Investigation of trace element mobility in river sediments using ICP-OES

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Abstract

In this study, the column method was used to determine the leachable trace metals present in selected river sediments. In addition the sediments were investigated using a shaker method and these two methods were compared for reliability. For both these methods extract solutions associated with a sequential extraction method were used. However, the sediments were only subjected to one extractant solution and not to the whole sequential procedure. The river sediments were also subjected to a digestion procedure to determine the total trace metal content. Simulated pollution experiments were performed where the sediments were also spiked to give known concentrations of trace metals. These results were very useful, especially in cases where certain trace metals were not currently present in river sediments. From the results achieved in this study the general trace metal status of the sediments can be established. From the results achieved it was established that in the case of the less impacted rivers (Crocodile and Olifants Rivers) only slight changes in the river conditions are needed to mobilise the trace metals present. From the results of the Blesbokspruit it was seen that urgent attention is needed to prevent further damage to the system.

Keywords: river sediments; pH dependent extraction; trace metal content; acid digestion; column extraction method; shaker extraction method; simulated pollution; experiments

Introduction

In the past, water quality assessment techniques were the main tools used to assess the impact of humans on the aquatic environment. However, soil and river sediments are also prone to contamination from atmospheric and hydrological sources. In South Africa, this indicator of pollution is not that intensively investigated in comparison to the water resource component. In the past decades, both industrial development and urbanisation have led to a dramatic increase in the amounts of effluents discharged into the natural environment (Fangueiro et al., 2002).

This study was done to establish ambient concentration values of trace metals in the chosen river sediments. These river sediments originated from the Blesbokspruit (near Witbank in the Mpumalanga Province (25°49'23" S and 29°12'33" E)), the Crocodile River (near Hartbeespoort Dam in the Gauteng Province (25°47'47" S and 27°53'42" E)) and the Olifants River (near Ohrigstad in the Northern Province (24°22'44" S and 30°39'58" E)) (see Fig. 1). The sediment samples were investigated to establish their ability to adsorb or retain trace metals. The mobility of the trace metals was also investigated to establish the possibility that trace metals present in the sediments could be mobilised under certain environmental conditions. Two different methods were used to extract the trace metals and these methods were evaluated to determine their suitability as assessment tools. The river sediment samples were also subjected to a total digestion procedure to determine the total trace metal content. After sample preparation, all of the samples were analysed using an inductively coupled plasma optical emission spectrometer (ICP-OES).

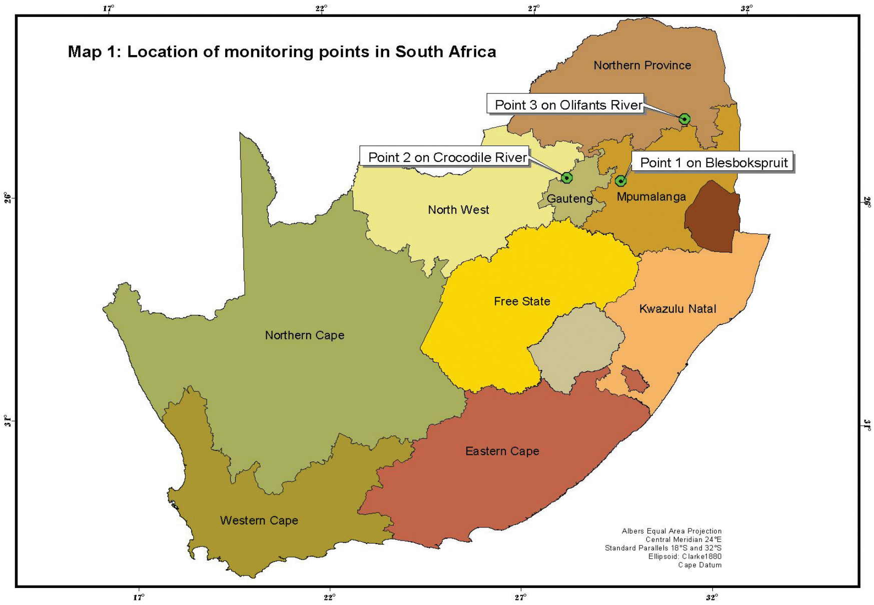

Figure 1
Map showing location of sample points

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Two main catchments were identified to investigate the trace metal levels in the sediments and the water components of the selected rivers. The rivers that were chosen for this investigation were the Olifants River (Mpumalanga and Northern Province) and the Crocodile River (Gauteng Province). The sample area covers land-use activities ranging from predominantly coal- and iron-mining to agriculture and forestry (Hill et al., 2001).

The Blesbokspruit is a tributary of the Olifants River and is classified as part of the Upper Olifants River catchment. This area is heavily impacted upon by point- and non-point source discharges. The main land-use activities are mining, especially coal- and ferro-metal mines. Acid mine drainage problems are found especially in the case of abandoned coal-mines, resulting in sulphate pollution. The increased levels of nutrients in the water stimulate aquatic vegetation growth, resulting in encroachment of the water bodies (DWAF Mpumalanga, 2002). Urban developments including Middelburg, Witbank and Bronkhorstspruit also have a role to play in the overall impact on the environment and the water quality. Large industries and power stations can also have a significant impact on the environment. Farming is not practised extensively in the area (Quibell and Belcher, 1997).

