

Mercury Monitoring Activities by NIMD and other organizations in Japan

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(NIMD)

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Monitoring for atmospheric mercury & other heavy metals in Japan

Organizations:

- Ministry of the Environment, Japan (MOEJ)
- National Institute for Environmental Studies (NIES)
- National Institute for Minamata Disease (NIMD)
- College of Niigata Institute of Technology (NIIT)

Framework:

- Our monitoring activities are carried out individually.
- We have no monitoring network for atmospheric Hg.

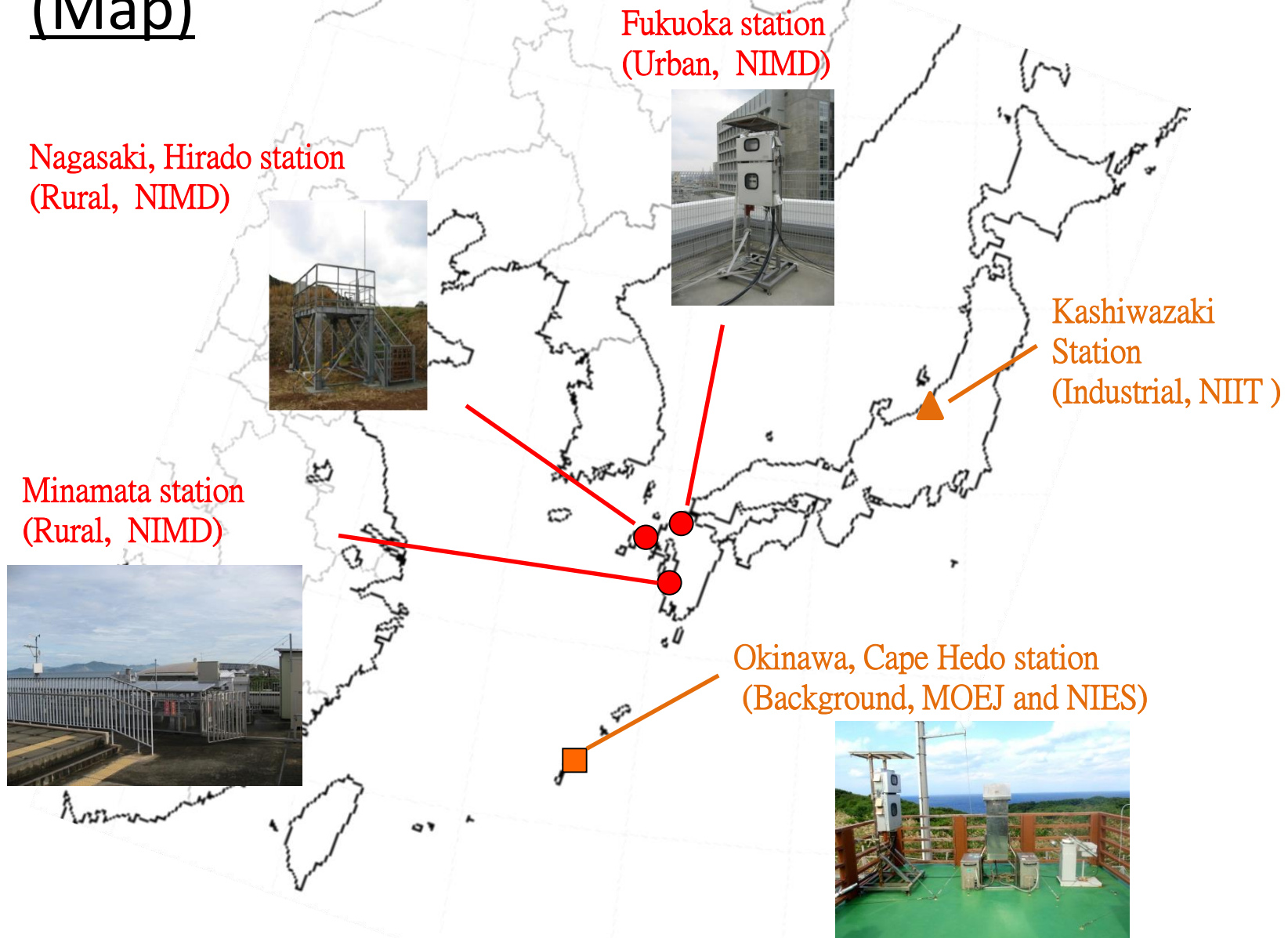
Monitoring for atmospheric mercury & other heavy metals in Japan

Objectives:

- Monitor current levels of mercury (Hg) and other heavy metals in air, particles, and precipitation;
- Obtain useful information on the long-range transportation of mercury and other heavy metals in Asia-Pacific region;
- Develop monitoring Methodologies;
- Contribute to the international efforts in atmospheric monitoring

On-going mercury monitoring sites in Japan

(Map)



On-going mercury monitoring sites in Japan

(Site description 1)

Sites	Organizations	Latitude	Longitude	Height	Monitoring Start
Cape Hedo (Background)	MOEJ and NIES	26.87 N	128.26 E	60m a.s.l.	From 2007/02 ~
Minamata (Rural)	NIMD	32.20 N	130.37 E	20m a.s.l.	From 2008/09 to 2010/08 and From 2011/01~
Hirado (Rural)	NIMD	33.35N	129.58 E	50m a.s.l.	From 2011/06 ~
Fukuoka (Urban)	NIMD	33.55N	130.36 E	55m a.s.l.	From 2012/06 ~
Kashiwazaki (Industrial)	NIIT	37.34 N	138. 58 E	40m a.s.l.	From 2010/07 ~

