Total Hg and Hg isotopes in soils, street dust, and lake sediment around a large scale Zinc smelter in Hunan, China

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Outline

1. About the large scale smelter
2. Hg in soils
3. Hg in street dust
4. Hg in lake sediment

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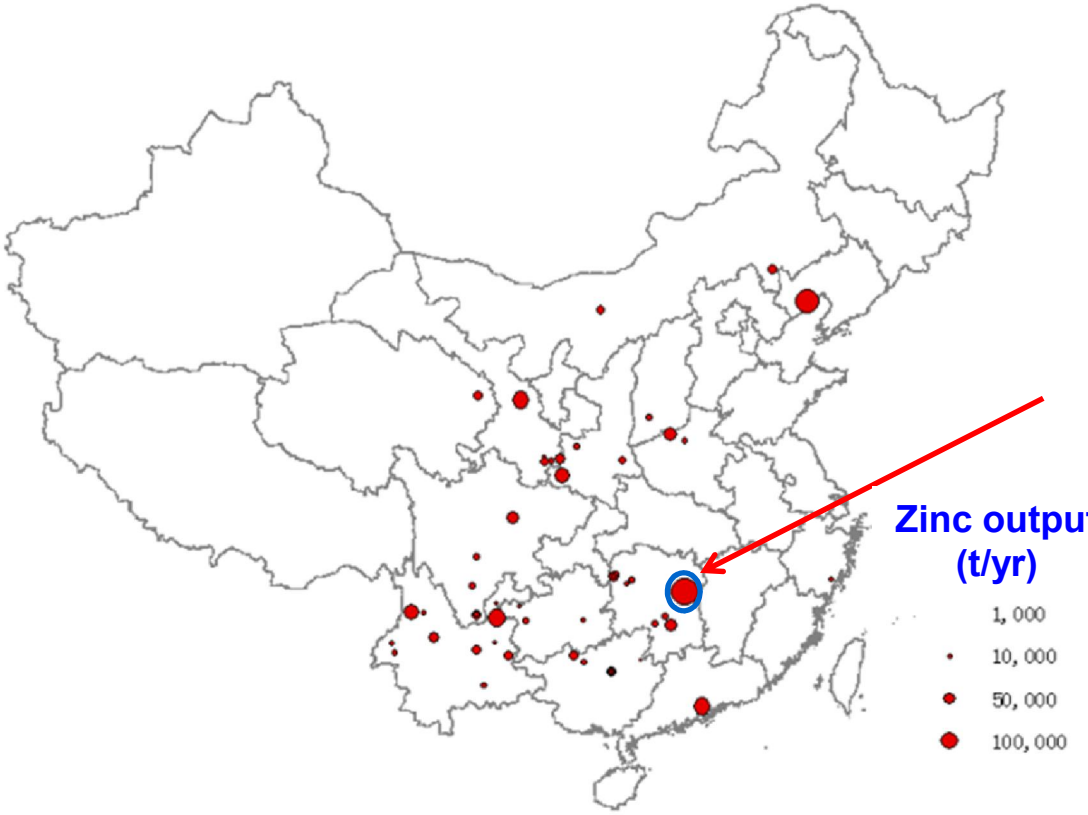
Study area



The largest zinc smelter in China,

Started into operation since late 1950s

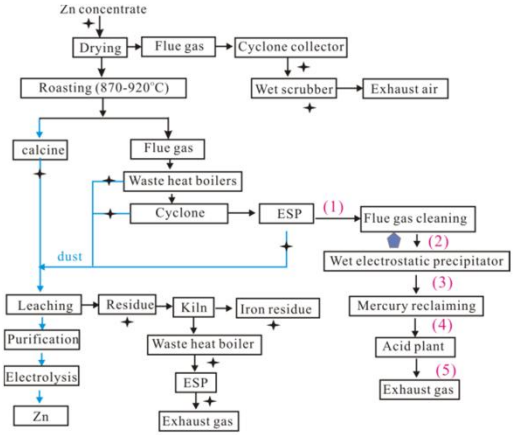
Zn ingot output: 0.50 Mt/yr

Pb ingot output: 0.10 Mt/yr

Process of the large-scale zinc smelter

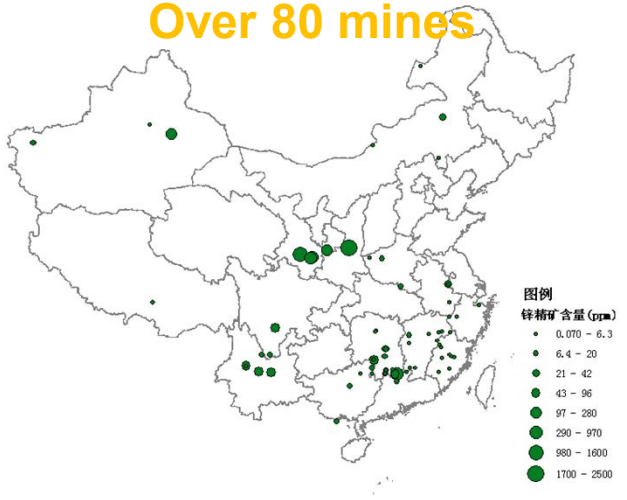
Zhuzhou smelter

Production procedure



Zn ore sources

Over 80 mines



The hydrometallurgical process (electrolysis process) for zinc production:

(1) Roasting (700-1000C): $2\,ZnS + 3\,O_2 \rightarrow 2\,ZnO + 2\,SO_2$ **Most Hg ↑**

(2) Electrolysis process : Leaching, purification, electrolysis, melting and casting

Historical air pollution control measures

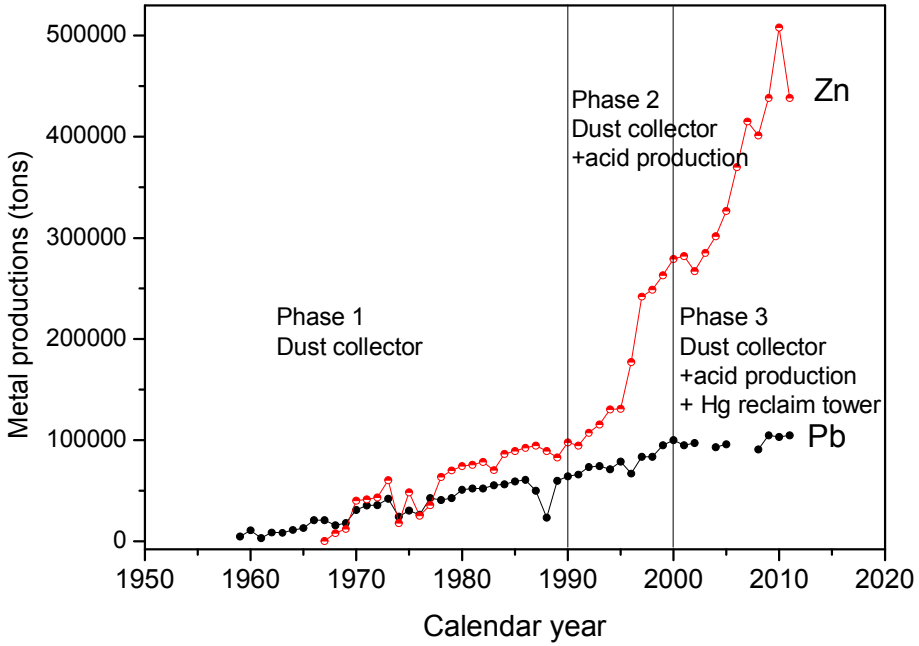
The developing history of the smelter.

