

## Seasonal variations of trace metal chemical forms in bed sediments of a karstic river in Lebanon: implications for self-purification

Samira Ibrahim Korfali<sup>1,3</sup> & Brian E. Davies<sup>2</sup>

<sup>1</sup>Natural Science Division, Lebanese American University, P.O.Box, 13-5053, Chouran Beirut: 1102 2801, Beirut, Lebanon

<sup>2</sup>107 Teeside Drive, Anerson, SC 29625, USA

<sup>3</sup>Author for correspondence (fax: 009611867098; e-mail: skorfali@lau.edu.lb)

Received 9 January 2004; Accepted 2 December 2004

**Key words:** chemical speciation, karst, metals, seasonal variation, sediment, self-purification

### Abstract

Although Lebanon has abundant water, its rivers are polluted and aquifer water mismanaged. Effective river water usage requires an understanding of the geochemistry of polluting metals in catchments. Climate is “Mediterranean”: wet winters and dry summers. Active sediment flushing is restricted to winter high discharge episodes. Except in winter, water column pollutants are removed by precipitation or sorption to the surface of static bed sediments. Hence (1) does winter flushing of contaminated sediment and replacement by clean sediment favour self purification? (2) does the distribution of metals between extractable fractions change seasonally and thereby affect metal bioavailability? Results on the distribution of metals are reported for Fe, Pb, Zn, Cu and Cd in bed sediments from Nahr Ibrahim (a karstic river) for summer and winter. A Tessier-like sequential extraction scheme was applied to samples (< 75 µm) for five locations along a 13 km stretch to the sea. Water pH was above 8.2 at all locations implying a very low solubility for Fe. Sediment was derived from catchment soils and limestone. Total sediment Fe increased in winter at all sites following deposition of eroded soil from upstream. Cadmium, Cu and Pb derived from polluting sources; the sources of Zn were more complex. Dilution by clean sediment explained winter reductions in total Cd, Cu and Pb; Zn changes were less consistent. Iron occurred mostly (> 77% sum of fractions) in the residual fraction compared with 6–31% for pollutants; residual Cu and Zn showed a small increase in winter whereas Cd and Pb did not change. All readily exchangeable metals decreased in winter and the carbonate bound forms predominated in both seasons. Nahr Ibrahim has a high capacity for self purification and metal resolubilisation from sediment will be limited by the solubility of carbonate forms.

### Introduction

Lebanon has, potentially, an abundant water supply but utilization of its ground water is increasingly limited by generally unregulated exploitation and, along the populous coast, saline intrusions into aquifers (Sene *et al.* 1999) through over-pumping of private wells. A better utilization of river water is regarded as making a possibly significant contribution to national water needs (Jurdi *et al.* 2001). Technical studies have recommended that Lebanon build 16–20 dams in

various parts of the country (Amery 2002). However, Lebanese rivers are subject to pollution from many point sources (Jurdi *et al.* 2002) and development of an effective water usage strategy requires effective pollution remediation and, in turn, better information on the geochemical properties of the rivers and their capacities for self purification.

Many trace metals of toxicological significance (e.g., Cd, Pb) have low solubilities in the range of Eh and pH conditions found in natural waters and river sediments are sinks for trace metals mobilised

in the drainage basin (Salomons and Förstner 1984). Bed sediment metal contents reflect the influence of catchment lithology, anthropogenic contamination and chemical reactions (precipitation, complexation, adsorption) between the water column and the sediment particle surfaces. Transport, deposition, resuspension and solubilisation of these metals in the fluvial system is dominated by hydrological processes and by the chemistry of the water column; there are many gaps in our understanding of this complex system (Foster and Charlesworth 1996).

The climate of Lebanon is typically 'Mediterranean', i.e. characterised by cool, wet winters and hot, dry summers. Lebanon's precipitation is limited to 80–90 winter days every year and river discharge is low in the summer dry season (Amery 2002). Active downstream flushing of sediment is restricted to the high discharge episodes of the winter wet season. For much of the year pollutants entering the fluvial system will be incorporated into bed sediments by precipitation on and sorption to the surface layer of static bed sediments.

This paper reports sediment trace metal data for Nahr Ibrahim, a major Lebanese river subject to industrial metal pollution in its lower reaches. Its drainage basin is largely floored by limestone. In the wet winter season the river Nahr Ibrahim carries a high suspended sediment load which gives it a reddish colour whereas during the dry summer season the river runs slow and clear. Two questions were identified:

- (1) Whether high winter discharge contributes to effective 'self-cleansing' through flushing contaminated sediments towards the Mediterranean sea and replacement by uncontaminated sediment derived from the river's upper reaches on Mount Lebanon. An overall reduction of total contents of polluting metals in the winter samples would be evidence in favour of a process of self-purification.
- (2) Whether the distribution of polluting metals in chemical fractions of the sediment differs between the two seasons. The occurrence of toxic metals in sediment labile chemical pools in summer would indicate that pollutant capture was through sorption or precipitation processes at the water-sediment interface.

In an earlier paper (Korfali and Davies 2000) the total and extractable metal (Fe, Cu, Pb, Zn) con-

tents of bed sediments (< 75 µm fraction) were reported for five locations along the lower 13 km stretch of Nahr Ibrahim. The data were for samples collected during the dry season of 1996. It was concluded that water pH (8.2–8.7) was typical for a karstic river, that Fe in the sediments was derived from geological sources whereas Cu, Pb and Zn were anthropogenic in origin.

