CD AND PB EXTRACTABILITY WITH EDTA IN SEDIMENTS OF THREE CONTRASTED SITES OF THE LEBANESE COAST

C. Abi-Ghanem, A. Bermond[1], S. Besançon[1], K. Nakhlé and G. Khalaf
Centre National des Sciences Marines, CNRSL, P.O. Box 534, Batroun, Lebanon
[1]Agro-ParisTech, 16, rue C. Bernard, F.75231 Paris cedex 5, France
carine.a.ghanem@hotmail.fr

(Received 15 October 2008 - Accepted 26 February 2009)

ABSTRACT

Cd and Pb extractability with EDTA were measured from sediment samples collected at three contrasted sites along the Lebanese coastal zones: Akkar, Dora and Selaata. Akkar is located away from any direct source of contamination, while Dora and Selaata receive respectively urban and industrial wastes. The extractability of Cd and Pb from sediments of the aforementioned sites was studied by applying kinetic and equilibrium extractions with EDTA 0.05M. The adjustment of Pb kinetic extractions curves to a two-first order reactions model permitted to kinetically fractionate Pb in the studied sediments into three fractions (readily extractable, less extractable and non extractable) and allowed to conclude that Pb in Selaata represents the highest environmental risk.

Keywords: cadmium, lead, sediments, mobility, extraction, EDTA, Lebanon

INTRODUCTION

The coastal zone of Lebanon is subjected in many areas to trace metal contamination from domestic and industrial wastes discharged directly into the sea or into several rivers which drain rapidly into the sea (CDR/ECODIT-IAURIF, 1997). These anthropogenic activities have lead to an increase in trace metal levels in the water column and marine sediments in some heavily urbanized and industrialized zones of the Lebanese coast. Among these trace metals water and sediment enrichments, high levels of Cd and Pb were previously detected by several authors in many coastal areas (Shiber, 1980; Nakhlé, 2003; Nassif, 2005; Abi-Ghanem *et al.*, 2008). Studies conducted on Pb and Cd contamination in the solid phase of some Lebanese coastal marine sediments, were always limited to a superficial trace metal total quantification and, till now, no work has been done regarding these trace metal extractability.

However, since the quantification of total metal concentrations in sediment does not give a clear idea on their mobility and thus on their potential ecological risk, a particular attention is generally given to the study of trace metal bioavailability in the sediments of many parts of the world and to the estimation of the amount of metal mobilized from the solid phase of the sediment in specific environmental conditions. The kinetic approach to the speciation of trace metals with EDTA is a new operational speciation approach, recently applied to soils and sediments (Fangueiro, 2004; Bermond *et al.*, 2005; Manouchehri, 2006). It is based on the desorption fluxes of the metal from the sediment by the action of a single reagent (EDTA) (Fangueiro *et al.*, 2005). EDTA is a synthetic chelating agent that forms strong complexes with metals associated to the sediment components throughout various ways: ion exchange, adsorbtion, organically bound, or occlusion into inorganic compounds as Fe and Mn oxides and clay minerals (Paya-Perez *et al.*, 1993). In general kinetic extraction of trace metals with EDTA allows fractionating trace metals into three fractions i) fraction quickly extracted (called labile) which is supposed to represent the highest potential environmental risk, ii) a less quickly extracted fraction (called slowly labile) and iii) a non extracted fraction (Fangueiro, 2004; Manouchehri, 2006).

Due to the fact that these trace metal mobilization with EDTA were never applied to the Lebanese coastal sediments, this preliminary study was conducted with the following aims: 1) to test EDTA extraction potential regarding Cd and Pb present in three different sites of the Lebanese coast (Akkar, Dora and Selaata) and also 2) to verify the feasibility of applying EDTA kinetic extractions to the aforementioned trace elements, which could clarify Cd and Pb bioavailability in the studied sediments (Varrault, 2001; Fangueiro *et al.*, 2005).

MATERIAL AND METHODS

Study area

The prospected zone is the coastal zone located between Akkar in the north of Lebanon and Beirut. This zone is selected for its relatively high domestic and industrial activities; it contains more than 30% of the Lebanese industries and more than 40% of the population of Lebanon (Nakhlé, 2003) (Fig. 1, Table 1).

Akkar is one of the less studied areas in Lebanon from an environmental point of view. The chosen site is located in front of a seemingly non contaminated bay of Akkar, away from any important industrial activity or urbanization. Dora is a heavily urbanized and industrialized zone of the St Georges bay adjacent to the Beirut harbour, characterized by a dumpsite peninsula that received 120x10^6 kg of solid wastes per year until 1998, the year of its closure (CDR/ECODIT-IAURIF, 1997). The Selaata site is nearby a chemical plant established in 1957, which produces phosphoric acid, triple superphosphate, aluminium sulfate and sulfuric acid (Al-Hajj & Muscat, 2000).

