A pH-dependent sequential extraction procedure to determine mobilisation and transport of metals in sediments

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Abstract

A pH-dependent sequential extraction procedure to determine mobilisation and transport of metals from sediments in the Vaal River-Koekemoerspruit confluence area was developed. The study was preformed on the less than 0,2 mm particle size of the dried sediments. Ammonium/acetate extracting reagents were used and the extracts were analysed by using inductively coupled plasma (ICP) emission spectroscopy. The performance of the sequential extraction procedure was evaluated relative to a standard sediment. Differences can arise in using this sequential extraction procedure when naturally occurring soil types and ligands, which influence the extraction behaviour, are other than those used in this study. Arsenic, copper, zinc and manganese are mobile elements in the Vaal River-Koekemoerspruit confluence area and may have a possible environmental impact on the water phase.

Introduction

Sediments are important sources of trace metals as they receive physical debris and are sinks for a wide variety of chemicals (Adams et al., 1992; Adriano, 1986; Martin et al., 1987). They provide a matrix for living aquatic organisms (Pickering, 1981) and therefore, from the viewpoint of pollution to the environment, it is important to know whether trace metals in the sediment are in a readily available form. Metals are not necessarily permanently sorbed by sediments and can be released to the water column with changes in different environmental conditions such as pH, redox potential, concentration of inorganic and organic complexation agents (Adriano, 1986; Calmano and Förstner, 1983), salinity and dredging (Donze et al., 1990). Many workers (Aualiitia and Pickering, 1988; Brümmer, 1986; Förstner et al., 1981; Gibbs, 1977; Meguellati et al., 1983; Tessier et al., 1979; Zeien and Brümmer, 1989) have developed sequential "selective" extraction procedures for partitioning particulate trace metals into chemical forms likely to be released into solution under various environmental conditions. Non-selectivity of extraction procedures and trace element redistribution among phases during extraction are two major experimental problems with species-specific sequential procedures according to Kheboian and Bauer (1987). Furthermore, Nirel and Morel (1990) have shown that sequential extraction techniques cannot provide actual particulate speciation. For this reason it was decided to develop a sequential extraction procedure for a specific environmental problem.

South Africa is a water-poor country with considerable mining activities occurring inland. Treated acidic mine discharges into rivers inevitably have an impact on their water. Without doubt the resultant pH fluctuation will play a role in dissolving trace metals from the river bed sediment and changing the water-solid phase equilibrium. In investigating the effect of pH of extractant on the release of copper and lead from a sediment, Rauret et al. (1991) found that not only is the pH of the extractant solution of importance in release of metals, but also the rate at which the acid extractant is added as the pH is decreased. In the interior of South Africa rainfall tends to be sporadic and intense, with the result that rapid dilution of acid drainage occurs. During a rain storm large amounts of decomposing organic matter are washed into the rivers, thereby elevating ammonium ion concentrations. For this reason ammonium salt based buffers were used in designing the sequential pH extraction procedure.

The purpose of this study was to develop a sequential pH-dependent extraction procedure to determine whether various metals present in the sediment would be available to the water phase if the pH of the overlying water fluctuates. The data from the sequential extraction procedure will be useful in evaluating the pollution potential for mobilisation and transport of metals from the sediment under fluctuating pH conditions.

Materials and methods

Study areas and sampling

The Vaal River is one of the most important rivers in South Africa, being the principal water source for the many activities in the industrial heart of the country (Van Vliet, 1986). The catchment area is approximately 194 000 km^2. Industrial activity near the sampling site is dominated by the mining industry where mainly gold and uranium is mined. Using a core sampler, core sediment samples were collected from the riverbed at the Vaal River-Koekemoerspruit confluence region in the Vaal River catchment (Fig. 1). This area is geologically characterised by the Transvaal System which consists mainly of shale, quartzite and dolomite (Van Eeden, 1972). The reason these points were chosen was as a result of the historical study of Bruwer et al., (1983) who found high metal values in the sediments as well as in the water and because of the extensive mining activities in the Vaal River-Koekemoerspruit confluence area (Fig. 2). Ammonia is used in the uranium mining process and concentrations of approximately 1 mg/ℓ N were found in the bottom waters. Periodic increases in ammonia are possibly due to releases from point and diffuse sources. The effluent standard for NH_4^+-N in point sources in South

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Received 1 April 1993; accepted in revised form 5 November 1993.

