

THE EFFECT OF INDUSTRIAL EFFLUENT AND LEACHATE FROM LANDFILLS ON THE LEVELS OF SELECTED TRACE HEAVY METALS IN THE WATERS OF UPPER AND MIDDLE MUKUVISI RIVER IN HARARE,ZIMBABWE

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ABSTRACT. Mukuvisi River passes through industrial and residential areas of the city of Harare before it discharges into lake Chivero, the main water source of the city. The river receives leachate from land-filled areas, as well as effluent from industries situated along its banks. The effect of this landfilling, as well as that of industrial effluent discharged into the river, on the levels of Cu, Zn, Pb, Co, Cd, Fe, Ni and Cr was studied by comparison of the levels of these elements in a leachate canal and in two industrial effluent canals discharging into the river to their levels at points upstream and downstream of the canals. Levels of Pb, Cr(III), Co and Cd in the section of river studied were found to be far in excess of the World Health Organisation guidelines for drinking water. The study further confirmed that both leaching of heavy metals from the landfilling along the river banks and pollution from industrial effluent contribute to the pollution of the river by heavy metals.

INTRODUCTION

Zimbabwe is currently experiencing considerable industrial expansion. Much of this development is taking place in Harare, the capital city, which has a population of 1 million and covers an area of 559 sq km. The city draws its water from lake Chivero, situated some 2 km to the S. West (Fig. 1).

Figure 1 shows that the lake receives its water from three major rivers: Mhanyami, Mukuvisi and Marimba. Both Mukuvisi and Marimba rivers have their sources in the city, so that the city is the catchment area for its own water supply. This situation, coupled with this considerable industrial expansion above, is now causing much concern as regards the quality of the water reaching the lake. Indeed pollution of the lake waters by organochlorine pesticides, polychlorinated biphenyl (PCB's), hexachlorobenzene, as well as toxic heavy metals such as lead, cadmium, cobalt and mercury, has been reported [1,2]. This concern is further exacerbated by the fact that the lake is now plagued by water hyacinth which at its worst can cover up to two-thirds of the 2500 ha lake, an indication of the high eutrophic levels in the lake.

The aim of the present study was to establish the sources of heavy metals that may reach the lake. Possible sources include industrial and sewage effluent discharged into the rivers, and leachate from the landfilled areas along the city sections of the rivers (i.e. legal waste dumping areas) and leachate from illegal waste dumping in the river

valleys which is not uncommon. In this paper we report on a study we conducted to evaluate the impact of industrial effluent and the city's landfill programme on the levels of selected heavy metals in the waters of upper and middle Mukuvisi river.

The section of Mukuvisi river studied stretches from the Mutare road Bridge near the source of the river just below Cleveland Dam to the Cripps Road Bridge in the Graniteside Industrial area (Fig. 1). The underlying rocks for most of the length of river studied are composed of granite, except for the distance below the Seke (or Hatfield) Road Bridge where the river lies along the contact between the granite to the south and red ironstones to the north.

In its upper reaches the river receives effluent from a phosphate fertilizer manufacturing plant and several other sundry industries in the recently expanding Masasa industrial area. Below the Mutare Rail bridge (sampling point No. 3), the river runs past a tobacco processing plant, after which it runs through the Mukuvisi Woodlands, a forest area reserved for game. After this the river runs past the residential areas of Hillside and Braeside, the city Railway station and marshalling yard, and the main commercial area of the city.

The area bordering the river between old Chiremba road and Cripps road (Fig. 1) has been the target of landfill programmes dating back to the 1950's. The area between old Chiremba road and Seke road was landfilled between the 1950's and about 1972. Landfilling below Seke road began in 1972 and is still in progress.

Samples were collected from eleven sites along the river as indicated in Table 1. Sampling point X lies on an effluent canal from the fertilizer plant which discharges into upper Mukuvisi. The influence of this effluent canal on the levels of trace heavy metals in the waters of the river can therefore be assessed by comparison of the levels of each element in the canal with the levels at sampling points in the river immediately above and below the point at which the canal enters the river.

