Millennial mercury records derived from ornithogenic sediment on Dongdao Island, South China Sea

Hong Yan¹, Yuhong Wang²*, Wenhan Cheng¹, Liguang Sun¹,*

1. Institute of Polar Environment, University of Science and Technology of China, Hefei 230026, China. E-mail: yanhong19860124@hotmail.com
2. National Institutes of Health, Bethesda, MD 20892, USA

Received 10 November 2010; revised 08 March 2011; accepted 10 March 2011

Abstract

Two ornithogenic sediment cores, which have a time span of 1000 years and are influenced by red-footed booby (Sula sula), were collected from Dongdao Islands, South China Sea. The determined mercury concentrations of the two cores show similar and substantial fluctuations during the past millennium, and the fluctuations are most likely caused by the changes in mercury level of the ocean environment and in anthropogenic Hg emission. For the past 500 years, the mercury concentration in the red-footed booby excrement has a striking association with global anthropogenic mercury emission. The mercury concentration increased rapidly after AD 1600 in corresponding to beginning of the unparalleled gold and silver mining in South Central America that left a large volume of anthropogenic mercury pollution. Since the Industrial Revolution, the mercury level has increased at a fast pace, very likely caused by modern coal combustion, chlor-alkali and oil refining industries. The comparison of mercury profiles from different places on earth suggested that anthropogenic mercury pollution after the Industrial Revolution is more severe in Northern Hemisphere than in Antarctica.

Key words: South China Sea; red-footed booby; ornithogenic sediment; mercury; anthropogenic source

DOI: 10.1016/S1001-0742(10)60603-1


Introduction

Mercury, a well known global contaminant, has a significant bioaccumulation by food chain, especially in the form of methyl-mercury, which is highly toxic to human beings and animals (Sun et al., 2006). Mercury exists in nature as elemental mercury (Hg⁰), inorganic, or organic compounds. Due to its chemical inertness, vaporizable nature (a low enthalpy of vaporization as 59.15 kJ/mol), and low solubility in water (at 20°C, 2×10⁻⁶ g/g), gaseous Hg⁰ has a long atmospheric residence time of over one year, a long range atmospheric transport, and a global distribution (Fitzgerald et al., 1998; Roos-Barraclough et al., 2002).

Both anthropogenic emissions and natural factors, such as climatic conditions, biological productivity in ocean, volcanic eruption, and photochemical reaction, can affect mercury deposition at a site (Fitzgerald et al., 1998; Roos-Barraclough et al., 2002). For anthropogenic emissions, the historical quantitative records are still lacking even though related ancient activities, such as gold and silver mining using amalgamation process in Europe and America and alchemy in China and India, have been well documented (Lacerda, 1997; Sun et al., 2006). Nriagu (1994) estimated that the cumulative losses of mercury to the environment due to the production of precious metals in the Americas from AD 1580 to AD 1900 totaled approximately 257,400 tons. The global production of metallic Hg during the last 500 years is close to one million tones and mainly from anthropogenic emissions (Hylander and Meili, 2003). Approximately 60%–65% of elemental mercury in the amalgamation process of extracting gold and silver from mines was released to the atmosphere, and became a major source of atmospheric mercury pollution (Nriagu, 1994). For natural factors, the Hg deposition process is favored by both higher ocean biological productivity (Vandal et al., 1993) and cooler climate (Martinez-Cortizas et al., 1999), especially during pre-anthropogenic times. A recycling of mercury at about 5%–6% proportion to deposited mercury may partly be responsible for the high fluxes in some areas of North and South America (Nriagu, 1994).

In the past decade, many efforts have been made to study the fate of mercury in natural environments and the historical deposition fluxes based on its profiles in peat bogs, lake and marine sediments, and ice cores (Martinez-Cortizas et al., 1999; Biester et al., 2002; Lindeberg et al., 2003).
2006; Sun et al., 2006). Most of these profiles, however, were located in polluted areas, and they mainly reflected regional mercury deposition history due to the fact that the background of local deposition was far higher than the outer inputs (Schuster et al., 2002). For example, the mercury profile in the Spanish peat bog near Almaden mine, the biggest mercury mine in the world, unambiguously recorded ancient European mining activities and natural events (Martinez-Cortizas et al., 1999), but it did not show any well-known Asian and American ones. Therefore, the global profile of total mercury emission for the past thousands years remain absent (Balogh et al., 1999).

