Observations on concentrations of the heavy metals zinc, manganese, nickel and iron in the water, in the sediments and in two aquatic macrophytes, *Typha capensis* (Rohrb.) N.E. Br. and *Arundo donax* L., of a stream affected by goldmine and industrial effluents

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Abstract

The occurrence of the heavy metals Zn, Mn, Ni and Fe and their uptake by two emergent aquatic weeds *Typha capensis* and *Arundo donax* in the water and sediments of a stream polluted by acid mine drainage water, was investigated. Results showed that, with the exception of Fe, the deposition of the other three metals increased as the stream water became more alkaline. At the same time, higher concentrations of these metals were present in the tissues of both species. *A. donax* and *T. capensis* differed in their capacity to accumulate metals. The possibility of the removal of metals from the ecosystem by cropping *A. donax* was discussed.

Introduction

The Elsburgspruit in the Transvaal is situated within the boundaries of the Witwatersrand (Fig. 1). Because of intensive goldmining activities over many decades in the headwater region of this stream, its waters are at places severely contaminated by effluents from disused and active mines. Water pumped from these mines varies in pH and contains a variety of heavy metals. The volume released into the Elsburgspruit could amount to as much as 10 938 m^3/d (Wells, 1989), reaching the spruit directly, or indirectly through seepage. These volumes of low pH, highly saline effluent waters discharged into the Elsburgspruit were found to exert a marked influence on the biology of the affected streams (Schoonbee and Van der Merwe, 1989). Effluents from metal-processing industries containing Zn, Ni and Cu further complicated the presence and composition of certain of these metals in the water and in the stream sediments (Schoonbee and Van der Merwe, 1989).

The effects of the acidification of streams on the macro-invertebrate fauna, caused mainly by effluent waters from mines, were first studied in South Africa by Harrison (1958; 1961). The role of mine effluent waters containing heavy metals on stream ecosystems has also received considerable attention elsewhere in the world ((Eyres and Pugh-Thomas, 1978; Salomons and Mook, 1980; Burrows and Whitton, 1983; Burton *et al.*, 1983; Campbell and Stokes, 1985; Norris, 1986). From these and other related investigations it is evident that heavy metals could not only have a deleterious effect on the composition and presence of certain stream biota (Wood, 1974), but that changes in the pH of the water could have a direct bearing on the water solubility as well as the depositing capacity of such metals in the substrata of standing and flowing water ecosystems (Förstner and Prosi, 1979). Research by Abo-Rady (1980) and Mortimer (1985), to name but two researchers, showed that aquatic macrophytes and certain algae could be used as bio-indicator organisms to evaluate the presence of selected heavy metals in aquatic ecosystems.

In this study the concentrations of the heavy metals Zn, Mn, Ni and Fe in the water environment and stream sediments were investigated, as well as their accumulation by two emergent aquatic plants *Arundo donax* and *Typha capensis* under acidic and alkaline water quality conditions at four selected localities in the Elsburgspruit catchment area near Germiston in the Transvaal. The investigation was carried out in summer during the active growth phase of both plants and before the onset of senescence.

Selection of sampling sites

The four different sampling localities on the Elsburgspruit and on one of its tributaries (Fig. 1) were largely selected on the basis of prevailing pH conditions in the streams, but also for the reasons that follow. Sampling locality 1 was used to evaluate the effects of the acidic mine waters on the metal contents of the water, the sediments and the two aquatic plants just before it enters the main stream of the Elsburgspruit. Previous investigations (Schoonbee and Van der Merwe, 1989) had shown that the water of the Elsburgspruit at that point contained abnormally high concentrations of various heavy metals and that the pH of the water was very low, fluctuating between 3,6 and 6,6. Sampling locality 2 was situated approximately 2,5 km downstream from locality 1 where the pH of the water showed some improvement, varying mainly between 4,4 and 6,9. Locality 3, situated on a tributary which also receives acidic mine effluent waters, was also shown to receive fluxes of relatively high concentrations of the heavy metals concerned (Schoonbee and Van der Merwe, 1989). Sampling locality 4 was situated on the main stream again in a predominantly wetland area (Fig. 1), after the stream had flowed through densely-vegetated *T. capensis* and *A. donax* communities for more than 6 km. At this point the pH of the water already showed some recovery by fluctuating between 6,1 and 8,8.

