Exploring the sources and pathways of mercury entering a lake ecosystem using a stable mercury isotope mass balance model

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Mercury (Hg) is a global atmospheric pollutant of international concern

Mercury is a highly toxic heavy metal

- Methyl mercury (MeHg) poisoning can cause human death in acute cases (Minamata disease, Japan)
- Long-term low-dose MeHg exposure in pregnant women affects fetal mental development

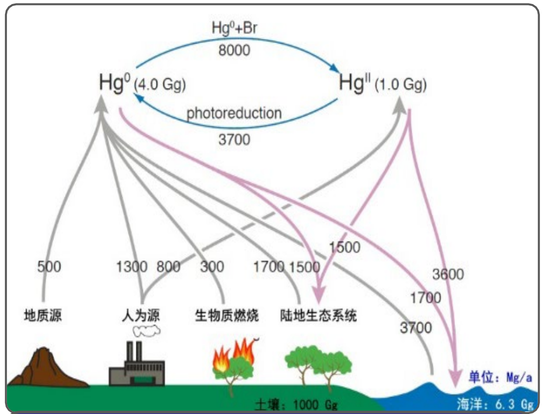
Mercury is transported globally mainly via the atmosphere

- Fish Hg levels in many remote lakes in Europe and the United States are exceeding the limit

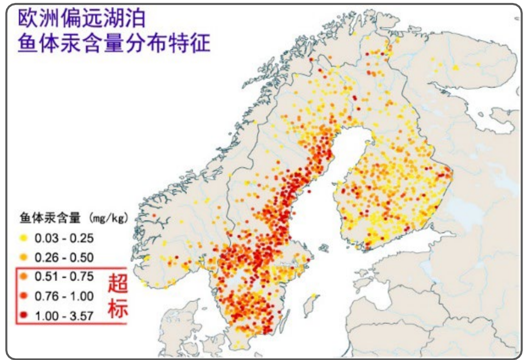
Minamata Convention implementation in 2017

- Objective of the Convention: To control and reduce atmospheric mercury emissions

Minamata disease incident in Japan



Global atmospheric mercury transport

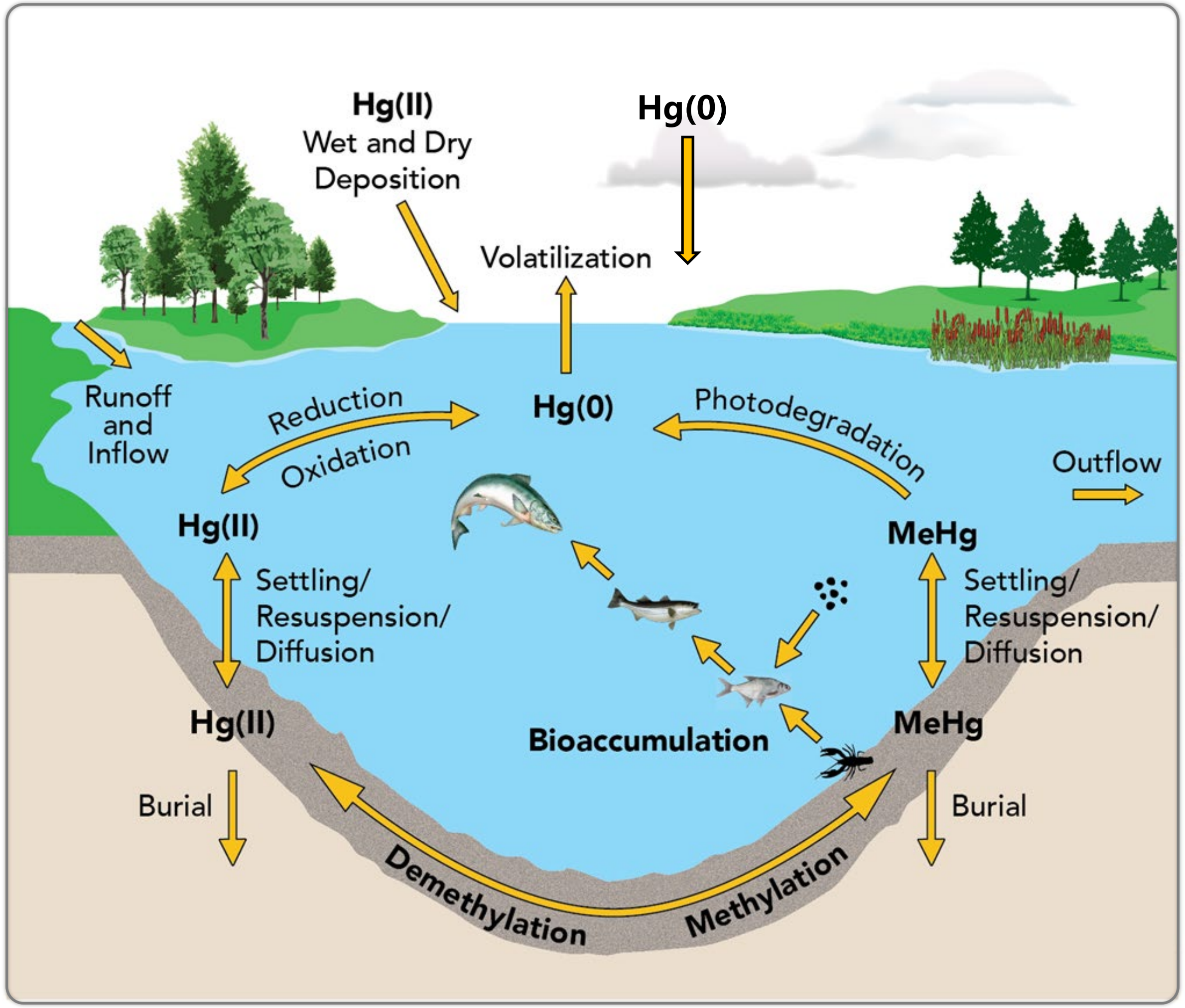


Mercury contamination of fish in Europe and the United States

Conference of the Parties to the Minamata Convention

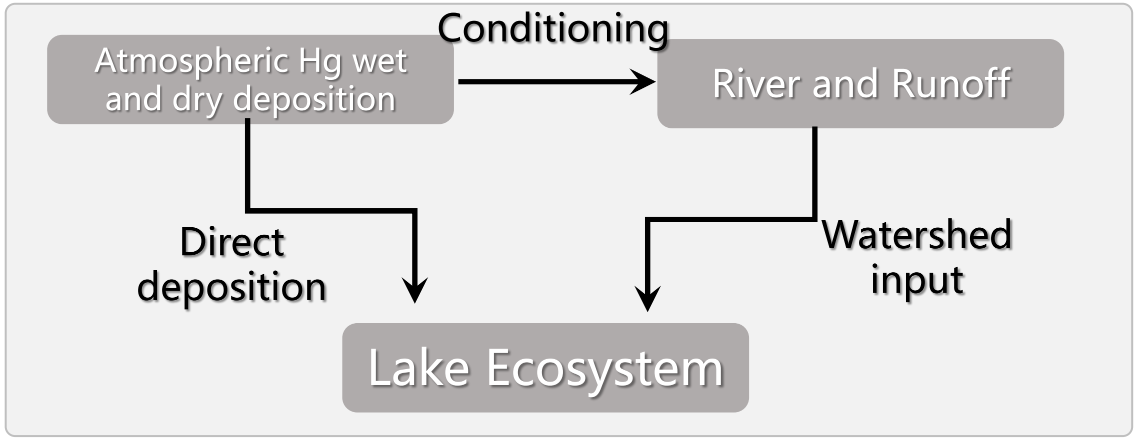
Holmes et al., 2010, ACP; AMAP/UNEP, 2018

Sources of Hg in lake ecosystems



Sources of Hg in lake ecosystems

- Atmospheric Hg(0) dry deposition
- Atmospheric Hg(II) wet deposition (PBM and GOM)
- Dry deposition of GOM and PBM
- Riverine input
- Surface runoff input

