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# Distribution and diagenesis of trace metals in marine sediments of a coastal Mediterranean area: St-Georges Bay (Lebanon)

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## Abstract:

St-Georges Bay (Lebanon) is an open bay, to the Mediterranean Sea and it is exposed to numerous anthropogenic activities such as industrial effluents, non-treated wastewater discharge and maritime activities leading an increasing chemical contamination especially with trace metals. Contamination with trace metals (Cu, Cd, Co, Pb, As, Ag and Hg) and the influence of early diagenesis on their distribution are studied on both sediments and waters transect. For this purpose, sediment cores were collected, then treated under inert atmosphere to retrieve pore waters and solid fraction. The area appeared to be seriously impacted by the transport through Beirut River and/or by direct inputs, and the recent landscaping done with dumpsite material. The sediments showed a significant level of contamination. Element mobility was studied by selective extraction on sediments. The mobility of the studied trace elements from solid fraction to pore waters is controlled by Fe/Mn cycle and organic matter.

**Keywords:** Mediterranean, trace metals, early diagenesis, sediments, pore waters.

## 1. Introduction

Numerous anthropogenic activities such as maritime traffic, harbor activities, discharge of wastewater, solid waste disposal or industrial effluents in coastal areas had negatively impact on the surrounded

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4 environment, seriously releasing several pollutants such as trace metals as point sources in the  
5 surrounding environment. Industrial activities (e.g. tannery, foundry or paper processing) can release trace  
6 metals wastewaters contaminating the coastal areas and causing a massive ecological impact on water  
7 organisms (Qian et al., 2015). Trace metals are also introduced into estuarine and coastal zones from non-  
8 point sources through aeolian and/or alluvial processes for example atmospheric transport, underground  
9 waters, rivers, run-off and ocean outfalls (Chester, 1990; Lu et al., 2014). Once in coastal areas, trace  
10 metals are distributed in different phases such as aqueous, colloids or suspended matter and sedimentary  
11 phases. Trace metals are non-degradable contaminants; they can be adsorbed onto settling particles,  
12 which turn the sediment into the ultimate sink but also into an essential source of contaminants for the  
13 surrounding ecosystem due to natural or anthropogenic disturbance (Pan and Wang, 2012; Rigaud et al.,  
14 2013; Shaw et al., 1990; Singh et al., 2005). In the sediments, trace metals can remain adsorbed to clay  
15 surfaces or Fe/Mn (oxy)hydroxides, complexed with organic matter (OM) or incorporate in amorphous  
16 materials (Lu et al., 2014; Peng et al., 2009). However, high concentration of trace metals in sediments  
17 reflect the degree of contamination but not the toxicity for the aquatic systems, which is related to  
18 chemical speciation. This contamination can later affect directly aquatic organisms, presenting a long-  
19 term accumulative effect (Lu et al., 2014; Pan and Wang, 2012). Hence, many biogeochemical processes  
20 occurring in the estuarine-coastal mixing area may affect the solid-liquid repartitioning of these metals,  
21 and their input to the water column such as diffusive flux, resuspension of sediments and early diagenesis  
22 (Elbaz-Poulichet, 2005; Rigaud et al., 2013; Scholz and Neumann, 2007). Early diagenesis is a set of  
23 chemicals (e.g. sorption, dissolution/precipitation), biologicals and physicals (e.g. sedimentation)  
24 processes taking place in the sediments and controlled by benthic life and bacterial activities. These  
25 processes control the trace metal mobility from sediment to surface waters and allow understanding their  
26 distribution in the sediments (Elbaz-Poulichet, 2005; Tankere-Muller et al., 2007). The mineralization of  
27 organic matter is the driving force of early diagenesis where the organic matter is degraded close to  
28 water/sediment interface (Chester, 1990).

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47 Diagenetic primary processes start with aerobic oxidation of OM by using dissolved oxygen from the  
48 overlying or interstitial waters as an oxidant near the sediment-water interface (SWI). When oxygen is  
49 completely consumed or falls to very low levels, OM decomposition can occur by using sequentially  $\text{NO}_3^-$   
50 , Mn (oxy)hydroxides ( $\text{MnO}_x$ ), Fe (oxy)hydroxides ( $\text{Fe}_2\text{O}_3$  or  $\text{FeOOH}$ ) as electrons acceptors (Chester,  
51 1990; Froelich et al., 1979). The reductive dissolution of Mn/Fe (oxy)hydroxide releases in pore waters  
52 trace metals previously bound/incorporated to the settled oxides. Sulfate reduction occurs in the sulfidic  
53 anaerobic areas where  $\text{SO}_4^{2-}$  is used as electrons acceptors. In the contrary, sulfate reduction to sulfide  
54 could sequester dissolved trace metals in sulfide precipitates (Burgos et al., 2018; Froelich et al., 1979;  
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4 Hyacinthe et al., 2001; Lesven et al., 2008). In anaerobic conditions, following sulfate reduction, the last  
5 reaction, methanogenesis, occurs where biogenic dissolved methane can be formed (Burdige and  
6 Komada, 2011; Chester, 1990; Froelich et al., 1979). These primary redox reactions are vertically  
7 stratified depending on their energy yield and the reduced species produced such as  $\text{NH}_4^+$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{HS}^-$   
8,  $\text{CH}_4$  take part in secondary redox reactions in diagenetic reactions (Canavan et al., 2006). Moreover,  
9 primary and secondary redox reactions divide sediments into different zones of redox conditions (e.g.  
10 oxic, sub-oxic, anoxic and sulfidic) (Canavan et al., 2006; Chester, 1990; Rigaud, 2011). However, this  
11 order can be disturbed due to the presence of a set of microenvironments with redox condition controlled  
12 by different bacterial populations (Achard, 2013). Several studies related to trace metal contamination in  
13 marine sediments were conducted in the Mediterranean Sea (Álvarez-Iglesias et al., 2006; Cossa et al.,  
14 2014) and along the Lebanese coasts (Abi-Ghanem et al., 2009; Nakhle, 2004; Nassif, 2010) (Table1).  
15 The Lebanese studies that focused on solid phase contamination, have shown that Dora area in Beirut is  
16 the most contaminated zone of Lebanon. However, there is a lack of study aiming at shedding light on the  
17 impacts of diagenetic process on metal-mobilization in pore waters and at identifying the link between  
18 sedimentary accumulation and water column transport processes. Therefore, the aim of this study is: 1) to  
19 assess the contamination status of the Lebanese coastal sediments of St-Georges Bay – Dora; 2) to study  
20 the influence of early diagenesis on trace metal distribution and their distribution between the solid phase  
21 and pore waters in the studied sites. For this, diagenetic tracers, organic carbon and a series of  
22 minor/major/trace elements (Al, Ag, As, Cd, Co, Cu, Fe, Hg, Mn, Pb and Rb) were measured in pore  
23 water and solid fraction (sediments) in three Dora bay sites.

## 2. Area of study

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43 St-Georges Bay is located in the coastal area of Beirut-Lebanon (Eastern Mediterranean Sea). This bay is  
44 subjected to pollution pressures and a variety of runoff water regimes between a rainy winter-spring and  
45 dry summer seasons. This bay suffers from serious environmental pollution issues due to fuels containers,  
46 non-treated industrial effluents, maritime traffic and the former massive solid waste dump ‘‘Dora  
47 Dumpsite’’ in direct contact with water. The dumpsite has been releasing pollutants to water for 20 years  
48 until it was closed in 1998 (Nakhle, 2004). Recently, a new land (green area, Figure 1) was built from the  
49 solid waste of the dumpsite (blue area, Figure 1). In the north of the bay, the Beirut River flows into the  
50 bay. It takes its source in Mount of Lebanon at an altitude of 1,890 m. It is a karstic and seasonal river;  
51 consequently, monthly flow rate varies between 0.01 and 16 m<sup>3</sup>/s, in addition, non-treated domestic and  
52 industrial wastewater discharged are transported into the Beirut River. These sewage waters represent  
53 almost the entire flow of the water transported by the river during the dry season (Maatouk, 2015).  
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### 3. Materials and methods

#### 3.1. Sampling

Sediment sampling campaigns were carried out in September 2016 and July 2017 at St-Georges Bay-Lebanon. Samples were collected at three stations “D0” in front of the estuary of Beirut River, “D1”, and “D2” in front of the dumpsite and an industrial effluent (Figure 1). For each sampling point, seawater was collected in FEP bottles at 0.5, 2.5, 5 and 6 m from the surface. In addition, three sediment cores were collected using 10-cm diameter and 1-m long Plexiglas® tube at each station with the support of the scientific boat “CANA” and its divers (Figure 1). The first sediment core (pre-drilled holes each 2 cm) was collected to measure pH and redox potential (ORP). In parallel, a second core was stabilized for 24h to collect supernatant water (SW), then SW was simultaneous recovered at 2, 5 and 15 cm from sea water interface (SWI) and filtered (0.2 µm, cellulose nitrate, *Sartorius*). The third core was sliced with a 2 cm resolution from top to bottom under an inert atmosphere (N<sub>2</sub>) to preserve redox conditions. The collected sediments were then centrifuged (for 15 min, 3,077 g, 20 °C). Then, pore waters were collected also under inert atmosphere, filtered (0.2 µm, cellulose nitrate, *Sartorius*). The solid fraction was homogenized and deep-frozen, then freeze-dried (-18 °C), 2 mm sieved, crushed and kept deep-frozen until analysis.

