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DETERMINATION OF SOME DISSOLVED TRACE METALS FROM GROUNDWATER IN MAURITIUS USING INDUCTIVELY-COUPLED PLASMA -MASS SPECTROMETRY

by

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ABSTRACT

The concentrations of some dissolved trace metals: aluminium, chromium, manganese, nickel, copper, zinc, cadmium and lead (Al, Cr, Mn, Ni, Cu, Zn, Cd and Pb) were determined in groundwater in the Flic en Flac and Grand River North West (GRNW) areas to assess groundwater contamination arising from agricultural and industrial activities of the Export Processing Zone (EPZ) in Mauritius during 1998. Inputs of dissolved Al, Ni, Cu, Cd and Pb originating from both anthropogenic and natural activities and leading to the contamination of the groundwater at both Flic en Flac and GRNW were not significant in 1998. However, dissolved Zn was significantly higher in rainwater compared to Flic en Flac groundwater samples. The data demonstrated the potential for concentrations of some dissolved trace metals in groundwater samples to be below the proposed revised pollution limits in Mauritius. However, dissolved Cr in groundwater samples in the GRNW catchment area, which may arise from textile industries exceeded the proposed revised environmental inland water limits in Mauritius. There is at present an urgent need to review the guidelines for groundwater standards for trace metals in Mauritius which are to be proposed under Sections 34 and 74 of the Environmental Protection Act 1991 and cited as the new Environmental Protection Regulations 2000.

Keywords: Dissolved tracemetals, ICP-MS, groundwater, rainwater

INTRODUCTION

The coastal zone of the oceanic island of Mauritius, (1850km^2, 20°S and 57°E, South Western Indian ocean) is made up of terrestrial and marine interfaces where industrial activities (textiles, food processing and light industries) and coastal resort development are superseding traditional activities such as sugarcane plantation. Concern that trace metals in drinking water present a potential health hazard if they exceed certain concentrations has prompted the Ministry of Environment in Mauritius to propose a revised maximum allowable concentrations for these elements in inland water (Anon., 1991; Anon., 1996; Ramessur *et al*. 1998). The groundwater resources used for domestic consumption conflict with environmental protection as many boreholes in Mauritius are situated in industrial areas where much of the wastewater of textile origin remain untreated (Heeramun, 1997). There are at present about 400 industries most of which lack clean technology and 50 of which are dye-houses and stone washing industries on the island and the amount of hazardous wastes produced daily is estimated at 200 tonnes (Anon., 1997). In addition, the inland transport consisting of about 200 300 vehicles in Mauritius rely heavily on leaded petrol and diesel. So far emissions of hazardous air pollutants are unknown in Mauritius and there is very little information on exposure to the most toxic air pollutants at ambient concentrations. Beceiro-Gonzalez *et al*. (1997) reported that Zn and Cd associated with diesel and fuel products presented the broadest ranges in an industrial area whereas Pb reflected a pollution pattern originating mainly by automobile exhausts in an airborne metal particulate study in a coastal city in North West Spain. In a coal-fired power station environmental impact study in Delhi, Mehra *et al*. (1998) concluded that fly ash leachates from coal-fired power generation were a source of alkali, alkaline earth and to some extent heavy metals whereas Paul *et al*. (1998) reported that coal combustion residues accumulating in ponds and landfills in Illinois, USA, raised the risk of groundwater contamination due to leaching of trace elements. The increasing use of groundwater for domestic consumption, industrial and coastal tourism development and the corresponding volume of waste water which must be disposed of, has given rise to serious concern for water pollution and the protection of the integrity of water resources in Mauritius. One of the recent papers describing the analysis of groundwater using ICP-MS is that of Nkono & Asubiojo (1997) which assesses the quality of bottled waters and mineral waters in Nigeria from spring waters and boreholes. In this paper, some trace metals in the groundwater samples from an industrial area were determined and compared to an agricultural area and rainwater using inductively coupled plasma – Mass Spectrometry (ICP-MS). Temporal variations in the distributions of dissolved Cr, Ni, Cu, Zn, Cd and Pb originating from both natural and anthropogenic sources in the boreholes in the Flic en Flac and Grand River North West areas and in rainwater in Mauritius were followed at monthly intervals from January to May 1998.

