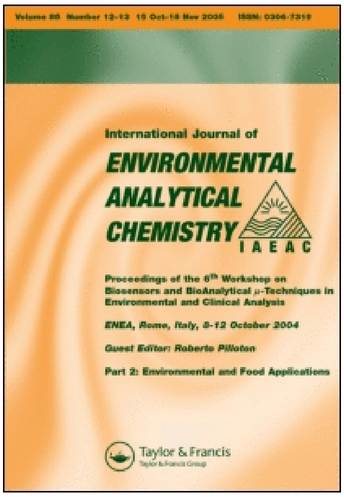

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

# Trace Metal Speciation and Research in Marine Geochemistry

C. Latouche[a]; J. C. Dumon[a]; G. Lavaux[a]; Ph. Pedemay[a]
[a] Département de Géologie et Océanographie, Université de Bordeaux I, Talence, France

**To cite this Article** Latouche, C. , Dumon, J. C. , Lavaux, G. and Pedemay, Ph.(1993) 'Trace Metal Speciation and Research in Marine Geochemistry', International Journal of Environmental Analytical Chemistry, 51: 1, 177 — 185
**To link to this Article: DOI:** 10.1080/03067319308027623
**URL:** http://dx.doi.org/10.1080/03067319308027623

*Intern. J. Environ. Anal. Chem.*, Vol. 51, pp. 177-185
Reprints available directly from the publisher
Photocopying permitted by license only

# TRACE METAL SPECIATION AND RESEARCH IN MARINE GEOCHEMISTRY

C. LATOUCHE, J.C. DUMON, G. LAVAUX, and Ph. PEDEMAY

*Département de Géologie et Océanographie, Université de Bordeaux I, 351 cours de la Libération,33405 Talence, France*

*(Received in final form, 31 August 1992)*

In order to precise the origin and behaviour of trace metals associated with coastal marine sediments, marine geochemists frequently utilize various methods of sequential extraction. The main objective is to test the potential mobility / stability of particulate metals in the natural environments. Several examples are presented in the article, namely: i/ Exchangeable Pb from podzolic soils of the drainage basin of a lagoon which sediments and phreatic waters are for a large part inherited from the surrounding soils; ii/ Evolution of particulate metals in an estuary; iii/ Mobility of metals at the sea bottom interface; iv/ Role of amorphous components of estuarine sediments and suspended matter; v/ Effects of dredging activities on solubility of metals in an estuary; vi/ Behaviour of heavy metals in lagoons.

Main results obtained from the extraction procedures are described, as well as particular difficulties encountered when applying some classical methods.

**KEY WORDS:** Trace metals, metal speciation, sequential extraction, estuaries, sediments, geochemistry.

## INTRODUCTION

Marine geochemists are interested in a great deal of problems related to the behaviour of metallic elements in oceanic systems, or in coastal environments, and even in the surrounding drainage basins controlling coastal terrigenous sedimentation. It is for instance the case for soils in the immediate proximity of a lagoon deeply inserted in the continent. If the soils are of podzolic type, with a very weak cation exchange capacity, the mobility of adsorbed elements towards rivers, lagoons or sea is very high. Moreover correlative pollution of nearshore environments having always to be considered, it is necessary in such an environment to take into account, not only the marine system itself, but also the surrounding drainage basins and soils. In the marine environments, the problems related to heavy metals are highly complex ones due to the fact that the origin of these metallic elements is twofold. For the first part, they are *natural* components of sediments and suspended matter (SM), i-e: either major components, (e.g. iron); minor components (e.g. Mn) or, more often, trace-elements (Zn, Cu, Pb, Ni, Co, Cd, Cr. etc ...). The second part is of *anthropogenic origin*, e.g. metal emission into the atmosphere, such as lead from gazoline combustion, or direct input into the hydrocycle such as Zn, Cd, Cr, from wastes of various industries such as: ore processing, metallic surface treatments, tanneries etc ... In addition to this diversity of origin and pathways, metallic elements in marine environments have a large diversity of physical states and chemical bonds, easily passing from particulate matter to dissolved matter and reciprocally.