TABLE 1

Description of the Core Sampling Sites

Site	Core	Coordinates (latitude, longitude)	Water column depth above the core (m)
Akkar	A	34°33’700N; 035°58’127E	18.5
Selaata	S6	34°17’205N; 035°39’685E	15
Dora	D	33°54’155N; 035°33’218E	8

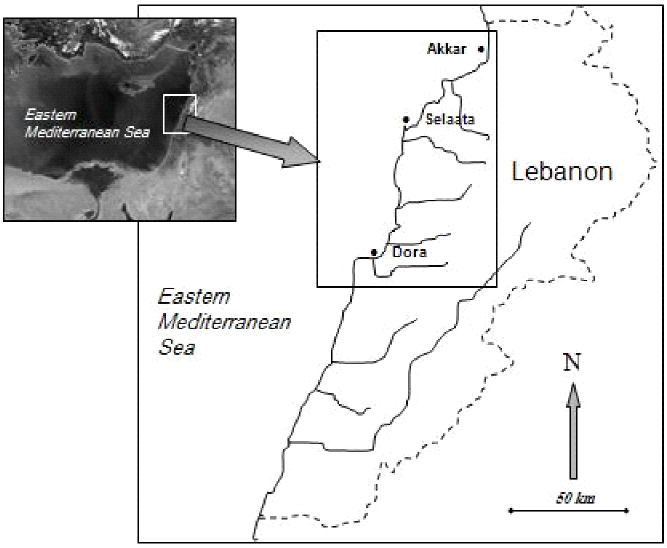

Figure 1. Studied area and locations of the sampling sites.

Sampling methods

The three stations were sampled for solid phase sediment between October and November 2006. For this purpose, acid pre-washed (immersion in HNO_3 50% at 40 ºC for three days, rinsing with deionised water, immersion in HNO_3 10% for three days, rinsing with deionised water) plastic (methacrylate) cores (40 cm high and 7 cm inner diameter) (A, D, S6) (Table1) were vertically introduced in the sediments by divers.

Laboratory analyses

Prior to the analysis, 1 cm layers of sediments were put in polyethylene bags and air-dried in an oven at 50°C until reaching constant weight, with frequent manual agitation in order to avoid their cementation. Then the sediment slices were dry sieved (<63 µm) using an acid pre-cleaned (immersion in HNO_3 50% at 40 ºC for three days, rinsing with deionised water, immersion in HNO_3 10% for three days, rinsing with deionised water) nylon sieve, the fraction (<63 µm) being used for further analysis. It is noteworthy that kinetic extraction analysis of Selaata S6 sediments were conducted on the total fraction of the sediments because of insufficient quantity of fine fraction (<63 µm).

X and γ ray measurements

Samples for the X-ray mineralogical determinations were finely crushed in an agate mortar and sieved on a zero background silicon plate. X-ray powder diffraction patterns were performed on a Philips PW 3710 diffractometer using Co $_{K\alpha}$ radiation (λ = 1.79 Å) with a secondary flat graphite monochromator. The diffractometer optic used to record all samples was a front fixed slit of 1°, a 1° scattered radiation slit after the sample and a detector slit of 0.2 mm. The X-ray tube operating conditions were 40 kV and 40 mA. The 2θ range was 3.5 – 78° in 0.02 steps and a counting time of 12 s. X'Pert Highscore plus software (Panalytical) with ICDD PDF-2 database was used to identify and quantify minerals in the samples.

Total concentrations

In order to determine total Ca, Mg, Fe, Al, Si, Cd and Pb concentrations in these sediments, 200 mg of dry sediment were digested for 2h 30min at 120°C with 250µl HNO_3 (65%), 750 µl HCl (30%) and 6 ml HF (48%) in Teflon bombs according to the protocol described by Loring and Rantala (1990). All reagents used were SupraPur® from Merck. Then, the digested samples were transferred into polypropylene tubes where 2.7 g of boric acid were added. The solution was then diluted to a final volume of 50 ml with deionised distilled water. The concentrations of analyzed elements were determined using an inductive coupled plasma mass spectrometer (ICP-MS, Thermo Electron Corporation, Element X Series). The determinations were validated using certified reference materials MESS-3 and BCSS-1 provided from the National Council of Research-Canada. A blank sample (prepared by mixing in the Teflon bombs the same quantities of acids and deionised water as in the analyzed series) was included with each batch of 15 samples in the total digestion procedure and then analyzed with ICP-MS. The values obtained for the blank are below detection limits (DL) ($Ca_{(DL)} = 0.34$ mg g^{-1}; $Mg_{(DL)} = 0.003$ mg g^{-1}; $Fe_{(DL)} = 0.12$ mg g^{-1}; $Pb_{(DL)} = 0.02$ µg g^{-1}; $Cd_{(DL)} = 0.01$ µg g^{-1}). On the other hand, values obtained for the certified reference materials were within the range of the certified values.

Organic carbon analysis

Organic carbon content was analysed using the Carlo Erba analytical system CHNS-O microanalyser EA 1110 according to the technique described by Quian (1993). Sediments are decarbonised under vacuum in a dessicator containing a small container of concentrated HCl 37% for 2 hours, before being dried in an oven at 50°C. For each sample, two to three aliquots of sediment were analysed, the coefficient of variation was <10%. Quality control and quality assurance of the results were performed using standard reference materials from the National Council of Research-Canada: B2150 and the MESS1 as well as with the MS68 which is a material used in interlaboratory comparison and which undergoes the same protocol as for decarbonised sediments. While certified percentage in mass for B2150, MESS1 and MS68 were 6.72±0.17, 2.99±0.09 and 2.23 respectively, the obtained result was were in the range of the accepted concentrations: 6.53±0.23, 2.95±0.09 and 2.21±0.04 respectively.

