Biogeochemical Cycle of Mercury in Wetlands Ecosystem Affected by Gold Mining in a Semi-Arid Area

Ewa Cukrowska[1], Julien Lusilao-Makiese[1], Hlanganani Tutu[1], Luke Chimuka[1] and Isabel Weiersbye[2]

1. Molecular Sciences Institute, University of the Witwatersrand, South Africa,

2. School of Animal, Plants and Environmental Science, University of the Witwatersrand, South Africa

ABSTRACT

Wetlands are essential habitats in the environment since they fulfill a variety of ecological functions and support rich biodiversity. One major characteristic of wetlands is their ability to act as chemical sinks. There have been biogeochemical models developed for wetlands in Europe and North America but these systems differ from those found in South Africa, where most wetlands are river-fed and therefore undergo seasonal saturations, with periods of flooding in summer followed by drying during winter. High evapotranspiration rates also concentrate pollutants to very high levels. The nature, level and impact of mercury in the environment have not been extensively studied in South Africa, particularly in areas that have been significantly affected by gold mining activities.

Aims of this research were to determine the biogeochemical cycling of mercury in permanent and seasonal aquatic ecosystems (rivers, dams, natural and manmade wetlands) that have been heavily affected by mining activities (acid rock drainage) in semi-arid areas with extreme seasonal changes.

Research methodology included seasonal sampling, sequential extractions, determination of mercury speciation and modeling.

Results show that natural wetlands in South Africa have a greater capacity to trap mercury than manmade wetlands. Most leachable mercury exists in oxidizable form followed by unleachable residue. Organomercury species are produced in anaerobic deeper levels where organic carbon and reduced sulfur content is high. Evapotranspiration and surface precipitation during the dry season exhibited a strong seasonal relationship to acidity and redox conditions.

These research results are supported by a biogeochemical model may be used for identification and implementation of potential mercury remediation measures.

Keywords: mercury, wetlands, biogeochemical cycling, sequential extraction, bioavailability

INTRODUCTION

Changes in chemical and physical properties in the lithosphere can influence the release of heavy metals from mine tailings into the ecosystem and increase the likelihood of uptake by living organisms (Kim et al. 2001). These changes include acid rock drainage (ARD) (Durkin and Hermann 1994; Wildeman et al. 1991, Han et al., 2003).

Understanding the processes that influence the distribution, concentration, and bioavailability of potentially toxic metals, such as arsenic (As), cadmium (Cd), lead (Pb), mercury (Hg), and selenium (Se) is critical for successful management of chronically affected ecosystems. Such understanding can be used to identify and target pathways that have the greatest immediate and long-term impact on the environment. Such knowledge provides the scientific foundation for making decisions, developing strategy, and assessing remediation alternatives by governmental institutions as well as mining companies or local agencies charged with minimizing the environmental and health impacts of these toxic elements.

Gold mining has played a significant role in the socioeconomic life of South Africa (SA) for over one hundred years. Unfortunately, the wastes from this activity have been identified as a significant source of Hg and other heavy metals contamination of the environment. Heavy metals associated with mining are of particular interest for a number of reasons. They exhibit a tendency to accumulate in sediments and soils and persist as they are not biodegradable. Metals can be derived from the erosion of source rocks, or can accumulate following application of metal-enriched water as well as via deposition of atmospheric dust and fluvial reworking mined sediments (Getaneh W., 2006).

Acid rock drainage (ARD) is considered one of the mining industry's toughest challenges. Most water remediation techniques are time-consuming and costly, and ARD can continue in perpetuity, long after the mining activities cease. Constructed wetlands (CW) have been considered a possible solution to the long-term remediation of ARD. Wetlands successfully support improved water quality, providing a continuous, low-cost and effective solution to the ARD problem in some settings (Fennessy & Mitsch 1986; Kadlec 1985; Perry & Kleinman 1991; Snyder & Aharrah 1985). .

Wetlands functions that aid in the amelioration of ARD .include adsorption and ion exchange, bioaccumulation, biotic and abiotic oxidation, sedimentation, neutralization, reduction, and dissolution of carbonate minerals (Perry & Kleinmann 1991).

