

# Trace Metals in Wastewater Ponds in Qatar

Jamal A. Sweileh and Ibrahim S. Al-Naimi

Department of Chemistry

Hussain A. Abulfatih, Roda F. Al-Thani, Mahmoud M. Kardousha

Department of Biological Science

Elhaj A. Elhaj

Department of Marine Science

Faculty of Science, University of Qatar,

P.O. Box 2713, Doha, Qatar

## العناصر المعدنية الشحيحة في برك المياه العادمة في قطر

جمال أمين صويلح ، إبراهيم النعيمي - قسم الكيمياء

حسين أبو الفتح ، روضة آل ثاني ، محمود كردوشة - قسم العلوم البيولوجية

الحاج أبو جبر الحاج - قسم علوم البحار

كلية العلوم - جامعة قطر

تم تقدير كميات العناصر الشحيحة في بركتي المياه العادمة في منطقتي أبو هامور (ذات المياه غير المعالجة) وأبو نخلة (ذات المياه المعالجة) وذلك بأخذ وتحليل عينات مائية ورواسب بمعدل مرة واحدة شهرياً لمدة عام واحد. وبينت دراسة الترسيبات أن ترتيب معدل التركيز المتاح للعناصر الشحيحة على النحو التالي : منجنيز < نحاس < كروم < رصاص < نيكل .

وكما بينت الدراسة أن محتوى الكاديوم والزنك في العينات المائية والرواسب أقل من حد الكشف باستخدام مطياف الامتصاص الذري بالتدريجية الكهروحرارية. وأظهرت دراسة الرواسب أن تركيز عناصر النحاس والنيكل والمنجنيز لا تختلف عن نظيراتها في عينات من التربة أخذت من مواقع تبعد حوالي ١,٥ إلى ٣ كيلو متر من حدود البركتين، وهذا يدل على عدم تأثير التربة بطرح المياه العادمة في البركتين. أما بالنسبة لعنصري الكروم والرصاص فإن تركيزهما في رواسب كلا الموقعين يفوق تركيز نظيرهما في عينات التربة التي جمعت من مواقع بعيدة عن هاتين البركتين مما يدل على تلوثهما بهذين العنصرين وعلى سبيل المثال يبلغ معدل تركيز الرصاص في ترسيبات بركة أبو هامور ٦٠ مايكروجرام لكل كيلو جرام بينما يبلغ معدل تركيز الرصاص في التربة المجاورة الغير ملوثة بالمياه العادمة ٣٢ مايكروجرام لكل كيلو جرام. أما بالنسبة للمياه العادمة في كلا البركتين فإن تركيز العناصر أعلاه تقل كثيراً عن الحدود العليا المسموح بها لإعادة استخدامها للري الزراعي مما يوحي بخلوها من التلوث المعدني وامكانية استخدامها لهذا الغرض.

**Key Words:** Atomic absorption, Cadmium, Chromium, Copper, Graphite furnace, Lead, Manganese, Nickel, Sediments, Trace metals, Wastewater.

## ABSTRACT

A one-year monitoring program was conducted to determine the extent of metal contamination in two wastewater ponds in Qatar. Abu-Hamour pond receives untreated domestic and industrial waste while Abu-Nakhla pond receives treated wastewater from two nearby wastewater treatment plants. The concentration of available metals in wastewater samples ( $\mu\text{g/L}$ ) and in sediment samples ( $\mu\text{g/kg}$ ) follows the order  $\text{Mn} > \text{Cu} > \text{Cr} > \text{Pb} > \text{Ni}$ . The order of available metal concentration in un-impacted control soil samples taken from locations 1.5 to 3 km from the ponds is  $\text{Mn} > \text{Cu} > \text{Cr} = \text{Pb} > \text{Ni}$ . Levels of available mercury and cadmium are close to or below the limits of detection (LOD) for the employed graphite furnace atomic absorption spectroscopic method. Available metals in wastewater of both ponds are significantly less than the recognized permissible upper limits for agricultural reuse.

The available Mn, Cu and Ni in sediments are statistically equal to those obtained for unimpacted "control" soil samples. This indicates no environmental impact of wastewater discharge in the area on available Mn, Cu and Ni. Available Pb in pond sediments is statistically higher than that of control soil samples; Abu-Hamour pond sediments contain an average of  $60 \mu\text{g}$  lead /kg compared with  $32 \mu\text{g/kg}$  for the control samples. The average available Cr in the sediments of both ponds are statistically higher than the corresponding values for the control soil samples, indicating appreciable environmental impact.

