

**Mercury concentrations in water resources potentially impacted by coal-fired power stations
and artisanal gold mining in Mpumalanga, South Africa**

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ABSTRACT

Total mercury (TotHg) and methylmercury (MeHg) concentrations were determined in various environmental compartments collected from water resources of three Water Management Areas (WMAs) – viz. Olifants, Upper Vaal and Inkomati WMAs, potentially impacted by major

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anthropogenic mercury (Hg) sources (i.e coal-fired power stations and artisanal gold mining activities). Aqueous TotHg concentrations were found to be elevated above the global average (5.0 ng/L) in 38% of all aqueous samples, while aqueous MeHg concentrations ranged from below the detection limit (0.02 ng/L) to 2.73 ± 0.10 ng/L. Total Hg concentrations in surface sediment (0-4 cm) ranged from 0.75 ± 0.01 to 358.23 ± 76.83 ng/g wet weight (ww). Methylmercury accounted for, on average, 24% of TotHg concentrations in sediment. Methylmercury concentrations were not correlated with TotHg concentrations or organic content in sediment. The concentration of MeHg in invertebrates and fish were highest in the Inkomati WMA and, furthermore, measured just below the US EPA guideline for MeHg in fish.

Keywords: Mercury, methylmercury, coal-fired power stations, water, sediment, invertebrates, fish.

INTRODUCTION

Mercury (Hg) has been regarded as a major environmental pollutant for several decades. In recent years, numerous studies have focused on improving our understanding of the dynamics of Hg, and its effects on aquatic ecosystems and human health. Atmospheric deposition, from both natural and anthropogenic sources, is the primary source of Hg and other heavy metals to aquatic ecosystems,

^[1-2] either directly from wet/dry deposition to the water surface or indirectly via runoff. ^[3]

Atmospheric Hg is reported to contribute approximately 50% to the global anthropogenic Hg emissions. ^[4] Hylander and Meili ^[5] reported that the anthropogenic Hg emissions have doubled the global Hg deposition rates since pre-industrial times, although Mason and Sheu ^[6] have reported a three-fold increase. Emissions from coal-fired power stations and artisanal gold mining practices have been identified as major anthropogenic Hg sources. ^[7-8]

Recently, Pacyna et al. ^[8] ranked South Africa as the second highest anthropogenic Hg emitter, and reported that the country contributed > 10% to the global Hg emissions. Pacyna et al.'s ^[8] statement was largely based on coal combustion and artisanal gold mining. Dabrowski et al. ^[9] and Leaner et al. ^[10] have since reported such Hg emissions in South Africa to be significantly lower than previously reported. Nevertheless South Africa is recognized as the sixth largest coal producer in the world ^[11] and uses relatively low grade coal for combustion and energy generation. Although Hg is present in trace amounts in coal, it can contribute significantly to the Hg load as coal-fired power stations are the main source of energy production in South Africa. Any increase in the amount of coal combusted will lead to increased Hg emissions to the environment, concomitant with an increase in the demand for electricity. ^[9-10] Nonetheless, the Hg contribution to the global Hg cycle is significant when coal is combusted. ^[12]

In terms of artisanal gold mining, Veiga ^[13] reported that as much as 50% of Hg vapours produced during artisanal gold mining practices are emitted and dispersed in the air. These are subsequently deposited via wet and dry deposition onto land and into aquatic ecosystems. Furthermore, Hg wastes from artisanal gold mining can remain in the soil and sediment for several years ^[14] with long-term deposition and bioaccumulation of Hg-contaminated soil and sediment posing an environmental threat.

Although often confined to urban areas, the contamination of aquatic ecosystems far removed from point sources is still possible due to the long-range atmospheric transport of Hg. ^[3]

The work presented here was aimed at assessing the TotHg and MeHg concentrations in various environmental compartments in water resources of three WMAs located in close proximity to potential anthropogenic Hg sources in South Africa. As such, an intensive TotHg and MeHg assessment study was undertaken in 2007 to 2008 in the Olifants and Upper Vaal, and Inkomati WMAs, where coal-fired power stations and artisanal gold mining activities, respectively, are potentially the major sources of Hg in the Mpumalanga province.

MATERIALS AND METHODS

Study Area, Site Selection and Site Characterization

The Mpumalanga Province, which borders Gauteng in the west and Swaziland and Mozambique in the east, is the centre of South Africa's electricity sector. Witbank, a major town in the area, is the largest coal producer in Africa and therefore most of South Africa's coal-fired power stations are located in this province. Intense coal mining and emissions from power stations have contributed to the deterioration of both air and water quality which subsequently has raised environmental concerns. In response, the Department of Environmental Affairs (DEA) has declared the Vaal Triangle and Highveld areas (situated in close proximity to the coal-fired power stations) National Priority Areas for air quality. ^[15-16]

In South Africa, ca. 13 power stations (ten operational and three mothballed) exist, of which eight of the operational coal-fired power stations are located in the Mpumalanga Province. These are Arnot, Hendrina, Kendal, Kriel, Majuba, Matla, Tutuka, and Duvha power stations (Fig. 1).

Gold amalgamation practices are also still being used by artisanal gold miners (an illegal practice in South Africa) in the Inkomati WMA in Mpumalanga Province.

These practices occur mostly along the Noordkaap, Suidkaap, and Queens Rivers near the town of Barberton, in the Inkomati WMA (Fig. 1).

Sampling Protocol and Collection

Sampling for water, sediment and biota was undertaken in selected water resources of the Olifants, Inkomati and Upper Vaal WMAs of the Mpumalanga Province. As sampling was undertaken during several phases, the letters “a, b, c, d” at the end of each site ID on Figures 2 and 4 – 7 denote the sampling period, i.e. June 2007 (dry season), November 2007 (wet season), July 2008 (dry season) and October 2008 (wet season), respectively. In this study, sampling sites selected within these WMAs were selected on the basis of their proximity to potential Hg sources (i.e. coal-fired power stations and artisanal gold mining activities) (Fig. 1; Table 1).

Clean handling techniques were employed throughout sample collection since contamination of sampling equipment is the most common source of erroneous results. Accordingly, all samples were collected using residue-free nitrile gloves, while sampling equipment were acid-cleaned and double-bagged, using the standard protocols for collecting samples for TotHg and MeHg analysis.

[17]

Surface water samples (~500 mL) were collected in acid-cleaned Teflon® bottles, using a peristaltic pump system fitted with acid-clean C-flex tubing, with the inlet immersed ca. 10 cm below the water surface. Additional water samples were collected for ancillary measurements of nutrients (SO_4^{2-} , NO_3^- , PO_4^{3-}) and dissolved organic carbon (DOC). Surface sediment cores (up to 4 cm in

depth) were extruded using an acid-clean polypropylene cylindrical corer and sectioned at 2 cm intervals, after which each section was individually transferred into clean 50 mL centrifuge tubes. Biota samples (invertebrates and fish) were collected using a 1 mm-meshed net. All samples were double-bagged and stored on ice until transported to the laboratory at CSIR (Stellenbosch, South Africa), where they were stored frozen until analyzed.

Ancillary water quality parameters (viz. pH, temperature, dissolved oxygen - DO, electrical conductivity - EC, total dissolved solids - TDS and turbidity) were measured on-site, and provided an account of the present ecological state at each site. Temperature (°C), EC (mS/cm), TDS (ng/L) and pH were measured using a Hanna Instrument Model 991302 and DO (mg/L) was measured using a Hanna Instrument Model 9143.

Sample Preparation and Analytical Techniques

Total mercury analyses

Details of the analytical procedures used for the quantification of TotHg in water have been previously described.^[18] In brief, the determination of TotHg in water followed US EPA Method 1631^[19] which includes the oxidation of Hg with bromine monochloride (BrCl), pre-reduction with

hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) and further reduction with stannous chloride (SnCl_2). Quantification of TotHg was performed by cold vapour atomic fluorescence spectrometry (CVAFS) following gold amalgamation trapping. ^[20]

The TotHg in solid samples, i.e. sediment and biota, were measured using a DMA-80 Solid Phase Direct Mercury Analyzer (Milestone Inc., Monroe, CT, USA). Details on the procedure have been described. ^[21] In brief, ca. 0.1 – 1.0 g homogenized wet sample was weighed out into a quartz boat of a DMA-80 Direct Mercury Analyser and loaded into the combustion chamber of the DMA-80, pre-programmed for automatic TotHg detection.