As a consequence, the knowledge of origin and behaviour of these elements requires reliable analytical tools. In order to understand the factors responsible of their concentration and also to predict their possible evolution in a natural system and then to appreciate their possible impact on human health, it is necessary to have the more exact informations on the physico-chemical forms in which heavy metals exist in sediments and SM.

The main objective of this paper is to present some case studies for which sequential extractions -in a very general sense- unabled us to precise the origin of metals and to better understand their geochemical cycles and mobility. Most of the examples presented below are relative to coastal environments. For several reasons, this environment is probably one of the more critical ones. First of all because it is the most exposed to the fluxes of pollutants, among them heavy metals. Second, because the fresh-water / saline-water interface is characterised by drastic changes of the main physico-chemical parameters (ionic concentrations of waters, pH, Eh and often temperature and light-transmission effects). The examples mainly concern estuarine systems and lagoons, more or less isolated from the open sea. They address to sediments and suspended matter but in consideration with reciprocal exchanges with water. The role of organic components, living or non living, is also considered in the cycle of these heavy metals in coastal systems.

Finally, thanks to trace metal speciation and/or selective extractions various important processes relative to the transfer of metallic elements from the continent to the ocean have been identified; the following examples are presented in this paper (Table 1).

- Adsorption of Pb from motor fuel additive, by podzolic soils(i-e: deprived of any cation-retention, what is capital in such a context), in the vicinity of a marine-lagoonal environment: Arcachon Basin.
- Solubization of particulate organic matter and associated trace metals in Gironde estuary.
- Mobilization of Mn at the sea bottom interface.
- Role of amorphous inorganic components as support of metallic elements in estuaries.
- Effect of dredging activities on the mobility of metallic elements in an estuary.
- Behaviour of heavy metals in lagoons.

## CASE STUDIES

### *Adsorption by soils of lead from motor fuel additive*

Distribution of Pb, on its exchangeable form, has been studied in soils of the drainage basin of a famous French lagoon: Bassin d'Arcachon. The drainage basin of the lagoon (Leyre

**Table 1** Overview on various case studies presented in the article.

| *Objectives of Studies* | *Methods* | *Extracts* | *Results* |
|---|---|---|---|
| Adsorption of Pb by soils of drainage basins. | Ammonium acetate(N,pH7) on Ao Horizon | Exchangeable Pb | Impact of highways on the environment |
| Evolution of particulate metals in an estuary | Brannon and al (1976) | 1 - Exchangeable. phase<br>2 - Easily reducible phase<br>3 - Organic+ sulfide phase<br>4 - Moderatly reducible phase<br>5 - Residual phase | Solubilization of metals associated with Particulate Organic Matter (POM) along the estuary |
| Metal exchanges at the sea bottom interface | Chester et Hughes (1967)<br>Presley and al.(1972) | 1 - Hydroxyde phase<br>2 - Organic+ sulfide phase<br>3 - Residual phase | - Relative mobility of Fe and Mn at the interface. Effect of Eh;<br>- Consequences on Zn, Pb,Cu, Ni distributions |
| Amorphous components of estuarine sediments and Suspended Matter (SM). | Biermans and Baert (1977) | Amorphous silica et associated Fe and Al | Comparisons of various estuarine systems |
| Effects of dredging activities on metals solubility in estuary | Experimental extraction with pure water and saline water (5‰) | Fe Mn Cu Zn Cd soluble | Limited effects of dredgings compare to the effect of natural processes |
| Heavy metals mobility in lagoons | HCl 0,1 mol.l$^{-1}$ | Cu, Zn, Ni, Sr easily mobilisable | Role of aquatic plant on metals mobility |

river) is crossed by an important highway (R.N.10, Bordeaux to Bayonne), responsible, given the intense traffic, of a pollution by hydrocarbons and Pb from fuel motor additives. In order to appreciate this pollution at its source, analysies have been made on samples of forest litter collected at increasing distances from the highway. Extractions have been classically carried out by ammonium acetate (1 mol.l$^{-1}$) and at pH 7.0. The results (Figure 1) show that the distribution of exchangeable Pb in horizons $A_o$ is maximum along the highway itself and decreases with the distance; 30 meters away the road, the content of exchangeable Pb becomes quite normal.(1 mg.kg$^{-1}$ dry matter). Also, the results clearly show that the distribution of Pb depends on the direction of prevalent winds.

