Mercury contamination history of an estuarine floodplain reconstructed from a $^{210}$Pb-dated sediment core (Berg River, South Africa)

T.J. Kading a,*, R.P. Mason b, J.J. Leaner c

a Wesleyan University, Department of Earth and Environmental Studies, 265 Church Street Middletown, CT 06457, United States
b University of Connecticut, Department of Marine Science, 1080 Shennecossett Road, Groton, CT 06355, United States
c Council for Scientific and Industrial Research, 11 Jan Cilliers Street, Stellenbosch, Western Cape 7602, South Africa

ARTICLE INFO

Keywords:
$^{210}$Pb
Mercury
South Africa
Berg River

ABSTRACT

Mercury deposition histories have been scarcely documented in the southern hemisphere. A sediment core was collected from the ecologically important estuarine floodplain of the Berg River (South Africa). We establish the concentration of Hg in this $^{210}$Pb-dated sediment core at <50 ng g$^{-1}$ Hg throughout the core, but with 1.3 ng g$^{-1}$ methylmercury in surface sediments. The $^{210}$Pb dating of the core provides a first record of mercury deposition to the site and reveals the onset of enhanced mercury deposition in 1970. The ratio of methylmercury to total mercury is relatively high in these sediments when compared to other wetlands.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

The history of mercury deposition can be reconstructed using $^{210}$Pb – dating of accreting sediments from lakes, bogs, and salt marshes. Such studies have been carried out extensively in the northern hemisphere (Hornberger et al., 1999; Varekamp et al., 2003; Roos-Barracough and Shotyk, 2003), but few studies have focused on the history of mercury deposition in the southern hemisphere (Biester et al., 2002; Lamborg et al., 2002; Sanders et al., 2006) and still fewer in Africa (Ramlal et al., 2003). Wetland sediments have been widely used as records of mercury and other metal accumulation (Hung and Chmura, 2006; Varekamp et al., 2003; Spencer et al., 2003; Cochran et al., 1998). These sediments retain deposition histories because they serve as a sink for particle-reactive pollutants from both the atmosphere and the watershed (Spencer et al., 2003; Cochran et al., 1998). Anoxic conditions exist immediately below the sediment surface largely preventing bioturbation, and the thick roots of marsh grasses prevent physical sediment reworking, which limits post-deposition mobility of particle-bound elements (McCaffrey and Thomson, 1980). Furthermore, organic matter in these sediments binds and immobilizes metals like lead and mercury (Benoit et al., 1998). This study presents chemical data for a core from an estuarine floodplain wetland in western South Africa.

The Berg River estuary is a high-priority site for conservation efforts in South Africa, because it is inhabited by a wide variety of birds and serves as a nursery for commercially valuable fish species (Birdlife International, 2008). This ecosystem also suffers from decreased freshwater inputs due to increased agricultural water demand in the watershed (UNEP, 2006). Previous studies have documented elevated heavy metal concentrations (Jackson et al., 2007) and the onset of eutrophication (de Villiers, 2007), and have attributed these to anthropogenic processes. Mercury is a relatively ubiquitous heavy metal in coastal environments through atmospheric and point source inputs. The toxicity and biomagnification of methylated mercury in ecosystems is particularly detrimental to species high in the food chain, such as piscivorous birds and humans (Wiener et al., 2003). The regional usage history of the Berg River watershed suggests the presence of elevated mercury levels that have the potential to harm this ecologically important ecosystem in South Africa.

