

A COMPARISON OF METALS IN SEDIMENTS AND WATER IN THE RIVER NAHR-IBRAHIM, LEBANON: 1996 AND 1999

SAMIRA IBRAHIM KORFALI¹ and BRIAN E. DAVIES²

¹Natural Science Division, Lebanese American University, P.O. Box, 13-5053, Chouran Beirut, 1102 2801, Beirut, Lebanon; ²Department of Geological Sciences, 340 Brackett Hall, Clemson University, SC 29634, USA (e-mails: skorfali@lau.edu.lb; bdavies@clemson.edu)

Received 20 May 2001; accepted in revised form 20 October 2001

Abstract. Rivers whose basins are underlain by carbonate rocks exhibit high pH, lower desorption of metals and possess high buffering capacity against acidic inputs to the river. The catchment of River Nahr-Ibrahim, Lebanon, is largely underlain by limestone. Compared to neighbouring countries, Lebanon is relatively fortunate since precipitation is high. However, recently a warming in temperature and a drop in precipitation has occurred, thus causing low water levels in rivers. The objective of this study is to investigate the variation of the total metal content (Fe, Mn, Zn, Cu, Pb and Cd) in bed sediments and water of River Nahr-Ibrahim between 1996 and 1999 (two years); and relate these variations to the effect of changes in human activities and/or due to the variations of precipitation rate, temperature and pH of water. Bed load sediments and stream water were collected simultaneously from five sampling sites. Water pH and temperature were determined *in situ*. Sediment samples were dried at room temperature and sieved; the sediment size < 75 μm size was retained. Water was analysed for major constituents and trace metals. Metals were extracted from sediments with aqua regia. Metal concentration in water and sediments were determined using ICP-MS technique. Data revealed a drop in metal concentrations (Zn, Cu, Pb, Cd) in sediments at quarry site after its closure. The decrease in precipitation rate, lowering the level of water and the dilution of industrial discharges and decrease in water pH led most probably to the desorption of metals from sediments into the water.

Key words: human activities, metal content, sediment, variation, water

1. Introduction

Suspended and bed load sediments are sinks for heavy metals entering rivers from pollutant discharges due to human activities (Hudson-Edwards *et al.*, 1997; Large and McGoldrick, 1998). The deposition of metals in sediments occurs through an interaction between sediment and water (Piron *et al.*, 1990), whereby variations of metal contents of sediments and water depend on variation of water chemistry, for example, temperature, pH and solute concentration. Rivers whose basins are underlain by carbonate rocks exhibit high pH, lower desorption of metals and possess high buffering capacity against acidic inputs to the river (Jarvie *et al.*, 1997). The catchment of River Nahr-Ibrahim, Lebanon, is largely underlain by



Environmental Geochemistry and Health 25: 41–50, 2003.

© 2003 Kluwer Academic Publishers. Printed in the Netherlands.

limestone. Lebanon has a warm/hot dry summer and cool wet winter. Compared to neighbouring countries, Lebanon is relatively fortunate since precipitation is high (832 mm annually) and the high mountain areas receive 1400 mm annually (Khair *et al.*, 1994). However, recently a warming in temperature and a drop in precipitation has occurred, precipitation dropped annually to 440 mm in the year 1999 (Lebanese Meteorology Department), thus causing low water levels in rivers. The objective of this study is to investigate the variation of the total metal content (Fe, Mn, Zn, Cu, Pb and Cd) in bed sediments and water of River Nahr-Ibrahim (located north of Beirut near Byblos) and relate these variations to the effect of changes in human activities such as the closure of the quarry on the river banks and/or due to the variations of precipitation rate, temperature and pH of water. The metal concentration in sediments and water between the years 1996 and 1999 are compared.

2. Material and methods

Water and sediment samples were collected in the dry season (October 1996 and 1999). The same five sampling sites were chosen. They stretched along 13 km of the river (Nahr-Ibrahim) upstream of its confluence with the Mediterranean Sea (Figure 1). The choice of these sites in 1996 was based upon the observed potential contamination from domestic waste or industrial discharge and vehicle motion. While, Table I provides the other relevant characteristics of the sampling sites with the variations that these sites encountered in the year 1996 and 1999. The major variation between the two-studied years is that the excessive vehicle movement encountered in 1996 ceased completely at site 4 due to the closure of the quarry (was excessively exploited for extraction of calcite and marble rocks for construction works). The Lebanese Ministry of Environment recommended in November 1997 closure of the Nahr-Ibrahim quarry (MOE, 1997), but the cease of the works at the quarry was in May 1998.

