# Spatial variations of mercury in sediment and speciation of mercury in bottom water in Minamata Bay, Japan

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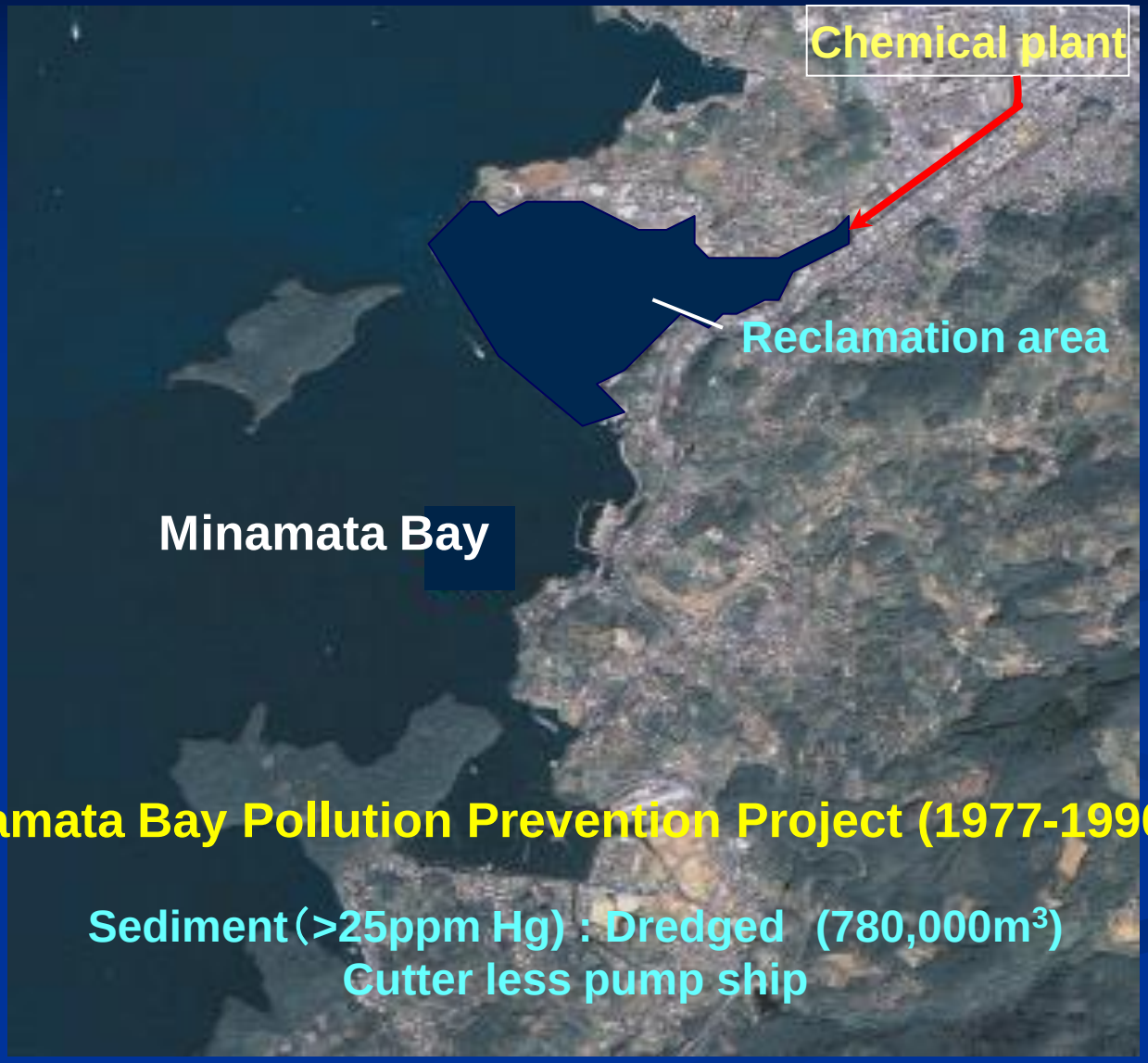
# Plan of presentation

- Vertical and Horizontal distribution of mercury in sediment of Minamata Bay
  - History of contamination of Minamata Bay sediment
  - Estimation of the background level
- Speciation of Hg in bottom water of Minamata Bay
  - Movement of mercury from bottom sediment into water column
- Vertical and Horizontal distribution of mercury in sediment of Yatsushiro Sea
  - Dispersion of Hg from Minamata Bay to Yatsushiro Sea




**Minamata Bay Pollution Prevention Project (1977-1990)**

Sediment（>25ppm Hg) : Dredged (780,000m$^3$)
Cutter less pump ship

# Vertical and Horizontal distribution of mercury in sediment of Minamata Bay

History of contamination of Minamata Bay sediment

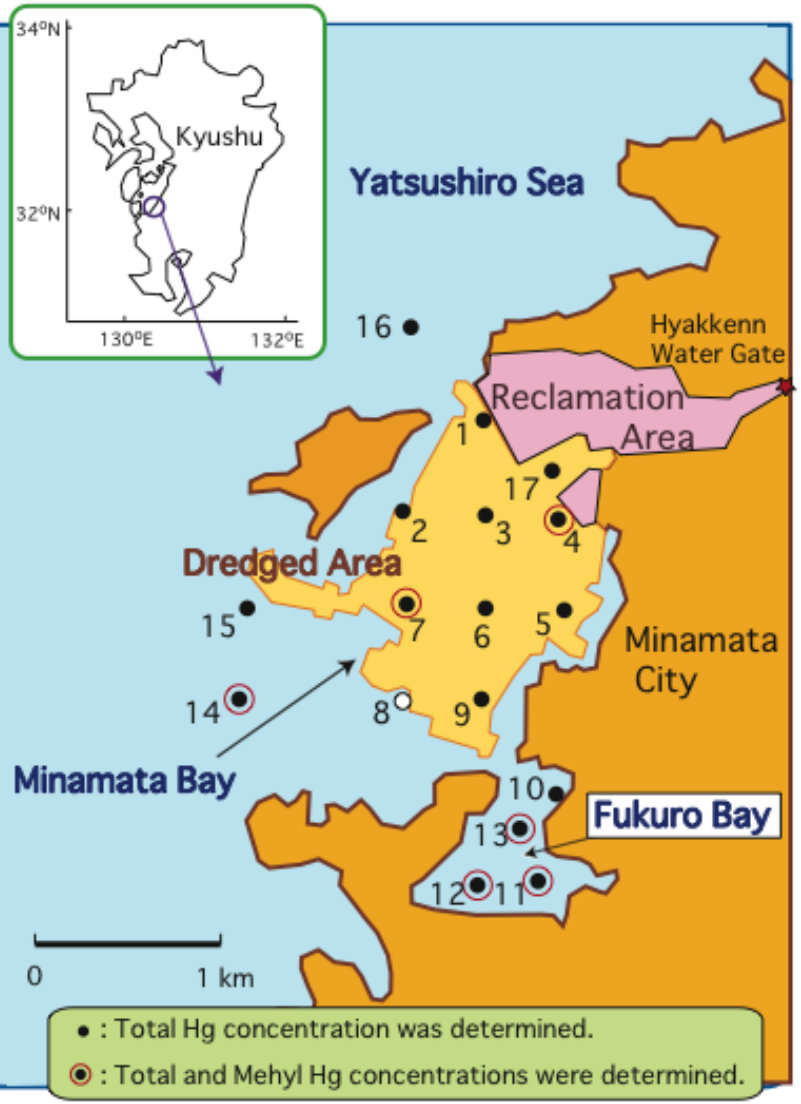
Estimation of the background level

## Sampling

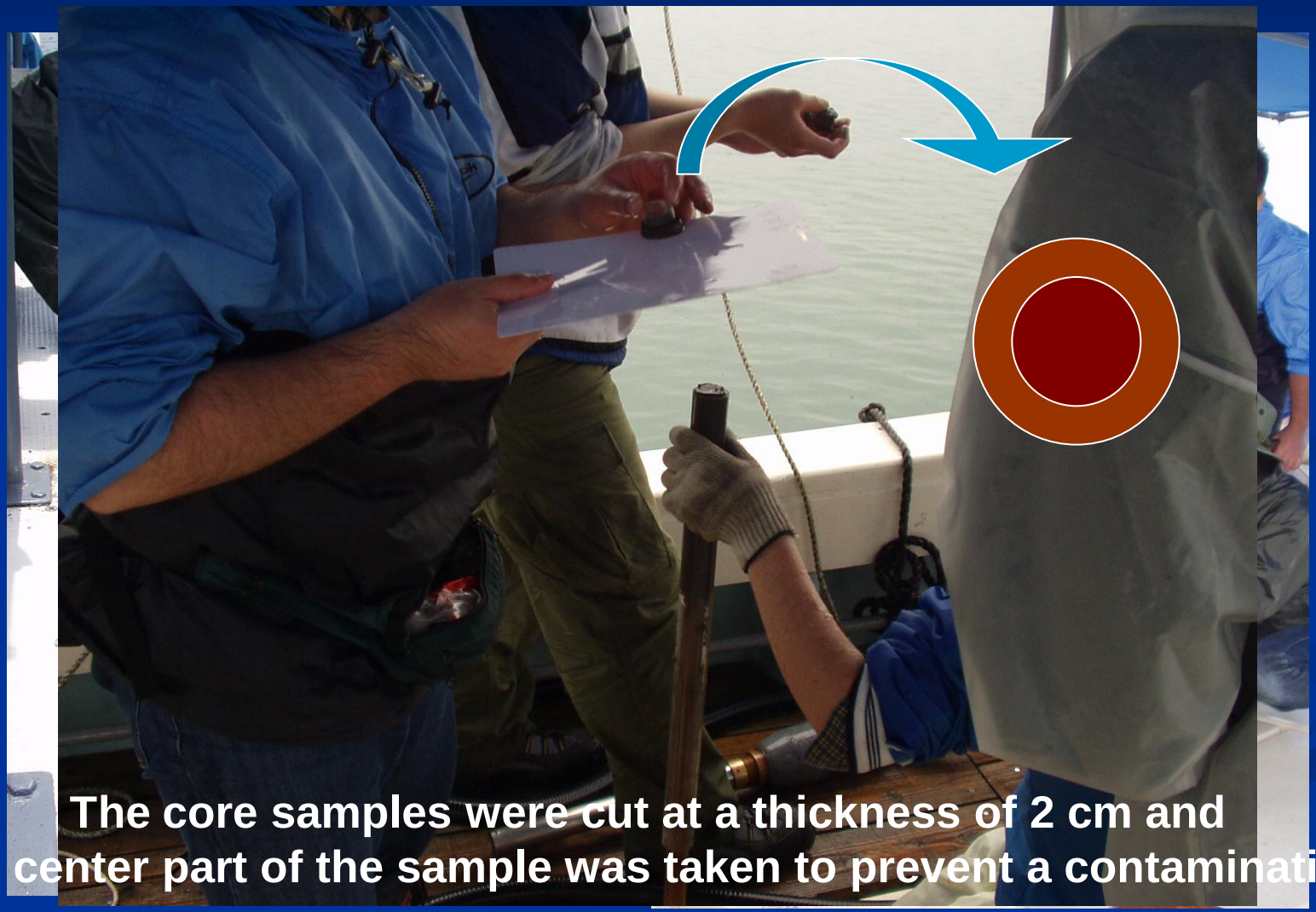
**Columnar samples** were taken from
**17 sampling sites**
using a **PHLEGER gravity core sampler**
in **June 26, 2002.**

