

Session II-2

Study on the Mercury Speciated Concentrations and Atmospheric Wet Deposition of Total Mercury (TM) in Seoul, Korea



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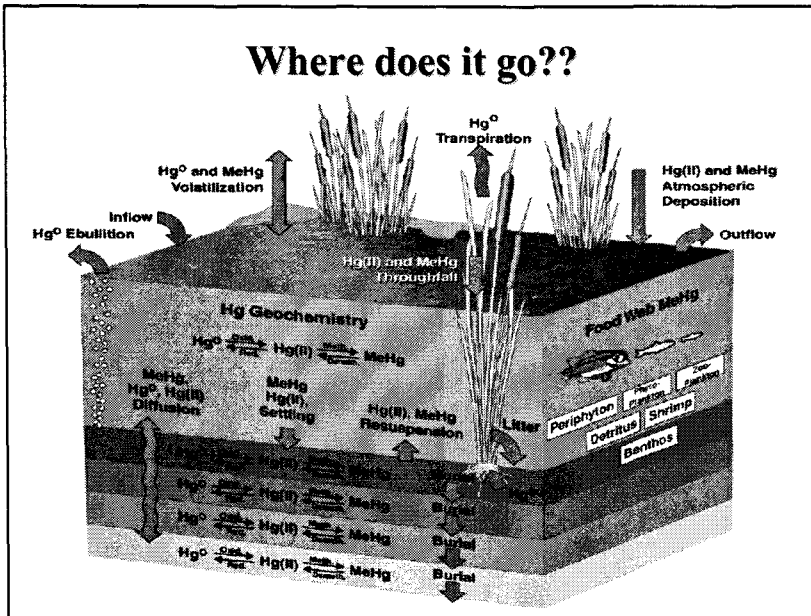
What is mercury??

- **Mercury is a cationic metal : Excellent conductor of electricity**
- **Elemental Mercury (Hg^0) (2.55 tons/yr, U.S. 1999)**
 - Predominant species, Long range transport**
 - Residence time: 0.5 – 2 yrs.**
 - Globally distributed**
- **Gaseous divalent mercury (Hg^{2+}) (1.50 tons/yr, U.S. 1999)**
 - Oxidized mercury: Hg(II) : HgCl_2 , other species?**
 - Highly water soluble -> short atmospheric life time (1 – 2 days)**
 - Local and Regional effects**
- **Particulate Mercury (Hg_p) (0.45 tons/yr, U.S. 1999)**
 - Species largely unknown**
 - Local and Regional Effects**

Where does it come from??

- **Natural sources: the mobilization or releases of geologically bound mercury by natural processes**
- **Anthropogenic sources (EPA, 1999) (2,143 - 2400 tons/yr)**
 - 1. Coal-fired electric utilities (40%)**
 - 2. Industrial boilers (10%)**
 - 3. Hazardous waste incinerators (5%)**
 - 4. Chlorine production (5%)**
- **Re-emitted mercury (2000 – 2134 tons/yr): previously deposited to the earth's surface by anthropogenic sources**
- **2/3 of Hg atmospheric emissions (6,060 – 6,600 tons/yr) – direct or re-emitted anthropogenic sources**

Where does it go??



How does mercury affect health??


- **Methylmercury accumulates most efficiently in the aquatic food web (four times more efficient than inorganic Hg).**
- **Dominant exposure for human: Fish consumption**
 - : Dietary methylmercury is almost completely absorbed into the blood.
 - : Freshwater fish: Walleye, Bass, Northern Pike
 - : Saltwater fish: Shark, Swordfish, Tilefish, Tuna
- **Neurotoxicity – women of childbearing age**
- **Tremors, inability to walk, convulsions, death**

