

Determination and speciation of heavy metals in sediments of the Hartbeespoort Dam by sequential chemical extraction

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Abstract

The speciation of 10 heavy metals Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn in Hartbeespoort Dam sediments was determined by applying a sequential extraction procedure.

Environmental risks associated with the potential remobilisation probability of these metals were evaluated. The results showed that with regard to total metal content, the sediments of the Hartbeespoort Dam would compare with moderately to heavily polluted fluvial systems in Europe and North America. The observed metal distribution patterns in the different sediment fractions, however, indicated that major proportions of most metals seemed to be associated with the inert fraction and could therefore be classified to be of geochemical origin. This result is supported by the extraordinary metal-rich rock types of the Transvaal complex in the area surrounding the Hartbeespoort Dam.

Introduction

The ecological significance of heavy metals follows from their general toxicity and the fact that they are non-biodegradable (Förstner, 1990). Metals released into an ecosystem tend to accumulate in sediments through various adsorption and precipitation processes. They thus become part of the ecosystem more or less permanently. Remobilisation processes in which natural waters provide the main pathways, can reintroduce these metals into the ecosystem in a bio-available form. The biomethylation of mercury in sediments by bacteria to form toxic methyl mercury is well-known. The destructive effect that such an event can have on fish and human populations was tragically demonstrated in Minamata, Japan, not so long ago (Ishimure, 1991). Metals can also be released into the water phase when conditions like pH, redox potential, ionic strength and the concentration of organic complexing agents, change (Calmano et al., 1990).

It is generally accepted that the composition of top sediment layers reflects the current quality of a natural water system. The determination of heavy metals in sediments and in particular the physico-chemical forms in which they occur, can provide information that is essential to the proper assessment of risk and to the long-term conservation and management of a natural water system. Speciation data can address the question of metal reactivity, which to a large extent determines its impact on the environment. Reactivity is dependent on the metal's physico-chemical form which in turn will dictate its interaction capacity with other components or biota and consequently its bio-availability and toxicity.

The physico-chemical forms of metals bound to sediment phases may be determined by sequential extraction procedures (Förstner, 1982). A series of chemical extractants are applied in order of increasing strength to extract metals from the sediment sample into each of 5 speciation categories. The contamination risks associated with polluted sediments can be assessed from the distribution of the metals among the different fractions of the sediment. The speciation fractions are essentially operationally defined by the chemical properties of the extractants used. Metals associated with the "adsorptive or exchangeable" fraction, the "carbonate", the "reducible" and organic fraction are considered to

be more mobile, therefore more easily released from the sediment and potentially more dangerous. These 4 fractions would include metals from anthropogenic sources and therefore give some indication of the degree of pollution to which a particular sediment has been exposed. Metals reporting to the "inert" fraction could be interpreted as originating from geochemical or natural sources.

In this study sediments from the Hartbeespoort Dam were subjected to the sequential extraction procedure proposed by Tessier et al. (1979). The purpose was to get some indication of metal distributions in the different sediment categories and to predict possible environmental risks associated with the 10 metals included in this investigation.

Metal speciation studies have been reported for many major natural water systems in Europe (Pardo et al., 1990; Rauret et al., 1989) and North America (Campbell and Tessier, 1987). Speciation data for South African natural water resources are, however, practically non-existent. This work is an attempt to make a contribution in this regard.

Materials and methods

Sampling and sample treatment procedures

Sediment samples were taken during March 1992 at 3 locations around the Hartbeespoort Dam as indicated in Fig. 1. A standard Ekman grab (Håkanson and Jansson, 1983) was used to collect about 1 kg of sediment at each of the sampling points. The inner core of each sample was transferred to polyethylene bottles and stored under nitrogen at -4°C.

Water samples were taken at Site 1 near the dam wall and analysed for major components by the Hydrological Research Institute at Roodeplaat Dam. The depth sampled varied between 0 and 22 m. Samples were taken at least every 2 weeks, totalling about 30 samples per month.

The moisture content of centrifuged sediment was determined in order to relate results to mass of dry sediment. The wet (i.e. centrifuged at 3 000 r/min for 30 min) equivalent of 1 g of dry sediment was used in the sequential extraction procedures. During all procedures samples were kept under nitrogen atmosphere to prevent oxidation of the anoxic sediments. Samples were analysed in triplicate. Sample treatment, extraction and subsequent analytical determinations were performed in a clean laboratory. All

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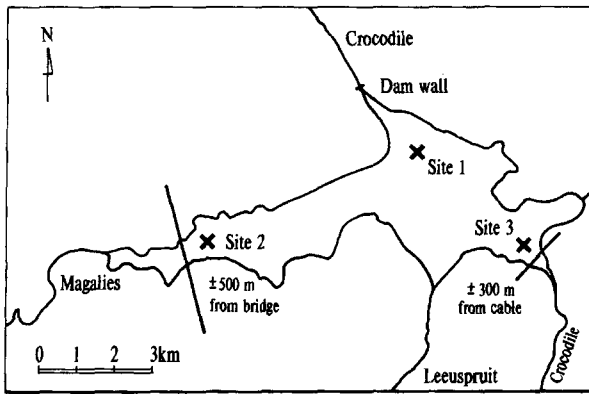


