

# Mercury concentrations at a historically mercury-contaminated site in KwaZulu-Natal (South Africa)

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## Abstract

**Introduction** A mercury (Hg) processing plant previously operating in KwaZulu-Natal Province (South Africa) discharged Hg waste into a nearby river system causing widespread contamination since the 1980s. Although the processing plant ceased operation in the 1990s, Hg contamination (due to residual Hg) remains significant. Previous studies in the area since the plant's closure have found elevated Hg concentrations in fish, and that these concentrations were as a direct consequence of widespread contamination of the Hg processing plant operations conducted between the 1980s and 1990s.

**Objectives** This study aimed at investigating the impacts of residual Hg almost 20 years after the plant's closure.

**Methods** Water, sediment and biota (invertebrates and fish) were collected in water resources in the vicinity of the processing plant to determine the Hg concentrations in these compartments, as a proxy for assessing the extent to which residual Hg that is reintroduced to the water column becomes bioavailable to biota. For water and sediment samples, higher total mercury (TotHg) and methylmercury (MeHg) concentrations were measured at sampling sites immediately downstream of the Hg processing plant when compared to the upstream sites, while concentrations decreased with distance from the plant. Fish MeHg concentrations measured just below the US EPA guideline for Hg in fish muscle tissue.

**Results** The results show that the historically Hg-contaminated river system is a potential Hg pollution source due to the residual Hg present in sediment. Any dredging of sediment as a form of remediation in the Mngceweni River is not recommended; however, a Hg monitoring programme is recommended for assessing the bioavailability of resuspended Hg from sediment.

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## Abbreviations

CVAFS	Cold vapour atomic fluorescence spectrometry
DOC	Dissolved organic carbon
DO	Dissolved oxygen
Hg	Mercury
TotHg	Total mercury
MeHg	Methylmercury
OM	Organic matter
US EPA	United States Environmental Protection Agency

## 1 Introduction

Mercury (Hg) contamination has become a global concern due to its impacts on ecosystems and human health. When present in the aquatic environment, Hg has a high affinity for suspended particles, which promotes its removal from the adjacent water column and settlement in sediment (Lee et al. 1998). Inorganic Hg ( $\text{Hg}^{2+}$ ) is methylated to its more toxic organic form, methylmercury (MeHg) under favourable environmental conditions, where it is primarily controlled by pH, temperature and presence of organic matter (OM) (Scheuhammer and Graham 1999; Gilbertson and Carpenter 2004). Sediments are the primary reservoir where such methylation occurs (Benoit et al. 1999), and any Hg that is sequestered in sediments can be remobilized and reintroduced to the surrounding water column (Covelli et al. 1999). MeHg bioaccumulates in aquatic organisms (Boudou and Ribeyre 1997; Mason et al. 2000; UNEP 2002) and it is well documented that it also biomagnifies along the aquatic food chain (Cabana et al. 1994).

Historically contaminated Hg sites are important for assessing the bioavailability of resuspended Hg to aquatic organisms. Such assessments can provide important information to decision-makers (e.g. government) as to the need for further remediation and/or Hg monitoring programmes at such sites. In South Africa, the discharge of Hg-containing effluent into the Mngceweni River (KwaZulu-Natal) during the 1990s has resulted in an area that is now considered “historically contaminated with Hg”. Studies undertaken immediately after the incident reported elevated Hg concentrations in sediment and fish caught in the vicinity (Johnston et al. 1991; Oosthuizen and Ehrlich 2001; Barrat and Combrink 2002). Papu-Zamxaka et al. (2010), recently measured Hg concentrations in sediment, fish and human hair samples. Since Hg concentrations in the latter study were measured in only two compartments of the aquatic food chain, a more in-depth study of various other compartments of the Mngceweni River is required.

Total Hg (TotHg) and MeHg concentrations in water, sediment, invertebrates and fish were measured and used as a proxy for determining the bioavailability of resuspended Hg in the aquatic food chain of the Mngceweni River. These compartments were assessed almost 20 years after the incident and the plant’s closure, and the data was used to determine whether future Hg remediation actions or Hg monitoring programmes are required in the Mngceweni River. This study also provides valuable information as to whether historically Hg-contaminated sites should undergo further Hg remediation or remain in its existing condition with a Hg monitoring regime in place.

## 2 Materials and methods

### 2.1 Site description

The Umgeni River and its tributary, viz. Mngceweni River, is located ca. 23 km from Pietermaritzburg, and ca. 56 km from Durban in the KwaZulu-Natal Province of South Africa. The Inanda Dam, located ca. 35 km downstream of the Hg processing plant at Cato Ridge, is the primary source of drinking water of the city of Durban (Oosthuizen and Ehrlich 2001) and is a location for subsistence fishing for residents in the Valley of a Thousand Hills in the area. The Nagle Dam, on the other hand, is located ca. 20 km upstream of the plant.