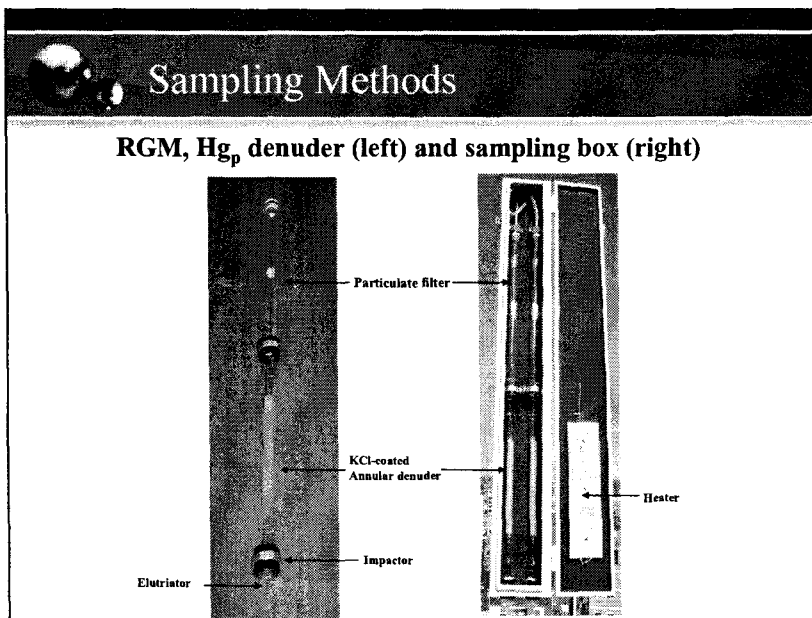
What is EPA doing to reduce mercury emissions??

- **Final regulations for large municipal waste combustors were issued on October 31, 1995 → reduce by 88%**
- **Emission standards for medical waste incinerators were issued on August 15, 1997 → reduce by 95%**
- **Emission standards for hazardous waste combustors were issued on February 1999.**
- **Emission standards for chlor-alkali production were issued on August 27, 2003**
- **EPA wrote proposals that would reduce mercury emissions from coal power plant by 70% by 2018.**

Motivations

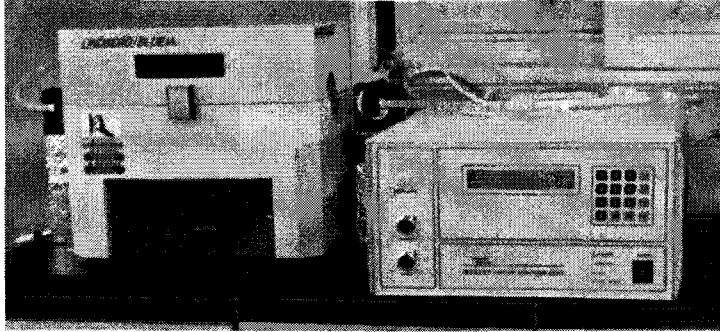
- **Atmospheric mercury is origin of anthropogenic mercury.**
- **Mercury can transport in long range in atmosphere.**
- **Mercury pollution is not only local problem but also global problem because of the air.**
- **Measuring accurate mercury concentration in ambient air and finding out important atmospheric mercury sources are the first step to regulate mercury in environment.**

 Sampling Methods			
Mercury species	Sampling site	Sampling period	Sampling methods
TGM	Roof of Graduate School of Public Health at SNU in Seoul Korea (37.514°, 127.001°, 17 m)	February 2005 – February 2006	CVAES (Tekran Model 2537A)
RGM		June 2005 – February 2006	denuder (URG) coated with KCl
Hg _p (<2.5µm)			denuder (URG) with quartz fiber filter



Mercury Analysis

Mercury species (TGM, RGM, and Hg_p) analysis



- RGM and Hg_p : tube furnace (Lindberg 55035C) &CVAFS (Tekran Model 2537A)
- TGM : CVAFS (Tekran Model 2537A)

Quality Assurance and Quality Control (QA/QC)

☐ TGM (Tekran 2537A)