**Samples** were taken **at a thickness of 2 cm**
from the **center of the column**
to prevent a contamination.

**The Hg concentration**, based on wet weight,
was converted to **a dry weight value**
**by using water content**
which was measured separately
**by heating the sample at 110°C for 6 h.**



# Sediment sampling with gravity core sampler



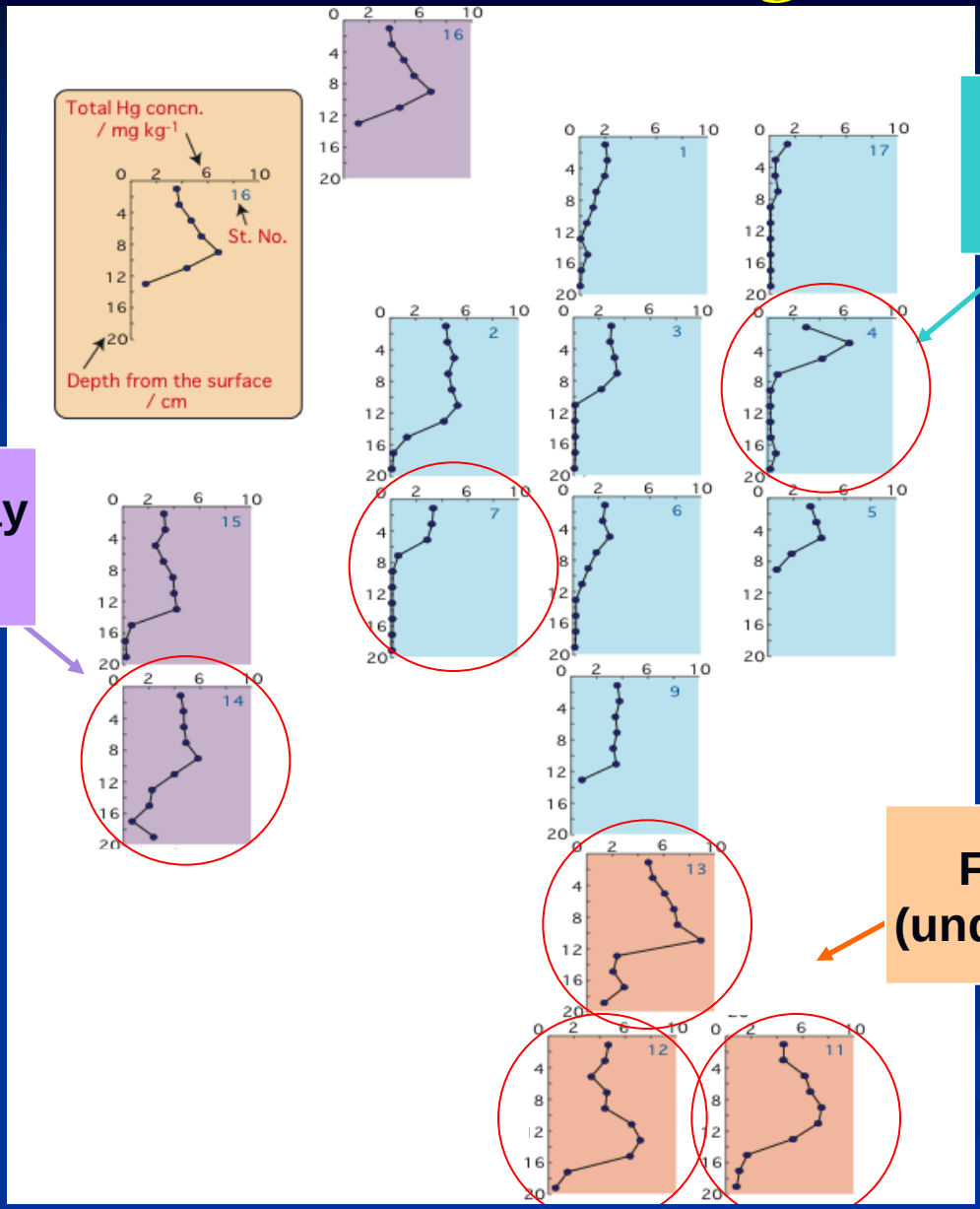
The core samples were cut at a thickness of 2 cm and the center part of the sample was taken to prevent a contamination

# Analytical Procedures

- **T-Hg** : determined by CVAAS after wet digestion at 230°C using $H_2SO_4$-$HNO_3$-$HClO_4$ mixture.
- **MeHg** : Samples were treated with KOH-ethanol solution and MeHg eluted in the liquid was extracted with toluene as dithizonates and determined by GC-ECD.

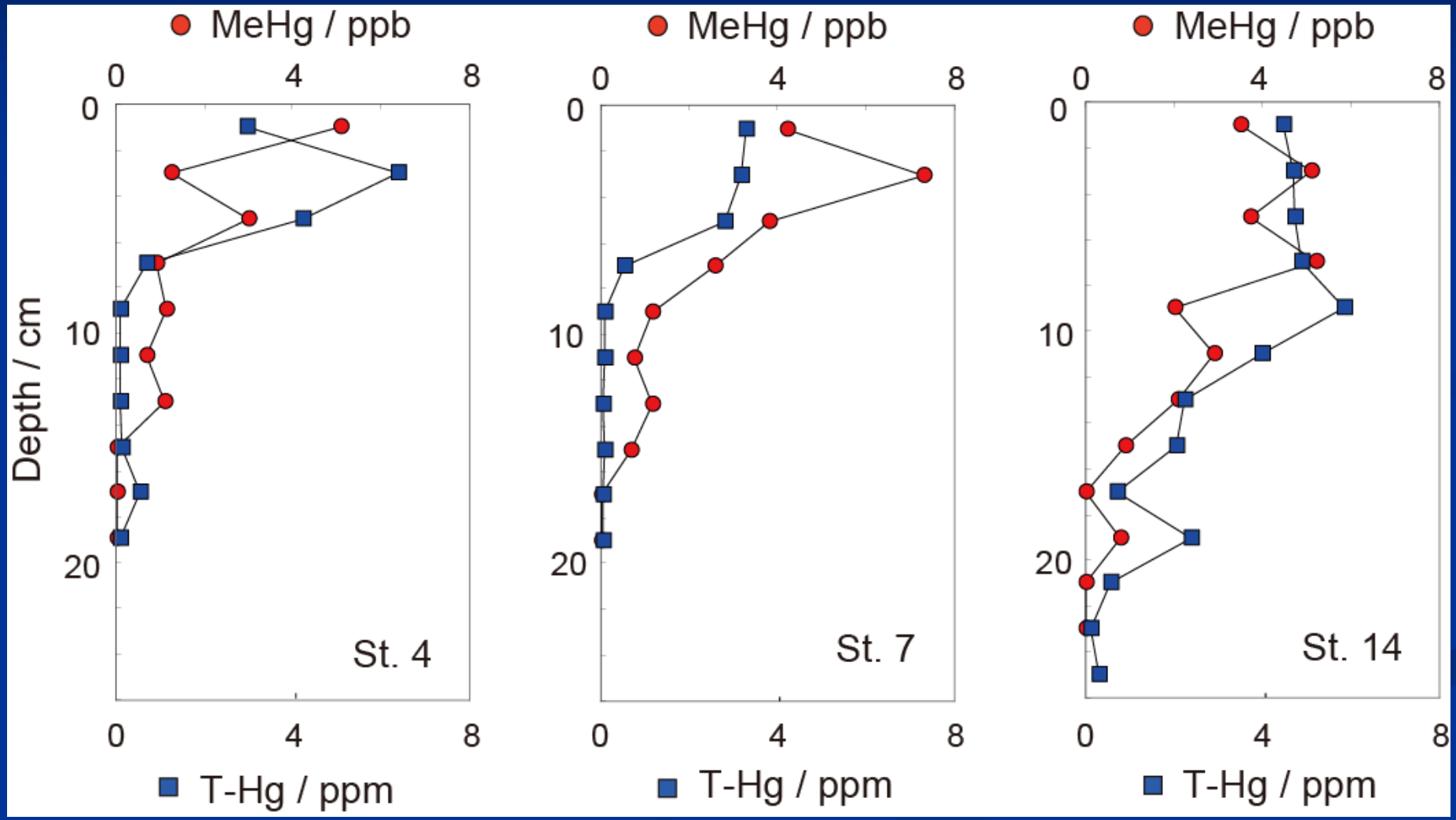
Hg concentration obtained in wet basis was converted to dry weight basis by using water content (110°C, 6 hr).