## Introduction

Because of the ever-increasing interest in a cleaner and healthier living environment, the determination of the concentration of toxic metals in water and sediment is becoming detrimental. The impact of toxic metals on the environment is more pronounced than that of organic pollutants because these metals are not biodegradable as is the case with most organic pollutants [1]. Metals tend to accumulate on sediments by adsorption, sorption or complexation, and may be released and re-mobilized by various physical and chemical processes [2,3].

Current analytical methods for trace metal determination are well established and straightforward. However, the determination whether such concentration levels lead to significant pollution is still controversial [4]. Because pollution is only observed by its ill effect on the ecosystem. Biological availability of metals is a function of several complex variables associated with the nature of the metal species, the physico-chemical nature of the underlying sediment and the nature of exposed animals or plants [5].

In Qatar, the largest wastewater bodies close to urban areas are Abu-Hamour and Abu-Nakhla ponds. Literature search showed a severe lack of attention to those ponds and their impact on the quality of the environment in the area. Abu-Hamour pond receives untreated domestic and industrial wastewater while Abu-Nakhla pond receives treated wastewater from two sewage treatment plants in the area.

This project is aimed at characterizing the two ponds for trace metal contamination with the view of shedding some light on their status, compare them with similar ponds in the area, and recommend some reuse options. We have chosen to determine the "acid-soluble" metals in the wastewater and sediments

because this corresponds with the fraction of total metal that may be used to estimate the potential impact of such metals on aquatic life and water quality [6]. The elements selected were lead (Pb), cadmium (Cd), copper (Cu), nickel (Ni), chromium (Cr), manganese (Mn) and mercury (Hg).

## **Experimental Method**

### ***Study Site***

Abu-Hamour pond is located at the southern outskirts of Doha neighboring the industrial city. It receives both domestic and industrial wastewater. Abu-Nakhla pond is located about 7-km southwest of the industrial city on Salwa Road and receives treated wastewater only from two wastewater treatment plants in the area. Figure 1 shows the schematic shape of the two ponds and the sampling points.

### ***Sampling***

For each pond, samples of water and sediments were taken monthly between November 2000 and October 2001 at four locations indicated in Figure 1. Grab samples of water were taken in 1-L size acid-washed polypropylene bottles about 1.5 m from the shore at a depth of 10 to 25 cm. Using surgical gloves wet sediment samples were collected and transferred into seal-able polypropylene bags. All samples were shipped to the laboratory in ice-boxes and stored at 4°C. Six control soil samples were collected some 1.5 to 3 km away from each wastewater pond. Each sample was processed similar to pond sediments and analyzed for the targeted elements in duplicate.

### ***Sample treatment***

For the determination of acid soluble metals [7], 100 ml of each water sample (equilibrated at room temperature) was dispensed into a polypropylene beaker and acidified by addition of nitric acid (1:1, v/v) to pH  $1.75 \pm 0.1$  and left standing for 16 hours. Next, pH was rechecked and adjusted if necessary by addition of the above nitric acid or ammonia solution (1:10, v/v) and a portion of this sample was filtered using 0.45- $\mu$ m pore size cellulose filter (Millipore). The filtrate (about 35 ml) was then acidified with two drops of nitric acid and submitted for atomic absorption analysis in disposable plastic centrifuge tube. Turbid water samples were allowed to settle and the 100-ml aliquot was taken from the clear supernatant portion.

For sediments, the sample was dried at 90 °C, pulverized and homogenized. Then, 4.000 g of the powder was mixed with 100 ml of distilled de-ionized water and acidified with drops of nitric acid to pH  $1.75 \pm 0.1$  and agitated for 30 minutes. After standing at room temperature for 16 hours, the pH was re-adjusted, filtered using 0.45  $\mu$ m filter and the filtrate was treated as described above for water samples.

For the determination of mercury [8] 100 ml of the water sample was transferred to a biological oxygen demand (BOD) bottle and digested for 2 minutes with 5 ml of freshly prepared Aqua-Regia; mixture of hydrochloric and nitric acid (3:1, v/v) at 95 °C on a water bath. After cooling, 15 ml of 5% (w/v) potassium permanganate was added and the content was mixed thoroughly and digested on the water bath for 30 min. The solution was cooled and 6 ml of an aqueous solution of sodium chloride-hydroxylamine sulfate (12% each component, w/v) was added to reduce the excess permanganate. This solution (115ml) was

submitted for cold vapor atomic absorption determination using sodium borohydride reduction.

For sediments, 0.2000 g of the dried powdered sample was digested for 2 min. in a BOD bottle using 5 ml of Aqua-Regia and 5 ml of water at 95°C. After cooling, 50 ml of water and 15 ml of potassium permanganate solution were added and the treatment was concluded as described above for water samples.