In the Crocodile River catchment the major land use centres mainly on agriculture and forestry. Agriculture is divided into two components, namely dry-land and irrigation agriculture. Dry-land agriculture produces crops like maize, subtropical and citrus fruits and nuts. The most important of the crops cultivated under irrigation are citrus and sugar-cane. Both types of agriculture may lead to increased levels of nutrients in the water and soils if fertilisers are used in excess of the crop's requirements and with irrigation return flows. The mining activities in the area consist of chromium, platinum and vanadium mining. Urban development and informal settlements have a detrimental influence on the quality of the environment in this area due to industrial and domestic wastes. Smaller game farming and cattle ranching activities when properly managed have a lesser impact on the state of the catchment, from a water quality perspective (Quibell and Belcher, 1997).

The sampling point on the Olifants River was in the mountainous region and in the lower catchment area. The most important land-use activities in the mountainous region are small- and large- scale irrigation farming, afforestation, stock watering and urban developments, e.g. Lydenburg, Steelpoort and Burgersfort. In the lower part of the catchment the following land-use activities are of importance: Precious and base-metal mining, small-scale irrigation farming and urban development, e.g. Phalaborwa. The mining activities are mainly concentrated in the Steelpoort River valley and at Phalaborwa (phosphate mining) (Quibell and Belcher, 1997). The Olifants catchment is experiencing an extreme demand for natural resources. This is closely associated with land modification and pollution (Balance et al., 2001).

Materials and methods

Sampling procedure

The equipment used in the sampling of river water and sediment was washed using Merck Extran® MA2 soap (sample bottles and sample tubes). Thereafter it was placed in a solution of 1% (v/v) hydrochloric acid (HCl) for a period of 6 h. The apparatus was removed from the acid solution and was rinsed with Milli Q® quality water.

The sediment sampling was done in river flow conditions where the water level was not too deep for sampling. The core sampler and sampling tubes with a length of 500 mm were made of Perspex. This tube was inserted into the sediment, and the rubber stopper placed in the top of the tube. The tube was slowly removed and the bottom rubber stopper was inserted at the moment when the tube was free from the bottom sediment. The sample tubes were kept at 4°C until the sample preparation stage.

The river water samples were taken in 1 ℓ polyethylene bottles using the subsurface grab method. The water samples were not preserved at sampling, instead they were transported to the laboratory in cool- boxes where on arrival they were prepared and preserved. The samples were kept at 4°C until analysis (Gismera et al., 2004).

Sample preparation

The water samples were filtered using a vacuum-type filtration apparatus directly after arrival at the laboratory. A conditioned 0.45 μm membrane filter was used to filter the water samples. The 0.45 μm membrane was conditioned before use by filtering 50 mℓ of Milli Q® water followed by 50 mℓ 1% nitric acid (HNO_3) (v/v). Both these fractions were discarded and thereafter 100 mℓ of river water was filtered and preserved using 1 mℓ of concentrated HNO_3 (Schillack and Duma, 2003a).

The sediment samples were divided into the different layers where needed. The samples were dried in a drying oven at 30°C for a period of 1 d. After the drying stage, the sediment was ground using a mortar and pestle and sieved with a stainless steel sieve (0.2 mm mesh size). The smaller than 0.2 mm fraction was collected for further sample preparation (Schillack and Duma, 2003b).

TABLE 1
Preparation of the mobile phases

Mobile phase	**Extract solution**
Mobile alkaline phase pH 8	1 mol·dm^{-3} ammonium nitrate (NH_4NO_3), pH adjusted to pH 8 with sodium hydroxide (NaOH)
Mobile neutral phase pH 7	1 mol·dm^{-3} ammonium acetate (CH_3COONH_4)
Easily reduced phase pH 6	1 mol·dm^{-3} ammonium acetate (CH_3COONH_4) and 0.1 mol.dm^{-3} hydroxyl ammonium chloride (NH2OH.HCl)
Weak acid soluble phase pH 5	1 mol·dm^{-3} sodium acetate (CH_3COONa), pH adjusted to pH 5 with glacial acetic acid (CH_3COOH)
Acid soluble phase pH 3	0.1 mol·dm^{-3} hydroxyl ammonium chloride ($NH_2OH.HCl$), pH adjusted to pH 3 with glacial acetic acid (CH_3COOH)
Milli Q water® phase	Water with resistivity of better than 18 MΩ. cm^{-1} mm^{-1} please with measured pH of 6.9
River water phase	River water with measured pH values

Extract solutions

The extract reagents used in the investigation were prepared using AR grade chemicals from Merck (BDH® chemicals) and Milli Q® quality water. The salts were weighted using a 4 decimal analytical balance. The extract solutions were prepared using calibrated A grade volumetric flasks. The extract solutions were pH corrected and measured with a Knick® pH Meter 761 Calimatic calibrated with Radiometer Analytical® (pH 4 and 10) buffer solutions. All the chemicals and acids used to adjust the pH were also AR chemicals. River water from the different sample points and Milli Q® water were also used as a mobile phase in the column and shaker procedures (Tokalioglu et al., 2000; Ngiam and Lim, 2001; Kaasalainen and Yli-Halla, 2003; Dahlin et al., 2002; Dang et al., 2002; Van der Merwe et al., 1994; Fernandez Espinosa et al., 2002).