Processes within natural wetlands (NW) have been found to remediate contaminants found in ARD: imitation of these processes can work similarly in constructed wetlands. Wetlands have organic-rich substrates which capture/exchange dissolved metals (Wildeman et al. 1991). Wetland sediments are generally anaerobic below a thin oxidized surface layer and contain organic carbon needed for microbial growth (Gambrell & Patrick 1978). The anoxic zone of the sediments provide conditions which favor microbial and chemical reducing processes (Fenessy & Mitsch 1989). Soluble metals are converted to insoluble forms by the anoxic conditions of wetland sediments. Plants, microflora and bacteria also generate microenvironments that assist in oxidation and reduction processes (Wildeman et al. 1991; Mitsch & Gosselink 1986).

The toxicity of mercury depends strongly on the chemical form of the element (its speciation) but also on water environmental conditions like pH, redox potential, and the presence of dissolved and suspended carbon. Also dramatic differences may occur through time (high seasonality) and space. This is very important when establishing links between mercury emissions and levels in biota (Harris et al. 2005). The reactions and interactions may also vary with depth in wetland zones. For

example, the biogeochemical processes of complexation, adsorption, and precipitation may release or sequester certain metal species due to varying levels of biological activity (Baird and Cann 2012). Mercury behaves differently from other metals, forming volatile elemental mercury and even more volatile and toxic organomercury species under the anaerobic conditions which exist in deeper wetland sediments (Harris et al. 2005).

The nature, extent and impact of mercury in the environment have not been extensively studied in South Africa, particularly in areas that have been significantly affected by mining activities. To date, no analysis of seasonal changes in mercury bio-accessibility has been reported. This study addresses that gap, providing a detailed assessment and evaluation of the impact of mercury in Gauteng area of SA, very densely populated area with associated intensive water usage. The results would be useful in considering various remediation strategies.

Sequential extraction procedures (SEPs)

The toxicity, bioavailability and mobility of metals are related to their species (Quevauviller et al, 1994). However, the determination of chemical species is difficult and sometimes impossible. Therefore, the use of sequential extraction procedures for environmental studies provides an important tool for the determination of the different chemical forms or ways of binding between trace metals and sediment components (Rauret et al, 1999).

Sequential extraction procedures (SEPs) are employed to assess operationally defined metal fractions, which can be related to chemical speciation, as well as compound mobility, bioavailability or ecotoxicity. It is generally accepted that the ecological effects of metals (e.g., their transport, bioavailability, and ecotoxicology) are related to such mobile fractions rather than to the total metal concentration (Cordos et al, 2003).

Chemical fractionation schemes for partitioning trace metals in soils and sediments have been used extensively (Tessier, A., et al, 1979; Rauret G., et al, 1999; Han, F. X., et al, 2003; Ianni, C,et al, 2001; Navas, A., Lindhorfer, H. 2003; Hlavay, J., 2004. The European Community Bureau of Reference, the BCR method, standardizes SEPs (Ure et al. 1993) in order to: 1) minimize errors in the treatment and analysis of samples, 2) identify the most appropriate analytical procedure and 3) to supply reference materials for comparisons of the results. This standardized method appears to be more operationally effective than others previously proposed. (Sheppard and Stephenson, 1997).

