METAL CONCENTRATIONS IN MARINE SEDIMENTS FROM LEBANON

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Abstract. Nearshore shallow marine sediment was collected from fourteen points along the Lebanese coast and analyzed for heavy metals. The samples consisting of medium to fine sand (those from Khaldé, Rmeileh, and Sidon) had generally lower metal concentrations than those made up of very coarse to coarse sand (Tabarja, Beirut, Adloun), fine to very fine sand (Beirut), and very find sand to coarse silt (Nahr Ibrahim Village). The sediments which had the highest Pb, Zn, and Mn were from Beirut and Adloun. Those with the highest Fe concentrations came from Beirut and Nahr Ibrahim Village, and the highest Cu occurred in sediments collected from Beirut and Tabarja. The metal levels found do not seem to reflect abnormal contamination in the areas sampled. More extensive work is recommended.

1. Introduction

Sediments have aptly been called 'trace element traps' (Chester and Stoner, 1975) because they eventually receive almost all the trace metals which are introduced into the aquatic environment (Greig and McGrath, 1977). The 220 km coastline of Lebanon, which is characterized by high sea cliffs of limestone with smaller ones of alluvium, is undergoing increased erosion (Emery and George, 1963; Beydoun, 1976). Although there is a small percentage of sand beaches which are comprised of about 25% heavy minerals (mainly hematite) with an average of 31% Ca and Mg carbonate (shell fragments and limestone grains), the majority of the beaches are chiefly made up of dolomitic limestone gravel (Emery and George, 1963). Ten of the fifteen principal rivers which emanate from the mountains in the western part of the country drain areas with good clastic exposures and are the major source of suspended sediment reaching the sea (Beydoun, 1976).

Along with these natural contributions of heavy metals to the sediment, there are the anthropogenic contributions, through untreated sewage, fertilizer and pesticide residues, industrial effluents, and atmospheric 'fallout', which are probably quite significant here. Yet, until now, no studies had been made with regard to the heavy metal content of these sediments. The present work reports the Pb, Cd, Cu, Ni, Fe, Zn, Cr, and Mn levels in shallow sediments taken from certain points along the Lebanese coast.

2. Collection and Analysis

Two sediment samples (top 5 to 10 cm) were collected approximately 500 to 1000 m apart at each of seven locations off the coast of Lebanon from Nahr (River) Ibrahim Village

