The 14th International Symposium on
BIOGEOCHEMISTRY OF WETLANDS & AQUATIC SYSTEMS

Mercury properties and transformations in the sediments of wetlands in the Yangtze River Estuary

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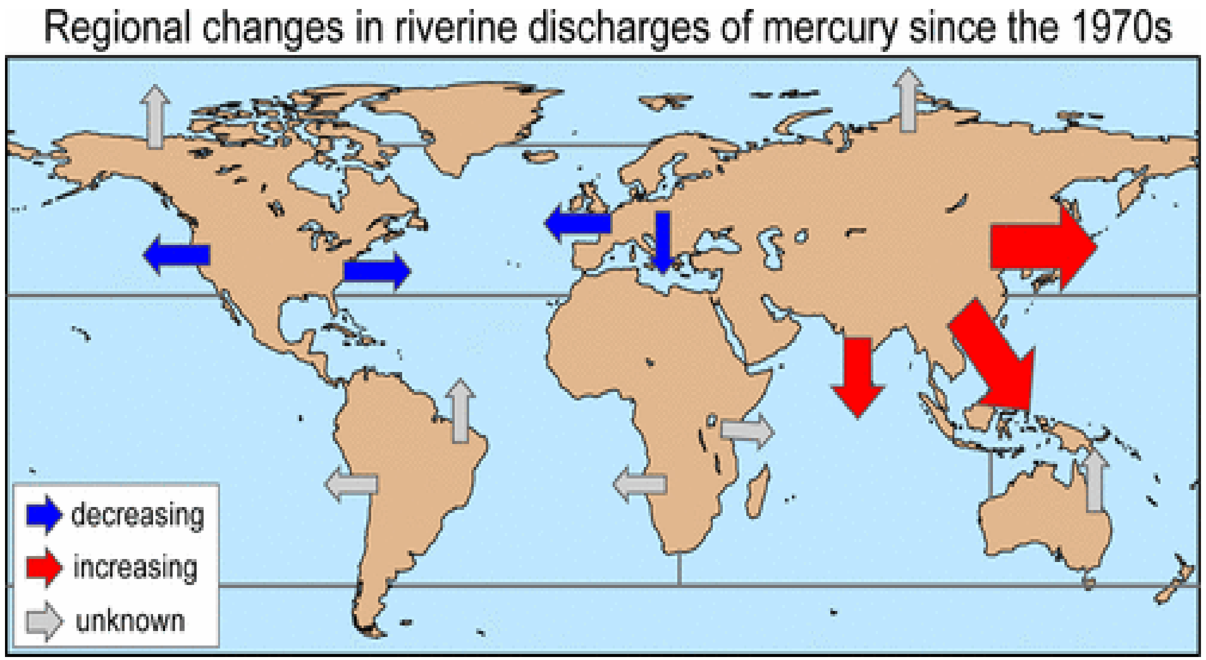
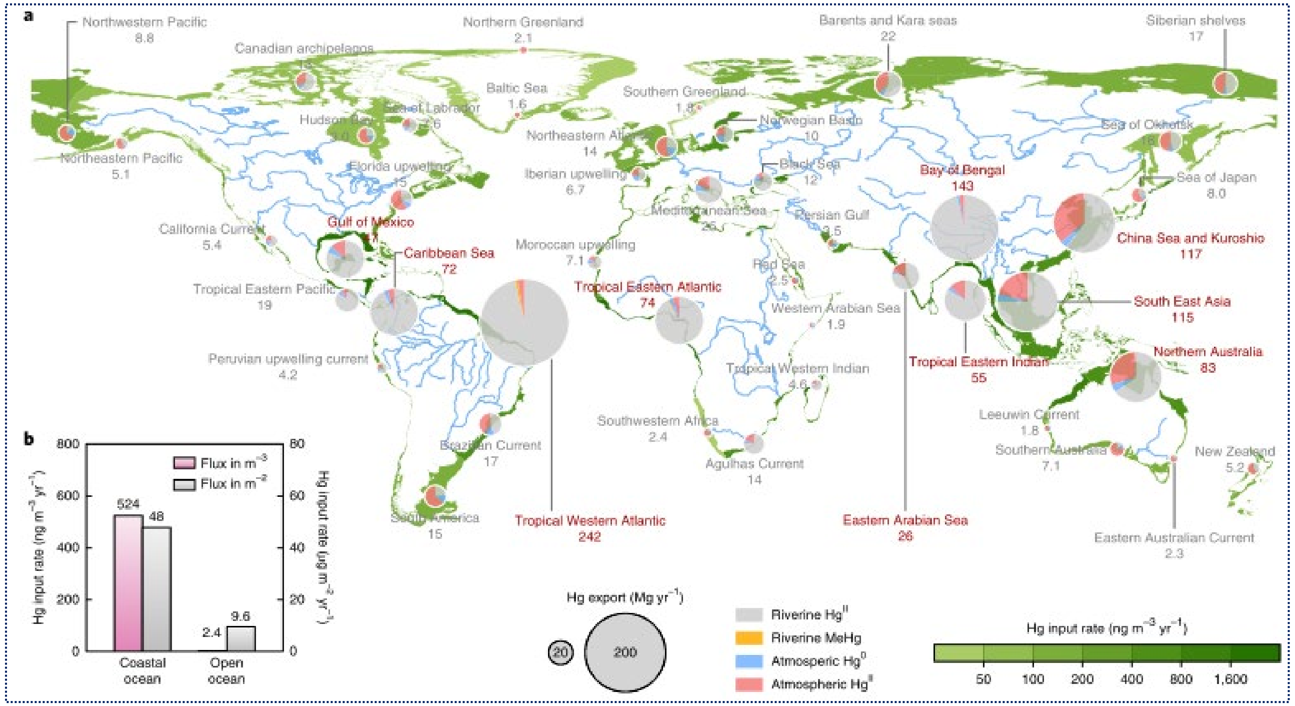
Rivers are the largest source of mercury for coastal oceans worldwide

Mercury is a global pollutant that affects human and ecosystem health



Amos et al., 2014, Environ. Sci. Technol.



Liu et al., 2021, Nat. Geosci.

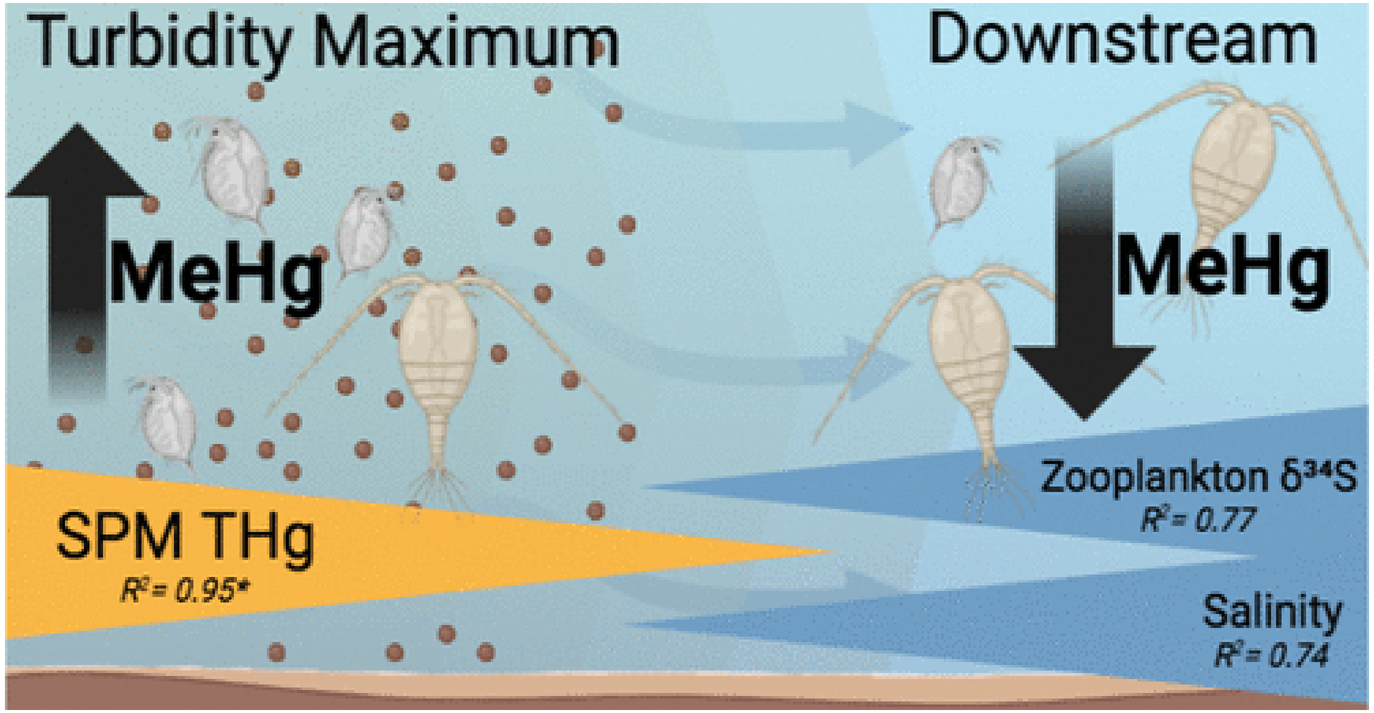
For example, based on the observed data before 2015, the riverine Hg increased in Asia (Amos et al., 2014, Environ. Sci. Technol.)

Estuaries are important locations for the cycling of Hg, which results in the bioaccumulation of MeHg in estuarine fish and shellfish

Bacteria → Invertebrates → fish and shellfish

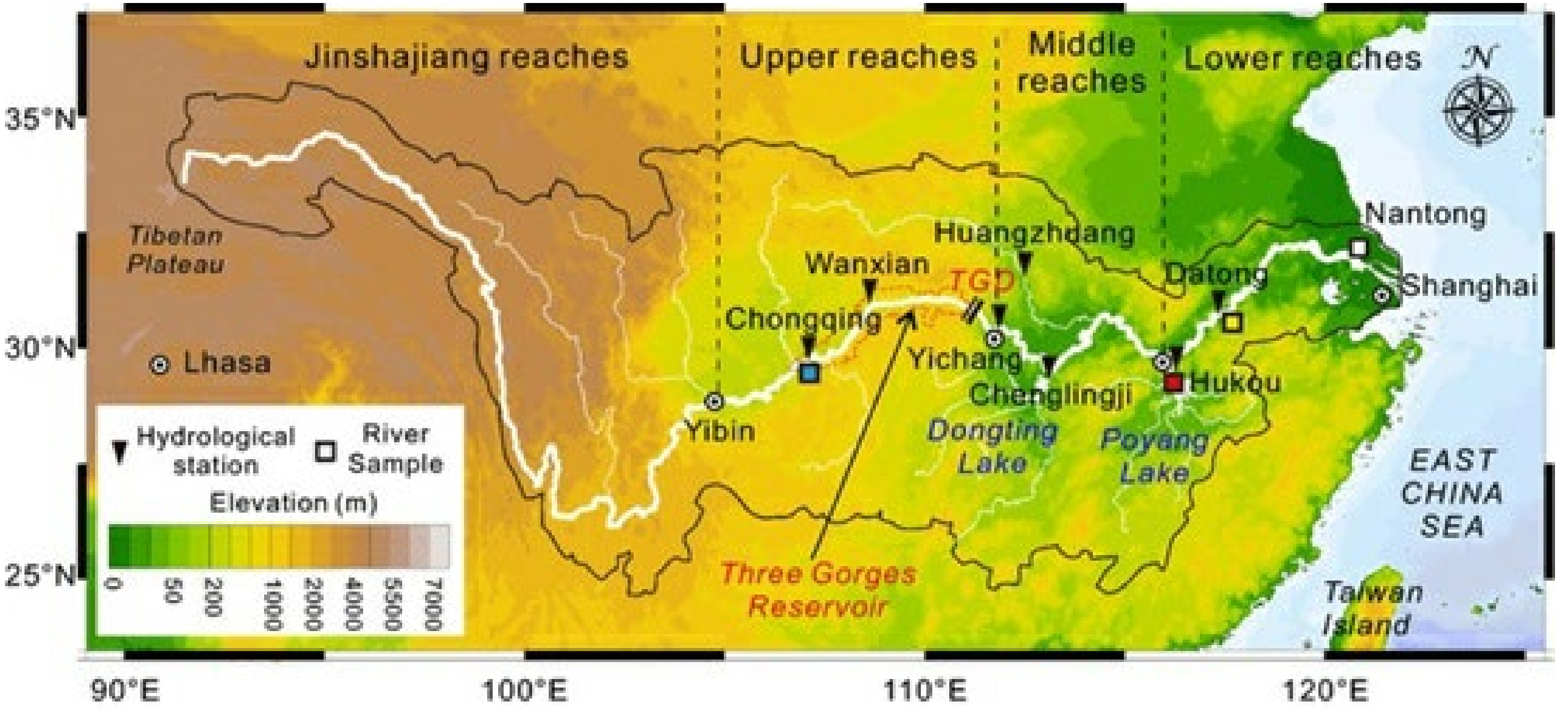
Hg(II) MeHg MeHg

Willacker et al., 2017, Environ. Sci. Technol.