Materials and methods

Selected chemical and physical analyses of the water according to APHA (1971) were done monthly during the survey. These included analysis of pH, conductivity, alkalinity, total hardness and sulphates as well as of the presence of the four heavy metals Zn, Mn, Ni and Fe. Organic material (detritus) was separated from the sand taken from the soft bottom substrates sampled by means of a

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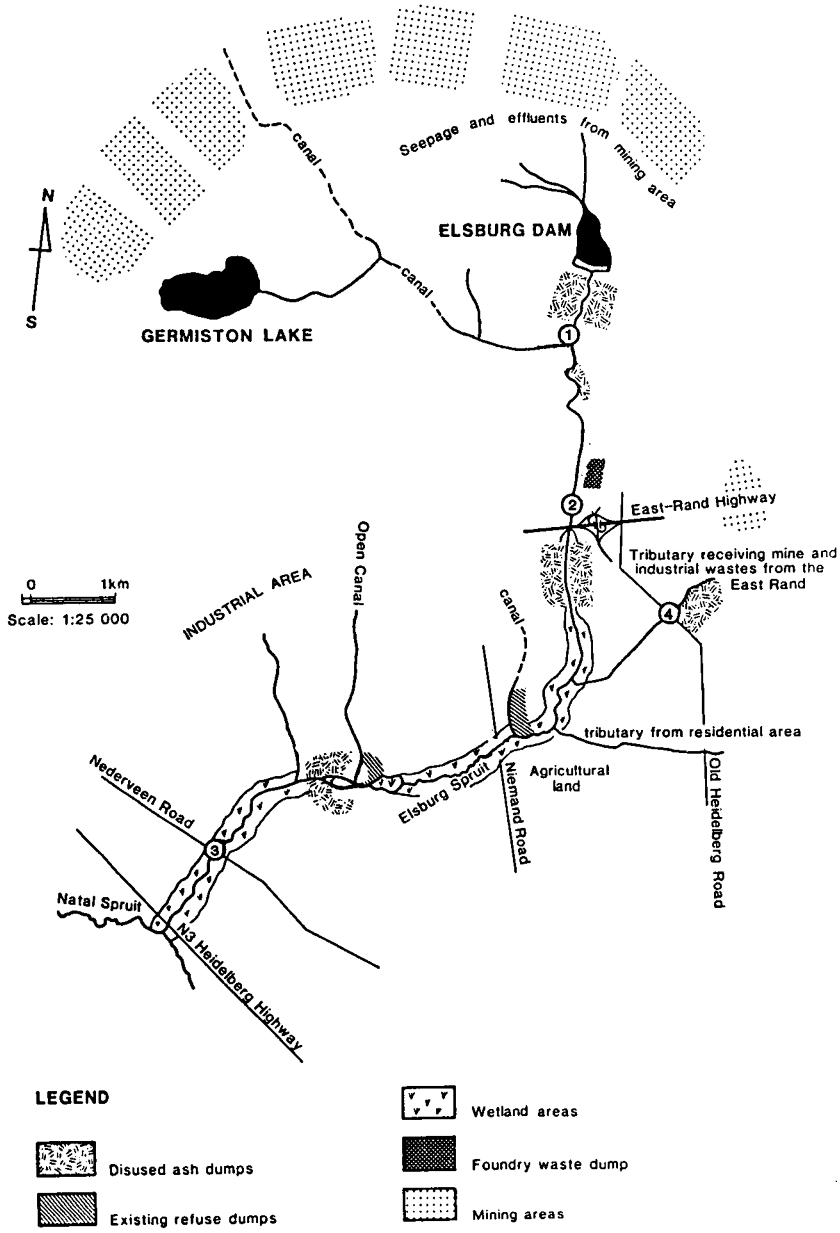

Figure 1
Sampling localities on the Elsburgspruit and one of its tributaries with an indication of the possible sources of pollution in the catchment area of this stream

thorough repetitive rinsing process. Settling was followed by drying the detritus for approximately 72 h at 90°C. Approximately 1 g (accurate to 0,01 mg) of the detritus, derived from the sediments at each locality, was carefully weighed and then digested in a Buchi digester at boiling-point in a mixture of 5 mℓ concentrated nitric acid (55%) and 5 mℓ concentrated perchloric acid (70%) for a minimum period of 4 h or until a clear solution was obtained (Houba *et al.,* 1983; Mortimer, 1985; Norris, 1986). These samples were then filtered and rinsed with distilled water through a 0,45 μm membrane filter, and made up to 100 mℓ with distilled water for further analysis.

