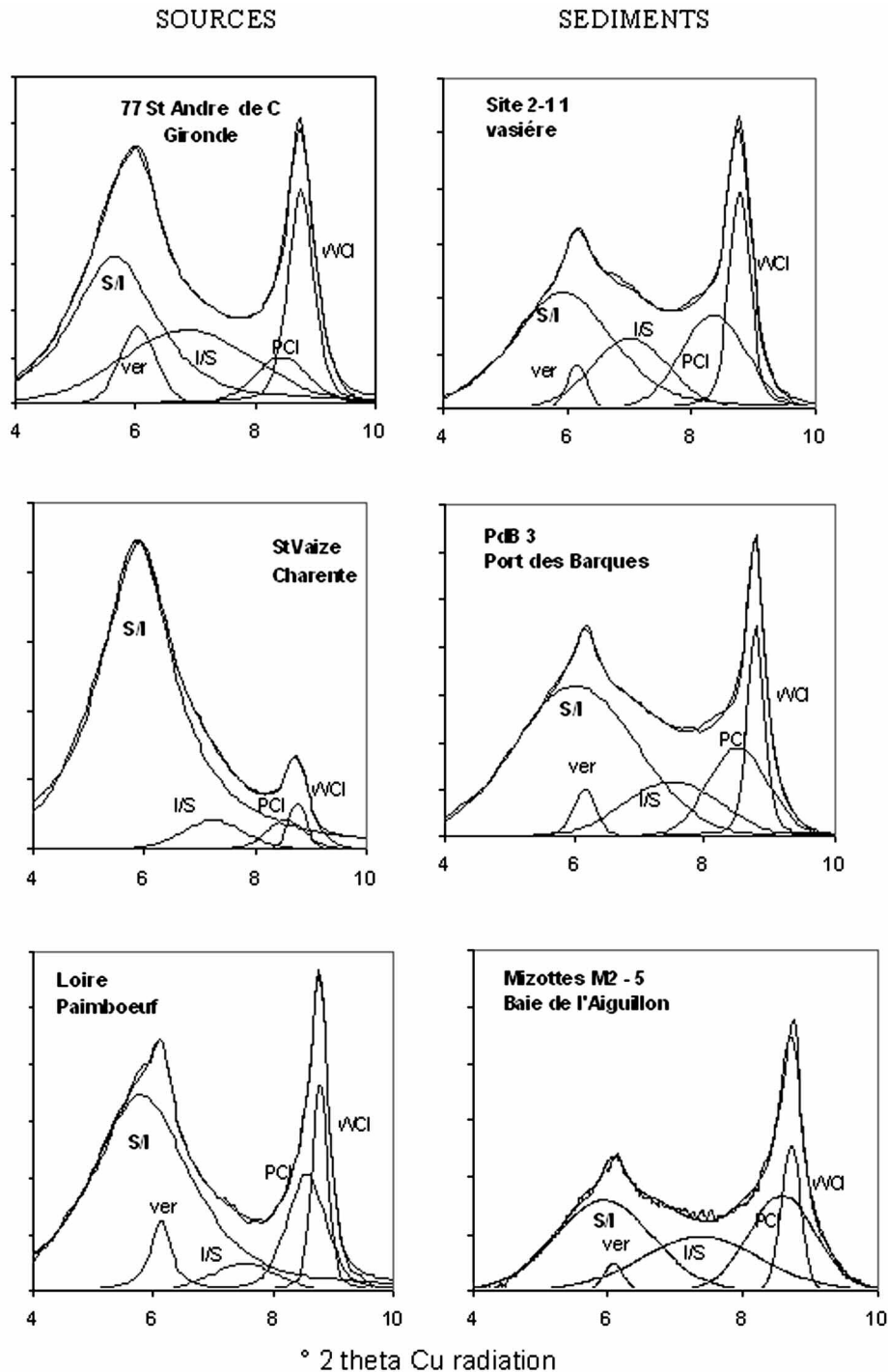


Figure 3. Treated X-ray diffractograms (smoothed and decomposed according to the method of Lanson, 1997). Comparison between river bank sediments and mud bank (Site 2-1), slikke (Port des Barques) and salt marsh (Aiguillon) deposits. Note the apparent loss of the S/I (smectite rich illite/smectite mixed layer) mineral during the process of transport in the ocean environment. Mineral peaks are S/I (smectite-rich mixed layer), I/S (illite-rich mixed layer), mineral ver (vermiculite-chlorite), PCI and WCI (illite peaks).

