Mercury Deposit Distribution on the Intertidal Zones of Minamata Bay

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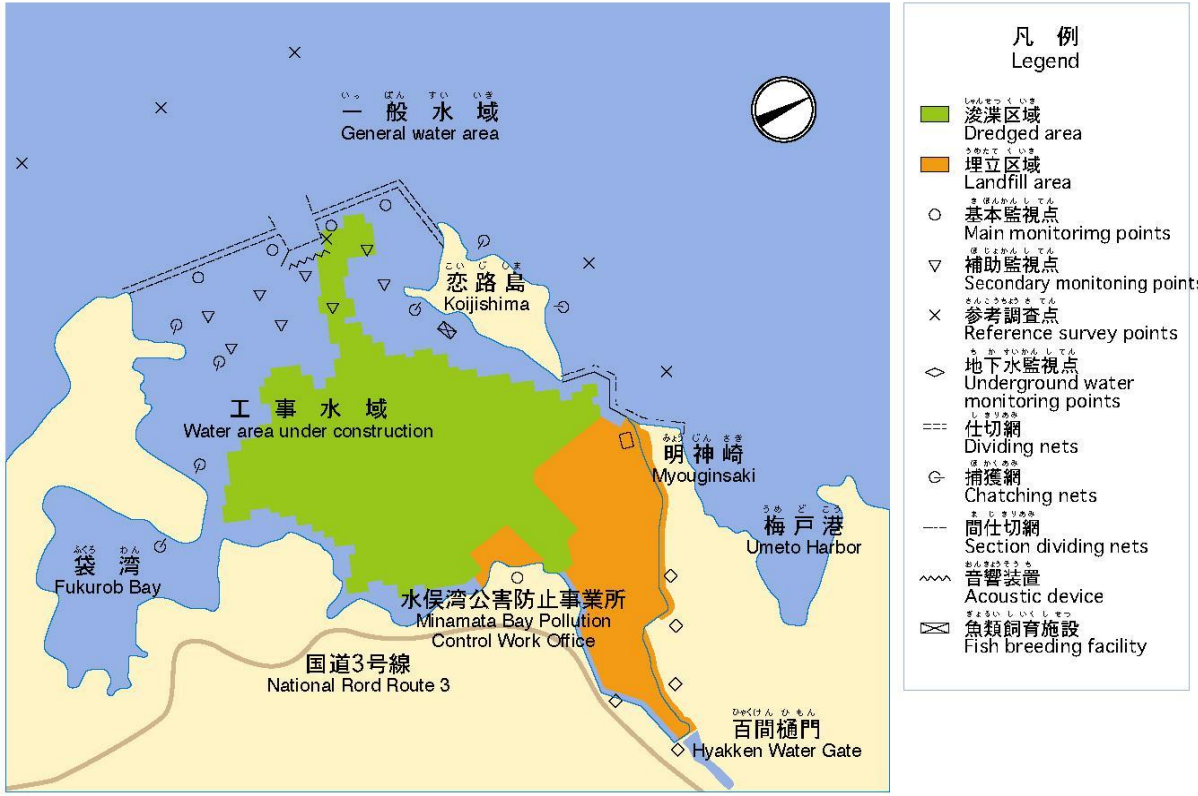
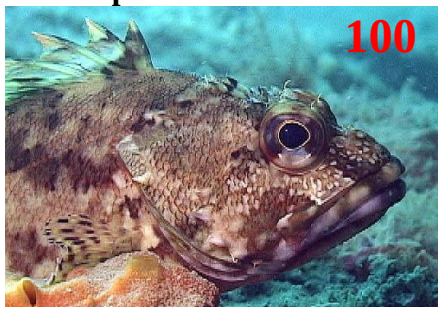
Remediation
1977 - 1990

4. Environmental restoration

Sludge containing mercury was deposited over an extensive area at the bottom of Minamata Bay. The area covered with sludge of over 25 ppm mercury concentration reached 2.09 million square meters. The volume of this highly polluted sludge is estimated at 1.51 million cubic meters. To confine the sludge in a reclaimed land section of Minamata Bay, an extensive construction project was carried out. Since the project necessitated various measures to prevent the spread of the pollutant, it took as long as 14 years from 1977 to 1990, including an intermission of three years. The total project cost of approximately 48.5 billion yen was shared by the national government, Kumamoto Prefecture, and Chisso Corp.; of the three, Chisso Corp. paid more than 60%. In addition to this project, Marushima fishing port and Hyakken drainage were dredged.



Scorpion fish



The rate of MeHg concentration in each species to that of Scorpion fish is shown in red character (? is not mesured yet)

Baits of Scorpion fish

10 | 30 | 30 | 15 | 15

(number is the rate of each biota)

Leptodius sp. 6.2

10

60

10

10 10

Alpheus sp.

30 ?

20

50

Gaetice sp.

5

? Hermit crabs

20

Polyplacophora sp.

?

40

30

50 50

Snails

Limpets

3

100

Small crastaceans

?

10

90

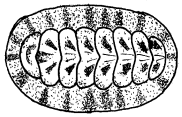
10 17

Lugworms

10 80

? Bibalb

100



100

Algae, Bacteria ?

