

Total mercury and mercury isotope signatures in reservoir sediment reflecting the landscape changes and agricultural activities in northeast China

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ABSTRACT

Northeast China possess large areas of agricultural farmlands that were reclaimed from earlier marsh wetlands in the past several decades, while the response of trace element like mercury (Hg) in this process were not fully understood. In the present study, total mercury (THg) and Hg isotope composition were determined in reservoir sediment cores of a reservoir, agricultural soils and forest soils in Northeast China to reveal the possible impacts of agricultural activities on Hg geochemistry in the reservoir. The more negative $\delta^{202}\text{Hg}$ ($\downarrow 0.35\text{‰}$), increased concentrations of THg ($\uparrow 22.4 \text{ ng g}^{-1}$), and higher organic matter (OM) ($\uparrow 10\%$) in the deeper than the upper layer sediments indicate noticeable Hg input about 50–60 years ago, which is coincident with the grand reclamation of marsh wetland in the study area. The gradual decrease in THg content and the increase of $\delta^{202}\text{Hg}$ value in the upper sediment layer reflect the weakened reclamation and thus less Hg input in the later decades. Using a triple mixing model, it is estimated that more than half of Hg in this reservoir sediment was originated from the reclamation of marsh wetlands into farmlands in the earlier stage and soil erosion in the later period. The study demonstrated that Hg isotope signatures in reservoir sediment core can reflect the landscape changes, such as reclamation.

1. Introduction

Mercury (Hg) is a known neurotoxin that enters into environment as a result of different natural and anthropogenic processes (Bigham et al., 2005). A series of biogeochemical processes, like weathering and erosion, can affect the migration and transformation of Hg in the environment (Jiskra et al., 2017). In recent years, plants have been found to play a pivotal role in the environmental cycling of Hg due to the sequestering of gaseous elemental Hg from atmosphere by leaves and subsequent shedding as litterfall into soil (Demers et al., 2013; Washburn et al., 2017; Yuan et al., 2019; Wang et al., 2016). It is estimated that the amount of Hg in global litter material controls the spatial distribution of Hg in surface soil (Wang et al., 2016). The

dissolution of Hg in litter forms an important source of Hg in the surrounding environment, such as streams and lakes (Jiskra et al., 2017). Marsh wetland has a high diversity of plant species, especially herbaceous plant, and covers a land area of ca. 2.2% of China in 2017 (Data from: China Statistical Yearbook, 2018). Marsh wetland is found to be an important Hg sink (Wang et al., 2002), with much Hg being stored in the buried humus and peat layers. The destruction of such ecosystem may induce Hg disturbance. Sediments can be an effective chronographer of environmental change due to its continuity and integrity of profile preservation (Zeng et al., 2009). The environmental pollution by heavy metals and organic pollutants has been well registered in sediments since the industrial revolution (Combi et al., 2019; Li et al., 2019; Wang et al., 2019).

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To facilitate the development of mechanized and productive agriculture in China, plenty of marsh wetland has been transformed into farmland. In northeastern China, where half of the national marsh wetlands were originally located (Liu et al., 2005), the number and size of wetlands have dramatically decreased after several high tides of reclamation since 1950s. In the Sanjiang Plain of Heilongjiang province alone, 22831.3 km² of marsh wetland, which accounts for 89.5% of the original total 50 years ago, has been reclaimed (Bu et al., 2008; Li et al., 2002) and changed into an important agricultural base producing soybean, corn and rice (photos shown in Fig. S1). However, the reclamation activities may have promoted changes in the local climate from “cold and wet” to “warm and dry” (Wang et al., 2003), and intensively reduced the species diversity and the ecosystem services. Furthermore, this process has deteriorated the soil quality and impacted the geochemistry of nutrients (e.g., N, P) and harmful elements (e.g., Hg, Pb) (Q. Wang et al., 2012; Y. Wang et al., 2012). Liu et al., 2003a observed organic matter (OM) in wetland soil decreased by ~15% in the first several years after reclamation. Luan et al. (2003) found significant degradation in soil fertility and reduction in OM and total nitrogen after the wetland reclamation in Naoli River Basin of Sanjiang Plain. To date, the fundamental knowledge is still lacking regarding the regional Hg cycle, knowing that it can be strongly affected during sharp changes in soil conditions and climate.

Besides total Hg (THg), Hg isotope compositions could provide deeper insights in the complex geochemical processes involved (Bergquist and Blum 2007; Blum and Bergquist 2007; Blum et al., 2014; Perrot et al., 2010). Based on this principle, Hg isotope signals have been successfully applied in the source tracing of forest soil Hg (Wang et al., 2016; Yuan et al., 2019), lake/riverine sediments (Feng et al., 2010, 2013; Liu et al., 2011), etc.

