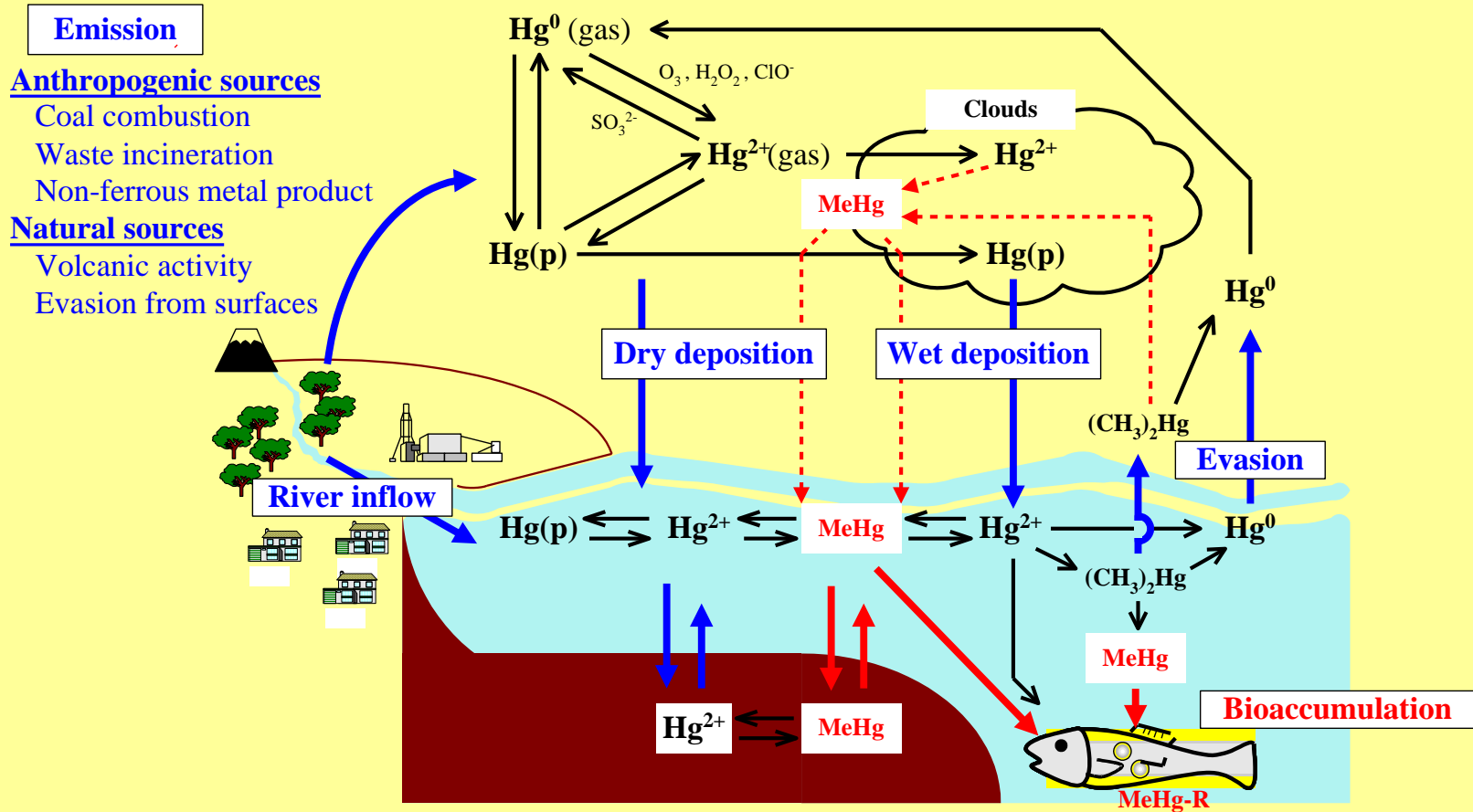


# Wet deposition fluxes of total and methyl mercury into Minamata Bay

National Institute for Minamata Disease

Kohji Marumoto, Akito Matsuyama

# Introduction(1)



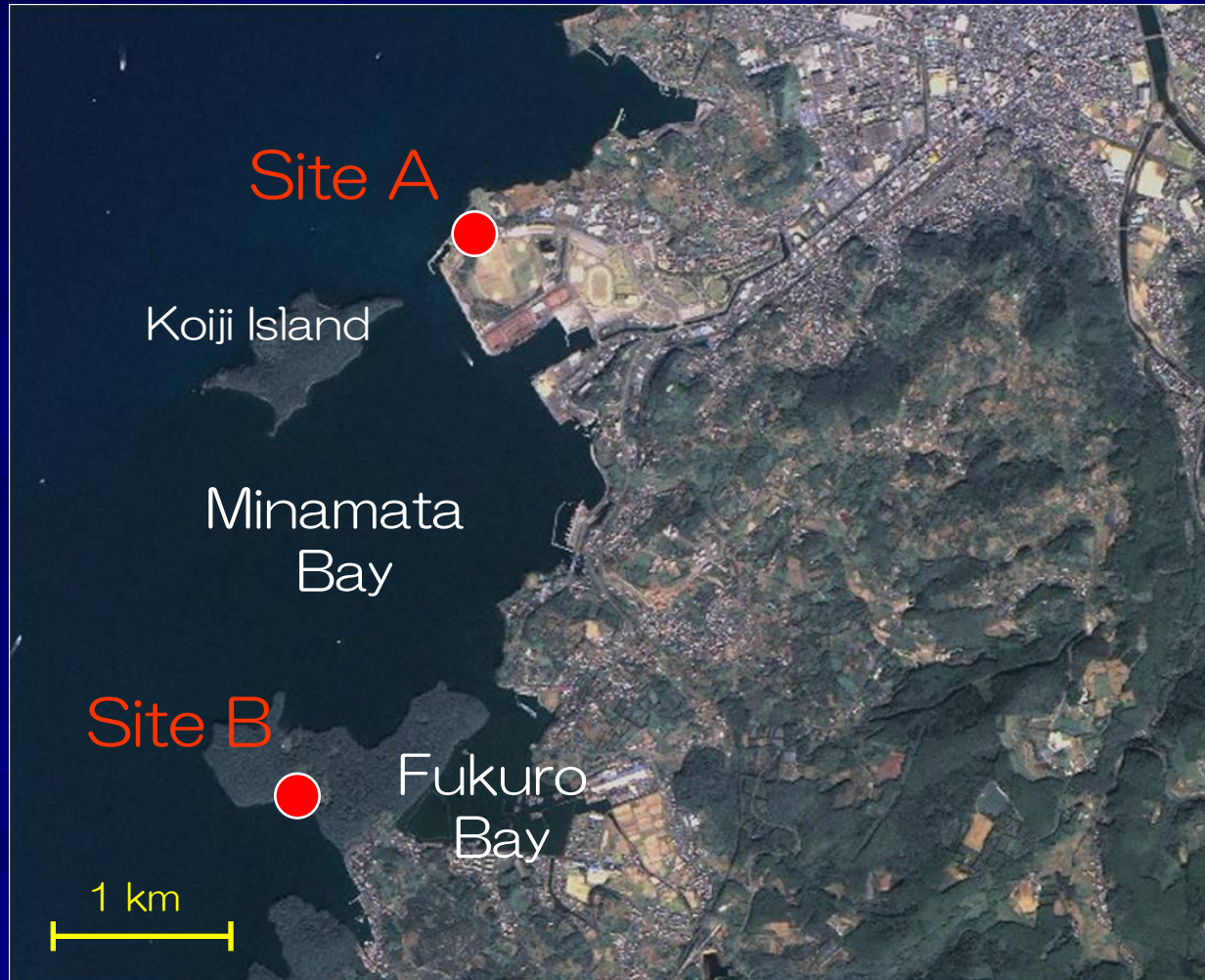
# Introduction(2)

- Atmospheric Hg is finally reached into aquatic environments through both wet and dry deposition processes.
  - Wet deposition process : Rain and Snow
  - Dry deposition process : Diffusion of gaseous Hg and  
Gravitational settling of particulate Hg
- In general, wet deposition plays a dominant role in total deposition of atmospheric Hg, compared to dry deposition.
- In case with atmospheric MeHg, there is little data on its wet deposition fluxes and deposition processes.

