



Determination and partitioning of heavy metals in sediments of the Vaal Dam System by sequential extraction

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Abstract

The partitioning of 12 heavy metals in sediments of the Vaal Dam system was determined by applying a sequential extraction procedure. Environmental risks associated with the potential remobilisation of these metals, the capacity of the sediment to continue functioning as a sink and the possible origin of the metals were assessed. Despite the fact that the water level was at record lows, ca. 13% in the Vaal Dam, the extractable metal content of the sediments was low, indicating a relatively unpolluted system. Major proportions of most metals seemed to be associated with the inert phase and could therefore be classified as of geochemical origin.

Introduction

Approximately 99.5% of all water abstracted and treated by Rand Water is surface water obtained from the Vaal Dam and the Vaal River Barrage. Rand Water supplies potable water to some 60% of South Africa's industrial undertakings and to about 9 m. people. The raw water abstracted from the Vaal River Barrage is normally of inferior quality when compared to the water abstracted from the Vaal Dam. The Vaal Dam water is low in electrolytes, turbid and relatively unpolluted, and drains a rural agricultural area. The Klip and Suikerbosrant Rivers, draining the industrialised Witwatersrand area, are high in mineral content and have low turbidity. Approximately 55% of Rand Water's purified water is supplied to the southern side of the Witwatersrand divide. Of this water, 65% finds its way into the Vaal River Barrage as treated domestic and industrial effluent, mainly through the Klip River (Information from Rand Water).

Since the Vaal Dam is of great importance to millions of people, it is necessary to monitor the quality of the water. This is done on a continual basis by various organisations like Rand Water, Department of Water Affairs and Forestry and the CSIR. It is, however, not enough to monitor only the water quality and not the condition of sediments, since sediments accumulate pollutants, in particular trace metals. The resuspension of sediments and remobilisation of pollutants from sediments because of shifts in water/sediment equilibria, can substantially affect water quality. Analytical data on the particulate speciation of metals in different sediment phases could therefore provide valuable information to assess the condition of the system and to predict potential environmental risks.

The ecological significance of heavy metals follows from their general toxicity and the fact that they are non-biodegradable. The composition of sediments, in particular the top layers, affects the current quality of the natural water system. Sequential extractions (Batley, 1989) have been used for more than a decade to obtain data regarding the particulate speciation of metals in sediments. A series of chemical extractants is applied in order of increasing strength to extract metals from the sediment sample into each of four speciation categories. The contamination risks

associated with polluted sediments can then be assessed from the distribution of the metals among the different phases of the sediment. Despite many pitfalls in the interpretation (Nirel and Morel, 1990) of sequential extraction data, the procedures are widely used in Europe (Pardo et al., 1990). With extensive validation (Coetzee et al., 1995) of the procedure and the proper appreciation of the chemistry of the extraction processes involved, we believe that sequential extraction can provide useful information to environmental scientists, water authorities and sedimentologists. The procedure is very successful in distinguishing between metals originating from anthropogenic sources and metals of geochemical origin.

Particulate speciation data on sediments of rivers and lakes are common in Europe and North America. Speciation data for South African river and dam sediments are, however, not readily available. Coetzee (1993) studied the sediments of the Hartbeespoort Dam by sequential chemical extraction using the Tessier scheme. Kempster et al. (1991) carried out sequential pH extractions for iron, manganese, copper and vanadium on the sediments of the Loskop Dam and Phalaborwa Barrage.

In this work we applied the BCR (Community Bureau of Reference, Paris, France) protocol. This procedure (Ure et al., 1993) is being proposed as a standard method for sequential extractions which will enable comparison of results on a global basis when in general use. The BCR extraction scheme was validated by Coetzee et al. (1995) using defined model sediments prepared by mixing appropriate natural components found in typical South African sediments. The BCR procedure was used to obtain data on the sediments of the Vaal Dam system at a particularly interesting time in its historical cycle. Samples were taken in February 1995 when the dam was at a record low of 13%.

Materials and methods

Instrumentation and reagents

A Heto F.D. 1.0 freeze-drying apparatus was used to freeze-dry the sediment samples. Centrifugation was performed using a BHG Roto Uni II centrifuge. An ARL 35 000 sequential inductively coupled plasma atomic emission spectrometer (ICP-AES) was used for all metal determinations. Particle size determinations were performed on a small amount of freeze-dried sediment sample suspended in water by photo-correlation spectroscopy using a Malvern Zetamaster. A Phillips PW 1700 X-ray powder

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Received 16 July 1996; accepted in revised form 18 December 1996.

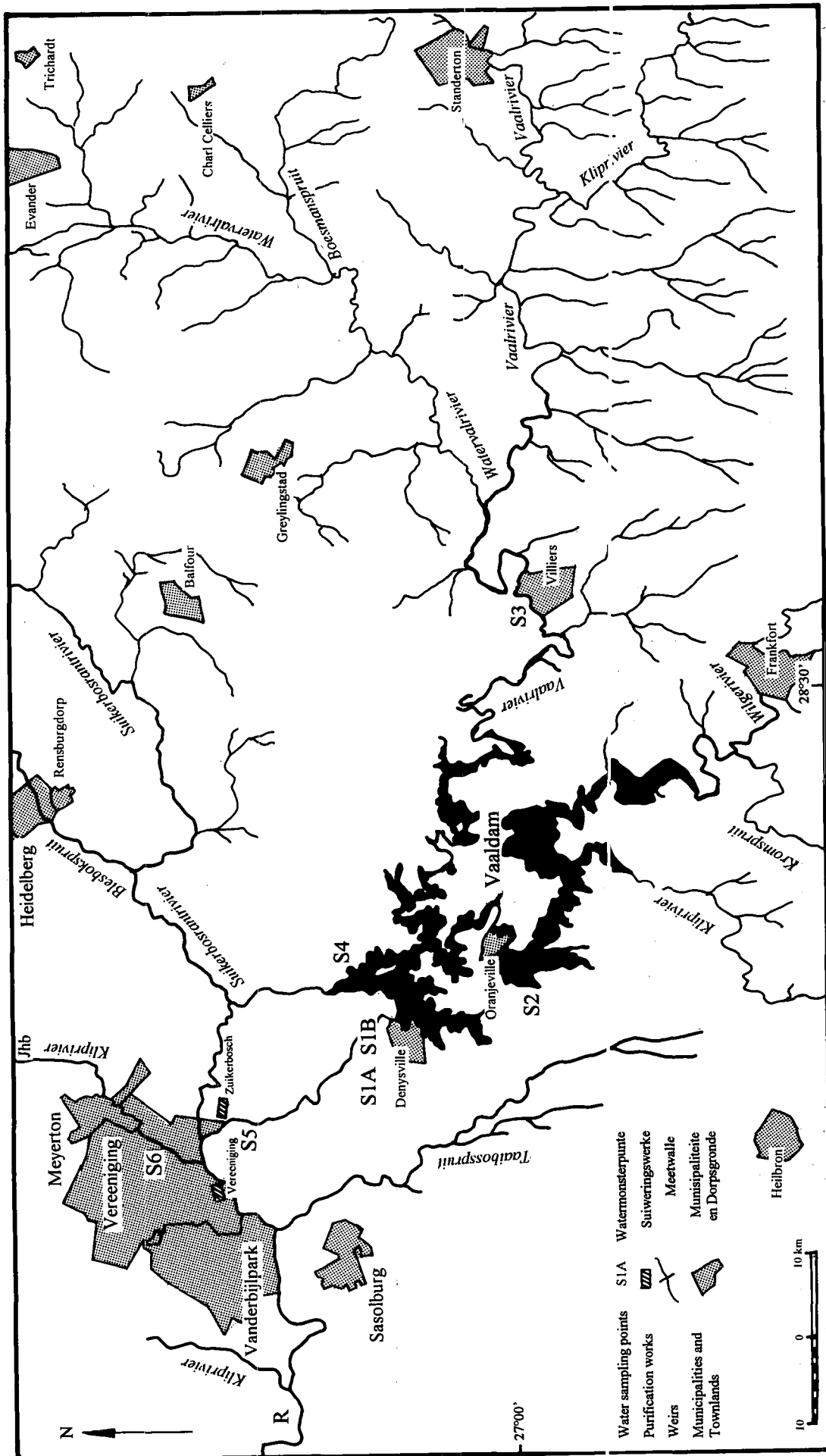


Figure 1
Location of sediment sampling points in the Vaal River catchment area

diffractometer was used to determine the quartz content of sediment samples with CoK α radiation generated at 40 kW and 40 mA. Standards were prepared from a 1 000 mg/l multi-element ICP standard and single element ICP standards obtained from Merck. All other reagents were analar quality also obtained from Merck. 0.45 μ m filters were used to filter the supernatant.

