Mercury Accumulation and Bio-transportation in Wetlands Biota Affected by Gold Mining - Modelling and Remediation

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Abstract Phytoremediation is cost-effective, eco-friendly technology for the removal of metals contaminating aquatic ecosystems. Biogeochemical models for mercury in wetlands were developed by monitoring its accumulation, speciation, methylation and bio-transportation with seasonal changes, emissions, transformations of environmental parameters and biological responses. The lowest bioaccumulation factors were during the wet season indicating lower macrophyte uptake capacity. Translocation factors show mercury accumulation in roots in the wet season; opposite to the dry season. Few plants are proposed for constructed wetlands for mercury phytoremediation. The different uptake and speciation patterns suggest that the most effective wetlands should include few different plant species working together.

Key words mercury, wetlands, bioaccumulation, methylation, phytoremediation

Introduction

Wetlands have several functions that aid in the removal of metals and ameliorate AMD. Sulphates and metals are trapped by wetlands (Perry and Kleinmann 1991). The ability of wetland to act as chemical sinks is due to the presence of plants. Phytoremediation is economically viable biological soil remediation method alternative for the removal of metals contaminating aquatic ecosystems (Padmavathiamma et al. 2007). Biosorption capacity depends on: the metal ion (atomic mass, ionic ray, and valence), environmental conditions (pH, temp. conductivity, contact time, biomass), nature of a biosorbent (Wang and Chen 2009). Many wetlands contain higher concentrations of total and methylmercury and have been shown to be sources and sinks of mercury and most always sources of methylmercury (Guentzel, 2009). Nevertheless, these ecosystems not only respond to direct environmental changes but to the combined or integrated influences of different anthropogenic activities taking place along their watersheds. Indeed, they are permanently at risk. This project was inspired by the paucity of research on mercury and methylmercury in wetland biota growing in semi-arid areas affected by mining and other industrial activities. Unfortunately there are very few long term records of mercury and methylmercury in wetland plants in SA, moreover, no seasonal changes of the mercury loads in affected areas were reported until very recently (Lusilao-Makiese et al. 2014, 2016), thus establishing widespread baselines or current trends is presently difficult. Understanding the bio-transportation and accumulation of mercury in wetland biota is necessary in order to predict the potential impacts and hazards associated with mercury contamination. In addition, it also important to determine how these seasonal changes will affect the Hg speciation in this type of ecosystems.

Materials and Methods

Sampling area

The main wetland area chosen for this study is Germiston in the east of Johannesburg, South Africa (fig.1).

The sampling site is down the slope of the reprocessed tailing footprint (TF). Thus, metals from the tailing footprint are washed to the sampling site via fluvial transportation and erosion. The water from the Natalspruit River flows through the wetland and lend up ultimately in the Vaal River which is used as a water source for greater Johannesburg.

Two sampling campaigns were conducted during the wet and late dry seasons. Plants, water and topsoil from where the plants grew were collected from the wetland adjacent to the tailing footprint. The wet and dry seasons sampling was motivated by the need of understanding the seasonal impact on the Hg accumulation, bio-transportation and distribution in wetland in the semiarid area. Sampling points were selected based on data obtained from the wet season sampling.

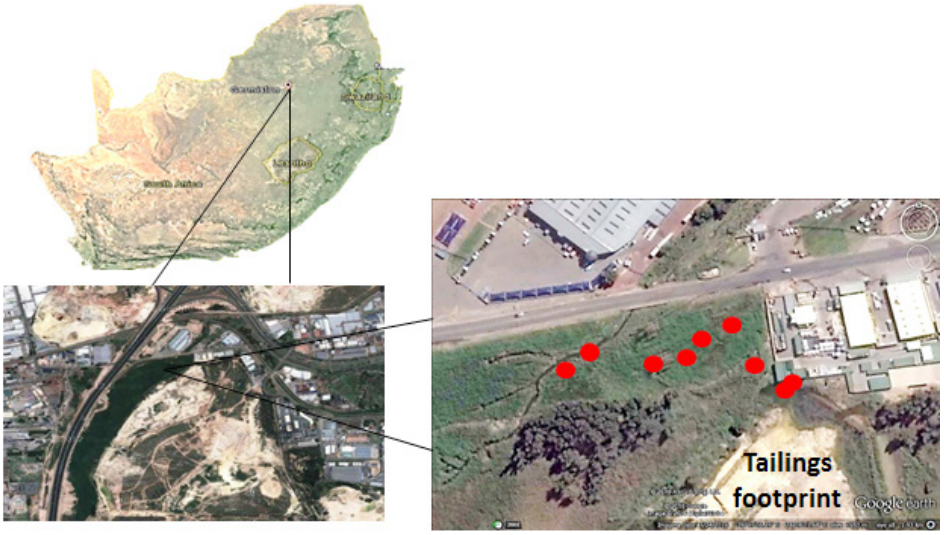

Figure 1 *Geographical location of the Germiston sampling site together with points where samples were collected..*