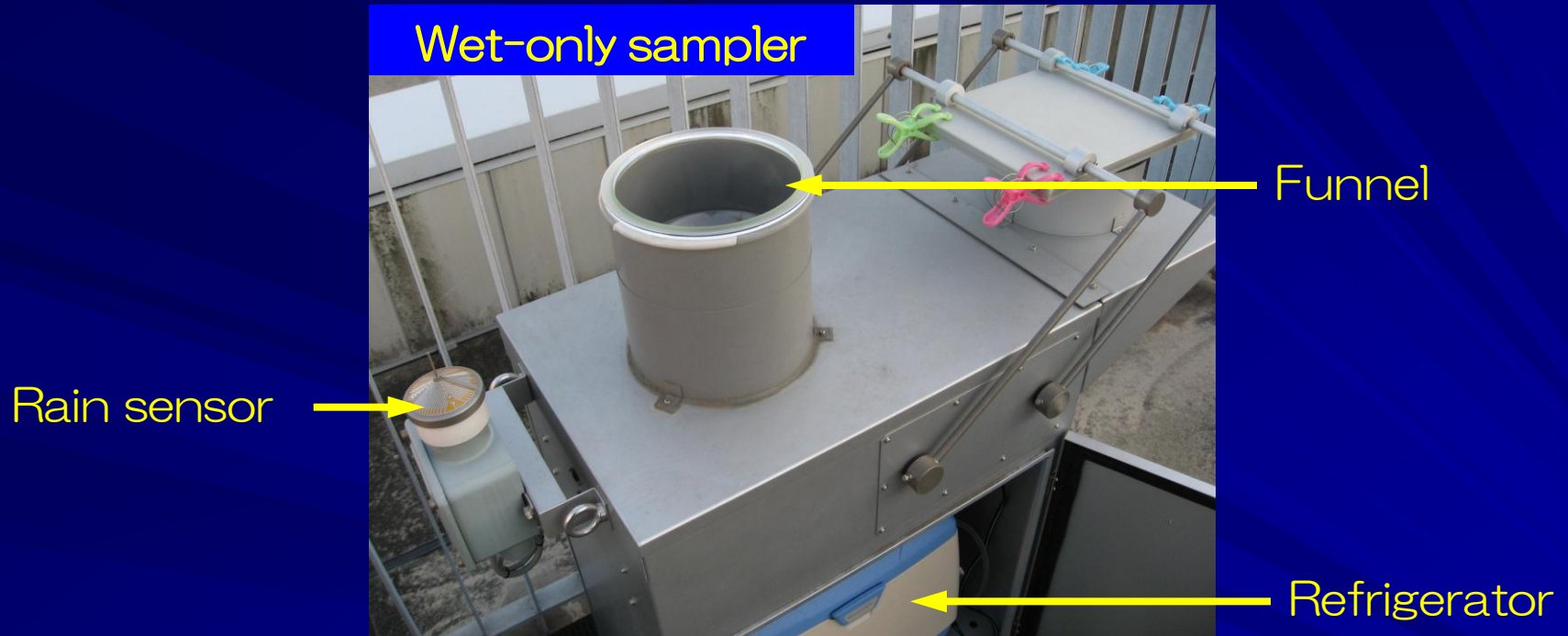
# Objectives in our research

- To investigate the wet deposition fluxes of total Hg and methyl Hg into Minamata Bay, one-year observation of them in wet depositions were carried out.
- In addition, other chemical components such as major ions and dissolved organic carbon (DOC) were also measured to elucidate factors influencing the variations of total and methyl mercury concentrations and to obtain information about their emission sources in the atmosphere.
- Minamata Bay area is selected for our research because total Hg and methyl Hg in seawater in the bay have been decreased in recent years. So, it is possible that the atmospheric loading of Hg significantly contributes as a source of Hg in the seawater.

# Location of sampling sites



# Sampling

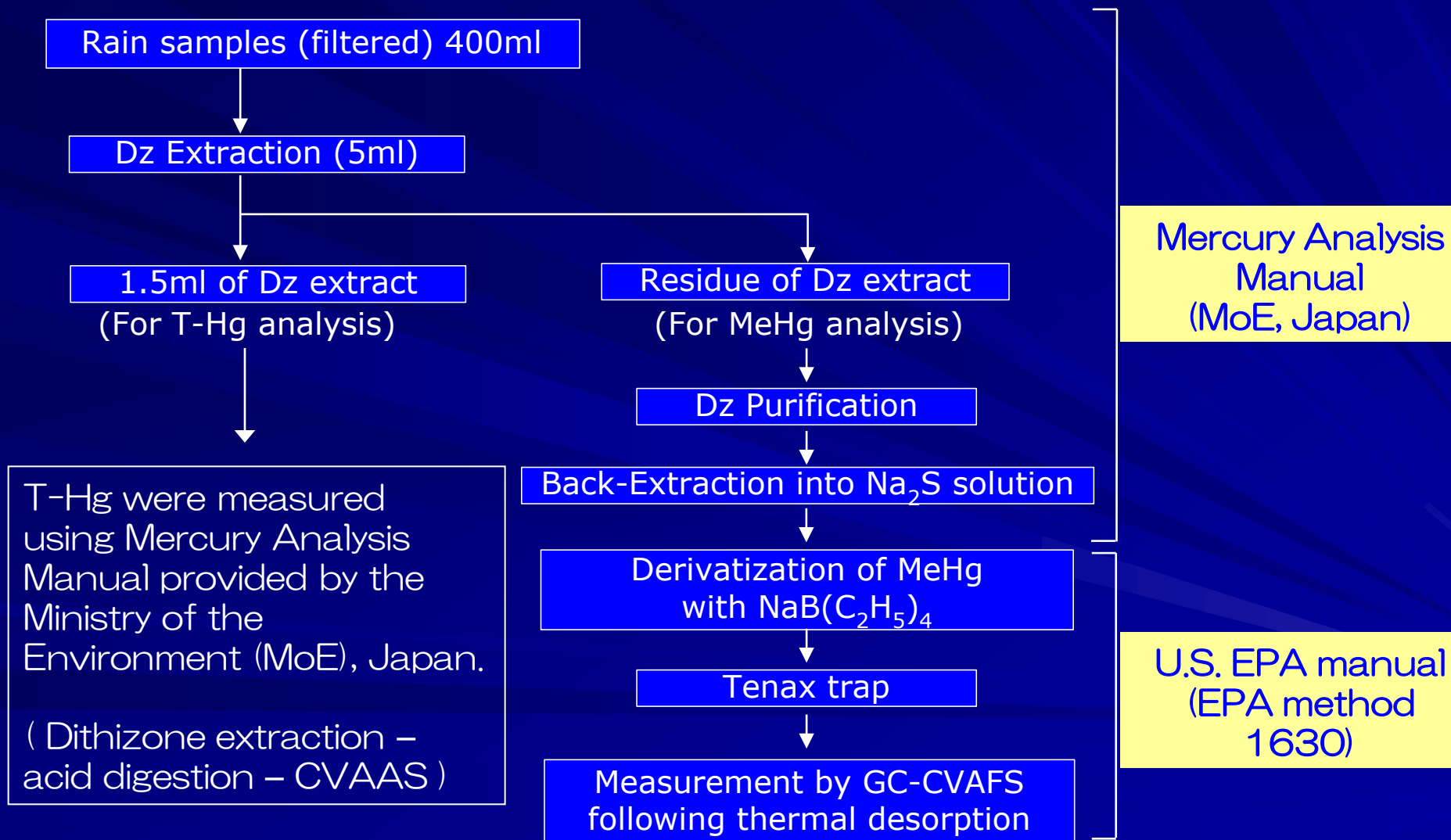


- Weekly wet deposition samples were collected using a wet-only sampler.
- The sample was filtered by itself using a  $0.45\ \mu\text{m}$  membrane filter and were stored at  $5^\circ\text{C}$  during the sampling.

