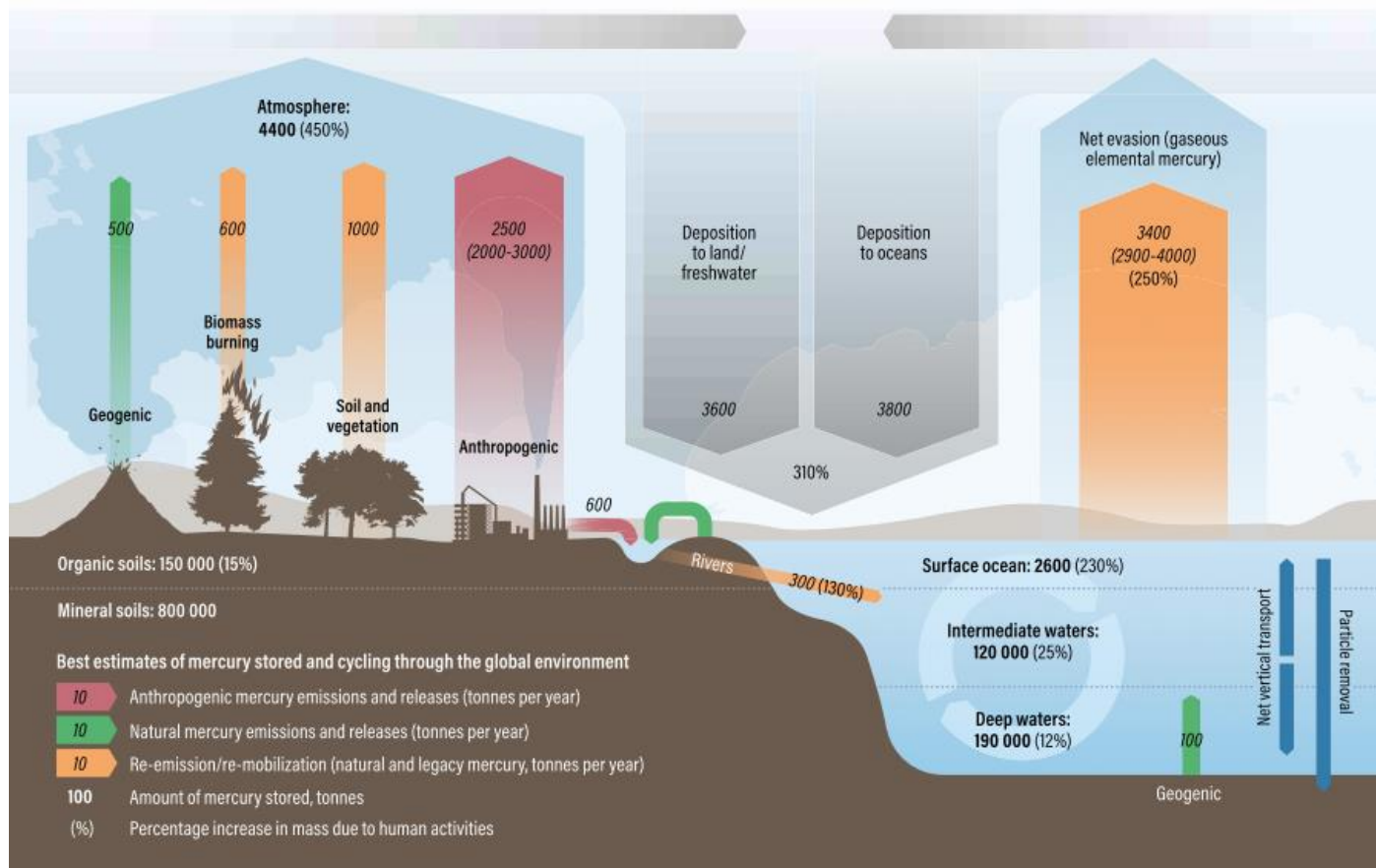


Hg surveys in the East China Sea and western North Pacific Ocean

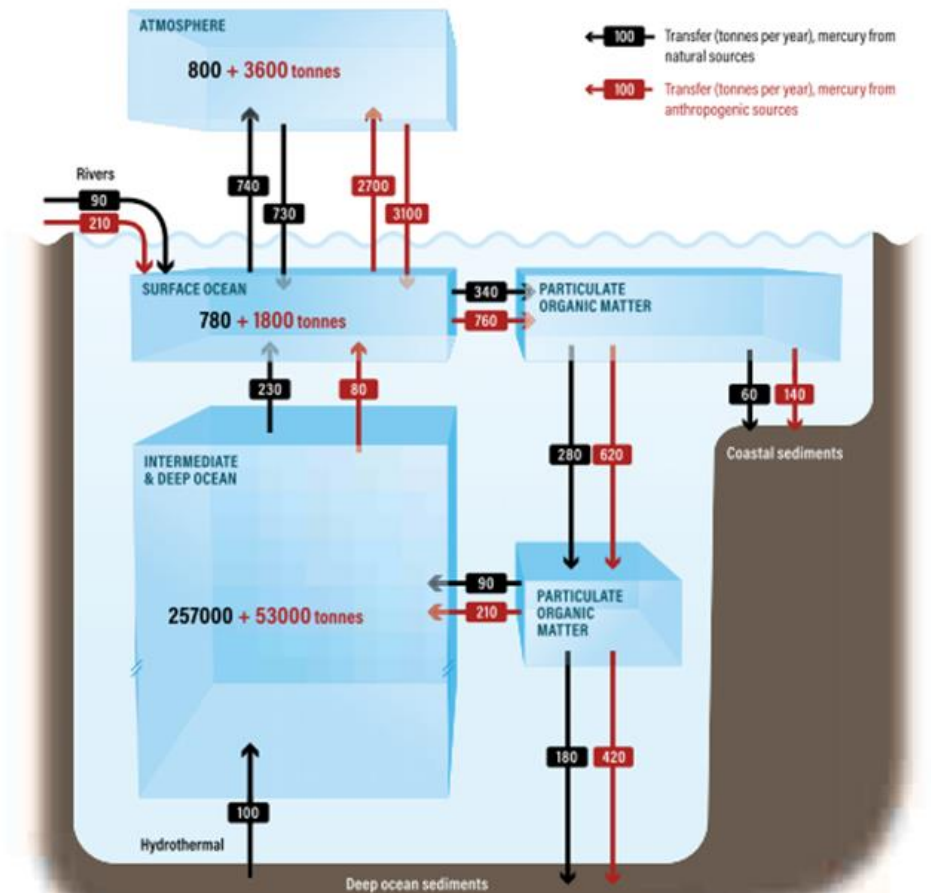
National Institute for Minamata Disease
Environmental Chemistry Section

Kohji Marumoto

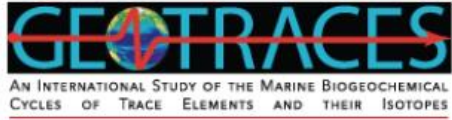
UNEP Global Mercury Assessment 2018



Ocean is one of the most important media because the main pathway of the methyl Hg exposure for human is fish consumption.



International monitoring program for oceanic mercury



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GEOTRACES

An International Study of the Marine Biogeochemical Cycles of
Trace Elements and Isotopes

 **2021** United Nations Decade
2030 of Ocean Science
for Sustainable Development

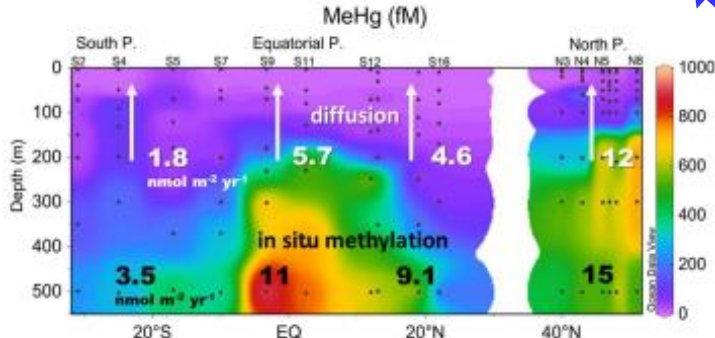


Hg surveys in the North Pacific Ocean

* 100 fM = 20 pg/L

Western Pacific Ocean

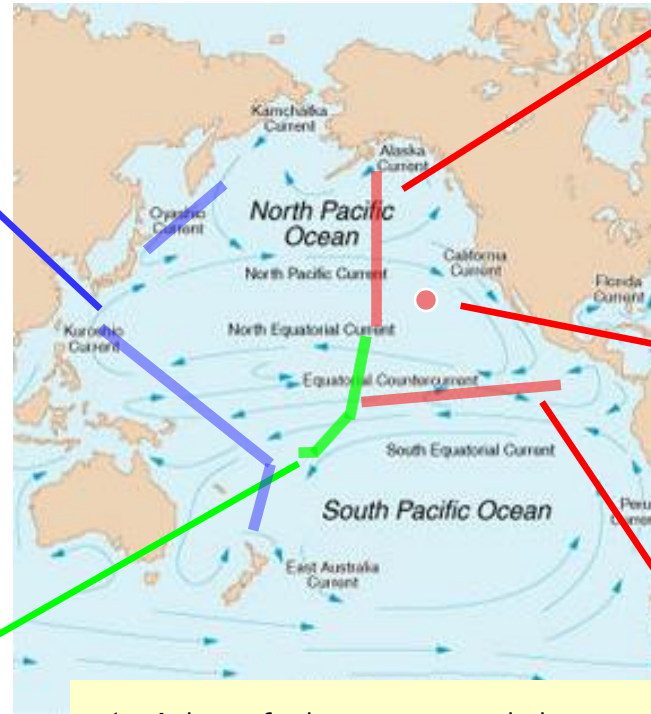
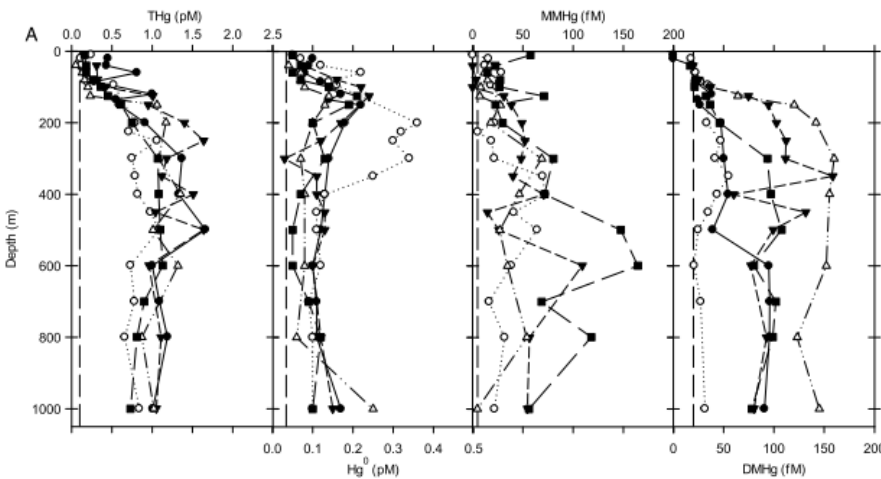
Kim et al. (2017) Environmental Science and Technology 51(3), 1186-1194