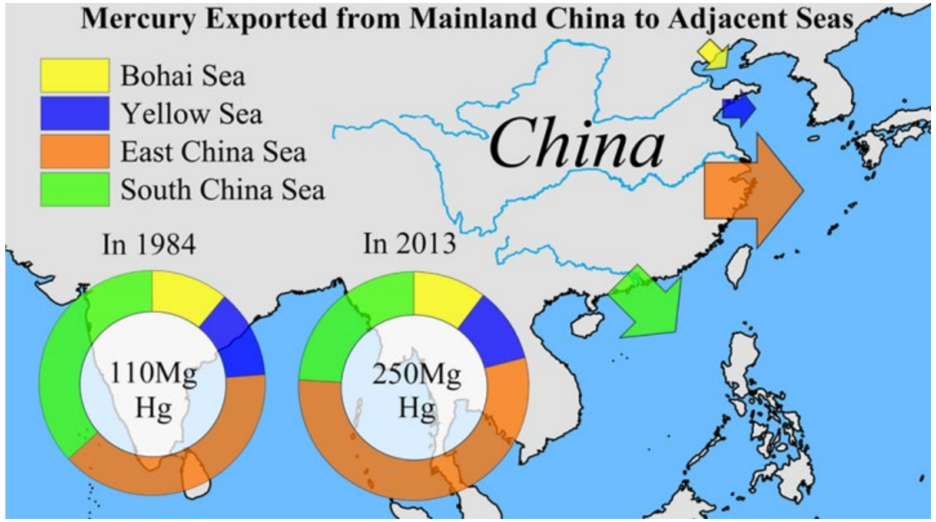


Vogl et al., 2025, Environ. Sci. Technol.

The Yangtze River is a major contributor to riverine Hg flux in East Asia



Topographical map of the Yangtze River basin
(Li et al., 2020, Environ. Sci. Eur)



Liu et al., 2016, Environ. Sci. Technol.

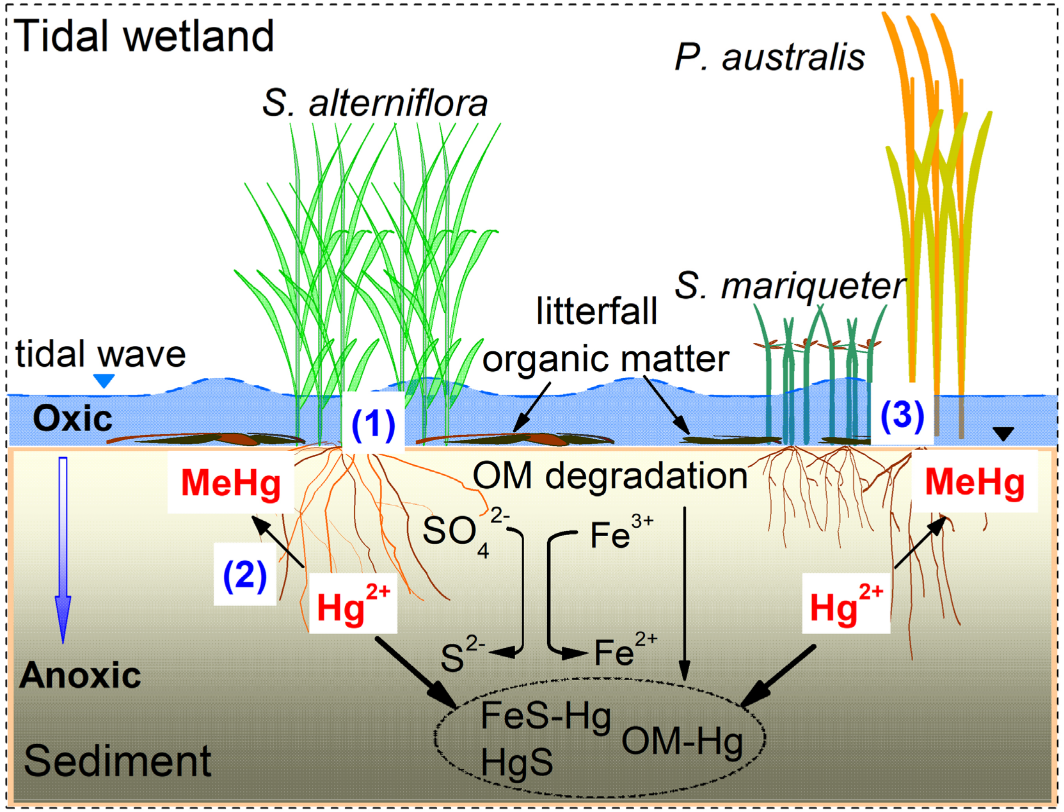
It is estimated that 48 ± 8.4 Mg Hg were released into the East China Sea in 2016 (Liu et al., 2021, Environ. Sci. Technol.)

Problem

➢ Mercury (Hg) enters Yangtze River Estuary (YRE) and its adjacent sea.

- The properties and fate of Hg in sediments in estuarine environments, particularly with regard to net MeHg production, are unclear.

- The linkages between external Hg inputs and the formation of MeHg under frequent redox oscillations are of interest.



(1) The plants facilitate riverine Hg deposition

(2) MeHg production in sediments

(3) Sediment resuspension affects suspended particulate Hg dynamics

Objectives

- ✓ To better understand the biogeochemical reactivity and mobility of Hg in sediments in YRS by using thermo-desorption techniques and chemical extraction methods

- ✓ To examine the potential of Hg methylation under scenarios of external Hg input and periodically changing redox conditions by microcosm experiments.

Study area

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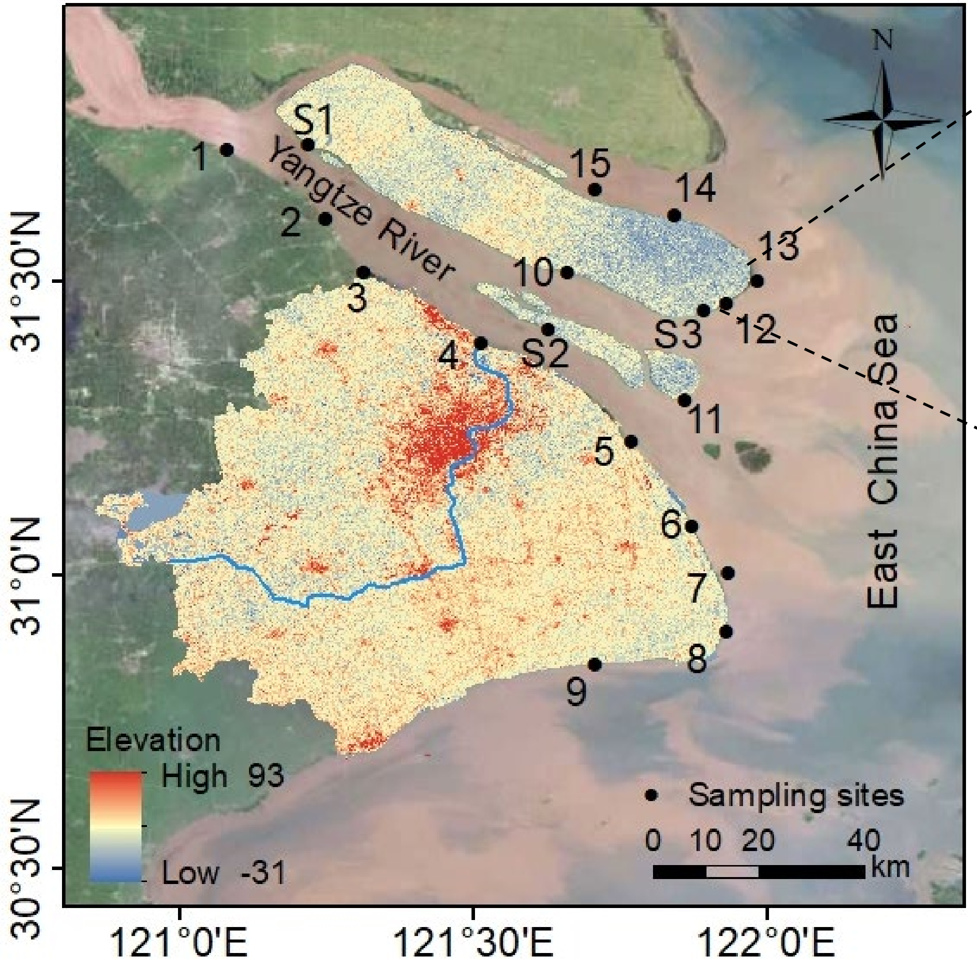

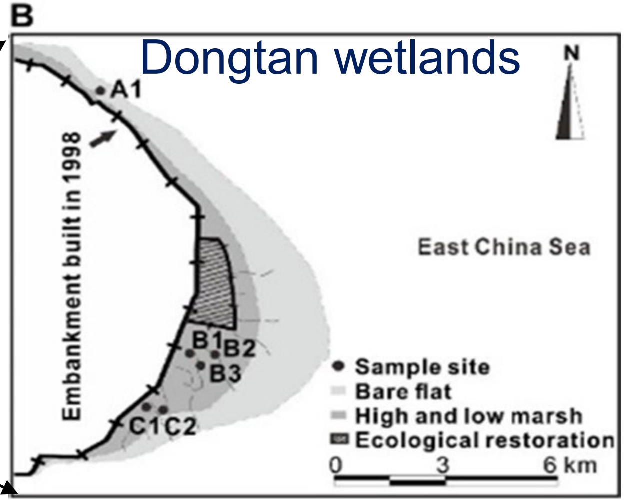

Sediment deposition has led to the formation of a wide variety of wetlands in YRS.

