Mercury speciation in gold-mining environments – determination and development of predictive models for transformation, transport, immobilisation and retardation

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Abstract Mercury speciation was determined in areas impacted by gold mining. Both inorganic and methylmercury were detected at high concentrations in all watersheds where mining occurred. Migration of mercury from pollution sources due to seasonal influences was determined. Enhancement of mercury methylation occurred in deeper sediments at the lowest redox potential, higher pH, carbon and sulphur and enrichment of inorganic mercury.

Key Words Mercury, speciation, gold mining, tailings, models

Introduction

The Witwatersrand Basin in South Africa (SA) is the biggest gold mining region in the world. Mercury, which occurs in gold-bearing ores, was also used for gold recoveries till 1915 and is still used in illegal artisanal mining. Consequences of these activities are the release of Hg to the environment. It was reported that the Hg emissions in SA are second only to China (Paycna et al. 2005). This is due mainly to coal combustion and gold mining.

Risk assessment of Hg pollution in South Africa is based on total element concentrations. Unfortunately, the determination of total Hg is not sufficient to understand its transport and fate in the environment. The purpose of this study was to carry out a quantitative assessment of mercury pollution in areas of four watersheds suspected to have elevated concentrations of total mercury due to a long history of gold mining activities. It is necessary to evaluate Hg speciation, and characterize potential sources, pathways, receptors and sinks in order to implement mitigation strategies and minimize environmental risk.

This paper describes Hg speciation in selected water, soil and sediment samples from Val River watershed during two sampling campaigns (dry and rainy season). Mining operations in the region commenced in the late 19th century, and used amalgamation techniques. Sampling sites were identified from historical aerial photographs (post-1948), showing extensive shallow mining of the Black Reef, and large spillages from old mine tailings facilities. Deep-level mining is being undertaken now alongside reprocessing of old tailings to recover gold left-over by previous extraction methods. However, environmental degradation from mining operations is widespread in the region, and there are anecdotal reports of artisanal mining using Hg amalgamation.

Methods

A sub-set of the data from two sampling campaigns (the late dry season – September 2008, and late wet season – February 2009) is presented to illustrate Hg trends in different substrata. Water, soil and sediment samples were collected from adjacent to gold tailings facilities, from a licensed pollution control dam (which receives dirty water discharges from tailings facilities and recycles these back to the metallurgical process), and from a stream known to have received spillages (pre-1940’s) from tailings facilities and drainage from other sources (including tailings, industries, graveyards and artisinal mining activities; Fig.1, Table 1). Soil pits were excavated to a maximum depth of 3 metres, and all field parameters measured in situ. Water samples were collected in acid-washed polypropylene containers, and sediment samples stored in double plastic bags in the dark within cold boxes. Samples were prepared using the methodology of Rodriguez Martin-Doimeadios et al. (2003), and Hg species, inorganic Hg (IHg) and methylmercury (MHg), were determined using GC-ICP MS. Analyses were validated using a certified reference material (IAEA405 estuarine sediment) certified at 810 ± 140 ng g^{-1} IHg and 5.49 ± 0.53 ng g^{-1} MHg.

Figure 1 Sampling area

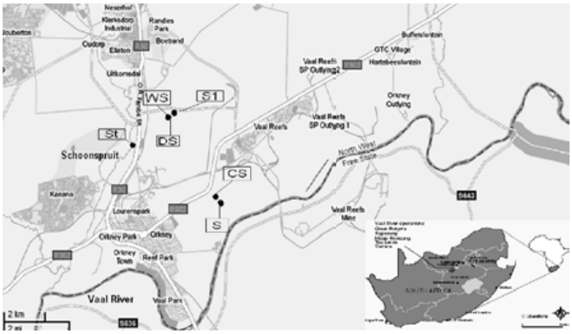

Table 1 Description of sediment samples

Sample ID	Description
DS	Surface dry soils adjacent to the tailings facility
WS	Surface wet soils adjacent to the tailings facility
S1, 2 and 3	Soil profiles adjacent to the tailings facility
SS	Surface sediment within the pollution control dam
CS	Composite sediment from within the pollution control dam
CS	Sediment profiles collected from within the pollution control dam
S	Sediment below the pollution control dam
St	Sediment of stream draining mines and a town in the catchment

Results and Discussion

The CRM IAEA 405 results agreed well with the certified values, at 820 ± 20 ng g^{-1} for IHg and 5.50 ± 0.42 ng g^{-1} for MHg, with LOD of 0.39 pg L^{-1}. Back-ground mercury values in the area were relatively low - <50—80 ng g^{-1}. Mercury concentrations were ranging from 20.96 ng L^{-1} in waters to approximately 4300 ng g^{-1} in sediments (Tables 2,3).

Our sampling was biased towards contaminant sinks, and nearly 80% of surficial sediments had Hg concentrations above the Threshold Effect Level (TEL) of 174 ng g^{-1} (USEPA 1997). Enrichment in Hg_{TOT} was evident in deeper soils adjacent to tailings facilities, reaching concentrations of mg g^{-1}. Most sediment profiles showed enrichment in MHg concentration near or at the layer corresponding to the lowest redox potential and the highest IHg concentration (Figure 2) and were closely related to sulphur and carbon levels (Table 2).