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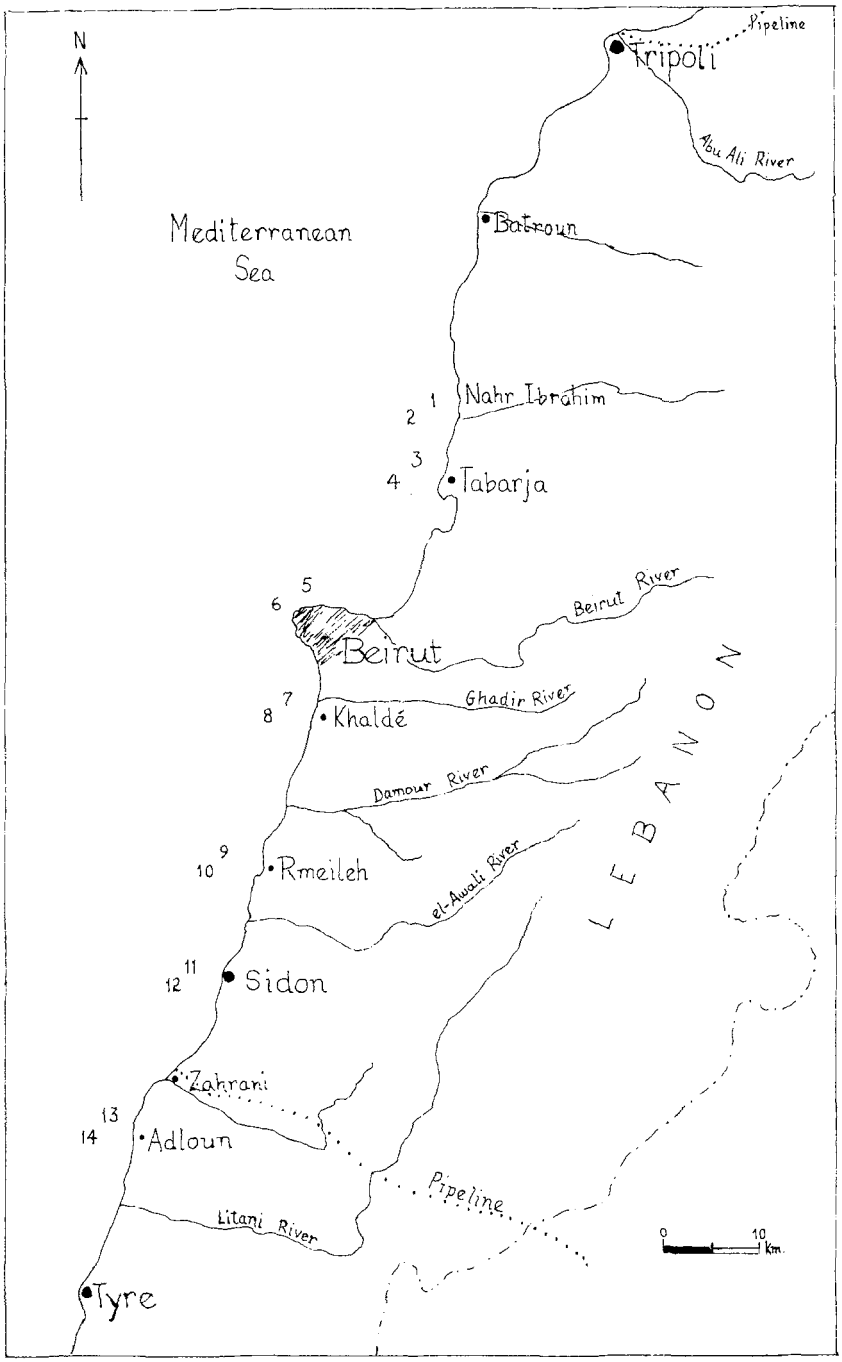

Fig. 1. The coast of Lebanon from Tripoli to Tyre indicating the approximate locations from which fourteen samples of surface sediment were collected.

in the north, to Adloun in the south (Figure 1). The area sampled covers about 110 km of the Lebanese coastline. Except for the Beirut samples (Nos. 5 and 6), which were taken in November 1977 all sediment was collected in April and May 1978. Divers collected the samples in glass bottles which had been cleaned by soaking overnight in detergent, rinsing several times in distilled water (Bernhard, 1976) and then oven-drying. The bottles were immediately sealed with cleaned plastic covers after each sample was taken. Details of the distance from shore and depth of sampling at each location are included in Table I.

Sediment samples were sieved through a 1.75 mm (0.75 ϕ) nylon mesh and rinsed two-to-three times in distilled water. A portion of each sample was retained for classification purposes (see Table I) since grain size, organic matter content and minerology are important factors in the trace element concentration of sediment (Eisler *et al.*, 1977). These samples were air-dried for at least 24 h. The remainder of the sediment was frozen at $-2°C$ to $0°C$ in covered, plastic Petri dishes to await processing for analysis.

Once thawed, the sediment samples were transferred to 150 ml Pyrex flasks (previously cleaned according to the aforementioned method), weighed, and oven dried at 80 to 90°C for 24 to 48 h. An agate mortar and pestle were used to grind the dried sediments to fine powder. Subsamples, weighing 0.5 g each, were placed in cleaned flasks, to which 10 ml of nitric–perchloric acid (3:1) was added. The flasks containing the samples were placed in an oven at 150°C for 12 to 24 h, or until no visible signs of the liquid remained. Each

TABLE I

A brief description of the surface sediment (top 5–10 cm) sampled off the coast of Lebanon including the location, approximate distance from shore and depth of sampling

