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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

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

Diagenetic primary processes start with aerobic oxidation of OM by using dissolved oxygen from the overlying or interstitial waters as an oxidant near the sediment-water interface (SWI). When oxygen is completely consumed or falls to very low levels, OM decomposition can occur by using sequentially NO_3^-, Mn (oxy)hydroxides (MnO_x), Fe (oxy)hydroxides (Fe_2O_3 or FeOOH) as electrons acceptors (Chester, 1990; Froelich et al., 1979). The reductive dissolution of Mn/Fe (oxy)hydroxide releases in pore waters trace metals previously bound/incorporated to the settled oxides. Sulfate reduction occurs in the sulfidic anaerobic areas where SO_4^{2-} is used as electrons acceptors. In the contrary, sulfate reduction to sulfide could sequestrate dissolved trace metals in sulfide precipitates (Burgos et al., 2018; Froelich et al., 1979;

Hyacinthe et al., 2001; Lesven et al., 2008). In anaerobic conditions, following sulfate reduction, the last reaction, methanogenesis, occurs where biogenic dissolved methane can be formed (Burdige and Komada, 2011; Chester, 1990; Froelich et al., 1979). These primary redox reactions are vertically stratified depending on their energy yield and the reduced species produced such as NH_4^+, Mn^{2+}, Fe^{2+}, HS^-, CH_4 take part in secondary redox reactions in diagenetic reactions (Canavan et al., 2006). Moreover, primary and secondary redox reactions divide sediments into different zones of redox conditions (e.g. oxic, sub-oxic, anoxic and sulfidic) (Canavan et al., 2006; Chester, 1990; Rigaud, 2011). However, this order can be disturbed due to the presence of a set of microenvironments with redox condition controlled by different bacterial populations (Achard, 2013). Several studies related to trace metal contamination in marine sediments were conducted in the Mediterranean Sea (Álvarez-Iglesias et al., 2006; Cossa et al., 2014) and along the Lebanese coasts (Abi-Ghanem et al., 2009; Nakhle, 2004; Nassif, 2010) (Table1). The Lebanese studies that focused on solid phase contamination, have shown that Dora area in Beirut is the most contaminated zone of Lebanon. However, there is a lack of study aiming at shedding light on the impacts of diagenetic process on metal-mobilization in pore waters and at identifying the link between sedimentary accumulation and water column transport processes. Therefore, the aim of this study is: 1) to assess the contamination status of the Lebanese coastal sediments of St-Georges Bay – Dora; 2) to study the influence of early diagenesis on trace metal distribution and their distribution between the solid phase and pore waters in the studied sites. For this, diagenetic tracers, organic carbon and a series of minor/major/trace elements (Al, Ag, As, Cd, Co, Cu, Fe, Hg, Mn, Pb and Rb) were measured in pore water and solid fraction (sediments) in three Dora bay sites.

2. Area of study

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

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_2) to preserve redox conditions. The collected sediments were then centrifuged (for 15 min, 3,077 g, 20 ºC). 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 ºC), 2 mm sieved, crushed and kept deep-frozen until analysis.

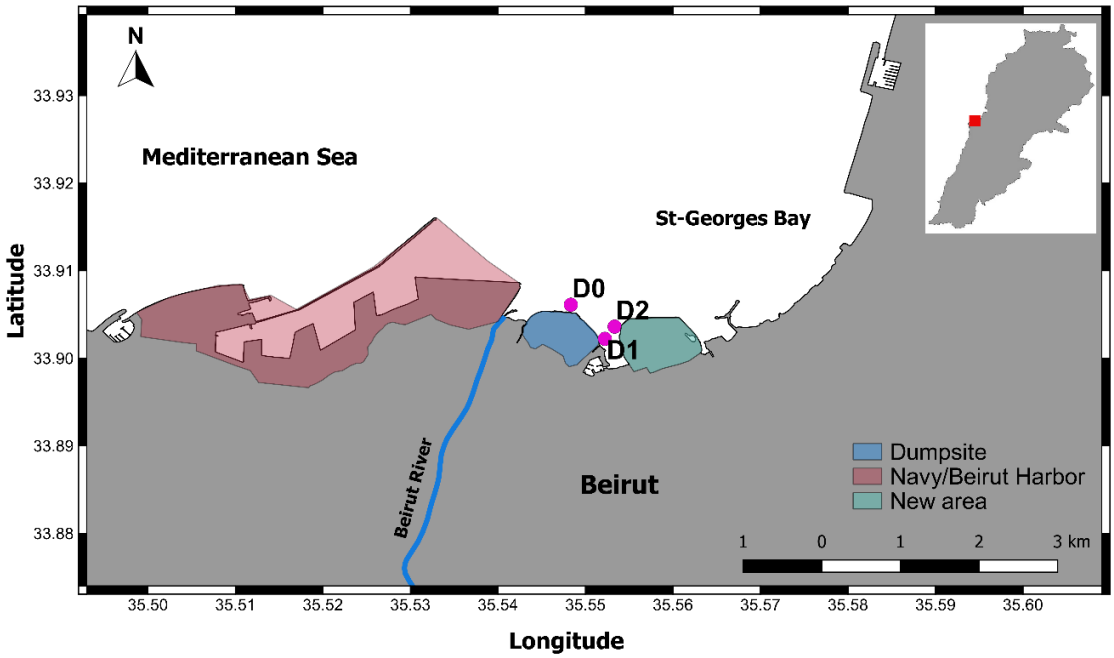

Figure 1: Map of the studied area and location of the sampled sediment cores D0, D1 and D2.

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 (Malvem hydro 2000G) respectively. Elements concentrations were determined after an aqua regia and microwave assisted digestion of sediments. The obtained solutions were filtered (0.2 µm, 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.