The objectives of this paper are to compare and contrast two bed sediment trace metal data sets, the previously published (Korfali and Davies 2000) August 1996 data and unpublished February 1997 data in an attempt to assess the river's self cleansing capacity and to infer possible hydrochemical controls on bed sediment trace metal composition. Total Fe, Cd, Cu, Pb and Zn sediment concentrations are reported as well as the partitioning of these metals among (operationally defined) chemical pools derived from a sequential chemical extraction procedure. Iron was presumed to be a marker element for uncontaminated sediment while the other metals are those commonly carried into water ways from pollution sources. Selected water chemistry data are also reported.

### The study area

The research concerned the lower 13 km of the river Nahr Ibrahim, down to its confluence with the sea (Figure 1). The Nahr Ibrahim basin encompasses 330 km<sup>2</sup> in central Lebanon. The river discharges into the Mediterranean Sea south of the city of Byblos (Jubayl) and stretches 30 km inland to its two main sources, the Afqa and Roueiss springs, located at an altitude of 1200 m on Mount Lebanon. Much of the valley is canyon-like, occasionally broadening out to small floodplains, before entering the coastal lowland. Most of the rocks exposed in the valley are fractured karstic limestone of Cenomanian age and fractured karstified massive dolomite, dolomitic limestone and bedded limestone of the Jurassic period. Sandstone and sandy limestone are of limited occurrence. Rocks outcropping in the bottom of the valley belong to the middle and upper Cretaceous period (Sannine and Maameltain Formations) limestones and dolostones. Quaternary alluvial deposits occur near the river mouth and upstream, basaltic volcanic rocks outcrop (Abdel-Rahman and Nader 2002). The water chemistry is

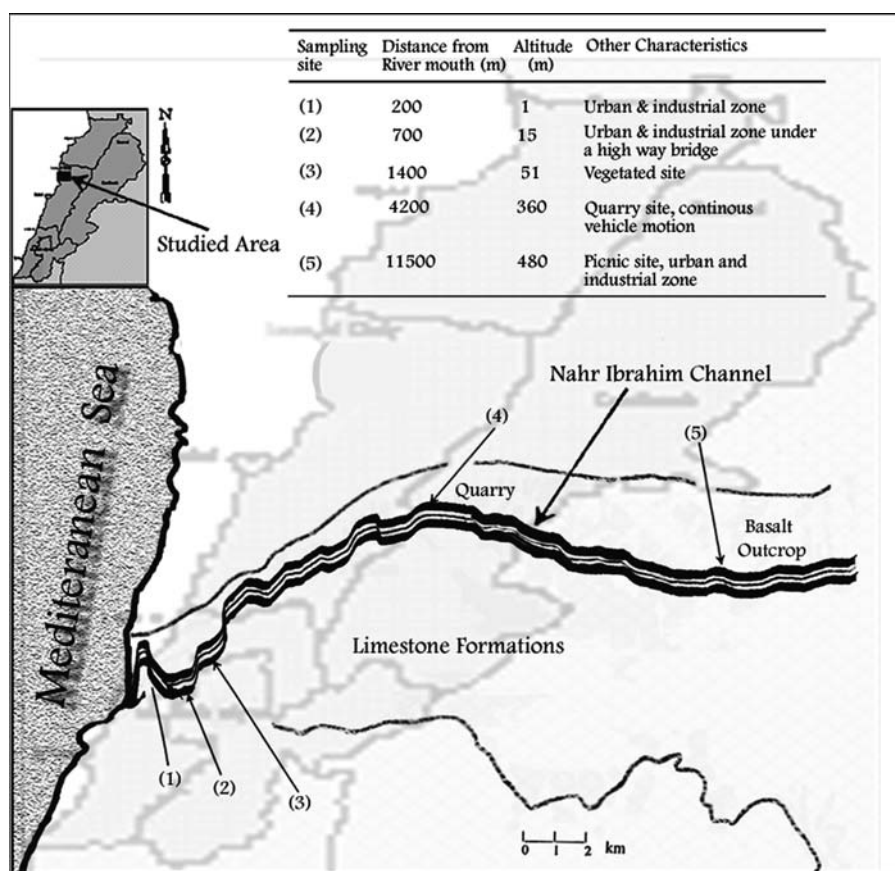


Fig. 1. Locations and sampling sites with respective characteristics.

controlled by the carbonate bedrock (Korfali and Davies 2000).

Lebanon has a warm/hot, dry summer and a cool/cold, wet winter. Heaviest precipitation occurs between November and April and no rain falls in June, July and August (Sene *et al.* 1999). The hydrological characteristics of the river reflect this marked seasonality. In the wet winter season, the river Nahr Ibrahim carries a high suspended sediment load but during the dry summer season the river runs clear and discharge is low. The average annual discharge of the river Nahr-Ibrahim is  $12.77 \text{ m}^3 \text{ s}^{-1}$ ; the average discharge for the wet season is  $20.88 \text{ m}^3 \text{ s}^{-1}$  and that of the dry season is  $4.65 \text{ m}^3 \text{ s}^{-1}$ . Discharge for the first dry season sampling on August 24, 1996 was  $1.06 \text{ m}^3 \text{ s}^{-1}$  and February 26, 1997 it was  $25.3 \text{ m}^3 \text{ s}^{-1}$  (Lebanese Ministry of Hydraulics and Electrical Resources – MHER). Figure 2 depicts the climatic and discharge data.

## Materials and methods

### Sampling methods

Five sampling sites were chosen (Figure 1) along a 13 km stretch of the river Nahr Ibrahim upstream of its confluence with the Mediterranean Sea. The choice of these sites was based, firstly, on the practicability of collecting bed load sediments (especially accessibility) and secondly the observed likelihood of metal contamination by domestic wastes, industrial discharges and high vehicle movements.

