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# Metal binding in soil cores and sediments in the vicinity of a dammed agricultural and industrial watershed

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**Abstract:** The environment is witnessing a downgrade caused by the amelioration of the industrial and agricultural sectors, namely soil and sediment compartments. For those reasons, a comparative study was done between soil cores and sediments taken from two locations in the Qaraaoun reservoir, Lebanon. The soil cores were partitioned into several layers. Each layer was analyzed for several physico-chemical parameters, such as functional groups, particle size distribution,  $\zeta$ -potential, texture, pH, electric conductivity, total dissolved solids, organic matter, cation exchange capacity, active and total calcareous, available sodium and potassium and metal content (cadmium, copper and lead). The metal content of each site was linked to soil composition and characteristics. The two sites showed distinguishable characteristics for features such as organic matter, pH, mineral fraction, calcareous and metal content. The samples taken towards the south site, though contain lower organic matter than the other but more calcareous, showed higher metal content in comparison to the other site (average Cd: 3.8>1.8mg/Kg, Cu: 28.6>21.9mg/Kg, Pb: 26.7>19mg/Kg). However, the metal content in this study did not correlate as much to the organic matter; rather it was influenced by the location of the samples with respect to the dam, its hydrodynamics, the calcareous nature of the soil and the variation of the industrial and agricultural influence on each site.

**Keywords:** Qaraaoun, calcareous, mineral fraction, organic matter, Cu, Cd, Pb.

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## Introduction

The soil is considered as a settling compartment for metals that are discharged due to variable agricultural and industrial activities (Cottenic and Verloo 1984). Lebanon, for example, is witnessing an evolution in the agricultural and industrial sectors in the recent decades (MoE/LEDO 2001). The industrial sector is showing a 20% gross domestic production (GDP) in 2013, with a five year average of 19%, while the agricultural one has a 5% GDP in 2013 and a five year average as well (Matabadal 2013). This evolution is unfortunately accompanied with environmental degradation and consequently health hazards (Van der Gaag et al. 1991), especially in cases where effluent quality is not monitored. As is the case in the Qaraaoun area located in the Bekaa Valley, containing one

of the most viable water bodies in Lebanon, i.e. the Litani River. The Qaraaoun dam is the biggest in Lebanon, it was built in 1959 to collect and store up to 2.2Mm<sup>3</sup> of water (Shaban and Nassif 2007). The development of the industrial and agricultural sectors in that water-rich area is worsening the environmental compartments (Buccolieri 2006), especially soil, sediment and water (BAMAS 2005a), since effluents and discharges from those sectors are being released into the Litani River, or its tributaries, without preliminary treatment in many cases (Abi-Ghanem et al. 2009). In addition, agricultural run-offs in the Qaraaoun watershed will eventually reach the Qaraaoun reservoir along with pollutants and contaminants (such as heavy metals). However, heavy metal assessment in soils is a triggering case, because it depends on many parameters, such as the composition of soil's organic matter (dissolved and particulate), mineral content, pH, biogeochemical fractionation, speciation, calcareous content, cation exchange capacity (CEC), redox state of the soil, water content, texture and background levels of metals (Sukreeyapongse et al. 2002; Mclean and Bledsoe 1992; Eriksson 1988; Zaranyika and Chirinda 2011). Those factors are determining factors for the immobilization or leaching of heavy metals, hence the changing of environmental conditions can alter those factors that in turn have an influence on the pollution level and bioavailability of metals (Soares et al. 1999; Demirbas et al. 2005). Heavy metal pollution assessment in soil and sediment samples, and their leachability to underlying groundwater has been reported countless times, because they are non-biodegradable and can cause serious environmental and health problems (Tokalioglu et al. 2003; Hafizur Rahman et al. 2012; Shafie et al. 2013; Kumar et al. 2011; Yisa et al. 2012; Bentu et al. 2011). For those reasons per se, and because the Qaraaoun region is witnessing an exponential population growth and proliferation in the industrial and agricultural sectors, this study was conducted. A comparative study was done between two sites in the Qaraaoun dam vicinity.

The aims of this study are to link the metal content with different physico-chemical characteristics of soil and sediment samples, to have an insight about the influence of the industrial and agricultural sectors on the quality of the soil and sediment compartments, to determine the influence of the hydrodynamics of the Qaraaoun reservoir on nearby sediments and soil samples, and lastly to indicate the possibility of trace metal transfer at soil-water interface (whether surface or ground).

## **1 Materials and methods**

### **1.1 Sampling site**

The studied site is the Qaraaoun reservoir, located between Mount and Anti-Mount Lebanon ranges, since it is an indispensable water body for the agricultural sector in the Bekaa Valley. A core and a sediment sample was taken from each site, named Q1 and Q2, both lying on the East side of the reservoir (Q1: 33°33'57.66"N, 35°42'26.87"E and 858m altitude; Q2: 33°35'0.53"N, 35°42'37.08"E and 857m altitude) (Fig. 1). The two cores were taken via a motorized core drill (Carottage à Percussion) on March 2013. The 50cm cores were partitioned into six layers, 5cm for the two upper most layers, and 10cm for the deeper four. The sediment samples were taken from the shoreline of each sampling site by a polyethylene shovel (sediments from Q1 and Q2 will be referred to as S1 and S2 respectively). The soil samples were collected in polyethylene bags and stored at 4°C till further analyses were performed, while sediments were stored at -80°C to be freeze-dried by Alpha 1-4 LD plus freeze-drier.

### **1.2 Sample preparation**

The soil samples were disaggregated gently and air dried at ambient room temperature, sediment samples were freeze-dried. All samples were sieved at 2mm to remove particles coarser than sand. Soil samples

were further oven dried (105°C for one day) before experimentation took place. Soil and sediment preparation were in accordance with the Organization for Economic Cooperation and Development (OECD 312 2004).