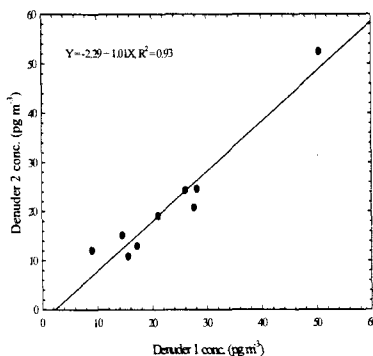
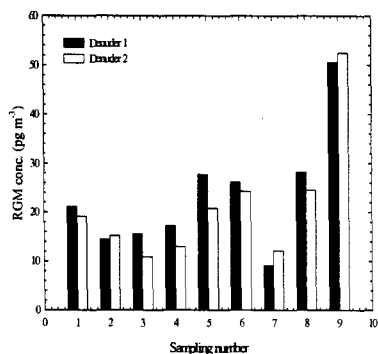
- Internal permeation source calibration
 - ✓ six steps: clean A, B, zero A, B and span A, B
 - ✓ auto calibration interval was set every 24 hrs
- Zero test
 - ✓ detection limit: $0.03 \pm 0.29 \text{ ng m}^{-3}$
- Source calibration & manual calibration response factor
 - ✓ overall precision: $0.038 \pm 0.023\%$
- Span (spike) recovery
 - ✓ $96 \pm 3\%$
- Recovery
 - ✓ $97 \pm 3\%$



Quality Assurance and Quality Control (QA/QC)

☐ RGM

- Side by Side: $17.75 \pm 12.41\%$ (n=9)



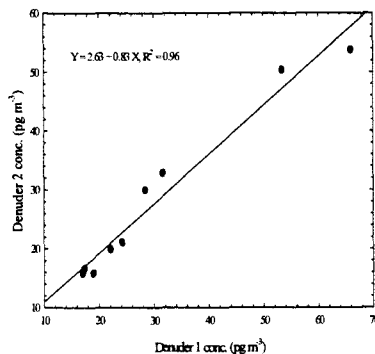
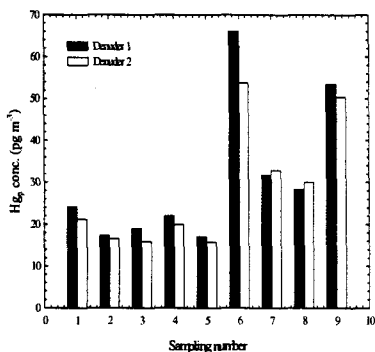
- Field Blank: 1.4 ± 0.77 pg (n=5)



Quality Assurance and Quality Control (QA/QC)

☐ Hg_p

- Side by Side: $9.81 \pm 6.08\%$ (n=9)



- Field Blank: 1.05 ± 0.88 pg (n=5)



Result

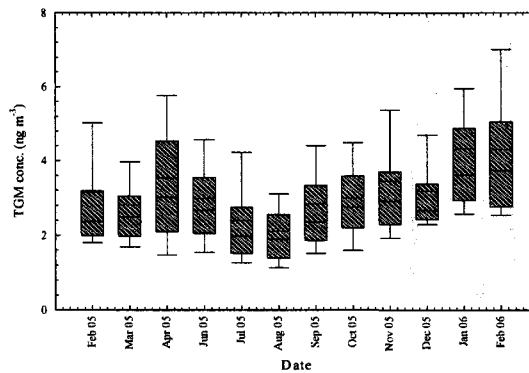
Summary of TGM, RGM, and Hg_p concentrations measured in Seoul

	TGM ^a (ng m ⁻³)	RGM ^b (pg m ⁻³)	Hg _p ^b (pg m ⁻³)
Average	3.21	25.63	23.38
Median	3.14	14.41	19.31
SD	2.15	17.6	19.65
Sample number	25623	76	74