Bed load sediments and stream water were collected according to standard methods (Chapman, 1992; Lewis and McConchie, 1994; APHA, 1998). At each collecting site four sub-samples of sediments were taken and bulked in one polyethylene bag. Water samples were collected simultaneously with sediments at each sampling site at mid depth from the surface using two 1 L polyethylene bottles. Water pH and temperature were determined *in situ* and water samples subsequently filtered through 0.45 μm membrane in the laboratory. Sediment samples were dried at room temperature and sieved; the sediment size $<75 \mu\text{m}$ size was retained. This sediment size exhibited higher metal content compared to other larger sediment sizes (250 and 1180 μm) in the former conducted study of the year 1996 (Korfali, 1999; Korfali and Davies, 2000). Water was analysed for major constituents and

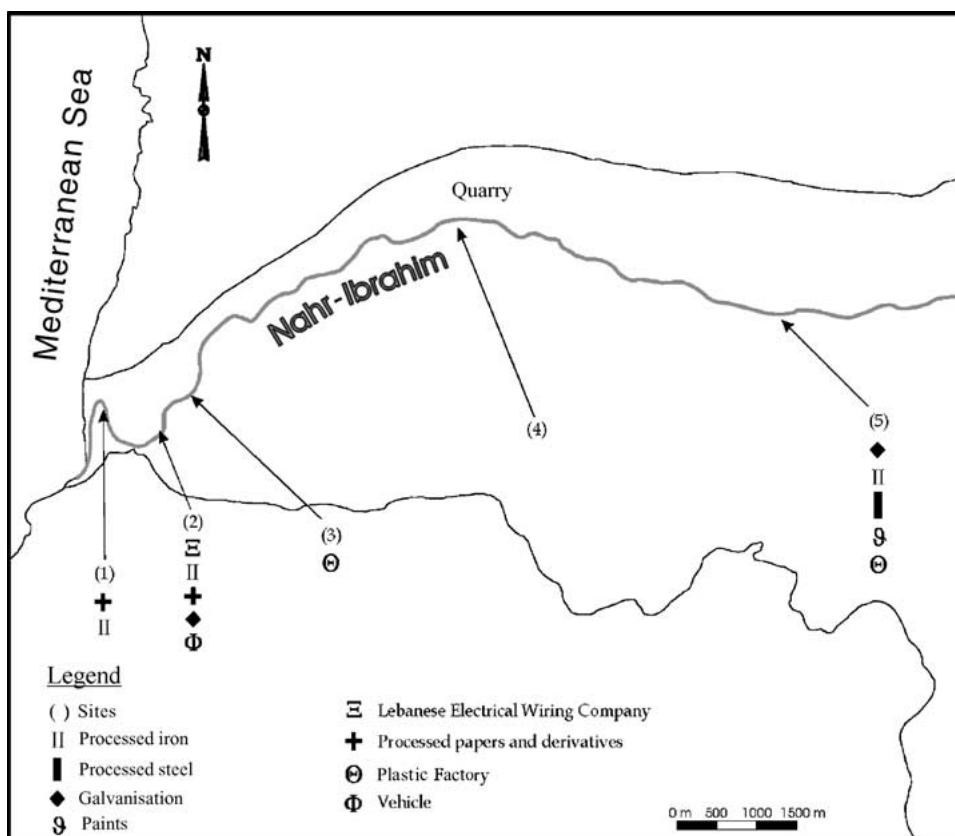


Figure 1. A graphical representation of the sampling sites with their respective industries.

TABLE I
Relevant characteristic and variations of the year 1996 and 1999 of the sampling sites

Sampling sites	(1)	(2)	(3)	(4)	(5)
1996	Urban site	Urban site, under a highway bridge	Vegetated site	Quarry, continuous vehicle movement	Plantation site, downstream from an urban highly industrial zone
1999	Urban site	Urban site, under a highway bridge	Vegetated site, plastic factory	Closed quarry, nil vehicle movement	Plantation site, downstream from an urban highly industrial zone

trace metals. Total metals were extracted from sediments (1 g) with hot aqua regia (Baghdady and Sippola, 1983; Kersten and Förstner, 1989). Metal concentration in water and sediments was determined using ICP-MS technique. Analytical quality was assured through the use of reference material (sediment RM 8704, water SRM 1643 d from NIST-USA) and appropriate replicates (eight replicates). Water solute speciation was modelled by PHREEQC.