Sample collection and preparation

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Surface sediments	Sediment cores	Total number
Jul. 12–31, 2024		16*
2023		24
Nov. 16–26, 2019		15*
	Nov., 2020 and Jan., Apr., and Aug., 2021	24 cores
2012	2017–2019	32; 20 cores

*Unpublished data

Lyophilization → Samples were powdered with an agate mortar → Samples were sieved through 150-μm nylon mesh

Methods-1

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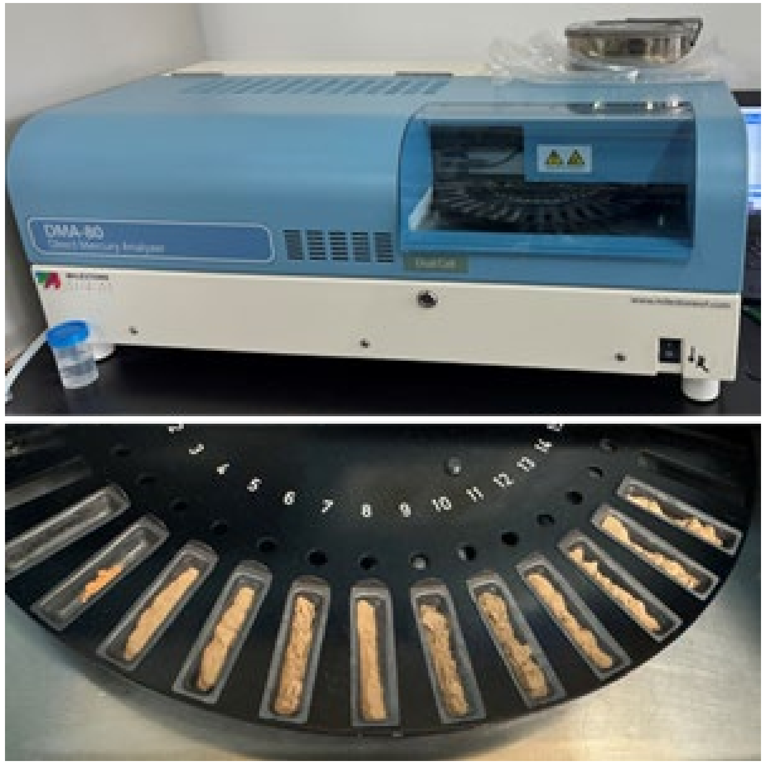
Thermo-desorption methods*

Temperature	T1 (s)[a]	T2 (s)[b]	Hg Compounds	Abbreviation
175 ℃	120	540	HgI_2, Hg_2Cl_2, $HgBr_2$, $HgCl_2$	Hg_{175}
225 ℃	120	480	MeHg, Hg bound to humic acids	Hg_{225}
325 ℃	180	540	HgS	Hg_{325}
750 ℃	180	180	HgO, $HgSO_4$, HgF, Hg embedded in mineral matrices	Hg_{750}
650 ℃	90	90	Total Hg	THg

[a]The heating time required to reach a target temperature;
[b]The duration over which the target temperature was maintained.



Direct mercury analyzer (DMA-80, Milestone, Italy)

* A modified method according to protocol of Saniewska & Bełdowska, 2017.

Methods-2

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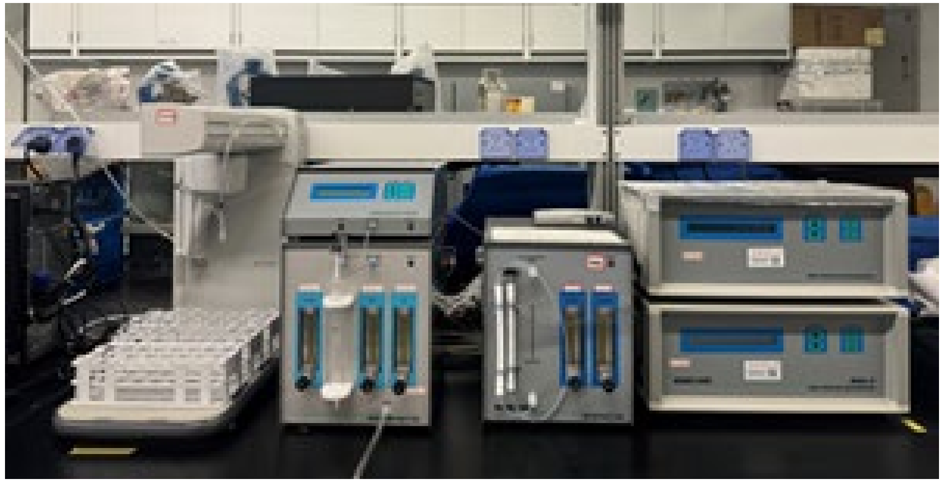
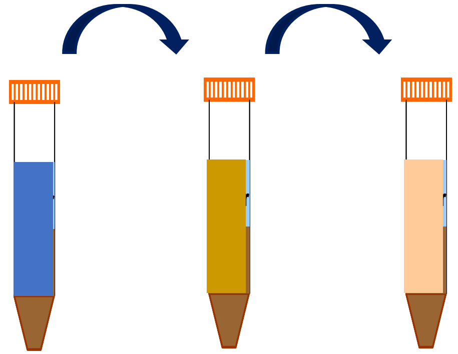
Sequential selective extraction method*

Solution	Extraction	Hg Compounds	Abbreviation
0.5 M HCl	1 h, 1:1000 (w/v)	Fractions closely associated with highly reactive and poorly crys-talline iron oxides	**HCl-extractable Hg**
1 M KOH	18 h, 1:1000 (w/v)	Hg bound to humic acids	**KOH-extractable Hg**
0.2 M BrCl	120 h, 2-5% (v/v)	Residual compounds	**BrCl-extractable Hg**



CVAFS (Model III, Brooks Rand, USA)



* A modified method according to protocol of Olund et al., 2004, Reis et al. 2016 and Bloom et al. 2003

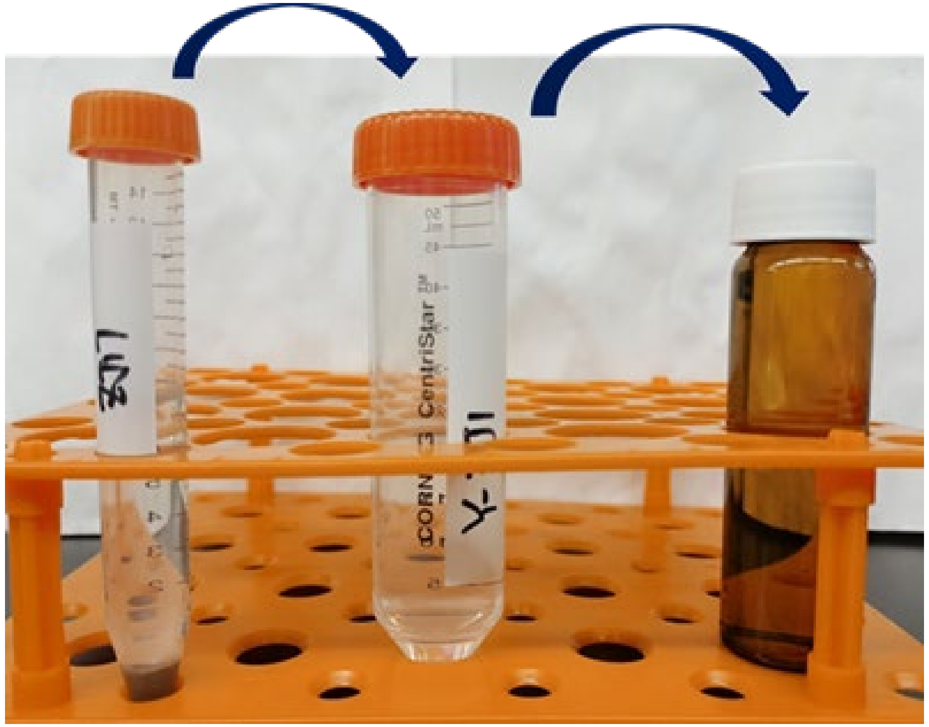
Measurements of THg in solution were performed following the U.S. EPA method 1631

Methods-3

The determination of MeHg concentrations in sediments was performed using a $CuSO_4$–HNO_3–CH_2Cl_2 extraction method (Liang et al., 2004) and was analyzed by CVAFS following USEPA Method 1630 (USEPA, 2001).

The reference materials of GBW07305 for sediment Hg (NRCCRM, China), and ERM-CC580 for estuarine sediment MeHg (IRMM, Belgium) were used to ensure the quality of digestion and analysis.

The recoveries were 92.2%, RSD= 6% (n=7) for Hg and 80.2%, RSD=4.6% (n=5) for MeHg.



Results and discussion

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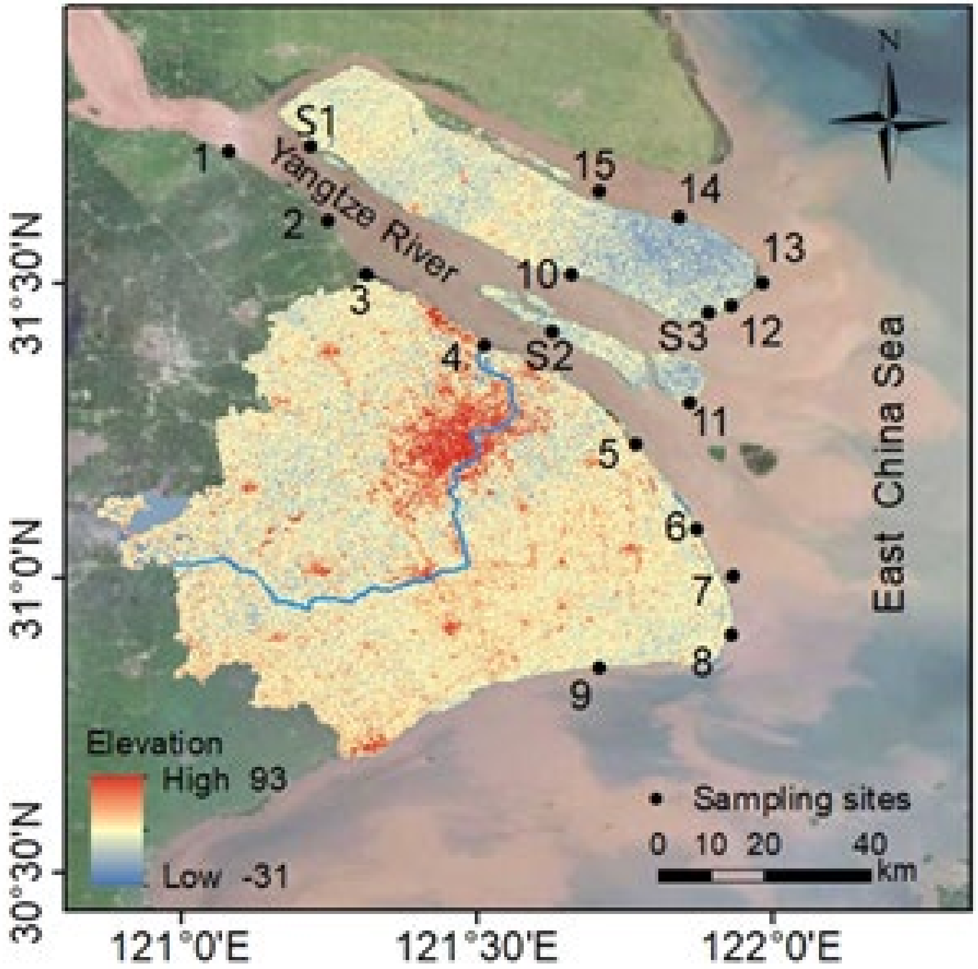
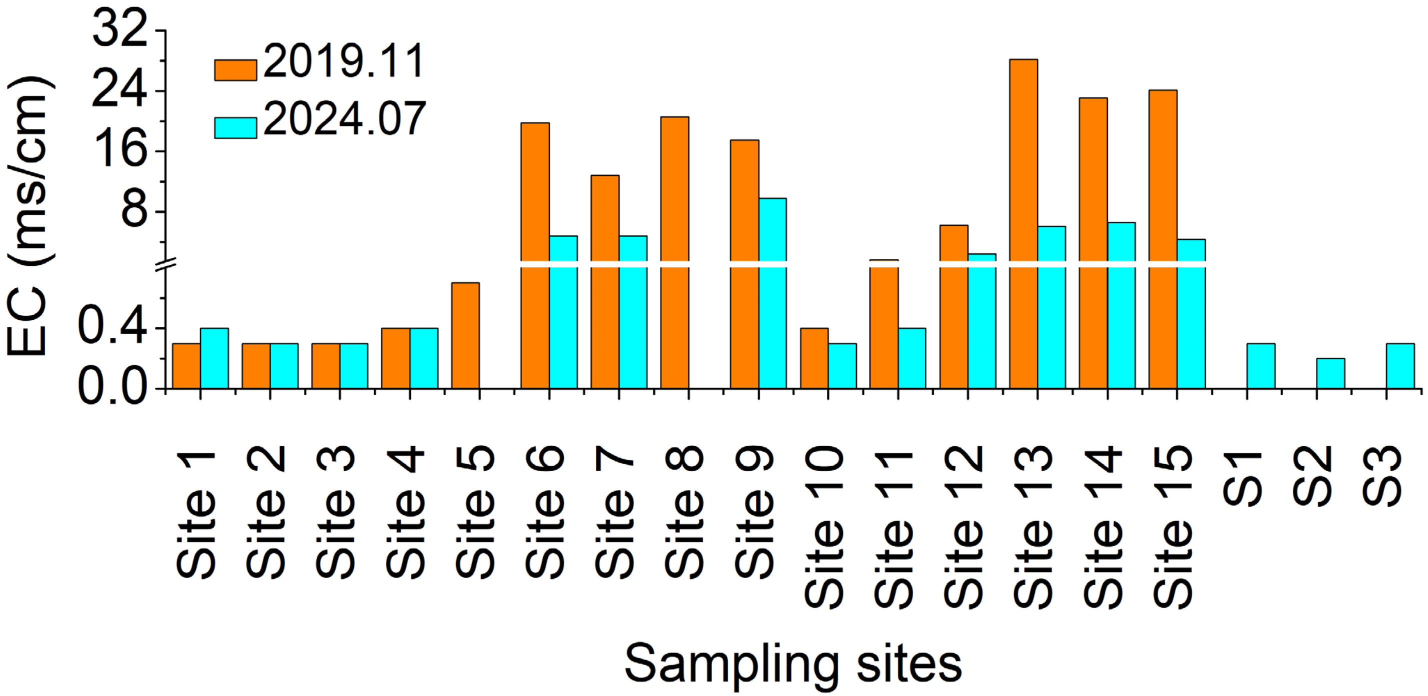