MATERIALS AND METHODS

Description of sites

The Grand River North West (GRNW) aquifer is situated south of Port Louis next to GRNW river with a catchment area of 116km^2 receiving wastewater from the Coromandel industrial zone downstream and from St. Louis river which flows through Pailles and Plaine Lauzun industrial area (Fig 1.). The GRNW area receives wastewater discharges from both domestic and industrial origins such as dye houses, battery manufacturers, soap and detergent industries, ethanol distilleries, chemical industries, paint manufacturers, food and beverages processors, galvanising and electroplating plants downstream from more than 70 industries in Coromandel and the Export Processing Zone in Plaine Lauzun. (Anon., 1992). The Flic en Flac area is situated in the Western Tourist Zone of Mauritius and has seven hotel complexes along the beach with sugarcane plantation in the hinterland above a groundwater aquifer in the Medine area.

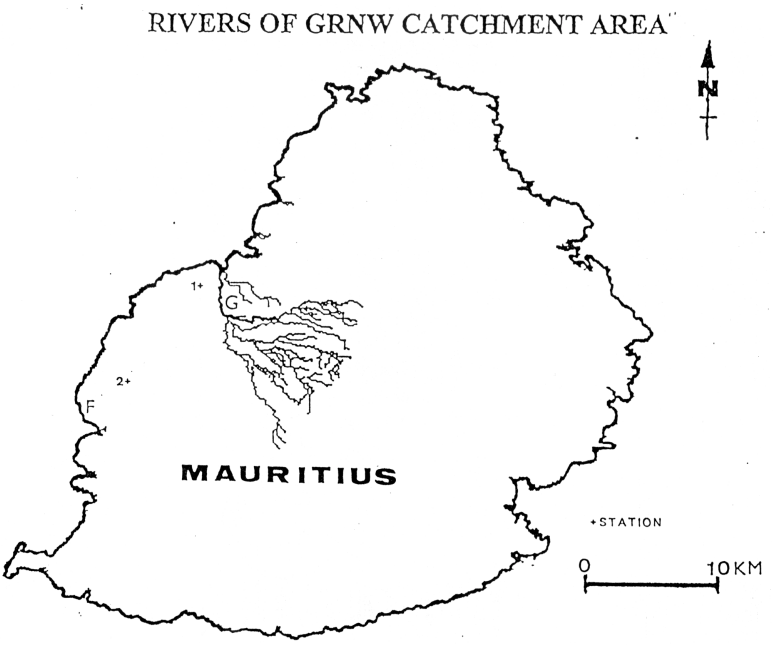

Fig.1 GRNW and Flic en Flac study areas (G & F).

Sample collection

Samples of groundwater were collected monthly in the Flic en Flac and GRNW boreholes (20-70m deep) from January to May 1998 in pre-acid washed 100mL plastic bottles, filtered using 0.45μm Whatman cellulose nitrate membrane filter and stabilized by acidification to pH <2 with 2% analar grade nitric acid (B.D.H, U.K) to reduce chemisorption of trace metal ions onto surfaces and to prevent the hydrolysis and precipitation of cations. Samples were subsequently stored at 4°C for trace element analysis to reduce loss or change of labile constituents. Rainwater in the GRNW catchment area was also collected and stored at monthly intervals in 100mL plastic bottles at Réduit for trace element analysis to establish atmospheric inputs and for comparison purposes.

Trace element determination

The dissolved trace metals (Al, Cr, Mn, Ni, Cu, Zn, Cd and Pb) were determined in the samples collected using a VG Elemental PlasmaQuad II+ ICP-MS. Multi-elemental standard solutions were prepared from a $10mgL^{-1}$ multielemental standard ICPMS2 (SPEX Multi-element plasma, U.S.A) by dilution in deionized water in the range 10-50 ng mL^{-1}. All samples or reagent preparation and handling was conducted under a laminar flow clean hood to minimise contamination. Sample solutions were nebulized (cross flow nebulizer) into the VG Elemental Plasma Quad II+ ICP-MS with operating conditions shown in Table 1 and data collected in the scanning mode of operation. Elements determined were Al (27m/z), Cr (52 m/z), Mn (55m/z), Ni (60m/z), Cu (65m/z), Zn (66m/z), Cd (111m/z) and Pb (208m/z). The accuracy of the method was verified by triplicate analysis of Standard Reference Material NIST 1643d, Trace Elements in Water (USGS) and 3σ detection limits were calculated from blank solutions. The reported results are the mean values of triplicate determinations and are expressed as ng mL^{-1}. The values were also compared to Anon. (1996) and to those in river/ natural waters and rainwater (Thompson & Walsh, 1989; Ihnat *et al.* 1993; Bensimon *et al.* 1994; Santosa & Tanaka, 1995; Fifield & Haines, 1996) as shown in Table 2 to reveal any potential breach of the proposed revised pollution limit. Fe, As and Se were not determined because of significant polyatomic ion interferences which resulted in a degradation of detection limits.