EDTA extractions

EDTA-extraction kinetics were conducted on the superficial (0-1) cm and the deep (21-23) cm layers for Akkar and Dora sediment cores and on the superficial (0-1) cm and the deep (15-17) cm layer of Selaata S6 sediments. The protocol used was optimized by Fangueiro *et al.* (2002) and insures high extraction capacity of EDTA without competitive extraction by H^+. The chelatant agent is disodium EDTA 0.05M adjusted at pH 6.5 with NaOH 8M. The Pb desorption kinetic was studied at different period of time (5, 10, 15, 20, 25, 30, 45, 60, 90, 120, 150, 200, 300, 500, 800, 1100 and 1440 min). For each time period, a flask (60 ml) containing 0.5 g of sediment and 50 ml of the EDTA solution was used and the flasks were stirred with an end-over-end shaker. After agitation with the sediments, the EDTA solution was filtered through a 0.45 µm cellulose acetate membrane (Millipore). To facilitate the filtration step, a preliminary centrifugation of the solution (for 3 min at 6000 rpm) was done prior to its passage through the cellulose acetate membrane. The pH of the obtained EDTA extracts was measured and the solutions were then stored at 4°C prior to analysis. In addition to Pb concentrations measurements, Fe, Mg, Ca and Cd concentrations were also analyzed in the EDTA extracts obtained at the extraction time of 24 h. All the reagents used were of analytical-reagent grade and purchased from Merck. The concentrations of the aforementioned metals were determined by atomic absorption spectrometry (Hitach Z-5000), air-acetylene flame is applied in the case of Ca, Fe and Mg analysis and electrothermal in the case of Pb and Cd. Matrix modifier ($NH_4H_2PO_4$) and the technique of standard addition was used to overcome matrix interferences in the case of Pb and Cd analysis. Three replicates were made for each sample at the extraction time of 24h; their relative standard deviation was < 5%. Metal concentrations in blanks were below these detection limits (DL) ($Ca_{(DL)} = 0.1$ mg l^{-1}; $Mg_{(DL)} = 0.1$ mg l^{-1}; $Fe_{(DL)} = 0.1$ mg l^{-1}; $Pb_{(DL)} = 0.02$ µg l^{-1}; $Cd_{(DL)} = 0.01$µg l^{-1}).

Estimation of kinetic parameters

Experimental curves resulting from kinetic extraction with EDTA were adjusted to a two first-order reactions model using a non-linear regression program Sigma-Plot® software. The quality of the fitting process was controlled by several statistical parameters such as the coefficient of correlation (r), the standard error of estimate (S.E.) and the P value.

RESULTS AND DISCUSSION

Mineralogical composition and sediment organic carbon content

The sediment mineralogical composition analyzed by X-ray diffraction indicates that Akkar sediments are the most enriched with dolomite and ankerite (40-45%), while Dora's sediments exhibit the highest content in quartz (SiO_2) (70-80%). The Selaata sediment mineralogical composition is mainly represented by the two compounds quartz (25-55%) and fluorite CaF_2 (25-55%) which presence in Selaata deposits testifies of the input of the phosphogypsum industries (Abi-Ghanem *et al.*, 2008).

Total organic carbon contents vary from 0.91% to 2.82% with the highest percentage in mass obtained for Akkar sediments 2.5% ± 0.32. In contrast Dora and Selaata sediments had the lower percentage of organic carbon 1.3 %± 0.39 and 1.28%± 0.32 respectively. These percentages are the mean and standard deviation of the concentration obtained for the different levels (15-18 sediment samples) of each core.

Chemical components (Ca, Fe, Mg, Cd and Pb) total concentrations in upper and deep sediment layers of Akkar, Dora and Selaata sediments

Ca, Fe, Mg, Pb and Cd total content in the studied sediment levels of Akkar, Dora and Selaata are presented in Table 2.

Akkar sediment layers are the most enriched with Ca (21-23%) and Mg (4-5%) globally originating from dolomite, calcite and ankerite rocks erosion. On the other hand, Dora sediments exhibit the highest percentage in mass of Fe (5%) with relatively low concentrations of Ca and Mg. Selaata sediment layers which present the lower Fe percentages (1-2%) are relatively enriched with Ca (15%). The highest Pb (78-101 µg g^{-1}) and Cd (0.65-0.71 µg g^{-1}) concentrations comparable to values obtained in contaminated sediments, are obtained in Dora sediments, whereas relatively low concentrations of theses trace elements are obtained in Akkar and the total fraction of Selaata S6 sediments.

TABLE 2

Major Element (Ca, Fe, Mg) and Trace Element (Pb, Cd) Concentrations in the Studied Sediment Layers (into Bracket Is the Depth of the Sediment Layer in cm). Ca, Fe and Mg Concentrations are Expressed in Percentage in Mass of the Fraction (<63 µm) for Akkar and Dora Sediments and of the Total Fraction for Selaata S6 Sediments

	Ca (%)	Fe (%)	Mg (%)	Pb (µg g^{-1})	Cd (µg g^{-1})
A(0-1)	23.21	3.54	4.23	12.20	0.14
A(21-23)	21.07	3.67	5.11	8.52	0.14
S6 (0-1)	15.13	1.69	1.54	4.59	0.31
S6 (15-17)	15.27	1.72	1.76	5.48	0.30
D(0-1)	12.91	4.98	1.07	78.36	0.71
D(21-23)	11.27	4.90	0.96	101.06	0.65

Major element Ca, Mg and Fe extractability with EDTA at equilibrium

In order to clarify the sediment major element attitude regarding EDTA extraction and to verify that EDTA is always in excess, the percentages in mass of Ca, Mg and Fe extracted after 24 hours of extraction time were studied. This period of time is considered as sufficient to reach the thermodynamic equilibrium especially for Ca and Mg (Bermond *et al.*, 1998; Fangueiro *et al.*, 2002).