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

3.3. Enrichment factors (EF)

To explain the origin of trace elements in sediment and show the influence of anthropogenic activities, enrichment factors (EF) were calculated by comparing trace elements concentrations to the geochemical background of the studying area, using the following equation:

$$EF = \frac{\left(\frac{Me}{X}\right) sample}{\left(\frac{Me}{X}\right) background}$$

Where used X is Al. Since there is no accepted pollution ranking by authors five categories system of enrichment are proposed by Sutherland, 2000:

EF < 2: absence to low enrichment; crustal origin

2 < EF < 5: moderate enrichment

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

20 < EF < 40: Highly enriched

EF > 40: Extremely enriched

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 (µg.g^{1})	Cd (µg.g^{1})	Pb (µg.g^{1})	Cr (µg.g^{1})	Co (µg.g^{1})	Cu (µg.g^{1})	As (µg.g^{1})	Hg (µg.g^{1})
D0 (8)[a]	**Range**	0.6 - 0.9	0.4 - 0.5	25.1 - 44.3	86.9 - 107.7	12.6 - 16.3	34.8 - 53.1	6.5 - 9.8	0.1 - 0.1
	Average	0.7 ± 0.7	0.4 ± 0.03	35.2 ± 5.5	99.5 ± 7.0	14.9 ± 1.5	47.5 ± 10.8	8.2 ± 1.2	0.1± 0.03
D1 (15)	**Range**	1.0 - 2.6	0.5 - 1.1	58.7 - 140.0	126.2 - 298.8	14.5 - 26.0	73.2 - 142.0	10.0 - 16.4	0.1 - 0.3
	Average	1.5 ± 0.5	0.7 ± 0.2	92.1 ± 18.6	189.2 ± 52.5	19.78 ± 3.5	96.7 ± 16	12.9 ± 2.2	0.2 ± 0.05
D2 (15)	**Range**	1.5 - 5.6	0.6 - 0.9	64.3 - 376.1	158.3 - 230.9	16.4 - 23.6	66.6 - 201.4	13.1 - 18.6	0.2 - 0.7
	Average	2.9 ± 1.3	0.7 ± 0.3	118.4 ± 75.9	182.6 ± 19.3	18.3 ± 2.2	93.2 ± 32.1	15.3 ± 1.89	0.4 ± 0.1
Aguada Bay – India (Prajith et al., 2016)	**Average**	-	-	10.7 ± 2.91	218 ± 115	20.5 ± 4.85	65.9 ± 39	-	-
San Simón Bay – Spain(Álvarez-Iglesias et al., 2006)	**Average**	-	-	46.4 ± 27.7	79.5 ± 24.8	6.0 ± 2.5	32.1 ± 5.6	-	-
Cap de Creus Canyon – France(Cossa et al., 2014)	**Average**	0.12 ± 0.01	0.13 ± 0.01	46.3 ± 4.7	85.4 ± 3.4	16.2 ± 0.5	29.3 ± 2.3	-	-
Selaata – Lebanon(Abi-ghanem, 2008)	**Average**	0.5 ± 0.3	0.3 ± 0.1	12.0 ± 4.4	145.2 ± 30.7	-	18.9 ± 3.1	-	0.04 ± 0.01
Akkar background – Lebanon[b]	**Average**	0.08 ± 0.01	0.2 ± 0.02	10.9 ± 2.44	102.5 ± 12.0	-	11.1 ± 2.8	-	0.02 ± 0.01
UCC[c]		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 ± 0.15, 1.47 ± 0.06, 1.57 ± 0.26). Results of grain size showed that predominant fraction size in all the studied sediments was between 20 - 60 µm and 60 – 200 µm *(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** (%)	**TS** (%)	**Al** (%)	**Mn** (%)	**Fe** (%)	Rb ($\mu g.g^{-1}$)
D0(8)	Average	Quartz/Calcite/Ankerite/ Dolomite	0.3 ± 0.1	0,5 ± 0,2	3.2 ± 0.5	0.03	4.0 ± 0.2	13.7 ± 5.3
D1(15)	Average	Quartz/Calcite/Pyrite /Dolomite	0.2 ± 0.07	0,6 ± 0,2	3.4 ± 0.6	0.04 ± 0.01	5.0 ± 0.7	15.1 ± 3.2
D2(15)	Average	Quartz/Calcite/Pyrite/ Dolomite	0.47 ± 0.9	0,8 ± 0,2	3.4 ± 1	0,04	5.1 ± 0.5	11.2 ± 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