Sampling points Y and Z are in canals within the landfilled area and drain to the river (Fig. 1). These canals have weep holes draining the landfill. Thus the influence of the landfill on the levels of trace heavy metals in the waters of the river can be evaluated by comparison of the level of a given element at points 5, Y and 6 and points 7, Z and 8 as described above for the evaluation of the influence of industrial effluent.

Table 1. Sampling points and their designations

River section	Sampling point No	Designations
Upper Mukuvisi	1	Mutare Road Bridge
	X	Effluent canal from fertilizer plant
	2	Buck Road Bridge
	3	Mutare Rail Bridge
Middle Mukuvisi	4	Old Chiremba Road Bridge
	5	Arcadia Mainstream Foot Bridge
	Y	Arcadia Landfill Drainage Canal
	6	Seke Road Bridge
	7	Magaba bend
	Z	Effluent canal from Graniteside Industrial area
8	Cripps Road Bridge	

EXPERIMENTAL

Equipment. A Pye Unicam SP9 atomic absorption spectrophotometer (AAS) was used in conjunction with the appropriate Varian Techtron hollow cathode lamps (Varian Techtron (Pty) Ltd, Australia) for the determination of Cu, Co, Zn, Ni, Pb, Fe, Cr(III) and Cr(VI) while a Perkin Elmer Model 3100 AAS and Perkin Elmer hollow cathode lamps were used for the determination of Mn and Cd. Air-C₂H₂ and/or N₂O-C₂H₂ flame systems were used.

Samples were collected into 1 litre white polythene bottles. The polythene bottles, as well as all glassware used in the analysis, were washed with soap solution prepared using deionized water. The apparatus were rinsed with deionized water thoroughly before filling them with a 10% v/v nitric acid solution and letting them soak for at least 48 hrs. The apparatus were rinsed twice with distilled water and then once with deionized water before being used.

Materials. The following A.R. grade metal salts were used to prepare calibration standard solutions: copper sulphate pentahydrate, cobalt chloride dihydrate, ferric nitrate monohydrate, lead nitrate, nickel chloride dihydrate, cadmium metal and zinc metal.

Ammonium pyrolydinedithiocarbamate (APDC) and methylisobutylketone (MIBK) (reagent grade), pH 4.2 ammonium acetate buffer, pH 4.0 potassium hydrogen phthalate buffer solution, and other reagents used, were of A.R. grade.

Sampling and sample pretreatment. Samples from upper Mukuvisi were collected during May and July 1990, while samples from middle Mukuvisi were collected during May, June and July 1991. Samples were collected during the dry season to avoid surface run-off during the summer months influencing the results.

After collection water samples were, immediately upon arrival at the laboratory, filtered using a 0.45 µm cellulose nitrate filter paper mounted on a Pyrex filter holder and then acidified to pH 2 with nitric acid in order to keep the metals in solution. Thereafter the samples were stored in the dark at room temperature. Dissolved oxygen (DO) and the pH of the water samples were determined prior to filtration.

Sediment samples were collected from the top 25 cm of sediment directly below the point from which water samples were collected. The samples were collected using a polythene scoop into polythene bags previously soaked in dilute nitric acid for 48 hr and then rinsed thoroughly with deionised water. Once at the laboratory the sediments were centrifuged at 5000 rpm for 30 min to remove excess water and then stored under refrigeration. For analysis the sediment was thawed, air-dried and sieved through an 80 mesh sieve.

Analytical procedures. Copper, cobalt, zinc, nickel, lead, iron and manganese in the water samples were determined by atomic absorption spectrometry (AAS) following chelation with APDC at pH 5 and solvent extraction of the chelate with MIBK [3]. The organic layer was aspirated into the AAS without further concentration (the samples were concentrated by a factor of 10 after the solvent extraction).

