Distribution and bacterial bioavailability of selected metals in sediments of Ismailia Canal, Egypt

Hanan S. Ibrahim[a], Medhat A. Ibrahim[b],*, Farag A. Samhan[a]

[a] Water Pollution Research Department, National Research Centre, Dokki, Cairo, Egypt
[b] Spectroscopy Department, National Research Center, NRC, Dokki, Cairo, Egypt

ABSTRACT

The spatial and temporal variability in concentrations of heavy metals, and the portion of the bioavailable metals for bacterial community of Ismailia Canal sediment were conducted. Furthermore, Fourier Transform Infrared Spectroscopy (FTIR) was employed to elucidate the molecular structure of the same sediment samples. Results indicate that Cu, Cr and Zn concentrations showed temporal variation ($p \leq 0.05$). However Pb and Zn showed significant spatial variation ($p \leq 0.05$). Also, the mean value of Pb and Zn in sediment is higher than the shale reference value. There were no temporal or spatial significant in the total viable bacterial count (TVBC) for all sites while Zn shows the highest affinity for bacterial uptake followed by Ni > Pb > Cu > Cr > Co. Also, the shift in the C=O suggested that hydrated divalent metals are interacting with organic acids to form hexahydrated metals carboxylate. There were non-significant interactions between temporal and spatial variation for all the studied metals.

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1. Introduction

Nile River is the main water source for Egypt and the traditional concern with securing sufficient water for Egypt's survival and economic development cannot be overemphasized. At the same time, uncontrolled wastewater discharges are causing immediate and long-term water quality health impacts on the users [1]. Heavy metals have a great ecological significance due to their toxicity and accumulative behaviour [2]. They are not biodegradable, contrary to most pollutants, and undergo a global ecobiological cycle in which natural waters are the main pathways [3]. Sediments are considered to be the ultimate sink for many contaminants and therefore pose the highest risk to the aquatic environment as a source of pollution [4–15]. Therefore, the analysis of river sediments is a good indicator of the river water quality [16].

On the other hand Fourier Transform Infrared Spectroscopy (FTIR) can be potentially used to identify the structural characteristics of matter. It is of diagnostic value for reactive functional groups; and being used by many researchers for studying soil organic matter [17,18]. Recently; FTIR is used extensively to elucidate the structure of sediment [19,20]. Furthermore, both molecular modelling as well as FTIR was used to study the molecular structure of Nile sediment in greater Cairo region [21].

Ismailia Canal is one of the largest freshwater canal branched from the Nile and has become of importance since it provides water for irrigation; navigation; industrial and domestic purposes to areas in the eastern region of Egypt. It is 294.35 km long and the average of each of water depth is 2.8 m, water velocity is $0.28\,\mathrm{m\,s^{-1}}$ and its discharge reached $7 \times 10^6\,\mathrm{m^3\,s^{-1}}$ [22]. The present work was established to evaluate temporal and spatial variability in concentrations of selected metals namely Cd, Cu, Cr, Pb, Ni, Co, and Zn; molecular structure as well as bacterial count and content of metal uptake for surface sediments in Ismailia Canal at 12 sites covering the industrial activities such as petroleum, petrogas, iron and steel and detergent industries as well as water treatment plants and power station.

2. Material and methods

### 2.1. Reagent and standard solutions

All reagents used were of analytical grade (AR) and deionised water was used throughout. All standard metal solutions for atomic absorption spectrometric determinations were prepared from certified atomic absorption metal stock solutions (Merck chemicals Ltd., Germany) by appropriate dilutions. Calibration curves were constructed composed of a blank and three standards.

2.2. Sample collections and preparations

Sediment samples were collected from 12 sites along Ismailia Canal East of Shubra El-Khema as indicated in the map (Fig. 1). Samples were collected by means of stainless steel Ekman dredge sediment sampler. Possible contamination from the metal con-

