ANNUAL REPORT ON GEOTRACES ACTIVITIES IN CHINA-BEIJING

May 1st, 2023 to April 30th, 2024

New GEOTRACES or GEOTRACES relevant scientific results

- **^{90}Sr in coastal oceans**

The behavior and source of ^{90}Sr in the coastal ocean remain uncertain. Here, we investigated the distributions of ^{90}Sr in coastal fresh groundwater, river water, pore water, and seawater in three bays along the southeastern coast of China between 2019 and 2021 and evaluated the potential of submarine groundwater discharge (SGD) as a source of coastal ^{90}Sr. The ^{90}Sr activity in coastal fresh groundwater was higher than that in river water and seawater, while the ^{90}Sr activity in pore water was comparable to that in adjacent seawater. In addition, nonconservative mixing behavior of ^{90}Sr along the salinity gradient between river water and seawater was observed. These observations indicated that fresh SGD may serve as an additional source of ^{90}Sr in coastal seawater. Combining our groundwater ^{90}Sr data with the reported fresh SGD flux data, the estimated fresh SGD-derived ^{90}Sr fluxes into the three bays were comparable to or even higher than those supplied by riverine sources. These results revealed that fresh SGD is a major but overlooked source of ^{90}Sr in the coastal ocean. This subterranean pathway for transport of ^{90}Sr to the coastal ocean should be considered in the monitoring and risk assessment of coastal areas, especially those near nuclear facilities.

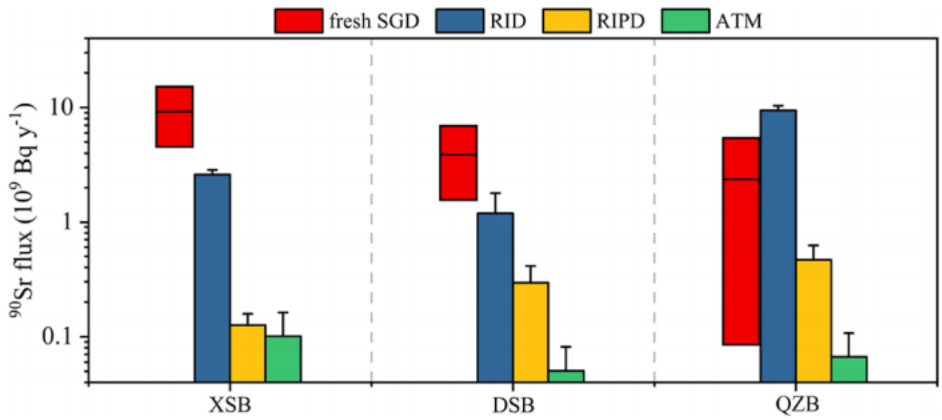

Figure 1. Comparison of the estimated fresh SGD-derived ^{90}Sr fluxes to the river inputs of dissolved ^{90}Sr (RID), river particulate desorption (RIPD), and atmospheric deposition (ATM) in XSB, DSB, and QZB.

- **New insights on Fe, Ni, Cu and Zn behaviours in the Pearl River Estuary**

The concentration data showed that Fe, Ni and Zn experienced removal, but Cu remained conservative along the salinity gradients. The metal isotopes reveal more complex estuarine processes, like the two-stage process which involved particle adsorption and colloidal flocculation at low salinities, followed by conservation at high salinities, as well as the three-endmember mixing process which is dominated by riverine, oceanic endmembers and external sources. Specifically, capturing δ^{56}Fe fully proves challenging, yet it appears strongly influenced by inputs of benthic Fe within the PRE, characterized by dFe > 13 nmol kg^{-1} and δ^{56}Fe < -0.80‰. δ^{60}Ni and δ^{66}Zn can be described by either two-stage or there-endmember mixing processes. The description of δ^{65}Cu is best achieved by a three-endmember mixing process, with the external source having dCu > 20 nmol kg^{-1} andδ^{65}Cu <

+1.3‰, indicative of processes like organic matter remineralization or discharge from wastewater treatment plant. This study highlights the need for more extensive and detailed studies on estuarine settings to elucidate their potentially crucial role in global dTMs budgets.

Table 1. The concentrations of dFe, dNi, dCu and dZn, and their isotopic compositions of $\delta^{56}Fe$, $\delta^{60}Ni$, $\delta^{65}Cu$ and $\delta^{66}Zn$ (values ±2 SD) along a salinity gradient in the Pearl River Estuary. We assume the long-term 2SD reproducibility of the secondary standards to represent uncertainty on each analysis, unless the internal precision is larger, in which case the latter is used.