3. Results and discussion

3.1. COMPARATIVE VARIATION OF METAL CONTENT IN SEDIMENTS

Figure 2 shows the variation of sediment total metal content (Zn, Cu, Pb and Cd) at the different sampling sites between the years 1996 and 1999. Since, Fe and Mn content in sediments did not vary significantly, they are not reported in Figure 2. The mean value of content for 1996 (Fe: $23,054 \mu\text{g g}^{-1}$, Mn: $208 \mu\text{g g}^{-1}$) and for 1999 (Fe: $22,138 \mu\text{g g}^{-1}$, Mn: $170 \mu\text{g g}^{-1}$). This is in accordance with the previous conducted study (Korfali, 1999; Korfali and Davies, 2000), where Fe and Mn derived their source origin primarily from natural sources.

What is clearly explicit (Figure 2) is the drop in sediment metal concentration in 1999 at site 4 (the quarry). The factor decrease of the metal content was 2.4 for Zn, 2.2 for Cu, 7.2 for Cd and 11.3 for Pb. It seems that the closure of quarry led to a significant reduction in the sediment metal content, due to the decrease of truck traffic and discharges from human activities at this site. This suggestion is reinforced at sites 1 and 2 where the sediment Pb content remained very similar between 1996 and 1999 (Figure 2) due to continued excessive vehicle motion, and where the sediment Pb content ($160 \mu\text{g g}^{-1}$) sustained to very high compared to the standard average shale value, $20 \mu\text{g g}^{-1}$ (Martin and Meybeck, 1979). However, at site 5 (near the industrial zone, galvanization, steel works, electroplating, battery factory, paint and furniture factories), the sediment content of Cu and Zn continued to be the highest of all sites and much higher than the standard shale value (Zn: $95 \mu\text{g g}^{-1}$, Cu: $45 \mu\text{g g}^{-1}$). The increase in Cu content at site 3 in 1999 is linked most probably to the discharges of the PVC factory that was recently established (Stephenson *et al.*, 1998). While the decrease in sediment Cd content at all sites in the year 1999 compared to 1996 may be attributed to the diffused non-point source origin of Cd as suggested by the conducted study of the year 1996. The former study estimated Cd source to be most probably derived from the dumping and/or open air burning of the garbage (Korfali, 1999). Recently, when political stability has been restored, the government has implemented strict rules of landfill disposal. Open air burning of garbage has been reduced with a consequent decrease of the sediment Cd content. However, the sediment Cd content at all sites continued to be