Samples were collected in 2019 and 2024



➢ The results showed that the predominant size of sediment is medium silt (< 32 μm), more than 65%.

Changes in total Hg

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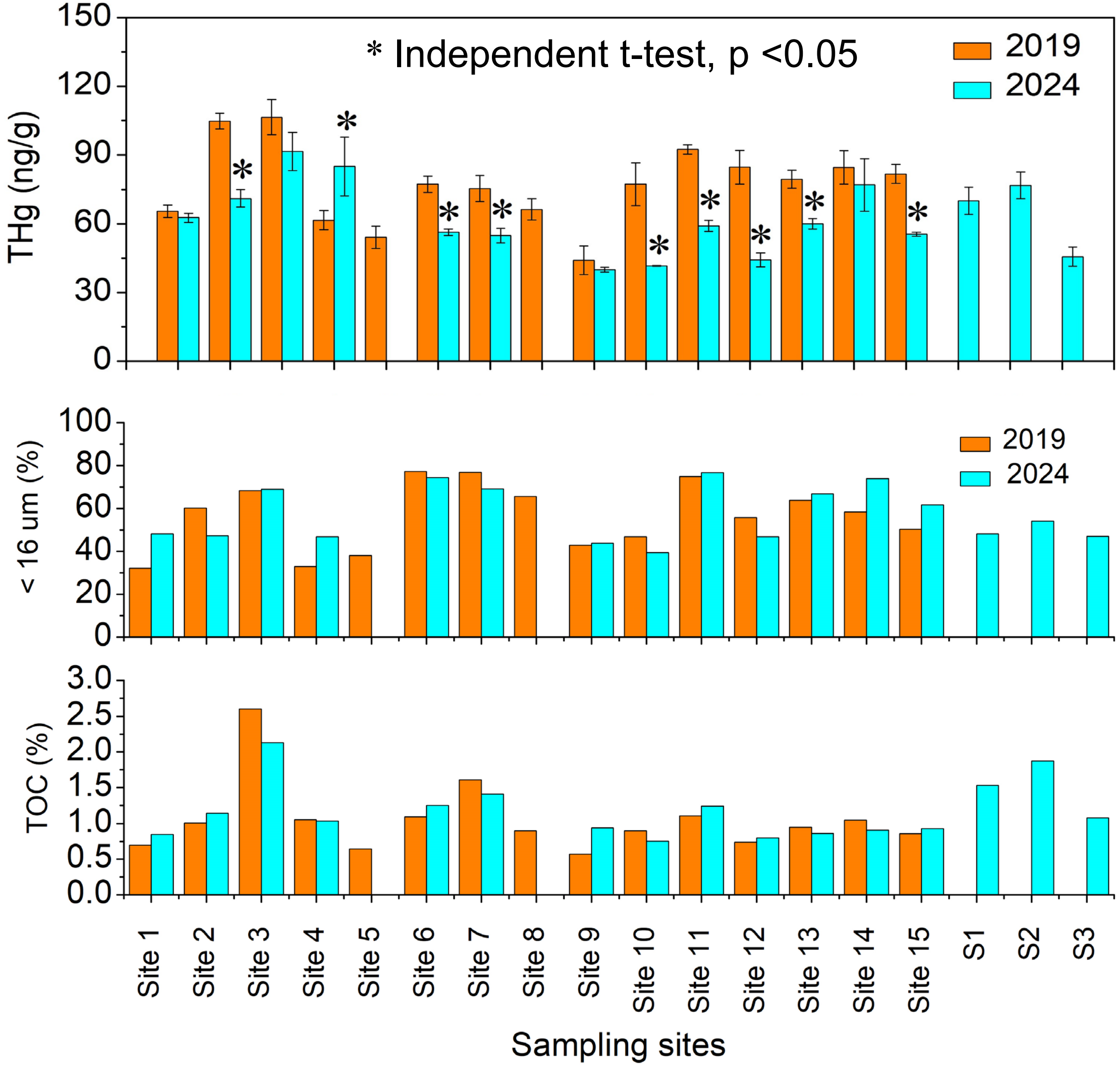
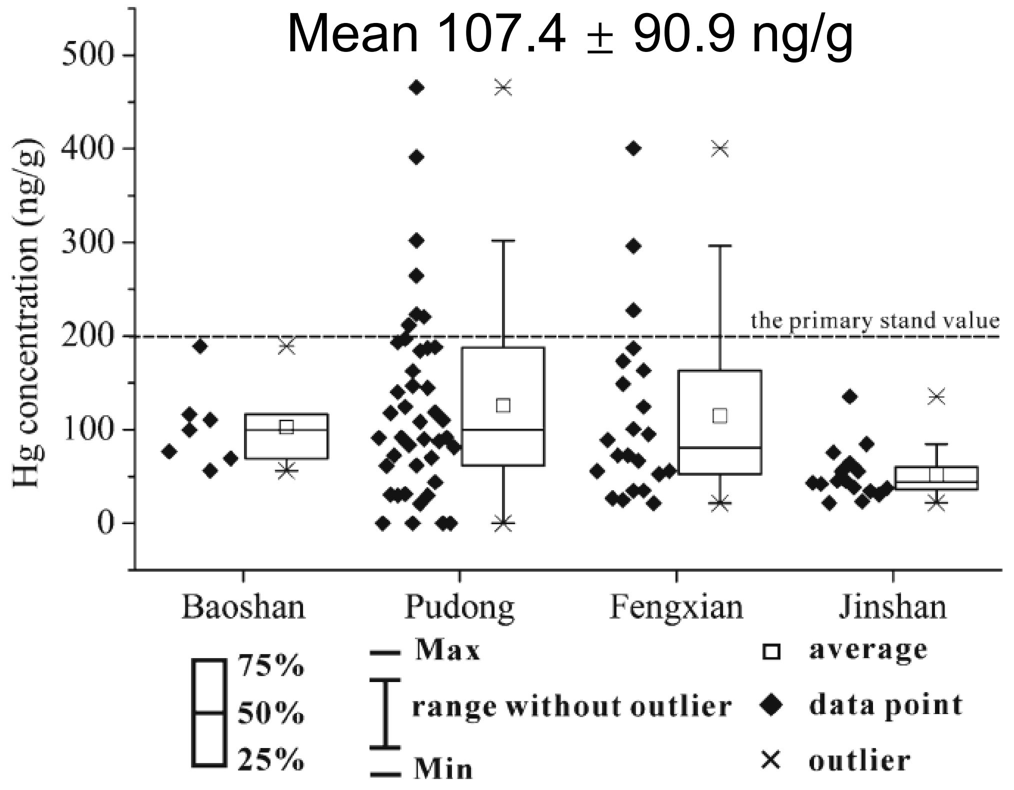


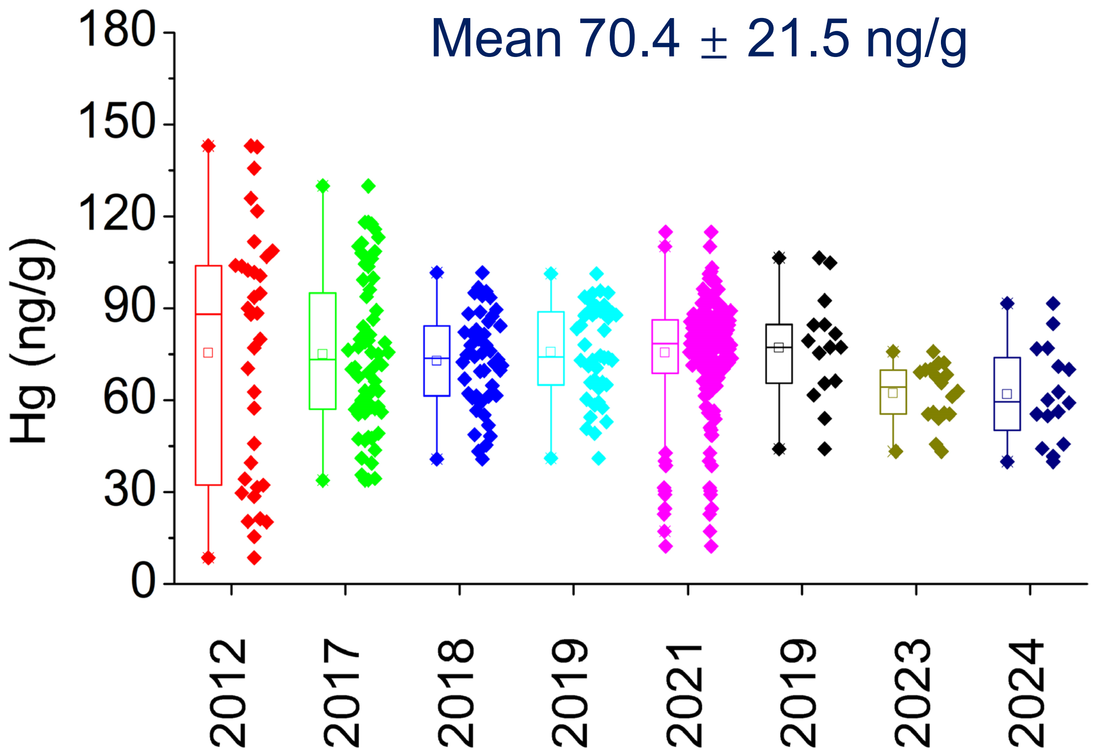
- THg < 200 ng/g (Class Ⅰ Hg limit for marine monitoring in China, GB, 18668–2002).
- THg in sediments generally decreased by 4.3–47.7% in 2024 compared to those in 2019.
- However, the decrease in fine silt (< 16 μm) and total organic carbon (TOC) was not the same as the decrease in THg.