On-going mercury monitoring sites in Japan (Site description 2)

Sites	Organizations	Hg speciation (GEM, GOM, PHg) In air	TGM	Hg in precipitation	Heavy metals In air and precipitation
Cape Hedo (Background)	MOEJ and NIES	○ Continuous (by Tekran)		○ Wet-only Weekly	○ LVS sampling Weekly
Minamata (Rural)	NIMD	△ Manual sampling 1 week a month	○ Continuous	○ Wet-only Weekly	△ (Air only) HVS sampling Weekly
Hirado (Rural)	NIMD	△ Manual sampling 1 week in <u>each season</u>		○ Wet-only Weekly	△ (Air only) HVS sampling Weekly
Fukuoka (Urban)	NIMD	○ Continuous (by Tekran)			
Kashiwazaki (Industrial)	NIIT	○ Continuous (by Tekran)			

Minamata Station

Weather station



Wet-only sampler
for precipitation



Manually operated offline
sampling system for GEM,
GOM and PHg



TGM monitor
CO monitor



High volume air sampler

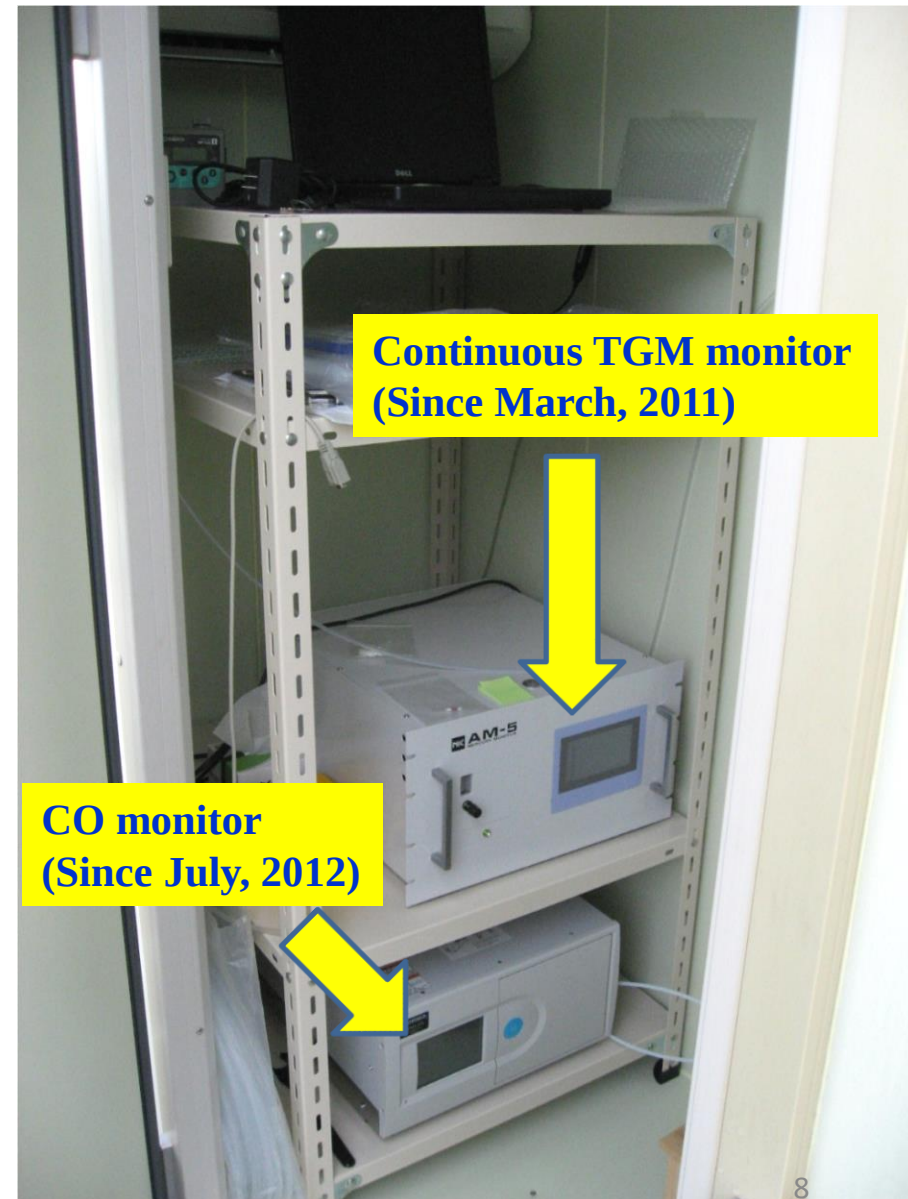


Minamata Atmospheric Mercury
Monitoring Station was set up at
the rooftop of Minamata Disease
Archive in the coastal area of
Minamata Bay (32.20N, 130.37E).

Minamata Station

Total gaseous Hg (TGM) is measured at 15minutes intervals using a continuous TGM monitor (AM-5, Nippon Instruments Corporation) since March, 2011 . The monitor is manually calibrated once a week using a standard gas of Hg(0).