Methylmercury analyses

The analytical methods for the determination of MeHg are well documented ^[22-24] and followed US EPA Method 1630. ^[25] In brief, water and sediment samples were distilled with 1 mL 50% H_2SO_4 and 0.5 mL 20% KCl. The distillate was ethylated with sodium tetraethyl borate which converts MeHg to volatile methylethylmercury. Following ethylation, all samples were purged through a Tenax™ trap, separated by isothermal gas chromatography, and followed by quantification using CVAFS. ^[26]

Since MeHg is the most toxic and predominant form (~90%) of Hg in tissues of invertebrates and

fish, ^[24] and due to sample mass limitations in the biota collected, only the MeHg concentration was measured in the invertebrates and fish. Therefore, for MeHg concentrations in biota, all homogenized samples were digested with 25% KOH-methanol and placed in a 65°C oven for 24h. Sample analysis and quantification were performed using CVAFS.

Ancillary analyses

The percentage organic content of each sediment layer was determined as loss on ignition (LOI) at approximately 550°C overnight. ^[27]

Quality Control Procedures

Analytical quality assurance/quality control (QA/QC) criteria were maintained for all analytical methods using a standard calibration curve having a regression coefficient (r^2) of at least 0.998 at the beginning and end of each day. Matrix spikes (MS), matrix spike duplicates (MSD), standard reference material (SRM) and matrix blanks were included as part of the daily QA/QC protocol.

Where sample size was not limited, duplicate samples were analysed to establish the precision of the analytical techniques used. The following SRM's were employed for the determination of Hg in

sediment or biota: (i) MESS-3 Marine Sediment SRM (0.091 ± 0.009 mg/kg) (National Research Council, Canada); (ii) PACS-2 Marine Sediment SRM (3.04 ± 0.20 mg/kg) National Research Council, Canada); (iii) IAEA-405 Trace Elements and Methylmercury in Estuarine Sediment SRM (0.00549 ± 0.00053 mg/kg) (International Atomic Energy Agency, Austria); (iv) TORT-2 Lobster Hepatopancreas Marine SRM (0.27 ± 0.06 mg/kg) (National Research Council, Canada) for biota; and (v) DORM-2 Fish Protein SRM for biota (0.382 ± 0.060 mg/kg) (National Research Council, Canada). Duplicate and triplicate samples analysed yielded a marginal error of $< 10\%$ while all SRM's analysed were within the certified ranges.

Statistical Analyses

The means and standard deviations were obtained for all duplicate and triplicate samples, and were statistically compared. Linear regression equations were determined using Sigmaplot (Sigmaplot 8.0; SPSS Inc., Chicago, IL), and MS Excel (Microsoft Office Excel 2003, Washington, USA). The comparisons of the regression coefficients, using both Simaplot and MS Excel, were not significantly different. A one-way analysis of variance (ANOVA), followed by the Tukey-Kramer HSD means comparison test (JMP 8.0, SAS Institute; SPSS Inc.) was undertaken to determine any significant differences ($p < 0.05$) in the TotHg and MeHg concentrations of the samples analysed.

RESULTS AND DISCUSSION

Mercury in Water

Aqueous TotHg concentrations ranged from 0.32 ± 0.02 to 19.06 ± 0.99 ng/, 0.84 ± 0.01 to 26.65 ± 3.53 ng/L, and 0.06 to 16.60 ± 0.28 ng/L in the Olifants, Upper Vaal and Inkomati WMAs, respectively (Fig. 2). The aqueous TotHg concentrations, on average, exhibited the following order for the WMAs: [TotHg in Upper Vaal] > [TotHg in Olifants] > [TotHg in Inkomati]. A comparison of the mean TotHg concentrations in water analysed for each WMA demonstrated significant differences ($p < 0.05$) between the Upper Vaal and Inkomati WMAs. All TotHg concentrations were within the water quality range of 40 ng/L set for TotHg levels in aquatic ecosystems in South Africa.

^[28] However, 38% were above the global average of 5.0 ng/L and a total of 19% were above the concentration that would result in chronic effects to aquatic life (i.e. 12 ng/L). ^[29]

The highest TotHg concentration was measured at site ThU1 (26.65 ng/L \pm 3.53) in the Upper Vaal WMA. The TotHg concentrations measured in the Inkomati WMA were well below the ranges reported in filtered water analysed for TotHg concentrations in an artisanal gold mining centre (10 to 70 ng/L). ^[30]

Seasonal trends in TotHg concentrations were also observed in the Inkomati WMA where sites were sampled during both the wet and dry season (i.e. BnK1, BsK1 BK2, BK3, BK5, BQ1 – see Table 1 for sampling frequency). Higher TotHg concentrations were measured in all samples collected in the wet season, when compared to the dry season, except at BsK1, BK3 and BK5. Periods of high rainfall and river discharge most likely cause physical remobilization of fine-grained sediments and resuspension of Hg in the water column, similar to what has been reported by others.^[31] The TotHg concentrations were also higher in the downstream sites when compared to the upstream sites (i.e. Olifants: WAR1b vs. OdR2b; Olifants: RtR1b vs. RtR2b; Inkomati: BK2d vs. BK4d; Upper Vaal: VR1 vs. VR3). This can likely be attributed to the downward flow and hence transportation of TotHg in the water column, to the lower reaches of the sampled water resources.

Aqueous MeHg concentrations ranged from below the detection limit (0.02 ng/L) to 0.50 ng/L, 0.05 to 0.89 ± 0.02 ng/L and 0.05 to 2.73 ± 0.10 ng/L in the Olifants, Upper Vaal and Inkomati WMAs, respectively (Fig. 2). The aqueous MeHg concentrations, on average, exhibited the following order for the WMAs, [MeHg in Inkomati] > [MeHg in Upper Vaal] > [MeHg in Olifants]. In contrast to TotHg, the highest MeHg concentration was measured at site BK5 (BK5d in the Inkomati WMA).

Evidence of seasonal variation was observed in the MeHg concentrations of water samples collected in the Inkomati WMA, but not in the Olifants and Upper Vaal WMAs (Fig. 2), since samples in the Inkomati WMA were collected during both the wet and dry seasons for most of the sites sampled.

Up to a 5-fold increase in MeHg concentrations was observed in water samples collected at most sites in the Inkomati WMA during the dry season compared with the wet season, except for sites BnK1 and BQ1 (Fig. 2). Since water is transient, any MeHg present upstream will be transported downstream (or deposited in sediment), similar to what has been observed for TotHg concentrations in this study. As such, MeHg concentrations were generally higher downstream than at the upstream sampling sites, except at sampling sites BK2 and BK4.

The TotHg and MeHg concentrations in the Olifants and Upper Vaal WMAs were weakly correlated ($r^2 = 0.36$ and $r^2 = 0.76$, respectively) and suggest that MeHg concentrations were relatively independent of TotHg concentrations. This is in contrast to what is typically expected.^[32]

Metal speciation is also affected by organic ligands present in the water column.^[33] Dissolved organic carbon (DOC) concentrations were inconsistent across WMAs, and ranged from 3.62 to 11.53 mg/L, 3.62 to 14.59 mg/L and 1.00 to 10.97 mg/L, in the Olifants, Upper Vaal and Inkomati WMAs, respectively. When TotHg and MeHg concentrations were correlated with DOC, weak positive correlations were observed in the Upper Vaal (TotHg $r^2 = 0.51$ and MeHg $r^2 = 0.78$), Olifants (TotHg $r^2 = 0.15$ and MeHg $r^2 = 0.10$) and the Inkomati WMAs (TotHg $r^2 = 0.04$ and MeHg $r^2 = 0.07$). These results suggest that Hg complexation with DOC was probably insignificant in all three WMAs. Additional sampling should be conducted in future to understand the behavior of TotHg and MeHg in correlation with DOC for this specific area.