✓ It is possible as a result of the implementation of the Minamata Convention in 2017.

Changes in total Hg



THHg in surface sediments in 2006-2007 in south bank of YRE
(Deng et al., 2013, Environ Sci Pollut Res)



(2012-2021 samples collected in Dongtan wetlands;
The other sites in 2019-2024 in YRE)

✓ A decline in Hg levels in recent two decades, possible due to the enhanced adoption and implementation of wastewater treatment policies over past decades in China (Cai et al., 2024)

The fractionation of Hg in sediments

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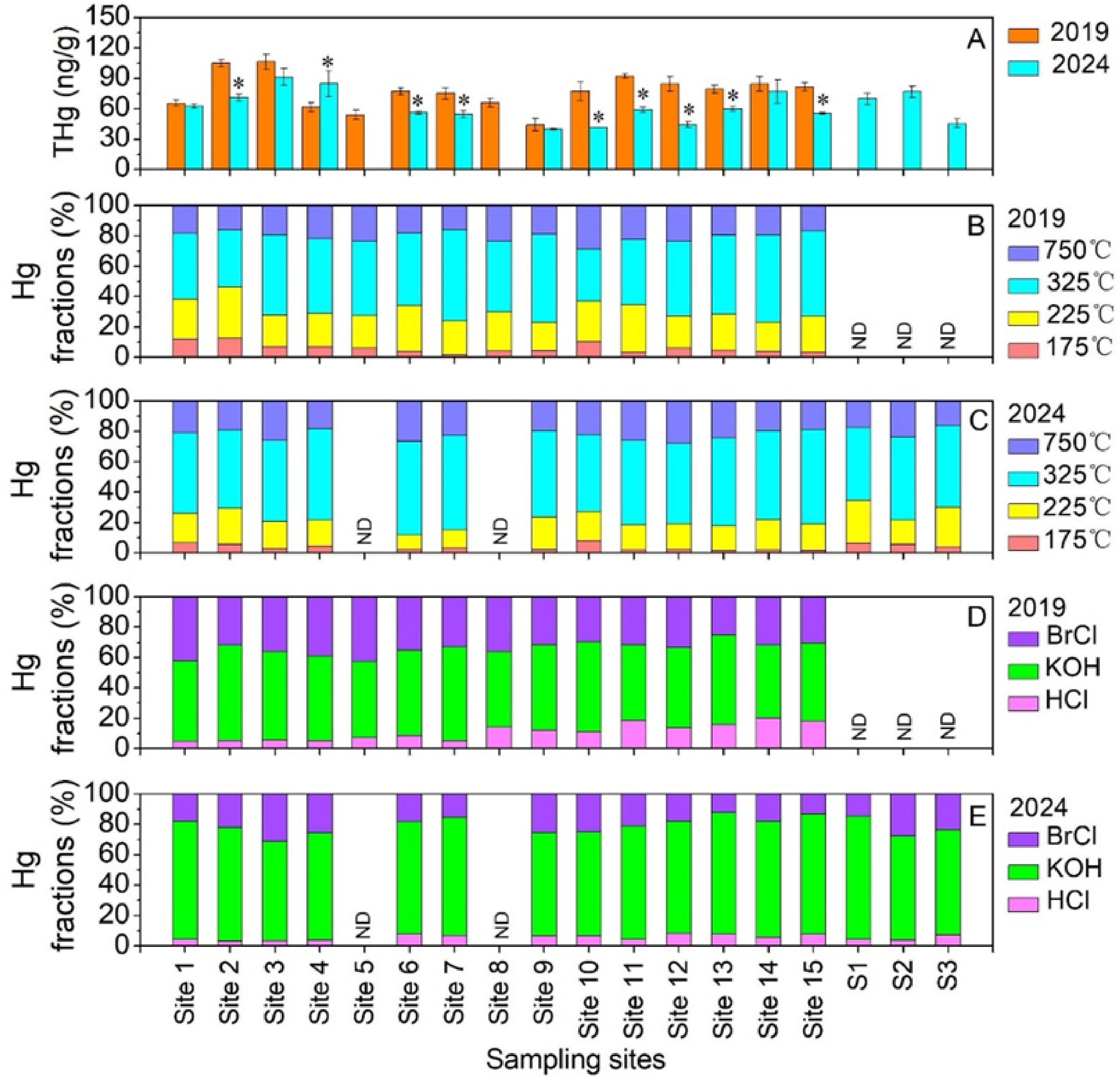

- The fractions of Hg_{325} is the highest percentage (52.6%) in sediments.
- However, the KOH-extractable Hg was the major Hg fractions in the sediments (65.1%).

The fractionation of Hg in sediments

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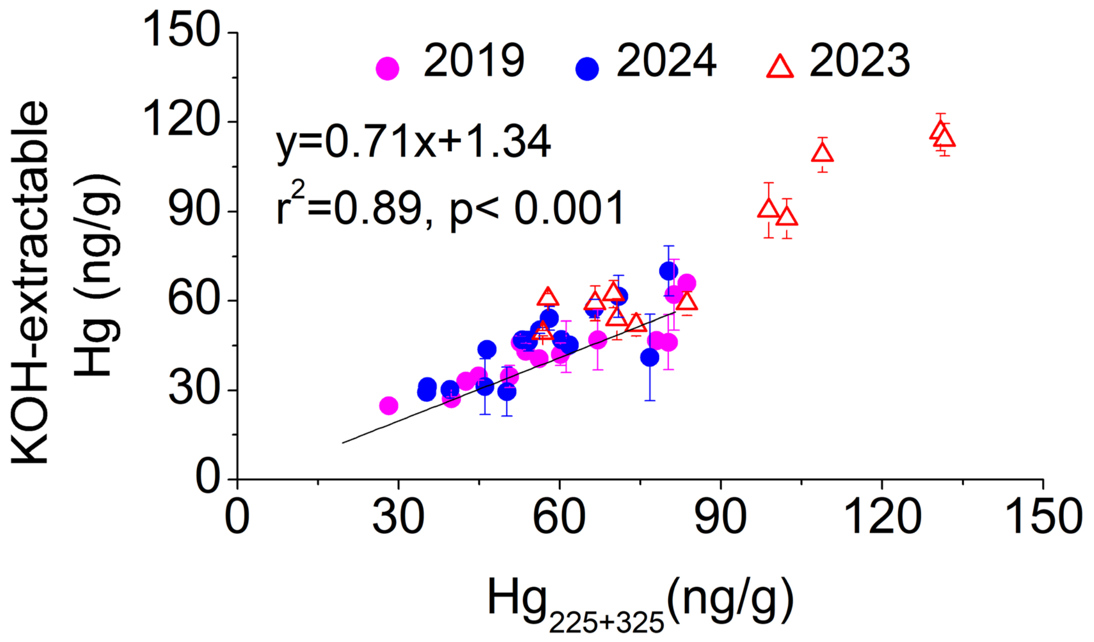
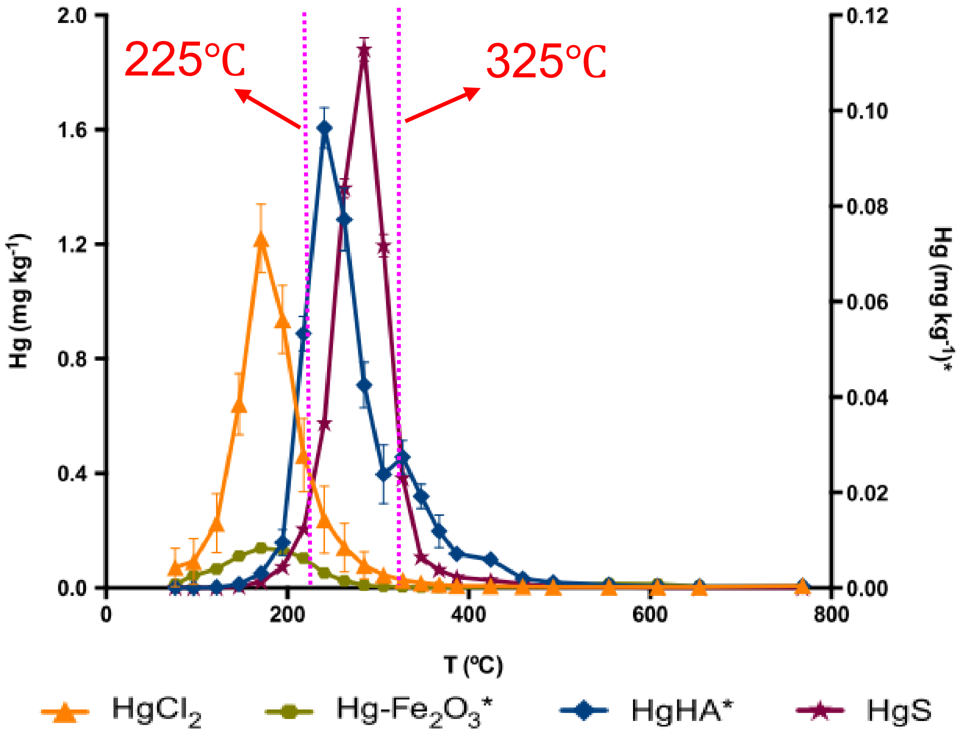


Linear fit of the data obtained in 2019 and 2024; The red up triangle indicate the centrifuged sediments that collected in 2023 (Bi et al., 2024)



Thermo-desorption curves (n = 10) for Hg species in synthetic standard materials: $HgCl_2$ and HgS — left Y axis; HgHA and to Hg-Fe_2O_3 — right Y axis (**Reis et al., 2015**)

A significant positive correlation between $Hg_{225+325}$ and KOH-extractable Hg indicates that organic matter may play a key role in controlling Hg in sediments.

- ✓ We proposed that the compounds of HgS in the studied sediments could be overstated.