Experimental procedure

The digestion of the different fractions was performed using a mixture 20% (v/v) of HCl and HNO_3 in the ratio 3:1. One gram of the sediment was weighed on a 4 decimal analytical scale (Mettler®AE 200) and transferred to a 200 mℓ glass beaker. The sample was then digested using an open beaker digestion technique on a hotplate for 2 h whereupon the samples were filtered into clean 350 mℓ polyethylene bottles using an 80 mm funnel fitted with a Whatman® 42 filter paper (Van der Merwe, 1998; Martin et al., 2001; Bettinelli et al., 2000; Sastre et al., 2002).

Column experiment procedure

For the column experiments, 100 g of the sieved fraction was weighed on a 4 decimal analytical balance and placed in a 50 mm inner diameter glass tube. The glass tube was held in place with the aid of a support stand and clamp and it rested on an 80mm funnel fitted with Whatman® 42 filter paper. The extract solution was added to the sample using a Gilson Minipuls 2® peristaltic pump fitted with tubing with inner diameter of 1.3 mm. The peristaltic pump was set up to produce a flow rate of 1mℓ·min^{-1} and the delivery amount of extract solution was 100 mℓ. The total addition time of the extract solution was 100 min. This set-up was used for all the extract solutions mentioned in Table 1. The tubing was centred at the top of the glass tube to prevent irregular flow conditions. The filtrate was collected in a clean 350 mℓ polyethylene bottle and the samples were left to stand for 3 h after the extract solution was added. The samples were done in duplicate to minimise the heterogeneity of the sediments. The filtrate's volume was measured and then stored in a cool-room at less than 4°C until analysis (Yong et al., 2001).

Shaker experiment procedure

For the shaker test, 5 g of sediment was weighed on a 4 decimal analytical balance and placed into a 350 mℓ polyethylene bottle for all the different fractions. 100 mℓ of the particular extract solution was added to the 5 g sample. The sample bottles were placed on a Labotec Model 202 shaker at setting 4 for a period of 100 min after which the samples were taken off the shaker and were filtered through a Whatman® 42 filter paper into a clean 350 mℓ polyethylene bottle (Schillack and Duma, 2003b).

Trace element spiking procedure

For the column and shaker tests the sediment was wetted with 15 mℓ of Milli Q® water and then spiked using 1 000 mg/ℓ single element (Merck) ampoule standards. The ratio of sediment and standard added for the two methods was the same.

Quality assurance

All the calculations were done with a 99% confidence level and a certified reference material sample was used to investigate the suitability of the digestion method. All the analysis readings were performed in triplicate and the samples were prepared in duplicate and analysed.

Analytical results of the river water and sediments

The results for the river water samples were as follows:

TABLE 2
River water analytical results using ICP-OES (Spectroflame Modula)

Determinant	Blesbokspruit water No 1 ($\text{mg}\cdot\ell^{-1}$)	Crocodile River water No 2 ($\text{mg}\cdot\ell^{-1}$)	Olifants River water No 3&4 ($\text{mg}\cdot\ell^{-1}$)
As	0.038	0.051	0.023
Ba	0.050	0.025	0.045
Cd	< LOD	< LOD	< LOD
Co	0.169	< LOD	< LOD
Cr	0.015	0.014	0.011
Cu	0.023	0.027	0.023
Fe	0.612	0.018	0.262
Hg	< LOD	< LOD	< LOD
Mn	3.566	< LOD	0.037
Mo	0.045	0.047	0.044
Ni	0.140	0.035	0.034
Pb	0.085	0.091	0.103
V	0.025	0.030	0.025
Zn	0.115	< LOD	1.378
Zr	0.012	< LOD	< LOD

<LOD shows that the results were lower than the limit of detection of the ICP-OES

TABLE 3
River water pH results using a Knick® pH Meter 761 Calimatic

Determinant	Blesbokspruit water No 1 (pH units)	Crocodile River water No 2 (pH units)	Olifants River water No 3&4 pH units
pH	3.12	7.23	7.39

The results for the different river sediment samples were as follows:

TABLE 4
River sediment digestion results using ICP-OES (Spectroflame Modula)

