The role of humic substances in metal attenuation in leachates emanating from abandoned gold tailings footprints

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Abstract Mine leachates from gold tailings around Johannesburg, South Africa have been documented to contain a wide variety of trace elements. Natural wetlands occurring adjacent to most of the pollution sources have helped in attenuating these pollutants. In this work, we aimed at studying the role of humic substances in metal removal in these wetlands by assessing the isolated humic fractions (namely fulvic acids, humic acids and humin) and low molecular weight organic acids (LMWOAs). Metals held within the humic fractions were determined. The findings of the study revealed that a significant proportion of the metals were associated with fulvic and humic acids. This was higher than metal concentrations found to be associated with other phases.

Keywords mine leachates, gold tailings, humic substances, wetlands, low molecular weight organic acids

Introduction

Wetlands of the Witwatersrand Basin are mainly vegetated by reeds of the type Phragmites and Typha and their partially decomposed remains form the bulk of the organic matter (inset in Fig. 1). Wetland plants, including Phragmites australis, are tolerant of more extreme chemical conditions, such as elevated metals, nutrients, and organic carbon (Peverly *et al.* 1995). The high organic content in wetlands is mainly due to the decomposition of the plant material (Garnier-Sillam *et al.* 1999). Sulphate-reducing microorganisms (SRMs) play an important part in decomposing organic matter in wetlands. Huge expanses of wetlands, occurring mainly at inlets of dams, along streams and as buffers between tailings storage facilities (TSFs) and streams and dams (Tutu *et al.* 2008) form an important component of the catchment in the study area (Fig. 1).

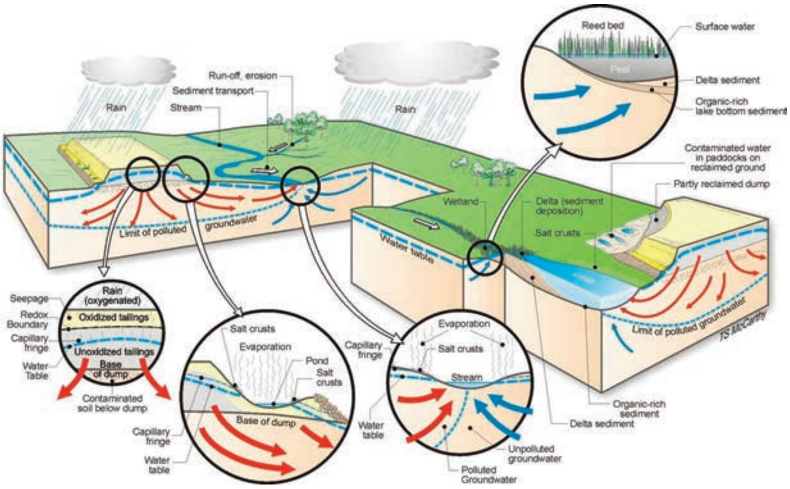

***Fig. 1** Generic model for water pollution and distribution pathways around gold mining activities (Tutu et al. 2008)*

Their role as sinks and mitigation zones for metals and other pollutants emanating from gold mining activities is fairly established (Tutu 2008; McCarthy and Venter 2006; Roychoudhury and Starke 2008). However, the role played by organic moieties in these important features has not been well researched. For instance, information regarding the most influential pools of these moieties that sequester metals is not available. To this end, this study has been pursued.

Materials and methods

The study site (Fig. 2) is located in the Central Goldfield (S26°13′ E028°07′). The area features a stream (the Natalspruit) draining through a wetland. The wetland is located between the stream and an abandoned tailings footprint. On the footprint used to be a mixed tailings dump (*i.e.* a sand dump and a slimes dump) which was reprocessed around 2004. Since then, it was abandoned with little or no proper management to contain pollutants emanating from it. The pond also acts as a holding sink for polluted water which gradually drains out into the wetland and stream. Sediment samples were collected from four sites on the wetland using a hand-held auger (to depths of 90 cm).