# The vertical variations of T-Hg in sediment

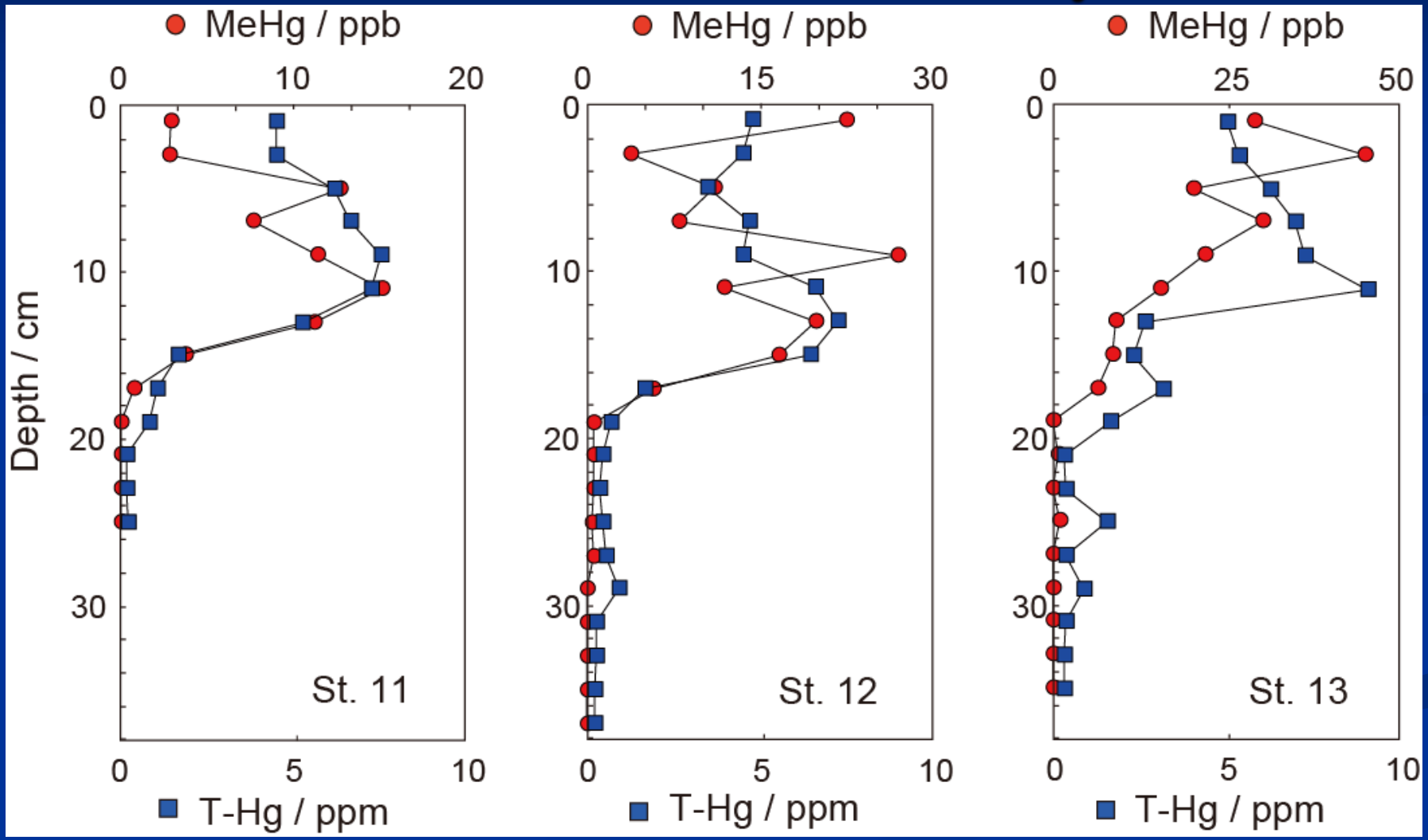



T.Tomiyasu, A.Matsuyama, T.Eguchi, Y.Fuchigami, K.Oki, M Horvat,R.Rajar and H.Akagi, Sci. Tot. Environ., 368, 283 – 290 (2006)

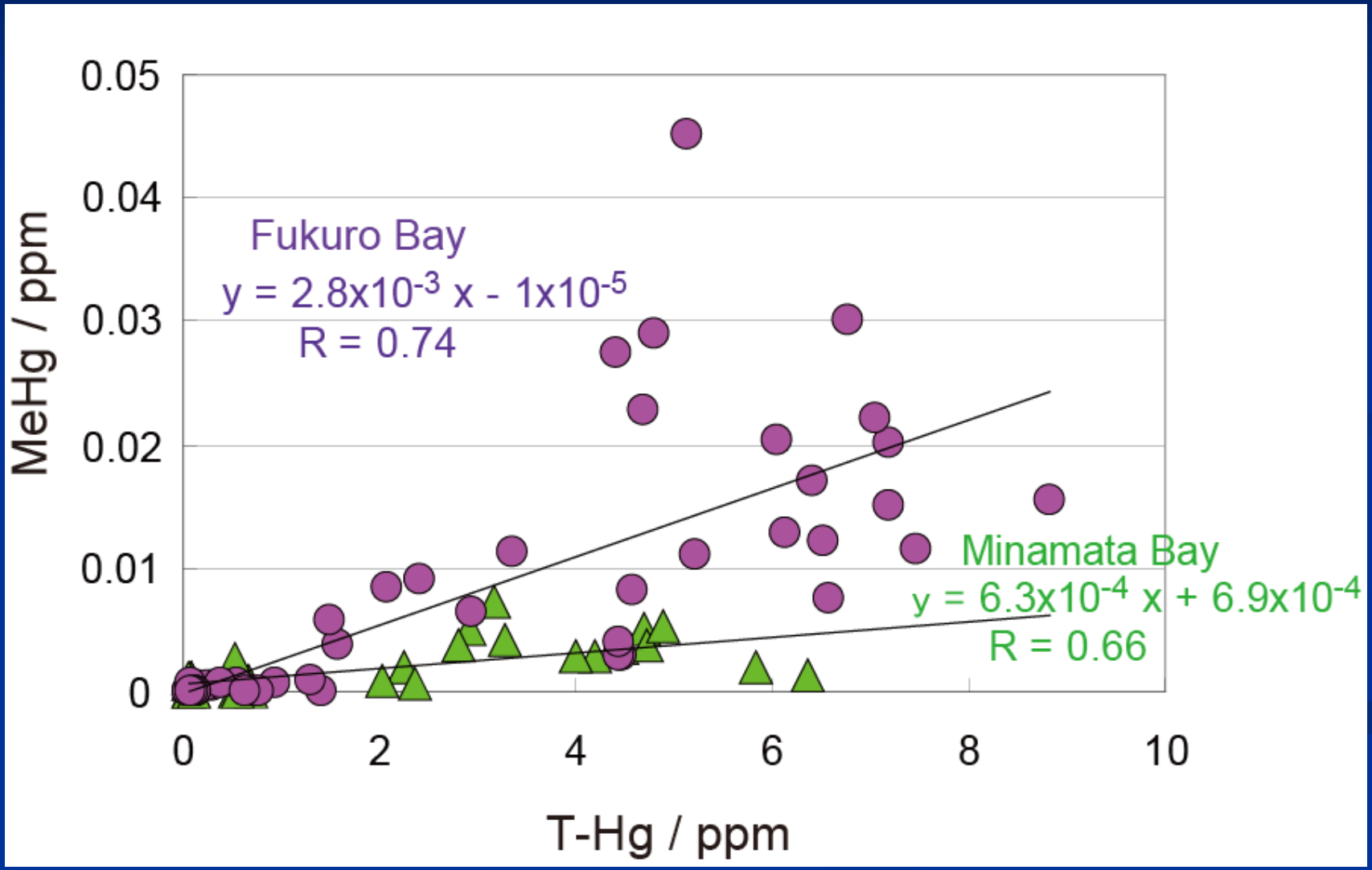
# Vertical variations of T-Hg and MeHg in sediment of Minamata Bay