# Measurements of chemical components in wet deposition samples

- T-Hg (Dissolved + Particulate)
- MeHg (Dissolved only)
- Major ions
  - $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$   $\Rightarrow$  Sea salt (Particle)
  - $\text{Ca}^{2+}$   $\Rightarrow$  Soil (Particle)
  - $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$   $\Rightarrow$  Human activity  
(Gas and Particle)
- pH ( $\text{H}^+$ )
- DOC (Dissolved Organic Carbon)  $\Rightarrow$  Organic matters

# Analytical method for T-Hg and MeHg in our research





# Advantages and disadvantages of our MeHg analysis

- Our method is simple, compared with the MoE method, but is more complicated than the EPA method.
- More than 100 ml of a sample can be treated. Therefore, our method has a high sensitivity because MeHg in large amount of a sample can be concentrated into Dz.
- Interferences of MeHg determination caused by organics in the sample are cancelled because CVAFS which has selectivity for Hg is installed for the detection of MeHg.
- The detection limit ( $3\sigma$ ) of our method is less than  $0.010 \text{ ng L}^{-1}$  ( Sample volume : 400ml ).

# Intercomparison of MeHg determinations with EPA method 1630

MeHg (ng L <sup>-1</sup> )	A: Distillation- Etylation (EPA method 1630)	B: Dz Extraction Etylation (Our method)	Difference/% $\frac{[A - B]}{(A+B)/2} \times 100$
Sample A	0.16	0.17	- 6.4%
Sample B	0.15	0.17	-13.7%

# Concentrations of T-Hg and MeHg

- Comparison with other regions -

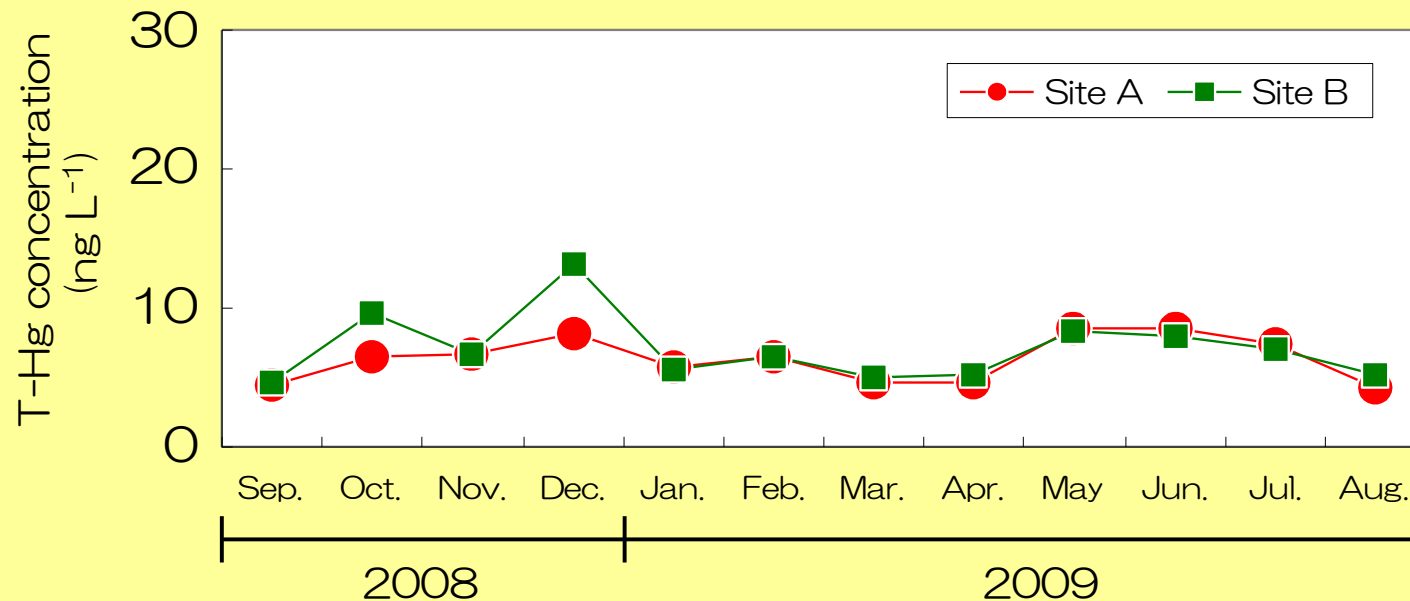
Site	MeHg (ng L <sup>-1</sup> )	Total Hg (ng L <sup>-1</sup> )	Reference
Wisconsin (Snow)	0.030	3.3	Lamborg et al, 1995
Wisconsin	0.10	7.9	Lamborg et al, 1995
NW Ontario	0.12	10.0	St. Louis et al., 2001
Ellesmere Island (Snow)	0.052	3.2	St. Louis et al., 2005
Maryland	0.040	10.8	Mason et al., 1997
Conneticut	0.18	6.7	Balcom et al., 2004
Equatorial Atlantic	< 0.008	4.6	Lamborg et al., 1999
Minamata (Site A)	0.071 * <sup>1</sup>	6.0	This work
Minamata (Site B)	0.070 * <sup>1</sup>	6.4	This work

The data in other regions from Hammerschmidt et al. (2007) Atmos. Environ. 41, 1663-1668