Figure 3. Diffractogrammes rayons-X d'après les méthodes préconisées par Lanson (1977). Comparaison entre les sédiments de la rivière et la vasière (Site 2-1), les dépôts de slikke (Port des Barques) et des marais salés (Aiguillon). Notez la perte apparente de S/I au cours du transport en milieu marin. Les pics de minéraux sont S/I (interstratifié smectitique), I/S (interstratifié illitique), ver (vermiculite-chlorite), PCI et WCI (pics d'illite).

smectite/illite minerals. These are shown in Figure 3 where the source (river or estuarine) materials are compared to shore and slikke sediments. The Gironde is compared to the Brouage site, the Charente river (Saint Vaize) is compared to the Port des Barques site and the Loire is compared to the baie de l'Aiguillon site. The smectite/illite minerals with major peaks near $6^{\circ}2\theta$ (Cu radiation, 15 Å interlayer spacing in the Sr saturated, air dried state) are dominant in the river sediments while the illite/smectites and illites are relatively more abundant in the shore-slikke sediments. This suggests a loss of smectite in the sedimentation process. Since the smectite-rich minerals (smectite/illites) are of smaller grain size, it is probable that this fine grained material remains in suspension and is carried to the sea where it is eventually deposited in the deep sea zones as indicated by Biscaye (1965) for the Atlantic Ocean.

A method which can be used to determine possible diagenetic (sedimentation environment) change in the clays is a comparison of the peak positions of the mixed layer illite/smectite minerals, the smectite rich S/I and illite rich I/S mineral typical of soils (see Righi et al., 1995). Figure 4 indicates that the samples from the Gironde and Charente rivers fall into the range of the coastal sediments except for the Port des Barques series. Oxidation of the samples (removal of organic matter) does not significantly change the peak positions for the samples.

We can conclude that the deposited clay minerals are little affected by the sedimentation processes and contact with marine organic material. The only effect on the clays through the process of transportation and sedimentation on the coastal sites is partial loss of the grained fraction, smectite – rich smectite illite mixed layer minerals.

Chemistry

Major elements (Table 1). Major element abundances do not change greatly from one sample to the other. The only element of significance directly related to the silicate clay minerals is calcium, a typical exchange cation whose abundance will be affected by the relative abundance of smectite in the mixed layer minerals. However, phosphorous, more likely related to organic matter is strongly concentrated by the oxidation process. No relationship between phosphorous and calcium was found. These two elements could be related to each other through the formation of calcium phosphate in the samples. However, the abundances of these two elements seem to be independent of each other.

Minor elements (Table 2). Even though some of the experimental variation is relatively high for some of the minor elements, the results presented show variations well beyond the experimental variation excepting for Pb which is not presented. However, given the sparsity of data it was not considered advisable to do statistical correlations on the