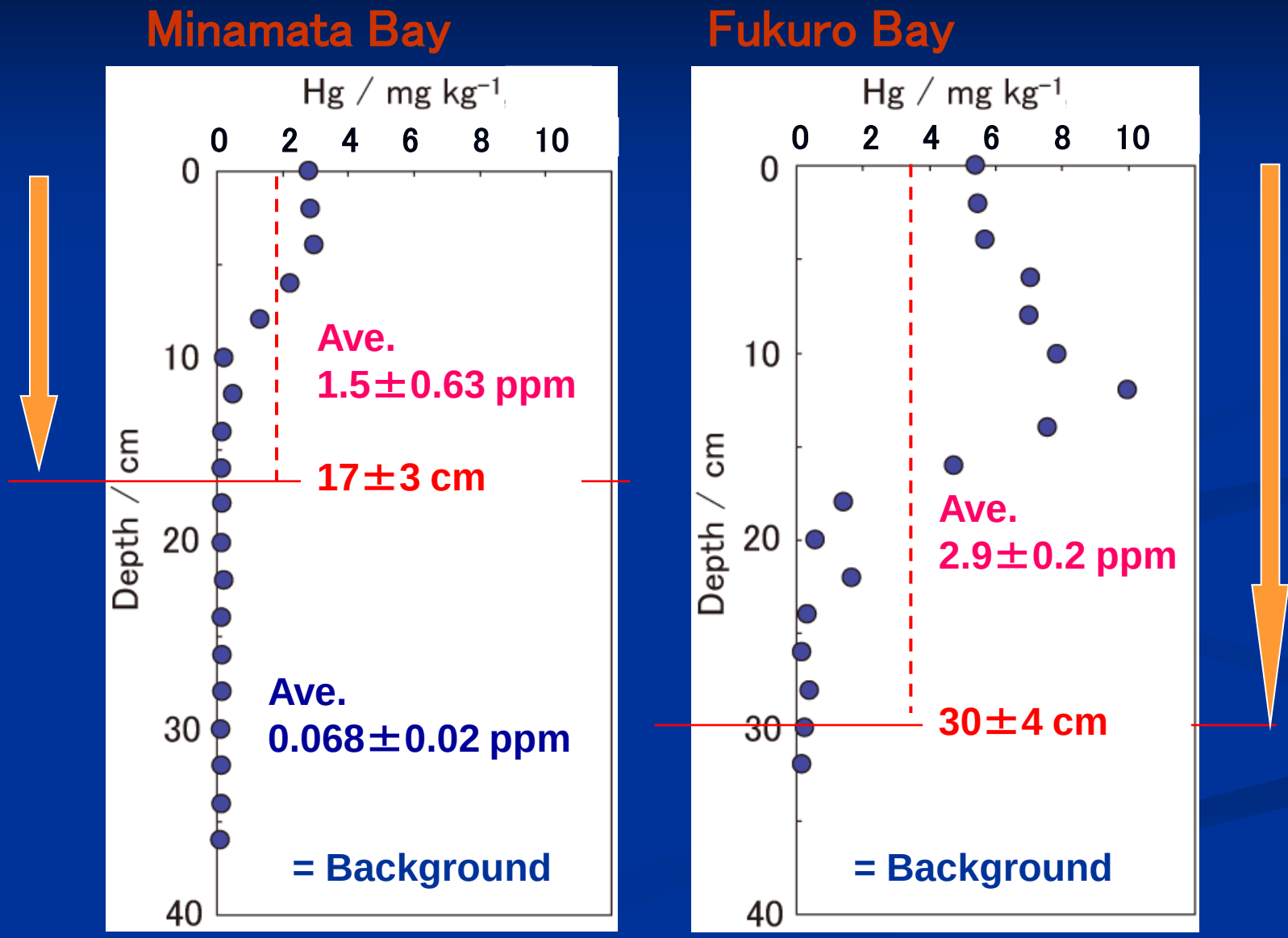
# Vertical variations of T-Hg and MeHg in sediment of Fukuro Bay



# T-Hg vs. MeHg plots



# Typical vertical profiles of Hg in sediments



# Conclusion 1

- In the lower layer of cores, Hg concentration showed no apparent trends with lower value.（The Hg concentration increased toward the surface.）

  →From the Hg concentration in the lower layers, background level of the study area was estimated as 0.068 mg/kg (dry weight basis).

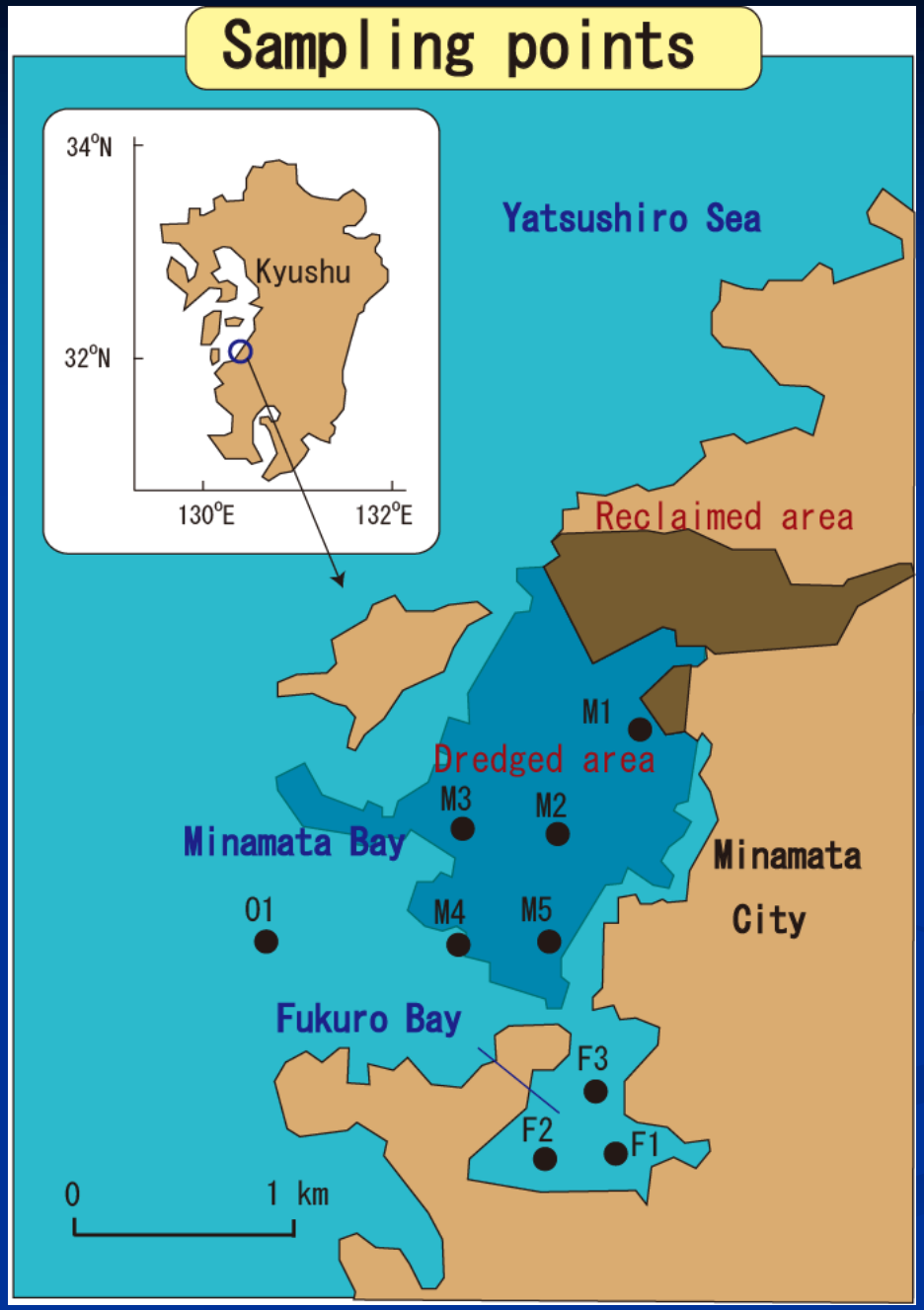
- The thickness of contaminated layers of the sediment were 17 cm and 30 cm for Minamata Bay and Fukuro Bay, respectively.

  → Hg concentration in the layer, 1.5 and 2.9 mg/kg for Minamata Bay and Fukuro Bay, respectively, are 20 – 40 times higher than the background level. (<<25 mg/kg)

# Speciation of mercury in bottom water in Minamata Bay, Japan

To assess the remobilization of mercury from bottom sediment into water column,

T-Hg and MeHg concentrations in bottom water, suspended particles and surface sediments were determined.


Sampling points
34°N
32°N
130°E
132°E
Kyushu
Yatsushiro Sea
Reclaimed area
M1
Dredged area
M3
M2
Minamata Bay
Minamata
City
01
M4
M5
Fukuro Bay
F3
F2
F1
0
1 km

# Sampling


Gravity core sampler


Bottom water layer
= clear water layer
= turbid layer
→ water layer
→ suspended particles


Surface sediment (0-2 cm)

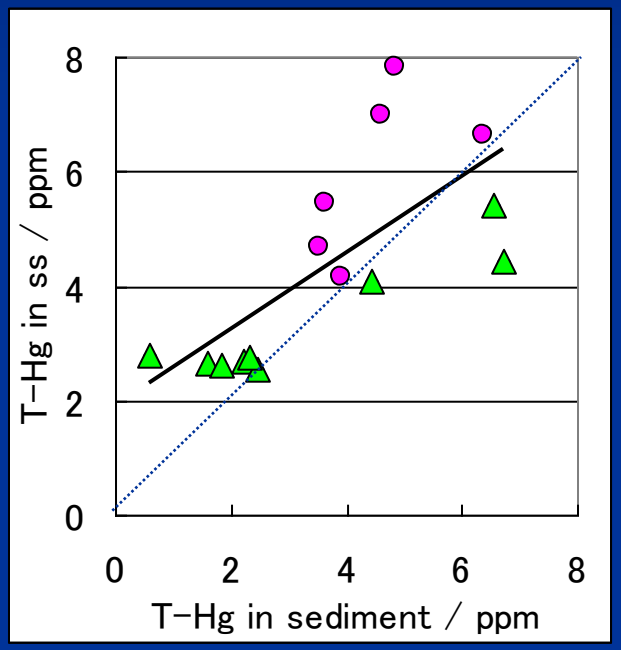
# Hg concentrations in sediment and ss

| area | sediment | | |
|---|---|---|---|
| | T-Hg /mg kg$^{-1}$ | MeHg /ug kg$^{-1}$ | Me/T (%) |
| Minamata Bay | 3.2±2.2 | 4.2±2.1 | 0.19±0.13 |
| Fukuro Bay | 4.5±1.1 | 16.6±16.6 | 0.39±0.41 |
| Whole data | 3.7±1.9 | 9.2±11.9 | 0.27±0.28 |

| area | suspended particles | | |
|---|---|---|---|
| | T-Hg /mg kg$^{-1}$ | MeHg /ug kg$^{-1}$ | Me/T (%) |
| Minamata Bay | 3.3±1.0 | 4.1±1.9 | 0.12±0.05 |
| Fukuro Bay | 6.0±1.4 | 14.1±12.8 | 0.26±0.24 |
| Whole data | 4.4±1.8 | 8.1±9.3 | 0.18±0.17 |