During the reclamation of wetlands into farmland, a lot of small-scale reservoirs were built to receive the drainage produced from the reclamation process, and these reservoirs are also used to control the flood and to store water (Wang et al., 2013). Information concerning the landscape changing as well as the cultivation activities might be registered in such reservoir sediment.

Hence, in this study, we aimed to investigate the possible impacts of landscape changes on the Hg geochemistry in the local ecosystem by collecting samples of the reservoir sediment cores, agricultural soil and forest soil core in northeast China and analyzed THg contents, OM content and Hg isotope composition. Through analysis of the collected data we revealed the influence of natural and human activities on the biogeochemical cycle of Hg in the reservoir sediments. Knowledge obtained from this study is critical for understanding Hg cycling in this wetland-agricultural area during the past decades.

2. Materials and methods

2.1. Study area

The Xingkai reservoir (N45°27'22"; E132°16'58") located in east Mishan county, Jixi City, Heilongjiang Province was selected for this investigation (Fig. 1). The region belongs to the cold temperate zone with a semi-humid continental monsoon climate. The annual average temperature is 4°C and annual precipitation is 550 mm. Large-scale reclamation was initiated in 1958 and reached its climax during the following two decades in the county (Liu, 2006). During the process of transforming marshland to agricultural land, wide drainage channels were dug to drain water and to achieve a lower water level, and then the wetland plants were buried by ploughing. As a result, the land was excavated and cultivated. Xingkai reservoir was built in 1958 to serve the local reclamation, which has a water surface area of 2 km², an average water depth of 3 m and the drainage basin area of 64 km². The surrounding topography is dominated by plains and a small number of hills with height < 100 m. The main crops in the surrounding areas are corn and soybean seeded in May and harvested in late September or

early October, and the land lies fallow in winter.

2.2. Sample collection and preparation

Undisturbed reservoir sediment core samples were collected in October 2016 with a SWB-1 type portable reservoir sediment sampler being designed by Wang et al. (1998). The PVC tube for holding the reservoir sediment sampler has a 5.75 cm inner diameter and an 80 cm length. Two reservoir sediment cores (up to 37 cm length) were taken 5 m apart in the center of the reservoir and were divided at 1 cm intervals. The reservoir sediment core reached to the reservoir bottom that corresponds to the time the reservoir was built in late 1950 s (Mishan County Local Chronicles Compilation Committee, 1993). In addition, agriculture soils were taken at two sites to reflect the local soils, with one being very close (< 1 km) to the reservoir (Soil A) and another (Soil B) being about 50 km away northwest of the reservoir, both sites were reclaimed from the wetland and planted with corn. These two soil samples were used as the local erosion source as they have the same soil type of marsh soil. At each site, two soils, with one represents the surface (plough) layer (0–20 cm) and the other for the sub-surface layer (40–60 cm), were taken. In addition, a soil profile of a poplar-oak forest floor near the reservoir was collected, and this soil core has a total length of 57 cm from the surface litter layer to the bedrock layer which is used to reflect the local Hg background information. In addition, degradation layer (0–10 cm) samples and the wetland plants from the Sanjiang Plain Wetland Research Station in Heilongjiang province (ca. 240 km northeast of the reservoir) were collected to reflect the marsh wetland plant input during the reclamation. All these samples were freeze dried, homogenized and sieved to minus 200 meshes (0.075 mm) in the laboratory prior to chemical analysis, and all the parameters discussed below are reported on a dry-mass basis.

2.3. Determination of total mercury concentrations

Total Hg (THg) concentrations in reservoir sediments and soils were determined following the US EPA Method 7473 (USEPA, 2007). Solid samples were heated at 800° and the released Hg⁰ was measured by cold-vapor atomic absorption spectrometry (CVAAS) (Lumex RA915+, Russia) with a detection limit of 0.1 µg kg⁻¹. Each solid sample was determined at least three times to obtain a mean value. Accuracy was assessed using the certified reference material GBW07427 (GSS-13, soil, with certified THg of 52 ng g⁻¹), and the recovery of THg is 95%–106%.