Mercury in Sediment

The TotHg distribution in sediments in the three WMAs is represented in Figure 3. A large variability in TotHg concentrations were observed between the different WMAs. Overall, the TotHg concentrations in the Olifants WMA ranged from 1.79 ± 0.38 to 31.43 ± 2.71 ng/g ww and 1.50 to 34.25 ± 2.74 ng/g ww, in the < 2 cm and > 2 cm depths, respectively. In the Upper Vaal, TotHg concentrations ranged from 1.90 ± 0.54 to 16.10 ± 2.52 ng/g ww and 1.00 to 7.33 ± 0.24 ng/g ww, in the < 2 cm and > 2 cm depths, respectively. In the Inkomati WMA, TotHg concentrations ranged from 0.87 ± 0.09 to 358.23 ± 76.83 ng/g ww and 0.75 ± 0.01 to 115.71 ± 3.09 ng/g ww, in the < 2 cm and > 2 cm depths, respectively (Fig. 3).

Significant differences ($p < 0.05$) were observed in TotHg concentrations between the Olifants, Upper Vaal and Inkomati WMA in the < 2 cm depth, and between the Olifants and Upper Vaal WMAs, and the Inkomati WMA in the > 2 cm depth. The highest TotHg concentrations were observed in sediment collected in the Inkomati WMA (Fig. 3). This could be attributed to the Hg:Gold amalgam processes employed in the illegal artisanal gold mining industry taking place in the Inkomati WMA. Any Hg released from artisanal gold mining is likely deposited either directly through runoff or from atmospheric deposition into water resources and sediments. Sediment TotHg

concentrations in the Inkomati WMA also exceeded the US EPA's quality guideline of 200 ng/g. ^[34]

However, this result is below the range reported elsewhere for TotHg in sediments impacted by artisanal gold mining activities. ^[35-36]

Since this is an illegal trade in South Africa, the scale of artisanal gold mining in the Inkomati WMA could be much lower than in areas where artisanal gold mining is practiced legally in other countries. If this is indeed the situation, then the lower TotHg concentrations observed in sediment collected in water resources in the Inkomati WMA, when compared to the published studies, ^[35-36] is not unexpected.

Sediment methylation occurs either through biological (bacterially) ^[37-38] or chemical mediated. ^[39]

The formation of MeHg is affected by several parameters such as sediment TotHg concentration, microbial activity, ^[40] and sediment organic carbon (OC). The MeHg concentrations in the surface sediments showed a high degree of variability among the three WMAs (Fig. 4). The MeHg concentrations in the Olifants WMA ranged from 0.02 ± 0.01 to 2.45 ± 0.08 ng/g ww and 0.08 to 1.75 ± 0.28 ng/g ww in the < 2 cm and > 2 cm depths, respectively. In the Upper Vaal WMA, the MeHg concentrations ranged from 0.02 to 1.95 ± 0.28 ng/g ww and 0.13 to 1.74 ± 0.04 ng/g ww in the < 2 cm and > 2 cm depths, respectively. In the Inkomati WMA, the MeHg concentrations ranged from < 0.02 to 6.90 ± 2.25 ng/g ww and 0.02 to 10.99 ng/g ww in the < 2 cm and > 2 cm depths, respectively.

The MeHg concentrations measured were highest in the Inkomati WMA at sites BK2 and BF1, when compared to all sites. This can also possibly be attributed to the artisanal gold mining activities that take place in the Inkomati WMA.

Conway et al. ^[41] and Warner et al. ^[42] showed covariance between TotHg and MeHg concentrations in surface sediment. However, the weak relationship found in the results of this study suggests that this may not be the case in the three WMAs. This suggests that sediment MeHg concentrations in the three WMAs were not controlled by sediment TotHg concentrations. Equivalently, there are likely several co-depending controlling factors that determine the MeHg concentrations.

Mercury in Biota

Lower trophic levels play an important role in the bioaccumulation of Hg in fish. Predatory and benthic species often contain relatively elevated Hg concentrations. A list of the invertebrate and fish species collected appears in Table 2.

The MeHg concentrations for all invertebrates are illustrated in Figure 5, and ranged from 5.29 ± 0.23 to 32.25 ± 1.40 ng/g ww, 2.80 ± 0.73 to 20.12 ± 2.34 ng/g ww and 3.59 ± 1.09 to 76.18 ± 4.97 ng/g ww, in the Olifants, Upper Vaal and Inkomati WMAs, respectively. The highest MeHg concentrations were measured in invertebrates collected in the Inkomati WMA (Fig. 5). All biota

(invertebrates and fish) analysed in this study are typically benthic organisms, living and feeding at the water-sediment interface or in sediment (Table 2). Benthic organisms generally contain higher Hg concentrations than other (pelagic-dwelling) organisms, ^[22] and therefore provide for the transfer of sedimentary Hg to the aquatic food chain. ^[43] Benthic invertebrates also provide an indication of the bioavailability of Hg in sediments to biota ^[22]. However, weak correlations were observed between sediment MeHg and invertebrate MeHg in the three WMAs ($r^2 = 0.22$; $r^2 = 0.34$; $r^2 = 0.1$, respectively) which suggests that sediment-associated MeHg is not readily available for uptake by biota. The MeHg concentrations in invertebrates collected in the Upper Vaal and Inkomati WMAs, were significantly different ($p < 0.05$) to invertebrates collected in the Olifants WMA. The MeHg concentrations in fish samples collected in the three WMAs are represented in Figure 6. Fish feeding on organisms at the lower trophic levels bioaccumulate less MeHg when compared to fish that feed on organisms at higher trophic levels. ^[44] The MeHg concentrations in all fish collected (Table 2) ranged from 20.03 to 75.40 ± 5.82 ng/g ww, 10.06 ± 1.44 to 33.92 ± 3.44 ng/g ww, and 14.40 ± 2.48 to 217.82 ± 4.13 ng/g ww in the Olifants, Upper Vaal and Inkomati WMA, respectively (Fig. 6). The highest MeHg concentration in fish was measured in the Inkomati WMA, which can again possibly be attributed to the artisanal gold mining industry in the area and other factors described below.

Fish species caught in this study feed primarily on invertebrates and organic sediments (Table 2). A

comparison of MeHg concentration in invertebrates and fish collected in the Inkomati WMA supports the fact that benthic invertebrates facilitate the transport of sedimentary Hg to fish. A positive correlation in fish MeHg concentrations and fish length was observed in the Olifants and Upper Vaal WMAs ($r^2 = 0.88$; $r^2 = 0.90$) similar to that reported by others.^[44] However, such a correlation was not observed for fish collected in the Inkomati WMA, as higher concentrations were measured in fish of smaller size class. These differences can possibly be attributed to the location of Hg point sources in the Inkomati WMA compared to those in the Olifants and Upper Vaal WMAs. Mercury in sediment is also a source of Hg to fish.^[45] Brumbaugh et al.^[46] supports this reasoning, and reported positive correlations with aqueous and sedimentary MeHg concentrations. Fish MeHg concentrations were also positively correlated to aqueous MeHg and sediment MeHg concentrations in the Inkomati WMA. Although all fish MeHg concentrations were below the US EPA guideline for MeHg (300 ng/g ww)^[47], some MeHg concentrations, particularly in the Inkomati WMA, were approaching this value. These findings can possibly be attributed to direct Hg inputs into the water resources of the Inkomati WMAs where artisanal gold mining activities take place.