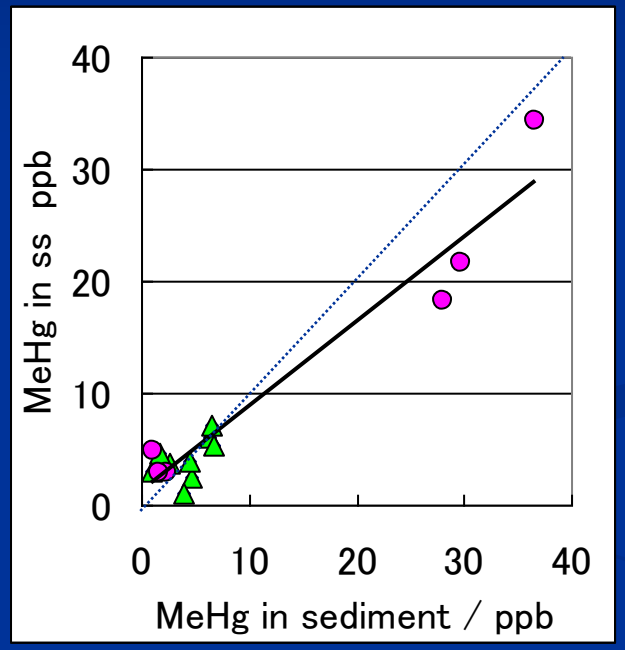
# Correlations between sediment and ss

**T-Hg concentration**



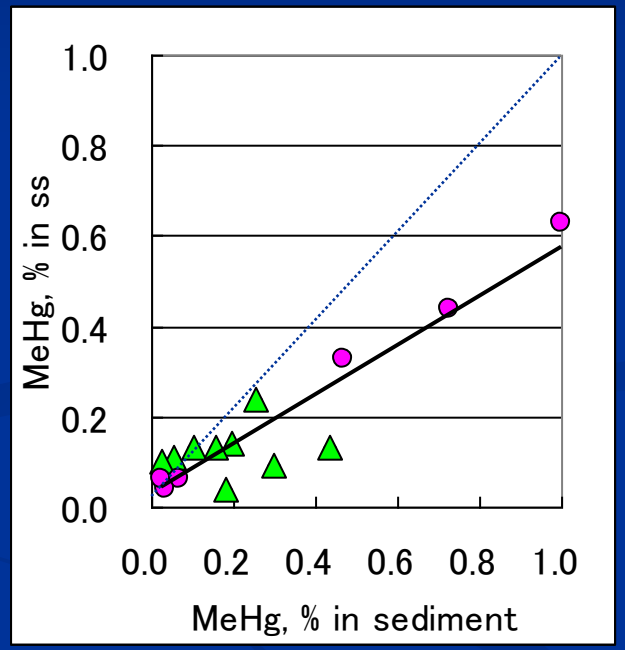

**Y = 0.67x + 1.7**
**r = 0.73, *p* <0.01**

**MeHg concentration**




**Y = 0.76x + 1.1**
**r = 0.96, *p* <0.01**

**MeHg / T-Hg, %**



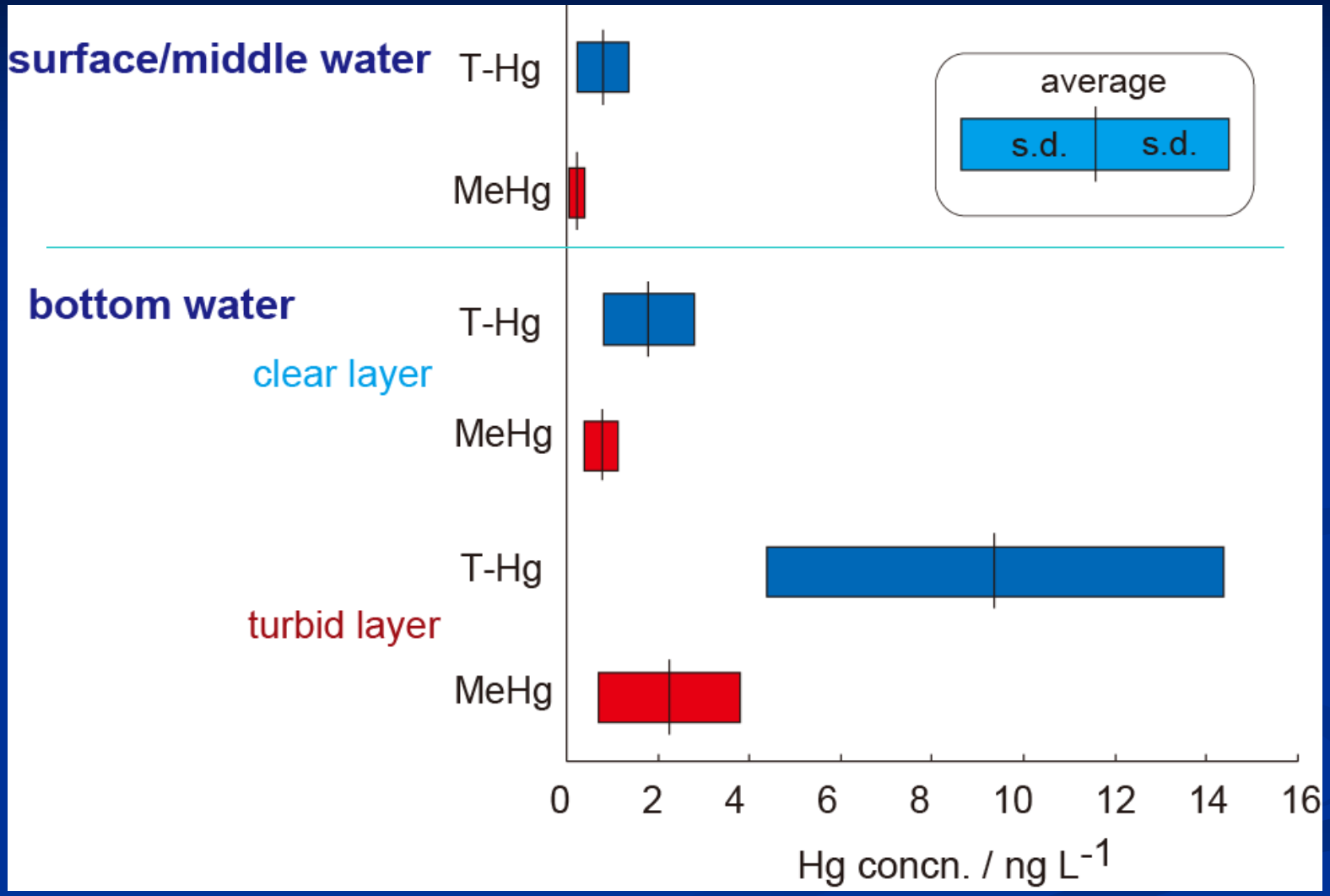

**Y = 0.55x + 0.03**
**r = 0.93, *p* <0.01**

By the resuspension of sediment, MeHg readily elutes from solid phase..?.

# Hg concentrations in bottom water samples

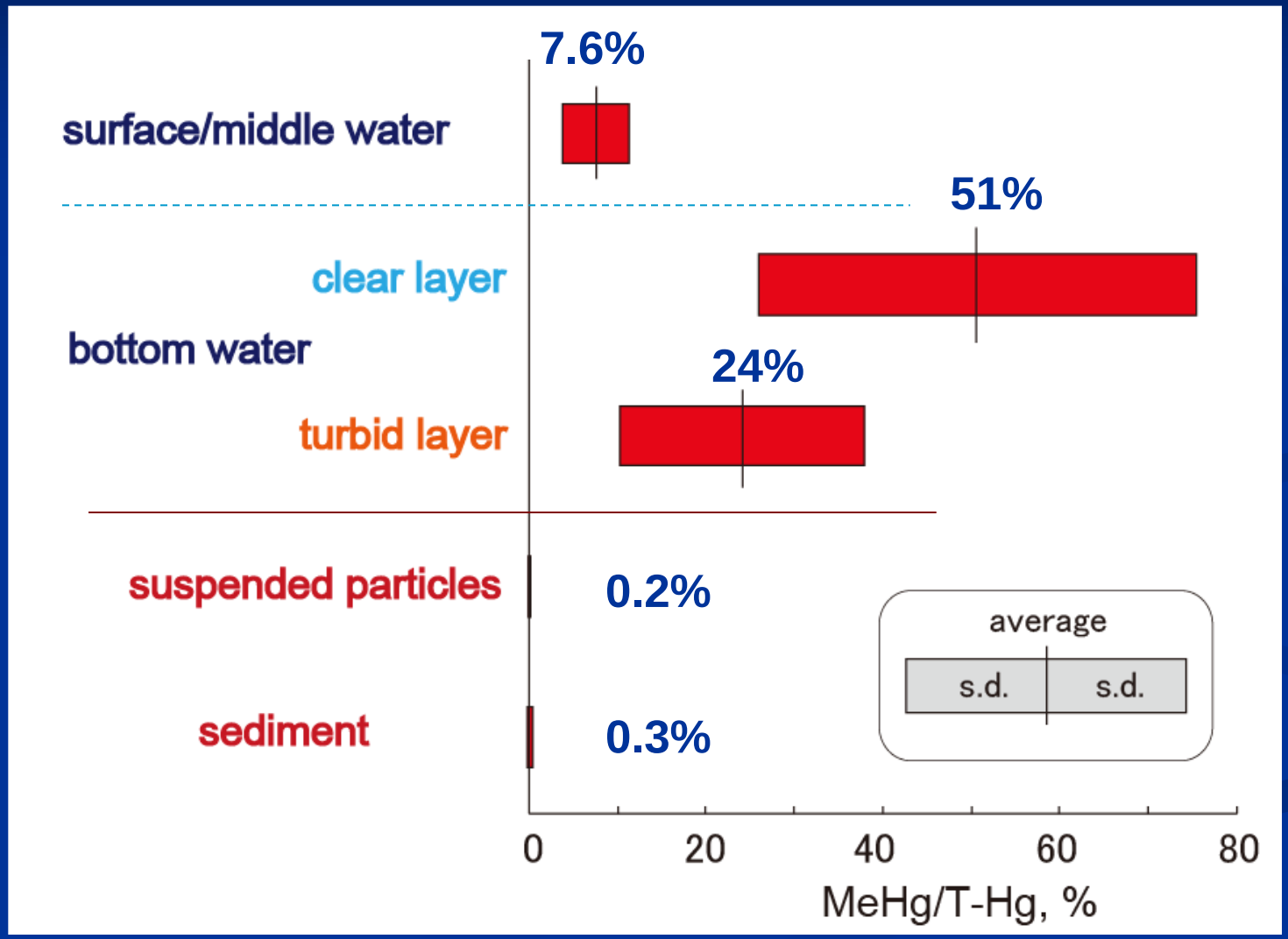
| | Oct. 2002 | | | | | | April 2005 | | |
|---|---|---|---|---|---|---|---|---|---|
| | clear layer | | | turbid layer | | | clear layer | | |
| St. | T-Hg | MeHg | MeHg | T-Hg | MeHg | MeHg | T-Hg | MeHg | MeHg |
| | (ng $L^{-1}$) | | (%) | (ng $L^{-1}$) | | (%) | (ng $L^{-1}$) | | (%) |
| M1 | 1.7 | 1.0 | 62 | 9.8 | 2.9 | 30 | 0.9 | 0.6 | 62 |
| M2 | 1.3 | 1.1 | 80 | 7.8 | 4.1 | 53 | 0.8 | 0.7 | 88 |
| M3 | 3.3 | 0.3 | 10 | 9.3 | 1.2 | 13 | - | - | - |
| M4 | 1.4 | 0.8 | 59 | 7.1 | 1.5 | 22 | 1.0 | 0.3 | 35 |
| M5 | 4.3 | 0.5 | 12 | 22.3 | 5.2 | 23 | - | - | - |
| F1 | 2.6 | 0.7 | 29 | 8.0 | 1.0 | 12 | 0.9 | 0.5 | 51 |
| F2 | 1.5 | 0.9 | 60 | 7.4 | 0.8 | 10 | 1.6 | 0.3 | 17 |
| F3 | 2.0 | 1.2 | 59 | 5.6 | 2.1 | 36 | 1.0 | 0.8 | 74 |
| O1 | 2.6 | 1.7 | 64 | 7.1 | 1.3 | 18 | - | - | - |
| ave | 2.3 | 0.9 | 48 | 9.4 | 2.2 | 24 | 1.1 | 0.5 | 54 |
| stdev | 1.0 | 0.4 | 25 | 5.0 | 1.6 | 14 | 0.3 | 0.2 | 26 |