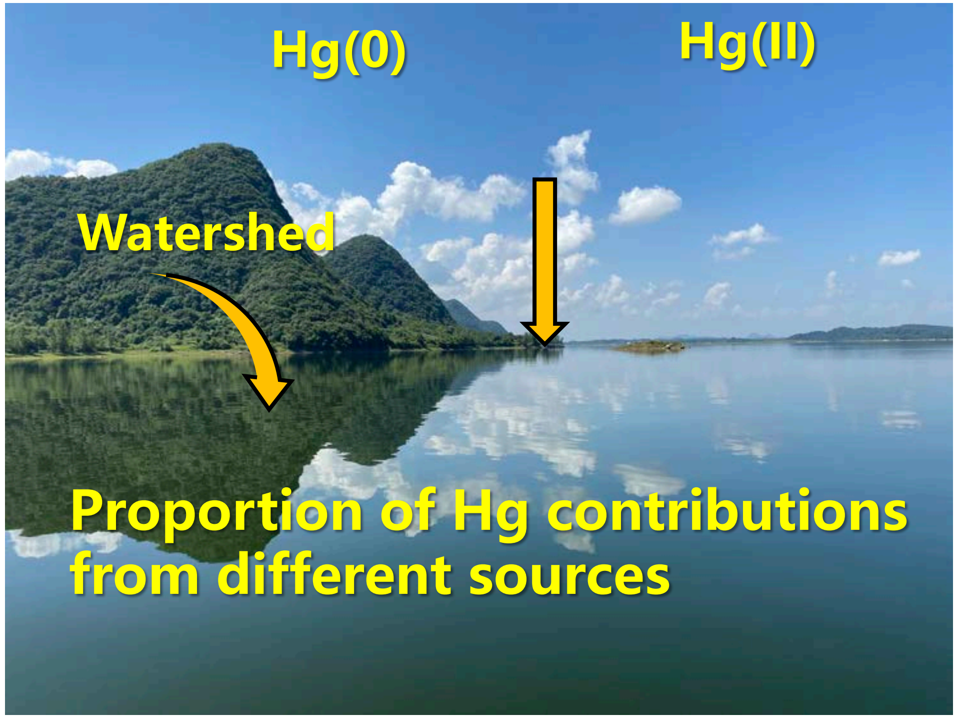


Engstrom et al., 2007, PNAS

Lack of quantification of sources of Hg in lake ecosystems

Status of Research:

- Focus on water column Hg concentration, morphology and flux analysis
- Focus on qualitative analysis of sources of mercury in water bodies and sediments
- Lake mercury levels and isotopic composition have not been systematically investigated

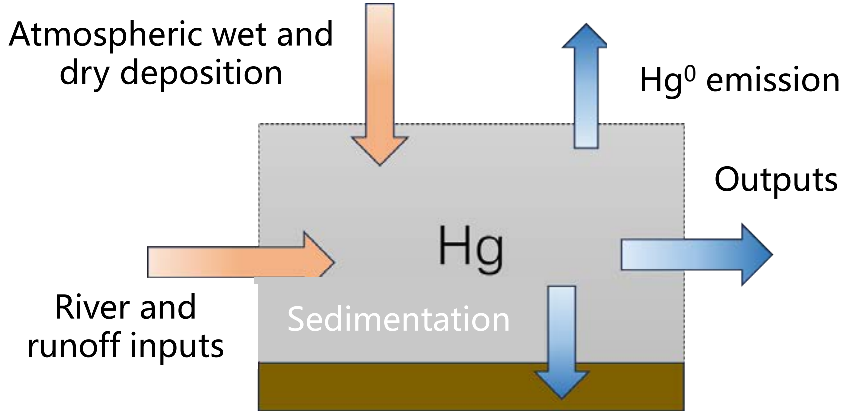


A complete understanding of the sources and transport pathways of Hg in lake ecosystems is still lacking

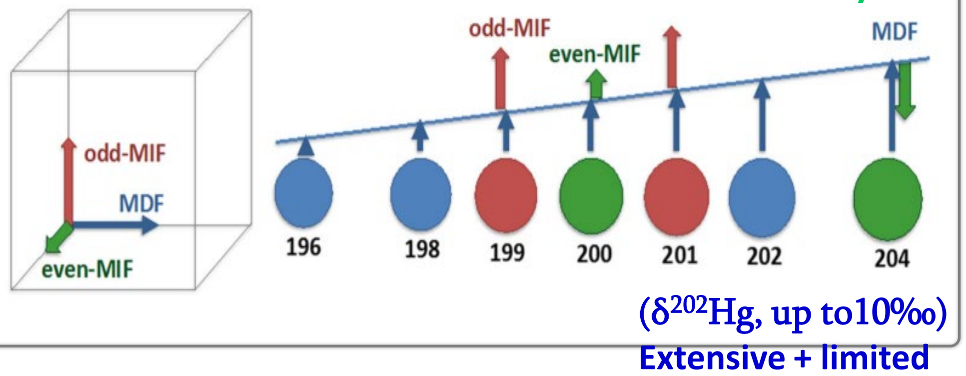
Tsui et al., 2020, STOEN

Hg stable isotopes may provide a precise, even exclusive, means of analyzing the sources of mercury in lake ecosystems

