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On-site preconcentration and trace metal ions determination in the Okavango Delta water system, Botswana

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Abstract

Microcolumns containing 8-hydroxyquinoline azo-immobilized on controlled pore glass were incorporated in a field sampler for on-site collection, isolation and preconcentration of trace metal ions in waters of the Okavango Delta, Botswana. Sequestered trace metal ions were recovered by elution with 0.5 ml of 1.5 M nitric acid, and determined by graphite furnace atomic absorption spectrometry (GFAAS). This sampling and enrichment method minimizes sample contamination, and collection of large volumes of water samples for transporting, over long distances, to analytical laboratories is avoided.

Data reported comprise one of the initial surveys on trace metal ion concentrations in waters of the Okavango Delta, Botswana. In waters with more efficient mixing, dissolved metal ion concentrations found were generally low with slightly elevated levels of manganese (7–19 $\mu g\,l^{-1}$), zinc (2.7–4.8 $\mu g\,l^{-1}$), nickel (0.2–2.5 $\mu g\,l^{-1}$) and copper (0.3–2.1 $\mu g\,l^{-1}$). For each trace metal ion, concentration levels seem to reflect zones of varying water conveyance, and show no obvious temporal and spatial variations apart from a slight increment from the inlet in the upper Delta to the outlets in the lower Delta.

Keywords: Trace metal ions; Okavango Delta; 8-Hydroxyquinoline; Preconcentration

1. Introduction

Due to the ever-growing awareness of how the natural environment should be managed, water quality monitoring programs became necessary even in geographical areas where heavy pollution is largely non-existent and where concentrations of toxic metal ions may be too small for accurate measurement. However, the adverse effects of those trace metals in the environment should not be ignored.

Reliable data on trace metal ion concentrations in natural water systems in Africa is scanty. This is largely attributable to the sheer size of the water bodies, inaccessibility of good sampling locations and their remoteness from laboratories with good analytical facilities. Also, pollution levels are generally low due to little industrial and other human developments. As a consequence, most metal ions are in extremely low concentrations and occur together with much higher concentrations of compounds likely to cause interferences during the analysis. Generally, the metal ions are below the detection capabilities of the conventional analytical methods [1], i.e. methods without sample enrichments and cleanup.

Several methods using chelating ion-exchange resins have been developed for multi element preconcentration and selective determination of trace metal ions from natural waters [2–6]. A number of laboratories have demonstrated that extraction of metal ions from aqueous solutions onto immobilized ligands is useful in clean-up and preconcentration of metal ions for ultra-trace detection [7–9]. However, and in spite of all the inherent advantages, there are not many reported applications of this approach in actual field sampling and analysis.

The work described in this paper was part of a study aimed at provision of data on the occurrence and concentration levels of trace metals in the Okavango Delta water system, Botswana. This interest is not only due to the possible detrimental effects of trace metals in these natural waters, but such information is required in establishing hydrochemical and productivity models necessary for future management of the water system.

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Data on trace metal ions in the Okavango Delta was obtained using a novel sampling technique, i.e. a suitably designed microcolumn packed with immobilized 8-hydroxyquinoline was incorporated in a fabricated field sampler to collect, isolate and preconcentrate trace metal ions, on-site.