# Hg concentrations in water




*1. Logar M, *et al*., Appl Organometal Chem 2001;15:515-526.
*2. current study (Tomiyasu T, *et al.,* Marine Chemistry, in press.)

# Percentages of MeHg in samples



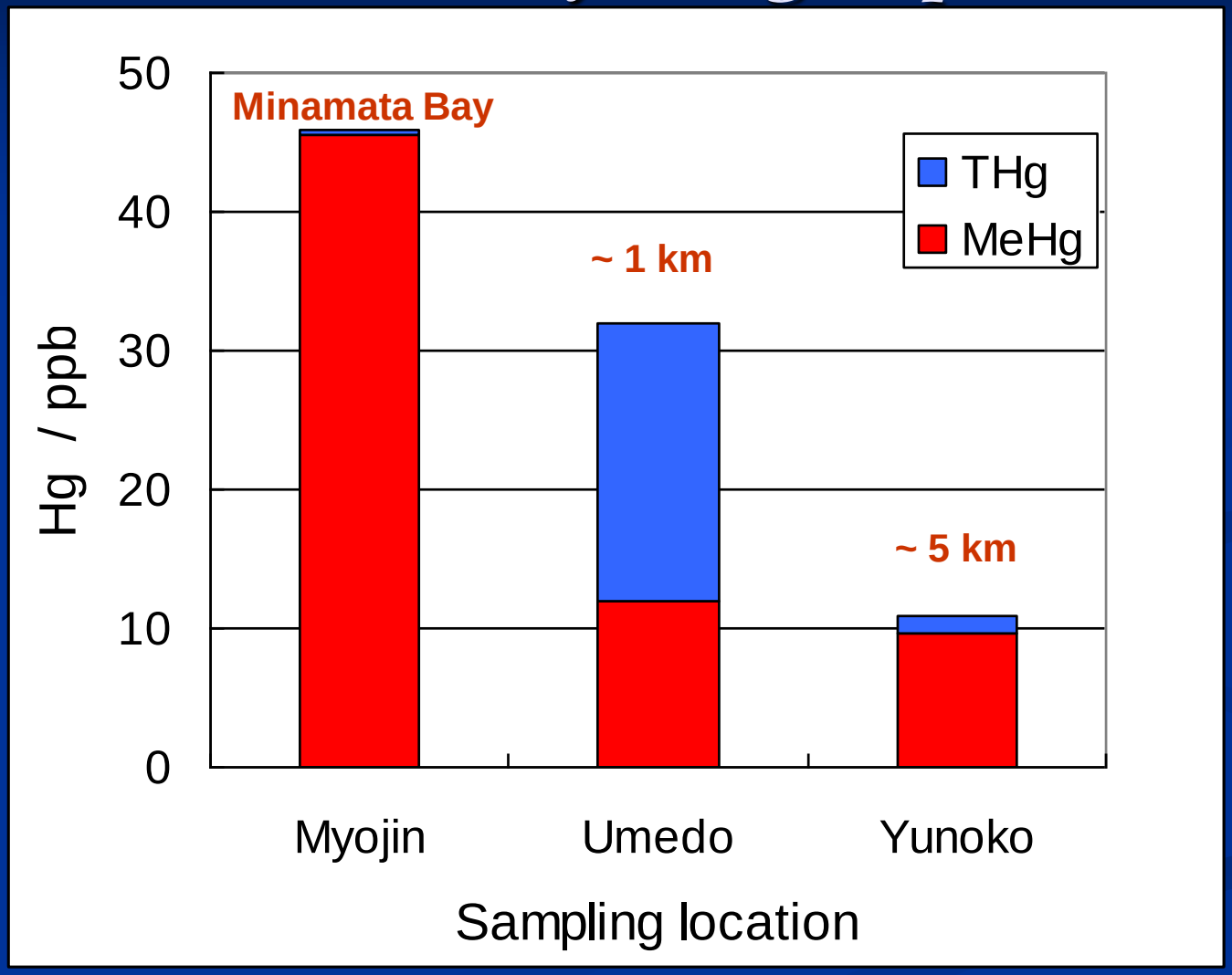
# Hg concentration in Mussel collected from Minamata Bay

Mussel *Mytilus galloprovincialis*

- Sedentary filter-feeding bivalves
- Commonly used as biological indicators of water quality

5 organs
- adductor muscle
- mantle
- gonads
- gills
- digestive gland

# Concentration of T-Hg and MeHg in adductor muscle of Mussel *Mytilus galloprovincialis*




M. Sato, K. Haraguchi, T. Ando, T. Tomiyasu and H. Akagi, Environmental Sciences, 5, 4 (1997)

# Conclusion 2

- A gradation of T-Hg concentration in water phase could be seen clearly.

  → The main source of mercury in water of Minamata Bay is the sediment.

- MeHg concentration in bottom water is also high and about 24-50% of T-Hg is MeHg. The values are two orders of magnitude larger than that in sediment and ss.

  → The predominant form of mercury at the elution step from sediment into water column is MeHg.

- The Hg concentration in adductor muscle of Mussel decreased with distance from Minamata Bay.

  → The MeHg eluted from sediment may be readily adsorbed aquatic organisms and accumulated with food chain.

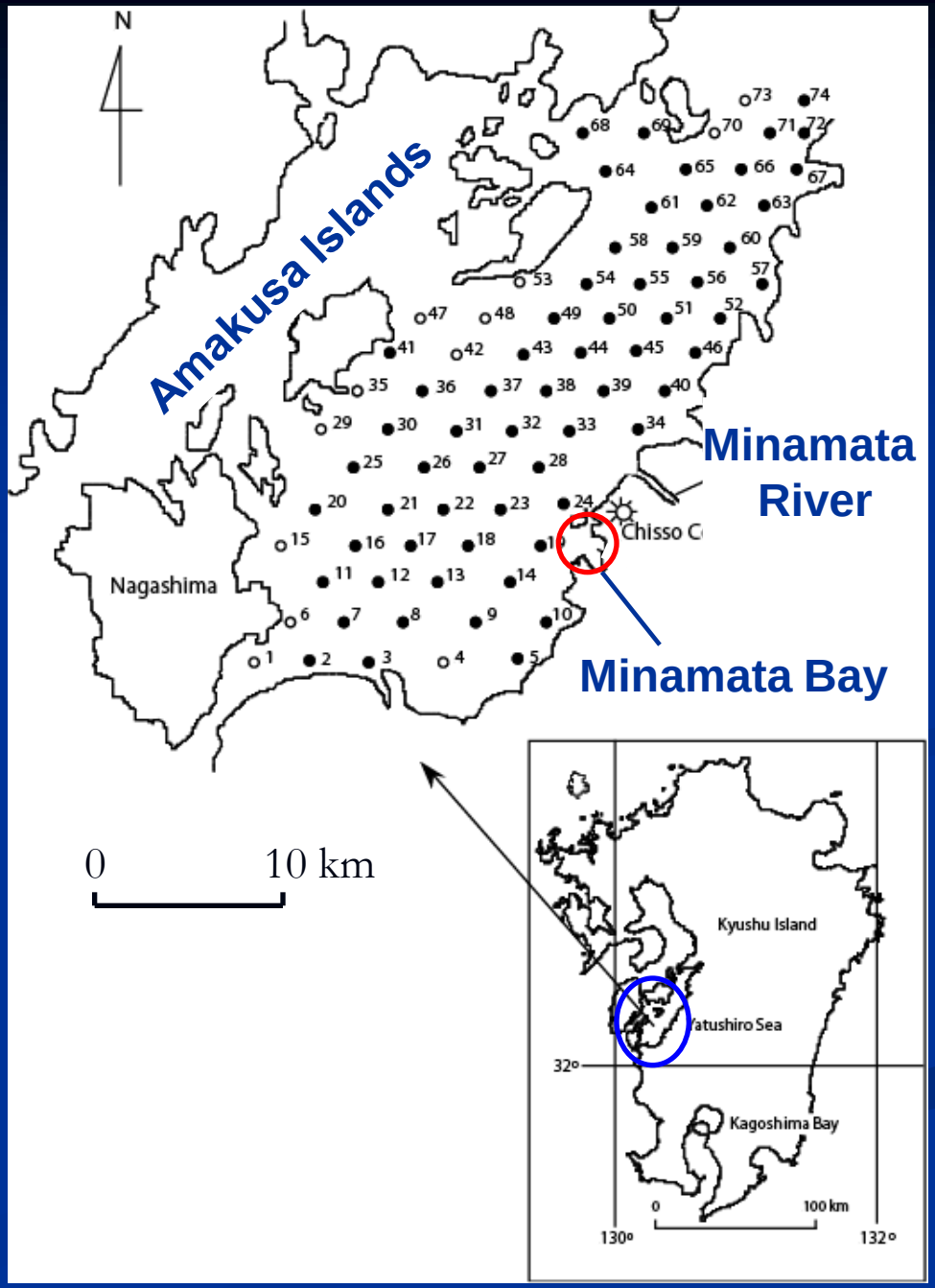
# Vertical and Horizontal distribution of mercury in sediment of Yatsushiro Sea