\*1 Dissolved only

# Seasonal variations of T-Hg concentrations

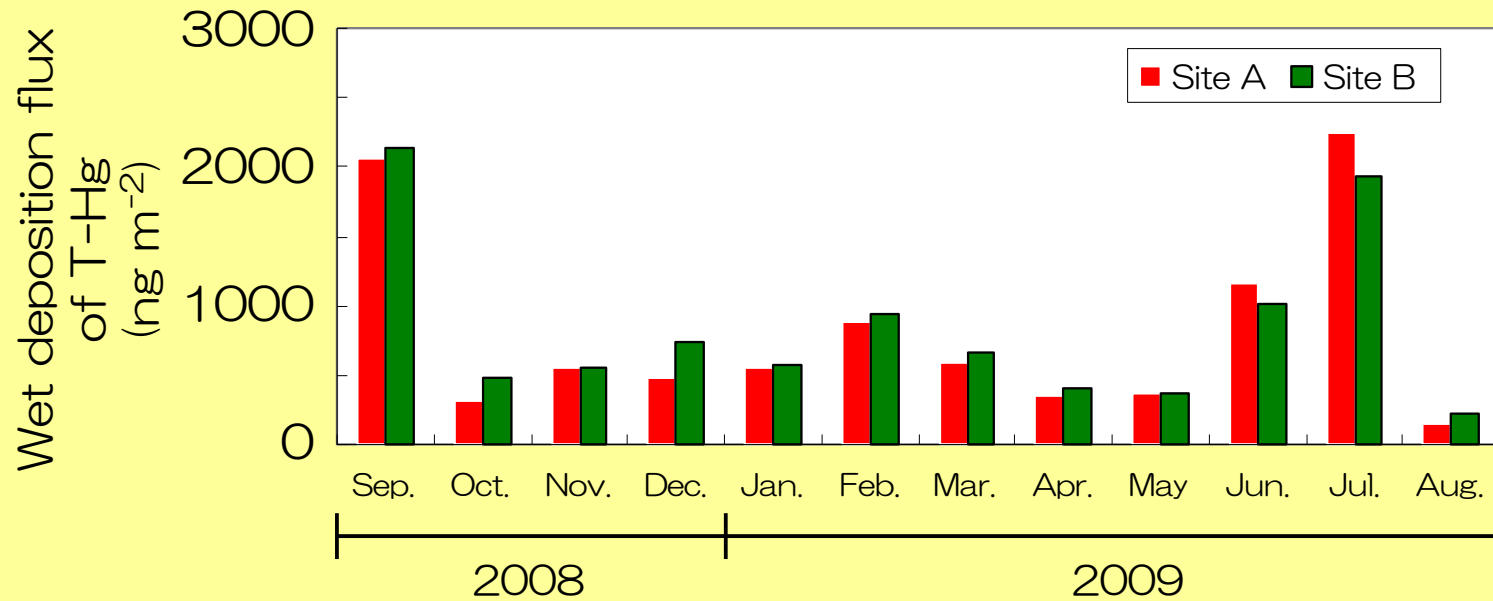
- Monthly volume-weighted average concentrations -



- T-Hg concentrations showed no seasonal variations.
- There were no differences of T-Hg concentrations at Sites A and B.



# Monthly wet deposition fluxes of T-Hg

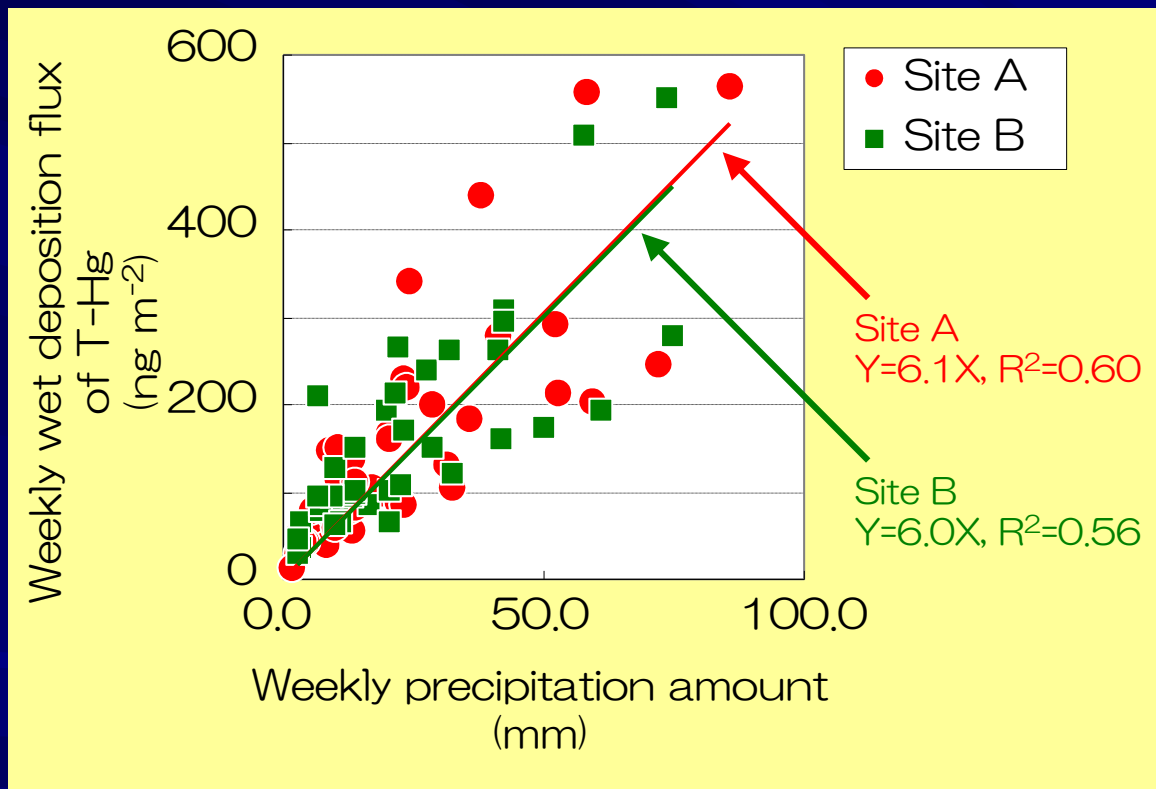


- The wet deposition fluxes of T-Hg increased in rainy season.
- Annual wet deposition fluxes during the period from September, 2008 to August, 2009