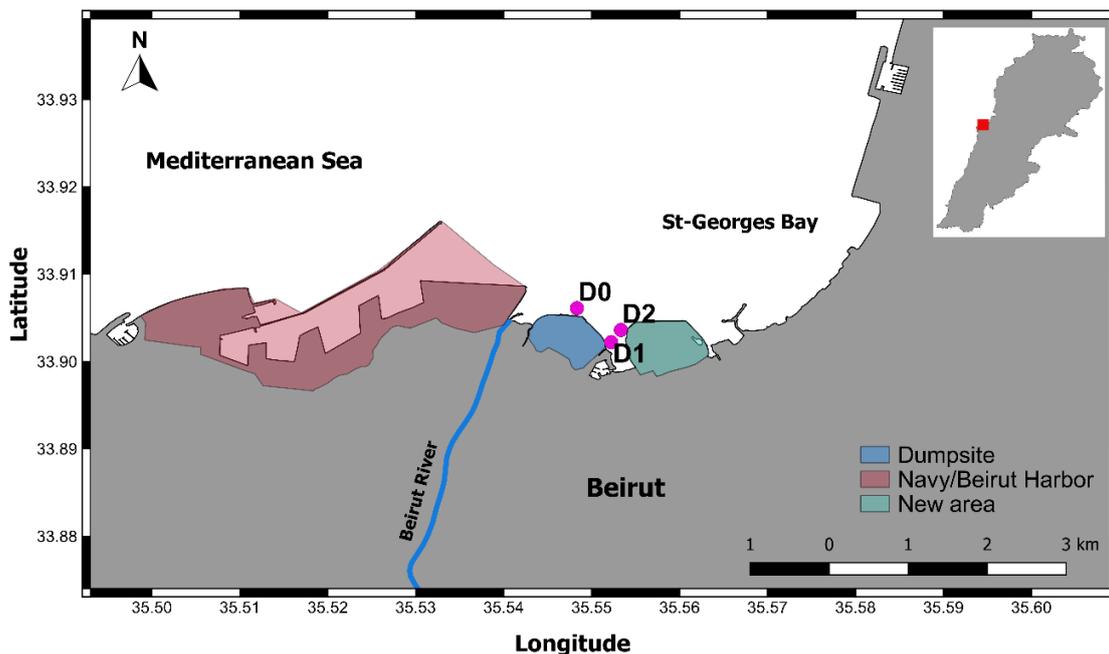


Figure 1: Map of the studied area and location of the sampled sediment cores D0, D1 and D2.

### 3.2. Sediment analysis

Total and particulate organic carbon (TC/POC) and total sulfur (TS) in sediments were analyzed using a TOC- $V_{CHS}$  analyzer (*Shimadzu*). The organic carbon content was measured after treating sediments with 6M HCl. TS was measured after mixing ~ 3 mg of freeze dried sediments with ~ 1.5 mg of vanadium pentoxide  $V_2O_5$  (*Thermo Fisher scientific*). For both measurements of carbon and sulfur, two reference soils were used Soil Reference material NC and NCS (*Thermo Fisher scientific*). Mineralogy and granulometry of studied sediment were measured by DRX (Panalytical X'Pert PRO) and Laser (Malvern hydro 2000G) respectively. Elements concentrations were determined after an aqua regia and microwave assisted digestion of sediments. The obtained solutions were filtered (0.2  $\mu m$ , cellulose nitrate, *Sartorius*) and diluted for analysis. Concentrations of minor/trace elements were measured by High Resolution Inductively Coupled Plasma – Mass Spectrometer (HR – ICP/MS, *Element 2, Finnigan*) and validated by using CASS-5 (Nearshore seawater certified reference material, National Research Council of Canada - NRC) and SLRS-5 (River water certified reference material – NRC) for water samples and PACS2 (NRC) for sediments. Hg concentrations were measured using an Advanced Mercury Analyzer AMA-254 on ~ 5 to 30 mg of sediments without pre-treatment and MESS-3 (NRC) was used as a certified reference material. For all measurement, the analytical recovery was within 10 % comparing to certified concentration.

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4 In order to explore the behavior and the distribution of trace metals (TM), “Spearman” correlation  
5 matrices and PCA were performed by using toolboxes within R programming environment for all the data  
6 set. Selective extractions with HCl 1M, NaOH 0.1 M and ascorbate (pH= 8.2) solutions were performed  
7 on freeze-dried sediments of each cores. Ascorbate extraction was performed to selectively extract trace  
8 elements associated to easily reducible iron (oxy)hydroxides (Haese et al., 2000). HCl extraction was  
9 applied to determine elements associated to carbonates, iron oxides and iron phosphate as well as acid  
10 volatile sulfide AVS (Haese et al., 2000; Leleyter and Baraud, 2005). Alkaline extraction is performed to  
11 extract a significant fraction of trace elements associated to organic matter (Ho et al., 2012). The same  
12 protocol was used for the three extractions: a solid/liquid ratio 300 mg / 10 mL of samples were prepared  
13 than head-over-head shaken for 24h, centrifuged (3,077 g , 15 min), filtered through 0.2 µm syringe filter  
14 for the whole layers at each sediment cores. In results and discussion part, we will present and discuss  
15 only the mean percentage of extracted elements.  
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### 25 3.3. Enrichment factors (EF)

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27 To explain the origin of trace elements in sediment and show the influence of anthropogenic activities,  
28 enrichment factors (EF) were calculated by comparing trace elements concentrations to the geochemical  
29 background of the studying area, using the following equation:  
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$$33 EF = \frac{\left(\frac{Me}{X}\right)_{sample}}{\left(\frac{Me}{X}\right)_{background}}$$

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38 Where used X is Al. Since there is no accepted pollution ranking by authors five categories system of  
39 enrichment are proposed by Sutherland, 2000:  
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43 EF < 2: absence to low enrichment; crustal origin

44 2 < EF < 5: moderate enrichment

45 5 < EF < 20: Significant enriched; non - crustal source

46 20 < EF < 40: Highly enriched

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Table 1 Range and mean values of trace elements in sediments core from St-George Bay - Dora - Lebanon. Average of trace elements concentrations found in sediment

|   |                | Ag<br>( $\mu\text{g}\cdot\text{g}^{-1}$ ) | Cd<br>( $\mu\text{g}\cdot\text{g}^{-1}$ ) | Pb<br>( $\mu\text{g}\cdot\text{g}^{-1}$ ) | Cr<br>( $\mu\text{g}\cdot\text{g}^{-1}$ ) | Co<br>( $\mu\text{g}\cdot\text{g}^{-1}$ ) | Cu<br>( $\mu\text{g}\cdot\text{g}^{-1}$ ) | As<br>( $\mu\text{g}\cdot\text{g}^{-1}$ ) | Hg<br>( $\mu\text{g}\cdot\text{g}^{-1}$ ) |
|---|----------------|---|---|---|---|---|---|---|---|
| <b>D0 (8)<sup>a</sup></b>   | <b>Range</b>   | 0.6 - 0.9                                 | 0.4 -<br>0.5                              | 25.1 -<br>44.3                            | 86.9 -<br>107.7                           | 12.6 -<br>16.3                            | 34.8 -<br>53.1                            | 6.5 - 9.8                                 | 0.1 -<br>0.1                              |
|   | <b>Average</b> | 0.7 $\pm$ 0.7                             | 0.4 $\pm$<br>0.03                         | 35.2 $\pm$<br>5.5                         | 99.5 $\pm$<br>7.0                         | 14.9 $\pm$<br>1.5                         | 47.5 $\pm$<br>10.8                        | 8.2 $\pm$<br>1.2                          | 0.1 $\pm$<br>0.03                         |
| <b>D1 (15)</b>  | <b>Range</b>   | 1.0 - 2.6                                 | 0.5 -<br>1.1                              | 58.7 -<br>140.0                           | 126.2 -<br>298.8                          | 14.5 -<br>26.0                            | 73.2 -<br>142.0                           | 10.0 -<br>16.4                            | 0.1 -<br>0.3                              |
|   | <b>Average</b> | 1.5 $\pm$ 0.5                             | 0.7 $\pm$<br>0.2                          | 92.1 $\pm$<br>18.6                        | 189.2 $\pm$<br>52.5                       | 19.78 $\pm$<br>3.5                        | 96.7 $\pm$<br>16                          | 12.9 $\pm$<br>2.2                         | 0.2 $\pm$<br>0.05                         |
| <b>D2 (15)</b>  | <b>Range</b>   | 1.5 - 5.6                                 | 0.6 -<br>0.9                              | 64.3 -<br>376.1                           | 158.3 -<br>230.9                          | 16.4 -<br>23.6                            | 66.6 -<br>201.4                           | 13.1 -<br>18.6                            | 0.2 -<br>0.7                              |
|   | <b>Average</b> | 2.9 $\pm$ 1.3                             | 0.7 $\pm$<br>0.3                          | 118.4 $\pm$<br>75.9                       | 182.6 $\pm$<br>19.3                       | 18.3 $\pm$<br>2.2                         | 93.2 $\pm$<br>32.1                        | 15.3 $\pm$<br>1.89                        | 0.4 $\pm$<br>0.1                          |
| <b>Aguada Bay –<br/>India (Prajith et<br/>al., 2016)</b>                  | <b>Average</b> | -   | -   | 10.7 $\pm$<br>2.91                        | 218 $\pm$<br>115                          | 20.5 $\pm$<br>4.85                        | 65.9 $\pm$<br>39                          | -   | -   |
| <b>San Simón Bay<br/>– Spain (Álvarez-<br/>Iglesias et al.,<br/>2006)</b> | <b>Average</b> | -   | -   | 46.4 $\pm$<br>27.7                        | 79.5 $\pm$<br>24.8                        | 6.0 $\pm$<br>2.5                          | 32.1 $\pm$<br>5.6                         | -   | -   |
| <b>Cap de Creus<br/>Canyon –<br/>France (Cossa et<br/>al., 2014)</b>      | <b>Average</b> | 0.12 $\pm$<br>0.01                        | 0.13 $\pm$<br>0.01                        | 46.3 $\pm$<br>4.7                         | 85.4 $\pm$<br>3.4                         | 16.2 $\pm$<br>0.5                         | 29.3 $\pm$<br>2.3                         | -   | -   |
| <b>Selaata –<br/>Lebanon (Abi-<br/>ghanem, 2008)</b>                      | <b>Average</b> | 0.5 $\pm$ 0.3                             | 0.3 $\pm$<br>0.1                          | 12.0 $\pm$<br>4.4                         | 145.2 $\pm$<br>30.7                       | -   | 18.9 $\pm$<br>3.1                         | -   | 0.04 $\pm$<br>0.01                        |
| <b>Akkar<br/>background –<br/>Lebanon<sup>b</sup></b>                     | <b>Average</b> | 0.08 $\pm$<br>0.01                        | 0.2 $\pm$<br>0.02                         | 10.9 $\pm$<br>2.44                        | 102.5 $\pm$<br>12.0                       | -   | 11.1 $\pm$<br>2.8                         | -   | 0.02 $\pm$<br>0.01                        |
| <b>UCC<sup>c</sup></b>  |                | 0.05                                      | 2   | 17 - 20                                   | 35.0                                      | 10 - 17                                   | 14.3                                      | 1.5                                       | 0.06                                      |