Mercury has several anthropogenic sources, such as coal and oil burning, production of steel and non ferrous metals, cement manufacturing, and municipal waste burning (Pacyna and Pacyna, 2002). Most energy production in South Africa relies on coal burning and the potential mercury releases from electricity generation and related activities is substantial (Dabrowski et al., 2008). The extraction and processing of gold and other mineral resources represent an additional source. Significant natural sources of mercury to the atmosphere are volcanism and geothermal activity (Nriagu and Becker, 2003), biomass burning (Brunke et al., 2001), and volatilization from minerals and soils (Poissant and Casimir, 1998). Local mercury sources to the study site include the now defunct Athlone coal fired power plant, situated 125 km to the south, and a large cement factory 13 km from the Berg River (Ninham Shand, 2006). The metropolis Cape Town, 140 km south of this site, could be a source of fuel burning related mercury emissions. The
watershed of the Berg River flows through agricultural and urban areas (Fig. 1). A recent forest fire south of the site was linked to an episode of elevated gaseous elemental mercury concentrations in the region (Brunke et al., 2001).

Sediments are the primary sink for mercury in aquatic systems, primarily due to its association with organic matter and oxide mineral surfaces, and this ensures its post-depositional retention within the sediments (Fitzgerald et al., 1998). Sulfur reducing bacteria at the oxic/anoxic boundary in the sediment mediate the transformation of ionic mercury to highly toxic methylmercury, and this process is responsible for most of the methylmercury found in aquatic food chains (Fitzgerald and Lamborg, 2003). Although methylmercury and total mercury have been shown to co-vary in estuarine systems in some instances (Sunderland et al., 2004), other factors such as the presence of sulfide, pH, and DOC can profoundly impact the rate of methylation (Benoit et al., 2003). Seasonally inundated flood plains such as the Berg River estuary may be environments with enhanced rates of methylation due to the seasonal anoxia, as Roulet et al. (2001) demonstrated in the Amazon Basin. Therefore, marsh and flood plain sediments are important as both a mercury sink and the site of significant methylation.

2. Materials and methods

2.1. Study site

The Berg River drains an area of 7715 km² along South Africa’s west coast (Fig. 1). During the rainy winter, the high-tide salt water intrudes about 10 km upriver, whereas salt water can be found 64 km upstream from the ocean during the dry summer (Slinger and Taljaard, 1994). The Berg River has experienced major changes in its flow over the last century. In 1966, the river mouth closed up completely during the dry season, and had to be dredged to allow local boaters to use the harbor (Slinger and Taljaard, 1994). This decrease in flow may be an indication of the high extent of recent water withdrawal within the catchment for agricultural activity: more than 50% of the catchment area supports agriculture (de Villiers, 2007). Dams have been constructed since 1947 to provide drinking and irrigation water, thus reducing stream flow.
2.2. Sample collection

A 30 cm long sediment core was collected in late July 2007 from a salt marsh in the flood plain 6 km upstream from the Atlantic Ocean (32°47’26”S, 18°12’05”E) with a 4.76 cm ID acid-washed, acryllic tube (Fig. 1). The sediment surface was approximately 10 cm below water at the time of collection. The core was extruded and cut using a plastic knife in one centimeter intervals, applying a custom-made extruder where only an acid-washed silicon bung made contact with the sediment. Samples were transferred into clean centrifuge tubes and sample jars and stored frozen in ziplock bags (double bagged). Once in the lab, samples were freeze-dried and then sieved through a stainless steel 180 µm sieve to remove roots, pebbles and sand from the sample.

2.3. Mercury and methylmercury analysis

The <180 µg fraction of the sediment was then analyzed for mercury concentration using a Milestone DMA-80 mercury analyzer, which uses dual cell atomic absorption spectrometry to quantify the absorption of elemental Hg at the 253.65 nm wavelength. Samples are combusted, decomposed, and interfering substances are removed by a catalytic column at high temperature prior to entrance into the absorption cell. Aliquots of 0.1–0.5 g of sediment were introduced into the sample boats yielding 3–8 ng of mercury. Methylmercury analysis followed the protocol described in Kim et al. (2006) and was only performed on a ground fraction of the sediment from this core.