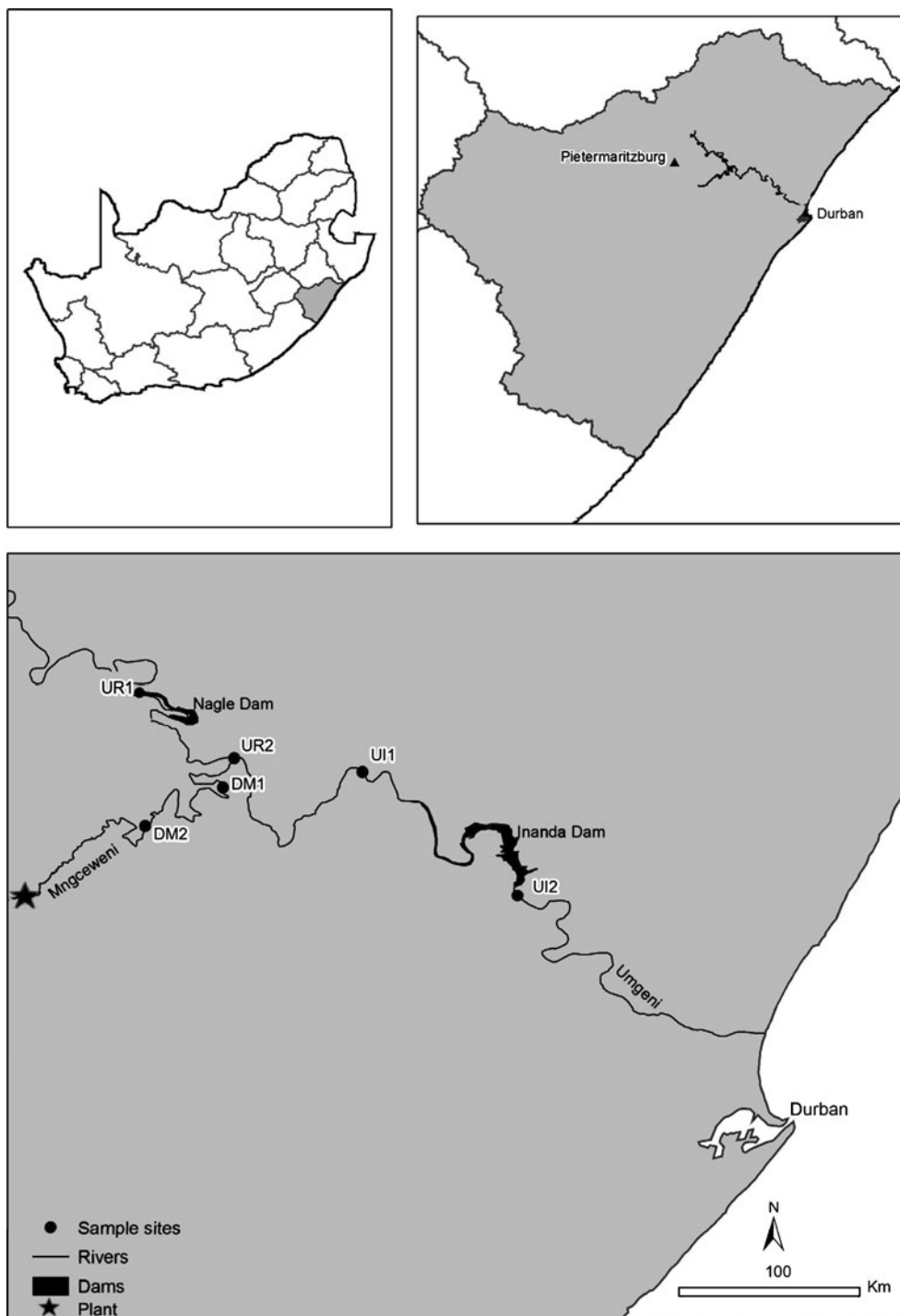
Sampling sites were located on the Mngceweni River (immediately below the processing plant that had released Hg effluent into the river during the 1990s) and on the Umgeni River (upstream and downstream of the Nagle and Inanda dams) (Fig. 1).

Water, sediment and biota were collected during the dry season in June 2007 and July 2008, as well as during the wet season in December 2008. The letters “a, b and c” at the end of each site ID in Figs. 2, 3, 4 and 5 denote the sampling period, viz. June 2007 (a), July 2008 (b) and December 2008 (c).

### 2.2 Sample collection

Standard protocols for collecting samples for TotHg and MeHg analysis were employed throughout sample collection (US EPA 1996; Mason and Sullivan 1998). Surface water samples for TotHg and MeHg analysis were collected in acid-cleaned Teflon<sup>®</sup> bottles, using ultra-clean sampling protocols (Mason and Sullivan, 1994). Additional water samples were collected for ancillary measurements of nutrients ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ) and dissolved organic carbon (DOC). Ancillary water parameters (viz. pH, temperature, dissolved oxygen—DO, electrical conductivity—EC, total dissolved solids—TDS and turbidity) were measured on site. These provided an account of the present ecological state at each site. Temperature ( $^{\circ}\text{C}$ ), EC (mS/cm), TDS (ppt) and pH were measured using a Hanna Instrument Model 991302 portable sensor; while DO (ppm) was measured using a Hanna Instrument Model 9143 portable sensor. Surface sediment cores (up to 3 cm in depth) were extruded using an acid-cleaned polypropylene cylindrical corer and sectioned at 1-cm intervals, after which each section was individually transferred into clean 50-mL centrifuge tubes. Invertebrates and fish (Table 1) were collected using a 1-mm meshed net. All samples were double-bagged and stored on ice while transported to the Mercury Laboratory at Council of Scientific and Industrial Research (CSIR) (Stellenbosch, South Africa), where they were stored frozen until analysed.