Location	Sample No.	Distance offshore (m)	Depth (m)	Sediment description
Nahr Ibrahim Village	1, 2	150	15	Very fine sand and very fine sand to coarse silt populations nearly equal; 85% detritals, 10% allochemicals, 5% shell tests in fragmental angular debris, red algae, etc.
Tabarja	3, 4	800	20	Coarse sand; 95% allochemicals, 5% detritals
Beirut	5	150	15	Fine sand to coarse silt, but predominantly fine to very fine sand; 80% detritals, 20% allochemicals
	6	150	10	Coarse sand; chiefly allochemicals consisting mainly of skeletel debris
Khaldé	7, 8	600	15	85% medium to fine sand, 15% coarse and very fine sand equally distributed; 95% detritals, 5% allochemicals
Rmeileh	9, 10	250	10	90% medium to fine sand, 5% coarse, 5% very find sand; 80% quartz grains, 15% heavy minerals (hematite, limonite), 5% allochemicals
Sidon	11, 12	150	10	80% fine sand, 10% medium sand, 10% very fine sand; 50% allochemicals, 50% detritals
Adloun	13	200	10	100% very coarse to coarse sand; 100% allochemicals
	14	200	10	98% very coarse to coarse sand; 100% allochemicals

sample was then brought to volume with 75 ml of 0.1N HCl. Blanks were processed in the same manner.

The analysis of the sediments for Pb, Cu, Fe, Zn, and Mn was performed on a Varian Techtron AA–5 spectrophotometer with an air–acetylene flame in the Department of Chemistry at the University of Birmingham, Birmingham, England. The Nahr Ibrahim, Tabarja and Adloun samples were also analyzed (for Pb, Cd, Cu, Ni, Fe, Zn, and Cr) at the Purdue University School of Civil Engineering in Lafayette, Indiana, U.S.A. on a Perkon–Elmer Model 306 atomic absorption spectrophotometer using a flame with a lean mixture of air and acetylene. All values were given in mg l^{-1} and then converted to $\mu g\ g^{-1}$ dry weight, as presented here.

3. Results and Discussion

The results are shown in Table II. The highest Pb, Zn, and Mn readings appeared in the Beirut and Adloun sediment samples, and with the exception of the high reading in sample No. 4 (Tabarja), the Beirut samples also had the highest Cu values. Iron was highest in the Beirut and Nahr Ibrahim sediments. Of the six samples analysed for Cd, Ni, and Cr, sample No. 4 at Tabarja had the highest Cd, No. 1 at Nahr Ibrahim had the

TABLE II

Metal concentrations in shallow marine sediments from the coast of Lebanon. All samples were analyzed on a Varian Techtron AA-5 atomic absorption spectrophotometer (AAS). The results of a second analysis of samples No. 1–4, 13, and 14 on a Perkin-Elmer Model 306 AAS also appear and are indicated by asterisks. Values given are in $\mu g\ g^{-1}$ (ppm) dry weight; n.d. = not detected

Sample No.	Pb	Cd	Cu	Ni	Fe	Zn	Cr	Mn
1	9.4	–	3.8	–	23975.0	64.6	–	255.0
	*n.d.	< 0.8	15.9	38.4	28381.3	52.6	13.0	–
2	26.3	–	11.2	–	25640.0	94.6	–	217.5
	*13.1	< 0.8	17.8	19.7	28193.8	42.4	13.0	–
3	63.8	–	18.8	–	12305.0	79.6	–	270.0
	*n.d.	< 0.8	26.3	28.1	13662.5	74.3	10.8	–
4	33.8	–	3.8	–	14645.0	64.6	–	255.0
	*26.3	3.8	195.0	18.8	17037.5	48.8	10.8	–
5	104.6	–	44.2	–	24784.7	105.4	–	405.5
6	83.8	–	44.2	–	26425.0	134.6	–	385.0
7	n.d.	–	3.8	–	7310.0	n.d.	–	105.0
8	n.d.	–	3.8	–	7970.0	64.6	–	105.0
9	18.8	–	3.8	–	16640.0	19.6	–	165.0
10	n.d.	–	3.8	–	11315.0	49.6	–	120.0
11	33.8	–	3.8	–	10640.0	19.6	–	240.0
12	18.8	–	3.8	–	9980.0	19.6	–	240.0
13	63.8	–	3.8	–	3980.0	154.6	–	465.0
	*n.d.	2.3	1.9	18.8	5581.3	21.8	8.5	–
14	93.8	–	3.8	–	3635.0	79.6	–	525.0
	*n.d.	2.3	1.9	18.8	5206.3	12.8	5.9	–