Bed sediments were collected during the dry season (August 1996), and the wet season (February 1997). The method of collecting bed sediments followed published methods for collection in shallow streams (Chapman 1992; Lewis and McConchie 1994) and were reported in full in our earlier paper (Korfali and Davies 2000). At each

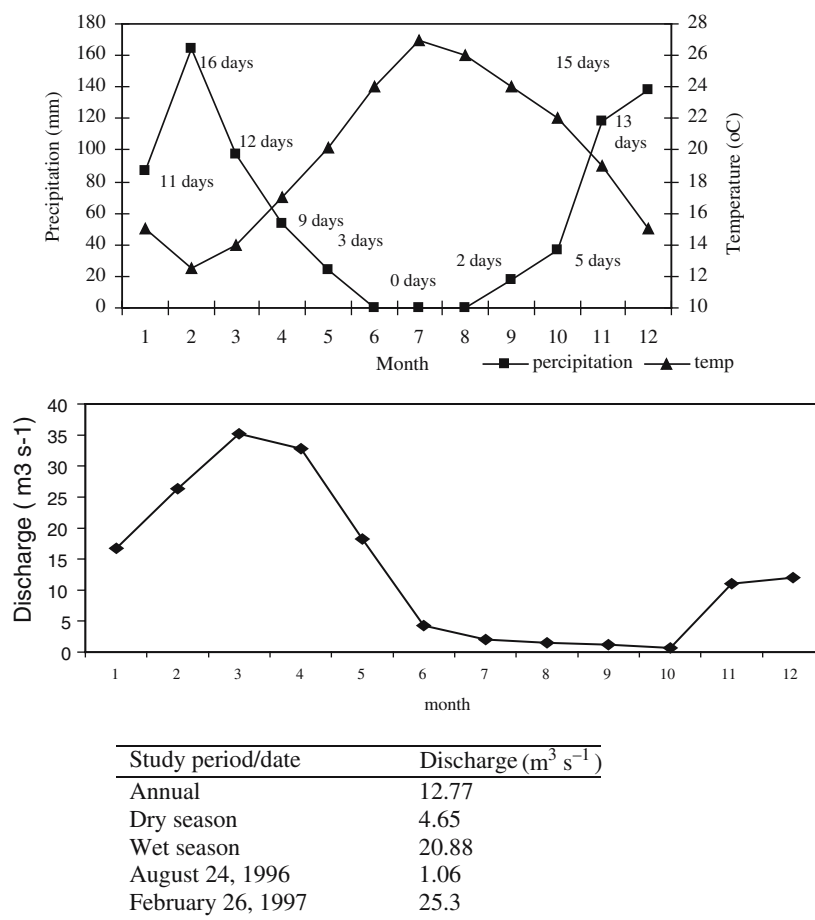


Fig. 2. Variation of climate and discharge of studied area.

collection site four, sub-samples were taken and bulked in one polyethylene bag. Careful note was made in August 1996 of the positions of the sampling sites so that the identical locations could be resampled the following February.

Measurements of water pH and temperature were made in the field using a Hach Model 44,600 m. Water samples were collected using one-litre polyethylene bottles that had been soaked overnight in 10% (v/v) nitric acid and then rinsed with distilled water. Before filling with the sample they were also rinsed twice with river water. Each water bottle was labelled with its sampling site number, time and date of collection.

#### Experimental methods

Methods were reported in full in Korfali and Davies (2000) and are repeated here in shortened form.

#### Water analysis

After arriving at the laboratory, water samples were immediately filtered through 0.45  $\mu\text{m}$  pore cellulose filters by vacuum suction into Pyrex™ flasks that had been previously washed in 10% v/v nitric acid. The water samples were transferred into one-litre polyethylene bottles, acidified and stored at 4 °C prior to analysis.

#### Sediment treatment and analysis

Sediments were dried and sieved and the < 75  $\mu\text{m}$  fraction was retained for analysis.

A modified sequential chemical extraction procedure was used based on Chao (1972), Tessier *et al.* (1979), Baghdady and Sippola (1983), Kersten and Förstner (1989). One gram of each sediment sample was used and six (operationally defined) fractions were derived:

- F1: exchangeable, extracted by 1 mol L<sup>-1</sup> CH<sub>3</sub>COONH<sub>4</sub>  
 F2: specifically sorbed or carbonate-bound, extracted by CH<sub>3</sub>COONa/CH<sub>3</sub>COOH at pH = 5  
 F3: easily reducible, extracted by 0.1 mol L<sup>-1</sup> NH<sub>2</sub>OH.HCl  
 F4: moderately reducible, extracted by 0.04 mol L<sup>-1</sup> NH<sub>2</sub>OH.HCl  
 F5: organically bound, extracted by 0.02 mol L<sup>-1</sup> HNO<sub>3</sub>/30% H<sub>2</sub>O<sub>2</sub>  
 F6: residual extracted by hot *aqua regia*.

Metals in solution (Fe, Cd, Cu, Pb and Zn) were determined by flame atomic absorption spectrometry on three replicates. The total metal content in sediment was calculated by summing the metals in each sediment fraction. Analytical quality control was monitored by analysis of the standard certified reference Buffalo River sediment, Ohio, USA (SRM 2704, National Institute of Standards and Technology – NIST, USA). Eight replicates of SRM 2704 were analysed by the same experimental analytical procedure; the percentage relative standard deviation (%RSD) was < 10%.