The two aquatic macrophyte species involved were collected in the streams at each of the four localities, a garden fork being used to dislodge the plants intact from the stream bed. The plants were then thoroughly washed to remove sediments from the roots. Each plant was separately dried for the same period and at the same temperature as specified for the detritus, and then macerated. Samples of approximately 1 g were digested and prepared for analysis according to the same procedures described for the detritus.

The heavy metal analyses of the digested samples were done using a Varian AA 875 series atomic absorption spectrophotometer. Results obtained were expressed as μg of the metal present in 1 g of the material analysed.

Results

Physico-chemical conditions of the water

The wide range in temperature fluctuations of the stream from winter to summer (readings were usually taken between 09:00 and 12:00) are emphasised by the results obtained (Table 1), where the lowest winter day temperatures fluctuated between 4° and 7°C with summer maxima of 18° to 20°C. The effects of the larger volumes of acidic effluents from mines on the pH of the main stream and on its tributary can be observed clearly at Localities 1, 2 and 4 (Fig. 2). There were, however, definite signs of a recovery to normal alkaline stream conditions, with pH values exceeding 7 at Locality 3 during most months of the year, except during March (6,2) and June (6,1) (Fig. 2). Values for conductivity also indicated the considerable contribution of solids dissolved in the effluents from the mines towards the mineral loads of the stream at all four Localities, with values fluctuating between 55 and 303 mS/m (Table 1). The acidic conditions resulted in low values for alkalinity, which largely prevailed at Localities 1, 2 and 4. Increased values for alkalinity which fluctuated between 86 and 170 mg/ℓ at Locality 3, coincided with expected higher pH values (Fig. 2). Values for hardness and sulphates were exceptionally high and followed approximately the same pattern at Localities 1, 2 and 4, as was the case for conductivity, showing the marked influence of mine effluent waters on the water chemistry of the stream system. Acidic conditions accompanied by the release of sulphates in the water are usually caused by the oxidation of sulphur found in a pyritic form, e.g. iron pyrite (FeS_2) in the mine rock formations (Koryak *et al.*, 1972). During the mining process, water and sulphur oxidising bacteria, when exposed to air, will convert the inorganic sulphur to a water soluble sulphate and sulphuric acid according to the chemical reaction:

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2\,FeSO_4 + 2H_2SO_4$$

Although concentrations for nitrates were not exceptionally high at all four stations (Table 1), phosphates were present in much lower concentrations. Even so, values for chemical oxygen demand (COD) together with those for nitrates and phosphates suggested the presence of some organic enrichment of the stream water which cannot be accounted for by the effluents from the mines alone (Table 1).

Heavy metal concentrations in the water, stream sediments and aquatic plants

A comparison of the concentrations of the different metals in the water medium, in the sediments and in the plant species clearly showed that changes in the concentrations of zinc, manganese and nickel in the various constituents analysed were closely associated, and possibly determined by the pH regime at the different localities. For instance, Zn, Mn and Ni had the highest concentrations in the water where the lowest pH conditions prevailed, with a definite, substantial decline of the metal concentrations in the water at Locality 3 under generally alkaline environmental water conditions (Fig. 3). Changes in pH from acidic to alkaline conditions in turn coincided in most cases with marked increases of the three metals in the sediment. At the same time, the concentrations of these metals in the two plants also increased significantly under more alkaline conditions such as those experienced at Locality 3 (Table 2), suggesting that the capacity of both plants to accumulate these metals may be largely pH-dependent. The relatively high values for Zn in *A. donax* at Locality 3 somewhat contradicted the findings for the main stream. This tributary showed fluxes of

TABLE 1
MEAN VALUES FOR SELECTED CHEMICAL AND PHYSICAL PARAMETERS REFLECTING CONDITIONS IN THE WATER OF THE ELSBURGSPRUIT (LOCALITIES 1, 2 AND 3) AND ON A TRIBUTARY (LOCALITY 4) DURING THE DIFFERENT SEASONS OF 1988