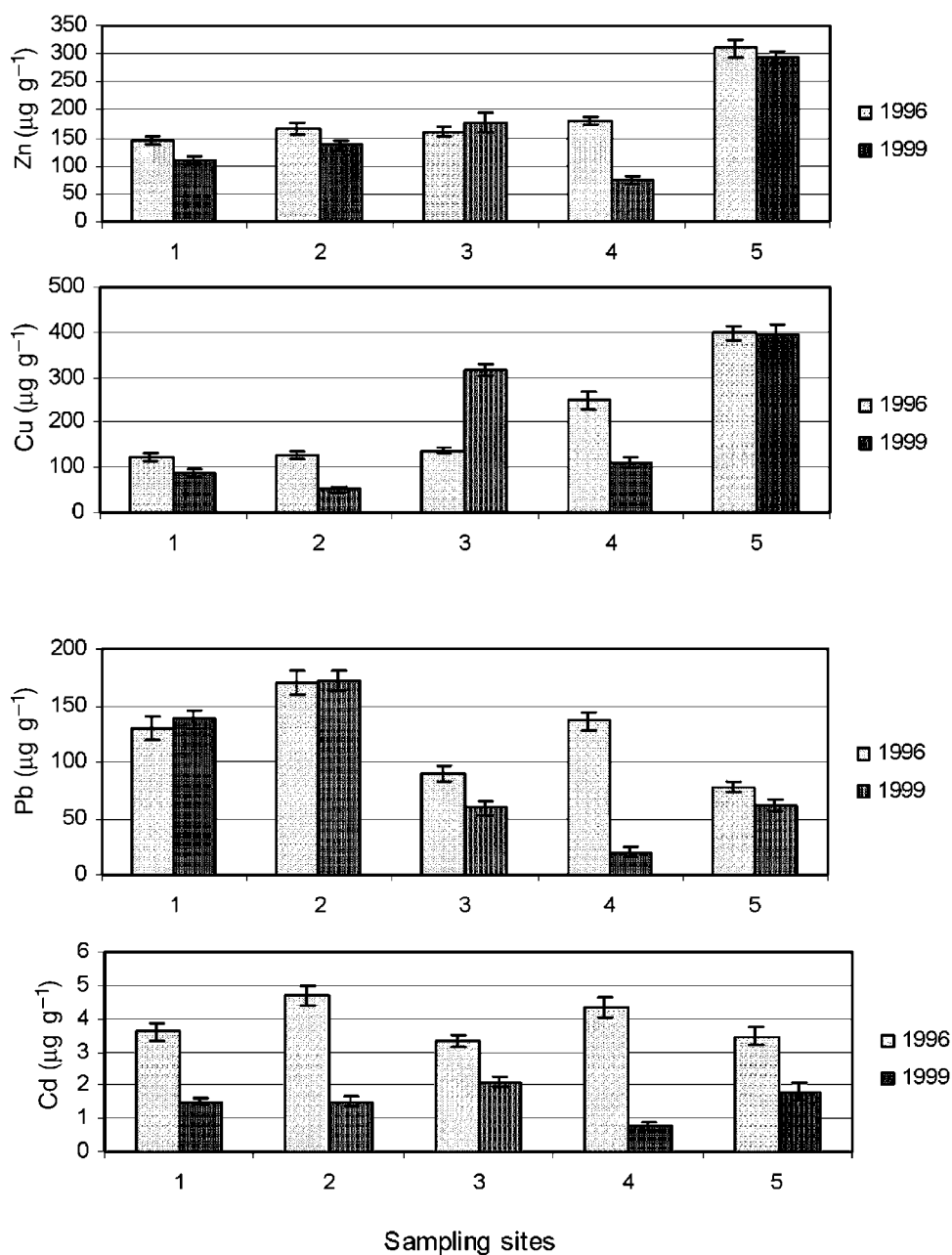


Figure 2. Variation of total metal concentration in bed load sediment between the years 1996 and 1999. Data columns and error bar represent means ($n = 3$) and SD, respectively.

of higher values than the standard shale content ($0.3 \mu\text{g g}^{-1}$), and this is a reflection to other Cd sources such as fertilizers and stabilizing pigments used in painting, which is explicit at sites 3 and 5 (Figure 2).

3.2. COMPARATIVE VARIATION OF METAL CONTENT IN WATER

Table II presents the variation of the metal concentrations in the river water for the years 1996 and 1999. A decrease occurred at sites 1 to 4 in the concentration of Pb, Cd, and Mn in the year 1999 as compared to those of 1996. Cu concentration's change was similar to those previously mentioned except slight increase at site 1, while fluctuations were recorded for Zn and Fe concentrations. However, what is evident from Table II is the large increase in the year 1999 at site 5 in the concentrations of Fe, Mn, Zn and Pb. The factor increase was 8.6 for Fe, 2.3 for Mn, 18.3 for Zn and 2.5 for Pb. The increase in water concentrations of these metals at site 5 probably is expected to be from the excessive industrial discharges from the industrial zone at site 5 (Figure 1), and where in Lebanon the control on these discharges in a zone further from main cities is limited. Furthermore, the increase in the aforementioned metals at site 5 is also due to the yearly variation in water macro parameters, such as pH and temperature (Table III). These variables influence the release or adsorption of each metal into the different sediment chemical fractions. The pH value had dropped from 8.5 (1996) to 7.9 (1999). The pH decrease is most probably related to the lower precipitation rate of 1999 (830 mm in 1996, 430 mm in 1999 according to the Lebanese Meteorology Department), thus increasing the concentration of solute particles such as the acids from the discharges of the battery factory. This may also explain the increase in SO_4^{2-} and the decrease of NH_3 and PO_4^{3-} in 1999 (Table III). The pH decrease may have led to desorption of metals (Mn, Zn, Pb) from the moderately reducible sediment chemical fraction (Fe oxide/hydroxide) to water column (river water). The assumption of the release of these metals from the reducible fraction is based on results of the conducted study of metal fractionation of 1996 sediments (Korfali, 1999; Korfali and Davies, 2000). In bed load sediment, Mn, Zn and Pb fractionated mainly in the carbonate and moderately reducible fractions. The desorption process of Mn, Zn and Pb from the sediment carbonate fraction is of a lower probability since the carbonate minerals have a lower solubility at higher temperatures. Cu did not appear to be affected by pH changes. This may be due to Cu fractionation in the sediment carbonate and organic fraction. Accordingly, a deposition process of Cu rather than dissolution might have occurred in the year 1999. During this year the temperature increased which lowered both the carbonate mineral solubility and the oxidation of organic constituents (lower oxygen content in water), and consequently lowering concentration of Cu in the water.