Table 3 shows that Ca is highly mobilised with EDTA (82-99%) at the superficial and the deep sediment layers of Akkar and Dora. This Ca behaviour and also the lower amount of Ca extracted from Selaata sediments (31-38%) have to be related to the mineralogical composition of the sediments. Ca at Akkar and at Dora sediments is mostly present as calcite $CaCO_3$, dolomite $CaMg(CO_3)_2$ and ankerite $Ca(Mg,Fe)(CO_3)_2$ (Abi-Ghanem *et al.*, 2008) originating mainly from the weathering of the dominant coastal dolomite and calcite rocks (Sanlaville, 1977), while in Selaata sediments Ca is mainly present as fluoride (CaF_2) which results from the processing of the phosphate rock in Selaata chemical plant (Abi-Ghanem *et al.*, 2008). Thus one can conclude that the Ca extracted with EDTA from Dora, Akkar and Selaata sediments, originates mainly from calcite and dolomite compounds. However, the Ca present as fluoride in Selaata sediments is less extracted with EDTA.

Mg is more extracted from Dora sediments where the percentage of Mg is (0.84-1.07%) than from Akkar sediments or from Selaata sediments where Mg content is (3-5%) and (1.5-1.7%) respectively. X-ray mineralogical analysis have shown that Mg is naturally present in Akkar as dolomite and ankerite (40-45%) (Abi-Ghanem *et al.*, 2008) with lower quantity (<10%) of augite (Ca, Mg, Fe) SiO_3, whereas in Dora and Selaata sediments it is present as dolomite and ankerite. Thus the relatively low percentage of Mg extracted from Akkar sediments could be related to the fact that a fraction of Mg is present as augite especially that as previously shown, dolomite and ankerite can be highly mobilised with EDTA, thus Mg which is associated with dolomite and ankerite is also highly mobilised.

TABLE 3

Percentage of the Total Ca, Mg, and Fe Extracted with EDTA at Equilibrium

	A(0-1)	A(21-23)	S6(0-1)	S6(15-17)	D(0-1)	D(21-23)
Ca (%)	85,95 ±2.00	82,13 ±0.75	31,44 ±0.47	38,14 ±1.00	86,69 ±3.45	99,26 ±0.22
Mg (%)	47,56 ±1.20	46,83 ±0.57	56,87 ±1.28	50,51 ±1.26	61,73 ±2.24	64,36±1.07
Fe (%)	3,28 ±0.05	3,90 ±0.05	7,92 ±0.17	6,88 ±0.42	9,97±0.63	14,12 ±0.27

Fe is more mobilised in Dora sediments where total Fe content varies from 4.3 to 5% than in Selaata or Akkar sediments where the percentages of total Fe are 2% and 3-3.6% respectively. Compared to Ca and Mg, Fe is very weakly extracted which could be explained by its abundant presence as oxyhydroxides and Fe-oxides whose dissolution in the presence of EDTA is very slow and does not easily reach the equilibrium even after 24 hours of extraction (Bordas & Bourg, 1998; Ghestem, 1997). Semi-quantitative X-ray mineralogical analysis results are in the favour of this hypothesis, they indicate that Akkar sediments contain hematite Fe_2O_3 (1-2.5%), goethite FeO(OH) (0.8-2%) and magnetite Fe_3O_4 (0.4-1.5%), while in Dora sediments, the presence of these Fe-oxides is limited to low quantity of goethite (1-1.5 %), the dominant Fe mineral in Lebanese soils (Darwish & Zurayk, 1997). On the other hand, Selaata's mineralogical analysis revealed the presence of low quantity (0.1-0.4%) of magnetite Fe_3O_4.

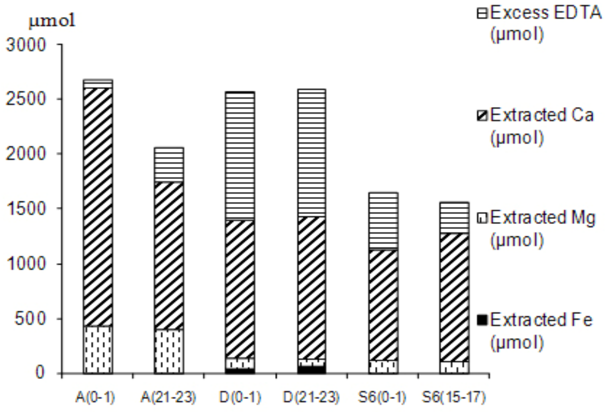

Figure 2. Ca, Fe and Mg (µmol) extracted with EDTA 0.05M at equilibrium.

According to these results and assuming that Ca, Mg and Fe are the main major cations extracted by EDTA, the mass balance established for Akkar, Dora and Selaata sediments (Fig. 2) indicates clearly that under these experimental conditions there is an excess of EDTA even though this excess is not important for some sediment layer as A(0-1). Thus one can consider that EDTA is, from a kinetic point of view, not limitant for the extraction of the studied major (Ca, Fe and Mg) and trace elements (Cd, Pb). This excess EDTA also allows the application of the simple kinetic hypothesis to these results.