Data only for depths down to 500m

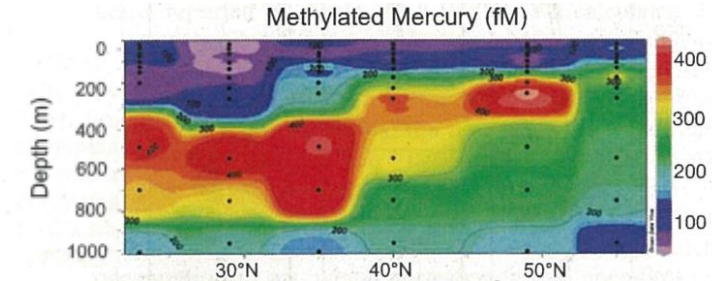
Central tropical Pacific Ocean

Munson et al. (2015) Global Biogeochemical cycles 29, 656-676



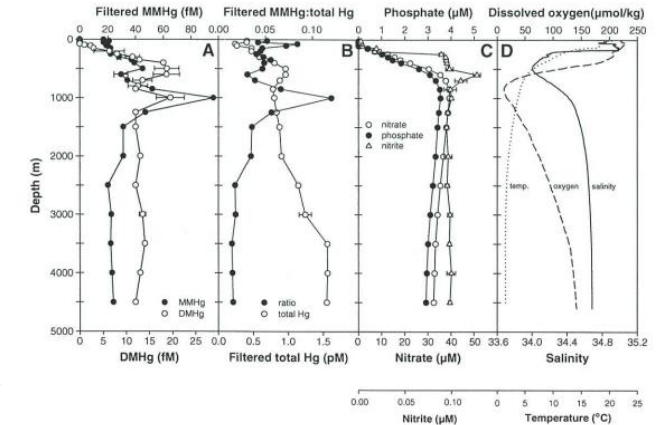
152° W Line

Sunderland et al. (2009) Global Biogeochemical cycles 23, GB2010



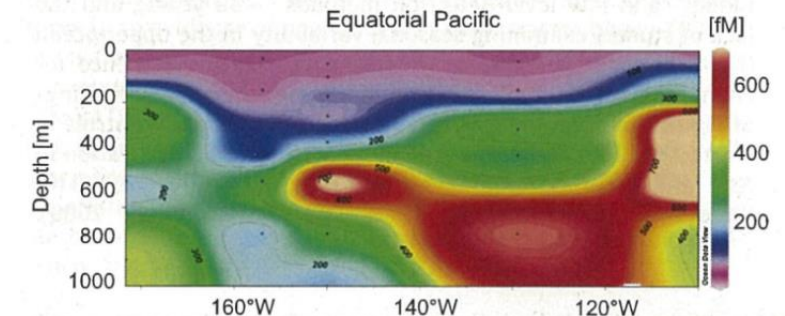
SAFe station (30° N, 130° W)

Hammerschmidt and Bowman (2012) Marine Chemistry 132-133, 77-82



Equatorial pacific (180° W~85° W)

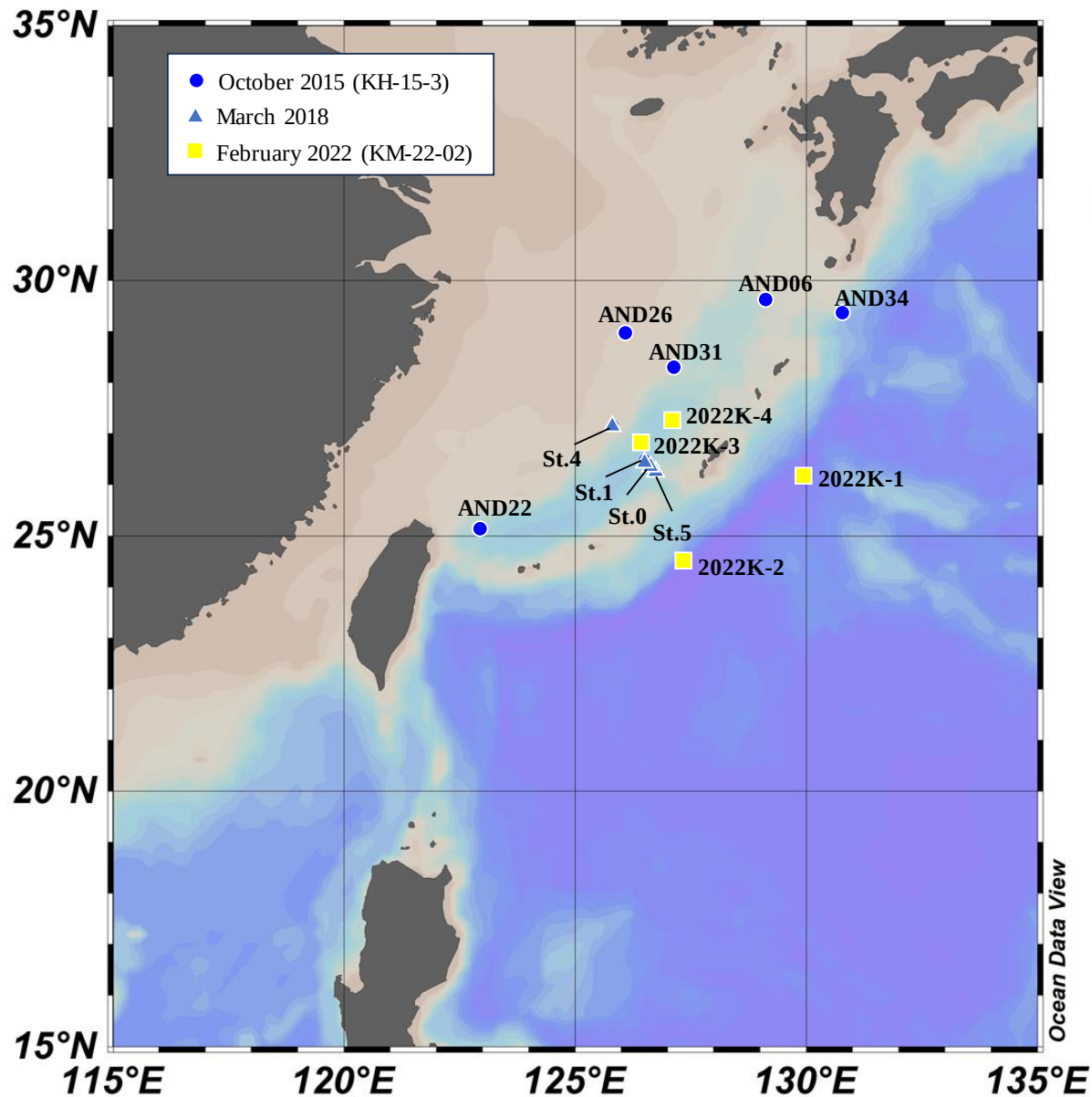
Mason and Fitzgerald (1993) Deep Sea Research I 40, 1897-1993



- ✓ A lot of observational data exist in the Mediterranean Sea, North Atlantic Ocean and Arctic Ocean.
- ✓ There are observational data in the east region of the Pacific Ocean, but in western region, the published data is scarce.

Surveys on Hg in seawater and planktons of the East China Sea

Sampling points of Hg survey in the East China Sea



– ANDROMEDA Expedition – AISIAN GEOTRACES_III (GP06)

Biogeochemical studies in the East
China Sea and Kuroshio area



R/V Kaimei Cruise Report
KM22-02

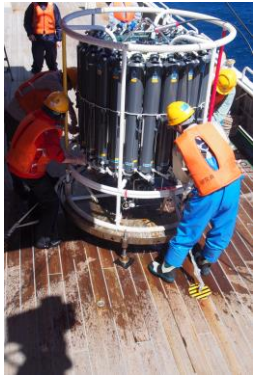
Understanding the actual condition of marine pollutants
and their impact on marine ecosystems

March 2018
Offshore of Kume Islands



R/V Kaimei

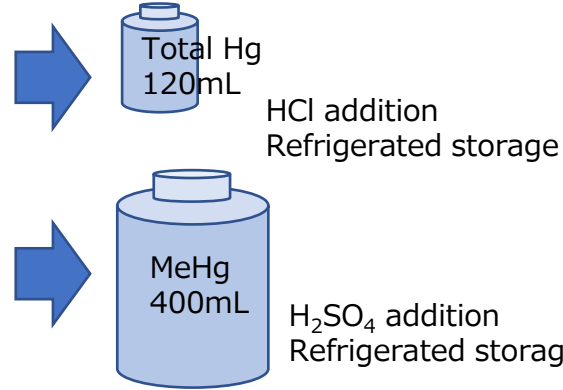
Speciation for mercury in seawater



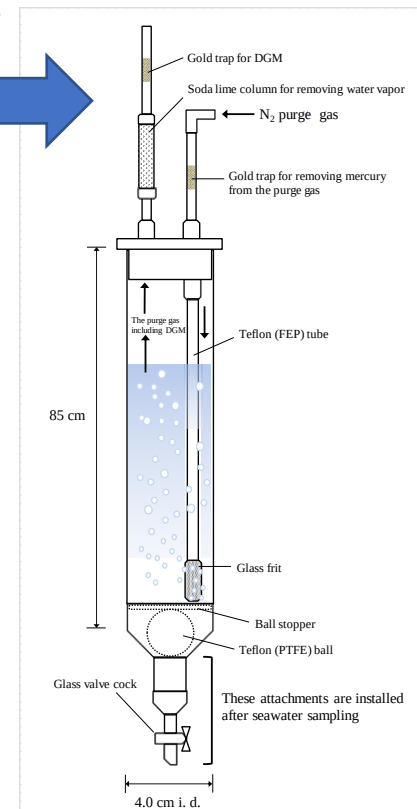
Seawater sampling



Clean technique and filtration using a polycarbonate filter (pore size is 0.2 μm)



Nitrogen purge and trap



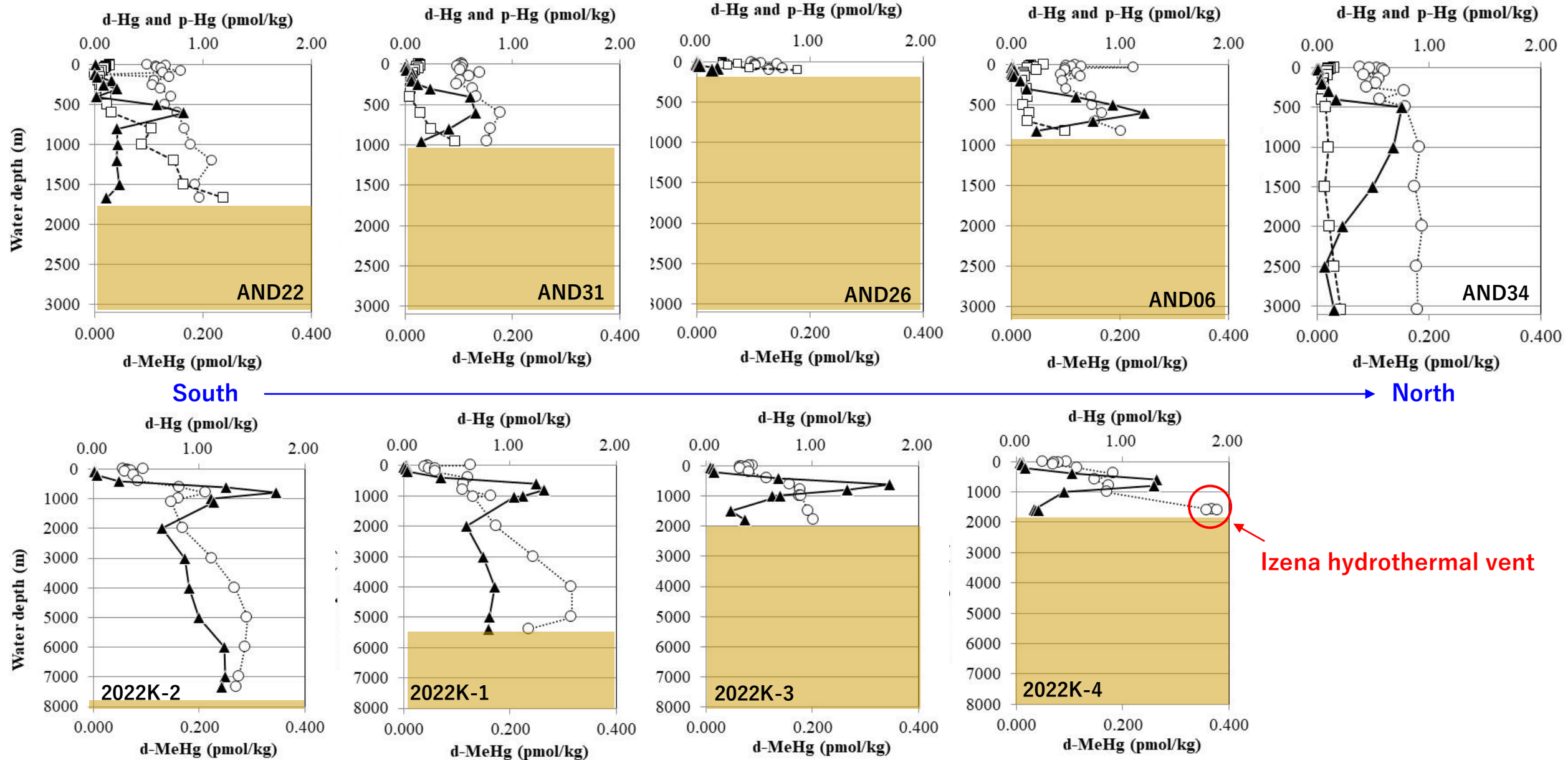
H₂SO₄ addition
Refrigerated storage

Hg species	Analytical method	Detection Limit
Hg(0) [Gas]	N2 purge – Gold cartridge – CVAFS	2 pg/L (0.01 pM) (500mL of sample)
DMHg: Dimethyl Hg [Gas]	N2 purge – Bond Elute ENV Trap – Gold cartridge – CVAFS	2 pg/L (0.01 pM) (500mL of sample)
MMHg: Monomethyl Hg Or MeHg Methylated Hg	Dithizone extraction – Reversed extraction to Na ₂ S solution ⇒ Derivatization using STEB – Tenax Trap – GC separation – CVAFS detection (Hybrid method with mercury analysis manual and draft EPA method 1630)	2 pg/L (0.01pM) (400mL of sample)
Total Hg	EPA method 1631	20 pg/L (0.1 pM)
* Hg(II) = (Total Hg) – (Hg(0)+DMHg+MMHg)		