**Fig. 1** Location of sample sites on the Umgeni River (up and downstream of the Nagle and Inanda dams) and Mngceweni River (KwaZulu-Natal, South Africa)



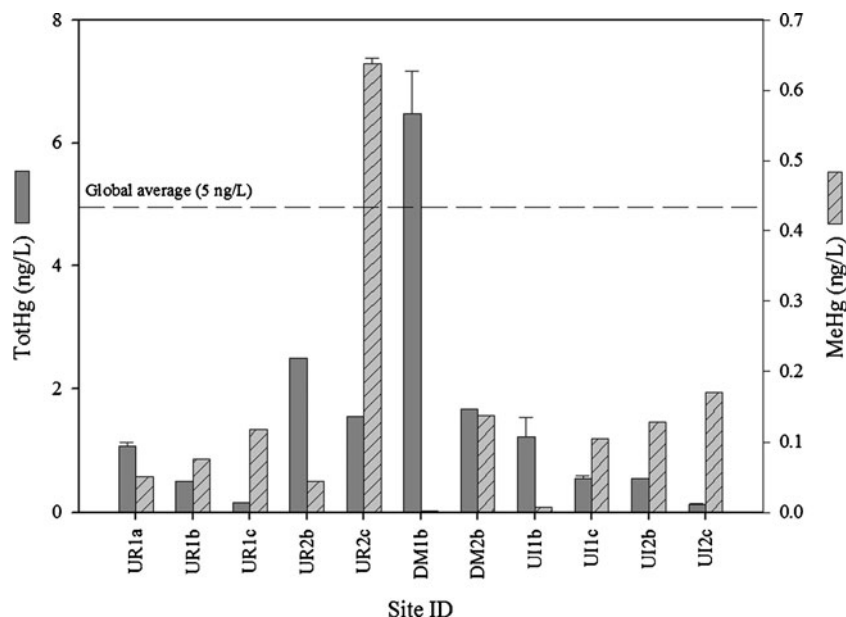
### 2.3 Analytical techniques

The determination of TotHg in water followed United States Environmental Protection Agency (US EPA) method 1631 (US EPA, 2002) which included the oxidation of Hg with bromine monochloride, pre-reduction with hydroxylamine hydrochloride and further reduction with stannous chloride. Quantification of TotHg was performed by cold vapour atomic fluorescence spectrometry (CVAFS) following gold

amalgamation trapping (Bloom and Fitzgerald 1988). The TotHg concentrations in solid samples, i.e. sediment were measured using a DMA-80 Solid Phase Direct Mercury Analyser (Milestone Inc., Montoe, CT, USA). Briefly, ca. 0.1–1 g homogenized wet sample was weighed into a quartz boat (Boylan et al. 2001) and placed on the loading tray of the DMA-80 Direct Mercury Analyser.

The analytical methods for the determination of MeHg are well documented (Mason and Lawrence 1999; Leaner

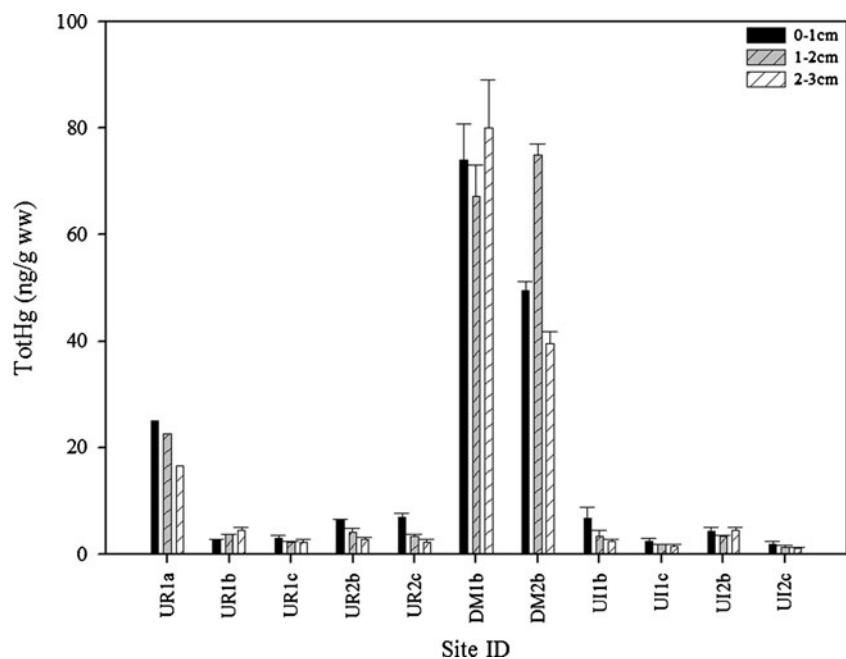
**Fig. 2** Total mercury (TotHg) and methylmercury (MeHg) concentrations in surface water collected on the Umgeni River (UR), Mngceweni River (DM) and Inanda Dam (UI) (*a* = June 2007; *b* = July 2008; *c* = December 2008)



