

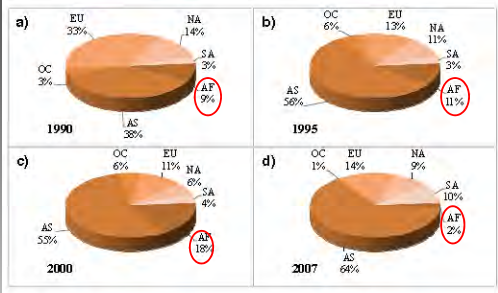
Mercury speciation in the gold-mine polluted environment– determination and development of predictive models for transformation, transport, immobilisation and retardation

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Trend of global anthropogenic mercury emissions by region



a) Pirrone et al. (1996), b) Pacyna et al. (2003), c) Pacyna et al. (2006), and d) Pirrone et al. (2010).

Data reported on d) are for most contributing countries.
AF-Africa; AS-Asia; EU-Europe; NA-North America; OC-Oceania; SA-South America

The Witwatersrand Basin in South Africa (SA) is the biggest gold mining region in the world.

Mercury, which occurs in some gold-bearing ores, was also used for gold recoveries till 1915 and presently in illegal artisanal mining.

The consequences of these mining activities are the release of Hg to the environment, mainly due to AMD from tailings dumps.

It was reported that the Hg emissions in SA are second only to China, contributing more than 10% of the global Hg emissions (Pacyna et al. 2005).


This is due mainly to coal combustion and gold mining.

The information is very controversial and many studies are required to find the real figures for mercury pollution in Southern Africa.

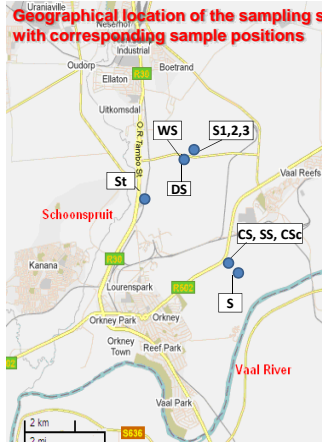


The presentation describes Hg speciation in selected water, soil and sediment samples from Val River watershed during two sampling campaigns (dry and rain season).

- ❑ 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.



Geographical location of the sampling site with corresponding sample positions



Sample ID	Description of soil and sediment samples
DS	Surface dry soils adjacent to the tailings facility
WS	Surface wet soils adjacent to the tailings facility
S1,2,3	Soil profiles adjacent to the tailings facility
SS	Surface sediment within the pollution control dam
CS, SS, CSC	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


Methods

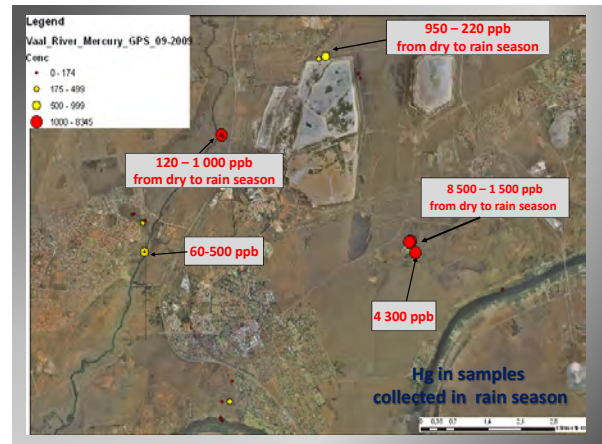
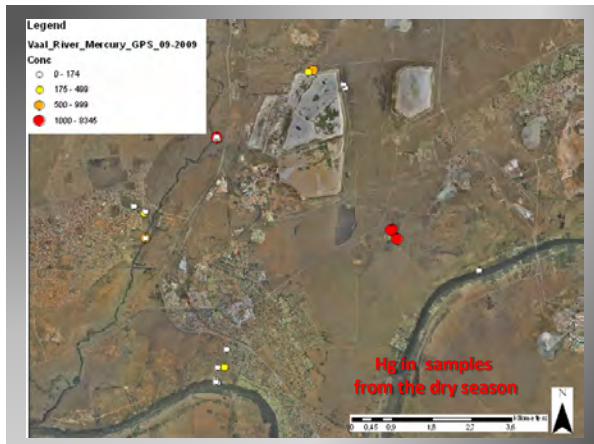
A sub-set of the data from two sampling campaigns (the late dry season – September 2008, and late wet season – February 2009) is presented to illustrate Hg trends in different substrata.