Collection of DMHg and Hg(0) using Bond Elut trap and Gold cartridge

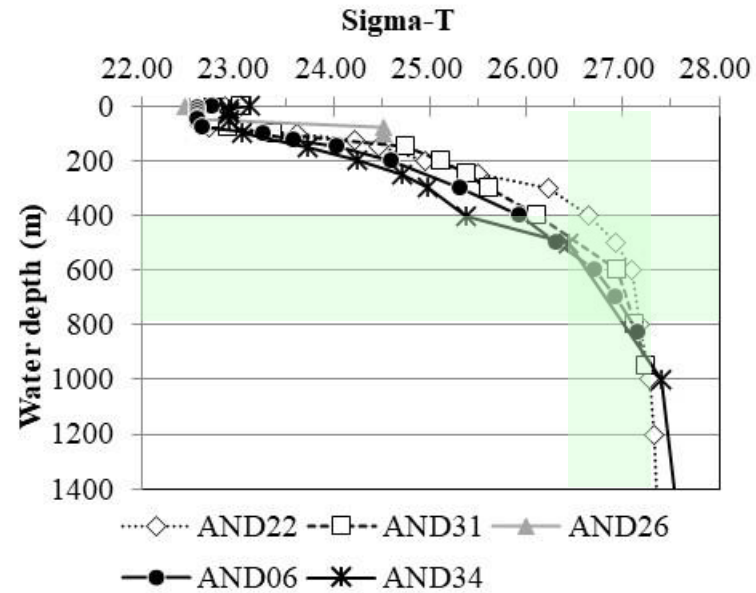
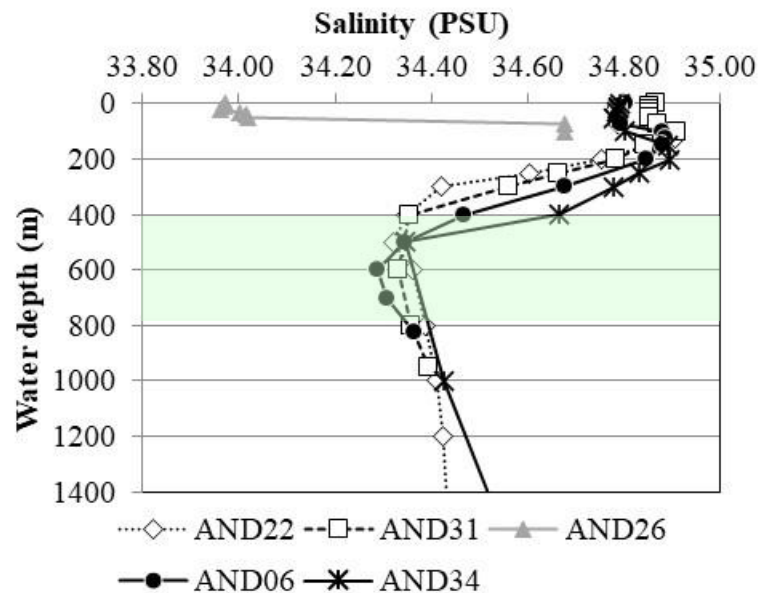
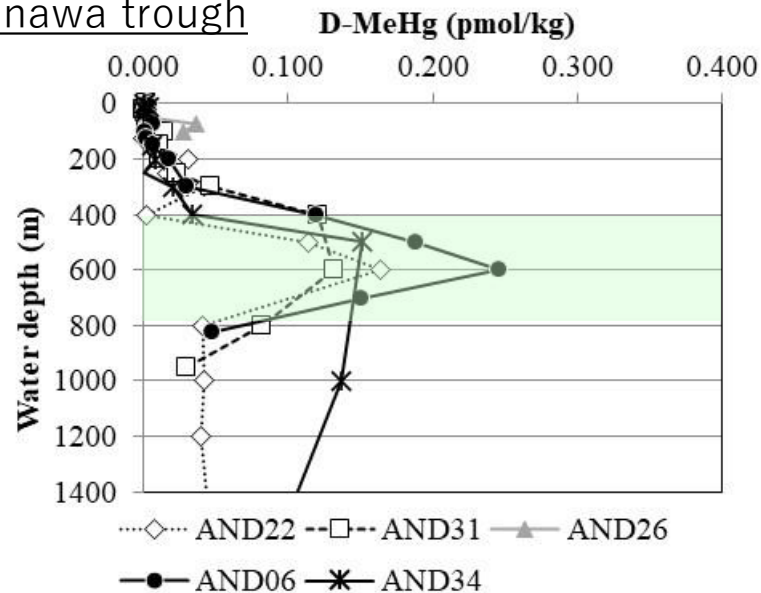
Full depth profile of seawater Hg in the East China Sea

○····· d-Hg □····· p-Hg ▲····· d-MeHg

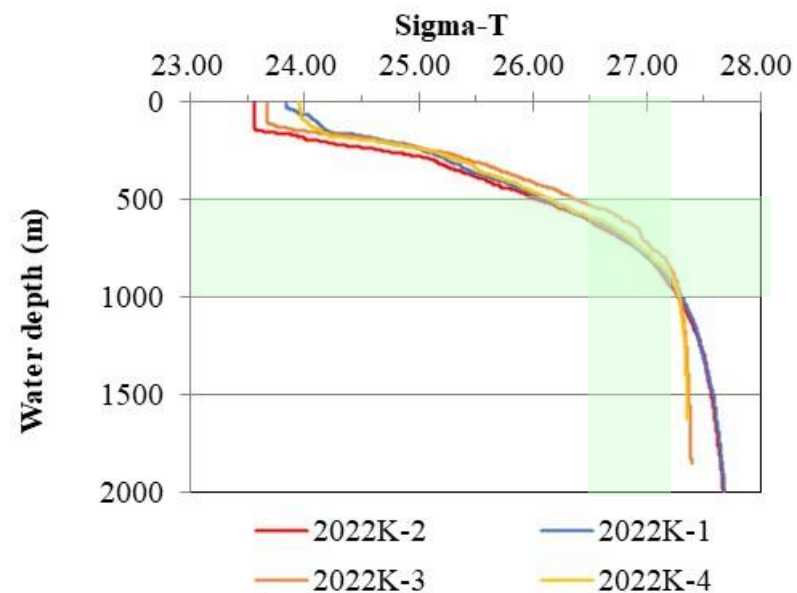
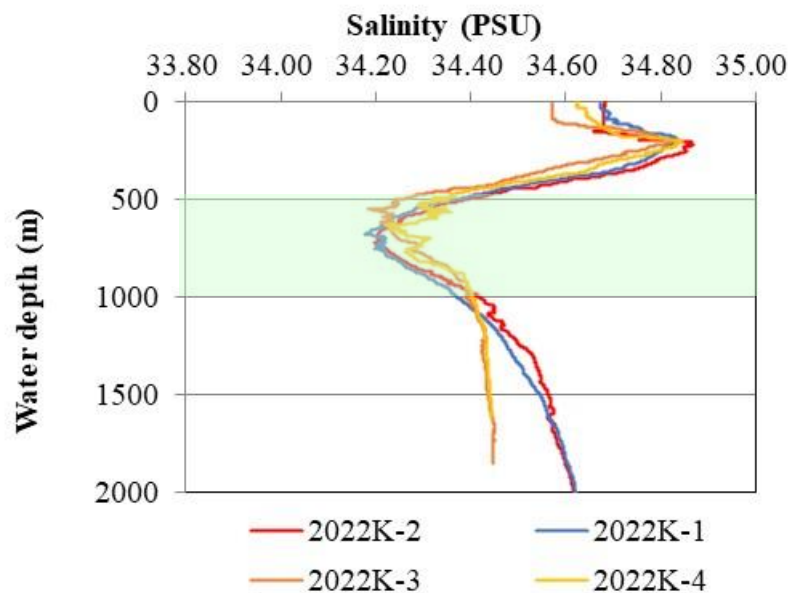
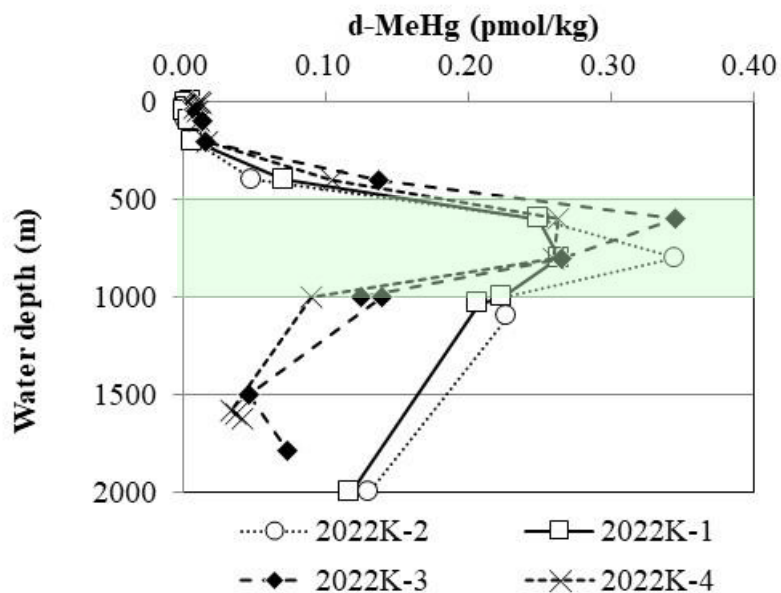


Maximum MeHg were observed at low salinity water mass ($\sigma_t=26.5\sim27.2$)

Okinawa trough



Ryukyu trench and Okinawa trough



Is the North Pacific Intermediate Water (NPIW) associated with MeHg maxima?