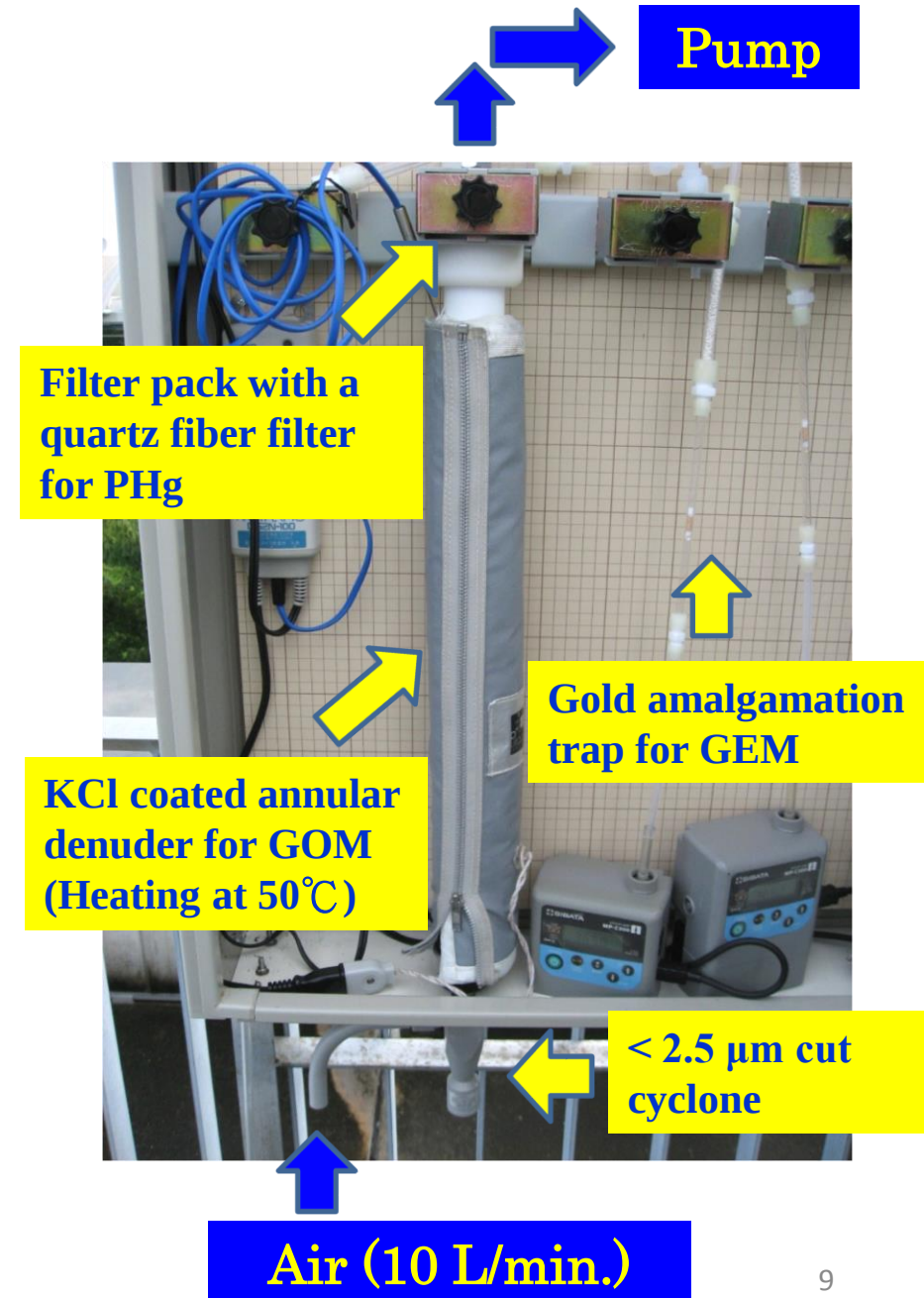
Monitoring of Carbon monoxide (CO) , which is an indicator (TGM/CO) of influences on long range transported Hg from Asian continent, are operated from July, 2012 to the present.