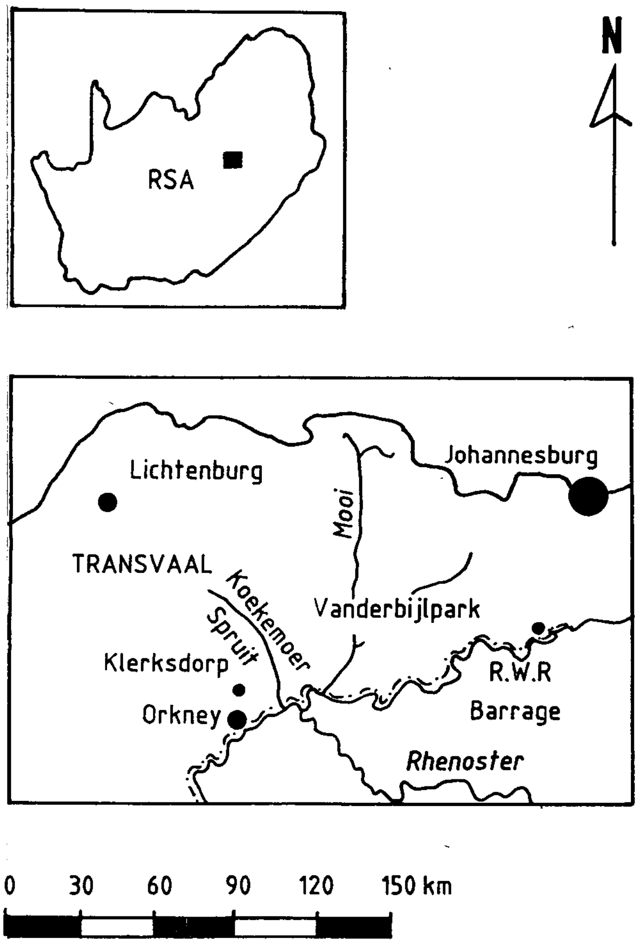

Figure 1
Vaal River-Koekemoerspruit confluence sampling areas in the Vaal River Catchment, South Africa.

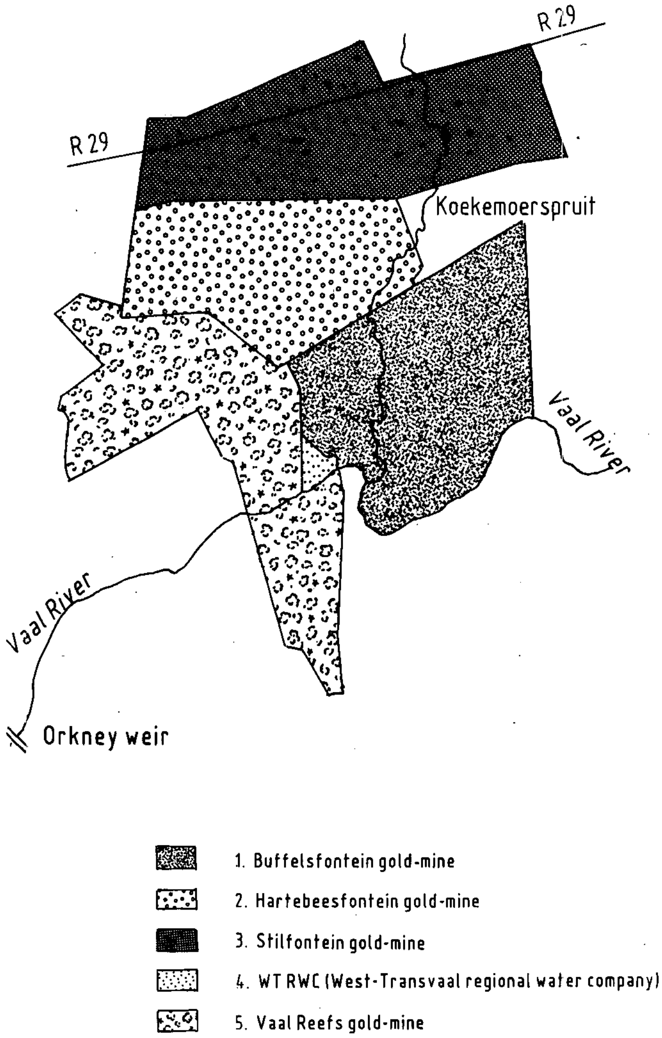

Figure 2
Mining activities in the Vaal River-Koekemoerspruit confluence area.