2.4. Measurement of mercury isotope compositions

Hg isotopes in different solid samples (reservoir sediments, soils, and plants) were determined by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS, Nu Instruments Ltd., UK) with the method developed by Yin et al., 2010). Hg has seven natural stable isotopes: ¹⁹⁶Hg (0.15%), ¹⁹⁸Hg (9.97%), ¹⁹⁹Hg (16.87%), ²⁰⁰Hg (23.10%), ²⁰¹Hg (13.18%), ²⁰²Hg (29.86%) and ²⁰⁴Hg (6.87%). All of the isotopes except ¹⁹⁶Hg have sufficient abundance for precise measurements of isotope ratios (Blum and Bergquist, 2007). Of the two reservoir sediment cores, only one is subject for Hg isotope analysis due to the similarity of Hg concentration and other parameters in the twin cores. Briefly, solid samples were pre-concentrated into 5 mL of a 40% mixed acid solution (v/v, 2HNO₃/1HCl) using a double-stage combustion protocol for Hg isotope analysis (Sun et al., 2013). The standard-sample-bracketing method was used, and Tl standard solution (NIST SRM 997) was used as an internal standard to eliminate the instrument's shifting effect. Concentrations between the diluted samples and bracketing standards (NIST SRM 3133) were matched within 10%.

All Hg isotope ratio variations are expressed relative to the bracketing Hg standard. The mass-dependent fractionation (MDF) was used by the δ-notation (‰), and defined by the following equation:

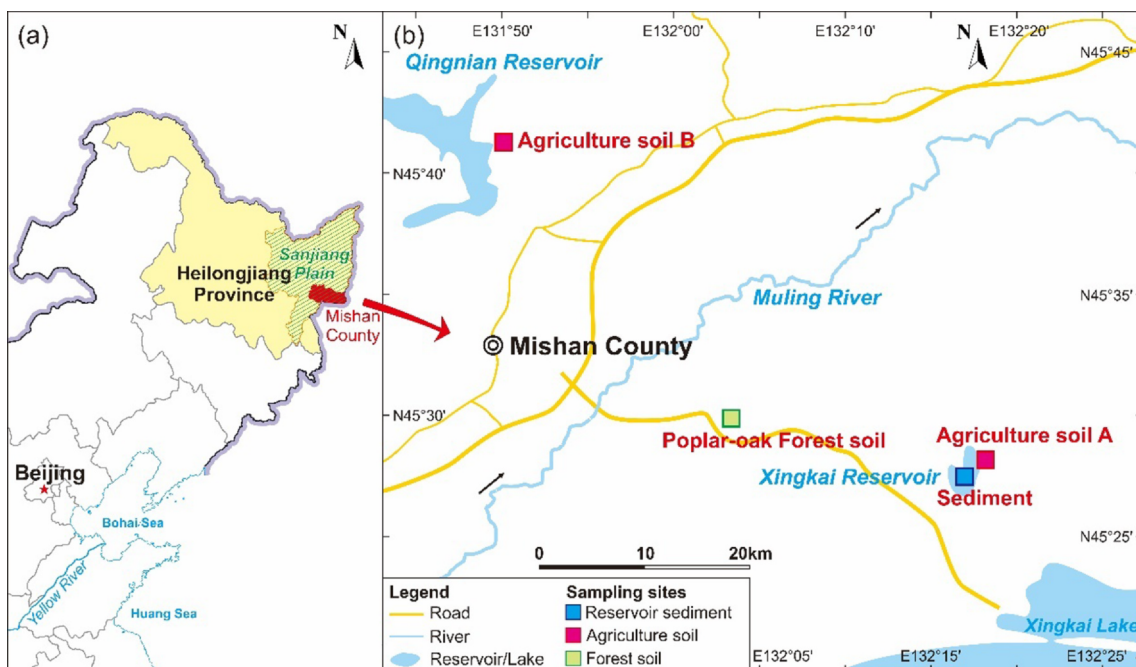


Fig. 1. Location of the sampling sites.

$$\delta^{xxx}\text{Hg}(\text{‰}) = 1000 \times \left[\frac{(\text{xxxHg}/^{198}\text{Hg})_{\text{sample}}}{(\text{xxxHg}/^{198}\text{Hg})_{\text{NIST3133}}} - 1 \right] \quad (1)$$

Where ^{xxx}Hg is ^{199}Hg , ^{200}Hg , ^{201}Hg or ^{202}Hg . $^{xxx}\text{Hg}/^{198}\text{Hg}_{\text{std}}$ is the isotope ratio of the reference standard solution (NIST SRM 3133). Mass independent fractionation (MIF) is reported as Δ -values and represents the difference between the measured and theoretically predicted value of $\delta^{xxx}\text{Hg}$ (Blum and Bergquist, 2007).

$$\Delta^{199}\text{Hg}(\text{‰}) = \delta^{199}\text{Hg} - 0.2520 \times \delta^{202}\text{Hg} \quad (2)$$

$$\Delta^{200}\text{Hg}(\text{‰}) = \delta^{200}\text{Hg} - 0.5024 \times \delta^{202}\text{Hg} \quad (3)$$

$$\Delta^{201}\text{Hg}(\text{‰}) = \delta^{201}\text{Hg} - 0.7520 \times \delta^{202}\text{Hg} \quad (4)$$