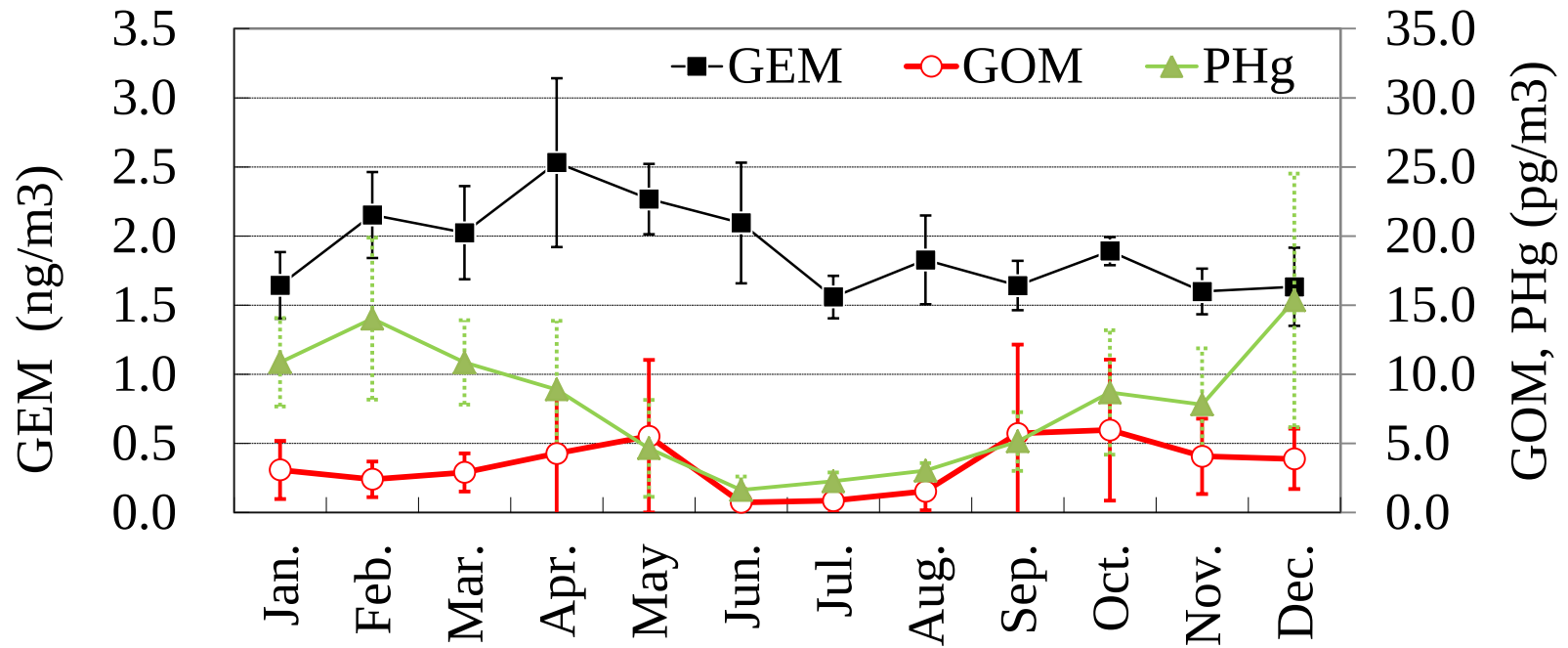
Minamata Station

Gaseous elemental Hg(GEM), gaseous oxidized Hg (GOM) and particle associated Hg (PHg) are sampled using a manually operated offline sampling system at about 12 hour intervals in 6 days a month.

After sampling, these Hg species are measured by CVAFS or CVAFS following thermal desorption. The detection limits (3σ) of GEM, GOM and PHg are 0.3 ng/m^3 , 0.6 pg/m^3 and 1.7 pg/m^3 , respectively.



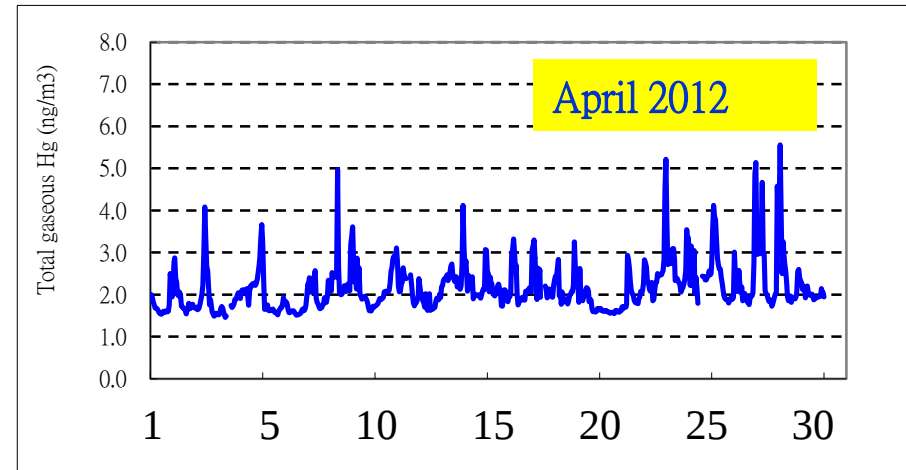
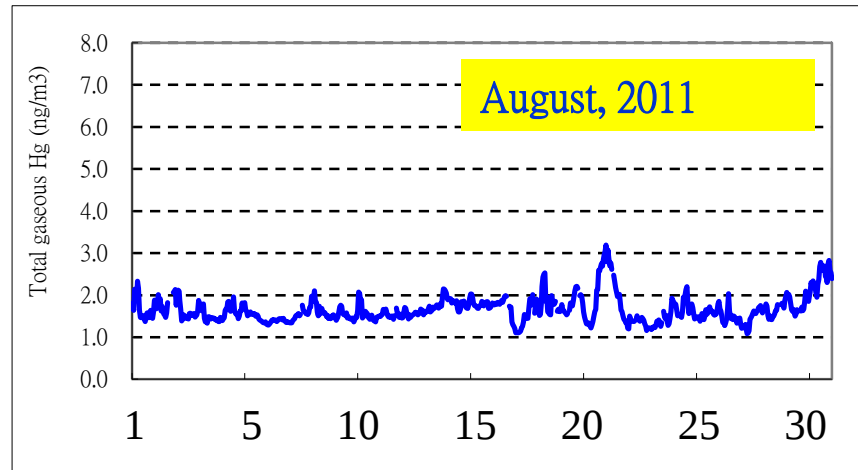
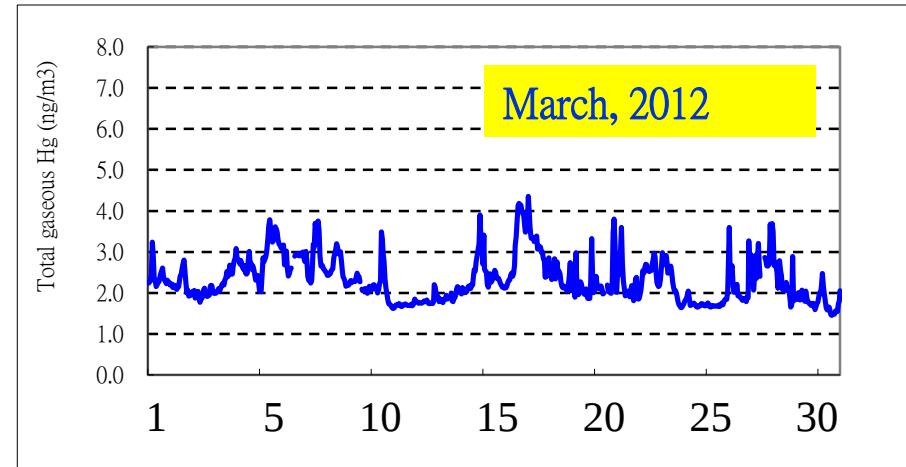
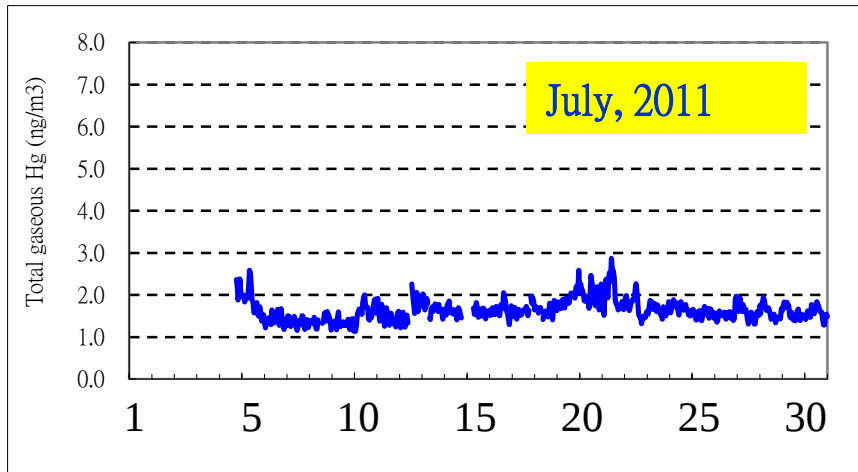
Seasonal variations on concentrations of GEM and GOM, particulate Hg(PHg) at Minamata in 2011