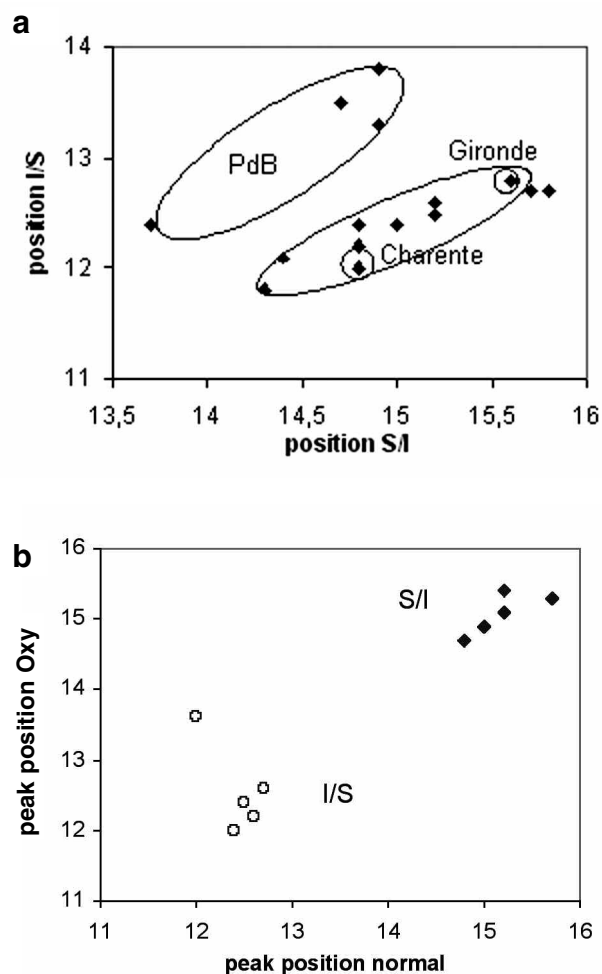


Figure 4. a. Relations between the peak positions (indicating composition of illite and smectite layers) for the sediments (diamonds) compared to Gironde and Charente river sediments for the two types of interstratified mixed layer mineral I/S and S/I (most samples within the same range excepting the Port des Barques (PdB) sequence). **b.** Peak position for normal and treated (oxidized, organic-free) samples showing a strong similarity indicating little effect on the silicates by the treatment.

Figure 4. a. Relations entre les positions des pics pour les deux types de minéraux interstratifiés I/S (illitique) et S/I (smectitique). **b.** Positions pour les échantillons non traités et traités (oxydés, sans matière organique) montrant une forte similitude, signe d'un effet faible du traitement sur les silicates.

data. It is presented for visual interpretation only. Only Cd and Sn were of insufficiently low abundance in the reference clay sample to preclude precise measurement in variations of the abundance. However, the range in values and inter-element correlations indicates reasonable accuracy for these measurements. Elements with significant variations in abundance are Cu (50-300 ppm), Zn (400-1100 ppm), As (40-100 ppm), Cd (2-110 ppm) and Sn (20-1200

Table 1. Major elements in clay sized fraction samples**Tableau 1.** Elements majeurs dans la fraction argileuse des échantillons.

	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	TiO ₂	MnO	FeO
mudbank										
site 2 - 1 1	0.44	2.4	24.88	53.9	0.78	3.78	3.94	0.36	0.34	9.17
site 2 - 1 3	0.61	2.76	25.06	53.22	0.11	3.79	4.02	0.9	0	9.56
Site 2 - 1 5	0.44	2.88	25.92	52.7	0.68	4.09	3.38	0.8	0.2	8.92
Brouage										
Brou 1 - 3	0.39	2.45	25.57	54.52	0.37	3.8	2.8	0.78	0.15	9.18
Brou 1 - 5	0.55	2.55	25.55	53.64	0.24	3.58	3.19	0.87	0	9.84
Brou 1 - 7	0.74	2.81	23.65	52.96	0.2	3.52	5.38	0.98	0	9.8
Brou 1 - 9	0.73	2.7	23.91	53.36	0.44	3.83	2.8	0.86	0.02	11.35
Brou 2 - 1	0.44	2.67	24.05	53.67	0.53	2.7	3.22	0.52	0.27	8.92
Brou 2 - 3	0.87	2.51	24.35	53.95	0.84	3.88	4.02	0.67	0	8.98
Brou 2 - 5	0.75	2.88	25.43	54.69	0.85	3.57	2.34	0.84	0	8.81
Brou 2 - 7	0.41	2.76	25.32	53.39	0.45	3.95	4	0.58	0.24	8.89
Brou 2 - 9	0.27	2.97	25.47	53.52	0.34	4.23	4.56	0.82	0.06	7.77
Brou 3	0.65	2.99	24.63	52.05	0.55	3.87	3.93	0.83	0.00	10.54
Soubise										
Sou 0	0.31	2.11	22.06	55.72	0.97	3.27	5.94	0.99	0.31	8.33
Sou 3	0.45	2.16	24.02	54.29	0.53	2.67	5.73	0.61	0.10	9.45
Sou 5	0.43	2.64	24.76	53.53	0.46	3.46	4.25	0.83	0.14	9.49
Sou 7	0.39	2.68	24.49	54.06	0.45	3.39	4.43	0.76	0.07	9.28
Port des Barques										
PdB 1	0.53	2.69	25.18	53.77	0.41	3.92	4.24	0.23	0.00	9.29
PdB 3	0.50	2.87	24.70	53.27	0.44	3.41	4.45	0.96	0.03	9.37
PdB 5	0.50	2.74	24.68	53.33	0.40	3.99	3.77	0.73	0.02	9.83
PdB 7	0.80	2.61	23.98	52.99	0.72	3.69	4.07	0.87	0.17	10.10
PdB 9	0.86	2.66	24.62	53.44	0.48	3.76	4.11	0.76	0.25	9.06
St Vaize	0.47	2.37	25.09	51.16	0.58	3.16	6.03	0.83	0.36	9.94
StAdCubzac	0.44	2.40	25.66	54.38	1.59	3.10	3.10	0.31	0.03	8.98
Average	0.54	2.63	24.70	53.56	0.56	3.60	4.07	0.73	0.09	9.36
2 - 1 4 oxy	0.55	2.3	24.5	53.39	1.96	3.5	3.18	0.6	0.12	9.88
Brou 1-1 oxy	0.33	2.31	24.2	52.98	4.03	2.57	3.82	0.43	0	9.45
Brou 2-1 oxy	0.37	2.2	25.17	53.52	2.24	3.43	3.09	0.53	0	9.67
Brou 2 -5 oxy	0.74	2.34	23.87	53.15	0.83	4.07	4.7	0.61	0	9.74
Sou 1 oxy	0.34	2.36	24.37	53.03	1.42	3.16	4.37	0.69	0.54	9.73
Sou 5 oxy	0.44	2.26	24.72	52.38	1.29	3.3	4.12	1.02	0	10.46
PdB 1 oxy	0.36	2.42	23.85	52.27	6.03	2.13	3.44	0.25	0.18	9.08
SAdC oxy	0.66	2.66	23.71	54.34	0.52	3.37	5.3	0.84	0.07	8.53
Average	0.47	2.35	24.30	53.13	2.29	3.19	4.00	0.62	0.06	9.56