Figure 1

Map of study area showing the sampling sites:
 Site 1: near the dam wall (Longitude: 27°51'00";
 Latitude: 25°43'30")
 Site 2: at the Crocodile River inflow
 Site 3: at the Magalies River inflow

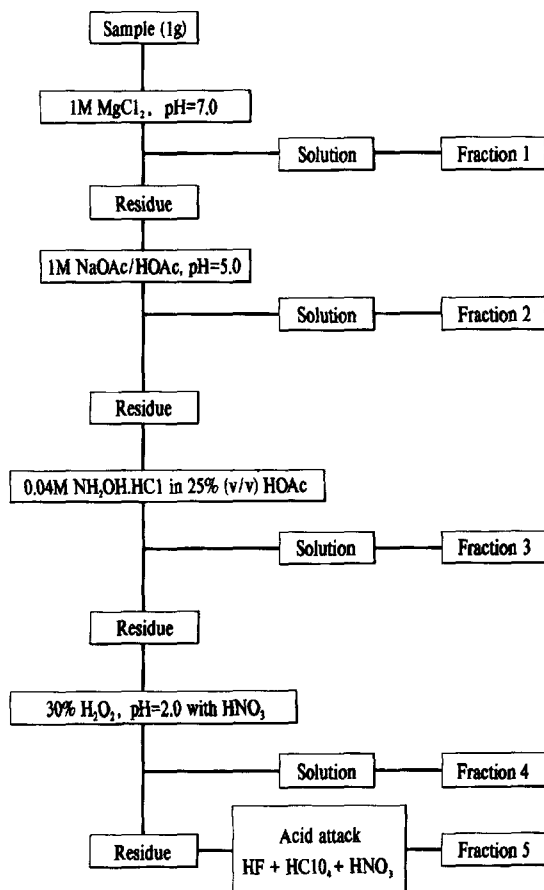


Figure 2

Flow diagram for Tessier sequential extraction scheme

glassware and plasticware used during analytical procedure were previously soaked in 10% (v/v) high purity nitric acid for 24 h and rinsed thoroughly with 18 Ω deionised water.

Sequential extraction procedure

The sequential extraction scheme of Tessier et al. (1979) was followed as summarised in the flow diagram shown in Fig. 2. All extractions were carried out in 50 ml glass centrifuge tubes. Continuous magnetic stirring or agitation in a mechanical shaker ensured proper mixing of sediment and extraction solution. Suspensions were centrifuged at 3 000 r/min for 30 min subsequent to each extraction step and the extracted metals then separated from the residual sediment by decantation.

A short description of the 5 fractions most likely to be relevant in assessing the effect of changing environmental conditions on polluted sediments is given below. A more detailed discussion may be found in the literature (Tessier et al., 1979).

Fraction 1: Exchangeable

Metals extracted in the exchangeable fraction would include weakly adsorbed metals particularly those retained on the sediment surface by relatively weak electrostatic interaction and those that can be released by ion-exchange processes. Changes in the ionic composition of the water would strongly influence these adsorption-desorption and ion-exchange processes of metal ions with the major constituents of sediments like clays, and the hydrated oxides of iron and manganese.

Procedure

1 g of sediment was extracted at room temperature for 1 h with 8 ml magnesium chloride solution (1 M MgCl₂, pH 7).

Fraction 2: Bound to carbonates

Significant amounts of trace metals like manganese can be co-precipitated with carbonates like calcite present in many sediments. Lowering of the pH could cause remobilisation of metals from this fraction.

Procedure

The residue from Fraction 1 was leached with 8 ml 1 M sodium acetate/acetic acid buffer at pH 5 for 5 h at room temperature.

Fraction 3: Bound to iron and manganese oxides

Iron and manganese oxides which can be present in sediments as concretions, cement between particles or coatings on particles, are excellent substrates with large surface areas for adsorbing trace metals. Reduction of Fe(III) and Mn(IV) under anoxic conditions and their subsequent dissolution, could release adsorbed trace metals.

Procedure

The residue from Fraction 2 was extracted under mild reducing conditions with 20 ml of 0,4 M hydroxyl amine hydrochloride (NH₂OH.HCl) in 25% (v/v) acetic acid at 96 ± 3°C in a waterbath for 6 h.

Fraction 4: Bound to organic matter

Various forms of organic matter like detritus, living organisms,

and coatings on mineral particles may bind trace metals through complexation or bioaccumulation processes. Under oxidising conditions these substances may be degraded thus leading to a release of soluble metals. Some uncertainty with regard to the behaviour of sulphide minerals in the Tessier scheme still remains, but it can be expected that substantial amounts of these minerals might extract in this fraction. More stable sulphides are expected to report to the inert fraction.

Procedure

The residue from Fraction 3 was treated with 3 ml 0,02 M nitric acid and 5 ml 30% (v/v) hydrogen peroxide. The mixture was heated to $85 \pm 2^\circ\text{C}$ in a waterbath for 3 h. After cooling, 5 ml of 3,2 M ammonium acetate in 20% (v/v) nitric acid was added to the sample and diluted to 20 ml.

Fraction 5: Residual or inert fraction

The residual fraction largely consists of mineral components where metals are firmly bonded within the crystal structure of the minerals comprising the sediment. These metals are not likely to be released into solution under normal environmental conditions.