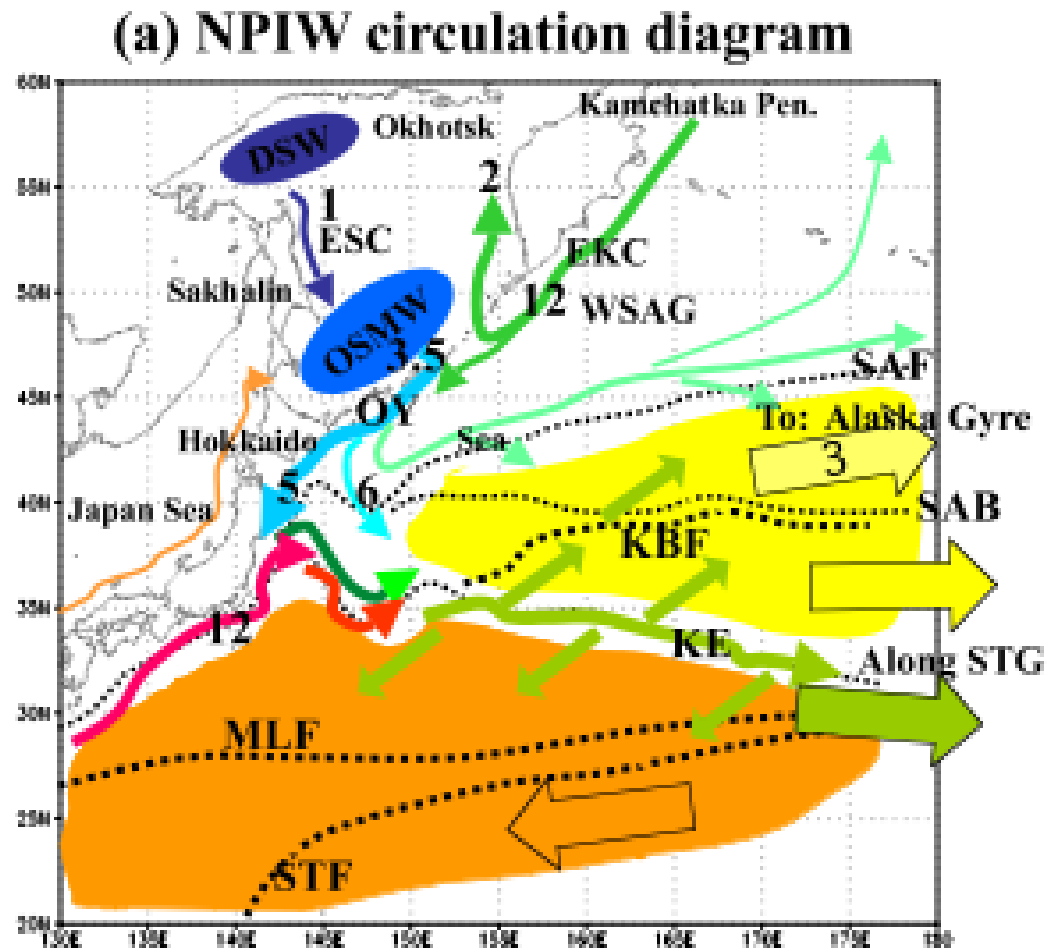


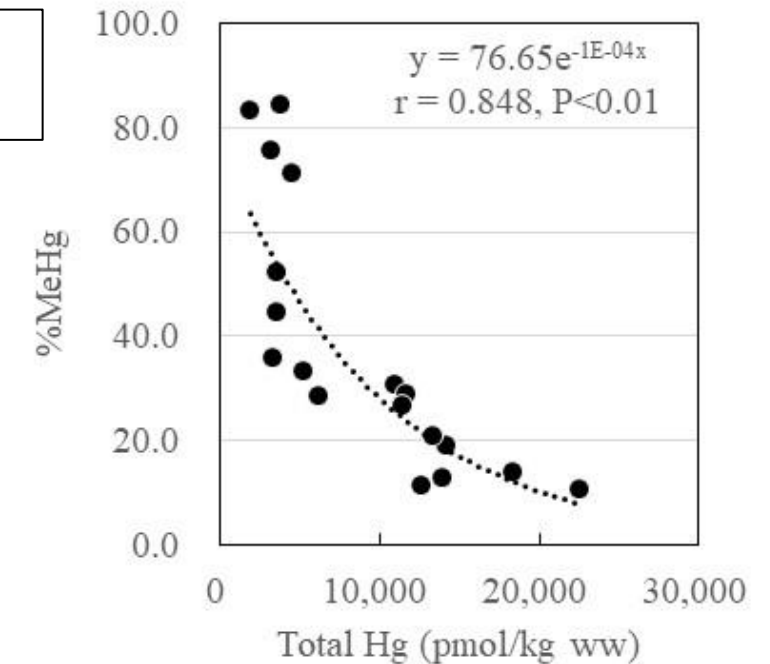
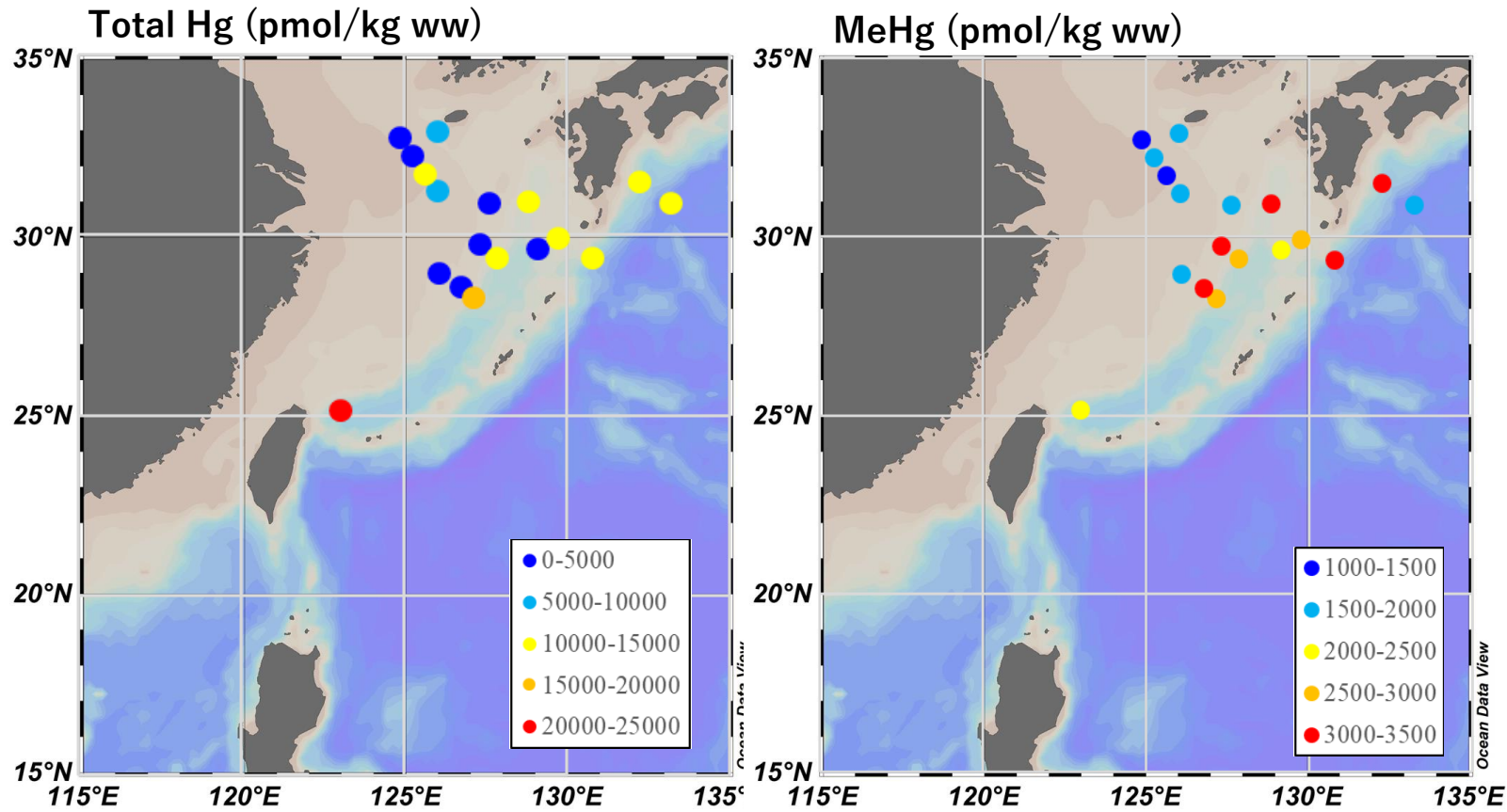
Fig. 1. (a) Schematic illustration of water mass distribution, transformation and transport related to North Pacific Intermediate Water (NPIW). The transport values are in Sv ($=10^6 \text{ m}^3/\text{s}$) in the density range between $26.7-27.4 \sigma_\theta$. EKC: East Kamchatka Current, WSAG: Western Subarctic Gyre, ESC: East Sakhalin Current, OY: Oyashio, KE: Kuroshio Extension, DSW: Dense Shelf Water, OSMW: Okhotsk Sea Mode Water. Broken curves represent the Subarctic Front (SAF), Subarctic Boundary (SAB), Kuroshio Bifurcation Front (KBF), and Mixed Layer Front (MLF) Subtropical Front (STF) from north to south.



Concentrations of THg and MeHg in zooplankton in the East China Sea (KH-15-03 cruise)

Sampling : Norpak net (Mesh size $100\mu\text{m}$) , Vertical towing to a depth of 200 m.

Preparation : The entire seawater is frozen, and collected on a filter after thawing. The filter is freeze-dried.

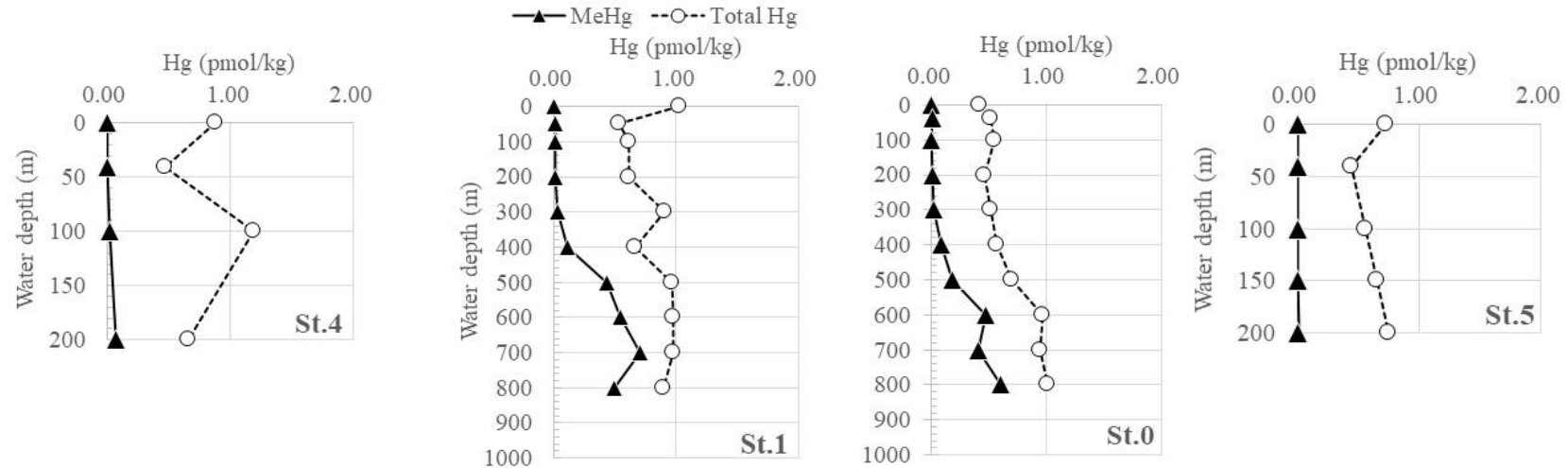
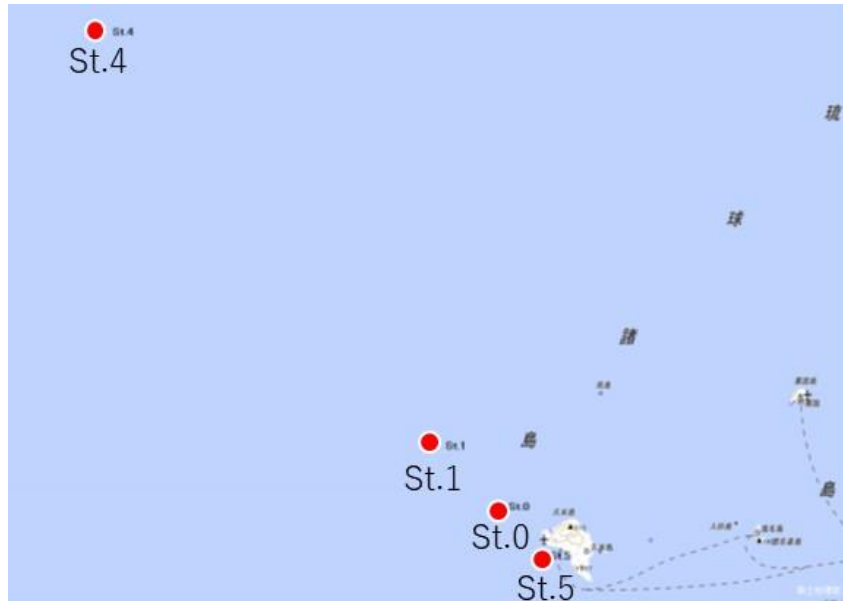


Partition Coefficient* (L/kg)	Total Hg	MeHg
平均	2.12×10^4	1.56×10^6
標準偏差	1.50×10^4	1.64×10^6
最小値	0.52×10^4	0.17×10^6
最大値	3.68×10^4	4.18×10^6

Both Total Hg and MeHg concentrations tend to be higher in the Kuroshio Current region.