This trend was also observed by Hines et al. (2004). They concluded that redox potential, advective transport, or higher temperatures stimulating microbial sulfate reduction should explain

Table 2 Results for selected sediment and water samples collected during rainy season

Sediment	pH	Eh (mV)	Ec (mS cm^{-1})	% Moisture	%C	%S	HgT (ng g^{-1})	IHg (ng g^{-1})	MHg (ng g^{-1})
DS	5,8	409,6	2,39	10,8	0,64	0,06	353,2	na(*)	na
WS	4,0	406,3	3,01	19,5	0,14	0,32	373,7	na	na
S1(0-20)	4,8	322,3	0,845	2,4	1,40	0,02	353,2	282,7	8,27
S1(20-40)	4,5	324,7	0,141	0,3	0,63	0,06	373,7	158,2	bdl(**)
S1(40-60)	5,6	332,5	2,98	3,7	0,57	0,08	216,6	213,4	6,0
S1(60-80)	5,7	349,2	4,22	6,5	0,35	0,34	165,9	446,8	2,0
S1(80-100)	5,9	206,1	6,14	13,5	0,11	0,81	187,2	959,4	13,8
S1(100-120)	5,9	277	5,23	15,8	0,09	0,57	462,3	1007,6	8,9
S1(120-140)	6,5	137	11,22	17,6	0,20	0,74	1103,1	801,6	3,3
S1(140-160)	5,7	214	0,257	1,3	0,57	0,01	1272,6	175,7	6,9
CS	7,2	373,8	2,34	29,5	0,85	0,85	1432,2	na	na
S(0-20)	6,3	418	1,03	25,4	2,76	0,24	4286,8	4114,3	13
S(20-40)	6,5	397	1,88	10,1	1,10	0,09	125,9	110,4	9,5
S(40-60)	6,6	407	0,98	8,1	1,51	0,59	59,6	103,8	6,2
S(60-80)	6,8	421,5	0,94	8,8	0,58	0,04	56,2	147,6	3,8
S(80-100)	6,8	428,9	1,07	12,3	0,70	0,01	76,4	48,0	2,4
S(100-120)	6,8	366	1,48	10,1	0,54	0,02	89,1	60,6	3,7
S(120-150)	6,9	410	1,25	14,5	0,92	0,18	45,2	87,0	1,4
St(0-20)	7,4	373,2	3,19	28,7	2,56	1,59	1004,1	872,0	17,1
St(20-40)	7,4	376,1	1,91	21,6	1,13	0,01	347,3	219,8	bdl
St(40-60)	7,3	332,9	2,19	20,6	1,29	0,57	5482,8	3099,8	140,5
St(60-80)	7,7	350,1	2,11	18,6	0,92	0,07	481,5	302,7	37,8
St(80-100)	7,7	371,5	1,85	21,9	1,39	0,68	77,2	129,9	22,8
Water							(ng l^{-1})	(ng l^{-1})	(ng l^{-1})
CS W1	7.4	452	4.4				1940	651	605
CS W2	7.6	454	4.4				1040	478	461
St W	7.5	482	0.8				92	46	26

(*): Not analyzed (**): Below detection limit

***Table 3** Comparative selected data obtained during dry season*

Sediment	pH	Eh (mV)	Ec (mS cm^{-1})	HgT (ng g^{-1})	IHg (ng g^{-1})	MHg (ng g^{-1})	%MHg
S1	6.5	160	4.06	939.8	768.0	3.2	0.4
CS	7,4	407	2,36	10245,6	8478,8	12,9	0,2
St	7,8	112	1,78	103,4	119,5	2,1	1,7
Water				(ng l^{-1})	(ng l^{-1})	(ng l^{-1})	
St W	7.3	279	1.15	bdl	bdl	bdl	
CS W	7,8	335	3,41	5,483	5,260	0,222	4,1

this trend. Furthermore, Harris et al. (2007) reported maximum MHg concentrations where the inorganic pool of mercury in sediments was the most bioavailable to methylation processes. Metal ions adsorbed in acid media increase with pH, until the threshold value required for partial dissolution of solid and formation of soluble metal-humic complexes is exceeded (Lacerda et al. 1998). Increases in HgTOT were correlated with pH (Figure 3). Methylation occurs in deep sediments at higher pH but, due to its mobility, MHg migrates to shallow levels.

The concentration of HgTOT in waters of the pollution control dam was above 1 ng mL^{-1}, with nearly 50% in the form of MHg. We observed different trends in the dry and rainy seasons, with only 0,005 ng mL^{-1} in water during the rains, despite concentrations in bottom sediments of up to 8500 ng g^{-1} Hg.

