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EVALUATING CHEMICAL POLLUTION ON THE COAST OF LEBANON: LEAD AND CADMIUM CONTENT IN SEDIMENTS

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Being of a toxic nature, lead and cadmium present a high risk for both marine ecology and human life. Studying the concentration of these elements in marine sediments serves to raise awareness about their threat. In this study, samples from selected localities were collected from different sediment layers and at different depths of seawater. These localities, namely Beirut, Jounieh, and Batroun, represent major cities with intensive human activities. The analysis was designed to detect the effect of sediment layers, depths, and location on the concentration of heavy metals. Results show that different layers in Batroun contain varied lead and cadmium concentrations at the same water depth. However, in Jounieh, the concentrations varied in relation to water depth and are not influenced by the sequence of sediment layers. In Beirut, the concentration of lead varies with depth, but the concentration of cadmium is not affected by the depth of water or even by the sequence of layers. As an empirical result, and compared to French tolerable concentration limits, the lead and cadmium concentrations in Lebanon are within normal limits. This conflicts with the expectation regarding heavy metals in sediments along the littoral zone at major Lebanese cities.

INTRODUCTION

Pollution by heavy metals is a recent worldwide problem that concerns all coastal zones, which worry about maintaining a good quality of their seawater. This issue is anticipated to affect the Lebanese coast in general; especially the region of Beirut, Jounieh, and Batroun where heavy population growth is ongoing supplemented by growing tourism, industry and agriculture. These activities, which are the principal drivers for economic growth, will affect the use of marine resources (e.g., fisheries, exploitation of algae, etc.). It is expected that marine resources will be impacted by many releases (e.g., industrial and chemical products, agricultural fertilizers, oil residues, etc.), thus adding negative consequences to the quality of the marine environment in these regions.

During the past 30 years, most Western countries have introduced programs to control discharges; especially in aquatic environments. For their part, developing countries control to a much lesser degree the sources of contamination of their seawater (Philips and Rainbow, 1993). Knowledge is necessary about inputs to coastal environments for a nation eager to conserve and sustainably manage its marine resources. The protection of coastal areas is one of the major challenges for countries with a coastline. For this purpose, many programs that keep track of coastal pollutants (mostly organic but also heavy metals) have been put in place (e.g. NOAA networks in the United States and an observational network of water quality in France: www.ifremer.fr/envlit/surveillance/). This study is conducted to detect the influence of sources of pollution on the concentration of lead (Pb) and cadmium (Cd) in the marine sediments of costal Lebanon. As an example of a pollution source, the political conflict that took place in Lebanon in July 2006, after bombing the Jiyeh Electrical Station, Pb to a huge release of fuel oil into the sea. The second target of this study is to detect and determine the difference of Pb and Cd concentrations on a spatial basis, and between sediment layers and depths of the same site.

This is the first study in Lebanon of the concentration of these heavy metals in marine sediments. It provides important preliminary information about the presence and concentrations of Pb and Cd in individual sediment layers.

Many published works during the last decade have clearly demonstrated the important role of sediments in the geochemical cycle of pollutants (Forstner and Wittman, 1981; Robbe, 1981; Salomons and Forstner, 1984). In the hydro-chemical cycle, sediments play a crucial role not only as important vectors, but they also constitute the principal reservoirs of many toxic metals that have accumulated over the years. As a result, sediments are considered as inclusive and plotters of metal pollution (Kaimoussi et al., 2000). The analysis of pollutants in sediments provides the amount of contamination of an area by monitoring the surficial levels of sediment, and a view of the temporal evolution of pollution when studying the distribution of contaminants in deeper layers of sediment collected by coring methods (RNO, 2001; RNO, 2005).