Chromium (III) was determined by AAS after preconcentration by coprecipitation with Fe(III) hydroxide followed by acid digestion to redissolve the precipitate [4]. Cr(VI) was preconcentrated by co-precipitation using cobalt pyrrolidinedithiocarbamate (Co-APDC) as the gathering agent. The Co-APDC was filtered off using a Whatman No. 1 filter paper, then acid digested to redissolve the precipitate for AAS [5].

Total element levels in the sediment samples were determined by AAS after wet

ashing of the air-dried and sieved sediment with a 1:1:3 mixture of nitric acid, perchloric acid and hydrofluoric acid [6]. Teflon beakers were used for the acid digestion step.

Exchangeable cations in the dried sediment were determined by AAS after extraction with 1 M acetic acid, evaporation of the acetic acid and dissolution of the residue in hydrochloric acid [7].

Quantification was done using the calibration curve technique. Freshly prepared standard solutions were used for each run. All the standards were subjected to the same treatment as the samples. Blank determinations on the materials used in the analysis were carried out for all determinations. Concentration levels obtained for the various elements analysed at the different sampling sites are shown in Table 2 (upper Mukuvisi water samples), Table 3 (middle Mukuvisi water samples) and Table 4 (upper Mukuvisi sediment samples).

Dissolved oxygen (DO) values were determined by the Winkler method [8].

Table 2. Concentration of the metals listed for water collected along upper Mukuvisi river and the pH values at each point.

Sample		Concentration of metals (mg/L)							
No.	pH	Cu	Zn	Pb	Co	Fe	Ni	Cr(III)	Cr(VI)
1(a)	7.82	0.06	0.0595	0.030	0.016	0.056	0.038	0.056	0.007
(b)	7.14	0.035	0.0650	0.010	0.045	0.025	0.0293		
2(a)	5.80	0.084	0.685	3.380	0.240	0.130	0.040	0.200	0.008
(b)	5.49	0.040	0.850	3.960	0.125	0.150	0.052		
3(a)	6.18	0.070	0.645	0.480	0.200	0.500	0.080	0.260	ND
(b)	6.73	0.020	0.625	0.575	0.150	0.575	0.065		
WHO limit for drinking water									
		1.0	5.0	0.05	0.05	0.3	0.2 [*]	0.05	

ND = not detected, (a) = first sampling 19/05/90, (b) = second sampling 13/07/90, * = no use restriction.

RESULTS AND DISCUSSION

From Table 2 it is apparent that base levels for Cu, Zn, Pb, Co, Fe, and Ni at sampling point 1 are all well within acceptable levels in terms of the 1989 World Health Organization, WHO, water quality guidelines for drinking water [9]. Fig. 2 shows, however, that the levels of all the metals studied rise sharply between sampling points 1 and 2. This is attributed to industrial effluent discharged into the river, especially from the fertilizer manufacturing plant. This is confirmed in Table 4 which shows that the sediments in the effluent canal from the fertilizer plant are heavily polluted compared to sediments at point 1. The result is that levels of Pb, Co, Fe and Cr(III) in the river at sampling point 2 lie well above the WHO water quality guidelines [9]. Lead exceeds the recommended upper limit by factors of 79 and 10 at sampling points 2 and 3 respectively, while Cr(III) exceeds the recommended upper limit by a factor of 5 at point 2. The source of these elements is probably the raw materials used by the fertilizer plant, especially the phosphate rock concentrate [10]. Table 4 also shows that the effluent from the fertilizer plant was very acidic at pH 3.6.

Table 3. Mean concentration of ten trace metals in water samples taken from the middle Mukuvisi river (mg/L) for the period May to July, 1991.