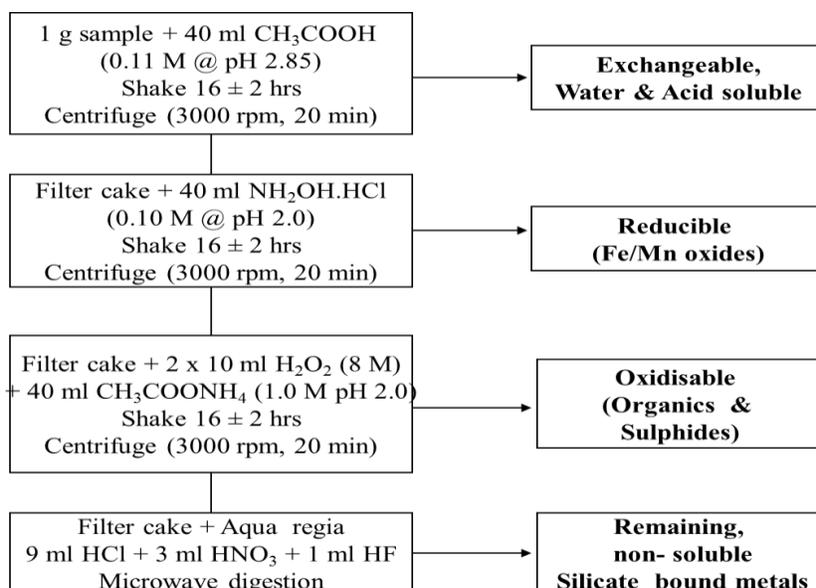### METHODOLOGY

Sampling sites and sample pre-treatment

Samples were collected from a deposit of mine tailings (West Wits (WW)) in the Witwatersrand basin of South Africa (Figure 1). The sampling included natural and constructed wetlands, tailings and the soil next to the tailings. Redox potential, pH, temperature and conductivity were measured during sample collection. Samples were freeze dried and stored prior to analysis.

a.

b.
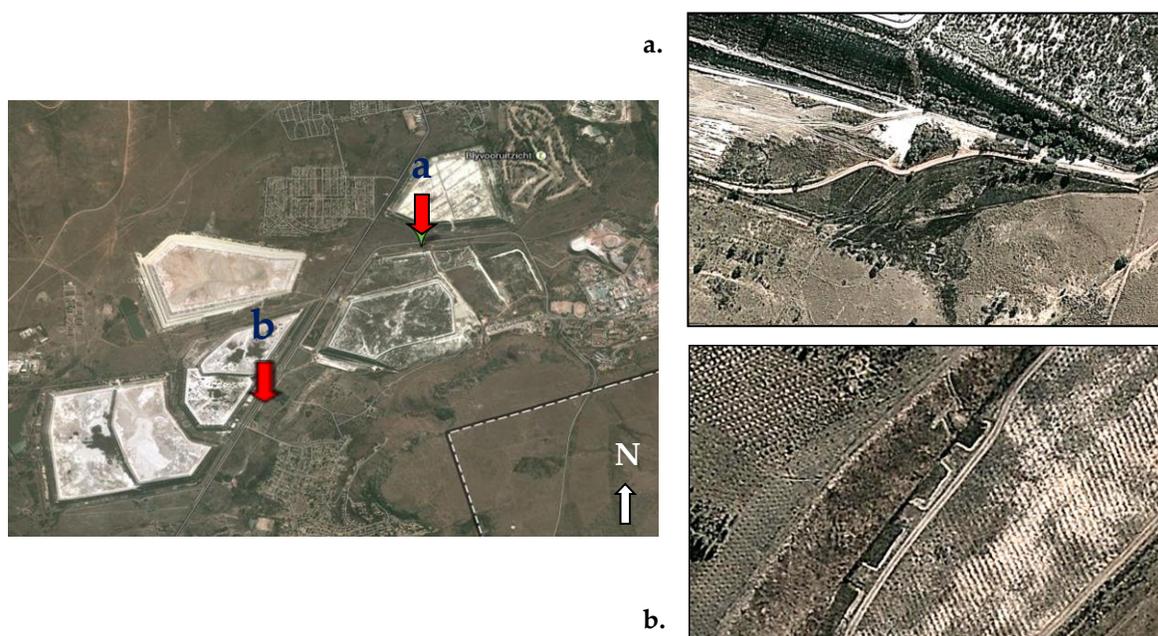
Figure 1 West Wits sampling site. a. natural wetlands (NW), b. constructed wetlands (CW)

Three stage BCR sequential extraction (BCR SE)

The BCR sequential extraction scheme with reagents and extracted fractions is shown on Figure 2.