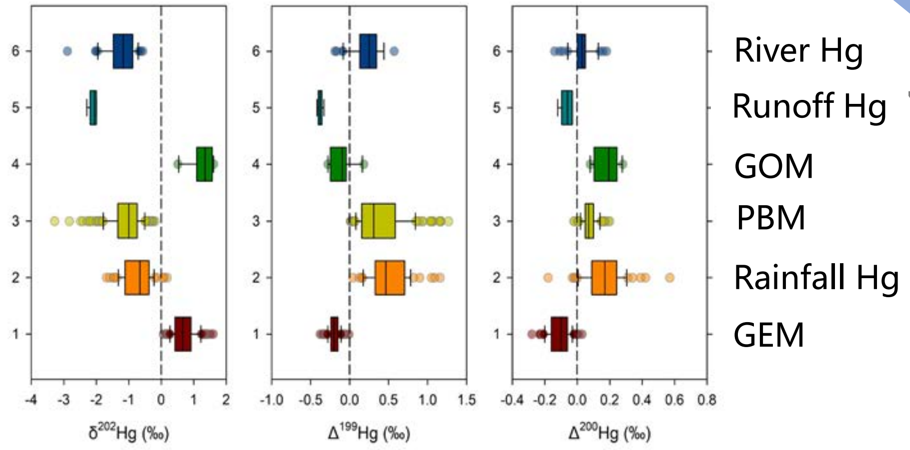
Hg mass balance studies



Hg isotope studies



Isotope fingerprinting of Hg input sources to lakes

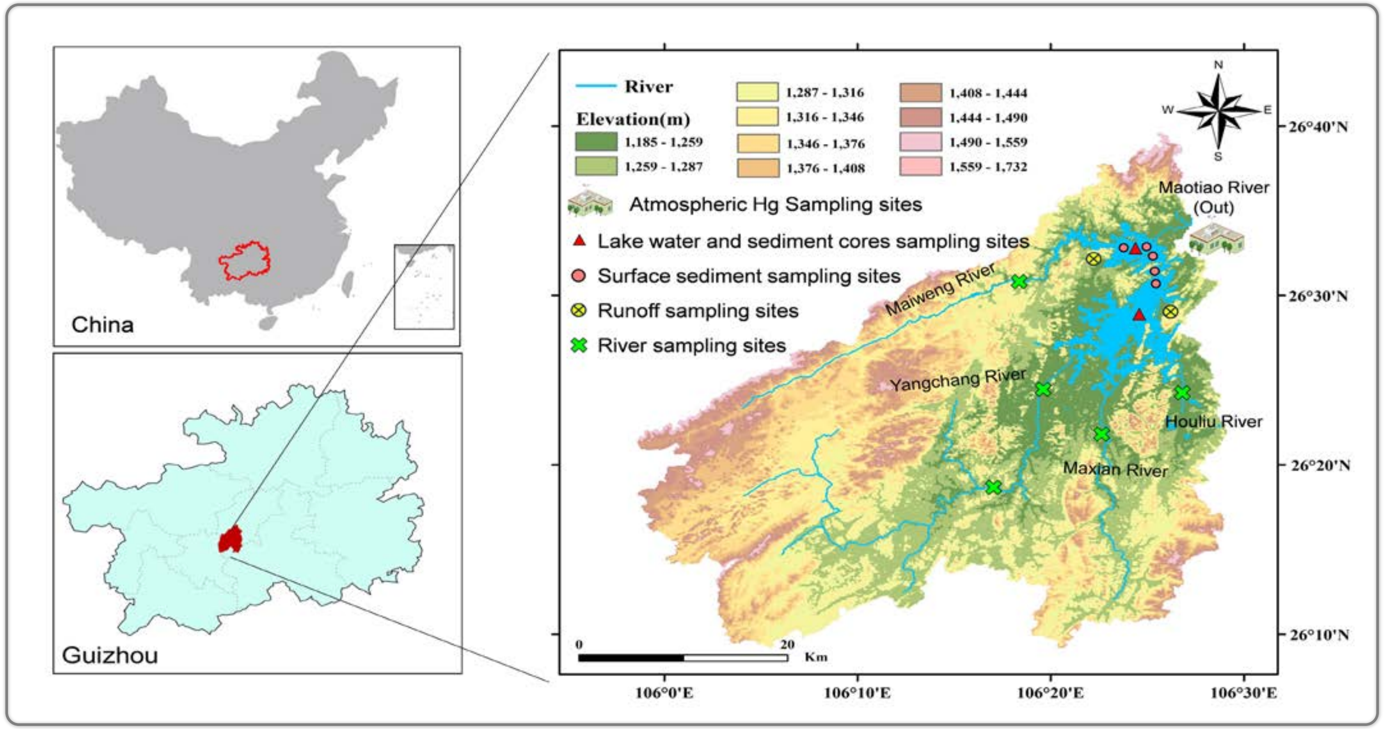


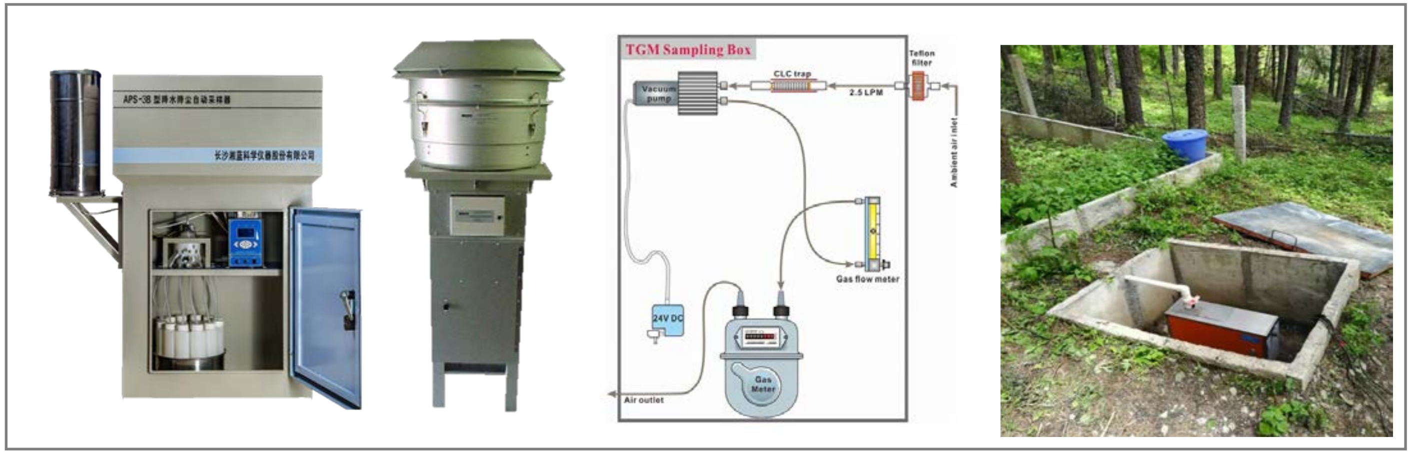
Hg isotope techniques

- Identify source information for Hg
- Indicative geochemical processes of Hg

Tsui et al., 2020; Kwon et al., 2020; Blum et al., 2014; Jiskra et al., 2017

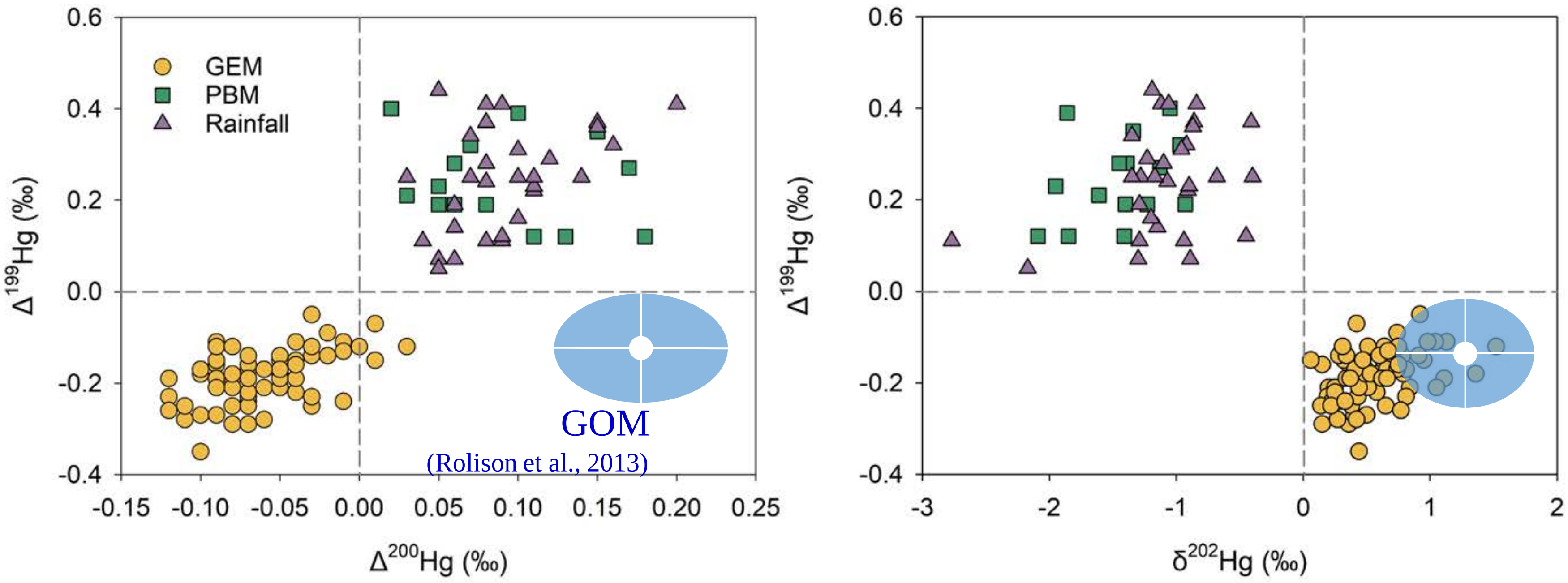
Study sites and methods





Sample Information	Sampling time	Descriptions
GEM	2020.1-2020.12	10 days/each
Rainfall Hg	2020.1-2020.12	Period of precipitation
PBM	2020.1-2020.12	10 days/each
River Hg	2020（1/5/7）	Surface layer
Runoff	2020.6~2020.8	Period of precipitation
Lake water	2020（1/5/7）	Water column（2m interval）
Surface sediments	2021.1	0~10cm
Sediment core	2021.1	50cm length