For accuracy and precision check laboratory blanks and spiked blanks as well as duplicates for water and sediment samples were carried out through the whole procedure for all parameters.

### ***Instrumental analysis***

The determination of all metals was performed using Perkin-Elmer model AAnalyzer 700 atomic absorption spectrometer. The instrument is equipped with a deuterium lamp background corrector. Metals were determined using a Perkin-Elmer model HGA graphite furnace unit and an AS 800 auto-sampler. Mercury was determined by cold vapor technique using the flow injection accessory in a quartz tube atom cell. Mercury reduction was achieved by a solution was 0.2% (w/v) sodium borohydride in 0.05% (w/v) sodium hydroxide. Instrumental parameters for the each element are those recommended by the manufacturer. The atomic absorption instrument is controlled by a micro-computer based data acquisition system comprised of a Perkin-Elmer AAnalyzer software, a Dell GXI micro computer and a Hewlett-Packard model 895CXI printer.

### **Results and Discussion**

Initial data indicated very little variability in available metal content between sampling point in both wastewater and sediment samples. An exception is the second sampling point of Abu-Hamour pond, which is characterized by high oil content in both water and sediment. Therefore, a composite sample was made from sampling points H1, H3 and H4 only, while the second sampling point, H2 was treated as a separate sample. Figure 2 depicts month-to-month concentration of available trace metals in wastewater and sediment samples in both ponds.

The available concentrations of Cd and Hg in the study sites are below or close to the limits of detection (LOD). These limits of detection were calculated as the average laboratory blanks plus three times its standard deviation ( $n = 8$  to 12). The limit of quantification (LOQ) is taken as the average blank value plus 10 times its standard deviation [9]. The analytical precision for each element was calculated from the analysis of the field duplicate samples ( $n = 8$  to 12) [10]. Table 1 summarizes the data obtained for LOD, LOQ and analytical precision (expressed as the relative standard deviation, RSD) for available metal determination in wastewater and sediment samples.

The average available Pb concentration in wastewater of Abu-Hamour pond (1.92  $\mu\text{g/L}$ ) and Abu-Nakhla pond (1.65  $\mu\text{g/L}$ ) are statistically insignificantly different. However, month-to-month variability in Abu-Hamour pond is higher as indicated by the larger confidence interval of the mean value at 95% probability. For sediment samples, lead levels seem to have increased steadily during the study period (Figure 2).

For both ponds the average available Mn, Cu and Ni in ponds sediments are statistically similar (at 95 % confidence level) to the corresponding average available trace metals of the control soil samples. However, average available lead concentration in pond sediments is statistically higher than that of the control soil samples. For both locations the average available chromium concentration is higher than that of the corresponding control samples, which indicates a certain level of environmental impact. A summary of t-testing data is given in Table 2.

The “total” metal concentration in water is usually performed after strong acid addition and digestion. The “available “ metal concentration in wastewater performed in this work is similar to the total metal obtained by strong acid digestion because sediment-free water samples were used, and because GFAAS gives the total metal content of such samples. Therefore it is legitimate to compare the wastewater data with the international guidelines of the permissible metal content for water reuse. The concentration of available target metals in Abu-Hamour and Abu-Nakhla ponds are less than the upper limits of the Saudi Arabian guidelines for wastewater re-use [11] and even less than those of the World Health Organization’s guidelines for drinking-water quality [12].

### **Conclusions and Recommendations**

This work is the first systematic attempt to study the metal contamination of Abu-Hamour and Abu-Nakhla wastewater ponds and underlying sediments. The choice of “available” metal (leaching at pH = 1.75) rather than the total metal should yield the same values for water samples, but may give lower values for sediment samples. Available metal concentration is a better indicator of environmental vulnerability of the ecosystem to man-made pollution such as acid rain. Also, it could serve as an indicator for potential transfer of such pollutants to vegetation and aquatic life.

Overall, available metal contamination is low and if other aspects of water quality are favorable, the wastewater can be used for agricultural irrigation. A future study might correlate metal concentration in sediments and water to those in plants, birds and fish species inhabiting the area. Core sediment samples from several locations in the water body may shed some light on the history of waste discharge.

During the twelve sampling trips conducted in the two areas, we witnessed a thriving community of plants, fish species and different birds such as ducks, flamingos, kites, hawks, making the area a paradise for hunters and naturalists. Discharge in Abu-Nakhla pond was stopped for few months in spring 2001 that resulted in killing thousands of fish in dried out areas.