a. Sample number in sediment core

b. Natural Background values of the Lebanese coastal sediments (Abi-ghanem, 2008).

c. Natural background values of the Upper Continental Crust (Wedepohl, 1995).

### 3.4. Pore waters analysis

Diagenetic tracers (ammonium, phosphate) were analyzed by using a Visible spectrophotometer (DR 2800, Hach Lange). Ammonium analysis were carried out using Merck Spectroquant (1.14752). Orthophosphate were analyzed by the method as described by Murphy and Riley (1958). Dissolved

organic and inorganic carbon (DOC and DIC) were analyzed using a TOC-VCSH meter (*Shimadzu*) coupled with ASI-5000A module. DOC/DIC analysis were validated using a certified reference material (SUPER 05, Environment and Climate Change Canada). Dissolved minor/trace elements concentrations in pore waters were determined directly with HR – ICP/MS (Element 2 – Thermo *Finnigan*) by diluting by 10.

## 4. Results

### 4.1. Minor/Major/trace elements in sediment cores.

Correlation between TM concentration of the three sediment cores are presented in Figure 2. Al and Fe were well correlated in D0, D1 ( $r^2 = 0.71$  and  $0.93$  respectively) and they were not significantly correlated at D2 ( $r^2 = 0.46$ ). In addition, a significant correlation was observed between Al and Rb in D0, D1 and D2 ( $r^2 = 0.76, 0.90$  and  $0.86$  respectively). Al and Mn were only strongly correlated in D0 and D1 ( $r^2 = 0.90$  and  $0.76$  respectively). Between D0, D1 and D2, Fe/Al ratios presented close average values ( $1.27 \pm 0.15$ ,  $1.47 \pm 0.06$ ,  $1.57 \pm 0.26$ ). Results of grain size showed that predominant fraction size in all the studied sediments was between  $20 - 60 \mu\text{m}$  and  $60 - 200 \mu\text{m}$  (*Supplementary information 1*). In addition, the three sediment cores showed a superficial sediment enrichment in quartz, dolomite and calcite (Table2). Only D0 core showed the presence of ankerite and absence of pyrite in deep sediments.

Table 2: Average values of grain size, mineralogy, POC, TS, Al, Mn, Fe and Rb in the studied sediments

|        |         | Mineralogy                           | POC<br>(%)     | TS<br>(%)     | Al<br>(%)     | Mn<br>(%)       | Fe<br>(%)     | Rb<br>( $\mu\text{g.g}^{-1}$ ) |
|--------|---------|--------------------------------------|----------------|---------------|---------------|-----------------|---------------|--------------------------------|
| D0(8)  | Average | Quartz/Calcite/Ankerite/<br>Dolomite | $0.3 \pm 0.1$  | $0.5 \pm 0.2$ | $3.2 \pm 0.5$ | 0.03            | $4.0 \pm 0.2$ | $13.7 \pm 5.3$                 |
|        |         | Quartz/Calcite/Pyrite /Dolomite      | $0.2 \pm 0.07$ | $0.6 \pm 0.2$ | $3.4 \pm 0.6$ | $0.04 \pm 0.01$ | $5.0 \pm 0.7$ | $15.1 \pm 3.2$                 |
| D2(15) | Average | Quartz/Calcite/Pyrite/ Dolomite      | $0.47 \pm 0.9$ | $0.8 \pm 0.2$ | $3.4 \pm 1$   | 0.04            | $5.1 \pm 0.5$ | $11.2 \pm 4.0$                 |

The highest particulate organic carbon (POC) content (3.3 %) were found in superficial layer of the sediment core D2 then decrease rapidly along profile and reach low values (~ 0.2 %) (Figure 3). POC in the sediment cores D0 and D1 were lower than 0.5 %. In the sediment core D0, there was no correlation between POC and the studied elements except a significant negative correlation with POC and Fe and Co ( $r^2 = -0.83$  and  $-0.67$ , respectively). At the contrary, in the sediment core D1, there was a significant correlation between POC and all elements, for example with As ( $r^2=0.75$ ) and Cd ( $r^2 = 0.45$ ). In the sediment core D2, there was no correlation between POC and Fe, Pb, Cd and Co, on the other hand, a significant correlation is observed between POC and Cu ( $r^2 = 0.61$ ). All the studied trace elements in the three sediment cores (Figure 2) present different correlation with POC due to different cores processes. Total content profiles of minor and trace elements are presented in Figure 3. The studied elements in the

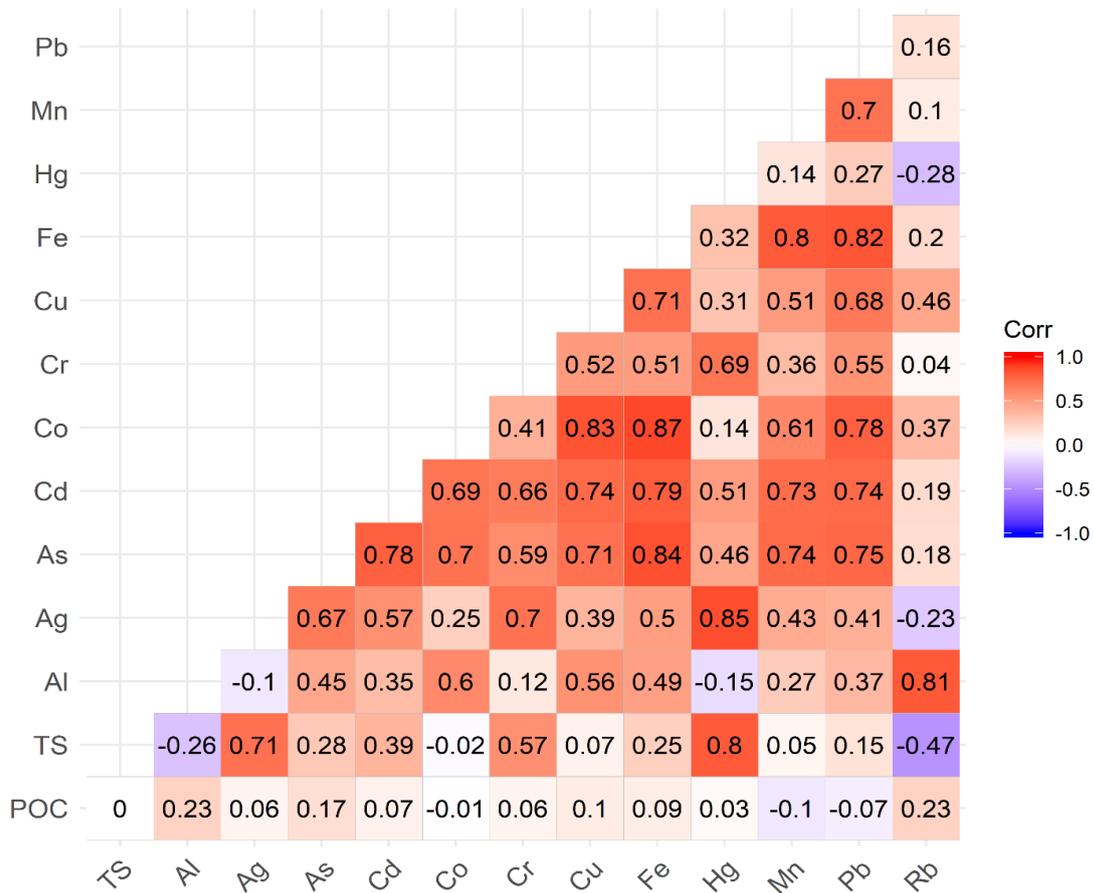


Figure 2: Correlation of POC, TS and all studied elements in the sediments.