Sediment 0.5

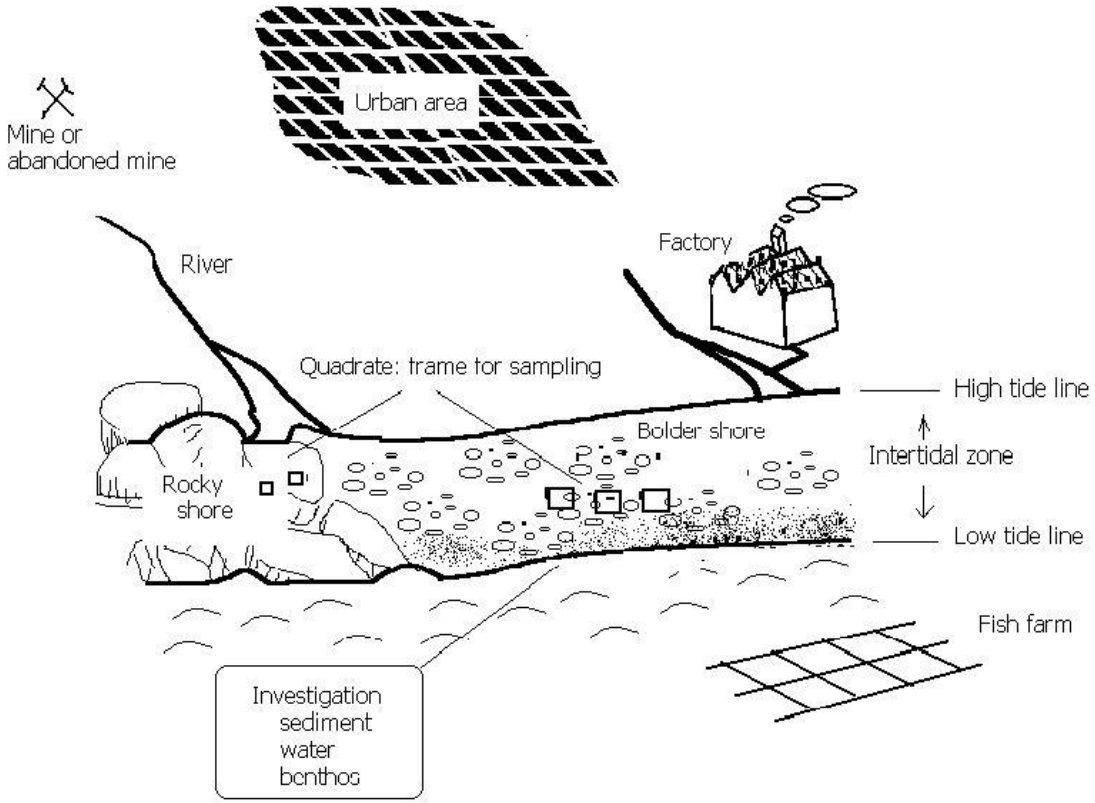
K. Mori & Y. Yasuda 2005

Intertidal zone

Border between land and sea, showing several types of shore profile (see right list).
Inportance of this zone in emvironmental area is based on the follows. Pollutant usually derived from land and diffuse through this zone. Biota at this zone (majority is invertebrate) is consumed as food by many kind of littoral fishes

Intertidal zone in Minamata Bay (inside m)

1. Rocky shore 1200 18.6%
2. Bolder shore 3150 48.9%
3. Sandy shore 0
4. Muddy shore 45 0.7%
5. Artificial sea bank 2045 31.8%



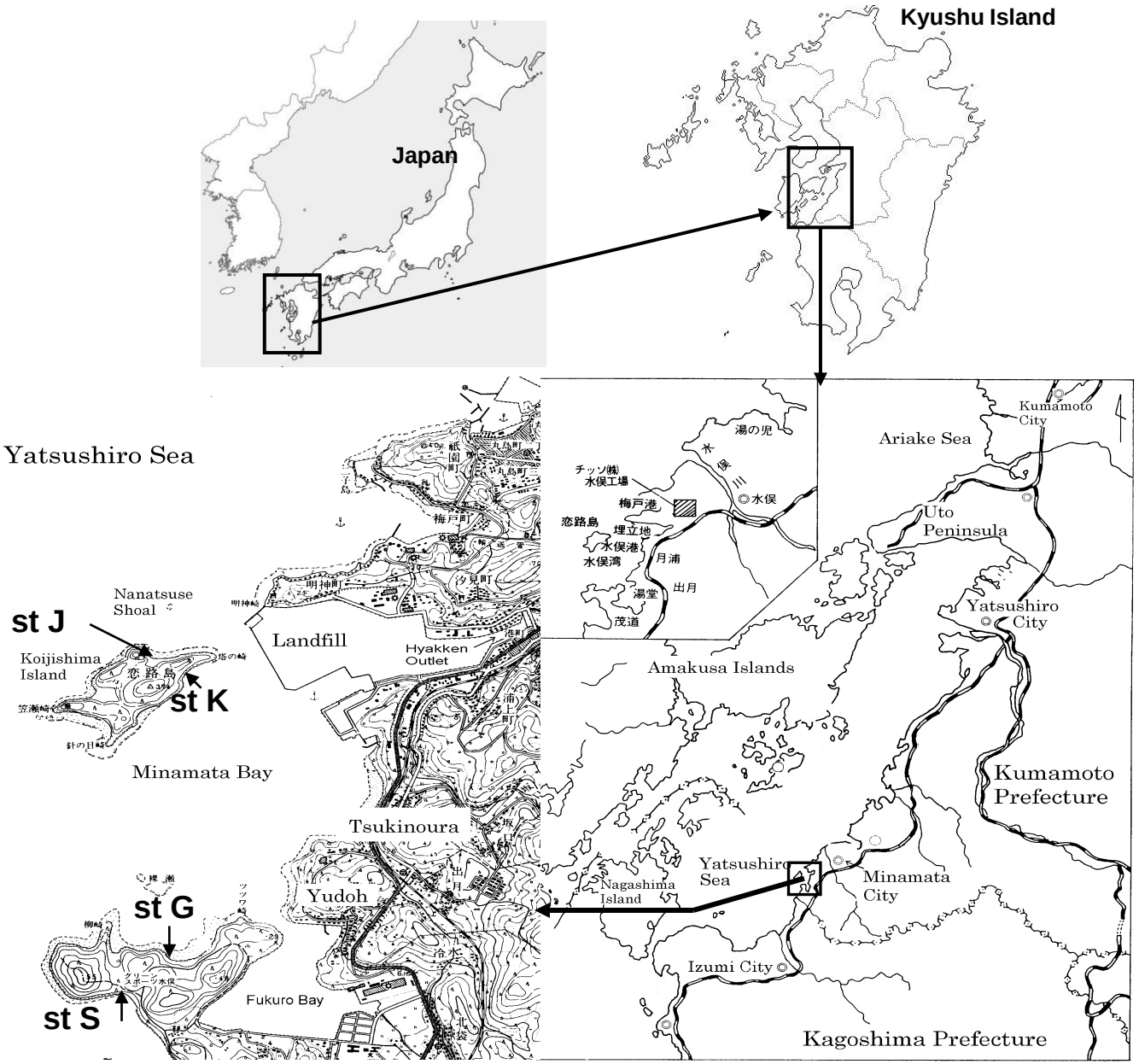
Objects of the present study:

Clarify the mercury deposit distribution at intertidal zones of Minamata Bay as a start point of the bio-accumulation and bio-magnification through food web

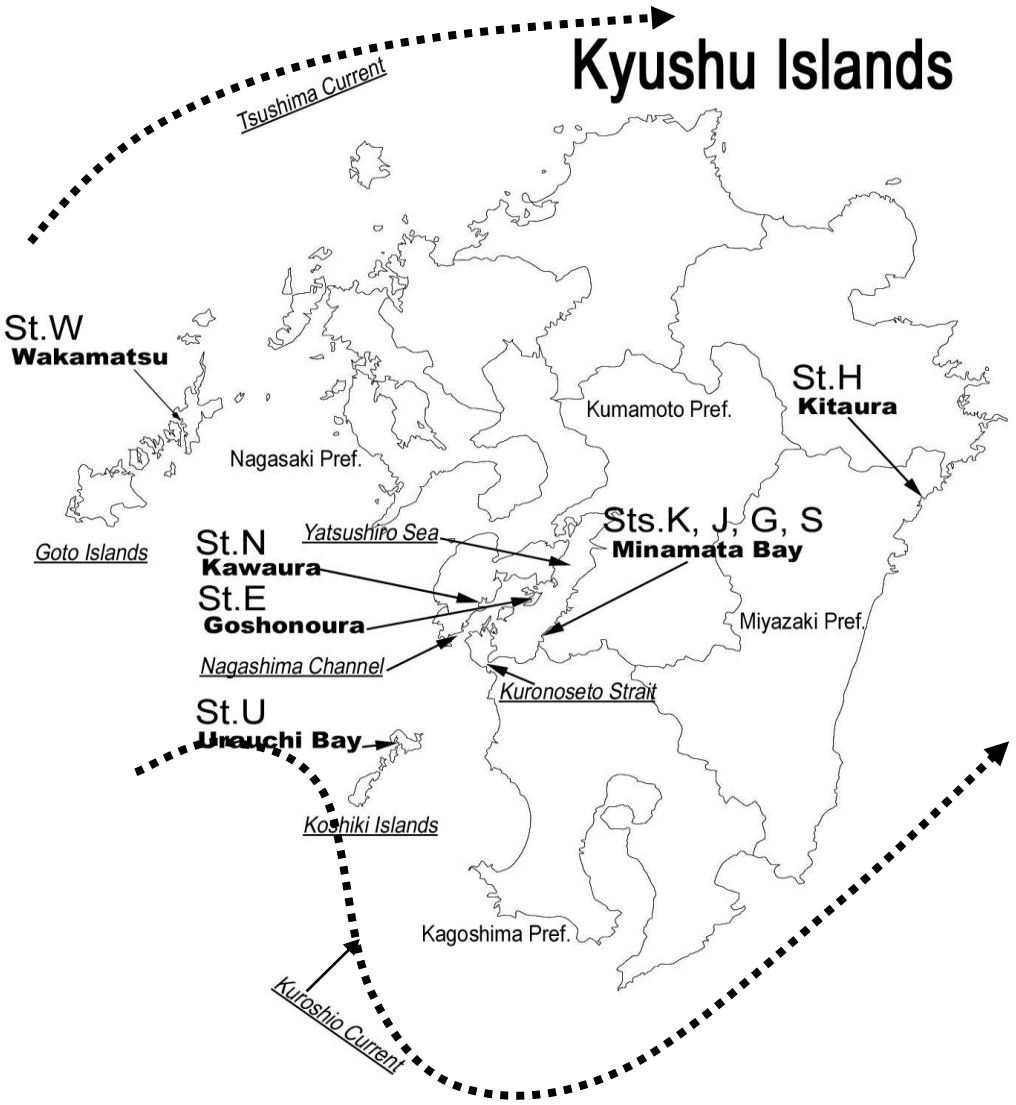
Procedure for the present study:

Total and methyl mercury analyses of sediments at intertidal zones of two stations inside and other two outside the bay. Data are compared with that of the control stations set at other region.