Sampling and sample treatment procedures

Sediment samples were collected at nine different locations in the Vaal Dam area during February 1995. These points are shown on the map in Fig. 1. The first collection point was in the Vaal Dam, 50 m from the dam wall. Samples S1A and S1B were collected about 50 m apart. Sample S2 was taken at Oranjeville 100 m upstream from the bridge in the Wilge River. The Wilge River feeds the Vaal Dam during drought seasons from the Sterkfontein Dam. Sample S3 was collected from the Vaal River at the picnic area at Villiers. Sample S4 was taken from the jetty at the Vaal Marina. The next two samples were collected in Vereeniging. Sample S5 was taken in the Vaal River just upstream from the area where the Klip River enters the Vaal River. Sample S6 was collected in the Klip River about 500 m before it enters the Vaal River. Samples B1 and B2 were taken in the Vaal River Barrage 50 m from the sluices. Sample R2 was collected in the Rietspruit at the bridge before it enters the Vaal River Barrage. Sample R1 was obtained by sampling at Loch Vaal 50 m from the north-eastern river bank.

About 1 kg of sediment was collected at each of the sampling points using a Birge-Ekman grab. The grab consists of a stainless steel box with a pair of jaws and free-moving hinged flaps. The spring-tensioned, scoop-like jaws are mounted on pivot points on opposite sides of the box. The jaws are held open by stainless steel wires which lead to an externally mounted trigger assembly, activated by a messenger weight. After closure the jaws meet tightly to prevent washout during retrieval. Pole attachments were used for sampling in flowing water or in the case where sediment contained gravel.

The sediment sample was transferred to polyethylene bottles with the aid of a plastic spatula, taking care not to use possibly contaminated sediment near the sides of the metal grab. The samples were then stored at 4°C in a cooler box.

The samples were freeze-dried within a few hours after sampling and the remaining sediment was stored in a refrigerator. Sample treatment, extraction and analysis were conducted in a clean laboratory. All glass- and plastic-ware used during these processes was soaked in 10% (v/v) nitric acid for 24 h and then rinsed thoroughly with 18 M Ω deionised water.

Sequential extraction procedure (BCR protocol)

The BCR extraction scheme is summarised in the flow diagram shown in Fig. 2. All extractions were carried out in 50 ml glass centrifuge tubes. Continuous magnetic stirring ensured proper mixing of the sediment and the extraction solution. The magnets were inspected regularly to ensure that the protective coating was secure. After each extraction step the suspensions were centrifuged at 3 000 r/min for 15 min. The supernatant was filtered through 0.45 μ m filters, before analysis, to remove any remaining particles. Samples that contained very high amounts of a metal, for example Fe in Step 4, were diluted.

Step 1: Extraction with 0.11 mol/l acetic acid

The dissolution of carbonate and dolomite minerals with their

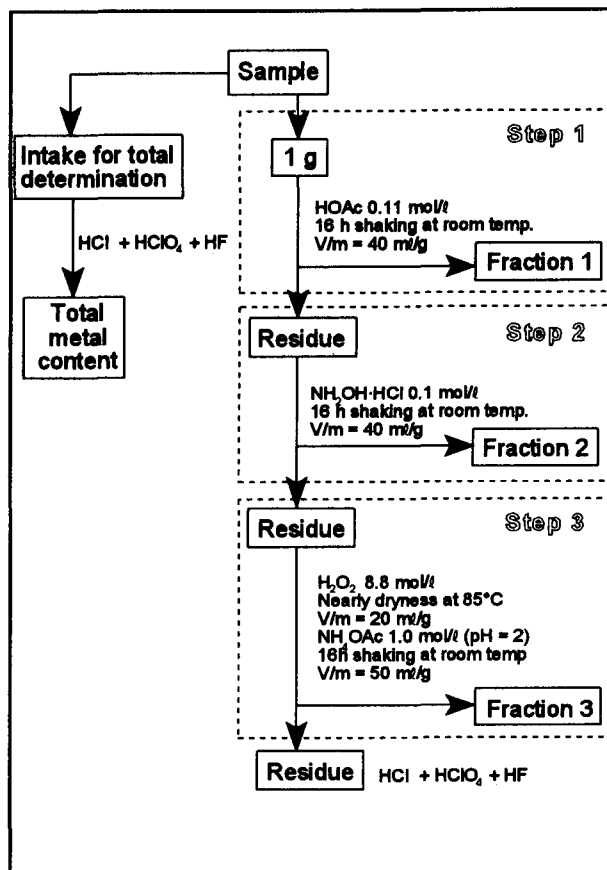


Figure 2
Schematic representation of the BCR sequential extraction procedure

occluded trace metals is nearly quantitative with dilute acetic acid. Trace metals adsorbed onto the surfaces of the different fractions can also be remobilised forming acetate complexes. Therefore a decrease in pH can cause remobilisation of metals loosely bound to sediment surfaces and metals bound to or incorporated in the carbonate phase.

Procedure

1 g of sediment was extracted overnight (16 h) at 20°C with 40 ml of 0.11 M acetic acid.

Step 2: Extraction with 0.1 M hydroxylamine hydrochloride

Hydroxylamine hydrochloride is used to bring reducible species into solution, particularly iron and manganese oxides and thereby release adsorbed or occluded trace metals.

Procedure

The residue from Step 1 was extracted overnight (16 h) at 20°C with 40 ml 0.1 M hydroxylamine hydrochloride.

Step 3: Extraction with 30% hydrogen peroxide and 1 M ammonium acetate

The hydrogen peroxide is used to attack oxidisable matter, particularly organic matter. The hydrogen peroxide is acidified to

pH 2, to prevent scavenging of metal ions by Fe(III) hydroxide precipitations which occur at higher pH values. The ammonium acetate is used to keep ions in solution and to prevent readsorption.

Procedure

The residue of Step 2 was treated with 10 ml 30% H₂O₂. This solution was digested at room temperature for 1 h with occasional manual shaking. The digestion was continued for another hour at 85°C until the volume was reduced to a few millilitres. A further aliquot of 10 ml of the 30% H₂O₂ was added and digested for another hour after which the volume was reduced again to a few millilitres. 50 ml of the 1 M ammonium acetate was added to the residue and extracted overnight (16 h).

Step 4: Total digestion of residual or inert fraction with hydrofluoric acid and perchloric acid

Procedure

The residue of Step 3 was first digested in a teflon beaker with a solution of concentrated HClO₄ (2 ml) and HF (10 ml) to near dryness. Subsequently a second addition of HClO₄ (1 ml) and HF (10 ml) was done and the solution evaporated to near dryness. Finally HClO₄ (1 ml) alone was added and the sample was evaporated until the appearance of white fumes. The residue was dissolved in 12 M HCl and diluted to 25 ml.

The effect of pH on adsorption

25 ml of 100 mg/l of each metal (Zn as ZnSO₄·7H₂O, Cr as Cr(NO₃)₃·9H₂O and Mn as MnCl₂·4H₂O) at each of the following pH values 3.5, 5.5, 6.5 and 7.5 were added to 2.5 g sediment (S1) in a centrifuge tube and shaken for 24 h at 24°C. After centrifugation the pH values were measured and the supernatant was analysed by ICP-AES.

Total metal analysis

1 g of sediment was treated with HF according to Step 4 of the extraction procedure.

Adsorption and desorption study

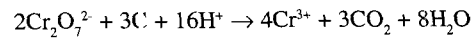
This study was conducted on sample S1 which was collected at the dam wall. For the sorption study, standard solutions (10, 50, 100, 300 and 500 mg/l) of Mn, Cr and Zn were prepared in deionised water. 25 ml of a standard solution was added to 2.5 g of dry, sieved sediment in a centrifuge tube. The pH for the different metals was then adjusted to ensure proper adsorption. The pH for Mn was 6.5, for Cr 5.5 and for Zn 7 and was obtained from pH adsorption curves (Coetzee et al., 1995). The tubes were then stoppered and shaken for 24 h at 24°C. After centrifugation for 10 min, the supernatant was filtered and analysed by ICP-AES. This was done in triplicate.