sediment core D2, except Ag, show the same pattern: high superficial concentration and rapid decrease. A strong correlation between trace metals within the three sediment cores (Figure 2). Beside the strong

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4 correlation, solid profiles for Mn, Fe, Co, Cd and As showed the same pattern variation along the three  
5 sediment profiles (Figure 3), where D0 showed the lowest concentration comparing to D1 and D2.  
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9 The Mn profile in cores fluctuated between 270 and 520  $\mu\text{g. g}^{-1}$ , and showed large amplitude peaks at  
10 sub-superficial layer. A high enrichment of trace elements in superficial sediment (from - 1 cm to - 3 cm)  
11 was observed at cores D1 and D2 for Pb and Ag, but for Hg and Cu the enrichment was observed only at  
12 D2. A constant and slight decrease of these trace metals levels was observed in deeper sediments of D2  
13 (Figure 3). A superficial enrichment of trace elements (from - 1 cm to - 3 cm) were observed at D2 and it  
14 was strongly and significantly correlated with POC and TS ( $r^2= 0.99$ ). However, Ag profiles at point D1  
15 showed a slight increase with depth and a peak at - 12 cm, yet, D2 showed two peaks at superficial layer  
16 and at -17 cm sediment depth. In contrast, D0 trace elements profiles showed a different trend, it showed  
17 more and less a constant profile with depth. At D0, a sub-superficial peak was detected for As and Cd  
18 associated to Mn, in contrary, a peak was detected for Ag, Co, Cu and Hg associated to Fe (Figure 3).  
19 Spearman correlation was used to evaluate the source of elements and their influence on sediment  
20 characteristics. Positive correlation was observed between all studied trace elements, indicating a similar  
21 spatial distribution at the bay and same source input(Wang et al., 2017) (Figure 2). When studying each  
22 core alone, a significant positive correlation was still observed between most of trace elements in D1 but  
23 no more specifically in D0 or D2 where it appears poor correlations and sometimes negatives correlations  
24 (*Supplementary information 2, Supplementary information 3*).  
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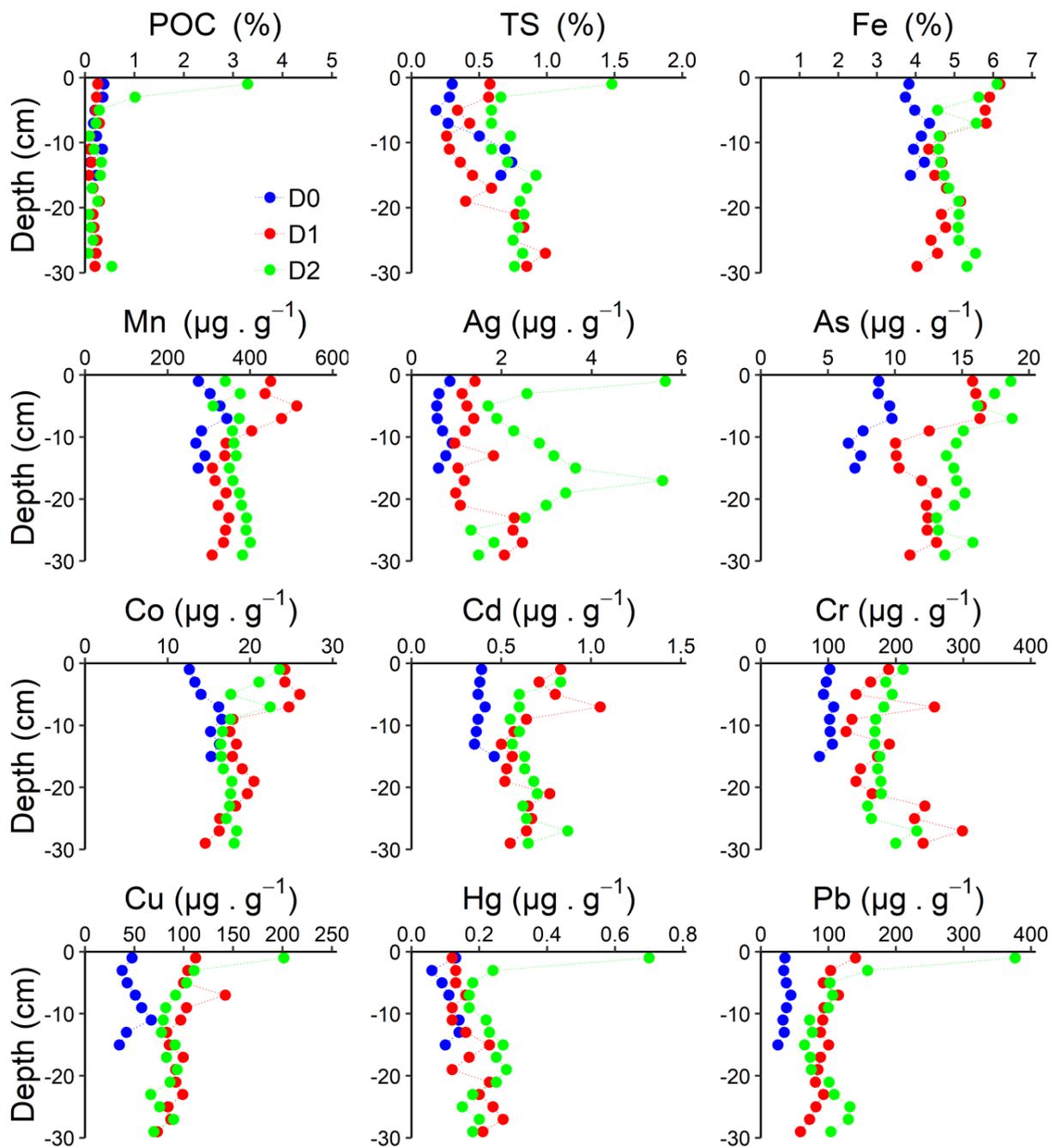


Figure 3: POC, TS, Fe, Mn, Ag, Cd, Pb, Co, Cr, Cu, As and Hg profiles in the three sediments cores D0 (blue), D1 (red) and D2 (green).

As an example, Cu was correlated with Mn, Fe, As, Cd, Co and Pb in D1 ( $0.66 < r^2 < 0.78$ ) which was not the case in D0 and D2 expect for Cu/As correlation in D2 that were stronger ( $r^2 = 0.87$ ). Pb was correlated with Mn and Fe in the three cores. Gathering all data: particulate organic/inorganic content (POC/PIC) and 33 elements (studied elements of this study and Li, Be, Rb, Mo, Sn, Sb, Cs, Tl, Bi, U, Al, Ti, V, Ni,

Sr and Ba) measured by ICP-MS, a principal component analysis (PCA) was performed using R toolboxes. In purpose, to see correlation and similarities between the three stations (D0, D1 and D2) and the studied elements. Three principal components (PC1, PC2 and PC3) were able to explain 52.1 %, 17.5 % and 11 % respectively of the dataset variance (Figure 4).

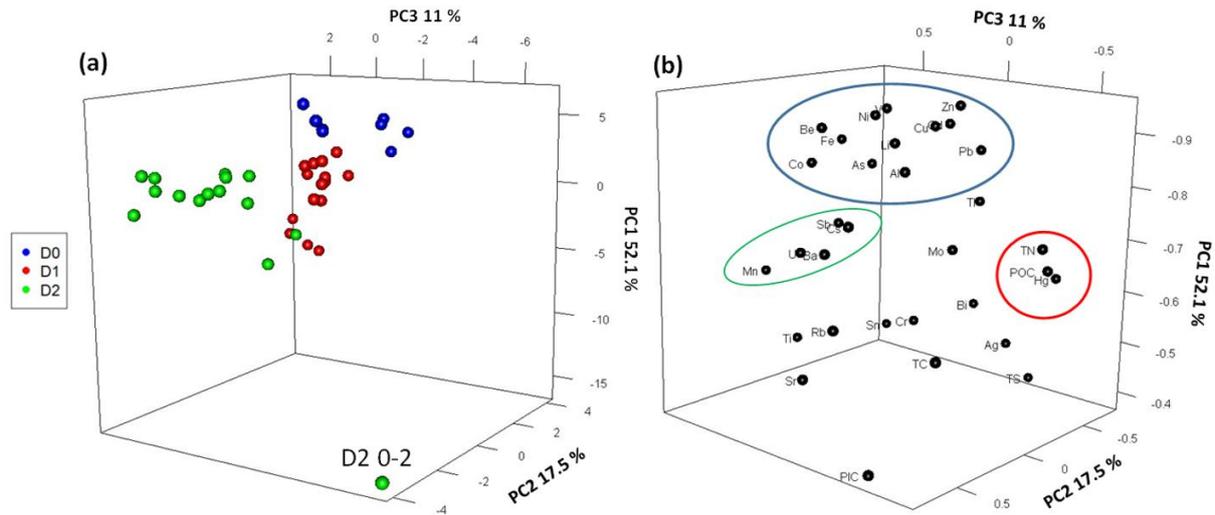


Figure 4: 3D representation of the three principal components obtained by PCA treatment of the dataset for (a) the sediments samples of D0 (blue), D1 (red) and D2 (green) and (b) the 33 elements. Blue circle are elements driving D1 (blue circle), red circle the correlation between Hg and POC and green circle elements driving D2.