The first studies along this highway are rather old[1]. Since this period, monitoring have been carried on considering a probable interesting environmental evolution: the expected decrease of Pb emission since the reduction of using of Pb additive in motor fuels and corresponding decrease in soils and lagoon sediments originating from the erosion of these soils.

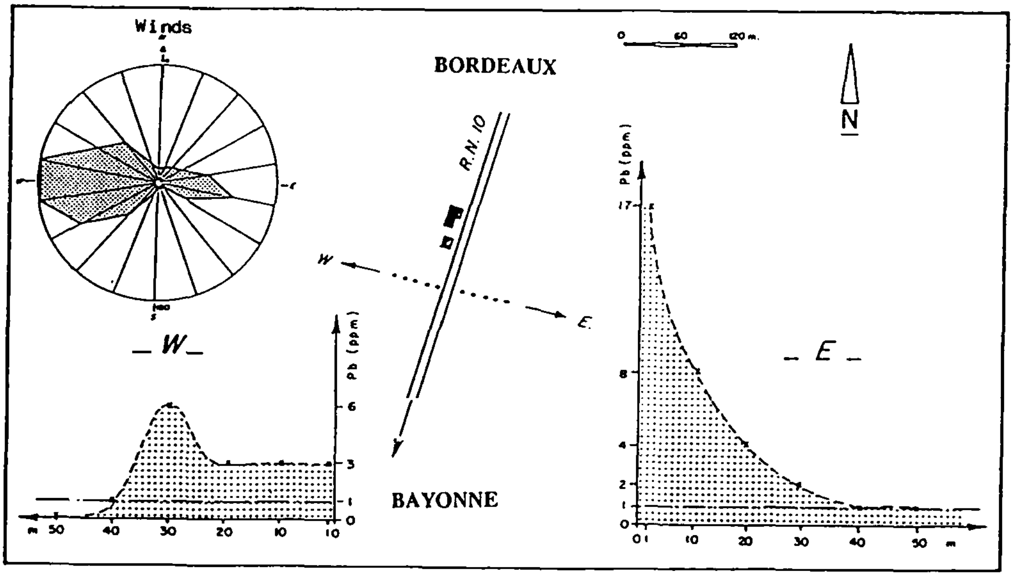

**Figure 1** Exchangeable Pb in soils along RN 10 highway.

### *Solubilisation of particulate organic matter and associated trace metals in a macrotidal estuary*

Macrotidal estuaries such as Gironde (tidal range 4 to 6 m) are characterised by an important oscillating stock of suspended matter enabling such systems to accumulate heavy metals. In the Gironde estuary however, the study of their distribution and their subsequent flux quantification during several consecutive years showed that the accumulation of metals associated with sediments is limited. It has been demonstrated that the residence time of SM in the estuary before their expulsion to the open ocean, is 2 years. In such a context the majority of particulate metallic elements (about 80%) pass into solution, before escaping to the atlantic marine environment[2].

Mechanisms responsible of such an evolution have been studied on the basis of various approaches. By sequential extraction, Bertrand[3] examined the repartition of various forms of metals associated with SM along the estuary. Using the method proposed by Brannon and al.[4], he demonstrated that the strong upstream / downstream decrease of particulate Zn is mainly due (Figure 2) to the decrease of organic fraction, other fractions (exchangeable, hydroxydes, residual) remaining rather constant along the estuary. Conversely for Ni, no major variation of metal content appears along the estuary. For this metal, sequential extractions showed that the most important form is the residual one.

Following the study of Bertrand (quoted above), several methods demonstrated that the results obtained from sequential extraction methods are reliable. On the basis of examination of the balance of organic matter in the estuary, it was demonstrated[5] that a large part of the particulate organic matter considered, from the results of sequential extraction, as the main support of metals, either pass into solution or is mineralized along