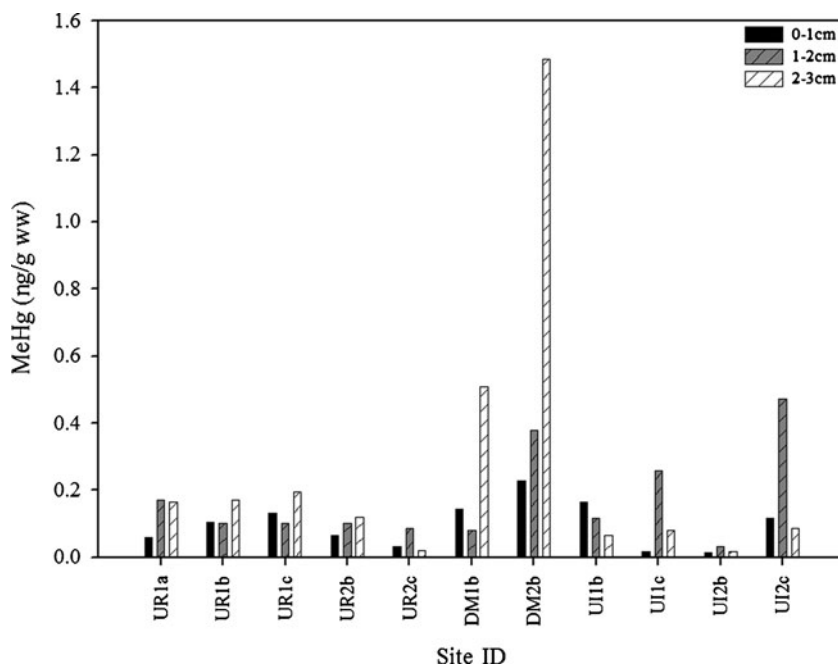
and Mason 2002; Leaner and Mason 2004) and followed the US EPA method 1630 (US EPA 2001a). In brief, water and sediment samples were distilled in 1 mL of 50% H<sub>2</sub>SO<sub>4</sub> and 0.5 mL 20% KCl. The distillate was ethylated with sodium tetraethyl borate, which converts MeHg to volatile methylethylmercury. Following ethylation, all samples were purged through a Tenax<sup>®</sup> trap, separated by isothermal gas chromatography and followed by quantification using CVAFS (Mason et al. 2006). The percentage organic content of each sediment layer was determined as loss on ignition (LOI) at approximately 550°C overnight (Kim et al. 2006)

Due to sample mass limitations in the biota collected, only MeHg concentrations were measured in the invertebrates and fish. Since MeHg is the most toxic and predominant form (~90%) of Hg in tissues of invertebrates and fish (Leaner and Mason 2004), MeHg concentrations measured would also provide a reasonable assessment of the Hg concentrations in invertebrates and fish collected. Therefore for MeHg concentrations in biota, all homogenized samples were digested with 25% KOH-methanol and placed in a 65°C oven for 24 h. Sample analysis and quantification of MeHg followed methods similar to those described above.

**Fig. 3** Total mercury (TotHg) concentrations in surface sediment collected on the Umgeni River (UR), Mngceweni River (DM) and Inanda Dam (UI) (*a* = June 2007; *b* = July 2008; *c* = December 2008)



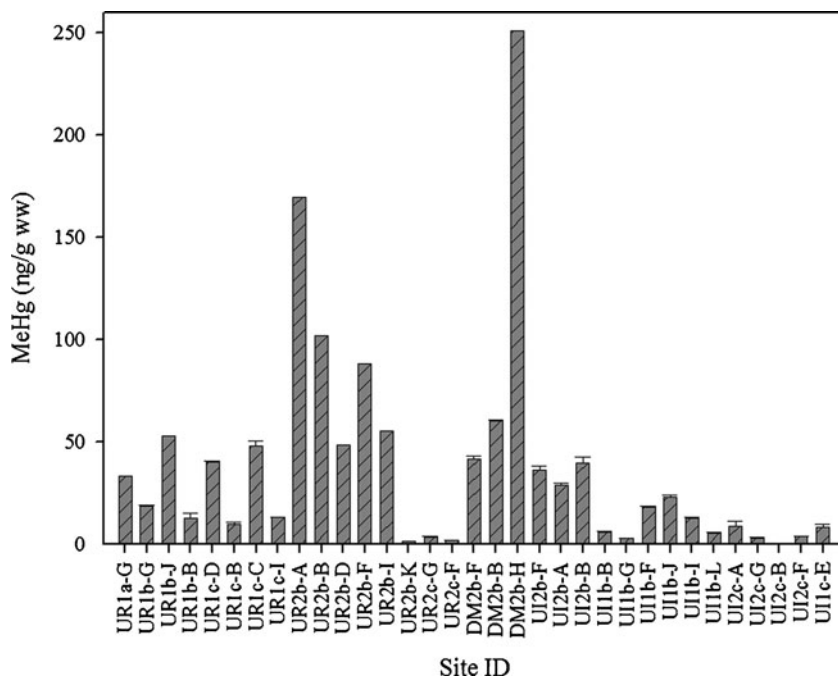
**Fig. 4** Methylmercury (MeHg) concentrations in surface sediment collected on the Umgeni River (UR), Mngceweni River (DM) and Inanda Dam (UI) (*a* = June 2007; *b* = July 2008; *c* = December 2008)



