2015 International Conferences on
Mercury Pollution Prevention and Control
Beijing, China, Dec. 8-9, 2015

Effects of Existing APCDs and BATs Applications on Mercury Removal at Annex D Sources in Minamata Convention

Yong-Chil Seo

Professor, Dept. of Environmental Engineering, Yonsei University

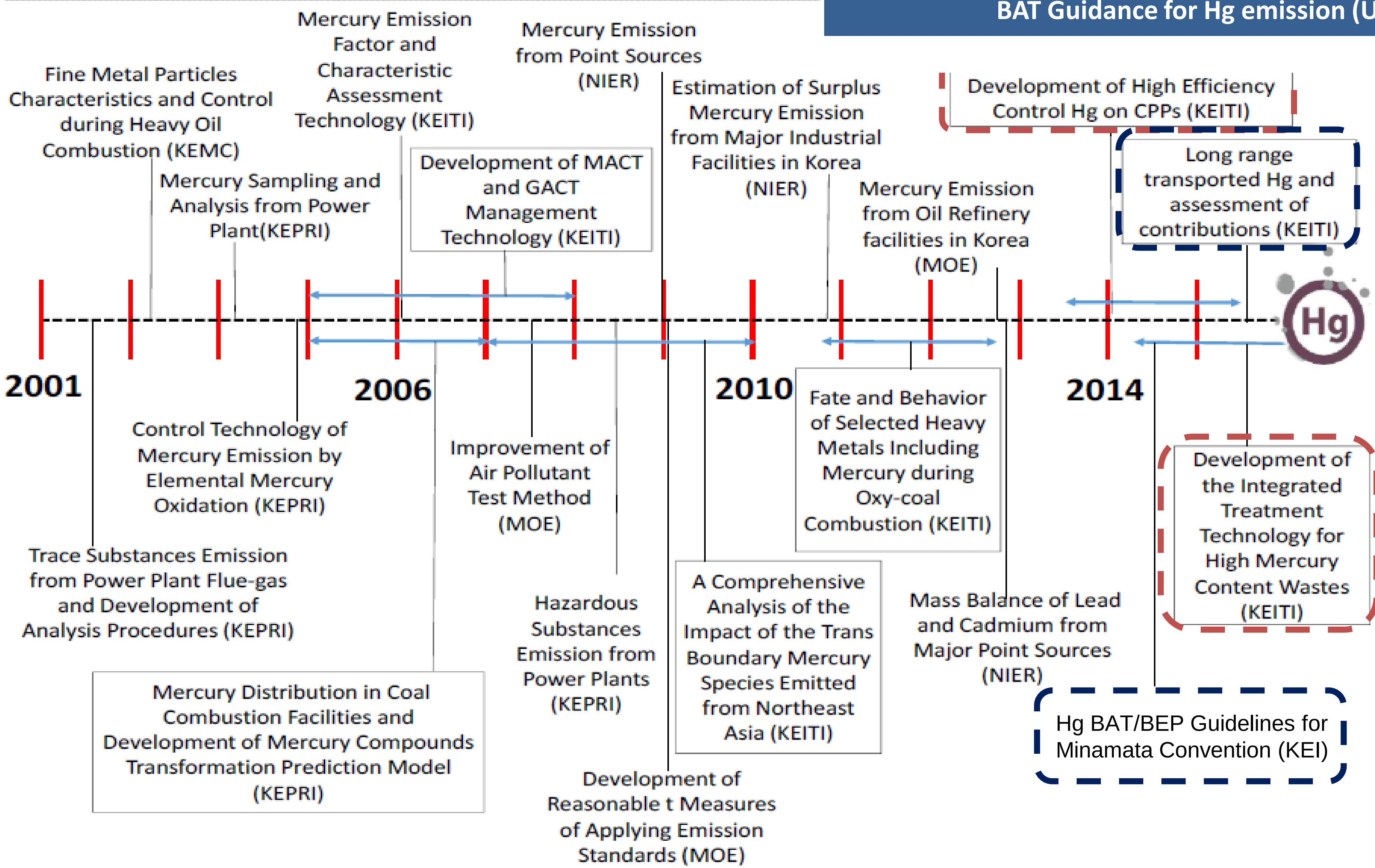
Republic of Korea

Contents

History of Hg in Prof. SEO Laboratory

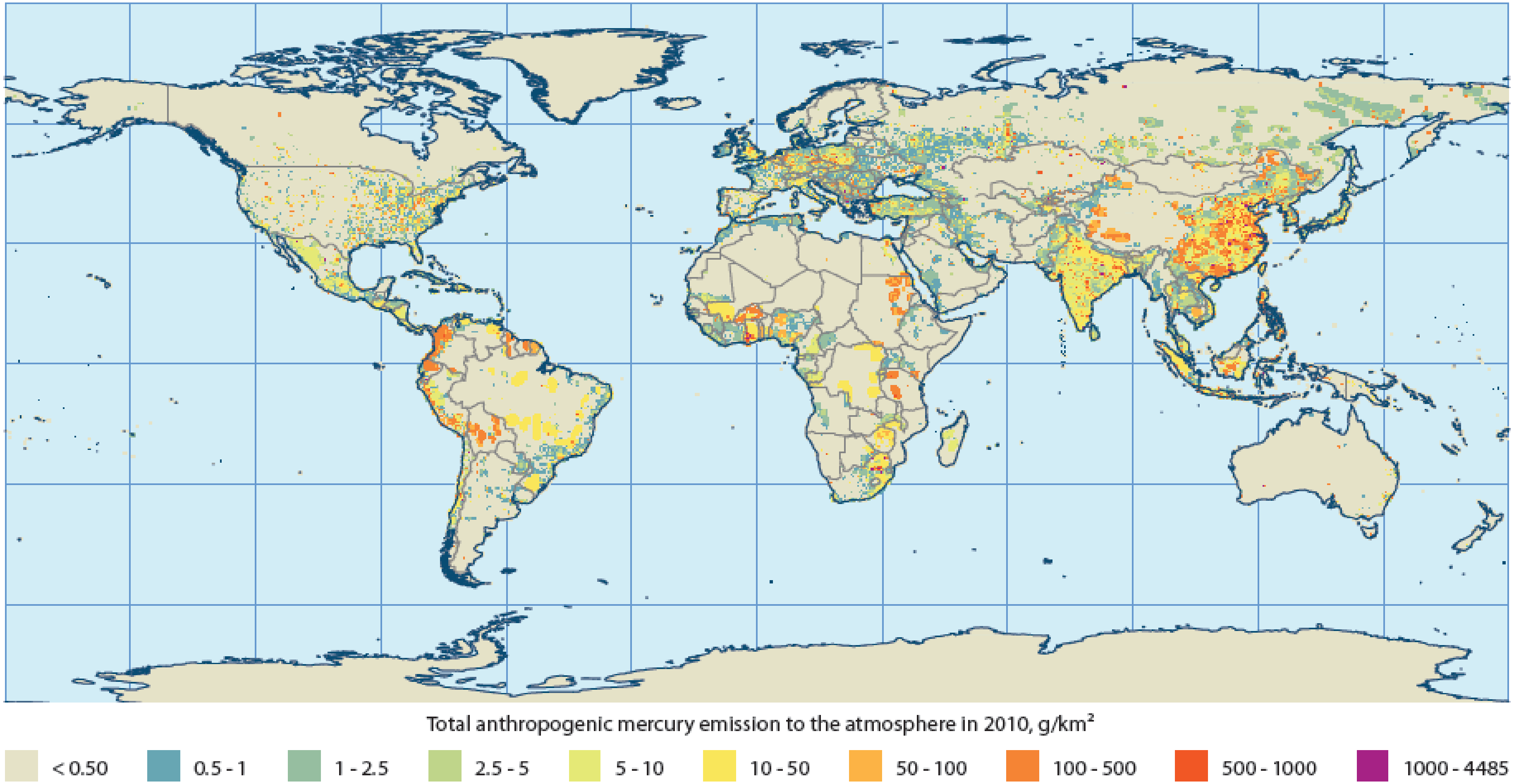
2008- : UNEP Partnership Programs: Reduce from Coal, Waste Management
2011-2012 : Working Member for Global Assessment Report (UNEP, 2013)
2014-2015 : Experts Group Member for Developing BAT Guidance for Hg emission (UNEP)