EDTA-extraction of Cd and Pb

In order to clarify Cd and Pb remobilization with EDTA from the studied sediments and to study the feasibility of kinetics extractions with EDTA to these deposits, Cd and Pb extraction with EDTA on the upper and deep sediment layers of cores collected at the three sites were conducted (Akkar, Dora and Selaata) (see § on EDTA extractions).

Cd extraction at equilibrium

EDTA extractions applied to the superficial and to deep sediment layer of Akkar, Dora and Selaata sediments indicates that 45-50% of Cd is extracted from Dora's sediment layers and around 60% of Cd at Akkar is extracted after 24 h of extraction time while (62-65%) of Cd present at Selaata sediments is extracted within the same time (Fig. 3). Compared to data in literature, these percentages are comparable to those of Cd extracted from uncontaminated carbonate soils (Manouchehri, 2006) and lower than the percentages of Cd mobilized from contaminated sediments (73-80%) or from contaminated soils (70-90%) (Ghestem, 1997; Fangueiro *et al.*, 2002). Despite its higher concentrations at Dora sediments, Cd is more mobilized in Akkar sediments. Compared to Dora, Cd is also more mobilized in Selaata sediments where Cd concentrations in the total fraction of the sediment are lower (Table 2).

These findings lead to the conclusion that the amount of Cd desorbed with EDTA from the studied sediments seems to be imposed by its association with the solid phase of the sediment which is in accord with results obtained by Bordas and Bourg (1998).

Cd in Akkar and Selaata sediments is more easily mobilized than Cd in Dora's sediments which indicate its lower affinity to Akkar and Selaata sediments than to Dora's sediments.

The high affinity of Cd to Dora's sediments rich in quartz, could be explained by the possible integration of Cd in the lattice of silicate primary minerals and also could be related to the possible presence of Cd in a precipitated form *e.g.* octavite $CdCO_3$ (Fuller & Davis, 1987).

These factors allow a very strong metal association with the solid phase of the sediments and thus decrease its mobilization with EDTA. On the other hand, the highest percentage of Cd extracted with EDTA (65%) corresponds to the superficial sediment layer of Selaata sediments which indicates that, compared to Akkar and Dora sediments, Cd present in Selaata sediments and discharged by Selaata chemical plant is the most loosely bound to the sediment.

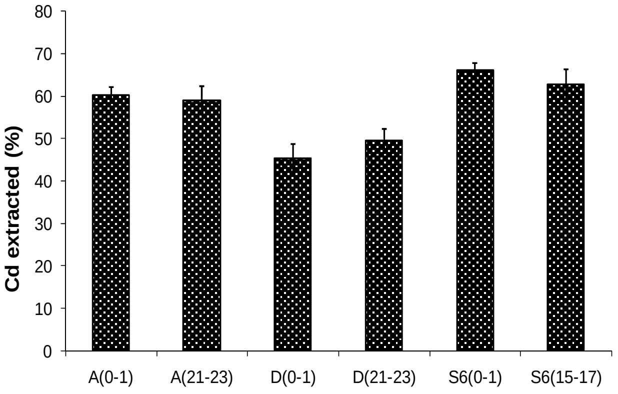

Figure 3. Percentage of Cd extracted at equilibrium from superficial and deep sediment layers of Akkar (A), Dora (D) and Selaata (S6).

The extractability of Cd with EDTA at equilibrium from the three sites Akkar, Dora and Selaata has been modelized with Multiple Regression Analysis using Statgraphic centurion Software. The different factors used are major elements Ca, Si, Fe, Mg, organic carbon expressed in percentage of mass and total Cd (µg g^{-1}). The best model obtained is presented in equation (1):

$$\log Cd_{extr} = -6.07 + 5.53 \log Ca - 2.61 \log Mg + 2.85 \log Fe \ (p<0.01;\ R^2=0.98)\ (n=12) \qquad (1)$$

Thus one can clearly see that 98% of the variability of the quantity of extracted Cd at equilibrium is explained by a positive impact of Ca and Fe and a negative impact of Mg.

Pb extraction (equilibrium and kinetics)

Equilibrium study

EDTA extractions applied to the superficial and deep sediment layers of Akkar, Dora and Selaata deposits indicate that the percentages of lead mobilized with EDTA 0.05M from different sediment levels of Akkar and Selaata are comparable and vary between 72 and 77% (Fig. 4).

On the other hand 93% of lead is extracted from Dora D(0-1) cm sediment layer and 67 % is extracted from D(21-23) cm sediment layer.

Thus one can clearly see that lead is highly mobilised with EDTA in these sediments which is consistent with the high value of the complexation constant of Pb with EDTA (log K= 18.3).

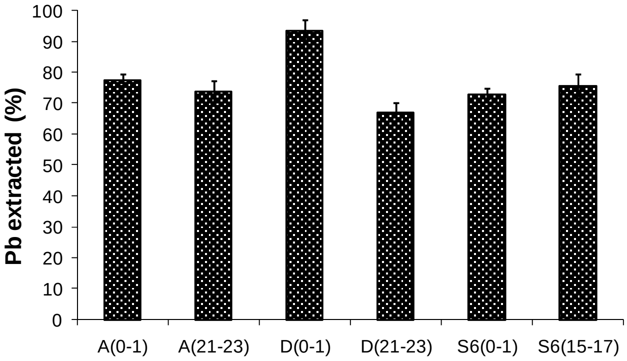

Figure 4. Percentage of Pb extracted at equilibrium from superficial and deep sediment layers of Akkar (A), Dora (D) and Selaata (S6).