Station	Longitude	Latitude	Salinity	dFe	dNi	dCu	dZn	$\delta^{56}Fe$	$\delta^{60}Ni$	$\delta^{65}Cu$	$\delta^{66}Zn$
	◦ E	◦N		nmol kg^{-1}	nmol kg^{-1}	nmol kg^{-1}	nmol kg^{-1}	‰	‰	‰	‰
1	113.5160	23.0500	0.13	44.07	67.63	22.38	24.92	+0.04 ± 0.10	+0.92 ± 0.08	+2.50 ± 0.07	+0.63 ± 0.10
2	113.5676	22.9159	0.16	63.47	76.94	26.67	20.28	+0.08 ± 0.16	+1.25 ± 0.08	-	+0.52 ± 0.11
3	113.6865	22.6731	3.19	12.92	31.99	21.58	15.99	− 0.76 ± 0.09	+1.25 ± 0.08	+2.27 ± 0.07	+0.69 ± 0.06
4	113.7411	22.5130	6.95	6.98	21.25	16.02	8.44	− 0.18 ± 0.09	+1.15 ± 0.08	+1.77 ± 0.07	+0.64 ± 0.06
5	113.7615	22.4114	7.85	6.68	28.14	17.61	10.17	− 0.06 ± 0.08	+1.09 ± 0.08	+1.63 ± 0.07	+0.67 ± 0.06
6	113.8283	22.2078	13.03	2.71	31.63	16.56	9.79	− 0.45 ± 0.06	+1.13 ± 0.08	+1.60 ± 0.07	+0.76 ± 0.07
7	113.8379	22.1787	22.03	2.54	38.59	13.19	6.78	− 0.24 ± 0.07	+1.13 ± 0.08	+1.44 ± 0.07	+0.92 ± 0.07
8	113.8542	22.1346	24.24	1.95	20.94	11.94	3.65	+0.69 ± 0.09	+1.12 ± 0.08	+1.25 ± 0.07	+0.66 ± 0.10
9	113.8736	21.9807	28.19	0.48	13.11	8.26	0.87	+0.04 ± 0.10	+1.07 ± 0.08	+1.24 ± 0.07	+0.36 ± 0.31
10	113.8385	21.7213	32.95	1.37	4.09	3.61	0.69	+0.04 ± 0.19	+0.94 ± 0.08	+0.82 ± 0.07	+0.25 ± 0.30
11	114.1640	21.4562	33.78	0.62	2.59	1.15	0.23	+0.49 ± 0.13	+1.38 ± 0.08	+0.69 ± 0.07	− 0.05 ± 0.29
12	114.2785	21.1695	33.71	0.36	2.47	1.21	0.47	− 0.31 ± 0.12	+1.33 ± 0.08	-	− 0.17 ± 0.35
13	114.3970	20.8376	33.69	0.79	2.60	1.06	0.07	− 0.56 ± 0.20	+1.63 ± 0.08	+0.68 ± 0.07	-
14	114.4809	20.6295	33.81	0.13	2.39	1.08	0.24	+0.05 ± 0.25	+1.63 ± 0.08	+0.60 ± 0.07	− 0.14 ± 0.44

- data not available due to measurement failure.

- **Methylmercury cycling in the Bohai Sea and Yellow Sea: reasons for the low system efficiency of methylmercury production**

Coastal seas contribute the majority of human methylmercury (MeHg) exposure via marine fisheries. The terrestrial area surrounding the Bohai Sea and Yellow Sea (BS and YS) is one of the mercury (Hg) emission “hot spots” in the world, resulting in high concentrations of Hg in BS and YS seawater in comparison to other marine systems. However, comparable or even lower Hg levels were detected in seafood from the BS and YS than other coastal regions around the word, suggesting a low system bioaccumulation of Hg. Reasoning a low system efficiency of MeHg production (represented by MeHg/THg (total Hg) in seawater) may be present in these two systems, seven cruises were conducted in the BS and YS to test this hypothesis. MeHg/THg ratios in BS and YS seawater were found to be lower than that in most coastal systems, indicating that the system efficiency of MeHg production is relatively lower in the BS and YS. The low system efficiency of MeHg production reduces the risk of Hg in the BS and YS with high Hg discharge intensity. By measuring *in situ* production and degradation of MeHg using double stable isotope addition method, and MeHg discharge flux from various sources and its exchange at various interfaces, the budgets of MeHg in the BS and YS were estimated. The results indicate that *in situ* methylation and demethylation are the major source and sink of MeHg in the BS and YS. By comparing the potential controlling processes and environmental parameters for MeHg/THg in the BS and YS with the other coastal seas, estuaries and bays, lower transport efficiency of inorganic Hg from water column to the sediment, slower methylation of Hg, and rapid demethylation of MeHg were identified to be major reasons for the low system efficiency of MeHg production in the BS and YS. This study highlights the necessity of monitoring the system efficiency of MeHg production, associated processes, and controlling parameters to evaluate the efficiency of reducing Hg emissions in China as well as the other countries.