R&Ds on Mercury Performed last 15 years



1. Mercury Air Emission Inventories

- **Global Distribution of Anthropogenic Mercury Emissions to air in 2010**

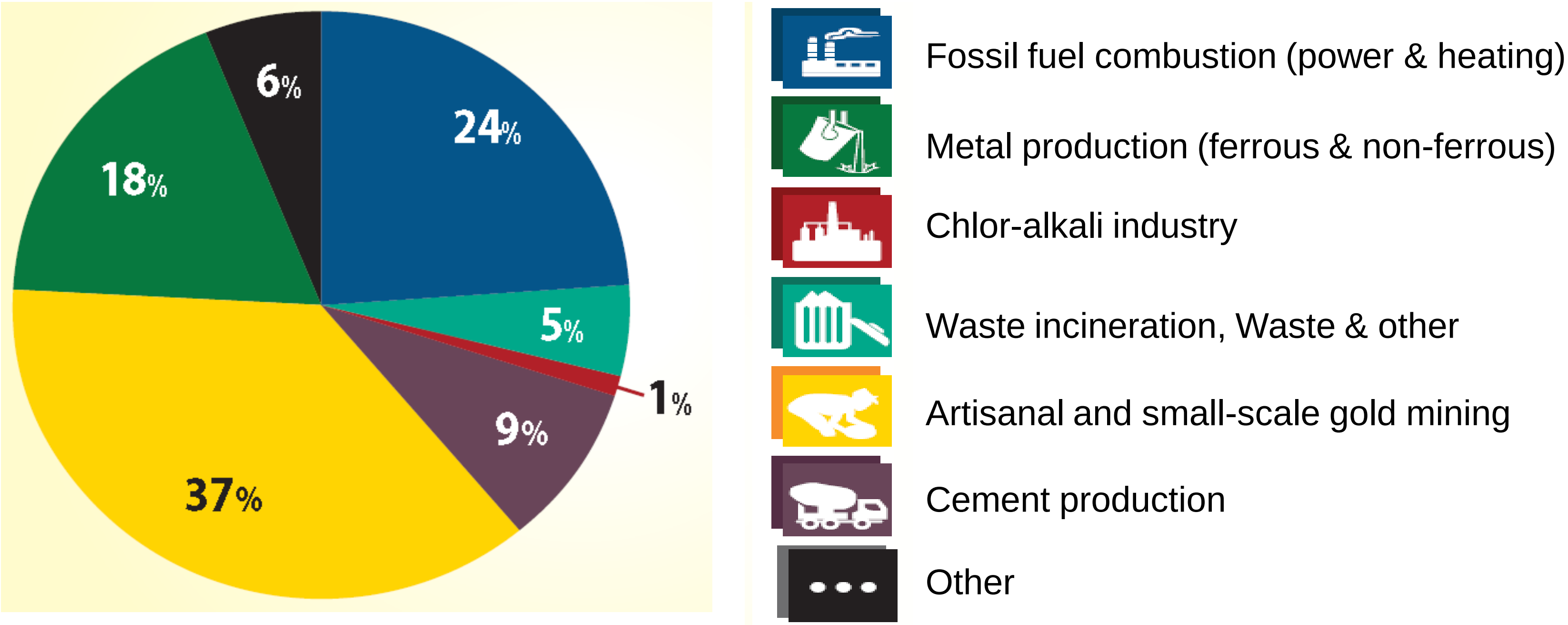


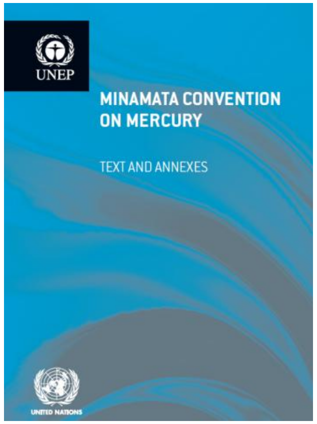
Global Grand Total (2010) : Ave. 1,960 ton-Hg (1,010 ~ 4,070 ton-Hg)

Reference : - UNEP, Global Mercury Assessment 2013

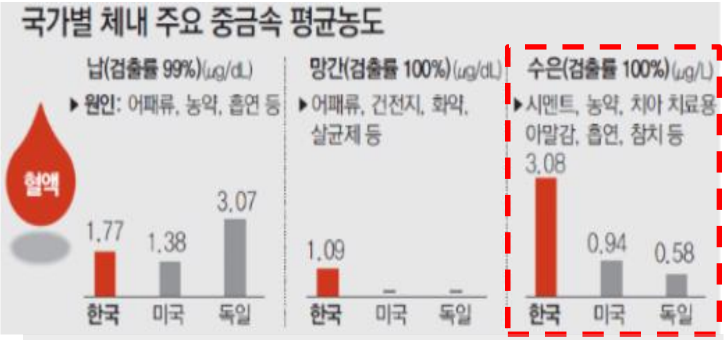
1. Mercury Air Emission Inventories

- Global Anthropogenic Mercury Emissions in 2010





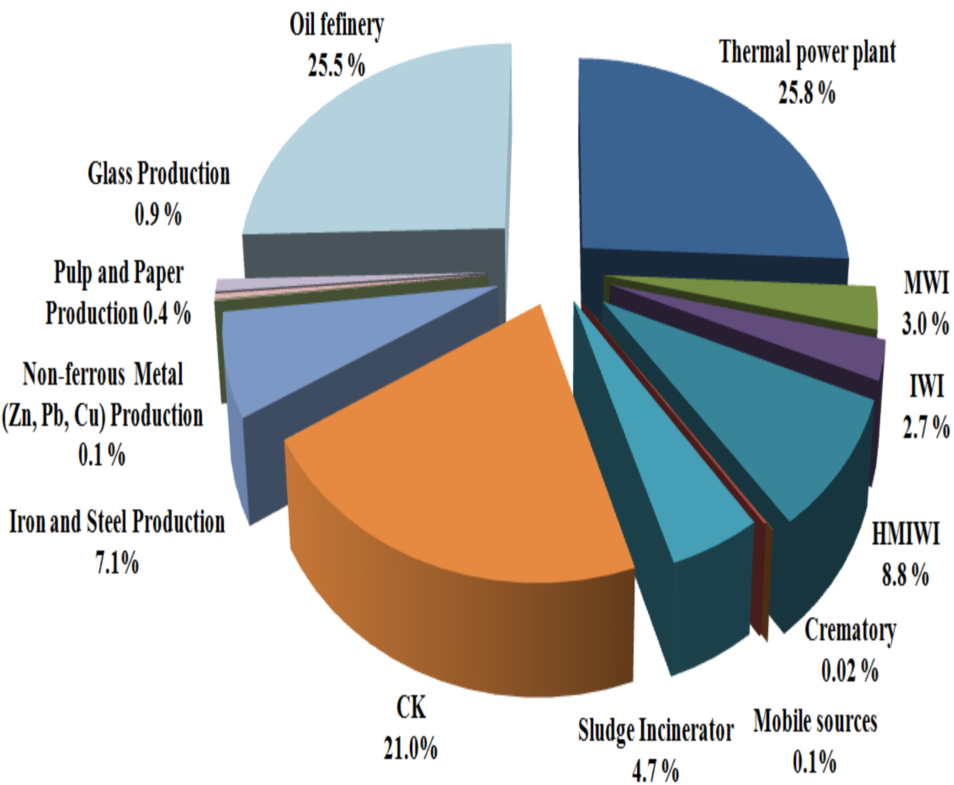
- Minamata Convention adoption (`13.10)
- ANNEX D (major management source)
  1. Coal-fired power plants;
  2. Coal-fired industrial boilers;
  3. Smelting and roasting processes used in the production of non-ferrous metals
  4. Waste incineration facilities;
  5. Cement clinker production facilities.



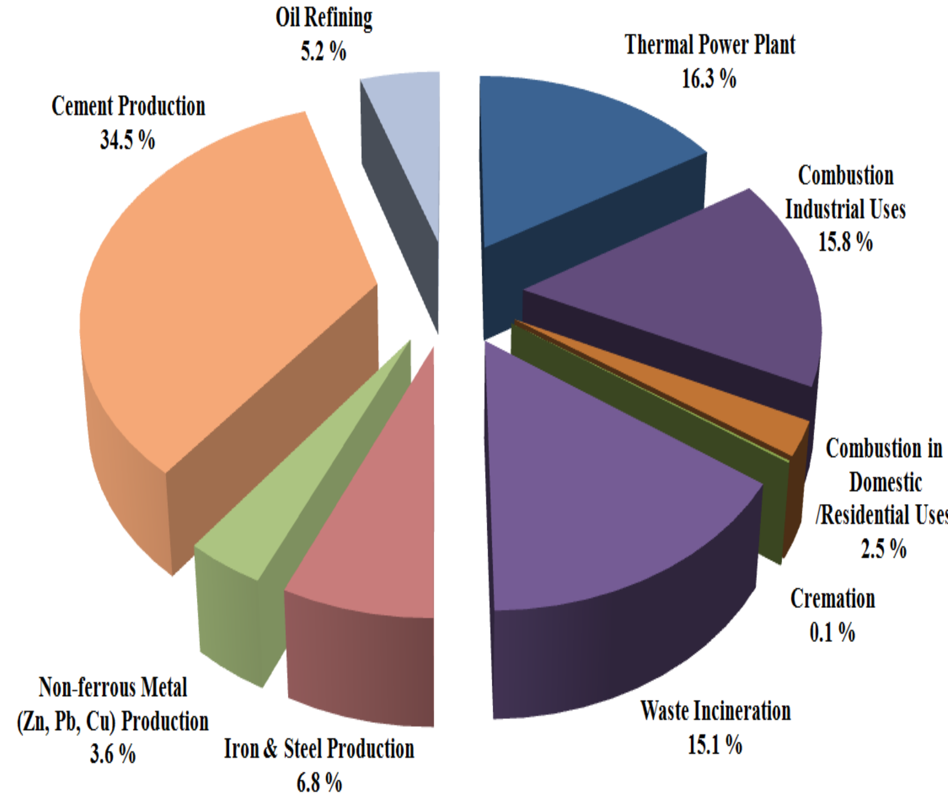
Blood Hg concentration in other countries

1. Mercury Air Emission Inventories

- ## Anthropogenic Mercury Emission (Air) in Korea



Annual Hg Air Emission (2007) : Ave. 12.8 ton-Hg



Annual Hg Air Emission (2010) : Ave. 7.2 ton-Hg

Kim et al., 2010; Atmospheric Environment 44 (23), 2714-2721.