CONCLUSION

This assessment provides an indication of the TotHg and MeHg concentrations in water, sediment,

and biota of three WMAs, viz. Olifants, Upper Vaal and Inkomati WMAs in South Africa. The TotHg and MeHg concentrations in water samples collected were higher at downstream sites relative to the upstream sites, and were higher during the wet season relative to the dry season. The highest sediment Hg concentrations occurred in the Inkomati WMA. Elevated Hg concentrations as also reflected in both invertebrates (primarily benthic invertebrates) and fish (species feeding on benthic invertebrates and organic matter). The positive correlations between fish MeHg concentrations and sedimentary MeHg concentrations lends support to the significance of sediment, and benthic invertebrates in particular, as the primary mechanism for the transport of sedimentary Hg to aquatic food chains. The results of this study suggest that coal-fired power plants and artisanal gold mining activities may possibly have some environmental impact in the Mpumalanga Province. In general, the Inkomati WMA appears to be more impacted by anthropogenic sources of Hg relative to the Olifants and Upper Vaal WMAs. The impacts of artisanal gold mining activities in the Inkomati WMA could be sustained in the cycling and mobilization of Hg-contaminated sediments in the water column. Furthermore, the elevated MeHg concentrations in fish collected in the Inkomati WMA indicate that MeHg is more readily available in the latter WMA, than in the Olifants and Upper Vaal WMAs. This study demonstrates that more long-term monitoring is needed to fully assess the Hg concentrations in the Inkomati WMA, particularly since subsistence fishing forms part of the daily livelihoods of the communities living

near the water resources sampled in this study. Such studies are particularly important in this WMA since MeHg concentrations in fish were approaching the US EPA regulatory limits for fish (i.e. 300 ng/g ww).^[47] Overall, the results demonstrate that the impacts of coal-fired power plants and artisanal gold mining activities on water resources and its ecosystems need to be assessed over a much longer timeframe and at a more regular frequency. Such a monitoring programme (with increased samples, sampling sites and sampling frequency) will prove more conclusive in determining the potential impacts of these anthropogenic Hg sources on water resources in these WMAs.

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REFERENCES

- [1] Mason, R.P.; Lawson, N.M.; Sheu, G.R. Mercury in the Atlantic Ocean: factors controlling air-sea exchange of mercury and its distribution in the upper waters. *Deep-sea Res.* **2001**, *48*, 2829-2853.
- [2] Mason, R.P.; Lawson, N.M.; Sheu, G.R. The urban atmosphere: an important source of trace metals to nearby waters? In *Chemicals in the Environment*; Lipnick, R.L., Mason, R.P., Phillips, M.L., Pittman, C.U., Eds.; Oxford University Press, **2004**; 203-222.
- [3] Mason, R.P.; Lawson, N.M.; Sheu, G.R. Annual and seasonal trends in mercury deposition in Maryland. *Atmos. Environ.* **2000**, *34*, 1691-1701.
- [4] Douglas, J. Mercury in the environment. *EPRIJ*, **1991**; 4-11.
- [5] Hylander, L.D.; Meili, M. 500 years of mercury production: a global annual inventory by region until 2000 and associated emissions. *Sci. of the Tot. Environ.* **2003**, *304*, 13-27.
- [6] Mason, R.P.; Sheu, G.-R. The role of the ocean in the global mercury cycle. *Glob. Biogeochem. Cycl.* **2002**, *16*(4), 1093-1106; doi: 10.1029/2001GB001440.
- [7] Nriagu, J.O.; Pacyna, J.M. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature.* **1988**, *333*, 134-139.
- [8] Pacyna, E.G.; Pacyna, J.M.; Steenhuisen, F.; Wilson, S. Global anthropogenic mercury emission inventory for 2000. *Atmos. Environ.* **2006**, *40*, 4048-4063.
- [9] Dabrowski, J.D.; Ashton, P.J.; Murray, K.; Leaner, J. Anthropogenic mercury emissions in South

Africa: coal combustion. South African Mercury Assessment Programme. **2008**.

[10] Leaner, J.J.; Kim, E-H.; Mason, R.P.; Hendricks, M.; MacMillan, P.; Hendricks, D.T.;

Dabrowski, J.M.; Murray, K.; Ashton, P.J.; Bernier, G. Preliminary assessment of total mercury and methylmercury in selected rivers of the Western Cape and Mpumalanga Provinces, South Africa.

2008, CSIR Report No. CSIR/NRE/WR/EXP/ 2007/0040/A.

[11] DME (Department of Minerals and Energy). *Digest of South African energy statistics*.

Department of Minerals and Energy. **2004**, Pretoria, South Africa.

[12] Knobeloch, L.; Gliori, G.; Anderson, H. Assessment of methylmercury exposure in Wisconsin.

Environ. Res. **2007**, *103*, 205-210.

[13] Veiga, M.M.; Bermudez, D.; Pacheco-Ferreira, H.; Pedroso, R.L.R.M.; Gunson, A.J.; Berrios,

G.; Vos, L.; Huidobro, P.; Roeser, M. Mercury pollution from artisanal gold mining in block B, El

Callao, Bolivar State, Venezuela. In *Dynamics of Mercury Pollution on Regional and Global Scales*;

Pirrone, N., Mahaffey, K., Eds; Springer, NY, **2005**; 421-450.

[14] Ramirez Requelme, M.E.; Ramos, J.F.F.; Angelica, R.S.; Brabo, E.S. Assessment of

mercury-contamination in soils and stream sediments in the mineral district of Nambija, Ecuadorian

Amazon (example of an impacted area affected by artisanal gold mining). *Appl. Geochem.* **2003**, *18*,

371-381.

[15] DEAT (Department of Environmental Affairs and Tourism). *Vaal Triangle Airshed Priority*

Area – Macro Siting Report. Pretoria, South Africa. **2006**, Report No. DEAT_RN_060001.

[16] DEAT (Department of Environmental Affairs and Tourism). *Highveld Priority Area Ambient Air Quality Monitoring – Micro-Scale Siting Report*. Pretoria, South Africa. **2007**, Report No. SIA_RN_070002.

[17] Mason, R.P; Sullivan, K.A. Mercury and methylmercury transport through an urban watershed. *Water Res.* **1998**, *32*, 321-330.

[18] Horvat, M.; Liang, L.; Bloom, N.S. Comparison of distillation with other current isolation methods for the determination of methylmercury compounds in low environmental samples: part II. *Water. Anal. Chim. Acta.* **1993**, *282*, 153-168.

[19] US EPA (United States Environmental Protection Agency). *Mercury in water by oxidation, purge and trap, and cold water atomic fluorescence spectrometry*. Washington DC, USA. **2002**, EPA Publication No.: EPA-821-R-02-019.

[20] Bloom, N.S; Fitzgerald, W.F. Determination of volatile mercury species at the pictogram concentration by low temperature gas chromatography with cold-vapour atomic fluorescence detector. *Anal. Chim. Acta.* **1988**, *208*, 151-161.

[21] Boylan, H.M.; Richter, R.C.; Kingston, H.M.; Ricotta, A. Rapid mercury analysis for the field: Method development and application to natural gas utility sites. *Water, Air and Soil Poll.* **2001**, *127*, 255-270.

[22] Mason, R.P.; Lawrence, A.L. Concentration, distribution, and bioavailability of mercury and methylmercury in sediments of Baltimore Harbour and Chesapeake Bay, Maryland, USA.

Environ. Toxicol. and Chem. **1999**, *18* (11), 2438-2447.

[23] Leaner, J.J.; Mason, R.P. Methylmercury accumulation and fluxes across the intestine of channel catfish, *Ictalurus punctatus*. Comp. Biochem. and Physiol. Part C. **2002**, *132*, 247-259.

[24] Leaner, J.J.; Mason, R.P. Methylmercury uptake and distribution kinetics in sheepshead minnows, *Cyprinodon variegates*, after exposure to CH₃Hg-spiked food. Environ. Toxicol. and Chem. **2004**, *23* (9), 2138-2146.

[25] US EPA (United States Environmental Protection Agency). *Method 1630: Methylmercury in water by distillation, aqueous ethylation, purge and trap, and CVAFS*. Washington DC, USA, **2001a**.

EPA Publication No. 821 –R-01-020.

[26] Mason, R.P.; Kim, E.; Cornwell, J.; Heyes, D. An examination of the factors influencing the flux of mercury, methylmercury and other constituents from estuarine sediments. Mar. Chem. **2006**, *102*, 96-110.

[27] Kim, E-H.; Mason, R.P.; Porter, E.T.; Soulen, H.L. The impact of resuspension on sediment mercury dynamics, and methylmercury production and fate: A mesocosm study. Mar. Chem. **2006**, *102*: 300-315.

[28] DWAF (Department of Water Affairs and Forestry). *Water Quality Guidelines: Aquatic*

Ecosystem Use. First Edition. Department of Water Affairs and Forestry, Pretoria, South Africa.