Procedure

The residue from Fraction 4 was digested with a 5:1 mixture of hydrofluoric acid and perchloric acid in Teflon beakers.

Instrumentation and reagents

All reagents were analar quality obtained from Merck. ICP standard solutions were obtained from Johnson Matthey.

An ARL 35 000 sequential inductively coupled plasma (ICP) atomic emission spectrometer was used for all metal determinations.

A Philips PW 1700 X-ray powder diffractometer was used to determine the mineralogical composition of the sediment samples with CoK_α radiation generated at 40 kV and 40 mA. Samples were ultrasonically disaggregated, air-dried, sieved and the $< 63\mu$ fraction presented for X-ray diffraction analysis. The clay fraction, defined as less than 2μ in particle size, was separated using the method of Hardy and Tucker (1988) to identify the mineral components. The quartz content was determined quantitatively by using external standards consisting of 5, 10 and 15% SiO_2 in a known mixture of montmorillonite and muscovite.

Results and discussion

Composition of sediments

Table 1 summarises the mineralogical composition of the sediment samples as determined qualitatively by X-ray diffraction analysis.

All 3 samples were essentially similar mineralogically and consisted of about 15 to 20% quartz and less than 5% organic material.

Chemical analyses of Hartbeespoort Dam water

The results for the chemical analyses of the Hartbeespoort Dam water for major components are summarised in Table 2 for the period March 1992 to March 1993. The data show that the water quality remains fairly constant throughout the year as far as major

TABLE 1
MINERAL COMPOSITION OF SEDIMENTS

Mineral	Structure*	Possible host mineral for
Quartz	SiO_2	
Calcite	$\text{A}^{+2}(\text{CO}_3)$ $\text{A}^{+2} = \text{Ca, Cd, Co, Fe, Mg, Mn, Ni, Zn}$	Cd, Co, Mn
Clinocllore	$(\text{Mg, Fe}^{2+})_3\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$	Mn, Ni, Zn, Fe
Mica (muscovite)	$\text{K Al}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH,F})_2$	Cr, V, Zn
Feldspar	XZ_4O_8 X=Ba, Ca, K, Na, NH_4 , Sr Z = Al, B, S:	
Amphibole	$\text{A}_{0-1}\text{B}_2\text{Y}_5\text{Z}_8\text{O}_{22}(\text{OH, F, Cl})$ A = Ca, Na, K, Pb B = Ca, Fe^{2+} , Li, Mg, Mn^{2+} , Na Y = Al, Cr^{3+} , Fe^{2+} , Fe^{3+} , Mg, Mn^{2+} , Ti Z = Al, Be, Si, Ti	Pb, Cr, Cd, Fe
Clay minerals (montmorillonite)	$\text{Y}_{2-3}\text{Z}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ Y = Al, Cr^{3+} , Cu, Fe^{2+} , Fe^{3+} , Li, Mg, Ni, Zn Z = Al, Si	Cr, Cu, Ni, Zn, Fe

*Fleischer and Mandarino, 1991

TABLE 2
CHEMICAL ANALYSIS DATA FOR HARTBEEPOORT DAM. MONTHLY AVERAGE VALUES

Date	Elec. cond. mS/m	Total diss. salts	pH	Na µg/ml	Mg µg/ml	Ca µg/ml	Cl µg/ml	NO ₃ +NO ₂ as N µg/ml	SO ₄ µg/ml	PO ₄ as P	Total alkal. as CaCO ₃	K µg/ml
3/92	61,44	390,41	8,42	51,76	18,00	29,76	58,76	0,59	82,41	0,023	111,53	10,46
SD	1,79	4,69	0,13	1,09	0,35	1,39	1,44	0,39	4,08	0,034	5,21	0,11
4/92	60,93	401,33	8,01	54,67	18,29	31,92	58,08	0,77	85,67	0,012	113,25	11,02
SD	1,00	7,85	0,39	0,64	0,62	0,97	1,56	0,09	3,61	0,004	3,79	0,20
5/92	60,93	417,25	8,10	60,0	18,75	33,50	55,88	1,14	89,25	0,012	117,88	11,05
SD	2,36	1,28	0,09	0,0	0,46	0,53	0,64	0,01	0,46	0,001	1,46	0,053
6/92	64,8	418,14	8,36	55,71	18,14	34,64	60,29	1,42	89,86	0,094	116	11,18
SD	2,46	5,93	0,15	0,99	0,36	0,63	1,27	0,22	1,17	0,180	2,04	0,11
7/92	63	430,77	8,35	57,77	19,00	36,92	59,31	1,53	92,00	0,018	121,07	11,3
SD	2,39	5,23	0,12	1,42	0,00	1,04	0,63	0,07	1,73	0,010	0,64	0,082
8/92	67,08	448,00	8,54	60,50	18,50	38,19	58,94	1,71	92,94	0,017	130,38	11,49
SD	1,24	5,48	0,22	0,73	0,52	1,04	2,38	0,10	1,61	0,009	1,26	0,23
9/92	66,45	461,13	8,96	61,75	19,88	39,38	65,00	1,56	89,50	0,024	136,63	11,79
SD	3,64	4,19	0,28	1,04	0,35	0,74	2,27	0,89	0,93	0,008	1,77	0,12
10/92	67,08	467,60	8,77	66,00	19,27	36,47	64,80	1,00	96,53	0,020	137,27	12,01
SD	3,10	7,98	0,32	2,83	0,59	1,30	4,33	0,26	4,26	0,008	6,51	0,32
11/92	67,07	450,28	8,59	62,22	18,00	34,94	60,83	0,95	89,78	0,14	131,39	11,93
SD	1,44	9,90	0,19	1,56	0,34	1,31	3,71	0,29	3,93	0,10	20,13	0,25
12/92	62,22	414,84	9,09	58,95	17,16	33,53	54,14	1,10	83,74	0,11	120,79	11,47
SD	2,97	16,83	0,48	2,57	1,07	1,50	11,80	0,23	3,74	0,07	7,22	0,91
1/93	59,54	393,26	9,07	55,42	15,74	31,79	54,00	0,57	78,16	0,14	117,37	11,05
SD	2,60	13,96	0,39	1,46	0,65	1,44	3,02	0,28	3,72	0,11	8,28	0,58
2/93	53,97	389,18	9,00	54,09	15,27	32,09	54,55	0,42	73,91	0,22	118,45	11,091
SD	2,34	10,74	0,53	1,22	0,47	0,30	1,75	0,26	2,98	0,18	8,99	0,77
3/93	52,94	395,38	9,30	56,38	15,63	31,75	52,75	0,84	74,38	0,37	121,5	11,78
SD	3,17	3,54	0,33	1,30	0,52	0,89	1,28	0,67	1,19	0,64	2,83	0,23