Period	Zinc producing lines (Zn1 & Zn2)			Lead producing line (Pb1)			Total Hg emitted from smelter (t)	Total Hg accumulated in soil (t)
	Production (kt yr^{-1})	Ore consumption (kt yr^{-1})	APCDs[a]	Production (kt yr^{-1})	Ore consumption (kt yr^{-1})	APCDs[a]		
1960–1968[c]		–	–	20	34	None	2	0.1
1969–1990	100	208	DC	30	50	DC	95	14.2
1991–2000	170	350	DC + AP_d	70	120	DC + AP_s	3	0.4
2001–2005	450	930	DC + AP_d/DC + AP_d + RT[b]	100	170	DC + AP_s	3	0.1
2006–2011	500	1040	DC + AP_d + RT	100	170	DC + AP_s	2	0.1

[a] Air pollution control devices for smelting flue gas. None — no air pollution control devices; DC — dust collector; AP_d — acid plants with double conversion and double absorption tower; AP_s — acid plants with single conversion and single absorption tower; RT — Hg reclaim tower.

[b] During 2001–2005, about 60% of smelting flue gas from zinc smelter was treated with AP_d + RT.

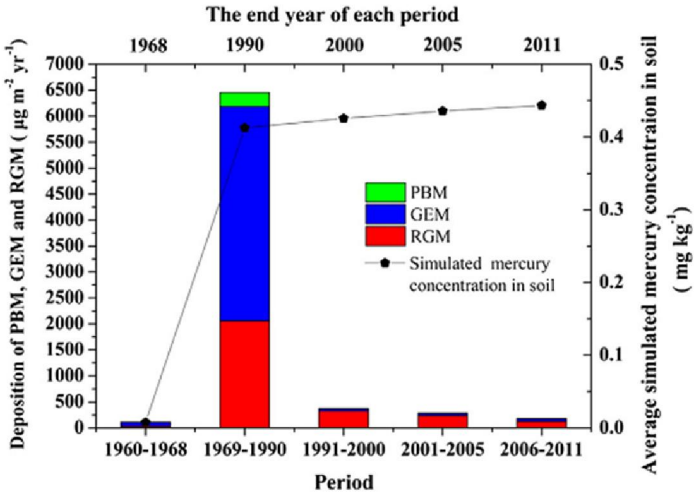
[c] The lead line was operated in August of 1959. Considering the unstable production in that year, we have not considered its impact in this study.



Time series of Zn and Pb output;

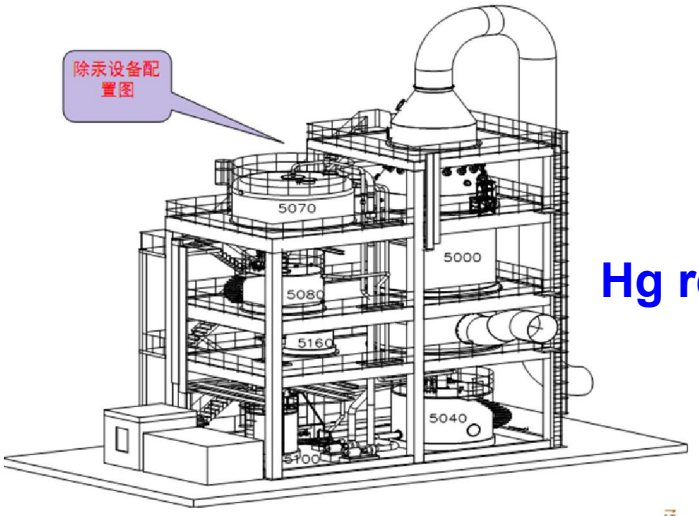
with flue gas control techniques in different times