Table 1. ICP-MS instrument operating conditions

Plasma conditions—	PlasmaQuad STE
Instrument	1350
Forward power /W	<5
Reflected power/W	14
Coolant gas flow/ l min^{-1}	0.80
Nebulizer gas flow/ l min^{-1}	0.5
Auxiliary gas flow/ l min^{-1}	
Interface—	Ni 1 mm orifice
Sampling cone	Ni mini-skimmer, 0.7 mm orifice
Skimmer cone	
Nebulizer—	De Galan V-groove
Type	0.5
Solution up-take rate/ ml min^{-1}	
Data acquisition parameters—	160
Dwell time per channel/μs	20 per mass unit
Number of channels	60
Total measurement time/s	10-210
Scan range/m/z	120-200
Skipped mass regions/m/z	

Table 2. Proposed revised pollution limits in 1996 for Mauritius and typical concentration of trace metals in natural freshwater and rainwater.

Trace metals	Proposed revised Pollution Limits, Mauritius, 1996. ng mL^{-1} WHO[2] Limits For drinking water (1984) ng mL^{-1}	EEC[1] (1980) maximum admissible concentrations Thompson and Walsh (1989). EEC[2] (1975) Guideline. Rump and Krist, 1992. ng ml^{L-1}	Groundwater and natural water. Bensimon *et al.*, 1994. Fifield and Haines., 1996 ng mL^{-1}	Rainwater in Japan Santosa and Tanaka, 1995. ng ml^{-1}
ALUMINIUM	—	200[1]	0.3	29.5
CHROMIUM	2.0, 50[2]	50[1,2]	0.4	0.3
MANGANESE	—100[2]	50[1]	0.5	5.8
NICKEL	88.0, 50[2]	50[1]	0.03	1.9
COPPER	6.5, 1000[2]	100[1] 50[2]	3	8.0
ZINC	59.0, 5000[2]	100[1] 3000[2]	0.2	23.0
STRONTIUM	—	—	70-330	—
CADMIUM	0.70, 5[2]	5.0[1,2]	0.01	0.3
LEAD	1.3, 10[2]	50[1,2]	0.08	2.8

RESULTS AND DISCUSSION

The linearity for the calibration line for the multi-elemental trace standards used in ICP-MS was good showing a correlation coefficient of 1.0 during analysis of Flic en Flac, rainwater and GRNW samples. The detection limits for the trace metals calculated using five replicate runs of the standard blank were in the range 0.006-3.0ng/mL and were comparable to values quoted from other researchers for freshwater (Santosa & Tanaka, 1995; Hall *et al.* 1996). The precision at the concentration of 10ng/mL based on three runs of the same solution given as % RSD (i.e. St. dev/Mean x 100) were as follows: 2% (Pb, Mn); 3% (Cr, Cu, Cd,); 4% (Al, Ni, Zn). The accuracy of the procedure was good for the suite of trace elements determined as shown in Fig 2. The variation of trace elements for the period January 98-May 98 in groundwater samples from Flic en Flac and GRNW and in rainwater collected at Réduit during January -May 1998 are shown in Fig 3-5. The mean concentration of the trace elements in rainwater and groundwater at Flic en Flac and GRNW during summer and winter is shown in Tables 3 and 4. Pairwise comparisons of rainwater and groundwater at Flic en Flac and GRNW during 1998 using t-test at 5% significance level are shown in Table 5.