Reproducibility of the isotopic data was assessed by measuring one replicate sample digests in every 10 samples. UM-Almadén solution was also analyzed as a secondary standard. Our repeated measurements of UM-Almadén ($\delta^{202}\text{Hg}$: $-0.51 \pm 0.06\text{‰}$; $\Delta^{199}\text{Hg}$: $-0.02 \pm 0.05\text{‰}$; $\Delta^{201}\text{Hg}$: $-0.04 \pm 0.05\text{‰}$; 1SD, $n = 12$), BCR-482 ($\delta^{202}\text{Hg}$: $-1.60 \pm 0.05\text{‰}$; $\Delta^{199}\text{Hg}$: $-0.61 \pm 0.03\text{‰}$; $\Delta^{201}\text{Hg}$: $-0.54 \pm 0.02\text{‰}$; 1SD, $n = 2$) and GBW07405 (GSS-5, $\delta^{202}\text{Hg}$: $-1.88 \pm 0.01\text{‰}$; $\Delta^{199}\text{Hg}$: $-0.37 \pm 0.01\text{‰}$; $\Delta^{201}\text{Hg}$: $-0.27 \pm 0.00\text{‰}$; 1SD, $n = 2$) were consistent with previously reported ones (Blum and Bergquist, 2007; Estrade et al., 2009; Huang et al., 2015).

2.5. Analysis of organic matter

The organic matter (OM) content in all reservoir sediment and soil samples was determined by sulphuric acid–potassium dichromate hydration method (GB 9834–1988).

2.6. Statistics

In this study, all data analyses were carried out using Microsoft Excel 2019 and SPSS 21.0, and the significance level for all statistical analyses (one-way ANOVA) was $p < 0.05$. Origin 2017 and Corel draw 2018 were used to draw the figures.

3. Results

3.1. THg concentrations in reservoir sediments and soils

THg concentrations in the reservoir sediment cores were in the range of $38.2\text{--}60.6 \text{ ng g}^{-1}$. The average THg concentrations were very close between the two reservoir sediment cores, with $43.3 \pm 4.2 \text{ ng g}^{-1}$ for core #1 and $42.2 \pm 3.2 \text{ ng g}^{-1}$ for core #2. An identical vertical distribution pattern was found for these two cores (Fig. 2), indicating that they both reflect a similar geochemical process of Hg. There was a clear increasing trend of THg from the upper layer to the deeper layer (Fig. 2). The sharp increase of THg concentration appeared in the deepest several centimeters, namely, 30–37 cm depth, with a maximum increase of 22.4 ng g^{-1} .

There are significant differences ($p < 0.01$) in THg concentration between the reservoir sediment and soil samples (Fig. 3, Table S1). The highest THg concentrations were observed in reservoir sediments, followed by the agricultural soils at the two sites (range:

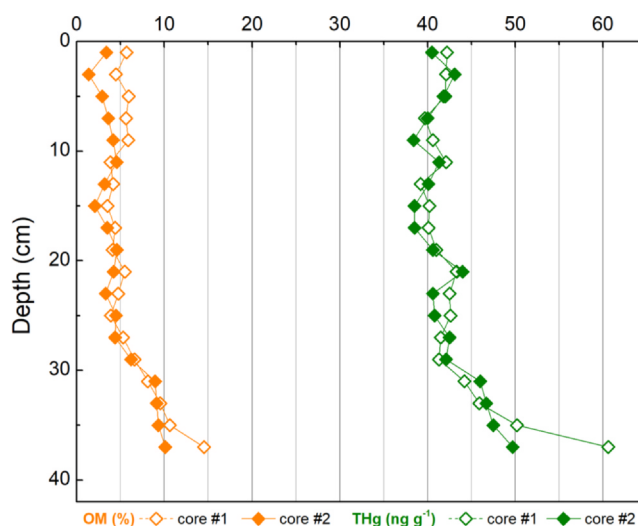


Fig. 2. Distribution of THg and OM in reservoir sediment cores.