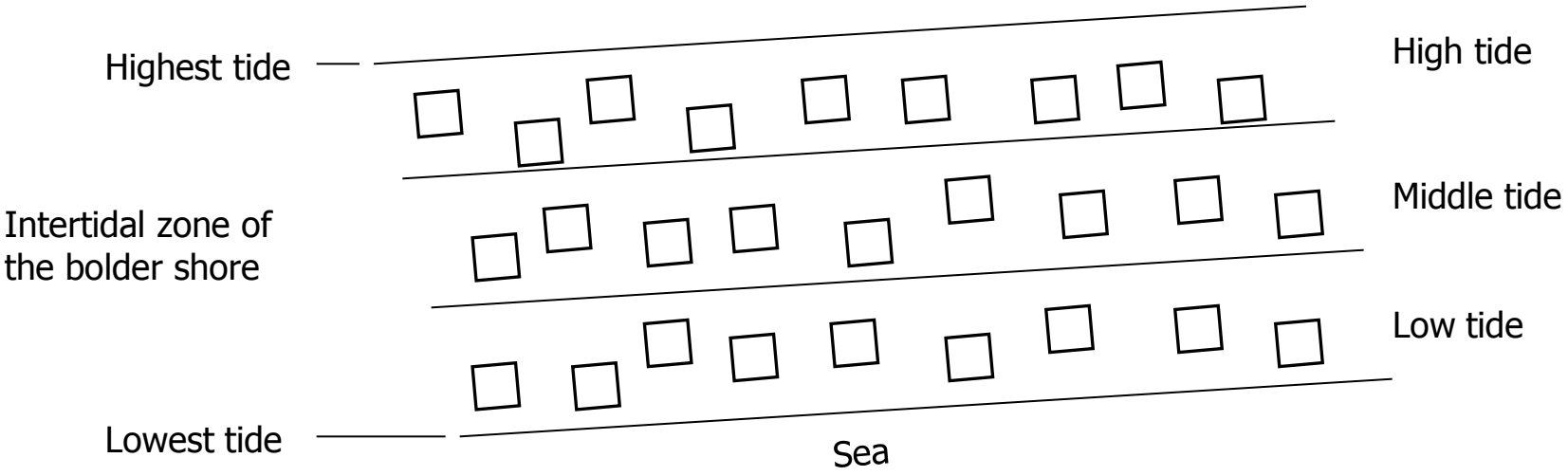
Locations of the sampling stations in Minamata Bay

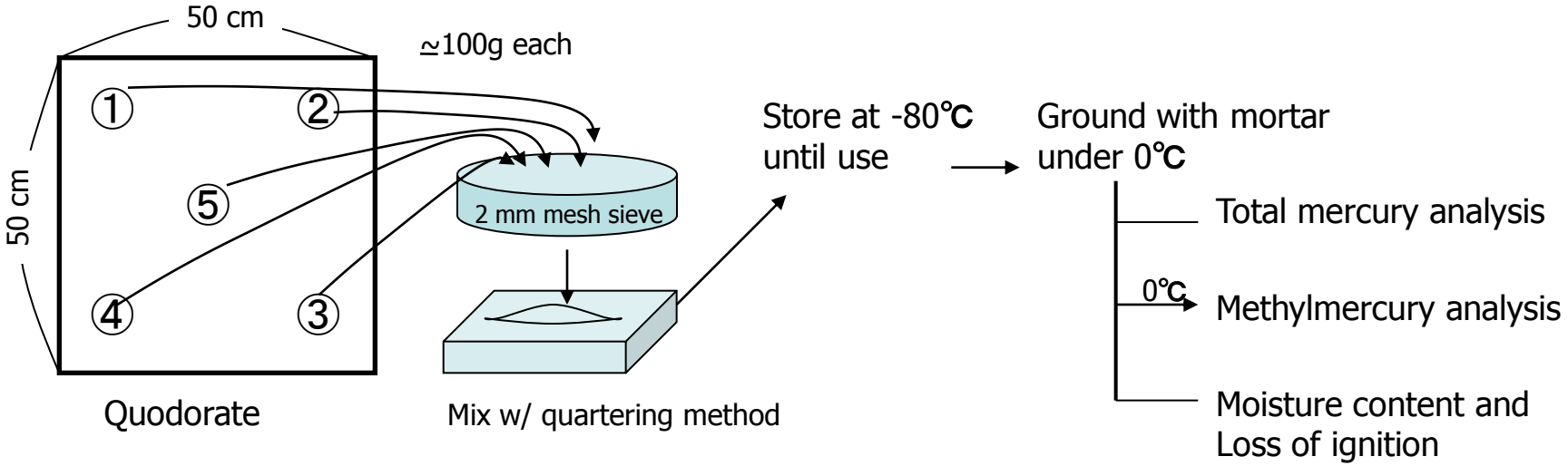


Locations of stations (controls)



Sampling method





Procedure for THg measurement

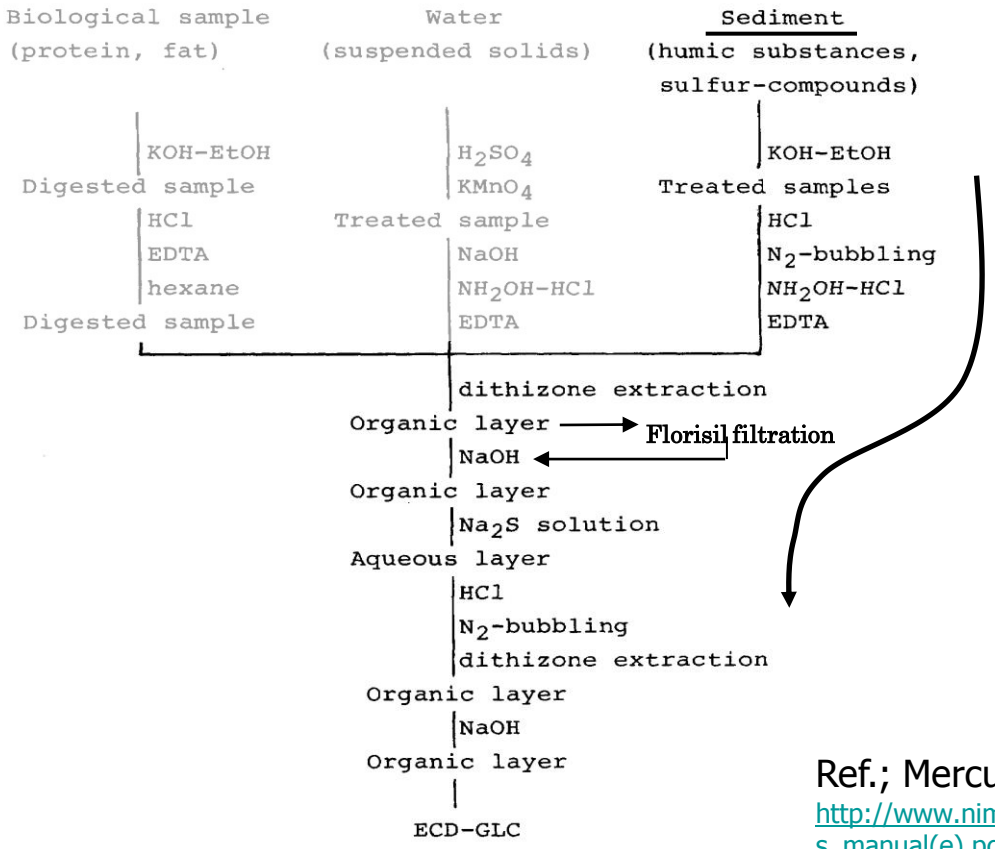
Sample (<0.4g) → Digest with acid mixture (1 ml H_2O, 2 ml (HNO_3+$HClO_4$, 1:1), and 5 ml H_2SO