NIER , Report of Integrated Hg Management, 2013

2. Emission, Speciation, and Behavior of Hg in Anthropogenic Sources

- **Mercury Compounds Analysis in Annex D**

Mercury Stack Sampling

EPA Method 7470, 7471

EPA Method 1631

2. Emission, Speciation, and Behavior of Hg in Annex D Sources

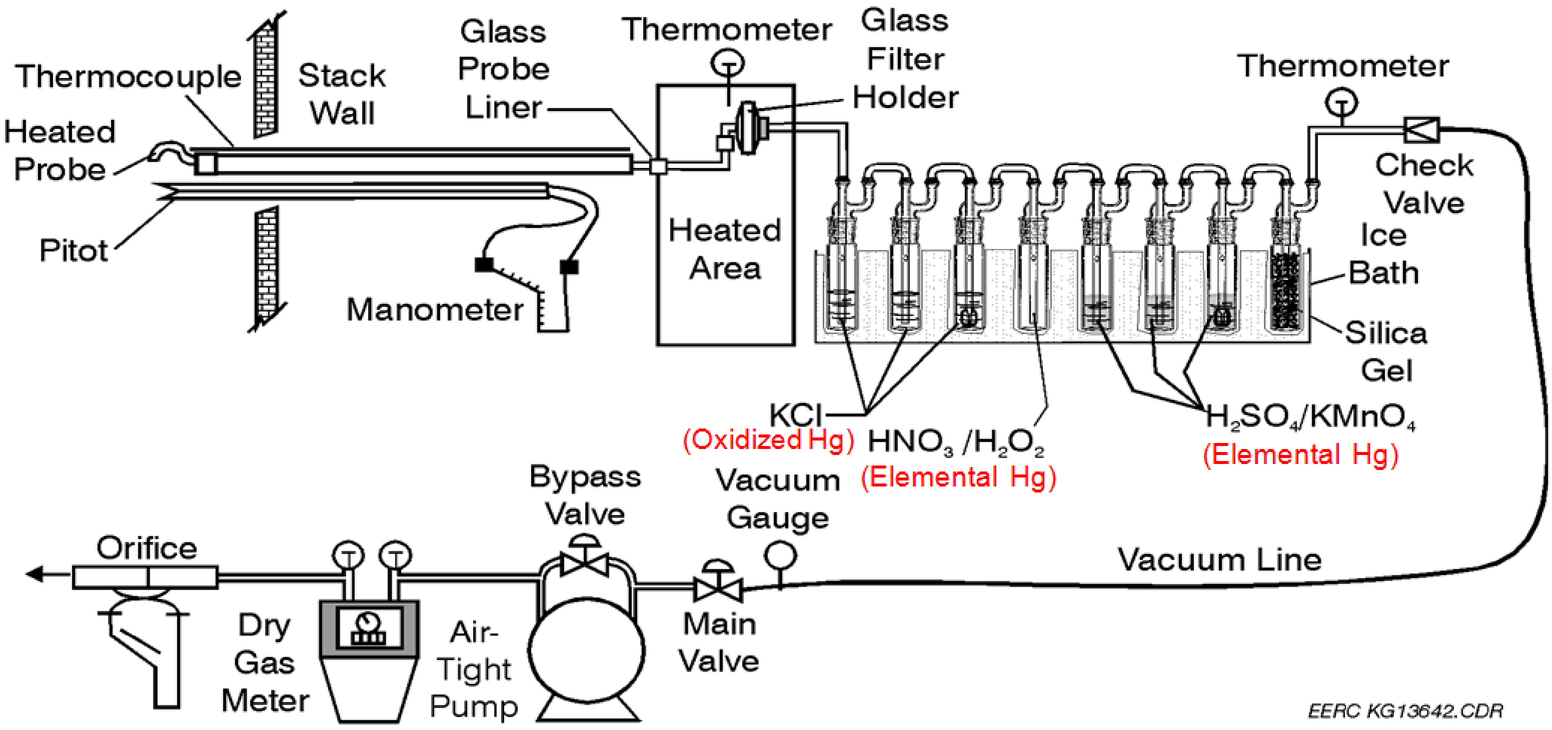
- **Mercury Compounds Analysis Method**

Ontario Hydro Method (ASTM, D 6784-02)

1^{st} - 3^{rd} Train 1N KCl (100ml)

4^{th} Train 5% HNO_3-10%H_2O_2 (100ml)

5^{th} - 7^{th} Train 4wt%$KMnO_4$-10%H_2SO_4 (100ml)



2. Emission, Speciation, and Behavior of Hg in Annex D Sources

▪ Oxidation Trend of Hg

Hg^0 → Hg^{2+}

1. Temperature increase : Hg^{2+} ↓

2. Chlorine (Cl) content increase : Hg^{2+} ↑

3. NO_2, HCl, NO & SO_2 complex : Hg^{2+} ↑

4. Passing through ESP : Hg^{2+} ↑

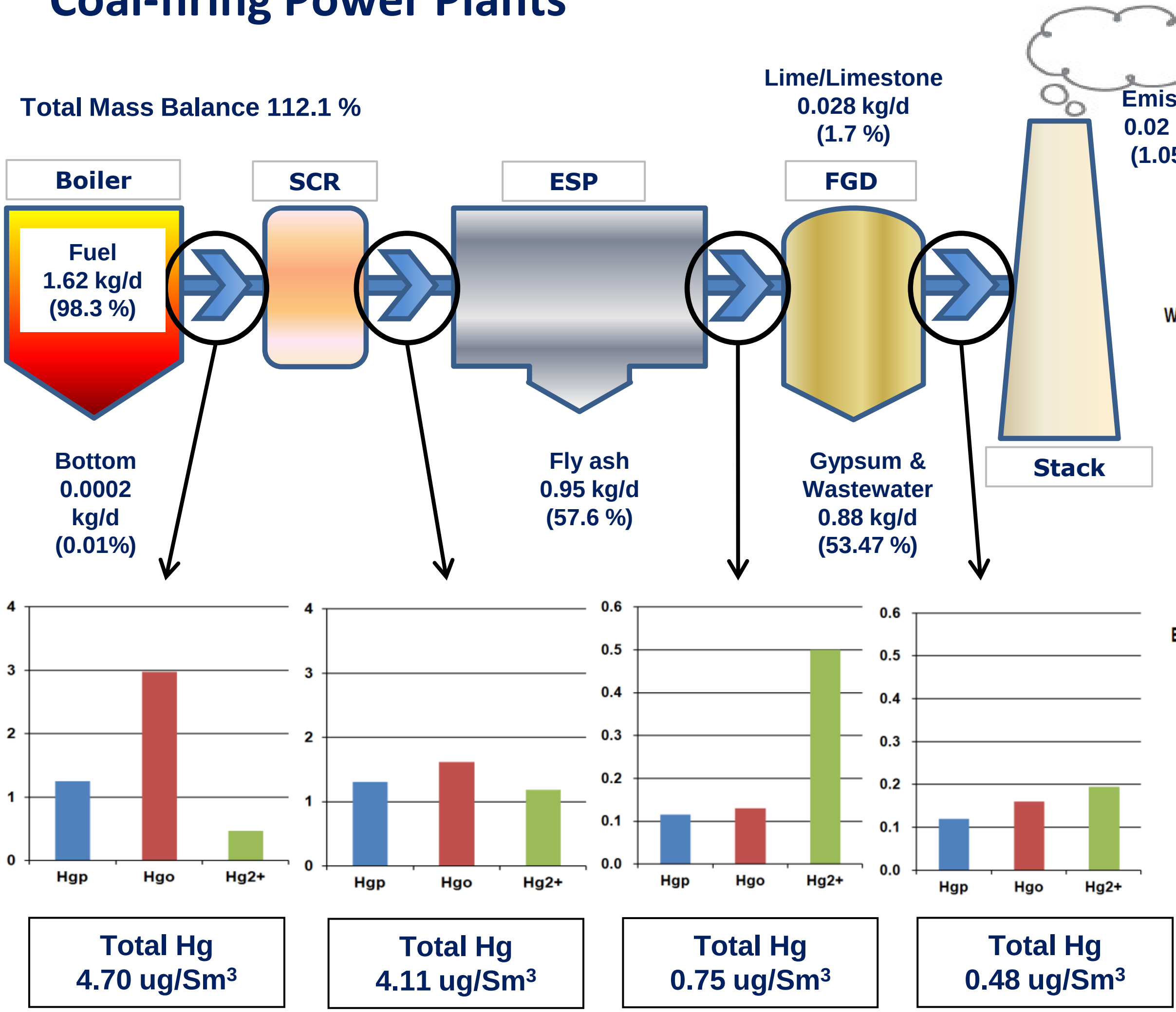
5. Passing through wet FGD : Hg^{2+} ↓

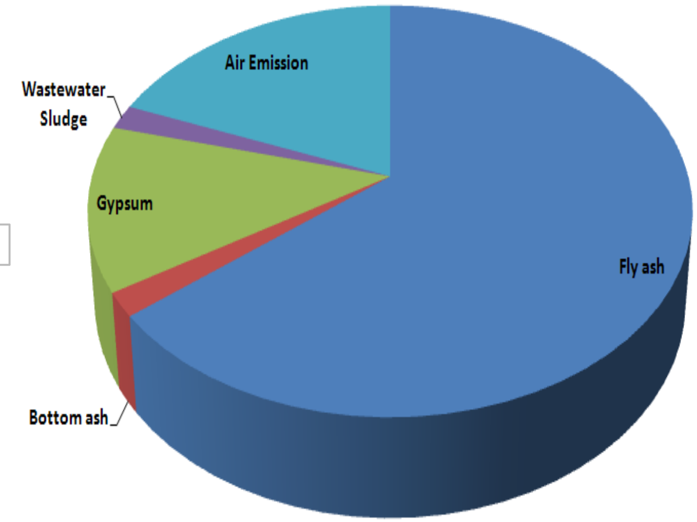
6. Passing through SCR : Hg^{2+} ↑

Reference : - Pudasainee and Seo (2009) Atmospheric Environment 43

2. Emission, Speciation, and Behavior of Hg in Annex D Sources

▪ Coal-firing Power Plants





Coal Power Plant
Hg Emission Contribution
Mass balance Ave. (97.0 %)