To obtain data for the desorption study, the supernatant was decanted to obtain the solid phase. 25 ml of 1M MgCl₂ was added to the solid phase and was shaken for 24 h at 24°C. After centrifugation the supernatant was analysed by the ICP-AES.

Determination of the organic content

The percentage organic material in the sediments was determined by the Walkley Black method (Hesse, 1971). Organic material in soil may be oxidised by treatment with a hot mixture of K₂Cr₂O₇

and sulphuric acid, according to the equation:



After completion of the reaction, the excess dichromate is titrated with iron(II)ammonium sulphate hexahydrate. The reduced dichromate is assumed to be equivalent to the organic C present in the sample, assuming that soil organic matter has an average valence of zero.

Results and discussion

Composition of the sediments

The basic composition of the sediments, summarised in Table 1, was established by determining the organic content, quartz content and the particle size distribution. The organic content was less than 2% while the quartz content varied between 9 and 65% for the different sediment samples. The high quartz values of 65% for sample R2 obtained from the Rietspruit and 50% from the Klip River were to be expected because the river beds consisted mostly of sand and clay. The organic content in Barrage sediments was the highest, just less than 2%, while less than 1% was found for the dam and river sediments.

Sample	% C	% Quartz	Particle size nm
S1A	0.85	50	470 ± 11
S2	0.97	12	-
S3	0.31	9	581 ± 24
S4	0.90	9	737 ± 9
S5	0.76	30	455 ± 24
S6	1.69	50	739 ± 25
B1	1.14	16	744 ± 28
B2	1.82	-	544 ± 9
R1	1.03	-	729 ± 39
R2	0.56	65	548 ± 32

Mineralogy of surrounding rocks

The drainage area of the Vaal Dam is underlain by rocks predominantly of the Karoo Supergroup. When these rocks erode they mainly liberate illitic clay minerals. Illite is therefore the most abundant clay mineral in the Vaal Dam and the rivers under discussion, but decreases in abundance toward the wall of the Vaal Dam. Smectite clay minerals (from volcanic and feldspathic rocks of the Ventersdorp Supergroups) and kaolinite (from volcanic and feldspathic rocks of the Witwatersrand Supergroup) also occur, especially in the Wilge River tributary, lower down in the Vaal River upstream of the dam and the Vaal Dam. The relative abundance of smectite and kaolinite increases towards the dam wall and downstream of the Vaal Dam (Birch, 1983). Clay minerals (typical composition: Y₂₋₃Z₄O₁₀(OH)₂nH₂O where Y=Al, Cr³⁺, Cu, Fe²⁺, Fe³⁺, Li, Mg, Ni, Zn and Z=Al, Si) are possible host minerals for Cr, Cu, Ni, Zn, Fe.

The effect of pH on adsorption

A limited characterisation of the sediments of the Vaal Dam system was undertaken by studying the adsorption and desorption properties of one of the sediment samples (S1) taken at the dam wall for three selected metals. These metals were selected to represent different chemistries of incorporation in and remobilisation from sediments.

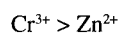
The percentage adsorption for the metals Zn, Mn, and Cr as a function of pH is summarised in Table 2. The metals were quantitatively adsorbed at pH levels above 6.1 except Mn for which the result was only 80%. Zn and Mn were only partially adsorbed at a pH value of 5.2 whereas the adsorption for Cr was still 100%. These results reflect the different adsorption chemistries of the metals for this sediment. It stresses the fact that remobilisation or incomplete adsorption could occur if the pH should drop to around 6.1.

pH	% metal adsorbed		
	Mn	Cr	Zn
7.3	95	100	100
6.9	90	97	100
6.1	80	100	100
5.2	40	100	80

Adsorption and desorption study

The results obtained in these studies are given in Table 3.

The bold result pairs indicate the metal concentration in solution after completion of the adsorption process (first value) for each metal at different initial concentrations and the metal concentration after desorption with 1M MgCl₂ (second value). Ni was added as a control for indicating possible contamination or instrumental drift. It was observed that, as the loading concentration of Cr increased, more and more Mn was released (see italicised values in column 3 of Table 3) during the adsorption process of Cr. Highly charged Cr species effectively displaced Mn, since this metal was not strongly retained on the sediment. Zn also caused the remobilisation of Mn but to a much lesser extent than Cr. From these results the following sequence could be established for the effectiveness of metal ions to remobilise Mn:



This sediment sample had a relatively high capacity for Cr, as can be seen in Table 4. Even at a loading concentration of 500 mg/l almost all the Cr was adsorbed. The capacity of the sediment for Zn was also high, whereas the capacity for Mn was lower. At a loading concentration of 500 mg/l, only 65% of the Mn was adsorbed. The sediment could therefore act as a sink for these metals since it could effectively remove them from the water. It must be kept in mind though, that the adsorption of one metal, could promote the desorption of another in a cation-exchange process.

Since the desorption was accomplished by using a 1M MgCl₂ solution, similar to the first step of the Tessier et al. (1979) procedure, only the loosely bound species were removed despite the fact that the extractant represented a TDS (total dissolved solids) level about 50 times what is generally found in the Vaal River. Extractions at more realistic concentration levels would, however, be too time-consuming to be practical. In the desorption processes it was observed that a constant amount of Mn was released with MgCl₂ in the samples that had not been spiked with these metals. A background concentration for each metal was

Adsorption conc (mg/l)	Adsorbed element	Element concentration (mg/l)							
		Mn*	Mn des**	Ni*	Ni des**	Cr*	Cr des**	Zn*	Zn des**
50	Mn	5.4	92.7	<0.02	0.39	0.12	0.24	0.12	0.42
	Cr	7.6	63.8	0.21	0.42	0.29	0.44	0.14	0.55
	Zn	4.5	69.4	0.14	0.44	0.35	0.78	0.99	26.01
100	Mn	13.6	160.8	0.17	0.56	0.24	0.54	0.02	0.48
	Cr	<i>12.1</i>	69.2	<0.02	0.81	0.08	0.98	0.06	0.77
	Zn	6.6	70.7	<0.02	1.06	0.05	0.78	2.89	68.45
300	Mn	82.6	258.6	0.06	0.35	0.19	0.55	0.04	0.57
	Cr	<i>44.8</i>	43.7	0.05	0.32	3.79	24.63	0.37	1.42
	Zn	20.9	53.1	0.14	0.38	0.25	0.74	40.47	182.67
500	Mn	177.1	398.5	<0.02	0.67	<0.01	0.67	0.05	0.61
	Cr	<i>68.1</i>	49.2	0.66	0.94	15.00	107.15	0.67	0.94
	Zn	30.8	70.4	0.29	1.00	<0.01	0.39	87.45	255.70

* Amount of metal left in supernatant after adsorption
 ** Amount of metal after desorption with 1 M MgCl₂.

Element	% adsorped				% desorped from loading			
	50 mg/l	100 mg/l	300 mg/l	500 mg/l	50 mg/l	100 mg/l	300 mg/l	500 mg/l
Mn	89	86	86	65	65	100	72	100
Cr	99	100	95	98	0	0	9	22
Zn	98	97	86	83	52	70	71	62

therefore determined and used as a correction to calculate the percentage desorption. Some of the Mn was most probably adsorbed onto the sediment by weak Van der Waals forces. The effect on Cr and Zn could not be considered because the sediment did not contain these metals in measurable amounts. The effectiveness of the sediment to remove Cr from solution and to prevent remobilisation was shown by the fact that only 9% Cr was released at a loading concentration of 300 mg/l and 22% at a loading concentration of 500 mg/l. Cr(III) was used for loading, since Cr(III) is readily adsorbed by suspended particulates and by bottom sediments. Cr(III) forms strong, inert complexes with a wide range of naturally occurring organic and inorganic ligands.