components are concerned. Trace element data for the Hartbeespoort Dam proved difficult to find. Our own data for sampling Site 1 give some indication of the metal concentrations in the water during February 1993. Dissolved metal concentrations were extremely low which could be expected for water with pH values generally above 8. Metal concentrations were below 10 µg/l for all metals except iron (59 µg/l), chromium (95 µg/l) and zinc (54 µg/l). This result seems to indicate that metal transport to the sediments could largely be through particulate matter. During this period the dam level decreased from 14,38 m in March 1992 to a minimum of 9,52 m in October 1992. From November 1992 the water level steadily

rose to 11,85 in February 1993. Water level, as is to be expected, seems to be the main determinant in explaining the temporal variation in component concentrations which show an inverse correlation with water level.

Mineralogy of surrounding rocks

The catchment area of the Hartbeespoort Dam can be divided into 4 main mineralogical areas for the purpose of correlating the metal distribution in the dam sediments with the host minerals of these metals in the surrounding rocks. These are shown in Fig. 3 and

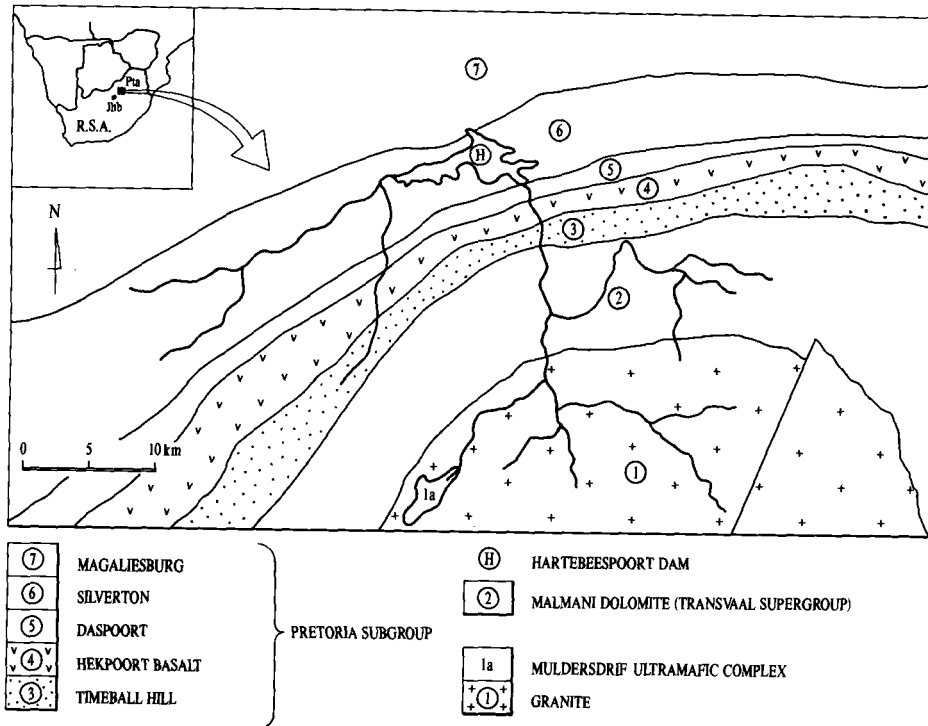


Figure 3
Catchment area of the Hartbeespoort dam showing typical rock types

consist of the Johannesburg Dome (area No.1), the Muldersdrif Ultramafic Complex (area No.1a), the Malmani Dolomites (area No.2) and the Pretoria Group (area No.3 to 7). The Crocodile River and its tributaries originate in the Johannesburg Dome area shown as area No. 1 in Fig. 3. This area consists mainly of granite (Table 3). The river then flows northwards toward the dam, first through the Malmani Dolomites (area No. 2) which contains (Table 3) up to 8% iron as Fe_2O_3 and 1% manganese as MnO. These dolomites are also known (Button, 1973) to have anomalously high zinc concentrations of up to 445 $\mu g/g$. Lead can be present in spots in substantial quantities. Black shale which is common within Malmani Dolomites is rich in most transition metals (Table 3). The dam itself is located within the Pretoria Group of rock types (area No. 3 to 7) which consist of quartzite conglomerate, shale and basaltic andesite (Table 4). The Magalies River also passes over rocks of this type.