Historical pollution control measures

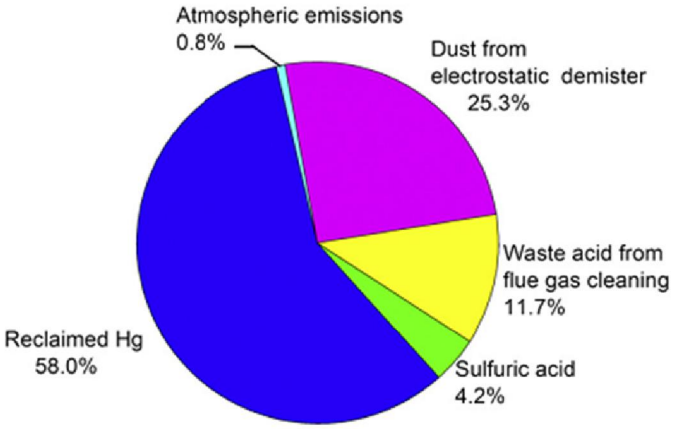


105 t Hg was lost into atmosphere during 1960-2011

Wu et al., STOTEN, 2014



Hg reclaim tower



Wang et al., Environ. Pollut., 2010

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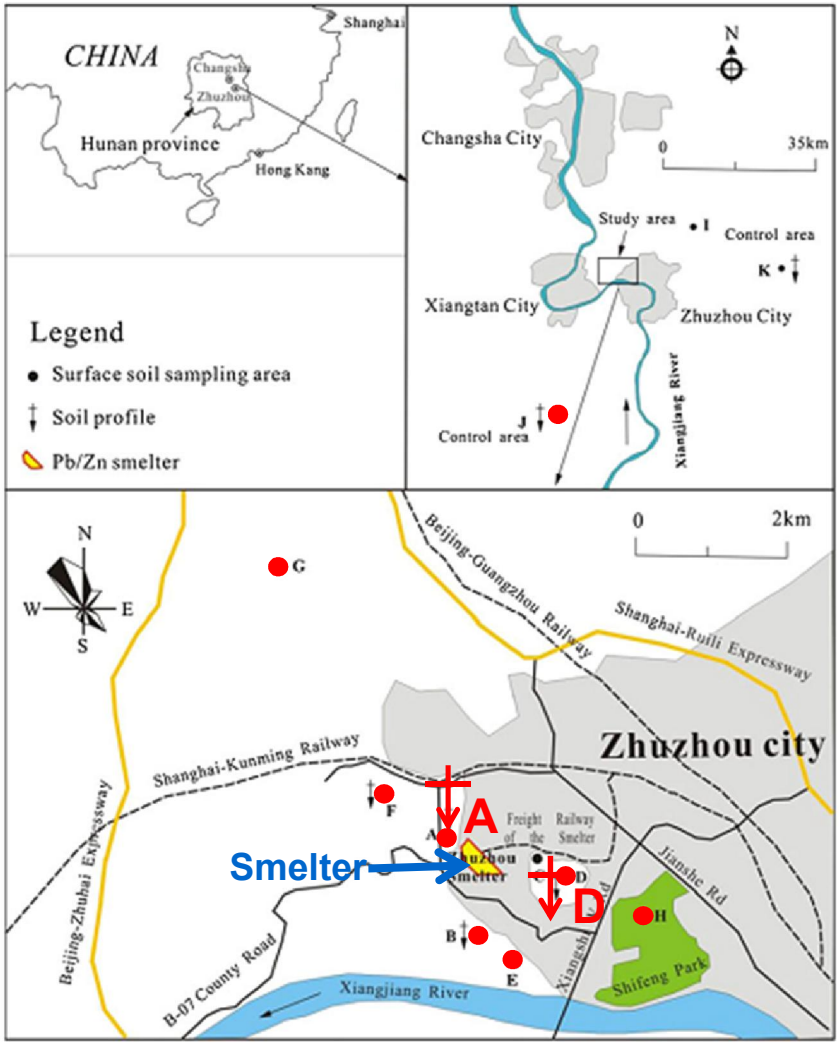
Soil sampling sites



Totally 11 sampling areas, within 38 km to the smelter

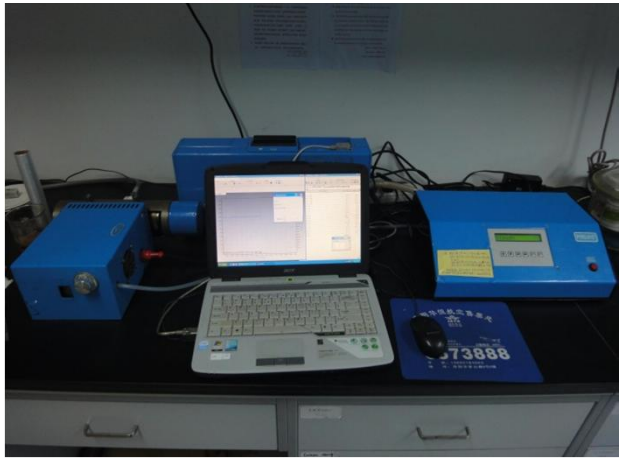
Agricultural soils

Surface soil (0-20cm)

Soil cores (0-50cm)

- **Total Hg**
- **Hg isotope**

Analysis for total Hg



Total Hg: LUMEX direct Hg analyzer (RA-915+ & PYRO-915)

Analysis for Hg isotopes

HGX-200 Hydride generation system

HGX-200 Cold Vapor System (CETAC)

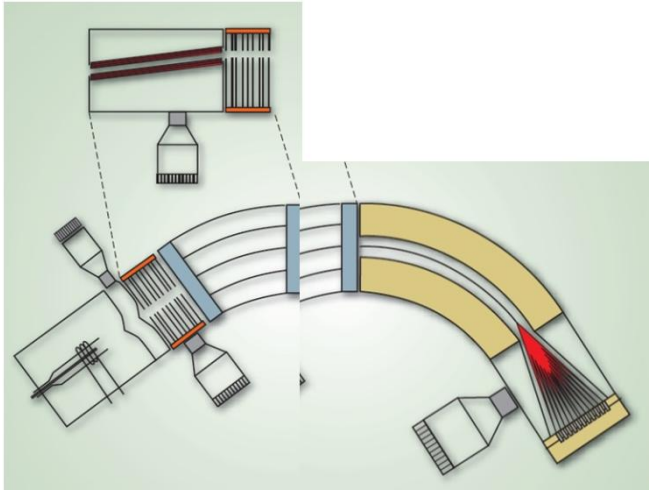
Apex-Q nebulizer

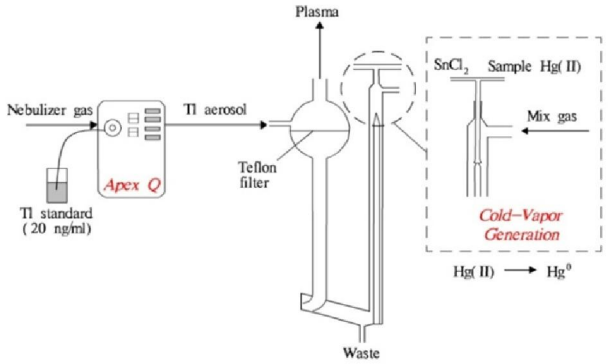
Apex-Q desolvation unit (CETAC Technologies, Omaha, USA)

peristaltic pump

Gilson minipuls3 (Gilson Corp., USA)

Nu-Plasma MC-ICP-MS (Nu Instruments)





On-line introduction systems

Instrumentation（MC-ICP-MS, Nu Instruments, Nu plasma model）

Analysis for total Hg and Hg isotopes

Mass dependent fractionation (MDF):

$$\delta^{xxx}\mathrm{Hg}\ (^{0}/_{00})=\left\{\left[\frac{^{xxx}\mathrm{Hg}/^{198}Hg_{sample}}{^{xxx}Hg/^{198}\mathrm{Hg}_{standard}}\right]-1\right\}\times 1000$$

Where xxx is 199, 200, 201, 202

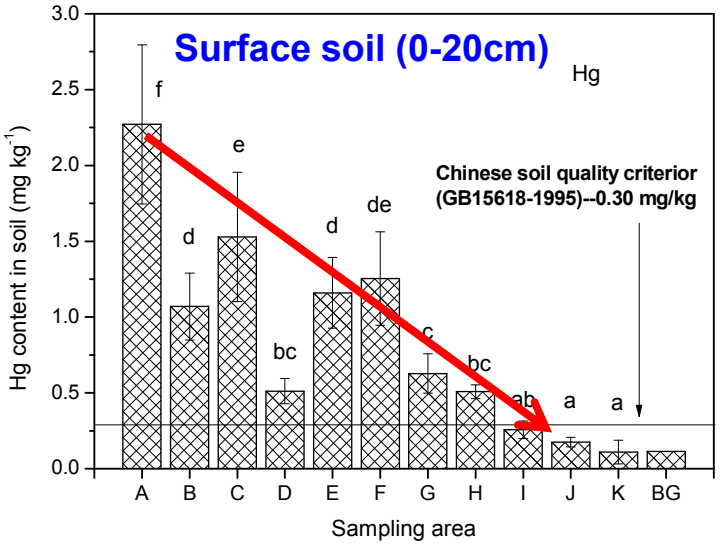
Mass independent fractionation (MIF):