1996, Vol. 7.

[29] US EPA (United States Environmental Protection Agency). *Water quality standards; establishment of numeric criteria for priority toxic pollutants; states' compliance; final rule*. Federal Register 40 CFR Part 131 57. **1992**, 246 (60) 847-860, 916.

[30] Taylor, H.; Appleton, J.D.; Lister, R.; Smith, B.; Chitamwebwa, D.; Mkumbo, O.; Machiwa, J.F.; Tesha, A.L.; Beinhoff, C. Environmental assessment of mercury contamination from the Rwamagasa artisanal gold mining centre, Geita District, Tanzania. *Sc. of the Tot. Environ.* **2005**, 34, 111-133.

[31] Churchill, R.C.; Maethrel, C.E.; Suter, P.J. A retrospective assessment of gold mining in the Reedy Creek sub-catchment, northeast Victoria, Australia: residual mercury contamination 100 years later. *Environ. Poll.* **2004**, 132, 355-363.

[32] Watras, C.J.; Back, R.C.; Halvorsen, S.; Hudson, R.J.M.; Morrison, K.A.; Wentz, S.P. Bioaccumulation of mercury in pelagic freshwater food webs. *Sci. of the Tot. Environ.* **1998**, 219, 183-208.

[33] Ravichandran, M. Interactions between mercury and dissolved organic matter – a review. *Chemos.* **2004**, 55, 319-331.

[34] US EPA (United States Environmental Protection Agency). *Guidance for assessing chemical*

contamination data for use in fish-advisories. Vol 1: field sampling and analysis, Third Ed.

Washington DC, US EPA, Office of Water. **2000**, EPA publication no. EPA-823-B-00-007.

[35] Ikingura, J.R.; Akagi, H.; Mujumba, J.; Messo, C. Environmental assessment of mercury dispersion, transformation and bioavailability in the Lake Goldfields, Tanzania. *J. of Environ. Manag.* **2006**, *81*, 167-173.

[36] Loredó, J.; Ordoñez, A.; Álvarez, R. Environmental impact of toxic metals and metalloids from the Munon Cimero mercury-mining area (Asturias, Spain). *J. of Hazard. Mater.* **2006**, *136*(3), 455-467.

[37] Scheuhammer, A.M.; Graham, J.E. The bioaccumulation of mercury in aquatic organisms from two similar lakes with differing pH. *Ecotoxicol.* **1999**, *8*, 49-56.

[38] Gilbertson, M.; Carpenter, D.O. An ecosystem approach to the health effects of mercury in the Great Lakes basin ecosystem. *Environ. Res.* **2004**, *95*, 240-246.

[39] Celo, V.; Lean, D.R.S.; Scott, S.L. Abiotic methylation of mercury in the aquatic environment. *Sc. of the Tot. Environ.* **2006**, *368*, 126-137.

[40] Benoit, J.M.; Gilmour, C.C.; Heyes, A.; Mason, R.P.; Miller, C.L. Geochemical and biological controls over methylmercury production and degradation in aquatic ecosystems. ACS Symposium Series. 2002.

[41] Conway, C.H.; Squire, S.; Mason, R.P.; Flegal, A.R. Mercury speciation in the San Francisco

Bay estuary. *Mar. Chem.* **2003**, *80*, 199-225.

[42] Warner, K.A.; Bonzongo, J. J.; Roden, E.E; Ward, G.M.; Green, A.C.; Chaubey, I.; Lyons, W.B.; Arrington, D.A. Effect of watershed parameters on mercury distribution in different environmental compartments in the Mobile Alabama River Basin, USA. *Sci. of the Tot. Environ.* **2005**, *347*, 187-207.

[43] Lawrence, A.L. and Mason, R.P. Factors controlling the bioaccumulation of mercury and methylmercury by the estuarine amphipod *Leptocheirus plumulosus*. *Environ. Poll.* **2001**, *111*, 217-231.

[44] Sveinsdottir, A.Y.; Mason, R.P. Factors controlling mercury and methylmercury concentrations in largemouth bass (*Micropterus salmoides*) and other fish from Maryland reservoirs. *Arch. of Environ. Contamin. and Toxicol.* **2005**, *49*, 528-545.

[45] Gilmour, C. C.; Henry, E. A.; Mitchell, R. Sulfate stimulation of mercury methylation in freshwater sediments. *Environ. Sci. and Techn.* **1992**, *26*, 2281-2287.

[46] Brumbaugh, W.G.; Krabbenhoft, D.P.; Helsel, D.R.; Wiener J.G.; Echols, K.R. A national pilot study of mercury contamination of aquatic ecosystems along multiple gradients: bioaccumulation in fish. U.S. Geological Survey. **2001**, USGS/BRD/BSR-2001-0009.

[47] US EPA (United States Environmental Protection Agency). *Mercury update: impact on fish advisories*. US EPA, Washington DC. **2001b**, EPA-823-F-01-012.

FIGURE CAPTIONS

Figure 1. Map of sampling sites located in the Olifants, Upper Vaal and Inkomati Water Management Areas, as well as locations of coal-fired power stations in the Mpumalanga Province, South Africa.

Figure 2. Aqueous total mercury and methylmercury concentrations for sampling sites located in the Olifants, Upper Vaal and Inkomati Water Management Areas. (Solid line indicates US EPA TotHg guideline of 12 ng/L; dotted line indicates global TotHg average of 5.0 ng/L)

Figure 3. Total mercury concentrations in surface sediment layers (< 2 cm and > 2 cm) for sampling sites located in the Olifants, Upper Vaal and Inkomati Water Management Areas.

Figure 4. Methylmercury concentrations in surface sediment layers (< 2 cm and > 2 cm) for sampling sites located in the Olifants, Upper Vaal and Inkomati Water Management Areas.

Figure 5. Methylmercury concentrations in invertebrates for sampling sites located in the Olifants, Upper Vaal and Inkomati Water Management Areas.

Figure 6. Methylmercury concentrations in fish for sampling sites located in the Olifants, Upper Vaal and Inkomati Water Management Areas.