Determinant	Blesbokspruit <0.2 mm No 1 ($\mu g \cdot g^{-1}$)	Crocodile River <0.2 mm No 2($\mu g \cdot g^{-1}$)	Olifants River <0.2 mm No 3 ($\mu g \cdot g^{-1}$)	Olifants River <0.2 mm No 4 ($\mu g \cdot g^{-1}$)
As	7.17	4.20	3.33	< LOD
Ba	23.95	123.44	24.27	53.76
Cd	< LOD	< LOD	< LOD	< LOD
Co	32.82	18.39	7.57	17.94
Cr	58.50	60.64	38.83	135.22
Cu	16.73	48.02	< LOD	< LOD
Fe	13320	22 740	16 090	43 110
Hg	< LOD	< LOD	< LOD	< LOD
Mn	31.12	1 406	249.1	411.3
Mo	< LOD	< LOD	< LOD	< LOD
Ni	21.26	29.61	10.89	30.22
Pb	12.81	90.39	< LOD	< LOD
V	43.42	39.89	47.46	208.8
Zn	53.09	346.7	< LOD	< LOD
Zr	4.12	3.27	2.65	2.84

TABLE 5
Blesbokspruit fraction column method blank sediments using ICP-OES (Spectroflame Modula)

Determinant	Milli Q water ($\mu g \cdot g^{-1}$)	pH 3 ($\mu g \cdot g^{-1}$)	pH 5 ($\mu g \cdot g^{-1}$)	pH 6 ($\mu g \cdot g^{-1}$)	pH 7 ($\mu g \cdot g^{-1}$)	pH 8 ($\mu g \cdot g^{-1}$)	River water ($\mu g \cdot g^{-1}$)
As	0.04	0.23	0.16	0.23	0.22	0.28	0.13
Ba	0.06	0.16	0.13	0.64	0.45	1.12	0.04
Cd	0.01	0.14	0.06	0.08	0.04	0.04	0.09
Co	5.99	19.22	6.48	22.98	15.29	16.51	12.56
Cr	0.06	0.44	0.47	0.85	0.60	0.24	0.28
Cu	0.18	0.22	0.13	0.16	0.11	0.05	0.12
Fe	9.30	338.7	54.11	76.04	41.58	43.23	132.19
Hg	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Mn	38.69	76.26	55.48	20.92	14.96	15.21	63.39
Mo	0.01	0.19	0.05	<LOD	<LOD	<LOD	0.12
Ni	2.45	12.09	5.36	8.81	6.47	8.55	9.07
Pb	<LOD	0.03	0.02	0.04	<LOD	0.02	<LOD
V	<LOD	0.16	0.03	0.67	0.49	0.11	0.05
Zn	3.83	18.73	7.07	24.25	18.14	20.89	14.86
Zr	0.05	0.23	0.29	0.41	0.32	0.14	0.13

TABLE 6
Crocodile River fraction column method blank sediments

Determinant	Milli Q water ($\mu g \cdot g^{-1}$)	pH 3 ($\mu g \cdot g^{-1}$)	pH 5 ($\mu g \cdot g^{-1}$)	pH 6 ($\mu g \cdot g^{-1}$)	pH 7 ($\mu g \cdot g^{-1}$)	pH 8 ($\mu g \cdot g^{-1}$)	River water ($\mu g \cdot g^{-1}$)
As	0.02	0.02	0.02	0.03	0.02	<LOD	0.01
Ba	0.43	0.48	6.08	13.34	5.07	5.43	0.25
Cd	0.01	<LOD	0.24	0.19	0.09	0.05	<LOD
Co	0.08	0.08	0.37	0.59	0.25	0.13	0.04

TABLE 6 (continued)

Determinant	Milli Q water ($\mu g \cdot g^{-1}$)	pH 3 ($\mu g \cdot g^{-1}$)	pH 5 ($\mu g \cdot g^{-1}$)	pH 6 ($\mu g \cdot g^{-1}$)	pH 7 ($\mu g \cdot g^{-1}$)	pH 8 ($\mu g \cdot g^{-1}$)	River water ($\mu g \cdot g^{-1}$)
Cr	<LOD	<LOD	0.19	0.22	0.08	0.04	<LOD
Cu	0.17	0.19	0.60	0.35	0.33	0.24	0.26
Fe	0.48	0.73	1.70	1.05	0.24	0.14	0.27
Hg	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Mn	15.53	20.94	414.7	478.2	236.7	94.32	4.72
Mo	0.07	0.08	0.34	0.35	0.31	0.30	0.05
Ni	0.19	0.18	1.05	0.67	0.40	0.22	0.15
Pb	<LOD	<LOD	0.48	0.50	<LOD	<LOD	<LOD
V	<LOD	0.01	0.09	0.25	0.03	0.01	<LOD
Zn	1.02	1.14	24.50	15.71	4.13	2.18	0.71
Zr	0.02	0.11	0.07	0.12	0.01	0.01	0.02