## Dispersion of Hg from Minamata Bay to Yatsushiro Sea

# Sampling points

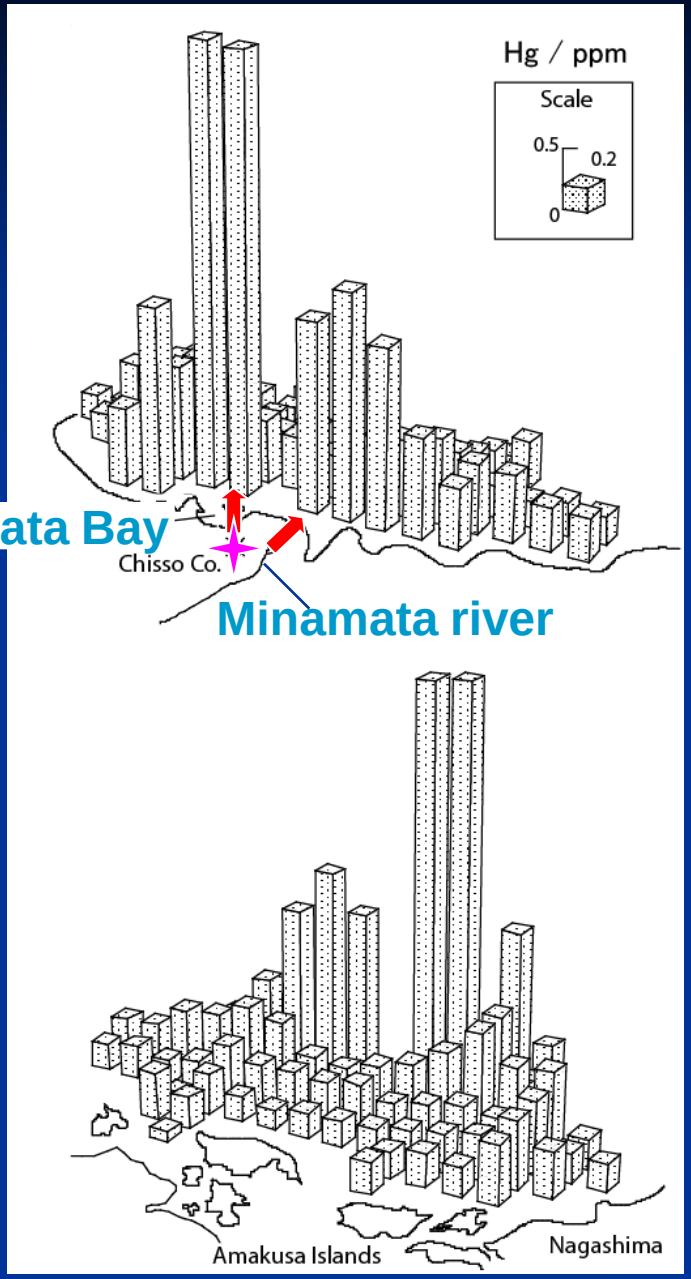
At 62 locations throughout southern part of the Yatsushiro Sea, columnar samples were taken from the bottom using a Phleger gravity core sampler.

Samples were taken at a thickness of 1 cm and layers every 3 – 5cm were used for Hg measurement.




T. Tomiyasu, A. Nagano, N. Yonehara, H. Sakamoto, Rifardi, K. Oki, H. Akagi, Sci. Total Environ, 257, 121-132 (2000)

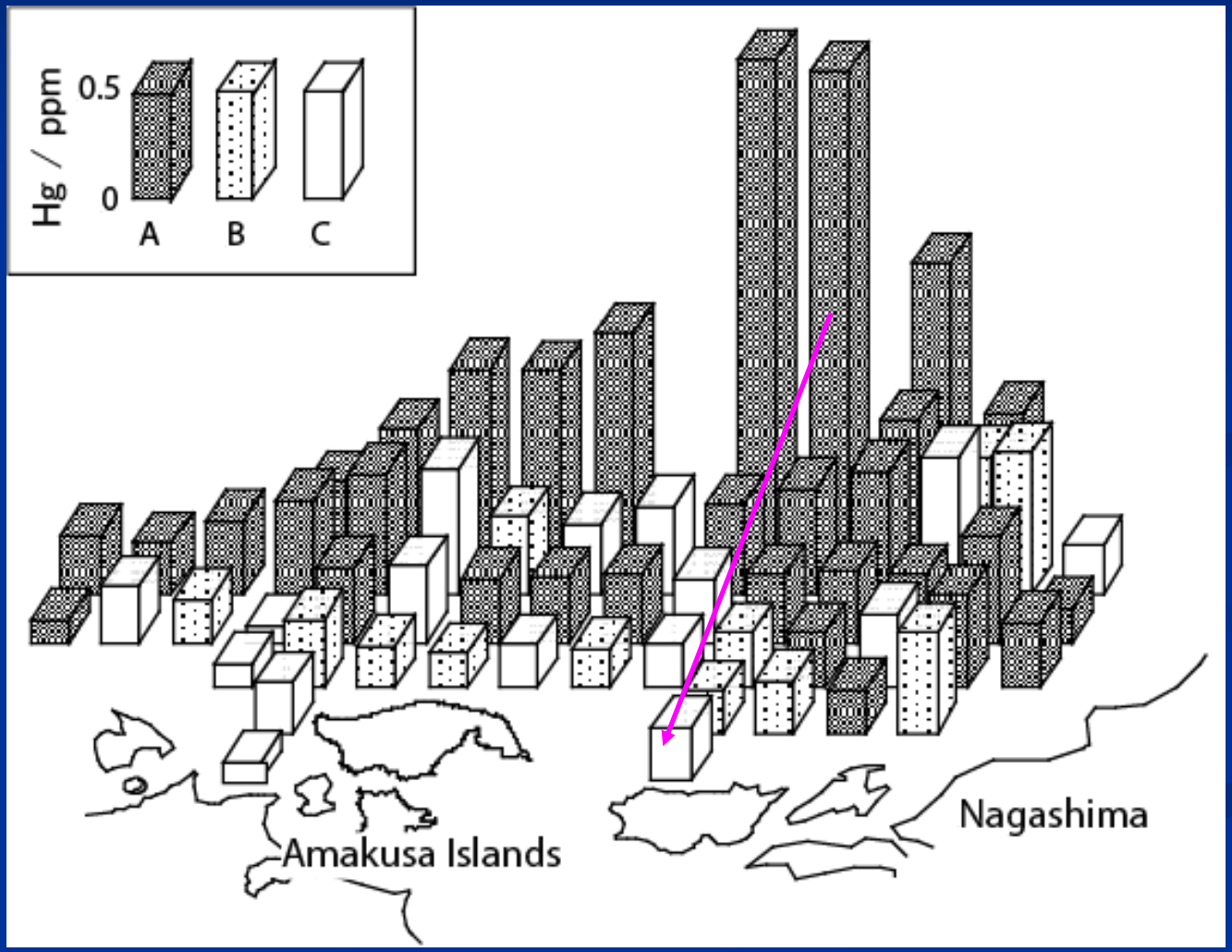
# The highest Hg concentration observed at each station.