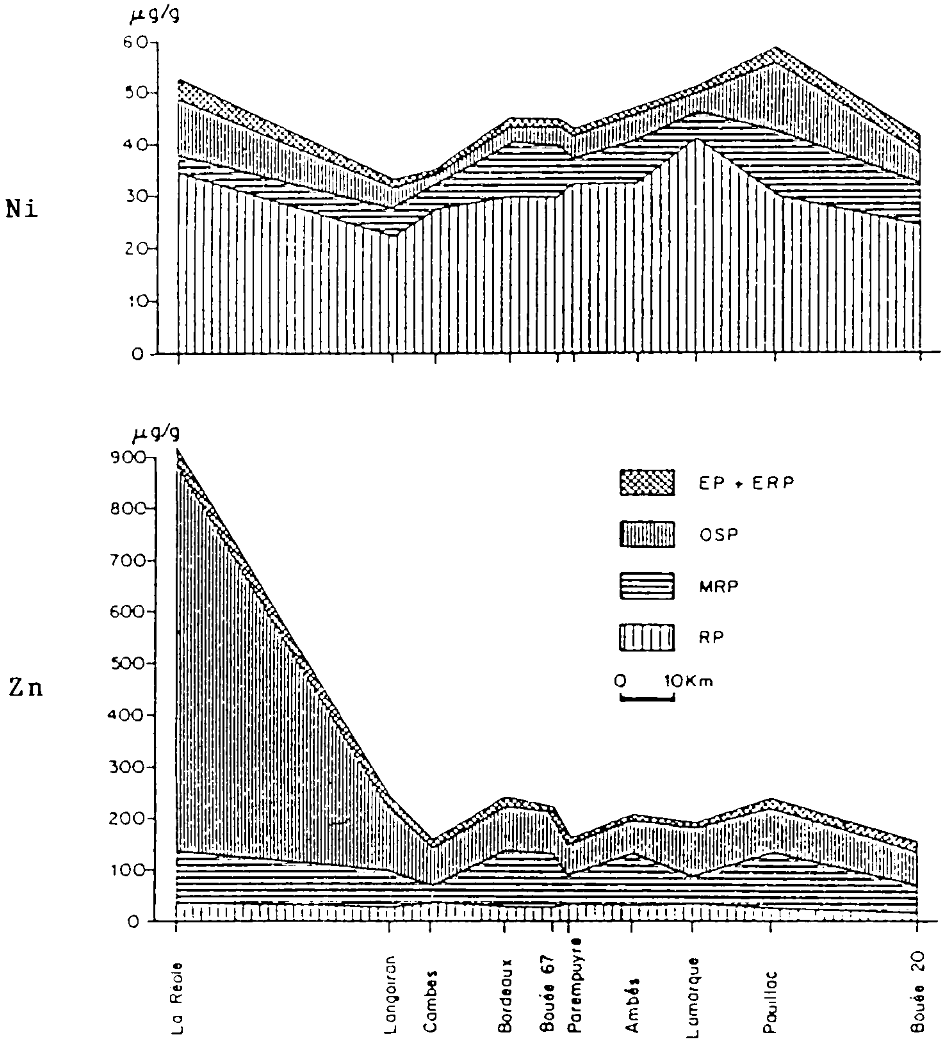

**Figure 2** Upstream (La Réole) / downstream (Bouée 20 ) distribution of Zn and Ni in the various fractions of suspended matters of the Gironde estuary (from Bertrand 1980).

EP + ERP : Exchangeable phase
OSP : Organic + sulfide phase
MRP : Moderatly reducible phase
RP : Residual phase

the estuary. Moreover an experiment of simulation of pollution by radioactive tracers ($^{65}$Zn and $^{179}$ $^{181}$Hf) demonstrated[6] that, as expected from the results of the sequential extraction, Zn associated with SM at the entrance of the estuary pass into solution during the transfer of particles in the estuary.