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 artisanal mining activities).

Soil pits were excavated to a maximum depth of 3 m, 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 (MeHg), were determined using GC-ICP MS.
- Analyses were validated using a certified reference material (IAEA405 estuarine sediment) certified at $810 \pm 140 \text{ ng g}^{-1}$ iHg and $5.49 \pm 0.53 \text{ ng g}^{-1}$ MeHg.





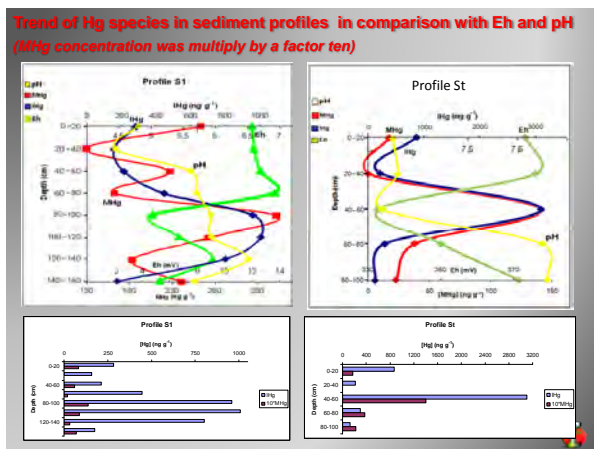
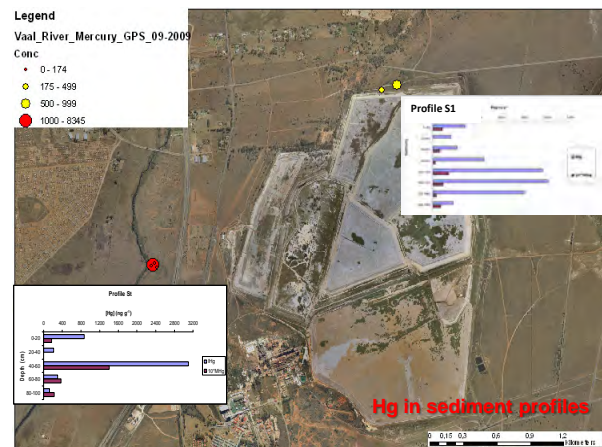
In areas where mining operations involve milling of Au-bearing ores and tailings deposition, metallic Hg can be mobilized through particle transport and leaching (Lacerda et al. 1998).

Seasonal migration of metallic Hg could explain the patterns observed in the stream sediments.

In the rain season, 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 they were build in the first half of the 20th century.

Concentrations of Hg in surficial sediments near the later TSF (which commenced construction in the 1940s and is still in operation), were about 300-1000 ng g⁻¹



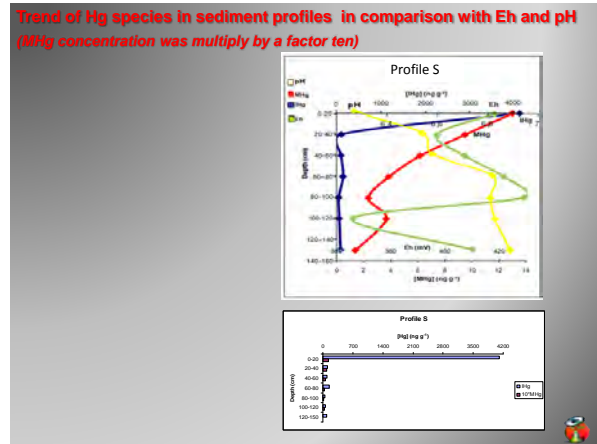
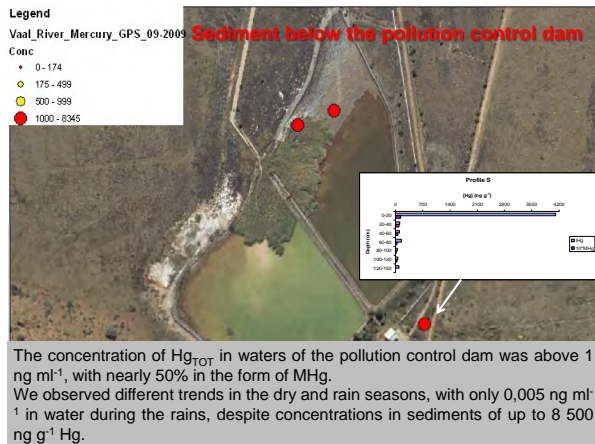
Hg_{TOT} was evident in deeper soils adjacent to tailings facilities. Most sediment profiles showed enrichment in MHg near the layer with the lowest redox potential and the highest IHg concentration and were closely related to sulphur and carbon levels.