highest Ni, and all six had similar Cr levels although sample No. 14 at Adloun had the lowest.

It is not surprising to see the elevated metal levels in the Beirut sediments since Beirut is the most heavily populated and industrialized area sampled. It might be interesting to note that there was a sharp contrast in general type between these two sediments which were taken only a few hundred meters from each other (Table I). Sample No. 5 was chiefly made up of detritals, whereas sample No. 6 consisted mainly of allochemicals. Yet, there was no appreciable difference between the metal levels which each sample concentrated.

The raw sewage, garbage and industrial waste input along the coast of Lebanon is particularly heavy in the Beirut area. For example, according to Ahmad (1972), the volume of sewage which is carried from inland by the Ghadir River (south of Beirut) alone exceeds the river's flow in all seasons, and as of 1970 the Beirut River (north of the city), which also empties into the Mediterranean, discharged at least 178 500 m^3 of wastewater daily. No up-to-date figures are available, but it would probably be safe to assume that the volume of wastes entering the Mediterranean from Lebanon has increased from year to year, particularly around Beirut. Many investigators have reported that the highest metal levels occur in sediment taken closest to the points of sewage entry (Carmody *et al.*, 1973; Oliver, 1973; Halcrow *et al.*, 1973; Boyden, 1975; Amiel and Navrot, 1978).

Ahmad (1972) suggested that the south-to-north surface currents of the Mediterranean along the Lebanese coast might indicate that the coastal areas in the northern parts of the country are subject to a higher degree of contamination than those in the south. This does not explain, however, the elevated Pb, Cd, Zn, and Mn concentrations in the sediment samples from the southern town of Adloun. Perhaps the close proximity of this town to the oil refinery and terminal at Zahrani (Figure 1), where there is a considerable amount of tanker traffic, would partially account for the high readings in the Adloun sediment. About 8×10^5 tonne of crude oil were refined and 20.9×10^6 tonne were shipped yearly from Zahrani between 1966 and 1969 (Ahmad, 1972). These figures have probably increased considerably since then, in spite of the recent civil war here. There is also an oil terminal just north of Beirut and one at the northern city of Tripoli, plus approximately four to five other major oil pipelines which terminate at the eastern Mediterranean.

The sediment samples from Nahr Ibrahim might be expected to have high metal concentrations since they were taken close to the point at which the river enters the sea, the sediment of the type at this station (see Table I), i.e., very fine sand to coarse silt, seems to concentrate higher levels of trace elements than fine to medium sands (Jones, 1973) or coarse sands (Oliver, 1973). But the only metal in the Nahr Ibrahim samples which had very elevated levels in relation to all the other samples (except Beirut) was Fe. Unfortunately, the volume and type of wastewater this river carries, which is probably a significant determinant of its heavy metal input, has not yet been investigated.

Many factors could be playing a role in the level of trace metal concentration in the

marine environment here and they should be considered carefully before conclusions are drawn. Abdullah *et al.* (1972), for instance, concluded that natural runoff, sewage, and industrial effluent input in areas with limited water circulation could result in an increase in Pb and Cd levels. According to Jenne (1968), hydrous Fe and Mn oxides can control the concentration of different metals. The nature of the Fe and Mn in the sediments analyzed here has not been determined, but some of the readings, particularly of Fe, seem to be high.