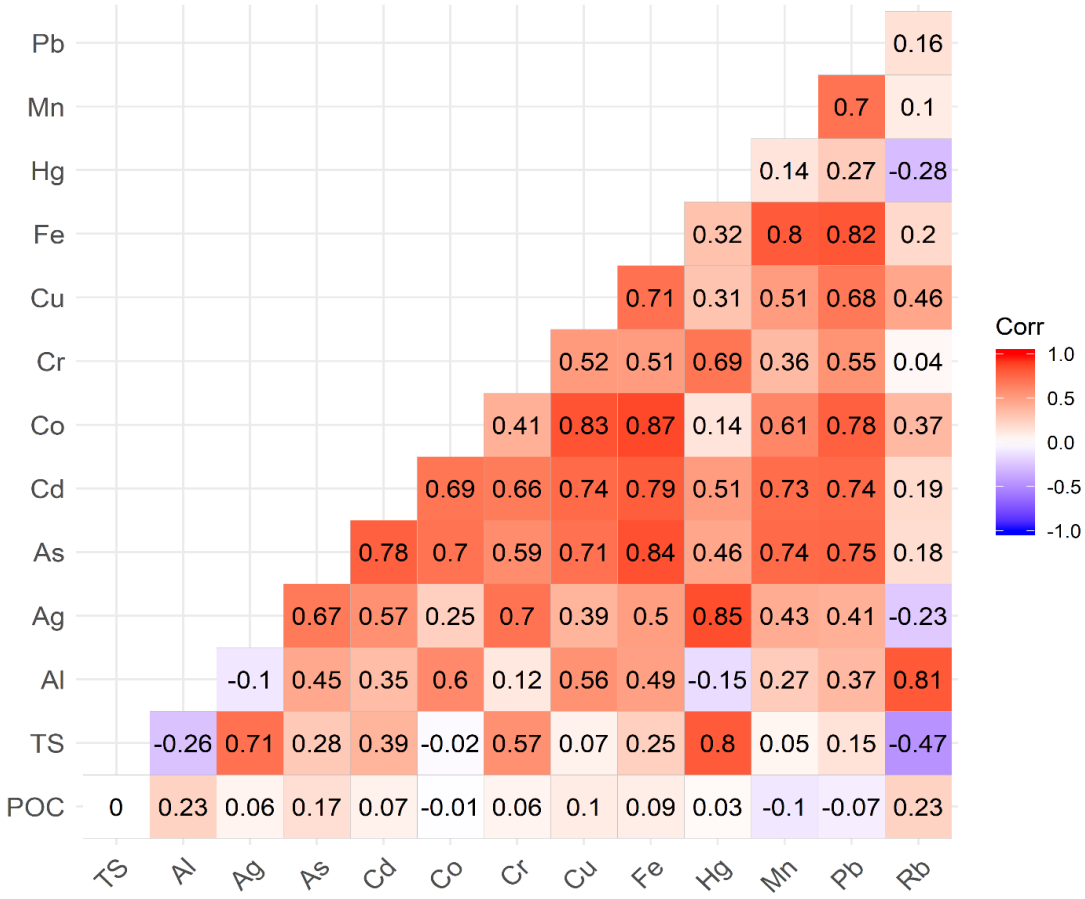

Figure 2: Correlation of POC, TS and all studied elements in the sediments.

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

correlation, solid profiles for Mn, Fe, Co, Cd and As showed the same pattern variation along the three sediment profiles (Figure 3), where D0 showed the lowest concentration comparing to D1 and D2.

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

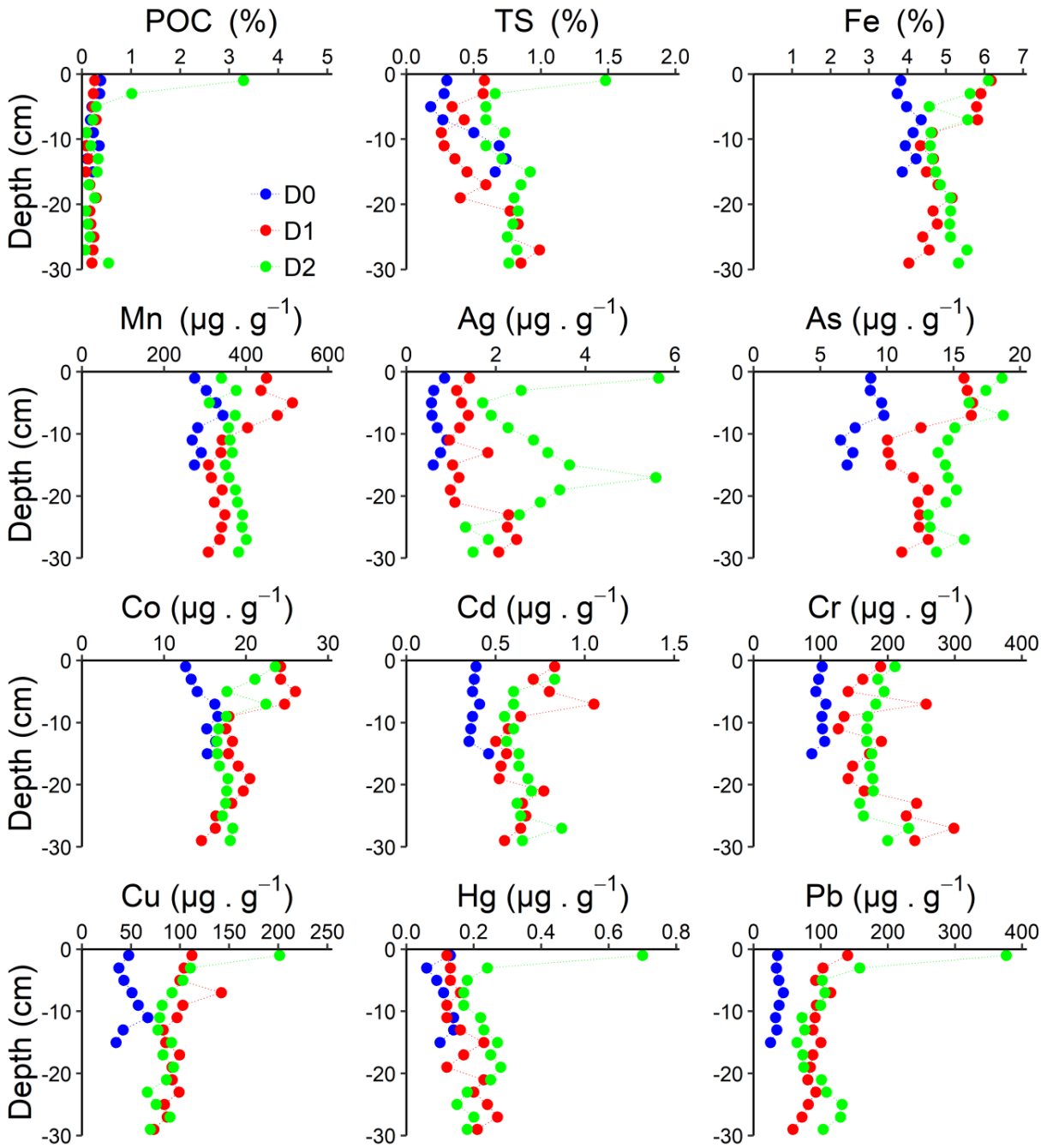

Figure 3: POC, TS, Fe, Mn, Ag, Cd, Pb, Co, Cr, Cu, As and Hg profiles in the three sediments cores D0 (blue), D1 (red) and D2 (green).