- Air Emission standard in Korea
  (Coal-firing power plant) : 0.05 mg/Sm^3

SCR: Selective Catalytic Reactor

CS-ESP: Cold side Electrostatic Precipitator

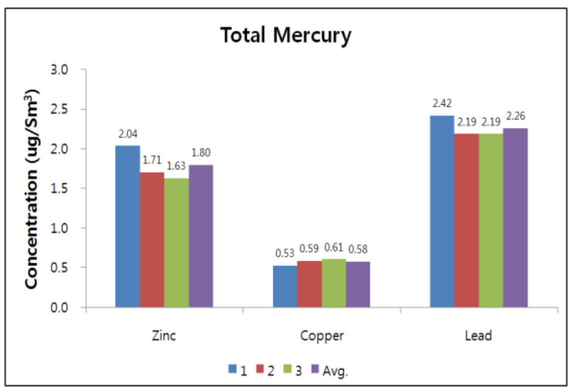
FGD: Flue Gas Desulphurization

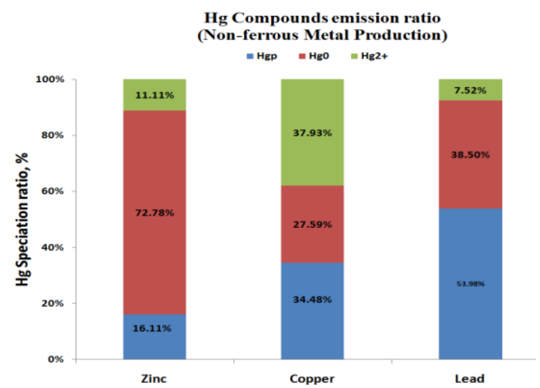
Reference : 1)Kim and Seo (2010) Ind. Eng. Chem. Res., 49(11)
2) Study on Emission of mercury for the atmospheric emissions facilities (II)
(2010) NIER, Conducted and Reported by Yonsei University

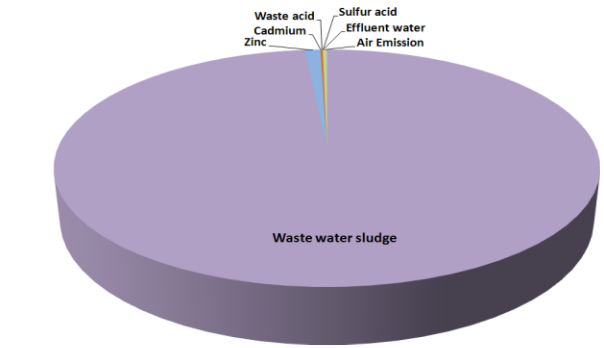
2. Emission, Speciation, and Behavior of Hg in Annex D Sources

▪ Non-ferrous Metal Facilities

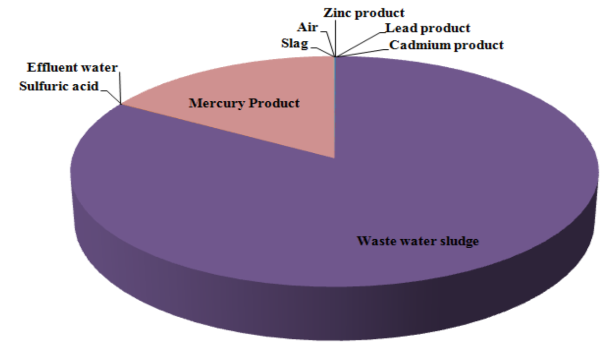
ID	Status of APCDs and Sampling Point	APCDs Type
Zinc & Lead #1	ESP – Venturi Scrubber – ESP – Boliden Norzink – Dry Tower – SO_2 1st Adsorp. Tower – SO2 2nd Adsorp. Tower – Scrubber – Stack	Wet
Copper #1	WS – ESP – Dry Tower – SO_2 1st Adsorp. Tower – SO2 2nd Adsorp. Tower – FGD – Stack	Wet



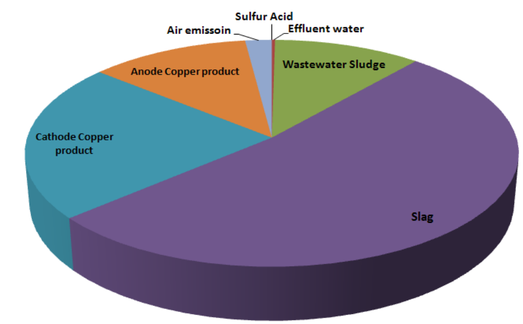




Zinc Facility Hg Emission Contribution
Mass balance Ave. (68.26 %)



Zinc & Lead Facility Hg Emission Contribution
Mass balance Ave. (over 100 %)



Copper Facility Hg Emission Contribution
Mass balance Ave. (97.06 %)

- Total Hg Concentration (outlet APCDs)
  - Zinc Facility : 1.80 ug/Sm^3
  - Cupper Facility : 0.58 ug/Sm^3
  - Lead Facility : 2.26 ug/Sm^3

- Measured Facility has High Efficiency APCDs for Hg reduction
  - B/F : Remove Hg-p
  - Wet APCDs & FGD : Remove Hg^{2+}
- Air Emission standard in Korea (Non-ferrous smelting Facility) : 0.05 mg/Sm^3

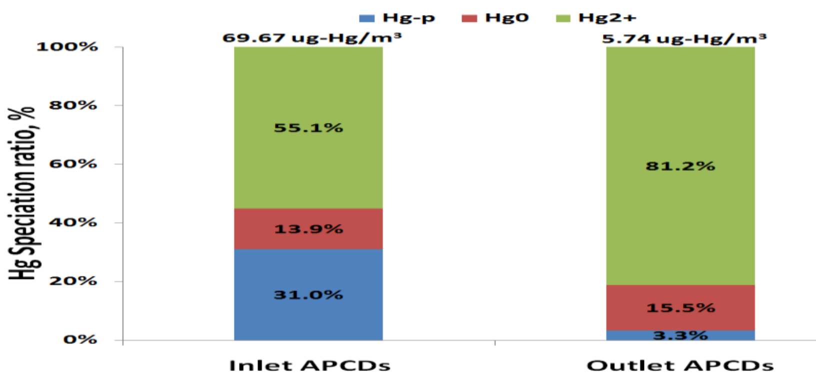
Reference : - Study on Emission of mercury for the atmospheric emissions facilities (I) (2008) NIER , Conducted and Reported by Yonsei

2. Emission, Speciation, and Behavior of Hg in Annex D Sources

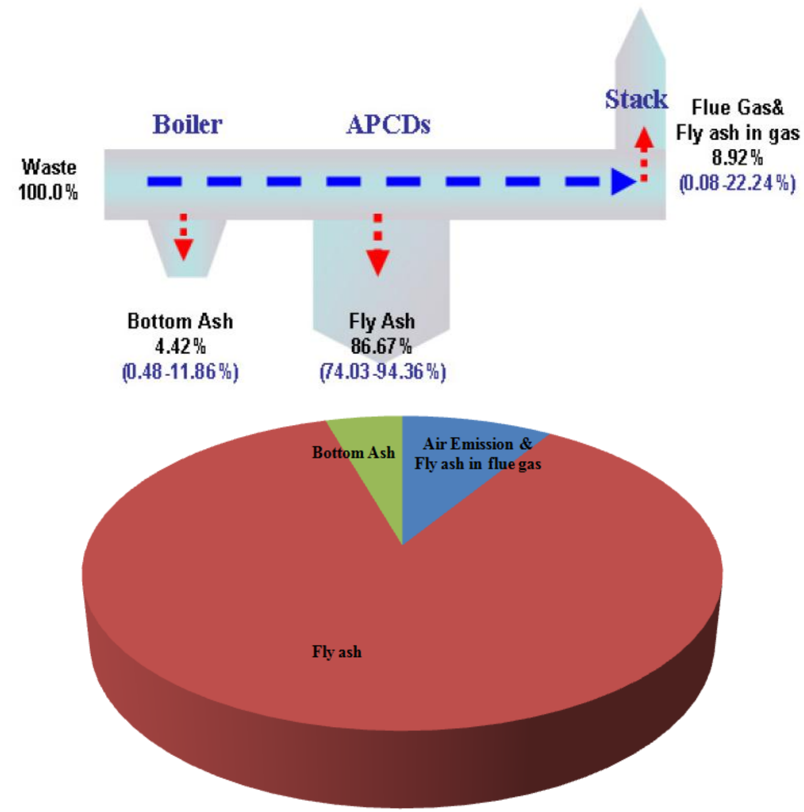
▪ Municipal Waste Incineration

ID	Status of APCDs and Sampling Point	APCDs Type
MWI #3	Incinerator → (200℃, Sampling Point) → SDA → BF → SCR → (200℃, Sampling Point) → Stack	Dry
MWI #6	Incinerator → (220℃, Sampling Point) → ESP → WS → ACI → BF → SCR → (180℃, Sampling Point) → Stack	Wet

- Input Waste : Variety type of waste at the same time
  → Various chemical reactions & effects



- High efficiency APCDs is equipped compared with other facilities
- Air Emission standard in Korea
  (Incineration Facility) : 0.08 mg/Sm^3