Obviously the adsorption capacity of the sediment is far from being saturated. Incomplete adsorption only occurs at metal concentrations above 300 mg/l, values not likely to be reached in the water column. The capacity of the Vaal Dam sediment to function as a sink was therefore considered to be adequate. Adsorption-desorption experiments were performed on sample S1(dam wall) which was assumed to be a representative Vaal Dam sediment. This assumption was deemed acceptable in view of the similar extraction results obtained for the five dam sediments, S1 to S4. It was found, however, that remobilisation or desorption of Mn and Zn was highly likely even with a weak extractant like MgCl₂. An increase in the salt content of the water column could for instance increase remobilisation.

Sequential extractions

The results for the sequential extractions appear in Table 5. No measurable concentration of Cd and Co was obtained in any step of the sequential extraction procedure for all the samples. Practically no Pb, Cu, Cr and Ni species were extracted in the first three steps, indicating that none of these metals were anthropogenically introduced into the sediments. Significant quantities of these elements were, however, found in the final step (HF dissolution) which could indicate that they were incorporated into the mineral phase and are therefore of natural geochemical origin.

Detectable quantities of Cr were extracted only under oxidising extraction conditions in Step 3 as is shown in Fig. 3. This phenomenon was also found in the extraction of model sediments (Coetzee et al., 1995) and explained in terms of the oxidation of Cr(III) to Cr(VI) by the H₂O₂ present in the extractant. In the case of Cr, extraction in the HF dissolution step does not necessarily indicate a geochemical origin for this element. The chemistry of Cr simply does not allow its extraction in the mild extractions applied in Steps 1 and 2.

The Ca extracted in Step 1 most probably originated from the dissolution of calcite (Fig. 4). The bulk of the Ca in most samples was extracted in the final step.

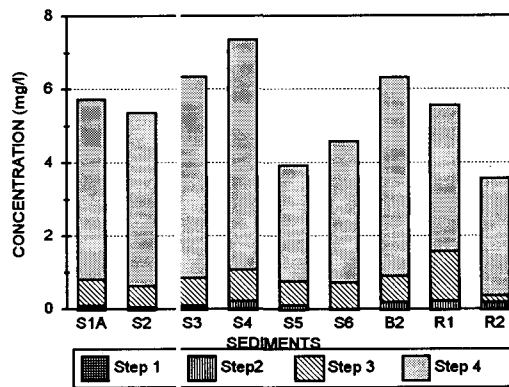


Figure 3
The sequential extraction results for Cr

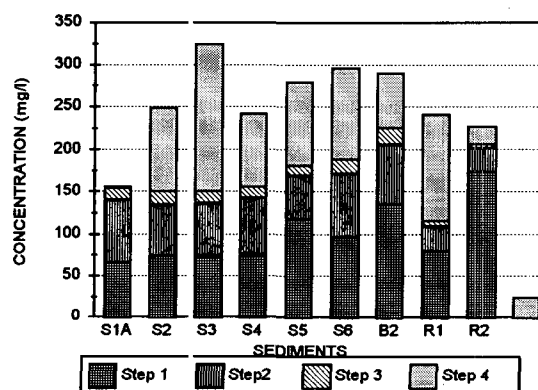


Figure 4
The sequential extraction results for Ca

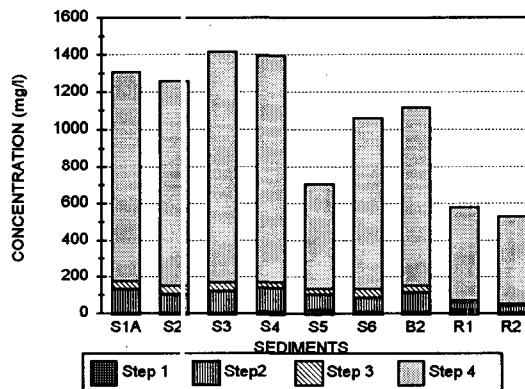


Figure 5
The sequential extraction results for Sn

TABLE 5
RESULTS OF SEQUENTIAL EXTRACTIONS OF SEDIMENTS FROM THE VAAL DAM AND CONTRIBUTING RIVERS.
ALL CONCENTRATIONS IN mg/l (n=3)

Element	Sample	Step 1	Step 2	Step 3	Step 4	Total sequential extraction	Total analysis
Ni	S1A	7 ± 3	12 ± 4	5 ± 1	37 ± 9	61 ± 9	84 ± 18
	S1B	7 ± 4	12 ± 1	4 ± 2	58 ± 6	81 ± 12	82 ± 12
	S2	4 ± 3	9 ± 3	3 ± 2	32 ± 15	48 ± 19	69 ± 13
	S3	6 ± 4	14 ± 1	3 ± 1	37 ± 13	60 ± 13	55 ± 1
	S4	5 ± 3	9 ± 5	4 ± 3	37 ± 23	55 ± 44	105 ± 2
	S5	63 ± 6	40 ± 1	18 ± 7	19 ± 9	707 ± 74	146 ± 9
	S6	58 ± 8	75 ± 11	59 ± 2	51 ± 17	243 ± 68	264 ± 3
	B1	37 ± 2	32 ± 2	23 ± 2	42 ± 2	134 ± 1	70 ± 5
	B2	38 ± 1	27 ± 2	15 ± 2	35 ± 4	115 ± 8	67 ± 10
	R1	15 ± 3	8 ± 1	15 ± 1	21 ± 5	59 ± 3	39 ± 2
R2	32 ± 2	32 ± 23	66 ± 32	19 ± 5	149 ± 46	80 ± 2	
Mn	S1A	616 ± 36	532 ± 44	101 ± 12	110 ± 25	(1.4 ± 0.1)×10 ³	(1.4 ± 0.2)×10 ³
	S1B	52 ± 56	548 ± 39	96 ± 17	120 ± 10	816 ± 48	700 ± 25
	S2	636 ± 56	376 ± 12	80 ± 15	244 ± 53	336 ± 75	700 ± 125
	S3	728 ± 44	564 ± 32	160 ± 96	128 ± 28	(1.6 ± 0.1)×10 ³	685 ± 76
	S4	508 ± 44	385 ± 32	69 ± 34	95 ± 33	(1.1 ± 0.1)×10 ³	907 ± 56
	S5	1000 ± 240	291 ± 2	39 ± 14	78 ± 35	(1.4 ± 0.3)×10 ³	(1.3 ± 0.2)×10 ³
	S6	760 ± 140	496 ± 72	100 ± 22	98 ± 23	(1.5 ± 0.2)×10 ³	(1.1 ± 0.1)×10 ³
	B1	819 ± 28	382 ± 5	92 ± 3	133 ± 8	(1.4 ± 0.1)×10 ³	184 ± 4
	B2	868 ± 43	256 ± 2	72 ± 3	143 ± 15	(1.3 ± 0.1)×10 ³	249 ± 12
	R1	364 ± 10	140 ± 37	21 ± 4	73 ± 8	598 ± 112	111 ± 12
R2	615 ± 35	127 ± 8	23 ± 2	83 ± 10	848 ± 33	164 ± 7	
Co	S1A	6 ± 1	13 ± 5	2 ± 2	17 ± 5	38 ± 3	36 ± 3
	S1B	6 ± 3	10 ± 1	3 ± 4	17 ± 2	36 ± 4	30 ± 5
	S2	6 ± 3	9 ± 1	1 ± 1	16 ± 8	32 ± 12	33 ± 2
	S3	6 ± 4	15 ± 3	1 ± 1	16 ± 5	38 ± 6	39 ± 5
	S4	4 ± 2	9 ± 1	1 ± 1	14 ± 3	28 ± 7	41 ± 4
	S5	24 ± 3	14 ± 1	12 ± 7	8 ± 4	58 ± 16	49 ± 3
	S6	34 ± 4	43 ± 9	26 ± 2	26 ± 9	129 ± 30	122 ± 2
	B1	6 ± 1	6 ± 2	3 ± 1	19 ± 1	34 ± 2	20 ± 5
	B2	8 ± 2	5 ± 1	1 ± 1	17 ± 1	31 ± 2	20 ± 1
	R1	4 ± 1	2 ± 1	2 ± 1	9 ± 1	17 ± 3	17 ± 6
R2	7 ± 1	17 ± 4	23 ± 18	83 ± 5	130 ± 15	103 ± 4	
Cr	S1A	2 ± 1	3 ± 2	28 ± 2	122 ± 23	155 ± 13	186 ± 16
	S1B	4 ± 3	2 ± 1	26 ± 3	136 ± 50	168 ± 35	177 ± 10
	S2	1 ± 1	3 ± 1	22 ± 4	118 ± 72	144 ± 50	149 ± 17
	S3	2 ± 1	3 ± 2	29 ± 3	137 ± 50	171 ± 34	165 ± 20
	S4	2 ± 1	9 ± 5	32 ± 10	157 ± 119	201 ± 48	250 ± 24
	S5	4 ± 3	1 ± 1	26 ± 3	78 ± 40	309 ± 82	202 ± 41
	S6	1 ± 1	1 ± 1	28 ± 2	96 ± 32	126 ± 76	186 ± 17
	B1	<DL	7 ± 2	27 ± 6	135 ± 10	170 ± 4	167 ± 1
	B2	<DL	10 ± 1	16 ± 6	136 ± 28	162 ± 22	155 ± 8
	R1	<DL	11 ± 5	53 ± 3	99 ± 4	163 ± 2	169 ± 2
R2	<DL	8 ± 2	8 ± 5	79 ± 3	258 ± 21	156 ± 1	
Zn	S1A	10 ± 2	23 ± 3	7 ± 2	74 ± 15	114 ± 17	130 ± 14
	S1B	8 ± 1	16 ± 2	6 ± 2	77 ± 11	107 ± 11	111 ± 2
	S2	5 ± 2	13 ± 1	7 ± 2	76 ± 20	101 ± 25	93 ± 22
	S3	7 ± 3	15 ± 1	6 ± 2	79 ± 18	107 ± 16	48 ± 3
	S4	64 ± 5	288 ± 56	6 ± 4	70 ± 33	428 ± 137	104 ± 11
	S5	125 ± 10	62 ± 2	16 ± 3	33 -	236 ± 53	192 ± 7
	S6	260 ± 30	390 ± 10	134 ± 19	183 ± 47	1203 ± 164	878 ± 52
	B1	46 ± 2	36 ± 3	4 ± 1	75 ± 1	161 ± 3	77 ± 17
	B2	40 ± 1	28 ± 2	3 ± 1	62 ± 1	294 ± 7	87 ± 18
	R1	304 ± 36	128 ± 15	8 ± 1	28 ± 15	468 ± 64	403 ± 52
R2	87 ± 3	32 ± 1	4 ± 2	26 ± 1	149 ± 4	123 ± 27	