### 1.3 Physical and chemical parameters

The soil samples were analyzed for several features. Spectral analysis for mineral content of the dried soil and sediment samples was determined by Fourier Transform Infrared (FT-IR-6300 from JASCO). The samples were homogenized with KBr and compressed into 0.7cm holding disks and then subjected to infrared radiation (IR). The size of the samples' particles was determined by Partica Laser Scattering Particle Size Distribution Analyzer LA-950V2 (from HORIBA). In addition, zeta potential ( $\zeta$ -potential in mV) of the colloidal particles of the samples was determined by Zeta Meter 4.0 equipped with electrodes, electrophoretic cells, a microscope, a direct video imaging assembly, a pattern generator and monitor.  $\zeta$ -potential was performed to determine the stability of the colloidal systems in each sample.

Other physico-chemical characterizations, namely pH,  $\text{pH}_{\text{KCl}}$ , electric conductivity (EC), total dissolved solids (TDS), organic matter (OM), cation exchange capacity (CEC), active and total calcareous ( $\text{CaCO}_3$ ), texture and available sodium and potassium content, in duplicates for each ( $n=2$ ), were performed (Table 1). Lastly, sediment and soil samples were sieved by a 64 $\mu\text{m}$  mesh and later acid digested for total metal content.

### 1.3 Metal content

Metal content of the soil and sediment samples were quantified after acid digestion was performed according to ISO 11466. A few milliliters of  $\text{H}_2\text{O}_2$  were added to three grams of each dried sample before the aqua regia solution (1:3 of  $\text{HNO}_3$ : $\text{HCl}$ ) was added (Hseu et al. 2002). The samples were left to incubate in flasks connected to reflux condensers for 16 hours with few millimeters of  $\text{H}_2\text{O}_2$ , 21ml of 12M  $\text{HCl}$  and 7ml of 15.8M  $\text{HNO}_3$ . The samples were heated at 50°C and kept for 30min (Shafie et al. 2013), then heated till 120°C was reached and kept for 2 hours. The samples were left to cool, filtered by a 0.45 $\mu\text{m}$  filter, transferred to a 50ml flask and made up to the line mark with 0.5M  $\text{HNO}_3$ . The samples were then stored at 4°C till copper (Cu), Cadmium (Cd) and lead (Pb) quantifications were performed by Atomic Absorption Spectroscopy (AAS Rayleigh WFX-210) equipped with a WF-10A autosampler and flame and graphite furnace modes.

### 1.4 Statistical analysis

Statistical analyses were performed by SPSS 17.0. ANOVA test ( $P<0.05$ ) was done to determine the significant influence of the site location, the deepness of the soil layer and both, for the different physico-chemical characteristic and metal content. ANOVA test, in case significant difference was found, was followed by Duncan test ( $P<0.05$ ) to partition different soil profiles according to their physico-chemical characteristics. Eta square was done to indicate whether the difference of the physico-chemical parameter values is due to different locations, depths or the combination of both.

## 2 Results

### 2.1 Elemental and physical composition

Even though the two cores were taken from the East side of the Qaraaoun reservoir, at approximately 2km apart (Fig. 1), they showed peculiar characteristics in several parameters. The FT-IR results of the soil and sediment samples taken from Q1 and Q2 showed similar functional groups, such as O-H (alcohol), S-H (mercaptan), C=O (acid chloride), O-H (carboxylic acid), S=O (sulfoxide), C-H (Aromatic) and C-Br (alkyl bromide) at wavenumbers 3436, 2513, 1798, 1428, 1031, 795 and 500 $\text{cm}^{-1}$  respectively. Sediment and soil samples

towards the North (i.e. Q2) exclusively showed N-H (primary amine) and C=O (anhydride) at 1630 and 1875 $\text{cm}^{-1}$  respectively, while the latter site (Q1) showed C-H (alkane) at 2981 $\text{cm}^{-1}$ . Even though some functional groups were common in both locations (Fig. 2), however, the transmittance of those functional groups was dissimilar in the soil profile of the same and different locations (Table 2). It is worth mentioning that transmittance % is inversely proportional to the functional group detection. Alcohol and aromatic containing compounds were detected in higher amounts in Q2, while acid chloride and mercaptan containing compounds were more prominent in Q1. The presence, absence, noticeable or negligible content is very dependent on the state of soil and its aspects.

The particle size distribution of the samples indicates the range of the particles (from 0.19 to 1531.91 $\mu\text{m}$  in this case). The minimum and maximum particles size, in addition to the size of the particle where 50% of the particle population is under is shown in Table 3. Almost all samples were found to have sizes as low as 1 $\mu\text{m}$ , however, the maximum range of the size varied from sample to other, where the lowest two profiles of Q1 and uppermost Q2 layer recorded size of 1.53 and 1.3mm respectively. The size of the soil reflects the texture and organic matter content, which both are suitable indicators of metal sorption ability. By comparing the size of soil where 50% of the soil population is under, the first 30cm deep profiles of Q1 is finer than Q2, while the latter depths, in addition to S1, is coarser than Q2.

The stability of the colloidal particles, as indicated by zeta potential (Fig. 3), ranged from -53 to -62mV, except for S1, that had the least negative value (-32.3mV). The variation of  $\zeta$ -potential of Q1 and Q2 were opposite, indicating different soil stability and colloidal behavior. In general, the high negative values of the samples indicate relatively higher stability of the colloidal systems, which can be in the form of OM that is slightly susceptible to association-dissociation mechanisms (Greenwood and Kendall 1999).