Sampling and sample pre-treatment

Waters were collected as duplicate samples into acid-washed and conditioned borisilicate bottles with PTFE-lined caps, according to commonly accepted sampling procedures (USEPA, 2007). Each sample was divided into two parts: the one was filtered under vacuum with 0.45 μm filter papers (Millipore, USA) and used for the determination of anions (Cl^- and SO_4^{-2}) by ion chromatography (IC); the other was acidified with 1% (v/v) HCl suprapure (37%, Sigma Aldrich). The samples were transferred in borosilicate bottles with PTFE-lined caps and stored at 4°C until analysis.

Field parameters such as temperature (T), pH and redox potential (Eh) were measured *in situ* using portable meters (WTW multi-parameter instrument pH/Cond 340i and ORP, Germany). GPS coordinates were taken at each sampling point and were used for mapping. Plant species were randomly collected in triplicates. The entire above ground tissues of the plant material together with the roots and sediments from where the plant grew were collected. Vegetation samples consisted of six different plant species (fig. 2).

To rid the samples of any metals that could be attached to the surface, they were thoroughly rinsed with de-ionized water and kept in polyethylene bags. Later, the plant material was cut into smaller pieces and appropriately sorted out into categories of roots, stem, leaves and seeds. Vegetation samples were then frozen and lyophilized at -40°C for 48 hours. Lyophilized samples were ground into fine homogenous powder using a pestle and a mortar with the aid of liquid nitrogen (Heller and Weber 1998). These were kept in cleaned polystyrene bottles in the dark, to prevent photodegradation (Yu and Yan 2003).

The method employed for plant sample treatment was acquired from an existing sample pre-treatment method developed by the United States Environmental Protection Agency (USEPA 1996).

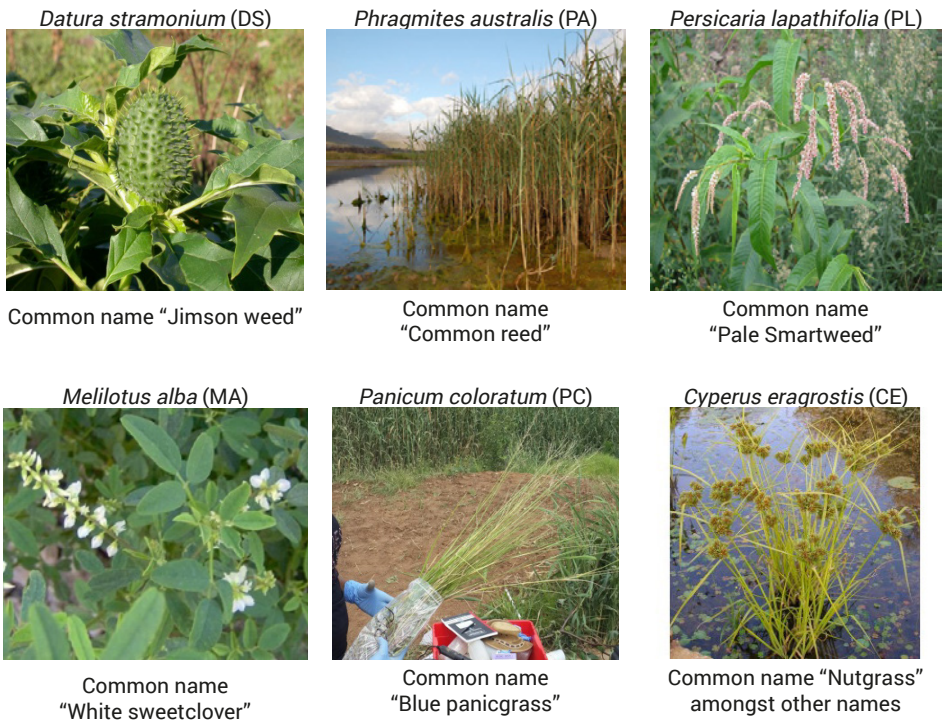

Figure 2 *Plant species used in the study*

Results and Discussion

Field measurements

Table 1 shows the measured parameters in sediments where plants were collected. In the wet season, pH was slightly acidic to neutral. In dry season the pH of sediments samples ranged from 4.1 to 6.4 and the redox potential from 0.26 to 0.49 V. Sediments samples in dry season are acidic in all studied sites. The lower pH values observed in dry season is an evidence of the acidification of the area through pyrite oxidation.