## Results and discussion

### Water

Water pH, temperature and dissolved calcium values are given in Table 1 for each site in August 1996 and February 1997. In both months the pH values are around 8 (i.e. the river samples are alkaline) but those for February are generally lower. Lower pH values in the February samples are accounted for by dilution due to the higher discharge in that month. Water temperature was lower in February (mean

12.2 °C) compared with the previous August (mean 18.4 °C). Water temperature reflects summer/winter ambient temperatures.

Dissolved calcium was higher in August (mean 68.8 mg Ca L<sup>-1</sup>) compared with February (mean 56 mg Ca L<sup>-1</sup>). The decrease is also explained as dilution when discharge is high. Both sets of values are high. Published solubility constants for calcite (CaCO<sub>3</sub>) tabulate  $K_{so} = 8.35$  and the saturated equilibrium solution is 2.68 mg Ca L<sup>-1</sup>. Except for site 4 in February, all values are in excess of the calculated saturated solution concentration for water in contact with calcite. A known problem with conventional sample treatment in water analysis is that the 0.45 µm microfilter does not exclude colloidal forms (Benoit and Rozan 1999) and this permeability to colloidal precipitates would explain the apparent Ca over-saturation in the water samples. The conclusion is that water column conditions favour formation of colloidal calcium carbonate and subsequent precipitation on to bed sediment particles especially during the dry season. Work to test this hypothesis is in hand.

### Total sediment metals

Total metal contents (i.e., sum of six fractions) are given as mg metal kg<sup>-1</sup> in Table 2 for each site and in each month (August, the dry season and February, the wet season). The percentage change from summer to winter (wet/dry-season samples) is also recorded.

### Iron

In classical Greek times Nahr Ibrahim was known as the river Adonis and heavy rain made it “run red into the sea with dislodged soil”. The consistent red colour of the river in spate was the basis

Table 1. Main characteristics of Nahr Ibrahim River.

Site	Distance from mouth (m)	Altitude AMSL (m)	pH		Temp (°C)		Ca (mg L <sup>-1</sup> )	
			Aug	Feb	Aug	Feb	Aug	Feb
1	200	1	8.7	8.3	18.0	11.5	68	56
2	700	15	8.5	8.4	18.0	13.2	80	64
3	1400	50.5	8.5	8.4	18.5	12.5	60	80
4	4200	360	8.6	8.3	18.5	12.6	56	24
5	11500	480	8.5	8.2	19.0	11.0	80	56

Table 2. Variation of metal content (mg metal kg<sup>-1</sup>) among sites and seasonal (D is dry and W is wet season) and compared to other standard values.

Site	1	2	3	4	5	Mean	Shale <sup>a</sup>	Limestone <sup>b</sup>
Fe_D	13987	13496	18231	20551	23034	17860	34000	3651
Fe_W	30770	24337	21604	25318	25081	25422		
%changeFe	220.0	180.3	118.5	123.2	108.9	150.2		
Pb_D	112	149	110	140	76	117.4	20	2.82
Pb_W	54	52	44	62	35	49.4		
%changePb	48.2	34.9	40.0	44.3	46.1	42.7		
Zn_D	110	141	132	170	221	154.8	160	30.1
Zn_W	159	159	140	154	199	162.2		
%changeZn	144.5	112.8	106.1	90.6	90.0	108.8		
Cu_D	107	118	138	245	335	188.6	45	23.4
Cu_W	57	104	38	86	182	93.3		
%changeCu	53.3	87.7	27.5	35.1	54.3	51.6		
Cd_D	4.01	5.39	4.01	4.78	3.89	4.4	0.3	0.07
Cd_W	2.46	3.01	2.22	3.18	1.8	2.5		
%changeCd	61.3	55.8	55.4	66.5	46.3	57.1		

<sup>a</sup> Shale value adapted from Li (2000).

<sup>b</sup> Limestone values adapted from Abdel-Rahman and Nader (2002) and Li(2000).

for a myth involving the bloody death of a fertility god (Grant 1988). Rendell (1997) has reviewed earth surface processes in the countries of the Mediterranean Basin. Erosion has stripped soil from many areas of karst limestone outcrops and although limestone constitutes a substantial proportion of the bedrock in the Mediterranean Basin it provides very little suspended sediment.

Soils at the higher altitudes of Lebanon have been described by Darwish and Zurayk (1997). Loosely described as Red Mediterranean soils, they are, taxonomically, Ultisols (Ustalfs, Xeralfs). Soil colour (Munsell notation) is overall yellow-red, range 2.5-5yrs. Erosion of these soils is presumed to furnish the fresh sediment entering the river system in the winter period, especially at snow melt in early spring. Their iron contents (whole soil) are reported to range from 30,000–85,000 mg Fe kg<sup>-1</sup>.

Comparison with a 'shale standard' is a quick and practical means of assessing metal enrichments or depletions (Forstner and Wittmann 1979) in sediments. Soils and sediments are usually compared with standard shales. The tabulation of Li (2000) is used here for comparison and the cited values for shale are given in Table 2.

X-ray diffraction data for sediments from the Nahr Ibrahim River (Korfali and Davies, unpublished) indicate the dominance of calcite, dolomite and quartz in the mineralogy of the <75 µm fraction. Most of the visible coarse material in the stream bed is limestone/dolostone. These observations raise the question whether a standard limestone rather than shale should be used as the reference rock. In Table 2 the mean values for the dominant Sannine Formation limestone (Abdel-Rahman and Nader 2002), are entered (except for Cd and Cu, which were not reported) and the reference limestone values of Li (2000) are used. The (reference) value for Fe in Sannine limestone is 3651 mgFe kg<sup>-1</sup>. The mean dry season sediment Fe content is 4.5 times the reference value; similarly the wet season ratio is 7.0. The sediment iron data (Table 2) appear to match the shale standard better and is used as the basis for comparison in this discussion.