## 2.2 Physico-chemical analysis of Q1 and Q2

The dominant textures in all samples were clay and clay loam. Clay content as a function of depth showed a general increasing trend, especially in the top 30cm horizon of both cores (Table 4). A high content of sand was only seen in the bottom 20cm layer of Q1 (sandy clay loam). Silt content, however, in Q2 showed a stable content in the soil profile. The pH values in both soil cores and sediment samples were basic in nature (INRA, 1995); however, the value was stable and significantly the same throughout the profile of Q1, while it showed a slight variation through the profile of Q2. In both cases, the pH value of the sediment was significantly different than the soil in the same location. As for  $\text{pH}_{\text{KCl}}$ , that indicates the pH variation in case of salt or fertilizer residue addition, they shifted the pH values of both cores to comparable values between Q1 and Q2. The greatest variation of  $\text{pH}-\text{pH}_{\text{KCl}}$  was in the 40-50cm layer of Q2 (18.4%), the same layer had the lowest EC and TDS values (461 $\mu\text{S}/\text{cm}$  and 49mg/L respectively), while the other samples had fluctuating values, with lower values for the sample lying towards the north of the Qaraaoun reservoir (i.e. Q2). Most samples have moderate EC values, except for the superficial layers of Q2 and S1 that have high EC values ( $\text{EC}>1\text{mS}/\text{cm}$ ), while 40-50cm layer of Q2 has a weak EC value (according to AFNOR X 31-113). The variation of pH in the different samples is attributable to location (76.6%), while  $\text{pH}_{\text{KCl}}$ , EC and TDS are rather affected majorly by the factors of location and depth combined (42.87, 46.07 and 42.47% respectively) (Table 7).

Q1 showed a decreasing value for the OM content in the soil profile (from 5.5 to 2.8%) (Table 5). There is a significant difference in those layers (0-5, 5-20, 20-30 and 30-50cm) with a poor OM content in the 20-50cm profile, however Q2 shows a rise and fall in OM, yet all are OM-rich soils (AFNOR X 31-109). The variation of

the OM is due to the different nature of each location; this is proven by eta square test that indicates that location is 70% responsible for OM variation between the samples, the same is said about active and total calcareous (97.8 and 95.9% respectively), while CEC variation is due to the combined effect of location and depth (Table 7). All CEC values lie in the moderate range (12-20meq), except for the 20-30cm layer and sediment of Q1, which have elevated values of CEC (INRA 1992). The 0-20 and 20-50cm layers of Q1 showed significantly different behavior regarding CEC and active calcareous content. As for calcareous, Q2 had very weak CaCO<sub>3</sub> content, only the surface layers (0-20cm) contained a few percentage of active CaCO<sub>3</sub>. In general, the surface layers had higher calcareous content than the bottom ones (Table 5). Q1 samples, however, are very calcareous in nature (Total Calcareous>45% according to AFNOR X31-106).

### 2.3 Trace elements and cation content

The cationic and total metal content varied in an element dependent manner throughout the soil profile. Potassium and sodium content in Q1 and Q2, respectively, was the highest in the sediment (50.15 and 39mg/L) followed by the superficial soil layer (36 and 35.2mg/L) (Table 6). Sodium was found in higher concentrations in the top profiles of Q1, thus 72% of Na<sup>+</sup> variation is location dependent (Table 7). As for potassium, it is mostly influenced by the factor of depth (42.68%), and it was found in higher concentrations in the top 20cm of Q1 and in the other layers in Q2. Regarding the metal content, the sediment samples had generally the lowest values (22.1 and 17.7mg/Kg Cu, 2.5 and 1.6mg/Kg Cd, and 24 and 16.4mg/Kg Pb in Q1 and Q2 respectively). Pb in the 5-10cm layer in both locations (Q1: 30.5mg/Kg and Q2: 24mg/Kg), Cu in the 30-40cm layer of Q1 (33mg/Kg), Cd in the 40-50cm layer of Q1 (4.6mg/Kg), Cd in the 0-5cm layer in Q2 (2mg/Kg) and Cu in the 10-20cm layer of Q2 (24.2mg/Kg) had the highest concentrations (Table 6). Nonetheless, the distribution of Cu, Cd and Pb, according to eta square analysis (Table 7), was majorly dependent on the location (72, 86 and 71% respectively), with significantly higher content in Q1.

## 3 Discussion

### 3.1 Initial soil characterization

Both cores were taken from the East side of the Qaraaoun reservoir, and the resemblance of IR detected functional groups present in the soil and sediment samples of each location indicates that the sediments in the reservoir bed are originated from soil erosion, especially Q2, in which the sediment and top soil have the same texture (Fig. 2 and Table 4), while S1 is rather influenced by the settling of the particulate matter that reach the bed's periphery as a function of the wind direction and hydrodynamic action of the dam. Another indication of the results given by the samples functionality is the higher composition of mineral and organic fractions in Q1 and Q2 respectively. The mineralogical fraction in Q1 can be explained by the higher abundance of mercaptan and acid chlorides (Table 2), which reflect the presence of mineral salts (Takai and Asami 1962), the former is also found further in anaerobic conditions (Smil 2002), which is prominent in the 30-50cm profile of Q1, indicating full water saturation at that depth during the wet season. On the other hand, the organic fraction of Q2 is explained by the dominance of aromatic, primary amines, alcoholic and carboxylic functional groups (Mclean and Bledsoe 1992). The relatively higher particle sizes in 30-40 and 40-50cm of Q1 and 0-5cm of Q2 are correlated to the higher sand content of those soils (Table 3 and 4). However, the fine particle distribution of the other layers gives a notion about higher particulate organic matter or clay content (Thien and Graveel 2003); however, an increase in one indicates higher possible metal retention (Mclean and Bledsoe 1992; Carrillo-Gonzalez et al. 2006). In some cases,

the zeta-potential is correlated to the clay content of the soil, as seen in Q1, because the clay content is dependent and inversely proportional to zeta-potential (Fig. 3 and Table 4) (Chesworth 2008). Higher clay content and lower (or more negative) zeta-potential indicates the presence of highly stable colloids, and hence higher retention capacity of metals (Murray et al. 2004). Most layers (0-5, 10-20, 20-30 and 30-40cm of Q1 and 0-5, 5-10, 30-40 and 40-50cm of Q2) showed good colloidal stability, S1 is of moderate stability, while the rest are of excellent stability (Greenwood and Kendall 1999).