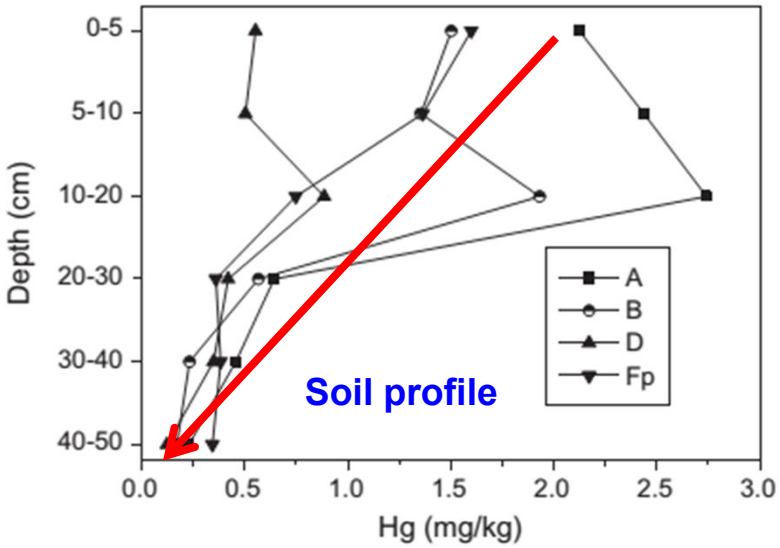
$$\Delta^{199}\mathrm{Hg}(‰)=\delta^{199}\mathrm{Hg}-(0.2520\times\delta^{202}\mathrm{Hg})$$

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

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

Total Hg in surface soil and soil cores

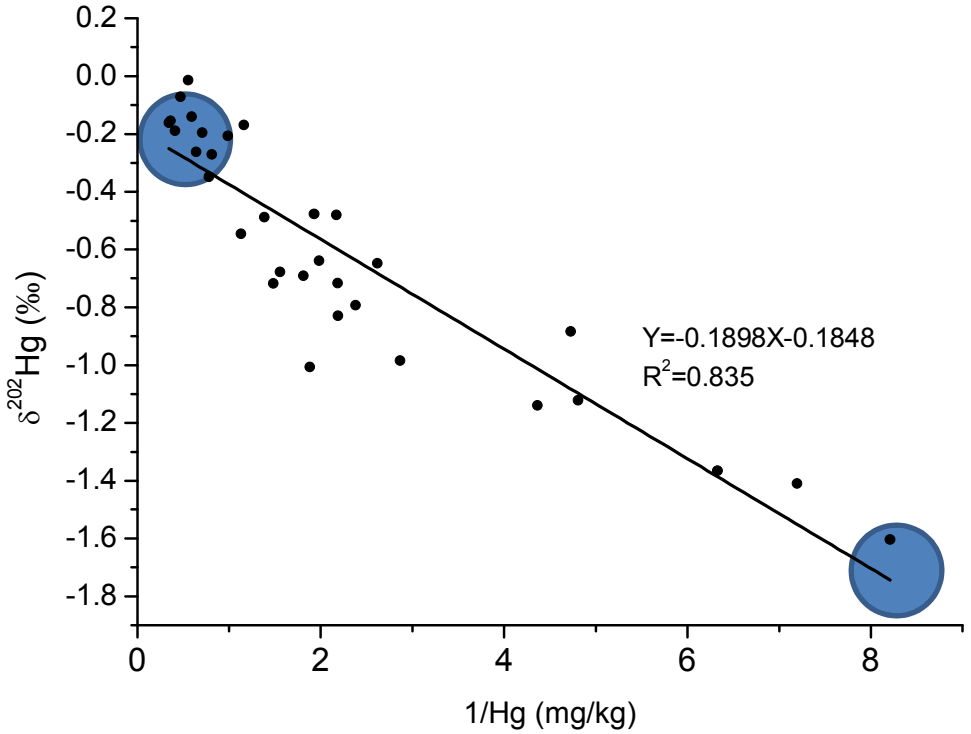




Li ZG et al., Appl. Geochem. 2011

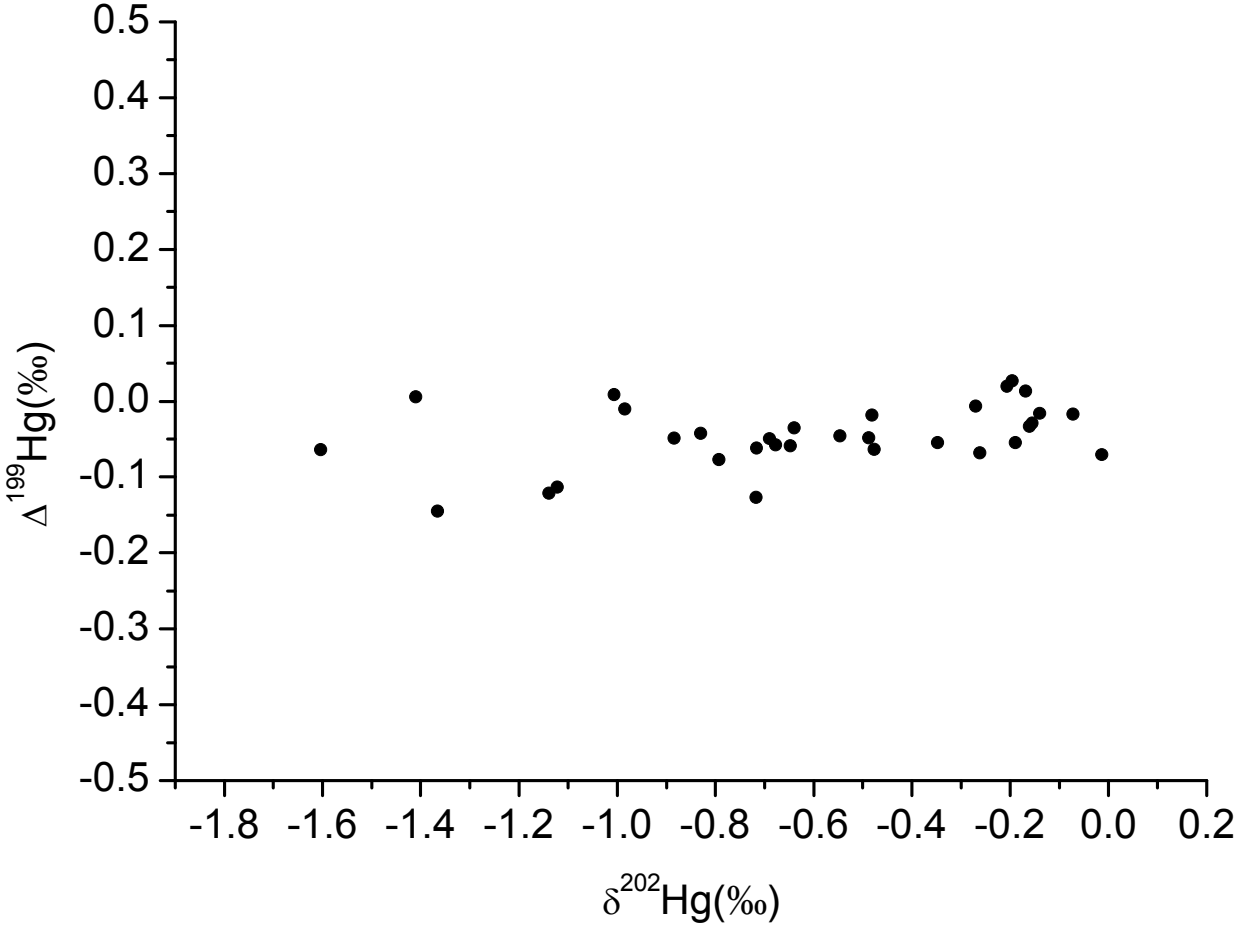
Hg contamination decreased with distance to the smelter and soil depth, the maximum Hg content is about 2.8 mg/kg (with background of 0.1 mg/kg), and the most impacted zone is the upper 20 cm soil layer (cultivated horizon), around 6.5 t Hg was accumulated in the soils within 4 km to the smelter