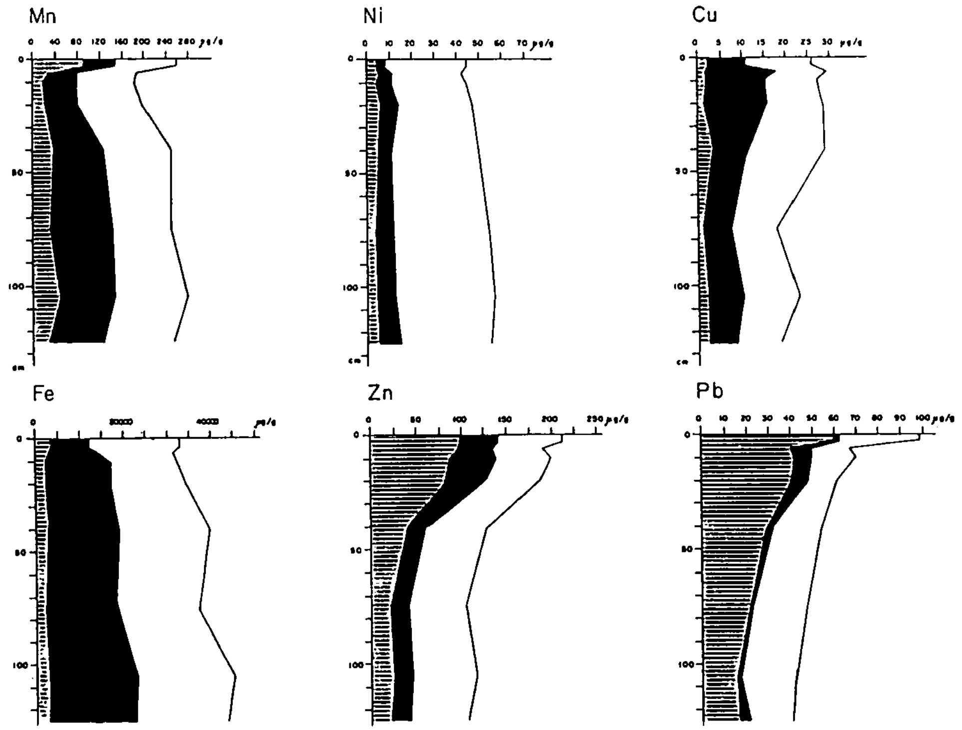

**Figure 3** Arcachon Basin: reducible, oxidizable and residual fractions in ug per g. dry sediment in core.

*Mobility of metals at the sediment water interface*

In order to study the effects of early diagenesis on the partitioning of Mn, Fe, Cu, Zn, Pb, and Ni in nearshore sediments from Aquitaine coast (France), El Ghobary[7] performed sequential extractions on thin layers of cored samples of the four following coastal environments of the SW of France: Marennes-Oléron Bay, Gironde estuary, Vasière Ouest-Gironde, and Arcachon Bay. Extractions were made according to the method proposed by Chester and Hughes[8]; Presley and al.[9]. The sequential extraction steps were performed as follows (Figure 3):

1 sediment was leached for 4 hours with hydroxylamine hydrochloride—acetic acid v/v: $NH_2OH$, HCl (1 mol.$l^{-1}$) in HOAc (0,25 mol.$l^{-1}$)
2 after, the sample was submitted for 4h to hydrogen peroxyde (50 ml of $H_2O_2$ (10,2 mol.$l^{-1}$); 5 ml are added at the time while heating 85°C)
3 and then, takes place a dissolution in HF-$HClO_4$-HCl.

These three steps were respectively attributed by the authors to the reducible fraction, for the first, the oxidizable one for the second, and to the residual fraction for the last.

Concerning $H_2O_2$ extraction, the ratio extractant / sediment has been increased in comparison with other methods (e.g. 10), but without adding HCl, because the pH would be too much acid and, in this case, silicates could be attacked.

It has to be emphasized that some more detailed methods of sequential extractions have been proposed with the aim of distinguishing: exchangeable, carbonate, oxide and hydroxide, organic and residual fractions[10,11]. Other methods also differentiate sulfide and organic fractions. Nevertheless, taking into account some lack of specificity of very detailed sequential extractions[12] it appeared better to prefer a method regrouping the so called exchangeable, carbonate, oxide and hydroxide fractions.

Despite its simplicity, this sequential extraction method enabled us[13] to better understand the roles of organic matter, sulfides, oxides, carbonates, water chemistry and rates of sedimentation on the associations and diagenesis of metals. In the surficial sediments, an important part of the mobile fractions of metals is associated with oxides and carbonates. In "Bassin d' Arcachon" however, under highly reducing conditions which prevail at the bottom, a high percentage of the mobile fractions of Fe, Cu, Mn and Ni is associated with sulfides. An intense dissolution of Mn oxides close to the water sediment interface could account for the low Mn content of surficial sediments.

In the Gironde estuary, the establishment of reducing conditions following burrial, solubilization may lead to the precipitation of metals with carbonates.