### 3.2 Soil and sediment analytical experimentation

Soil content (sand, silt and clay) does not follow a steady behavior in the soil profile; rather it depends on the geology and nature of the site (Bai et al. 2012). The clay content in Q2 showed a general increasing trend in the soil depth, while silt content did not have a wide range of variation, the same was observed by Hubert (2006); however that was not the case of Q1. Hubert (2006) also stated that pH doesn't follow a certain trend in the soil profile; this is shown in the eta square values that statistically prove that pH variation is location dependent (Table 7). The pH values of the soil samples lie between 7.5 and 8.3, and thus are considered calcareous, which is the case of many soils belonging to floodplain of humid regions (Foth 1990), such as the Qaraaoun reservoir. The basic pH value is an indication of high calcareous content in Q1 (Table 4 and 5), the same pH variation range in the soil profile was indicated by Kassir et al. (2012) in a study done in North Lebanon of a clayey soil. The 40-50cm profile of Q2 has the lowest EC, TDS and  $pH_{KCl}$  values (Table 4); the values are significantly different from values of other depths. This depth is very susceptible to pH variation (as seen by the difference in pH and  $pH_{KCl}$  in Table 4); the low buffering capacity is due to a low mineralogical content, yet high OM content, thus higher available/exchangeable sites are present that enable higher proton exchange with the soil particles (Table 5) (Foth 1990). Furthermore, the higher pH values of Q1 create more negative charges in the soil matrix that are consequently able to immobilize metals and make them unavailable (Zheng and Zhang 2011). The higher EC and TDS values of Q1 are due to higher mineralogical fraction of the site (Table 2 and 4) and the hydrodynamics of the dam, where its location is in favor of the wind direction and water flow originated from the reservoir mouth. In addition, the stratification of the soil, regarding EC and TDS (as proven by Duncan's multiple range test in Table 4), indicates the variation of those solids as induced by the fluctuation in the water content of the soil layers (Foth 1990). Unlike Hubert (2006), the CEC values neither showed an increase with greater depths nor with increasing clay content, rather it was generally correlated with OM (McClean and Bledsoe., 1992), this is most prominent in the 40-50cm layer of Q1 (Table 4 and 5). Higher CEC values are found in cases where the particle size of the sample is lower (Table 3 and 5). Although many authors reported a strong correlation between CEC, OM and clay content (Shriadah 1999; Callaway 1998; Horowitz et al. 2006; Du Laing et al. 2007), this was not visible in either site. Organic matter in Q1 showed an undisturbed soil profile, while the fluctuation of OM in Q2 indicates plowing or other activities that cause the disturbance of the soil depths (Table 5); In fact, higher OM content in Q2 is due to the agricultural activity and littering process taking place in that location (see Fig. 1 for agricultural nature in the proximity of Q2). The relatively higher values of  $CaCO_3$  in Q1 are correlated to higher mineralogical fraction and alkalinity of the soils (Table 2, 4 and 5) (Du Laing et al. 2009; BAMAS 2005b); in this case, total and active calcareous and pH are all dependent on location (76, 96 and 98% respectively) (Table 7). The carbonate fraction can serve as metal immobilizers (Adriano., 2001), either by precipitation or chemisorption in general (Papadopoulos and Rowell 1988), by creating a nucleating or adsorbing surface for Cu and Cd in

particular (Santillan-Medrano and Jurinak 1975; Cavallaro and McBride 1978; McBride and Bouldin 1984), or by Cu restraining via CaCO<sub>3</sub> (Dudley et al. 1988; Dudley et al. 1991).

### 3.3 Metals and cation variation in comparable cores and sediments

Total sodium and potassium are found in high amounts in natural soils since they are building structures of soil minerals, however, only a small fraction is available in the ionic form, the rest is mostly adsorbed to clay minerals, OM and silt (Chesworth 2008). In the undisturbed nature of Q1, the available potassium content decreases with depth (Table 6), as did OM (Table 5), this correlation is due to the nature of the weak interaction between K<sup>+</sup> and OM, where higher OM are able to hold higher potassium cations (Abdel- Salam and Salem 2012), and this was the case of sediment samples (Table 5 and 6). The saturation of colloidal complexes with exchangeable bases, such as sodium hydroxide, constructs the alkalinity of the soil, thus higher sodium concentrations were linked to the more basic site of Q1 (Table 4 and 6) (Chesworth 2008).

The average values of cadmium, copper and lead content of the soils of this study were compared to other studies done in the same area (Qaraaoun) and same country (North Lebanon), and later compared to guidelines and general metal content of soil (Table 8). Cd content is highly variable in the Qaraaoun watershed; it ranged from 0.01-11mg/Kg (Jurdi et al. 2011), and 0.02-5.16mg/Kg (BAMAS 2005a), nonetheless, the average Cd content in this study exceeded other averages done in the Qaraaoun area and North Lebanon, and it was higher than the Canadian guidelines (NGSO 2005; ISQG 2002) and proposed background concentrations by Martin and Whitfield (1983). Cu concentrations ranged in the same interval as in previous studies done in the Qaraaoun basin (Kanbar 2012; Jurdi et al 2011), yet the average was the lowest in this study. Pb, on the other hand had comparable values with nearby sites (Kanbar 2012), and the average lied between the average values of the other two studies done in that area (Jurdi et al. 2011; Kanbar 2012). However, copper and lead concentrations in this study did not exceed the permissible limits set by NGSO (2005), ISQG (2002) or Martin and Whitfield (1983).