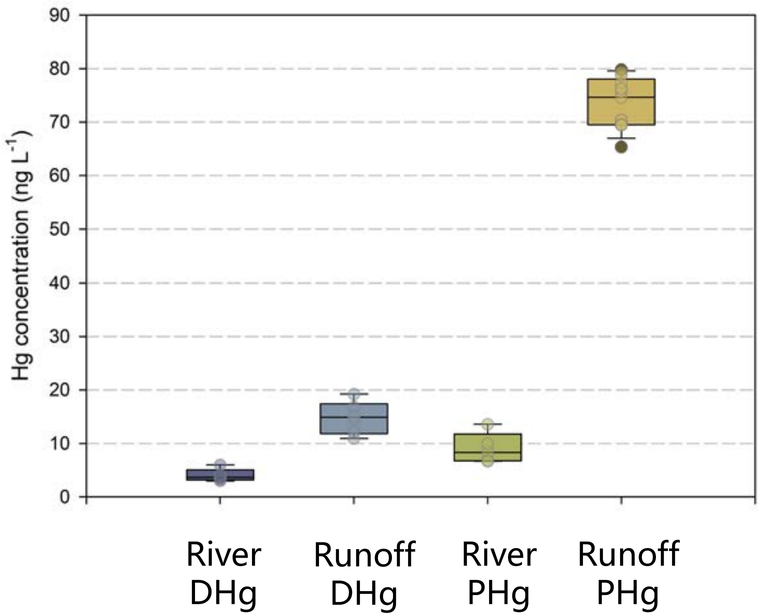
Isotopic signatures of atmospheric Hg in different forms

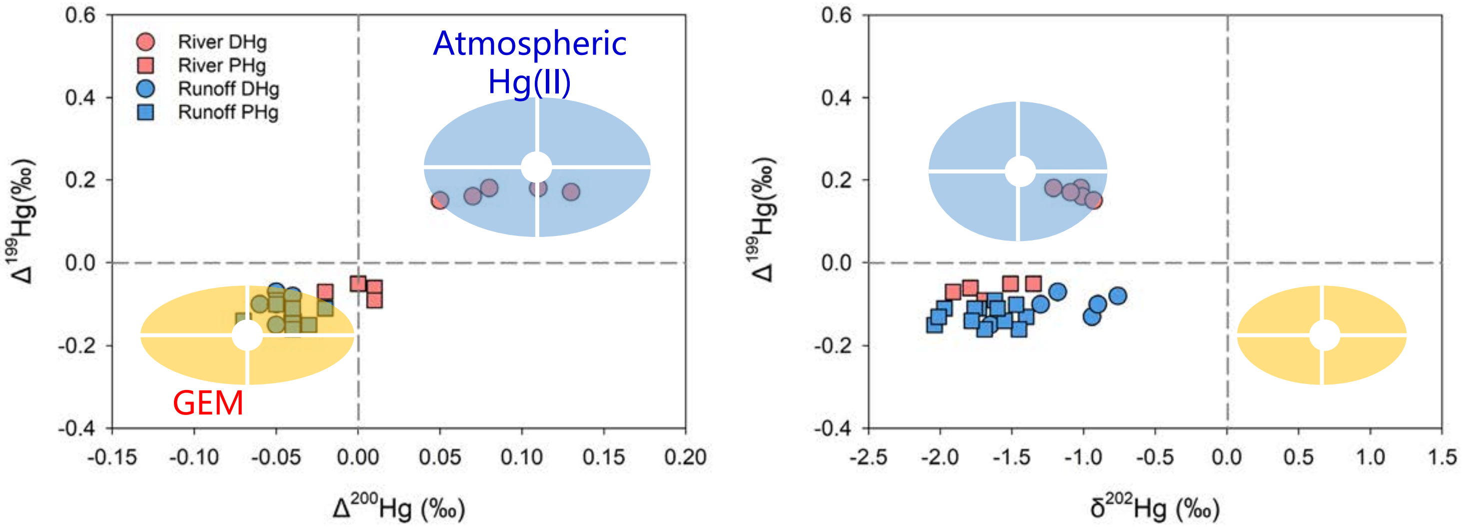


- No significant seasonal variation in Hg concentrations and isotopic compositions of different forms of Hg → associated with regional anthropogenic activities and vegetation cover
- GEM: positive δ^{202}Hg, negative Δ^{199}Hg and Δ^{200}Hg; PBM and rainfall Hg(II): negative δ^{202}Hg, positive Δ^{199}Hg and Δ^{200}Hg, and are similar in atmospheric Hg isotopic compositions to the background region
- Atmospheric mercury isotope variability: mainly related to atmospheric photochemical reactions

Tsui et al., 2020; Kwon et al., 2020; Fu et al., 2021; Chen et al., 2012

Isotopic signatures of Hg in rivers and runoff



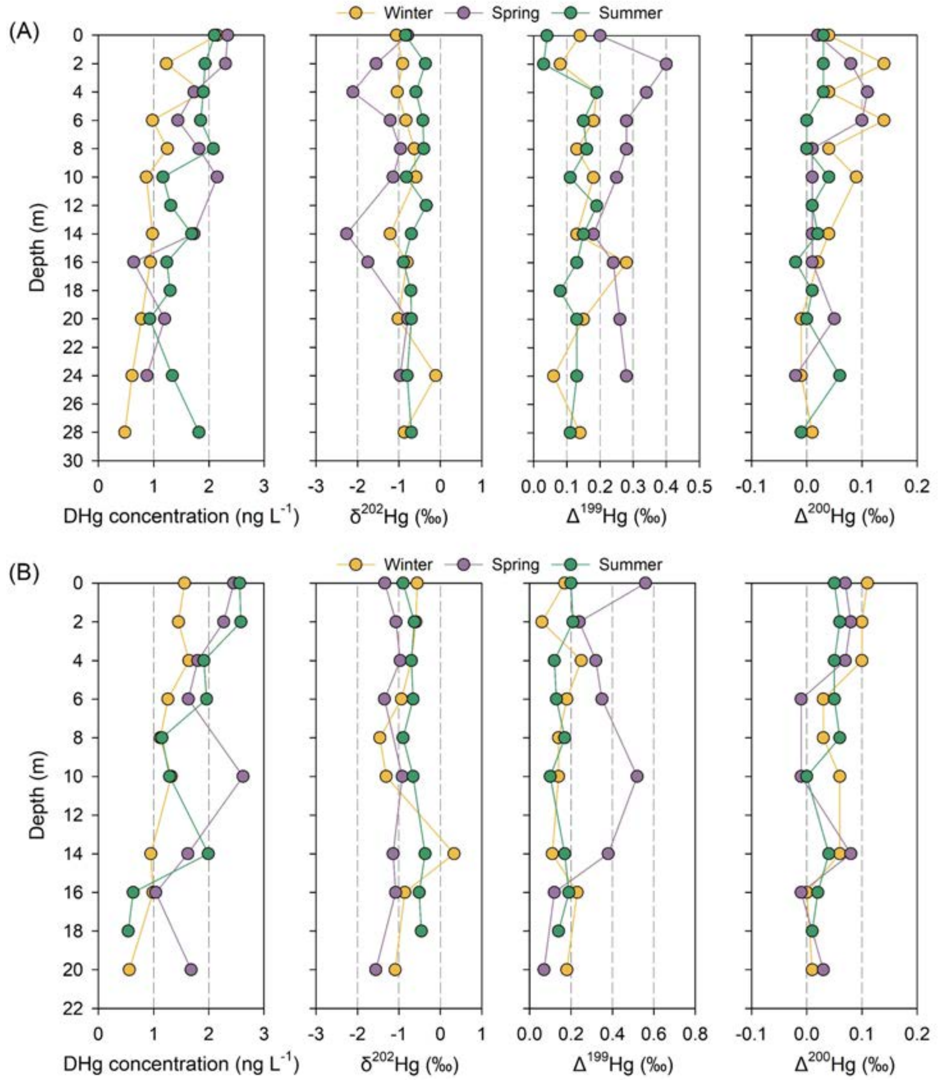


- Higher levels of Hg in particulate(PHg) than in dissolved form (DHg)
- Higher levels of Hg in surface runoff than in rivers