1 g sample + 40 ml CH_3COOH
(0.11 M @ pH 2.85)
Shake 16 ± 2 hrs
Centrifuge (3000 rpm, 20 min)
→ **Exchangeable, Water & Acid soluble**

Filter cake + 40 ml $NH_2OH.HCl$
(0.10 M @ pH 2.0)
Shake 16 ± 2 hrs
Centrifuge (3000 rpm, 20 min)
→ **Reducible (Fe/Mn oxides)**

Filter cake + 2 x 10 ml H_2O_2 (8 M)
+ 40 ml CH_3COONH_4 (1.0 M pH 2.0)
Shake 16 ± 2 hrs
Centrifuge (3000 rpm, 20 min)
→ **Oxidisable (Organics & Sulphides)**

Filter cake + Aqua regia
9 ml HCl + 3 ml HNO_3 + 1 ml HF
Microwave digestion
→ **Remaining, non- soluble Silicate bound metals**

Figure 2 European Community Bureau of Reference (BCR) SE

4

Reagents and stock solutions

The following extraction solutions were prepared: (a) 0.11 M CH_3COOH solution adjusted to a pH of 2.0 by super pure grade HNO_3; (b) 0.10 M $NH_2OH.HCl$ solution adjusted to a pH of 2 with ultra-pure grade HNO_3; (c) 30 % H_2O_2 and 1.0 M CH_3COONH_4 adjusted to pH 2 with HNO_3 (d) ($HCl+HNO_3+HF$). Aqueous solutions of 3 % HCl (v/v) and 1.1 % $SnCl_2.2H_2O$ (in 3 % HCl v/v) were also prepared for the determination of Hg. Reagents used for Hg analysis were all certified heavy metals free (i.e. 99.999% pure).

Instrumentation

The determinations of metals in the extracts were performed by ICP – OES (Spectro, Germany) whereas Hg was analysed using an automated Hydride Generation Flow Injection Atomic Absorption Spectrometer (HG-FI-AAS, Perkin Elmer).

RESULTS AND DISCUSSION

The pH, Eh and organic carbon profiles recorded in wetlands sediments during the wet season are shown in Figure 3.
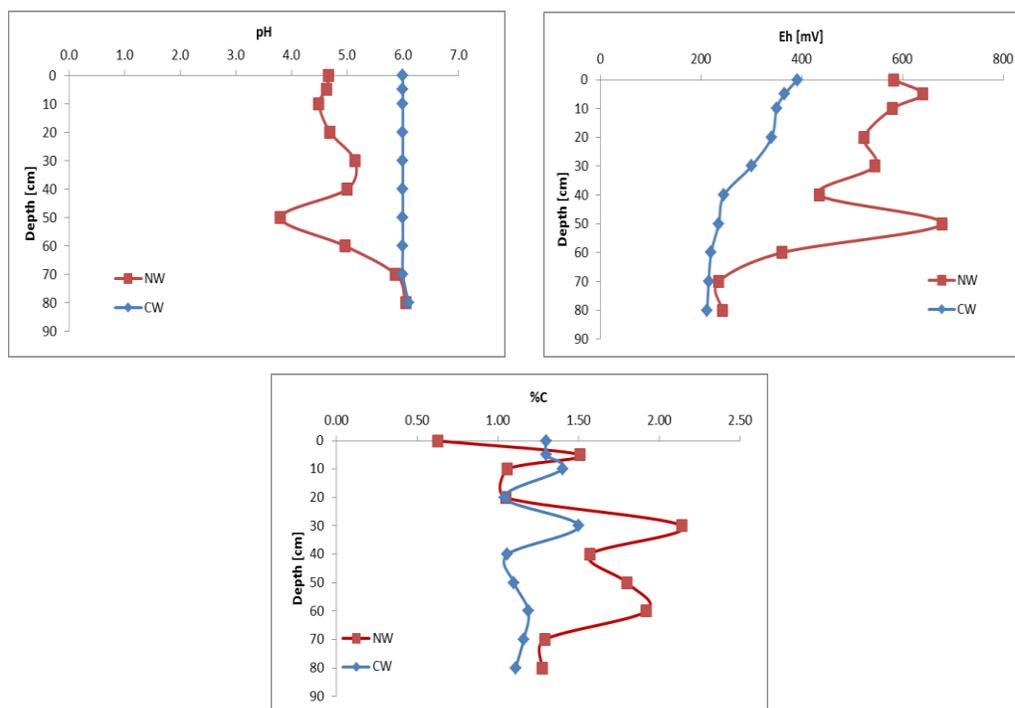

Figure 3 Sediment profiles of pH, Eh and carbon in NW and CW during wet season.