The studied area corresponds to the Okavango river which spreads out in northwest Botswana into swamps known as Okavango Delta water system. The Okavango Delta water system is located between longitudes 22° east to 24° east and latitudes 18° south to 20° south. It is a unique ecological system famous for its fauna and flora, and covers an area of about 28,000 km^2 of which about 6000 km^2 is perennial swamp and about 12,000 km^2 seasonal swamp. Annual inflow of water in the Delta averages 10.6×10^9 m^3, with a range of 16.0×10^9 to 7.4×10^9 m^3. Annual precipitation averages 5.0×10^9 m^3 but evapotranspiration losses account for an estimated 14.9×10^9 m^3, leaving a surface outflow of only about 0.4×10^9 m^3 and a groundwater flow of assumed equal magnitude [10]. Average water depth is 1.5–2.0 m but can, in some lagoons and larger channels attain 5.0–7.0 m. The inundation zone is very dynamic with the highest flood peak resulting from rains in the headwaters of the Okavango river in neighboring Angola. Like other inundation zone in sub-tropical Africa such as the Barotse flood plain (Zambia), the Niger inland delta (Niger) and the Sudd (Sudan), the Okavango Delta is a region of considerable economic potential and an important water resource for Botswana. The Okavango Delta is the main source of water for many small communities within and on the peripheries of the Delta; a population of about 51,000. These riverine communities rely on raw, untreated water for their domestic needs, as do over 180,000 cattle and huge wildlife population (Okavango Delta is a preserve of one of the most outstanding nature sceneries in the world). Information on the occurrence and concentrations of toxic trace metals is therefore of primary importance for the sustainable use and development of the Okavango Delta region.

2. Experimental

2.1. Reagents

Ultra high quality water, prepared using the Elgastat UHQ-PS unit (Elga Ltd., Bucks, UK), was used to make all solutions. A 65% suprapure nitric acid (Merck, Darmsdat, Germany) was used. UnivAR element stock standard solutions of 1000 mg l^{-1} concentration (Sarchem, South Africa) were diluted to prepare working aqueous standard solutions. 8-Hydroxyquinoline azo-immobilized on controlled pore glass (mesh size: 120–200 nm; pore diameter: 24 nm) was prepared according to Hill's [11] procedure in the laboratories of the Department of Analytical Chemistry, University of Lund, Sweden.

2.2. Instrumentation

A Masterflex variable speed portable sampling pump (Cole-Parmer Instruments Co., Chicago, USA) was used for fieldwork. Gilson Minipuls 2 peristaltic pumps (Gilson, France) fitted with four channel pump heads were used in the laboratories for on-line elution of trace metal ions from the samplers. A Varian Spectra AA-400 plus Zeeman atomic absorption spectrometer equipped with Varian Spectra GTA autosampler (Varian Australia Pty., Ltd., Australia) and interfaced with an Epson Computer (Vacutek Pty., Ltd., South Africa) were used. Varian type pyrolytically coated graphite tubes were exclusively used. Furnace programme parameters were mostly those recom-