MWI Hg Emission Contribution

SDA: Semi-Dry Absorber

BF: Bag Filter

SCR: Selective Catalytic Reactor

WS: Wet Scrubber

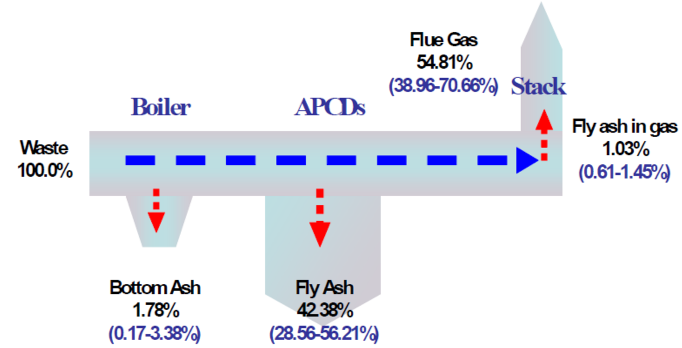
ACI: Activated Carbon Injection

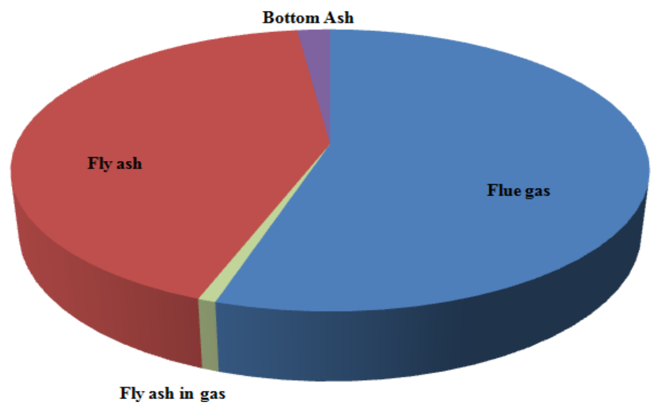
Reference : - Study on Emission of mercury for the atmospheric emissions facilities (I) (2008) NIER , Conducted and Reported by Yonsei

2. Emission, Speciation, and Behavior of Hg in Annex D Sources

▪ Industrial Waste Incineration

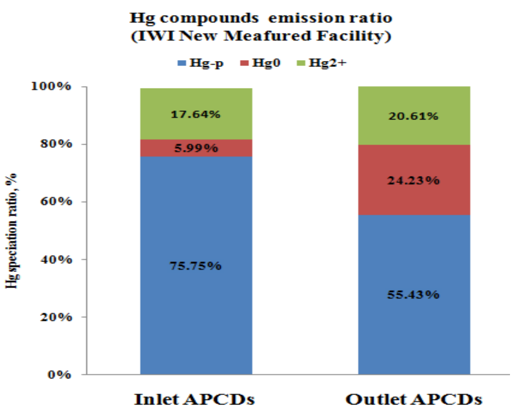
ID		Status of APCDs and Sampling Point	APCDs Type
IWI #1	Existing Measured Facilities	Incinerator – Dry Cyclone – (438℃, Sampling Point) – BF – (145℃, Sampling Point) – Stack	Dry
IWI #6	New Measured Facility	Incinerator – (980℃, Sampling Point) – SNCR – CT – BF – WS – (67℃, Sampling Point) – Stack	Wet

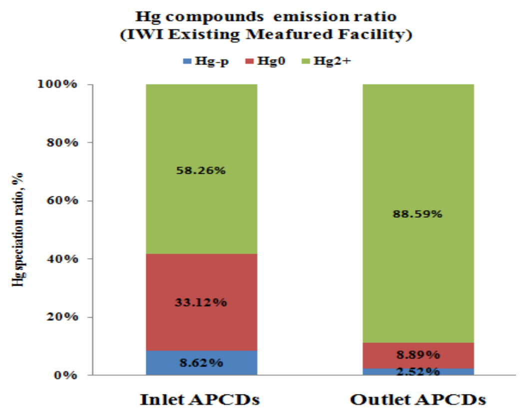




IWI Hg Emission Contribution

- Input Waste : Various type of wastes
- Emission Concentration : large Variation range





- U.S. EPA(1999) Data : 0.48~1,396 ug/Nm^3 (Outlet APCDs) : large variation range
- Air Emission standard in Korea
  (Incineration Facility) : 0.08 mg/Sm^3

BF: Bag Filter

SNCR: Selective Non-Catalytic Reactor

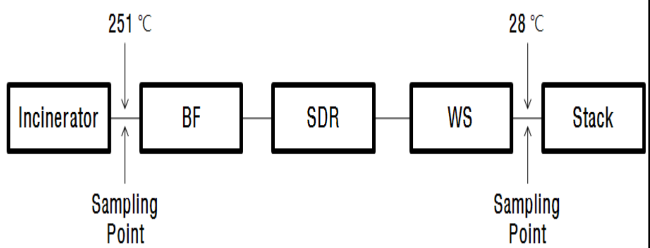
CT: Cooling Tower

WS: Wet Scrubber

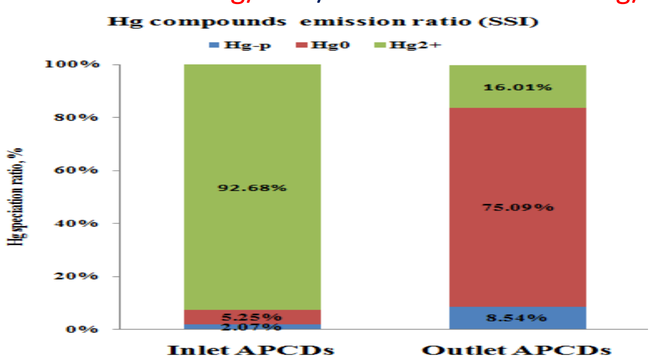
Reference : - Study on Emission of mercury for the atmospheric
emissions facilities (Ⅱ) (2010) NIER, Conducted and Reported by Yonsei

2. Emission, Speciation, and Behavior of Hg in Annex D Sources

Sewage Sludge Incineration

ID	Status of APCDs and Sampling Point	APCDs Type	Etc.
SSI #1 ~ #2		Wet	Fluidized Incinerator

- Total Hg Concentration
- Inlet APCDs : 670.02 ug/Sm^3 / Outlet APCDs : 2.81 ug/Sm^3

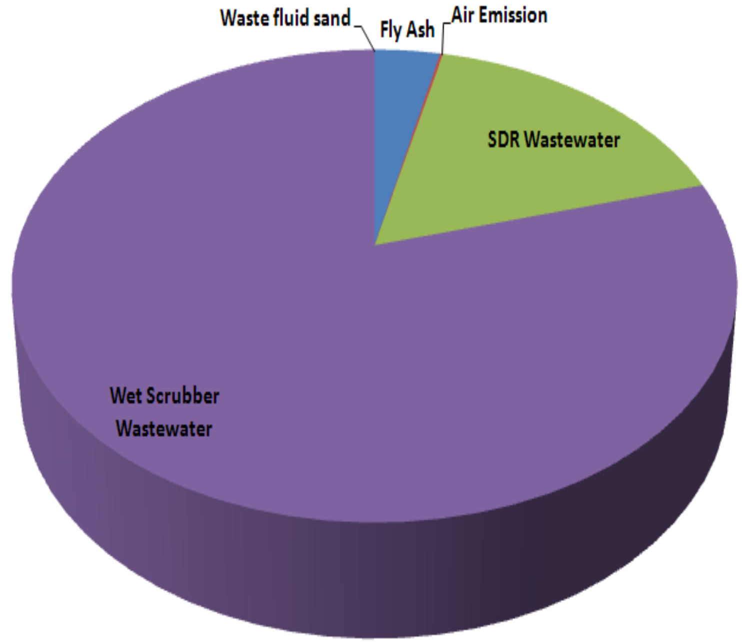


- Measured Facility has High Efficiency APCDs for Hg reduction.

- B/F : Remove Hg-p

- SDR & Wet Scrubber : Remove Hg^{2+}

- Air Emission standard in Korea (Incineration Facility) : 0.08 mg/Sm^3



Sewage Sludge Incinerator
Hg Emission Contribution
Mass balance Ave. (72.4 %)

BF: Bag Filter

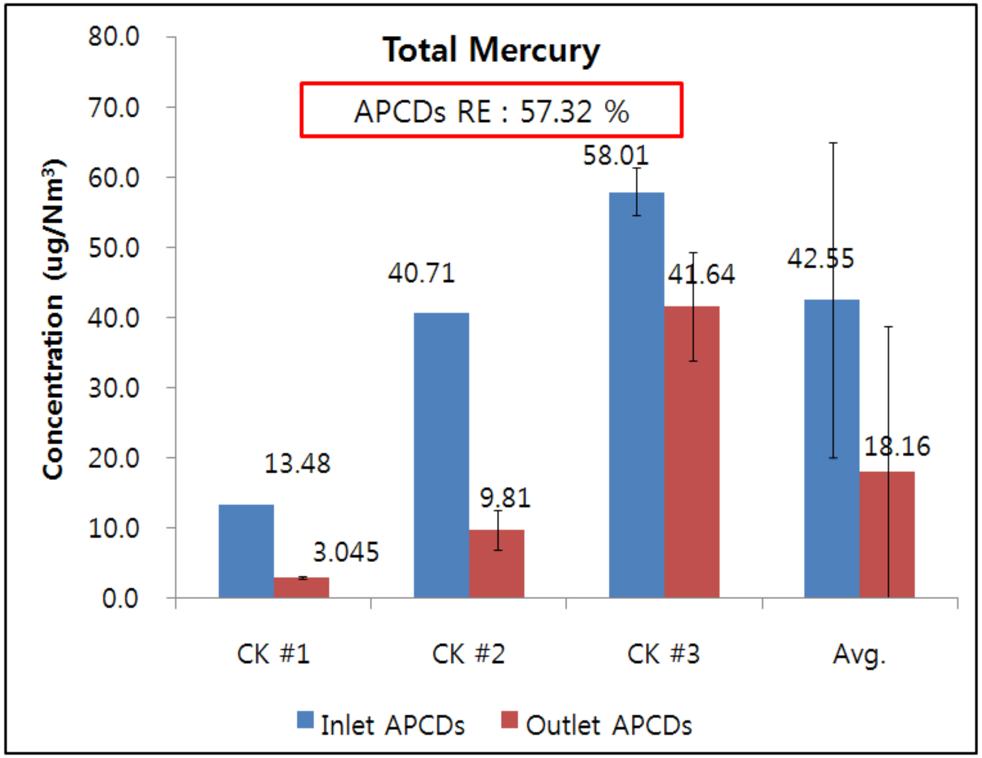
SDR: Semi-Dry Reactor

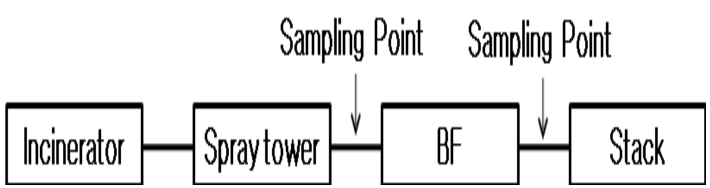
WS: Wet Scrubber

Reference : - Study on Emission of mercury for the atmospheric emissions facilities (I) (2008) NIER , Conducted and Reported by Yonsei