The CW profile was much more uniform to a depth of 70 cm, with a higher pH and lower redox potential and organic carbon content than the NW profile. , exhibiting almost the same levels in the lower-most sediments in both NW and CW. This might be attributed to the ageing process and to

the accumulation of organic matter. The CW is younger with sediments being removed operationally every few (3-4) years.

The total concentrations of Hg, iron (Fe) and sulfur (S), among others, were determined in wetlands, the tailings facility (TSF) and soil near the TSF (Table 1). The results of BCR sequential extraction for the same elements are presented in Figure 4.

Table 1 Total Hg, Fe and S in the wetlands and tailings

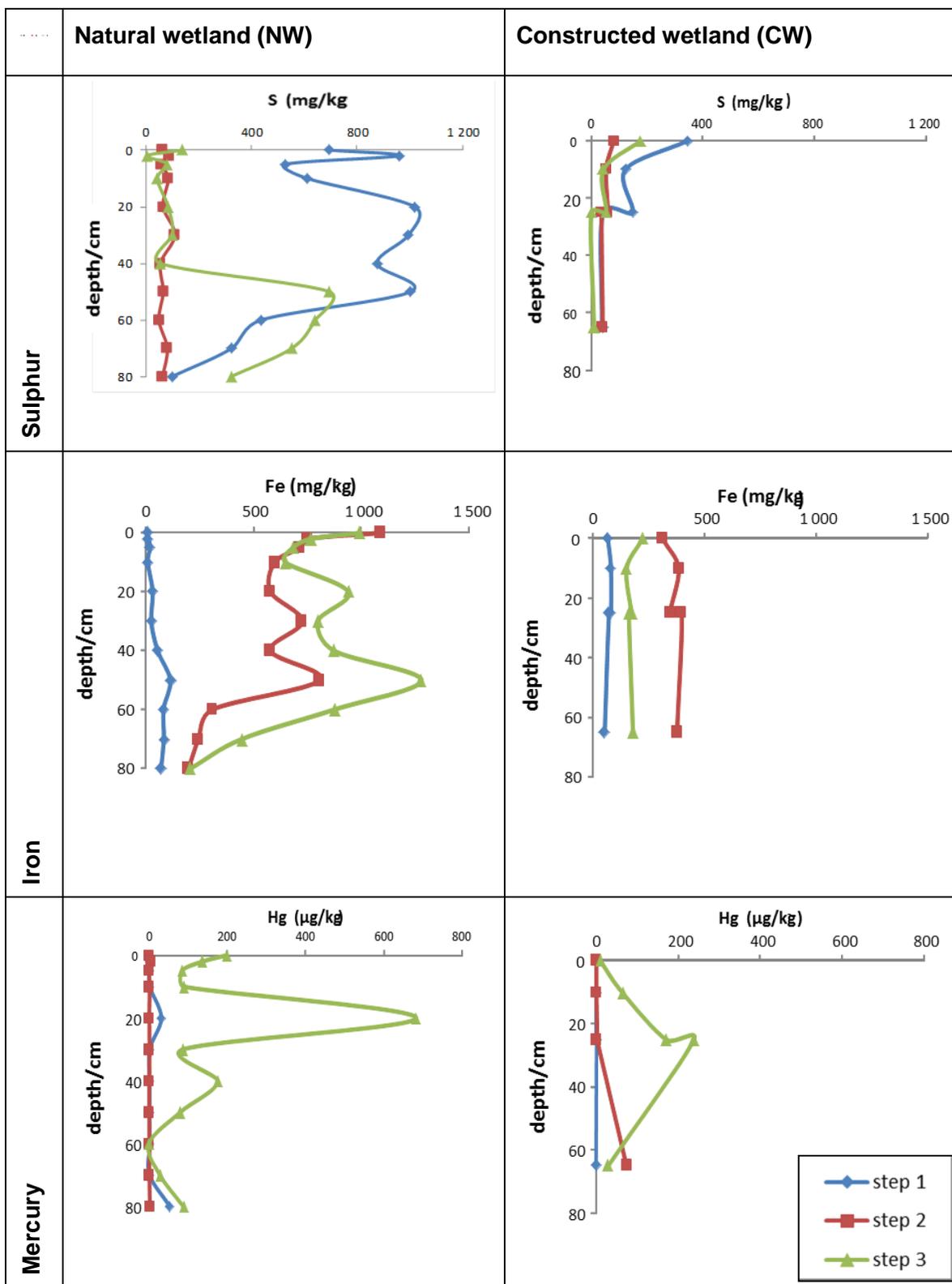| Sample ID	Depth (cm)	Hg (µg Kg^{-1})	Fe (mg Kg^{-1})	S (mg Kg^{-1})
Soil near	0	1162	42459	1157
TSF	10	1196	34783	914
	20	987	38386	795
	30	1450	38460	692
	40	1171	38485	572
	50	1390	43693	544
	60	1198	41386	320
Tailings	0	1670	35205	1575
	10	1619	36551	1788
	20	1614	36712	1711
	30	1774	37598	1847
	40	1893	37258	1930
NW (WW)	0	312	33301	1070
	5	195	32247	1049
	10	207	27787	857
	20	803	34597	1298
	30	202	35042	1648
	40	294	31890	1321
	50	184	61115	2603
	60	207	26228	2112
	70	106	36164	1999
	80	237	47232	1421
CW (WW)	0	39	28571	1176
	20	111	41121	589
	40	234	39796	784
	60	315	61310	409
	80	194	51476	226