Recent studies (UNEP, 1986-1989; CEDRE, 2002; Nassif, 2004; Nakhle, 2004) conducted in Lebanon highlighted the variation of levels of metal pollutants, including Pb and Cd in sediments and in Lebanese coastal waters according to the selected site and the period during which the samples were taken. Their results showed that despite the geographic difference between sites, the concentration of Cd and Pb is close to those usually encountered in the Mediterranean basin. This study aims, in addition to assessing the impact of site location and depth, to assess the effect on sediment layer sequence at the same site, which has yet to be quantified. For this purpose, the two heavy metals Pb and Cd were determined in the coastal sediments at 11 sites at Beirut, Jounieh, and Batroun.

The selection of these two elements for analysis is based on their ubiquity as chemical contaminants (Calabrese, 1981) and toxicity (Sadiq, 1992) which justify their presence in the list of priority contaminants of international conventions and regulations (OSPAR, EU, USEPA, Barcelona Convention for the Mediterranean, 1976). The selection of site localities and types of heavy metals depends also on results from recent studies to monitor the levels of Pb and Cd in the littoral region (Nassif, 2004; Nakhle, 2004).

The three selected cities for the study are situated adjacent to major ports. Industries and a variety of human activities are expanding at these sites. The sea and the river systems are frequently used to dump wastewater and refuse. The wastewater from these cities is discharged directly to the sea near the beach without any treatment.

MATERIALS AND METHOD

The sediment samples originated from sediments cored at three sites: Beirut, Jounieh, and Batroun (Figure 1). At each site, the samples were taken from 3 or 4 depths (Table 1), as follows:

- Beirut: 0, 5, and 10 meters.
- Jounieh: 0, 4, 10, and 60 meters.
- Batroun: 50cm, 5, and 10 meters.

The sampling conducted during the summer, when the weather was stable.

The main purpose was to study each layers (1 cm thick) separately, but due to the small weight (<0.5g) of sediments less than 63 micrometers in size in each layer, we were obliged to mix more than two layers together (Figure 2).

Figure 1. Location map of the studied coastal stretch.

Table 1. Location of selected samples.

Region	Depth	Coordinates	
		N	E
Beirut	0 meter	33°52.550'	035°28.820'
	5 meters	33°52.662'	035°28.657'
	10 meters	33°52.668'	035°28.458'
Jounieh	0 meter	33°59.333'	035°38.235'
	4 meters	33°59.137'	035°37.870'
	10 meters	33°59.318'	035°37.755'
	60 meters	33°59.813'	035°37.081'
Batroun	50 cm	34°17.037'	035°39.526'
	5 meters	34°16.709'	035°39.115'
	10 meters (250m far from the chemical factory); I	34°16.169'	035°39.226'
	10 meters (in front of CNRS); II	34°15.092'	035°39.211'

The precise concentration of Pb and Cd was determined using a Unicam 969 Z Atomic Absorption Spectrometer equipped with a graphite furnace, following dissolution in a mixture of hydrofluoric and nitric acids to permit the digestion on the residual fractions and to fractionate heavy metal chemical forms.

All the extracts were kept in thoroughly cleaned plastic bottles. All glassware used for the experiments were previously soaked in 5‰ HCl, then 5‰ HNO_3 for 24 hours each, and rinsed with double deionized water. For each experiment 0.5g of sediment was used.

The accuracy of the total extraction procedure and the analytical quality of the data were controlled by including one sample of standard reference materials (MESS-2) of known composition in each analytical batch of samples, the value of Pb and Cd measured in the MESS-2 was 21.55 ± 1.26 and 0.239 ± 0.004 knowing that the certified value is respectively 21.9 ± 1.2 and 0.24 ± 0.01 for Pb and Cd.