Accuracy and precision of total mercury analysis was excellent. Duplicates were run on 50% of the samples, and standard reference material and blanks were run between every 10 samples. Blank values remained low through the two days of running samples for mercury (N = 5, 0.05 ± 0.03 ng Hg). Between 0.035 and 0.080 g of NRCC marine sediment MESS-3 (certified value: 91 ± 0.9 ng Hg g⁻¹) was used after every ten sample runs, and high recovery and precision was found in this study (N = 5, 91.5 ± 1.4 ng Hg g⁻¹). The mean percent recovery of this SRM was 100.6%. The coefficient of variation between samples was low (N = 12, mean%CV = 0.86%).

2.4. Carbon and nitrogen analysis

Carbon and Nitrogen analysis was performed on the <180 µg fraction of sediments using a CE Elantech Flash 1112 CHNSO Elemental Analyzer. The instrument was calibrated using Aspartic Acid (10.5200% N, 36.0900% C) and L-Cystine (11.6130% N, 29.9490% C). Aspartic Acid and L-Cystine were run to check instrument performance after every set of nine samples. Precision and accuracy were good on these reference materials (Aspartic Acid: N = 3, %N = 10.637 ± 0.324, %C = 36.489 ± 0.581; L-Cystine: N = 2, %N = 11.570 ± 0.122, %C = 30.189 ± 0.233). Duplicate analyses were performed for every five samples. The differences between these duplicates was minimal (N = 4, nitrogen mean%CV = 1.9%, carbon mean%CV = 0.5%).

2.5. 210Pb analysis

210Pb analysis was performed by polonium extraction from the <180 µg sediment fraction following the procedure of Eakins and Morrison (1978). Briefly, the sediments were spiked with 209Po as a yield tracer and then digested in concentrated HCl at 95–100°C overnight. Polonium was collected by distilling it at high temperature in a test tube furnace onto a plug of steel wool, which was then digested for 30 min in 0.5 N HCl. A silver disc was then suspended in the solution with one side exposed for five hours. Alpha particle emissions from the silver disc were counted using surface barrier detectors until 1000 counts were collected for both 210Po and 209Po peaks. The activity of 210Pb is assumed to be in secular equilibrium with the 210Po activity in sediments.

3. Results

3.1. Sediment chronology

The 210Pb dating of the sediments to determine age and sediment accumulation rate was done following the Periodic Flux (PF) model (Sanchez-Cabeza et al., 2000). The results of the application of this model are shown in Fig. 2. This model calculates the age of each sediment interval based on the ratio of the total unsupported 210Pb inventory to the unsupported 210Po interval below the sediment interval divided by the mean life of 210Pb. The sediment accumulation rate was calculated by dividing the dry mass of the interval by the formation time based on PF model ages. The supported 210Pb activity was estimated by taking the average of the four samples at the bottom of the core where no appreciable decrease appears to be occurring anymore. This activity was then subtracted from all overlying sediment activities to determine the unsupported 210Pb activity.

One potential complication to this method of dating sediments is that the supported 210Pb may be changing over time if the sediment source is changing. However, on the decadal time scale, it is probably reasonable to assume that this is constant as sedimentation processes are dominated by in situ plant growth and seasonally deposited suspended matter. Another potential shortcoming of this model is the use of the <180 µg fraction for calculation of sediment ages. Duplicate 210Pb measurements were performed on bulk samples from 2 to 18 cm. These measurements showed only a slight enrichment (mean: 113% ± 15%) associated with the <180 µg fraction relative to bulk samples, which suggests these measurements are applicable to bulk calculations. Furthermore, sediment ages calculated when only the <180 µg fractions inventory and mass are used as the parameters are very similar (R² = 0.99) to those calculated when <180 µg fraction is assumed to be bulk composition despite large difference in accumulation rates due to change in accumulated mass. This indicates that the <180 µg fraction is representative of the bulk sample in a majority of the samples.