* (Hg in planktons; ng/kg ww) / (Hg in seawater; ng/L)

MeHg concentration in planktons at offshore of Kume Island in the ECS



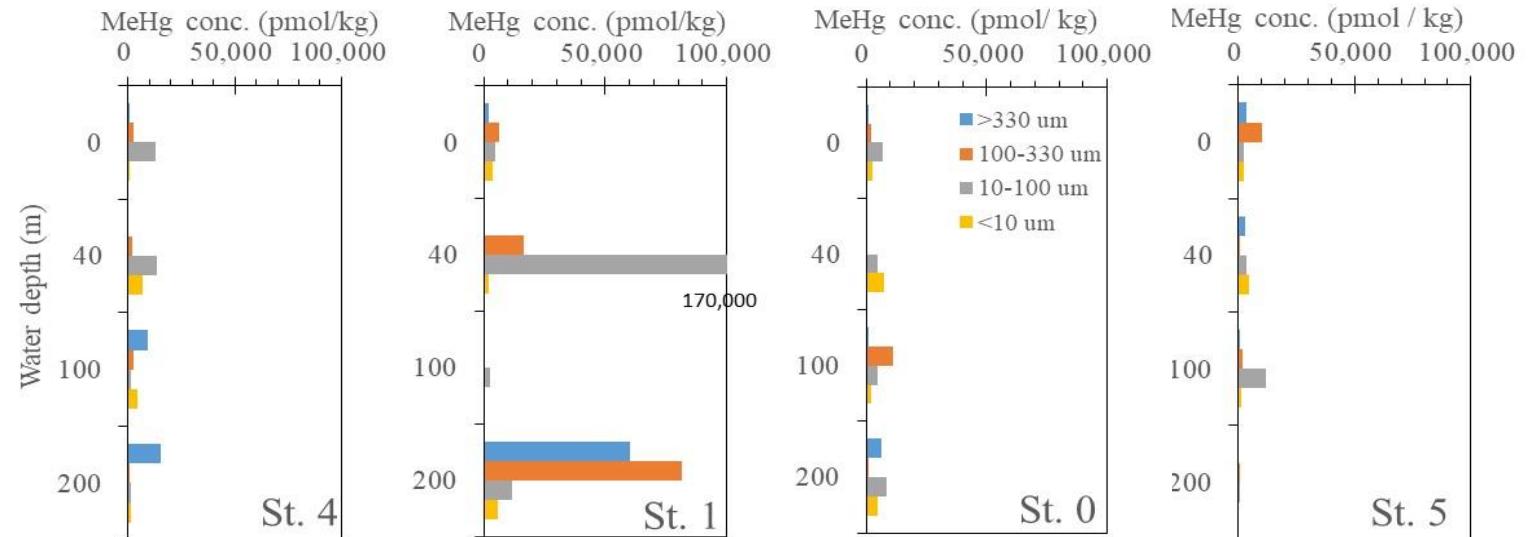
Concentrations of total Hg and MeHg in unfiltered seawaters

調査地点	St.0	St.1	St.4	St.5
調査日	2018/3/14	2018/3/13	2018/3/15	2018/3/16
調査開始時刻	7:55	9:10	9:56	12:40
～	～	～	～	～
調査終了時刻	15:10	18:45	15:02	16:50
開始時位置	北緯 26° 24' 16.2"	26° 30' 08.2"	27° 10' 04.0"	26° 19' 29.2"
東経	126° 37' 35.8"	126° 30' 00.2"	125° 49' 54.9"	126° 42' 37.3"
開始時水深	1100m	1700m	211m	223m
終了時位置	北緯 26° 26' 25.6"	26° 33' 31.8"	27° 10' 18.2"	26° 19' 22.7"
東経	126° 34' 02.5"	126° 32' 42.7"	125° 31' 39.7"	126° 42' 27.5"
終了時水深	1700m	1800m	238m	297m
出航時刻	7:03	7:05	2:59	12:15
帰航時刻	16:15	20:20	22:36	17:15

Sampling : Plankton net (Surface, SCM, 100m, 200m)

Size fraction: 0.2-10、10-100、100-330、>330 μ m

Preparation : The entire seawater is frozen, and collected on a filter after thawing. The filter is freeze-dried.

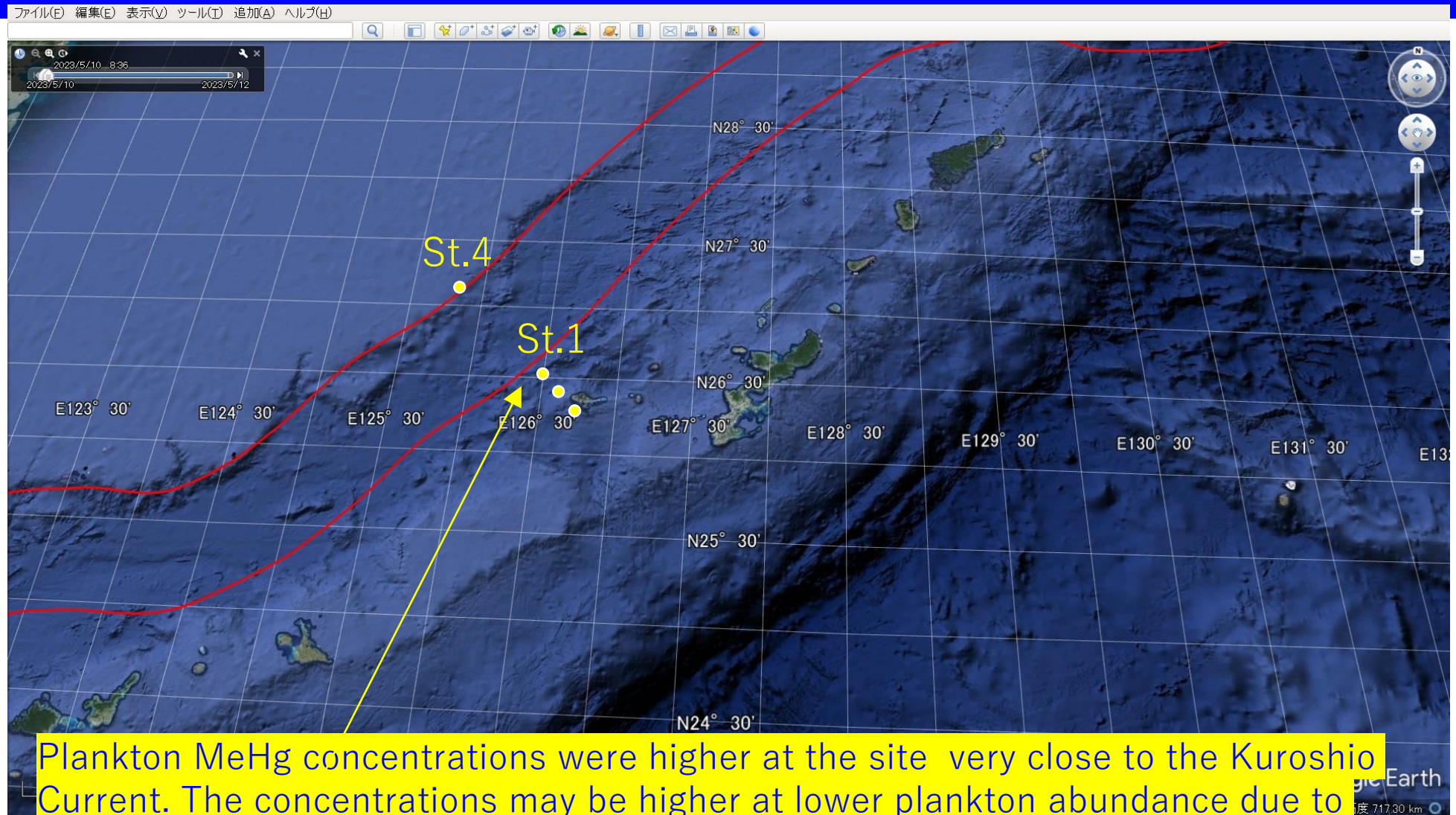


MeHg concentrations in planktons with each size

High MeHg in planktons at St. 1 were observed regardless of size

Kuroshio Current at the sampling day, 13 March 2018

(Data from Maritime Intelligence Division of Japan Coast Guard)



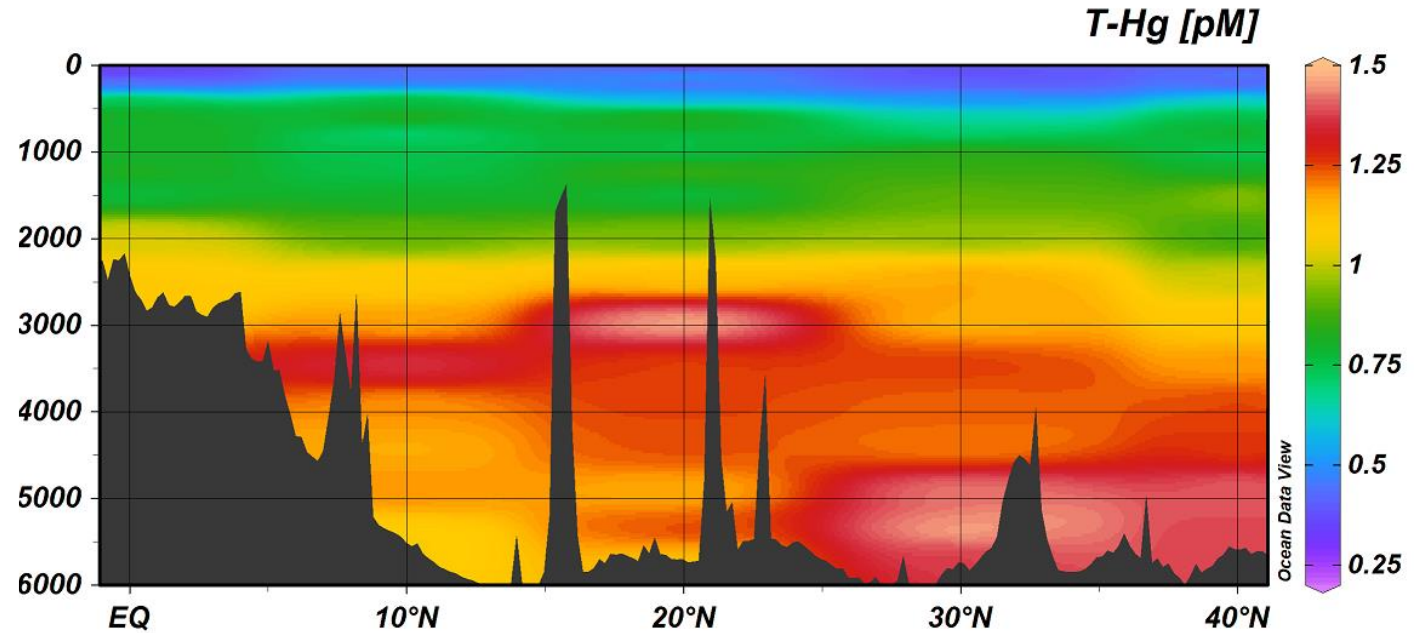
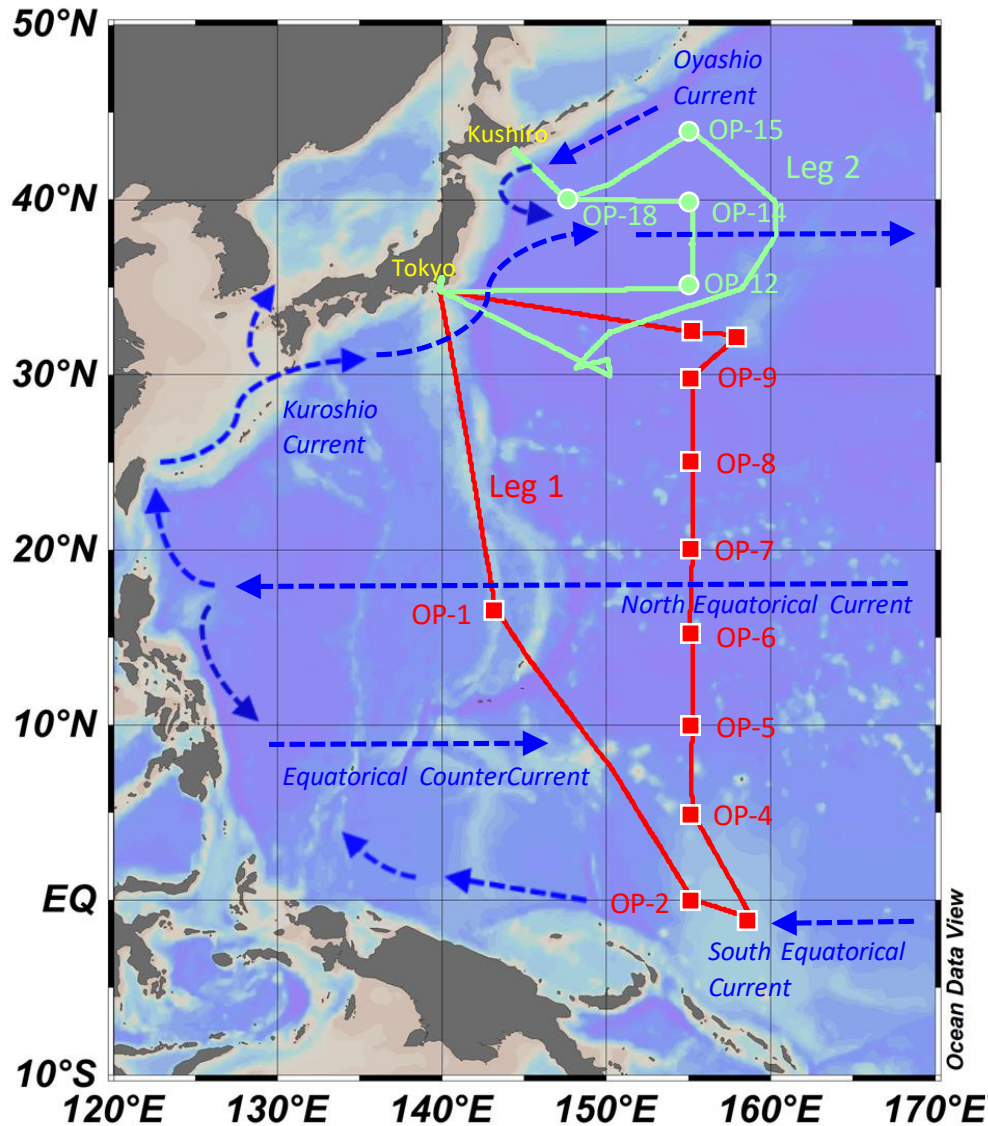
Plankton MeHg concentrations were higher at the site very close to the Kuroshio Current. The concentrations may be higher at lower plankton abundance due to oligotrophic currents. This could be the opposite of the bio-dilution effect.