ppm) for un-treated samples of the clay fractions (< 2 µm).

No attempt has been made to establish statistical regression for the experimental points. It is considered by the author that the quantity of data points and possible errors in

experimental determinations do not warrant such treatment. The existence of rather un-ordered groups in a number of cases tends to justify this attitude. No use of linear correlations should be made from the information presented here.

However, certain elements show good relations as would be expected, Th and U, Ti and V, and Ba vs Cs. Th and U represent the detrital non-silicate fraction of the fine-grained sample, Ti and V the non-silicate (oxide) and also

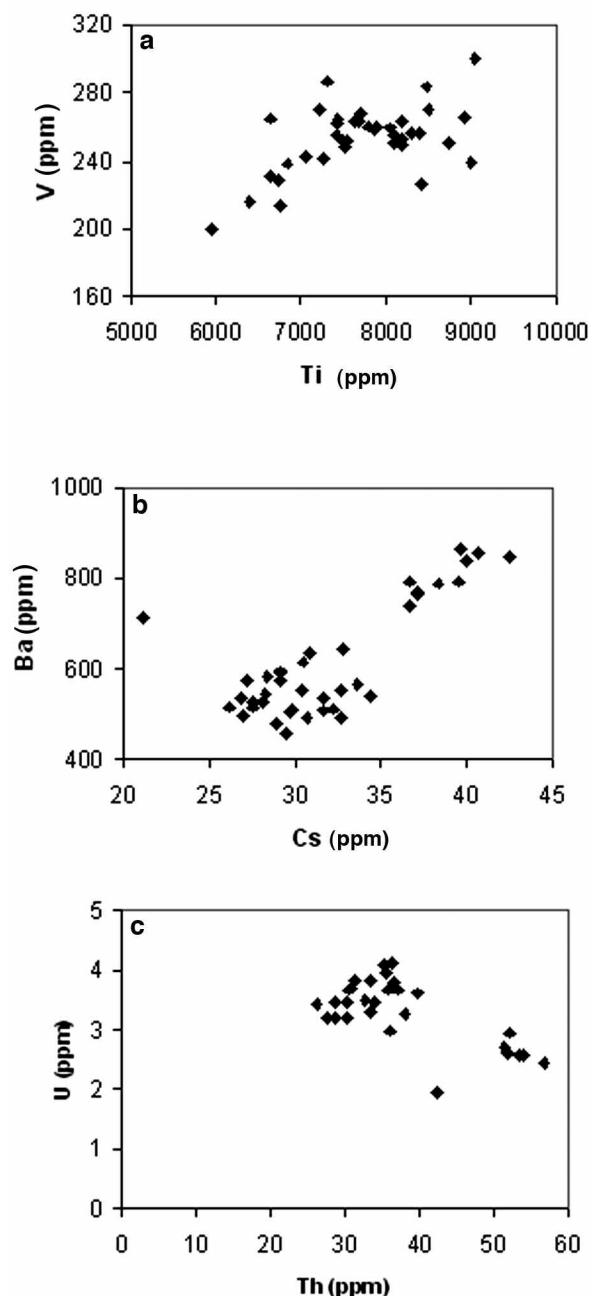


Figure 5. a. Relation between V and Ti (ppm) in the clay fraction of the sediments. **b.** Relation between Ba and Cs (ppm). **c.** Relation between U and Th (ppm).