On Xisha archipelago (16°39′–16°41′N, 112°43′–112°45′E) of South China Sea, red-footed booby (Sula sula) is the dominant seabird species. This tropic seabird, long-lived and at the top of food chain, is an excellent bio-indicator for spatial and temporal distribution of ocean contaminants (Gochfeld and Burger, 1998) due to accumulation in food chain (Bargagli et al., 1998). In this study, we collected two ornithogenic sediment deposition profiles that are influenced by red-footed booby (S. sula) in Xisha Islands, reconstructed 1000-year records of calibrated mercury concentration in the excrement of red-footed booby (S. sula), examined the impacts of anthropogenic and natural mercury deposition on South China Sea marine ecosystem, and discussed the association between these mercury profiles and global historic gold and silver mining.

These sediment deposits from Xisha Islands provide a number of advantages for studying mercury fluxes. First, Xisha atolls are regarded as a privileged observatory for research on global changes caused by human activities due to their remoteness (Liu et al., 2006; Yan et al., 2010). Second, most previous research on historic Hg deposition focused on high latitude regions such as Europe and America, and few research have been published for tropic regions like Xisha Islands. Third, Xisha Islands are far from two historically dominant Hg emission spots, Europe and South America, and few research have been published for tropical regions like Xisha Islands. Third, Xisha Islands are far from two historically dominant Hg emission spots, Europe and South America, and it could record the Hg emissions all over the world rather than local ones. Fourth, as one of the top predators in the oceanic food chain, red-footed booby has high concentrations of mercury due to biomagnification (Bargagli et al., 1998). As a result, it is a prominent bio-monitor for the historical pollution in the ecosystem of South China Sea (Bargagli et al., 1998). Finally, the lake sediment cores from tropical Xisha islands have higher resolution than those from polar area, and they have a relatively simple composition of mainly corals and guano.

1 Materials and methods

1.1 Study area and sampling

Dongdao Island is located in the east of Xisha Islands of South China Sea and is about 18 sea miles from Yongxin Island, the largest one of Xisha Islands. It is a tropic coral reef island with an elliptical shape and a northwest-southeast orientation (Fig. 1). This small island has a land area of 1.55 km² and an elevation of about 3–6 m above the sea level, and it is completely composed of coral sand and coral rock. The eastern, southern and western shores of this island are surrounded by 5-6 m high sand barriers. The sand barriers are covered with thriving shrubs. The interior of this island is an up to 3 m high flat. A Pisonia grandis woodland covers the center and roughly half the area of the island, providing a good and shaded nesting place for numerous seabirds. Dongdao Island has also been identified as the natural reserve area for red-footed booby (S. sula).

Cattle Pond was discovered on Dongdao Island during our field investigations in 2003. It is a crescent-shaped freshwater lake, located within the southwestern sand barrier. It is about 150 m long and has a maximum width of 15 m. The pond appears hydrologically closed, and the lake water is mainly fed by atmospheric precipitation and lost predominantly through evaporation. The water depth of Cattle Pond varies with the alternation of dry and wet seasons; in the dry season, the lake surface area becomes small. However, according to investigation in the field, we never saw Cattle Pond completely drying out and the water depth remained steady at about 0.5 m for most of time, probably caused by the seepage between Cattle Pond and South China Sea. As judged by the progressive sedimentary lithology and the results of 14C dating as discussed below, sediment hiatus does not seem to occur or is insignificant. Cattle Pond is the only fresh water source for the seabirds living on Dongdao Island. Field observation also showed that a large number of seabirds are clustered in this area and the pond is significantly influenced by seabird droppings (Liu et al., 2006; Yan et al., 2010, 2011).

From Cattle Pond, we collected two lake sediment cores DY2 and DY4 of 126 cm and 117 cm long, respectively, using PVC plastic gravity pipes of 12 cm in diameter in the field. Sampling distance between the two coring sites was about 100 m. We also collected some fresh seabird droppings and coral rock samples on Dongdao Island to determine the background element concentrations.

1.2 Analysis

In laboratory, the DY2 and DY4 cores were opened, photographed, and described, then sectioned at 1-cm intervals. During sectioning, the loose surface sediments were kept half-frozen to avoid collapsing. Each sliced portion of the DY2 and DY4 cores was sealed in separate plastic bags to prevent contamination, and bags were stored in a refrigerator prior to analysis.

