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# Lead and its isotopes in the sediment of three sites on the Lebanese coast: Identification of contamination sources and mobility

C. Abi-Ghanem<sup>a,\*</sup>, J.F. Chiffoleau<sup>b</sup>, A. Bermond<sup>c</sup>, K. Nakhlé<sup>a</sup>, G. Khalaf<sup>a</sup>, D. Borschneck<sup>d</sup> and D.

Corresponding author : C. Abi-Ghanem, Fax: +961 6 741 584, email address: carine.a.ghanem@hotmail.fr

#### Abstract:

Lead concentrations and isotopic composition of sediment samples collected from three sites within the Lebanese coastal zones were measured; at Akkar. Dora and Selaata. Akkar is located far from any direct source of contamination, while Dora and Selaata receive urban and industrial wastes, respectively. Low Pb concentrations (6-16 µg g<sup>-1</sup>) were detected in the Akkar sediments, and high concentrations of Pb (70-101 µg g<sup>-1</sup>) were detected in the Dora sediments. Measuring stable isotope ratios of Pb makes it possible to identify the principal sources of Pb in the Akkar sediments as Pb emitted from gasoline combustion and Pb originating from natural sources. On the other hand, Pb stable isotopic ratios in Dora sediments indicate that they are more highly influenced by anthropogenic sources. Isotopic Pb ratios in the Selaata deposits, where Pb concentrations range between 5 and  $35~\mu g~g^{-1}$ , have an exceptional radiogenic signature for marine sediments  $1.25 < ^{206} Pb/^{207} Pb < 1.6$  and  $0.5 < ^{206} Pb/^{208} Pb < 0.67$ , which shows the impact of the phosphogypsum discharged by Selaata's chemical plant. Isotopic Pb analysis applied to EDTA extracts, to test the mobility of Pb, shows that that this mobility is high (>60%) after 24 h of extraction, and that the extracted Pb is less radiogenic than the residual Pb.

<sup>&</sup>lt;sup>a</sup> Centre National des Sciences Marines, CNRSL, P.O. Box 534, Batroun, Lebanon

<sup>&</sup>lt;sup>b</sup> Ifremer, LBCM, Centre de Nantes, BP 21105, F.44311 Nantes cedex 3, France

<sup>&</sup>lt;sup>c</sup> Agro-ParisTech, 16, rue C. Bernard, F.75231 Paris cedex 5, France <sup>d</sup> CEREGE CNRS, Aix-Marseille University, Europôle Méditerranéen de l'Arbois, BP 80, 13545 Aix-en-Provence, France

## 1. Introduction

Lead is present in the continental crust as a trace element. Its presence in near-shore marine sediments is the result of the mixing of material from various sources: coastal erosion, biogenic and mineral components, river borne particles and atmospheric deposits. Each of these materials has its own natural Pb concentration and is, to various degrees, impregnated by anthropogenic inputs (Callender, 2005). The main anthropogenic sources for Pb are non-ferrous metallurgy, fuel combustion (especially coal), waste incinerators, glass production and gasoline additives, (e.g., Snakin and Prisyazhaya, 2000; Nriagu, 1990; Nriagu and Pacyna, 1988). In the last century, Pb contaminated the global atmosphere. The analysis of ice sheet data indicates that early Pb smelting was responsible for beginning the increase in the concentration of Pb in the atmosphere (Murozumi et al., 1969). At the end of the 18th century this increase was heightened by the industrial revolution, and then a sharp increase in atmospheric Pb emissions occurred around 1950, due to the burning of Pb alkyls in gasoline. Finally, atmospheric Pb fluxes decreased 6.5-fold in the last decades of the 20<sup>th</sup> century, in response to the banning of leaded gasoline throughout most of the world (Candelon et al., 1995; Callender, 2005). The impact of this anthropogenic Pb on surficial pelagic sediments from the North Atlantic was clearly revealed by Hamelin et al. (1990). . On the other hand, many authors have studied anthropogenic Pb input to coastal and continental shelf regions, because of the rapid removal process of Pb from seawater in these regions, which are characterized by high accumulation rates. These facts permit a precise reconstruction of the increase of Pb pollution over time (Nriagu and Patterson, 1982; Ridgway and Price, 1987). It should be noted that the combustion of Pb additives in gasoline has been revealed as the main source of Pb contamination in many coastal sediments such as those along the Southern California coast (Chow et al., 1973; Hamelin et al., 1990).

To determine the amplitude of Pb contamination in coastal marine sediment, the capacity to discriminate natural from anthropogenic Pb must be improved. It is thus important, first of all, to define the nature and the origin of the coastal sedimentary deposits, before trying to qualify the "contamination level" of the sediments.

Following the pioneer work of Patterson et al. (1976), stable Pb isotope composition is now frequently used for tracing the sources and the movement of Pb in the environment. There are 4 stable isotopes of Pb: 204Pb, 206Pb, 207Pb and 208Pb. The first is not radiogenic, and its abundance has remained constant since the formation of the solar system, while the other 3 are produced by the radioactive decay of <sup>238</sup>U, <sup>235</sup>U and <sup>232</sup>Th, respectively. The ratios of these isotopes in Pb ores vary according to the geographical regions where they are extracted (Doe, 1970). This geographical variability is due to differences in Pb accumulation generated by radioactive decay over geological time in the different regions, and to how long the Pb and its radioactive parents were together in the mantle and crust before the Pb was separated into ore bodies (Patterson and Chow, 1962; Doe, 1970). The isotopic signal of Pb in the environment now stems from 3 major sources: natural, gasoline additives and metal industries (smelters). The Pb generated from natural sources is characterized by its high <sup>206</sup>Pb/<sup>207</sup>Pb, <sup>206</sup>Pb/<sup>208</sup>Pb and  $^{206}$ Pb/ $^{204}$ Pb ratios; 1.2 ± 0.01, 0.48 ± 0.001 and 18.95 ± 0.016, respectively (Luck and Othman, 1998). The lowest ratios are generally obtained for leaded gasoline ( $^{206}$ Pb/ $^{207}$ Pb = 1.11 ± 0.02;  $^{206}$ Pb/ $^{208}$ Pb = 0.46 ± 0.006 and  $^{206}$ Pb/ $^{204}$ Pb = 17.34 ± 0.48), especially tetra-ethyl and tetramethyl Pb distributed by Octel and Novoktam in Western Europe and in North Africa, while gasoline distributed by Ethyl Corporation has higher isotopic ratios (Chow et al., 1975; Alleman, 1997; Ferrand et al., 1999). The industrial emissions have different Pb isotopic compositions, which are in general more radiogenic than the Pb emitted by gasoline combustion (Monna et al., 1995; Alleman, 1997; Ferrand et al., 1999; Veron et al., 1999).

Numerous studies concerning Pb isotopes have been conducted in the North Western Mediterranean area (Maring et al., 1987; Alleman, 1997; Luck and Othman, 2002; Mirailles et

al., 2003). In the Eastern Mediterranean zone such studies are rare; Erel et al. (1997) used the isotopic ratios to trace anthropogenic Pb in the atmosphere and in soils of the Eastern Mediterranean region. He found that anthropogenic Pb existing in aerosols and soils was influenced by alkyl-Pb produced in France and Germany, by aerosols traveling across the Eastern Mediterranean basin from Turkey, and others originating in Greece and the Ukraine. These findings agree with the results of a more recent study conducted by Erel et al. (2002), who showed that Pb detected in the atmosphere of Jerusalem (Israel) originates from local petrol Pb and also from anthropogenic Pb transported to Jerusalem from Egypt, Turkey and Eastern Europe. On the other hand, Teutsch et al. (2001), who studied Pb in soils of nearby Eastern Mediterranean countries, have shown that petrol-Pb, mainly produced in North America, has penetrated all of the roadside soil, and has reached the aluminosilicate fraction in the upper layer of the soil.