Figure 5. a. Relation entre V et Ti (ppm) dans la fraction argileuse des sédiments. **b.** Relation entre Ba et Cs (ppm). **c.** Relation entre U et Th (ppm).

clay fraction, Ba and Cs are associated with the exchange ion portion of the clay assemblages (Ca, Mg, Na, K). The inter relations are shown in Figure 5. Heavy metal inter relations appear exist between As and Zn, Cd and Sn. No apparent relations were found for Cu. Similar relations have been found by Velde et al. (2003) for sediments in similar situations.

Oxidation of the samples (destruction of the organic matter) changes the distributions of several elements, notably P, Sn and Cd. Figure 6 indicates the increase in Cd for normal and treated samples. The high values are shown by bold characters in Table 2. Given that there was a notable increase in phosphorus content in the treated samples also, one can consider the effect using P and the heavy elements Cd, Sn and As. Figure 7 indicates the relations for all samples for these elements. It is clear that there is a strong relationship between P and Cd, a similar but less well expressed relationship for P and Zn and possibly two trends for As and P, one untreated samples (P less than 3000 ppm) and the other in the treated samples. Hence we see a relationship between P, Zn, Cd and As.

Looking at the untreated samples one finds inter relations for As and Zn (Fig. 8) and Cd-Sn. There are no other clear cross relations between these elements. One can surmise that the input of these heavy elements is from two different sources.

Samples from river banks near the ocean-river interface indicate a generally lower concentration of the heavy metals Cd, Sn for the Charente River (Saint Vaize) and the Gironde (Saint André de Cubzac) river samples compared to the coastal sediments. This could suggest a concentration effect in the cycles of sedimentation and re-mobilization of the inner coastal basin of the La Rochelle-Brouage area.

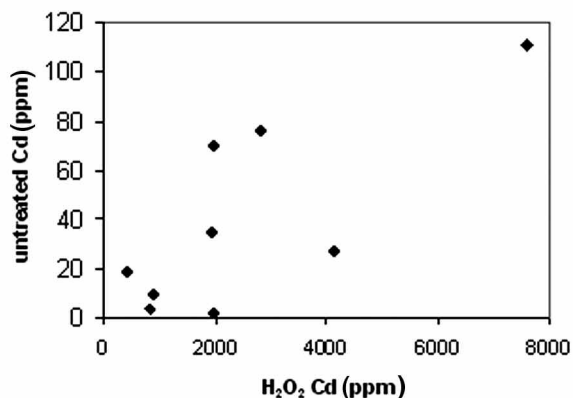


Figure 6. Relation between Cd in normal and oxidized samples showing the strong concentration of Cd by the treatment.

Figure 6. Relation entre le Cd avant et après traitement (oxydation) mettant en évidence la forte concentration du Cd due au traitement.

Table 2. Values in ppm for different minor elements in sediment samples determined by laser ablation ICP MS methods for untreated samples and oxydized samples (H₂O₂).
Number after the element is the isotope used for the determination.
Table 2. Valeurs (ppm) pour les différents éléments lourds dans les échantillons étudiés, déterminées par les méthodes laser ablation ICP MS. Echantillons non-traités et oxydés (H₂O₂). Le numéro après l'élément est l'isotope observé.