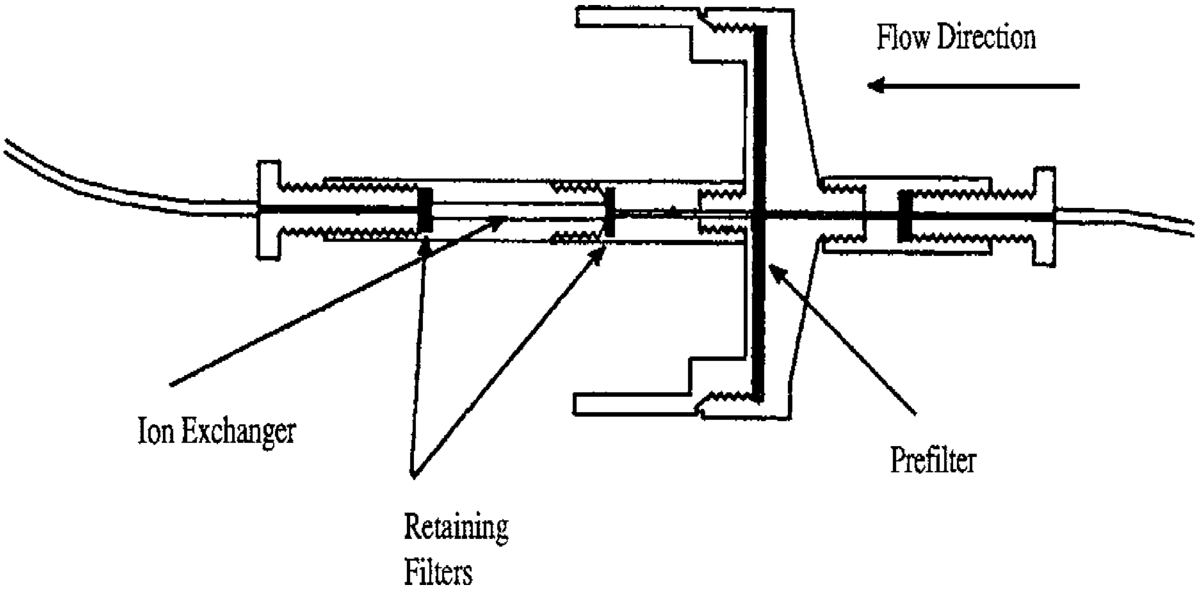

Fig. 1. Field sampler incorporating immobilized 8-hydroxyquinoline ion exchanger.

mended in the instrument manual from the manufacturer [12].

2.3. Sampler design

Malmas et al. [3] reported successful laboratory benchwork using microcolumns packed with immobilized 8-hydroxyquinoline, for on-line preconcentration of several metal ions in filtered water samples. For fieldwork in the Okavango Delta, Teflon microcolumns of 2.7 mm internal diameter, 35 mm length and with a 240 μl volume capacity, were used. Fig. 1 shows a field sampler incorporating the packed microcolumn. Approximately 80 mg of 8-hydroxyquinoline immobilized on controlled pore glass could be packed in this optimized design which had also been tested for ease of packing, sample flow-through, and for absence of on-line sample leakages. The immobilized chelating ion-exchanger was held in position by fiberglass retaining filters (0.45 μm pore size). The inlet end of the packed microcolumn was screwed on to the flow through Teflon tubing connected to a large size polypropylene Swinex type disc filter holder (25 mm, Millipore) to hold membrane prefilters.

2.4. Sampling and analysis

Water samples were collected at 22 locations mostly along Boro river, the main channel in the Okavango Delta water system. Over the study period, at least eight samples were collected at each location. The field sampler was assembled as indicated in Fig. 1 with the inlet end connected to a peristaltic pump. A known volume (50–250 ml) of water was pumped directly through the sampler at optimized flow rates of between 3 and 5 ml min^{-1}. The metal-ion loaded microcolumn was then unscrewed from the sampler, outlet and inlet ends sealed with Teflon screw caps, labeled and transported in sealed clean bags to the laboratory. Subsequently, trace metal ions were eluted from each microcolumn using the elution scheme shown in Table 1 and Fig. 2. Solutions were pumped through the reassembled sampler at appropriate flow rates. Sequestered trace metal ions were recovered from the sampler using 0.5 ml of 1.5 M HNO_3, and the eluate diluted to 5.0 ml, with ultra high purity water in the Varian autosampler vials. Trace metal ions were determined by GFAAS. At selected sampling locations, water samples were simultaneously collected in acid washed polyethylene bottles, acid preserved and transported to the laboratory for comparative conventional determination of trace metal ions [1].

Table 1
Metal ions preconcentration and elution scheme

Pumped solutions	Volume (ml)	Flow rate (ml min^{-1})
Water sample	50–250	3–5
1.5 M HNO_3 eluent	0.5	1.0
Ultra high purity water	15	3.0
2.0 M HNO_3	5	3.0
Ultra high purity water	10	3.0

3. Results and discussion

3.1. Method validation

Previous studies have established the characteristic performance of 8-hydroxyquinoline, azo-immobilized on controlled pore glass, as an ion exchanger in terms of capacity, fast exchange kinetics and selectivity towards most transition metal ions [3,13,14]. Prior to analysis of real water samples, validation of the method was undertaken using metal ion standard solutions and certified reference materials. Recoveries of selected trace metal ions, from the microcolumns packed with immobilized 8-hydroxyquinoline, were ascertained using single and mixed metal ion standard solutions. Analysis was done using equimolar mixtures of metal ions and mixtures containing different concentrations of the metal ions. Fig. 3 shows the mean percentage recoveries of metal ions in equimolar standard solution mixtures of selected metal ions. For the metal ions studied, all metal ion percentage recoveries were above 85% with good precision (%R.S.Ds. < 5), and were generally similar to recoveries