The PCA results of the studied elements (Figure 4 - b) showed that Hg is correlated with POC. Contaminants such as Pb, Cu, Cd and As were correlated with terrigenous elements such as Al, Li and Fe evidencing a terrigenous source. On the other hand, the PCA projection of samples showed the sediments were distributed along with terrigenous elements (Figure 4- a). Moreover, the cores pool from D0 to D2 shift from terrigenous influence to more marine one (Mn, U, Ba, Sb, Sr, Rb) revealing a core gradient. A particular behavior was observed at the first layer of D2 (Figure 4) which is driven by PIC; spearman's correlation also showed a strong correlation between PIC and all the studied elements in this specific layer.

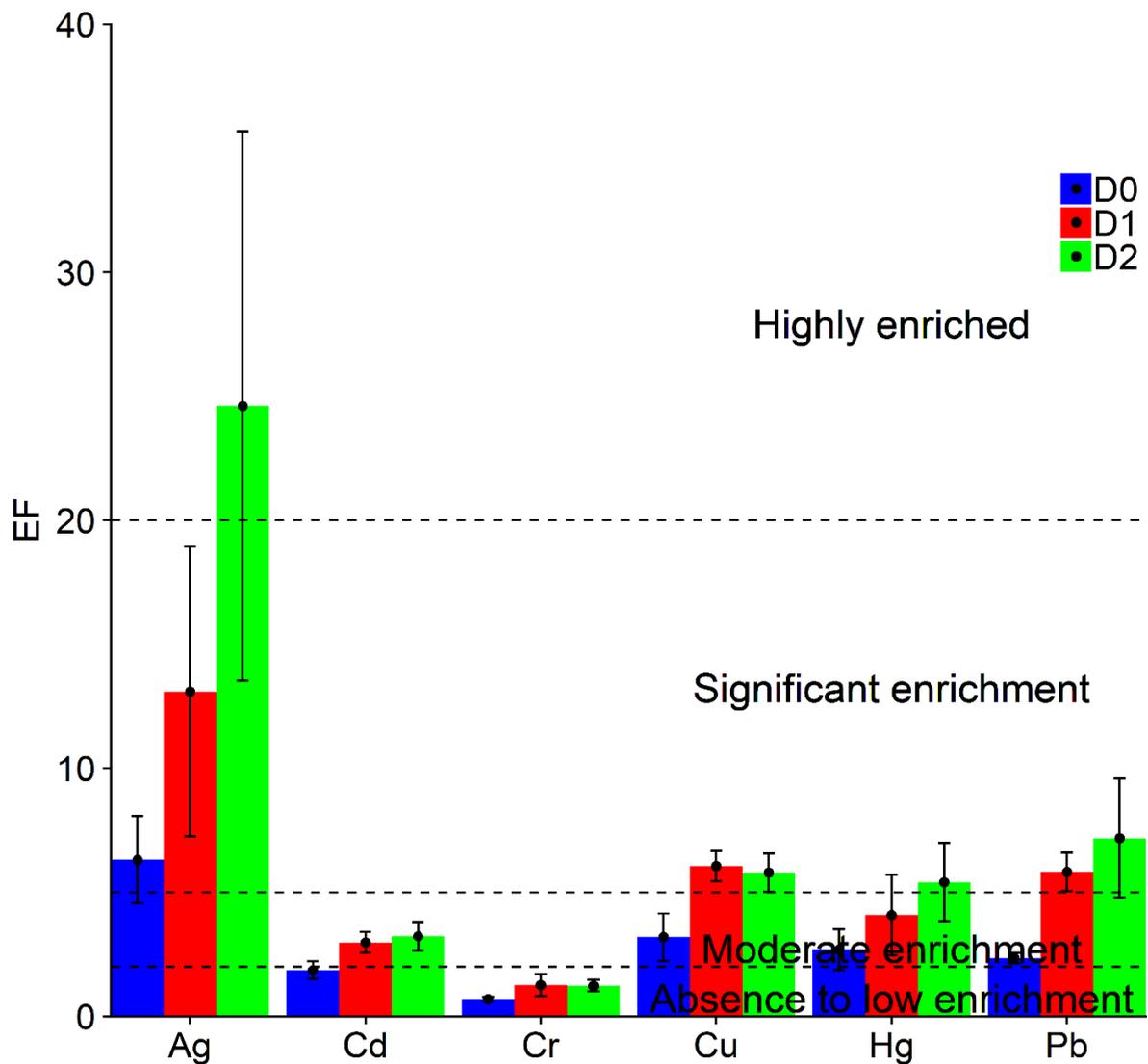


Figure 5: Average and standard deviation of metal enrichment factor (EF) in three sediments core "D0 (blue), "D1" (red) and "D2" (green). The dashed lines indicate four of five categories cited in section 3.3.

Geochemical normalization was based on the concentration of a conservative element, in this work; aluminum was used for normalization since it had been the most commonly used in the geochemical literature.(Kontas, 2008; Mahu et al., 2015; Prajith et al., 2016; Tessier et al., 2011) In addition, aluminum is non-reactive to diagenetic changes in the sediments and it is a lithophilic element representing aluminosilicates. The natural background metal/Al ratio used in the normalized EF calculation was from a non-polluted area called Akkar located north of Beirut collected and analyzed for TM by Abi-ghanem, 2008.(Abi-ghanem, 2008) Enrichment factors calculated for Ag, Cd, Cr, Cu, Hg and Pb were presented in (Figure 5). Enrichment factor of trace elements showed significant enrichment to

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4 moderate enrichment for Ag, Pb, Cu, Hg and Cd (Figure 5). These studied sediments were enriched in  
5 metals in the following order: Ag > Pb > Cu > Hg > Cd > Cr. To be noted that D2 and D1 were found  
6 more enriched than D0. EF values were detected above 20 (Highly Enriched) just for Ag at core D2. In  
7 addition, for all the elements cited, EF values indicated even a significant enrichment for Pb, Cu at D1  
8 and D2 and for Hg at D2. Alternatively, a moderate enrichment for Cu, Pb at D0 and for Hg at D1 and  
9 D0. On the other hand, no or minimal pollution was detected for Cr.

#### 14 4.2. Selective extractions

17 Total concentration of trace elements was not sufficient to estimate mobility of trace elements and their  
18 bioavailability in sediments by measuring. So selective extractions were applied on sediments with three  
19 extractants (HCl 1M, ascorbate pH=8.2, NaOH 0.1M) in order to clarify the distribution of trace elements  
20 in the solid phase of the sediment (Audry et al., 2006). Averaged percentages of elemental extractability  
21 all along the sediment cores in the three points D0, D1 and D2 are presented in Figure 6, representing the  
22 potential mobile fraction of an element (Leleyter and Baraud, 2005). Extraction with ascorbate give a  
23 primary information about easily reactive reducible Fe and Mn (oxy)hydroxides (Canavan et al., 2006)  
24 which are terminal electron acceptors in the organic matter degradation reaction and also bearing phases  
25 for trace elements in suboxic zone. Trace metals percentages extracted with ascorbate were very low and  
26 tended to be negligible expect for As. In this study, the order of extractable elements by ascorbate  
27 solution was  $Cd \approx Cu \approx Ag \approx Pb < Mn \approx Cd < Cr < Fe \approx Co < As$ . Along D0, the averaged percentage  
28 showed that As was the most extracted ( $12.9 \pm 3.5 \%$ ) then Co ( $5.7 \pm 0.8 \%$ ) and Cr ( $1.9 \pm 0.3 \%$ ) were  
29 slightly extracted with ascorbate solution. However, Pb, Cd, Cu and Ag were not extracted with  
30 ascorbate. Alkaline extraction was negligible for most of elements expect for As, Cu and Cd. Arsenic was  
31 the most extracted element ( $31.4 \pm 3.0 \%$ ), then Cu ( $7.4 \pm 2.0 \%$ ) and Cd ( $3.0 \pm 1.4 \%$ ) were slightly  
32 extracted with alkaline extraction. Acid extraction allowed the extraction of potentially “bioavailable”  
33 trace elements by dissolving oxides and carbonates (Dang et al., 2015; Larrose et al., 2010). The extracted  
34 percentage with HCl varied between 4 % and 87 % depending on element. As an example, in D2, arsenic  
35 was the less extracted element ( $4.4 \pm 2.1 \%$ ) by HCl compared to Cd ( $56.2 \pm 6.5 \%$ ) and Pb ( $53.1 \pm 5.1$   
36 %). Ag, Pb, Cd and Cu were the most extracted elements with HCl extraction. For all the sample, the  
37 order of extractable elements by HCl was  $As < Cr < Co < Cu < Ag < Pb \sim Cd$ , similar to the order  
38 obtained in sediment rich in pyrite (Scholz and Neumann, 2007).