	Li7	P31	V51	Cr53	Mn55	Fe57	Co59	Ni60	Cu65	Zn66	As75	Sr88	Cd114	Sn120	Sb121	Cs133	Ba136	Th232	U238
untreated																			
site2-1 1	93	3125	248	211	773	91720	28	102	127	907	99	340	70	1101	5	37	762	52	3
site 2-1 3	88	3073	284	278	973	95621	34	138	237	1016	109	418	22	236	6	43	846	54	3
Brou 1 - 1	1005	1264	262	216	3031	91820	38	103	77	542	60	224	27	292	4	32	538	40	4
Brou 1 - 3	318	1054	251	197	912	91820	26	79	55	482	44	232	2	15	2.3	28	516	31	3.7
Brou 1 - 5	300	1252	271	406	1013	98422	27	105	43	599	54	251	6	53	3.1	28	583	36	4.1
Brou 1 - 7	288	1155	268	223	720	98021	26	82	48	495	47	215	48	333	2.7	30	552	36	3.7
Brou 2 - 1	265	1249	255	208	1149	89220	28	113	52	462	50	328	35	239	2.6	26	517	29	3.5
Brou 2 - 5	312	1372	254	206	916	88119	27	83	47	469	48	266	76	722	2.4	28	528	30	3.7
Brou 2 - 7	85	2848	256	222	1148	88919	27	104	70	905	100	352	2	22	4	40	794	51	3
Brou 2 - 9	101	2632	265	235	1208	77717	28	100	305	961	72	484	13	124	11	41	854	52	3
Sou 0	249	1107	238	202	1012	83318	29	90	38	509	37	296	10	83	2.2	28	526	28	3.2
Sou 3	243	1157	260	213	1216	94521	29	83	43	502	39	321	11	103	2.2	29	588	34	3.5
Sou 5	217	1160	264	210	1367	94921	29	81	45	495	41	354	4	35	3.2	30	617	37	3.8
Sou 7	978	1417	265	211	1291	92820	29	170	51	551	45	268	30	317	3	30	458	30	3
PdB 1	843	1709	270	240	1110	92920	47	146	272	565	54	277	111	1246	3	31	492	31	4
PdB 3	252	1115	243	199	825	93721	28	95	123	514	42	259	4	35	2.4	27	497	29	3.2
PdB 9	277	1069	261	216	866	90620	27	84	53	443	36	302	2	17	2.6	28	546	35	4.0
St Vaize	227	1592	216	406	645	99422	26	85	130	1301	53	207	15	81	3.8	29	595	26	3.4
St André Cubzac	187	1047	231	220	1131	89820	32	108	79	611	52	204	19	157	3.0	27	573	30	3.5
Average	333	1595	256	236	1128	91665	30	103	133	649	57	293	29	274	4	31	595	36	3
H₂O₂																			
Site 2-1 1 oxy	218	18313	239	220	769	98822	30	123	104	1036	80	322	1970	24698	5	40	865	57	2
Brou 1 - 1 oxy	996	13074	251	208	792	94521	28	96	55	579	40	205	4135	49783	3	32	509	34	3
Brou 2 - 1 oxy	990	7797	253	222	680	96021	452	153	66	598	39	221	1963	24115	3	34	564	38	3
Brou 2-5 oxy	302	8883	250	242	574	93821	32	98	56	502	35	200	2827	25949	2.6	29	575	33	3.5
Sou 1 oxy	76	11139	226	199	878	97321	29	85	109	1349	85	408	916	11340	5	37	791	53	3
Sou 5 oxy	1093	5668	264	258	986	104623	32	200	185	763	38	247	828	10099	3	33	490	34	4
PdB 1 oxy	128	45088	215	204	551	90820	27	100	273	2073	77	269	7598	93711	5	37	768	42	2
PdB 9 oxy	313	6132	249	205	772	90820	49	86	69	635	28	270	1989	18487	2.3	31	635	37	3.7
St André Cubzac	206	2922	213	180	1401	85319	34	92	85	590	45	263	445	4167	3.4	21	716	35	4.1
average	480	13224	240	215	823	94676	79	115	111	903	52	267	2519	29150	4	33	657	40	3