For analysis of grain size distribution, all subsamples were sieved through a 2-mm sieve, and 0.5 g of material from each sample was analyzed using a laser particle analyzer (Mastersizer 2000, Malvern Instruments Co., Worcestershire, UK) at the Institute of Geology and Geophysics, Chinese Academy of Science. In this study, we report results as mean grain size (MGS) which is calculated by weight sum.

All subsamples were analyzed for the following 20 elements: Na, K, Ca, Mg, Mn, Fe, Al, Si, Zn, Pb, Co, As, Cd, Se, Sr and P, total organic carbon (TOC), total...
nitrogen (TN), total sulfur (TS), and the percentages of loss on ignition at 550 (LOI_{550}) and 950°C (LOI_{950}). The analytical methods were given in detail by Liu et al. (2006). For mercury analysis, all subsamples of DY2, DY4, fresh feces and coral rock were ground and passed through a 212-µm sieve after air dried in a laboratory and homogenized, and then dried at 60°C for 12 hr. About 3 g of each dried powder sample was taken, precisely weighed, and then digested by multi-acid (high purity grade HNO_3, HF, HClO_4, 10:1:1) in a Pt crucible with electric heating. The total mercury concentration was determined by atomic fluorescence spectrometry (AFS-930, Beijing Vital Co., China), with detection limit of 0.1 µg/kg. The concentration of mercury is expressed in µg/kg. For quality control purpose, the national standard sediment and soil samples of GBW07120, GBW07108 (two replicates) were measured as “unknowns” with every batch analysis. The analytical accuracy of the mercury data, estimated as relative percentage difference between duplicates, was ±1.7%. Analytical precision, estimated as the mean percentage recovery for matrix spikes, was 97.4%. The average residual concentration of standard samples relative to their certified values was +0.52 µg/kg, representing a mean relative difference of 3.25%.

Radiocarbon analyses for the DY2 and DY4 cores were performed on terrestrial organic matter (plant caryopsis, 13 samples) and TOC (Table 1). After HCl treatment, a total of 16 samples were determined using the Accelerator Mass Spectrometer facility at Institute of Heavy Ion Physics in Beijing University (Table 1). The AMS radiocarbon dates are expressed in conventional 14C yr BP (Before Present). The determined dates are corrected for isotopic fractionation and normalized to a δ^{13}C_PDB value of −25‰ on the PDB (Pee Dee Belemnite) scale. The quoted errors in the dates are based on the reproducibility of measurement. The determined radiocarbon dates were then calibrated into calendar years before present (cal yr BP) using the program OxCal version 4.4 and atmospheric data from Stuiver et al. (1998). Since the radiocarbon dates of terrestrial plant remains in lake sediments are not subject
to reservoir effects, the consistent dating results between plant seeds and TOC show that the measured radiocarbon dates do not need to be corrected for reservoir effect. For the upper 20 cm of sediments from DY2, we performed recent radionuclide analyses (210Pb, 226Ra and 137Cs) at 1-cm intervals by direct gamma spectrometry using Ortec HPGe GWL series (Wu et al., 2004), but the resulting profiles were not suitable for dating.

2 Results and discussions

2.1 Lithology and chronology

Detailed geochemistry analysis in our previous study (Liu et al., 2008) suggested that DY2 and DY4 have similar lithologies (Fig. 2). Three sediment units were identified based on color, LOI (Loss On Ignition), CaO, LOI, TOC, TN and presence of laminations (Fig. 2). The bottom sediment units (Unit 3) of DY2 (126–96 cm) and DY4 (117–87 cm) cores consist of fragments of grey-white coral, shell and sandy gravels. These bottom sediments probably represent deposition in a lagoon environment, and they do not contain any plant remains. Above these sediments, both cores consist of ornithogenic sediments (Unit 1) with exception of the well-sorted coral sand layers between 83–88 cm of DY2 and 58–69 cm of DY4 (Unit 2). The interbedded coral sand layers (Unit 2) have distinctly different lithology from the overlying and underlying sediments. The analyses on grain-size component, elemental geochemistry and biological remained showed that the interbedded coral sand layers (Unit 2, 83–88 cm of DY2 and 58–69 cm of DY4) correspond to a precipitous marine sedimentation event happened at about AD 1024 (Supporting by 8 AMS 14C dating results, Table 1), and this event could be interpreted as intense typhoon or even tsunami (Liu et al., 2008). After the interbedded coral sand layers, the sediments displayed minor disturbance. In order to avoid the influence of the precipitous marine sedimentation event, the present study is mainly based upon the top 83 cm and 58 cm sediment layers of DY2 and DY4, respectively, with a time span from AD 1024 to present (Liu et al., 2008, Yan et al., 2011). The sediment grain size-versus-depth profiles of DY2 and DY4 and the radiocarbon dating results are consistent (Table 1 and Fig. 2). The date of the surface sediment is assumed AD 2000 and the age between two consecutive dating results is calculated by interpolation by linear accumulation.