	SAMPLING LOCALITIES AND SEASONS							
	1				2			
Analysis	Autumn	Winter	Spring	Summer	Autumn	Winter	Spring	Summer
Temperature °C	19	7	14	20	19	5	15	20
pH*	4,2-5,0	5,0-5,4	3,9-6,6	3,6-3,7	4,4-6,0	5,0-6,9	5,0-6,5	4,8-6,9
Conductivity mS/m	283	300	303	230	267	230	250	163
Alkalinity as $CaCO_3$ mg/ℓ	5,33	7,17	7,7	0	10,7	32,3	7,6	20,3
Total hardness as $CaCO_3$ mg/ℓ	2076	2137	2167	1503	1909	1435	1653	950
Sulphates mg/ℓ	2210	2227	1990	1527	1997		1480	970
Nitrate mg/ℓ	3,6	3,5	4,0	2,8	3,6	5,85	4,87	3,27
Total phosphate mg/ℓ	0	2,11	0	0,13	0,11	0,24	0,15	0,11
COD mg/ℓ	5	4	18	9,7	5	105	25,3	29,3

	3				4			
Analysis	Autumn	Winter	Spring	Summer	Autumn	Winter	Spring	Summer
Temperature °C	16	4	11	18	18	5	15	20
pH*	6,2-8,1	6,1-7,5	6,8-8,2	8,2-8,8	5,1-6,8	4,7-4,9	4,4-5,6	5,2-7,1
Conductivity mS/m	136	203	173	55	166,7	208	208	153
Alkalinity as $CaCO_3$ mg/ℓ	94	86	86	170	8,17	2,33	2,17	11,5
Total hardness as $CaCO_3$ mg/ℓ	833	1225	1163	238	1033	1330	1317	930
Sulphates mg/ℓ	718		105	87	1040	1360	1445	930
Nitrate mg/ℓ	1,93	3,65	3,03	1,52	3,8	7,6	7,2	4,0
Total phosphate mg/ℓ	0,22	0	0,12	0	0,54	0,13	0	0,12
COD mg/ℓ	12	14	20	11	12	0	8,7	15

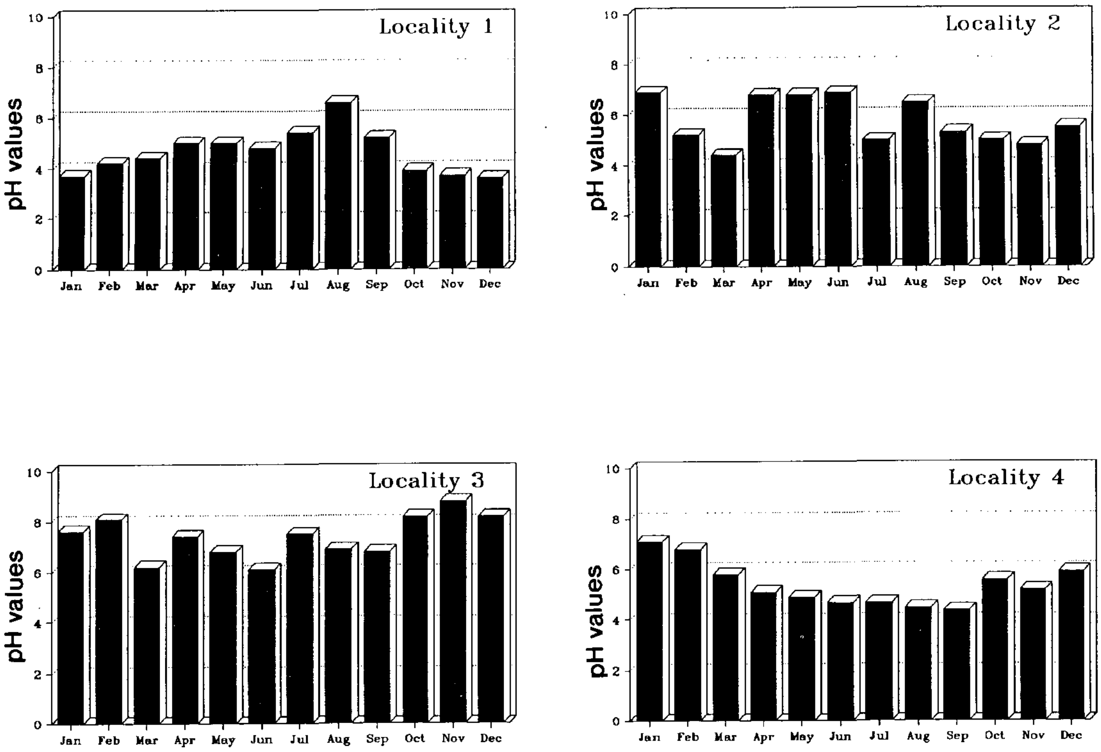

Figure 2

Monthly variations in pH during 1988 at the four localities on the Elsburgspruit (Localities 1-3) and one of its tributaries (Locality 4).