Hg isotopes in soils



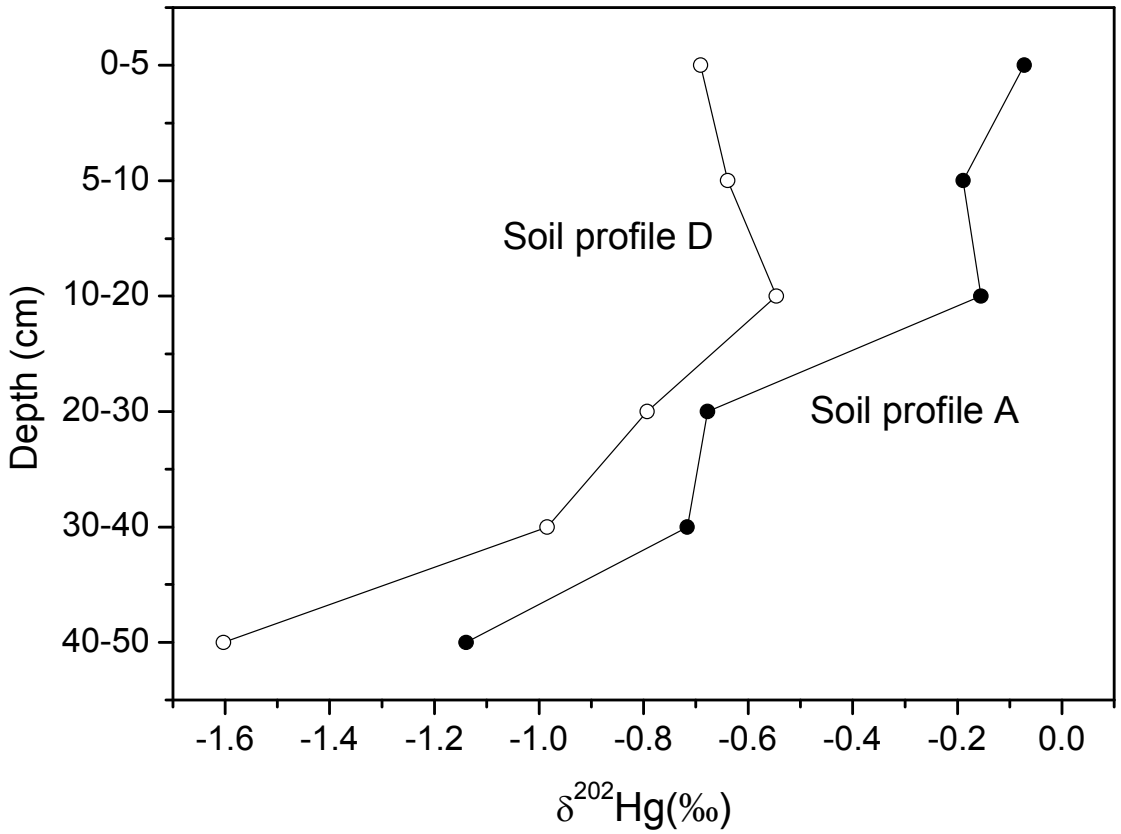
δ^{202}Hg(‰) is a function of Hg content in soils, and a binary mixing-model can be built up