Annual averaged concentrations

GEM (ng/m ³)	GOM (pg/m ³)	PHg (pg/m ³)
1.9 ± 0.4	3.4 ± 2.8	8.1 ± 6.0

Results on the continuous TGM monitoring at the Minamata station (hourly mean)

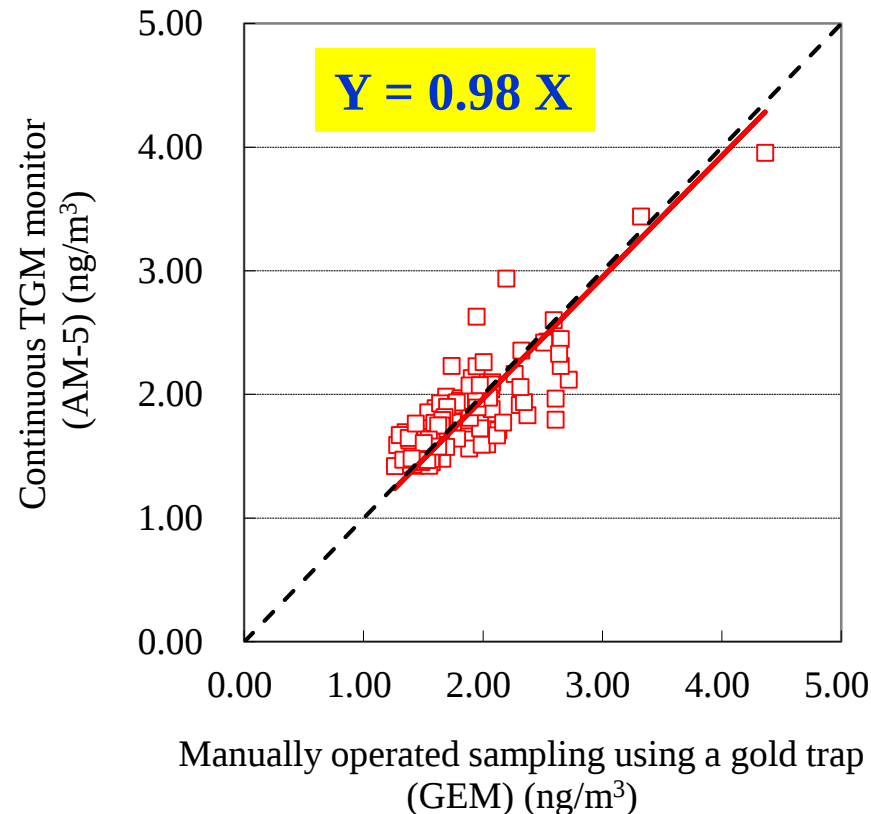


Comparison of Hg(0) measurement values at the Minamata Station

Continuous TGM monitor (AM-5)