In the four nearshore studied environments of the Aquitaine Coast the enrichment of Zn, Pb and Cu in the surficial sediments appears to have resulted from an increase in the anthropogenic fluxes of this metals during recent years. (Figure 3).

## *Amorphous fraction of estuarine suspended matter and sediments*

In order to precise the relative abundance and metallic adsorption capacity of amorphous fraction of estuarine suspended matter and sediment, various extraction methods were experimented[14]. Preliminary comparisons of 10 methods described by several authors, conducted to select 3 methods. The first one[15] is the extraction of amorphous Si and Al by NaOH (0,5 mol.l$^{-1}$ boiling). It has been completed by the solubilization of the Fe components by Na citrate and dithionite treatment at 80°C[16]. A third method was the extraction by NaOH and Tiron (0,1 mol.l$^{-1}$) at 80°C,[17].

None of these methods can be totally considered as specific of the amorphous fraction. A small part of crystalline components, particularly clay fraction, is always attacked by this kind of extraction. Nevertheless, comparisons of extracts from sediments and suspended matter of Gironde and Loire estuaries allowed to demonstrate the higher content of amorphous fractions in Loire samples (mean value: 14.1%) than in Gironde estuary (mean value: 8%). This is probably due to the shorter residence time of solid material in Loire than in Gironde estuary (2 years), and to the evolution of SM estuarine systems during its transfer in the freswater/seawater interface,[3,6].

## *Effect of dredging activities on solubilization of metals in Gironde estuary*

Recent attempts to chemically evaluate the quality of dredged sediments and the impact of dredging activities on the quality of the environments has been conducted in the Gironde

**Table 2** Total trace metal contents of dredged sediments of the Gironde estuary (dry matter).

| *Elements* | *Pb* $\mu g.g^{-1}$ | *Cu* $\mu g.g^{-1}$ | *Zn* $\mu g.g^{-1}$ | *Ni* $\mu g.g^{-1}$ | *Cd* $\mu g.g^{-1}$ | *Fe* % | *Mn* % |
|---|---|---|---|---|---|---|---|
| 1 | 63 | 66 | 251 | 43 | 0,68 | 4,42 | 0,09 |
| 2 | 219 | 79 | 811 | 69 | 1,95 | 6,65 | 0,07 |

1- uncontaminated sample
2- polluted sample

estuary. The comparison of trace metal contents (Fe, Mn, Cu, Cd, Zn) of sediments from the dredged sites with metal contents of sediments from dumping areas showed a decrease of 10 to 20% of the metallic load during dredging operations. With a view to precise the significance of this decrease, experiments of solubilization by freshwater and then by saline water (5‰) were conducted on sediments of various dredged areas of the Gironde estuary. The availability of trace metals associated with dredged sediments (Table 2) was first estimated by agitation of mixtures of sediments in water (1/3 sediment, 2/3 water). In order to avoid any risk of post-extraction readsorption, percolation experiments were then conducted with the same samples and extractants. Extracts were 10 times more important using percolation columns. Nevertheless, compared to the total metal contents, extractable contents do not exceed 0,6% for Cu; 0,07% for Cd; 0,04% for Mn.

Consequently from these extraction experiment results one can assume that dredging activities have limited effect on trace metal solubility into the Gironde estuary. In fact it appeared that the decrease of metal content recorded before and after dredging operations was mainly due to grain size effects. Dumping of sediments resulted in a dispersal of fine grained suspended material. On disposal site boundary, sediments are coarser and then have a lesser content of trace metals.

### *Importance of Eelgrass in the heavy metal budget of Arcachon basin (SW France)*

Eelgrass (*Zostera noltii*) is a very abundant aquatic plant in the Arcachon Basin. With the aim to study the role of this plant on the cycle of Zn, Cu, Fe, and Mn, Wasserman[18] considered the mobility of these elements in superficial sediments. For this purpose, mild reagent (30 ml of HCl 0,1 mol.$l^{-1}$) / 1g sediment, shaken 24 hours), was used to appreciate the bioavailability of metals. Such acid-soluble metals can be considered as the fraction possibly chelated by agents produced by plants. In comparison to the total contents of metals in sediments, the extraction provided for each metal an index of mobility. Zn and Cu are the most easily extracted from sediments, respectively 40,4% and 74,9% of the total content, acid-soluble Fe and Zn fraction presented good correlations (0,855 and 0,825 respectively) with particulate organic carbon (POC). In relation with their greater bioavailability, these elements are easily fixed by aquatic plants and then they return to the sediment under an easily mobilizable form, associated with organic detritus. Few quantity of Mn (11,7% of the total content) were extracted from sediments; this is due, for a large part, to the very low content of Mn in sediments.