An interesting potential source of metals is found in the Muldersdrif ultramafic complex (area No. 1a) which is situated at the source of the Crocodile River. This complex is especially rich in chromium and nickel (Table 3).

Weathering of the dominant rock types in the catchment area of the Hartbeespoort Dam would typically yield (Klein and Beukes, 1989) the minerals found in the sediment samples. These mineral types therefore seem to be appropriate host minerals to explain the metal content in the inert fraction as determined by sequential extraction (see next section).

Speciation of heavy metals

The results obtained for the sequential extraction of heavy metals from Hartbeespoort Dam sediments are summarised in Table 5. The table shows the percentage distribution of the 10 metals

among the 5 sediment fractions. It also gives the total metal content which was calculated by summation of metal concentrations in the individual fractions for each sediment. The average standard deviation for the triplicate determinations was less than $\pm 10\%$. The results show a marked similarity in the speciation patterns for the 3 sampling sites. The behaviour of the individual metals however, showed significant differences.

The iron content of all 3 sediment samples was very high, almost 10%. This somewhat unexpected result was confirmed by X-ray fluorescence analysis. The reason is to be found in the iron-rich basaltic rocks (rock type 4 in Fig. 3). These rock types contain up to 10% iron as iron oxides. The Magalies and the Crocodile Rivers flow through these regions. In addition the Malmani Dolomites (rock type 2 in Fig. 3) contain about 1,4% iron as Fe_2O_3 .

The relatively high manganese content of 0,3% is largely, i.e. between 65% and 80% associated with the "carbonate" fraction (Table 6). The predominant source of manganese therefore seems to be the Malmani Dolomites (rock type 3 in Fig. 3) which contain an average of about 0,5% manganese as MnO.

The Malmani Dolomites are anomalously high in zinc (range : 10 to 445 $\mu g/g$) and also contain metals like lead (range: 5 to 60 $\mu g/g$) copper, nickel and vanadium in substantial amounts.

Cadmium, cobalt and chromium seem to be absent from the rocks in the immediate vicinity of the dam. A small part of the dome, called the Muldersdrif Ultramafic Complex which is rich in heavy metals like chromium, is connected to the dam through one of the tributaries of the Crocodile River. Further study would, however, be necessary to prove this connection. It would therefore seem possible that lead, cadmium, cobalt and chromium may be derived from anthropogenic sources.

TABLE 3
CHEMICAL ANALYSES OF THE MULDERSDRIF
ULTRAMAFIC COMPLEX, JOHANNESBURG DOME
AND THE MALMANI DOLOMITES

Major element oxide	Johannesburg Dome ⁽¹⁾ (%)	Malmani Dolomites ⁽²⁾ (%)	Muldersdrif Ultramafic Complex ⁽¹⁾ (%)
SiO ₂	72,3	0,7 - 31	40 - 51
Al ₂ O ₃	14,4	-	1,05 - 15
Fe ₂ O ₃	0,5	0,3 - 7,7	1,2 - 5,5
FeO	1,1	-	1,2 - 10,5
MnO	0,04	0,1 - 1,0	0,1 - 0,3
MgO	1,6	14 - 23	7,6 - 38
CaO	4,3	18 - 23	0,25 - 15,5
K ₂ O	4,0	-	0,1 - 1,7
TiO ₂	0,23	-	0,07 - 1
Trace metal	(µg/g)	(µg/g)⁽³⁾	(µg/g)
Cd	-	-	-
Cr	-	3 - 286	152 - 4200
Co	-	2 - 43	57 - 126
Cu	-	10 - 100	15 - 138
Zn	-	10 - 445	-
Pb	-	5 - 60	-
Ni	-	30 - 180	245 - 2760
V	-	30 - 180	-

(1) Anhaeusser (1978)
(2) Button (1973)
(3) Klein and Beukes (1989)

Cadmium and zinc

Cadmium and zinc usually show similar environmental behaviour (Förstner, 1990). These results, however, indicate that Cd was primarily extracted from the residual or inert fraction while Zn was distributed through all fractions with a predominance of about 65% in the organic and reducible fractions. The differing distribution of Cd and Zn is probably not significant because the relatively low total concentration of Cd made its quantitative determination difficult in the sequentially extracted fractions. The detection limit for Cd in the ICP measurements on the extracted solutions was 0,15 µg/ml which was equivalent to about 4 µg/g in the dry sediment. It means that an extraction percentage of less than 50% in any of the fractions would not be detectable. The Cd reporting in Fraction 5 is therefore total Cd and cannot necessarily be classified as inert metal - in fact this would be a most unlikely explanation.