Other studies of Pb in marine sediments from the Eastern Mediterranean have determined total Pb content (Krumgalz and Fainshtein, 1991; Herut et al., 1993), without discussing their sources. In Lebanon, there are 4 major potential sources of Pb: gasoline combustion, industries (thermoelectrical, cement and fertilizer industries), untreated urban waste combustion and the weathering of rocks (Nassif, 2004). The emission of Pb generated in the atmosphere from gasoline combustion decreased between 1993 (the year of the introduction of unleaded gasoline in Lebanon) and 1999, from around 700 tons a<sup>-1</sup> to around 400 tons a<sup>-1</sup>, with the highest Pb concentration found in the air of some urbanized industrial zones (Hashisho and El-Fadel, 2004). No recent data are available from environmental samples within the last decade, and the atmospheric Pb generated by industrial plants has never been precisely monitored: the only available data come from estimates. For example, El-Fadel et al. (2000) indicate that the water near the electrical power plant of Jiyeh (South of Lebanon) has a Pb concentration 9 times higher than that of other industrial sites within the Lebanese coastal zone, and studies conducted on the river-sediments and soils of the Nahr-Ibrahim region, which receives urban and industrial effluents, have shown that the mean Pb concentrations in the river sediments and in the nearby soils are 91 µg g<sup>-1</sup> and 297 µg g<sup>-1</sup>, respectively, comparable to those of polluted soils and sediments elsewhere in the world (Korfali and Davies, 2004). However, concerning Pb isotope determination, the only study in Lebanon was conducted by Bollhofer and Rosman (2000, 2001), who indicated that the isotopic signatures of atmospheric Pb in Chekka (North of Lebanon) in 1994 ( $^{206}$ Pb/ $^{207}$ Pb = 1.119 ± 0.001,  $^{208}$ Pb/ $^{207}$ Pb = 2.393 ± 0.001,  $^{206}$ Pb/ $^{204}$ Pb = 17.39 ± 0.02), were mainly determined by French and German alkyllead producers.

The aim of this paper is to characterize the anthropogenic Pb content of the Lebanese near-shore sediments of 3 bays: Akkar, Selaata and St Georges (Dora). These sites have been selected on the basis of previous work, which indicate that the Akkar bay is far from any direct contamination source, while the Dora and Selaata sites are characterized by urban and industrial inputs, respectively (Nakhlé, 2003; Nassif, 2004). In order to distinguish between natural variability and the influences of contamination, the mineralogy and the major ion composition of the sediments (Ca, Fe, Al, Mg, Si) was first determined, and then the stable isotopic Pb composition of the sediments. In addition, in order to try to determine the age of the deposit and time changes, short sediment cores were taken and analyzed for chemical chronometers (<sup>210</sup>Pb and <sup>137</sup>Cs). Finally, additional leaching experiments were designed to study the possible mobility of Pb associated with these coastal deposits and also to identify the main sources of the mobilized Pb at different periods of time.

## 2. Material and methods

# 2.1. Sampling and environmental settings

The Lebanese coastal zone, which constitutes a part of the carbonate platform that covers most of the Eastern Mediterranean basin, results geologically from the carbonate marine sedimentation between the Jurassic and the Quaternary periods (Abdel-Rahman and Nader, 2002). Geological surveys indicate the presence of a thick layer of dolomite, marls or chalk. In fact these carbonate rocks are the only ones that reach the littoral zone today. Volcanic rocks also exist in two different layers in the stratigraphic sequence. The volcanic complexes (basalts and ashes) of the Jurassic are exposed in the deep valleys of Mount-Lebanon. Volcanic rocks (mainly basaltic) of the Quaternary Miocene Age cover most of the plate of Akkar (Sanlaville, 1977).

Sediment cores were collected between October and November 2006 at 3 sites in the Lebanese coastal zone, : Akkar (A), Dora (D) and Selaata (S3-S6-S4), as indicated in Figure 1 and described in Table 1. From an environmental point of view, Akkar is one of the least studied areas in Lebanon. The site chosen is located facing the apparently non-contaminated bay of Akkar, distant from any important industrial activity or urbanization. Dora is a heavily urbanized and industrialized zone on the St George bay, adjacent to Beirut harbour, characterized by a dumpsite peninsula that received 120 x 10<sup>6</sup> kg of solid waste per year until 1998, the year of its closure (CDR/ECODIT-IAURIF, 1997). The Selaata bay is near a chemical plant, established in 1957, which produces phosphoric acid, triple superphosphate, aluminium sulfate and sulfuric acid (Al-Haij and Muscat, 2000).

One core was collected at Akkar, one at Dora, and 3 cores were sampled at Selaata : the first (S3) facing the chemical power plant and very close to its effluent, the second (S6) from a bay to the north of the Selaata plants, relatively protected from the marine currents, where higher amounts of fine sediments are thought to be present. A supplementary core, S4, located between S3 and S6, was also collected for mineralogical analysis. The cores were collected by using acid pre-washed metacrylate tubes (40 cm long, with an inner diameter of 7 cm) vertically introduced into the sediment by divers. They were plugged at both ends with plastic covered rubber stoppers and kept in a refrigerator in a vertical position at +4°C. In the laboratory, the cores were sliced at 1-cm thick intervals for the first 5 cm and at 3-cm intervals for the remaining length. The sediment sub-samples were put in polyethylene bags and were air-dried in an oven at 50°C until reaching constant weight, with frequent manual agitation, in order to avoid cementation. Finally, the sediment slices were dry sieved (<63  $\mu$ m) using an acid pre-cleaned nylon sieve. Only the fine fraction (<63  $\mu$ m) was used for the analyses.

### 2.2. Chemical analyses

### 2.2.1. Total digestion

For AI, Si, Mg, Ca, Fe, Pb and the stable Pb isotope ratios: <sup>206</sup>Pb/<sup>207</sup>Pb, <sup>206</sup>Pb/<sup>208</sup>Pb, <sup>206</sup>Pb/<sup>204</sup>Pb analysis, an aliquot of approximately 200 mg of dry sediment was digested for 2 h 30 min at 120°C with 250µL HNO<sub>3</sub> (65%), 750µL HCI (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. A blank sample and certified reference material were included with each

batch of 15 samples in the total digestion procedure and then analyzed by ICP-MS. The values obtained for the blank are below detection limits. The certified and the mean measured values of Mg, Al, Si, Ca, Fe and Pb in the two materials of reference MESS3 and BCSS1 are shown in Table 2. Mass fractionation in the Pb ratio measurements was monitored by frequent measurements of the Pb standard NIST-SRM 981 (common Pb isotopic standard). Differences between the NIST-SRM 981 measured and its certified standard ratios are used for mass corrections of Pb isotope ratios in the sediment samples. The relative standard deviation of measured isotope values varies between 0.2 % for <sup>206</sup>Pb/<sup>207</sup>Pb and <sup>206</sup>Pb/<sup>208</sup>Pb and 0.6% for <sup>206</sup>Pb/<sup>204</sup>Pb. The higher analytical precision of <sup>206</sup>Pb/<sup>207</sup>Pb and <sup>206</sup>Pb/<sup>208</sup>Pb led to using these ratios in the study of Pb sources throughout this work. This choice has been adopted in many environmental studies (Negrel et al., 2004; Monna et al., 1997).