Environmental implications of the thermal-desorption methods

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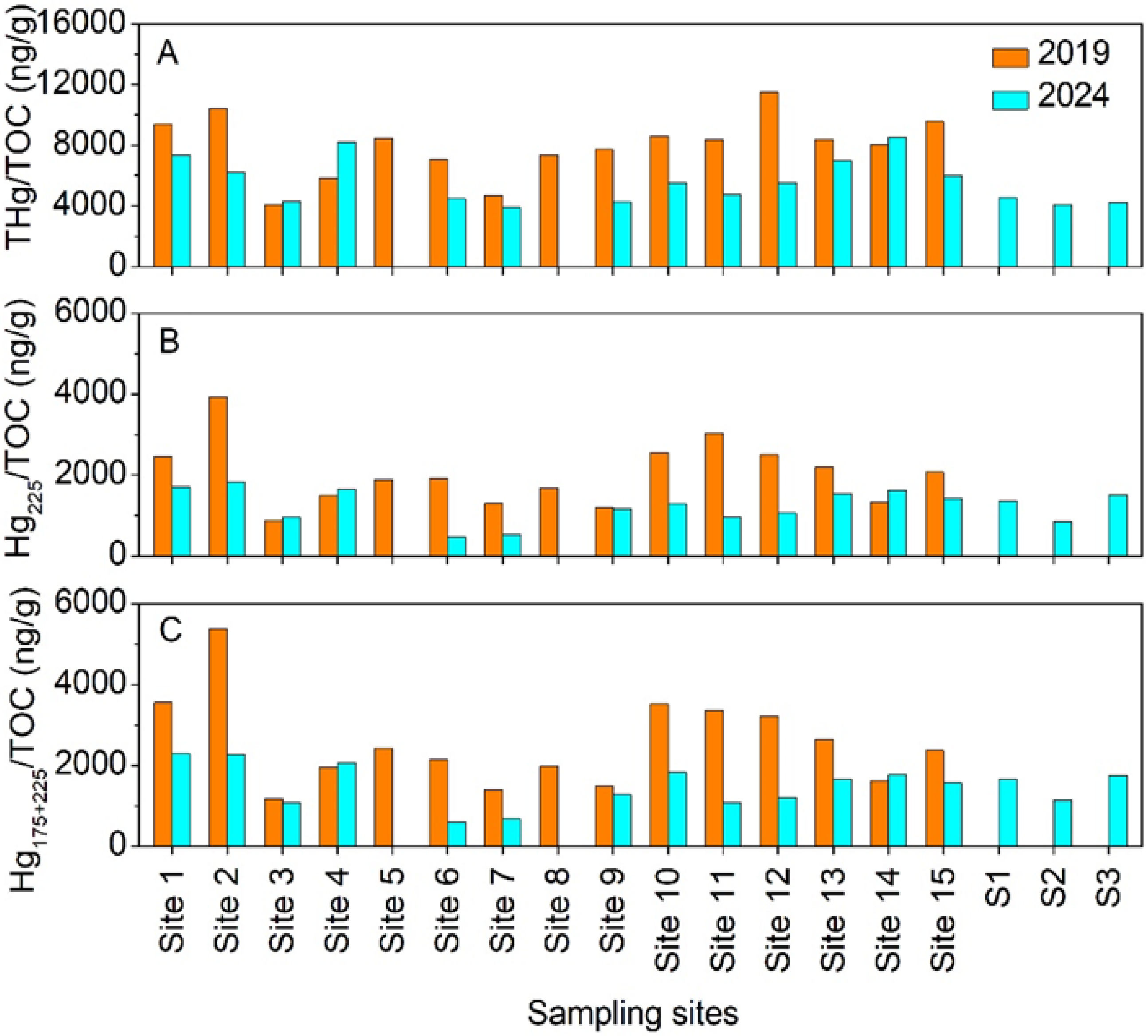

The spatial distribution of Hg_{225}/TOC or $Hg_{175+225}$/TOC ratios across the sampling sites showed patterns and changes similar to those of THg/TOC ratios in sediments.

- ✓ These results suggest that the determination of the $Hg_{175+225}$ by heating the sample directly at 225 ℃ could be a simple method to roughly assess the impact of human activities on Hg elevation in sediments.

MeHg in surface sediments

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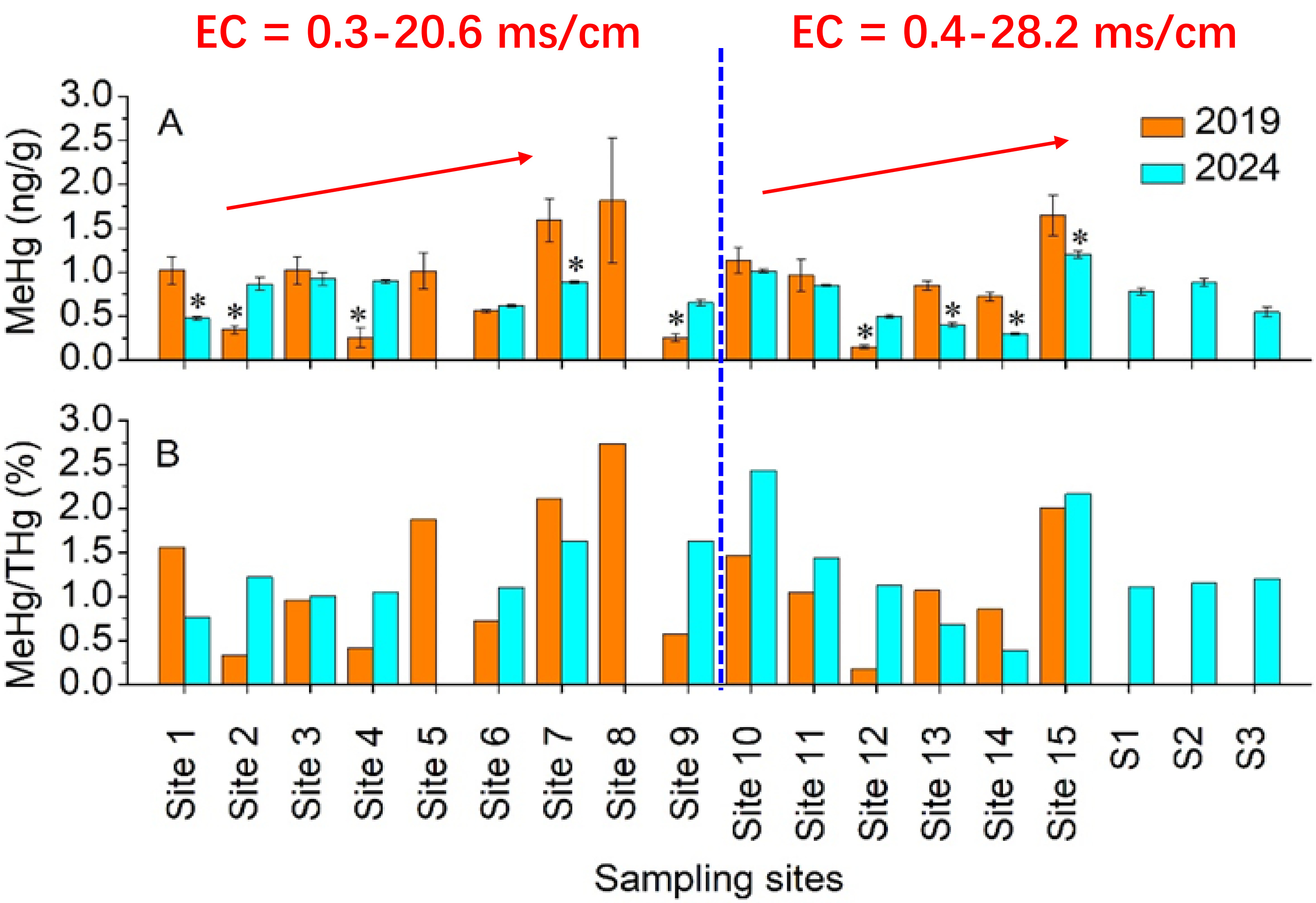
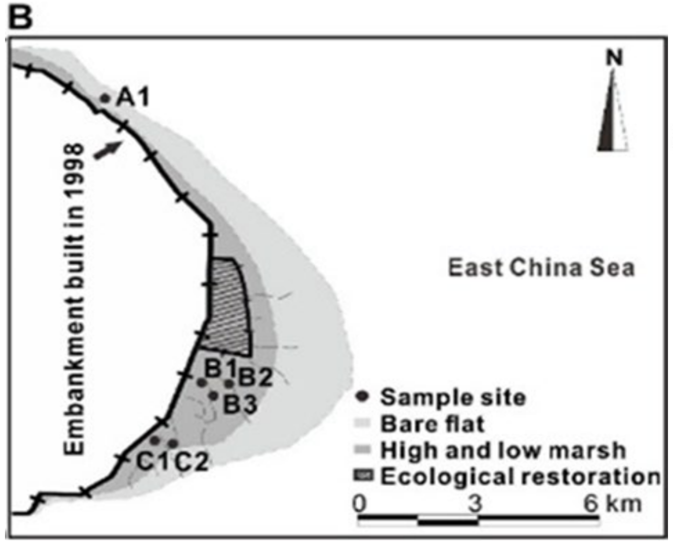
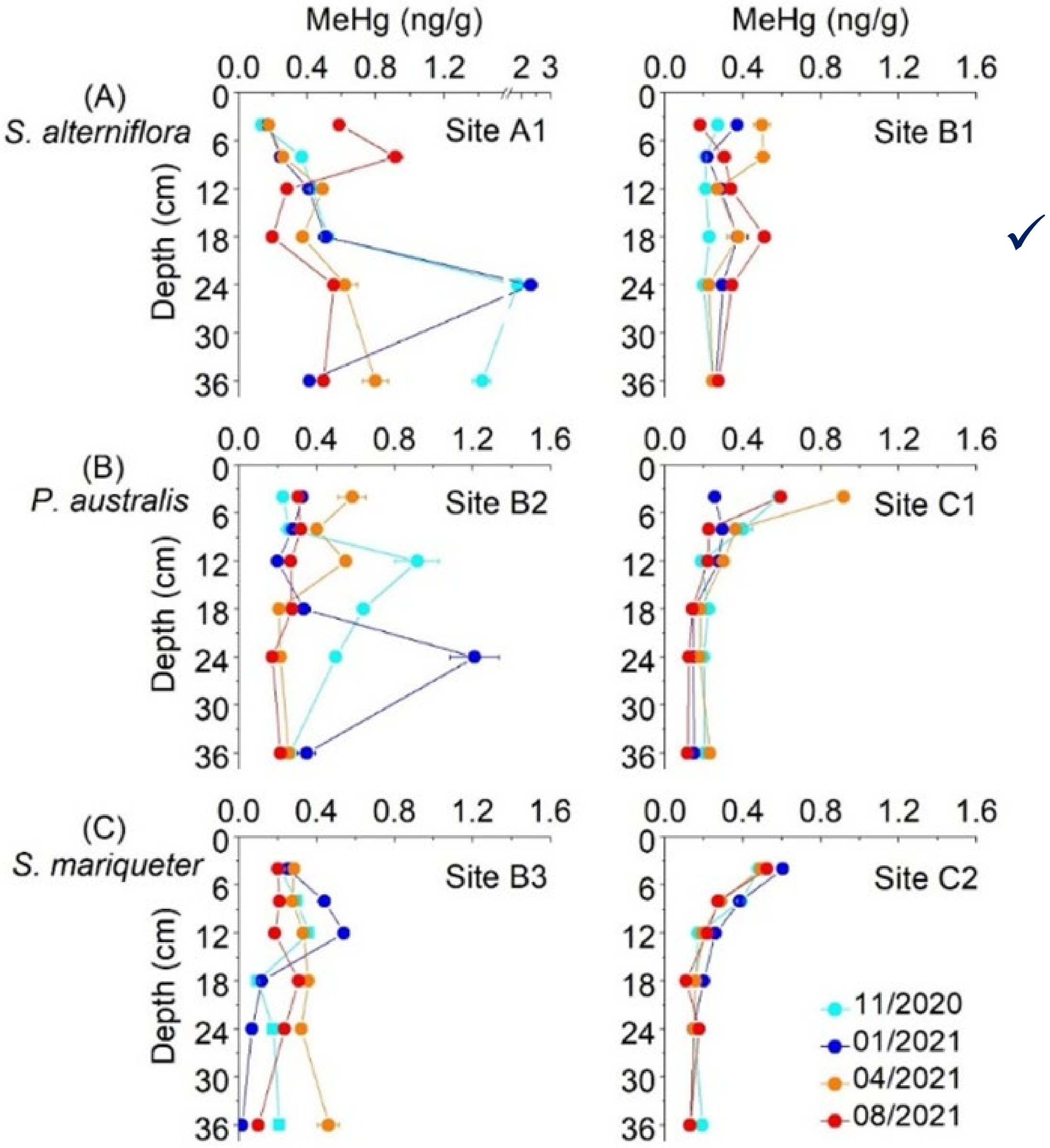


No significant positive correlation was found between MeHg and the characteristics of sediments such as THg, TOC, salinity, and each Hg fractions determined by the methods of thermal-desorption and sequential chemical extractions.