The variation of the metal concentrations in the Qaraaoun area is influenced by several factors, such as the physico-chemical characteristics of the soil sample (McClean and Bledsoe 1992; Foth 1990; Zheng and Zhang 2011; Du Laing et al. 2007), the fluctuation of the water content (Foth 1990) and time of sampling (wet or dry season) (Mohiuddin et al. 2011; Jurdi et al. 2011; BAMAS 2005a). On these notes, the higher values of cadmium may be explained by one of those factors. Cadmium content is thought to be originated from batteries and agricultural practices, copper from nearby smelting operation, while lead from smelting activities and automobile emissions (Jurdi et al. 2011). The proximity of the Qaraaoun is alive with agropastoral factories (Ablah and Chtaura), food and milk processing industries (Ferzol, Anjar and Jdita), paper mills (Kab Elias and Qaa Al-Rim), rock cutting industries (Chtaura and Zahle), wastewater treatment plants (Mekse, Chtaura, Zahle, Qab Elias and Zahle) and slaughterhouses (Zahle), all which contribute to polluting the Litani River, its tributaries and nearby soils, especially by heavy metals (BAMAS 2005a). Q1 higher metal content is thought to be originated from the particulate matter that comes from the effluents that are rejected in the Litani river course, and from nearby smelting and rock-cutting factories that lie in the Qaraaoun watershed. Lead, however, was found more prominently in Q1 that is more influenced by industrial and urban activities (Fig. 1) (ELARD 2011). So Pb in that area is more correlated to atmospheric (wet and dry) or direct effluents, domestic and diffuse industrial discharge (Abi-Ghanem et al. 2009). On another note, the fluctuation of the water level in the Qaraaoun reservoir is a key player in determining the metal behavior in those soils, since the alteration of the oxic/anoxic interface, redox



reactions taking place, humidity and exposure to the ambient environment can be factors in changing the metal fraction and speciation in that sample (Du Laing et al. 2009; Schulz-Zunkel and Krueger. 2009). So the increase in the water level during the wet season may come not just as a metal transporter, but also as a sinker (Du Laing et al. 2007).

Unlike Murray et al. (2004) and Mclean and Bledsoe (1992) reported, metals in this study were not held at higher concentrations in sites having higher clay content, CEC or OM, rather metals are believed to be held by the mineral fraction, especially the carbonate fractions. In this case, the metals may be bound more strongly to their support, and may not be as available as those held by organic matter; so metal leaching may be a serious thread in in the 0-10 and 40-50cm layers of Q2, since these layers have respectively higher organic matter and lower negative zeta-potential, since deformation or degradation of these particles may alter the metals available for surface water or underground water.

Q1 and Q2 are located in the same watershed, yet Q2 covers a higher area and thus gets higher volumes of runoffs. Nonetheless, runoffs reaching Q1 are originated from industrial and urban sources, since the proximity of Qaraaoun Square (with relatively higher population) lies less than 1km away from Q1, while those of Q2 are majorly agricultural (Fig. 1), therefore containing fertilizers, biocides or other chemical products and residues used in agriculture (ELARD 2011).

#### **4 Conclusions**

The two sites in the proximity of the Qaraaoun reservoir showed similar characteristics in functional groups, particle size distribution,  $\zeta$ -potential, texture and potassium content, yet they varied as a function of depth. Still, some parameters were significantly different between location, such as pH, OM, active and total calcareous, available sodium, Cd, Cu and Pb. As indicated by the samples functionality, Q1 can be concluded as a soil rich in calcareous and minerals, while Q2 is rich in OM. The variation of particle size distribution, CEC and OM in the soil profile of Q1 showed a natural stratification. Both samples have stable colloidal particles that do not associate-dissociate simply. Different ranges of pH, EC, OM and TDS were found between Q1 and Q2. The metal content was significantly higher in Q1 samples. Several factors cause that high metal content, the first is the mineral fraction, and to a larger extent the carbonate content that is able to adsorb and immobilize metals, while organic bound metals may cause a leaching thread to water bodies. Another factor is the spatial location of the sites, in which the first (Q1) is very much influenced by the domestic, industrial and urban activity, while the latter (Q2) is majorly influenced by agricultural practices that occur in the vicinity of the site. The last factor is the hydrodynamics of the reservoir, in which Q1 site is more influenced by wind and river water direction that can transport metals from the watershed to the reservoir beds and consequently to the nearby soils during the wet season.

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## List of tables

**Table 1** Experiments performed

Experiment	Norme
pH and $\text{pH}_{\text{KCl}}$	NF ISO 10390
EC (mS/cm)	NF ISO 11265
TDS (mg/L)	
OM (%)	ASTM D 2974
CEC (meq)	Thien and Graveel, 2003
Active $\text{CaCO}_3$ (%)	AFNOR X 31-106
Total $\text{CaCO}_3$ (%)	NF ISO 10693
Texture (%)	NF X31-107
Available $\text{Na}^+$ and $\text{K}^+$ (mg/L)	P05-001A

**Table 2** Functional groups of soil and sediment samples of various depths

		Functional Group Transmittance (%)												
Location	Depth (cm)	Functional Group	Alcohol	Alkane	Mercaptan	Acid chloride	Carboxylic acid	Sulfoxide	Aromatic	Alkyl bromide	Anhydride	Amine		
	Wavenumber (cm <sup>-1</sup> )		3436	2981	2513	1798	1428	875	1031	795	710	500	1875	1630
Q1	0-5		20.7	63.2	57.2	50.0	1.9	9.1	2.8	63.8	40.9	12.1		
	5-10		20.5	69.0	57.6	44.6	0.5	9.6	1.3	61.8	40.8	12.8		
	10-20		25.9	71.4	59.2	48.5	0.6	8.7	1.7	41.8	41.8	7.4		
	20-30		26.7	71.3	62.7	45.8	0.3	7.0	0.6	54.5	35.9	5.4		
	30-40		24.6	64.9	49.1	34.7	0.1	1.9	0.8	57.7	14.8	12.5		
	40-50		26.5	58.1	38.0	28.0	0.0	1.6	1.1	65.2	23.6	12.2		
	S1		27.4	67.0	59.6	43.8	0.6	5.4	0.7	54.4	30.4	5.9		
Q2	0-5		32.1		88.0	62.4		12.9	1.0	26.3	45.8	11.0	66.4	40.3
	5-10		4.2		89.3	53.0			0.0	2.1	4.0	0.5	48.8	19.2
	10-20		12.2			72.3		2.3	0.0	11.2	15.6	0.4	68.4	39.6
	20-30		2.9			62.8		4.1	0.0	5.8	0.0	0.8	60.5	21.6
	30-40		23.4			80.1		9.1	0.5	27.8	36.3	3.5	77.7	57.5
	40-50		11.1					3.0	0.1	19.8	21.4	0.6	75.9	42.4
	S2		13.9		87.5	59.8	19.4	2.2		7.7	13.5	0.6	61.3	28.6