Lorne (1978) has pointed out that the metal enrichment of sediment is related to the removal of metals from solution by terrestrial organic matter which eventually becomes incorporated with the sediment. Such a conclusion was reached with regard to algae (Helz *et al.,* 1975), the moults of certain crustaceans (Martin, 1970; Bertine and Goldberg, 1972) and the carbonate shell material of some molluscan species (Oreshkin, 1977). Studies recently conducted on the coast of Ras Beirut, Lebanon, have shown ranges of Pb, Cu, and Zn in various molluscs (Shiber and Shatila, 1978; Shiber, 1979b), algae (Shiber and Shatila, 1979; Shiber, 1979b), whole prawns and eggs of sea urchins (Shiber, 1979a), and crabs (Shiber, 1977) similar to those found in the Beirut samples of sediment in this study.

Nearshore surface seawater from the coast of Beirut has also been analyzed for heavy metals (Shiber and Shatila, 1978; Shiber, 1979a,b). However, the concentrations reported were abnormally high, except for possibly Cu, Fe, and Zn. This indicates that more work needs to be done along these lines before inter-relationships between metal levels of seawater and those of sediment and/or biota can be made.

The small amount of biogenous materials observed to occur in the sediment samples from Khaldé and Rmeileh (Table I) might partially explain the lower Pb, Cu, and Mn levels at these locations. Similarly, the very high percentage of biogenous materials in the Adloun samples and sample No. 6 from Beirut might be an important factor in some of their elevated readings. Furthermore, as mentioned earlier, coarser sands (such as comprise the latter samples) along with very fine sands may be more likely to have higher metal concentrations than medium-to-fine sands (Jones, 1973) of which the Khaldé and Rmeileh samples are comprised. This may be a partial explanation of the similarity in metal concentrations between the two very different Beirut samples, i.e., sample No. 6 had the higher percentage of biogenous materials, but No. 5 had fine to very fine sand.

Although little is known about the nature of the sediment in this region with regard to trace metal concentrations, there has been work done in some Mediterranean coastal areas (Table III). In their study of the Bay of Naples, Griggs and Johnson (1978) reported concentrations of Cr and Pb which are higher than values found in the present study and Cu levels which are generally similar. Papakostidis *et al.* (1974) found much higher Cr and Zn values in sediment taken from the Saronikos Gulf, especially in samples collected nearest a sewage outfall. The average concentrations of Cu and Fe in the present work are not very different from those found in surface sediments from the Bay of Roquebrune by Fukai (1965), but Zn and Mn are higher and Cr is lower.

TABLE III

Trace metal concentrations (ranges and/or averages) in sediment from Mediterranean coastal areas. Values are in ppm (dry weight) unless otherwise indicated

Location	Pb	Cd	Cu	Ni	Fe	Zn	Cr	Mn
Bay of Naples (Griggs & Johnson, 1978)	5 – 221 60.8		9 – 128 38.9				15 – 714 71.5	
Bay of Roquebrune* (Fukai, 1965)			28.5		18.9 mg g^{-1}	30	24	201
Rosh Hanikra-Haifa (Roth & Hornung, 1977)	3.9 – 19.7 8.4	0.3 – 2.2 0.7	0.3 – 2.9 1.6	2.3 – 9.3 4.8		2.1 – 18.2 7.0	1.7 – 12.4 4.2	
Saronikos Gulf (Papakostidis *et al.*, 1974)						45 – 1800	35 – 1000	
Tel-Aviv-Yaffo** (Amiel & Navrot, 1978)	s 15 – 27 w 14 – 18		7 – 40 5 – 13	5 – 15 8 – 13		22 – 85 20 – 47	30 – 60 30 – 40	
Lebanon (Present study)	† nd – 104.6 29.5	< 0.8 – 3.8 1.8	1.9 – 195 20.8	18.8 – 38.4 23.8	3635 – 28381 14865.4	12.8 – 154.6 60.2	5.9 – 13 10.3	105 – 525 268.1

*Readings are averages of two samples; **Readings (s: summer, w: winter) are approximate; † not detected.