Chromium

Chromium was primarily found in the inert fraction (76%) but also in the organic phase (20%).

TABLE 4
CHEMICAL ANALYSES OF PRETORIA GROUP
ROCK TYPES

Rock type Area No. in Fig. 3	Shale ⁽¹⁾ 3,6 (%)	Quartzite ⁽²⁾ 5 (%)	Basalts ⁽³⁾ 4 (%)
SiO ₂	62,37	94,3 - 95,5	50,5 - 55,6
Al ₂ O ₃	19,07	1,72 - 3,02	14,37 - 14,74
Fe ₂ O ₃	7,68	0,76 - 1,86	0,91 - 1,11
FeO	-	-	8,37 - 10,45
MnO	0,05	0-0,01	0,17 - 0,2
MgO	3,10	0 - 0,02	6,50 - 7,56
CaO	2,71	0,03 - 0,11	7,24 - 10,63
K ₂ O	3,58	0,34 - 1,1	0,15 - 1,47
TiO ₂	0,64	0,01 - 0,04	-
Cr ₂ O ₃	0,06	0,05 - 0,06	-
NiO	0,01	0,0 - 0,01	-
Trace metal	(µg/g)	(µg/g)	(µg/g)
Cd	-	-	-
Cr	130 - 173	147,4 - 175,1	-
Co	12 - 17	2,1 - 5,7	-
Cu	29 - 50	4,1 - 8,1	-
Zn	74 - 100	8,3 - 30,3	-
Pb	21 - 33	8,6 - 16,4	-
Ni	54 - 95	1,8 - 18,5	-
V	123 - 178	15,1 - 40,9	-

(1) Schreiber et al. (1992)
(2) Schreiber (1991)
(3) Button (1973)

Copper

The most remarkable feature of this metal is its strong association with the organic phase (> 50%). This is a well-known phenomenon according to previous reports in the literature (Salomons and Förstner, 1980).

Cobalt, nickel and vanadium

Cobalt, nickel and vanadium showed similar speciation patterns with 60 to 90% of the metals found in the inert phase and the rest evenly distributed between the reducible and carbonate phases.

Lead

Lead was found only in the inert phase. The detection limit for lead for the ICP determination was, however, relatively high at about 1 µg/ml. The amount of lead extracted from the other fractions might therefore have been too low for detection.

Iron and manganese

The iron and manganese contents were high in all samples as could

TABLE 5
SPECIATION PATTERN FOR METALS IN SEDIMENTS OF THE HARTBESPOORT DAM

Sampling site	Speciation category (%)					Total metal Hartbees sediment $\mu\text{g/g}$	Heavily* polluted sediment $\mu\text{g/g}$
	Fraction 1 Exchange-able	Fraction 2 Bound to carbonate phases	Fraction 3 Bound to oxide phases	Fraction 4 Bound to organic matter	Fraction 5 Inert metal		
Cadmium							
Hartbees	0,0	0,0	0,0	0,0	100	8,75	
Crocodile	0,0	0,0	0,0	0,0	100	8,43	
Magalies	0,0	0,0	0,0	0,0	100	7,78	
$\bar{x} \pm \text{SD}$	0,0	0,0	0,0	0,0	100	8,32 \pm 0,48	>6
Chromium							
Hartbees	0,0	0,0	8,7	19,4	71,9	180	
Crocodile	1,7	0,0	0,7	23,1	74,4	142	
Magalies	2,0	0,0	9,6	12,8	75,6	181	
$\bar{x} \pm \text{SD}$	1,2 \pm 1,1	0,0	6,3 \pm 4,8	18,5 \pm 5,3	74,0 \pm 2	168 \pm 22	>75
Cobalt							
Hartbees	0,0	5,0	10,4	0,0	84,7	79,9	
Crocodile	0,0	0,0	5,0	0,0	95,0	64,4	
Magalies	0,0	0,0	14,5	0,0	85,5	74,8	
$\bar{x} \pm \text{SD}$	0,0	1,8 \pm 2,8	10,2 \pm 4,8	0,0	88,0 \pm 5,7	73,1 \pm 7,9	
Iron							
Hartbees	0,2	12,8	16,1	5,7	65,1	108 770	
Crocodile	0,1	6,4	12,7	7,7	73,0	81 622	
Magalies	0,0	9,8	19,6	5,4	65,2	97 509	
$\bar{x} \pm \text{SD}$	0,1 \pm 0,1	10,0 \pm 3,2	16,3 \pm 3,4	6,2 \pm 1,2	67,4 \pm 4,5	95 967 \pm 13 600	>2 500
Copper							
Hartbees	0,0	0,0	0,0	50,0	50,0	61,8	
Crocodile	0,0	0,0	0,0	63,1	36,9	71,7	
Magalies	0,0	0,0	0,0	41,4	58,6	40,1	
$\bar{x} \pm \text{SD}$	0,0	0,0	0,0	53,4 \pm 10,9	46,6 \pm 10,9	57,8 \pm 16,1	>50
Zinc							
Hartbees	1,2	9,7	33,8	40,6	14,8	282	
Crocodile	0,9	8,2	54,9	27,5	8,5	380	
Magalies	0,4	5,8	17,2	60,1	16,5	183	
$\bar{x} \pm \text{SD}$	0,9 \pm 0,4	8,2 \pm 1,9	39,7 \pm 18,8	39,0 \pm 16,4	12,3 \pm 4,2	282 \pm 98	200
Lead							
Hartbees	0,0	0,0	0,0	0,0	100,0	178	
Crocodile	0,0	0,0	0,0	0,0	100,0	112	
Magalies	0,0	0,0	0,0	0,0	100,0	142	
$\bar{x} \pm \text{SD}$	0,0	0,0	0,0	0,0	100,0	144 \pm 33	>200
Nickel							
Hartbees	0,0	26,7	13,1	4,0	56,3	97,2	
Crocodile	1,2	17,2	14,1	11,9	55,6	108,8	
Magalies	0,0	0,0	27,7	9,5	62,7	76,3	
$\bar{x} \pm \text{SD}$	0,5 \pm 0,6	15,8 \pm 13,5	17,4 \pm 8,1	8,5 \pm 4	57,8 \pm 3,9	94,1 \pm 16,4	
Manganese							
Hartbees	4,5	81,2	6,5	2,9	4,9	2 900	
Crocodile	4,0	59,2	10,2	2,1	24,5	3 164	
Magalies	4,5	57,9	23,1	3,9	10,5	3 015	
$\bar{x} \pm \text{SD}$	4,3 \pm 0,3	66,8 \pm 13,3	12,1 \pm 8,7	2,8 \pm 0,9	14,0 \pm 10,1	3 026 \pm 132	>500
Vanadium							
Hartbees	0,0	1,1	23,4	11,2	64,4	127	
Crocodile	0,0	0,0	8,1	8,7	83,3	106	
Magalies	0,0	0,0	20,7	13,0	66,3	134	
$\bar{x} \pm \text{SD}$	0,0	0,4 \pm 0,5	18,0 \pm 8,1	11,1 \pm 2,1	70,5 \pm 10,4	123 \pm 14	