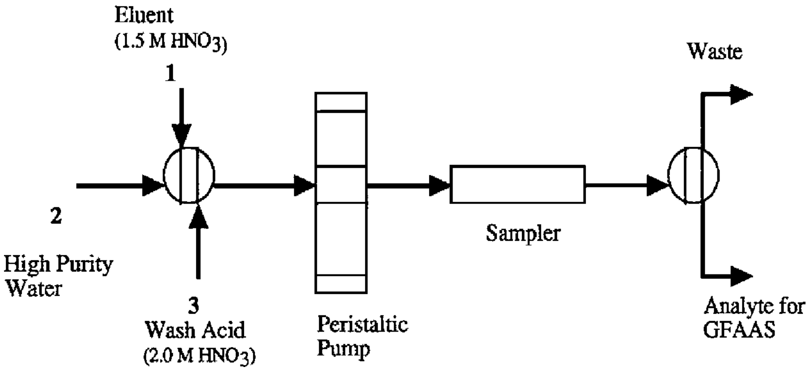

Fig. 2. Metal ions elution scheme.

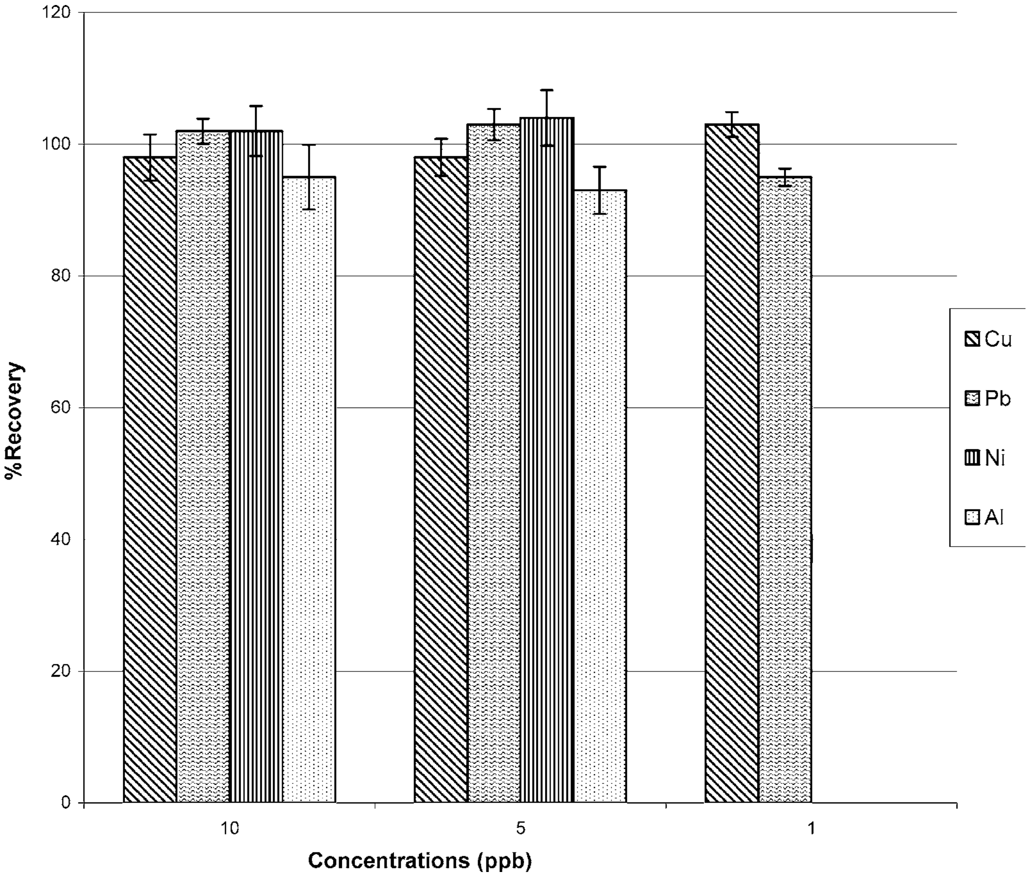

Fig. 3. Mean recoveries, of metal ions in standard solution mixtures, from immobilized 8-hydroxyquinoline ion exchanger columns.