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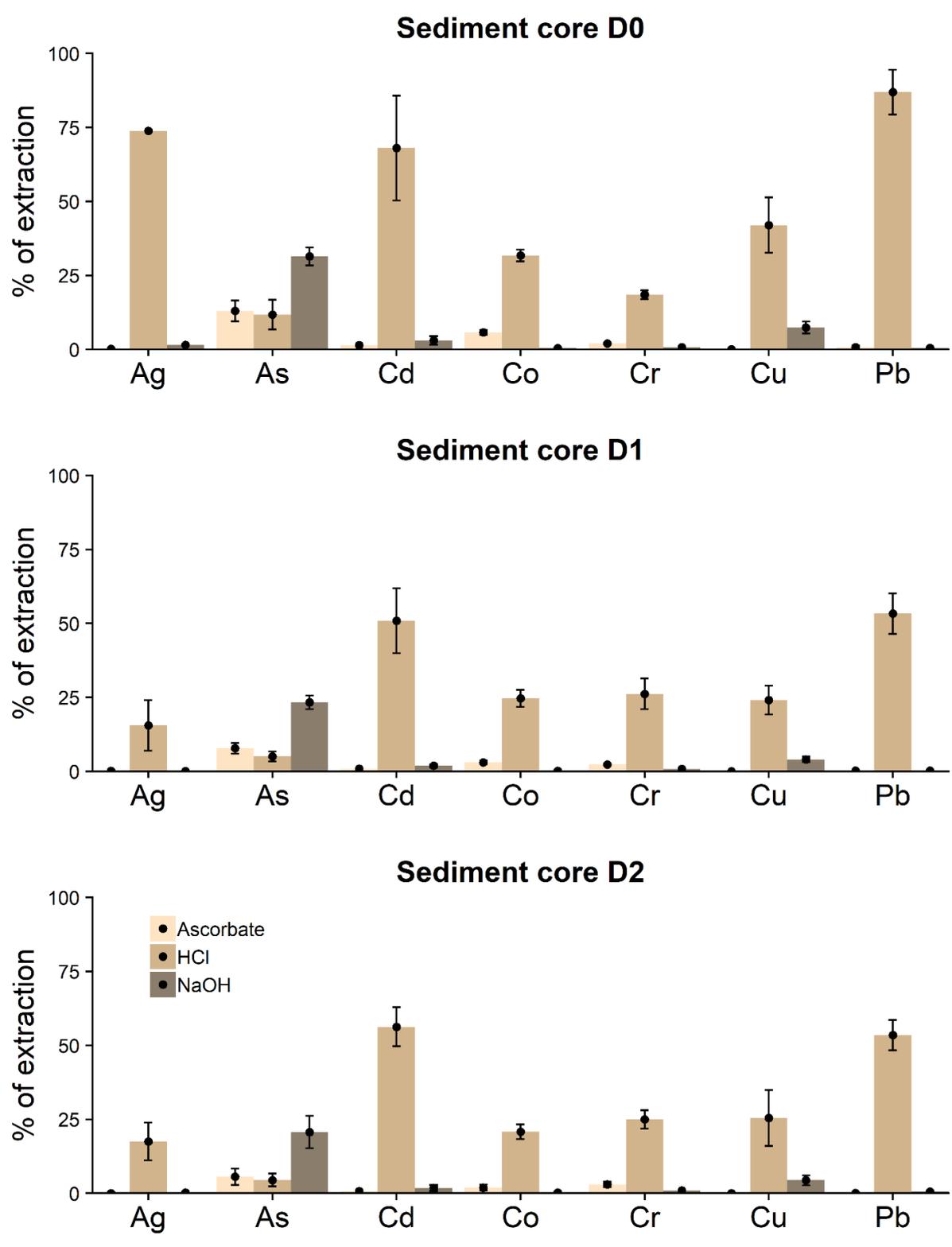


Figure 6: Mean percentage of trace elements extracted with Ascorbate pH=8.2, HCl 1M and NaOH 0.1M for each sediment cores "D0", "D1" and "D2" along all sediments depth.

### 4.3. Column and Interstitial water profiles

In water column, oxygen measurements showed 99 - 85.1 % saturation at the first meters of water column depth and oxygen was partially consumed (39 % sat of O<sub>2</sub>) below 3 m of water depth. In cores D0, D1 and D2, pH was around 8.0 ± 0.1 in surrounding column waters and fluctuated from 7.2 - 8.0 in interstitial waters. In sediment, redox potential values of interstitial water decreased slowly in D1 and D2 all along the core and reached -200 mV, however, redox potential decreased sharply from the surface to reach more negative values -300 mV in D0 (Figure 7).

Dissolved organic carbon (DOC) tended to increase with depth at D1 and D2, while in D0, DOC fluctuated but increased with depth. NH<sub>4</sub><sup>+</sup> profiles at D1 and D0 increased with depth, unlike D2 where a superficial peak is observed. To be noted that DOC was correlated with NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup> (r<sup>2</sup>= 0.63) only in D0. Mn (oxy)hydroxides reduction zones and release of dissolved Mn occurred at upper layer in D2 (at -3 cm) and a little bit deeper in D0 and D1 (at -7 cm). At deeper sediment layers, Mn concentrations decreased sharply at D2 (at -5 cm) and D0 (at -10 cm) where it tended to be negligible. In contrast, Mn concentrations decreased slowly at D1 but not completely removed. Furthermore, in D0 and D2, pore water peaks of Fe appeared above the large solid phase Fe peaks, yet, in D1 was vice versa. D0 showed a superficial peak at SWI interface with a concentration level of 680 nM (Figure 7). For D2, dissolved Fe profile showed a superficial peak and Fe concentrations were very low comparing to Fe contents in D0 and D1 and fluctuating between 1,000 and 3,000 nM (Figure 7). The highest concentration of dissolved Fe (20 mM) was observed at D1 at - 11 cm of sediment depth (Figure 7).

Concentrations of trace elements and DOC in column water did not vary significantly. In addition, a slightly increase in the concentration of some studied elements (Pb, Cu, Co and As) was detected in the supernatant water. The D1 interstitial water sediments core showed superficial peaks of dissolved Pb in the oxic/suboxic boundary. A strong correlation was observed between Fe and Pb in D1 (r<sup>2</sup>= 0.72) and D2 (r<sup>2</sup>= 0.86). For dissolved Co, a sub-superficial layer peak was detected at D0 associated with Mn (r<sup>2</sup>= 0.81) and Fe (oxy)hydroxide (r<sup>2</sup>= 0.61) in the reduction zone. On the other hand, dissolved Co profiles at D1 and D2 showed two peaks. The first one at superficial or sub-superficial layers at D1 associated with Mn (r<sup>2</sup>= 0.88) and Fe (oxy)hydroxide reduction zone (r<sup>2</sup>= 0.71) and slightly one with Mn oxides in D2 (r<sup>2</sup>= 0.41); the second peak was observed in deeper layer associated with DOC where a strong correlation was observed between Co and DOC in D1 and D2 (r<sup>2</sup>= 0.80). At D0 and D2, dissolved Cr profiles tended to increase with sediment depth.