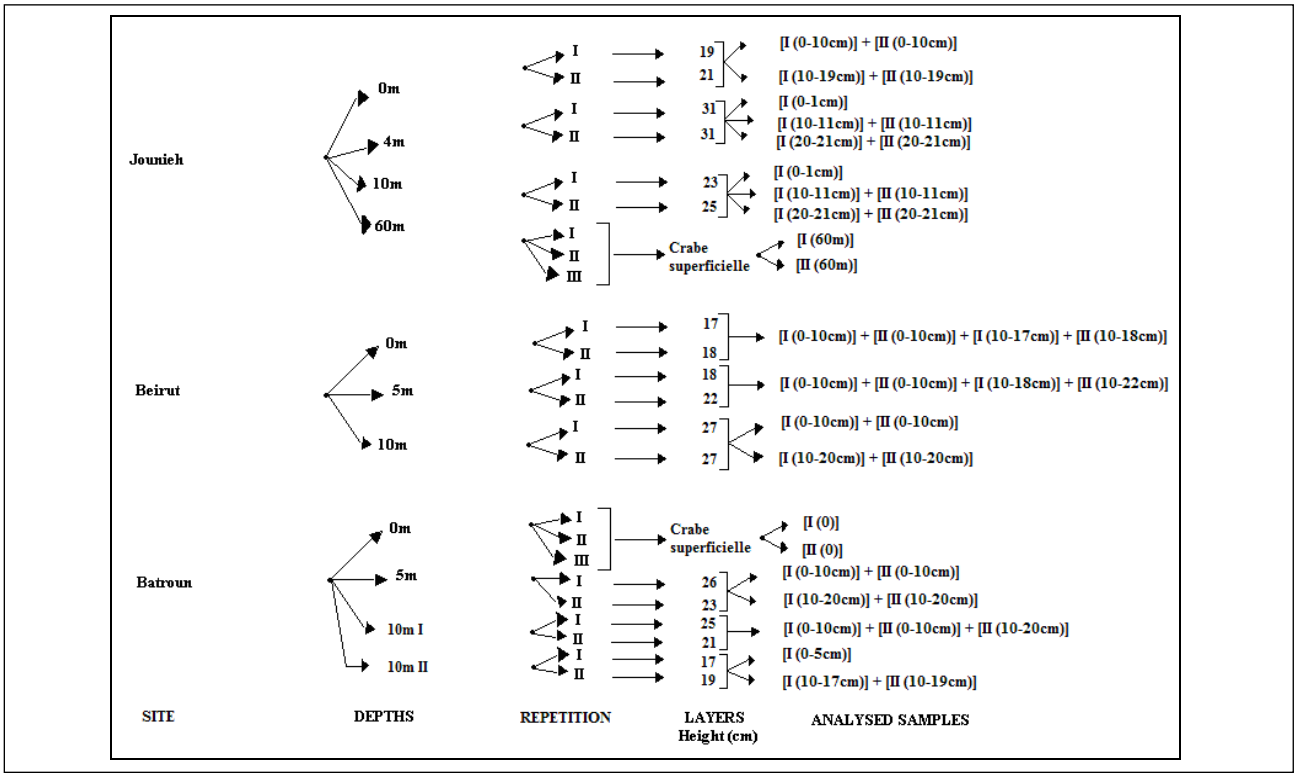

Figure 2. Schematic presentation of the sampling plan.

RESULTS AND DISCUSSION

The percentages of moisture content measured in the sediments vary from one site to another due to the difference of granulometry. In Beirut, it was 14.68% at 5m depth and 25.26% at 10m. The moisture percentage at Jounieh for the depth 0, 4 and 10m equaled 12.2%, but was higher at the 60m depth, where it reached 42.8%. In Batroun, the moisture percentage was 18.5% for all depths (Table 2).

The creditability of results is supported by:

- The heterogeneous composition of Beirut's sediments which contains: granular sand, fine sand, and mud.
- The homogeneous composition of Jounieh's sediment which contains only fine sand.
- The homogeneous composition of Batroun's sediment which contains fine sand, and mud. (Nassif, 2004)

In all sites, the concentrations of Pb and Cd in the marine environment was found to be lower than the accepted value of the French Standards – Pb <100 mg/Kg D.W and Cd < 1.2 mg/Kg D.W. (French decree, 2000).

The Pb concentration in Beirut sediments is much higher than those found in the other two sites. The layers 0-10cm and 10-20cm of Beirut at 10m depth contain the highest concentration of Pb; respectively, 29.18 and 27.8 $\mu g.g^{-1}$ D.W. (Figure 3).