Africa is 10 mg/ℓ N (Act 54 of 1956).

The upper 5 cm of the core samples were used for analysis. While it is recognised that wet sediment sieving is customarily done for soil particle fractionation, this procedure is inappropriate in this case as it would have changed the partitioning of metals between the solid and water phases. The wet sediment samples were dried overnight in an oven at 30°C, sieved through a 0,2 mm stainless steel sieve, and stored at 4°C until needed. The percentage sediment less than 0,2 mm particle size for samples taken upstream, at and downstream from the Vaal River- Koekemoerspruit confluence is, respectively 81, 76 and 40,9.

Leaching procedures and reagents

The steps in the chemical sequential extraction procedure were as follows:

(i) Mobile alkaline phase at pH 8

An 0,5 g mass of sediment was extracted at room temperature with 20 mℓ of 1 mol·dm^{-3} ammonium nitrate (adjusted to pH 8 with sodium hydroxide).

(ii) Mobile neutral phase at pH 7

The residue from (i) was leached at room temperature with 20 mℓ of 1 mol·dm^{-3} ammonium acetate.

(iii) Easily reducible phase at pH 6

The residue from (ii) was extracted with 20 mℓ 0,1 mol·dm^{-3} hydroxylamine hydrochloride and 1 mol·dm^{-3} ammonium acetate.

(iv) Weak acid soluble phase at pH 5

To the residue of (iii) 20 mℓ of 1 mol·dm^{-3} sodium acetate adjusted to pH 5 with acetic acid, was added.

(v) Reducible phase under acidic conditions at pH 3

The residue from (iv) was leached with 20 mℓ 0,1 mol·dm^{-3} hydroxylamine hydrochloride (pH adjusted to 3 with acetic acid).

(vi) Residual phase

The residue from (v) was digested with 14 mℓ of 4:10 hydrofluoric acid:aqua regia in a 85 mℓ polyfluor DG1:PTFE digestion vessel with pressure relief septa in a commercial microwave oven (5 power levels, 70 W to 700 W). Four vessels were placed in the microwave oven and the digestion was carried out as shown in Table 1. With each set of samples digested, a blank sample was included to correct for any possible contamination. After microwave digestion the vessels containing the sample were left in the microwave oven for 20 min and cooled in a freezer for another 20 min. The vessels were opened and the lids rinsed with deionised water so that the water flowed back into the vessels. Approximately 4 g boric acid was added to complex the fluoride ions. Each sample was then filtered through a Whatman No. 42 filter paper, previously rinsed with a 1% (v/v) nitric acid solution, into a 100 mℓ volumetric flask.

TABLE 1
MICROWAVE OVEN DIGESTION STEPS FOR SEDIMENT DISSOLUTION

Stage	Microwave oven setting	Time
1	High (700 W)	30 s
2	Medium High (490 W)	3 min
3	Medium (350 W)	3 min
4	Low (70 W)	5 min