Sediment samples were collected following recommended methods in literature (Hogan and Walbridge 2007). Recommended extraction protocols for humic substances in sediment samples were followed (Swift 1996) prior to determination of fulvic acids (FAs), humic acids (HAs), humin and low molecular weight organic acids (LMWOAs). Concentrations of carbon, nitrogen, hydrogen and sulphur were determined using the CHNS analyser (LECO) while LMWOAs were analysed using an ion chromatograph (Metrohm). The sediments were also digested in acid solutions in a microwave prior to metal determination. Metals in sediments and extracts of FAs and HAs were determined using inductively coupled plasma optical emission spectroscopy (ICP-OES).

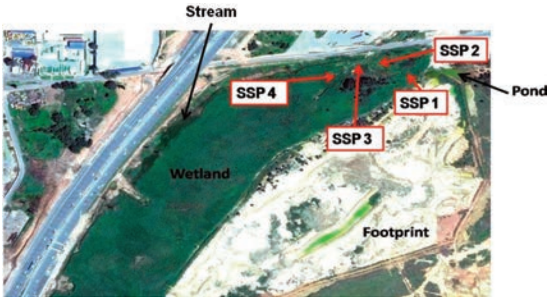

***Fig. 2** Aerial view of the study site*

Results and Discussion

The results for the average elemental concentrations in various phases of all sediment samples are presented in Table 1. The % values have been calculated based on total elemental concentrations in sediments.

The results show that FAs complex around 55 % of the metals while HAs complex around 30 % of the metals. FAs complex more metals than HAs due to their lower molecular weight, higher oxygen contents, number of functional group and exchange capacity (Yamamoto *et al.* 2010; Fujisawa *et al.* 2012). The extractable organic matter (FAs and HAs combined) complexed >80 % of metal ions, showing the importance of this phase in attenuating metals.

The formation and distribution of extractable organic matter is important and some of the salient features related to this are presented and discussed briefly in the following section of the results.

The results for C/N ratios in the sediments are presented in Fig. 3. The trend shows a decrease in this ratio with depth in all the sample sites.

The C/N ratio is an indication of organic matter decomposition and stabilization. Most wetland plants typically have a C/N ratio of >50 (Nair *et al.* 2001). As the plant matter decays in the soil, CO_2 is evolved while N is retained. This results in a decreasing C/N ratio and the new lower C/N ratios suggest an increasing stabilization of the HSs with soil depth.

The results for the internal oxidation rates (ω) in the profiles are presented in Fig. 4.

Element distribution	Average concentrations of selected elements / mg kg^{-1}																									
	Al	%	Bi	%	Ca	%	Co	%	Cr	%	Cu	%	Fe	%	Mn	%	Ni	%	Pb	%	S	%	Si	%	U	%	Zn	%
FAs	536.2	31	41.87	60	454.0	49	6.68	50	7.48	55	98.2	57	5484	55	91.73	53	42.6	47	8.07	42	1.22	0.3	46.39	neg	33.80	56	116.4	49
HAs	358.2	20	18.24	26	320.2	35	4.80	36	4.68	34	50.8	30	3191	32	64.26	37	28.5	32	6.13	32	1.81	0.5	23.93	neg	17.59	29	68.15	29
HSO and other phases	865.1	49	9.98	14	149.6	16	1.82	14	1.53	11	22.2	13	1239	13	16.81	10	19.2	21	4.98	26	367.9	99	3E+05	100	9.36	15	52.25	22
Soils	1760		69.09		923.8		13.3		13.7		171.2		9914		172.8		90.3		19.18		370.9		3E+05		60.75		236.8	

FAs – fulvic acids; HAs – humic acids; HSO – humin, silica and other phases; Soils – results for total concentrations after digestion

Table 1 *Average concentrations of selected elements in extractable OM and pseudo-total concentrations for selected elements in sediments*

The parameter ω (the degree of internal oxidation) is closely related to oxidation and degradation reactions. It is supposed that the degradation process involves the loss of CH_3 groups and partial oxidation, thus decreasing the number and length of aliphatic chains in the humic substance. High positive values of ω indicate a high degree of internal oxidation (Dębska 1997). According to literature, the atomic ratios O/C, O/H and ω indicate the degree of maturity of HSs (Gonet *et al.* 2010). From Fig. 4, ω showed that maturity of HSs increased with sediment depth.