Although there is a difference between the concentration of Pb in Beirut sediments at 0 and 10m depths, there is no difference between the layers at the same depth (Figure 3). This result reduces the influence of depth and allows a routine analysis to be conducted by studying only one layer.

The statistical procedures to analyze the concentration of Pb show the difference between the depths of 0 and 60m and between 10 and 60m at the Jounieh site. At 60m, we found the highest

Table 2. Humidity ratio at different depth.

N°	Sample origin	Sediment fresh weight	Sediment weight after drying	Water weight	% water - Humidity
1	J 0m I (8-9cm)	2,076	1,7288	0,3472	16,72
2	J 0m II (14-15cm)	2,2411	1,8626	0,3785	16,89
3	J 4m I (23-24cm)	1,9062	1,5493	0,3569	18,72
4	J 4m II (27-28cm)	2,3658	1,9073	0,4585	19,38
5	J 10m I (11-12cm)	2,351	1,8779	0,4731	20,12
6	J 10mII (12-13cm)	2,941	2,2687	0,6723	22,86
7	J 60m I	3,3853	1,9475	1,4378	42,47
8	J 60m II	3,8716	2,0886	1,783	46,05
9	J 60m III	4,4975	2,703	1,7945	39,9
10	B 5m II (12-13cm)	1,3714	1,1701	0,2013	14,68
11	B 10m I (11-12cm)	1,5068	1,1262	0,3806	25,26
12	BAT 1 I (10-11cm)	1,8919	1,5206	0,3713	19,62
13	BAT 1 II (17-18cm)	2,4394	1,9407	0,4987	20,44
14	BAT 2 I (11-12cm)	1,955	1,5176	0,4374	22,37
15	BAT 2 II (18-19cm)	1,5225	1,3316	0,1909	12,54
16	BAT 3 I (1-2cm)	1,2854	1,0448	0,2406	18,72
17	BAT 3 I (20-21cm)	1,6603	1,2655	0,3948	23,78
18	BAT 3 II (0-1cm)	1,2104	1,0497	0,1607	13,28
19	BAT 3 II (22-23cm)	1,2945	1,0364	0,2581	19,94
20	BAT 0 I	2,0898	1,6957	0,3941	18,86
21	BAT 0 II	2,136	1,7679	0,3681	17,23
22	BAT 0 III	1,7179	1,4206	0,2973	17,31

J: Jounieh - B: Beirut - BAT: Batroun.