2.2 Seabird droppings as the major source of mercury in DY2 and DY4

The important role of seabirds in the transportation of nutrient nitrogen and phosphorus of marine origin to terrestrial ecosystems has been well recognized (Anderson and Polis, 1999). Phosphate deposits have been shown to occur in islands of the Pacific and Indian Oceans as the result of phosphate being leached from the superficial coating of avian guano and subsequently re-precipitating in underlying calcareous sands (Trichet and Fikri, 1997; Baker et al., 1998). In Dongdao Island, the concentrations of P in seabird dropping, guano phosphatic rock and soil are much higher than those in the materials not influenced by seabird droppings, and the bird-derived phosphorus is a major nutrient source for the island ecosystem (Liu et al., 2006). The high phosphate (as P2O5) content of 1.63% (means of all subsamples) in DY4 confirmed the large amount of guano input into Cattle Pond. Zhao et al. (2007) reported that the ratios of Sr/Ca and Mg/Ca in the plant, coral sand and seabird dropping on Dongdao Island are quite different from each other and thus these three major sediment media could be distinguished by Sr/Ca and Mg/Ca ratios. Using three end-member mixing model, Zhao et al. (2007) calculated relative contribution of seabird dropping, coral sand and plant remains in the lake sediments (Fig. 3). The calculated results suggested that the DY4 core is deeply influenced by seabird droppings and has feces content over 50% in most sediment layers. The results also coincide with the observed lithology. For example, the content of seabird droppings in the interbedded coral sand layer (Unit 2, 58–69 cm of DY4) is much lower than that in the ornithogenic sediments (Unit 1).

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Dated material</th>
<th>Depth (cm)</th>
<th>14C conventional age (yr BP)</th>
<th>Calibrated age (cal yr BP)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Intercept 2 sigma</td>
<td></td>
</tr>
<tr>
<td>DY4-21</td>
<td>Plant caryopsis</td>
<td>20–21</td>
<td>305 ± 40</td>
<td>417, 314, 411, 474–289</td>
</tr>
<tr>
<td>DY4-36</td>
<td>Plant caryopsis</td>
<td>35–36</td>
<td>765 ± 35</td>
<td>675, 735–656</td>
</tr>
<tr>
<td>DY4-45</td>
<td>Plant caryopsis</td>
<td>44–45</td>
<td>900 ± 35</td>
<td>790, 924–730</td>
</tr>
<tr>
<td>DY4-58(1)</td>
<td>Plant caryopsis</td>
<td>57–58</td>
<td>1020 ± 30</td>
<td>932, 970–804</td>
</tr>
<tr>
<td>DY4-58(2)</td>
<td>Plant caryopsis</td>
<td>57–58</td>
<td>985 ± 30</td>
<td>926, 953–794</td>
</tr>
<tr>
<td>DY4-58(3)</td>
<td>Plant caryopsis</td>
<td>57–58</td>
<td>980 ± 30</td>
<td>925, 951–793</td>
</tr>
<tr>
<td>DY4-71(1)</td>
<td>Plant caryopsis</td>
<td>70–71</td>
<td>1025 ± 30</td>
<td>933, 971–917</td>
</tr>
<tr>
<td>DY4-71(2)</td>
<td>Plant caryopsis</td>
<td>70–71</td>
<td>960 ± 30</td>
<td>916, 945–790</td>
</tr>
<tr>
<td>DY4-71(3)</td>
<td>Plant caryopsis</td>
<td>70–71</td>
<td>1010 ± 40</td>
<td>930, 972–795</td>
</tr>
<tr>
<td>DY4-71(4)</td>
<td>Plant caryopsis</td>
<td>70–71</td>
<td>965 ± 30</td>
<td>919, 947–790</td>
</tr>
<tr>
<td>DY4-71(5)</td>
<td>Plant caryopsis</td>
<td>70–71</td>
<td>995 ± 35</td>
<td>928, 966–794</td>
</tr>
<tr>
<td>DY4-87</td>
<td>Plant caryopsis</td>
<td>86–87</td>
<td>1340 ± 35</td>
<td>1284, 1306–1181</td>
</tr>
<tr>
<td>DY2-20</td>
<td>Bulk organic carbon</td>
<td>19–20</td>
<td>250 ± 70</td>
<td>298, 475–1</td>
</tr>
<tr>
<td>DY2-54</td>
<td>Bulk organic carbon</td>
<td>53–54</td>
<td>850 ± 60</td>
<td>738, 923–667</td>
</tr>
<tr>
<td>DY2-95</td>
<td>Bulk organic carbon</td>
<td>94.5</td>
<td>1440 ± 65</td>
<td>1327, 1510–1262</td>
</tr>
<tr>
<td>DY2-C1</td>
<td>Plant caryopsis</td>
<td>94.5</td>
<td>1360 ± 40</td>
<td>1288, 1331–1184</td>
</tr>
</tbody>
</table>