TABLE 5 (CONTINUED)

Fe	S1A	228 ± 0.5	(8.2 ± 0.8) × 10 ³	(2.5 ± 0.3) × 10 ³	(4.8 ± 0.3) × 10 ⁴	(5.9 ± 1.4) × 10 ⁴	(6.4 ± 1.6) × 10 ⁴
	S1B	840 ± 2.5	(7.6 ± 0.6) × 10 ³	(2.1 ± 0.6) × 10 ³	(4.4 ± 0.5) × 10 ⁴	(5.5 ± 0.3) × 10 ⁴	(6.7 ± 0.2) × 10 ⁴
	S2	332 ± 1.0	(6.4 ± 0.5) × 10 ³	(2.8 ± 0.5) × 10 ³	(4.1 ± 0.8) × 10 ⁴	(5.1 ± 0.5) × 10 ⁴	(5.5 ± 0.7) × 10 ⁴
	S3	492 ± 1.4	(7.4 ± 0.3) × 10 ³	(2.6 ± 0.2) × 10 ³	(4.6 ± 0.5) × 10 ⁴	(5.7 ± 0.6) × 10 ⁴	(3.5 ± 0.7) × 10 ⁴
	S4	836 ± 1.1	(7.5 ± 0.1) × 10 ³	(1.9 ± 0.8) × 10 ³	(4.6 ± 1.3) × 10 ⁴	(5.6 ± 0.6) × 10 ⁴	(5.9 ± 0.4) × 10 ⁴
	S5	452 ± 1.9	(5.3 ± 0.3) × 10 ³	(1.8 ± 0.4) × 10 ³	(2.1 ± 1.0) × 10 ⁴	(3.0 ± 1.1) × 10 ⁴	(3.8 ± 0.7) × 10 ⁴
	S6	644 ± 1.3	(4.8 ± 0.4) × 10 ³	(2.9 ± 0.4) × 10 ³	(3.3 ± 0.6) × 10 ⁴	(4.2 ± 1.4) × 10 ⁴	(3.1 ± 2.3) × 10 ⁴
	B1	848 ± 1.2	(5.5 ± 0.1) × 10 ³	(1.8 ± 0.1) × 10 ³	(3.5 ± 0.1) × 10 ⁴	(4.3 ± 0.1) × 10 ⁴	(2.7 ± 0.4) × 10 ⁴
	B2	584 ± 0.4	(4.9 ± 0.1) × 10 ³	(1.5 ± 0.1) × 10 ³	(2.8 ± 0.1) × 10 ⁴	(3.5 ± 0.1) × 10 ⁴	(2.5 ± 0.1) × 10 ⁴
	R1	1284 ± 2.1	(2.4 ± 0.4) × 10 ³	(0.5 ± 0.1) × 10 ³	(1.8 ± 0.1) × 10 ⁴	(2.3 ± 0.1) × 10 ⁴	(1.7 ± 0.3) × 10 ⁴
	R2	400 ± 1.7	(2.1 ± 0.2) × 10 ³	(0.5 ± 0.1) × 10 ³	(1.5 ± 0.2) × 10 ⁴	(4.6 ± 0.1) × 10 ⁴	(3.0 ± 0.1) × 10 ⁴
	Ca	S1A	(2.6 ± 0.1) × 10 ³	(3.0 ± 0.8) × 10 ³	(0.6 ± 0.1) × 10 ³	(2.4 ± 0.4) × 10 ³	(8.6 ± 0.1) × 10 ³
S1B		(1.9 ± 0.1) × 10 ³	(2.7 ± 0.2) × 10 ³	(0.5 ± 0.1) × 10 ³	(4.5 ± 0.3) × 10 ³	(9.6 ± 2.6) × 10 ³	(3.6 ± 0.4) × 10 ³
S2		(1.9 ± 0.2) × 10 ³	(2.5 ± 0.2) × 10 ³	(0.6 ± 0.1) × 10 ³	(4.3 ± 0.2) × 10 ³	(9.2 ± 2.3) × 10 ³	(8.8 ± 0.6) × 10 ³
S3		(1.9 ± 0.1) × 10 ³	(2.5 ± 0.1) × 10 ³	(0.6 ± 0.1) × 10 ³	(2.1 ± 0.1) × 10 ³	(7.0 ± 1.3) × 10 ³	(3.9 ± 0.3) × 10 ³
S4		(1.9 ± 0.2) × 10 ³	(2.7 ± 0.3) × 10 ³	(0.6 ± 0.3) × 10 ³	(2.4 ± 0.3) × 10 ³	(7.6 ± 2.2) × 10 ³	(3.8 ± 0.3) × 10 ³
S5		(3.0 ± 0.1) × 10 ³	(2.1 ± 0.2) × 10 ³	(0.5 ± 0.1) × 10 ³	(2.7 ± 0.2) × 10 ³	(8.1 ± 0.2) × 10 ³	(3.9 ± 0.7) × 10 ³
S6		(2.4 ± 0.1) × 10 ³	(3.1 ± 0.1) × 10 ³	(0.7 ± 0.1) × 10 ³	(1.6 ± 0.1) × 10 ³	(7.8 ± 1.3) × 10 ³	(4.5 ± 0.2) × 10 ³
B1		(3.3 ± 0.4) × 10 ³	(2.8 ± 0.1) × 10 ³	(0.8 ± 0.1) × 10 ³	(3.1 ± 0.2) × 10 ³	(1.0 ± 0.2) × 10 ⁴	(6.4 ± 0.2) × 10 ³
B2		(3.4 ± 0.1) × 10 ³	(2.5 ± 0.1) × 10 ³	(0.7 ± 0.1) × 10 ³	(3.5 ± 0.1) × 10 ³	(1.0 ± 0.2) × 10 ⁴	(9.5 ± 0.4) × 10 ³
R1		(2.0 ± 0.5) × 10 ³	(1.2 ± 0.3) × 10 ³	(0.2 ± 0.1) × 10 ³	(0.5 ± 0.1) × 10 ³	(3.9 ± 0.7) × 10 ³	(5.6 ± 0.4) × 10 ³
R2		(4.4 ± 0.2) × 10 ³	(1.2 ± 0.1) × 10 ³	(0.2 ± 0.1) × 10 ³	(0.6 ± 0.1) × 10 ³	(6.3 ± 0.1) × 10 ³	(5.7 ± 0.7) × 10 ³
Sn		S1A	142 ± 5	(5.2 ± 0.3) × 10 ³	(1.7 ± 0.1) × 10 ³	(2.8 ± 0.1) × 10 ⁴	(3.3 ± 0.6) × 10 ⁴
	S1B	572 ± 60	(5.0 ± 0.4) × 10 ³	(1.2 ± 0.3) × 10 ³	(3.0 ± 0.1) × 10 ⁴	(3.7 ± 0.3) × 10 ⁴	(4.7 ± 0.2) × 10 ⁴
	S2	235 ± 36	(4.3 ± 0.4) × 10 ³	(1.8 ± 0.3) × 10 ³	(2.8 ± 0.1) × 10 ⁴	(3.4 ± 0.4) × 10 ⁴	(3.4 ± 0.1) × 10 ⁴
	S3	339 ± 44	(4.9 ± 0.2) × 10 ³	(1.7 ± 0.2) × 10 ³	(3.1 ± 0.1) × 10 ⁴	(3.8 ± 0.4) × 10 ⁴	(3.8 ± 0.1) × 10 ⁴
	S4	540 ± 20	(5.1 ± 0.2) × 10 ³	(1.2 ± 0.4) × 10 ³	2.5 × 10 ⁴	(3.1 ± 0.9) × 10 ⁴	(4.0 ± 0.1) × 10 ⁴
	S5	968 ± 18	(3.5 ± 0.2) × 10 ³	(1.2 ± 0.3) × 10 ³	(1.4 ± 0.1) × 10 ⁴	(2.0 ± 0.7) × 10 ⁴	(2.9 ± 0.1) × 10 ⁴