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).

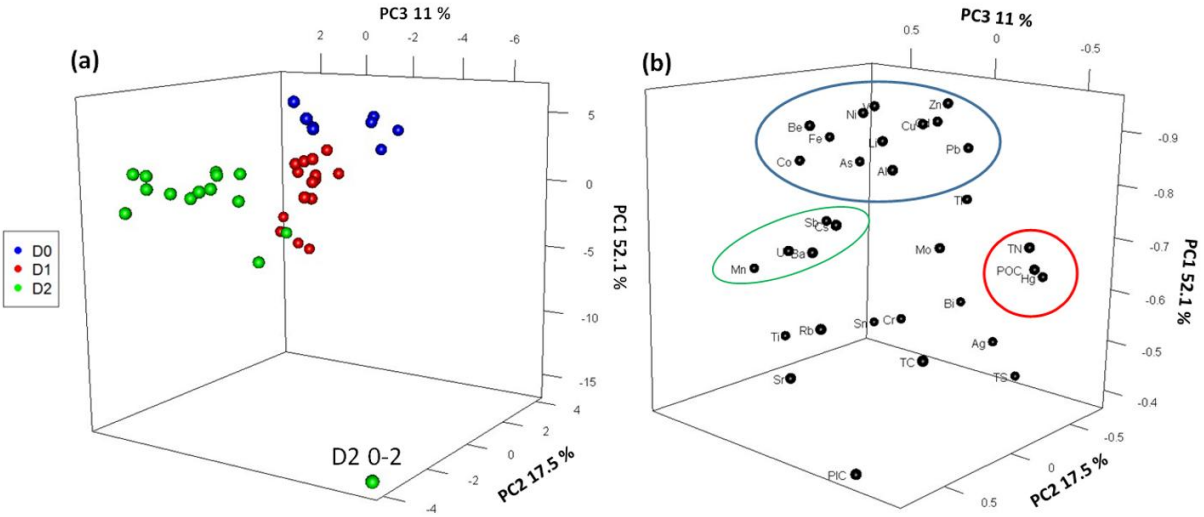

Figure 4: 3D representation of the three principal components obtained by PCA treatment of the dataset for (a) the sediments samples of D0 (blue), D1 (red) and D2 (green) and (b) the 33 elements. Blue circle are elements driving D1 (blue circle), red circle the correlation between Hg and POC and green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