vs

Manually operated sampling system using a gold trap for GEM

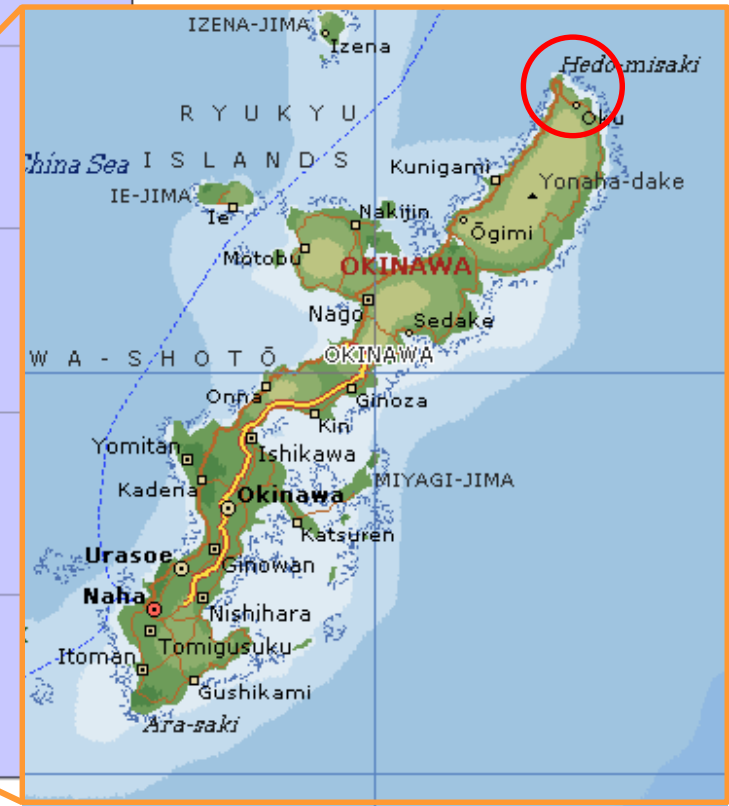


Cape Hedo Atmosphere and Aerosol Monitoring Station (CHAAMS)

Cape Hedo

26.87N 128.26E 60m a.s.l.

Okinawa



CHAAMS operated by National
Institute for Environment Studies 13

Cape Hedo Station

Mercury & other heavy metals monitoring systems

*Tekran mercury
speciation systems*

*Low-volume
sampler*

*Automatic
wet-only
sampler*

Measurement items, sampling, and analytical methods

Component	Measurement items		Sampling and analytical methods
Atmosphere	Mercury	Mercury speciation (Hg(0), RGM, PHg)	Continuous measurement with Tekran mercury speciation system
		Hg	24 hours continuous sampling by gold amalgamation method and followed by CVAAS
	Particulate matter	Pb, Cd, Cu, Zn, As, Cr, V, Ni, Se, Sb, Ba, Co, Mn, Sn, Te, Tl, Be, Al, Fe, Ca, Na, K	7 days continuous sampling by the low-volume sampler and analyzed by ICP/MS
Precipitation	Hg		Sampling by the automatic wet-only sampler and analyzed by CVAAS (EPA method 1631)

Summary of continuous mercury measurement (Fiscal year 2010)

Hourly data	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Annual
GEM (ng/m3)													
Mean	2.4	2.2	2.2	1.9	1.8	1.7	1.8	1.8	1.8	1.6	1.8	1.7	1.9
St Dev	0.5	0.4	0.8	0.1	0.2	0.2	0.3	0.3	0.5	0.3	0.5	0.4	0.5
Min.	1.6	1.7	1.4	1.6	1.4	1.4	1.4	1.2	1.2	1.3	1.3	1.2	1.2
Max	4.3	4.0	6.0	2.4	2.7	2.3	3.3	3.7	3.7	3.1	5.1	3.1	6.0
GOM (pg/m3)													
Mean	0.7	1.3	0.8	0.4	0.7	1.2	1.7	2.4	1.8	0.9	1.4	2.8	1.3
St Dev	1.0	2.5	2.4	0.6	1.5	4.2	5.1	2.9	2.7	1.4	2.6	5.5	3.1
Min.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Max	6.0	14.4	23.7	6.0	12.2	41.1	58.2	14.9	14.8	9.2	16.0	39.5	58.2
PHg (pg/m3)													
Mean	2.7	1.8	1.2	0.4	0.3	0.3	1.1	3.3	5.0	1.8	2.6	5.0	2.2
St Dev	3.4	2.4	3.6	0.6	0.7	0.7	1.9	4.3	8.1	3.3	3.8	5.3	4.2
Min.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Max	19.9	13.3	26.6	3.5	4.6	4.1	9.4	37.4	47.6	48.0	26.6	32.1	48.0

The data was provided by Ministry of the Environment, Japan (MOEJ)

Standard Operating Procedures for atmospheric Hg analysis using a Tekran analyzer at Cape Hedo

- Develop the QA/QC procedure **in hot and humid conditions** based on Draft USEPA's SOP (Oct. 2008)
- Hg(0): Good correlation with MOEJ manual method*
 - * Measurement of gaseous mercury including Hg(0) and GOM
- GOM and PHg: Good correlation with a manually-operated offline system including annular denuder and filter pack

Annual on-site maintenance schedule at Cape Hedo

Schedule	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar
Monthly	○	○	○	○	○	○	○	○	○	○	○	○
3 months			○				○			○		
6 months			○				○					
Annually							○					

On-site maintenance program & QA checks

Unit	Maintenance	Schedule
Overall system	Leak check the entire system	Weekly
	Check operation on outlet of air dryer and replace as necessary	Weekly
	Check and synchronize Tekran clock to NIST time source	6 months
	Spiked Recovery Test (Standard Addition Method) to confirm 100% recovery rate	6 months
	Monitor the instrument shelter air and indoor Hg concentration	6 months
	Rinse or install new Teflon tubing at key locations between the 2537 and 1130 including the heated sample line	6 months
Model 2537 (Analyzer)	Install new pre-purged soda lime trap	Bi-weekly
	Install trace-clean 2537 sample filter housing and zero air filter housing with new filter media in 2537	Monthly
	Audit the mass flow controller in the 2537	3 months
	Check the nichrome gold cartridge heating coils, reseal and tighten electrical connection and confirm operation	6 months
	Install new 2537A zero air canister and DFU filter if needed	6 months
	Replace the 2537 lamp and check the voltage	As needed