Figure 4 BCR sequential extraction (3 steps) for S, Fe and Hg in NW and CW sediments.

Mercury speciation in both wetlands shows the largest fraction leached in step 3 – oxidizable fraction; this situation is especially evident in the middle sediment levels. This is strongly correlated to sulphur and organic carbon for NWs. The relative quantities leached suggest the importance of ageing (maturity) in the case of CWs.

Seasonal distribution of mercury in wetlands

Distribution patterns for mercury were very similar in both wet and dry seasons. However, the total mercury (Hg^{TOT}) concentration in sediment was much higher in the latter (Figure 5). Also, in the dry season, pH was higher and redox potential was lower in water above the sediments. The equilibrium speciation modeling of Hg in wetlands waters was plotted on an Eh-pH diagram (Lewis and Plant, 2005) (Figure 6).
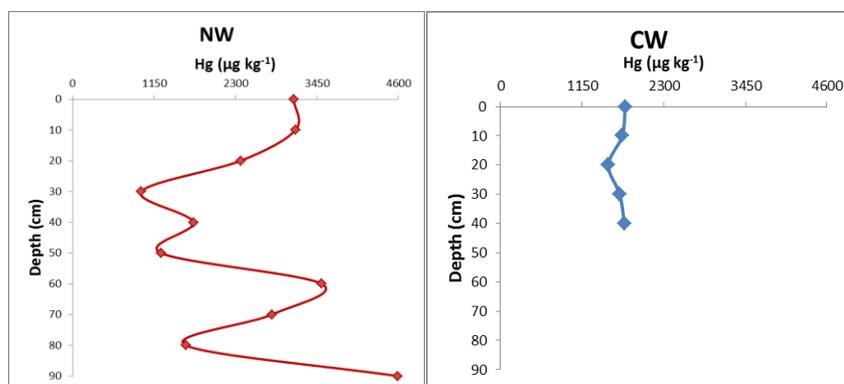