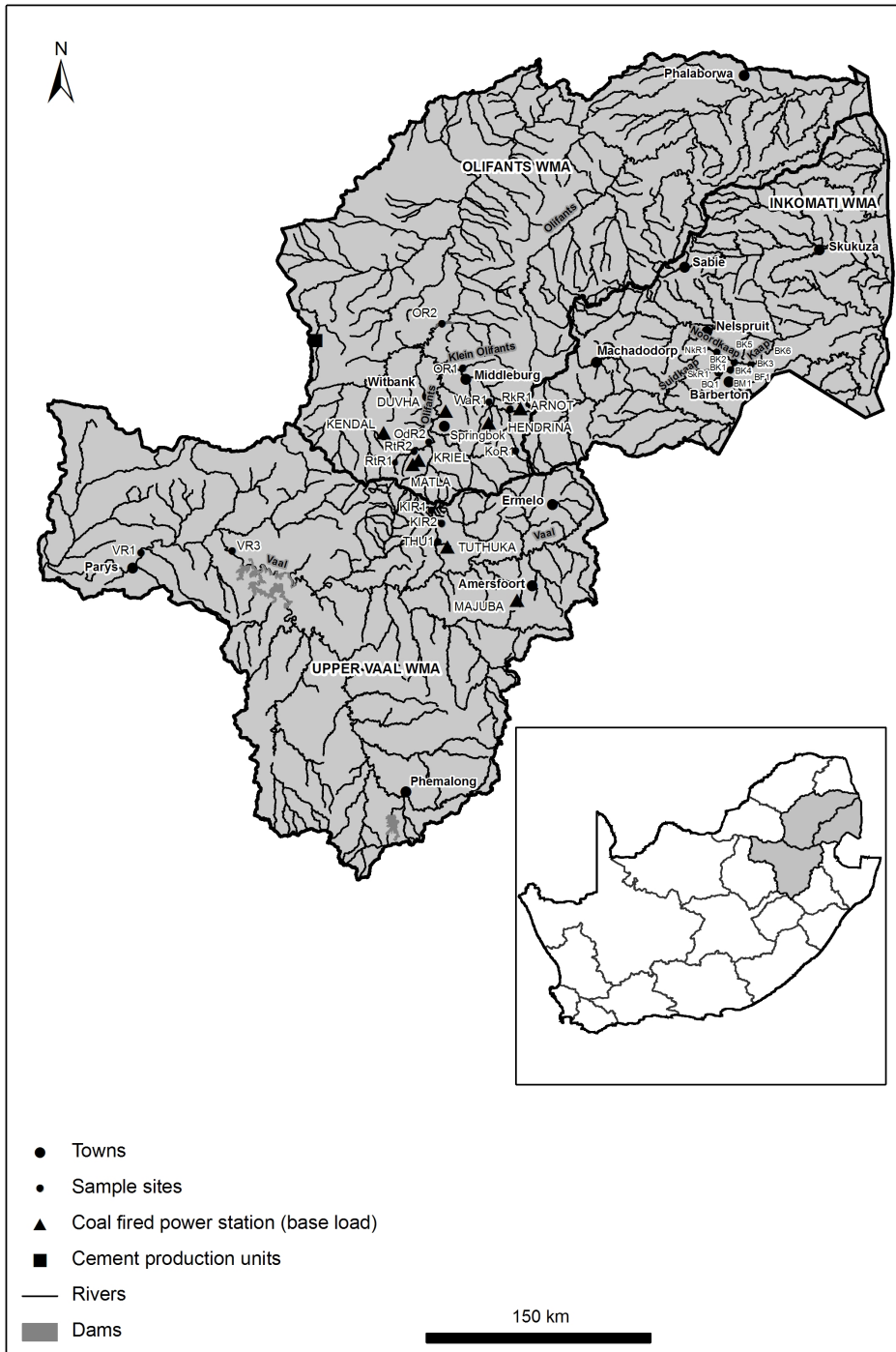


Fig.1

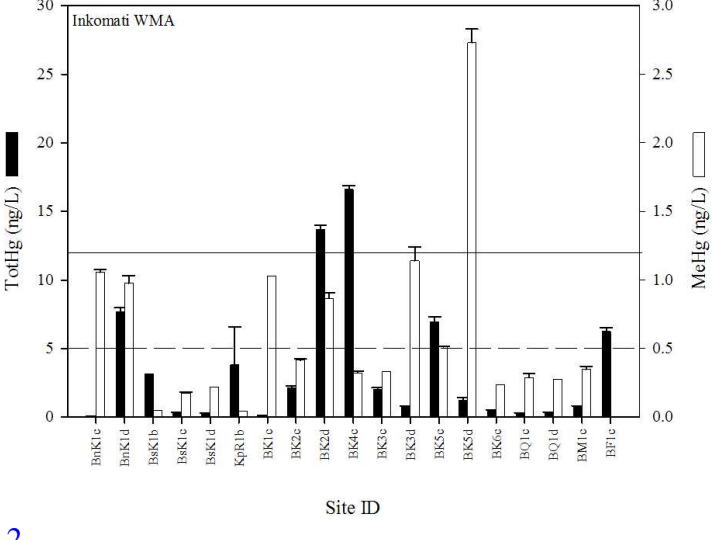
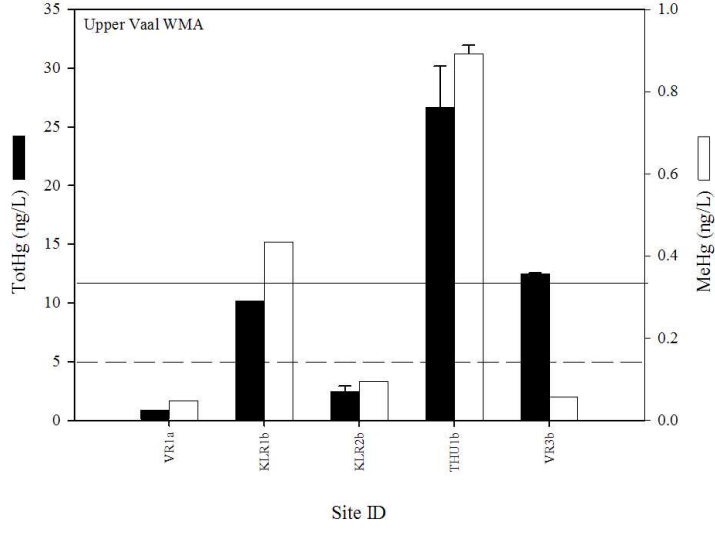
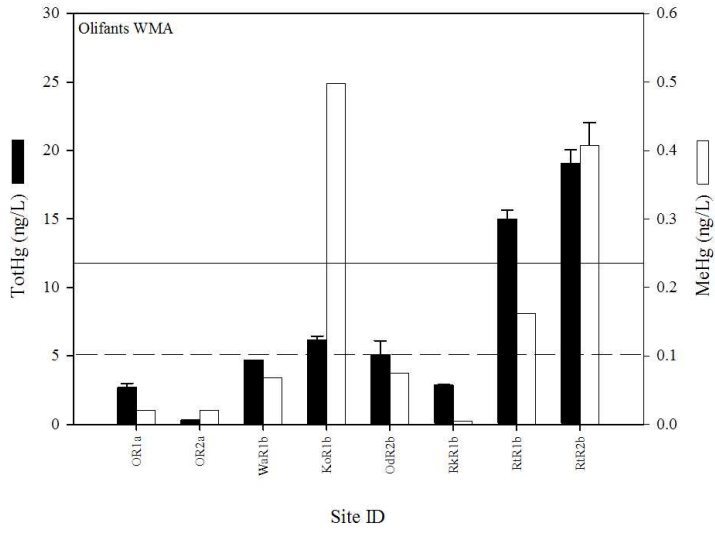


Fig.2

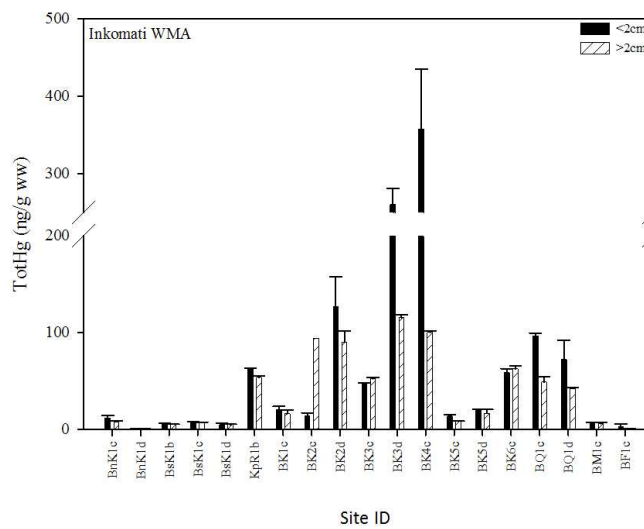
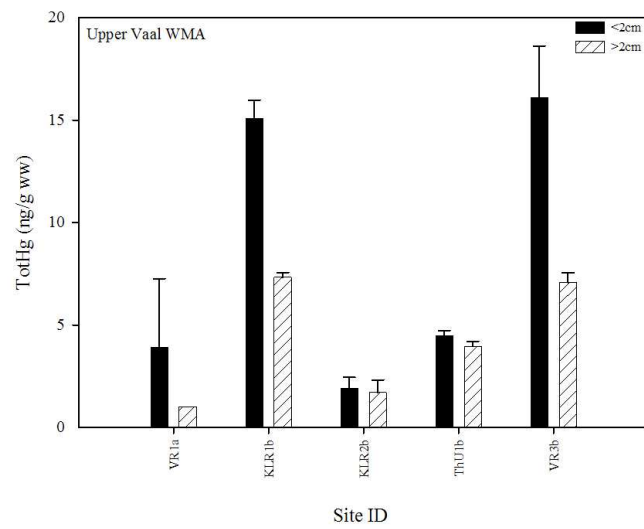
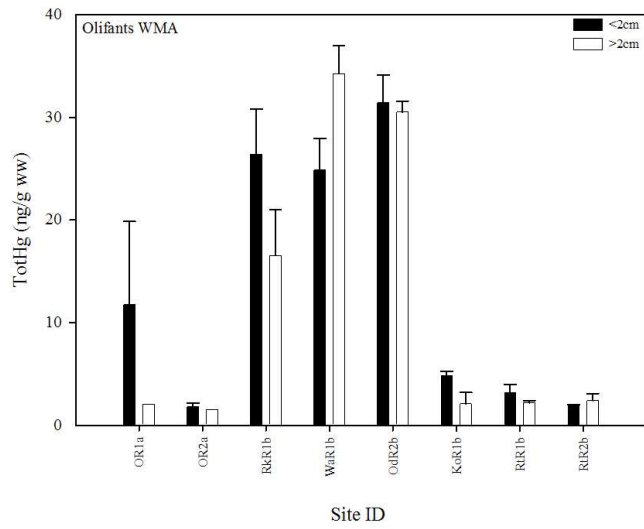