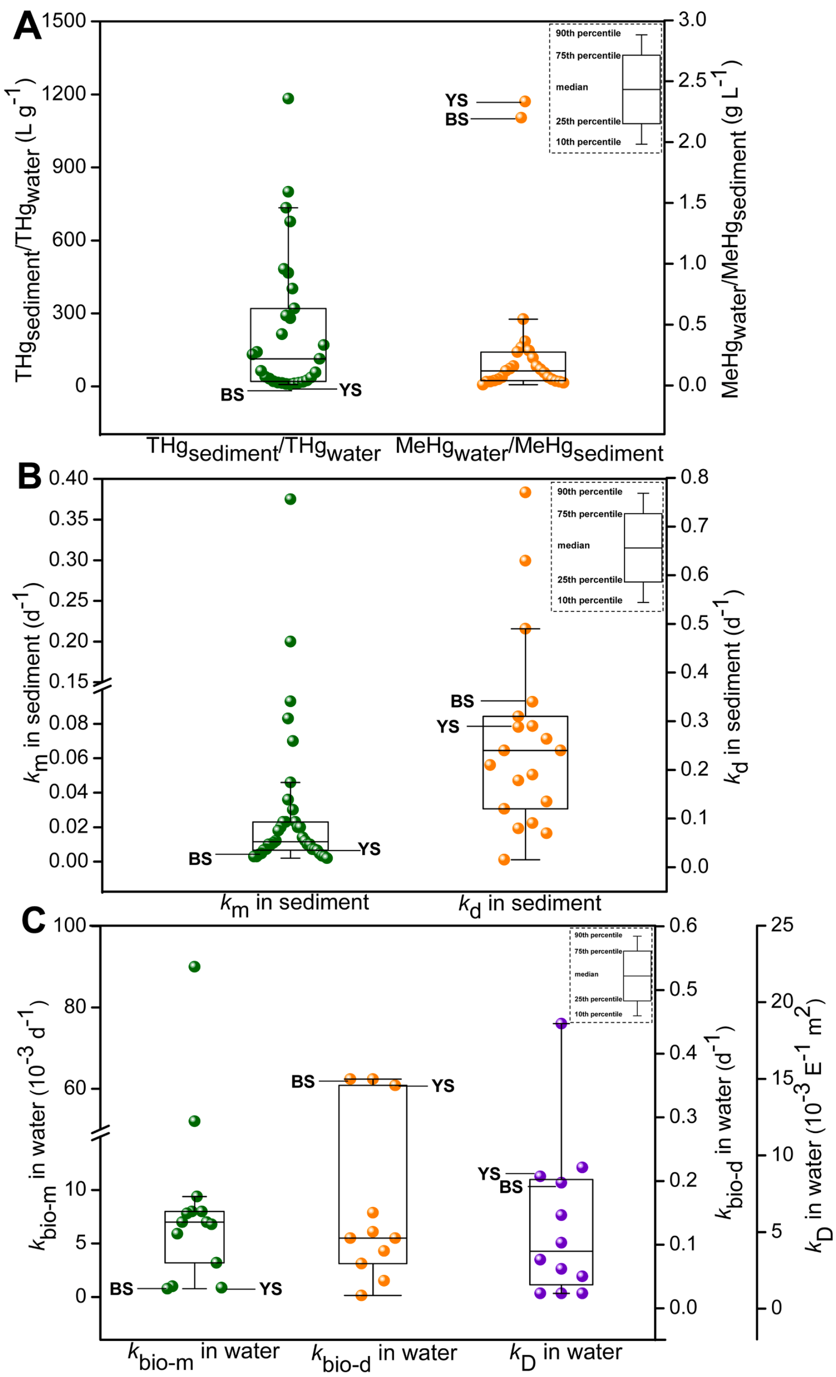

Figure 3. Comparisons of relevant parameters reflecting Hg methylation/demethylation potentials and transport efficiency of THg and MeHg among the BS, YS, and other coastal