#### 2.2.2. Kinetic extraction

The kinetic extraction of Pb was studied using the fine fraction (<63 µm) for Akkar and Dora and the total fraction for Selaata (S6). Because of time limitations, kinetic extraction was applied at only two sediment levels from each of the 3 sediment cores. The two sediment levels used in the extraction are the 0-1 cm and the 21-23 cm levels of the Akkar and Dora sediment cores, and the 0-1 cm and the 15-17 cm level of the Selaata sediment core. The protocol applied is the one proposed by Fangueiro et al. (2002). The chelatant agent used is EDTA 0.05M, adjusted to pH 6.5 with NaOH 8M. This EDTA concentration ensures an excess of EDTA, and the pH of 6.5 guaranties minimal variations of pH during the extraction. The Pb desorption kinetics was studied at 3 different time intervals (10 min, 30 min and 24 h). For each time period, a flask (60 mL) containing 0.5g of sediment and 50 mL of the EDTA solution was used, and the flasks were stirred with an end-over-end shaker. After agitation, the solution was filtered through a 0.45µm cellulose acetate membrane (Millipore). To facilitate the filtration step, a preliminary centrifugation of the solution (for 3 min at 6000 rpm) was made prior to its passage through the cellulose acetate membrane. Then the pH of the filtrate was measured and the solution stored at 4°C. All the reagents used were of analytical-reagent grade, purchased from Merck. The concentration of Pb extracted with EDTA was measured with a Hitach Z-5000 EAAS, equipped with a Zeeman correction. A matrix modifier (NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>) and the technique of standard addition were used to overcome matrix interferences. The relative standard deviation of Pb measurements obtained for the analysis of 3 discrete subsamples of selected samples was < 5%. After the measurements of the concentration of Pb, the pH of the extract was adjusted to about 4 with HNO<sub>3</sub> 1.54N, and stored at 4°C for further isotopic analysis. The Pb isotopic measurements were determined with the ICP-MS, following the procedure described above.

#### 2.2.3. 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  $_{\text{K}\alpha}$  radiation ( $\lambda$  = 1.79 Å) with a secondary flat graphite monochromator. The diffractometer optics used to record all samples were a front fixed slit of 1°, a 1° scattered radiation slit after the sample and a detector slit of 0.2mm. The X-ray tube operating conditions were 40kV and 40mA. The 2 $\theta$  range was 3.5 – 78° in 0.02 steps and a counting time of 12s. X'Pert Highscore plus software (Panalytical) with an ICDD PDF-2 database was used to identify and quantify minerals in the samples.

<sup>210</sup>Pb and <sup>137</sup>Cs measurements were made using a low background γ rayspectrometer equipped with a semi-planar Ge detector, coupled with a multichannel analyzer. Unsupported Pb (<sup>210</sup>Pb<sub>ex</sub>) was derived from the total <sup>210</sup>Pb activity, measured at 46.5keV, by subtracting the <sup>226</sup>Ra activity.

# 3. Results and discussion

In order to reduce the effect of sediment grain size on the variability of the physico-chemical measurements, the sediment fraction finer than 63 µm was used for the analyses.

## 3.1. Mineralogical composition

X-ray diffraction patterns show a high contribution of dolomite  $CaMg(CO_3)_2$  and ankerite  $Ca(Mg,Fe)(CO_3)_2$  (40-45%) in the Akkar sediments, with a lower contribution of calcite  $CaCO_3$  (20-25%) and quartz  $SiO_2$  (10-20%) (Table 3). The Dora sediments are highly enriched in quartz, (70-80%) with lower amounts of calcite (10-20%), ankerite and dolomite. The mineralogical composition of the Selaata sediment consists mainly of two minerals, quartz (25-55%) and fluorite  $CaF_2$  (25-55%), testifying to the input of the phosphogypsum industries (Table 3).

# 3.2. The major elements

At Akkar, the Ca and Mg concentrations show a lot of fluctuations, respectively, between 20-30% and 3-6%. At the 9 cm level, the ratio Mg/Ca increased from 0.15 to 0.26. Aluminium declined slightly with depth, from 1.8 to 3%. Iron and Si varied between 2.9 and 4.3% and between 6.7 and 8.7%, respectively. A superficial layer rich in Al and poor in Ca is noted.

The lowest values of Ca (10-14%) and Mg (0.8-1%) were found at Dora, where high Si concentrations (18.4-28.2%) were detected. Aluminium and Fe concentrations in the Dora sediment core varied, respectively, from between 2 and 3.1% and 4.3 and 5.8%.

At Selaata, Ca and Mg concentrations varied from 12 to 24%, and from 2.3 to 3.7%, respectively. Silicon concentrations fluctuate between 9 and 21%. Aluminium concentrations were also homogenous (1.4-2.2%). Iron concentrations at Selaata S3 varied from 3.1 to 4.9%, with highest concentrations in the first 6 cm.

The major element composition of the sediment is summarised by a ternary plot (Fig. 2), in which 3 different sample groups, corresponding to the sediments of Akkar (A), Dora (D) and Selaata (S6 and S3), can be distinguished. The Akkar sediments are the most highly enriched in  $CaCO_3$  and  $MgCO_3$  (70-80%), while the Dora sediments exhibit the highest content in  $SiO_2$  (45-60%). The results in the Selaata sediment fall between those of Akkar and Dora. It is ntable that the contribution in mass percentages of Fe and Al is similar for the 3 types of sediments, expressed as  $Fe_2O_3 + Al_2O_3$ , ranging from 5 to 15%. It can be concluded that the chemical composition of Akkar and Dora sediments is consistent with the mineralogical results. However, the specific mineralogy of the Selaata sediments, indicated by the analysis, is not clearly revealed in this ternary plot, given the fact that the major element analysis does not allow distinguishing between Ca from carbonates and that originating from fluorite.

# 3.3. <sup>210</sup>Pb and <sup>137</sup>Cs

<sup>210</sup>Pb is a radioactive isotope with a short half-life, 22.3 a. It is produced by the radioactive decay of i) <sup>222</sup>Rn emitted by the continental crust in the atmosphere and ii) <sup>226</sup>Ra present in the water column (Lu, 2007). Studying the activity of unsupported <sup>210</sup>Pb and <sup>210</sup>Pb<sub>ex</sub> in the sediments (<sup>210</sup>Pb produced by the radioactive decay of <sup>222</sup>Rn) enables dating them (Ferrand, 1996). Since the geochronology of the sediment, obtained by the study of the <sup>210</sup>Pb<sub>ex</sub> vertical profile, can be distorted by processes of mixture, bioturbation and compaction, this dating is verified by studying the profile of an independant time marker <sup>137</sup>Cs (Smith, 2001). <sup>137</sup>Cs is an artificial radioactive isotope originating in the atmospheric nuclear tests which took place between 1952

and 1972 and which were responsible for 90% of these emissions in 1963-1964. Its half-life is 30 a (Audry, 2003).