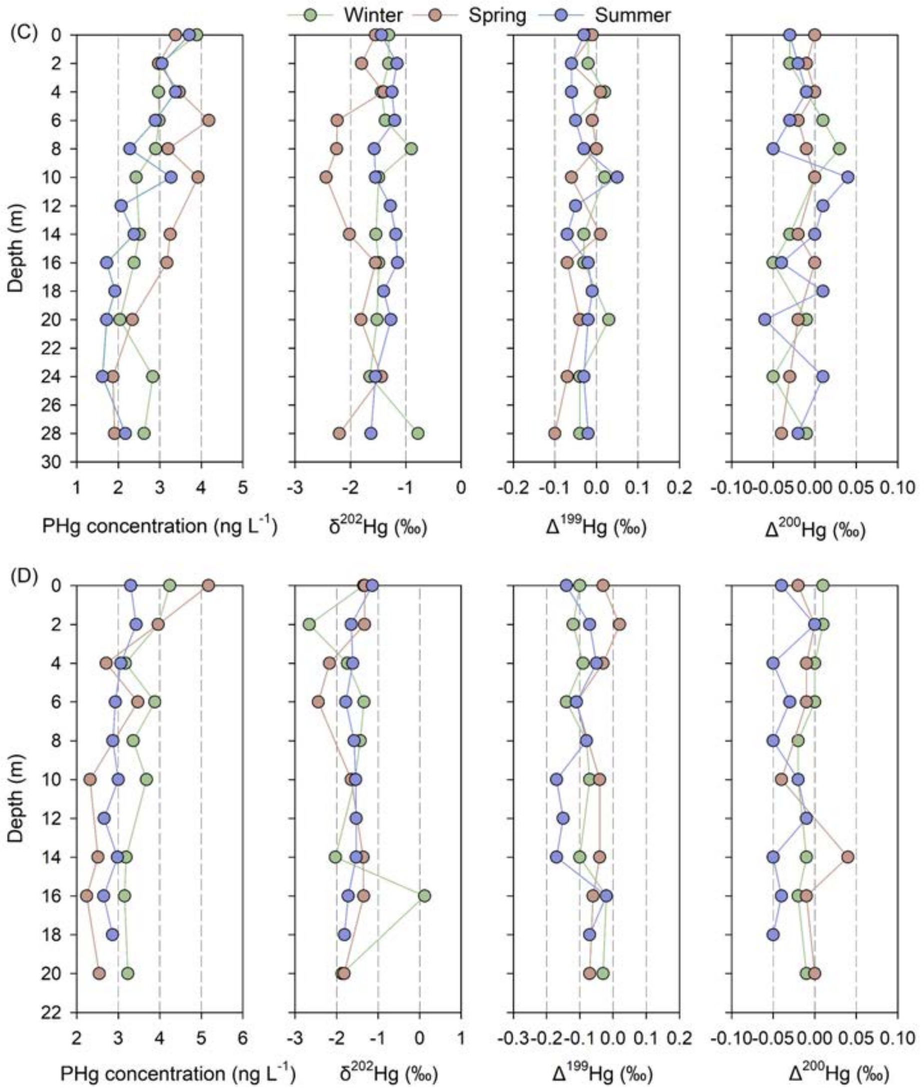
- River DHg: positive Δ^{199}Hg和Δ^{200}Hg; River PHg: relatively negative Δ^{199}Hg和 Δ^{200}Hg → Dissolved state from atmospheric precipitation Hg, particulate state from watershed runoff Hg
- Both DHg and PHg in runoff: negative Δ^{199}Hg和Δ^{200}Hg, consistent with the regional atmospheric Hg(0) → GEM through uptake by vegetation and apoptosis.

Trends in DHg and PHg concentrations and isotopes in lake profile waters

Concentrations and isotopic composition of lake DHg



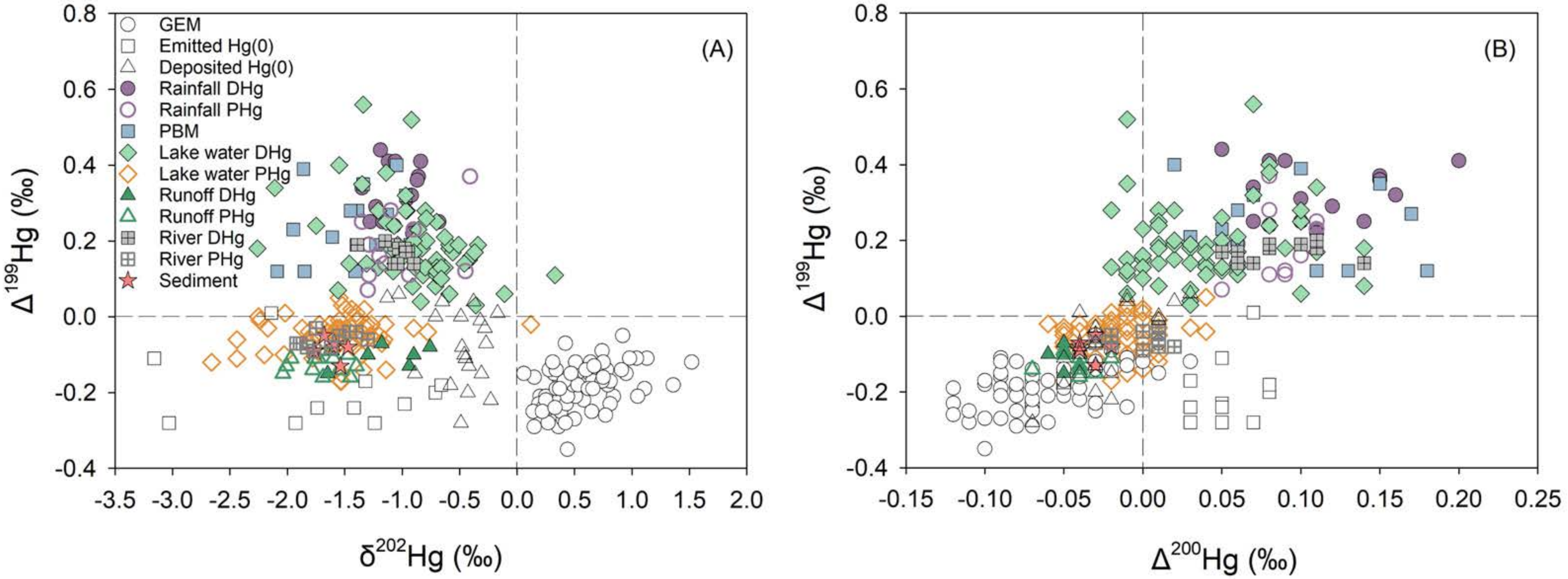
Concentrations and isotopic composition of lake PHg



Significant decreasing trend in Hg concentrations, but insignificant isotopic trend

High DOC in the surface layer; rapid vertical mixing action

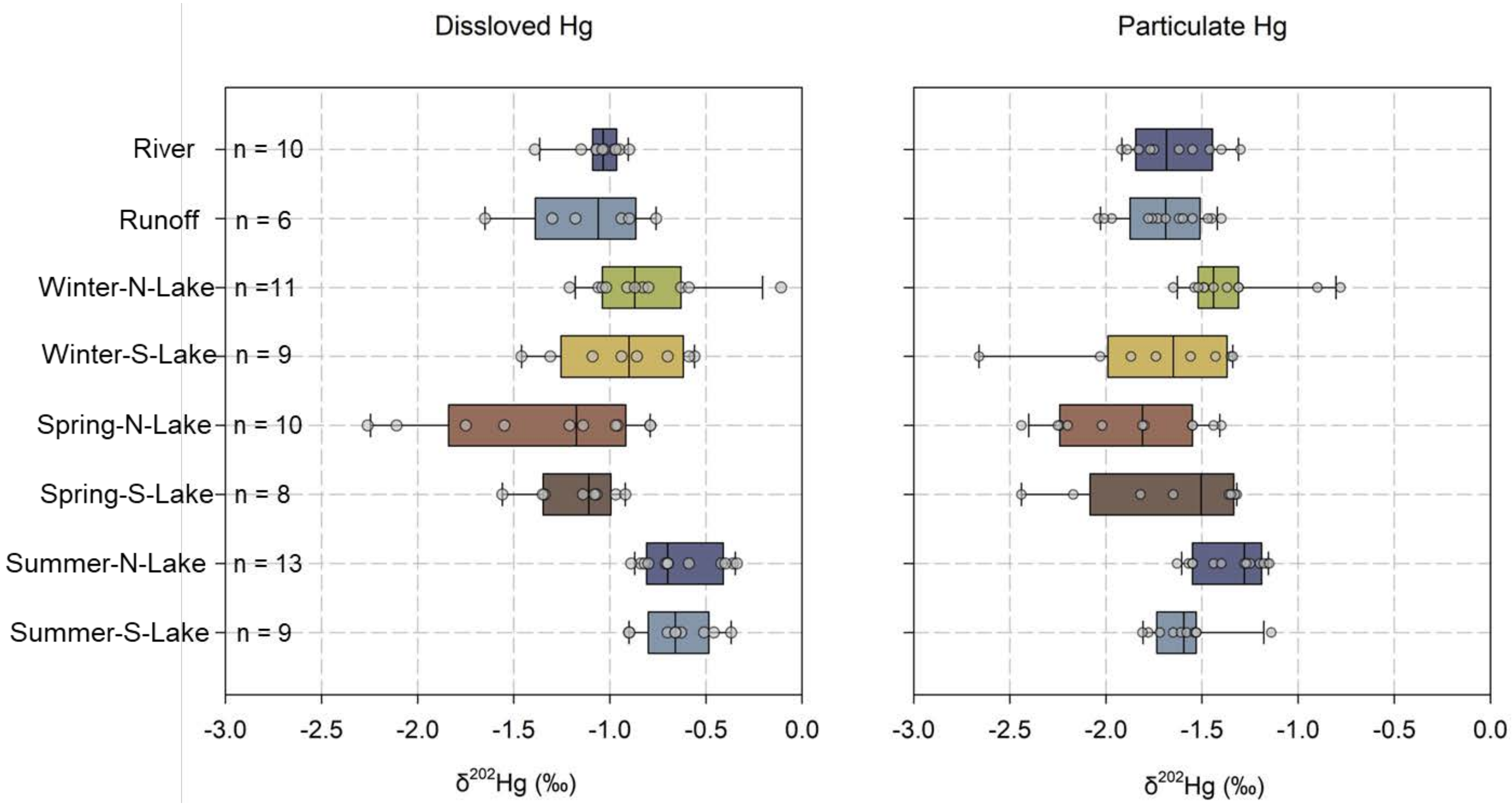
Hg isotope fingerprints of different environmental media in lake ecosystems