The large variation in the year 1999 in pH values of the river water did not only impinge on total metal content of the river, but also affected the Mn and Zn speciation in water. The range of the percentages of the main species of Mn and Zn as depicted from PHREEQC software among the sampling sites of the years 1996 and 1999 is presented in Table IV. A wider percentage range of the free hydrated metal ion species for the year 1999 is observed and the highest depicted percentage is for site 5. The free aqua ion of Mn (Mn^{2+}) and Zn (Zn^{2+}) were pH sensitive

TABLE II
Variation of total metal concentration ($\mu\text{g L}^{-1}$) in water between 1996 and 1999

Site	Fe		Mn		Zn		Cu		Pb		Cd	
	1996	1999	1996	1999	1996	1999	1996	1999	1996	1999	1996	1999
1	8.5	58	3.5	2.5	3.5	100	1.6	5	27	20	1.7	0.8
2	12.2	82.2	2.5	1.5	4.6	3.1	4.8	2	70	26	4.2	1.5
3	92	86	3.5	0.9	6.5	2.0	15	1.8	42	8	1.5	0.4
4	180	290	7.5	4.5	19	43	31	5.5	80	10	4.1	0.3
5	370	3200	7.6	17.0	38	700	55	11	16	40	1.1	1.0

TABLE III
Variation of macro parameters (mg L^{-1}) in water between 1996 and 1999

Site	pH		T ($^{\circ}\text{C}$)		HCO_3^-		NH_3		SO_4^{2-}		PO_4^{3-}	
	1996	1999	1996	1999	1996	1999	1996	1999	1996	1999	1996	1999
1	8.4	8.4	18.5	24.5	248	223	0.44	0.32	6.98	14.23	0.29	0.32
2	8.5	8.2	17.0	24.2	211	186	0.58	0.30	10.00	13.14	0.28	0.10
3	8.4	8.7	18.0	26.8	198	211	0.48	0.35	8.33	11.36	0.27	0.01
4	8.5	8.4	16.5	25.0	236	186	0.41	0.26	10.66	12.54	0.28	0.01
5	8.5	7.9	18.0	19.0	223	198	0.38	0.26	6.84	16.78	0.39	0.02

TABLE IV
Percentage speciation of total metal in water and correlation coefficients

Element	Species	% Range 1996	% Range 1999	R^2 (pH)	R^2 (HCO_3^-)
Zn	$\text{Zn}(\text{CO}_3)_2^{2-}$	42–49	11–58	0.990**	0.500
	ZnCO_3^0	35–41	20–47	–0.800*	–0.542
	Zn^{2+}	7–10	7–32	–0.925**	–0.333
Mn	MnCO_3^0	56–64	30–76	0.996**	0.427
	Mn^{2+}	29–35	20–57	–0.996**	–0.436

* $p < 0.05$, ** $p < 0.01$.

derived from the correlation attempt of the pH values and percentages of the free aqua ion of the five sampling sites. A correlation occurred between the free aqua ion of Mn and Zn with pH but not with HCO_3^- (Table IV). This correlation implies a perfect negative relationship between the pH and the speciation of Mn and Zn as free hydrated metal ion. The decrease in pH at site 5 in the year 1999 compared to 1996 caused the free aqua metal species in water to be high, rendering lower water quality. This suggestion is based on the widely reported literature that the toxicity of metal to an aquatic organism correlates primarily with the speciation of the metal as a free hydrated ion (Morel, 1983; Hall *et al.*, 1995; Traina and Laperche, 1999; Campbell *et al.*, 2000; Ritchie *et al.*, 2001). Though, two water sampling events 3 years apart cannot be assumed to reflect a true water quality and necessitates the continuous temporal water quality monitoring (Chapman, 1992). But, this study projected a situation of what might occur in a water body at a time of sample collection. This may trigger that certain unnoticed changes in the environmental conditions of water bodies can be of crucial significance for evaluating all process affecting the water quality.

4. Conclusion

Nahr-Ibrahim river is assumed to have a high buffering capacity for metal inputs due to its carbonate drainage and high pH, and where sediments are the sinks for metals. The decrease in precipitation rate, lowering the level of water and the dilution of industrial discharges led most probably to the desorption of metals from sediments into the water. Moreover, the ability of carbonate species to minimize the occurrence of free metal ions was reduced as the pH decreased. The determination of metal fractionation in sediment could have indicated which sediment chemical fraction was mostly affected by these environmental changes. The continuous monitoring of the water quality is of utmost need so as to predict what process might occur in sediments.