3.2. Excess 210Pb inventory

The measured 210Pb profile for the location is shown in Fig. 3. The value for the supported 210Pb was estimated at 0.8 dpm g⁻¹ based on the lack of continued change in activity with depth for the deepest section of the core. Based on this estimate, the inventory of excess 210Pb found at the site is 3920 Bq m⁻², comparable to the 3479 Bq m⁻² found in an eastern South African salt marsh (Ivanovitch and Harmon, 1992). The inventory of 210Pb found at this site is slightly higher than that predicted by an atmospheric transport model (2680 Bq m⁻², Turekian et al., 1977), which indicates that atmospheric deposition is responsible for ~70% of the excess 210Pb inventory, or a sediment focusing factor of 1.4.

3.3. Sediment characteristics

Visual inspection of this core reveals that the upper 2 cm are rich in roots and twigs, but the content of these intact floral remains gradually decreases to 10 cm depth, below which they can no longer be found. The <180 µg fraction varies considerably in the upper 10 cm due to the presence of larger bits of plant debris, and becomes increasingly more rich in this fraction with depth (Fig. 3).
3.4. Total mercury and methylmercury

The mercury concentrations ranged from 15.4 to 49.9 ng g\(^{-1}\) (Fig. 2), and show a trend of decreasing concentration with depth. The maximum mercury concentration (49.9 ± 2.5 ng g\(^{-1}\)) was found in the 6–7 cm depth interval. The methylmercury concentration in the surface sediment was 1.3 ng g\(^{-1}\) (Table 1). Methylmercury made up 4.0% of the total mercury found in surface sediments.

3.5. Carbon and nitrogen

Carbon and Nitrogen co-vary in this core (\(R^2 = 0.997\)). The surface sediment is 26.9% carbon and 2.5% nitrogen decreasing with depth to 2.0% carbon and 0.1% nitrogen at the base of the core. The atomic C:N ratio shown in Fig. 3 gradually increases with depth from 12.6 at the surface to 16.6 at the base, though the change is quite variable throughout the core. This decrease can be explained by either the preferential diagenesis of algae over higher plant material or a trend towards increased algal and microbial presence in deposited sediments due to the onset of eutrophication reported by de Villiers (2007).

3.6. \(^{210}\text{Pb}/\text{Hg} \text{ and carbon correlation}\)

There is a weak correlation between total mercury and carbon concentrations (\(R^2 = 0.19\)) and a stronger correlation between...
210Pb activity and carbon ($R^2 = 0.68$). However, the 210Pb-carbon correlation is best explained by high concentrations of carbon associated with the deposition of organic material and its depletion with depth due to diagenesis, which occurs over a similar depth range as enrichment in 210Pb due to atmospheric deposition of unsupported 210Pb.

### 3.7. Mercury accumulation rates

The pre-1970 mercury accumulation rate was 10–22 μg m⁻² yr⁻¹ with a mean value of 16 μg m⁻² yr⁻¹ (Fig. 2). The pre-industrial deposition rate for this region is 7–8 μg m⁻² yr⁻¹ based on atmospheric transport modeling (Selin et al., 2008), suggesting that the observed mercury accumulation rate in the Berg River does not reflect only in situ atmospheric deposition. This enhancement of the mercury accumulation rate could be explained by sediment focusing in the watershed (e.g., Engstrom et al., 1994) through the accumulation of material at the site from the overall watershed. The mean pre-1970 mercury accumulation rate is reduced to 11 μg m⁻² yr⁻¹ when the accumulation rate is corrected based on the excess 210Pb inventory determined sediment focusing factor, which indicates pre-industrial levels had not yet been reached in the first half of the 20th century. The average post-1970 mercury accumulation rate is 100 μg m⁻² yr⁻¹ (29–149 μg m⁻² yr⁻¹) and the mean peak-deposition rate is approximately six times the pre-1970 rate.

### 4. Discussion

#### 4.1. Reconstructed mercury contamination history

If the source of the sediments is relatively constant in terms of supported and unsupported 210Pb over the last century then the PF model can be used to interpret the 210Pb data. This study lacks age confirmations through independent dating horizons, such as would be provided by 137Cs determination, nor is there independent measurement of supported 210Pb, but the results nonetheless provide a reasonable set of initial dates for these sediments that will be further developed with validated records in the future.