Redox potential, advective transport, or higher temp. stimulating microbial sulfate reduction should explain this trend.

Harris et al. (2007) also reported max. MHg concentration where the inorganic pool of mercury in sediments was the most bioavailable to methylation processes.

Metal ions adsorbed in acidic 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 Hg_{TOT} were correlated with pH. Methylation occurs in deep sediments at higher pH but, due to its mobility, MHg migrates to shallow levels.

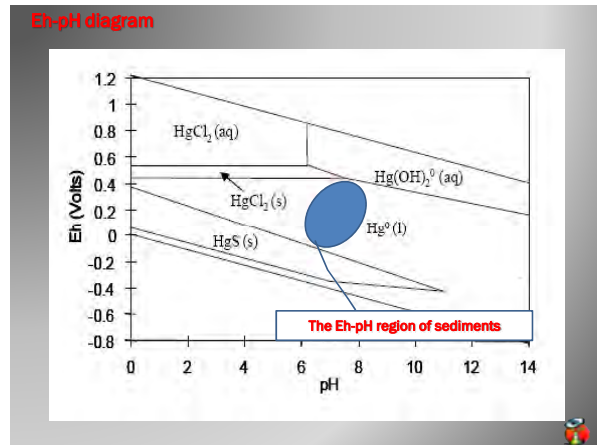


In our study, pH in the pollution control dam decreased from the dry to the rainy season (from 7.8 to 7.5) and redox potential increased (from 335 to 450 mV), with an increase in Hg concentration in the (unfiltered) water.

A drastic increase in the redox potential and Hg concentrations in suspended particles was also observed (Lacerda et al. (1998)).

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 Mercury from contaminated particles surfaces take place, resulting in a decrease in Hg concentration in the drainage bottom sediments and exportation away from mining sites.

This process explains the high Hg concentration (4300 ng g^{-1}) measured during the rain season in the upper layer of sediments in receipt of run-off from the pollution control dam.

The decrease in Hg concentration with depth within the control dam sediments (8500 to 1500 ng g^{-1}), and in the directly adjacent sediment (4286 ng g^{-1} at $0\text{-}20 \text{ cm}$ to 126 ng g^{-1} at $20\text{-}40 \text{ cm}$), suggests that the localized surface accumulation of Hg is from recently deposited particles and leached Hg.

Conclusions

Mercury contamination from the mining and recovery of gold during the late 19th and early 20th centuries is widespread in environmental compartments near historic gold mines in the Vaal River West region.

Mining operations has led to severe contamination of the bottom sediments of reservoirs downstream of the mines (Schoonspruit).

High levels of mercury accumulation found from mine sites, receiving waters, and even sediments downstream of mines indicate that a large part of the mercury used in gold ore processing was lost to the environment.

Remobilization of mercury from the bottom sediment at the dam and its drainage by runoff during rainy season seems to be the cause of contamination of sediments away from pollution source.

Mercury in sediments mostly speciated as Hg^0 . Enhancement of mercury methylation occurred mainly in bulk sediments at regions corresponding to the lowest redox potential, higher pH and enrichment of inorganic mercury.

Thank you

Acknowledge:
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