Noteworthy that the absence of significant differences between the percentage of lead mobilized with EDTA at equilibrium from Akkar sediments and that from Selaata sediments suppose that Pb is associated in similar ways to these latter deposits, especially that the rate limiting step for Pb complexation with EDTA is the detachment of Pb^{2+} from the surface of the sediment (Nowack *et al.*, 2001). As for Cd, modelizing the extractability of Pb with EDTA at equilibrium from the three sites Akkar, Dora and Selaata with Multiple Regression Analysis (Statgraphic Centurion Software) leads to the model presented in equation (2):

$$\log Pb_{extr} = -4.2 + 0.99 \log Pb_{tot} - 0.96 \log Corg - 2.02 \log Si + 6.43 \log Ca - 3.16 \log Mg \quad (p<0.01;\ R^2=0.98)\ (n=12) \qquad (2)$$

Thus it can be concluded that 98% of the variability of extracted Pb at equilibrium from Akkar, Dora and Selaata sediments are explained: i) by a positive contribution of Pb_{tot}, and Ca and ii) by a negative contribution of Corg, Si, and Mg. On the other hand, high lead percentages extracted with EDTA at equilibrium (Fig. 4) correspond to high extracted Pb concentrations especially at Dora sediments (57 to 78 µg g^{-1}). These high lead percentages extracted with EDTA at equilibrium have lead to apply Pb kinetic extractions with EDTA to the studied sediment layers. The aforementioned kinetic extractions allowed a finer partitioning of extracted lead into rapidly extracted and less rapidly extracted (Ghestem, 1997; Manouchehri, 2006). However, relatively low Cd concentrations (0.08-0.3 µg g^{-1}) extracted with EDTA at equilibrium from the studied sediments did not allow to successfully apply these kinetic extractions to Cd.

Kinetic extraction of Pb

Extraction kinetics of lead were studied on Akkar and Dora and Selaata first and deep sediment levels (see the third section). The extraction rate data of Pb with EDTA from the studied sediments is presented in Figure 5 where one can see that the extraction process consists of a rapid extraction in the first 30 minutes, followed by much slower extraction one can also see that the amount of metal extracted reaches a plateau after 5-8 h of extraction time.

The model that fits successfully the extraction kinetic of lead at Akkar and Dora sediments and to a lower extends Selaata sediments is the two first-order (or pseudo-first-order) reaction model. This model has been widely used in trace metal extractions kinetics with EDTA from soils (Bermond *et al.*, 2005; Manouchehri, 2006) and sediments (Yu & Klarup, 1994; Fangueiro *et al.*, 2005). It's a simplified form of the multiple first-order reactions model which is based on the assumption that the desorption of a trace metal from a specific bounding site of the sediment is governed by a first-order reaction (Lin & Chen, 1998).

The two first-order reactions model is presented in the following equation:

$$Q = Q_1^0 (1 - \exp^{-k1}t) + Q_2^0 (1 - \exp^{-k2}t) \qquad (3)$$

where: Q (μg g^{-1}) is the fraction of metal extracted from the sediment at time t
Q_1^0 (μg g^{-1}) is the fraction of metal readily extractable associated to the rate constant k_1
Q_2^0 (μg g^{-1}) is the fraction of metal less extractable associated to the rate constant k_2

The adjustment of the former equation to the extraction rate data allows the non-linear regression calculations effectuated by the Sigma-Plot® software the calculation of Q_1^0, Q_2^0, k_1 and k_2.

On the other hand, the fraction of metal not extractable Q_3^0 (μg g^{-1}) is obtained by calculating the difference between the total concentration of lead in the sediment Q_{tot} and the concentration of lead extracted at equilibrium:

$$Q_3^0 = Q_{tot} - Q_1^0 - Q_2^0 \qquad (4)$$

Table 4 shows that the coefficient of correlation r is always higher that 0.95 (except for Selaata sediments because of low extracted Pb concentrations), the p value associated to each fit was always lower than 0.0001 and the standard error of estimate S.E. was relatively low.

The readily extractable fraction Q_1^0 is always higher than the fraction of metal less extractable Q_2^0. The rate constant k_1 which is also higher than k_2, varies between 0.25 and 0.6 min^{-1} according to the sediment level and its geographical position. On the other hand k_2 is almost constant and correspond to 0.005-0.006 min^{-1}.

The variability in k_1 values indicates that the fraction rapidly extracted from the studied sediments is bound in different ways to the solid phase of the sediment. In other words, one can say that the readily extractable fractions of lead in Akkar sediments and Dora superficial sediment levels are bound to the solid phase of the sediment in similar ways which permits obtaining comparable k_1 values (0.3-0.4 min^{-1}), whereas higher k_1 value (0.6 min^{-1}) obtained in Selaata S6 superficial sediment layer shows that the fraction rapidly extracted from these sediments is more loosely bounded to the solid fraction of the sediments than this latter in Akkar and Dora sediments. Regarding the fraction of lead less extractable Q_2^0, one can say that this fraction is bounded to the solid phase of Akkar, Dora and Selaata sediments in similar ways which assures comparable k_2 values (0.005-0.006 min^{-1}). It is noteworthy that the low concentrations of lead extracted with EDTA resulting from applying kinetic extractions to deep sediment layer of Selaata S6 core (Fig. 5) did not allow the successful adjustment of S6 (15-17) cm kinetic curve to the two first-order reactions model. Thus one cannot calculate corresponding Q_1^0, Q_2^0, k_1 and k_2.