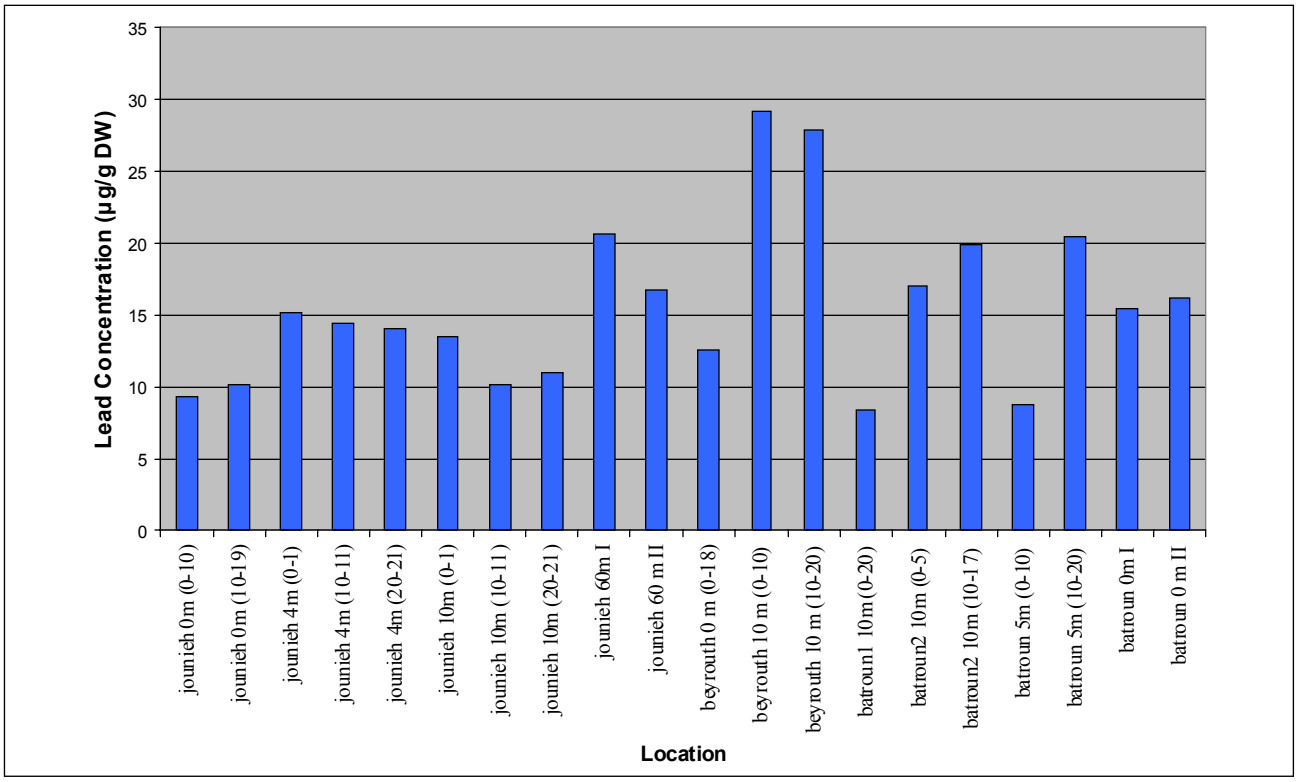

Figure 3. Lead concentration per region and layer.

concentration of Pb. On the other hand there is no difference between layers of the same depth (Figure 3). This result is almost similar to that found by Nassif (2004) and Mebazaa (2004).

At Batroun, there is no significant difference between the depths concerning the concentration of Pb (Figure 3). The zero meter depth contains the highest concentration due to different causes such as:

- Atmospheric pollution, which holds Pb particles derived from different sources toward the shoreline.
- The effect of oil releases from the Jiyeh Power Station during the 2006 conflict.

At 10m depth, there is a difference between the layers 0-20cm and 0-5cm; 0-20cm and 10-17cm. At 5m of depth, the difference is found between the layers 0-10cm and 10-20cm (Figure 3). This difference might be caused by the recurrent accumulation of pollution through different periods of time, taking into consideration that no perturbation occurred between these layers.

The Cd concentration in Batroun sediments is much higher than those found in the other two sites. The layers 10-17cm and 0-20cm of Batroun 10m depth and the layers 0-10cm and 10-20cm of Batroun 5m depth contain the highest concentration of Cd (Figure 4).

The statistical analyses reflect the absence of a significant difference between depths and layers concerning Cd concentration in Beirut (Figure 4).

The analyses show the difference between the depths 0 and 60m (highest concentration) at Jounieh, and the absence of this difference between the layers of the same depth (Figure 4).

Although in Batroun, there is no significant difference between the depths concerning the concentration of Cd, yet an obvious difference was found at 10m depth between the layers (Figure 4):