The study showed that <sup>210</sup>Pb<sub>ex</sub> was undetectable (<0.05 Bq g<sup>-1</sup>) in the Akkar and Dora samples. This result precludes the aging of these sediments and suggests that the two sites are mainly composed of detritic sediments from coastal erosion (or anthropogenic quarry material), with a very slight influence of recent continental alluvial or atmospheric deposits. At Selaata <sup>210</sup>Pb<sub>ex</sub> values in the S6 samples were low (0.19-0.25 Bq g<sup>-1</sup>, ±20%) and quite homogenous in the 11 samples analyzed between the benthic interface and a depth of 16 cm. This suggests that the origin of the <sup>210</sup>Pb<sub>ex</sub> is to be found in the waste from the Selaata phosphoric acid plant. The fact that <sup>210</sup>Pb<sub>ex</sub> in the Selaata deposits does not exhibit any linear decrease makes it very difficult to date these sediments. On the other hand, <sup>137</sup>Cs was also undetectable in the sediment studied core, which did not enable us to locate sediment layers that settled in the sixties. The very low concentrations of <sup>137</sup>Cs obtained lead to two conclusions: i) The impact of the nuclear tests on this area of the Eastern Mediterranean is insignificant, and/or ii) The nature of the sediments, rich in carbonate and quartz and very poor in clay content, limits the adsorption of <sup>137</sup>Cs which, as is well known, has a much greater affinity for clays (Poinssot et al.., 1999).

#### 3.4. Lead distributions and sources

Lead concentration profiles were established for the 3 sites (Fig. 3). The variation of Pb concentrations in sediment can result from differences in the grain size, the mineralogy, the redox potential, and from anthropogenic impact. For this reason the grain-size normalization approach, by selecting for analysis the fraction of sediment finer than 63 µm, was completed by a geochemical correction, which consists of a normalizing technique using a tracer element (Kersten and Smedes, 2002). The tracer element chosen in this study is Al because of its capacity to represent the clay sediment fraction, and also because it is scarcely influenced by anthropogenic inputs and by organic matter degradation (Roussiez et al., 2005). Then, once the total Pb concentration distribution was described, an attempt was made to trace the different origins of Pb by calculating Pb isotopic ratios. Particular attention was given to the <sup>206</sup>Pb/<sup>207</sup>Pb ratio, which gives a better understanding of the impact of anthropogenic Pb, especially since this stable isotope ratio is subject to only a very small analytical error and is insensitive to mineralogical changes in the sediments (Monna et al., 1995; Roussiez et al., 2005).

The results were plotted on a <sup>207</sup>Pb/<sup>206</sup>Pb and <sup>208</sup>Pb/<sup>206</sup>Pb diagram (Fig. 4), using as end-members data from literature concerning the isotopic composition of some leaded and unleaded gasoline, some Mediterranean aerosols and certain rocks (Table 5).

# 3.4.1. Akkar

Pb concentrations in the sediments of Akkar ranged from between 6.2  $\mu g$  g<sup>-1</sup> in the deepest layer to 15.8  $\mu g$  g<sup>-1</sup> in the superficial layer (Fig. 3a). These levels are in the low range of the mean earth crust composition (Table 4) especially for carbonate rocks which, according to Kabata-Pendias and Pendias (1992), have Pb concentrations that fluctuate between 3 and 10  $\mu g$  g<sup>-1</sup>, while typical Pb concentrations are 23  $\mu g$  g<sup>-1</sup> in schist and granite, 10  $\mu g$  g<sup>-1</sup> in sandstone and very low in some magmatic rocks such as gabbro (2  $\mu g$  g<sup>-1</sup>). However, they are comparable to the first measurements made in the Akkar watershed sediments (Thomas et al., 2005) and the marine sediment of the adjacent Batroun region (Table 4).

The vertical profile of Pb concentrations exhibited its highest value (16  $\mu g$  g<sup>-1</sup>) and quite large variations within the first 12-14 cm below the water sediment interface, and then regularly decreased from 14 to 6  $\mu g$  g<sup>-1</sup> downward in the core (Fig. 3a). It should be noted that this 12-14 cm change was also detected in the Mg/Ca ratio values that regularly increased below the 12-14 cm level from 0.18 to 0.26% . Change in the Mg/Ca ratios are important, since they indicate

a modification in the mineralogical composition of the sediment, especially that Mg is mainly present in the sediment as dolomite CaMg(CO<sub>3</sub>)<sub>2</sub> and ankerite Ca(Mg,Fe)(CO<sub>3</sub>)<sub>2</sub>. The variability between 0 and 12 cm completely disappears (except for two points) when plotting the Pb/Al ratio versus depth (Fig. 3a). The regular Pb concentration decreases between 20 cm and 28 cm and is related to changes in Si concentrations (Pb ( $\mu g g^{-1}$ ) = -1.7 %Si + 21.3; R<sup>2</sup>= 0.84, p<0.05 and n= 5), and also to higher amounts of ankerite [Ca(Fe,Mq,Mn)(CO<sub>3</sub>)<sub>2</sub>] and lower amounts of quartz (Table 3). However, the regular increase of Pb concentrations and Pb/Al in the lower part of the core (12cm down) is not solely accounted for by these mineralogical changes. To clarify whether or not the Pb distribution is affected by anthropogenic inputs, the Pb isotopic signature is useful. Applying stable Pb isotopic analysis to Akkar sediments clearly shows that the Akkar  $^{206}$ Pb/ $^{207}$ Pb ratio has low values in the first 20cm (1.165<  $^{206}$ Pb/ $^{207}$ Pb <1.18), but this ratio becomes more radiogenic (1.18< <sup>206</sup>Pb/<sup>207</sup>Pb <1.22) in the deepest 10 cm, and attains a value of 1.22 without reaching any constant value. The increase in Pb concentrations in the upper 20 cm of the sediment core (Fig. 3a), correlates well with the low <sup>206</sup>Pb/<sup>207</sup>Pb ratio at these levels. This feature, classically obtained by other authors (Ferrand et al., 1999), indicates the anthropogenic origin of the Pb enrichment.

The small fluctuations of the <sup>206</sup>Pb/<sup>207</sup>Pb ratio in the first 20cm may be related to the various contributions of different types of gasoline combustion and industrial emissions (Table 5). The increase in the <sup>206</sup>Pb/<sup>207</sup>Pb profile between 10 and 5 cm from 1.16 to 1.18 may be related to a higher contribution of industrial Pb and to the decrease in leaded gasoline emissions in 1993, when unleaded gasoline was introduced in Lebanon (Nakhlé, 2003). In addition, the <sup>206</sup>Pb/<sup>207</sup>Pb profile shows an increase between 16 and 22 cm, at the same depth as a decrease in total Pb concentration (Fig. 3a). However, these conclusions must be considered carefully, because of the absence of any stratigraphic evidence in the core, and also because of the impact of turbidity currents and bioturbation, which can be present in the area studied and could strongly influence the Pb profile (Barusseau and Radakovitch, 1996; Puig et al., 2001).

In the deepest layer of the sediment core the  $^{206}$ Pb/ $^{207}$ Pb ratio 1.22 is almost equal to the signature of Miocene silicate rock (Luck and Othman, 1998) and is more radiogenic than the value considered to be the natural isotopic composition of Mediterranean sediment  $^{206}$ Pb/ $^{207}$ Pb = 1.2  $\pm$  0.005 (Ferrand et al., 1999; Alleman et al., 2000). These findings suggest that the Pb in this deepest sediment layer of the Akkar core corresponds to natural pre-anthropogenic Pb, and is likely to originate from the erosion of Miocene Limestone, abundant in Akkar (Sanlaville, 1977).