Result

Monthly variations on TGM concentrations

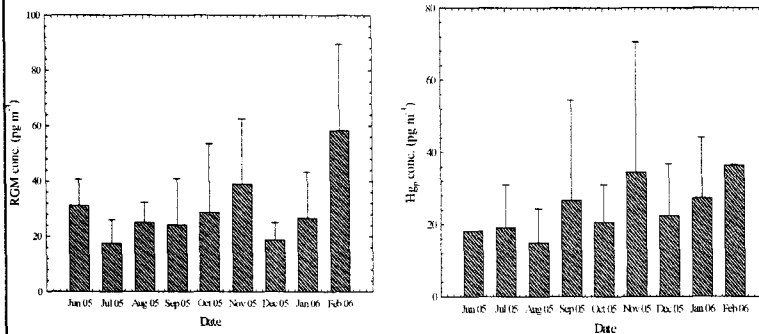


Black lines: median; red lines: mean; upper edge of the box: 75th percentile; lower edge of box: 25th percentile; error bar above and below the box: 90th and 10th percentiles.



Result

Monthly variations on RGM and Hg_p concentrations

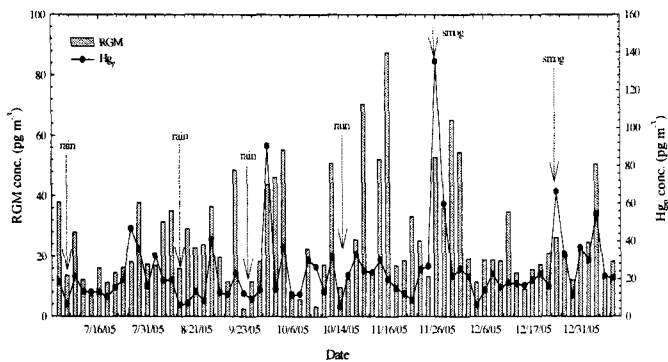


Error bars indicate standard deviations for each month.



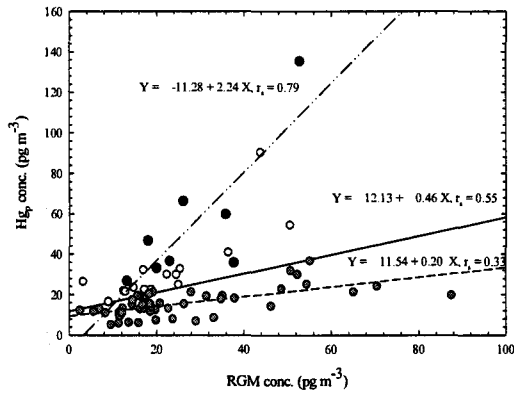
Result

Daily concentrations of RGM and Hg_p



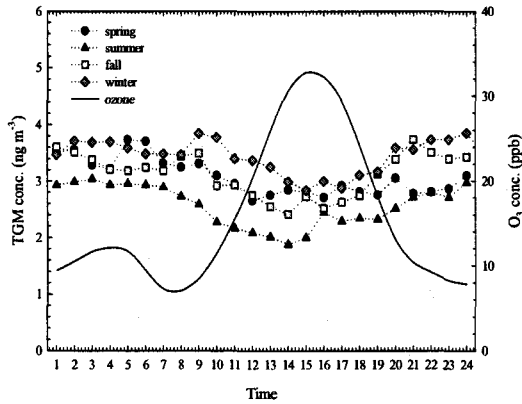
Result

Relationship between RGM and Hg_p concentrations



Result

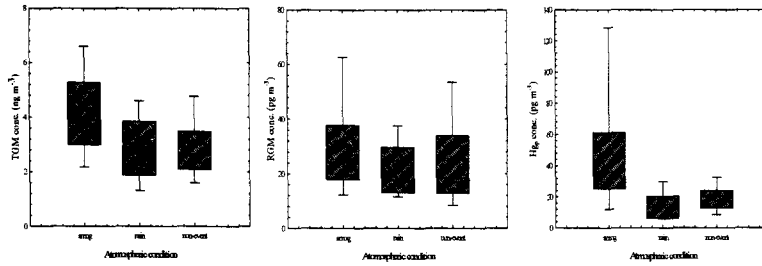
Diurnal variations on TGM concentrations during four seasons