Sampling point	Cd	Co	Cu	Cr(III)	Cr(VI)	Fe	Mn	Ni	Pb	Zn	pH	DO
4	0.408	0.399	0.167	0.054	0.007	0.439	0.049	0.385	0.293	0.322	7.55	4.97
5	0.443	0.425	0.150	0.118	0.004	0.454	0.060	0.220	0.241	0.541	7.82	3.61
Y	0.403	0.457	0.137	0.060	0.003	0.469	0.074	0.246	0.341	0.445	7.85	8.25
6	0.387	0.401	0.141	0.131	0.004	0.460	0.046	0.257	0.318	0.355	7.58	5.07
7	0.397	0.395	0.150	0.246	0.004	0.501	0.061	0.197	0.314	0.466	7.73	4.32
Z	0.424	0.470	0.178	0.120	0.008	1.380	0.080	0.207	0.393	0.525	7.73	1.65
8	0.397	0.477	0.153	0.187	0.004	0.559	0.086	0.195	0.251	0.289	7.78	4.41
WHO (Ref. 9) limits for drinking Water												
	0.005	0.05*	(1.0)	0.05	---	(0.3)	(0.1)	0.2*	0.05	(5.0)	(6.5-8.5)	>4**
Zimbabwe (Ref. 11)												
limits	0.01	---	0.05	0.05	---	0.3	0.1	0.3	0.05	1.0	6-9	>6

* = No use restriction.

** = Low quality water limit in India for river waters used for public supply.

Table 4. Total element (unbracketed) and 1 M acetic acid exchangeable cation (unbracketed) levels in the sediments of upper Mukuvisi river.

Sampling Point	pH (water phase)	Concentration levels of elements ($\mu\text{g/g}$)							
		Pb	Cr(III)	Cu	Zn	Ni	Co	Fe	
1	5.38	0.68 (0.31)	4.8 (4.6)	7.0 (0.25)	0.85 (0.25)	0.47 (0.52)	4.4 (3.9)	154 (154)	
X	3.60	97 (2.7)	14 (10)	17 (1.5)	5.9 (1.5)	0.78 (0.52)	11 (6.0)	243 (186)	
2	4.90	3.8 (0.35)	15 (11)	15 (4.5)	3.7 (3.0)	1.9 (1.1)	7.4	241 (225)	
3	5.78	3.5 (11)	15 (11)	20 (1.3)	6.3 (4.5)	2.6 (0.48)	14 (6.6)	240 (189)	

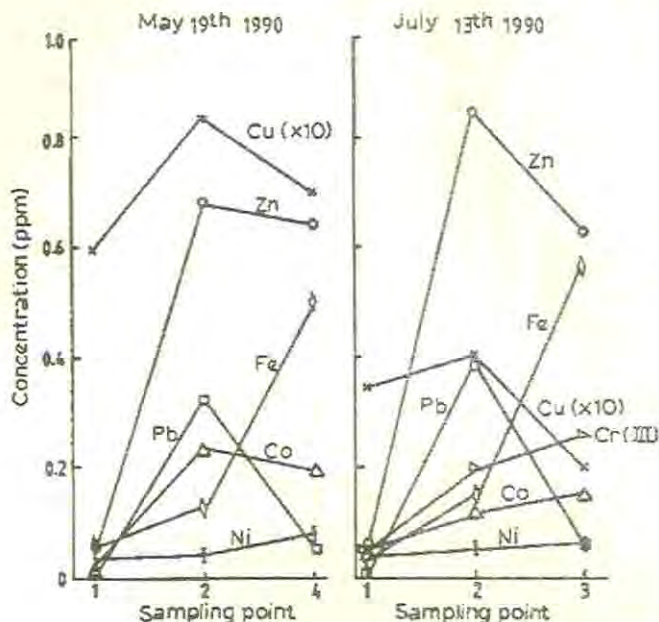


Fig. 2. Concentration levels of heavy metals in the water phase on May 19th and July 13th, 1990 at sampling points 1, 2 and 3.

Table 3 lists mean levels of the various heavy metals obtained for samples from middle Mukuvisi for the three months May to July 1991. Cu, Mn, and Zn fell within the WHO recommended upper limits. Cd, Co, Cr(III), Fe, Ni and Pb exceeded the recommended upper limits by factors of 89, 10, 5, 2, 2 and 6 respectively.