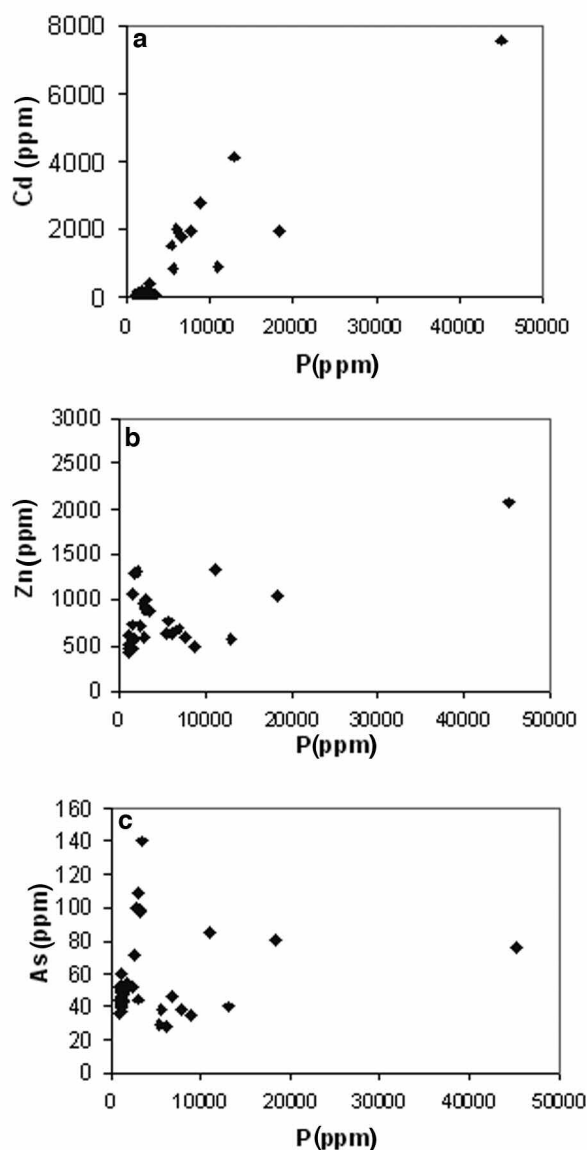


Figure 7. a. Cd-P relation in ppm concentrations for all samples (normal and treated). **b.** Sn and P relation in ppm concentrations for all samples (normal and treated). **c.** As and P relation in ppm concentrations for all samples (normal and treated).

Figure 7. Relations entre l'abondance (concentration en ppm) des éléments **a.** Cd-P, **b.** Sn-P et **c.** As-P pour l'ensemble des échantillons (traités et non traités).

Discussion

From the above study it is apparent that there is a sedimentation relation between Sn and Cd as well as As and Zn. Other heavy elements seem to be much less cross related in abundance in the clay fraction of the coastal sediments. These elements are not of high abundance in river sediment.

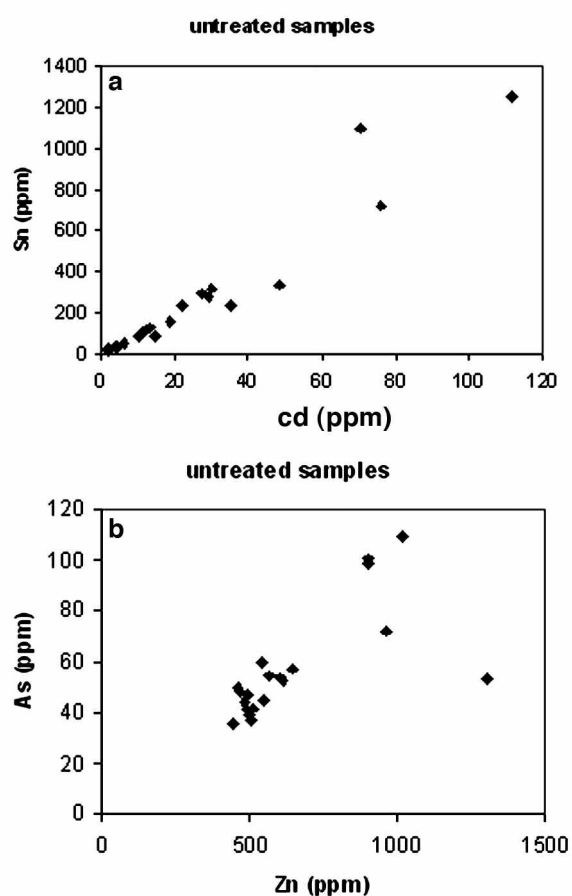


Figure 8. a. Sn-Cd relation in ppm concentrations for untreated samples **b.** As-Zn relation in ppm for un-treated samples.

Figure 8. a. Relation entre Sn et Cd (concentrations en ppm) dans les échantillons non traités. **b.** Relation entre As et Zn (concentrations en ppm) dans les échantillons non traités.

In comparing these data for clay size material ($< 2 \mu\text{m}$) with similar results for a finer fraction ($< 0.07 \mu\text{m}$) for river extracts of the Gironde and other rivers in the southwest of France (Schäfer & Blanc, 2002) significantly higher levels of As, Cd, Zn and Sn occur in clay sized fractions of both river and coastal sediments compared to the fine suspended fraction. One can conclude that the clay fraction probably carries more of the heavy element load than does the finer suspended material. The clays are transported to the littoral through dispersion and eventual flocculation in the off shore area to be re-deposited along the coastal mud flats through tidal action. However the eventual deposition of this clay material is probably determined by fixation by plants in the slikke part of the sedimentary structure. Material in the mudflats, at least at the surface, is most likely strongly re-mobilized during high energy storm events. Some high values indicate local pollution.