Analytical quality assurance/quality control (QA/QC) criteria were maintained using a standard calibration curve, having an  $r^2$  of at least 0.998, achieved daily. Matrix spikes and matrix spike duplicates, 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 and yielded no significant difference. The results obtained

for the SRM's analyses were within the certified ranges: PACS-2 Marine Sediment SRM ( $3.04 \pm 0.20$  mg/kg) National Research Council, Canada; IAEA-405 Trace Elements and Methylmercury in Estuarine Sediment SRM ( $0.00549 \pm 0.00053$  mg/kg) (International Atomic Energy Agency, Austria); TORT-2 Lobster Hepatopancreas Marine SRM ( $0.27 \pm 0.06$  mg/kg) (National Research Council, Canada) for biota. Duplicate and triplicate samples analysed yielded marginal error of <10%.

**Fig. 5** Methylmercury (MeHg) concentrations in invertebrates collected on the Umgeni River (UR), Mngceweni River (DM) and Inanda Dam (UI) (*a* = June 2007; *b* = July 2008; *c* = December 2008; *capital letters* denote species in Table 1)



**Table 1** List of biota species collected and respective diet of each of the species

ID	Species	Common name	Diet
Invertebrates			
A	<i>Aeshnidae</i>	Dragonfly	Insects; small fish
B	<i>Atyidae</i>	Freshwater shrimp	Aquatic plants; benthic invertebrates
C	<i>Belastomatidae</i>	Giant water bug	Crustaceans, fish, amphibians
D	<i>Coeangrionidae</i>	Damselfly	Daphnia; mosquito larvae
E	<i>Corixidae</i>	Water boatmen	Insects; small fish; tadpoles
F	<i>Gomphidae</i>	Dragonfly	Daphnia; small aquatic organisms
G	<i>Libellulidae</i>	Dragonfly	Daphnia; small aquatic organisms
H	<i>Nepidae</i>	Water scorpion	Invertebrates
I	<i>Naucoridae</i>	Creeping water bug	Insects; snails
J	<i>Notonectidae</i>	Backswimmer	Insects; small fish; tadpoles
K	<i>Thiaridae</i>	Cony snail	Aquatic plants
L	<i>Tabanidae</i>	Horsefly	Males: nectar/pollen; females: blood
Fish			
A	<i>Amphilius</i> spp	Catfish	Benthic invertebrates
B	<i>Labeobarbus natalensis</i>	Yellowfish	Detritus; invertebrates
C	<i>Micropterus dolomieu</i>	Small-mouthed bass	Fish; crabs
D	<i>Tilapia sparrmanii</i>	Banded tilapia	Aquatic plants; small invertebrates
E	<i>Tilapia rendalli</i>	Red-breasted tilapia	Aquatic plants; small invertebrates

## 2.4 Statistical analysis

The mean 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 Sigmaplot and MS Excel were not significantly different. A one-way analysis of variance, 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.

## 3 Results and discussion

### 3.1 Mercury in water

The concentrations of TotHg in surface water ranged from  $0.13 \pm 0.01$  to  $6.48 \pm 0.69$  ng/L (Fig. 2). All TotHg concentrations, except those at sampling site DM1b, were below the global average of 5.0 ng/L (Mason et al. 1994). All TotHg measurements were also below the South African water quality guidelines for aquatic ecosystems (40 ng/L; DWAF 1996), as well as the US EPA suggested value of 12 ng/L that could result in chronic effects in aquatic organisms (US EPA 1992). The TotHg concentrations measured were also much less than the concentrations

reported for river waters near Hg deposits, where the concentrations generally range between 500 and 100,000 ng/L (CRC Press 1997).