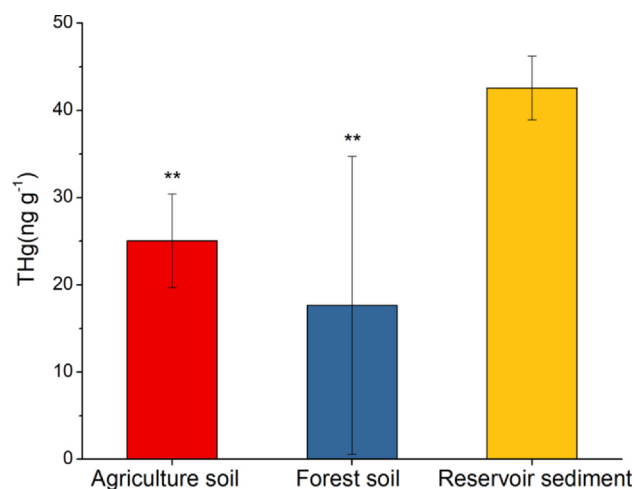


Fig. 3. Comparison of the average THg concentration in reservoir sediment and soil samples. (the error bar stands for the standard deviation; **, $p < 0.01$, significant difference with reservoir sediment.)

17.3–33.8 ng g⁻¹, mean: 25.0 ± 5.4 ng g⁻¹, $n = 4$), and the lowest values at the forest soil (range: 7.8–66.9 ng g⁻¹, mean: 17.2 ± 16.4 ng g⁻¹). THg value as low as 7.8 ng g⁻¹ was measured at the bottom layer (57 cm depth) of the forest soil core (Table S1 in the supporting information), which reflects the Hg level in the local bedrocks or the local soil background. Several folds of Hg enrichment were observed in the reservoir sediment and agricultural soils than the local soil background. In addition, Hg content in the marsh wetland, especially in the degradation layer (uppermost 10 cm) (113.6 ± 4.3 ng g⁻¹, $n = 3$), was notably higher than those in the other non-wetland environmental media, indicating the marsh wetland acting as an Hg sink of the local environment.

3.2. Organic matter

Similar to THg, there was no significant difference ($p > 0.05$) in average OM content between the two reservoir sediment cores (core #1: $6.13 \pm 2.80\%$, core #2: $4.92 \pm 2.58\%$), and the same vertical variation trend of OM in these two cores was observed (Fig. 2). Up to 15% of OM was found in the deeper sediment section (> 30 cm), while only < 5% in the most upper layer (10 cm).

3.3. Mercury isotope signatures

In this study, $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$ are used to represent the MDF and MIF, respectively, and only reservoir sediment core #1 was investigated for the Hg isotope composition. $\delta^{202}\text{Hg}$ values varied from -1.29 to -0.94% in the reservoir sediments of Xingkai reservoir (Fig. 4), with a positive shift of 0.35‰ from the deeper to the upper layer.

4. Discussion

4.1. Drivers of variation in reservoir sediment core THg and organic matter

The THg profile showed increasing concentration with depth in the reservoir sediment cores. A previous study revealed that the wetland Hg pool will be lost due to the reclaiming of marsh wetland into agricultural farmland in Sanjiang plain, especially in the early stages (1–7 yr) of reclamation and with a Hg lost rate of -3.7 ng/(g·yr) (Liu et al., 2002). The lost Hg is leached out and combined with OM (Jiskra et al., 2017) and settled down in the nearby reservoir. Liu et al. (2018) found a mean sedimentation rate for five lakes in Sanjiang Plain of 0.18–0.49 cm/yr for the past 180 yrs with a maximum of 1 cm/yr during the reclamation peak. The average sediment deposition rate

(0.62 cm/yr) of this study is somewhat higher than the previous study, which is due to the intensive disturbance occurred in the past 50–60 yrs.

Most of the wetland plants in northeast China are herbaceous plants (such as *Carex lasiocarpa*, *Carex meyeriana*, *Carex pseudocuraica*, etc.) with large leaf and biomass. THg content of these plant/biomass was relatively high (Liu et al., 2002), especially moss (94 ± 44 ng g⁻¹), *Carex limosa* (83 ng g⁻¹), *Carrel lasiocarpa* (51 ± 21 ng g⁻¹), and litter fall (113.6 ± 4.3 ng g⁻¹) (Liu et al., 2002; Liu et al., 2004). Hg, C, N and S in the marsh wetland ecosystem was found to be decreased in the process of reclamation in Sanjiang Plain (Liu et al., 2002; Wang et al., 2012). Hence, the higher THg concentration in the deeper sediment layer relative to the upper layer in present study records the landscape changes from the Great Northern Wilderness to the Great Northern Barn in this area during 1950s–1960s, which resulted in large amounts of Hg and OM lost with drainage that entered into the reservoir and recorded in the reservoir sediments.