Fig. 3 and 4 show the levels of each element at points 5, Y and 6 (Fig. 3) and points 7, Z and 8 (Fig. 4) respectively as a function of time. From Fig. 3 it is apparent that, except for Cd and Zn, all the metals show similar trends at the three sampling points 5, Y and 6. This is true also for Cu, Cr(III), Fe, Mn, Ni and Pb (Fig. 4). The similarity in the curves for the leachate canals and points in the streams is evidence of the influence of the land filling on the heavy metal content of the stream. The curves for zinc in both Fig. 3 and 4 show that the downstream sampling point curves (i.e. points 6 and 8 respectively) resemble the curves for the leachate canals more closely than the upstream sampling point curve. This is also true for Cd (Fig. 4).

The metals Mn, Cu, Ni, Co and Fe show increasing levels in both the stream water and leachate canal water with time. The rate is however different for the different elements with Mn showing the least levels and lowest rate of increase. On the other hand Cr(III) and Pb levels increased from May to June, then dropped below the May levels in July. These trends are indicative of the similarity in the speciation trends of these metals within the landfill soil system and the Mukuvisi river water system. Cd

and Zn display different trends in the canal and the stream waters. The increase in the levels of Mn, Cu, Ni, Co and Fe are attributed to the faster reduction in the flow rate

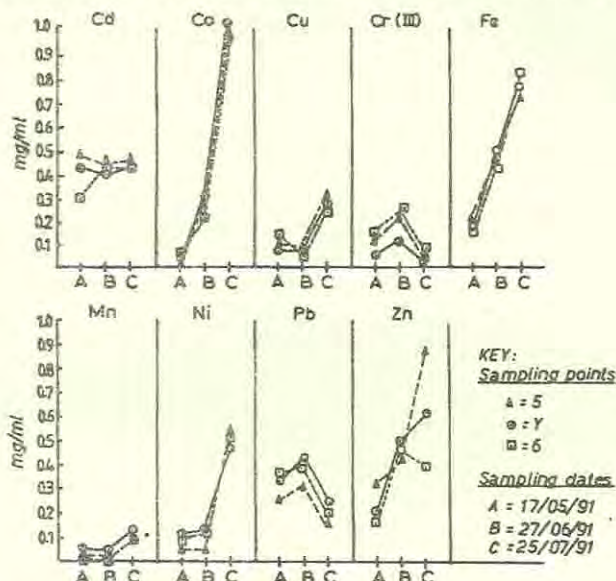


Fig. 3. Levels of heavy metals at sampling points 5, Y and 6 as a function of time.

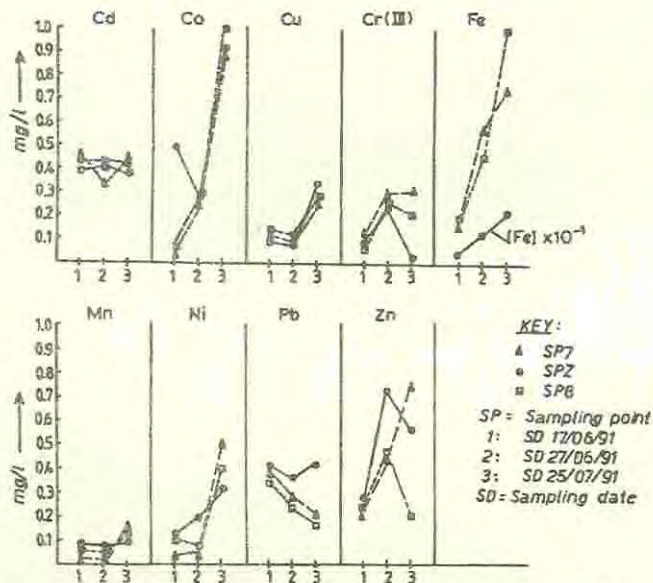


Fig. 4. Levels of heavy metals at sampling points 7, Z and 8 as a function of time.

of the river water compared to the flow rate of water within the landfill soil system as the dry season progresses.

The study overall confirmed that both leaching of heavy metals from the landfilling along the river banks and pollution from industrial effluent contribute to the pollution of the river by heavy metals.

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