Background TotHg concentrations at sampling site UR1 (upstream of the Nagle Dam) during all three sampling phases (i.e. UR1a, UR1b and UR1c) were generally in the range of  $0.16$ – $1.09 \pm 0.05$  ng/L, whereas TotHg concentrations at sites DM1b and DM2b (immediately below the chemical-manufacturing plant) measured  $6.48 \pm 0.69$  and  $1.67$  ng/L, respectively. Generally, TotHg concentrations decreased with distance from the plant; an 11-fold decrease from  $6.48 \pm 0.69$  to  $0.55 \pm 0.01$  ng/L was observed. Sites located immediately downstream from the plant were statistically different ( $p < 0.05$ ) to sites located upstream and furthest downstream of the plant. The decrease in TotHg concentrations further away from the plant could likely be attributed to possible sedimentation of particulate Hg (Cardona-Marek et al. 2007) or pollution dilution effects (Turner and Lindberg 1978; Synder and Hendricks 1997), similar to what has been observed in other historically Hg-contaminated sites (Berzas Nevado et al. 2003).

Seasonal trends were also observed at sampling sites UR1, UR2, UI1 and UI2, where TotHg concentrations generally showed a 50% reduction in the wet compared to the dry season, which indicates dilution effects (Turner and Lindberg 1978; Synder and Hendricks 1997).

Aqueous MeHg concentrations ranged from below the detection limit ( $< 0.02$  ng/L) to  $0.64 \pm 0.01$  ng/L, with a gradual increase in MeHg concentrations being observed in all sites sampled during 2007 and 2008 (Fig. 2). In contrast to TotHg,

MeHg concentrations increased more than 20-fold during the wet season (December 2008) and could likely be attributed to the resuspension of MeHg (from sediments) into the water column (Kim 2004). The highest MeHg concentration was measured at sampling site UR2 (below the Nagle Dam) during the dry season in December 2008 (i.e. UR2c). Overall, the increase in MeHg concentrations but decrease in TotHg concentrations suggests that methylation and resuspension of residual Hg are still prevalent in the system.

Since OM forms strong complexes with Hg, the extent to which Hg binds with DOC determines the efficiency of downstream transportation of Hg. DOC affects Hg speciation, solubility, mobility and toxicity (Ravichandran 2004), and controls the temporal TotHg distribution in aquatic systems. The extent of this influence is site specific and also depends on the season (Babiarz et al. 1998). The concentrations of DOC ranged from 3.10 to 14.81 mg/L. A positive relationship was observed for TotHg ( $r^2=0.58$ ) and MeHg ( $r^2=0.68$ ) concentrations correlated to DOC at each site during the wet season only. This suggests that during the wet season, Hg was organically complexed similar to what has been reported in other studies (Watras et al. 1998). This can likely be attributed to changes in freshwater flow and associated runoff processes, including flocculation of DOC as observed by Conaway et al. (2003).

### 3.2 Mercury in sediment

Total Hg concentrations in surface sediment ranged from  $1.82\pm 0.53$  to  $74.03\pm 6.71$  ng/g wet weight (ww) at 0–1 cm depths,  $1.38\pm 0.23$  to  $75.00\pm 2.10$  ng/g ww at 1–2 cm depths and  $1.04\pm 0.23$  to  $80.08\pm 8.97$  ng/g ww at 2–3 cm depths (Fig. 3). All TotHg concentrations were below the US EPA guideline of 200 ng/g for sediment (US EPA 2000a), and were below the mean TotHg concentrations previously reported by Barrat and Combrink (2002) for the same area. The TotHg concentrations were generally highest at DM1 and DM2—both sites are located immediately downstream of the chemical-manufacturing plant at Cato Ridge. Significant differences ( $p<0.05$ ) in TotHg concentrations were observed at sites located immediately downstream of the plant (Fig. 4). Furthermore, TotHg concentrations generally decreased (up to 90%) from June 2007 to July 2008 (Fig. 3) in all sediment layers.

Seasonally, higher TotHg concentrations were generally measured during the dry season (June 2007 and July 2008) when compared to the wet season (December 2008), although no statistical significant difference was observed. While most sites showed a decrease in TotHg concentrations with increase in depth (i.e. [TotHg] 1 cm in depth > [TotHg] 2 cm in depth > [TotHg] 3 cm depth), no trend (increasing or decreasing) was observed in sediment organic content.

The overall low TotHg concentrations measured at sampling sites UR1, UI1 and UI2 are expected. The Nagle Dam site (UR2) is located above the confluence of the Mngceweni River and Umgeni River, while the other two sites (UI1 and UI2) are located some distance from the Mngceweni River. Any residual Hg from the historical Hg contamination into the Mngceweni River would be trapped in sediment closest to the chemical-manufacturing plant, as evidenced by the higher TotHg concentrations measured at sampling sites DM1 and DM2 (Fig. 3).