Acknowledgements

The authors are grateful to the University Research Council-Lebanese American University (URC-LAU) and the Lebanese National Research Council (CNRS) for funding this study.

References

- APHA, AWWA, WEF: 1998, *Standard Methods for the Examination of Water and Wastewater*, 20th edn, American Public Health Association, Washington DC, USA.
- Baghdady, N.H. and Sippola, J.: 1983, Total heavy metal recovery by aqua regia in soils of different origin, *Annales Agriculture Fenniae* **22**, 175–185.
- Campbell, C.D., Hird, M., Lumsdon, D.G. and Meeussen, J.C.L.: 2000, The effect of EDTA and fulvic acid on Cd, Zn, and Cu toxicity to a bioluminescent construct (pUCD607) of *Escherichia*, *Chemosphere* **40**, 319–325.
- Chapman, D.: 1992, *Water Quality Assessments*, University Press, Cambridge, UK.
- Hall, L.W., Ziegenfuss, M.C., Anderson, R.D. and Lweis, B.L.: 1995, The effect of salinity on the acute toxicity of total and free cadmium to Chesapeake Bay copepod and fish, *Marine Pollution Bulletin* **6**, 376–384.
- Hudson-Edwards, K., Macklin, M. and Taylor, M.: 1997, Historic metal mining inputs to Tees river sediment, *The Science of the Total Environment* **194/195**, 437–445.
- Jarvie, H.P., Neal, C., Leach, D.V., Ryland, G.P., House, W.A. and Robson, A.J.: 1997, Major ion concentrations and the inorganic carbon chemistry of the Humber rivers, *The Science of the Total Environment* **194/195**, 285–302.
- Kersten, M. and Förstner, U.: 1989, Speciation of trace metals in sediments, in: Batley, G.E. (ed.), *Trace Element Speciation: Analytical and Problems*, CRC Press, Boca Raton, Florida, pp. 245–317.
- Khair, K., Aker, N., Haddad, F., Jurdi, M. and Hachach, A.: 1994, The environmental impacts of humans on ground water in Lebanon, *Water Air and Soil Pollution* **78**, 37–49.
- Korfali, S.I.: 1999, Metal Concentrations in The Nahr-Ibrahim River, Lebanon, PhD Thesis, University of Bradford, UK.
- Korfali, S.I. and Davies, B.E.: 2000, Total and extractable trace elements in Lebanese river sediments: dry season data, *Environmental Geochemistry and Health* **22**, 265–273.
- Lewis, D.W. and McConchie, D.M.: 1994, *Analytical Sedimentology*, Chapman and Hall, New York, USA.
- Large, R.R. and McGoldrick, P.J.: 1998, Litho-geochemical halos and geochemical vectors to stratiform sediment hosted Zn-Pb-Ag deposits, 1. Lady Loretta Deposit, Queensland, *Journal of Geochemical Exploration* **63**, 37–56.
- Lebanese MOE (Ministry of Environment): 1997, Resolution No. 1/182, *Official Gazette* **20** (in Arabic).
- Martin, J.M. and Meybeck, M.: 1979, Elemental mass balance of material carried by world major rivers, *Marine Chemistry* **7**, 173–206.
- Morel, F.M.M.: 1983, *Principles of Aquatic Chemistry*, Wiley-Interscience, New York.
- Piron, M., Pineau, A. and Mabele, R.M.: 1990, Sediment, parameters and distribution of metals in fine sediments of the Loire estuary, *Water, Air, and Soil Pollution* **50**, 267–277.
- Ritchie, J.M., Cresser, M. and Cotter-Howells: 2001, Toxicological response of a bioluminescent microbial assay to Zn, Pb and Cd in an artificial soil solution: relationship with total metal concentrations and free ion activities, *Environmental Pollution* **114**, 129–136.

- Stephenson, A., Labounskaia, I. and Stringer, R.: 1998, *Heavy Metal and Organic Screen Analysis of Environmental and Waste Samples Associated with Industrial Activities in Lebanon, September, 1997*, Greenpeace Research Laboratory, University of Exeter, UK.
- Trania, S.J. and Laperche, V.: 1999, Contaminant bioavailability in soils, sediments, and aquatic environments, *Proceedings of the National Academy of Sciences of the United States* **96**, 3365–3371.