Site A:  $9.7 \mu\text{g m}^{-2}$

Site B:  $9.8 \mu\text{g m}^{-2}$

# Relationships between the weekly wet deposition fluxes of T-Hg and the weekly precipitation amounts

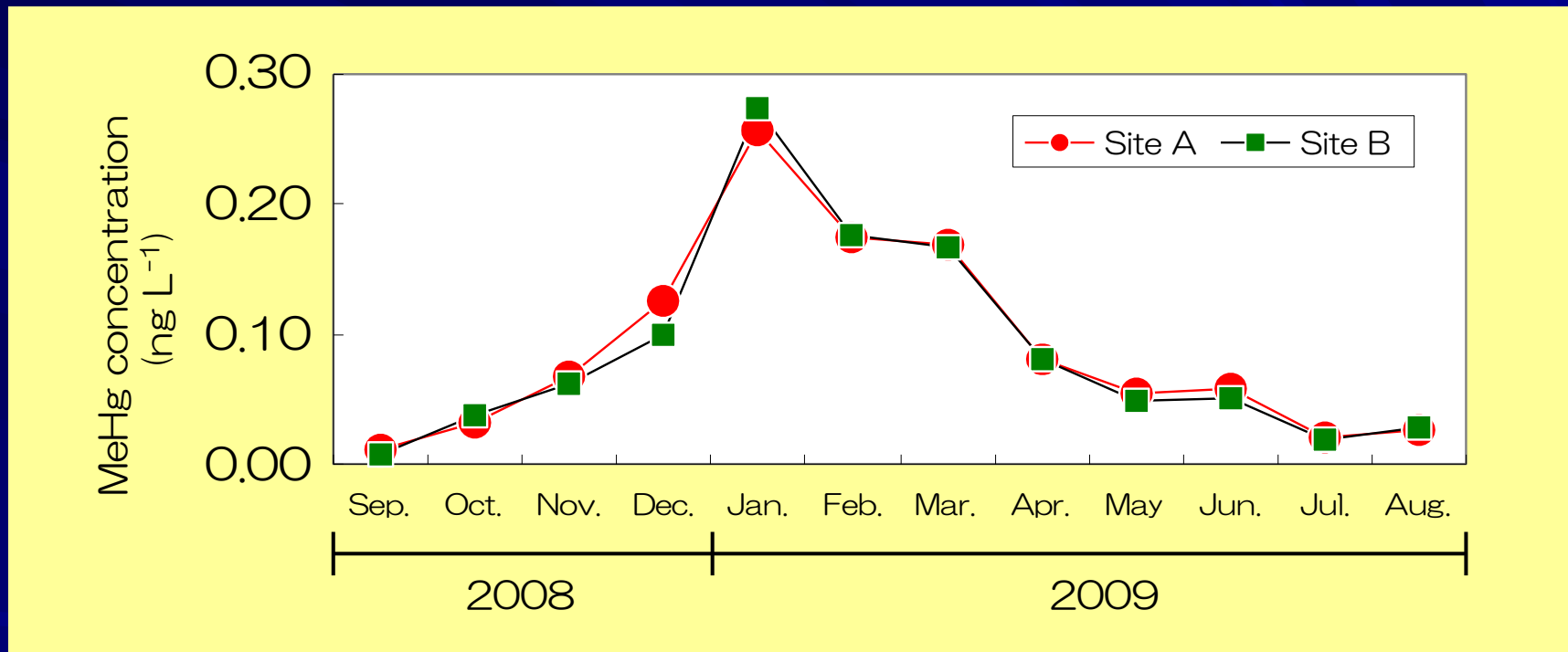


- This correlation is one of the specific characteristics on gaseous components in air, such as  $\text{NH}_3$  and  $\text{SO}_2$ .
- The wet deposition fluxes of T-Hg are dominated by scavenging of atmospheric gaseous divalent mercury because gaseous elemental mercury is difficult to dissolve into water.

\* The three overflow samples were excluded from the dataset.