On the other hand, the untreated wastewater pond of Abu-Hamour is an environmental liability; the shores and sediments are soaked with oil and an offensive odor is strong especially at the discharge point H1. Extensive effort is needed to improve or eliminate this health hazard.

### Acknowledgements

The authors highly valued the assistance of Masoud Abdul-Raheem in sample collection and processing and Adel Mostafa in atomic absorption analysis. The financial assistance of the Scientific and Applied Research Center (SARC), of The University of Qatar, under project number 1-11/2000, is highly appreciated. The support and valuable comments of Homaid El-Madfaa the Director of SARC are also appreciated.

### REFERENCES

- [1] **Breder, R.; Nurnburg, H. W.; Goiimowski, and Stoeppler, M., 1985.** Toxic metal levels in the River Rhyne. 205 - 225, In Nurnberg, editor. Pollutants and their toxicological significance, John Wiley & Sons, N.Y., USA.
- [2] **Bero, A. S., and Gibbs, R. J., 1990.** Mechanisms of pollution transport in the Hudson estuary. The Sci. Tot. Environ., 97/98: 9 - 22.
- [3] **Combest, K., 1991.** Trace metals in sediments: spatial trends and sorption processes. Water Resources. Bulletin, 27/1: 19 - 28.
- [4] **Ongly, D. E.; Birkholz, D. A.; Carey, J. H.; Samoilloff, J., 1988.** Is water a relevant sampling medium? an alternative environmental sensing strategy. Environ. Qual. 17/3: 391 - 401.
- [5] **White, K. D.; Tittlebaum, M. E., 1984.** Statistical comparison of heavy metal concentrations in various Louisiana sediments. Environ. Monit. & Assess. 4: 163 - 170.
- [6] **Kiffney, P. M.; and Clements, W. H., 1993.** Bio-accumulation of heavy metals in benthic invertebrates at the Arkansas River, Colorado. Environ. Toxicol. & Chem. 12: 1507 - 1517.
- [7] **Martin, T. D.; O Dell, J. W., and McKee, G. D., 1992.** Method 200.1 Determination of acid-soluble metals. ICP Inform. Newslett. 18/3: 138 - 141.
- [8] **USEPA 1974.** United States Environmental Protection Agency, Method # 245.5.
- [9] **Guidelines for Data Acquisition and Data Quality Control in Environmental Chemistry 1980.** Anal. Chem. 52: 2242 - 2249.
- [10] **Harvey, D. 2000.** "Modern Analytical Chemistry", first edition, McGraw - Hill. Chapter 15, 705 - 724.
- [11] **Zahid, W.M.K., and Al-Rehali, A.M., 2000.** Reuse of municipal wastewater in Saudi Arabia: treatment systems, reuse activities and criteria. Arabian Gulf J. Sci Res. 18/2: 134 - 142.
- [12] **World Health Organization, 1995.** Guidelines for drinking-water quality Eastern Mediterranean Regional Office, Regional Center for Environmental Health Activities (CEHA), Amman, Jordan.

**Table 1**  
**Analytical performance parameters for trace elements in**  
**wastewater ( $\mu\text{g/L}$ ) and sediments ( $\mu\text{g/kg}$ )**

Parameter	Element						
	Pb	Cd	Cu	Ni	Cr	Mn	Hg
LOD ( $\mu\text{g/L}$ )	0.52	0.081	0.92	0.10	0.39	2.7	0.15
LOD ( $\mu\text{g/kg}$ )	4.6	2.0	23.0	2.5	6.75	67.5	100
LOQ ( $\mu\text{g/L}$ )	1.34	0.21	2.39	0.29	0.95	6.9	0.48
LOQ ( $\mu\text{g/kg}$ )	13.2	5.25	59.8	7.25	16.8	172	310
RSD% (water)	5.8	8.2	3.1	2.2	2.7	4.6	10.1
RSD% (solids)	6.4	13.7	5.2	3.9	4.0	4.2	14.5

LOD: limit of detection; LOQ: limit of quantification; RSD: relative standard deviation.

Table 2

Test of significance for average available metal concentration ( $\mu\text{g}/\text{kg}$ ) in pond sediments and control soil samples from Abu-Hamour (H) and Abu-Nakhla (K) areas.