MeHg in sediments



The samples were collected in 2020-2021



- ✓ We proposed that the elevated MeHg in the upper surface layer (0–12 cm) could mainly be attributed to the enhanced activity of methylating bacteria.

Incubation experiments

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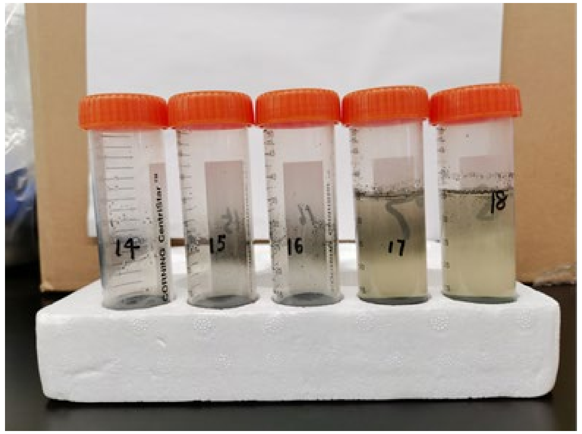
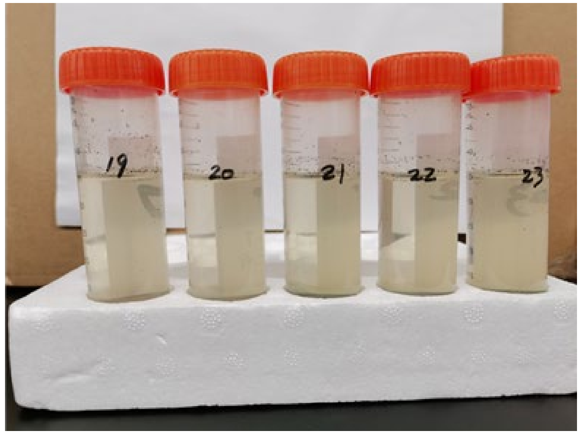
A short-term (14 days) incubation experiment

Sites	Treatments	Incubation conditions
Sites 1-15, 2019	**CK**: the control **OM-P**: the addition of the organic matter of plants	25–27℃; Anoxic; Dark

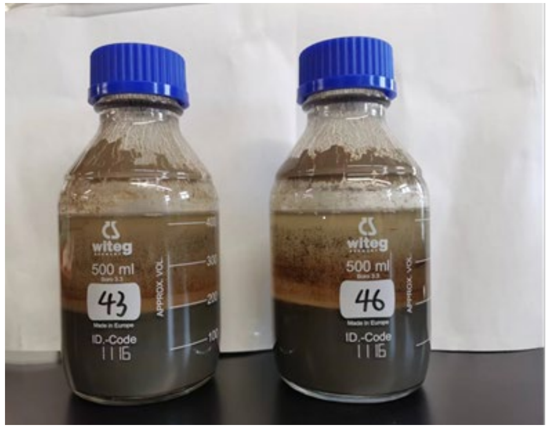




A long-term (252 days) incubation experiment

Sites	Treatments	Incubation conditions
Site S2, S3, 14 and 9, 2023	**CK**: the control **OM**: the addition of the organic matter of plants; **+Hg**: increased by 109–275% **+OM+Hg**: organic matter +Hg	25–27℃; Anoxic-oxic; Dark

Anoxic



Oxic

Microcosm incubation experiments

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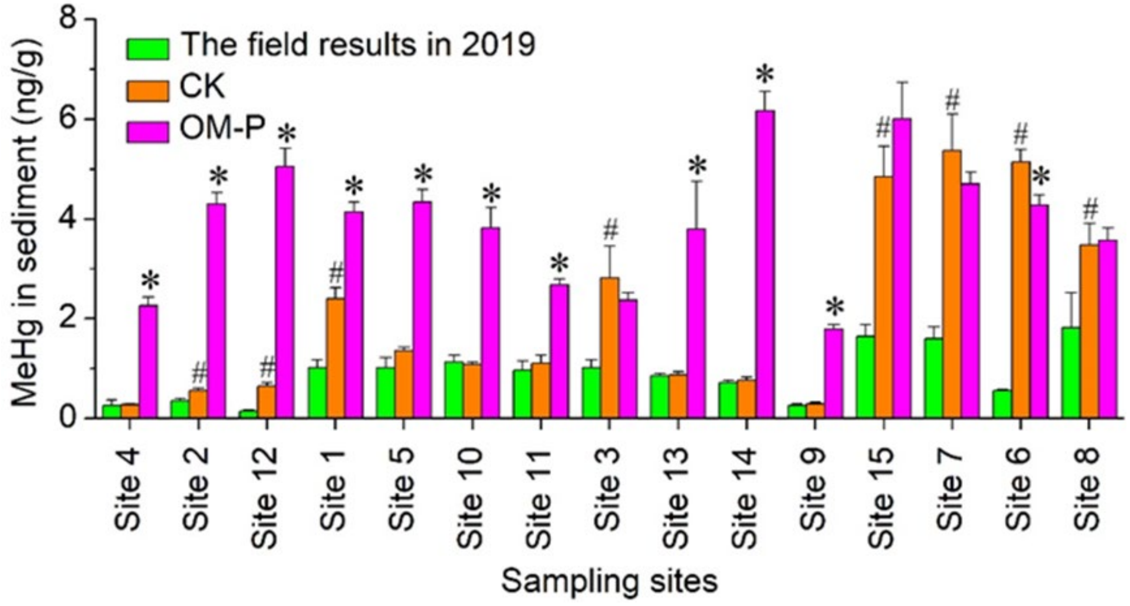
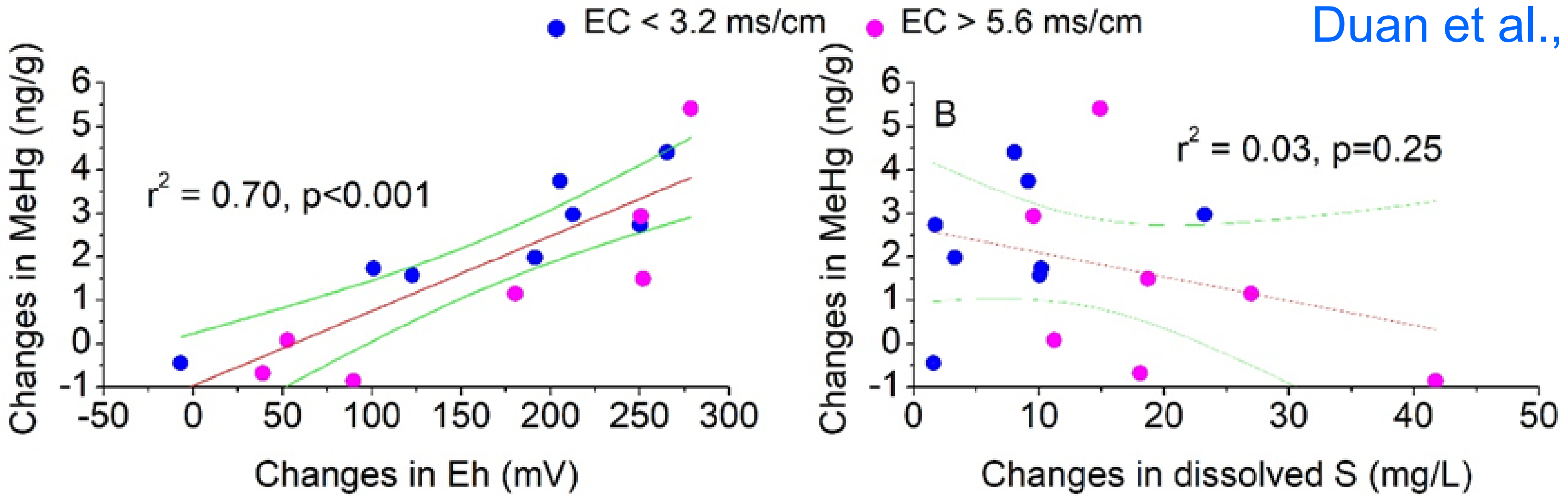


OM-P: the treatments with the addition of the power of plants.



Net MeHg production was enhanced significantly with addition of the labile organic matter of plant tissues.

✓ The observed results could be attributed to a stimulating effect of labile organic matter on microbial methylation activity (Ullrich et al., 2001; Bravo et al., 2017; Duan et al., 2021)

Changes in MeHg under different redox conditions

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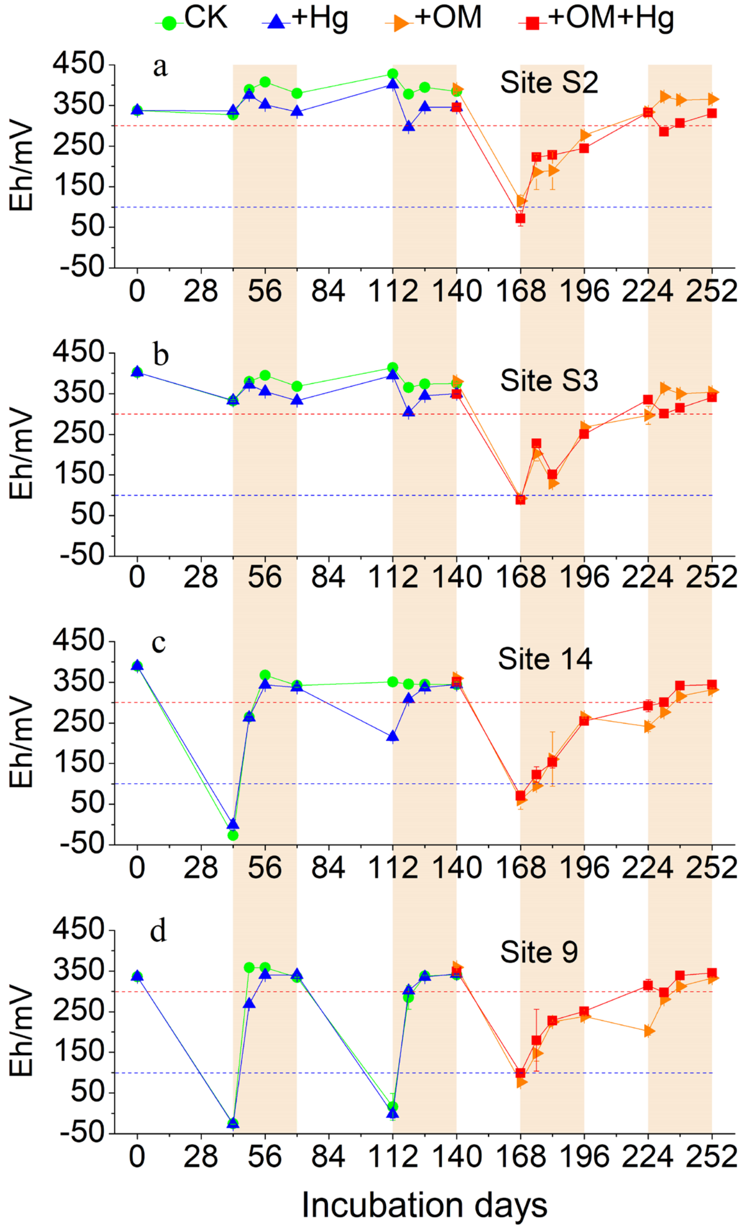