With regard to the easternmost coastal area of the Mediterranean, the only data which seem to be available for general comparison are the few studies done on the coast of Israel/Palestine (Roth and Hornung, 1977; Amiel and Navrot, 1978). The sediments sampled by Roth and Hornung (1977) between Rosh Hanikra and Haifa had lower Pb, Cu, Ni, and Zn levels, but both Cd and Cr concentrations were within ranges similar to those found in the present work. Amiel and Navrot (1978) studied the metal levels in sediment collected within close proximity to the Tel-Aviv–Yaffo sewage pipeline outlet, in both winter (January–February) and summer (June–September) and reported that the summer samples had the highest concentrations. The range of metal values reported here are more in line with those Amiel and Navrot found in their summer samples, but are still higher, except for Cr, which was considerably lower. Comparison data are lacking with regard to Fe and Mn in sediments from this area.

When compared with those reported from other geographical areas (Table IV), the metal concentrations reported here do not seem to reflect a picture of gross contamination of the sediment at the locations sampled. The average values of Cr, Mn, and Fe are much lower than the continental crust averages proposed by Taylor (1964). Copper and Zn are also lower, but Pb is twice as high. However, this work is preliminary and more extensive studies should be conducted here before any firm conclusions can be made. Such investigations might cover a greater portion of the coastal area and include sampling deeper in the sediment (i.e., layers unaffected by man), so that the distribution of heavy metals and the level of background concentrations in unpolluted sediment might be better understood. Moreover, studies regarding the volume and nature of the wastes entering the Mediterranean from Lebanon are greatly needed. Also, little is known

TABLE IV

Trace metal concentrations (ranges and/or averages) in sediments from various geographical areas. Values are in ppm (dry weight) unless otherwise indicated

Location	Pb	Cd	Cu	Ni	Fe	Zn	Cr	Mn
Portsmouth Harbour, UK (Soulsby *et al.*, 1978)	49 – 114 69.5	0.5 – 3.3 1.4	26 – 72 39.8	19 – 30 25.5		68 – 210 112.3	8 – 25 13.8	117 – 169 143.8
N.Y. Bight, USA (Carmody *et al.*, 1973)	25 – 370 144		8 – 390 141	3 – 35 24		26 – 1500 264	2 – 310 106	
New South Wales, Australia (deForest *et al.*, 1978)	4 – 53 21	0.2 – 2.5 1.6	4 – 15 6	1 – 24 14	0.1 – 4.3 0.9 (g/100 g)	2 – 144 40	5 – 125 38.3	
North Sea (Taylor, 1979)	17 – 238 45.4	0.1 – 0.8 0.2	2 – 49.4 8	6.5 – 22 10		19.7 – 197.5 74.1	4 – 41.1 9.9	108 – 3073 242.1
Inner German Bight (Gadow & Schafer, 1974)	152	15	44	73		459	176	
Narragansett Bay USA (Eisler *et al.*, 1977)	17 – 81 44	0.06 – 2.45 0.47	26 – 98 53	6 – 34 18	6.26 – 30.98 (g kg^{-1})	53 – 168 110	13 – 81 46	
Kaohsiung Harbour, Taiwan (Chen, 1977)	26 – 576 68	0.3 – 0.179 0.082	11 – 134 74	40 – 76 59	7.33%	103 – 3514 511	42 – 285 98	291 – 771 523
Lebanon (Present study)	*nd – 104.6 29.5	< 0.8 – 3.8 1.8	1.9 – 195 20.8	18.8 – 38.4 23.8	3635 – 28381 14865.4	12.8 – 154.6 60.2	5.9 – 13 10.3	105 – 525 268.1

*not detected.

about the effects that increasing land erosion might be having on the heavy metal content of the sediment here. This would be another worthwhile topic for future research.

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