The secondary relation of heavy metals and phosphorous revealed by the destruction of organic matter has some potential for understanding the eventual concentration of heavy metals in these sediments. It is known that phosphorous is fixed by oxy-hydroxide materials in wetland soils and stream sediments (Reddy et al., 1998) and a relation between Cd and P fixation in soils (Bolan et al., 1999). Thus a change in use of phosphorous by plant or algal organisms could be involved in P and Cd accumulation in marine and brackish sediment material. Therefore one can consider that there is a relationship between phosphorous and Cd in treated samples (involving destruction of the organic matter) but that the input of Cd into the sediment, which is not related to P content, but is related to another heavy metal, Sn. Cd is not selectively absorbed on clays and is highly pH sensitive (Reid & McDuffie, 1981). We assume that Cd is associated to released phosphorous after destruction of the organic matter. As and Zn are related but less strongly to concentration of phosphorous by destruction of organic matter. The re-mobilization of Sn and Cd in the sediments could be of great importance to the biology of coastal mud flats. If Cd is introduced into the bio-cycle it will be through organic (probably algal) matter associated with the clays (see Pigeot et al., 2006). The study by Miramand et al. (1998) indicates that such accumulation, seen in the brackish water of the Seine river, is apparently not magnified in the trophic web of carnivorous species.

Conclusion

Given the relatively small number of samples for the area concerned, this study must be considered as preliminary.

The Gironde-Charente-Loire River samples indicated that there is a loss of fine-grained clay, smectite rich, during the deposition process from river estuary to mud flat. The minor element compositions of the sediment clay fractions show higher content than those found in Gironde and Charente samples for the suspended ($< 0.07 \mu\text{m}$) and soluble matter reported by Schäfer & Blanc (2002). We assume that the clays are strong carriers of heavy metals. Sn and Cd as well as As and Zn concentrations could be correlated among the heavy metals in the untreated samples. Some

high concentrations indicate possible local pollution.

Destruction of organic matter by chemical oxidation concentrates phosphorous in the clay fraction and with it Cd and to a lesser extent Zn and As. Such re-organization of elements might be important for biological processes involving algal materials.

References

- Biscaye P. 1965.** Mineralogy and sedimentation of recent deep-sea clay in the Atlantic and adjacent seas and oceans. *Bulletin of the Geological Society America*, **76**: 803-823.
- Bolan S., Naidu R., Khan M., Tillman R., & Syers J. 1999.** The effects of anion sorption and leaching of cadmium. *Australian Journal of Soil Research*, **37**: 445-460.
- Lanson B. 1997.** Decomposition of experimental X-ray diffraction patterns (profile fitting) : A convenient way to study clay minerals. *Clay Minerals*, **45**: 132-146.
- Miramand P., Fichet D., Bentley D., Guary J.-C. & Caurant F. 1998.** Concentrations en métaux lourds (Cd, Cu, Pb, Zn) observées le long du gradient de salinité dans le réseau trophique pélagique de l'estuaire de la Seine. *Comptes Rendus de l'Académie des Sciences, Paris, Océanographie*, **327**: 259-264.
- Pigeot J., Miramand P., Guyot T., Sauriau P.-G., Fichet D., Lemoine O. & Huet V. 2006.** Cadmium pathways in an exploited intertidal ecosystem and chronic Cd inputs (Marennes-Oléron, Atlantic Coast, France). *Marine Ecology Progress Series*, **307**: 101-114.
- Reddy K., Connor G. & Gale P. 1998.** Phosphorous sorption of wetland soils and stream sediments impacted by dairy effluent. *Journal of Environmental Quality*, **27**: 438-447.
- Reid J. D. & McDuffie B. 1981.** Sorption of trace cadmium on clay minerals and river sediments: effects of pH and Cd (II) concentrations in a synthetic river water medium. *Water, Air and Soil Pollution*, **15**: 375-386.
- Righi D., Velde B. & Meunier A. 1995.** Clay stability in clay dominated soil systems. *Clay Minerals*, **30**: 353-364.
- Schäfer J. & Blanc G. 2002.** Relationship between ore deposits in river catchments and geochemistry of suspended particulate matter from six rivers in southwest France. *Science of the Total Environment*, **298**: 103-118.
- Velde B., Church T. & Bauer A. 2003.** Contrasting trace element geochemistry in two American and French salt marshes. *Marine Chemistry*, **83**: 131-144.