	S6	464 ± 14	(3.2 ± 0.3) × 10 ³	(1.7 ± 0.2) × 10 ³	(2.3 ± 0.1) × 10 ⁴	(2.9 ± 0.7) × 10 ⁴	(3.1 ± 0.1) × 10 ⁴
	B1	651 ± 10	(4.1 ± 0.1) × 10 ³	(1.5 ± 0.1) × 10 ³	(2.4 ± 0.1) × 10 ⁴	(3.0 ± 0.2) × 10 ⁴	(3.5 ± 0.1) × 10 ⁴
	B2	444 ± 2	(3.8 ± 0.1) × 10 ³	(1.2 ± 0.1) × 10 ³	(2.2 ± 0.1) × 10 ⁴	(2.7 ± 0.1) × 10 ⁴	(3.3 ± 0.1) × 10 ⁴
	R1	926 ± 11	(1.8 ± 0.2) × 10 ³	(0.4 ± 0.1) × 10 ³	(1.3 ± 0.1) × 10 ⁴	(1.6 ± 0.1) × 10 ⁴	(2.1 ± 0.1) × 10 ⁴
	R2	241 ± 19	(1.6 ± 0.1) × 10 ³	(0.4 ± 0.1) × 10 ³	(1.2 ± 0.1) × 10 ⁴	(1.4 ± 0.1) × 10 ⁴	(1.5 ± 0.1) × 10 ⁴
	Cd	S1A	2 ± 1	2 ± 1	<DL	3 ± 1	7 ± 1
S1B		2 ± 1	<DL	<DL	6 ± 2	8 ± 1	8 ± 1
S2		2 ± 1	2 ± 1	<DL	4 ± 1	8 ± 1	4 ± 1
S3		<DL	3 ± 1	<DL	3 ± 1	5 ± 1	4 ± 1
S4		<DL	3 ± 1	<DL	2 ± 1	5 ± 1	4 ± 1
S5		<DL	2 ± 1	<DL	<DL	2 ± 1	1 ± 1
S6		2 ± 1	3 ± 1	<DL	<DL	5 ± 1	2 ± 1
B1		<DL	<DL	<DL	1 ± 1	1 ± 1	1 ± 1
B2		<DL	<DL	<DL	3 ± 1	5 ± 1	1 ± 1
R1		<DL	<DL	<DL	2 ± 1	2 ± 1	2 ± 1
R2		<DL	<DL	<DL	3 ± 1	3 ± 1	2 ± 1
Pb		S1A	8 ± 3	8 ± 4	<DL	248 ± 95	268 ± 48
	S1B	11 ± 7	14 ± 4	<DL	258 ± 35	327 ± 33	155 ± 15
	S2	6 ± 2	10 ± 6	<DL	268 ± 95	288 ± 38	175 ± 385
	S3	7 ± 3	6 ± 2	6 ± 2	367 ± 24	366 ± 24	133 ± 60
	S4	8 ± 2	6 ± 3	8 ± 3	270 ± 56	292 ± 22	163 ± 10
	S5	<DL	11 ± 7	<DL	140 ± 63	151 ± 26	113 ± 35
	S6	<DL	7 ± 2	<DL	127 ± 11	134 ± 19	148 ± 3
	B1	<DL	10 ± 5	<DL	106 ± 21	116 ± 2	148 ± 33
	B2	<DL	6 ± 2	<DL	114 ± 1	120 ± 1	125 ± 10
	R1	<DL	<DL	<DL	49 ± 1	49 ± 1	98 ± 20
	R2	<DL	6 ± 2	<DL	40 ± 5	46 ± 3	60 ± 10

TABLE 5 (CONTINUED)

Al	S1A	37 ± 2	(7.0 ± 1.6) × 10 ³	(4.0 ± 0.02) × 10 ³	(8.7 ± 2.0) × 10 ⁴	(9.8 ± 1.4) × 10 ⁴	(7.2 ± 4.9) × 10 ⁴
	S1B	39 ± 2	(1.6 ± 0.4) × 10 ³	(3.6 ± 0.8) × 10 ³	(9.6 ± 1.7) × 10 ⁴	(10.1 ± 1.5) × 10 ⁴	(2.7 ± 3.8) × 10 ⁴
	S2	37 ± 1	(1.4 ± 0.4) × 10 ³	(3.4 ± 0.4) × 10 ³	(8.5 ± 1.0) × 10 ⁴	(9.0 ± 1.1) × 10 ⁴	(8.2 ± 5.1) × 10 ⁴
	S3	42 ± 3	(1.4 ± 0.4) × 10 ³	(3.2 ± 0.3) × 10 ³	(8.7 ± 2.6) × 10 ⁴	(9.2 ± 1.3) × 10 ⁴	(8.4 ± 1.6) × 10 ⁴
	S4	51 ± 14	(1.2 ± 0.4) × 10 ³	(3.0 ± 0.8) × 10 ³	(7.3 ± 1.4) × 10 ⁴	(7.8 ± 1.8) × 10 ⁴	(5.0 ± 1.5) × 10 ⁴
	S5	25 ± 3	(1.0 ± 0.4) × 10 ³	(2.9 ± 0.9) × 10 ³	(5.4 ± 1.9) × 10 ⁴	(5.9 ± 2.1) × 10 ⁴	(4.6 ± 0.5) × 10 ⁴
	S6	4 ± 1	7 ± 3	4 ± 0.2	128 ± 32	143 ± 21	148 ± 65
	B1	56 ± 6	(0.8 ± 0.01) × 10 ³	(2.8 ± 0.4) × 10 ³	(5.6 ± 1.0) × 10 ⁴	(5.6 ± 1.0) × 10 ⁴	(5.3 ± 1.3) × 10 ⁴
	B2	48 ± 1	(0.8 ± 0.02) × 10 ³	(2.3 ± 0.1) × 10 ³	(6.2 ± 0.3) × 10 ⁴	(6.5 ± 0.3) × 10 ⁴	(5.1 ± 0.2) × 10 ⁴
	R1	30 ± 8	(0.5 ± 0.03) × 10 ³	(8.0 ± 0.8) × 10 ²	(2.6 ± 0.2) × 10 ⁴	(2.7 ± 0.2) × 10 ⁴	(3.4 ± 0.2) × 10 ⁴
	R2	54 ± 18	(4.0 ± 0.04) × 10 ³	(5.0 ± 0.1) × 10 ²	(2.4 ± 0.1) × 10 ⁴	(2.8 ± 0.4) × 10 ⁴	(2.0 ± 0.1) × 10 ⁴
	Cu	S1A	4 ± 4	45 ± 26	23 ± 4	29 ± 10	101 ± 35
S1B		13 ± 12	23 ± 21	18 ± 7	34 ± 5	88 ± 26	102 ± 5
S2		3 ± 2	10 ± 2	30 ± 11	40 ± 7	83 ± 32	92 ± 13
S3		4 ± 2	16 ± 10	18 ± 1	29 ± 20	67 ± 23	56 ± 1
S4		62 ± 31	40 ± 27	63 ± 4	61 ± 65	226 ± 21	119 ± 10
S5		16 ± 3	23 ± 31	1 ± 1	46 ± 3	86 ± 27	76 ± 13
S6		10 ± 2	27 ± 22	58 ± 39	34 ± 13	129 ± 19	117 ± 4
B1		23 ± 4	14 ± 15	2 ± 1	50 ± 8	89 ± 7	31 ± 6
B2		<DL	2 ± 1	<DL	33 ± 2	35 ± 3	28 ± 3
R1		<DL	2 ± 1	16 ± 2	17 ± 3	35 ± 6	26 ± 5
R2		<DL	3 ± 1	10 ± 7	14 ± 1	22 ± 5	8 ± 5