↓ Reduce w/ $SnCl_2$

CVAA

Detection limit: 0.32 ng/g

Procedure for MeHg measurement



Detection limit: 0.12 ng/g

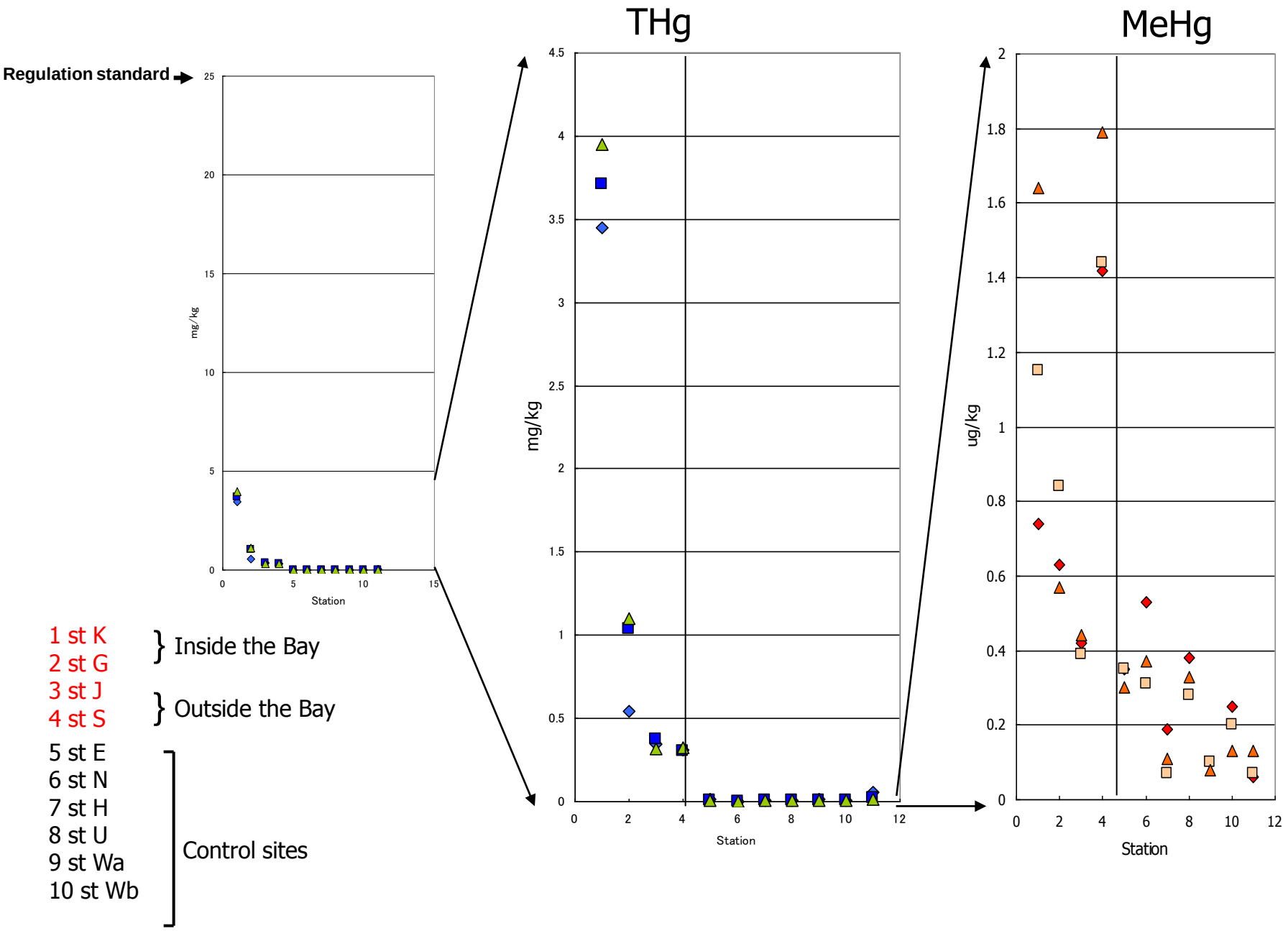
Ref.; Mercury Analysis Manual, 2004
http://www.nimd.go.jp/kenkyu/docs/march_mercury_analysis_manual(e).pdf

Quality checks of merucry analyses

Reference Materials			Certified values (ng/g)	*Measured values [average (ng/g) ± CI]
Dogfish meat by NRC	DORM-2	THg MeHg	4,640 ± 260 4,470 ± 320	4,670 ± 110 4,260 ± 100
Sediment by BCR	CRM-580	THg MeHg	132,000 ± 3000 75.5 ± 3.7	132,000 ± 2,000 76.0 ± 2.6
Sediment by IAEA	IAEA-405	THg MeHg	810 ± 40 5.49 ± 0.53	853 ± 13 5.52 ±0.34