* Toxicity classification of sediments according to EPA regulations (Thomas, 1987)

have been expected considering the rock types in the catchment area of the Hartbeespoort Dam (See Fig. 3). It is interesting to note that iron was mainly released from the inert fraction while manganese was released from the carbonate fraction. The reason for the former may be the incomplete dissolution of iron in Step 3 because of the exceedingly high iron content of the sediments.

Various interpretations can be given to these results. It should, however, be pointed out that extraction results do not necessarily prove the existence of any of the defined phases in a sediment but merely reflect the chemical behaviour of the metals with the different extracting solutions. More important is the understanding that the potential environmental impact of the metals could be estimated from the degree of remobilisation measured in the 5 extraction categories. The first 4 categories which could indicate the possible release of metals through the lowering of pH (exchangeable and bound to carbonate) and changes in redox potential (reducible and organic phases) are the most useful in assessing the potential pollution risk of contaminated sediments. Metals associated with the inert or mineralogical phase are often of natural origin and do not generally constitute an environmental risk. The stable nature of the compounds and the fact that the metals are bonded firmly within the mineral lattice, restrict the bio-availability of these metals.

Inspection of Table 5 shows the highest potential for pollution coming from zinc with 40% of the fairly high zinc content of 282 µg/g associated with organic matter, 40% with the reducible phase, and 8% with the carbonate phase. Almost 90% of zinc could therefore be potentially remobilisable. It also indicates that zinc in these sediments could primarily be of anthropogenic origin and therefore could be classified as a pollutant. The same behaviour would generally be expected from cadmium.

Copper was found primarily in the organic phase indicating that 50% of copper could be recycled. The same applies to chromium although the chromium content in the organic phase is lower at around 20%.

The average manganese concentration of 2 693 µg/g is relatively high and was found largely in the carbonate phase. A decrease in the pH of the dam water could release substantial amounts of manganese.

Other heavy metals were mainly associated with the inert phase and do not pose an immediate environmental problem.

The relative amount of metal present in the residual phase can be used as an indicator of the degree of contamination from

anthropogenic sources. The greater the relative amount of metal in the inert phase, the smaller the degree of pollution.

Comparison of our results for the Hartbeespoort Dam with results for zinc, copper and nickel from fluvial systems in Europe and North America, is shown in Table 6. Salomons and Förstner (1980) have shown that the lithogenous fraction of heavy metals increased in less polluted rivers. The Hartbeespoort Dam compares with an averagely polluted river system in Europe using this criterion.

Non-sequential extraction

An indication of the reliability of the sequential extraction procedure was obtained by carrying out extractions non-sequentially - that is applying each extraction step to a fresh aliquot of sediment. The results of this exercise are shown in Table 7. It is rather surprising to note that the total amount of metal extracted using the sequential and non-sequential procedures is in fairly good agreement. This in addition to the fact that the speciation patterns obtained in both experiments were essentially the same, is strong evidence that the extraction procedures are adequately selective for the type of sediments under investigation.