**Table 3** Range of particle size and size of soil having less than 50% population

Location	Depth (cm)	Minimum size ( $\mu\text{m}$ )	Maximum size ( $\mu\text{m}$ )	50% less than ( $\mu\text{m}$ )
Q1	0-5	1.51	300.518	26.111
	5-10	1.318	300.518	22.797
	10-20	0.197	300.518	17.377
	20-30	0.226	300.518	17.377
	30-40	1.51	1531.914	58.953
	40-50	1.51	1531.914	51.471
	S1	1.729	344.206	44.938
Q2	0-5	1.51	1337.481	44.938
	5-10	1.51	678.504	34.255
	10-20	1.318	300.518	34.255
	20-30	1.005	262.376	26.111
	30-40	1.151	300.518	34.255
	40-50	1.005	262.376	39.234
	S2	1.981	777.141	34.255



**Table 4** Physico-chemical characterization of the soil profiles and sediments

Depth (cm)	Texture (%)				pH	pH <sub>KCl</sub>	EC ( $\mu$ S/cm)	TDS (mg/L)	
	Sand	Silt	Clay	Class					
Q1	0-5	22	40	36	Clay loam	8.15 $\pm$ 0.005d	7.56 $\pm$ 0.035fg	899 $\pm$ 7.68f	98 $\pm$ 0.50fg
	5-10	37	24	38	Clay loam	8.10 $\pm$ 0.005d	7.54 $\pm$ 0.005efg	917 $\pm$ 8.64fg	99 $\pm$ 0.00gh
	10-20	32	23	44	Clay	8.15 $\pm$ 0.005d	7.50 $\pm$ 0.005ef	861 $\pm$ 0.32e	92 $\pm$ 0.00e
	20-30	31	24	44	Clay	8.11 $\pm$ 0.075d	7.51 $\pm$ 0.005ef	1001 $\pm$ 2.88 i	106 $\pm$ 1.50i
	30-40	52	18	29	Sandy Clay loam	8.10 $\pm$ 0.020d	7.55 $\pm$ 0.040fg	893 $\pm$ 14.08f	95 $\pm$ 1.50ef
	40-50	53	20	26	Sandy Clay loam	8.10 $\pm$ 0.010d	7.61 $\pm$ 0.010g	943 $\pm$ 6.08gh	100 $\pm$ 1.50gh
	S1	33	39	26	Loam	7.84 $\pm$ 0.050c	7.52 $\pm$ 0.065ef	1172 $\pm$ 23.36j	124 $\pm$ 3.00j
Q2	0-5	41	24	34	Clay loam	7.78 $\pm$ 0.010abc	7.52 $\pm$ 0.020efg	1154 $\pm$ 8.32j	123 $\pm$ 1.00j
	5-10	37	26	36	Clay loam	7.91 $\pm$ 0.035c	7.56 $\pm$ 0.020fg	815 $\pm$ 5.12d	87 $\pm$ 0.50d
	10-20	26	24	49	Clay	7.88 $\pm$ 0.015c	7.41 $\pm$ 0.005cd	774 $\pm$ 0.64bc	82 $\pm$ 0.00bc
	20-30	18	22	59	Clay	7.65 $\pm$ 0.005ab	7.13 $\pm$ 0.005b	786 $\pm$ 8.96cd	84 $\pm$ 0.50cd
	30-40	27	20	52	Clay	7.84 $\pm$ 0.175c	7.36 $\pm$ 0.000c	745 $\pm$ 16.00b	79 $\pm$ 2.00b
	40-50	17	22	59	Clay	7.82 $\pm$ 0.005bc	6.38 $\pm$ 0.045a	461 $\pm$ 1.28a	49 $\pm$ 0.00a
	S2	36	32	31	Clay loam	7.6 $\pm$ 0.010a	7.46 $\pm$ 0.025de	960 $\pm$ 9.60h	102 $\pm$ 1.00hi

The same letter in the same column indicates no significant difference according to Duncan's multiple range test ( $\alpha=0.05$ )

**Table 5** OM, CEC and calcareous content of all the samples

	Depth (cm)	OM (%)	CEC (meq)	Calcareous (%)	
				Active	Total
Q1	0-5	5.5±0.21d	19.6±0.31gh	16.8±0.31f	55.7±0.34e
	5-10	4.4±0.10c	18.7±0.40fg	17.1±0g	54.8±0.40e
	10-20	4.2±0.10c	18.9±0.01fgh	17.5±0.31f	50.3±0.01d
	20-30	3.8±0.08b	21.4±0.30i	13.7±0c	48.1±0.09c
	30-40	2.9±0.10a	16.7±0.13d	14.9±0d	65.9±1.51g
	40-50	2.8±0.02a	12.7±0.53a	13.7±0c	69.2±1.32h
	S1	6.8±0.13g	22.1±0.05i	15.4±0e	59.3±0.78f
Q2	0-5	7.0±0.15gh	17.6±0.04f	0.6±0b	6.7±0.03b
	5-10	5.2±0.04d	15.5±0.23c	0.6±0b	1.4±0.03a
	10-20	6.0±0.05e	14.5±0.43b	0.4±0b	0.5±0.01a
	20-30	7.1±0.04h	19.5±0.27gh	0a	0.3±0a
	30-40	6.3±0.01f	17.6±0.11f	0a	0.4±0a
	40-50	7.5±0.01i	19.8±0.06h	0a	0.1±0a
	S2	6.8±0.03g	18.4±0.15ef	0a	5.8±0.48b