Hg isotopes in soils



MIF: very small or insignificant

Hg isotopes in soils



Soil profile

Heavier in the upper layer
Lighter in the lower layer

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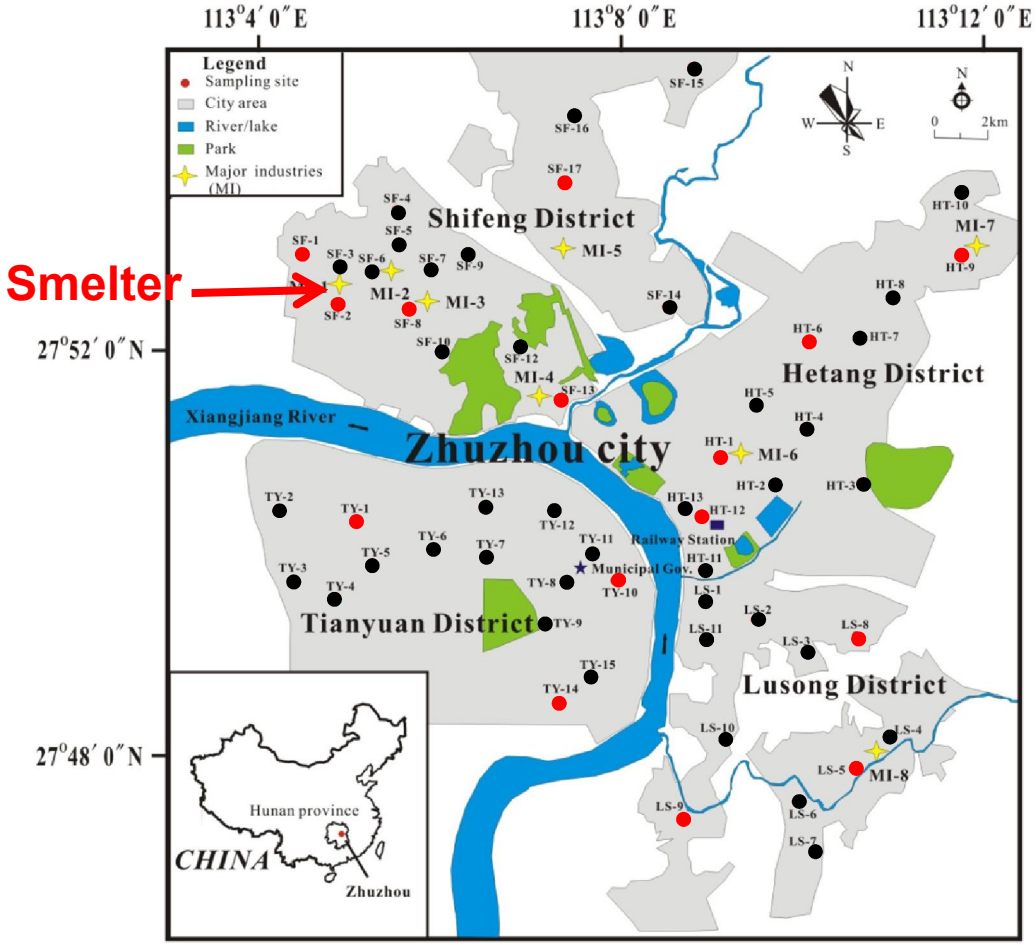
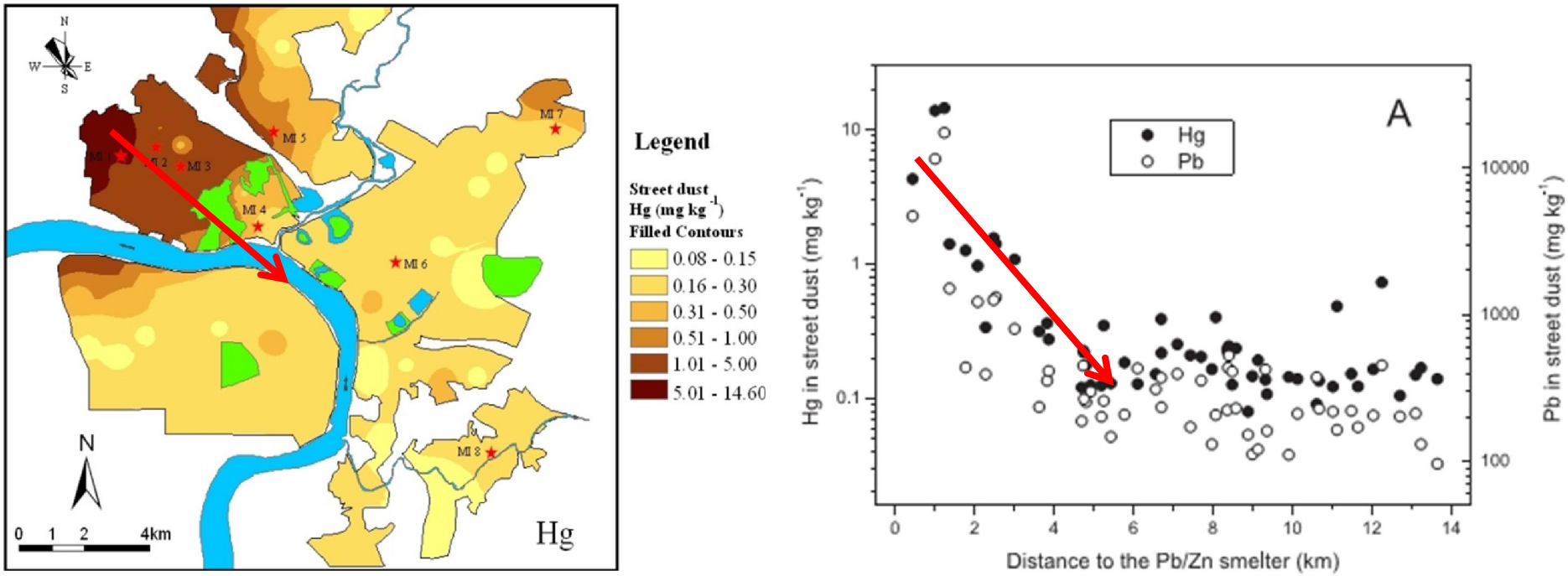
Sampling sites



55 sites within an area of 100 km^2

- Total Hg
- Hg isotope

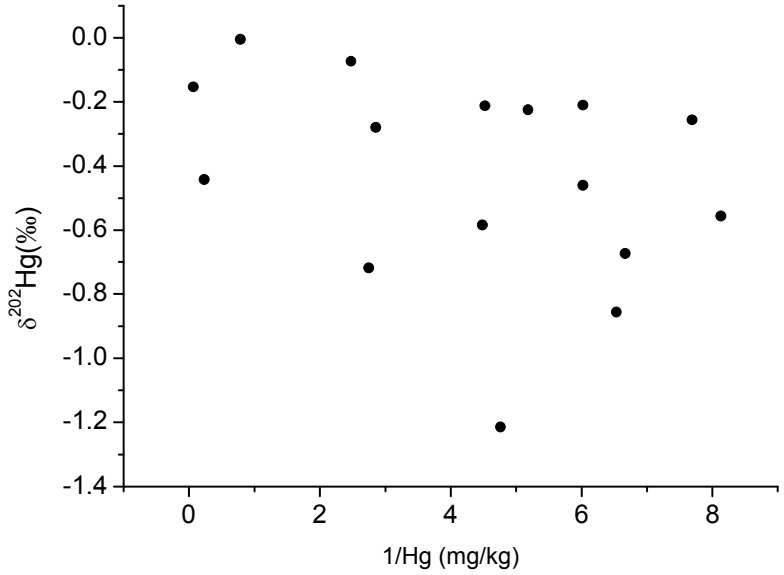
Total mercury in the street dust

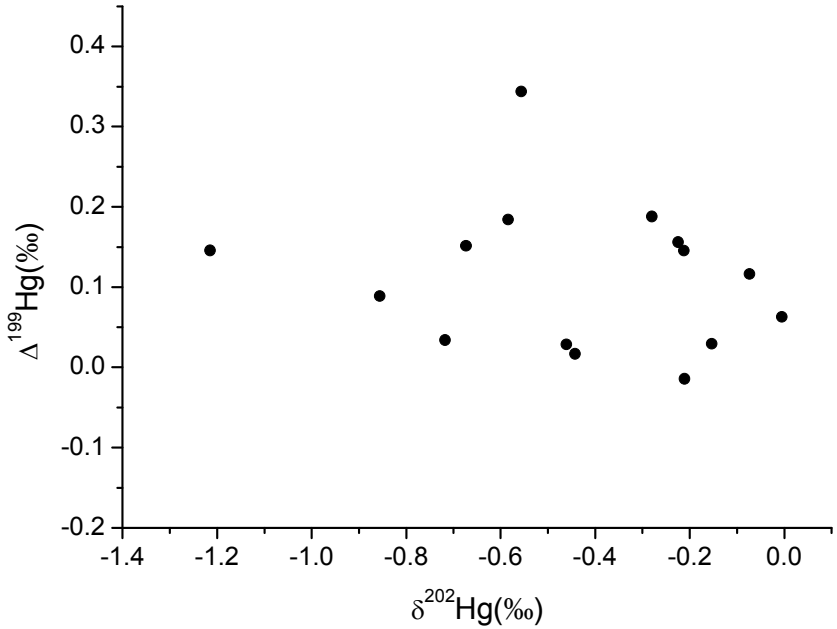


Li ZG et al., Environ. Pollut. 2013

Maximum Hg content is 15 mg/kg in the street dust, and most affected area is the nearest 5 km

Hg isotopes in the street dust





δ^{202}Hg : 0 ~ -1.21‰

The relation between δ^{202}Hg and mercury content is not clear (more sources?)