TABLE 7
Olifants River sand-layer fraction column method blank sediments

Determinant	Milli Q water ($\mu g \cdot g^{-1}$)	pH 3 ($\mu g \cdot g^{-1}$)	pH 5 ($\mu g \cdot g^{-1}$)	pH 6 ($\mu g \cdot g^{-1}$)	pH 7 ($\mu g \cdot g^{-1}$)	pH 8 ($\mu g \cdot g^{-1}$)	River water ($\mu g \cdot g^{-1}$)
As	<LOD	<LOD	<LOD	0.01	<LOD	0.01	<LOD
Ba	<LOD	10.42	9.82	16.39	6.76	6.75	0.05
Cd	<LOD	<LOD	0.01	0.01	<LOD	<LOD	<LOD
Co	0.46	0.39	0.02	1.43	<LOD	<LOD	<LOD
Cr	<LOD	<LOD	0.02	0.07	<LOD	<LOD	<LOD
Cu	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Fe	<LOD	0.39	0.31	1.32	<LOD	<LOD	<LOD
Hg	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Mn	0.01	100.5	11.93	135.9	0.23	<LOD	<LOD
Mo	<LOD	0.05	0.01	0.14	0.03	0.06	0.01
Ni	0.01	0.49	0.13	1.72	<LOD	<LOD	<LOD
Pb	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
V	0.01	1.18	<LOD	1.14	<LOD	<LOD	<LOD
Zn	<LOD	<LOD	<LOD	0.04	<LOD	<LOD	<LOD
Zr	0.02	0.02	0.03	0.04	0.01	0.02	0.02

TABLE 8
Olifants River clay-layer fraction column method blank sediments

Determinant	Milli Q water ($\mu g \cdot g^{-1}$)	pH 3 ($\mu g \cdot g^{-1}$)	pH 5 ($\mu g \cdot g^{-1}$)	pH 6 ($\mu g \cdot g^{-1}$)	pH 7 ($\mu g \cdot g^{-1}$)	pH 8 ($\mu g \cdot g^{-1}$)	River water ($\mu g \cdot g^{-1}$)
As	<LOD	<LOD	0.01	<LOD	0.02	<LOD	0.02
Ba	0.32	2.65	17.49	30.03	8.83	13.92	0.18
Cd	<LOD	0.02	0.05	0.04	0.04	0.04	0.01
Co	0.02	0.02	0.10	0.08	0.01	0.02	0.01
Cr	0.01	0.02	0.10	0.08	0.03	0.05	0.01
Cu	0.06	0.19	0.11	0.04	0.08	0.11	0.12
Fe	0.03	0.20	0.26	0.32	0.05	0.06	0.05
Hg	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Mn	1.58	5.80	81.89	77.49	3.11	7.38	0.67
Mo	0.16	0.36	0.50	0.57	0.48	0.54	0.18
Ni	0.04	0.32	0.29	0.16	0.08	0.10	0.06
Pb	0.05	0.10	0.12	0.08	0.17	0.17	0.15
V	0.02	0.68	0.06	0.71	0.04	0.05	0.04
Zn	<LOD	<LOD	0.02	0.05	<LOD	<LOD	<LOD
Zr	0.11	0.02	0.04	0.03	0.01	0.02	0.02

The recovery results for the spiked sediment samples were as follows.

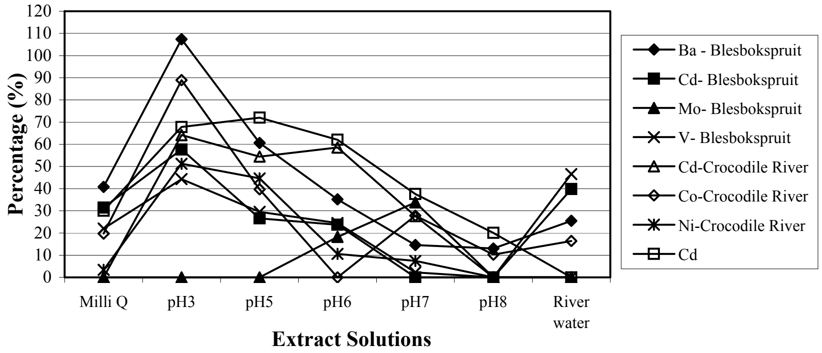

Figure 2
Recovery results of the spiked elements of column method for the Blesbokspruit and Crocodile River sediments

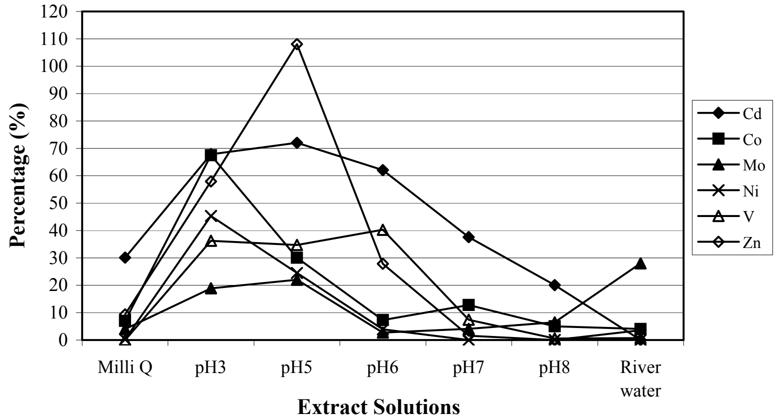

Figure 3
Recovery results of the spiked elements of column method for the Olifants River sand-layer sediments