On-site maintenance program & QA checks (Continued)

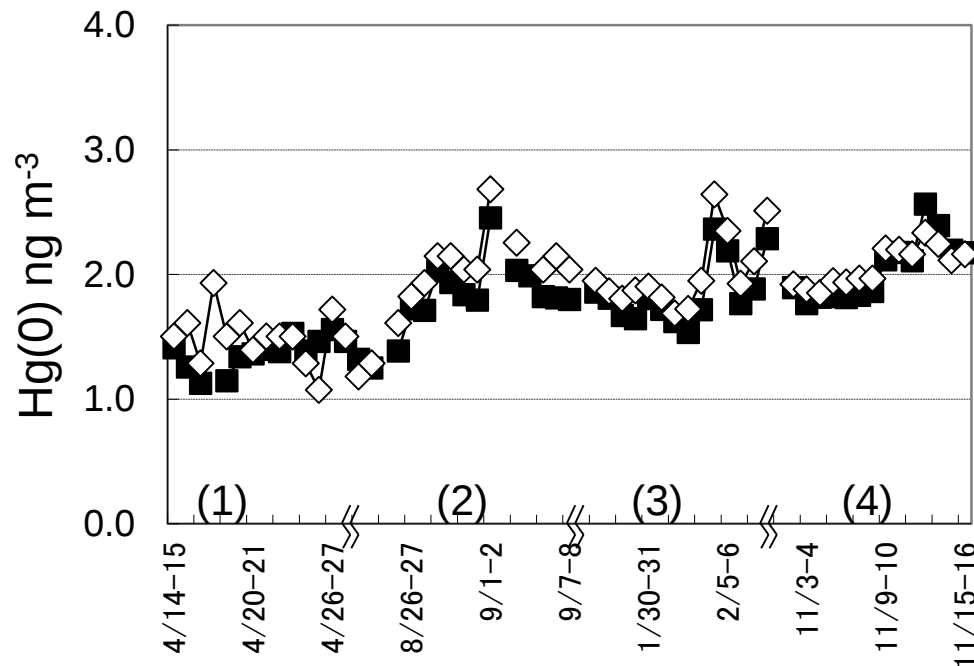
Unit	Maintenance	Schedule
Model 1130 (Denuder module) Model 1135 (Particulate module)	Install new blanked GOM denuder	Bi-weekly
	Install trace-clean inlet glassware including new frit	Bi-weekly
	Install trace-clean zero air filter housing and new filter media in 1130	Monthly
	Install trace-clean sample line filter housing and new filter media in 1130	Monthly
	Install new blanked regenerable particulate filter assembly	6 months
	Rinse or install new Teflon tubing at key locations in Modules	6 months
	Replace GL14-GL18 union fitting between denuder and RPF	6 months
Model 1130 (Pump Module)	Confirm inlet volumetric flow rate is between 8 to 11 L/min	Weekly
	Audit the mass flow meter in the 1130 pump module	6 months
	Replace the 1130 pump diaphragm and brushes	6 months
	Change both of the 1130 pump unit zero air carbon canisters and DFU filters	6 months

These maintenance program and QA checks are also installed in the monitoring at the Fukuoka station.