The onset of elevated mercury concentration and accumulation rates, probably associated with anthropogenic inputs, is found in 1970 (Fig. 2). This is in good agreement with the onset of mercury contamination found in dated cores from Lake Victoria (Ramalal et al., 2003). This suggests that regional sources may be more important relative to global sources in some regions of Africa, as this late onset date is at odds with the global increase in mercury contamination found in dated cores from Lake Victoria (Ramalal et al., 2003). This suggests that regional sources may be more important relative to global sources in some regions of Africa, as this late onset date is at odds with the global increase in mercury contamination found in dated cores from Lake Victoria (Ramalal et al., 2003). This suggests that regional sources may be more important relative to local sources (gold mining). In the Berg River estuary the dominant source of mercury contamination appears to be a regional source that began in the 1970's rather than global sources.

Peak mercury accumulation rates at this site were low relative to other estuaries. Varekamp et al. (2003) reported a mean anthropogenically-derived mercury accumulation rate of Long Island Sound as 260 μg m⁻² yr⁻¹, which is more than double the modern total mercury accumulation found in the Berg River estuary. This is probably related to the lower population density and fossil fuel consumption in the region surrounding the Berg River estuary relative to that surrounding Long Island Sound. Mercury accumulation rates of 120–270 μg m⁻² yr⁻¹ were found in Guaratuba Bay, Brazil (Sanders et al., 2006) dating back to the 1930's. As this site is far more pristine than Long Island Sound it is curious that the mercury accumulation rates are similar, albeit lower, in Brazil. This accumulation rate is still much higher than that found in this sediment core, which suggests that quantifying particle focusing may be very important for calculating estuarine mercury accumulation rates.

#### 4.2. Mercury and methylmercury

The total mercury concentrations found in these sediments are relatively low when compared to other environments with high organic content and intermittent flooding. The methylmercury concentration and percentage methylmercury of total mercury are quite elevated compared to other ecosystems, however (Table 1). This shows that, despite low mercury loading, methylmercury production rates were high in this location indicating that other factors are important in controlling methylation rate. Heyes et al. (1998) showed that anoxic decomposition of fresh plant matter can sustain high rates of methylmercury production and this data confirms that flood plain enhancement of methylation by rapid inundation of the area with fresh vegetal material occurs in estuaries as well as freshwater systems. This also indicates that the floodplains commonly found surrounding large rivers and their estuaries in the tropics may be important seasonal contributors of methylmercury to the system, as similar high levels of methylmercury are present in inundated Amazon Basin floodplains (Roulet et al., 2001).

Samples were collected from other sites in the Western Cape in addition to this location. Surface sediment samples taken 70 km upstream from sandy sediment in the bed of Berg River contained only 3.9 ± 1.5 ng g⁻¹ mercury. This indicates that the source of sediment to the core site is not simply river sediments but rather surface soils, and inputs from local sources. Surface sediment samples from the Kuils River near Cape Town were found to have more variation in concentration. An organic-rich sediment collected near a sewage outfall had a surface sediment mercury concentration of 540 ng g⁻¹, while two other sites in the watershed had much lower concentrations: 3 and 20 ng g⁻¹. The Berg River estuary sediments contain larger amounts of total mercury than other sampling.

---

Table 1

Summary data for total mercury (HgT) and methylmercury (MeHg) (in ng g⁻¹ dry weight) found in this study compared to values found in similar ecosystems worldwide.