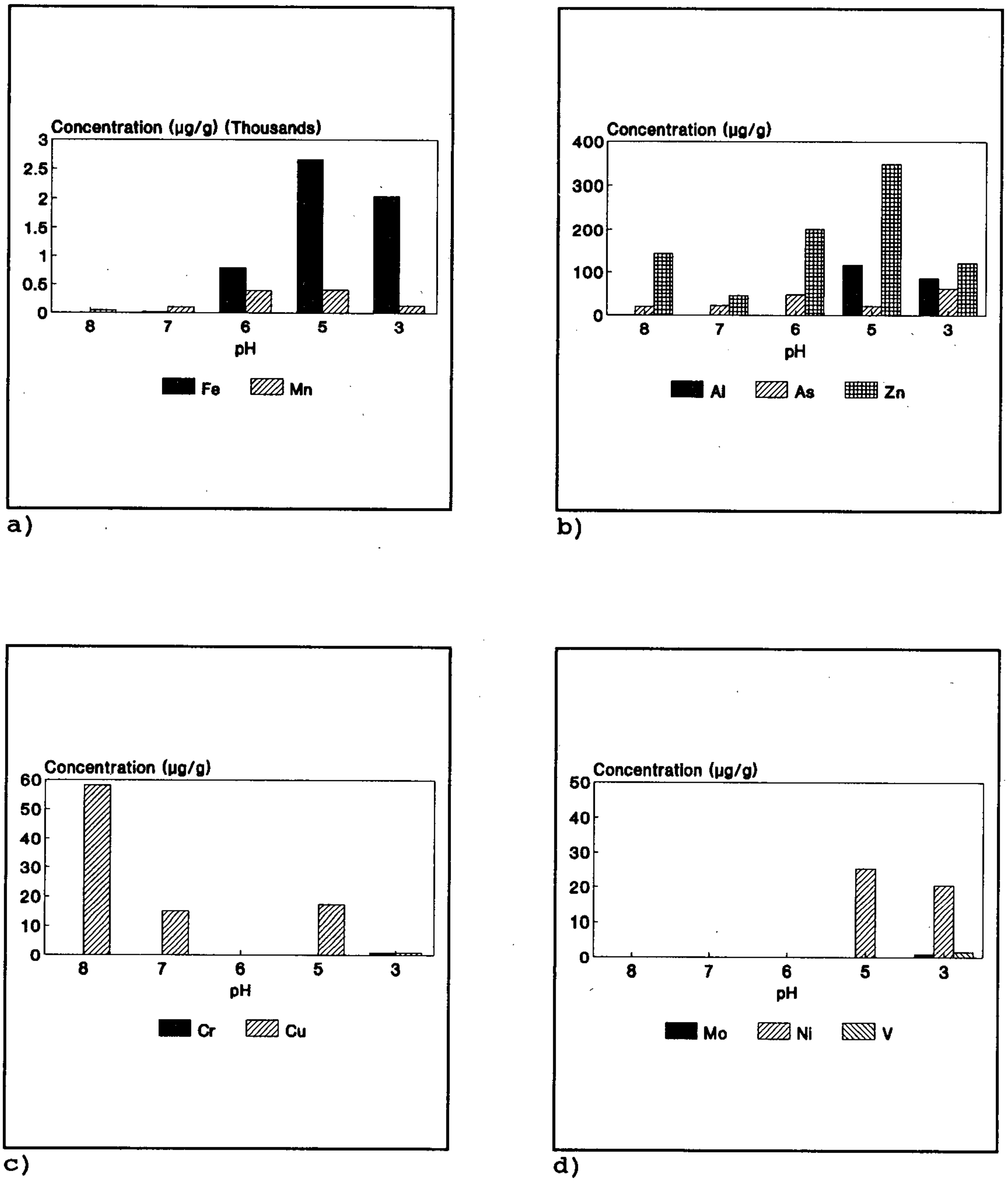

Figure 3
Metal concentrations leached out at each pH step of the sediment sequential extraction procedure from the sampling point at the Vaal River-Koekemoerspruit confluence.
a) Fe and Mn b) Al, As and Zn c) Cr and Cu d) Mo, Ni and V

TABLE 2
AVERAGE (n = 4) METAL CONCENTRATIONS LEACHED AT EACH PHASE OF THE SEQUENTIAL EXTRACTION PROCEDURE FROM REFERENCE SEDIMENT SAMPLE SL-1