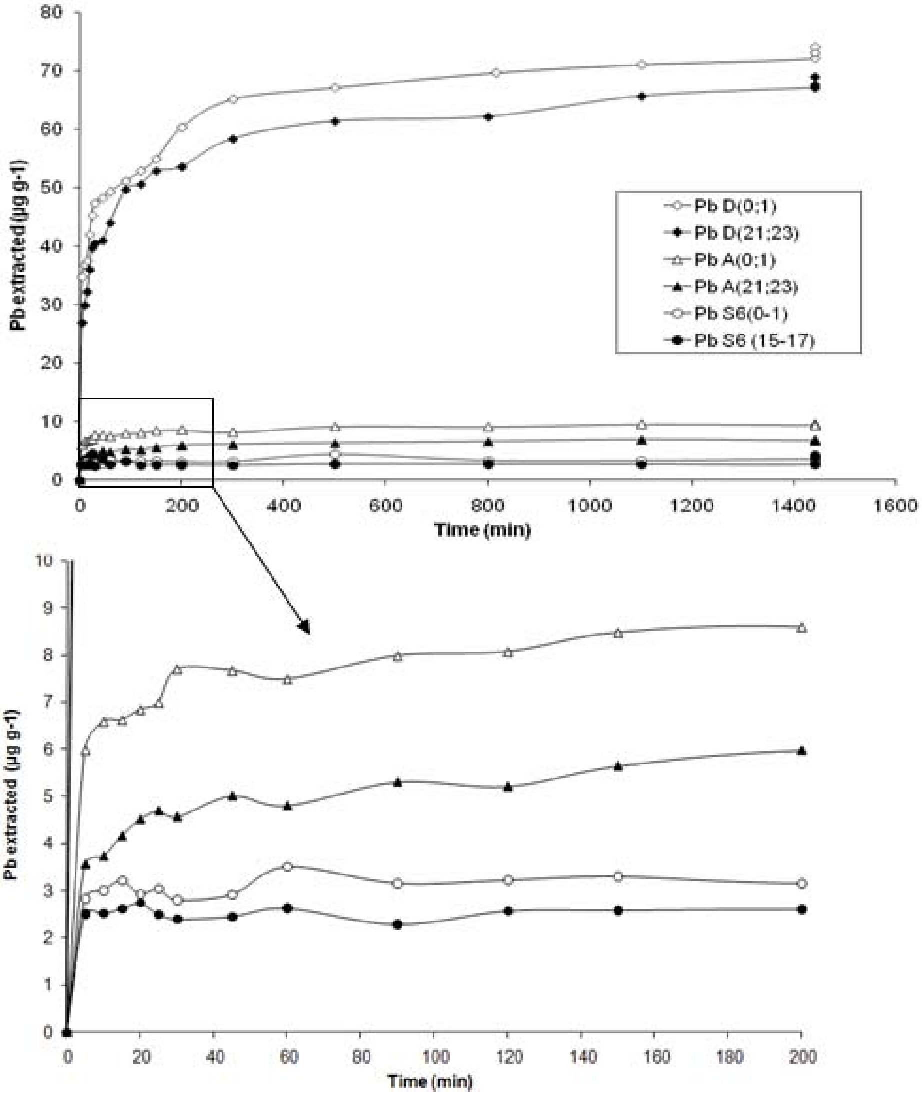

Figure 5. Pb extraction curves *vs* time in Akkar (A), Dora (D) and Selaata (S6) sediments.

TABLE 4

Q_1^0, Q_2^0, Q_3^0 (µg g^{-1}), k_1, k_2 (min^{-1}), Coefficient of Correlation (r) and Standard Error of Estimate (S.E.) (µg g^{-1}) of Two First-Order Reaction Model for Pb Kinetic Extraction by EDTA 0.05M from Akkar (A), Dora (D) and Selaata (S6) Sediment Layers

	A(0-1)	A(21-23)	D(0-1)	D(21-23)	S6(0-1)
Q_1^0	6.9	4.2	38.3	33.4	2.9
Q_2^0	2.5	2.6	32.35	32.4	0.52
k_1	0.4	0.3	0.4	0.25	0.6
k_2	0.005	0.005	0.005	0.005	0.006
R	0.98	0.98	0.96	0.98	0.85
S.E.	1.43	0.19	3.3	2.37	0.3
Q_3^0	2.8	1.72	7.71	35.26	1.17

Selaata S6 (15-17) kinetic parameters were not detected because of difficulties in adjustment S6 (15-17) kinetic curves to the two first-order reaction model

Interpretation of results corresponding to the kinetic extraction of Pb

The fractions Q_1^0, Q_2^0, Q_3^0 which result from fitting the extraction curves to the two first-order reaction model, are recalculated as fractions F_1, F_2 and F_3 of the total content by applying the equations presented below:

$$F_1 = Q_1^0 \times 100/ Q_{tot} \qquad (5)$$
$$F_2 = Q_2^0 \times 100/ Q_{tot} \qquad (6)$$
$$F_3 = Q_3^0 \times 100/ Q_{tot} \qquad (7)$$