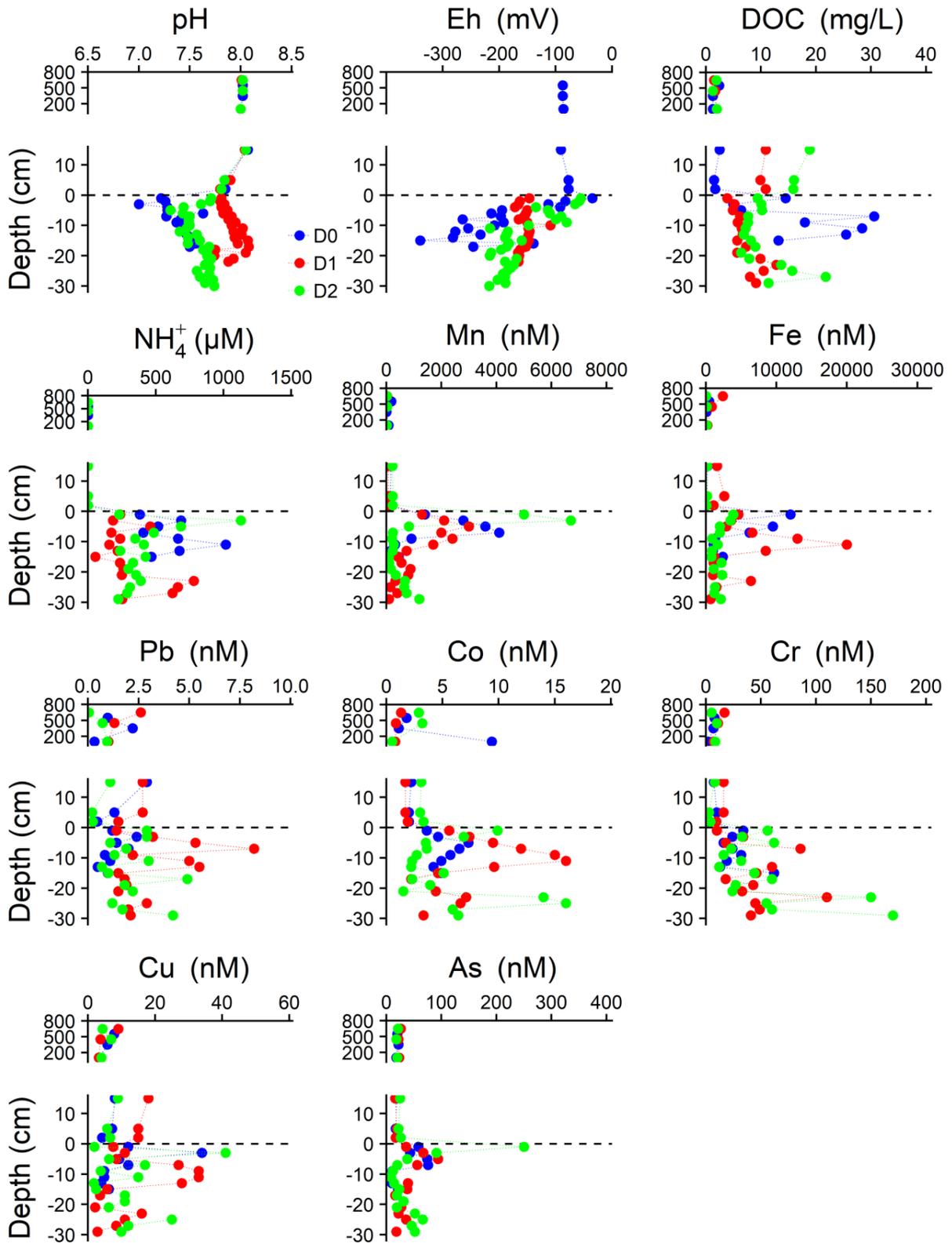


Figure 7: pH, Eh, dissolved organic carbon, nutrients and dissolved trace elements profiles in pore waters extracted at the three sediments cores "D0" (blue), "D1" (red) and "D2" (green).

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4 However, at D1, dissolved profile Cr showed two peaks, one at sub-superficial layer and the second at  
5 deeper layer attached to DOC; dissolved Cr in these layers were correlated with DOC ( $r^2= 0.50$ ). For  
6 dissolved Cu, profiles showed a superficial peak in the three sediment cores D0 (- 3 cm), D1 (- 11 cm)  
7 and D2 (- 3 cm). In D0 and D2 Cu was associated at the oxic/suboxic boundary in the Mn/Fe reduction  
8 zone and only with Fe reduction zone in D1. The release of dissolved arsenic occurred immediately below  
9 the SWI at D0, D1 and D2 indicating a release during organic matter oxidation and Mn or Fe oxides  
10 reduction.  
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## 18 5. Discussion

### 19 5.1. Sediments composition and solid profiles

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21 Grain size affects the accumulation of metals in sediments and fine fraction promotes the accumulation of  
22 trace elements in the sediments.(Blott S.J. and Pye K., 2001; Cauwet, 1987; Ujević et al., 2000) Mean  
23 percentage of grain size showed that the majority of particles were very coarse silt (20 - 50  $\mu\text{m}$ ) or very  
24 fine sand (50 – 200  $\mu\text{m}$ ) (*Supplementary information 1*) at the three sediment cores D0, D1 and D2.  
25 These results were co-variant with the mineralogy of the studied zone, rich in quartz, calcite and dolomite  
26 (Table 2). Elements concentrations such as Al, Rb, Fe, and Mn (Table 2) at the three points indicated that  
27 the mineral composition seems constant during sedimentation processes. The significant correlation  
28 between elements such as Al/Fe or Al/Rb or Al/Mn in D0 and D1 reflected a common source for these  
29 elements and indicated a signature of terrigenous fine particle such as aluminosilicates and oxy-  
30 hydroxides, however, the source in D2 do not present a completely to terrigenous source. These results  
31 could be related to high mixing of sediments or to the influence of alluvial continental deposits by Beirut  
32 river (Abi-Ghanem et al., 2009), such deposits came with the run-off of Beirut River after a big episodes  
33 of precipitation. This behavior was observed also with ascorbate and HCl extraction results. The ascorbate  
34 extraction showed an accumulation of Fe and Mn that correspond to Fe/Mn (oxy)hydroxide (Haese et al.,  
35 2000; Rigaud et al., 2013). In plus, ascorbate extraction of Al, Mn and Fe were low comparing to acid  
36 extraction but they showed the same trend and they were strongly correlated in the sediment cores D0 ( $r^2=$   
37 0.83) and D1 ( $r^2= 0.99$ ), less in D2 ( $r^2= 0.45$ ). The difference could be due to the presence of oxides,  
38 carbonates and monosulfide minerals in the sediments (Dang et al., 2014; Haese et al., 2000). The highest  
39 POC content detected at the superficial layer of D2 (Figure 3) indicated a superficial enrichment,  
40 supported by the highest dissolved organic carbon in the supernatant waters at D2, then a slight decrease  
41 with depth (Figure 7). This could be related to terrestrial OM inputs from rivers, to urban sewage  
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4 discharge or to biological production (Álvarez-Iglesias et al., 2006). POC profiles in D0 and D1, present  
5 lower starting point in D2, but also decreased with depth.  
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8 Vertical variability of trace elements presented in Figure 3, showed disrupted profiles of all studied  
9 elements with depth implied must probably the mixing sediment process “resuspension”, especially that  
10 this bay was very well known as a docking area. The Spearman’s correlation showed a significant  
11 positive correlation between concentrations of Al, Fe and the anthropogenic trace elements (Cd, Pb, Co,  
12 Cr, Cu and As) in this bay (Figure 2) and not Ag which was slightly correlated with POC (see section 4.1).  
13 These indicated that the primary accumulation of trace elements in the bay was governed by deposition of  
14 terrigenous material, particularly particles associated with terrigenous organic matter and Fe and Mn  
15 oxides and (oxy)hydroxides. Trace elements chemical extraction results appeared to be similar in the  
16 three sediments cores. These trace elements (Ag, Cd, Pb, Co, Cr and Cu) were more extracted with acid  
17 extraction, indicating they are mostly associated to exchangeable-carbonates or oxides. The high acid  
18 extraction percentage observed for Cu highlight the presence of a Cu desorption from organic sites or Cu  
19 release from oxides (Adamo et al., 2005). However, As was the most extracted with ascorbate and  
20 alkaline extraction. In plus, Cu was slightly extracted by alkaline extraction. This alkaline extraction of  
21 As and Cu could be attributed to the stable and soluble complexes formed with dissolved organic matter  
22 (Dang et al., 2015; Ho et al., 2012). As, Co, Cr and Cd were slightly extracted with ascorbate suggesting  
23 an interaction between these elements and Mn/Fe (oxy)hydroxide fraction but the contribution of other  
24 phases such as FeS are not negligible (Haese et al., 2000; Rigaud et al., 2013). These results confirmed  
25 the association of the studied trace elements to terrigenous organic matter and Fe and Mn oxides and  
26 (oxy)hydroxides which could be imported by the Beirut river or the industrial effluents or Beirut Harbor  
27 activities. Comparing concentrations of these trace elements in the three sediment cores to background  
28 level in the upper continental crust given by Wedepohl, 1995 or to background level of Akkar region  
29 (Table 1), the sediments in the area showed a highly mean content for Cd, Pb, Cu, As and Hg.  
30 Comparing to other studies in the Mediterranean Sea or outside (Table1), these studied sediments were  
31 highly contaminated especially, with Ag, Cd, Pb, Cu and Hg. High concentrations of trace elements were  
32 observed, especially, in sediment core D2. The superficial enrichment of trace elements and the strong  
33 correlation between trace elements and superficial high content of POC and Fe detected at station D2  
34 indicated that these elements could have terrestrial inputs from the river or point source input. This core  
35 was collected in front of fuels containers and an industrial effluent and under the influence of ships, which  
36 could be source of pollution. These results were confirmed with the EF values (Figure 5). Alkaline  
37 extraction showed a high percentage in superficial layer especially for As and Cu even for Ag and Cd  
38 (*data not shown*). These could be attributed to the stable and soluble complexes formed with dissolved  
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4 organic matter, as for Cd, could be attributed to the control of OM on the biogeochemistry of Cd.(Dang et  
5 al., 2015; Ho et al., 2012) In addition, acid extraction in these superficial layers showed the highest  
6 percentage of extraction indicating that the studied elements in the first layers are associated to oxides and  
7 carbonates (Dang et al., 2015; Larrose et al., 2010). These results indicated the influence of industrial  
8 activities in this bay and the presence of solid waste all around. This significant pollution could also be  
9 due to antifouling paints based on Cu or Pb or also to inputs arising from boat repainting (Burton et al.,  
10 2005). Noteworthy that the industrial effluents or urban storm water runoff transported without any  
11 treatment to the bay from the urbanized region by Beirut River could be a major source of trace metal  
12 pollution in the region. On the other hand, it could be due to resuspension of sediment as this area is faced  
13 to numerous activities such as rising of navy ships wrecks and this was reflected by a homogeneous  
14 distribution of metals (Briant et al., 2013). All these results confirmed the moderate and significant level  
15 of contamination in the St-Georges Bay sediments and highly contaminated with Ag. In addition, PCA  
16 results confirmed that the studied sediments of the three stations followed the contaminants elements  
17 which were correlated with terrigenous elements (clay-component elements Al and Fe) showing a  
18 contamination all down the core expect for the first layer of D2. These sediments mostly had  
19 anthropogenic origins from terrestrial inputs, which can be Beirut River or industrial effluents in this  
20 region. Such results confirmed the contamination of St-Georges Bay with Pb, Cd, Cu, Cd, As and  
21 particularly Ag. The studied elements showed a clear correlation between the anthropogenic and  
22 terrigenous and this could be related to their mixed origins and a significant contamination comparing to  
23 the background level.  
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## 39 5.2. Early diagenesis tracer evidences