obtained when working with single metal ion standard solutions. Hence at these metal ion concentration levels, there were no adverse effects due to metal ion competition for the of 8-hydroxyquinoline complexation sites. Using certified reference materials SLRS-3 (riverine water) and SLEW-2 (estuarine water) obtained from the National Research Council of Canada, accuracy and precision of the method were ascertained. Table 2 indicates the results obtained in the determination of Cu, Ni, and Pb. Good precision in metal ion determination was obtained, as indicated by the low standard deviation values. The mean concentration values were not significantly different from the certified values, for the respective metal ion, since the calculated Student's *t* (*t*-test) values were less than critical Student's *t*-values at the 95% confidence level. Also, at the 95% confidence level, differences in variances (s^2) of the mean values were not statistically significant as in all cases the calculated *F*-test values were less than the critical values of *F* [15].

Best metal ion recoveries from the microcolumns have previously been obtained within a sample pH range of 6–9, similar to that encountered in surface waters of the Okavango Delta [16]. Table 3 indicates the results obtained at three sampling locations where conventional determination of the trace metal ions was also undertaken. In general, results obtained using both methods were not significantly different. However, use of the field sampler to collect and preconcen-

Table 2
Method validation; determination of Cu, Ni and Pb in (a) SLRS-3 and (b) SLEW-2 certified reference materials

Metal	Mean concentration determined ($\mu g\, l^{-1}$, $n = 4$)	Certified value	Calculated *F*-test value ($P = 0.05$)	Calculated *t*-test value ($P = 0.05$)
(a) SLRS-3 certified reference material				
Cu	1.320 ± 0.03	1.350 ± 0.07	5.44	2.00
Pb	0.061 ± 0.009	0.068 ± 0.007	1.65	1.56
Ni	0.780 ± 0.04	0.830 ± 0.08	4.00	2.50
(b) SLEW-2 certified reference material				
Cu	1.560 ± 0.07	1.620 ± 0.1	2.47	1.71
Pb	0.024 ± 0.004	0.027 ± 0.005	1.56	1.50
Ni	0.720 ± 0.02	0.710 ± 0.05	6.02	1.00

Table 3
Analysis for dissolved metal ions in the Okavango Delta water using on-site samplers containing 8-hydroxyquinoline and conventional sampling methods for sample collection ($\mu g\,l^{-1}$; mean ± S.D.)

	Duba		Tichira		Boro junction	
	On-site sampling	Conventional sampling	On-site sampling	Conventional sampling	On-site sampling	Conventional sampling
Zn	3 ± 1	2.9 ± 0.8	2.9 ± 0.6	3 ± 1	5 ± 1	5 ± 1
Cd	0.24 ± 0.03	0.3 ± 0.2	0.12 ± 0.05	0.09 ± 0.05	0.2 ± 0.1	0.2 ± 0.2
Pb	0.15 ± 0.02	0.1 ± 0.1	0.13 ± 0.09	0.2 ± 0.1	0.25 ± 0.05	0.4 ± 0.2
Cu	0.84 ± 0.06	0.9 ± 0.3	1.1 ± 0.2	1.4 ± 0.7	0.6 ± 0.2	0.5 ± 0.2
Mn	14 ± 2	12 ± 2	14 ± 4	16 ± 4	15 ± 2	9 ± 3

trate the metal ions led to higher precision in analysis, as indicated by the lower standard deviations. Several dissolved metal ions could be determined in the same sampler eluate. A single sampler could be reused for over 10 cycles without any noticeable deterioration in performance. This method is relatively free from interferences and is fast because it involves minimum sample preparation. Sensitivity in detection is enhanced to ranges required for trace metal ions analysis. For water systems remotely located from good analytical laboratories, use of the sampler can therefore significantly reduce the many uncertainties in representativeness of data on trace metal analysis.