#### 3.4.2. Dora

Dora sediment has the highest concentration of Pb for this study (70-101 µg g<sup>-1</sup>). These values, compared to other sediments in the Mediterranean zone and in the world, reflect large anthropogenic inputs (Table 4). High Pb concentrations in the Dora sediments have been detected previously (Shiber, 1980; Nassif, 2004). These high concentrations are consistent with the high Pb level in water, up to 360 ng L<sup>-1</sup>, measured by Nakhlé (2003), while natural concentrations in Mediterranean waters are lower than 50 ng L<sup>-1</sup>. In addition, the evidence for anthropogenic effects is shown in the inputs of the Antélias River, which receives industrial and urban waste water from the city of Beirut, with a significant input of particulate Pb (Hashisho and El-Fadel, 2001; Nakhlé, 2003).

The Pb profile in the sediment core of Dora bay shows a two-layer pattern, below and above 9 cm. In the superficial 8cm, Pb concentrations were constant, with values being ~80  $\mu$ g g<sup>-1</sup> (Fig. 3b). In the deeper layers the Pb profile is much more heterogeneous with two peaks higher than 100  $\mu$ g g<sup>-1</sup> at 10 and 22 cm depth. The normalization of Pb to Al minimizes the vertical fluctuations in the profile. A slight tendency toward an upcore decrease of the Pb/Al ratio appears from the overall profile (Fig. 3b). This feature may be related to the closure of the Dora

dumpsite that took place in 1998. This hypothesis would suggest a 1cm year $^{-1}$  sedimentation rate in the area, which is reasonable for a coastal area. However, this is not corroborated by the  $^{210}\text{Pb}_{\text{ex}}$  values, which were undetectable.

The  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios at Dora are less radiogenic than those for Akkar, indicating a greater contribution from anthropogenic sources. In general the  $^{206}\text{Pb}/^{207}\text{Pb}$  vertical profile does not show significant variations with depth (1.16-1.17), which indicates that Pb sources have not changed with time. The lowest values of the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio for the highest Pb concentrations, confirms the anthropogenic origin of the Pb enrichment (Fig. 3b). In addition, the natural isotopic signature of Pb has not been detected in the sediment core of Dora, since the highest value for the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio is 1.17, less radiogenic than the natural isotopic signature (Table 5). The enrichment (up to 100 µg g<sup>-1</sup>) in the 10 and the 22 cm layers of Dora sediments is well correlated with the lowest  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio  $\sim 1.158\text{-}1.159$ , indicating an increase in the anthropogenic inputs of Pb.

The measured isotope ratios <sup>207</sup>Pb/<sup>206</sup>Pb and <sup>208</sup>Pb/<sup>206</sup>Pb in the sediment of Akkar and Dora, compared to data in the literature (Fig. 4), show that most of the results for the Dora plot are near the anthropogenic end-member (gasoline) and Mediterranean aerosols. This phenomenon indicates that Pb in the Dora sediment is more highly influenced by anthropogenic sources. However, because of the multiplicity of these sources at Dora, which is a highly urbanized and industrialized zone, it is difficult to determine the contribution of each. Isotopic values from the Akkar sediments shifted more radically towards the natural end-member, showing consistently in total Pb concentrations that these sediments are less contaminated than those of Dora.

# 3.4.3. Selaata

Lead concentrations in Selaata sediments range between 5 and 35  $\mu g~g^{-1}$  in the two cores analyzed (Table 4). The vertical distributions of Pb and its isotopes in Selaata sediment cores show considerable variability between cores and with depth (Fig. 3c). In S3, Pb concentrations range between 4.8  $\mu g~g^{-1}$  and 18.2  $\mu g~g^{-1}$ , with a minimum value at 10 cm. In the other layers Pb shows slight fluctuations around the value of 14.0  $\mu g~g^{-1}$ . The S6 sediment core collected in a bay to the north of the Selaata plants, is globally more highly enriched with Pb, especially in the superficial 10 cm, which may be due to its higher Pb loaded fine particles transported from Selaata discharges to the North by marine current. Nakhlé (2003) estimated that 13.612 kg of particulate Pb are discharged annually by the plant. The normalization of Pb to Al gives profiles very similair to the original Pb profile (Fig. 3c) and does not compensate for the enrichment in some levels, which indicates that the enrichment of Pb in the Selaata sediments is not due to a variation in the clay content of the sediments, but is more likely linked to Pb content in the industrial discharges.

The isotopic composition of Pb in the Selaata sediment  $(1.25<^{206}\text{Pb}/^{207}\text{Pb}<1.6$  and  $0.5<^{206}\text{Pb}/^{208}\text{Pb}<0.67)$  is very unusual for marine sediments. This isotopic signature is more radiogenic than most ore bodies, in which the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio ranges from between 0.92 and 1.3 (Sturges and Barrie, 1989). There is no specificity in the geological structure of the rocks in the Selaata area (Sanlaville, 1977) to relate these high radiogenic values to a particular source. It seems however that this source is Pb enriched. Indeed, the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio is inversely correlated to a high degree with total Pb concentrations in S6 ( $^{206}\text{Pb}/^{207}\text{Pb} = -0.007$  Pb ( $\mu$ g g<sup>-1</sup>) + 1.45; R<sup>2</sup>= 0.84, p<0.01 and n = 11). The Selaata plant uses phosphate rocks, imported from Syria, as a raw material. This raw material contains 48  $\mu$ g g<sup>-1</sup> of U (unpublished data K. Nakhlé). The major waste byproduct of the plant is phosphogypsum, discharged at a rate of 250 10<sup>3</sup> kg per day<sup>-1</sup> (Nakhlé, 2003), thus covering a large surface of the seabed sediments near the chemical plant (pers. comm. of divers of the CSM). This sediment can contain as much as 60 times the concentration of radioactive material normally found in phosphate rock (TEBODIN, 2000) and a "considerable content of the natural uranium radioactive decay series" was found in

the industrial wastewater of the plant (Al-Hajj and Muscat, 2000). These facts are consistent with the extremely radiogenic isotopic signature in Selaata sediment and suggest that the reason for this particular <sup>206</sup>Pb/<sup>207</sup>Pb ratio may be the characteristics of the phosphate rock processed in the Selaata plant. Selaata chemical plant inputs on nearby marine deposits is clearly revealed by X-ray mineralogical analyses, which have shown that 25-55% of the fine fraction of these sediments is composed of fluorite, CaF<sub>2</sub>, which is a compound naturally present in the phosphate rock Ca<sub>3</sub>(PO4)<sub>2</sub> processed in the Selaata plant (Al-Hajj and Muscat, 2000). Thus the high radiogenic isotopic ratios of the Selaata deposits and their fluctuations indicate the specificity and the original source of the sediments studied. They are quite different from other areas in the Lebanese coastal zone, and have a Pb isotopic signature greater than superficial coastal sediment collected in the Mediterranean basin, where the ratio <sup>206</sup>Pb/<sup>207</sup>Pb fluctuates from between 1.175 and 1.193 (Ferrand et al., 1999; Alleman etal., 2000; Miralles et al., 2003).