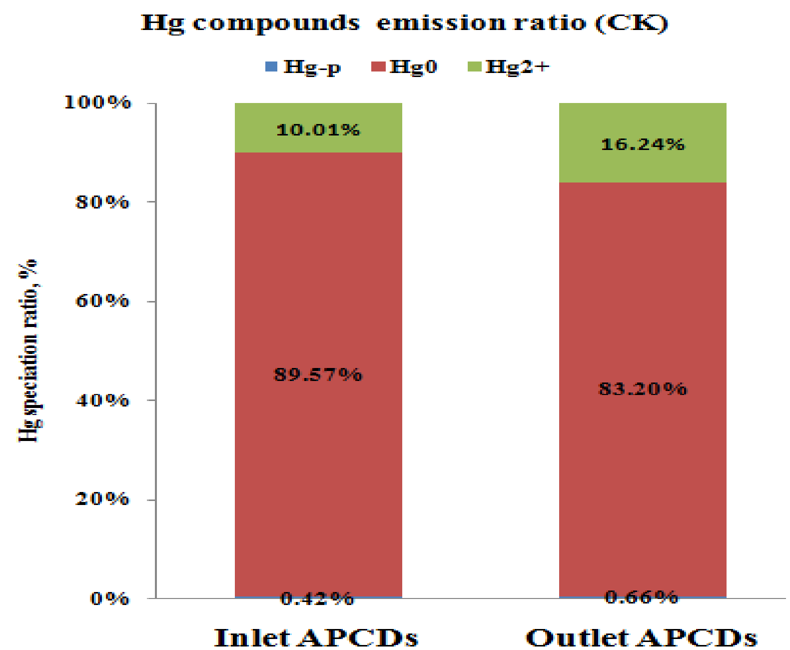
2. Emission, Speciation, and Behavior of Hg in Annex D Sources

▪ Cement Kilns



ID	Status of APCDs and Sampling Point	APCDs Type
CK #1 ~ #3		Dry

- Total Hg Concentration
  - Inlet APCDs : 42.55 ug/Sm^3
  - Outlet APCDs : 18.16 ug/Sm^3



- Input materials : Various type of Secondary fuel & Raw material → Impact on Hg Emissions
- Air Emission standard in Korea

  (Cement Clinker production) : 0.08 mg/Sm^3

BF: Bag Filter

Reference : - Study on Emission of mercury for the atmospheric emissions facilities (I) (2008) NIER , Conducted and Reported by Yonsei

3. Co-beneficial Effect of APCDs on Mercury Removal

▪ Coal-firing Power Plants

[ ] widely used configuration

Fuel	Portion (%)	Configuration of APCDs	Removal (%) Preceding research	Removal (%) Literature	Hg concentration (ug-Hg/m³)
Bituminous	62.79	Boiler – SCR – EP – FGD – Stack	68.87	67	1.64 (0.23~2.47)
	-	Boiler – EP – FGD – Stack	75.76	63	2.01 (1.63~2.27)
Anthracite	16.07	Boiler – SCR – EP – FGD – Stack	78.24	70	2.77 (2.08~3.33)
	42.56	Boiler – EP – FGD – Stack	80.10	81	2.80
	41.37	Boiler – EP – Stack	68.57	22	2.75

● Co-beneficial effect of APCDs

- ESP : only Hg_p is removed
- ESP + FGD : Hg_p and Hg^{2+} are removed
- Hg_p and Hg^{2+} are removed with more Hg^{2+} available at FGD intlet

References : 1) Study on Hg emissions from domestic industrial facilities (I)(2008) NIER, Conducted and Reported by Yonsei
2) Study on Hg emissions from domestic industrial facilities (II)(2010) NIER, Conducted and Reported by Yonsei
3) A study on integrated management of mercury using and emission facilities (2010) NIER
4) Kyu-Sik Park et al., (2008) Emission and speciation of mercury from various combustion sources, Powder Technology, 180, pp. 151-156
5) Jin-Ho Sung et al., (2014) Performance of Removal Efficiency for Mercury Compounds using Hybrid Filter System in a Coal-fired Power Plant, J. KOSAE, 30(3) pp.261-269
6) UNEP (2014) Guidelines BAT/BEP for mercury emission control from coal combustion
7) Technical Background Report for the Global Mercury Assessment 2013

3. Co-beneficial Effect of APCDs on Mercury Removal

- **Coal-firing Power Plants**

Existing Control Equipment	Qualitative Hg Capture
ESPc only	Good capture of particulate- or sorbent-bound
ESPh only	Low co-benefit capture
FF only	Good co-benefit capture of Hg^{2+}; Hg^0
ESPc + Wet FGD	Good co-benefit capture for bituminous coals
ESPh + Wet FGD	Moderate co-benefit capture for bituminous coals
SDA + FF	Very high co-benefit capture expected for bituminous coals
FF + Wet FGD	Good co-benefit capture for bituminous coal
SCR + ESPc	Good capture of particulate- or sorbent-bound Hg
SCR + ESPh	Low co-benefit capture
SCR + ESPc + Wet FGD	Good capture of particulate- or sorbent-bound Hg
SCR + HEX + LLT-ESP + Wet FGD	Very high co-benefit capture for bituminous coals, less for low rank coals
SCR + SDA + FF	Very high co-benefit capture for bituminous coals
SCR + ESPh + Wet FGD	Poor capture of particulate-bound Hg and total Hg for low rank coals
SCR + FF + Wet FGD	High level of Hg capture for all coals

Note: special considerations for seawater FGD
ESP = electrostatic precipitator   ESPc = cold side ESP
ESPh = Hot side ESP   FF = fabric filter
SCR = selective catalytic reduction   SDA = spray dryer absorber (dry scrubber)
Wet FGD = wet flue gas desulfurization scrubber

Reference : European IPPC Bureau (EIPPCB) (2013). Best Available Techniques (BAT) Reference Document for the Large Combustion Plants
Srivastava et al., (2006). Control of Mercury Emissions from Coal-Fired Electric Utility Boilers, Environ. Sci. Technol., vol. 40, pp. 1385–1392, 2006.

3. Co-beneficial Effect of APCDs on Mercury Removal

▪ Non-ferrous Metal Facilities

[ ] widely used configuration

Non-ferrous metal	Configuration of APCDs	Removal (%)		Hg concentration (ug-Hg/m³)
		Preceding research	Literature	
Zinc	ESP – Venturi Scrubber – ESP – Boliden Norzink – Dry Tower – SO_2 1st Adsorp. Tower – SO2 2nd Adsorp. Tower – Scrubber – Stack	99.9	99	1.23 (0.71~1.80)
Cooper	WS – ESP – Dry Tower – SO_2 1st Adsorp. Tower – SO2 2nd Adsorp. Tower – FGD – Stack	99.9	99	0.40 (0.20~0.58)
Lead	ESP – Venturi Scrubber – ESP – Dry Tower – SO_2 1st Adsorp. Tower – SO2 2nd Adsorp. Tower – Scrubber – Stack	99.9	99	3.09 (0.57~6.44)

● High Hg removal efficiency of APCDs for
- Hg oxidized in sulfuric acid process
- Most Hg^{2+} controlled from Boilden Norzink

Reference : 1) Study on Hg emissions from domestic industrial facilities (I)(2008) NIER, Conducted and Reported by Yonsei
2) Study on Hg emissions from domestic industrial facilities (II)(2010) NIER, Conducted and Reported by Yonsei
3) Technical Background Report for the Global Mercury Assessment 2013

3. Co-beneficial Effect of APCDs on Mercury Removal

- **Waste Incineration (MSW)**

widely used configuration

Waste	Scale (ton/hr)	Configuration of APCDs	Removal (%) Preceding research	Removal (%) Literature	Hg concentration (ug-Hg/m³)
Municipal Solid waste	0.67	SDS — BF — Stack	74.55	-	33.98
	1.87-8.47	SDR — BF — SCR or SNCR — Stack	98.14	-	1.40
	6.25-11.65	SNCR — SDR — BF — SCR — Stack	97.08	-	4.55
	8.30	SDA — BF — Stack	68.61	-	6.84
	7.50	SDA — BF — SCR — Stack	93.95	-	10.52
	2.79	SDA — ACI — BF — SCR — Stack	92.92	-	7.07
	5.30	SDA — ACI — BF — Stack	86.92	-	4.19
	4.75	EP — WS — ACI — BF — SCR — Stack	71.07	99	4.42

Reference : 1) Study on Hg emissions from domestic industrial facilities (I)(2008) NIER, Conducted and Reported by Yonsei
2) Study on Hg emissions from domestic industrial facilities (II)(2010) NIER, Conducted and Reported by Yonsei

3. Co-beneficial Effect of APCDs on Mercury Removal

▪ Waste Incineration (ISW)

widely used configuration (red dashed box)

Waste	Scale (ton/hr)	Configuration of APCDs	Removal (%)		Hg concentration (ug-Hg/m³)
			Preceding research	Literature	
Industrial Solid waste	3.00	CY – DR – BF – Wet EP – Adsorption – Stack	95.08	-	3.86
	0.40-2.00	CY – BF – Stack	41.79	-	918.71
	3.00-3.84	CY – BF or EP – WS – PT or SCR – Stack	60.52	-	6.98
	1.20-4.00	SNCR – SDR or ACI – CY – BF – WS – Stack	43.41	>95	41.31-64.48
	1.40-6.25	EP – WS – SCR – Stack	92.16	-	43.16
	6.00-6.25	EP – VS – WS – SCR – Stack	99.23	-	0.13-40.69

● Low removal efficiency & high Hg emission

- Some IWI need to apply BEP & BAT (ACI, WS etc.)