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41 At the three sites, pH was around 8 which is the common range for marine sediments (Burton et al., 2005)  
42 and it is a well-known factor that influence heavy metals transfer behavior in sediments (Peng et al.,  
43 2009). At the three points, sediments were strongly reduced (Figure 7) and reflected completely anoxic  
44 sediments (Burton et al., 2005) starting from - 14 cm of sediment depth in D1 and D2. During early  
45 diagenesis, the distribution of major/minor and trace elements between pore waters and sediments is  
46 affected by a set of complex processes (Heggie and Lewis, 1984). Many processes can lead to the  
47 removal and/or the release of elements from pore waters such as redox zone or biogenic material (Shaw et  
48 al., 1990). It is also important to note that the behavior of elements differ during early diagenesis in the  
49 same sedimentary environment. The common diagenetic sequence was clearly noticeable in the three  
50 sediment cores. Dissolved organic carbon (DOC) tended to increase with depth at the three sediment  
51 cores, which could be related to the mobilization of particulate carbon to the water. Ammonium profiles  
52 showed peaks at different sediment depths, i.e., at -10 cm for D0, and below -20 cm depth for D1 which  
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4 indicated sub-oxic degradation (Haese et al., 2000), unlike D2 where a peak was observed directly at  
5 superficial layer. The decrease of POC (Figure 3) in sediments and the increase of  $\text{PO}_4^{3-}$  (*Data not shown*),  
6  $\text{NH}_4^+$  and DOC with depth (Figure 7) in pore waters reflected directly the degradation of OM deriving  
7 primary and secondary redox reactions (Anschutz et al., 2007; Rigaud et al., 2013). A high mobilization  
8 of Mn/Fe occurred below the sediment-water interface (SWI) due to the reduction of Mn/Fe  
9 (oxy)hydroxides and released  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  into the pore waters (Figure 7). The release in the Mn  
10 reduction zone was attributed to the release of metals associated with Mn oxides in the solid phase (Shaw  
11 et al., 1990). Mn oxides reduction zones and release of dissolved Mn occurred at upper layer in the  
12 studied sediments. Fe (oxy)hydroxides reduction zones occurred after Mn oxide reduction but the order  
13 changed or overlap sometimes depending on inputs of reactive OM and bioavailability of  
14 Fe(oxy)hydroxides in the sediments (Canavan et al., 2006; Canfield et al., 1993). The high Mn peaks next  
15 to SWI are attributed to the reduction of amorphous Fe (oxy)hydroxide (Scholz and Neumann, 2007).  
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### 25 5.3 Trace metals and early diagenesis

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28 Almost at the 3 sediment cores, the release of trace elements was immediately below the SWI and occurs  
29 in the Fe and Mn (oxy)hydroxide reduction zone. Concentrations of trace elements in pore waters were  
30 higher than in the overlying water (Figure 7) indicating a possible diffusive flux from sediment to the  
31 water column (Rigaud et al., 2013). Dissolved Co profiles in the sediments and pore waters showed that  
32 Co was released in pore waters during reduction of Mn/Fe (oxy)hydroxide (Figure 7), indicating that Co  
33 was adsorbed onto manganese (oxy)hydroxide phases in the sediments as evidenced in different studies  
34 (Achterberg et al., 1997; Heggie and Lewis, 1984; Tankere-Muller et al., 2007). These results were  
35 confirmed with the strong correlation between Co and Mn or Fe; moreover, Co was mostly extracted with  
36 acid extraction. The second peak observed in station D1 (- 27 cm) and D2 (- 25 cm) was strongly  
37 correlated with DOC in deeper layer. Furthermore, Co was also slightly extracted with alkaline extraction,  
38 indicating that Co could be complexed to organic matter as described by different studies (Algeo and  
39 Maynard, 2004; Zhang et al., 1990) which showed the affinity of cobalt to humic substances and organic  
40 ligands. Dissolved Cr profiles tended to increase with sediment depth, except for D1, where two peaks, at  
41 sub-superficial layer (- 11 cm) and at deeper layer (- 27 cm) are present and associated to DOC. The  
42 release of Cr in superficial layer was due to reduction Mn/Fe (oxy)hydroxide. The increase of dissolved  
43 Cr concentrations in pore waters corresponded also to an increase in DOC concentrations, to an increase  
44 in Cr levels in sediment (Figure 3, Figure 7). And to a slight increase with depth in  $\text{Cr}_{\text{Asc}}$  and  $\text{Cr}_{\text{NaOH}}$   
45 profiles (*Supplementary information 4*). By this behavior, we could predict a strong affinity of Cr with  
46 OM and the presence of humic complexes (Shaw et al., 1990). The release of metals at the SWI or/and in  
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4 the reduction zone of Mn was attributed to biogenic materials or particles degradation which contain  
5 metals (Shaw et al., 1990). Release of Cu into pore waters occurred in the Mn/Fe reduction zone, which  
6 indicated that Cu was released from organic matter or from reductive dissolution of Fe (oxy)hydroxide in  
7 oxic/suboxic surface layer of the sediment. In the sediment, Cu is normally associated with fresh and  
8 easily metabolizable organic matter or adsorb onto particulate Mn/Fe (oxy)hydroxides (Algeo and  
9 Maynard, 2004; Scholz and Neumann, 2007). This hypothesis was also supported with the results of acid  
10 and alkaline extraction and the strong correlation between Cu and Fe ( $r^2 = 0.76$ ) in the sediment of the  
11 three sediment cores. The negligible values of  $Cu_{Asc}$  in the four sediment cores indicated the Cu is not  
12 associate to reducible fraction (amorphous Fe oxides). The release of dissolved arsenic occurred  
13 immediately below the SWI in the three cores was related to the reductive dissolution of Mn/Fe  
14 (oxy)hydroxide into pore waters in the form of As(III) and /or As(V), especially, that As was extracted  
15 with ascorbate and acid extraction. This behavior was similar to these observed in other studies (Chaillou  
16 et al., 2003; Couture et al., 2010; Dang et al., 2014). The second peak observed at deep layers of D1 (- 27  
17 cm) and D2 (- 25 cm) (Figure 7) could be linked to the presence of fresh organic matter from different  
18 source as there is a strong correlation between DOC and As in deep layers; moreover, As was mostly  
19 extracted with alkaline solution. Pb was mobilized near the SWI or at intermediate layer in the three cores  
20 during the reactive Fe oxides reduction or the aerobic degradation of organic matter. In addition, Pb was  
21 only extracted with acid extraction (Figure 6) confirming the release from these carrier phases and  
22 participating in the cycle of Fe dissolution, diffusion and re-precipitation (Gobeil and Silverberg, 1989).  
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## 38 6. Conclusion

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41 This study confirmed the significant contamination of the St-Georges Bay sediments, presenting  
42 significant (Hg, Cu, Pb) or high (Ag) levels of metals comparing to the marine background or to UCC  
43 levels and the EF values showed a significant to moderate enrichment especially for Ag, Pb, Cd, Cu and  
44 Hg in order. The principal component analysis PCA showed that the contaminants elements were  
45 associated to terrigenous elements inputs and a contamination gradient from D0 to D2. This pollution or  
46 inputs of contaminants were due to numerous anthropogenic activities in the area such as the discharge of  
47 industrial effluents and non-treated wastewater and the high maritime activities. Moreover, this maritime  
48 activity contributed to the resuspension of sediments, which modified and altered the diagenetic  
49 sequences. Selective extraction (acid, ascorbate and alkaline) indicated the carrier phases of the studied  
50 trace elements (organic matter and Mn/Fe oxides) and evidenced the mobility of trace elements in the  
51 sediments. More specifically, the main diagenetic processes influencing the remobilization of elements in  
52 pore waters were Mn/Fe (oxy)hydroxide reduction and this was proven with the release of dissolved trace  
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4 elements through these phases. The study of a spatial distribution of trace metals in the bay and along  
5 Beirut River appeared to be a necessity to identify more properly the source of inputs of the studied trace  
6 metals.  
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## 23 24 25 Conflict of interest

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27 There are no conflicts to declare.  
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