The same letter in the same column indicates no significant difference according to Duncan's multiple range test ( $\alpha=0.05$ )

**Table 6** Cation and metal content of Q1 and Q2

Depth (cm)	Available cation (mg/L)		Total metal content (mg/Kg)			
	Na <sup>+</sup>	K <sup>+</sup>	Cu	Cd	Pb	
Q1	0-5	51.65±0.25cd	36±0.00g	25.9±0.13e	3.8±0.07c	30±0.01g
	5-10	54.15±0.85d	25.1±0.40e	30.4±0.12g	3.6±0.01c	30.5±0.18g
	10-20	63.15±3.85e	19.85±0.25cd	30.1±0.35g	3.7±0.15c	25.5±0.92ef
	20-30	56.45±0.05d	20.25±0.25cd	30.3±0.86g	3.9±0.40c	23.1±1.45d
	30-40	40.2±0.10b	16.45±0.35ab	33±1.23h	4.6±0.15d	26.6±0.56f
	40-50	36.35±1.05b	13.95±0.15a	28.6±0.27f	4.7±0.76d	27.3±1.18f
	S1	47.05±0.15c	50.15±1.55h	22.1±0.18b	2.5±0.02b	24±0.07de
Q2	0-5	35.2±2.90b	31.2±0.90f	18.1±0.17a	2±0.00ab	19.3±0.08c
	5-10	23.1±0.70a	22.1±0.10d	23.7±0.17cd	1.8±0.10ab	24±0.03de
	10-20	25±0.20a	18.25±0.25bc	24.2±0.57d	1.8±0.04ab	17±0.01ab
	20-30	25.8±0.80a	32.7±0.50f	23.8±0.41cd	2±0.07ab	18.3±0.17bc
	30-40	25.6±0.50a	27.2±0.30e	22.6±0.07bc	1.6±0.05a	18.9±0.34bc
	40-50	24.85±4.55a	33±0.80f	23.5±0.36bcd	2±0.03ab	19.1±0.47c
	S2	39±1.70b	64.1±2.50i	17.7±0.02a	1.6±0.12a	16.4±0.09a

The same letter in the same column indicates no significant difference according to Duncan's multiple range test ( $\alpha=0.05$ )

**Table 7** ANOVA and influence of depth and location (Eta square) on the studied parameters

	Location		Depth		Location x Depth		Error (%)
	P(ANOVA)	% of influence	P(ANOVA)	% of influence	P(ANOVA)	% of influence	
pH	.000**	76.30	.307ns	6.32	.317ns	6.18	11.18
pH <sub>KCl</sub>	.000**	22.98	.000**	33.68	.000**	42.87	0.45
EC (μS/cm)	.000**	16.47	.000**	37.18	.000**	46.07	0.26
TDS (mg/L)	.000**	17.18	.000**	39.98	.000**	42.47	0.35
OM (%)	.000**	69.97	.000**	11.20	.000**	18.45	0.36
CEC (meq)	.003**	1.55	.000**	34.84	.000**	62.20	1.38
Active CaCO <sub>3</sub>	.000**	97.80	.000**	1.47	.000**	0.69	0.02
Total CaCO <sub>3</sub>	.000**	95.95	.000**	1.83	.000**	2.16	0.04
Na <sup>+</sup> (mg/L)	.000**	72.00	.000**	13.29	.000**	12.68	2.01
K <sup>+</sup> (mg/L)	.000**	15.32	.000**	42.68	.000**	41.59	0.39
Cu (mg/Kg)	.000**	72.35	.000**	21.91	.003**	4.20	1.52
Cd (mg/Kg)	.000**	86.48	.171ns	3.86	.109ns	4.73	4.92
Pb(mg/Kg)	.000**	71.44	.000**	22.56	.013*	3.97	2.01

\*\* : significant at 5%

ns: not significant

**Table 8** Comparison between the studied metals in several citations

Reference	Location	Metal Content (mg/Kg)		
		Cd	Cu	Pb
This study	Qaraaoun	2.8	25.3	22.9
Jurdi et al., 2011	Qaraaoun	0.83	54.2	11.3
Kanbar., 2012	Qaraaoun	0.73	-	32.2
Kassir et al., 2012	North Lebanon	0.28	30.54	9.25
BAMAS <sup>1</sup> , 2005a	Qaraaoun	1.84	37	-
NGSO <sup>2</sup> , 2005	CEQGS <sup>3</sup>	1.4	63	70
Martin and Whitfield, 1983	Elemental Composition in Soil	0.35	30	35
CCME <sup>4</sup> , 2002	CISQG <sup>5</sup>	0.6	35.7	35