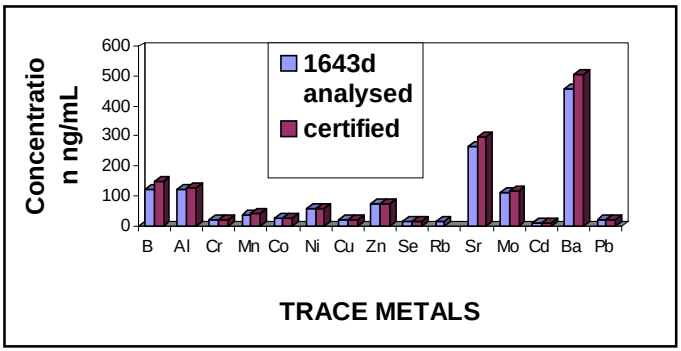

Fig. 2 Trace elements - certified 1643d values compared to analysed values

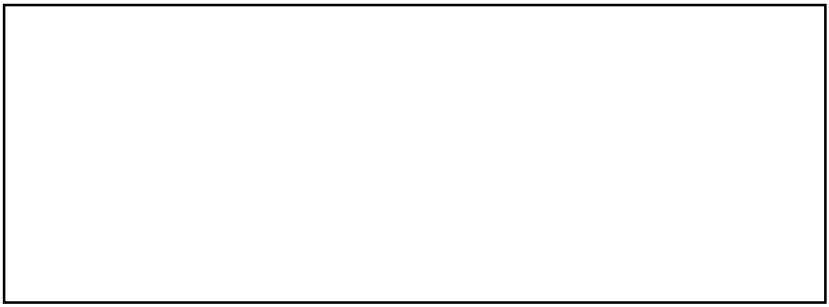

Fig. 3 Dissolved trace metals in groundwater in GRNW, Mauritius 1998.

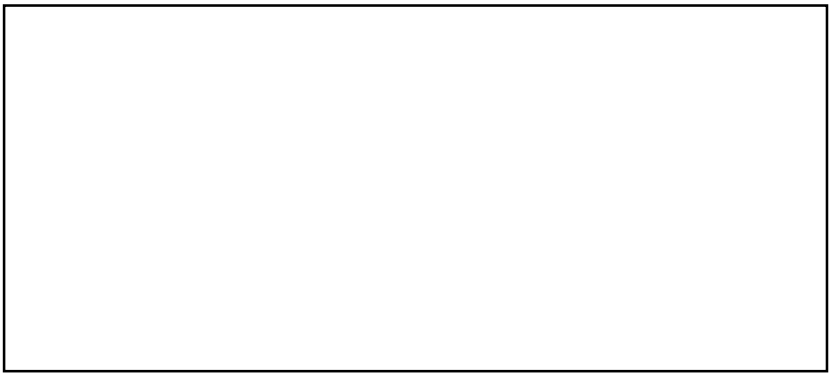

Fig. 4 Dissolved trace metals in groundwater at Filc en Flac, Mauritius 1998.

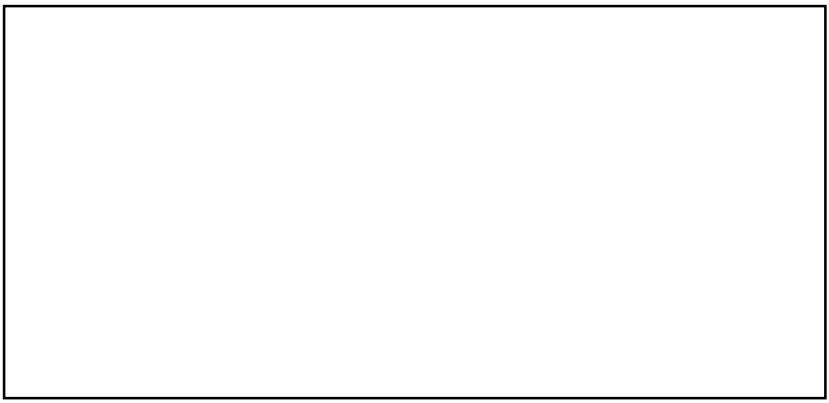

Fig. 5 Dissolved trace metals in rainwater , Mauritius 1998.

Table 3. Dissolved trace in groundwater in GRNW and Flic en Flac area

Trace metals	GRNW Groundwater Summer 98 ng mL^{-1}	GRNW Groundwater Winter 98 ng mL^{-1}	Flic en Flac Groundwater Summer 98 ng mL^{-1}	Flic en Flac Groundwater Winter 98 ng mL^{-1}
ALUMINIUM	<1.05	<1.05	<1.05	<1.05
CHROMIUM	2.97 ± 0.41	2.85 ± 0.37	2.38 ± 0.08	2.39 ± 0.04
MANGANESE	<0.05	<0.05	<0.05	<0.05
NICKEL	<0.26	<0.26	<0.26	<0.26
COPPER	1.05 ± 0.5	0.86 ± 0.3	1.5 ± 1.11	1.17 ± 0.49
ZINC	85.01 ± 78.11	63.41 ± 35.57	19.2 ± 0.69	19.05 ± 0.21
CADMIUM	<0.09	<0.090	<0.090	<0.09
LEAD	<0.07	<0.07	<0.07	<0.07

Table 4. Dissolved trace metals rainwater in Mauritius in 1998.