Large concentrations of Sn were extracted in the final step (Fig. 5). This means that Sn was probably originating from natural components in the surrounding rocks along the course of the rivers flowing into the dam. The Karoo sediment contains granites which again contains cassiterite (SnO₂). Since the Vaal River flows through Karoo rock formations, it could explain the occurrence of Sn in the sediments. Relatively high Sn values were also obtained in Step 2 which could indicate anthropogenic origins.

Sample S6 (Klip River) released relatively large amounts of Zn in the first three steps (Fig. 6). Zn released in the first step could either be Zn as ZnCO₃ which dissolves in acetic acid present in the extractant, or Zn loosely adsorbed onto sediment surfaces. The Klip River flows through highly industrialised areas and the Zn released in the first three steps could probably be introduced by these industries and informal settlements, since most of the other samples showed very low concentrations in these three steps.

Mn released in Step 1 (Fig. 7) could be indicative of Mn present as Mn carbonates together with calcite in the carbonate fraction and anthropogenic Mn is also a possibility. The extraction procedure as applied could, however, not provide a means of distinguishing between the two possibilities. A high Mn value was expected for sample S6, since the Klip River flows past SAMANCOR which processes Mn ores. The Mn content in this sample was, however, not significantly higher than the average values for the whole system. It could therefore be concluded that the manganese plant did not contribute to Mn pollution downstream in the Klip River to any significant extent.

Small amounts of Al were released in Steps 2 and 3 (Fig. 8) but the bulk of Al occurred as expected in the final step indicating the dissolution of the clay mineral fraction. Small amounts of Fe were released in Step 1, indicating the presence of FeCO₃ (siderite) or adsorbed Fe (Fig. 9). The Fe observed in Step 2 most

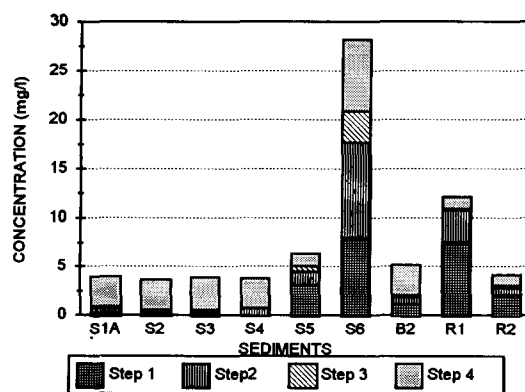


Figure 6
The sequential extraction results for Zn

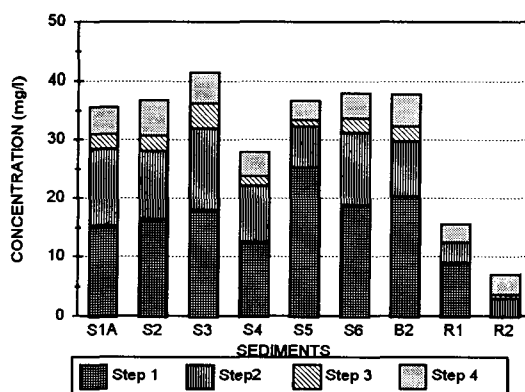


Figure 7
The sequential extraction results for Mn

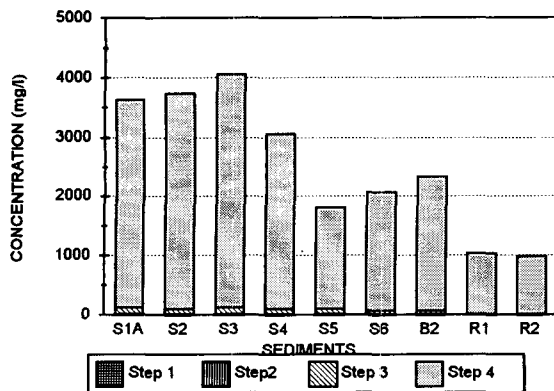


Figure 8
The sequential extraction results for Al

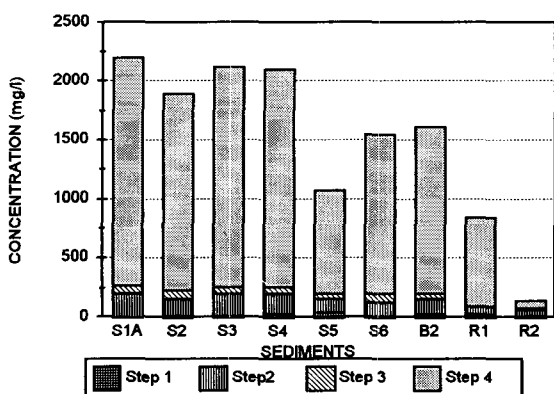


Figure 9
The sequential extraction results for Fe

probably originated from iron oxides, that should dissolve in the reduction step. The high values obtained in Step 4, could be caused by Fe which frequently occurs in association with clay minerals like smectite or vermiculite.

Total element analysis

The total element content shown in the last column of Table 6 is in reasonable agreement with the sum of the four extractions if the complexity of the samples is considered.

Conclusion

Sequential extraction results proved useful to distinguish between anthropogenic and geochemical sources of most metal species in sediments. Notable exceptions were Cr and Mn. The high proportion of metals in the residual phase and the generally low levels of extractable metals indicate that the sediments were relatively unpolluted. It was concluded that the capacity of the sediment to function as a sink for heavy metals was sufficient,

provided that pH values remain above 7 and the dissolved salt levels do not rise significantly above present levels. The precision obtained in the sequential extraction procedure was between 10 and 20%. This was not as good as those obtained in the model sediments analysis (Coetzee et al., 1995) but similar to the 20% found by Kim and Ferguson (1991).

Redistribution phenomena during the extraction process were not evaluated. We would assume, however, that the degree of redistribution would be less than that found in studies with model sediments (Coetzee et al., 1995). The natural sediment was probably in equilibrium, whereas the model sediment was a forced association. For example, if Cu were loaded onto kaolin in experiments with a model sediment, but would rather be associated with the humic acid component of the model sediment, it would redistribute to the humic acid fraction during extractions. In a natural system the Cu would have been associated with the humic acid in the first place

Acknowledgement

The authors thank the Department of Water Affairs and Forestry at Deneysville for assistance with the sampling of sediments near the dam wall and the Foundation for Research and Development for financial support.