Summary of Hg survey in the ECS

- Dissolved and particulate Hg concentrations in seawater increased with depth relative to the surface in the ECS, as in other marine areas.
- Dissolved MeHg in seawater reached a maximum around 600 m depth, which is consistent with a low-salinity water mass layer. Based on the density of seawater, there is a possibility of horizontal advection by the North Pacific Intermediate Water (NPIW). However, the reason for the high concentration of MeHg in the NPIW is unknown.
- Concentrations of total Hg and MeHg in planktons (including inorganic materials such as sediments) tend to be higher in the Kuroshio Current region. It is possible that the concentrations per unit weight are higher due to oligotrophic conditions which has lower plankton abundance. This could be the opposite of the bio-dilution effect.

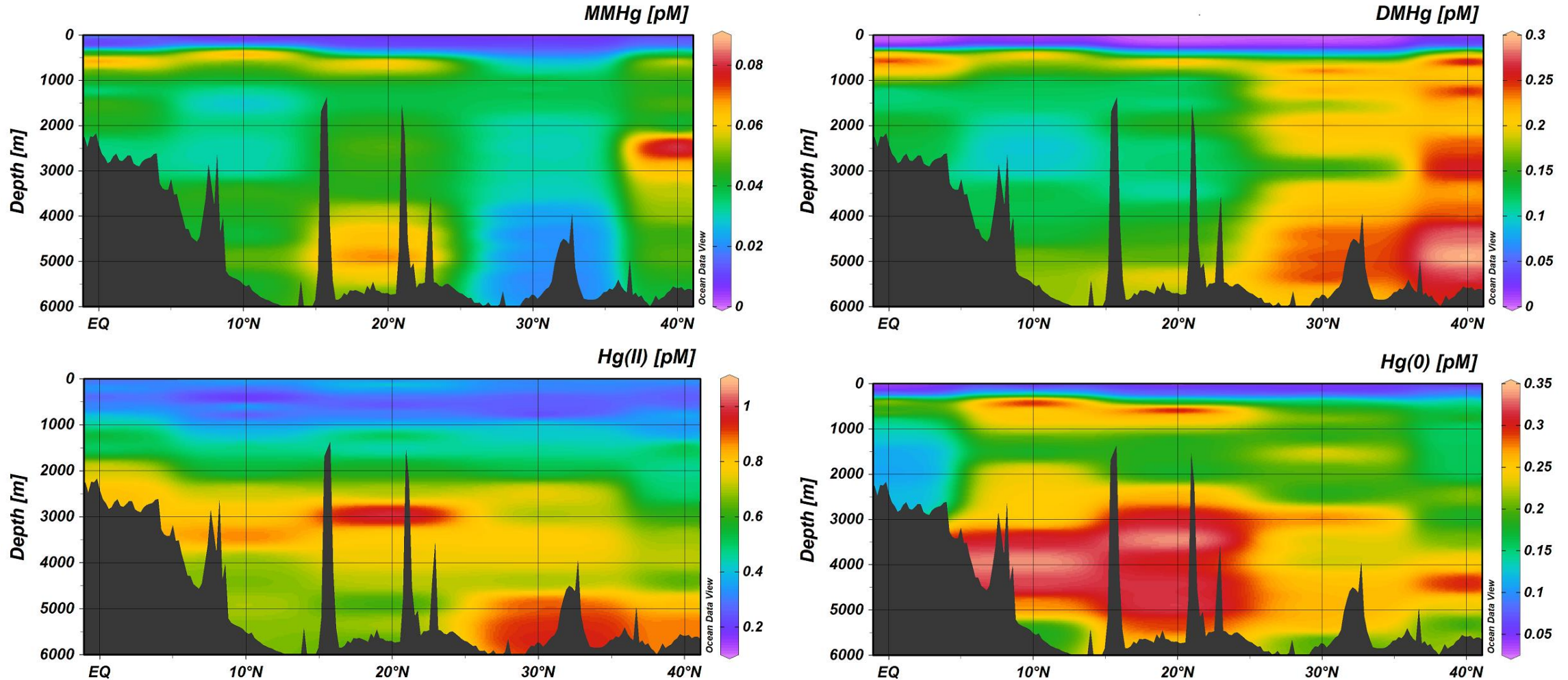
Survey on Hg in seawater and planktons of
the western region of North Pacific Ocean

Sampling points and vertical and horizontal distributions of total Hg in seawater



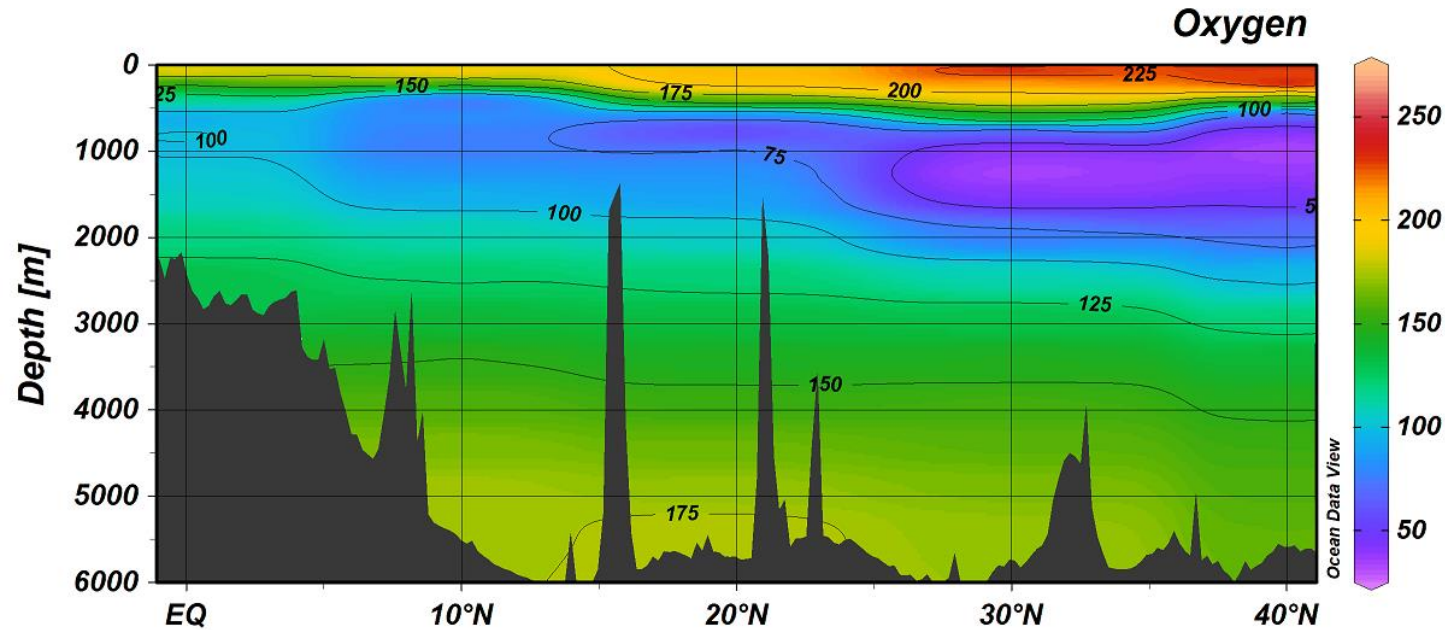
- Total Hg concentrations increased with depth.
- Concentrations tended to increase from south to north in the mesopelagic and deep layers.
- Concentrations may be higher in areas with complex topography.

Vertical and horizontal distributions of speciated Hg in seawater

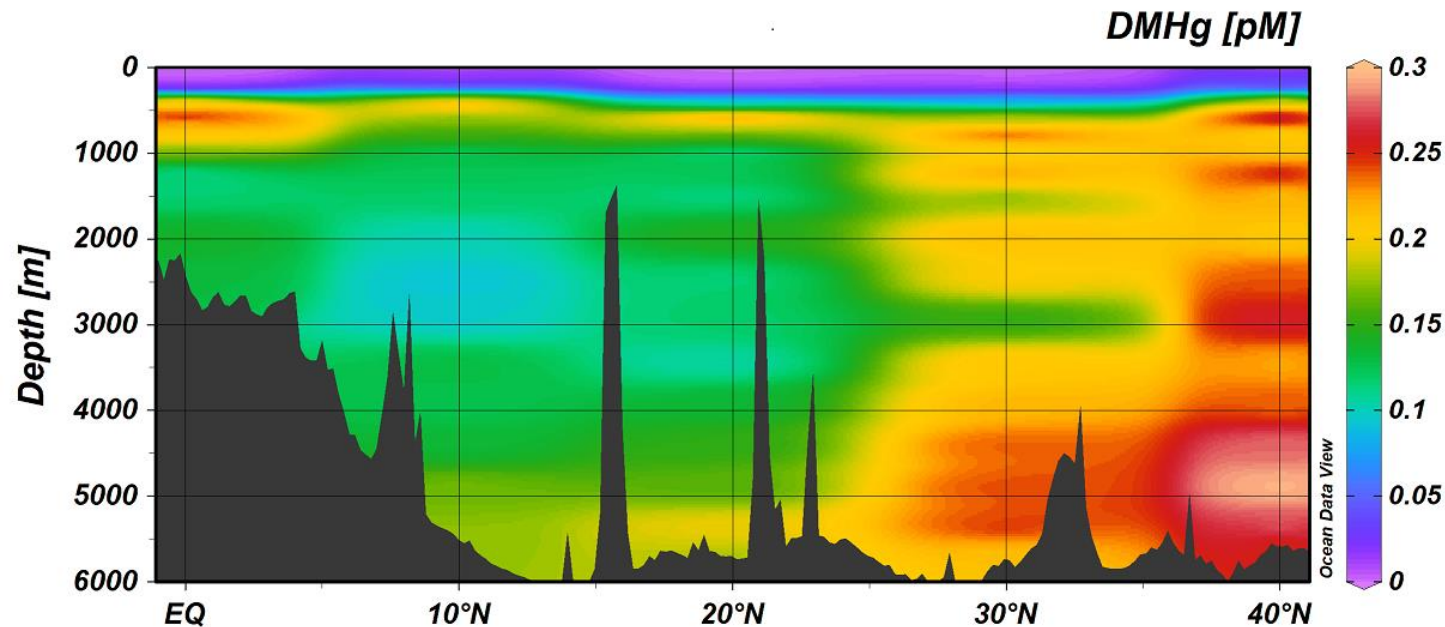


- The concentration of all Hg species increased with depth.
- MMHg, DMHg, and Hg(0) maxima in the mid-depth layer at around 500 m depth.
- DMHg concentrations tend to increase from south to north in the mesopelagic and deep layers.
- Hg(0) concentrations may be higher in areas with complex topography as well as total Hg

Distributions of Dissolved oxygen and DMHg in seawater



The MMHg, DMHg, and Hg(0) maxima were observed in the mesopelagic zone at a depth of about 500 m where the upper edge of the DO minimum was formed.