Figure 5 Comparison of Hg^{TOT} in constructed (CW) and natural (NW) wetland sediment in the dry season.
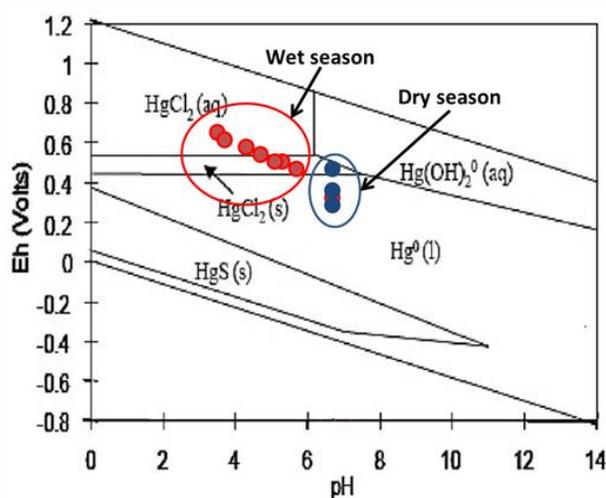

Figure 6 Eh-pH diagram showing seasonal mercury speciation in wetlands

The results showed that the predominant form of Hg in wet season waters is soluble $HgCl_2(aq)$ whereas the highly insoluble and volatile Hg^0 predominated in the dry season. This explains the elevated dissolved mercury concentration during the in wet season and its decrease in the corresponding sediment samples. This might be due to the acidification of the water during wet

8

season, which can occur when oxidation by products are flushed from mine tailings.. The lowering of the water pH during the rainy season is known to favour the solubilisation of heavy metals such as Hg, thus increasing Hg^{TOT}. There is, therefore a probable Hg remobilisation from the lower sediment horizons with the water's acidification during wet season and an eventual atmospheric release and/or re-precipitation during winter which explains its overall decrease in watersheds. The concentration of sulfate and chloride were also higher during the wet season, explaining the higher electrical conductivity values measured in these sampling time.

CONCLUSIONS

This study compares the performance of natural and manmade wetlands in trapping Hg as well the seasonal Hg distribution in both ecosystems. In general, natural wetlands performed better as "Hg sinks" compare to constructed ones. The lack of biodiversity in planting from the CWs and their younger ages could explain their lower effectiveness in Hg trapping. The constructed wetlands, therefore, require relatively more maturity and treatment prior to a meaningful assessment of their capacity retaining pollutants. Seasonal changes in Hg load in wetlands waters confirm that Hg is remobilized during the wet season and precipitates into sediment and/or evaporates into the atmosphere during the dry season. Selective extraction procedures revealed the predominance of in-soluble Hg compounds, especially at lower redox potential inorganic-rich sediments typical of wetlands. The fractionation of mercury in the BCR selective extraction depends strongly on the sample matrix as well as on the Hg concentration.

ACKNOWLEDGEMENTS

REFERENCES

Baird, C. and Cann, M. (2012). Environmental chemistry. W.H. Freeman, New York

Cordos E, Rautiu R, Roman C, Ponta M, Frentiu T, Sarkany A, Fodorpataki L, Macalik K, McCormick C, Weiss (2003). Characterization of the rivers system in the mining and industrial area of Baia Mare, Romania. The European Journal of Mineral Processing and Environmental Protection, 3 (3): 324-335.

Durkin, T.V. and J.G. Herrmann (1994). Focusing on the Problem of Mining Wastes: An Introduction to Acid Mine Drainage. IN Managing Environmental Problems at Inactive and Abandoned Mine Sites. US EPA Seminar Publication.

Fennessy, S. and W.J. Mitsch. (1989). Design and use of wetlands for renovation of drainage from coal mines. IN Ecological Engineering: an introduction to ecotechnology. W.J. Mitsch and S.E. Jorgensen (Ed.),. John Wiley & Sons, New York, NY, pp. 232-252

Gambrell, R.P. and W.H. Patrick Jr.. (1978) Chemical and microbiological properties of anaerobic soils and sediments. IN Plant Life in Anaerobic Environments. D.D. Hook and R.M.M. Crawford (Ed.). Ann Arbor, MI.

Getaneh W., Alemayehu T. (2006). Metal contamination of the environment by placer and primary gold mining in the Adola region of southern Ethiopia, Environ. Geol., 50(3), 339–352

Han, F. X., Banin, A., Kingery, W. L., Triplett, G. B., Zhou, L. X., Zheng, S. J., Ding, W. X. (2003) Advances in Environ. Research, vol. 8, pp. 113.