Trace metals	Rainwater Summer 98 ng mL^{-1}	Rainwater Winter 98 ng mL^{-1}
ALUMINIUM	10.46 ± 1.8	9.06 ± 2.81
CHROMIUM	1.9 ± 0.58	1.57 ± 1.04
MANGANESE	2 ± 0.42	1.61 ± 1.14
NICKEL	3.15 ± 0.97	2.43 ± 1.8
COPPER	3.63 ± 2.68	2.83 ± 2.2
ZINC	24.47 ± 4.45	24.56 ± 0.33
CADMIUM	<0.09	<0.09
LEAD	0.16 ± 0.14	0.11 ± 0.11

Table 5. Pairwise comparisons of rainwater and groundwater at Flic en Flac and GRNW during 1998 using t-test at 5% significance level. (ns-not significantly different).

Comparisons at 5% significance level using t-test (2tail)			
	GRNW 98 and Flic en Flac 98 Groundwater	**Rain 98 and GRNW 98 Groundwater**	**Rain 98 and Flic en Flac 98 Groundwater**
CHROMIUM	**significant** **t = 2.600** **t (crit) = 2.306**	**significant** **t =-3.573** **t (crit) = 2.306**	**ns**
COPPER	**ns**	**ns**	**ns**
ZINC	**ns**	**ns**	**significant** **t = 3.833** **t (crit) = 2.306**

GRNW

Dissolved Al, Mn, Ni, Cd and Pb were below the limits of detection of 1.05, 0.05, 0.26, 0.09 and 0.07ng mL^{-1} respectively and do not constitute a risk to human health in the GRNW groundwater samples. The concentration of of Cr, Cu and Zn in groundwater samples were comparable to values obtained by Fifield & Haines (1996) and Bensimon *et al.* (1994) for groundwater and natural waters in general. Dissolved Cr arising from textile industries was higher at GRNW compared to Flic en Flac groundwater and rainwater and also exceeded the environmental limits of 2.0ng/mL at the 5% significance level.

Flic en Flac

Of the eight dissolved trace metals determined in 1998, dissolved Al, Ni, Mn, Cd and Pb were not significant and below the limits of detection of 1.05, 0.26, 0.05, 0.09 and 0.07ng/mL respectively in the groundwater samples at Flic en Flac. The concentration of dissolved Cu and Zn in the Flic en Flac groundwater samples corresponded to those cited in the literature for groundwater and natural waters in general (Bensimon *et al.* 1994; Fifield & Haines, 1996) and were below the environmental limits proposed by the Ministry of Environment in 1996. However, dissolved Cr levels in groundwater exceeded the environmental limits of 2.0ng/mL during the period.

Rainwater

Al, Mn, Ni, Cu, Zn and Pb had similar concentrations to those values observed by Santosa & Tanaka (1995) for rainwater in Japan whereas Cr in rainwater was higher than the 0.3ng/mL value quoted and Cd was below the detection limit of 0.09ng/mL. The concentration of Cr was higher in rainwater than the proposed revised pollution limit of 2.0ng/mL only during February 1998 whereas Pb was below the 1.3ng/mL environmental limits during the period January – May 1998. Zn in rainwater was higher in rainwater compared to Flic en Flac groundwater samples at the 5% significance level.

CONCLUSION

The data demonstrate for concentrations of groundwater samples to be below the proposed revised pollution limits except for the potential of dissolved Cr to exceed the environmental limits (Anon., 1996) at GRNW, Flic en Flac and in rainwater. The contamination of rainwater by airborne zinc was significant in 1998. Dissolved Cr was significantly higher in groundwater from the GRNW industrial area and is a potential threat to the aquatic system in Mauritius. In general, the trace elements determined fell within the EEC (1975) Guideline of surface water for drinking water preparation, Category A_1 (filtration and disinfection) as reported by Rump & Krist (1992), the WHO (1984) limits for drinking water and the EEC maximum admissible concentrations as reported by Thompson & Walsh (1989). Finally, inputs of Ni, Cu, Cd and Pb that originated from both anthropogenic and natural activities and leading to the contamination of the groundwater at both Flic en Flac and GRNW were not significant. There is at present an urgent need to review the guidelines for groundwater standards in Mauritius which are to be proposed under Sections 34

and 74 of the Environmental Protection Act 1991 and cited as the new Environmental Protection Regulations 2000. Studies geared towards a better management and protection of groundwater aquifers, in particular, in the industrial and urban areas, will also provide baseline data for comparison purposes in the future.

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