#### 3.5. Kinetic extraction with EDTA

EDTA is a non specific strong complexant, able to extract elements that are sorbed or organically bound to the sediment. It is used in sequential extraction procedures and as a single extractant that estimates the mobility of an element in sediments or soils (Fangueiro et al., 2002). Kinetic extractions with EDTA applied to sediments are a time-based fractionation approach which uses one specific added chemical reagent (EDTA) to study the desorption fluxes of the metals from sediments at different periods of time within 24 h (Fangueiro et al., 2005). In general the kinetic extraction of trace metals with EDTA permits the division of these trace metals into 3 fractions: i) a fraction quickly extracted (called labile) which is thought to represent the highest potential environmental risk, ii) a more slowly extracted fraction (called slowly labile) and iii) a non extracted fraction (Fangueiro, 2004; Manouchehri, 2006). However, the main sources of these extracted trace metals has never been studied. Thus, the present study has been focused on the determination of the Pb isotopic signature of Pb extracted with EDTA, from the studied sediments, at different periods of time. The extraction times have been limited to 3 periods: 10, 30 and 1440 min. During the first period (10 min), the kinetics of Pb extraction is rapid. However, within 30 min, Pb is less rapidely extracted and the 1440 min period represents the equilibrium time of the extraction (Abi-Ghanem et al., 2009).

The percentages of Pb extracted with EDTA after 24 h of extraction time are in the range of 81%, 77% and 62 % for Akkar, Dora and Selaata respectively. Thus, more than half of the Pb is mobilized after 24h, which is consistent with the high value of the complexation constant of Pb with EDTA (log K= 18.3). The isotopic ratio of the residual fraction is predicted by applying the following equation, proposed by Bacon et al. (2006), for sequential extraction procedures:

 $R_{residue} = (R_{tot} \times C_{tot} - R_{1440} \times C_{1440}) / (C_{tot} - C_{1440})$ 

where  $R_{\text{residue}}$  is the isotopic ratio in the residual fraction,  $R_{\text{tot}}$  is the isotopic ratio in the unfractionated sediment and  $R_{1440}$  is the isotopic ratio of Pb extracted with EDTA after 1440 min of extraction time.  $C_{\text{tot}}$  and  $C_{1440}$  correspond to total Pb concentration in the sediment and the concentration of Pb extracted after 1440 min, respectively. The amplitude of variation in the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios of the extracted Pb was large. The highest values were found for the Selaata sediments (1.26< $^{206}\text{Pb}/^{207}\text{Pb}$ <1.43), and the least radiogenic isotopic ratio for the Dora sediments (1.14< $^{206}\text{Pb}/^{207}\text{Pb}$ <1.15). This indicates that EDTA can mobilize different types of Pb. Isotopic signatures of Pb extracted with EDTA from Akkar and Dora sediments are plotted in a  $^{207}\text{Pb}/^{206}\text{Pb}$ ,  $^{208}\text{Pb}/^{206}\text{Pb}$  diagram (Fig. 5) where it can clearly be seen that the residual fraction has an isotopic signature close to that of natural rocks for the superficial layer of Dora sediments, while the Pb extracted has an isotopic signature closer to Mediterranean aerosols for Akkar and to gasoline for Dora. It seems therefore that lithogenic Pb is not significantly extracted with EDTA (0.05M), while EDTA tends to rapidly mobilize the anthropogenic Pb.

# 4. Summary and conclusions

Based on mineralogy, chemical composition and the isotopic Pb analysis of sediment cores, the study clearly shows the anthropogenic influence on 3 distinct areas of the near-shore environment of the Lebanon coast. At Akkar, located far from any direct source of contamination, Pb concentrations (6-16  $\mu g$  g<sup>-1</sup>) are low, probably due to the presence of Miocene basaltic silicate and carbonate rocks. The mineralogical changes explain many fluctuations in the Pb vertical profile in the core. However, although the concentrations of total Pb are low in the Akkar sediments, the Pb isotopic signatures clearly show anthropogenic components.

The Dora bay, adjacent to a huge dumpsite in Beirut harbor (St Georges bay), is the most contaminated site. The high Pb concentrations (up to 100  $\mu$ g g<sup>-1</sup>), coupled with isotopic Pb signatures (i.e., low <sup>206</sup>Pb/<sup>207</sup>Pb ratios in Dora sediments: 1.16 - 1.17), indicate that this zone is highly influenced by anthropogenic inputs.

In the Selaata sediments, located near a chemical fertilizer plant and an urban area, Pb concentrations range from 5 to 35  $\mu g$  g<sup>-1</sup> and the Pb vertical profile shows great variability between cores and with depth. Stable Pb isotopic ratios at the Selaata deposits are highly radiogenic  $1.25 < ^{206} Pb/^{207} Pb < 1.6$ ,  $0.5 < ^{206} Pb/^{208} Pb < 0.67$ . These values are unexpected for marine sediments. Based on mineralogical X-ray determinations, which reveal the presence of phosphogypsum and fluorite, this isotopic signature is attributed to the effluents of the Selaata chemical plant, which processes phosphate rock. Lead isotopic analysis was also applied to EDTA 0.05M extracts, to try to identify the sources of the Pb mobilized by this technique. Results indicate that the Pb extracted with EDTA is more anthropogenic than the residual Pb. As a follow-up for the study, the authors suggest studying the isotopic Pb signature in the

aerosols emitted by the thermoelectrical power plants, cement industries and gasoline combustion in Lebanon. The determination of the isotopic imprint of major pollutant sources in the area studied will enable quantifying the impact of the anthropogenic activities on the geochemical cycle of Pb in Lebanon.

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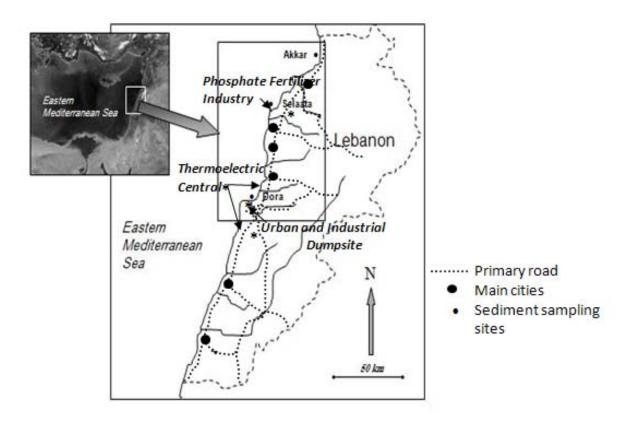


Figure 1. Area studied and locations of the sampling sites.

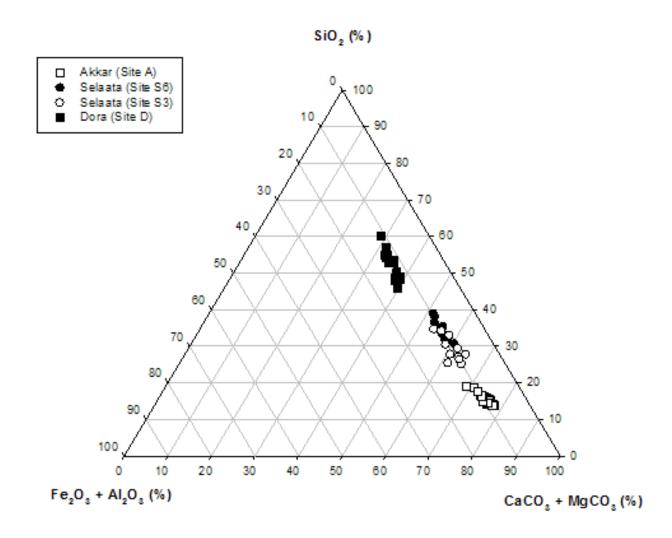


Figure 2. Ternary plot of major elements of Akkar, Dora and Selaata (S3 and S6) sediments.