Fig.3

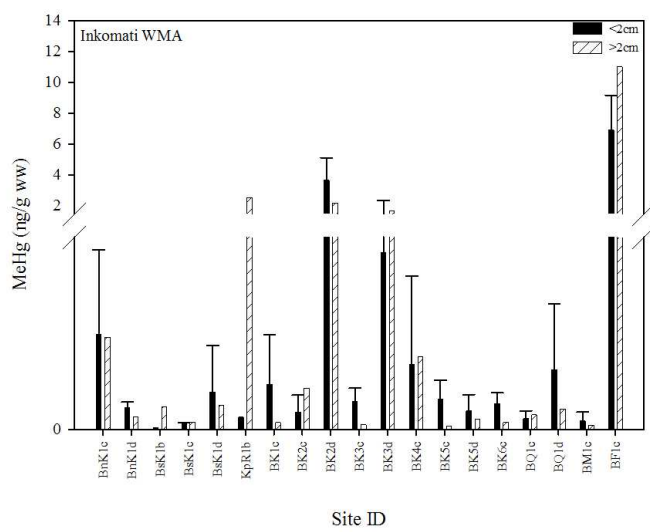
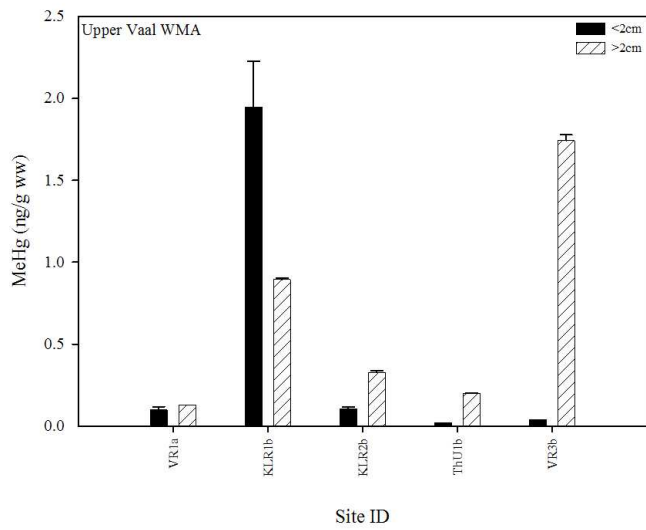
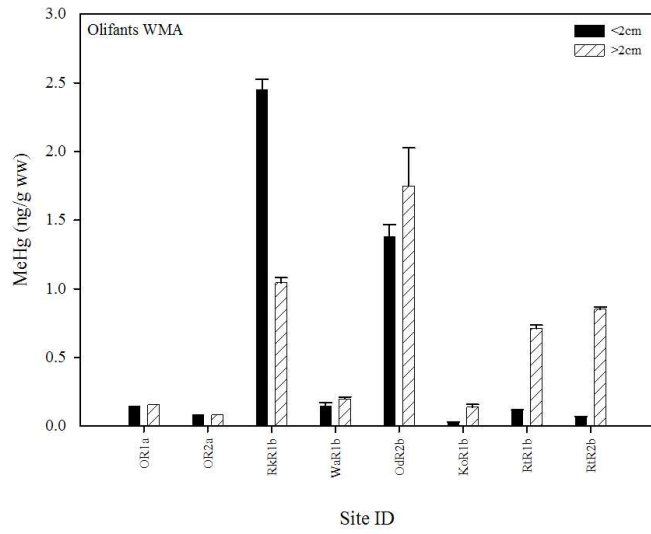


Fig.4

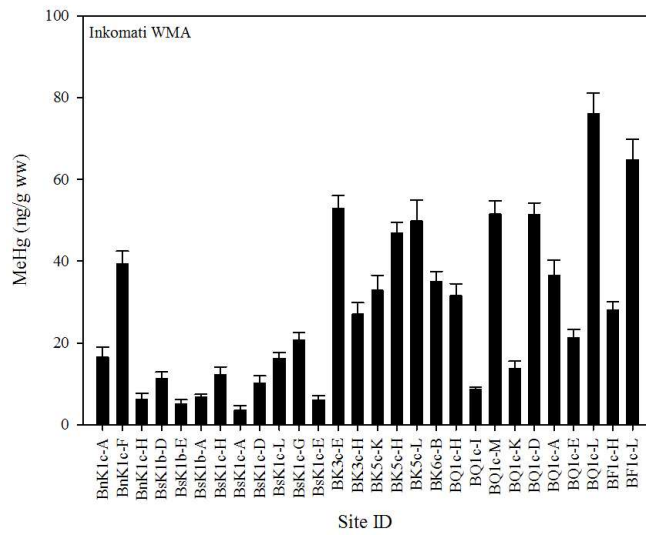
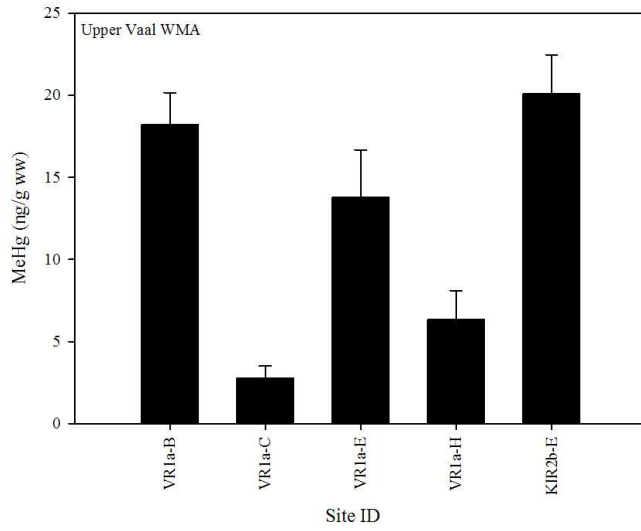
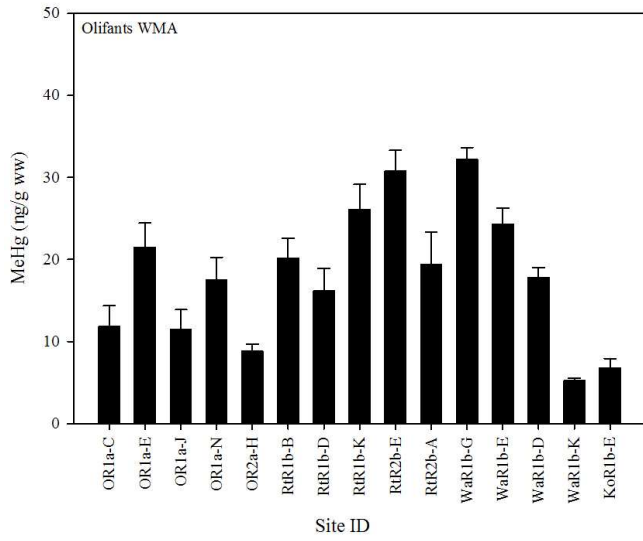