Metal	Area	Sediments		Control Soil		$t_{\text{exp.}}$ *
		Mean	S.D.	Mean	S.D.	
Lead	H	60.5	3.75	32.6	2.02	20.5
	K	25.8	1.65	23.8	1.47	2.61
Copper	H	109.5	5.69	104.3	5.42	1.88
	K	123	6.66	118.0	6.13	1.58
Nickel	H	21.4	1.05	20.5	1.00	1.76
	K	25.2	1.24	24.8	1.22	0.65
Chromium	H	62.2	2.49	40.7	1.63	22.0
	K	49.7	1.99	19.2	0.77	46.6
Manganese	H	5955	250	6105	256	1.18
	K	6061	255	6016	253	0.59

\*  $t_{\text{exp}}$  is for 16 degrees of freedom at 95% confidence level. Theoretical t-value is 2.12



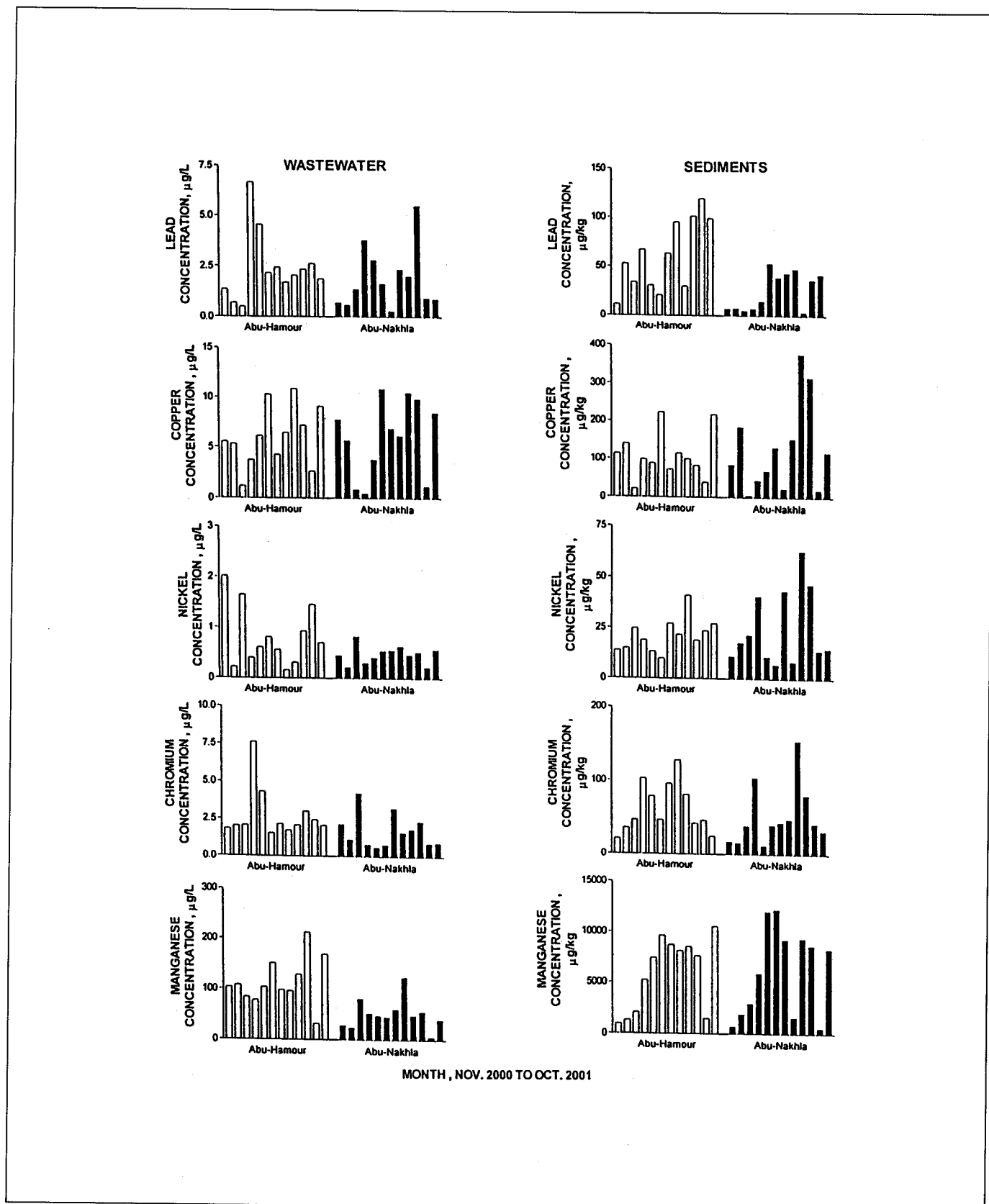


Figure 2. Available trace metal concentration in wastewater ponds ( $\mu\text{g/L}$ ) and sediments ( $\mu\text{g/kg}$ ).