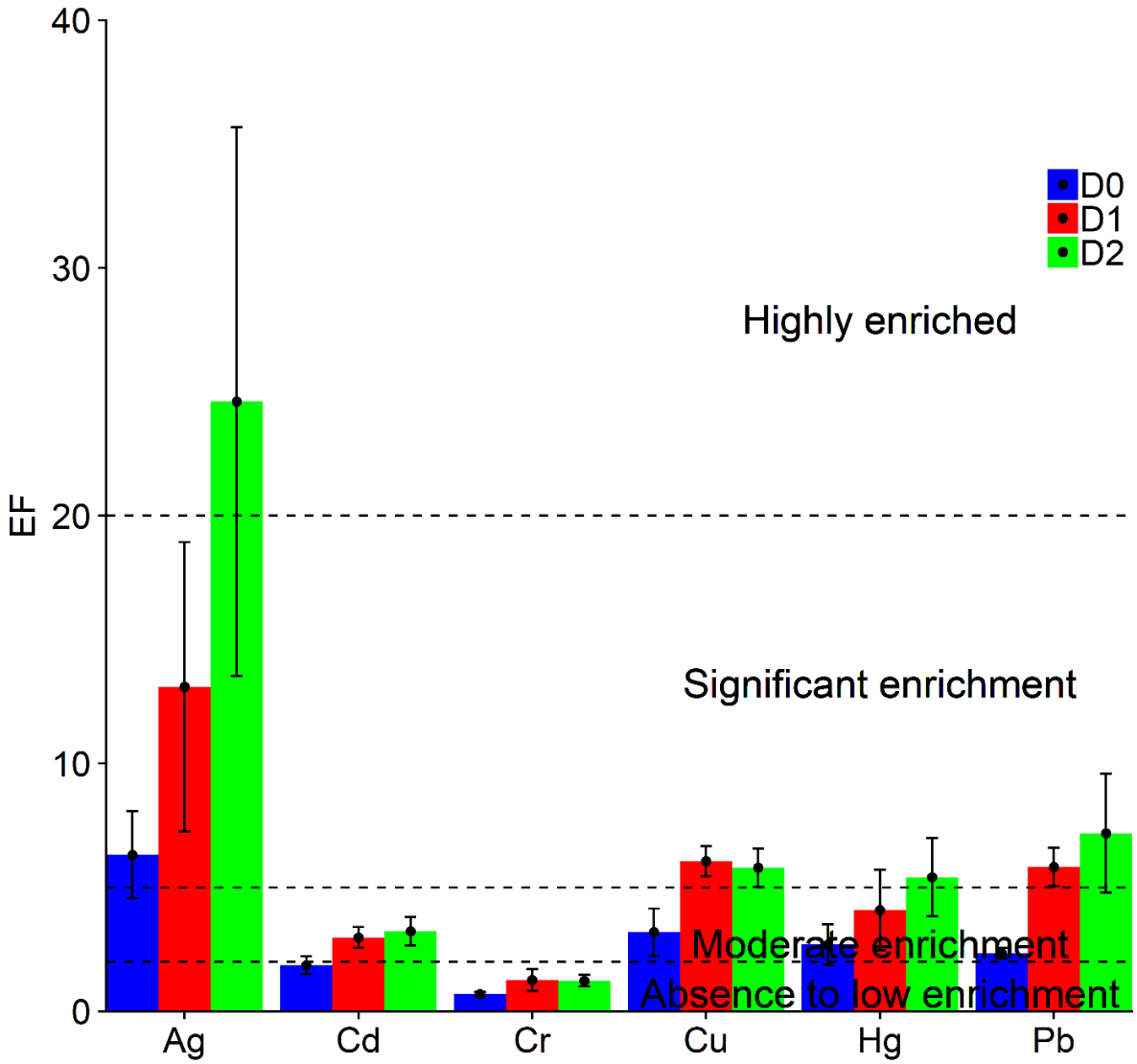

Figure 5: Average and standard deviation of metal enrichment factor (EF) in three sediments core "D0 (blue), "D1" (red) and "D2" (green). The dashed lines indicate four of five categories cited in section 3.3.

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

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

4.2. Selective extractions

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

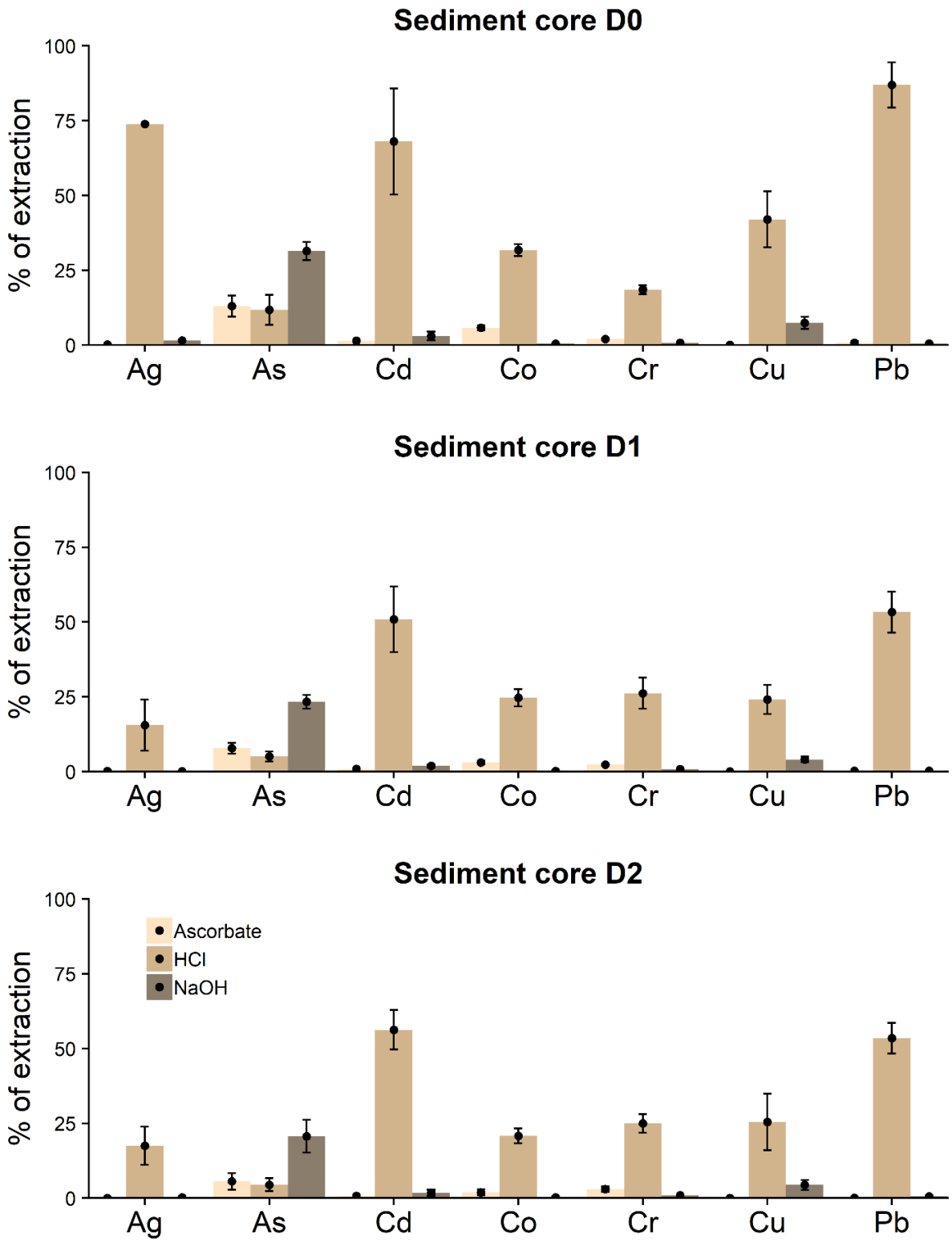

Figure 6: Mean percentage of trace elements extracted with Ascorbate pH=8.2, HCl 1M and NaOH 0.1M for each sediment cores "D0", "D1" and "D2" along all sediments depth.

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_2) 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_4^+ 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_4^+ and PO_4^{3-} (r^2= 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^2= 0.72) and D2 (r^2= 0.86). For dissolved Co, a sub-superficial layer peak was detected at D0 associated with Mn (r^2= 0.81) and Fe (oxy)hydroxide (r^2= 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^2= 0.88) and Fe (oxy)hydroxide reduction zone (r^2= 0.71) and slightly one with Mn oxides in D2 (r^2= 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^2= 0.80). At D0 and D2, dissolved Cr profiles tended to increase with sediment depth.