# Seasonal variations of MeHg concentrations

– Monthly volume-weighted average concentrations –

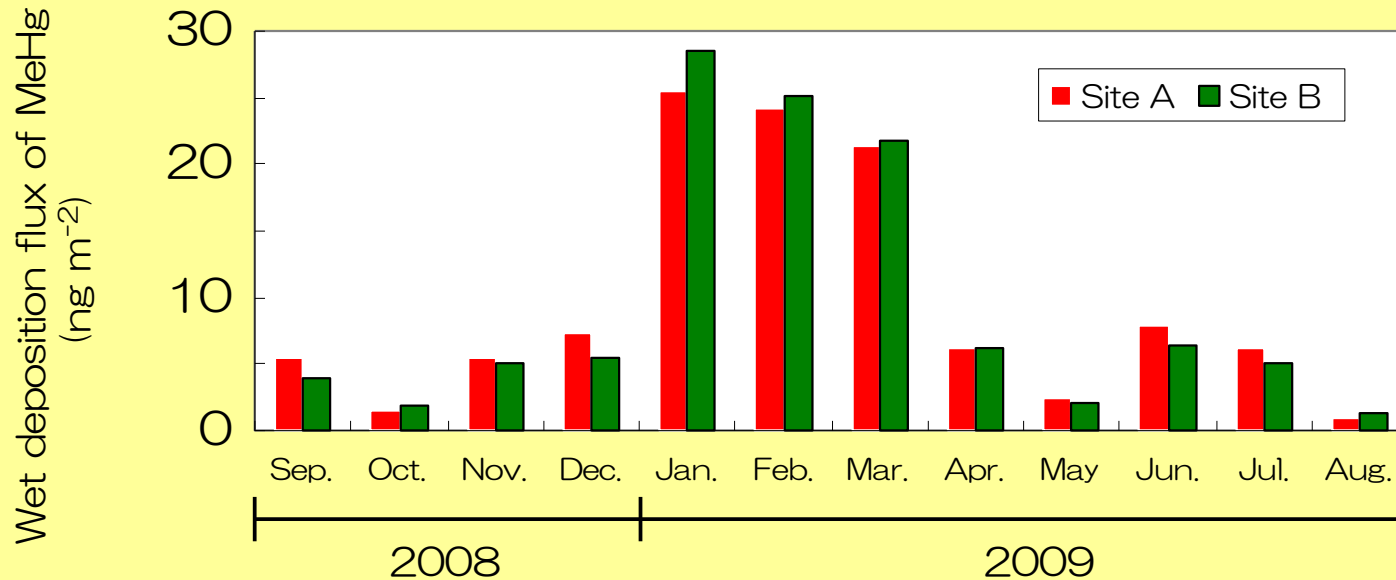


- MeHg concentrations were higher in winter than in summer.
- There were no differences of MeHg concentrations at Sites A and B.





# Monthly wet deposition fluxes of MeHg

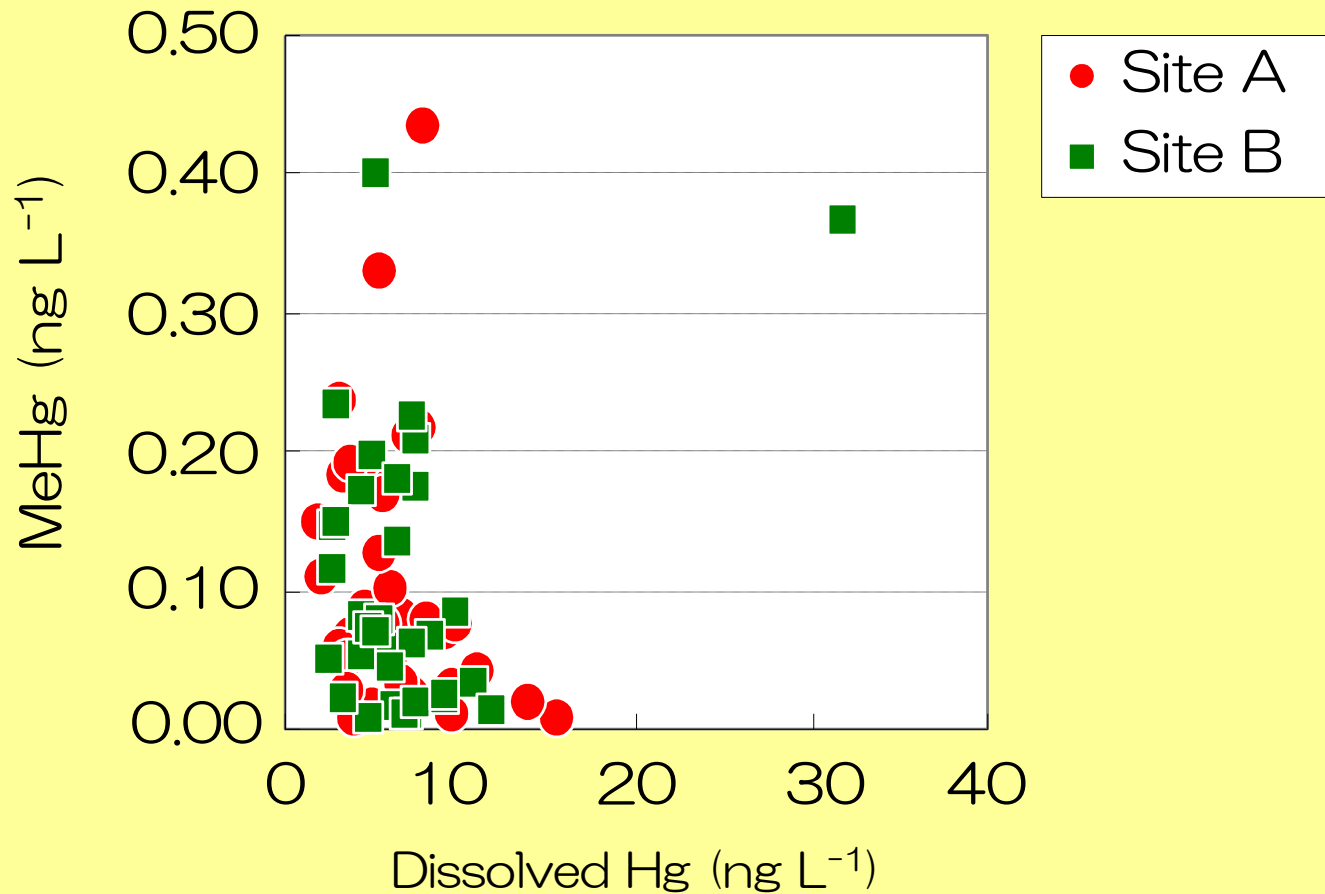


- The wet deposition fluxes of MeHg increased in winter.
- Annual wet deposition fluxes (dissolved form only) during the period from September, 2008 to August, 2009