3.2. *Metal ions in the Delta water*

Previous hydrochemical studies [16] characterized waters of the main channel in the Okavango Delta, Boro river, as generally soft, circum-neutral, low in conductance, with moderate alkalinity and moderate to high amounts of silica. Other studies [10] have also established that about 95% of the inflowing water, from neighboring Angola, is lost before it reaches the southern peripheries of the Delta due to intensive evapotranspiration in this semi-arid region. The subsequent evaporative concentration of the waters leads to a gradient of increasing concentrations of solutes, from the inlet to the southern peripheries of the Delta. Total dissolved solutes increase from about 30–95 $mg\,l^{-1}$ [16]. Trace metal concentrations, determined using the field sampler, are shown in Table 4. In flowing waters, i.e. with more efficient mixing, dissolved trace metal ion concentration were generally low, mostly in the sub-$\mu g\,l^{-1}$ levels, and in the absence of known pollution sources in the Delta, can safely be assumed as background concentrations. Most abundant were manganese (7–19 $\mu g\,l^{-1}$), zinc (2.7–4.8 $\mu g\,l^{-1}$), nickel (0.2–2.5 $\mu g\,l^{-1}$) and copper (0.3–2.1 $\mu g\,l^{-1}$).

3.3. *Spatial and temporal variation*

Taken collectively, distribution of trace metal ions seems to reflect zones of varying water conveyance in the Okavango

Table 4
Dissolved trace metal ions in the Okavango Delta water system ($\mu g\,l^{-1}$; mean ± S.D.)

Location		Cd	Mn	Cu	Co
1	Sepopa	0.30 ± 0.05	15 ± 1	1.20 ± 0.40	0.27 ± 0.08
2	Ok-Thaoge J	0.30 ± 0.1	15 ± 1	1.30 ± 0.2	0.25 ± 0.04
3	Seronga	0.22 ± 0.05	13 ± 0.4	1.50 ± 0.5	0.30 ± 0.1
4	Duba	0.24 ± 0.03	14 ± 2	0.84 ± 0.06	0.30 ± 0.1
5	Tichira	0.12 ± 0.05	14 ± 4	1.10 ± 0.2	0.21 ± 0.09
6	Plum tree	0.08 ± 0.05	15 ± 4	1.10 ± 0.4	0.20 ± 0.1
7	Xo-flats lgn.	0.17 ± 0.05	13 ± 2	0.60 ± 0.2	0.16 ± 0.08
8	Chao	0.21 ± 0.06	11 ± 4	0.28 ± 0.08	0.20 ± 0.1
9	Xakue	0.12 ± 0.05	11 ± 2	0.60 ± 0.2	0.18 ± 0.05
10	Xaxaba	0.39 ± 0.08	9 ± 1	1.02 ± 0.05	0.30 ± 0.1
11	Baboon cp	0.60 ± 0.2	7 ± 2	0.90 ± 0.4	0.32 ± 0.07
12	Wildlife cp	0.14 ± 0.08	9 ± 3	0.34 ± 0.05	0.25 ± 0.05
13	Odd balls	0.14 ± 0.05	7 ± 3	1.10 ± 0.8	0.20 ± 0.1
14	Moumo	0.13 ± 0.04	7 ± 1	0.31 ± 0.05	0.18 ± 0.09
15	Nxaraga	0.20 ± 0.1	14 ± 3	0.60 ± 0.1	0.30 ± 0.2
16	Mporota	0.17 ± 0.06	12 ± 3	1.10 ± 0.6	0.22 ± 0.09
17	Zebra cp	0.32 ± 0.09	12 ± 2	1.20 ± 0.3	0.27 ± 0.07
18	Bokwi	0.70 ± 0.1	10 ± 2	0.59 ± 0.08	0.30 ± 0.1
19	Buffalo fc	0.21 ± 0.08	14 ± 2	0.50 ± 0.1	0.38 ± 0.09
20	Boro Junction	0.20 ± 0.1	15 ± 2	0.60 ± 0.2	0.30 ± 0.2
21	Xaenga ledb.	0.41 ± 0.08	19 ± 2	2.10 ± 0.6	0.40 ± 0.1
22	Muanachira	0.26 ± 0.06	11 ± 2	1.60 ± 0.2	0.26 ± 0.09