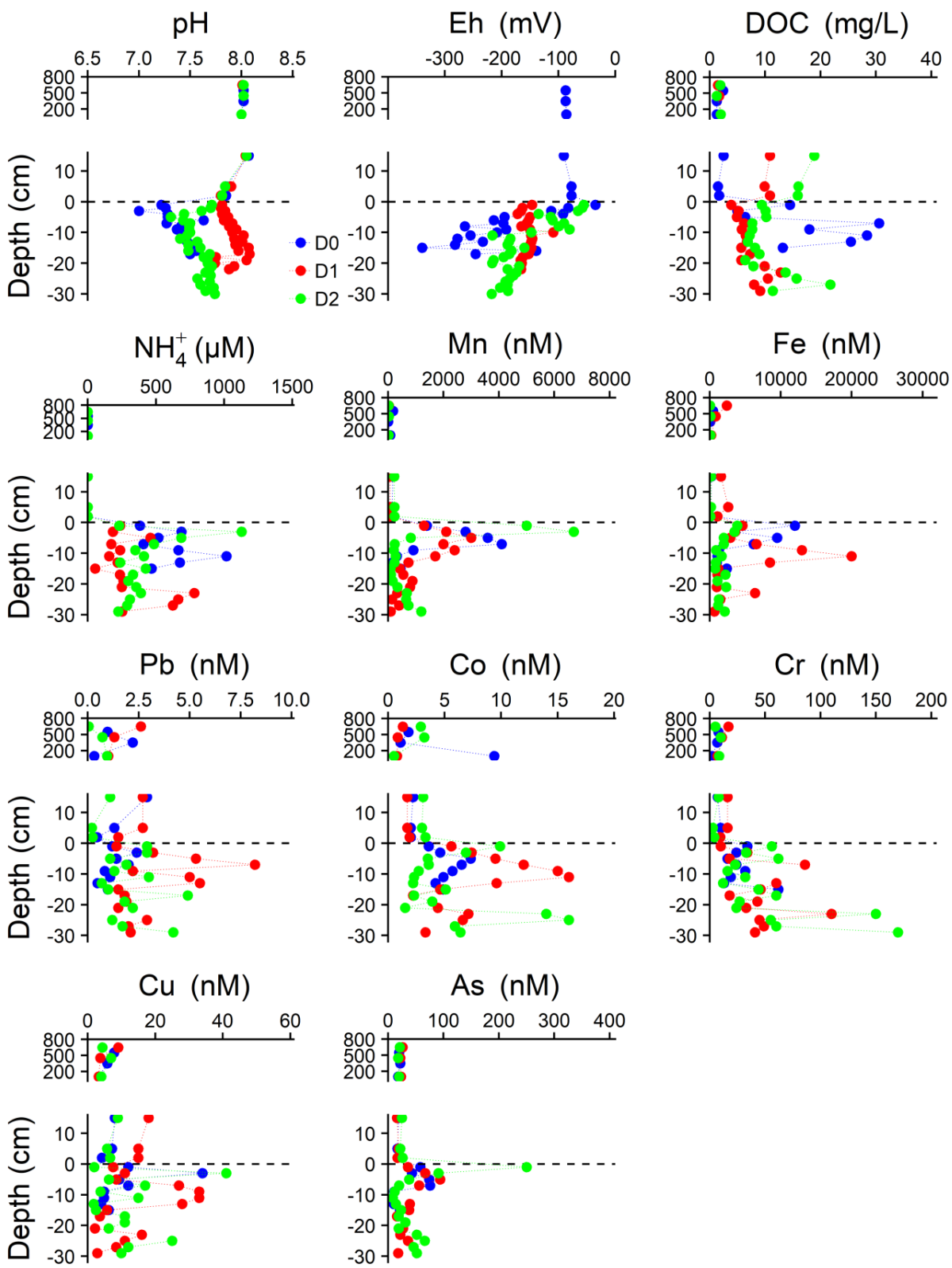

Figure 7: pH, Eh, dissolved organic carbon, nutrients and dissolved trace elements profiles in pore waters extracted at the three sediments cores "D0" (blue), "D1" (red) and "D2" (green).

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

5. Discussion

5.1. Sediments composition and solid profiles

Grain size affects the accumulation of metals in sediments and fine fraction promotes the accumulation of trace elements in the sediments.(Blott S.J. and Pye K., 2001; Cauwet, 1987; Ujević et al., 2000) Mean percentage of grain size showed that the majority of particles were very coarse silt (20 - 50 µm) or very fine sand (50 – 200 µm) (*Supplementary information 1)* at the three sediment cores D0, D1 and D2. These results were co-variant with the mineralogy of the studied zone, rich in quartz, calcite and dolomite (Table 2). Elements concentrations such as Al, Rb, Fe, and Mn (Table 2) at the three points indicated that the mineral composition seems constant during sedimentation processes. The significant correlation between elements such as Al/Fe or Al/Rb or Al/Mn in D0 and D1 reflected a common source for these elements and indicated a signature of terrigenous fine particle such as aluminosilicates and oxy-hydroxides, however, the source in D2 do not present a completely to terrigenous source. These results could be related to high mixing of sediments or to the influence of alluvial continental deposits by Beirut river (Abi-Ghanem et al., 2009), such deposits came with the run-off of Beirut River after a big episodes of precipitation. This behavior was observed also with ascorbate and HCl extraction results. The ascorbate extraction showed an accumulation of Fe and Mn that correspond to Fe/Mn (oxy)hydroxide (Haese et al., 2000; Rigaud et al., 2013). In plus, ascorbate extraction of Al, Mn and Fe were low comparing to acid extraction but they showed the same trend and they were strongly correlated in the sediment cores D0 (r^2= 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, carbonates and monosulfide minerals in the sediments (Dang et al., 2014; Haese et al., 2000). The highest POC content detected at the superficial layer of D2 (Figure 3) indicated a superficial enrichment, supported by the highest dissolved organic carbon in the supernatant waters at D2, then a slight decrease with depth (Figure 7). This could be related to terrestrial OM inputs from rivers, to urban sewage

discharge or to biological production (Álvarez-Iglesias et al., 2006). POC profiles in D0 and D1, present lower starting point in D2, but also decreased with depth.