The DO is consumed by microbial remineralization and such reducing Hg species may be produced in conjunction with it.

Proportion of each speciated Hg to total.

Site	Depth	<i>N</i>	%MMHg	%DMHg	%Hg(0)	%Hg(II)	%DMHg/MeHg
North Pacific 155° E line	Subsurface (10-100 m)	18	2.4 ± 1.8	1.9 ± 2.1	12.7 ± 3.0	83.1 ± 4.9	38.5 ± 29.3
	Upper Intermediate (100-1000 m)	36	5.1 ± 2.1	18.0 ± 11	25.2 ± 8.0	51.7 ± 18.2	69.5 ± 18.6
	Lower Intermediate (1000-3000 m)	25	4.2 ± 1.3	17.0 ± 6.4	19.9 ± 4.4	58.9 ± 8.0	79.1 ± 5.1
	Deep (Below 3000 m)	23	3.4 ± 1.3	15.7 ± 3.8	21.1 ± 4.5	59.8 ± 4.1	81.4 ± 7.9
	All depths	102	4.0 ± 2.0	14.4 ± 9.6	20.8 ± 7.2	60.8 ± 16.0	69.1 ± 22.6

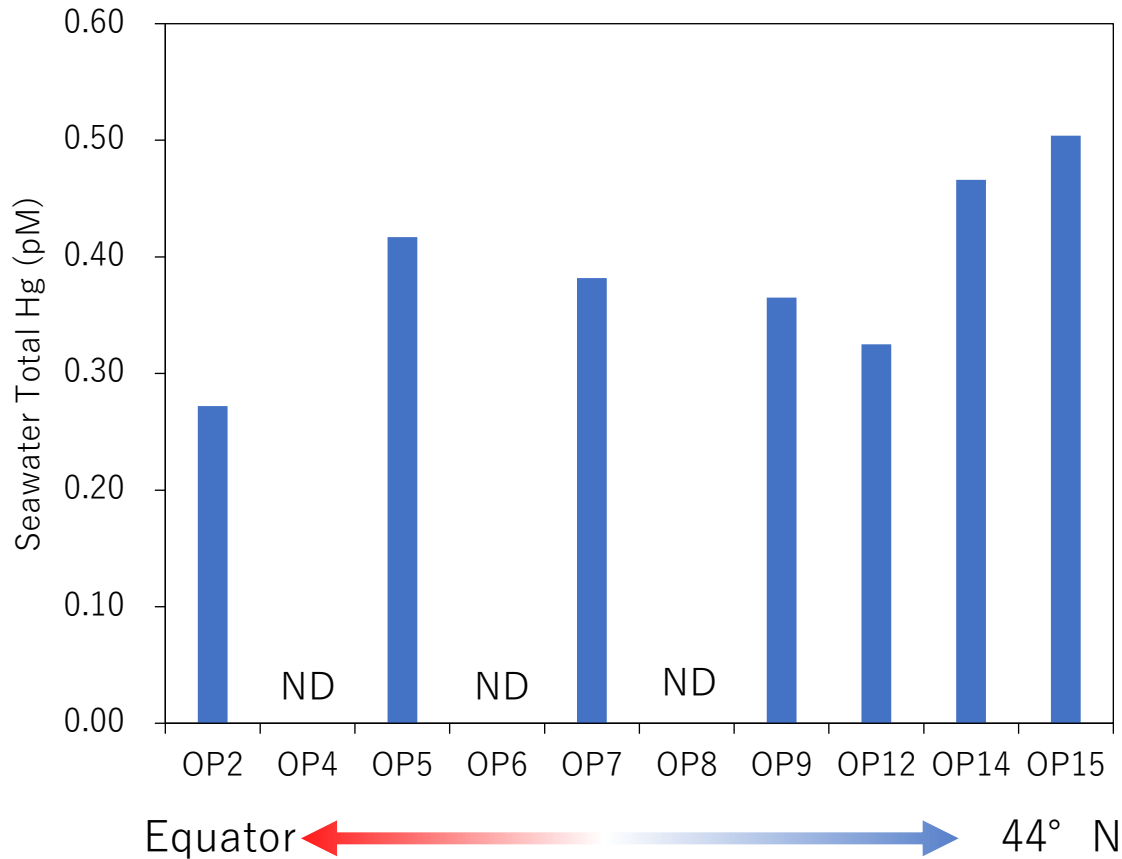
Percentage of DMHg to total MeHg in other sea areas

Sea area	Survey year	Sampling method of DMHg	DMHg (pM)	MMHg (pM)	%DMHg for MeHg	文献
North Atlantic Ocean: Sea area between Greenland and Iceland	1993	Carbotrap collection	0.08 ± 0.07	1.05 ± 0.11	7.1	(1)
Southern Ocean (SR3 CASO-GEPTRACES) AABW	2008	(MeHg) – (MMHg)	0.34 ± 0.14	0.18 ± 0.08	65.4	(2)
Eastern North Pacific Ocean SFe point (140° W, 30° N)	2009	Tenax collection	0.013 ± 0.001	0.024 ± 0.004	35.1	(3)
North Atlantic Ocean (U.S. GEOTRACES GA03)	2010-2011	Tenax collection	0.095 ± 0.10	0.095 ± 0.10	50.0	(4)
Central tropical Pacific Ocean	2013	Tenax collection	0.06 ± 0.07	0.032 ± 0.07	65.2	(5)
Eastern tropical South Pacific Ocean (U.S.GEOTRACES GP16)	2013	Bond Elut ENV Trap collection	0.07 ± 0.06	0.07 ± 0.07	50.0	(6)
Western Arctic Ocean including Bering Sea (U.S. GEOTRACES GN01)	2015	Bond Elut ENV Trap Collection	0.04 ± 0.027	0.055 ± 0.05	42.1	(7)
Arctic to Atlantic Ocean (GEOTRACES GN04 and GN05)	2015-2016	(MeHg) – (MMHg)	0.17 ± 0.12	0.07 ± 0.07	70.8	(8)

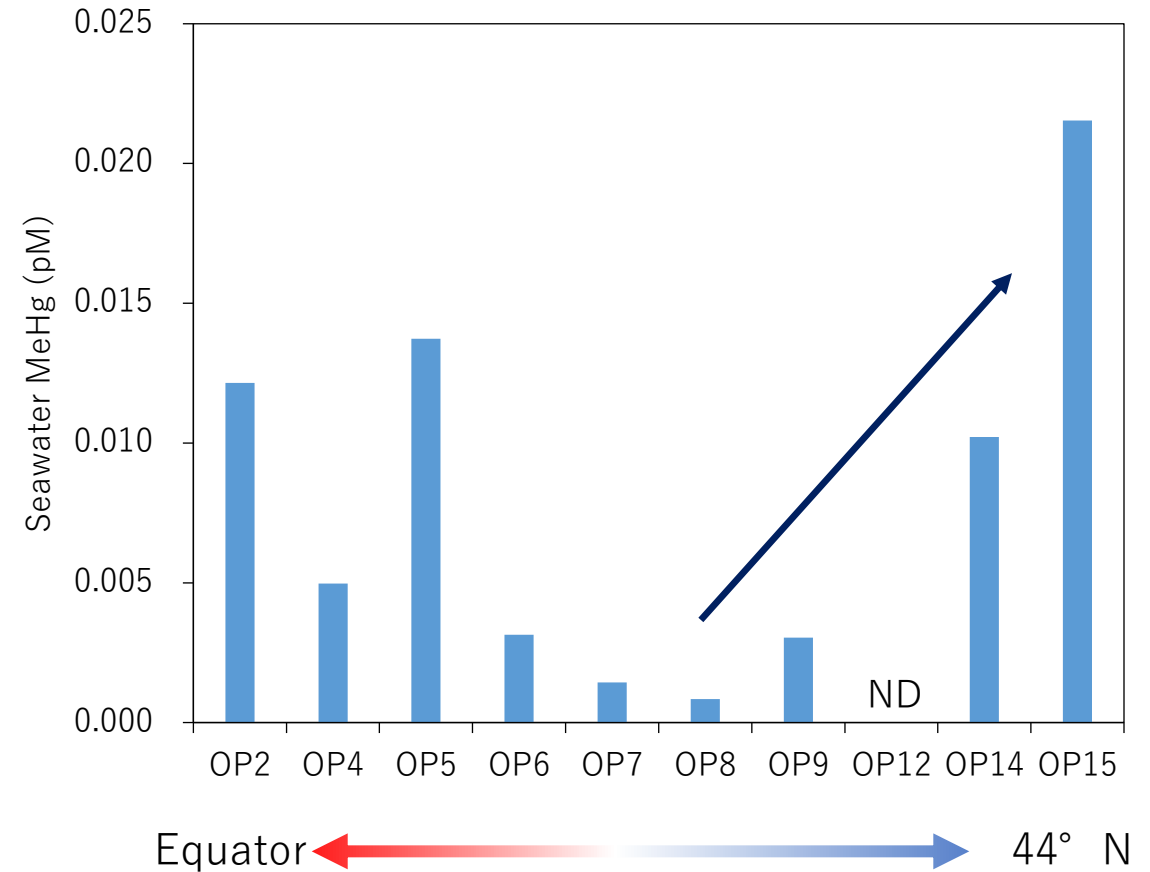
(1) Mason et al., 1998 (2) Cossa et al., 2011, (3) Hammerschmidt and Bowman, 2012, (4) Bowman et al., 2015, (5) Munson et al., 2015 (6) Bowman et al., 2016 (7) Agather et al., 2019, (8) Petrova et al., 2020

Total Hg and MeHg in subsurface seawaters

Seawater Total Hg (Average from 10 m to 150 m of depth)



Seawater MeHg (Average from 10 m to 150 m of depth)