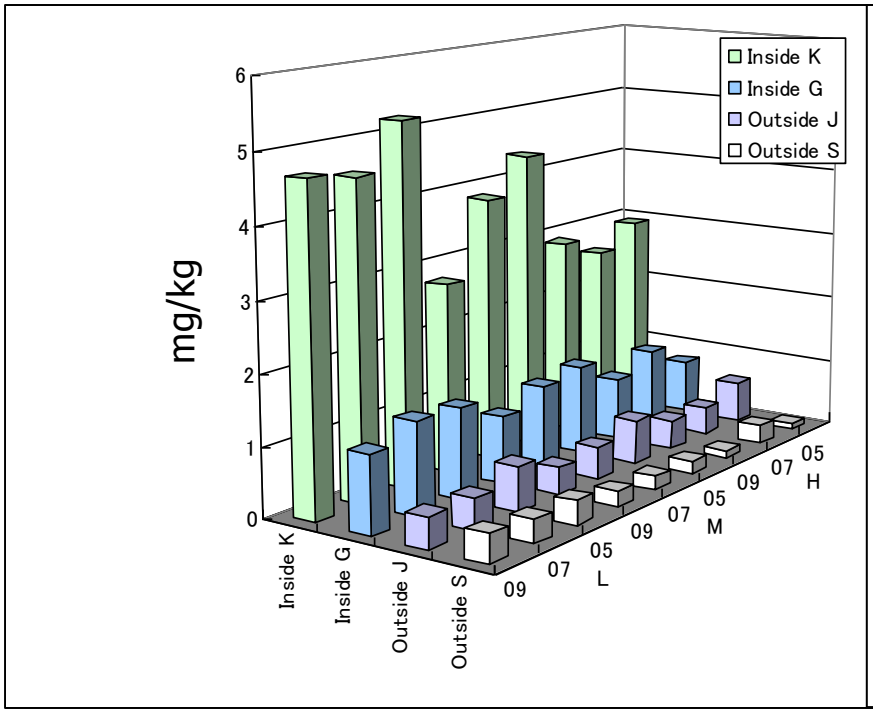
*Values are shown as means of 6 times repetitions
Whole data in this study is shown in the dry weight base
CI: 95% confidence interval
IAEA: International Atomic Energy Agency
NRC: National Research Council of Canada
BCR: Commission of the European Communities