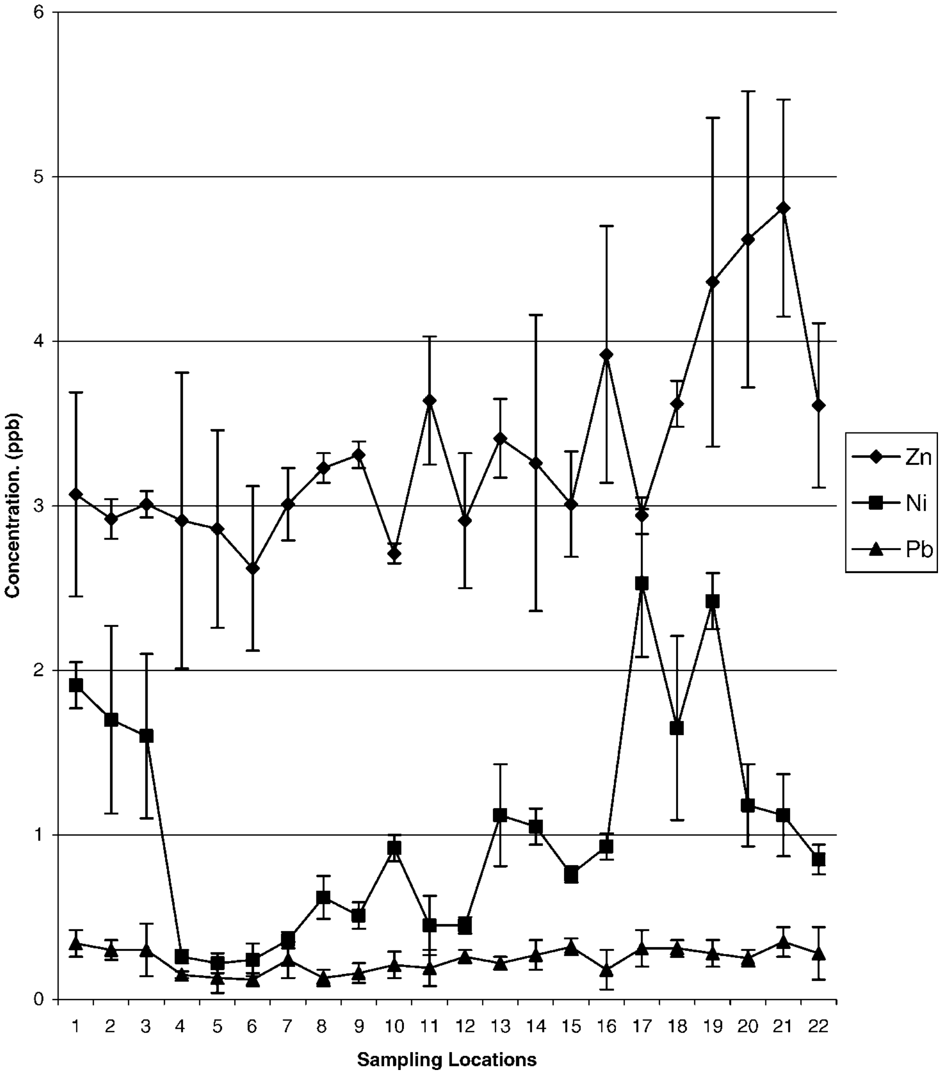

Fig. 4. Zn, Ni and Pb concentrations in the Okavango Delta water system, Botswana.