Harris, R., Krabbenhoft, D.P. Mason, R., Murray, M.W. Reash, R. , Saltman, T.ed. (2007). Ecosystem Responses to Mercury Contamination. CRC Press, Taylor & Fransis, New York.

Hlavay, J., Prohaska, T., Weisz, M., Wenzel, W., Stingeder, G.J., (2004) Determination of trace elements bound to soil and sediment fractions (IUPAC Technical Report). Pure Appl. Chem, , vol. 76, no. 2 pp. 415-442.

Ianni, C., Ruggieri, N., Rivaro, P. and Frache, R.: (2001) 'Evaluation and comparison of two selective extraction procedures for heavy metal speciation in sediments', Anal. Sci. 17, 1273–1278.

Kadlec, R.H. (1985). Aging phenomena in wastewater wetlands. IN Ecological Considerations in Wetlands Treatment of Municipal Waters. E.R. Kaynor, S. Pelczarski, and J. Benforado (Ed.). pp. 338-347. Van Nostrand Reinhold, NY.

Kim K.-K., Kim K.-W., Kim J.-Y., Kim I.S., Cheong Y.-W., Min J.-S., (2001) Characteristics of tailings from the closed metal mines as potential contamination source in South Korea, Environ. Geol., 41(3–4), 358–364

Lewis, R.A. and Plant, J.A. (2005) Mercury in the environment with reference to mining operations, Imperial College (ed), London.

Mitsch, W.J. and J.G. Gosselink. (1986). Wetlands. Van Nostrand Reinhold, NY.

Navas, A., Lindhorfer, H. 2003. Geochemical speciation of heavy metals in semiarid soils of the central Ebro Valley, Spain. Environ International 29 (1), 61-68.

Perry, A. and R.L.P. Kleinmann. (1991). The use of constructed wetlands in the treatment of acid mine drainage. Natural Resources Forum vol. 5, pp. 178-184.

Quevauviller, P., Rauret, G., Muntau, H., Ure, A. M., Rubio, R., Lopez-Sanchez, J. F., Fiedler, H. D., Griepink, B., (1994) Evaluation of a sequential extraction procedure for the extractable trace metal contents in sediments. Fresenius J. Anal. Chem., vol., 349, pp. 808-814.

Rauret, G López-Sánchez, J.-F. Sahuquillo, A. Barahona,E. Lachica,M. Ure,A.M. Davidson,C.M. Gomez,A. Lück,D. Bacon,J. Yli-Halla,M. Muntau H. and Quevauviller.,P. (2000) Application of a modified BCR sequential extraction (three-step) procedure for the determination of extractable trace metal contents in a sewage sludge amended soil reference material (CRM 483), complemented by a three-year stability study of acetic acid and EDTA extractable metal content J. Environ. Monit., vol. 2, pp. 228-233.

Sheppard, M.I., Stephenson, M., (1997). Critical Evaluation of Selective Extraction Methods for Soils and Sediments, Contaminated Soils. INRA (Les Colleagues, 85), Paris

Snyder, C,D. and E.C. Aharrah. (1985). The Typha community: a positive influence on mine drainage and mine restoration. IN Wetlands and Water Management on Mined Lands: Proc. of a Conf. 23-24 Oct. 1985 The Pennsylvania State University. pp. 187-188. University Park, PA.

Tessier,A.,Campbell,P.G.C., Bisson,M., (1979). Sequential extraction for the speciation of particulate trace metals. Anal. Chem. Vol. 51,pp. 844 – 851

Ure, A.M., Quevauviller, Ph., Muntau, H., Griepink, B., (1993). Speciation of heavy metal in soils and sediments. An account of the improvement and harmonisation of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities. Int. J. Environ. Anal. Chem. Vol. 51, pp. 135 - 151.

Wildeman, T., J. Gusek, J. Dietz and S. Morea. (1991). Handbook for Constructed Wetlands Receiving Acid Mine Drainage. US EPA, Cincinnati.