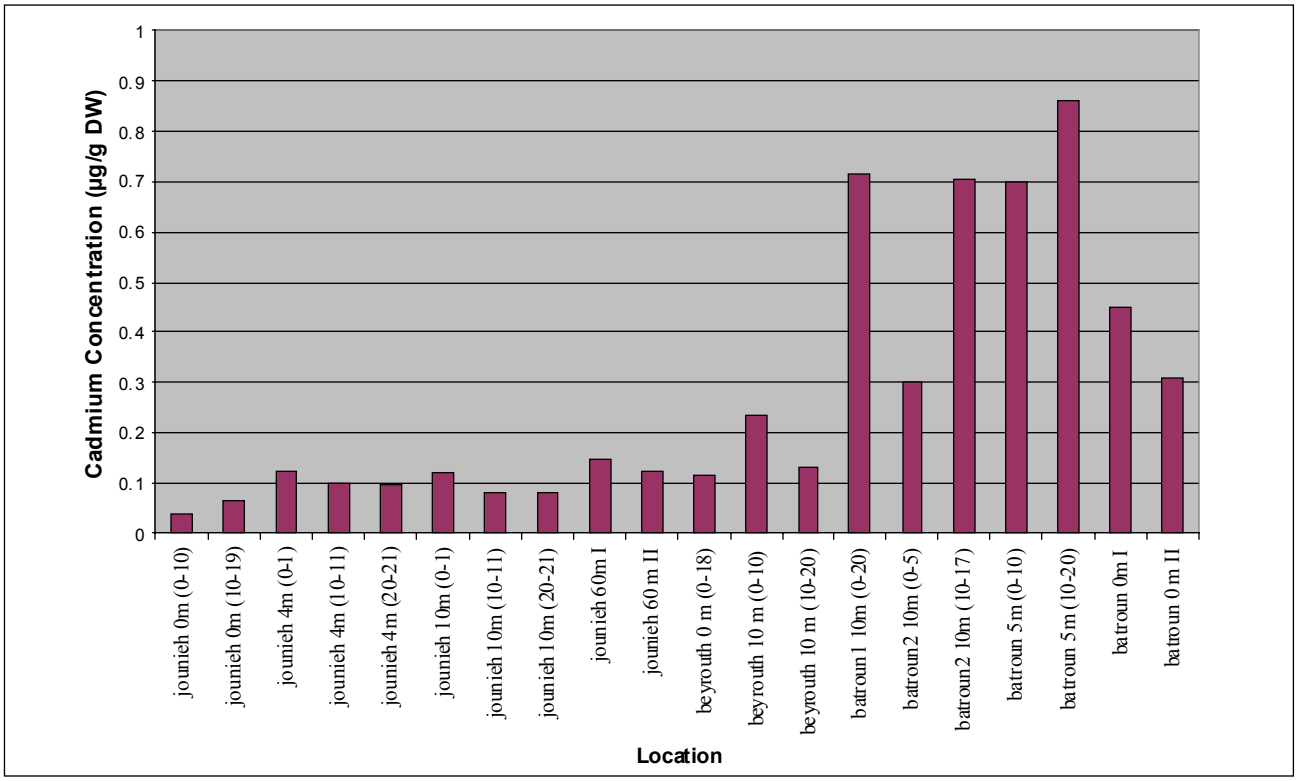

Figure 4. Cadmium concentration per region and layer.

- 0-20cm and 0-5cm
- 0-5cm and 10-17cm

A comparative analysis between Pb and Cd was carried out to detect the presence of a linear relation between these two metals. The results affirm the absence of this linear relation between them (Figure 5). Therefore, the concentration of one parameter cannot be used to show the concentration of the other one.