The maturity of the HSs can also be tracked using LMWOAs. The results for these are presented in Tables 2 and 3. Thus, the low molecular weight constituents of the extractable OM presented in Table 1 can be characterized. The trend shows a general decrease in the concentration of LMWOAs with depth. However, concentrations of succinic and citric acids increased with depth, most likely as a result of their increasing carbon content (*i.e.* more humification).

The extent of aromaticity or aliphaticity been classified in Fig. 5. The results pointed to more samples having less aromaticity. This is consistent with the trend observed in Table 1 and could suggest that more metals are held in the less aromatic phases of HSs, namely fulvic acids. Thus, these acids exert a greater influence in metal sequestration.

Conclusion

The results have pointed to the superior role that humic substances, particularly fulvic acids play in metal sequestration in wetlands. Characterisation of the HSs revealed interesting trends that relate to their evolution and resultant properties and that can be used to pre-

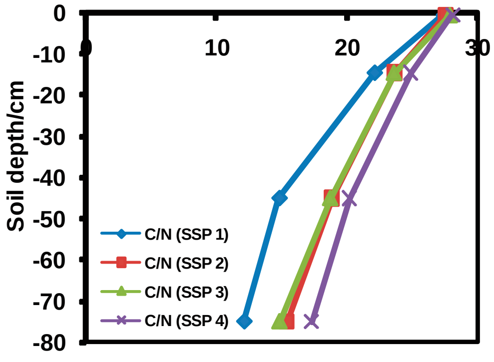

Fig. 3 *Variation of C/N ratios with sediment profiles*

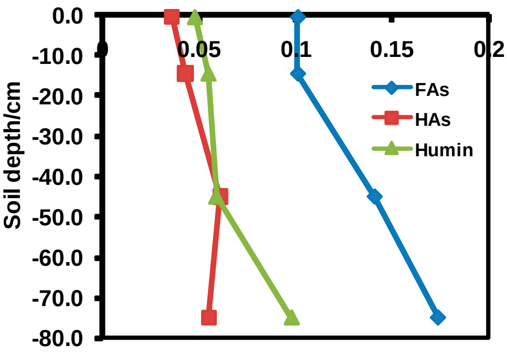

Fig. 4 *Variation of ω with sediment depth for Humic Substances in SSP 3.*

Soil depth	Concentration of organic acids at SSP 3			
	Acetic	Oxalic	Malonic	Citric
(cm)	(mg kg^{-1} of dry soil)			
0	46.4	2.6	nd	nd
15	94.2	6.1	8.6	16.8
45	64.8	66.4	26.3	34.0
75	20.6	25.7	32.1	80.4

Table 2 *Variation of concentration of LMWOAs at SSP 3*

Soil depth	Concentration of organic acids at SSP 4			
	Acetic	Succunic	Lactic	Maleic
(cm)	(mg kg^{-1} of dry soil)			
0	75.4	nd	24.7	nd
15	150.7	15.1	65.3	44.5
45	105.3	24.8	28.4	16.2
75	45.6	60.5	9.1	3.6

Table 3 *Variation of concentration of LMWOAs at SSP 4*

dict the metals likely to be distributed with them. For instance, LMWOAs were determined and these interact differently with various metals. This information is important for future studies that will focus on modelling the role of HSs in metal attenuation.

Acknowledgements

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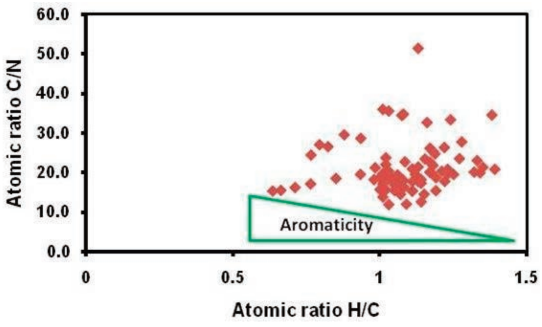

Fig. 5 *Atomic ratio C/N versus atomic ratio H/C for all the HSs from the study area*