1: Litani Basin Management Advisory Services

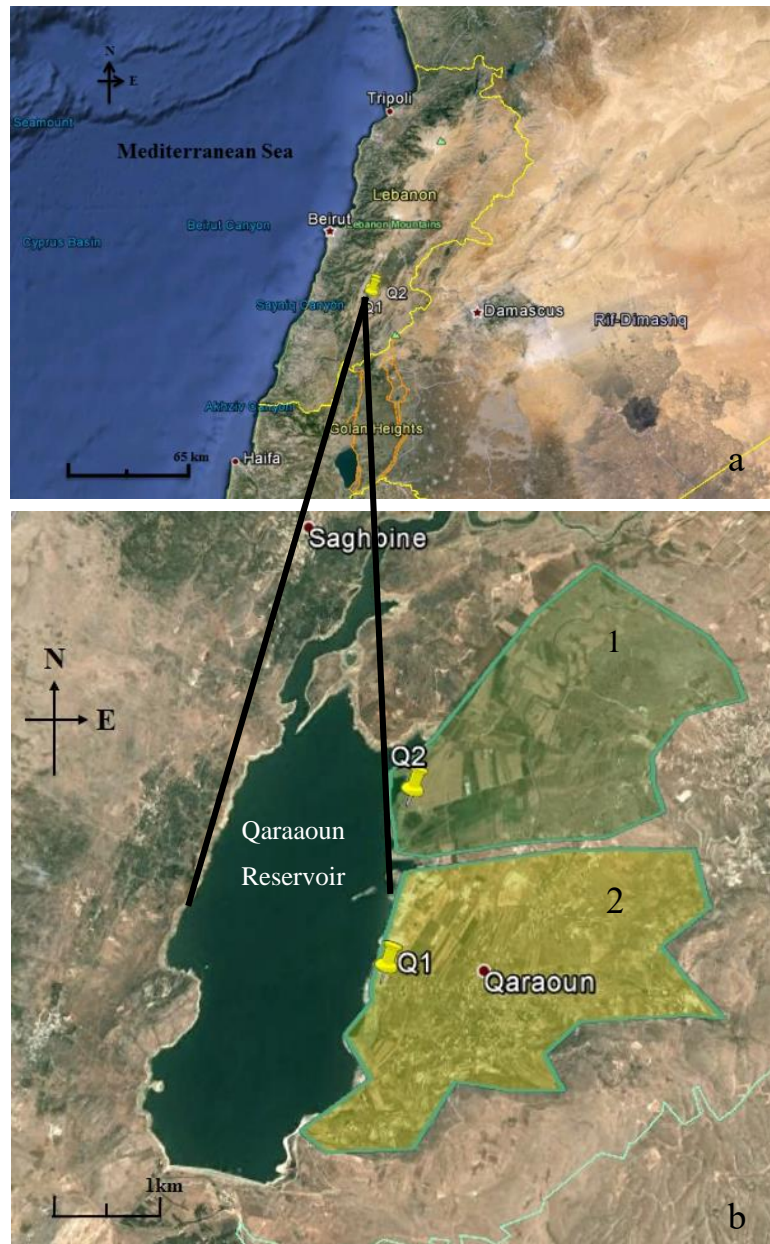
2: The National Guidelines and Standards Office

3: Canadian Environmental Quality Guidelines for Soil

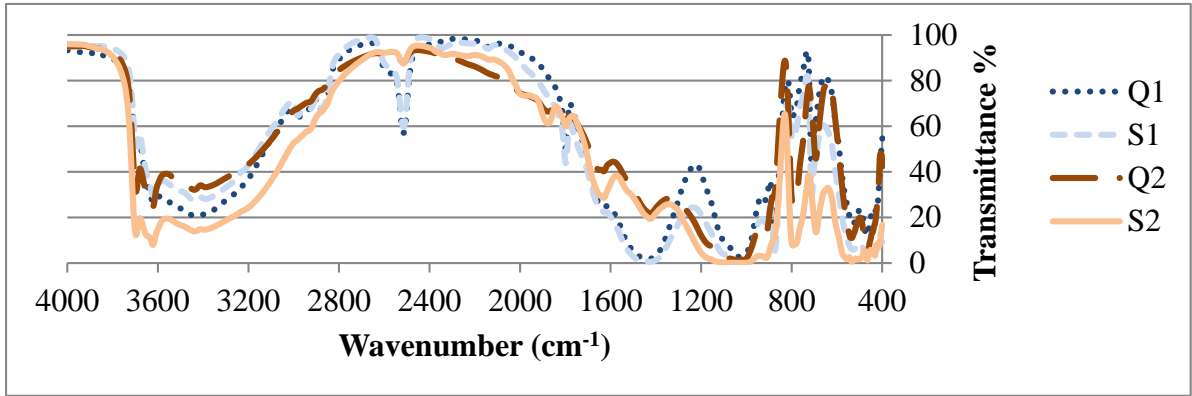
4: Canadian Council of Ministers of the Environment

5: Canadian Interim Sediment Quality Guideline

## List of figures



**Fig. 1** Sampling location (a: Lebanon map; b: Qaraaoun reservoir; 1: Q2 represents the sampling site towards the North of the reservoir, the highlighted area presents the agricultural nature of the site's proximity; 2: Q1 is the second sampling site, the highlighted area here points to the urban and industrial nature of the site's proximity)



**Fig. 2** FT-IR graph of upper layers and sediments of Q1 and Q2

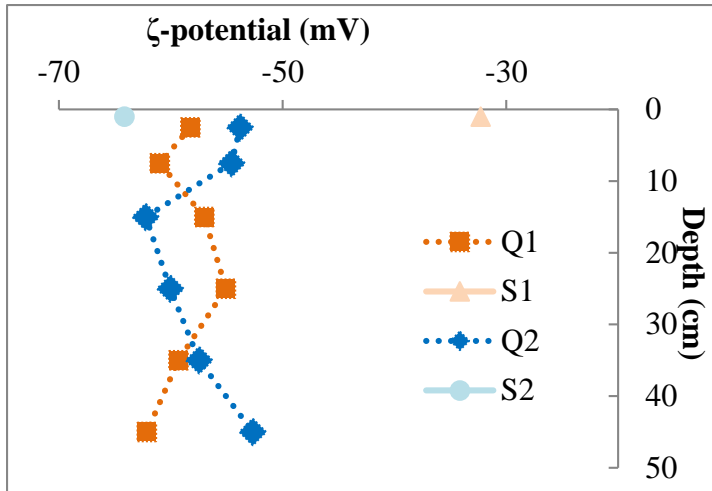


Fig. 3  $\zeta$ -potential