Reference : 1) Study on Hg emissions from domestic industrial facilities (I)(2008) NIER, Conducted and Reported by Yonsei
2) Study on Hg emissions from domestic industrial facilities (II)(2010) NIER, Conducted and Reported by Yonsei

3. Co-beneficial Effect of APCDs on Mercury Removal

▪ Cement Kilns

[ ] widely used configuration

Facility	Portion of production (%)	Configuration of APCDs	Removal (%)		Hg concentration (ug-Hg/m³)
			Preceding research	Literature	
CK (3)	35.74	SNCR — BF — Stack	51.43%	55%	18.17 (3.05~41.64)
CK (1)	7.98	SNCR — ESP — BF — Stack	-	77%	-

● Simple APCDs & low removal efficiency

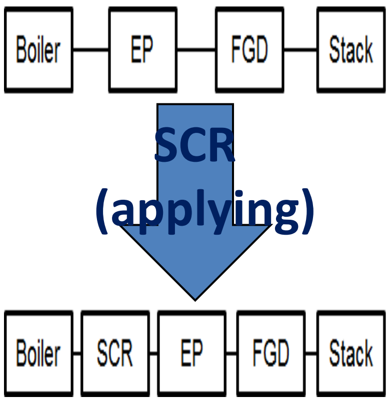
- Using alternative fuel(waste) → changes in mercury emssion
- Need to apply Best Available Technology & Best Environmental Practices

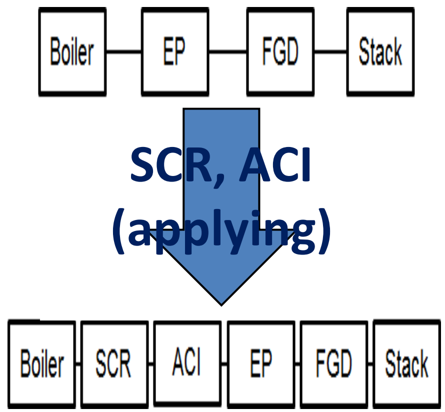
Reference : 1) Study on Hg emissions from domestic industrial facilities (I)(2008) NIER, Conducted and Reported by Yonsei
2) Study on Hg emissions from domestic industrial facilities (II)(2010) NIER, Conducted and Reported by Yonsei

4. Effect of BATs Application to Existing APCDs

- **Coal-firing Power Plants**

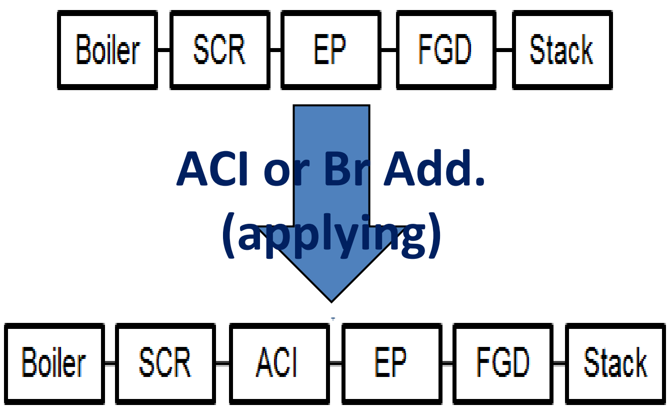
- Anthracite





	Removal (%)	Hg emission (ton/yr)
2010	80	0.002
SCR, FGD (Applying)	80	0.001
ACI (Applying)	90	0.001

- Bituminous



	Removal (%)	Hg emission (ton/yr)
2010	75	1.171
ACI or Br (Applying)	90	0.507

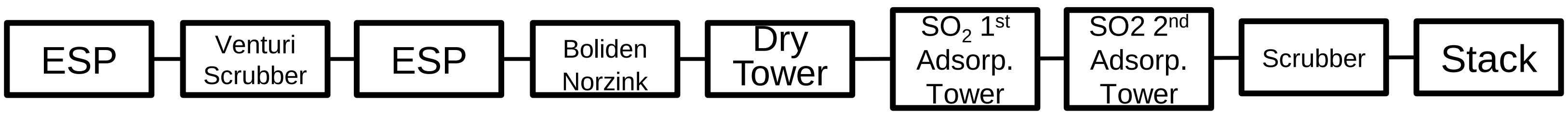
4. Effect of BATs Application to Existing APCDs

- **Non-ferrous Metal Facilities**

- Zinc

- Cooper

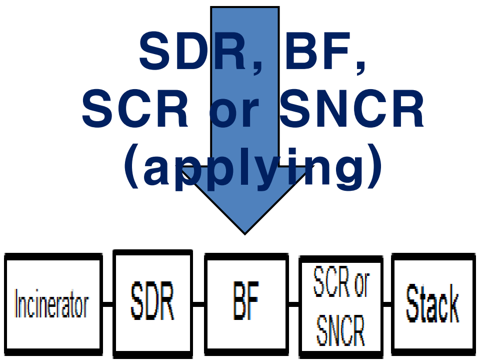
- Lead



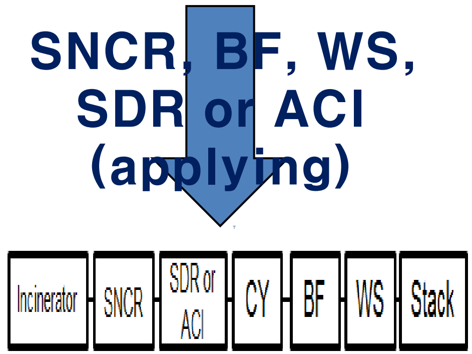
Division	Zinc	Cooper	Lead
Removal (%)	99.9	99.9	99.9
2010 (ton/yr)	0.005	0.004	0.003

4. Effect of BATs Application to Existing APCDs

- Waste Incineration



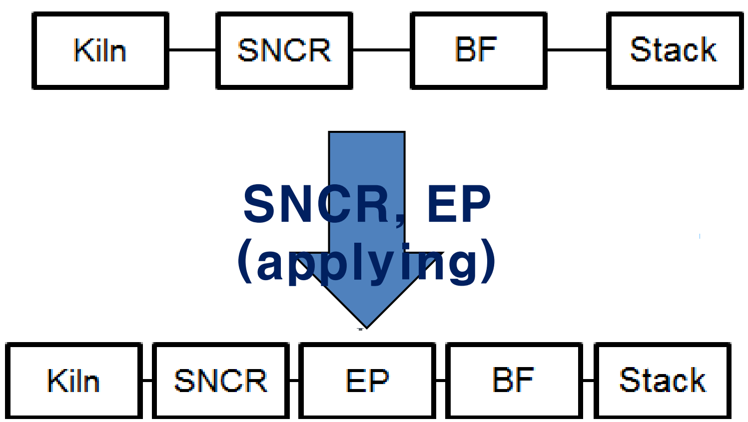
<Municipal Solid Waste>



<Industrial Solid Waste>

Division		Removal (%)	Hg emission (ton/yr)
MSW	2010	-	0.12
	SDR, BF, SCR or SNCR (applying)	98	0.04
ISW	2010	-	0.14
	SNCR, SDR or ACI, BF, WS (applying)	98	0.08

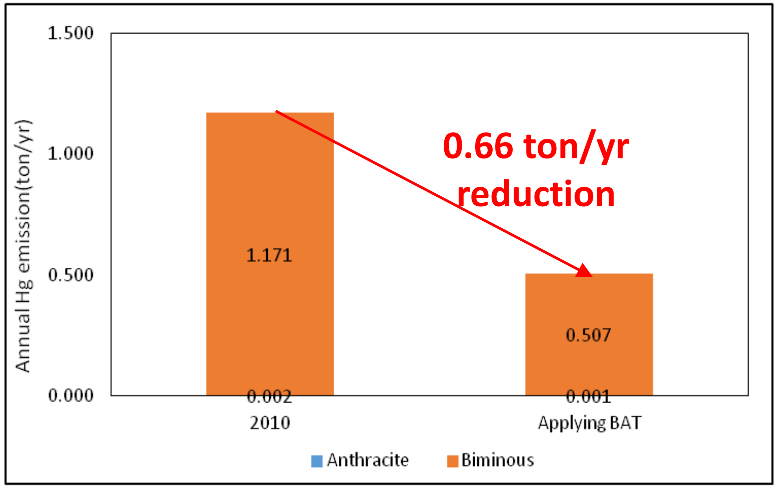
- Cement Kilns



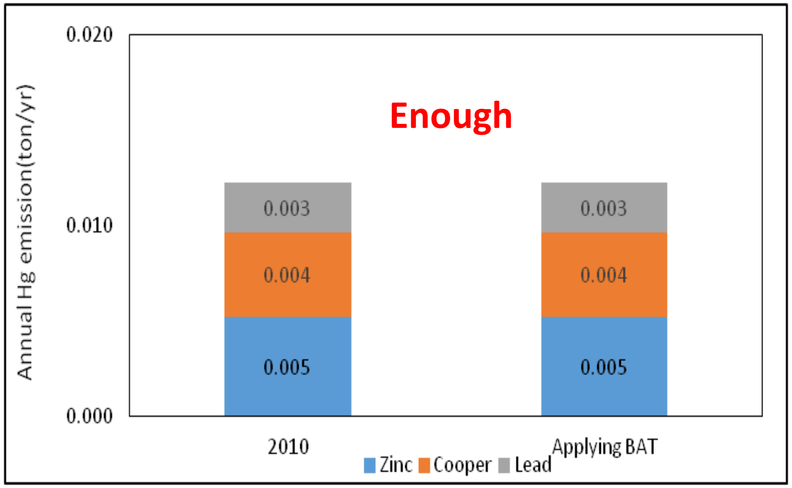
Division	Removal (%)	Hg emission (ton/yr)
2010	50	2.68
SNCR, EP (applying)	77	1.36