Table 1 *Field measurements for sediments in areas where wetland's plants were collected.*

Sample	Temp.	pH	Eh (V)	Temp.	pH	Eh (V)
	Wet season			Dry season		
DS	25	7.3	0.42	18	6.0	0.26
PA	23	7.3	0.42	19	4.1	0.38
PL	23	7.3	0.42	20	4.1	0.38
MA	21	7.3	0.42	18	6.0	0.49
PC	25	4.2	0.55	18	6.4	0.38
CE	26	7.3	0.42	18	4.1	0.39

Mercury concentration in sediments and plants

Total Hg and organo mercury concentrations in sediments and plants are shown in figure 3. PA showed the highest mercury concentrations in tissues. In most cases, HgT concentrations in sediments were significantly higher than those in roots in a wet seson. However, species such as CE and PC had a higher concentration in roots than in sediments. The highest root concentrations of Hg were observed in CE. CE had also the highest Hg concentration in stem (fig. 3). Generally, during a wet season the mercury levels were descending on the way roots-stem-leaves. The dry seasons patterns differ depends on the individual plant species. Generally MHg concentrations in a dry season are higher.

Bioaccumulation and translocation factors

The lowest BFs were registered for PA during the wet season indicating that Hg is mainly retained by sediments (tab. 2). The plant species with BF higher than 1 were CE and PC indicating a higher macrophyte uptake capacity. This trend was again observed with the behaviour of CE in the dry season. According to the TFs, metals were accumulated fundamentally in roots. TFs were greater than 1 for all mercury species in the dry season (tab.2). Some correlations were found varying according to species and plant tissue.

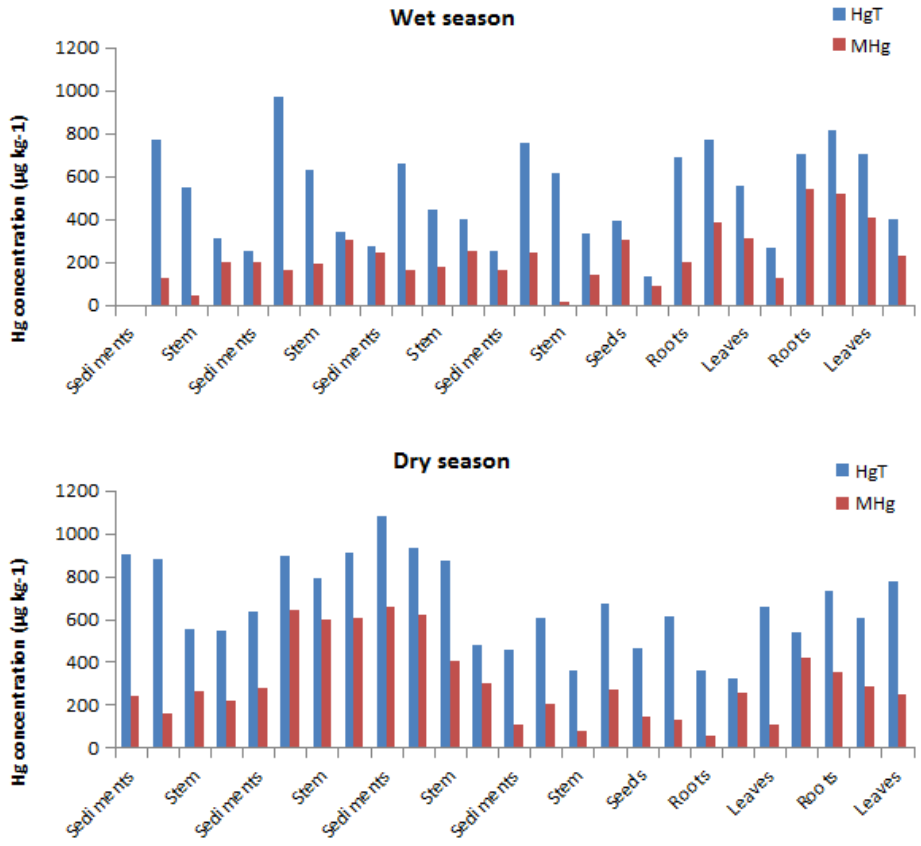

Figure 3 *HgT and MHg concentrations (µg kg^{-1} dry weight) in the sediments and plant tissues.*

Table 2 *Bioaccumulation factor (roots/sediment) and Translocation factor (leaves/roots).*

Sample	BF_s	TF_s	BF_s	TF_s
	Wet season		Dry season	
DS	0.81	0.64	1.31	1.11
PA	0.64	0.43	1.42	1.01
PL	0.70	0.45	0.98	0.62
MA	0.66	0.56	0.86	0.51
PC	1.11	0.34	0.58	1.83
CE	1.16	0.49	1.30	1.06