* Corresponding author.
 E-mail address: medahmed6@yahoo.com (M.A. Ibrahim).
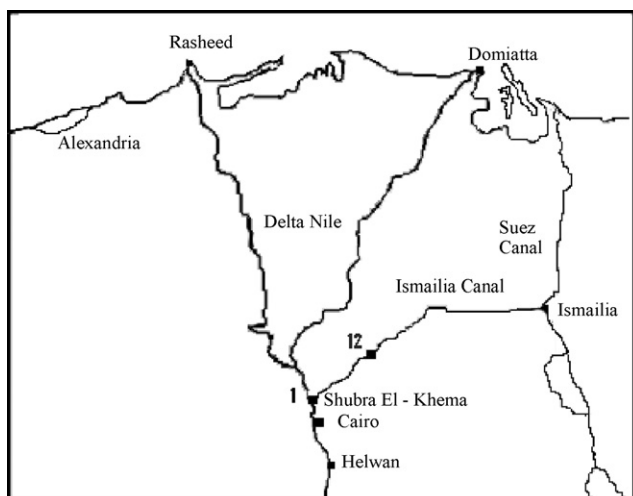
Latitude, 30.0667 N; longitude, 31.2667; Altitude, 10 m above sea level
(1 cm -----45 km)

Fig. 1. The sample locations at Ismailia Canal in Egypt.

struction of the dredge sampler could be avoided as sub-samples were taken from its centre with a fluorocarbon plastic tube. Samples were transferred into polyethylene vessels and stored at $-60\,°C$ till analyses [23]. Then samples were divided into three parts.

For heavy metals determination: sediment samples were dried at $65\,°C$, and powdered in an agate mortar then weighed and acid digested [23].

For bacterial count and analysis: the extraction of bacteria from sediment was adapted from Lehman et al. [24], 10 g from the sediment sample was taken from each sample and placed into a flask containing 90 ml of 0.1% sodium pyrophosphate solution. The culture solution was shaken continuously for 24 h at 150 rpm in a rotary shaker at room temperature ($\sim25\,°C$), enabling the bacteria to be eluted into the suspended solution from the sediment. After elution the tubes are left to setteldown for 2 h, the supernatant was transferred to another tube, where the total bacterial count was carried out according to "Standard Methods" [23] with poured plate technique (plate count agar, Difco), the rest of the culture solution was digested to measure the concentration of heavy metals.

For FTIR measurements, dried samples at $65\,°C$ were mixed with potassium bromide (KBr) (1 wt% per weight) and pressed in pellets.

All experimental procedures were repeated on 3 samples from each site to ensure precision and accuracy.

2.3. Instrumentations

Atomic Absorption Spectrometer Varian SpectrAA (220) with graphite furnace accessory and equipped with deuterium arc background corrector was used for determination of total metals concentration. To achieve the accuracy of measurements deuterium lamp was used to avoid back ground interferences especially for Cd, Co, Pb, Ni and Zn respectively. Also the operational conditions

in Table 1 were applied in order to analyze the studied samples; acetylene flow was kept constant at 2.0 l/min.

Fourier Transform Infrared Spectrometer JASCO, FTIR-300 E., in the range of $400–4000\,cm^{-1}$, was applied for elucidating the molecular structure of the sediment samples.

2.4. Statistical analysis

Data were analysed for spatial and temporal variations through SPSS version 14 using Multivariate Analysis and significance levels of tests were taken as $p \leq 0.05$.

3. Results and discussion

Sediment characteristics provide information about the accumulation and integration of metal discharges over time [25]. Therefore, analysis of Ismailia Canal sediments may provide important information on contaminant inputs into aquatic ecosystem. Spatial variations in the concentration for each metal are indicated in Fig. 2. The total metal concentrations in sediment samples were ranged from 36.88 to 17.07, 26.07 to 14.81, 67.03 to 27.50, 115.82 to 27.32, 44.03 to 18.53 and 108.3 to 61.03 mg/kg for Cr, Co, Cu, Pb, Ni, and Zn, respectively.

Cd was found below the detection limits. Table 2 presents the mean concentrations, standard error, spatial and temporal variations for each metal during the studied period. The average concentrations of the studied metals show the following decreasing order:

Zn > Pb > Cu > Ni > Cr

Several authors proposed that, reference shale compositions can be used as a quick and practical means of assessing metal enrichment or depletion in River sediments [26–28]. For all metals studied in the Ismaillia canal sediments, Pb and Zn content exceed the shale reference value, while Cu is comparable to the shale reference value. It is stated that Cu, Pb and Zn in the sediments have anthropogenic origin [29–31]. The presented result is in agreement with this statement. While the mean value for Cr, Co and Ni are found below reference shale value.