Sequential extraction procedures

Unit : µg/g **Standard sample : SL-1**

Determinant	pH 8	pH 7	pH 6	pH 5	pH 3	Residual	Sum of metal concentrations	Reference	Reference confidence interval
Aluminium	51,5 ±9,4	9,9 ±4,	43,4 ±10,6	45,3 ±0,3	27,6 ±0,9	71800 ±1490	71978	-	-
Arsenic	<4,0	<4,0	<4,0	<4,0	<4,0	<2,0	<22	27,5	23-32
Boron	<0,2	<0,2	<0,2	<0,2	<0,2	-	<1,0	-	-
Cadmium	<0,2	<0,2	<0,2	<0,2	<0,2	<1,0	<2	0,26	0,2-0,3
Chromium	3,87 ±1,21	<0,08	0,2	0,2	0,33 ±0,15	101± 3	105,6 -105,7	104	88-120
Copper	4,4 ±1,1	<0,2	<0,2	<0,2	<0,2	58,6 ±1,8	63,0 -63,8	30,0	26-35
Iron	51,4 ±9,8	12,5 ±3,9	508 ±87	886 ±46	1 520 ±56	67 800 ±1 980	70 778	67 400	57 300 -77 510
Mercury	<0,8	<0,8	<0,8	<0,8	<0,8	<4,0	<8	-	-
Manganese	2750 ±102	410 ±35	274 ±20	85 ±10	51,8 ±2,8	616 ±18	4187	3460	2941 -3979
Molybdenum	<0,2	<0,2	<0,2	<0,2	<0,2	10,9 ±0,4	10,9 -11,9	--	
Nickel	23,9 ±7,1	1,3 ±0,2	1,1 ±0,1	1,37 ±0,32	2,03 ±0,71	39,4 ±3,5	69,1	44,9	38-52
Lead	<2,0	<2,0	<2,0	3	<2,0	32,57 ±8,34	35,6 -43,6	37,7	32-43
Titanium	3,87 ±0,45	0,73 ±0,23	4,7 ±0,9	0,4 ±0,1	0,17 ±0,06	2820 ±92	2830	5170	4390 -5950
Vanadium	3,00 ±0,89	0,1	2,75 ±0,71	1,8 0,18	1,9 ±0,1	137 ± 4	146,6	170	144-195
Zinc	<0,16	3,9 ±0,4	13,6 ±2,5	5,73 ±1,55	9,1 ±0,6	163 ± 5	195,3 -195,5	223	190-256

TABLE 3
METAL CONCENTRATIONS LEACHED OUT AT EACH PHASE OF THE SEDIMENT SEQUENTIAL EXTRACTION PROCEDURE FROM THE SAMPLING POINT UPSTREAM OF THE VAAL RIVER-KOEKEMOERSPRUIT CONFLUENCE

Sequential extraction procedure concentrations						
Unit : µg/g	**Upstream of the Vaal River-Koekemoerspruit confluence**					
Determinant	**pH 8**	**pH 7**	**pH 6**	**pH 5**	**pH 3**	**Residual**
Aluminium	<4,0	<4,0	<4,0	49,7±2,2	46,1±19,8	34 700±2 260
Arsenic	<4,0	<4,0	<4,0	16,7 ±1,2	9 ±1	61,5 ±17,2
Boron	0,85 ±0,35	0,53 ±0,06	1,03 ±0,06	1,6	0,8 ±0,26	-
Cadmium	<0,2	<0,2	<0,2	<0,2	<0,2	<1,0
Chromium	7,3 ±4,9	<0,08	<0,08	0,53 ±0,06	<0,08	118±8
Copper	9,1 ±4,1	<0,2	<0,2	1,9 ±0,1	<0,2	54,7 ±1,1
Iron	12,3 ±2,5	6,2±3,3	243 ±29	682 ±17	848 ±78	42 600 ±3 120
Mercury	<0,8	<0,8	<0,8	<0,8	<0,8	<4,0
Manganese	97 ± 5	186 ±6	470 ±8	235 ±14	59,6 ±2,9	280 ± 6
Molybdenum	8,4 ±1,9	<0,2	<0,2	<0,2	<0,2	12,6
Nickel	7,2 ±3,5	<0,8	<0,8	12,4 ±0,5	2,4 ±0,1	31 ±22
Lead	<2,0	<2,0	<2,0	<2,0	<2,0	<10
Titanium	<0,04	<0,04	0,73 ±0,4	0,1	0,5 ±0,6	4 550 ±391
Vanadium	5,4 ±3,2	<0,04	8,3 ±0,4	6,93 ±0,45	2,7 ±0,2	88 ± 8
Zinc	0,75 ±0,21	8,53 ±0,15	31,3 ±0,8	32,9 ±1,0	14,4 ±10,1	79,6 ±6,1