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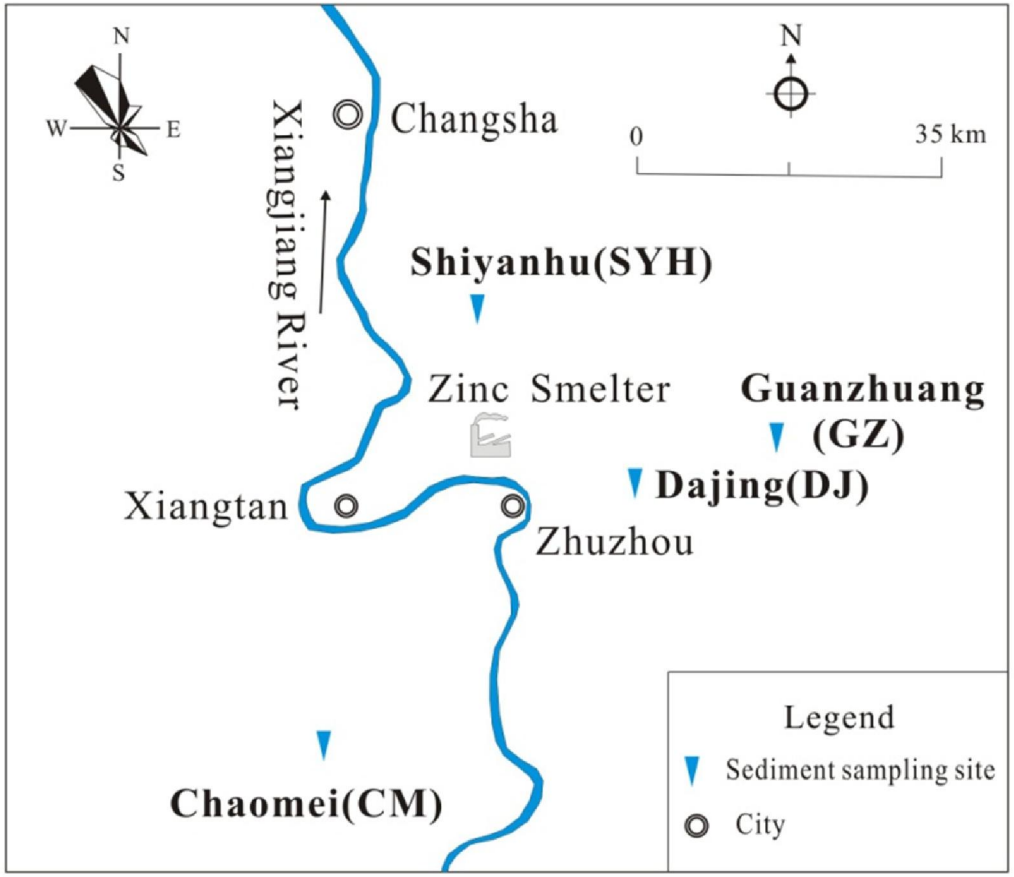
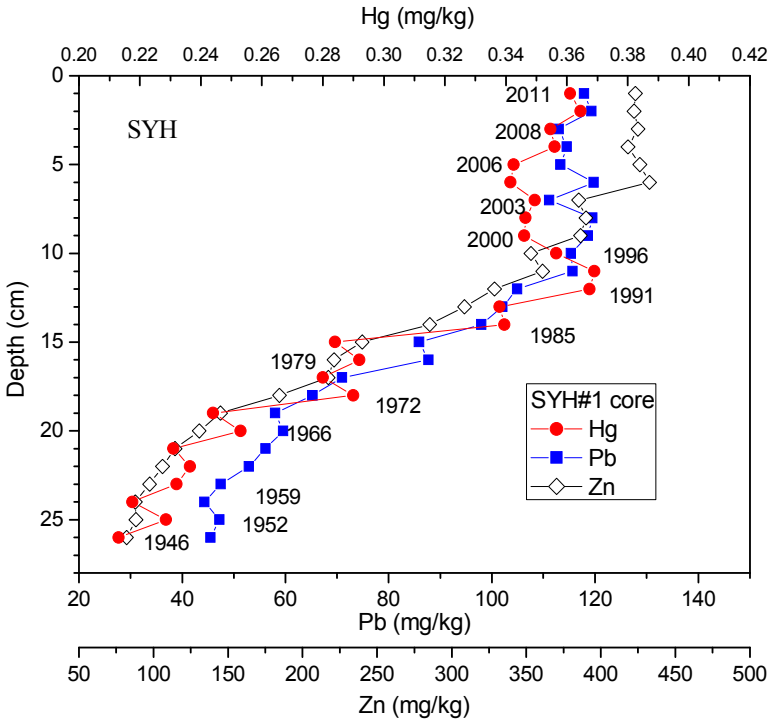
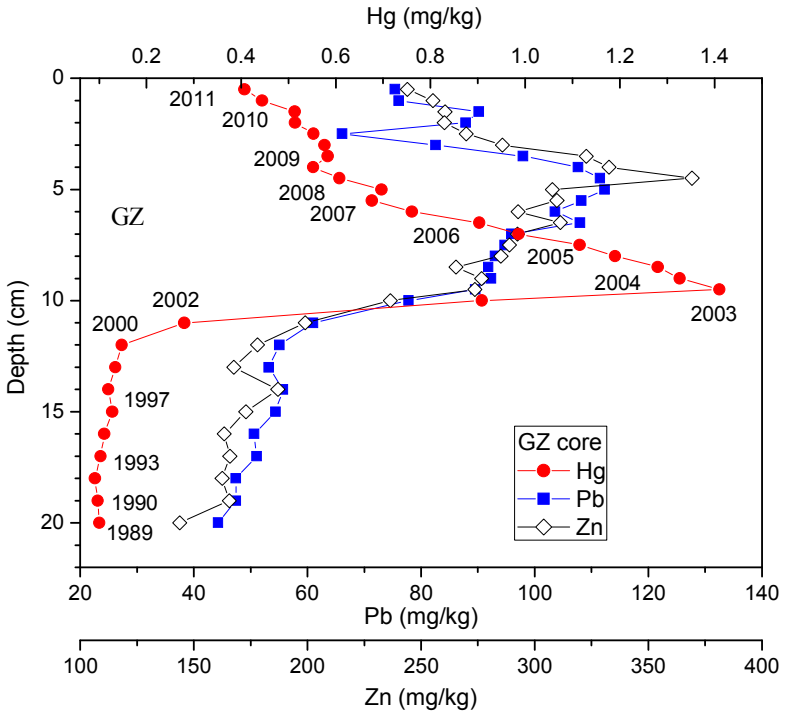