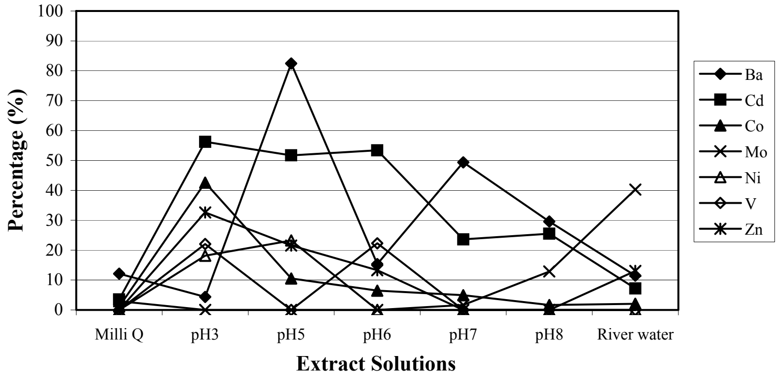

Figure 4
Recovery results of the spiked elements of column method for the Olifants River clay-layer sediments

Discussion of the Blesbokspruit sample results

The results from the Blesbokspruit water sample showed that 13 out of the 15 trace elements measured were present in varying concentrations. The main concentration contributions came from: Co, Fe, Mn, Ni and Zn. The pH of the water is also very low for natural water and was measured at 3.12 (pH units). This can definitely play a major role in the elevated levels of trace elements in the river's water. With the pH being this low it will promote the movement of the trace elements in the sediment and they will eventually end up in the groundwater source.

It was clear from the water analysis that very high concentrations were expected. After the digestion of the sediment samples this was confirmed. These elevated levels were proven throughout the results obtained.

In the column leach tests the trace elements that showed a concentration above their detection limits were Ba, Co, Cr, Cu, Fe, Mn, Ni, V, and Zn. Ba was present at very low concentrations throughout the extract solution series. From the results it is clear that a pH of between 6 and 8 is the best condition for mobility, with the highest concentration being at pH 8 (1.12 $\mu g \cdot g^{-1}$). The mobility of Co is relatively constant through the extract series and there is not a large difference between pH 3 and pH 6 in the concentrations measured. Co was also very mobile in the river water and the calculated value compared well with the other synthetic extract solutions. Cr displayed mobility from pH 3 through to pH 7. The concentration, however, was not high and ranged between 0.44 $\mu g \cdot g^{-1}$ (pH 3) to 0.85 $\mu g \cdot g^{-1}$ (pH 6). Cu was present at very low levels and the calculated values were between 0.05 $\mu g \cdot g^{-1}$ (pH 8) to 0.44 $\mu g \cdot g^{-1}$ (pH 3). It also showed a good relation between pH and mobility. Fe and Mn were present in very large amounts. The river water also leached considerable amounts, which showed that under normal river conditions Fe and Mn are very mobile. Ni was present at average concentrations and ranged from 12.09 $\mu g \cdot g^{-1}$ (pH 3) to 2.45$\mu g \cdot g^{-1}$ (Milli Q water). The river water again showed increased ability to mobilise Ni from the sediment under normal river conditions. V showed the highest mobility under conditions between pH 3 (0.16 $\mu g \cdot g^{-1}$) and pH 6 (0.67 μg·g^{-1}). From the results it could be seen that Zn is the most mobile under conditions of pH 6 to 8 and to a lesser degree under lower pH conditions.

In the shaker test the results exhibited the same characteristics. In general, however, the results had much larger deviations between the duplicate samples. This can be attributed to the smaller amounts of sediment used which will be more affected by subtle changes in trace metal content.

The results of the spiking exercise for the column method were only reliable for the following elements: Ba, Cd, Co, Ni and Zn (Fig. 2). The recovery of Ba varied from 0.86% (Milli Q water) to 11.92% (pH 3). The recovery was not high and this is an indication that the sediment adsorbs the element well. Cd on the other hand was mobile throughout the extract series with recovery ranging from 24.7% (pH 6) to 97.21% (pH 8).

Discussion of the Crocodile River sample results

The results from the Crocodile River water sample showed that 9 out of the 15 trace elements measured were present in varying concentrations. The pH of the water is considered normal for natural water sources and was measured at 7.23 (pH units). The main factor that influences the low concentrations of elements present in the river water is the neutral to slightly alkaline pH of the water. This is also an indication that little to no acid mine drainage is present in the river water.

The digested sediment sample analysis showed that 12 out of the 15 elements measured were present. The elements Cd, Hg and Mo were not present at detectable concentrations..