Fig.5

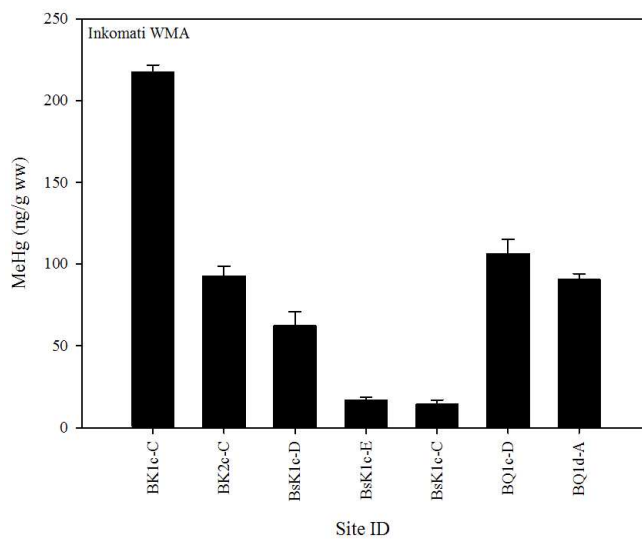
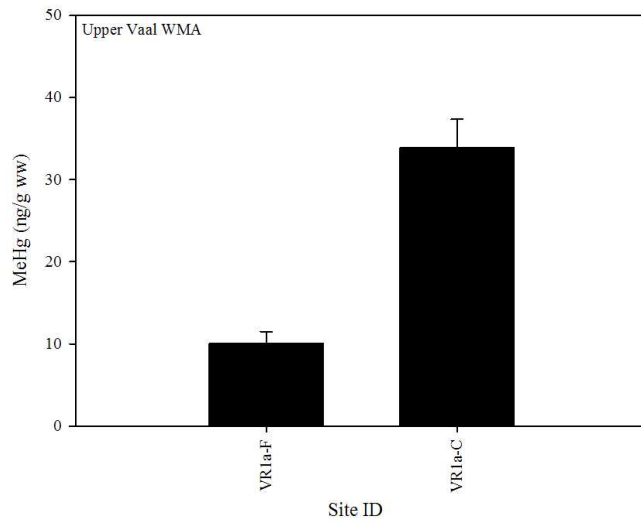
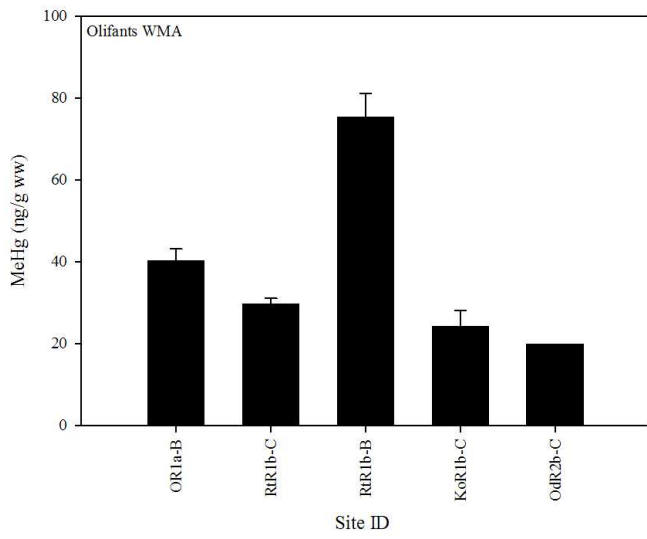


Fig.6

Table 1. Sampling sites for assessing mercury concentrations in water resources, sampling frequency and major anthropogenic mercury source.

Site ID	Site description	WMA	Major mercury source	Date(s) sampled
OR1	Olifants River – Middelburg	Olifants	Coal-fired power stations	June 07(a)
OR2	Olifants River – Loskop Dam	Olifants	Coal-fired power stations	June 07(a)
RkR1	Rietkuil River – Downstream of Arnot Power Station	Olifants	Coal-fired power stations	Nov 07(b)
WaR1	Woes-Alleen River – Upstream of Hendrina Power Station	Olifants	Coal-fired power stations	Nov 07(b)
OdR1	Olifants River – Downstream of Duvha Power Station	Olifants	Coal-fired power stations	Nov 07(b)
KoR1	Klein Olifants River – Downstream of Hendrina Power Station	Olifants	Coal-fired power stations	Nov 07(b)
RtR1	Riet River – Upstream of Kriel Colliery	Olifants	Coal-fired power stations	Nov 07(b)
RtR2	Riet River – Downstream of Kriel Colliery	Olifants	Coal-fired power stations	Nov 07(b)
VR1	Vaal River – Parys	Upper Vaal	Coal-fired power stations	June 07(a)
KIR1	Klip River	Upper Vaal	Coal-fired power stations	Nov 07(b)
KIR2	Klip River – Upstream of Sasol	Upper Vaal	Coal-fired power stations	Nov 07(b)
ThU1	Vaal River – at Thutuka Power Station	Upper Vaal	Coal-fired power stations	Nov 07(b)
VR3	Vaal River – Downstream of Lethabo Power Station	Upper Vaal	Coal-fired power stations	Nov 07(b)
BnK1	Noordkaap River – in nature reserve	Inkomati	Artisanal gold mining	July 08(c)

BsK1	Suidkaap River	Inkomati	Artisanal gold mining	Nov 07(b); July 08(c); Oct 08(d)
KpR1	Kaap River	Inkomati	Artisanal gold mining	Nov 07(b)
BK1	Kaap River – Downstream of Barberton	Inkomati	Artisanal gold mining	July 08(c)
BK2	Kaap River – at New Consort Mine	Inkomati	Artisanal gold mining	July 08(c); Oct 08(d)
BK3	Kaap River – at Eureka	Inkomati	Artisanal gold mining	July 08(c); Oct 08(d)
BK4	Kaap River – Downstream of New Consort Mine	Inkomati	Artisanal gold mining	July 08(c)
BK5	Kaap River – at Scotia Talc Mine	Inkomati	Artisanal gold mining	July 08(c); Oct 08(d)
BK6	Kaap River – Boulders turnoff at R38 and N4 crossing	Inkomati	Artisanal gold mining	July 08(c)
BQ1	Queens River – Barberton at R38	Inkomati	Artisanal gold mining	July 08(c); Oct 08(d)
BM1	Kaap River – at Barberton Mine Creek	Inkomati	Artisanal gold mining	July 08(c)
BF1	Kaap River – Figtree Creek	Inkomati	Artisanal gold mining	July 08(c)

Table 2. List of biota collected at the sampling sites in this study, species code, species name and diet.

ID	Species Name	Common Name	Diet
Invertebrates			
A	<i>Aeshnidae</i>	Dragonfly	Insects; small fish
B	<i>Atyidae</i>	Freshwater shrimp	aquatic plants; invertebrates (benthic)
C	<i>Baetidae</i>	Small minnow mayfly	aquatic plants
D	<i>Balastomatidae</i>	Giant water bug	crustaceans, fish, amphibians

E	<i>Coenagrionidae</i>	Damselfly	daphnia, mosquito larvae
F	<i>Corixidae</i>	Water boatmen	insects, small fish, tadpoles
G	<i>Dytiscidae</i>	Predacious diving beetle	tadpoles; glassworms; small invertebrates
H	<i>Gomphidae</i>	Dragonfly	daphnia, mosquito larvae, small aquatic organisms
I	<i>Gyrinidae</i>	Whirligig beetle	benthic invertebrates
J	<i>Heptageniidae</i>	Flat-headed mayfly	small invertebrates
K	<i>Hydropsyches</i>	Caseless caddishfly	small invertebrates
L	<i>Libellulidae</i>	Dragonfly	daphnia, mosquito larvae, small aquatic organisms
M	<i>Naucoridae</i>	Creeping water bug	insects; snails
N	<i>Oligochaeta</i>	Aquatic earthworm	detritus
O	<i>Perlidae</i>	Stonefly	aquatic invertebrates
P	<i>Simulidae</i>	Blackfly	organic matter

Fish

A	<i>Amphilius spp.</i>	Catfish	benthic invertebrates
B	<i>Gambusia affinis</i>	Mosquitofish	Small aquatic organisms
C	<i>Labeobarbus spp.</i>	Yellowfish	detritus; invertebrates
D	<i>Micropterus dolomieu</i>	Small-mouthed bass	fish, crabs
E	<i>Tilapia sarrmanii</i>	Banded tilapia	aquatic plants, small invertebrates