Hg, Pb, Zn in sediment cores

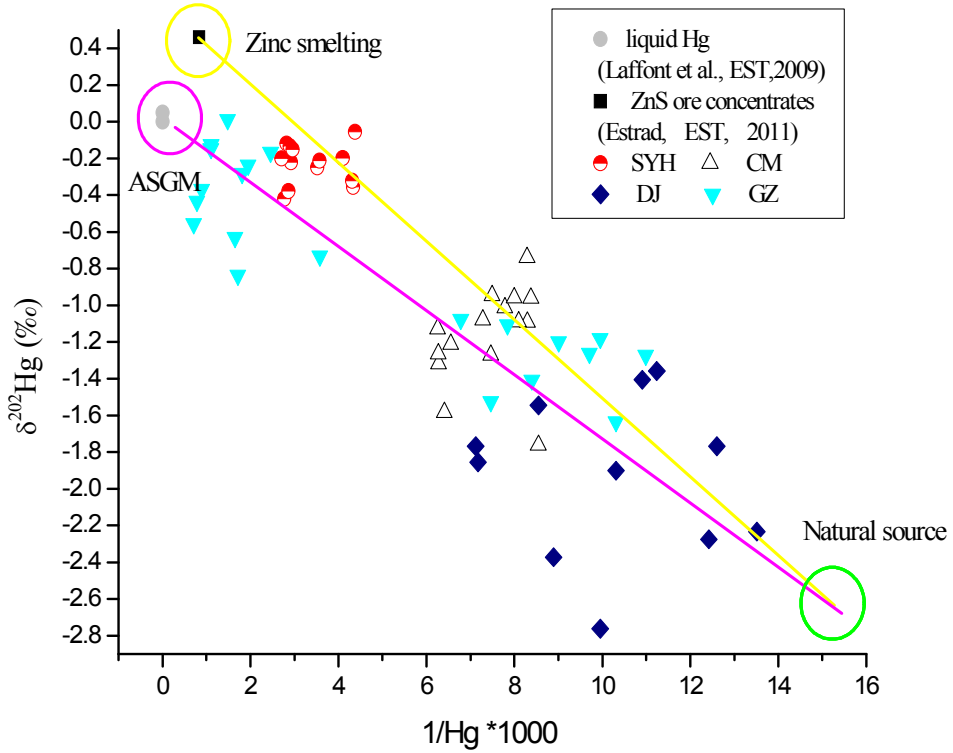


Lakes that mainly affected by the Zn smelter



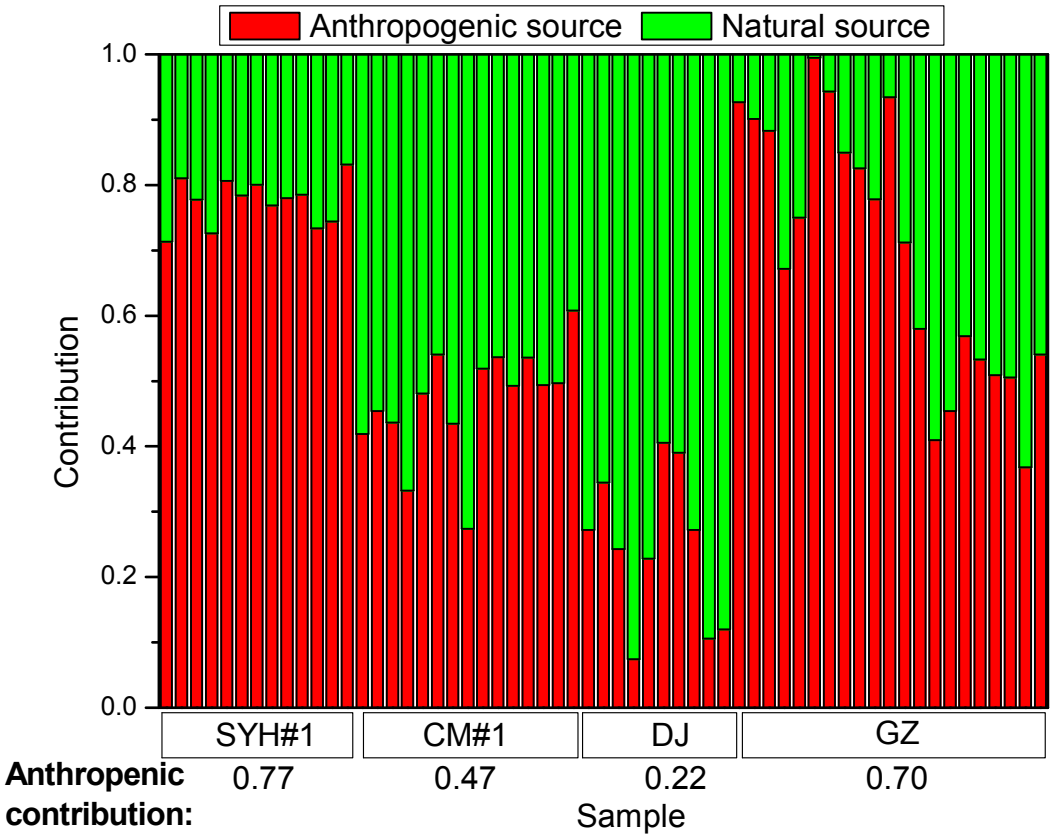
Lake that mainly affected by the artisanal and small-scale gold mining (ASGM)

Hg isotopes in the sediment



Hg isotopes in the sediment

Source apportionment



20-80% of Hg in sediment is attributed to the human activities

Summary

（1）Total Hg in agricultural soil and street dust is decreasing with distance to the Zn smelter.

（2）MDF ($\delta^{202}Hg$) is a function of soil Hg, while MIF ($\Delta^{199}Hg$) is negligible.

（3）Two distance sources in lake sediment, Zn smelting and ASGM, can be found.

Study plan

Collaborate with Swedish researches in two areas:

(1) Mercury isotopic signatures in seriously contaminated aquatic sediments (or soils) with different sources (such as paper pulp, chlor-alkali, Zn & gold extraction and smelting) ;

(2) Hg deposition flux and sources in less-impacted or remote lake sediment.

Thank you for your attention!