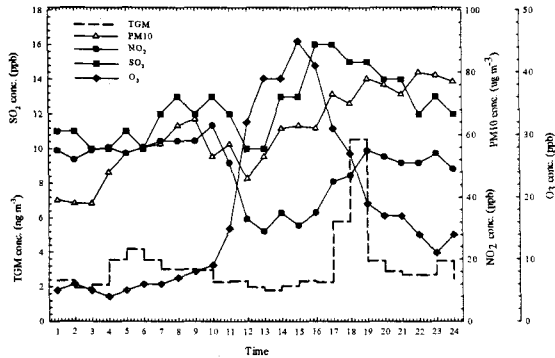
Result

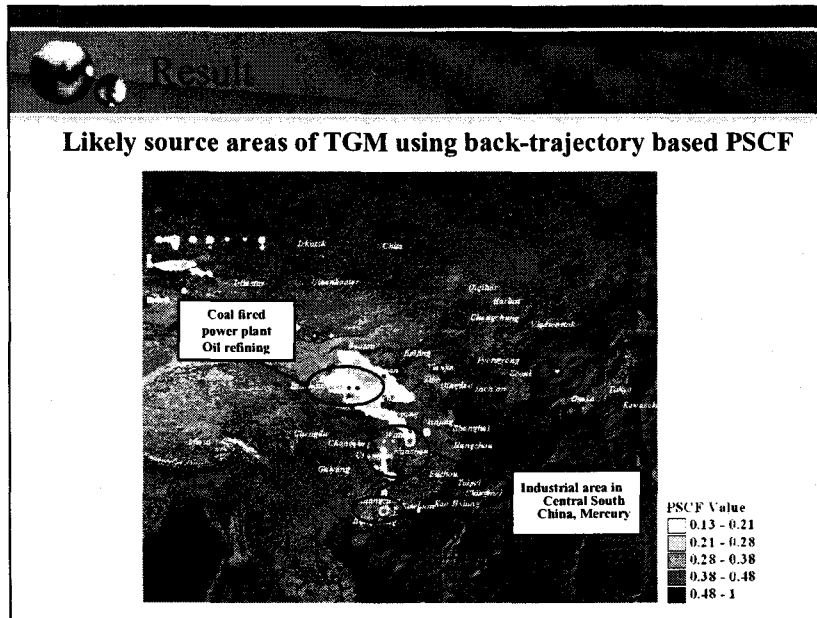
TGM (left), RGM (middle), and Hg_p (right) distributions for different atmospheric conditions



Result

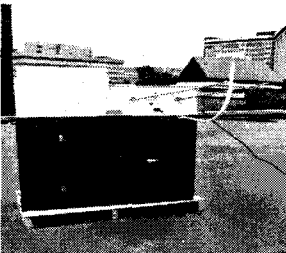
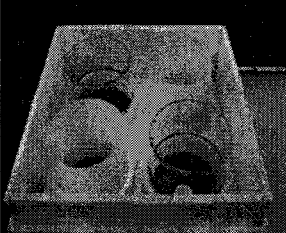
Variations on TGM and other air pollutants during smog event (March 15, 2005)





Sampling Methods

- Sampling Location : Roof of the School of Public Health building of Seoul National University
- Sampling Periods : February 2005 – January 2006
- Sampling Method : modified MIC-B sampler
 - 2 mercury sampling trains + 2 trace element sampling trains