The sequential extraction procedure was conducted in 50 mℓ polysulphone centrifuge tubes. For each step (i) to (v) of the sequential extraction procedure there was a 6 h contact time with shaking on a Labotex model 202 shaker. Between each extraction, separation was effected by centrifuging (Sorvall, Model RC2-B) at 10 000 r/min for 20 min. The supernatant was removed with a Pasteur pipette and analysed for trace metals with a 1978 Applied Research Laboratories (ARL) Model 34000 Polychromator and a 1983 Model ARL 3510 Scanning Monochromator inductively coupled plasma (ICP) emission spectrometer (Kempster, 1986). The residue was placed in a refrigerator at 10°C overnight between each extraction. Blank samples were also included and taken through the whole procedure. Blank values were subtracted from the sample values during the analysis. The time required to complete the whole extraction procedure was 5 d.

All reagents used were of Analar grade or better and the calibration standards to determine the metals were prepared from commercial stock solutions (Department of Water Affairs and Forestry, 1992).

All glassware used for the experiments was washed with 20% (v/v) EXTRAN soap and then soaked in a 1% (m/v) EDTA solution for 4 h, rinsed with deionised water, again soaked in 1% (v/v) hydrochloric acid for 4 h and rinsed with deionised water.

Choice of leaching agents

In the choice of reagents for the sequential extractions, emphasis was placed firstly on choosing reagents that would mimic conditions which could occur in the environment and secondly, those that could produce a pH sequence change from high pH to low pH. After studying leaching extraction methods used by other workers (Brümmer, 1986; Förstner et al., 1981; Tessier et al., 1979; Zeien and Brümmer, 1989), it was decided to use as far as possible ammonium/acetate extraction reagents throughout the extraction procedure. It is of importance to determine whether metals would dissolve in the water phase as the pH fluctuates and especially where the ammonium ion is present, as this is a common contaminant in sewage treatment plant effluents.

Precision and accuracy

The analytical precision for each step of the extraction procedure was tested by subjecting 4 subsamples of the standard sediment SL-1 of the International Atomic Energy Agency to the pH-dependent sequential extraction procedure described.

Results and discussion

The results obtained for standard sediment SL-1 are shown in Table 2. As expected the precision is generally poor where the concentration of the metals is near the detection limit of the instruments used, but improves for values well above the detection limit. When comparing the sum of the metal concentrations in the individual fractions with the reference confidence interval of the metal concentrations, it was found that chromium, iron, lead, vanadium and zinc concentrations all fell within the given confidence interval. Boron and cadmium concentrations were below the detection limit, while manganese and nickel concentrations were outside the confidence interval. The copper concentration is almost double and the titanium concentration is almost half of the reference value. The reference values supplied with the standard sediment were determined using analytical instruments which included research reactors, atomic absorption spectrometers, atomic emission spectrometers, X-ray fluorescence spectrometers and other instruments.

TABLE 4
METAL CONCENTRATIONS LEACHED OUT AT EACH PHASE OF THE SEDIMENT SEQUENTIAL EXTRACTION PROCEDURE FROM THE SAMPLING POINT AT THE VAAL RIVER-KOEKEMOERSPRUIT CONFLUENCE

Sequential extraction procedure concentrations

Unit : µg/g **At the Vaal River-Koekemoerspruit confluence**

Determinant	pH 8	pH 7	pH 6	pH 5	pH 3	Residual
Aluminium	<4,0	<4,0	<4,0	117 ±21	86,4 ±16,3	55 200 ±3 830
Arsenic	19,7 ±2,5	22,3 ±1,5	48 ±3	20,5 ±1,0	62 ±13	791 ±69
Boron	7,2 ±0,9	1,8 ±0,3	2,7 ±0,4	3,77 ±0,35	2,4 ±0,9	-
Cadmium	<0,2	<0,2	<0,2	<0,2	<0,2	<1,0
Chromium	<0,08	<0,08	<0,88	<0,08	0,83 ±0,25	176 ±6
Copper	58,1 ±4,1	14,7 ±3,5	<0,2	17,3 ±1,0	1,0 ±0,6	173 ±14
Iron	<0,8	20 ±3	786 ±44	2660 ±192	2040 ±303	35 200 ±2 100
Mercury	<0,8	<0,8	<0,8	<0,8	<0,8	<4,0
Manganese	40,5 ±3,5	100 ±11	392 ±29	407 ±7	126 ±14	369 ±37
Molybdenum	<0,2	<0,2	<0,2	<0,2	0,93 ±0,12	9,78 ±0,96
Nickel	<0,8	<0,8	<0,8	25,3 ±4,8	20,4 ±3,7	78,3 ±6,7
Lead	<2,0	<2,0	<2,0	<2,0	<2,0	<10,0
Titanium	<0,04	<0,04	<0,04	<0,04	<0,04	661 ±25
Vanadium	<0,16	<0,16	<0,16	<0,16	1,47 ±0,25	42,3 ±1,3
Zinc	144 ±12	46,3 ±9,5	202 ±9	349 ±8	122 ±16	369 ±43