4. Effect of BATs Application to Existing APCDs

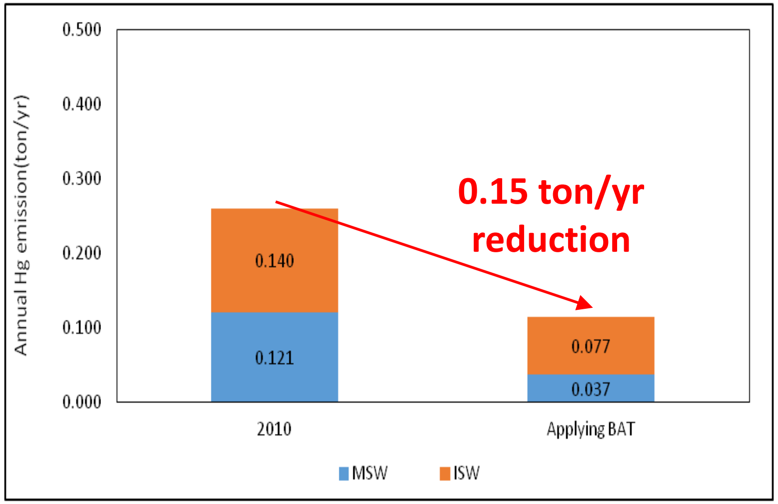
- Coal power plants



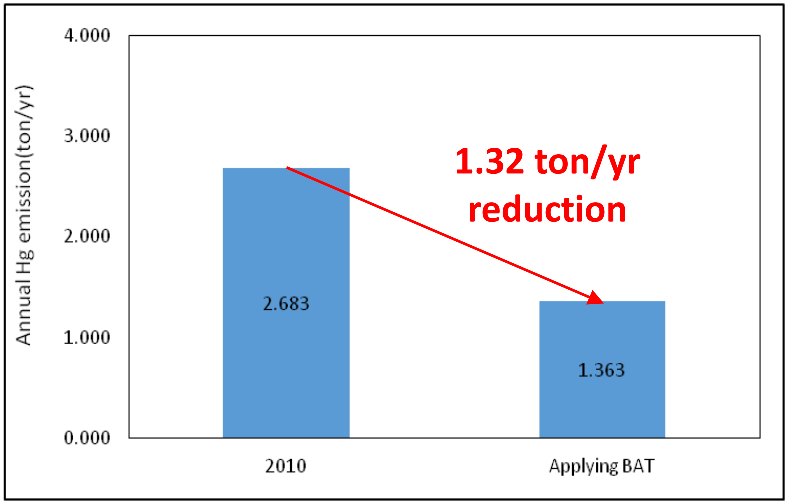
- Non-ferrous metal smelting facilities



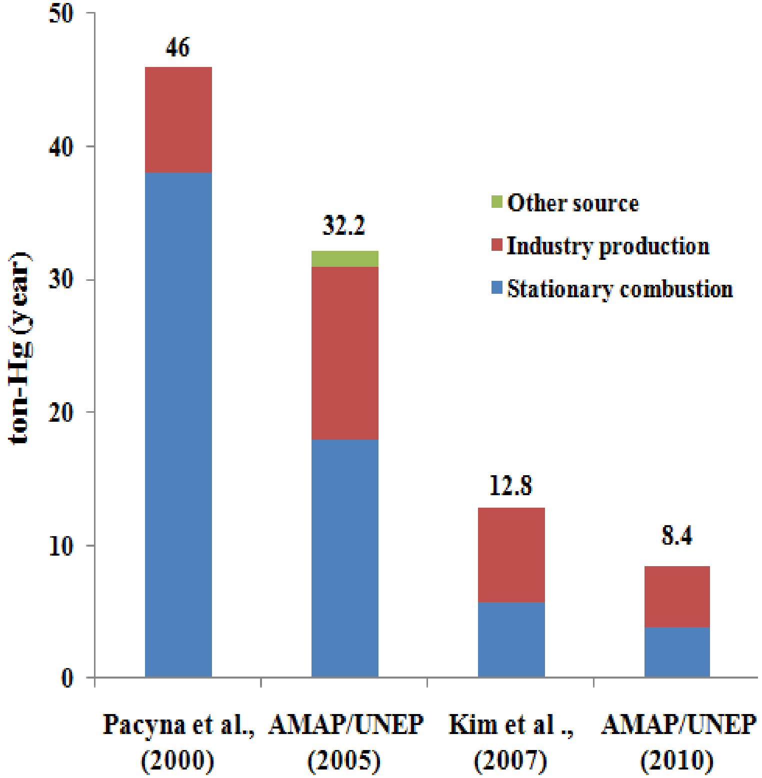
- Waste incineration facilities



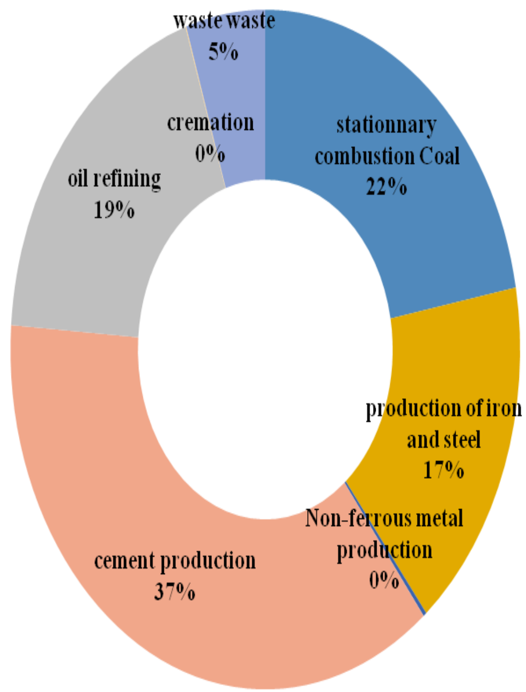
- Cement clinker production facilities



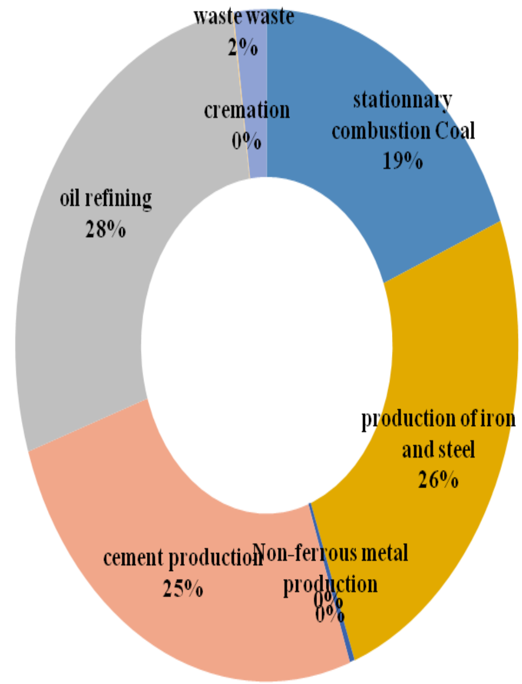
4. Effect of BATs Application to Existing APCDs



Decreasing Trend



AMAP/UNEP (2010)
8.04 ton/yr



Applying BATs (2010)
5.40 ton/yr

5. Summary

- International Convention on Mercury (Minamata Convention) was opened for signature by UNEP in 2013.
- Mercury in flue gas was mainly speciated into gaseous form, particle bound mercury was less. Elemental Hg was oxidized in dry APCDs.
  Hg^{2+} was absorbed in wet APCDs scrubber solution.
- Inclusion of real output distribution factors resulted decrease in share of mercury release into air, sector specific treatment/disposal and impurity in products, where as distribution in water and land increased; this is due to the use of efficient process technology and the co-beneficial effects by existing APCDs.
- Article 8 of the Minamata Convention on Mercury addresses controlling and where feasible reducing emissions of mercury (Hg) and Hg compounds (total Hg) to the atmosphere through measures to control emissions. BAT (Best Available Techniques) Guidance Documents for the control of Hg emissions will be soon available for Annex D facilities.
- The attempt to utilize such BATs to existing APCDs in Annex D facilities was made by suggesting proper BATs and which could be resulted in the reduction of mercury emission more. In conclusion the emission inventory of mercury would be reduced to under 5 tons annually by such application in South Korea.

THANK YOU FOR LISTENING

seoyc@yonsei.ac.kr