- Hg isotopes in lake and river waters are lying between atmospheric and runoff samples
- Hg isotopic compositions of lake sediment samples were similar to those of surface runoff samples, but differed significantly ($p<0.01$) from lake water isotopes of dissolved and particulate Hg（$p<0.01$）
- Mercury isotope mixing models indicate that 62% of the Hg in sediments is derived from surface runoff and 38% from the water column

Zhang et al., 2023, ES&T; Wu et al., 2023,JGR-a

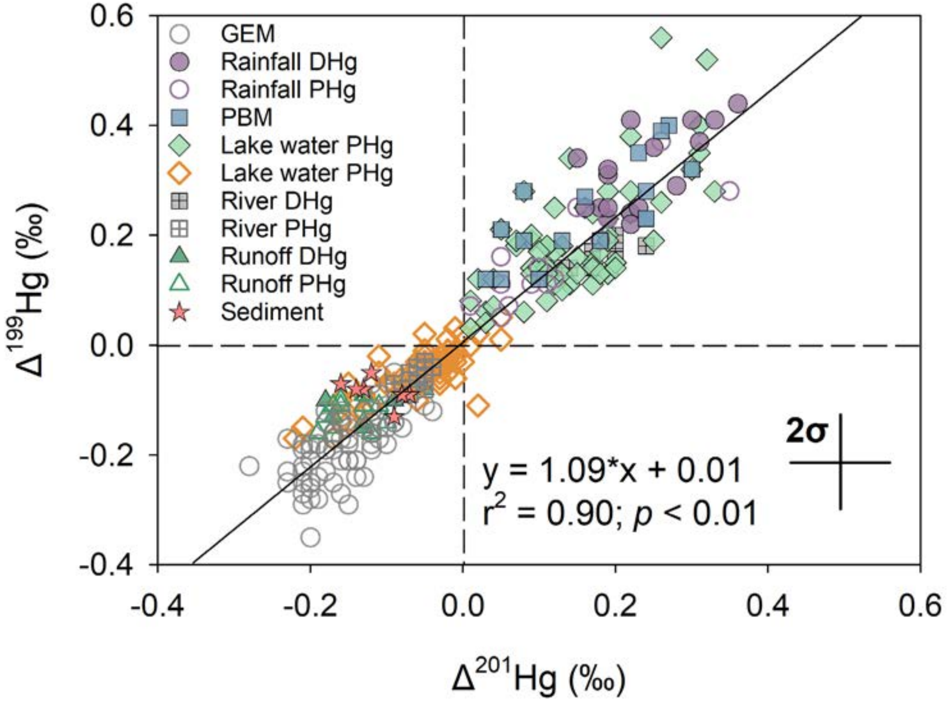
MDF in lake ecosystems

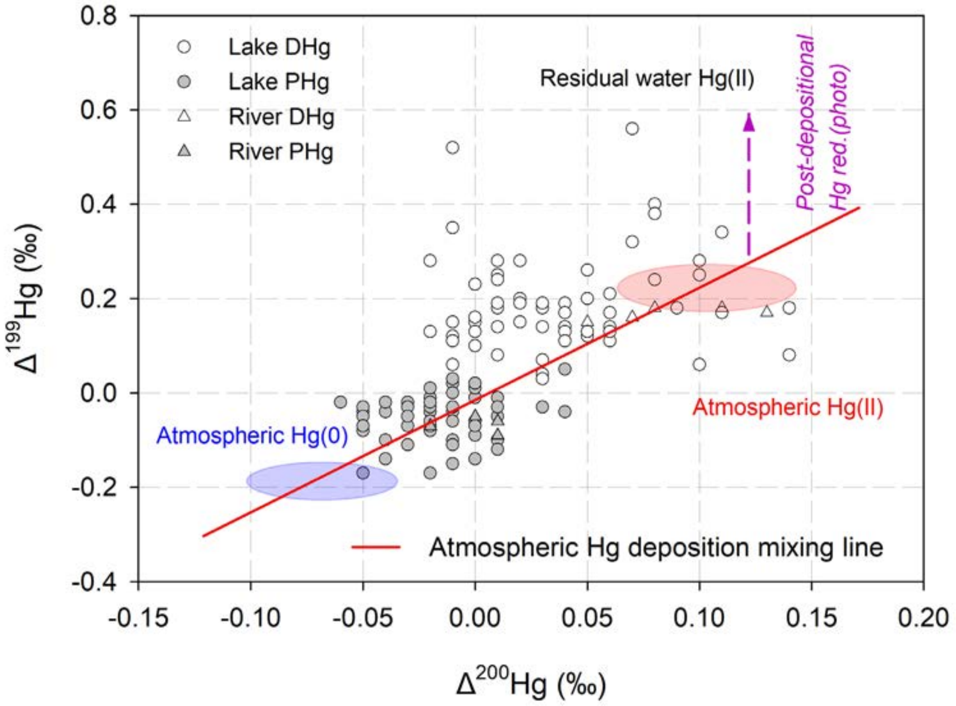


- Significant positive shifts of δ^{202}Hg in DHg relative to PHg in lake water, similar to that in river and runoff ($\delta^{202}Hg_{PHg\text{-}DHg}$ =-0.69 ~ -0.63‰)
- Sorption/adsorption processes between the dissolved Hg(II) and the organic colloids