Notable exceptions were observed for those metals showing a significant presence in the organic phase. For copper and zinc for instance the non-sequential procedure seemed to fail in extracting these metals to the same extent as the sequential procedure. This phenomenon might be explained, considering the absence of the reduction step, with hydroxyl amine which involves heating at 96°C for 6 h. Partial decomposition of the organic matrix might occur during this step. This might contribute to the ease with which these metals were released from the organic phase in the following step.

Conclusion

This work was a first attempt at studying the speciation of these 10 heavy metals in a South African sediment. For this purpose we used a proven extraction procedure which would allow comparison of results with those obtained for systems in other parts of the world.

The results provide a useful basis to indicate the level of heavy metal pollution in the Hartbeespoort Dam and may be used to assess the potential risks of remobilisation effects.

TABLE 6
PERCENTAGE OF METAL IN THE INERT FRACTION IN SOME NATURAL
WATER SYSTEMS

Natural water system						
Metal	Rhine	Schelde	Hartbees- poort	Seine	Garonne	Ottawa
← increasing pollution						
zinc	17,4	4,4	12,3	30,4	47,8	87,0
copper	23,9	17,4	46,6	47,8	69,6	91,3
nickel	17,4	56,5	57,8	60,9	73,9	87,0

TABLE 7
SPECIATION PATTERNS FOR METALS IN SEDIMENTS OBTAINED BY NON-SEQUENTIAL EXTRACTION

Sampling site	Speciation category (%)					Total metal ($\mu\text{g/g}$)	
	Exchange-able	Bound to carb. phases	Bound to red. phases	Bound to org. matter	Inert metal	Hartbees sediment	Mean* sediment
Cadmium							
Hartbees	5,1	0,0	15,0	0,0	79,9	11,52	
Magalies	9,8	0,0	0,0	0,0	90,2	6,73	
$\bar{x} \pm \text{SD}$	7,5 \pm 3,3	0,0	7,5 \pm 10,6	0,0	85,0 \pm 7,2	9,13 \pm 3,3	0,17
Chromium							
Hartbees	0,0	0,0	0,0	17,9	82,1	205,4	
Magalies	0,4	0,0	12,7	2,5	84,5	166,6	
$\bar{x} \pm \text{SD}$	0,2 \pm 0,3	0,0	5,7 \pm 8,9	11,0 \pm 10,8	83,1 \pm 1,7	186,0 \pm 27,4	72
Cobalt							
Hartbees	0,2	0,0	19,7	0,0	80,1	104,5	
Magalies	0,0	0,0	18,8	0,0	81,2	63,9	
$\bar{x} \pm \text{SD}$	0,1 \pm 0,1	0,0	19,4 \pm 0,6	0,0	80,5 \pm 0,8	84,2 \pm 28,7	14
Iron							
Hartbees	0,1	9,7	24,8	4,9	60,6	160 009	
Magalies	0,1	1,7	25,5	1,8	70,9	89 412	
$\bar{x} \pm \text{SD}$	0,1 \pm 0	6,8 \pm 5,6	25,0 \pm 0,5	3,8 \pm 2,5	64,3 \pm 7,2	124 710 \pm 49 900	41 000
Copper							
Hartbees	1,8	0,0	0,0	1,3	96,8	42,6	
Magalies	2,0	0,0	0,0	22,1	75,9	42,0	
$\bar{x} \pm \text{SD}$	1,9 \pm 0,1	0,0	0,0	11,7 \pm 14,7	86,4 \pm 14,7	42,3 \pm 0,4	50
Zinc							
Hartbees	0,2	1,5	44,4	19,7	34,3	240,1	
Magalies	0,8	9,1	34,0	17,0	39,1	82,3	
$\bar{x} \pm \text{SD}$	0,4 \pm 0,4	5,3 \pm 5,3	40,7 \pm 7,3	18,1 \pm 1,9	35,5 \pm 3,4	111	95
Lead							
Hartbees	0,0	0,0	0,0	0,0	100,0	167,9	
Magalies	0,0	0,0	0,0	0,0	100,0	89,9	
$\bar{x} \pm \text{SD}$	0,0	0,0	0,0	0,0	100,0	128,9 \pm 55,1	19
Nickel							
Hartbees	0,2	13,1	41,4	0,0	45,4	169,8	
Magalies	0,6	11,3	21,5	0,0	66,6	90,8	
$\bar{x} \pm \text{SD}$	0,4 \pm 0,2	12,5 \pm 1,2	34,3 \pm 14,1	0,0	52,8 \pm 14,9	130,3 \pm 55,8	52
Manganese							
Hartbees	1,4	36,0	28,0	15,8	18,8	8 413	
Magalies	2,9	31,1	27,7	15,1	23,2	3 330	
$\bar{x} \pm \text{SD}$	1,8 \pm 1,1	34,6 \pm 3,4	27,9 \pm 0,2	15,6 \pm 0,5	20,1 \pm 3,1	5 871 \pm 3 594	670
Vanadium							
Hartbees	0,0	0,0	23,7	8,1	68,2	163	
Magalies	0,0	0,0	23,0	9,1	67,9	130	
$\bar{x} \pm \text{SD}$	0,0	0,0	23,4 \pm 0,5	8,5 \pm 0,7	68,1 \pm 0,2	147 \pm 23	105

* Elemental composition of average earth sediment (Salomons et al., 1984)

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