Comparison of Hg(0) measurement values

■ Tekran Hg Analyzer

◇ MOEJ Manual Method*

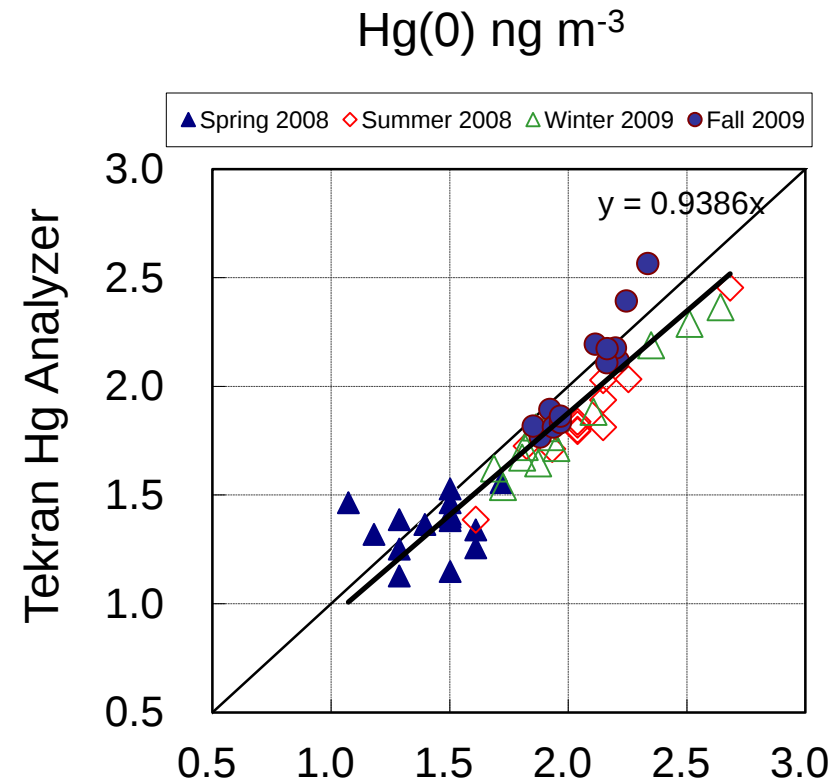


(1) Spring: 14 -30 Apr. 2008

(2) Summer: 25 Aug. - 8 Sep. 2008

(3) Winter: 26 Jan. - 8 Feb. 2009

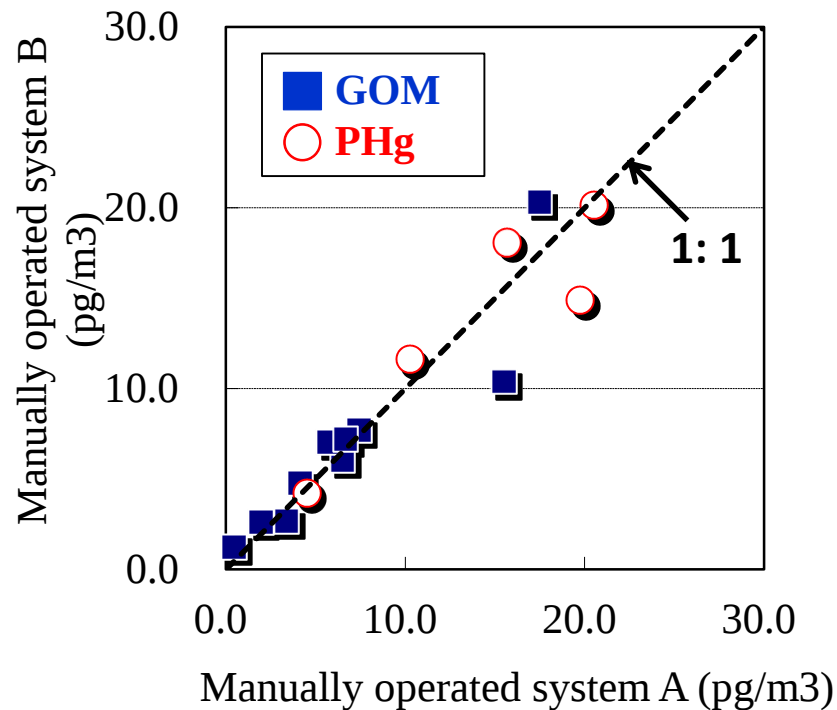
(4) Fall: 2 Nov. – 16 Nov. 2009



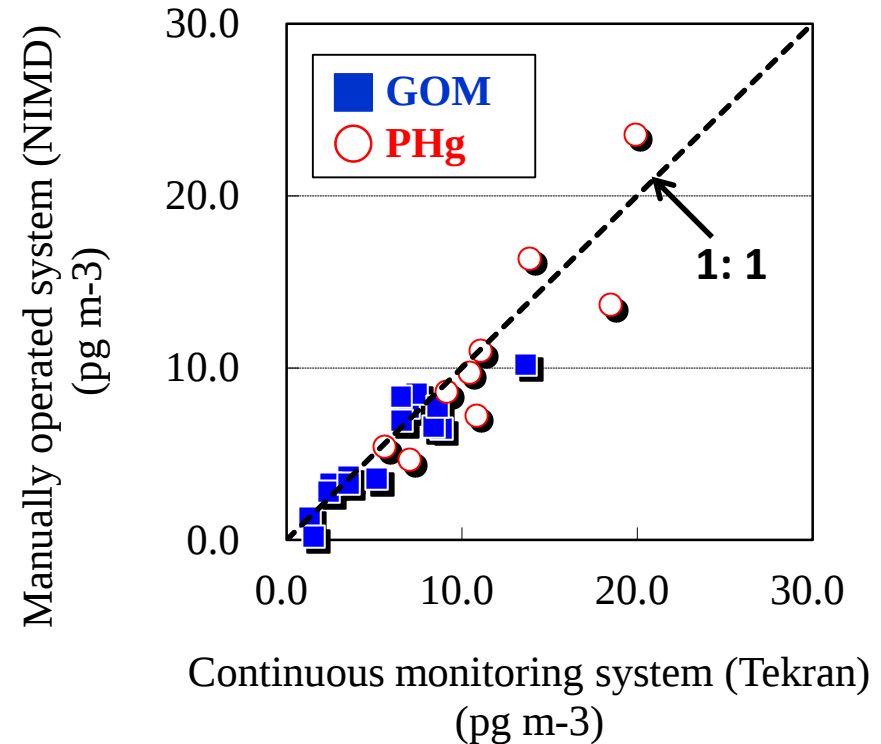
MOEJ Manual Method*

- * Install soda lime trap just before gold cartridge
- * Gaseous mercury including Hg(0) and GOM

Quality Control for GOM and PHg



Results on duplicate sampling
by a manually-operated offline
system



Results on simultaneous monitoring
By a continuous online monitoring
system (Tekran) and a manually-
operated offline system

Mercury monitoring activities in Japan in future

- Continuous monitoring are carried out at the existing stations as long as possible in collaboration with MOEJ, NIES, NIIT and NIMD.
- NIMD is preparing to establish a new station in the eastern part of Japanese islands, which has less influences of long-ranged transport of air mass, as a control site.
- NIMD is preparing to put the monitoring data obtained by NIMD on view through the internet after the data is checked by QC/QA program.