Table 1 AMS 14C dates and calibrated ages of the sediment cores DY2 and DY4 from the Cattle Pond on Dongdao Island.
As the two major sources of sediments in DY2 and DY4, seabird droppings and coral sand are composed of dissimilar elements (Table 2). Element P and trace metals Hg, Cd, Cu, Zn and Se have significantly higher concentrations in feces than in coral sands. Due to the great difference, a large amount of seabird droppings input will...
dramatically change the concentration ranges and characteristics of sediments. The concentration-versus-depth profiles of TOC, Se, P₂O₅, Cu, Zn, Hg and feces content in DY4 (Fig. 3) have similar fluctuations as confirmed by statistical analysis (Table 3), indicating that the major source of nutrient P and heavy metals Hg, Cd, Cu, Zn and Se in Cattle Pond is the fecal materials. This finding is consistent with previous study (Liu et al., 2006) in South China Sea and numerous studies in the remote islands of Antarctica and Arctic (Sun et al., 2000; Blais et al., 2005, 2007; Liu et al., 2005).

Except fecal materials, the mercury in the sediments of Cattle Pond could also be from direct atmospheric deposition. However, the contribution from atmospheric deposition is expected to be insignificant. First, atmospheric deposition of mercury could be low in Xisha atolls due to their remoteness and infrequent human activities, especially in historic times. Second, the rapid accumulation in Cattle Pond could dilute the mercury from atmospheric deposition. Third, the mercury from atmospheric deposition consists mostly of elemental mercury (Hg⁰) because only Hg⁰ has a long-range atmospheric transport and a global distribution (Fitzgerald et al., 1998; Roos-Barraclough et al., 2002; Wong et al., 2006). Most of mercury in biomaterials is present as inorganic and organic compounds (Houserova et al., 2007). In the present study, we homogenized subsamples and dried at 60°C for 12 hr before mercury analysis. In this process, most of Hg⁰ was lost (Martinez-Cortizas et al., 1999) and the measured Hg is mainly form inorganic and organic compounds.

### 2.3 Calibration of Hg concentrations in seabird droppings

The top 83 cm and 58 cm sediment layers of DY2 and DY4 have steady, continuous and abundant seabird droppings content and are suitable for investigating Hg concentration in historical red-footed booby droppings. To estimate Hg concentration in historical red-footed booby droppings, we calibrated it by the mass equation given as:

\[ M \times (x \times c_x + y \times c_y + z \times c_z) = M \times c_m \]

where, \( M \) (g) is the total weight of sediment, \( x \) (%) is the percentage of booby droppings in lake sediments, \( y \) (%) is the percentage of coral sands in lake sediments, \( z \) (%) is the percentage of plant remains in lake sediments, \( c_x \) (µg/kg) is the concentration of Hg in booby droppings, \( c_y \) (µg/kg) is the concentration of Hg in coral sands, \( c_z \) (µg/kg) is the concentration of Hg in plants, \( c_m \) (µg/kg) is the concentration of Hg in sediments.