In areas where gold mining operations involve milling of Au-bearing ores and tailings deposition, metallic Hg can eventually be mobilized through particle transport and leaching (Lacerda et al. 1998). Although Hg leaching from tailings seems to be a slow process, over the years the bulk migration of spilled tailings, and seasonal leaching from tailings and polluted soils, is important dispersal mechanisms for Hg. Seasonal migration of Hg could explain the patterns observed in

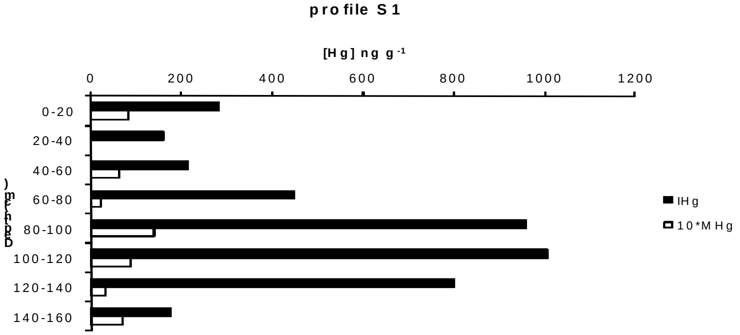

***Figure 2** Example of Hg trends in a sediment profile adjacent to the tailings facility. Note that MHg concentration is multiplied by a factor of ten*

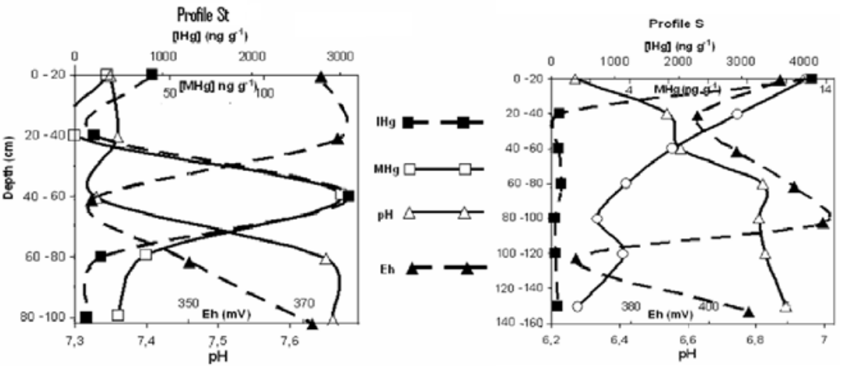

***Figure 3** Trends in Hg and MHg within sediment profiles in relation to redox potential (Eh) and pH: (a) sediments below the pollution control dam, and (b) stream bank sediments*

the stream bank sediments. In the rainy season (Figure 3b), Hg concentrations in surface sediment were 10 times higher than in the dry season. It was not possible to evaluate Hg in the bulk tailings which spilled into this stream, as this occurred in the first half of the 20th century. However, concentrations of Hg in surficial sediments near the later TSF (which commenced construction in the 1940s and is still in operation), were about 315 to 1000 ng g^{-1} (Figure 2).

Lacerda et al. (1998) studied changes in Hg concentrations in water and suspended particles, as well as major physico-chemical parameters in streams receiving drainage from tailings during storm events, and found a drastic increase in the redox potential and in Hg concentrations in suspended particles. In our study, pH in the pollution control dam decreased from the dry to the rainy season (from 7.8 to 7.5) and redox potential increased (from 335 to 450 mV), with an increase in Hg concentration in the (unfiltered) water. These results suggest that rain erodes fine particles enriched with Hg from sources, followed by Hg transport with suspended particles. The relationship between Hg dispersion, erosion and transport of suspended particles, supports a seasonal dispersal mechanism, with rainfall also diluting the existing Hg in water bodies. Hg-contaminated particles from tailings and secondary sources are transported during rains and deposited in sediments along drainage pathways. After this, remobilization of contaminated particles from sediment surfaces may take place, resulting in a decrease in Hg concentrations in the drainage bottom sediments and exportation to areas away from mining sites (Lacerda et al. 1998). This process explains the high Hg concentration of about 4300 ng g^{-1} measured during the rainy season in the upper layer (0—20 cm) of sediments in receipt of run-off from the pollution control dam. The decrease in Hg concentration with depth within the control dam sediments (from 8500 down to 1500 ng g^{-1}), and in the directly adjacent sediment (from 4286 ng g^{-1} at 0—20 cm to 126 ng g^{-1} at 20—40 cm, suggests that the localized surface accumulation of Hg is from recently deposited particles and leached Hg. In contrast, the enrichment of Hg at deeper levels in sediments adjacent to the old tailings facilities (Figure 2), might be due to historical loads of Hg in tailings and seepage from the facilities.

Conclusions

Mercury contamination, probably as a result of use in amalgamation, is to be widespread in the Witwatersrand Basin gold fields. This study identified Hg enrichment of sediments in the vicinity of gold mining activities. Although the function of pollution control dams and tailings storage facilities is to contain waste, the mitigation of Hg contamination may require additional measures to address all historic and artisinal sources. High concentrations of Hg were found at surface in over-flow pathways, and in deep sediments in receipt of seepage from tailings. This indicates that a big proportion of Hg used in gold ore processing was lost to the environment. Mercury in sediments mostly speciated as Hg^0. Enhancement of mercury methylation occurred mainly in deeper sediments at regions with the lowest redox potential, higher pH and enrichment of inorganic mercury.

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