There were significant temporal variations in concentration of Cu ($F = 3.763$; $p < 0.05$), Cr ($F = 3.303$; $p = 0.05$) and Zn ($F = 3.186$; $p = 0.05$) in the sediment, other metals are considered non-significant. Only Pb and Zn showed spatial variation; $p < 0.05$; which may be due to their high concentration levels as compared with that of shell level. Regarding the temporal and site interaction one can conclude that, there is no significance for all the studied metals.

For bacterial community, the average TVBC in sediment samples did not show sharp fluctuation from site to site or from season to other. The mean value of the TVBC ranged from 3×10^5 CFU/g to 6×10^6 CFU/g.

Spatial variations in the concentration for uptake of metals by bacterial community are indicated in Fig. 3. The bioaccumulation of metal by bacterial community in sediment samples were ranged from 1.05 to 0.14, 0.61 to 0.13, 0.85 to 0.14, 1.2 to 0.61, 1.1 to 0.30 and 1.85 to 0.28 mg/kg for Cr, Co, Cu, Pb, Ni, and Zn, respectively.

Table 1
Analytical conditions used in the analyses of the studied heavy metals using Varian SpectrAA 220 Flame Atomic Absorption Spectroscopy.

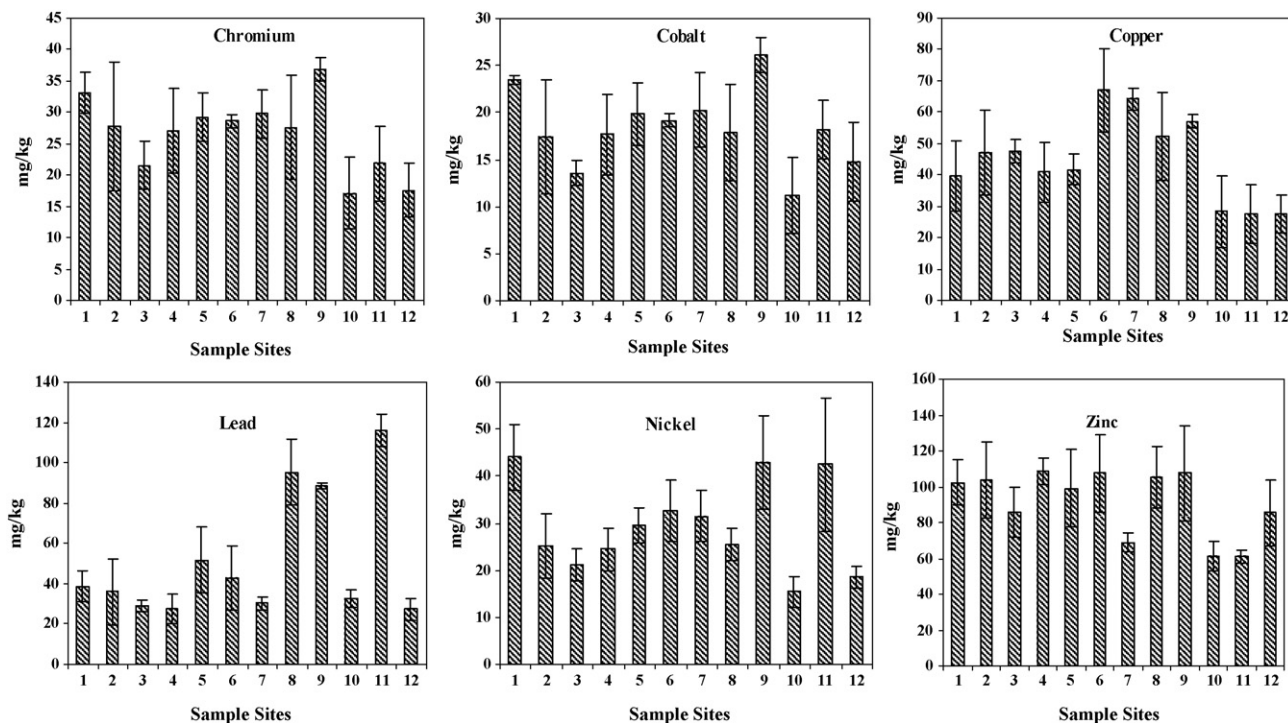| Metals	Wavelength (nm)	Slit width (nm)	Air flow (l/min)	Detection limit (mg/l)
Cadmium	228.8	0.5	13.5	0.010
Chromium	357.9	0.2	13.5	0.020
Cobalt	240.7	0.2	13.5	0.050
Copper	324.8	0.2	13.5	0.010
Lead	217.0	1.0	13.5	0.060
Nickel	232.0	0.2	13.5	0.030
Zinc	213.9	1.0	13.5	0.006