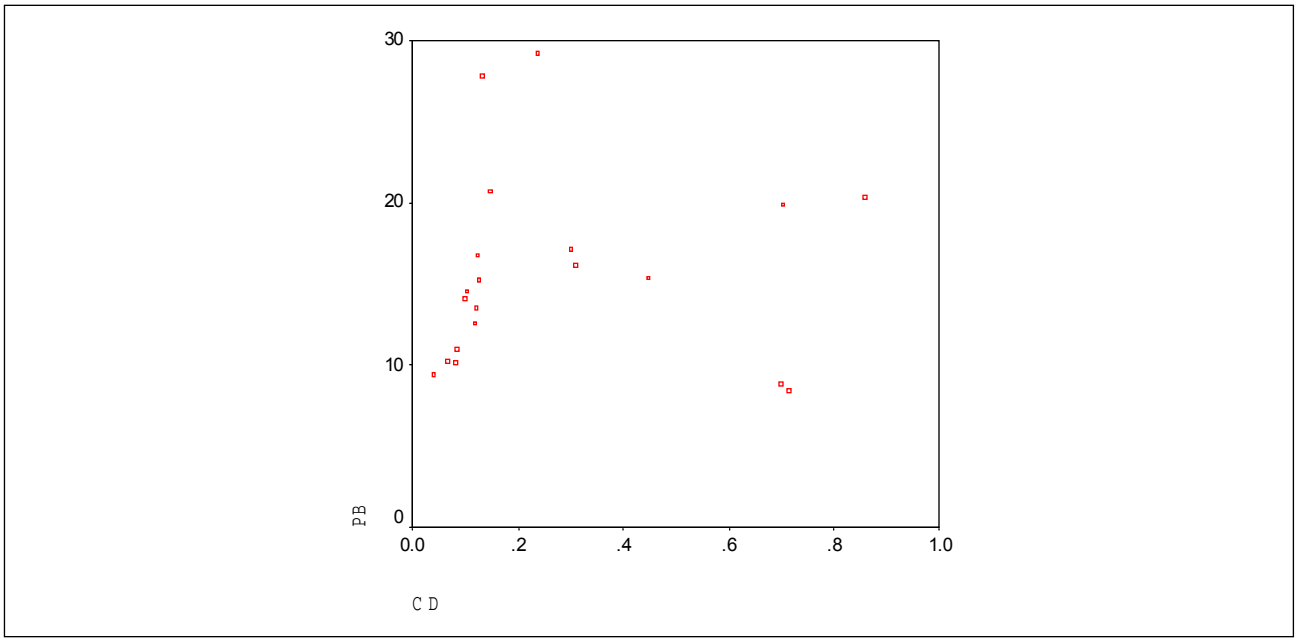

Figure 5. Correlation between lead and cadmium.

CONCLUSION

According to the French tolerable concentration levels (listed in the French decree-2000), the concentration of Pb and Cd in samples taken from Beirut, Jounieh, and Batroun are at the acceptable level; therefore these three cities are not considered as polluted regions based on Pb and Cd.

Beirut and Jounieh sediments contain a concentration of Pb higher than Cd. The sediments of Batroun contain more Cd than Pb. These results could be explained by the presence of an operational chemical factory near Batroun releasing its effluents into the sea. The exaggerated CO_2 present in the atmosphere due to the huge number of cars in Beirut and Jounieh, thus the fuel consumption increases the concentration of Pb in the sediments of these regions.

The results obtained after the 2006 political conflict (in this study) showed higher concentrations of Pb and Cd at the same regions and depths compared to the results obtained prior to the conflict (Table 3). This increase in concentration of Pb and Cd can be attributed to the huge quantity of sludge and debris resulting from bombs and fuel-oil, which raised the level of hydrocarbons in the seawater. Recent studies have shown a relation between hydrocarbons and heavy metals (Yu Li et al., 2006), which could explain this slight increase in heavy metals concentration.

Finally, the systematic surveillance of risk zones and the study of factors having an influence on the quality of the seawater, allow us to have more information. This contributes to risk values, management, and more efficient communication. It will be useful for fundamental progress to all stakeholders in the environment.

It recommended that this research be extended by applying the same study to the other coastal regions to confirm the distribution of Pb and Cd concentrations in sediment layers. It is also recommended to study sediments of diameters larger than 63 micrometers or to study layers with more than 1cm thickness; otherwise the weight of the samples might not be sufficient for the analysis.

Table 3. Comparison between lead and cadmium concentrations before and after the war.

Sites	Heavy Metals	Concentrations before the war[1] (µg.g^{-1} D.W)	Concentrations after the war[2] (µg.g^{-1} D.W)
Jounieh 4 m	Pb	4.9	14.6
	Cd	0.05	0.109
Jounieh 60 m	Pb	24.09	18.73
	Cd	0.21	0.135
Batroun 50 cm	Pb	2.44	15.78
	Cd	0.04	0.38
Batroun 10 m	Pb	1.92	8.36
	Cd	0.03	0.715

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