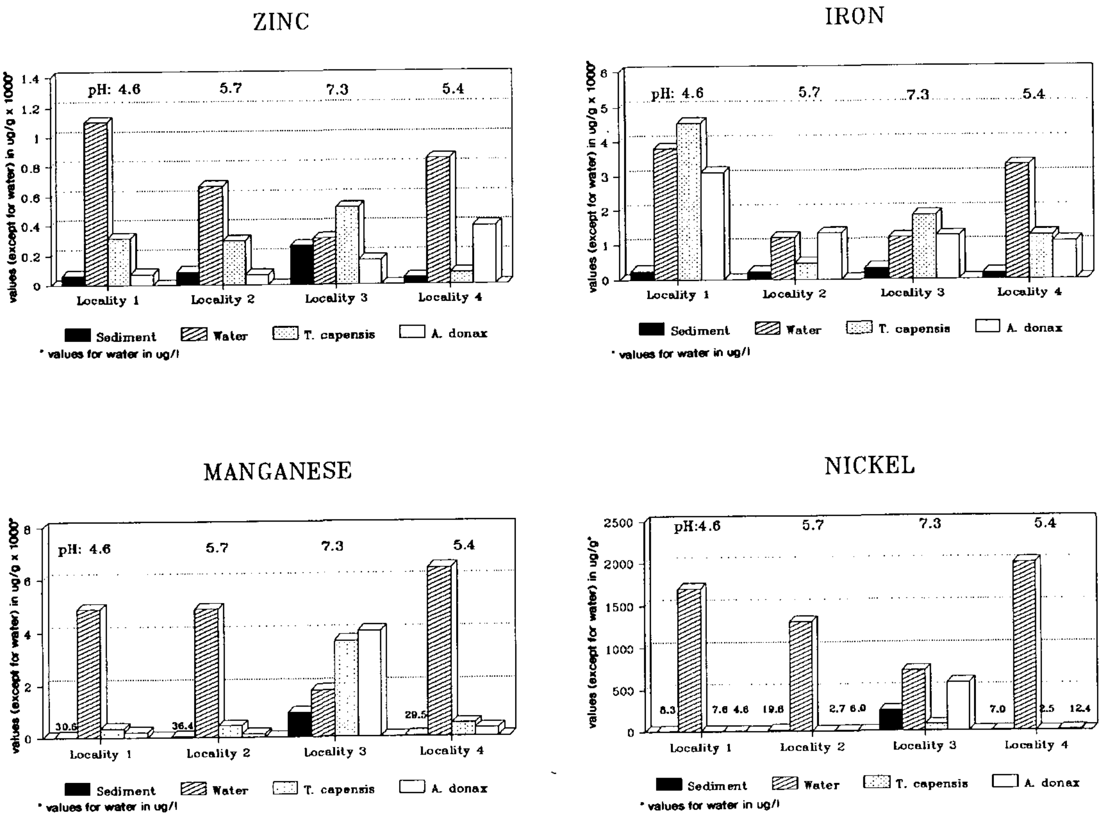

Figure 3

Heavy metal concentrations in the water, the sediments and the two aquatic macrophytes A. donax *and* T. capensis *at four localities on the Elsburgspruit and one of its tributaries during the summer of 1988.*

TABLE 2
HEAVY METAL CONCENTRATIONS IN THE WATER (μg/ℓ), THE SEDIMENTS (μg/g), *T. CAPENSIS* AND A. DONAX (μg/g) AT FOUR SELECTED LOCALITIES IN THE ELSBURGSPRUIT SYSTEM UNDER VARIOUS pH ENVIRONMENTAL CONDITIONS, WITH AN INDICATION OF CHANGES IN THE PERCENTAGE THEREOFF AT THE DIFFERENT SAMPLING LOCALITIES