Fig. 2. Spatial variations in the concentration (±SE) for each metal in the different sites from April to October 2006.

Table 2
Spatial and temporal variations in the means concentration (±SE) for each metal in the total samples from all sites during the studied period.

Metals	Shale	mg/kg		Studying period April to October 2006		Sample points		Studying period and sample sites	
		Means	SE	F-ratio	Significance	F-ratio	Significance	F-ratio	Significance
Chromium	90	26.49	1.64	3.303	$p = 0.05$	3.2	NS	0.493	NS
Cobalt	19	18.29	1.09	2.045	NS	0.657	NS	0.734	NS
Copper	45	45.05	3.15	3.763	$p < 0.05$	1.988	NS	1.38	NS
Lead	20	51.3	5.56	0.778	NS	5.406	$p < 0.05$	0.69	NS
Nickel	50	29.46	2.24	0.197	NS	0.197	NS	0.223	NS
Zinc	95	91.31	4.92	3.186	$p = 0.05$	4.67	$p < 0.05$	1.046	NS

Studying period: the significant effects of the differences of the season of collection on each metal. Sample sites: the significant effects of the difference of the collected sites on each metal. Studying period and sample sites: the significant effects of the interaction between the difference of the sample sites and the difference in the season of collection on each metal.

Bacteria as community as a living organism showed a significant temporal variation in concentrations of Cr ($F = 11.32$; $p < 0.005$), Pb ($F = 7.81$; $p < 0.01$), and Co ($F = 14.6$; $p < 0.001$). On other hand, all metals showed non-significant spatial variation in the concentration, which expressed in the invariable count of the total viable bacteria of the sediment samples (Table 3).

Cr and Co showed significant variation with regard to spatial and temporal interaction, which reflects the effect of seasonal variation of the studied metals rather than spatial effect.

Zn has the highest affinity for bacteria uptake followed by Ni > Pb > Cu > Cr > Co, these results complied with those obtained by [32]. Furthermore, the high percentage of the accumulated metals in bacteria may be a sign of potential pollution due to the greater mobility and thus indirectly increase the bioavailability as previously mentioned [33].

FTIR spectrum of sediment is studied in the region of 4000–400 cm^{-1} as indicated in Fig. 4. The assignment of the studied spectrum is listed in Table 4. The assignment is aided by our pre-

Table 3
Spatial and temporal variations in the means of metal concentration (±SE) in bacterial community in all sites during the half-year period from April to October 2006.

Metals	Heavy metals uptakes by bacteria (mg/kg)			Studying period April to October 2006		Sample sites		Studying period and sample sites	
	Means	%	SE	F-ratio	Significance	F-ratio	Significance	F-ratio	Significance
Chromium	0.34	1.3	0.09	11.324	$p < 0.005$	3.480	NS	4.690	$p < 0.05$
Cobalt	0.29	1.7	0.05	14.602	$p = 0.001$	2.708	NS	4.696	$p < 0.05$
Copper	0.49	1.3	0.07	0.485	NS	1.419	NS	2.240	NS
Lead	0.56	4.6	0.09	7.881	$p = 0.01$	0.003	NS	1.455	NS
Nickel	0.83	4.07	0.07	2.118	NS	0.107	NS	0.230	NS
Zinc	0.92	1.1	0.18	0.888	NS	0.425	NS	2.576	NS