Jiskra et al., 2012, ES&T; Wiederhold et al., 2010,ES&T

Odd- and even-MIF in lake ecosystems



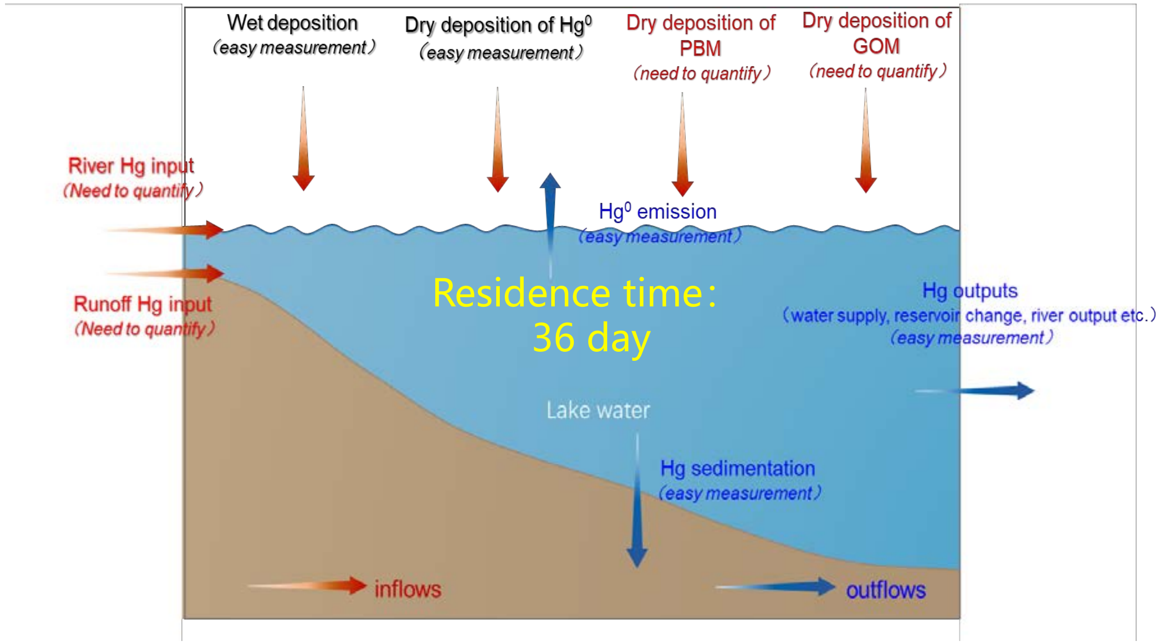


Photochemical processes are the main mechanism for mercury in lake ecosystems

- PHg in river and lake waters is located at the atmospheric Hg deposition line, but DHg is above the line.
- Low impact of particulate matter on the reduction process of Hg in the water column and easily reducible Hg in the dissolved state

Ci et al., 2016, ES&T; Aymot et al., 1999,GCA

Hg isotope mass balance models to quantify the sources of mercury in lakes

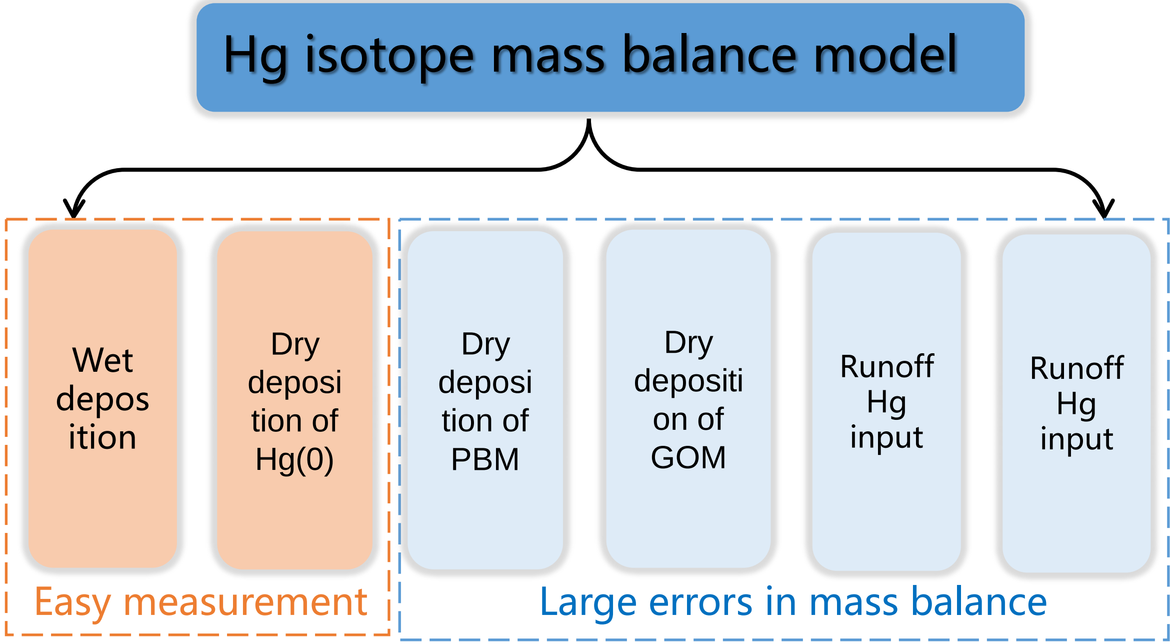


$$M_{inputs} * \delta^{202}Hg_{inputs} = M_{outputs} * \delta^{202}Hg_{outputs}$$
$$M_{inputs} * \Delta^{199}Hg_{inputs} = M_{outputs} * \Delta^{199}Hg_{outputs}$$
$$M_{inputs} * \Delta^{200}Hg_{inputs} = M_{outputs} * \Delta^{200}Hg_{outputs}$$

Sources	Mass fluxes ($kg\ yr^{-1}$)	
Wet deposition flux	1.87 ± 0.67	Calculated as the product of precipitation-weighted mean Hg concentration and precipitation amount
Dry deposition flux of Hg(0)	1.43 ± 0.37	Zhang et al., 2023
Dry deposition flux of PBM		Deposition velocity cannot be determined
Dry deposition flux of GOM		Deposition velocity cannot be determined
River Hg input		Flow rate could not be determined
Runoff Hg input		Flow rate could not be determined

Sinks	Mass fluxes ($kg\ yr^{-1}$)	
Hg(0) emission	2.30 ± 0.15	Zhang et al., 2023
Sedimentation	27.54 ± 1.85	Calculated from Hg sedimentation rate and surface sediment Hg concentrations
Outputs	4.23 ± 0.84	Calculated from output flow and lake water Hg concentration

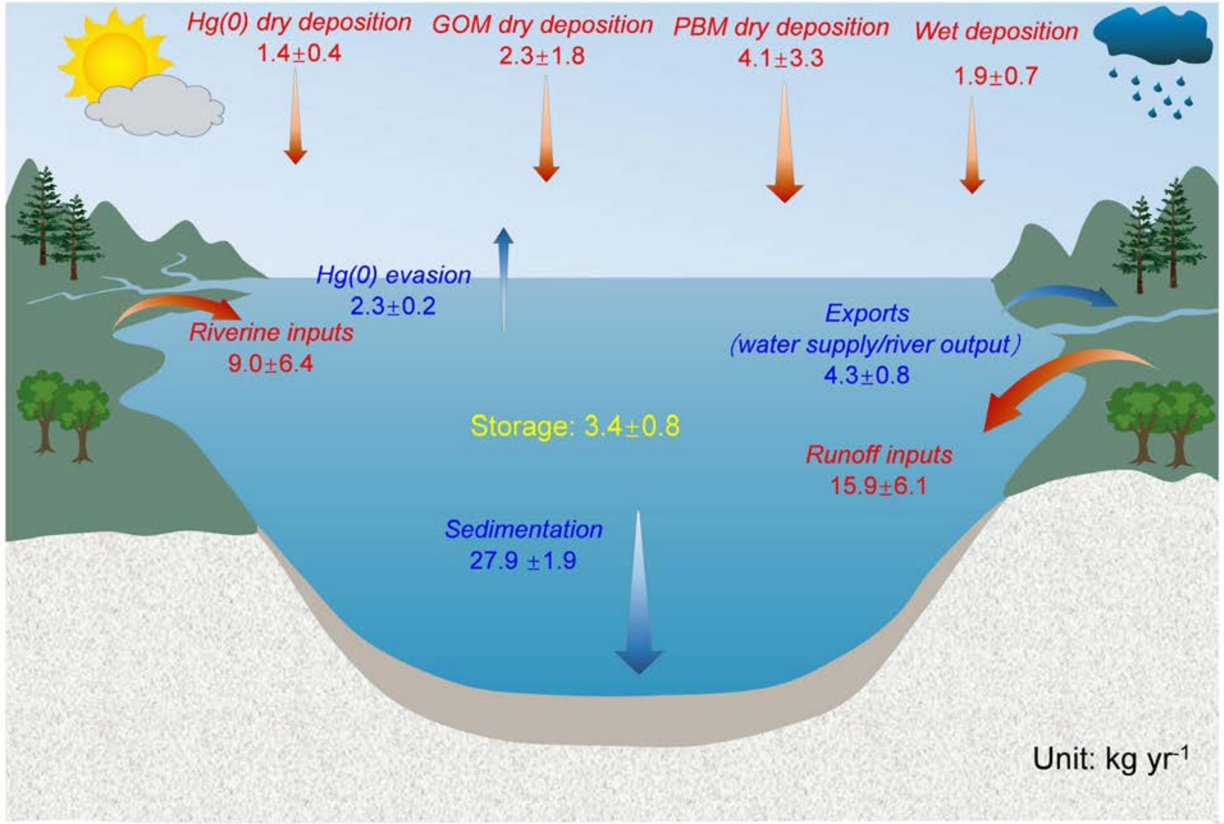
A comprehensive approach to flux- and stable isotope-based analysis of Hg sources in lakes