Previous studies revealed that free Hg ion and inorganic Hg species bind strongly with OM, and OM appears to be a key parameter to control the dynamics of Hg in reservoir sediment and water (Ravichandran, 2004; Rydberg et al., 2010; Sanei and Goodarzi, 2006). In this study, THg and OM correlated significantly for the reservoir sediment, agricultural soil and forest soil (Fig. 5), revealing that OM is a fundamental influencing factor of Hg in different environmental media of the study area. THg and OM in the reservoir sediments are both higher at the deeper than the upper layer, which is contrary to the trend observed in reservoir sediments in the barren Wujiang River Basin of Guizhou province, southwest China (Meng et al., 2016), where OM is built up by the action of endogenous microorganism over time (> 10 yr) after the reservoir was constructed. In the forest case of this study, an opposite vertical trend, namely, higher OM content in the upper than deeper layer, was found due to the Hg input by the litter fall or atmospheric dry deposition in forest ecosystem (Demers et al., 2007; Zheng et al., 2016). The close relationship of OM and THg in the study area suggests a common source, likely being plant, for these two chemical species.

With the reclamation weakened, both THg and OM in reservoir sediment dropped down. Nevertheless, THg in the surface (0–20 cm) reservoir sediments (40 – 42 ng g⁻¹) is higher than the local surface agriculture soils (21 – 28 ng g⁻¹), which might be caused by the leaching out/erosion of soil Hg and the lower Hg content in crop plants (5.7 – 51.9 ng g⁻¹) than the wetland plants (up to 142.1 ng g⁻¹) (Liu et al., 2003; Liu et al., xxxx).

4.2. Implications of Hg isotope signatures in reservoir sediment core

A recent study shows that light Hg is preferentially lost from the buried plants during the degradation process (Yuan et al., 2020), that might render the lighter $\delta^{202}\text{Hg}$ being leached out in the drainage water and preserved in the lower reservoir sediment layer during the reclamation stage. Negligible odd-MIF was observed in the reservoir sediment, e.g., the $\Delta^{199}\text{Hg}$ values ranged from -0.04 to $+0.11\%$, with a mean value of -0.02% . The ratio of $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ (~ 0.6) in this study is close to the ratio (0.86 ± 0.30) of Hg re-emissions from the leaf in the forest ecosystem (Yuan et al., 2019). Therefore, the MIF signals observed in the reservoir sediment should be related to the plant degradation process or the buried foliage re-emissions, rather than other processes, such as liquid–vapor evaporation of Hg (Wiederhold et al., 2010), Hg²⁺ dark reduction (Zheng and Hintelmann, 2010), or Hg²⁺-thiol adsorption (Bergquist and Blum, 2007), that have a distinct $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ ratio of 1.5–1.8, or Hg²⁺/methylmercury photo-reduction that has a $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ ratio of 1.00–1.36 (Bergquist and Blum, 2007; Zheng and Hintelmann, 2009).

Lighter $\delta^{202}\text{Hg}$ in deep reservoir sediments (> 20 cm) was likely due to the large amount of Hg imported from the wetland plants with relatively lighter $\delta^{202}\text{Hg}$, because light $\delta^{202}\text{Hg}$ has been observed for

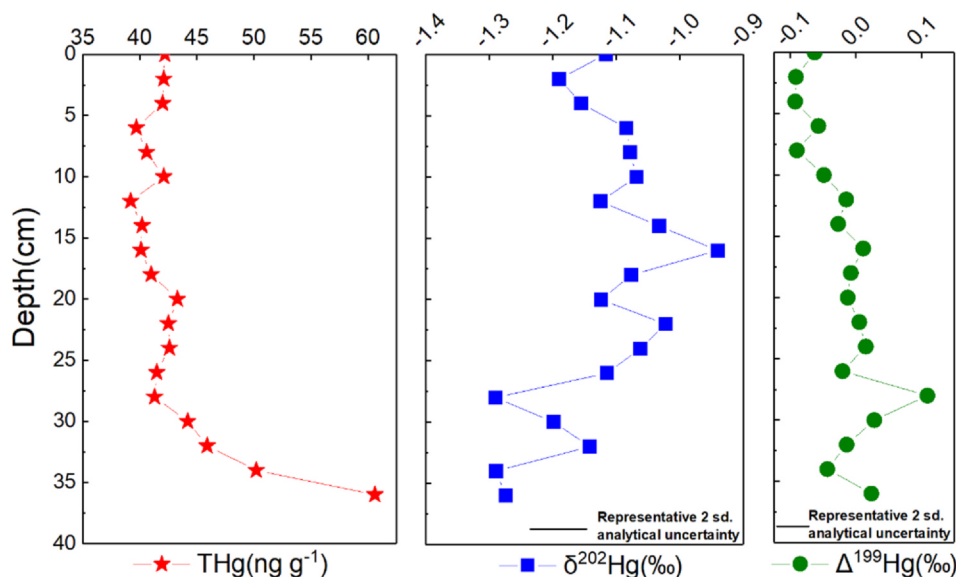


Fig. 4. THg, $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$ in reservoir sediment core.