Vertical variability of trace elements presented in Figure 3, showed disrupted profiles of all studied elements with depth implied must probably the mixing sediment process "resuspension", especially that this bay was very well known as a docking area. The Spearman's correlation showed a significant positive correlation between concentrations of Al, Fe and the anthropogenic trace elements (Cd, Pb, Co, Cr, Cu and As) in this bay (Figure 2) and not Ag which was slightly correlated with POC (see section 4.1). These indicated that the primary accumulation of trace elements in the bay was governed by deposition of terrigenous material, particularly particles associated with terrigenous organic matter and Fe and Mn oxides and (oxy)hydroxides. Trace elements chemical extraction results appeared to be similar in the three sediments cores. These trace elements (Ag, Cd, Pb, Co, Cr and Cu) were more extracted with acid extraction, indicating they are mostly associated to exchangeable-carbonates or oxides. The high acid extraction percentage observed for Cu highlight the presence of a Cu desorption from organic sites or Cu release from oxides (Adamo et al., 2005). However, As was the most extracted with ascorbate and alkaline extraction. In plus, Cu was slightly extracted by alkaline extraction. This alkaline extraction of As and Cu could be attributed to the stable and soluble complexes formed with dissolved organic matter (Dang et al., 2015; Ho et al., 2012). As, Co, Cr and Cd were slightly extracted with ascorbate suggesting an interaction between these elements and Mn/Fe (oxy)hydroxide fraction but the contribution of other phases such as FeS are not negligible (Haese et al., 2000; Rigaud et al., 2013). These results confirmed the association of the studied trace elements to terrigenous organic matter and Fe and Mn oxides and (oxy)hydroxides which could be imported by the Beirut river or the industrial effluents or Beirut Harbor activities. Comparing concentrations of these trace elements in the three sediment cores to background level in the upper continental crust given by Wedepohl, 1995 or to background level of Akkar region (Table 1), the sediments in the area showed a highly mean content for Cd, Pb, Cu, As and Hg. Comparing to other studies in the Mediterranean Sea or outside (Table1), these studied sediments were highly contaminated especially, with Ag, Cd, Pb, Cu and Hg. High concentrations of trace elements were observed, especially, in sediment core D2. The superficial enrichment of trace elements and the strong correlation between trace elements and superficial high content of POC and Fe detected at station D2 indicated that these elements could have terrestrial inputs from the river or point source input. This core was collected in front of fuels containers and an industrial effluent and under the influence of ships, which could be source of pollution. These results were confirmed with the EF values (Figure 5). Alkaline extraction showed a high percentage in superficial layer especially for As and Cu even for Ag and Cd *(data not shown)*. These could be attributed to the stable and soluble complexes formed with dissolved

organic matter, as for Cd, could be attributed to the control of OM on the biogeochemistry of Cd.(Dang et al., 2015; Ho et al., 2012) In addition, acid extraction in these superficial layers showed the highest percentage of extraction indicating that the studied elements in the first layers are associated to oxides and carbonates (Dang et al., 2015; Larrose et al., 2010). These results indicated the influence of industrial activities in this bay and the presence of solid waste all around. This significant pollution could also be due to antifouling paints based on Cu or Pb or also to inputs arising from boat repainting (Burton et al., 2005). Noteworthy that the industrial effluents or urban storm water runoff transported without any treatment to the bay from the urbanized region by Beirut River could be a major source of trace metal pollution in the region. On the other hand, it could be due to resuspension of sediment as this area is faced to numerous activities such as rising of navy ships wrecks and this was reflected by a homogeneous distribution of metals (Briant et al., 2013). All these results confirmed the moderate and significant level of contamination in the St-Georges Bay sediments and highly contaminated with Ag. In addition, PCA results confirmed that the studied sediments of the three stations followed the contaminants elements which were correlated with terrigenous elements (clay-component elements Al and Fe) showing a contamination all down the core expect for the first layer of D2. These sediments mostly had anthropogenic origins from terrestrial inputs, which can be Beirut River or industrial effluents in this region. Such results confirmed the contamination of St-Georges Bay with Pb, Cd, Cu, Cd, As and particularly Ag. The studied elements showed a clear correlation between the anthropogenic and terrigenous and this could be related to their mixed origins and a significant contamination comparing to the background level.

5.2. Early diagenesis tracer evidences

At the three sites, pH was around 8 which is the common range for marine sediments (Burton et al., 2005) and it is a well-known factor that influence heavy metals transfer behavior in sediments (Peng et al., 2009). At the three points, sediments were strongly reduced (Figure 7) and reflected completely anoxic sediments (Burton et al., 2005) starting from - 14 cm of sediment depth in D1 and D2. During early diagenesis, the distribution of major/minor and trace elements between pore waters and sediments is affected by a set of complex processes (Heggie and Lewis, 1984). Many processes can lead to the removal and/or the release of elements from pore waters such as redox zone or biogenic material (Shaw et al., 1990). It is also important to note that the behavior of elements differ during early diagenesis in the same sedimentary environment. The common diagenetic sequence was clearly noticeable in the three sediment cores. Dissolved organic carbon (DOC) tended to increase with depth at the three sediment cores, which could be related to the mobilization of particulate carbon to the water. Ammonium profiles showed peaks at different sediment depths, i.e., at -10 cm for D0, and below -20 cm depth for D1 which

indicated sub-oxic degradation (Haese et al., 2000), unlike D2 where a peak was observed directly at superficial layer. The decrease of POC (Figure 3) in sediments and the increase of PO_4^{3-} (*Data not shown*), NH_4^+ and DOC with depth (Figure 7) in pore waters reflected directly the degradation of OM deriving primary and secondary redox reactions (Anschutz et al., 2007; Rigaud et al., 2013). A high mobilization of Mn/Fe occurred below the sediment-water interface (SWI) due to the reduction of Mn/Fe (oxy)hydroxides and released Mn^{2+} and Fe^{2+} into the pore waters (Figure 7). The release in the Mn reduction zone was attributed to the release of metals associated with Mn oxides in the solid phase (Shaw et al., 1990). Mn oxides reduction zones and release of dissolved Mn occurred at upper layer in the studied sediments. Fe (oxy)hydroxides reduction zones occurred after Mn oxide reduction but the order changed or overlap sometimes depending on inputs of reactive OM and bioavailability of Fe(oxy)hydroxides in the sediments (Canavan et al., 2006; Canfield et al., 1993). The high Mn peaks next to SWI are attributed to the reduction of amorphous Fe (oxy)hydroxide (Scholz and Neumann, 2007).