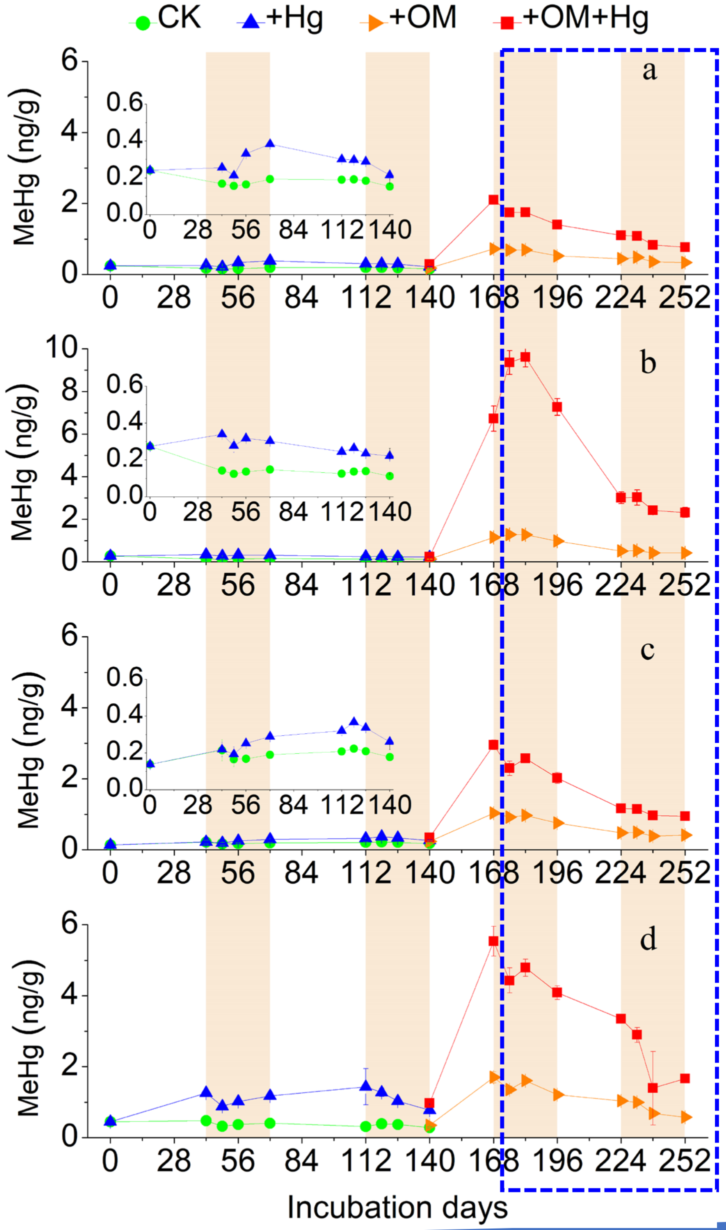

The rodox experiments further provided the evidence that a stimulating effect of labile organic matter on microbial methylation activity.

It is important that MeHg decreased under sunoxic and oxic conditions.

Changes in MeHg under different redox conditions

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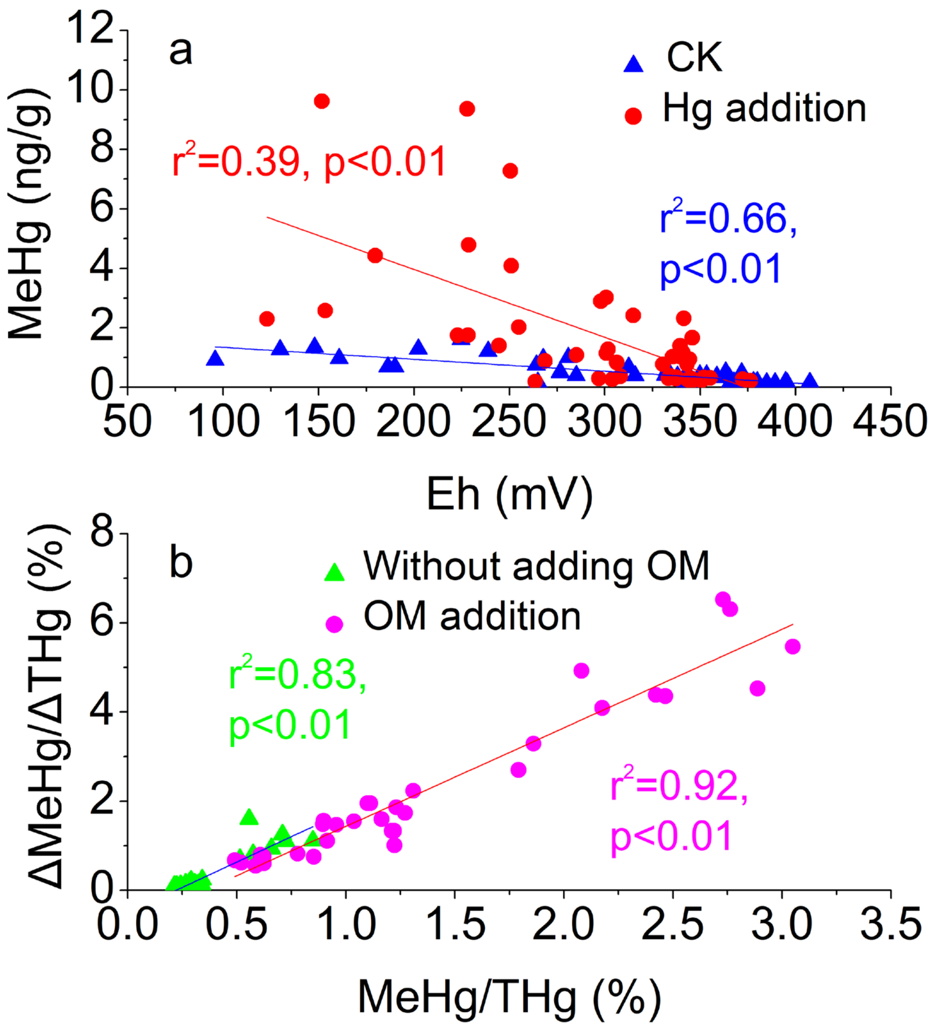

The up triangle (Δ) indicates the increases in THg and MeHg following Hg addition

- ✓ The results indicate MeHg degradation could be enhanced under oxic conditions.
- Following the addition of OM, the values of ΔMeHg/ΔTHg increased in Hg-added sediments, corresponding to the increase in MeHg/THg observed in the control without Hg addition.
- ✓ This suggests that the ambient Hg sources may be closely related to the input of reactive Hg associated with wastewater discharge in YRE basin.

Hg accumulation in sediments

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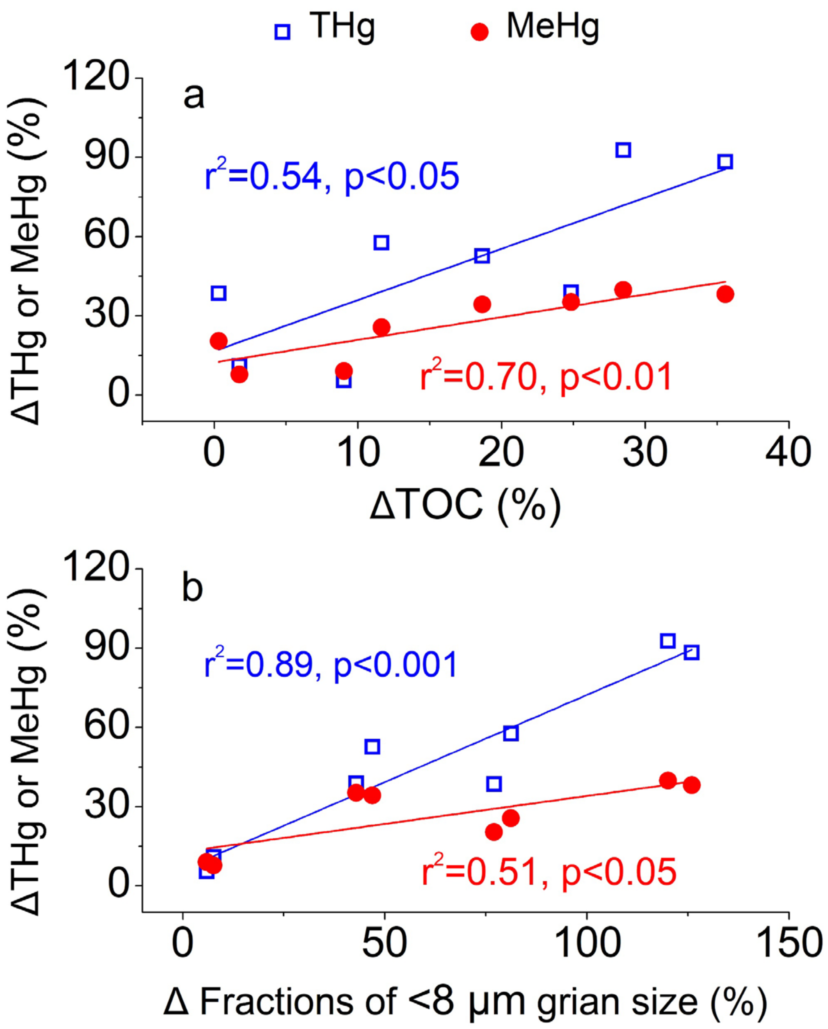

The up triangle (Δ) indicates
the increased percentage after centrifugation

We obtained the fine particles by centrifuging the sediments that had been incubated in our long-term experiment. The results showed that the centrifuged sediments were composed by fine particulate matter (D90 = 9.8~18.9 μm) and THg, MeHg and TOC increased after centrifugation.

✓ The results indicate both the organic matter and the very fine silt grain size are main factors for controlling Hg accumulation in sediments and mobility in water.

Conclusions

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- ✓ Directly heating the sample at 225 °C to determine Hg fractions could be a simple method of roughly assessing the impact of human activities on Hg elevation in sediments.
- ✓ The net formation of MeHg and its subsequent degradation following Hg loading were closely related to the degradation of labile organic matter.
- ✓ The risk of MeHg could be significantly reduced following long-term Hg ageing under a low-concentration input scenario.

Acknowledgments

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国家自然科学基金委员会

NSFC

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CMDT

Selected publications

ECNU

Lv S, Bi Q, Chen Y, Zhou L, Zheng X, **Wang Y*** . Mobility and transformation of mercury in the sediments of Changjiang estuarine wetlands following the soluble ionic mercury inputs: A long-term microcosm study. **Haiyang Xuebao** (in chinese), accepted in April, 2025.

Bi Q, Lv S, He Q, Liu X, Zhou L, Zheng X, **Wang Y***. 2024. Analysis of mercury fractions in the fine grains of surface sediments in the Changjiang Estuary wetlands using thermodesorption and chemical extraction methods. **Journal of Soils and Sediments**, 24: 3507–3514.

Zhu C, Lv S, Zhao Q, Liu X, Wang Z, Zheng X, Zhou L, **Wang Y***. 2023. Seasonal variation in mercury and methylmercury production in vegetated sediment in the Dongtan wetlands of the Yangtze River Estuary, China. **Marine Environmental Research**, 188, 105999.

Wang Y, Wang Z, Zheng X, Zhou L*. 2022. Influence of Spartina alterniflora invasion on mercury storage and methylation in the sediments of Yangtze River estuarine wetlands. **Estuarine, Coastal and Shelf Science**, 265, 107717.

Thank you for your attention