The MeHg concentrations in surface sediments were relatively low and ranged between  $<0.02$  and  $0.23\pm 0.05$  ng/g ww at 0–1 cm in depth,  $0.03$  to  $0.47\pm 0.04$  ng/g ww at 1–2 cm in depth, and  $0.02$ – $1.49\pm 0.02$  ng/g ww at 2–3 cm in depth (Fig. 4). Despite the relatively low sedimentary MeHg concentrations, it is significant since MeHg is capable of passing biological membranes (Kim 2004). An increase in MeHg concentrations were generally observed with increase in depth (i.e. [MeHg] 1 cm in depth > [MeHg] 2 cm in depth > [MeHg] 3 cm in depth). For most sites, MeHg concentrations increased from the dry (June 2007 and July 2008) to wet (December 2008) seasons. This suggests enhanced methylation due to resuspension of bottom sediment during the wet season, as reported previously by others (Heyes et al. 2004; Kim 2004). The highest MeHg concentration was measured at sampling site DM2 ( $1.49\pm 0.02$  ng/g ww) which is located on the Mngceweni River below the chemical-manufacturing plant. Trends in MeHg and TotHg concentrations in sediment were similar, and on average, the fraction of TotHg that occurred as MeHg was ca. 1.86%, 6.00% and 3.57%, for the respective sediment depths, i.e. 0–1, 1–2, and 2–3 cm.

Several studies have demonstrated the importance of TotHg concentration (Benoit et al. 2002; Conway et al. 2003) and sediment organic content (LOI) (Warner et al. 2005) in controlling methylation rate. Overall, MeHg concentrations were positively correlated with sediment OM ( $r^2=0.71$ , at 0–1 cm in depth;  $r^2=0.53$ , at 1–2 cm in depth;  $r^2=0.59$ , at 2–3 cm in depth). This suggests that MeHg concentrations were not primarily controlled by sediment OM. Overall, however, sediments in this region may be continuously eroded and remobilized, and consequently serve as a Hg source to sites downstream.

### 3.3 Mercury in biota

The bioavailability of Hg is dependent on several factors including the binding strength of Hg to sediments (Fan et al. 2002) and the ability of the organism to metabolize contaminants (Eggleton and Thomas, 2004). Thus, weakly adsorbed contaminants (such as those in the aquatic phase) are more bioavailable for uptake by biota than complex mineral-bound contaminants.

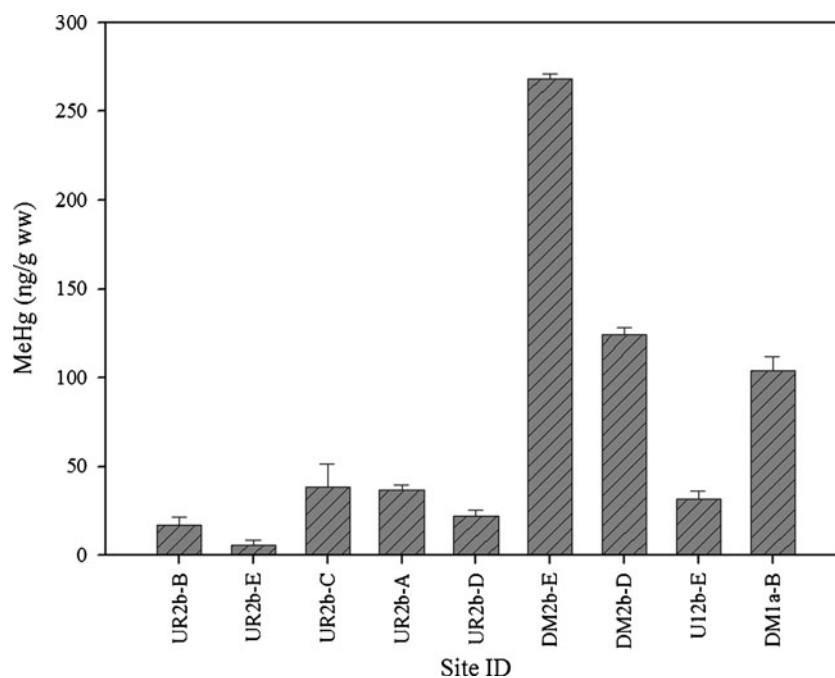
Invertebrate species collected in this study are mostly benthic invertebrates that live at the sediment–water interface or in sediments (Table 1). Generally, such invertebrates contain high MeHg concentrations (Mason and Lawrence 1999). Since sediments are the main repository for Hg in aquatic ecosystems, benthic invertebrates also provide a mechanism for Hg transport along the aquatic food chain.

In this study, MeHg concentrations in invertebrates extended over four orders of magnitude, and generally ranged between 0.16 to 251.19 ng/g ww (Fig. 5). The highest MeHg concentration (251.19 ng/g ww) was recorded in water scorpions at sampling site DM2 (DM2b) followed by MeHg concentrations (187.73 ng/g ww) measured in dragonflies collected at UR2 (UR2b). This is expected since the highest Hg concentration was measured in sediment collected at DM2. Thus, the MeHg concentrations in benthic invertebrates observed at this site could be attributed to the uptake of residual (sediment-bound) Hg present in the system (Lawrence and Mason, 2001). The ability of invertebrates to accumulate Hg from associated sediments were assessed using the biota–sediment accumulation factor (BSAF)—defined as the concentration of Hg (i.e. MeHg) in the organism relative to the concentration of Hg (i.e. MeHg) in the sediment. An average BSAF of 7.33 was obtained. A BSAF >1 indicates that invertebrates were able to accumulate Hg from sediment (Ruelas-Inzunza et al. 2009).