Studying period: the significant effects of the differences of the season of collection on each metal. Sample sites: the significant effects of the difference of the collected sites on each metal. Studying period and sample sites: the significant effects of the interaction between the difference of the sample sites and the difference in the season of collection on each metal.
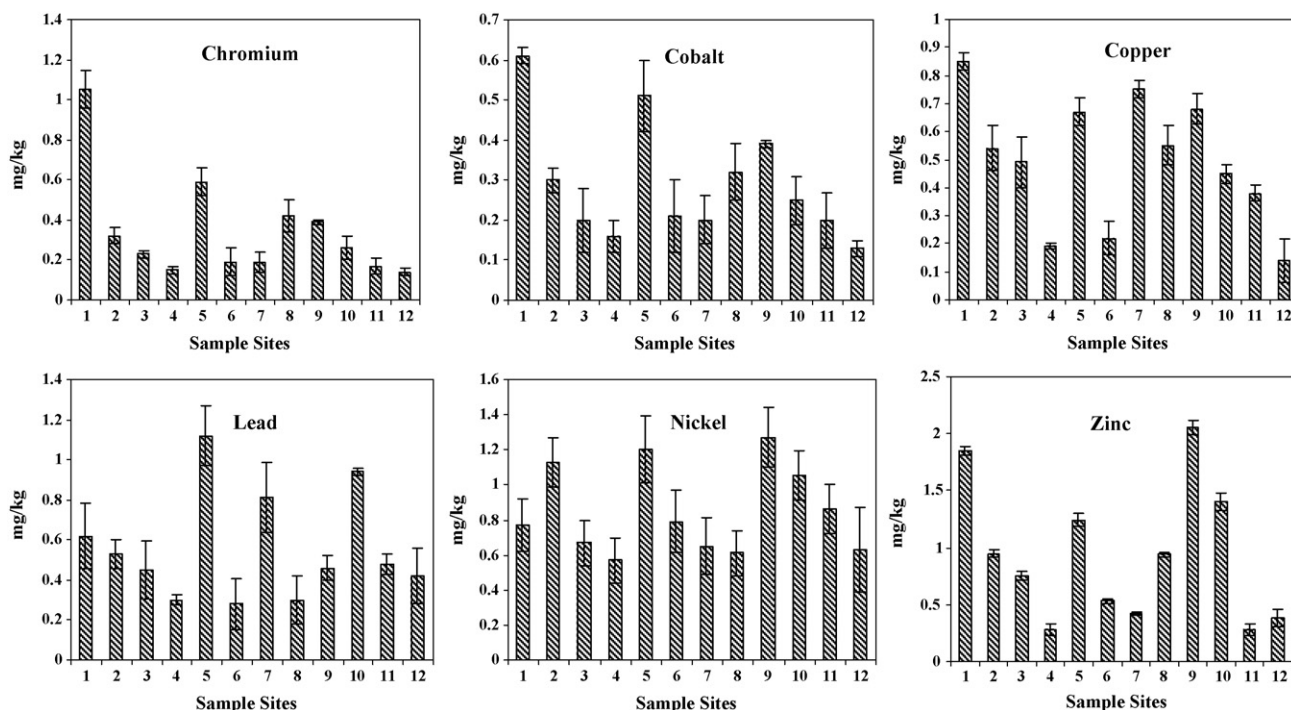
Fig. 3. Spatial variations in the concentration (±SE) for each metal in bacterial community from April to October 2006.

vious work on Nile sediment [21]. A band at $3696 cm^{-1}$ is assigned as the stretching vibration of kaolinite. The next band is assigned as aluminum hydroxide band which is followed by O–H stretching of water. The bands at 2900 up to $2337 cm^{-1}$ comes from the C–H symmetric as well as asymmetric stretching bands which may originates from aliphatic, aromatic and/or humic substances. Aluminum concentration was ranged from 115,00 mg/kg to 210,250 mg/kg and subsequently its band is varied from site to another according to the change in concentration and affect the band intensities as a result, especially at site 9 in front of Al-Amyria water treatment plant which used aluminium as coagulants. Furthermore, hydrated aluminum hydroxide is controlling the organometallic structure as it offers a wide surface for the organic structure to be adsorbed onto. Accordingly the increase in aluminium level leads