Difference of mercury concentration levels among stations in 2003 - 2006

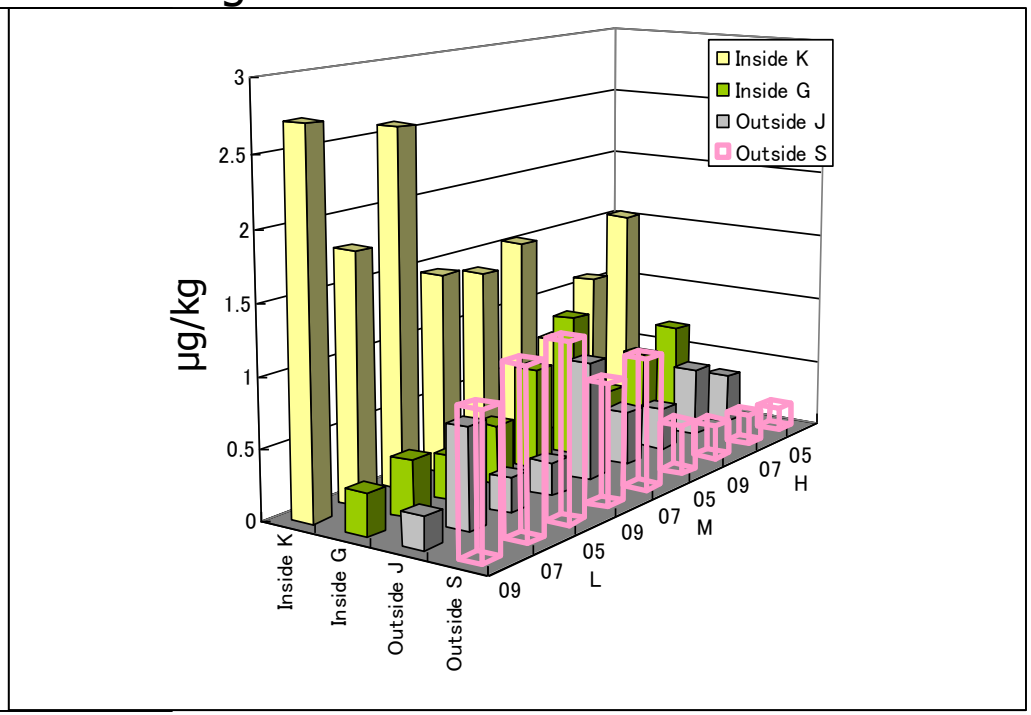


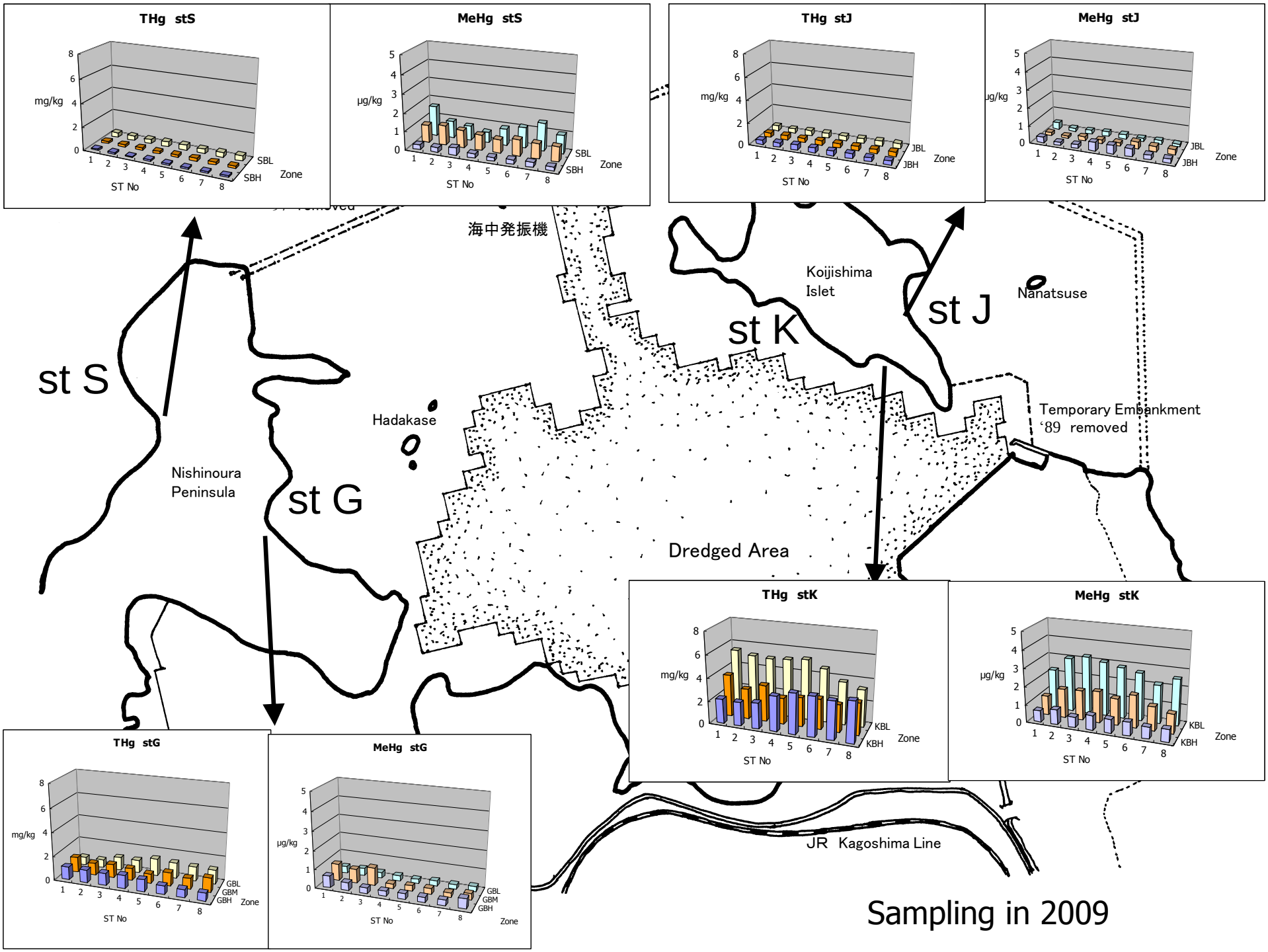
Mercury deposit distributions on the intertidal zones of Minamata Bay 2005 - 2009