Briefly, we assumed in this mass equation that the Hg concentration in coral sands and plants remain constant during the studied time period and used the Hg concentration in coral sands and modern plant as \( c_y \) and \( c_z \). The calibrated mercury concentration profiles of DY2 and DY4 are present in Fig. 4. The comparable Hg concentrations in the seabird droppings of the surface sediments and in fresh seabird droppings indicate that the calibration method is reliable (Fig. 4).

### 2.4 Possible causes for the variations of Hg\(_{\text{cal}}\) in seabird droppings

The calibrated mercury concentration profiles of DY2 and DY4 revealed similar and significant variations during the past millennium (Fig. 4). Both of them show rapid increase after about AD 1600, especially in recent decades. Such significant variations of Hg\(_{\text{cal}}\) concentration could be caused by the changes in species of seabirds, physiological process, diet composition, and mercury level in marine food web.

### Table 2

<table>
<thead>
<tr>
<th></th>
<th>P₂O₅-P (%)</th>
<th>Hg (µg/kg)</th>
<th>Cd (mg/kg)</th>
<th>Cu (mg/kg)</th>
<th>Zn (mg/kg)</th>
<th>Se (mg/kg)</th>
<th>Pb (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh seabird droppings-FSD (n = 3)</td>
<td>10.81</td>
<td>88.3</td>
<td>6.62</td>
<td>39.8</td>
<td>489</td>
<td>3.05</td>
<td>2.61</td>
</tr>
<tr>
<td>Coral sand background-BG (n = 3)</td>
<td>0.015</td>
<td>1.59</td>
<td>&lt;0.2</td>
<td>2.2</td>
<td>6.92</td>
<td>0.035</td>
<td>2.08</td>
</tr>
<tr>
<td>FSD/BG</td>
<td>986.86</td>
<td>55.53</td>
<td>&gt;33.1</td>
<td>18.09</td>
<td>70.66</td>
<td>87.14</td>
<td>1.25</td>
</tr>
<tr>
<td>Plant average (n = 5)</td>
<td>0.319</td>
<td>7.63</td>
<td>0.38</td>
<td>12.17</td>
<td>35.72</td>
<td>0.26</td>
<td>1.59</td>
</tr>
<tr>
<td>DY4 sediment average (n = 117)</td>
<td>1.65</td>
<td>14.34</td>
<td>2.34</td>
<td>6.63</td>
<td>28.5</td>
<td>1.55</td>
<td>3.26</td>
</tr>
</tbody>
</table>

* All correlations are significant at 0.01 level (2-tailed).

![Fig. 4](https://example.com/fig4.png)

---

**Fig. 4** Calibrated mercury concentration in historic seabird droppings of DY2 (a) and DY4 (b). Dashed lines show the mercury concentration in fresh seabird droppings.
The change of diet composition, physiological process and seabird species could have significant influence on trophic level of and Hg accumulation in seabirds, but it is expected to be insignificant. First, red-footed booby (S. sula) is the dominant seabird species on whole Xisha archipelago of South China Sea and its migration is insignificant due their remoteness (Cao et al., 2005). Second, biological characteristics of ancient pure guano granules and eggshells collected in the sandy mounds are similar to those of fresh biomaterials, indicating that the seabird species on Dongdao Island remained stable for the past 1000 years. Third, the δ¹⁵N values, a conventional isotopic ruler of trophic level (Sun et al., 2006), of the eggshells collected in the sandy mounds were stable (10.29 ± 0.60, n = 26, Fig. 5), again suggesting that the seabird species and their diet composition in Xisha atolls were stable (Xu et al., 2011). Furthermore, the variation in physiological process of individual seabird is expected to be averaged out as each subsample has a large amount of seabird droppings mixed.

Therefore, the change of mercury level in ocean environment, the bottom of the food chain in South China Sea, is probably the main factor for the observed and biomagnified variation of mercury concentration in the red-footed boobies on Dongdao Island.