TABLE 5
METAL CONCENTRATIONS LEACHED OUT AT EACH PHASE OF THE SEDIMENT SEQUENTIAL EXTRACTION PROCEDURE FROM THE SAMPLING POINT DOWNSTREAM OF THE VAAL RIVER-KOEKEMOERSPRUIT CONFLUENCE

Sequential extraction procedure concentrations

Unit : µg/g **Downstream of the Vaal River-Koekemoerspruit confluence**

Determinant	pH 8	pH 7	pH 6	pH 5	pH 3	Residual
Aluminium	<4,0	<4,0	13,2 ±3,2	47,2 ±4,6	69,9 ±12,7	28 300 ±2 770
Arsenic	<4,0	<4,0	<4,0	<4,0	<4,0	<20
Boron	<0,2	<0,2	1,1 ±0,1	<0,2	<0,2	-
Cadmium	<0,2	<0,2	<0,2	<0,2	<0,2	<1,0
Chromium	<0,08	<0,08	0,33 ±0,15	0,20 ±0,17	0,83 ±0,75	95,5 ±7,2
Copper	<0,2	<0,2	0,53 ±0,15	0,7 ±0,1	<0,2	43,3 ±4,7
Iron	<0,8	4,97 ±0,67	191 ±10	331 ±3	613 ±21	24 400 ±434
Mercury	<0,8	<0,8	<0,8	<0,8	<0,8	<4,0
Manganese	38 ±5	64,1 ±8,2	593 ±22	104 ±10	74,2 ±5,3	211 ±24
Molybdenum	<0,2	<0,2	<0,2	<0,2	<0,2	16,6 ±2,3
Nickel	<0,8	<0,8	3,7 ±0,6	2,8 ±0,6	3,7 ±2,1	33,7 ±2,5
Lead	<2,0	<2,0	<2,0	<2,0	<2,0	<10,0
Titanium	<0,04	<0,04	1,2 ±0,1	0,5 ±0,4	0,1	2 130 ±524
Vanadium	<0,16	<0,16	3,3 ±0,9	0,8 ±0,1	1,4 ±0,5	54,5 ±7,1
Zinc	<0,16	3,93 ±2,8	6,7 ±2,4	5,2 ±1,1	2,8 ±1,2	37,4 ±1,5

Sequential extraction

The results obtained from the sequential extractions on the sediments in the Koekemoerspruit-Vaal River confluence area can be seen in Tables 3, 4 and 5, and are discussed below. The concentrations found in the sequential extraction procedure of the sample at the Vaal River-Koekemoerspruit confluence are compared in Fig. 3.

pH 8 fraction

High manganese concentrations were found at all the sampling points with the highest concentration of 97 µg/g upstream of the Koekemoerspruit-Vaal River confluence. Chromium, copper, iron, molybdenum, nickel, vanadium and zinc were present at the sampling point upstream of the confluence. Relatively large amounts of arsenic (19,7 µg/g), copper (58,1 µg/g) and zinc (144 µg/g) leached out of the sample taken at the confluence.

pH 7 fraction

A similar amount of arsenic (22,3 µg/g) as in the pH 8 fraction leached out of the pH 7 fraction but lower concentrations of copper (14,7 µg/g) and zinc (46,3 µg/g) were found for the sampling point at the confluence of the Koekemoerspruit with the Vaal River. Higher manganese concentrations were found for all the sampling points than in the pH 8 fraction.