seas, bays, and estuaries. (A), transports of THg from seawater to sediment and MeHg from sediment to seawater; (B), methylation and demethylation of Hg in sediment; (C), biotic methylation/demethylation and photic demethylation of Hg in seawater. Systematic search was conducted in Web of Science using the keywords: (A), mercury, Hg, total mercury, total Hg, THg, methylmercury, methyl mercury, methyl Hg, or MeHg (Data of THg and MeHg in water and sediment of coastal seas, bays, and estuaries were subsequently utilized for doing the comparison); (B) and (C), mercury, Hg, methylmercury, methyl mercury, or MeHg and methylation, demethylation, production, or degradation (Data of Hg methylation and demethylation in water and sediment of coastal seas, bays, and estuaries were subsequently utilized for doing the comparison).

- **MOTES: A new facility designed for trace element sampling in seawater**

We present the modular trace element sampling facility that we have developed (MOTES). Vertical profiles of lead and iron, two trace metals particularly prone to contamination, are also shown to attest the reliability of MOTES.

The advantages of MOTES are that the improved Niskin-X sampling bottles could remain closed on the deck and open underneath the sea surface, and there is no need to remove and assemble the samplers during the whole process of sampling and filtration. Above the titanium CTD frame the Niskin-X bottles installed on, there is only a plastic-coated coaxial communication cable (12000 m) to minimize disturbance to the water column and potential contamination in the up-cast lift. There are three modular components in the facility, the winch system, the clean room and the L frame. The stainless-steel winch system and the clean room dedicated to sampling, and sample transfer and filtration are both installed in the standard-sized clean container which are very convenient to move. The hub part of winch system which contact with cable is cladded by nylon to avoid potential contaminations. The L frame system is installed in the 10 ft standard-sized container base. Last but not least, the three modular components can be detached for land transportation and reassembled on the deck of research vessels for sea-going cruises. Note also that the design concept can be adapted for other types of applications in a sea-going voyage, such as ships/cargo vessels and observational platforms, which require clean working conditions and must be self-sustaining in remote areas/situations.

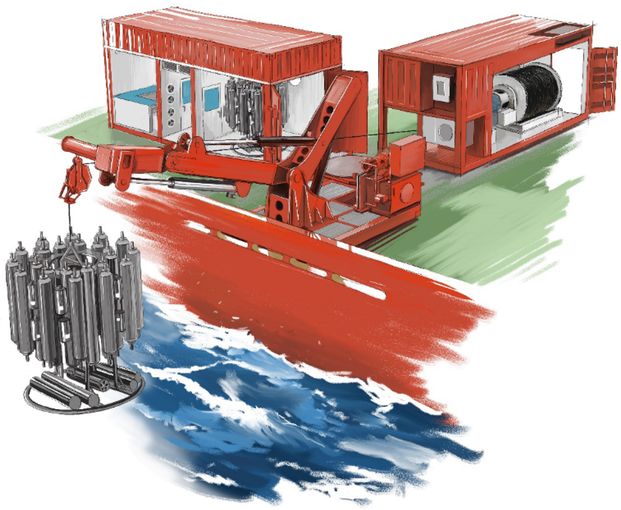

Figure 4. Configuration of MOTES facility on deck for a sea-going cruise, which includes a plastic-coated coaxial cable and stainless-steel winch (right), clean room (left), and L frame

with CTD and Niskin-X bottles (front). Winch and clean rooms are installed in standard-size container with clean air supply for road transportation and adaptation to different research vessels. For the purpose of illustration here, the side wall of container is “cut” so that the reader could see the set-up of winch and rosette Niskin-X inside.

GEOTRACES or GEOTRACES relevant cruises

- 2023 Northwest Pacific Ocean Multidisciplinary Cruise, water samples were collected to analyze monomethylmercury and dimethylmercury during this cruise.