2.5 Association between mercury in historic seabird droppings and global anthropogenic Hg emission

The mercury level at bottom of the food chain in South China Sea could be affected by short-term factors such as seasonal climate changes and long-term factors such as deposition conditions and emissions from natural and anthropogenic sources. Short-term factors are expected to be averaged out as each subsample have a time span of approximately fifteen years. The long-term atmospheric conditions for Hg deposition could be affected by climate such as air temperature; and cold climate is favorable for Hg deposition (Martinez-Cortizas et al., 1999). The effect of climate on Hg concentration in the seabird excrement, however, seems to be insignificant. We compared the Hgₑₛₑₚ profiles with the air temperature in southern China, and observed no remarkable association. For example, there are no peaks in Hgₑₛₑₚ profiles during the period from AD 1450 to AD 1650, the coolest time period during the past millennium called Little Ice Age. Natural emission such as volcanic eruptions does not seem to be a major factor either, and no significant correlation between Eastern Asia volcanic activities (Taira, 1980) and the Hgₑₛₑₚ profiles during the last 1000 years could be identified. Since the records from other geological sources are incomplete, their influences could not be completely excluded. As reported in previous studies (Nriagu, 1989; Lamborg et al., 2002; Bindler, 2003), however, natural Hg emissions are almost invariable at approximately 2000 tons every year. Martinez-Cortizas et al. (1999) reported that natural Hg emissions could contribute approximately 37–50 ng/g in Spain peat bog with a variation about 15% during the past 2000 years. The Hgₑₛₑₚ concentrations of DY2 and DY4 have a coefficient of variation about 132% and 69%, respectively, amplitudes too large to be explained only by natural variation. Therefore, anthropogenic events such as the consumption of Hg in gold and silver mining and alchemical activities might play an important role in the large fluctuations of Hg concentration in the seabird excrement (Fig. 6).

Previous studies suggested that about one million tons of anthropogenic Hg has been released into the atmosphere due to the Hg-amalgamation process in gold and silver mining since 500 BC (Nriagu, 1994; Camargo, 2002). The large volume of anthropogenic Hg release probably began in late of the 16th century in corresponding to beginning of the gold and silver mining in South Central America, which left an unparalleled legacy of massive mercury pollution. Between AD 1550 and AD 1930, over 260,000 tons of Hg was released into the atmosphere (Nriagu, 1994). Especially in the 18th century, the annual emission of Hg was 800–1200 tons (Sundelin and Eriksson, 2001). This large-volume anthropogenic Hg release was well reflected in sedimentary records from remote areas such as Antarctica and Europe (Martinez-Cortizas et al., 1999; Sun et al., 2006).

Since the Industrial Revolution in the 1840’s, coal combustion, chlor-alkali and oil refining industry have become the dominant sources of anthropogenic Hg (Biester et al., 2002; Sun et al., 2006). Many records from the different areas of the world, including the record of this study, indicated rapid increasing of mercury concentrations after the Industrial Revolution (Fig. 7). However, the amplitude of increase differs significantly. The ratio of the highest

![Fig. 5](image-url) Stable δ¹⁵N values in the eggshell collected from the sandy mound. The hollow dot is the stable δ¹⁵N values in the fresh eggshell.

![Fig. 6](image-url) Calibrated mercury concentration in the DY2 core (line a) and global mercury production in recent 500 years (line b) (Hylander and Meili, 2003).
Fig. 7 Calibrated mercury concentration in historic seabird droppings of DY2 (line a) and DY4 (line b). Hg accumulation in peat bog cores from Spain (line c) (Martinez-Cortizas et al., 1999), Hg concentration in Greenland lake sediment (line d) (Lindeberg et al., 2006) and Hg concentration in the Antarctic seal hairs (line e) (Sun et al., 2006).

calibrated Hg concentration over the lowest since 1840 is about 5 in South China Sea, Europe and Greenland, but only 2 in Antarctic seal hairs. This difference suggests that anthropogenic mercury pollution after the Industrial Revolution may be more severe in the Northern Hemisphere than in Antarctica (Sun et al., 2006). Three factors may account for this. First, the modern industry is centered in the Northern Hemisphere. Second, Antarctica is far away from the Northern Hemisphere, thus the mercury deposition in Antarctica from long distance transmission is less than that in other three sites. Third, Antarctica and South China Sea mercury records are derived from biomaterials and they could be affected by biological effects.

Acknowledgments

This work was supported by the Natural Science Foundation of China (NSFC) (No. 40730107) and the National Basic Research Program (973) of China (No. 2010CB428902). The authors would like to thank Nan Jia, Sanping Zhao, Xuebin Yin and Honghao Luo for their help in sampling and analyzing.

References


Millennial mercury records derived from ornithogenic sediment on Dongdao Island, South China Sea