THg

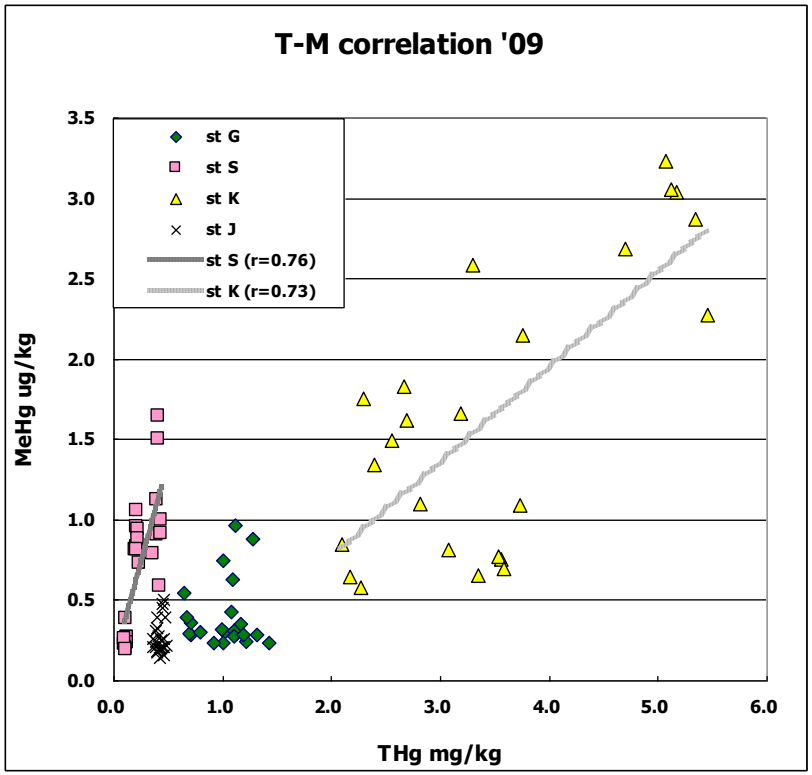


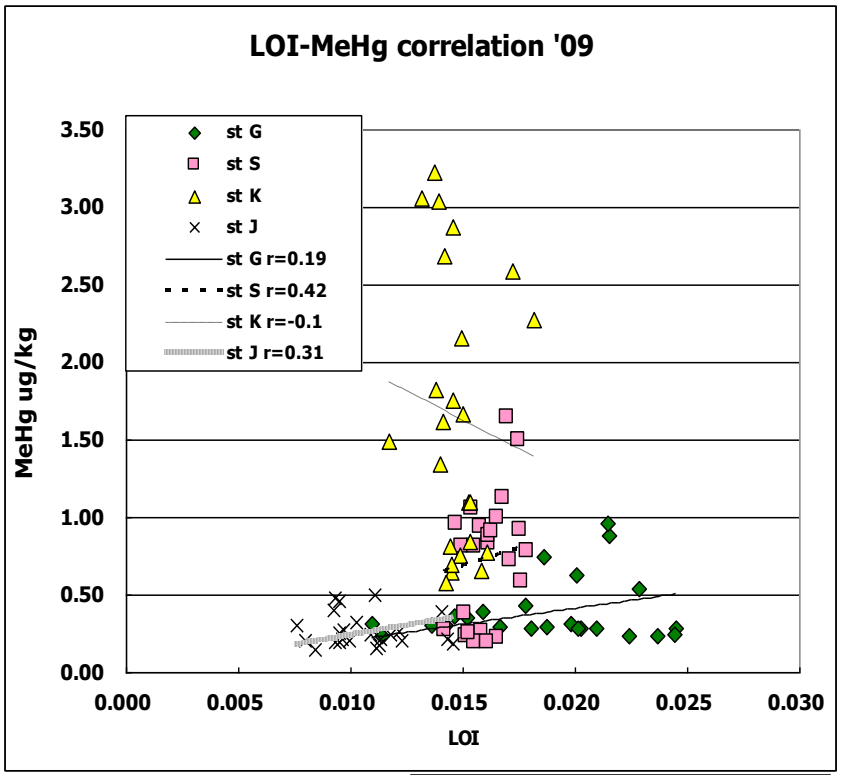
MeHg

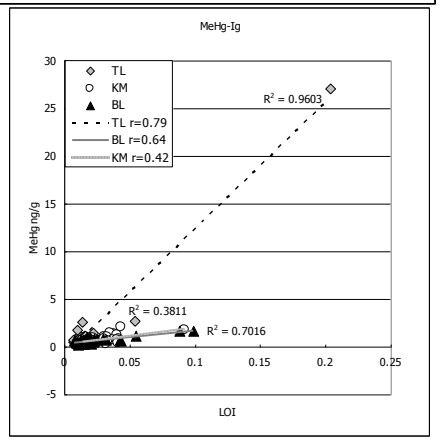



THg stS
mg/kg
ST No
SBL
SBH
Zone
MeHg stS
μg/kg
THg stJ
JBL
JBH
MeHg stJ
海中発振機
Koijishima
Islet
Nanatsuse
st J
st K
st S
st G
Hadakase
Nishinoura
Peninsula
Temporary Embankment
'89 removed
Dredged Area
THg stK
KBL
KBH
MeHg stK
THg stG
GBL
GBM
GBH
MeHg stG
JR Kagoshima Line
Sampling in 2009

Characteristics of mercury deposit on Minamata Bay intertidal zones







Correlation between MeHg and LOI of the sediment in rivers at gold mining area in North Sulawesi, Indonesia.

Conclusion

Mercury concentrations in sediment of intertidal zone of Minamata Bay bolder shores are less than 1/5 of the provisional standard value (25 mg/kg) but still higher than the background

A station at inside of Minamata Bay (st K) indicated highest concentration of both THg and MeHg

There seems to be an aliquot of MeHg exist in Minamata Bay which is a trace of that diffused by the anthropogenic activity in half a century ago

Acknowledgements

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On the Mercury Distribution at the Intertidal Zone of Minamata Bay

Abstract

Half a century after the serious mercury spill from a chemical factory, which resulted in an epidemic impact on the residents through consumption of a large amount of fish and shellfish in Minamata Bay polluted by methylmercury included in the effluent from the factory. A large-scale remediation project was undertaken from 1977 to 1990 in Minamata Bay by removing more than 1.5 million cubic meters of contaminated sediment (including more than 25 mg/kg dry of total mercury) which was used for land reclamation. After a decade from the completion of the recovery project, an updated situation report on the distribution of mercury deposits in the sediment of the intertidal zone of Minamata Bay was undertaken.

At two stations inside (stK, stG) and two more (stJ, stS) outside the Bay, mercury distributions in the surface sediment of the boulder intertidal shore were quantified and compared with those in control regions. The investigation was conducted from 2003 to 2009, and sampling was performed in February or March every other year in that period. Intertidal shore was divided into three zones with tide height (high, middle and low tide), and 8 quadrates (50 cm square) were randomly set for each tidal zone. Sediment was taken from inside the quadrate frames after removing all benthos. Total mercury analyses were performed with cold vapor atomic absorption after digestion and reduction with the acid mixture (HNO_3, $HClO_4$, H_2SO_4) and stannous chloride. Methylmercury was quantitated with an electron capture detector type gas chromatograph (GC-ECD) after extraction in KOH-ethanol (1:1) and concentrated by dithizone-Na_2S-dithizone stepwise extraction.

The results may be summarized as follows. The total mercury concentration in the low tide zone was relatively higher (3.7 – 4.7 mg/kg dry wt) at stK than the natural level, with lower levels at three other stations (0.3 – 1.4 mg/kg dry wt). The control regions, however, showed even lower levels (0.005 mg/kg dry wt) than at those three stations. However, methylmercury distribution was high at stK (1.1 - 12.7 μg/kg dry wt) as well as relatively high (1.0 – 1.5 μg/kg dry wt). At stK, where the highest concentration was detected, methylmercury concentrations indicated a positive correlation ($r=0.7$) with that of total mercury. On the other hand, methylmercury concentration at stK indicated no correlation ($r=-0.1$) with loss of ignition. That is unlike the situation in a metallic mercury polluted area such as is involved in gold mining. On the other hand, at stS outside the Bay, both correlations indicated positive ($r=0.7$ and 0.4). This situation at stS resembles the distribution situation in a gold mining field ($r=0.9$ and 0.8).

The majority of the mercury detected in a gold mining field is derived from the metallic mercury released from the workplace for gold collection process. In addition, the values in the loss of ignition experiment provide an amount of organic carbon, which emphasizes why the whole methylmercury detected in the gold mining field was synthesized *in situ* by some bacterial activity with the inorganic mercury derived form the metallic mercury of gold mine usage. Therefore, the mercury distribution situation in stK of Minamata Bay may be assumed that the methylmercury detected in the Bay includes both the aliquot synthesized *in situ* on the beach and the another aliquot as a residue of the factory-derived methylmercury released half a century ago and may be still circulating in the environment of the Bay. Instead, the methylmercury detected in stS is synthesized *in situ* with higher methylation activity than other stations, and a much lower contribution of residual mercury.