New projects and/or funding

- Research on the Mechanisms of Light Regulation on Iron Uptake in Marine Diatoms, General Program of National Natural Science Foundation of China, No. 42376158, 2024-2027, leading PI: Liangliang Kong
- Science Fund Program for Excellent Young Scholars of Shandong Province (Overseas), 2024HWYQ-039, 2024-2026, leading PI: Liangliang Kong
- Taishan Scholar Young Expert Program, 2024-2026, leading PI: Liangliang Kong
- Mercury species distribution and in situ formation mechanisms of methylmercury in the Northwestern Pacific Ocean impacted by intensive human activities, National Natural Science Foundation of China, 42373076, 2024-2027, leading PI: Yanbin Li

GEOTRACES workshops and meetings organized

- We organize the Training and exchange Seminar on techniques for monitoring radioactivity in the Marine environment during April 9 and 10 in Shanghai.

New GEOTRACES or GEOTRACES-relevant publications (published or in press)

- Peng, T., Yu, X., Liu, J., Zhu, Z., & Du, J. (2023). Capturing the influence of submarine groundwater discharge on nutrient speciation dynamics within an estuarine aquaculture ecosystem. Environmental Pollution, 336, 122467.
- Zhang, F., Wang, J., Huang, D., Zhong, Q., Yu, T., & Du, J. (2023). Fresh groundwater discharge as a major source of ^{90}Sr into the coastal ocean. Environmental Science & Technology, 57(32), 12033-12041.
- Yu, X., Liu, J., Chen, X., Yu, H., & Du, J. (2024). Fresh and saline groundwater nutrient inputs and their impacts on the nutrient budgets in a human-effected bay. Marine Pollution Bulletin, 199, 116026.
- Ruan, Y., Zhang, R., Yang, S. C., Jiang, Z., Chen, S., Conway, T. M., ... & John, S. G. (2024). Iron, Nickel, Copper, Zinc, and their stable isotopes along a salinity gradient in the Pearl River Estuary, southeastern China. Chemical Geology, 645, 121893.
- Cao, A., Liu, Q., Zhang, J., Shiller, A.M., Cai, Y., Zhang, R., Gilbert, M., Guo, X., and Liu, Z (2024), Dissolved rare earth elements in the North Pacific Subtropical Gyre: Lithogenic sources and water mass mixing control. Geochimica et Cosmochimica Acta, 372, 42-61.

- Cao, S., Liang, S., & Li, Y. (2023). Adsorption and environmental behavior of mercury on suspended particulate matter from the Yellow River and Xiaoqing River estuaries. Science of The Total Environment, 893, 164860.
- Zhou, Z., Tang, Z., Wang, H., Liu, K., Wang, Y., Xiao, X., ... & Li, Y. (2024). Spatial and temporal variations in the pollution status and sources of mercury in the Jiaozhou bay. Environmental Pollution, 123554.
- Chen, L., Cheng, G., Zhou, Z., Liang, Y., Ci, Z., Yin, Y., ... & Li, Y. (2024). Methylmercury cycling in the Bohai Sea and Yellow Sea: Reasons for the low system efficiency of methylmercury production. Water Research, 258, 121792.
- Li, D., Han, X., & Li, Y. (2024). Mechanism of methylmercury photodegradation in the yellow sea and East China Sea: Dominant pathways, and role of sunlight spectrum and dissolved organic matter. Water Research, 251, 121112.
- Zhang, J., Ni, Z. T., Ren, J. L., Yu, F., Diao, X. Y., Wang, Y., Zhang, S. J., Su, H., Cong, S. L., Lu, Z. J., Jiang, S., Ou, J., Chen, Y., Wang, Q., Zhang, Z. B., Ai, J. T., Wang, C. B., & Tao, Z. D. (2024). Modular ocean trace elements sampling for the international GEOTRACES studies – Evidence from analysis of dissolved Fe and Pb. Progress in Oceanography, 221, 103212.

Completed GEOTRACES PhD or Master theses

- Yaqing Ruan. The transport of trace metal Iron and Copper to the ocean through estuaries—using the Changjiang Estuary and Pearl River Estuary as examples. Master thesis. Shanghai Jiao Tong University, 2023.
- Cao AX. Sources, processes affecting the distribution, and application of rare earth elements in the Northwest Pacific. PhD thesis. Ocean University of China, 2023.
- Guan WK. Spatiotemporal distribution, sources and deposition fluxes of trace elements in aerosols from the Northwestern Pacific. PhD thesis. Ocean University of China, 2023.
- Sijing Cao. Effects of suspended particulate matter in estuaries on the transport and transformation of mercury. PhD thesis. Ocean University of China, 2023.

GEOTRACES presentations in international conferences

- Liangliang Kong. Invited Speaker for International Webinar Series for Young Scholars: “Cutting-edge Research on Marine Science and Engineering”, April 30, 2024, Hong Kong.

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