<table>
<thead>
<tr>
<th>Site</th>
<th>Hg (ng/g)</th>
<th>MeHg (ng/g)</th>
<th>MeHg (%)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface sediment, Hudson River wetland</td>
<td>190–1040</td>
<td>0.43–2.95</td>
<td>0.9</td>
<td>Zelewski et al. (2001)</td>
</tr>
<tr>
<td>Upper 20 cm average, Kirkpatrick marsh, Chesapeake Bay salt marsh</td>
<td>1.48</td>
<td>0.97</td>
<td>0.4</td>
<td>Mitchell and Gilmour (2008)</td>
</tr>
<tr>
<td>Upper 30 cm average, Marine Mississippi delta wetland</td>
<td>80</td>
<td>1.34</td>
<td>17</td>
<td>Kongchum et al. (2006)</td>
</tr>
<tr>
<td>Upper 30 cm average, Freshwater Mississippi delta wetland</td>
<td>140</td>
<td>4.19</td>
<td>30</td>
<td>Kongchum et al. (2006)</td>
</tr>
<tr>
<td>Litter horizon, Enseada igapo, Amazon flood plain</td>
<td>160</td>
<td>5.91</td>
<td>3.7</td>
<td>Roulet et al. (2001)</td>
</tr>
<tr>
<td>Litter horizon, Juturana igapo, Amazon flood plain</td>
<td>139</td>
<td>6</td>
<td>4.4</td>
<td>Roulet et al. (2001)</td>
</tr>
<tr>
<td>Surface sediment, Berg River estuine flood plain</td>
<td>32</td>
<td>1.3</td>
<td>4.0</td>
<td>This study</td>
</tr>
</tbody>
</table>

locations in the Berg River watershed, but less than some sites closer to the Cape Town metropolitan area.

4.3. Historical context

Cape Town’s Athlone coal fired power plant was brought into service in 1962 (Leeuwenaal, 2005), and it kept running until the mid-80’s, when it was mothballed due to the nearby construction of a nuclear power plant (van Gass, 2004). In Fig. 2, the overall mercury accumulation rate appears to mimic the potential changes in Hg deposition that may be associated with regional coal consumption by the Athlone plant, first increasing in the 1960’s and peaking in the late 1970’s. In 1995, as power demand began to overtake supply, the plant was brought back into operation during the winter and during times of peak demand to reduce the amount of energy bought from Eskom, South Africa’s power distributor (cbn.co.za, 2002). Concentrations begin to rise again in the mid 90’s and appear to decrease coincidently with the closing of the Athlone power station in 2003 (Marshall, 2007).

The coring site is far downstream from the nearest dam, so it is unlikely that this would have been a source of sediment to the site. However, the damming of the river has likely changed stream discharge rates and therefore altered sedimentation rates at the site. Evidence of this is seen in the decrease in sediment accumulation at PF model years 1976–1984 coinciding with the completion of the construction of the “Misverstand” dam, located 71 km upstream in Pikettsburg in 1977 (Fig. 2).

5. Conclusion

Comparison of modern mercury accumulation rates with pre-1970’s mercury accumulation rates reveal enhanced deposition related to regional and global sources. Elevated mercury accumulation rates and concentrations are found to begin in 1970. Surface sediments at this site contained 4% methylmercury which could indicate high rates of methylation. Total mercury concentrations were not very high when compared to other salt marshes and flood plains. This location provides evidence that regional changes in Hg deposition that have occurred over the last century and allow for a contrast with changes that have occurred and are well documented for the Northern Hemisphere.

Acknowledgments

This work was supported by the NSF International Program – “Developing Global Scientists and Engineers through the Study of Mercury Environmental Issues in Southern Africa”. We thank Chantel Petersen, Vernon Somerset, and Chavon Williams of the CSIR for assistance sample collection, preparation, and analysis. We thank Prentiss Balcom and Genevieve Bernier of UCONN for assisting with 210Pb geochronology, and Tim Ku of Wesleyan University for help with carbon and nitrogen analysis. We thank Johan Varekamp of Wesleyan University for the helpful criticism and review of this manuscript. We would also like to acknowledge the helpful suggestions of two anonymous reviewers in preparation of this manuscript.

References


Maurice-Bourgoin, L., Aalto, R., Rheault, I., Guyot, J.L. 2003. Use of 210Pb geochronology to explore the century-scale mercury contamination history and the importance of floodplain accumulation in Andean tributaries of the Amazon River. In: IV South American Symposium on Isotope Geology, pp. 449–452.