Seasonality of the mercury biogeochemical cycle

In a wet season four from the selected plant species had the lower concentration of HgT in roots compared to sediments. (species: PL, PA, MA and DS). The exclusion of metals from the root tissues has been suggested as a metal tolerance strategy (Weis and Weis 2004); a metal precipitates within the rhizosphere only by formation of insoluble complexes of mercury which results to lower bioavailability, thus reducing the uptake by the roots. This is confirmed by the bioaccumulation factor values calculated for these species were less than 1. A different trend was observed for PC and CE – the concentration of HgT in roots was greater than in sediments and the BF values were greater than 1 showing bioaccumulation of mercury. It could be inferred that these species have the ability to oxidise sediments in the rhizosphere. This leads to remobilisation of metal contaminants increasing their bioavailability.

The TF values of all the plant species in the wet season were less than 1 meaning the Hg was predominantly concentrated in the roots (tab. 2). This indicates limited mobility of mercury once inside the plant. Binding positively charged metal ions to negative charges in the cell walls of the roots, metal phytate formation, and chelation to phytochelatins followed by accumulation in vacuoles have been invoked as mechanisms to reduce metal transport and increase metal tolerance (Chaney 1993).

The levels of MHg concentrations were generally low in the wet season with the exception of CE and PC species. MHg is volatile and can easily evaporate in a hot season reducing its concentration in sediments and plant tissues. In South Africa, most wetlands are river-fed and therefore undergo seasonal changes with flooding in summer and drying out in winter. Due to high temperatures in summer, high evapotranspiration rates may result in loss of volatile methylmercury into the atmosphere. CE and PC had the highest concentration of MHg in the wet season and TF values greater than 1. This is indicative of significant translocation from sediments to roots. Mercury methylation occurs in the rhizosphere where sulfate reducing bacteria are found (Patty et al., 2009). Therefore for CE and PC some of HgT was converted to MHg in the rhizosphere and was translocated to the aerial tissues. Both these species shows similar pattern for THg and MHg with concentration of both forms decreasing from roots to leaves. Species PL, PA and MA shows similar pattern for MHg highest in stems than in roots and leaves. Only DS presented the highest MHg concentration in leaves in the wet season. In general the levels of mercury (HgT and MHg) were higher in the dry season. Mercury total cumulated in sediments serves as a reservoir for production of organomercury in anaerobic conditions. CE and PC had highest concentration of HgT in roots compared to sediments. However the leaves accumulated more HgT for both species in the dry season.

There changes noted in the distribution of HgT and MHg in PC, and DS during the dry season showed the highest MHg in leaves. Surface roughness could be one of the reasons as to why leaves and seeds of DS accumulated more mercury trapping particulates. MA and CE showed the pattern of decreasing MHg from roots to leaves during the dry season. PA

showed the biggest increase of MHg and HgT in all their tissues. The percentage conversion to organomercury was the highest. It also presented significant translocation of HgT from the sediments to the above ground plant tissues; the TF value greater than 1. This behaviour could be attributed to the presence of bacteria in the rhizosphere. The presence of microbial symbionts such as rhizosphere bacteria is one of the factors that can affect the accumulation of metals in wetland plants (Wies and Wies 2004). This was confirmed by a study that the presence of periphyton associated with PA in wetlands enhanced the ability to accumulate and retain metals (Lakatos et al. 1999). This specie is the most common in SA wetlands occupying 60 to 90% (in constructed wetlands) of areas.

Mercury has the ability to be transported over long-range distances in the atmosphere, can also be distributed from the mine tailings by wind, therefore its concentration in the leaves could also be from atmospheric deposition. Mercury can get translocated into the plants' system through foliar absorption. This process is more pronounced in the dry season due to the persistence of mercury particulates on the leaves and the absence of the washing rainfall. Furthermore, evaporation of water from sediments together with the dehydration of plant leaves by transpiration increase the metal concentration.

Conclusions

Wetland plants demonstrated that they can grow in mercury-polluted areas and have the potential to uptake the metal. Metal translocation into leaves appears to be restricted in some wetland plants, this is however not the case with other species such as CE and PC. Translocation factor gives an idea whether a plant can sufficiently take up Hg from the sediments to the aerial tissues. Besides their uptake capacity, plant species investigated developed mechanisms to cope with elevated levels of mercury and this enhances their phytoremediation capacity. CE, PC, PA and MA could be proposed as Hg biomonitors and phytoremediators, being useful species to be utilized in constructed wetlands for the treatment of industrial effluents. The different uptake and speciation patterns suggest that the most effective wetlands (including constructed wetlands) should include few different plant species working together.

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