5.3 Trace metals and early diagenesis

Almost at the 3 sediment cores, the release of trace elements was immediately below the SWI and occurs in the Fe and Mn (oxy)hydroxide reduction zone. Concentrations of trace elements in pore waters were higher than in the overlying water (Figure 7) indicating a possible diffusive flux from sediment to the water column (Rigaud et al., 2013). Dissolved Co profiles in the sediments and pore waters showed that Co was released in pore waters during reduction of Mn/Fe (oxy)hydroxide (Figure 7), indicating that Co was adsorbed onto manganese (oxy)hydroxide phases in the sediments as evidenced in different studies (Achterberg et al., 1997; Heggie and Lewis, 1984; Tankere-Muller et al., 2007). These results were confirmed with the strong correlation between Co and Mn or Fe; moreover, Co was mostly extracted with acid extraction. The second peak observed in station D1 (- 27 cm) and D2 (- 25 cm) was strongly correlated with DOC in deeper layer. Furthermore, Co was also slightly extracted with alkaline extraction, indicating that Co could be complexed to organic matter as described by different studies (Algeo and Maynard, 2004; Zhang et al., 1990) which showed the affinity of cobalt to humic substances and organic ligands. Dissolved Cr profiles tended to increase with sediment depth, expect for D1, where two peaks, at sub-superficial layer (- 11 cm) and at deeper layer (- 27 cm) are present and associated to DOC. The release of Cr in superficial layer was due to reduction Mn/Fe (oxy)hydroxide. The increase of dissolved Cr concentrations in pore waters corresponded also to an increase in DOC concentrations, to an increase in Cr levels in sediment (Figure 3, Figure 7). And to a slight increase with depth in Cr_{Asc} and Cr_{NaOH} profiles (*Supplementary information 4).* By this behavior, we could predict a strong affinity of Cr with OM and the presence of humic complexes (Shaw et al., 1990). The release of metals at the SWI or/and in

the reduction zone of Mn was attributed to biogenic materials or particles degradation which contain metals (Shaw et al., 1990). Release of Cu into pore waters occurred in the Mn/Fe reduction zone, which indicated that Cu was released from organic matter or from reductive dissolution of Fe (oxy)hydroxide in oxic/suboxic surface layer of the sediment. In the sediment, Cu is normally associated with fresh and easily metabolizable organic matter or adsorb onto particulate Mn/Fe (oxy)hydroxides (Algeo and Maynard, 2004; Scholz and Neumann, 2007). This hypothesis was also supported with the results of acid and alkaline extraction and the strong correlation between Cu and Fe (r^2 = 0.76) in the sediment of the three sediment cores. The negligible values of Cu_{Asc} in the four sediment cores indicated the Cu is not associate to reducible fraction (amorphous Fe oxides). The release of dissolved arsenic occurred immediately below the SWI in the three cores was related to the reductive dissolution of Mn/Fe (oxy)hydroxide into pore waters in the form of As(III) and /or As(V), especially, that As was extracted with ascorbate and acid extraction. This behavior was similar to these observed in other studies (Chaillou et al., 2003; Couture et al., 2010; Dang et al., 2014). The second peak observed at deep layers of D1 (- 27 cm) and D2 (- 25 cm) (Figure 7) could be linked to the presence of fresh organic matter from different source as there is a strong correlation between DOC and As in deep layers; moreover, As was mostly extracted with alkaline solution. Pb was mobilized near the SWI or at intermediate layer in the three cores during the reactive Fe oxides reduction or the aerobic degradation of organic matter. In addition, Pb was only extracted with acid extraction (Figure 6) confirming the release from these carrier phases and participating in the cycle of Fe dissolution, diffusion and re-precipitation (Gobeil and Silverberg, 1989).

6. Conclusion

This study confirmed the significant contamination of the St-Georges Bay sediments, presenting significant (Hg, Cu, Pb) or high (Ag) levels of metals comparing to the marine background or to UCC levels and the EF values showed a significant to moderate enrichment especially for Ag, Pb, Cd, Cu and Hg in order. The principal component analysis PCA showed that the contaminants elements were associated to terrigenous elements inputs and a contamination gradient from D0 to D2. This pollution or inputs of contaminants were due to numerous anthropogenic activities in the area such as the discharge of industrial effluents and non-treated wastewater and the high maritime activities. Moreover, this maritime activity contributed to the resuspension of sediments, which modified and altered the diagenetic sequences. Selective extraction (acid, ascorbate and alkaline) indicated the carrier phases of the studied trace elements (organic matter and Mn/Fe oxides) and evidenced the mobility of trace elements in the sediments. More specifically, the main diagenetic processes influencing the remobilization of elements in pore waters were Mn/Fe (oxy)hydroxide reduction and this was proven with the release of dissolved trace

elements through these phases. The study of a spatial distribution of trace metals in the bay and along Beirut River appeared to be a necessity to identify more properly the source of inputs of the studied trace metals.

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Conflict of interest

There are no conflicts to declare.

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