The reference shale Fe content is 34,000 mg Fe kg<sup>-1</sup> that is in the lower range of the published values for the Red Mediterranean soils. The mean Fe content for the dry season samples is 53% of the reference value and for the wet season samples, 75% of the reference values. It

should be noted that the Fe concentrations are probably an underestimate of the true total iron being the summation of the sequential fractionation sub-totals. Some iron is likely to remain in the sample even after the final *aqua regia* extraction. Further, X-ray diffraction analysis provides mineral data for crystalline material and peaks from microcrystalline material are difficult to separate while amorphous forms (e.g., recently precipitated ferrihydrite) cannot be identified. It is concluded that the fine bed sediment contains eroded and transported soil material as well as limestone/dolostone.

The total sediment Fe increased in the winter wet season compared with the previous summer (Table 2) at all sampling sites but there is no consistent variation trend downstream (Site 5 to 1) in wet season iron contents. In the dry (August) season, sediment iron contents decline progressively downstream until sites 1 and 2 (15 m apart). A weir between sites 1 and 2 would alter depositional processes.

We conclude from the iron data that sediment iron is naturally (geologically) derived. Delivery of fresh sediment from the uplands throughout this reach of the river can account for the overall increase in sediment iron and local variations of channel geometry can explain site-to-site variations. High winter discharge delivers fresh, presumably 'clean', sediment throughout the river length whereas in summer conditions of low flow, the sediment is neither disturbed nor transported but is subject to change through chemical deposition. The results are also consistent with Rendell's (1997) overview that suspended sediment in Mediterranean Basin karst rivers derives from eroded soil or soft sediments rather than the limestone bedrock.

#### *Lead*

Total lead values exceed the shale reference value in both months and at all sites. They also exceed the local limestone mean concentration by a factor of 42 (dry season) and 17.5 (wet season). The sediments are presumed to be contaminated. In the winter samples the Pb contents are (average) only 42.7% of the dry season values. Since there are no grounds for assuming water course pollution is significantly lower in the winter the simplest explanation for the decrease in Pb is that of dilution by the incorporation of

fresh clean sediment derived from headwater soil erosion.

#### *Copper*

The ratio of (mean) wet season copper to the shale reference value is 2.1 and the corresponding dry season ratio is 4.2. The sediments are therefore regarded as copper-contaminated. The wet season contents are consistently lower than those for the dry season (27.5–87.7%, Table 2) which again favours a dilution effect through the incorporation of clean sediment.

In the wet season the copper contents show no consistent site-to-site variation whereas in the dry season they decline progressively downstream. The maximum copper value (both seasons) is at site 5. Near this site is an industrial zone including an electroplating works and contamination from the works would explain the high values. Site 2 also peaks in the wet season data. The Lebanon Electrical Company manufactures electrical wires here. Such wires are commonly fabricated from copper and leaching of copper discharges by winter rains, or erosion of contaminated soil into the stream channel may be an explanation of the high value.

#### *Cadmium and zinc*

Table 2 shows that dry season zinc decreases progressively down stream from site 5 whereas wet season contents show no consistent pattern. The high concentrations observed at site 5 can also be explained by the proximity of electroplating in the industrial zone. Downstream dilution from this source can adequately explain the dry season progressive decline. The zinc sediment contents do not differ greatly from the shale reference value and there appear no grounds for considering them significantly contaminated. They are on average 5.3 times higher than the published value for the Sannine limestone formation.

Cadmium is geochemically a close companion to zinc and the Zn/Cd ratio for rocks, soils and sediments is commonly reported as around 100/1. For example, Ure and Berrow (1982) tabulated world soil means as Cd = 0.62 mg Cd kg<sup>-1</sup> and Zn = 59.8 mg Zn kg<sup>-1</sup>; Zn/Cd ratio = 96.5. The Zn/Cd ratio for the reference shale is 533. The average ratio for Zn/Cd in the wet season sediments is 67.9 and 35.8 for the dry season. Judged by the reference shale value all the sediments are Cd-contaminated but the Zn/Cd ratio is unusually

narrow in the dry season. Wet season sediment Cd values show a similar overall reduction as Cu and Pb (mean 57.1%) indicating a clean sediment dilution effect. Changes downstream are not consistent for either season. These contradictory trends for Cd compared with Zn suggest either that the source(s) of Cd for Nahr Ibrahim differ from those for Zn or that the two metals follow different chemical pathways before incorporation into the sediment sink.

#### *Metals in chemical fractions of sediments*

It has long been recognised that the determination of the total metal content of sediments is useful but inherently limited for interpreting processes or ecotoxicology and information on 'speciation' should be sought. The sequential extraction system of Tessier (Tessier *et al.* 1979) has been widely used in sedimentary geochemistry. Kersten and Förstner (1995) have reviewed the technique's limitations. The fractions analysed are to be understood only as 'operationally defined' and may not represent real sediment fractions; redistribution between fractions may take place during the procedure; sequence is important; the efficiency of each extractant may be different for different metals (Miller *et al.* 1986; Quevauviller 1996; Ariza *et al.* 2000). Although the procedures are not recommended for fundamental studies they have proved their value for environmental studies (Hirner 1992).