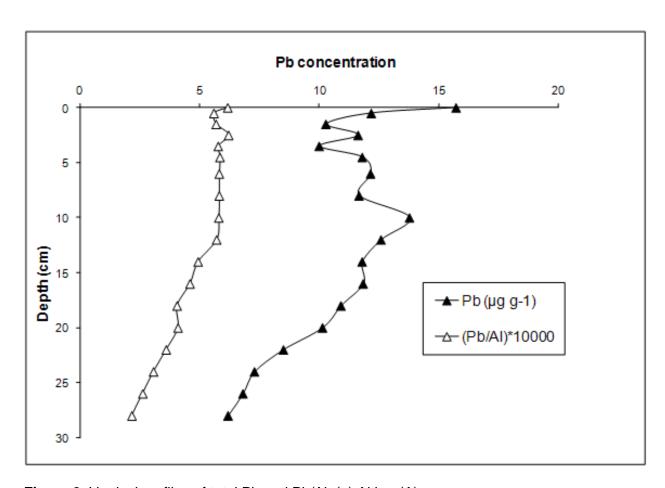
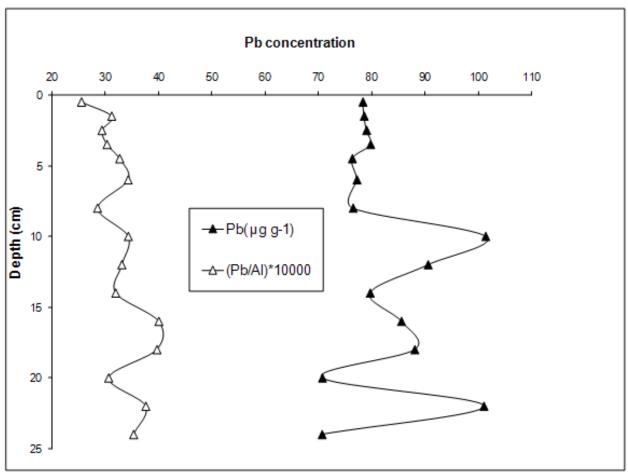
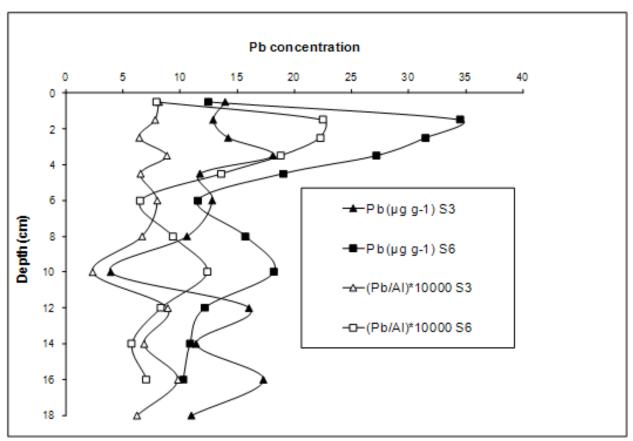


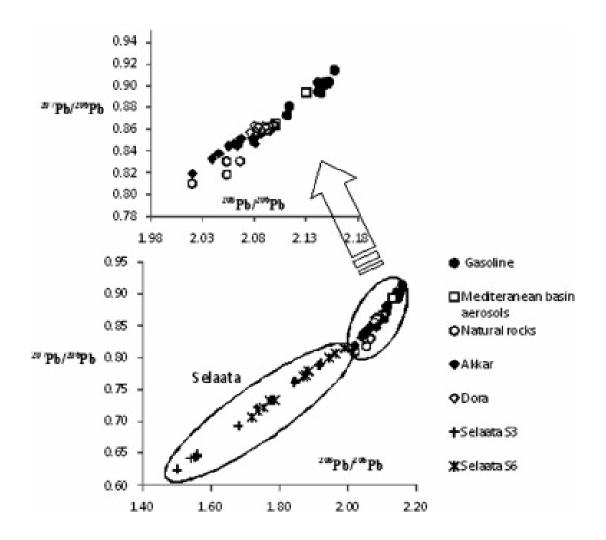
Figure 3. Vertical profiles of total Pb and Pb/Al. (a) Akkar (A),



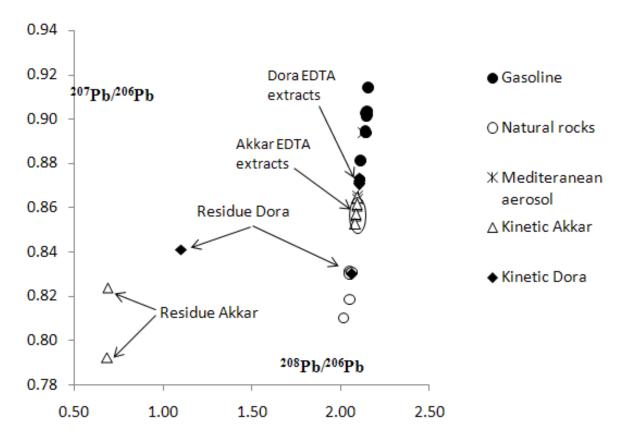
(b) Dora (D) and (c) Selaata (S3 and S6).



and (c) Selaata (S3 and S6).



**Figure 4.** Pb isotopic signatures of the sediments studied, with typical sources (Gasoline, Mediterranean basin aerosol and natural rocks from references of table 5).



**Figure 5.** Isotopic signatures of residual Pb and Pb extracted with EDTA at different periods of time from Akkar and Dora sediments with Pb isotopic signature of typical sources (Gasoline, Mediterranean basin aerosol and natural rocks from references of table 5).

# **Tables**

**Table 1.** Description of the core sampling sites.

| Site    | Core | Coordinates (Latitude, Longitude) | Water column depth above the sediment (m) |
|---------|------|-----------------------------------|---|
| Akkar   | Α    | 34°33'700N; 035°58'127E           | 18.5                                      |
| Selaata | S3   | 34°16'779N; 035°39'008E           | 14  |
| Selaata | S4   | 34°16'779N; 035°39'008E           | 6   |
| Selaata | S6   | 34°17'205N; 035°39'685E           | 15  |
| Dora    | D    | 33°54'155N; 035°33'218E           | 8   |

**Table 2.** Means and standard deviations of certified and measured values corresponding to the certified reference materials (CRM) MESS3 and BCSS1.

| CRM                      | Mg (%)    | AI (%)    | Si (%)    | Ca (%)    | Fe (%)   | Pb (µg g <sup>-1</sup> ) |
|--------------------------|-----------|-----------|-----------|-----------|----------|--------------------------|
| MESS-3 : certified value | 1.6       | 8.59±0.23 | 27        | 1.47±0.06 | 4.34±0.1 | 21.1±0.7                 |
| measured                 | 1.71±0.11 | 8.59±0.5  | 26.2±1.91 | 1.48±0.7  | 1        | 21.1±2.28                |
| value                    |           |           |           |           | 4.45±0.7 |                          |
| BCSS-1 : certified value | 1.47±0.13 | 6.26±0.22 | 30.9±0.5  | 0.54±0.05 | 3.29±0.1 | 22.7±3.4                 |
| measured                 | 1.4±0.02  | 6.34±0.13 | 31.1±0.59 | 0.66±0.14 | 3.3±0.17 | 22.3±1                   |
| value                    |           |           |           |           |          |                          |