Site A:  $0.11 \mu\text{g m}^{-2}$

Site B:  $0.11 \mu\text{g m}^{-2}$

# Relationships between dissolved Hg and dissolved MeHg



# Relationships between MeHg and other chemical components

Components	Physical forms in atmosphere	Correlation coefficients between MeHg and others	
		Site A (N=33)	Site B (N=33)
Cl <sup>-</sup>	Gas and Particle	0.34	0.33
NO <sub>3</sub> <sup>-</sup>	Gas and Particle	0.47 *	0.44 *
nss-SO <sub>4</sub> <sup>2-</sup>	Gas and Particle	0.41	0.27
Na <sup>+</sup>	Particle	0.34	0.34
NH <sub>4</sub> <sup>+</sup>	Gas and Particle	0.25	0.20
nss-K <sup>+</sup>	Particle	0.41	0.38
Mg <sup>2+</sup>	Particle	0.36	0.32
nss-Ca <sup>2+</sup>	Particle	0.39	0.35
H <sup>+</sup>		0.59 *	0.38
DOC **		0.60 *	0.63 *

\* P < 0.01

\*\* N=18 at Site A and N=17 at Site B

# Summary and Conclusions (1)

## T-Hg

- The volume weighted average concentrations at Sites A and B were 6.0 and 6.4 ng L<sup>-1</sup>, respectively. The concentrations had no seasonal variations.
- The annual wet deposition flux around Minamata Bay area was about 10 μg m<sup>-2</sup>. About 40 g of atmospheric Hg was directly deposited into the surface of Minamata and Fukuro bay via the wet deposition process.
- The fluxes showed a strong correlation with the precipitation amounts. In addition, about 80% of total was dissolved form. These indicates that Hg wet deposition fluxes is dominated by the precipitation scavenging of gaseous divalent Hg.

# Summary and Conclusions (2)

## MeHg

- The volume weighted average concentrations at Sites A and B were both  $0.07 \text{ ng L}^{-1}$ , respectively
- The annual wet deposition flux into Minamata Bay was about  $0.1 \mu\text{g m}^{-2}$  (1 % of total Hg). This is the first data in Japan.
- The concentrations and the wet deposition fluxes were higher in winter than in summer.
- MeHg concentrations were significantly correlated with DOC concentrations, suggesting that inorganic Hg are methylated by organics. However, it is unknown what kinds of organics mainly contribute Hg methylation in the atmosphere. Further research is needed.

## ■ Acknowledgement

We wish to thank Dr. Steve for useful collaboration with low-level MeHg analysis (EPA method 1630). We are also grateful to thank Y. Taniguchi, Y. Kawai and A. Kubo for their valuable assistance in this research.

**Thank you for your attention**

# Wet deposition fluxes of total and methyl mercury into Minamata Bay

Kohji Marumoto

(National Institute for Minamata Disease, Risk Evaluation Section)

To investigate the wet deposition process and fluxes of atmospheric inorganic and methyl mercury (Hg) in the Minamata Bay area, the concentrations of total and methyl Hg were measured at 2 sites around the Bay during the period from September, 2008 to August, 2009. Major ions ( $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{H}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ) and dissolved organic carbon (DOC) were also measured to obtain useful information on deposition processes of atmospheric gases and particulate matters and sources of atmospheric Hg. In addition, observation of meteorological parameters such as air temperature, humidity and solar radiation were conducted.

The volume weighted averaged concentrations of total Hg (soluble Hg + suspended Hg) in the wet depositions were approximately  $6.0 \text{ ng L}^{-1}$ , ranging from  $3.2 \text{ ng L}^{-1}$  to  $33 \text{ ng L}^{-1}$  at 2 sites around Minamata Bay. About 80% of total mercury in the wet depositions was soluble. The direct loading of total Hg by the wet deposition into the Bay during the sampling period was  $9.8 \mu\text{g m}^{-2} \text{ yr}^{-1}$ , which was slightly lower than the average wet deposition flux at 10 sites in Japan ( $12.8 \pm 3.9 \mu\text{g m}^{-2} \text{ yr}^{-1}$ ). The wet deposition fluxes of total Hg were significantly correlated with the precipitation volumes as with  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  that mainly exist in gaseous forms in the atmosphere. Therefore, this correlation is probably because Hg wet deposition is dominated by the precipitation scavenging of atmospheric gaseous Hg (reactive gaseous Hg, RGM). In our research on Hg speciation in air, it was clear that the RGM concentrations in air had a significant correlation with oxidants (primarily  $\text{O}_3$ ). This indicates that the RGM originates from the oxidation of elemental Hg ( $\text{Hg}^0$ ) by  $\text{O}_3$  as is the case with the Minamata Bay area.

On the other hand, the volume weighted average concentrations of soluble methyl Hg in wet depositions at 2 sites ranged widely from  $0.008$  to  $0.43 \text{ ng L}^{-1}$ . They were elevated during the period from late autumn to early spring (cold season), though the concentrations of total Hg had no seasonal variations. The concentrations of methyl Hg had significant positive correlations with the concentrations of  $\text{NO}_3^-$  and DOC. Therefore, it is possible that methyl Hg is produced by biochemical reactions including Hg methylation with microorganisms. However, it remains unclear that methyl Hg concentrations in the wet depositions become higher in the cold season. Further research on methylation and demethylation processes of atmospheric Hg including the behaviors of methylated agents such as organic substances and microorganisms is need.