pH 6 fraction

The highest concentrations for manganese (392 to 593 µg/g) of all the sampling points were found in this fraction, although the manganese concentration for the sampling point at the Vaal River-Koekemoerspruit confluence is similar to that in the leachate of the pH 5 fraction. High zinc and iron concentrations were present in the leachates for sampling points upstream and at the confluence with the Koekemoerspruit. Aluminium, chromium, copper and nickel were only present in the leachate of sampling points downstream of the confluence with the Koekemoerspruit. Arsenic was present (48 µg/g) at the confluence with the Koekemoerspruit.

pH 5 fraction

High zinc, aluminium, iron and manganese concentrations were found in the leachate of sampling points upstream, downstream and at the confluence with the Koekemoerspruit. The highest concentrations were present at the confluence with the Koekemoerspruit. Arsenic was found both at (20,5 µg/g) and upstream (16,7 µg/g) of the confluence point. Copper and nickel were found at all three sampling points, with the highest concentrations present at the confluence with the Koekemoerspruit.

pH 3 fraction

High concentrations of manganese, iron and aluminium were found at all the sampling points, with the highest concentrations at the confluence with the Koekemoerspruit. Arsenic was present at the sampling points at (62 µg/g) and upstream (9 µg/g) of the Koekemoerspruit. Traces of chromium were found in the samples from at and downstream of the confluence with the Koekemoerspruit while traces of molybdenum (0,93 µg/g) were found at the confluence. Nickel, zinc and vanadium were found in the leachate at all the sampling points.

Residual fraction

The highest metal concentrations were present in the residual fraction except for manganese. No arsenic was present at the sampling point downstream of the confluence with the Koekemoerspruit. Lead, mercury and cadmium were not present in detectable concentrations in the samples taken in the Vaal River-Koekemoerspruit confluence area.

Conclusions

It can clearly be seen from the data that arsenic, copper and zinc are present in relatively high concentrations in the mobile pH 8 and pH 7 phases of the sediment samples taken at the confluence of the Koekemoerspruit and the Vaal River (Fig. 3). Zinc and copper complexed with ammonia to form soluble compounds (Cotton and Wilkinson, 1962; Stumm and Morgan, 1970). It seems that the highest metal concentrations were present in this area. Zinc, manganese and copper were also present in the mobile phases of samples downstream and upstream of the Koekemoerspruit-Vaal River confluence. Zinc and manganese are the 2 elements in that area that are available to the water phase. Thus, the elements zinc, copper, manganese and arsenic are possible pollutants which may leach from the sediment to the water phase at the different pH values of natural water. If, for example, as a consequence of microbiological activity, the pH of the water becomes more acidic at the sediment-water interface, more metals would be available to the water phase (Moore and Luoma, 1990; Tackett et al., 1986).

Rauret et al. (1989) mention that high values found in the residual fraction may be due to incomplete metal solubilisation in previous fractions, particularly in the case of heavily polluted sediments. The ratio of solid matter to volume of extractant as well as the contact time are important variables. While this may be true for sandy type sediments, such as included in this study, we too found that the metals mainly concentrated in the residual fraction, yet when the contact time for each step was increased from 1 h to 6 h, this did not change the predominance of metals situated in the residual fraction. The 6 h extraction contact time is very time-consuming. Therefore it is suggested that a 1 h extraction time per step is used for monitoring purposes. Particularly in the case of a sandy-type sediment, it is expected that the mineral-associated metals will be limited almost entirely to the vigorous residual extraction step.

Pitfalls found in using this sequential extraction procedure can arise when naturally occurring soil types and ligands which influence the extraction behaviour are markedly different from those used in this study, for instance, in sandy, pristine rivers containing little organic pollution (Pickering, 1981). This sequential procedure should be applicable to a sediment environment in which high ammonium and acetate ions may occur as would be the case where run off high in organic matter, particularly of sewage origin, is found.

Acknowledgements

This paper is published with permission of the Department of Water Affairs and Forestry. Ms MC Pretorius is thanked for typing the manuscript, Ms HS van Rensburg and Ms MF Venter for assisting with the experimental work and Ms A Faber for preparing the figures.

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