The method used for this paper is adapted from the Tessier scheme. Fractions F1–F5 represent 'labile' fractions since they are removed by extractants which do not destroy the native minerals of sediments. The ammonium ion (as the acetate salt at pH 7), has commonly been the displacing ion of choice for readily exchangeable cations (outer sphere complexes) (Kersten and Förstner 1995). Fraction F1 is assumed to represent water soluble constituents plus readily exchangeable ions. The Tessier method extracts 'specifically sorbed or carbonate bound' ions with sodium acetate buffered to pH 5. Zwarich and Mills (1971) recommended this extractant for the quantitative determination of sedimentary calcite and dolomite. Fraction F2 is assumed to represent mainly soluble carbonates. Fractions F3 and F4 have been combined here as 'reducible' metals. Chao (1972) under experimental conditions reported acidified hydroxylamine hydrochloride as dissolving 85% manganese oxides and about 5% iron oxides. The combined F3 and 4 fraction is assumed to represent metals bound primarily to manganese oxyhydroxides with some contribution from iron oxyhydroxides. Fraction F5 is described in the Tessier scheme as dissolving organically bound metals. Residual metals are accounted for in fraction F6 and represent native forms.

Table 3 records the fractionation scheme results. The five sites were combined for each element and the data are as mean % total metal (sum of frac-

Table 3. Distribution of metals (average) in the different chemical fractions of sediment as percentages and metal content.

Fractions	August 1996					February 1997				
	F1 %	F2 %	F3_4 %	F5 %	F6 %	F1 %	F2 %	F3_4 %	F5 %	F6 %
Fe	0.11	0.90	16.21	6.20	76.87	0.07	0.58	10.71	4.74	83.90
Pb	3.17	44.94	29.60	12.45	9.62	1.17	42.83	34.00	12.70	9.11
Cu	18.26	25.02	8.72	25.27	22.83	6.22	22.02	10.44	23.22	39.02
Zn	11.15	25.22	28.16	4.66	30.82	3.00	13.36	25.68	6.61	51.36
Cd	10.0	53.4	26.1	4.0	6.4	6.8	48.6	32.3	6.0	6.3
Metal content	mg kg <sup>-1</sup>	mg kg <sup>-1</sup>	mg kg <sup>-1</sup>	mg kg <sup>-1</sup>	mg kg <sup>-1</sup>	mg kg <sup>-1</sup>	mg kg <sup>-1</sup>	mg kg <sup>-1</sup>	mg kg <sup>-1</sup>	mg kg <sup>-1</sup>
Fe	18.80	141.60	2870.40	1062.00	13833.80	16.80	142.00	2685.80	1224.80	21349.40
Pb	4.00	53.60	34.20	14.50	10.90	0.62	21.30	16.56	6.30	4.50
Cu	36.00	47.90	16.90	45.00	43.00	6.30	19.30	10.08	23.30	34.80
Zn	18.60	39.00	42.40	7.20	47.60	5.20	23.00	44.40	11.20	86.80
Cd	0.5	2.4	1.1	0.2	0.3	0.2	1.2	0.8	0.1	0.2



tions) and mean fraction metal (mg metal kg<sup>-1</sup>) for five fractions in summer and winter.

Iron speciation is dominated by the residual (F6) fraction and the labile fractions show proportional decreases from summer to winter. However, there are no significant decreases in the mean concentrations in each fraction except for the increase (1.5 fold) in the residual fraction. Darwish and Zurayk (1997) record goethite as the crystalline iron form in Lebanese red soils. Published solubility data for goethite ( $\alpha$ -FeOOH) show the equilibrium Fe<sup>3+</sup> concentration as negligible (10<sup>-24</sup> mol L<sup>-1</sup> at pH 8) (Lindsay 1979). It is unlikely that Fe will be solubilised from fresh incoming sediment to allow partitioning among the labile phases. The fresh sediment has increased total iron content but has not affected the partitioning of Fe in the summer bed sediment. It is concluded that the iron is naturally derived and is a marker of transported sediment.

Lead shows a 41.3% reduction in F6, residual Pb, from summer to winter. In fraction F3 and F4 absolute concentrations drop but proportionally rise from summer to winter. The significance of this is unclear at present. In both seasons, carbonate-bound lead is prominent (44.9% summer, 42.8% winter) with more lead (53.6 mg Pb kg<sup>-1</sup>) in this fraction in the summer than winter (21.3 mg Pb kg<sup>-1</sup>). This implies a probable role for carbonate precipitation or coprecipitation in removing polluting Pb from the water column under summer flow conditions. Two processes appear to be operative here. Fresh clean sediment brought in by turbulent flow in winter has decreased total sediment lead concentrations. In the summer low flow conditions Pb entering the water column is being sorbed to or precipitated on the bed sediment layer especially by carbonate precipitation or co-precipitation.

It was noted earlier that the total Cu decreased from summer to winter. The principal fraction change is in F1 where both absolutely and proportionally sorbed Cu decreases. Fraction F6 shows an increase proportionally and a decrease in absolute concentration of residual Cu. Decreases are principally in Cu bound in the labile fractions and carbonate-bound copper is prominent.

Total Zn (Table 2) changed relatively little (108.8%) from summer to winter. The data in Table III show that residual Zn (F6) increases by a

factor of 1.8 from summer to winter and there are major reductions in fractions F1 and F2, the exchangeable and carbonate-bound Zn. Compared with the shale reference the sediment is not Zn contaminated. These values are explained by assuming that about half the Zn is native Zn in winter. In summer sorption and coprecipitation of Zn from industrial effluents leads to partitioning among the labile fractions, especially the readily exchangeable and carbonate-bound pools.