The trace elements that gave a concentration above their detection limits were Ba, Mn and Zn. Barium was present in rather low concentrations ranging from 0.25 μg·g^{-1} (river water) to 13.34 μg·g^{-1} (pH 6). This shows that the best mobility of Ba was obtained between pH 5 to 6. Mn was present at very high concentrations in the digested sediments and was expected to be present in elevated levels in the leachate. Under normal river conditions though, Mn is not easily mobilised. Zn was present in low to moderate concentrations ranging from 0.71 μg·g^{-1} (river water) to 24.50 μg·g^{-1} (pH 5). The same applies to Zn as previously mentioned with Mn, very low mobility was seen in the river water. The shaker method gave correlating results with the column method, but Fe and Ni were also detected.

The elements that gave reliable recovery results were Cd, Co, Cr and Ni. The recovery values for Cd, Co and Ni were high and showed a good relationship between the mobility and lower pH levels (Fig. 2). Under river conditions it was illustrated that in the event of Cd and Co pollution, it is possible to mobilise these elements. Ni showed that in higher concentration levels it could be mobilised by the river water.

Discussion of the Crocodile River sample results

The results from the Olifants River water sample showed that 11 out of the 15 trace elements analysed for were present in varying concentrations. The concentrations of the elements present were higher than the Crocodile River and ranged between 0.011 mg·ℓ$^{-1}$ (Cr) and 1.38 mg·ℓ$^{-1}$ (Zn). Fe, Pb and Zn contributed the bulk of the concentrations in the water samples. The pH of the water, very much the same as that of the Crocodile River, is considered normal for natural water sources and was measured at 7.39 (pH units).

Sand-layer results

In the digested sediment samples 9 of the analysed elements were present in varying concentrations. The concentration varied from 2.65 μg·g^{-1} (Zr) to 28 120 μg·g^{-1} (Fe). The bulk contributors to the overall concentration that were measured were: Ba, Cr, Fe, Mn and V. Small differences in concentrations can be attributed to almost complete absence of clay particles present, which usually adsorb more trace elements and contribute more of the trace element measured concentration.

The concentrations found in the sand fraction of the Olifants River were very low, with the highest contribution being that of Mn. Ba was present at higher concentrations (ranging between 0.05 and 16.39 μg·g^{-1}) than in the sand fraction and exhibited the best mobility under pH 6 extract conditions. Co was present at very low concentrations ranging between 0.02 μg·g^{-1} (river water) and 1.43 μg·g^{-1} (pH 6). It was found that Co was the most mobile under pH 6 conditions. Mn was present at elevated levels in the pH 3 and 6 extract solutions and this agrees with the digested sediment results.

The same elements that were found to be mobile in the column test were found in the shaker test. The Fe and V, however, gave considerably higher concentrations than in the column method.

The elements that gave reliable recovery results were Cd, Co, Cr, Mo, Ni and V. The recovery values for Cd, Co and Ni were high and showed a good relationship between the mobility and lower pH levels, with the best being between pH 3 and 6. Under river conditions it was illustrated that in the event of Cd, Co and Ni pollution, it is possible to mobilise these elements. Mo and V showed good mobility under the extract conditions.

Clay-layer results

In the digested sediment samples 8 of the analysed elements were present in varying concentrations. The concentration varied from 2.84 μg·g^{-1} (Zn) to 43 110 μg·g^{-1} (Fe). The bulk contributors to the overall concentrations that were measured were: Ba, Cr, Fe, Mn and V. The Cr (135.2 μg·g^{-1}) and V (208.8 μg·g^{-1}) concentrations were noticeably higher than those in the sand layer. Overall the calculated concentrations were three times higher than those of the sand layer. The concentrations of the different fractions were not far from each other and this again can be attributed to the low amount of clay particles present.

In the column extract solution 12 out of the 15 elements measured were present. The two main contributions in concentration came from Ba and Mn. The other elements were present in very low concentrations and did not pose a possible pollution risk. Ba was, as with the sand layer, present in high concentrations between pH 5 and 6. Mn also exhibited the same characteristic and percentage mobility. All the other elements that were present were not present in the sand layer, but it is expected that the trace metal content will be higher in sediments with higher clay content.

In the shaker test the results exhibited the same characteristics. In general, however, the results had much larger deviations between the duplicate samples. This agrees with what was found with the Blesbokspruit samples.

The elements that gave reliable recovery results were Cd, Co, Hg, Mo, Ni, V and Zn. The recovery values for Cd, Co and Ni were high and showed a good relationship between the mobility and lower pH levels, with the best being between pH 3 and 6. Under river conditions it was illustrated that in the event of Cd, Co and Ni pollution, it is possible to mobilise these elements.

Mo and V showed good mobility under the extract conditions. Zn was also leached at detectable levels.