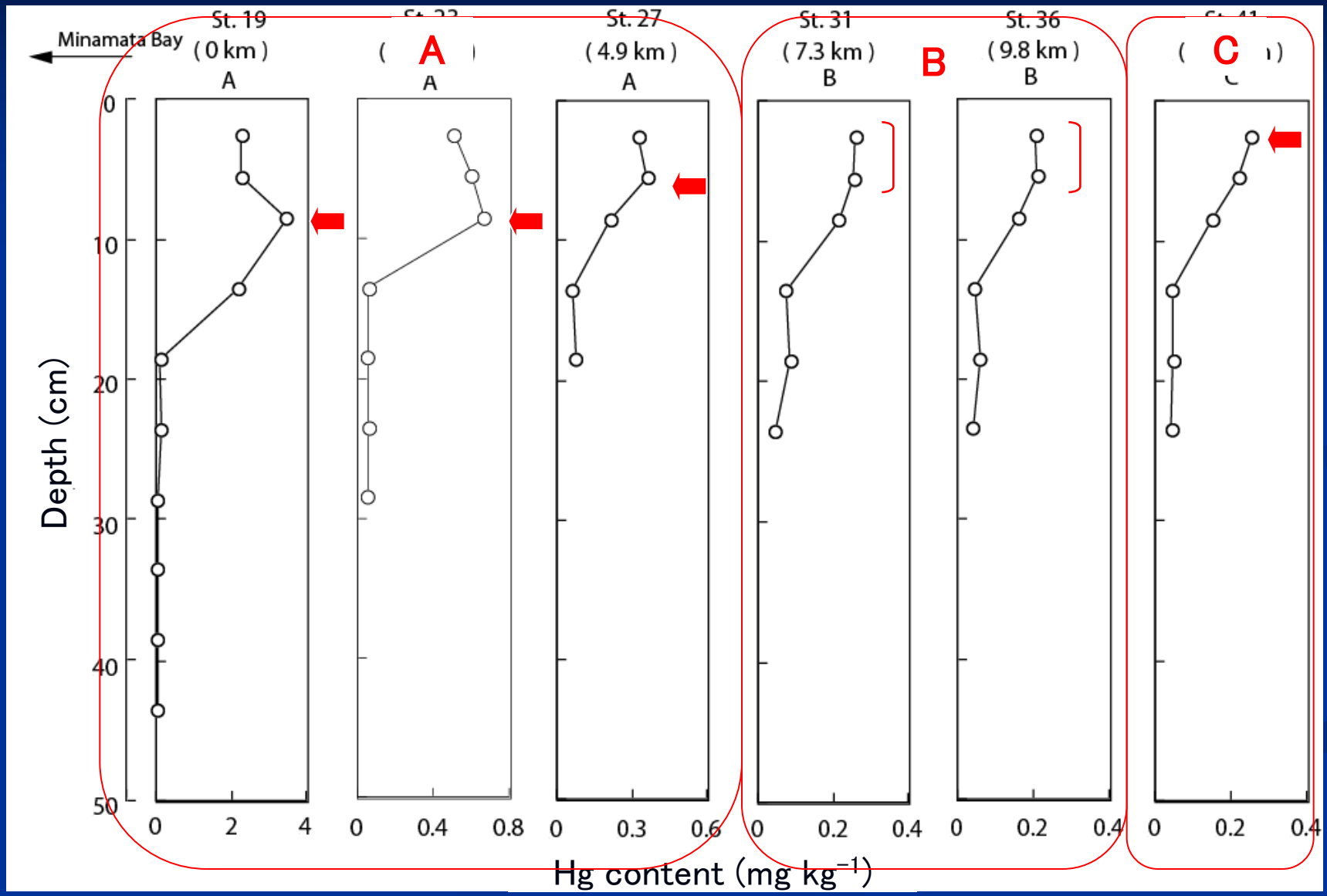

seen from Minamata City

seen from Amakusa Islands

# The distribution of mercury at sediment surface of Yatsushiro Sea (as viewed from Amakusa Islands)

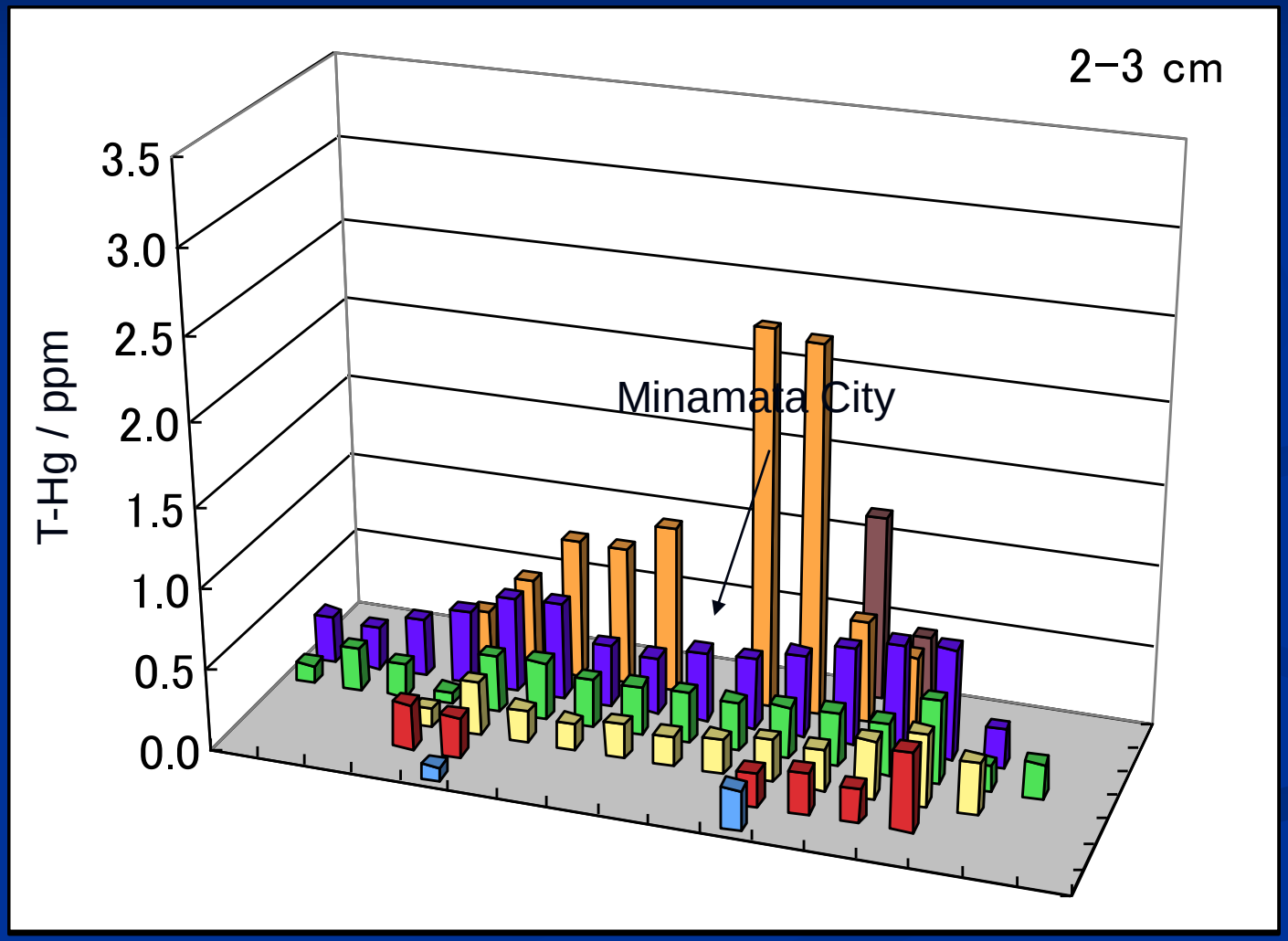


# Vertical profiles of Hg in core samples



# T-Hg distribution in each depth

## (as viewed from Amakusa Islands)



# Conclusion 3

Horizontal distribution

- The Hg concentration decreased with distance from Minamata Bay and Minamata river.

→The source of Hg in Yatsushiro sea sediment is the Hg discharged from chemical plant.

Vertical distribution

- The highest concentration of Hg in sediment at remote site was observed at the surface.

→The Hg-enriched sediment near Minamata Bay is still being redistributed even though 30 years have passed since the discharge ceased.

# Summary

In Yatsushiro Sea, the Hg-enriched sediment near Minamata Bay is still being redistributed.

During the resuspension and movement of sediment, MeHg readily elutes from the sediment into water column.

The eluted MeHg may be taken by aquatic organisms and accumulated in the aquatic food chain.

The long term monitoring of Hg in sediment, water, aquatic organisms in this area is important.

# Thank you for your attention!

# Spatial variations of mercury in sediment and speciation of mercury in bottom water in Minamata Bay, Japan

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From 1932, mercury-contaminated effluent was discharged into Minamata Bay from an acetaldehyde-producing factory for more than 30 years until 1968. Total mercury concentrations as high as 2000 mg $kg^{-1}$ were found in sediment near the overflow of the plant. The sedimentary sludge containing mercury concentrations higher than 25 mg $kg^{-1}$ were disposed by Minamata Bay Pollution Prevention Project. Through the project, most of the polluted sediment was dredged and removed from Minamata Bay. Just after the project mercury concentration of 0.06 – 12 mg $kg^{-1}$ at the sediment surface was reported by Kumamoto Prefecture. The value was, however, about 50 times higher than the background value of this area. When contaminated sediment is resuspended and transported, some mercury species may dissolve in the water column. Logar et al. (2001) reported the T-Hg and MeHg concentration in surface and middle water of Minamata Bay. The value was still higher than that in uncontaminated area. However, mercury concentration in overlying water just upper the bottom surface has not been investigated in Minamata Bay. In this study, total mercury and methylmercury concentrations in bottom water, suspended particle and surface sediments of Minamata Bay were determined to assess the remobilization of mercury from bottom sediment into water column.

The bottom water samples were taken with surface sediments by gravity core sampler in 9 locations of Minamata bay in October 2002 and 6 locations in April 2005. Average T-Hg concentration and the proportion of MeHg to the T-Hg in the surface sediment were 3.52 ± 1.98 mg/kg and 0.27 ± 0.27 %, respectively. The bottom water contained 1.80 ± 1.00 ng/l of T-Hg concentration, which was higher than the value reported for surface - middle waters of Minamata Bay. The fact suggests that the main source of mercury in water is the bottom sediment. The MeHg percentage of the bottom water was 50.7 ± 24.6%, which was also considerably higher than the surface – middle water. MeHg may be a predominant form of mercury released from sediment into water column.

In this presentation, the spatial variation of mercury in sediment of the Yatsushiro Sea is also shown and the dispersion of mercury with sediment will be discussed.

**Keywords:** mercury pollution, marine sediment, Minamata Bay, remobilization of mercury

Kumamoto Prefecture, Minamata-wan kankyo fukugen jigyou no gaiyou (in Japanease)（1998）

T. Tomiyasu et al., Science of the Total Environment, 257, 121-132 (2000)

M. Logar et al., Applied Organometalic Chemistry, 15, 515-526 (2001).

T. Tomiyasu et al., Science of the Total Environment, 368, 283-290 (2006)

T. Tomiyasu et al., Marine Chemistry, 112, 102-106 (2008)