Table 2 showed total Cd to reduce by 57.1%, from summer to winter. Table 3 shows that this is mainly due to reductions in the mobile phases, again suggesting a prominent role for Cd capture by sediments at the sediment-water interface.

The sequential fractionation results suggest complex chemical reactions are occurring as pollutant metals are removed from the water column and incorporated into the bed sediments. Further experimental work is needed to clarify these processes.

In brief Figure 3 is a schematic diagram that show the presumed/processes/going on that would anticipate the sediment metal content during the wet and dry seasons. Two season conditions-one is when the river is in spate and the chemistry operates in an environment of much suspended sediment and fast throughput including entrainment of bed material and transport of soil material from upstream bank erosion; other when flow is high but river runs clear, when little suspended sediment but nevertheless fast throughput of pollutants. In dry season, low discharge, no suspended sediment (but colloidal transport could be important), slow throughput of pollutants and emphases on sorption/precipitation of local pollutants.

## Conclusions

Sediment Fe is derived from sediments corresponding in composition to shale rather than to limestone. Although Nahr Ibrahim flows over karst limestone and much of the bed material is comprised of local carbonate rocks, the fine sediment Fe concentrations demonstrate incorporation of soil eroded higher in the drainage basin. In winter, when suspended sediment settles to the bed as the river fines down after a spate, the existing bed sediment is diluted by new material carried from upstream. For the moment, no direct evi-

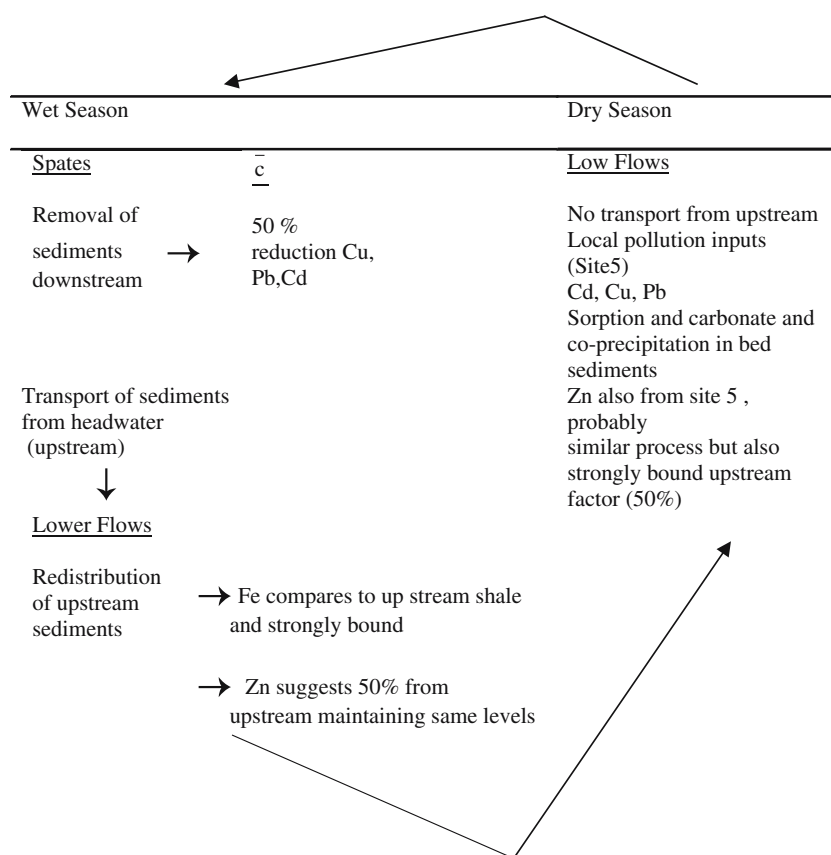


Fig. 3. Schematic diagram showing ongoing processes of metal deposition in sediment during dry and wet seasons.

dence is available to quantify any flushing process, through entrainment of bed sediment and its movement seawards, but the short river length (30 km) and the observation it runs red in winter indicates that flushing is probable. Further studies are planned to elucidate the flushing process.

Comparison of total toxic metal (Pb, Cu, Zn and Cd) contents with the shale standard shows that, except for Zn, these metals are primarily derived from pollution. Total cadmium, lead and copper reduce by an average of 50.5% from summer to winter. If this reduction is due to dilution by clean sediment then it is possible to make a very crude model estimate of the self purification capacity of Nahr Ibrahim if all pollution were to cease. Supposing the previous summer level is reduced by 50% each winter then between two to three years is all that would be needed to reduce each metal concentration to the shale reference. In practice this is unrealistic since

there are insufficient data to extrapolate a time series and floodplain storage represents a continuing source of potentially contaminated sediment (Walling *et al.* 1998). Nonetheless the estimate does highlight both the inherent self-purification capacity of the river and the urgency in controlling and reducing contemporary pollution.

The sequential fractionation results suggest complex water-sediment chemical processes. Bearing in mind that the fractions derived are operationally defined and may not correspond to actual chemical pools, the fate of polluting metals incorporated into bed sediments does appear to involve carbonate precipitation and bonding to oxyhydroxides. The solubilities of the metal carbonates are low (solubility products,  $K_{sp}$  are:  $CdCO_3 = 11.3$ ,  $CuCO_3 = 9.6$ ;  $PbCO_3 = 13.1$ ;  $ZnCO_3 = 10.8$ ) and carbonate compounds will minimise the aqueous concentrations of these metals.