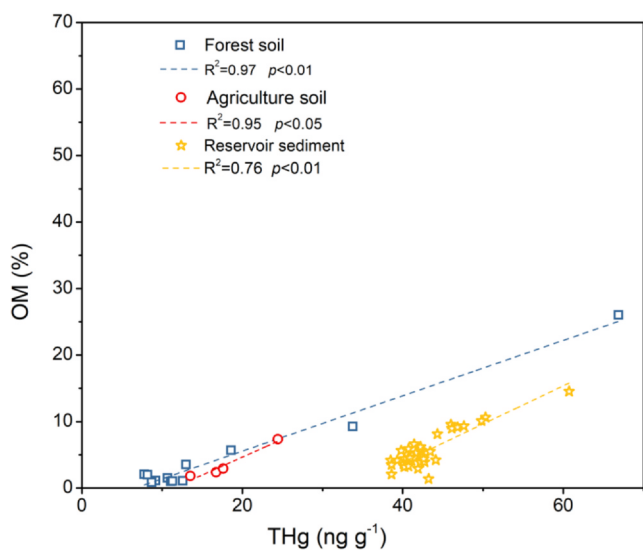


Fig. 5. Relationship between THg and OM in different samples.

plant leaves of different ecosystem (e.g., forest (-3.23‰) (Yuan et al., 2020), rice plant (-3.18‰) (Yin et al. 2013), corn (-3.25‰) (Sun et al., 2019), mangrove plant (-2.60‰) (Sun et al., 2017)), and Hg isotope of leaves is the lightest among different organs of a plant (Demers et al., 2013; Jiskra et al., 2017; Yin et al., 2013). The wetland plant leaf and degradation layer of the marsh in this study also featured with a relatively negative $\delta^{202}\text{Hg}$ signal (leaf: -1.86‰ , degradation layer: -1.15‰ , Tables S2 and S3). Thus, reclamation of wetland has led more isotopic light Hg transport out from the system by the drainage, which has then been recorded in the reservoir sediment. Therefore, $\delta^{202}\text{Hg}$ in the deeper reservoir sediments ($> 20\text{ cm}$) was the most negative, which should be mainly attributed to wetland plant leaves that is the mostly decomposable parts. With less human disturbance in this area after 1980s, reservoir sediment Hg was mainly imported from the leaching or erosion of agricultural soil at a lesser intensive level in terms of total input of THg, which resulted in more positive $\delta^{202}\text{Hg}$ in the upper layer ($< 20\text{ cm}$). In recent years, the thickness of black soil and OM content have decrease significantly due to the overuse of black soil in Northeast China (Wang, 2008), which led to Hg loss from soil and finally accumulated in the surrounding reservoir sediments.

The mixing-models have been successfully used to discriminate the Hg pollution sources in different environments based on the Hg isotope composition of different end members (Feng et al., 2010; Foucher et al., 2009; Lepak et al., 2015). In order to disclose the possible influencing factors that drives the Hg dynamics in the reservoir sediment, a triple mixing-model (equations 5–7 below) was used in this study. The possible sources considered here includes dry deposition (dry dep.), wet deposition (wet dep.), the erosion of farmland soil (erosion) and the buried plants (plants). Hg isotope signatures in the agricultural soils and wetland plant and upper most degradable layer (0–10 cm) measured in the present study were used for calculating the contributions from the farmland soils and the buried wetland plants, respectively. Dry and wet deposition data were not directly available for this region, therefore, the rainwater isotope ratio in North America with a similar latitude (Gratz et al., 2010) was used to represent the wet deposition in the northern hemisphere agricultural area. The particulate bound Hg (PBM) isotope composition in Changbai Mountain of the Northeast China was used for estimating the dry deposition (Fu et al., 2019).