Conclusions

Blesbokspruit

The results from the Blesbokspruit showed elevated levels of a number of trace elements present in the sediment. In the leaching experiments, it was seen that the elements were mobile to a high degree, and this was not expected in sediment with high clay content with which to bind the trace elements. Under normal river conditions, it was found that the mobility of the trace elements was very high especially with respect to Co, Fe, Mn, Ni and Zn. This was explained by the very low measured pH and higher than normal trace metal content of the river water. This is a worrying factor because it gives evidence that there need not be a drastic change in the river condition as previously assumed, for the trace elements to be mobilised. The trace elements are already mobile under existing river conditions. From the digested sediment samples, it can be seen that the trace element load of the river sediment is very high and the easily leached trace elements showed that the sediment does not have the capacity to strongly bind the trace elements.

The simulated pollution experiment gave good results for Cd, which was not present in the original sample. This showed that it could easily be mobilised. This showed that in the event of Cd pollution in the Blesbokspruit, it is possible for it to mobilise and cause possible deterioration of the groundwater resources. The overall state of the Blesbokspruit is undesirable and concerted action is needed to try and ameliorate the situation.

Crocodile River

The trace element content in the river water sample was low and the pH in the normal range of an unimpacted river. From the leaching methods the results showed that the major part of the leachable trace metal content occurs under pH conditions between five and six. The main contribution in the total concentration using the leach methods was shown to be Mn. Under current river conditions, low concentrations of the trace elements were found; however, there were detectable amounts of Ba, Cu, Fe, Ni and Zn. This indicates that it is possible to mobilise trace elements under the current river conditions. The fact that the best mobility was observed at pH 5 to 6 means that there need not be a drastic change in the river conditions to be able to mobilise trace elements from the river sediments and the acid rain may mobilise trace elements. At this stage, the elements (Cd, Co, Cr and Ni) that clearly showed mobility in the simulated pollution experiment are not present at high concentrations in the sediments. From the results, however, it can be deducted that in the event of possible pollution of the mentioned elements, it is possible to mobilise them from the sediment. Currently, the overall state of the Crocodile River is not heavily impacted upon, but careful monitoring is needed to keep the situation stable.

Olifants River

The trace element concentrations measured in the Olifants River sand and clay fractions were not extremely high. The main contributions in the sand fraction were from Ba and Mn, with smaller concentrations for Ni and V. The pH of the river water was 7.39 and this is normal for an undisturbed river system of this type. There were not any trace elements that gave significant values in the river water experiment and the main conditions of increased mobility were between pH 3 and 6. On the other hand, in the simulated pollution experiments it was clear that Cd, Co, Cr, Mo, Ni and V were mobile throughout the extract series at high levels. In the event of possible pollution of the above-mentioned elements, it is possible to mobilise trace elements under current river conditions. In the clay fraction there were many more different trace elements present; however, they were at low concentrations. The main concentration contributions arose from Ba and Mn. The best mobility conditions were shown to be between pH 5 and 6. Under normal river conditions, a number of elements were mobilised in small quantities, but in the long run they can contribute to the pollution of groundwater resources. The simulated pollution experiment showed the same elements to be as mobile as in the sand fraction with the same amount of mobility throughout the extract series. The overall trace metal status of the Olifants River at the sampling point was considered to be acceptable.

Analytical procedures

Column method of leaching trace elements

The column method gave repeatable and reproducible results with a low relative standard deviation between the different replicates. The use of a greater volume of sediment can have negative and positive implications on the analytical procedure. The positive aspects are that with the column method, the leaching process is more natural (simulating natural processes) and that using larger volumes of sediment can lessen the variability observed in the sediment samples. On the other hand, depending on the characteristics of the sediment, it is difficult to know exactly what the end volume of the extract will be once filtered. This means that the amount of extract solution retained in the sediment must first be determined before final decisions can be made on what volume to use. From the results obtained in this study, it can be said that the column method is a reliable way to measure leaching of trace elements if a sufficient volume of sediment is available.

Shaker method of leaching trace elements

The shaker method also gave reliable results and compared well with the column method. The relative standard deviation was higher between replications than in the case of the column method. The mechanical process of the method is also not natural and the leaching of elements is predominantly higher than in the column method. The biggest disadvantage of the shaker method is the small amount of sediment used in the sample preparation stage. The variability of the sediment composition can play a major role in the end concentration measured. This method can be used in the event that only a small amount of sediment is available, but then the results are prone to large variations in resultant concentrations. The advantage compared with the column method is that the end volume of the extract solution is not dependant upon the sediment type. With the results obtained in this study, the shaker method can be used, but the column test method gave better results.

Recommendations

In South Africa, sedimentation in the river systems is a common occurrence. The general feeling is that sedimentation can provide an inexhaustible sink to adsorb trace elements. From this study it is clear that the river sediment has only a limited capacity to adsorb trace elements and when the load on the river sediment increases this capacity could be breached. Under acidic or sometimes normal river conditions, the trace elements may leach and cause problems, for example, with groundwater quality degradation.

It is clear in the case of the Blesbokspruit that the water and sediment quality are heavily affected by anthropogenic activities. This is an example of a system that will take many years to rehabilitate if the process is started immediately. This shows the importance of constantly monitoring a river system's condition. This would then act as an early warning system that would warn the managing authorities before the damage sustained is no longer reversible.

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