Table 3. Mineralogical composition of the sediment core: Akkar (A), Dora (D) and Selaata (S4).

| Sample | Sample |          |        |         |                 |                 |
|--------|--------|----------|--------|---------|-----------------|-----------------|
| •      | depth  | Dolomite | Quartz | Calcite | <b>Ankerite</b> | <b>Fluorite</b> |
|        | (cm)   | (%)      | (%)    | (%)     | (%)             | (%)             |
| Α      | 1      | 36.9     | 17.9   | 17.0    | 6.9             | -               |
| Α      | 3      | 31.1     | 16.1   | 24.3    | 8.1             | -               |
| Α      | 5      | 25.6     | 20.0   | 26.4    | 8.1             | -               |
| Α      | 9      | 32.8     | 14.9   | 23.8    | 7.2             | -               |
| Α      | 15     | 33.6     | 11.6   | 28.6    | 7.3             | -               |
| Α      | 20     | 32.9     | 15.2   | 21.9    | 13.2            | -               |
| Α      | 25     | 27.8     | 13.7   | 22.3    | 11.6            | -               |
| Α      | 27     | 32.7     | 13.0   | 24.6    | 10.5            | -               |
| D      | 2      | 1.1      | 71.9   | 19.8    | 1.2             | -               |
| D      | 4      | 1.8      | 71.2   | 17.0    | 2.3             | -               |
| D      | 6      | 1.3      | 66.2   | 21.2    | 0.7             | -               |
| D      | 8      | 1.3      | 75.2   | 12.5    | 1.3             | -               |
| D      | 12     | 0.9      | 72.7   | 17.3    | 0.9             | -               |
| D      | 16     | 0.5      | 78.9   | 14.3    | 1.3             | -               |
| D      | 20     | 0.6      | 81.3   | 12.2    | 0.9             | -               |
| D      | 25     | 0.5      | 73.6   | 18.7    | 1.4             | -               |
| D      | 30     | 0.9      | 77.9   | 11.8    | 0.5             | -               |
| S4     | 10     | 2.2      | 30.7   | 7.1     | -               | 45.1            |
| S4     | 12     | 1.6      | 39.9   | 6.9     | -               | 39.4            |
| S4     | 14     | 2.0      | 56.6   | 6.0     | 3.0             | 24.3            |
| S4     | 16     | 3.9      | 29.4   | 5.8     | 2.3             | 47.7            |
| S4     | 18     | 1.6      | 25.6   | 3.7     | 0.9             | 54.5            |
| S4     | 22     | 3.8      | 29.1   | 4.7     | 1.8             | 48.0            |
| S4     | 24     | 1.2      | 23.5   | 7.2     | 0.9             | 52.9            |

**Table 4.** Pb concentrations in Lebanese coastal marine sediments compared to other regions.

| Type of sample                |            | Origin               | Рb<br>(µg g <sup>-</sup> | Fraction analysed / digestion method            | Reference                    |
|-------------------------------|------------|----------------------|--------------------------|---|------------------------------|
| Earth crust                   |            | World<br>average     | 16.0                     | HNO <sub>3</sub> + HCl + HF                     | Martin and Meybeck<br>(1979) |
| Northwestern Med              | iterranean | France               | 26-62                    | <63 μm / HNO <sub>3</sub> + HClO <sub>4</sub> + | Roussiez et al. (2005)       |
| marine sediments <sup>a</sup> |            |                      |                          | HF  |                              |
| Eastern Med                   | iterranean | Israel               | 4.0-5.0                  | $<$ 250 $\mu m$ / $HNO_3$                       | Herut et al. (1993)          |
| background marine sedi        | ment       |                      |                          |   |                              |
| Eastern Mediterranear         | coastal    | Israel               | 12.0-                    | $<250~\mu m / HNO_3$                            | Krumgalz and                 |
| sediment <sup>b</sup>         |            |                      | 14.0                     |   | Fainshtein (1991)            |
| Lebanese coastal sediment     | marine     | Lebanon,<br>Antelias | 21.5                     | <80 $\mu$ m / $HNO_3$ + $HF$                    | Nassif (2006)                |
| Lebanese coastal              | marine     | Lebanon,             | 11.0                     | <80 μm / HNO <sub>3</sub> + HF                  | Nassif (2006)                |
| sediment                      |            | Batroun              |                          |   |                              |
| Lebanese coastal sediment     | marine     | Lebanon,<br>Selaata  | 17.0-<br>24.0            | <80 μm / HNO <sub>3</sub> + HF                  | Nassif (2006)                |
| Lebanese coastal              | marine     | Lebanon,             | 6.2-                     | $<63 \mu m / HNO_3 + HCI + HF$                  | This study                   |
| sediment                      |            | Akkar                | 15.7                     |   |                              |
| Lebanese coastal              | marine     | Lebanon,             | 70.7-                    | $<63 \mu m / HNO_3 + HCI + HF$                  | This study                   |
| sediment                      |            | Dora                 | 101.4                    |   |                              |
| Lebanese coastal              | marine     | Lebanon,             | 4.8-                     | $<63 \mu m / HNO_3 + HCI + HF$                  | This study                   |
| sediment                      |            | Selaata              | 34.5                     |   |                              |

<sup>(</sup>a) Adjacent to industrial and urban areas, (b) deepest level in a core.

**Table 5.** Isotopic ratios reported from the literature.

| Sample                                   | Countr      | Dat      | <sup>208</sup> Pb/ <sup>206</sup> Pb | <sup>207</sup> Pb/ <sup>206</sup> Pb | Reference                      |
|--|-------------|----------|--------------------------------------|--------------------------------------|--------------------------------|
|  | у           | е        |                                      |                                      |                                |
| Leaded gasoline                          | Israel      | 199      | 2.142-2.158                          | 0.894-0.914                          | Erel et al. (1997)             |
|  |             | 5        |                                      |                                      |                                |
| Unleaded<br>gasoline                     | Israel      | 199      | 2.112-2.142                          | 0.873-0.903                          | Erel et al. (1997)             |
| gasomic                                  |             | 5        |                                      |                                      |                                |
| Aerosols <sup>a</sup>                    | Israel      | 199<br>5 | 2.101                                | 0.864/0.865                          | Erel et al. (1997)             |
| Aerosols <sup>b</sup>                    | Lebano<br>n | 199<br>4 | 2.130                                | 0.894                                | Bollhofer and Rosman<br>(2001) |
| Natural rock<br>(Miocene<br>carbonate)   |             | 199<br>8 | 2.053                                | 0.831                                | Luck and Othman (1998)         |
| Natural rock<br>(Paleocene<br>carbonate) |             | 199<br>8 | 2.053                                | 0.830                                | Luck and Othman (1998)         |
| Natural rock<br>(Miocene silicate)       |             | 199<br>8 | 2.053                                | 0.818                                | Luck and Othman (1998)         |
| Natural rock<br>(Paleocene<br>silicate)  |             | 199<br>8 | 2.066                                | 0.830                                | Luck and Othman (1998)         |
| Natural rock<br>(Basaltic rocks)         |             | 200<br>4 | 2.02                                 | 0.81                                 | Negrel et al. (2004)           |

<sup>(</sup>a) aerosols from Turkey travelling across the Eastern Mediterranean basin, (b) aerosols from an industrial area.