Source type	Results (%)
Dry deposition of Hg(0)	4.2%
Wet deposition	5.5%
Dry deposition of PBM	11.1%
Dry deposition of GOM	6.0%
River Hg input	22.6%
Runoff Hg input	**50.6%**

- The surface runoff is the largest source to HFL, accounting for 50.6% of the total
- Dry deposition of atmospheric Hg(II) is 3.1 times higher than wet deposition of Hg(II), confirming the contribution of dry deposition of Hg(II)
- Hg accumulation in HFL is primarily associated with changes in atmospheric Hg(0) levels due to watershed impacts

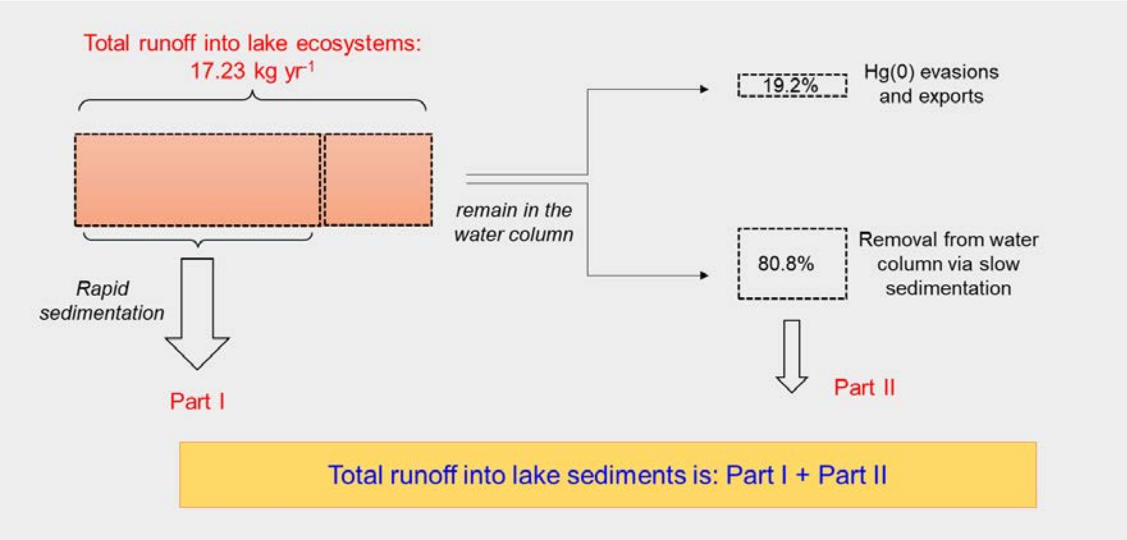
Implication: Biogeochemical cycling of Hg in lakes



- Dry deposition rates of PBM and GOM: 2.3 and 3.2cm s^{-1}
- Erosion rates of soil mercury in karst watersheds: 10.8 g km^{-2} yr^{-1}, much lower than the erosion of soil mercury in Guizhou in 2010 (320 g km^{-2} yr^{-1})

(Liu et al., 2018, ES&T)

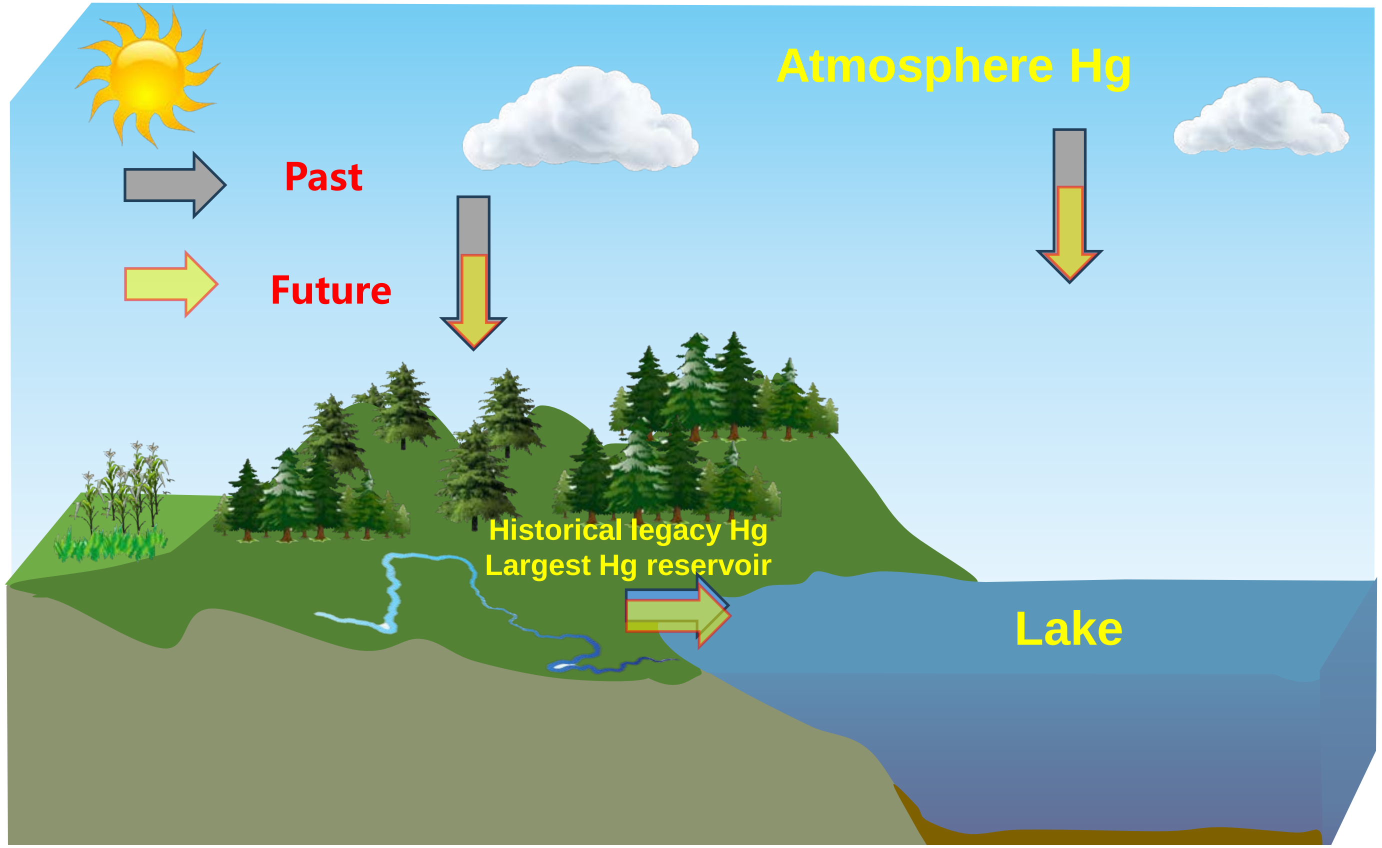
How much sediment Hg is derived from surface runoff?



Watershed area/ lake area of HFL=28:1

- 80% of Hg in sediments comes from surface runoff
- Isotopic changes in sediment Hg are mainly influenced by isotopic changes in watershed Hg and to a lesser extent by photochemical processes in water column Hg

Implication: Pollution control of regional Hg



- interprets the risk of mercury contamination of lakes as potentially persistent, even with future anthropogenic Hg reduction impacts
- Clarifies that the quality of Hg pollution in lakes is more difficult than we expected and that the prevention and control of Hg pollution in lakes is a continuous and long-lasting process

End of report

Thanks for listening and thanks for the comments!

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