	Zn Conc.	%	Mn Conc.	%	Ni Conc.	%	Fe Conc.	%
				Locality 1				
Water	1100	70,7	4900	89,4	1700	98,8	3800	32,5
Sediment	66,3	4,26	30,6	0,56	8,28	0,5	257	2,2
T. capensis	313,4	20,1	351,3	6,4	7,6	0,4	4534	38,8
A. donax	76,6	4,92	197,7	3,6	4,6	0,27	3106,6	26,6
				Locality 2				
Water	670	59,6	4900	89,2	1300	97,8	1200	37,3
Sediment	90,9	8,1	36,4	0,66	19,6	1,5	225,7	7,0
T. capensis	294,6	26,2	438,7	8,0	2,66	0,2	467	14,5
A. donax	68,6	6,1	120,3	2,2	6,02	0,5	1328,2	41,2
				Locality 3				
Water	310	20,9	1800	17,2	720	44	1200	26
Sediment	261,8	17,7	949	9,1	252	15,4	323,6	7
T. capensis	519,5	35	3666	35,1	81,9	5,0	1848	40
A. donax	391,2	26,4	4024	38,5	581,8	35,6	1247	27
				Locality 4				
Water	850	74,6	6400	88,3	2800	99,2	3300	56,8
Sediment	47,3	4,2	29,5	0,4	6,97	0,23	180,9	3,1
T. capensis	77,4	6,8	510,2	7,0	2,5	0,1	1254	21,6
A. donax	164,4	14,4	310,8	4,3	12,4	0,44	1079	18,6

severe mine effluent pollution when the pH of the water may [illegible] to as low as 4,4 (Table 1), but stream conditions there were also found to recover rapidly, with the pH exceeding 7, during which period this plant may well be able to accumulate some of the deposited Zn from the sediments. When the situation of Fe is compared with the other metals in the stream ecosystem at the different pH levels (Fig. 3), indications are that the uptake of this metal by the plants may be less affected by the pH of the water environment.

The results on the fall of the heavy metals in the water, sediments and plants obtained for Locality 4, where the pH was generally below 6 during most months of the year (Fig. 2), substantiated the findings recorded at Localities 1 and 2 regarding the water solubility and rate of deposit of the various heavy metals in the sediment under acidic environmental conditions.

Discussion

A number of research workers have shown that pH changes in the water could have a direct bearing on the solubility and/or precipitation of certain heavy metals in a freshwater aquatic environment (Shaw and Brown, 1974; Wood, 1974; Campbell and Stokes, 1985; Campbell and Tessier, 1985), affecting also the degree of toxicity of such metals (Whitley, 1968; Stumm and Morgan, 1970). The present study substantiates these findings (Table 2). In the case of *A. donax* and *T. capensis*, the concentrations of Zn, Mn and Ni in the sediments of the Elsburgspruit had a direct bearing on the increased uptake of these metals by the plants. This tendency coincided with an increase in the pH of the water, from mainly acidic to alkaline conditions. Mortimer (1985) suggested that differences in the uptake rate of metals by aquatic plants could depend upon factors such as the species of the plant and changes in seasonal growth rates, as well as the physical age of the plant and the metal ion involved in the absorption process. Our data showed that there were no clear-cut similarities in the absorption capacity of the metals between the two plants, with Zn and Fe being better accumulated under alkaline conditions by *T. capensis*, but with the reverse being the case for *A. donax*, where the absorption of Ni and Mn was more successful. Even though extremely high concentrations of Fe were recorded in the water environment at all four localities (Table 2), this metal appeared not to be detrimental to either *T. capensis* or *A. donax*, as both plants thrived under both acidic and alkaline conditions at the different localities. In contrast with Mn, Ni and Zn, Fe was more readily absorbed by both plants at lower pH levels (Locality 1, Fig. 3). With the exception of Locality 2, *T. capensis* was able to accumulate more Fe per mass in its tissues than was the case with *A. donax*.

From the results obtained it is evident that significant quantities of various metals are deposited in the stream sediments, particularly in the wetland areas from where they are taken up into the food chain. Estimates of the density and distribution of *A. donax* in the Elsburgspruit wetland region made by the authors showed this species to cover a surface area of approximately 43,5 ha, which at a peak summer standing may yield an estimated 3,75 kg dry mass plant material per m^2 area. This amounts to an estimated total summer yield of 1 630 t of *A.donax,* expressed us dry mass. Based on the heavy metal analysis, this tonnage of *A.donax* contained in its tissues an estimated 0,639 t of zinc, 6,561 t of manganese, 0,947 t of nickel and 2,033 t of iron. Should this plant be cropped regularly during the summer growing season, a substantial portion of these heavy metals present in the plants, and thus in the ecosystem, could effectively be removed. At present, *A.donax* is burned occasionally in the wetland regions of this stream during the dry winter months, with much of the ash and therefore the metals being returned directly into the stream ecosystem.

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