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TABLE 5 (CONTINUED)

Al	S1A	37 ± 2	(7.0 ± 1.6) × 10 ³	(4.0 ± 0.02) × 10 ³	(8.7 ± 2.0) × 10 ⁴	(9.8 ± 1.4) × 10 ⁴	(7.2 ± 4.9) × 10 ⁴
	S1B	39 ± 2	(1.6 ± 0.4) × 10 ³	(3.6 ± 0.8) × 10 ³	(9.6 ± 1.7) × 10 ⁴	(10.1 ± 1.5) × 10 ⁴	(2.7 ± 3.8) × 10 ⁴
	S2	37 ± 1	(1.4 ± 0.4) × 10 ³	(3.4 ± 0.4) × 10 ³	(8.5 ± 1.0) × 10 ⁴	(9.0 ± 1.1) × 10 ⁴	(8.2 ± 5.1) × 10 ⁴
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	S5	25 ± 3	(1.0 ± 0.4) × 10 ³	(2.9 ± 0.9) × 10 ³	(5.4 ± 1.9) × 10 ⁴	(5.9 ± 2.1) × 10 ⁴	(4.6 ± 0.5) × 10 ⁴
	S6	4 ± 1	7 ± 3	4 ± 0.2	128 ± 32	143 ± 21	148 ± 65
	B1	56 ± 6	(0.8 ± 0.01) × 10 ³	(2.8 ± 0.4) × 10 ³	(5.6 ± 1.0) × 10 ⁴	(5.6 ± 1.0) × 10 ⁴	(5.3 ± 1.3) × 10 ⁴
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R2	54 ± 18	(4.0 ± 0.04) × 10 ³	(5.0 ± 0.1) × 10 ²	(2.4 ± 0.1) × 10 ⁴	(2.8 ± 0.4) × 10 ⁴	(2.0 ± 0.1) × 10 ⁴	
Cu	S1A	4 ± 4	45 ± 26	23 ± 4	29 ± 10	101 ± 35	99 ± 17
	S1B	13 ± 12	23 ± 21	18 ± 7	34 ± 5	88 ± 26	102 ± 5
	S2	3 ± 2	10 ± 2	30 ± 11	40 ± 7	83 ± 32	92 ± 13
	S3	4 ± 2	16 ± 10	18 ± 1	29 ± 20	67 ± 23	56 ± 1
	S4	62 ± 31	40 ± 27	63 ± 4	61 ± 65	226 ± 21	119 ± 10
	S5	16 ± 3	23 ± 31	1 ± 1	46 ± 3	86 ± 27	76 ± 13
	S6	10 ± 2	27 ± 22	58 ± 39	34 ± 13	129 ± 19	117 ± 4
	B1	23 ± 4	14 ± 15	2 ± 1	50 ± 8	89 ± 7	31 ± 6
	B2	<DL	2 ± 1	<DL	33 ± 2	35 ± 3	28 ± 3
	R1	<DL	2 ± 1	16 ± 2	17 ± 3	35 ± 6	26 ± 5
R2	<DL	3 ± 1	10 ± 7	14 ± 1	22 ± 5	8 ± 5	

Large concentrations of Sn were extracted in the final step (Fig. 5). This means that Sn was probably originating from natural components in the surrounding rocks along the course of the rivers flowing into the dam. The Karoo sediment contains granites which again contains cassiterite (SnO₂). Since the Vaal River flows through Karoo rock formations, it could explain the occurrence of Sn in the sediments. Relatively high Sn values were also obtained in Step 2 which could indicate anthropogenic origins.

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Small amounts of Al were released in Steps 2 and 3 (Fig. 8) but the bulk of Al occurred as expected in the final step indicating the dissolution of the clay mineral fraction. Small amounts of Fe were released in Step 1, indicating the presence of FeCO₃ (siderite) or adsorbed Fe (Fig. 9). The Fe observed in Step 2 most

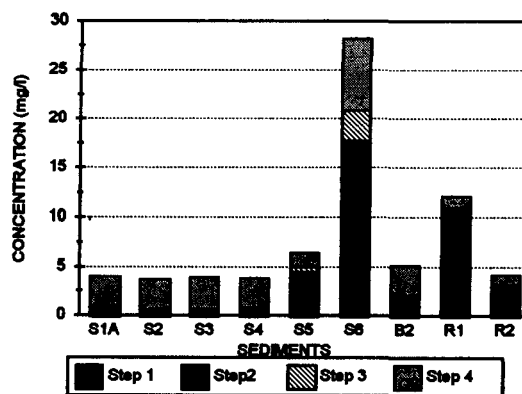


Figure 6

The sequential extraction results for Zn

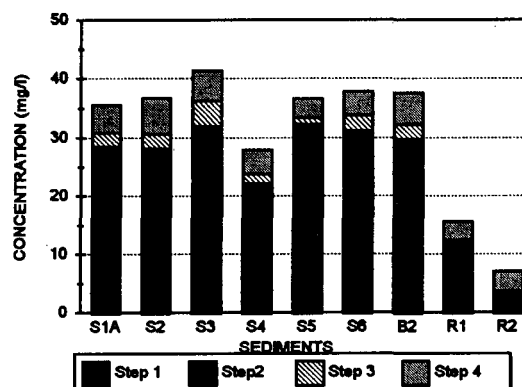


Figure 7

The sequential extraction results for Mn

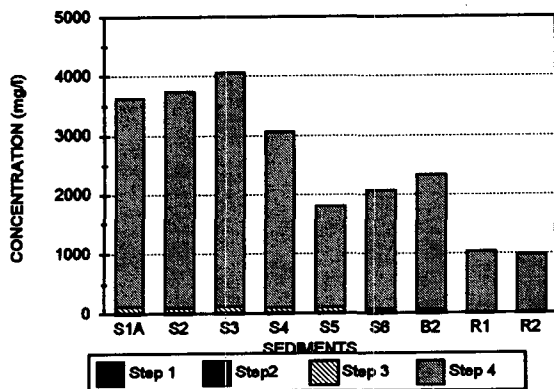


Figure 8
The sequential extraction results for Al

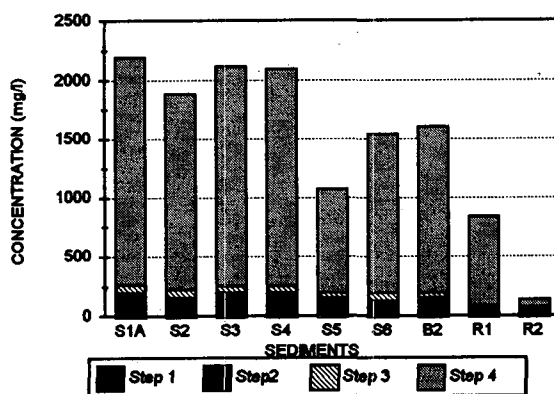


Figure 9
The sequential extraction results for Fe

probably originated from iron oxides, that should dissolve in the reduction step. The high values obtained in Step 4, could be caused by Fe which frequently occurs in association with clay minerals like smectite or vermiculite.

Total element analysis

The total element content shown in the last column of Table 6 is in reasonable agreement with the sum of the four extractions if the complexity of the samples is considered.

Conclusion

Sequential extraction results proved useful to distinguish between anthropogenic and geochemical sources of most metal species in sediments. Notable exceptions were Cr and Mn. The high proportion of metals in the residual phase and the generally low levels of extractable metals indicate that the sediments were relatively unpolluted. It was concluded that the capacity of the sediment to function as a sink for heavy metals was sufficient,

provided that pH values remain above 7 and the dissolved salt levels do not rise significantly above present levels. The precision obtained in the sequential extraction procedure was between 10 and 20%. This was not as good as those obtained in the model sediments analysis (Coetzee et al., 1995) but similar to the 20% found by Kim and Ferguson (1991).

Redistribution phenomena during the extraction process were not evaluated. We would assume, however, that the degree of redistribution would be less than that found in studies with model sediments (Coetzee et al., 1995). The natural sediment was probably in equilibrium, whereas the model sediment was a forced association. For example, if Cu were loaded onto kaolin in experiments with a model sediment, but would rather be associated with the humic acid component of the model sediment, it would redistribute to the humic acid fraction during extractions. In a natural system the Cu would have been associated with the humic acid in the first place.

Acknowledgement

The authors thank the Department of Water Affairs and Forestry at Deneysville for assistance with the sampling of sediments near the dam wall and the Foundation for Research and Development for financial support.

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