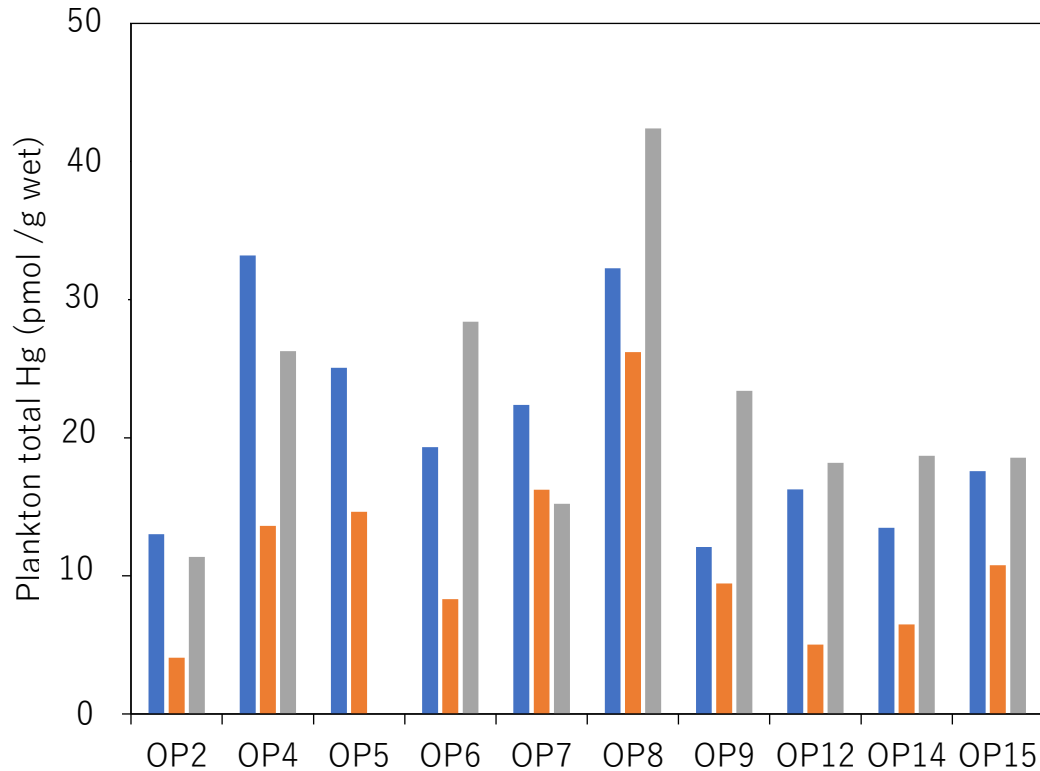


* ND = No data

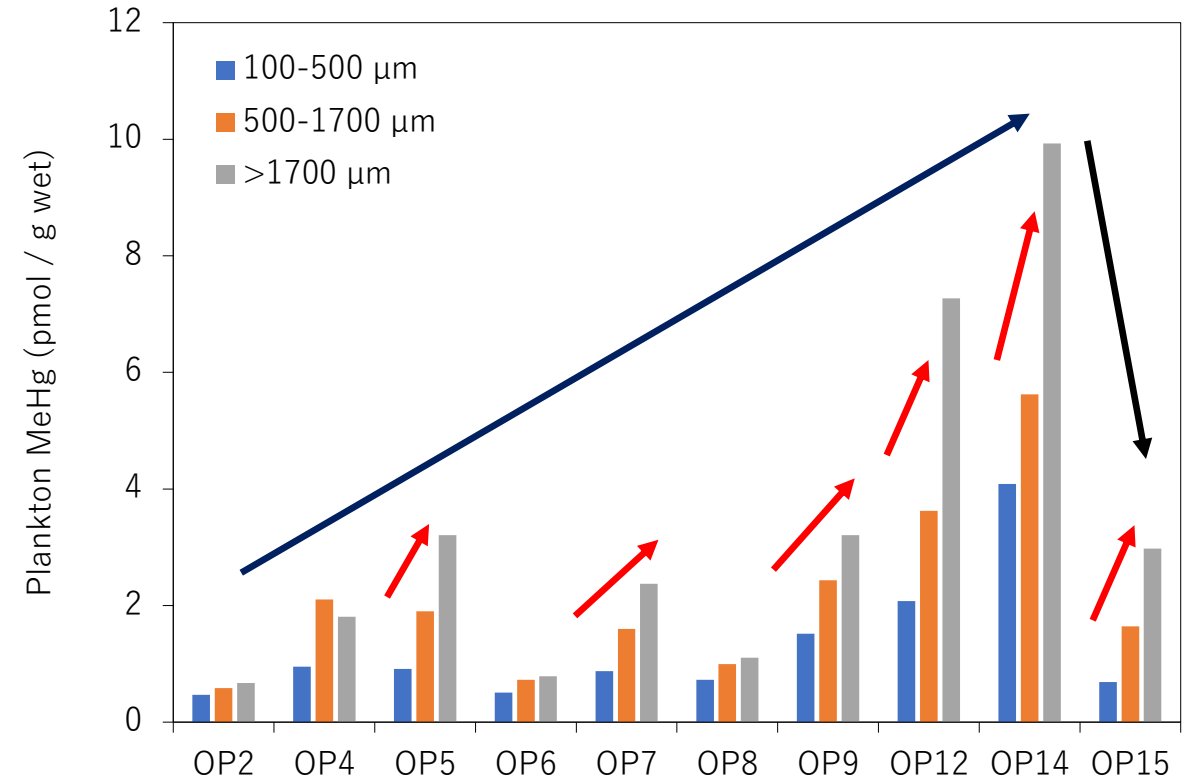
Seawater Total Hg : Higher in Oyashio Current region (Maximam: 0.5 pM)
Seawater MeHg : Higher in the equator region and Oyashio Current region
(OP15: 0.022 pM)

Total Hg and MeHg in zoo planktons

Plankton Total Hg (Calculated assuming 90% moisture content)



Plankton MeHg. (Calculated assuming 90% moisture content)



Equator ← → 44° N

Equator ← → 44° N

Plankton Total Hg : No relation to size and no significant north-south gradient

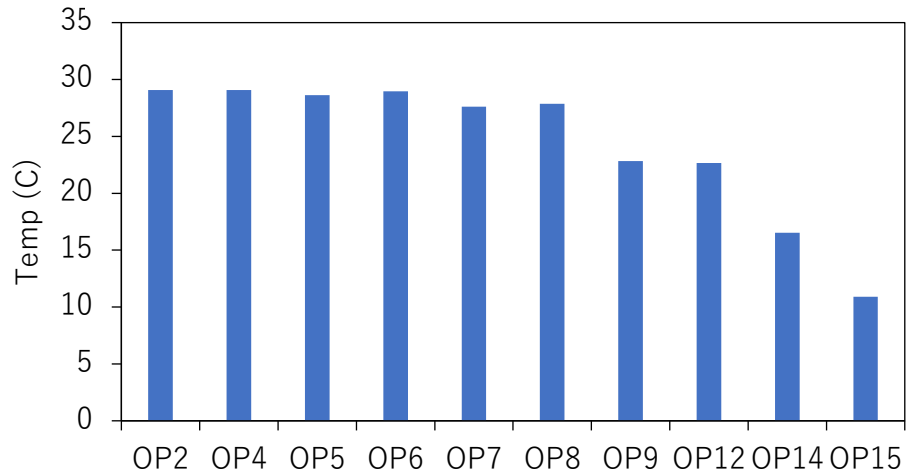
Plankton MeHg : Concentrations increased in proportion to size increase → Bio accumulation of MeHg

Concentrations were higher in north than in south, but they became lower in the northernmost point →

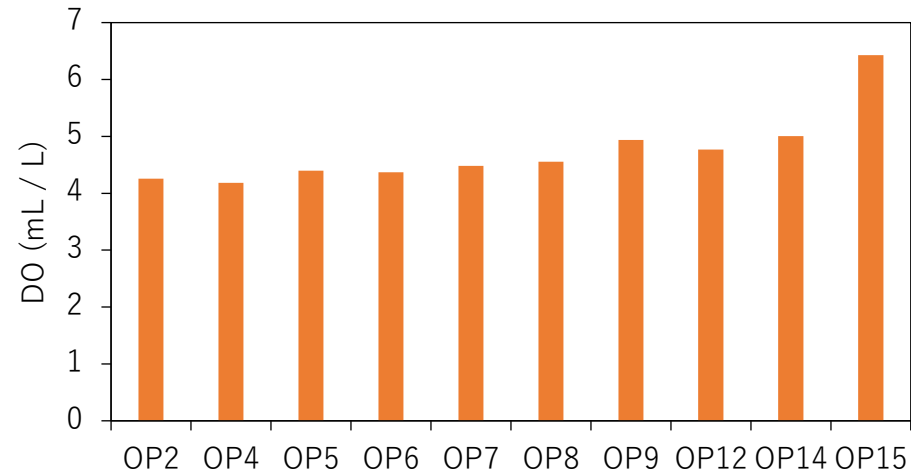
Accumulation rate varies depending on ocean area and currents

Why is the plankton MeHg is lower in the OP-15 point ?

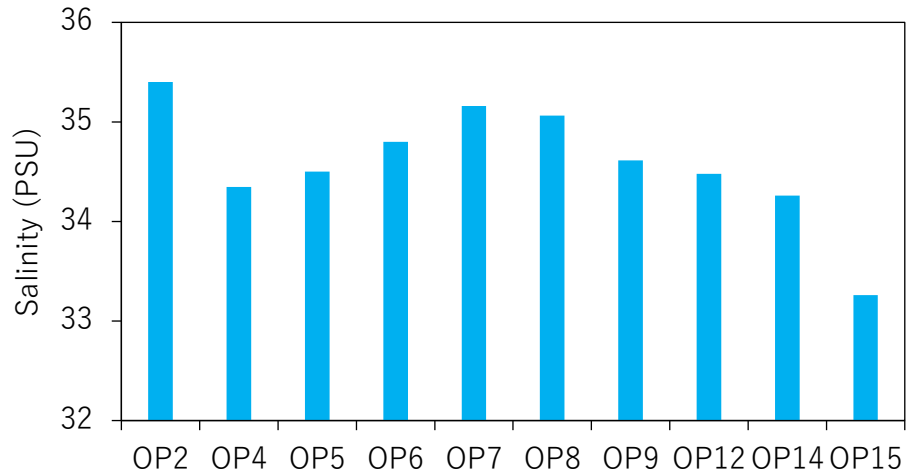
Surface water temperature



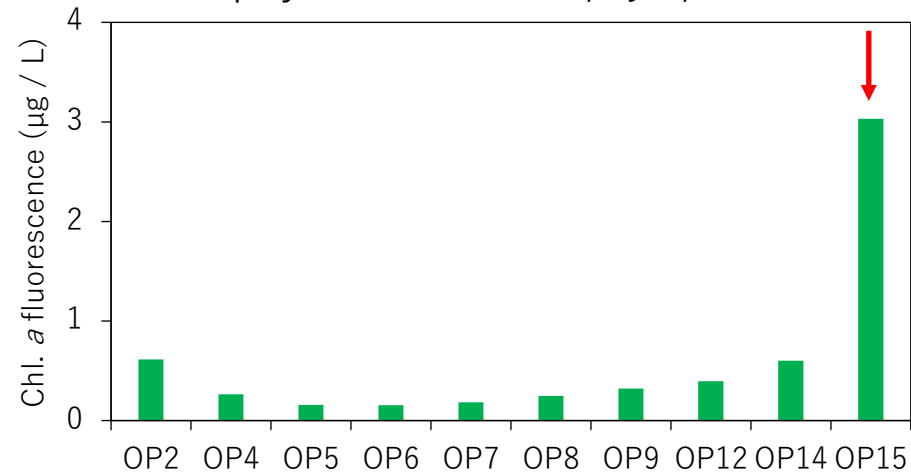
Surface DO concentration



Salinity in surface seawater



Chlorophyll a (Indicator of phytoplankton abundance)



The lower MeHg concentrations in planktons at OP-15 might be occurred due to bio-dilution with increased phytoplankton abundance.

Equator ← → 44° N

Equator ← → 44° N

Summary of Hg survey in the western North Pacific Ocean

- The concentrations of Hg(0), Hg(II), DMHg, and MMHg, the four main forms, were relatively low in the surface layer and higher in the intermediate and deep layers.
- The presence of MMHg, DMHg, and Hg(0) maxima in the mesopelagic zone at a depth of about 500 m and their formation at the upper edge of the oxygen minima suggest that oxygen is consumed by microbial remineralization and that reducing Hg may be produced in conjunction with it.
- DMHg concentrations became higher from south to north and were higher than MMHg concentrations in deeper layers. Around 70% of total MeHg concentrations were DMHg in the intermediate and deep layers.
- MeHg concentrations in plankton by size were observed in the western North Pacific Ocean (North-South transect and Oyashio region).
- Plankton MeHg concentrations increased in proportion to size increase, suggesting that bio-accumulation of MeHg is occurred.
- Plankton MeHg concentrations were higher in high latitude zone, but in areas with high chlorophyll-a concentrations, bio-dilution effect may cause a decrease in the concentration.

Acknowledgements

We would like to express our deepest gratitude to the members of the Environmental Chemistry Laboratory who assisted us in the preparation of atmospheric and oceanographic surveys and Hg analysis in conducting this research. We would also like to appreciate to the crew of the research vessel and many researchers for their assistance during the research cruise. This research was supported by a special research grant from the National Institute of Minamata Disease, a grant from the Environmental Research Promotion Fund, and a Grant-in-Aid for Scientific Research.



Thank you for your kind attention !