Acid-soluble method was also utilised for an experimental study of metal exchanges between sediments and senescent or recently dead *Zostera noltii*[18]. It appears that leaves of these plants deposited on sediments are able to absorb metals particularly those that are moderately linked to sediments. The results did not show any significant variations for the for acid-soluble metals tested.

## CONCLUSION

Trace metal speciation and selective chemical extractions enable geochemists to identify various important processes relative to the transfer of metallic elements to the continent e.g. mechanisms of transport mobilization, bioavailability, bioconcentration, accumulation, diagenesis at the interface water-sediment. In order to give to the results relative to these processes a quantitative basis that may be compared between various environments or case studies it is obvious that common procedures[19] has to be adopted by all scientists involved in earth sciences studies. Adoption of common schemes relative to sequential extractions clearly appears as a necessary condition for the comparison of data throughout the world, modeling application, theory development, etc ...

### *References*

1. J.C. Dumon and G. Vernette, *Bull. Inst. Geol. Bassin d'Aquitaine*, **16**, 121–126 (1974).
2. C. LaTouche, Ph. Bertrand, H. Etcheber, J.M. Jouanneau, *Mem. Soc. Geol. Fr.*, **144**, 155–160 (1982).
3. Ph. Bertrand, *Thèse 3°* cycle, Université de Bordeaux I, No 1547, (1980), 149 pp.
4. J.M. Brannon, R.M. Engler, J.R. Rose, P.G. Hunt, I. Smith, *U.S. Army Engineer Waterways*, D.76–18 Vicksburg, (1976), 33 pp.
5. Lin Rong Gen, *Thèse Université de Bordeaux I*, No 1218 (1988), 209 pp.
6. H. Etcheber, J.M. Jouanneau, C. LaTouche, P. Azoeuf, A. Caillot, R. Hoslin *Oceanol. Acta*. **3**, 477–486 (1980).
7. H. El Ghobary. *Thèse de doctorat d'Etat-ès-Sciences: Université de Bordeaux I*, (1983), 271 pp.
8. R. Chester and M.I. Hughes, *Chemical Geology*, **2**, 249–263 (1967).
9. B.J. Presley, Y. Kolodny, A. Nissebaub and I.R. Kaplan. *Geochim. Cosmochim Acta*. **36**, 1073–1090 (1972).
10. A. Tessier, P.G.C. Campbell, M. Bisson. *Anal. Chem.*, **51**, 844–851 (1979).
11. N. Meguellati. Thèse 3° cycle, Université Pau, (1982), 105 pp.
12. J.M. Jouanneau, C. LaTouche, F. Pautrizel. *Env. Techn. Letters*, **4**, 509–514 (1983).
13. H. El Ghobary and C. LaTouche, *in Proceedings of the third International Symposium on Interactions between Sediments and Water*, (P.G.Sly Edtr., Springer-Verlag New-York, Berlin, Heidelberg, 1984). pp. 27–31.
14. B. Roger. *DEA Université Bordeaux I*, (1983), 62 pp.
15. I. Hashimoto and M.L. Jackson. *Proc. 7ème Inter. Conf. on Clays and Clay Min.*, (A.Swineford Edtr., Washington DC 1960) pp. 102–113.
16. O.P. Mehra and M.L. Jackson. *Proc. 7ème Int. Conf. on Clays and Clay Min.*, (A.Swineford Edtr., Washington DC 1960) pp. 317–327.
17. U. Biermans and L. Baert, *Clay minerals*, **12**, 127–135 (1977).
18. J.C. Wasserman. *Thèse Université de Bordeaux I*, No 411, (1990), 263 pp.
19. A. Ure, P. Quevauviller, H. Muntau, B. Gripink B (1992). This issue.