The MeHg concentrations in fish species ranged from 6.00±2.40 to 268.47±2.82 ng/g ww (Fig. 6). All MeHg concentrations were well below the US EPA’s guideline for Hg in

fish muscle tissue (300 ng/g ww; US EPA, 2001b) as well as the World Health Organization guideline level of 500 ng/g (WHO 1990). However, MeHg concentrations measured in banded tilapia collected at sampling site DM2 (DM2b) were just below this guideline (268.47±2.82 ng/g ww; average fork tail length=13.46 cm). The MeHg concentrations in fish collected in the Umgeni River was 79% and 86% lower than MeHg concentrations reported in fish collected by Barrat and Combrink (2002) and Papu-Zamxaka et al. (2010), respectively. The concentrations obtained in this study are, however, based on a limited number of samples (*n*=3) and on different fish species. It is generally acknowledged that diet is the main route of Hg exposure to aquatic organisms. Thus, the high concentrations measured in banded tilapia (an omnivorous fish species feeding on small aquatic invertebrates) could likely be attributed to the high concentrations recorded in the dominant species of invertebrates at DM2. However, when analysing the statistical significance of MeHg concentrations taking diets into account, no significant difference was observed. Yet, statistical significant differences were observed in fish MeHg concentrations between fish collected at sites located downstream of the plant and immediately downstream of the plant. This observation identifies those sites situated immediately downstream of the plant as being a potential Hg “hotspot”. The high MeHg levels measured in sediment at DM2 could explain the fish MeHg concentrations also measured at DM2 illustrating that contaminated sediments are a continual source of Hg to biota, similar to what has been observed in other historically Hg-contaminated sites (Berzas Nevado et al. 2003). Rural communities in the area rely heavily on fish obtained from the river system and may

**Fig. 6** Methylmercury (MeHg) concentrations in fish collected on the Umgeni River (UR), Mngceweni River (DM) and Inanda Dam (UI) (*a* = June 2007; *b* = July 2008; *c* = December 2008; *capital letters* denote species in Table 1)





consume fish on a daily basis (Barrat and Combrink 2002). Based on this and the US EPA's fish consumption limits for Hg concentrations in the edible portion of fish (US EPA, 2000b), the consumption of fish in the downstream reaches of the Mngceweni River should be cautious.

#### 4 Concluding remarks

Several studies since the 1990s have measured Hg concentrations in the Mngceweni River near Cato Ridge (Johnston et al. 1991; Oosthuizen and Ehrlich 2001; Barrat and Combrink 2002), with the most recent study (Papu-Zamxaka et al. 2010) having measured only sediment and fish TotHg and MeHg concentrations. The MeHg concentrations of fish in this study were significantly lower than previously reported by Barrat and Combrink (2002) and Papu-Zamxaka et al. (2010). This difference can likely be attributed to Hg bioavailability, and contamination uptake mechanisms and rates during the respective sampling periods, as found by others (e.g. Eggleton and Thomas 2004). Regardless, this study provided a "snapshot" of the TotHg and MeHg concentrations in water, sediment, invertebrates and fish collected in the Umgeni and Mngceweni rivers of KwaZulu-Natal. The results suggest that the historically Hg-contaminated Mngceweni River still represents a potential Hg source to the surrounding area, similar to what has previously been observed at other historically Hg-contaminated sites in Europe (Berzas Nevado et al. 2003; Regnell et al. 2009), USA (Thomas et al. 2002) and South America (Pestana and Formoso 2003). The relatively high Hg concentrations measured in sediment and fish (particularly downstream of the plant) render this site a potential Hg "hotspot". Residual Hg remobilization from sediment appears to be minimal, although as expected, it is elevated during the wet season thereby making it more bioavailable for uptake in the aquatic food chain. Further remediation of Hg is not recommended for the Mngceweni River, as any dredging processes will resuspend Hg into the water column, as reported by others (Pestana and Formoso 2003; Bravo et al. 2009; Knott et al. 2009; Urban et al. 2010). However, a routine monitoring programme of sediment and fish is recommended, similar to what has been previously recommended for this area (Barrat and Combrink 2002; Papu-Zamxaka et al. 2010).

Although no risk assessment was undertaken in this study, there is some cause for concern concerning fish consumption by communities living near the Mngceweni River. Given the persistent and bioaccumulative nature of Hg, future research work is recommended to investigate both the environmental and human health implications of mercury exposure in this area, especially in light of the

recent Hg concentrations in hair samples collected in the same area (17% exceeded guideline values; Papu-Zamxaka et al. 2010).

The observations in this study are similar to what has been reported for other historically Hg-contaminated sites (Pestana and Formoso 2003; Pereira et al. 2009), and supports the notion that historically Hg-contaminated sites should remain in its existing condition, and that routine monitoring of water, sediment and biota can be used as a proxy for assessing the extent to which resuspended Hg that is reintroduced to the water column becomes bioavailable to biota. Such routine monitoring programmes are valuable for decision-making with regards to historically Hg-contaminated sites and its impacts to the aquatic environment.

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