$$X \cdot \Delta^{199}\text{Hg}_{\text{dry dep.}} + Y \cdot \Delta^{199}\text{Hg}_{\text{wet dep.}} + Z \cdot \Delta^{199}\text{Hg}_{\text{erosion or plants}} = \Delta^{199}\text{Hg}_{\text{reservoir sediment}} \quad (5)$$

$$X \cdot \delta^{202}\text{Hg}_{\text{dry dep.}} + Y \cdot \delta^{202}\text{Hg}_{\text{wet dep.}} + Z \cdot \delta^{202}\text{Hg}_{\text{erosion or plants}} = \delta^{202}\text{Hg}_{\text{reservoir sediment}} \quad (6)$$

$$X + Y + Z = 1 \quad (7)$$

where X, Y and Z represent the contribution of different Hg sources of the dry deposition, wet deposition and human activities (farmland tillage or the buried plants), respectively. As discussed above, the deeper ($> 20\text{ cm}$) and upper ($< 20\text{ cm}$) sediments were affected by different disturbances (reclamation or soil erosion induced by agricultural tillage), thus, different endmembers were used in the calculation, with input by dry/wet deposition and buried plants for the deeper sediment and dry/wet deposition and soil erosion for the upper sediment. There is no significant difference in isotope composition between the lower reservoir sediment ($> 20\text{ cm}$) and the marsh wetland degradation layer ($p > 0.05$) (Table S2; Fig. 6). It can be considered that the deeper reservoir sediment was formed by the degradation and decay of plants during the early development. The surface layer of the reservoir sediment ($< 20\text{ cm}$) is significantly close to the end-member of agriculture soils, indicating that it was greatly affected by the farmland soil in the later stage of sedimentation (Fig. 6). The results of

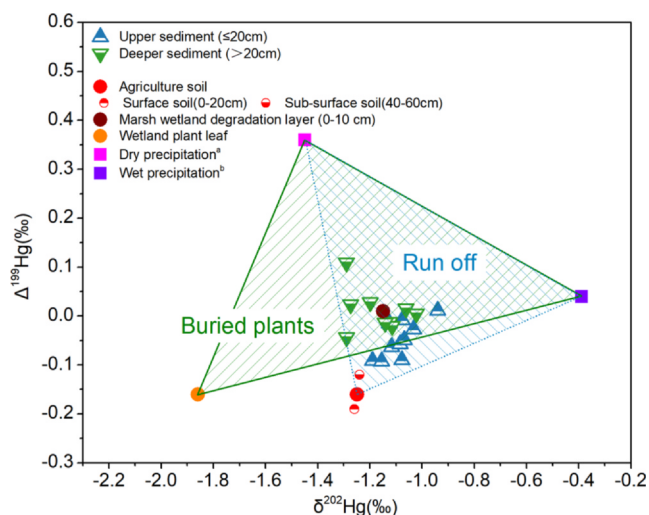


Fig. 6. A triple mixing-model describing the Hg source in sediments. (Solid squares represent isotopic ranges reported in selected previous relevant studies which contain dry deposition^a (particulate bound mercury) Hg isotopic composition data from Fu et al. (2019), wet deposition^b (rain) Hg isotopic composition data from Gratz et al. (2010). The green shadows indicate the Hg isotope composition of the deeper sediments (> 20 cm) and the blue shadows indicate the Hg isotope composition of the upper sediments (≤20 cm).)

the mixing model calculation indicated that agriculture soils in the later stage of reservoir sediment formation accounted for about two-thirds of Hg input, much larger than the atmospheric dry deposition and wet deposition (Table S2). Most nitrogen and potassium chemical fertilizer do not contain significant Hg (Tang et al., 2018), and thus the source of chemical additives could be neglected here. Therefore, we conclude that Hg in the sediments of this research were originated from the reclaimed marsh wetland in early stage and from the soil erosion in the later stage, while a smaller proportion was stemmed from the atmospheric dry/wet deposition. This study also implies that the isotope composition of wetland plants is preserved well in the reservoir sediments during the process of wetland reclamation, which might be similar to the coal forming process that inherit the isotope information of coal-forming plants (Sun et al. 2016).

5. Conclusion

Based on the analysis of a range of environmental parameters, including THg, OM and Hg isotope compositions in a reservoir sediment, the processes and mechanisms of Hg input to the reservoir close to farmlands reclaimed from marsh wetlands in northeast China are unveiled. THg concentrations in the reservoir sediment cores of Xingkai Reservoir ranged from 38.2 to 60.6 ng g⁻¹. Higher THg and OM content and lighter δ²⁰²Hg composition are observed in the deeper (> 20 cm) than the upper (< 20 cm) reservoir sediment layer, which reflects the reclamation processes of marsh wetlands into farmlands as the main Hg input in the early stages (~50–60 yrs ago) and the soil erosion/runoff as the main Hg input in the later periods (after 1980s). This work indicates that measuring total Hg concentration and isotope composition could provide an important clue for exploring the impacts of land scape changes and agricultural activities on the Hg biogeochemistry in northeast China for the past several decades. In the future, Hg input from the local dry/wet deposition, as well as soil erosions, should be quantified in order to acquire a more precise Hg geochemistry panorama of this area.

Declaration of Competing Interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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