to a subsequent increase in the organic substance in the surrounding area of the canal which has also been reported to mediate the cycling of both essential and toxic trace metals [34]. The asymmetric stretching of carboxyl C=O is noticed at $1632–1637 cm^{-1}$. It is stated that, the position of COO bands at $1650–1620 cm^{-1}$ provides an indication as to the metal coordinated to carboxyl group of humic acid [35,36]. Based on this consideration together with that obtained elsewhere [37,38]; the peak around $1632–1637 cm^{-1}$ could be assigned as asymmetric stretching of metal carboxylate. Carbonate gives rise to a band at $1438 cm^{-1}$, which represent the reservoir of potentially available metals [12]; the region from 1107 up to $914 cm^{-1}$ is attributed to the silicate followed by O–H stretching band at $873 cm^{-1}$. Finally two regions namely $676–691 cm^{-1}$ followed by $529–465 cm^{-1}$ are assigned as deformation bands of metal oxide. Then the characteristic bands for hexahydrated metal oxides around $465 cm^{-1}$ which is described in our previous study [39,40].

The change in the intensity of the band at $1632–1637 cm^{-1}$ colud be due to the variation of metal concentrations from site to another which in turn enhance the metal carboxylate band at that site.
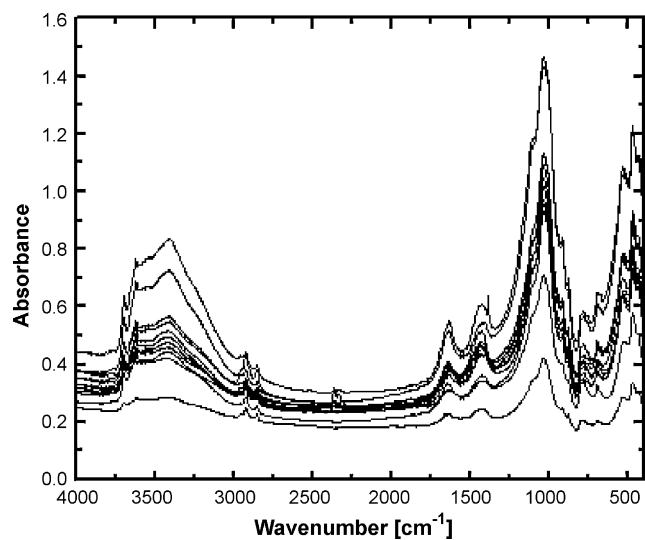

Fig. 4. FTIR spectra in the range from 4000 to $400 cm^{-1}$ for sediment samples which collected from Ismaillia canal.

Table 4
Band assignment for the obtained FTIR spectra of sediment samples.

Band frequency	Assignment
3696–3698	Str., vibr., of kaolinite
3619–3620	$Al_2(OH)_3$ smectites
3430–3436	O–H str.,
2924–2925	CH aliphatic
2851	CH aromatic
2358–2360	CH of humic substances
1632–1637	COO asymmetric stretching of metal carboxylate
1420–1434	Carbonate
1107	Asym., Si–O–Si
1030–1032	Silicate
913–914	$Fe(OH)_3$
874	OH vib.
778–693	Quartz
531–467	Deformation band of metal oxides

4. Conclusion

Sediments are an important trap for heavy metals, due to their temporarl storage capacity. Total metal concentrations generally decrease in the order: $Zn > Pb > Cu > Ni > Cr$.

Pb and Zn showed spatial variation; $p < 0.05$; which is due to their high concentration levels as compared with that of shell level.

The high percentage of the accumulated metals in bacterial community may be a sign of potential pollution due to the greater mobility and thus indirectly greater bioavailability.

FTIR indicate the presence of a shift in carboxyl group ($1632–1637\,cm^{-1}$) which reflects the interaction between the divalent hexahydrated metals and carboxyl group of the organic acid mainly humic acid. So that FTIR spectroscopy paves the way toward the possible release of some pollutants from the sediment. If a remobilization of this process takes place; divalent metals are then able to move towards the water column or accumulate in plants and consequently contaminate the food chain. Accordingly; these metals may undergo transformations and can have a large environmental, public health, and economic impact. Furthermore, the variations in band intensities from one site to another may be due to the release of divalent metals in one hand or to its bioavailability in the other hand. Therefore, enforcement activity by laws and regulations has been stepped up to protect the Nile as well as its branches from polluted wastewater discharges. Generally prohibit the use of waterways for the disposal of solid wastes and the discharge of untreated wastes from industries. Accordingly, the presence of organic structures play an important role in the distribution of studied metals rather than the industrial points of contamination which is located along the area of study.

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