The results obtained for Akkar, Dora and Selaata are presented in Figure 6 where one can clearly see that F1+F2 constitute more that 60% of total lead in each of the sediment levels of Akkar, Dora and Selaata. This kinetic fractionation allows to kinetically define more than 60% of lead present in the studied sediments, and up to 90% of Pb present in the superficial sediment layer of Dora. The most readily extracted fraction F1 constitutes the most abundant fraction (50<F1<60%) in the studied sediments (except for D(21-23)). The F1 values are higher than values obtained by Fangueiro *et al.* (2005) in contaminated sediments, but are comparable to the values obtained by Ghestem (1997) who studied lead kinetic extractions in contaminated soils.

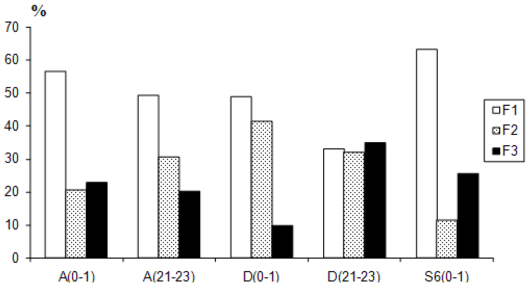

Figure 6. Distribution of lead into F1, F2 and F3 fractions in Akkar (A), Dora (D) and Selaata (S6) sediment layers.

If one takes into account that the fraction of lead more easily extracted is the more mobile in the sediment (Varrault, 2001; Fangueiro *et al.*, 2005), the studied sediment layers could be ranked as follows:

S6 (0-1) > A(0-1) > A(21-23) ≥ D(0-1) > D(21-23)

Thus one can conclude that lead in Selaata sediments is the most subject to potential mobilization and constitute the highest potential environmental risk to marine ecosystem. However and despite its high concentrations in Dora sediments and its low concentrations in Akkar sediments (Table 2), Pb in Akkar carbonated sediments is more rapidly mobilized which can be related to the high capacity of EDTA in extracting cations associated to carbonates (Ghestem, 1997). It is noteworthy that among the same sites (in the case of Akkar and Dora), Pb in the upper sediment layers is more rapidly mobilized than Pb in the deep sediment layers, which can be due to the fact that Pb in the upper sediment levels is freshly associated to the sediments and thus more loosely bounded to their compartment compared to Pb in deep sediment layers. These findings also could be an indicator that anthropogenic lead inputs (lead in the upper sediment layer of Akkar) is more rapidly mobilized with EDTA than the naturally derived Pb (Varrault, 2001; Abi-Ghanem *et al.*, 2008).

CONCLUSION

This preliminary study has proven that EDTA is efficient in extracting Pb and Cd from the studied contrasted sediments at the Lebanese coast. Applying extractions with EDTA 0.05M at equilibrium on Ca, Mg and Fe present in superficial and deep sediment layers of Akkar, Dora and Selaata clearly indicates that one is in excess EDTA and that Ca and Mg present in dolomite, ankerite and calcite compounds are highly extracted with EDTA. As regard Cd extractability at equilibrium with EDTA, these results show that (52-65%) of total Cd are mobilized after 24 hours of extraction time in Selaata sediments and (45-50%) in Dora sediments. This finding lead to conclude that Cd present in Selaata (namely in the upper sediment layer of Selaata) and in Akkar sediments is more loosely bound to the sediment compared to Cd present in Dora sediments.

Lead kinetic extractions with EDTA 0.05M applied to superficial and deep sediment layers of Akkar, Dora and Selaata sediments allowed to obtain kinetic extraction curves that were adjusted to a two first-order reactions model by non-linear regression calculations which permitted to determine the fractions of metal readily extractable Q_1^0 and less readily extractable Q_2^0, and also to calculate the corresponding rate constants k_1 and k_2. Thus one was able to kinetically "speciate" more than 60% of lead present in the sediments, the fraction non extracted with EDTA being (<40%). On the other, as regard lead potential environmental risk to marine ecosystem and biota, the studied sediments were ranked as follows:

S6 (0-1) > A(0-1) > A(21-23) ≥ D(0-1) > D(21-23)

This order correspond to the fraction of Pb rapidly extracted with EDTA calculated in percentage of total lead and which is considered as the most mobile in the sediment (Varrault, 2001; Fangueiro *et al.*, 2005). Thus one can say that, among the same site, lead freshly installed in the upper sediment layers presents the highest environmental risk whereas lead in the deep sediment layers is more strongly associated to the sediment components and thus less subject to remobilization. On the other hand, Pb in the upper sediment layer of

Selaata constitutes the highest environmental risk whereas Pb in the deep sediment layer of Dora presents the lowest environmental risk.

ACKNOWLEDGEMENTS

D. Auger, B. Averty, E. Rozuel and E. Teirik are gratefully acknowledged for their skilful help in the sampling operation and for analyses. Thanks are due to C. Gobeil (INRS-ETE) who provided the radioisotopic measurements and to D. Cossa for his for his comments on an early version of the manuscript. This research was funded by the CEDRE project (Convention N° 05 E F42/L6), the Lebanese CNRS, Ifremer and the "Agence Universitaire de la Francophonie" (AUF), which provides funding for student residence time in France.

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