## Acknowledgements

The authors are grateful to the Natural Science Division of Lebanese American University (LAU), Beirut, Lebanon for their provision of needed material and equipment and to the Learning Resources personnel for their quick provision of all needed documents.

## References cited

- Abdel-Rahman, A-FM Nader FH. 2002 Characterization of the Lebanese Jurassic-Cretaceous carbonate stratigraphic sequence: a geochemical approach. *Geol. J.* **37**, 69–91.
- Amery HA. 2002 Irrigation planning in Lebanon: challenges and opportunities. in Mehmet Ö, and Biçak HA (eds), *Modern and Traditional Irrigation Technologies in the Eastern Mediterranean*. Ottawa, Ontario Canada: IDRC 2002 publication, chapter 6.
- Ariza JLG, Giraldez D, Sanchez-Rodas D, Morales E. 2000 Selective assessment of a sequential extraction procedure for metal mobility characterization using model phases, *Talanta* **52**, 545–554.
- Baghdady NH, Sippola J. 1983 Total heavy metal recovery by aqua regia in soils of different origin. *Annales Agriculturae Fenniae* **22**, 175–178.
- Benoit G, Rozan TF. 1999 The influence of size distribution on the particle concentration effect and trace metal partitioning in rivers. *Geochimica et Cosmochimica Acta* **63**, 113–127.
- Chao TT. 1972 Selective dissolution of manganese oxides from soils and sediments with acidified hydroxylamine hydrochloride. *Soil Sci. Soc. Am. Proc.* **36**, 764–768.
- Chapman D. 1992 *Water Quality Assessments*. London, UK: Chapman and Hall, 583 pp.
- Darwish TM, Zurayk RA. 1997 Distribution and nature of Red Mediterranean soils in Lebanon along an altitudinal sequence. *Catena* **28**, 191–202.
- Forstner U, Wittmann GTW. 1979 *Metal pollution in the aquatic environment*. Berlin, Germany: Springer-Verlag, 486 pp.
- Foster IDL, Charlesworth SM. 1996 Heavy metals in the hydrological cycle: trends and explanations. *Hydrol. Proces.* **10**, 227–261.
- Grant M. 1988 *The ancient Mediterranean*. New York, Meridian (Penguin Group), 374 pp.
- Hirner AV. 1992 Trace element speciation in soils and sediments using sequential chemical extraction methods. *Int. J. Environ. Anal. Chem.* **46**, 77–85.
- Jurdi M Korfali SI, Karahagopian Y, Davies BE 2001 A prototype study for the management of surface water resources, Lebanon. *Water Policy* **3**, 41–46.
- Jurdi M, Korfali SI, Karahagopian Y, Davies BE. 2002 Evaluation of water quality of the Qaraaoun Reservoir, Lebanon. Suitability for multipurpose usage, *Environ. Monit. Assess.* **77**, 11–30.
- Kersten M, Forstner, U. 1989 Speciation of trace metals in sediments, in Batley GE (eds), *Trace Element Speciation: Analytical and Problems*. Boca Raton, Florida: CRC Press, Inc., pp. 247–317.
- Kersten M, Forstner U. 1995 Speciation of trace metals in sediments and combustion wastes. in Ure AM, Davidson CM (eds), *Chemical speciation in the environment*. London: Blackie Academic & Professional pp. 234–275.
- Korfali SI, Davies BE. 2000 Total and extractable trace elements in Lebanese river sediments: dry season data. *Environ. Geochem. Health* **22**, 265–273.
- Lewis DW, McConchie DM. 1994 *Analytical Sedimentology*. New York, USA: Chapman and Hall 197pp.
- Li Y-H. 2000 *A Compendium of Geochemistry*. Princeton, NJ, USA: Princeton University Press, 475 pp.
- Lindsay WL. 1979 *Chemical equilibria in soils*. New York: John Wiley and Sons, 449 pp.
- Miller WP, Martens DC, Zelazny LW. 1986 Effect of sequence in extraction of trace metals from soils. *Soil Sci. Soc. Am. J.* **50**, 598–601.
- Quevauviller P, Lachica M, Barahona E, Rauret G, Ure A, Gomez A, Muntau H. 1996 Interlaboratory comparison of EDTA and DTPA procedures prior to certification of extractable trace elements in calcareous soil. *Sci. Tot. Environ.* **178**, 127–132.
- Rendell H. 1997 Earth surface processes in the Mediterranean. in King R, Proudfoot L, Smith B (eds), *The Mediterranean: Environment and Society*. London: Arnold, pp. 45–56.
- Salomons W, Forstner U. 1984 *Metals in the Hydrocycle*. Berlin, Germany: Springer-Verlag, 349 pp.
- Sene KJ, Marsh TJ, Hachache A. 1999 An assessment of the difficulties in quantifying the surface water resources of Lebanon. *Hydrol. Sci.* **44**, 79–96.
- Tessier A Campbell PGC, Bisson M. 1979 Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry* **51**, 844–851.
- Ure AM, Berrow ML. 1982, The elemental constituents of soils. in Bowen HJM (eds), *Environmental Chemistry*. London: Royal Society of Chemistry, vol. **2**, pp. 94–204.
- Walling DE, Owens PN, Leeks GJL. 1998 The role of channel and floodplain storage in the suspended sediment budget of the River Ouse, Yorkshire, UK. *Geomorphology* **22**, 225–242.
- Zwarich MA, Mills JG. 1971 An evaluation of three methods for the quantitative determination of calcite and dolomite in soils and geological sediments. *Can. J. Earth Sci.* **8**, 967–972.