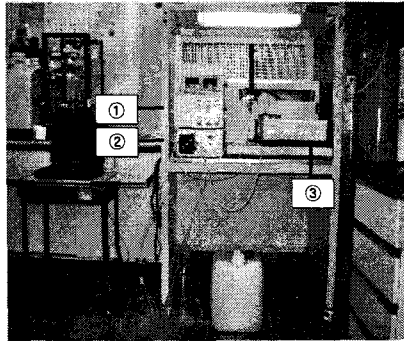





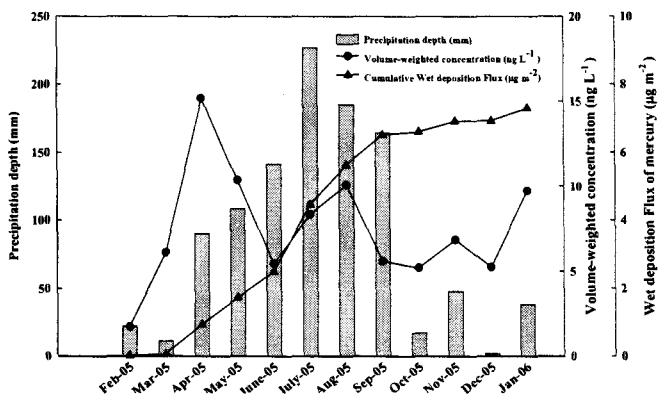
Analytical Method

- Sample Analysis
 - Tekran 2600 (CVAFS system)

- System Control Module
- Pump module
- Auto sampler

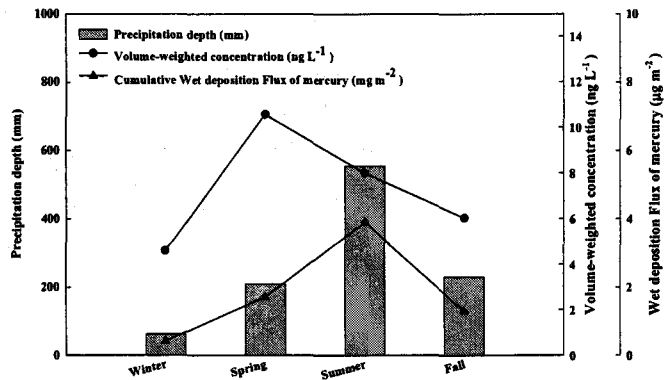


Result



Result

Seasonal Variations of Wet Deposition Flux of TM



Conclusions

□ Trend in TGM, RGM and Hg_p concentrations distribution

- Monthly and Seasonal variations
 - ✓ TGM (ng/m³): Winter (3.71 ± 2.54) > Summer (2.59 ± 1.48)
 - ✓ RGM & Hg_p (pg/m³)
 - Winter (23.94 ± 16.08, 24.76 ± 14.49, respectively) >
 - Summer (21.45 ± 12.10, 17.54 ± 20.09, respectively)
- Diurnal variation
 - ✓ TGM (ng/m³): Nighttime (3.31 ± 1.04) > Daytime (2.52 ± 1.31)
 - ✓ RGM & Hg_p (pg/m³)
 - Daytime (27.79 ± 22.22, 29.14 ± 24.53, respectively) > Nighttime
 - (15.46 ± 13.82, 17.23 ± 13.62, respectively)



Conclusions

Relationships with meteorological condition & other pollutants

- Rain

- ✓ RGM & Hg_p (pg/m³)

- Rainy day (21.21 ± 9.99, 14.67 ± 8.31, respectively)

- < non rainy day (26.59 ± 18.93, 23.78 ± 19.39, respectively)

- CO, PM₁₀

- ✓ TGM: CO ($r_s = 0.49$, $p < 0.01$), PM₁₀ ($r_s = 0.24$, $p < 0.01$)

- ✓ Hg_p: CO ($r_s = 0.41$, $p < 0.01$), PM₁₀ ($r_s = 0.45$, $p < 0.01$)



Conclusions

Relationships between smog event and mercury concentrations

- TGM (ng/m³)

- ✓ Smog event (4.32 ± 2.33) > Non smog event (3.09 ± 1.58)

- Hg_p (pg/m³)

- ✓ Smog event (47.28 ± 36.30) > Non smog event (20.83 ± 13.61)

Likely source areas of TGM

- TGM: Industrial areas in China – Coal fired power plant, Oil refining



Conclusions

- **Average Volume-weighted Concentration of TM:**
 8.16 ± 6.27 ng/L
 - **Maximum month: April (15.18 ± 12.83 ng/L)**

- **Cumulative wet deposition flux of TM: 7.30 mg/m²**
 - **Maximum season: summer (3.90 μ g/m²)**
 - **A significant positive correlation between wet deposition flux and rainfall depth ($r^2 = 0.68$)**



Acknowledgement

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