Delta; waters of more efficient mixing, e.g. in the swamps and main channel of Boro river between Xaxaba and Maumo sampling locations, show a general decrease in trace metal ion concentrations, while high trace metal ion concentrations coincide with zones of slower water flow, e.g. in the isolated pools at Xaenga ledb. and the Boro river at the Xo-flats lgn. Subsequently, some trace metal ion concentrations are likely to be exaggerated due to almost non-flow conditions in some sections of the main water channels during the long dry season. There is, therefore, no obvious spatial variation pattern apart from a slight gradient increase, in trace metal ion concentrations, towards the outlet of the Delta (Fig. 4). This is attributed to the already reported evapotranspiration processes that cause the evaporative concentration of solutes in the waters [10,16].

A major difficulty in analyzing the temporal variation in the trace metal ion concentrations of the waters of this complex hydrological system is the existence of a 4–5 months delay between the peak water flow at the inlet northern section of the Delta, the upper Delta, and the outlet southern peripherals of the Delta, the lower Delta. An ill-defined dilution pattern therefore arises; dilution effects upstream in the upper Delta being offset by intensive evapotranspiration effects in the lower Delta. Further complications arise from the existence, in both sections, of a distinct flood expansion phase during the rainy months of November to March and a distinct recession phase between April and October. Generally however, concentration minima for the majority of trace metal ions were observed at high discharges during the rainy period. Effects of desorption and remobilization from inlet headwaters, from Angola, seemed insignificant. Also in general, differences in concentrations of the trace metal ions at the individual sampling locations were insignificant for over four similar discharge periods during this study. Reflecting here that the metal ions in the waters are drawn mainly from the slow, physically changeable natural sources, e.g. land formations, rather that the highly varying impacts of pollution due to interventions associated with industrial and other human developments.

Some of the dissolved metal ion concentrations determined, in particular Ni, Zn, Cd and Cu, are slightly higher compared to those previously found in almost pristine systems for example the Niger [17], but lower than in relatively polluted environments, e.g. the Rhine [18]. There is no evidence that potentially toxic elements, e.g. Pb, Cd and Cu are currently present in concentrations deleterious to animal and plant life [19,20].

The results of this study highlight the interest in applying on-site sampling and preconcentration and this work constitutes part of an initial survey on trace metal ion concentrations in the Okavango Delta water system. It is widely accepted that most of the physico-chemical and biological processes controlling the quality of water in the main channels occur in the swamps, floodplains and islands, and therefore more work over the long term will be necessary, as well as the acquisition of hydrochemical data on rainwater and groundwater.

4. Conclusions

This study has demonstrated the use of 8-hydroxyquinoline, as a chelating ion exchanger, in a field water sampler for trace metal ions. The ability to achieve in-situ sampling and sample clean-up, coupled with analyte preconcentration, is demonstrated. The analytical results are precise and not significantly different to those obtained using the conventional methods. This sampling technique is most useful in quality studies of water systems remotely located from analytical laboratories. Metal-ion-loaded samplers can easily be transported and stored for several days before elution and determination of the metal ions. Samples could be taken and introduced in the detection system in a closed path, hence minimizing contamination and enhancing accuracy and precision in the results.

The results reported are part of the initial surveys, on trace metal ion concentrations, in the Okavango Delta. Heavy metal pollution is largely non-existent and in the absence of known significant sources of pollutants, the low trace metal ion concentrations found can safely be considered as background levels. The metal ion concentrations found had no defined spatial and temporal variation except for a slight increase from the inlet towards the outlet of the Delta, due to the gradual evaporative concentration of solutes in the water. The slightly elevated concentrations of some dissolved trace metals are of particular concern and an indication of the susceptibility of the Okavango Delta system to toxic metal pollution.

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