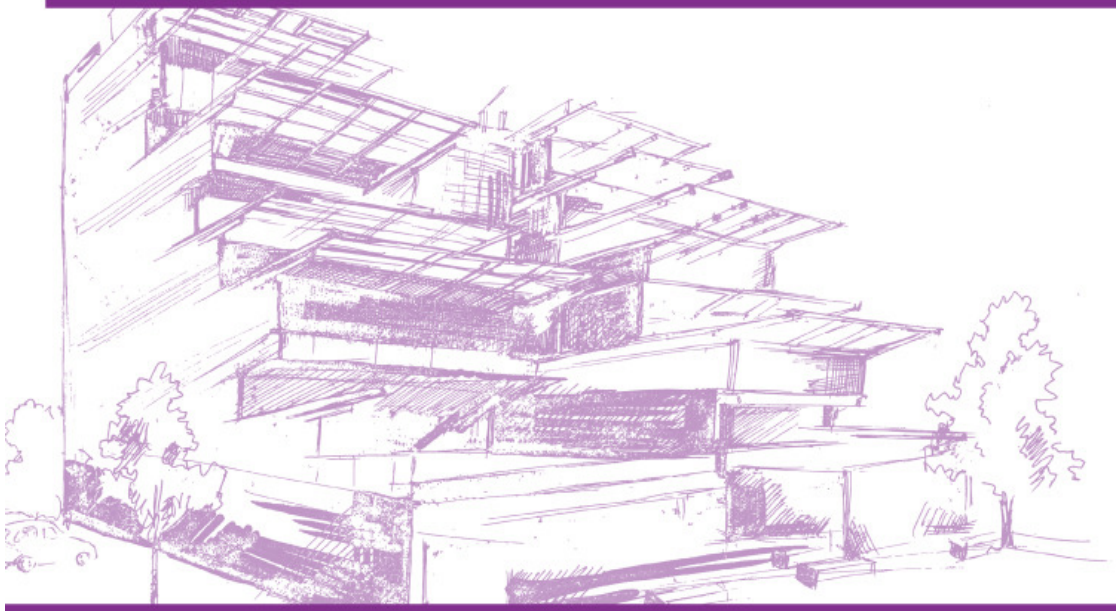
3rd International Conference on Earth Science & Climate Change, San Francisco, July 28-30, 2014

Overview of Speciated Mercury at Anthropogenic Emission Sources



Shuxiao Wang

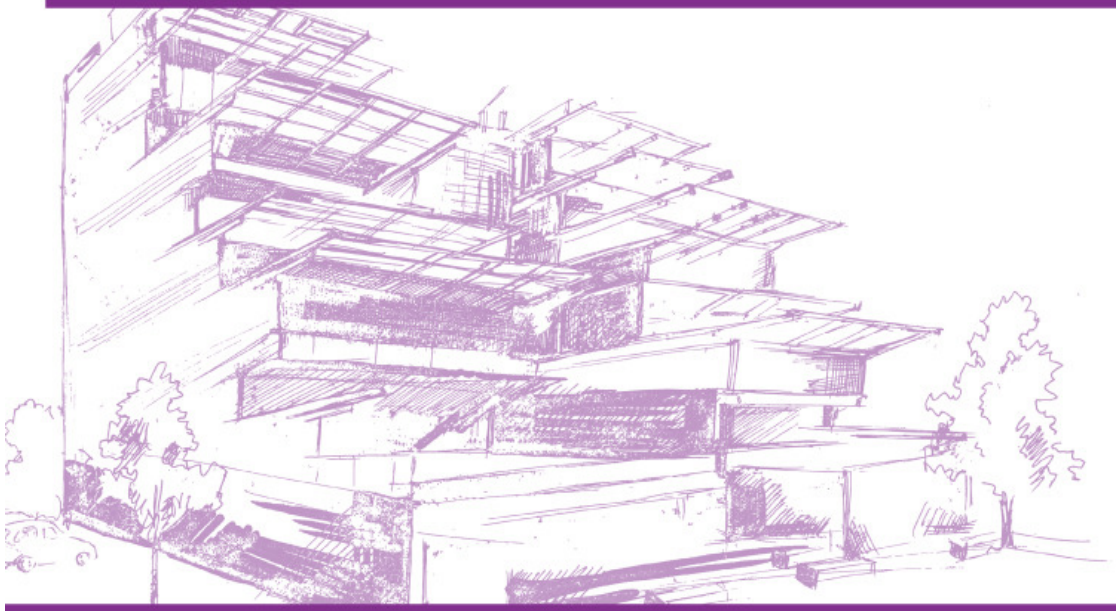
Tsinghua University

Contents

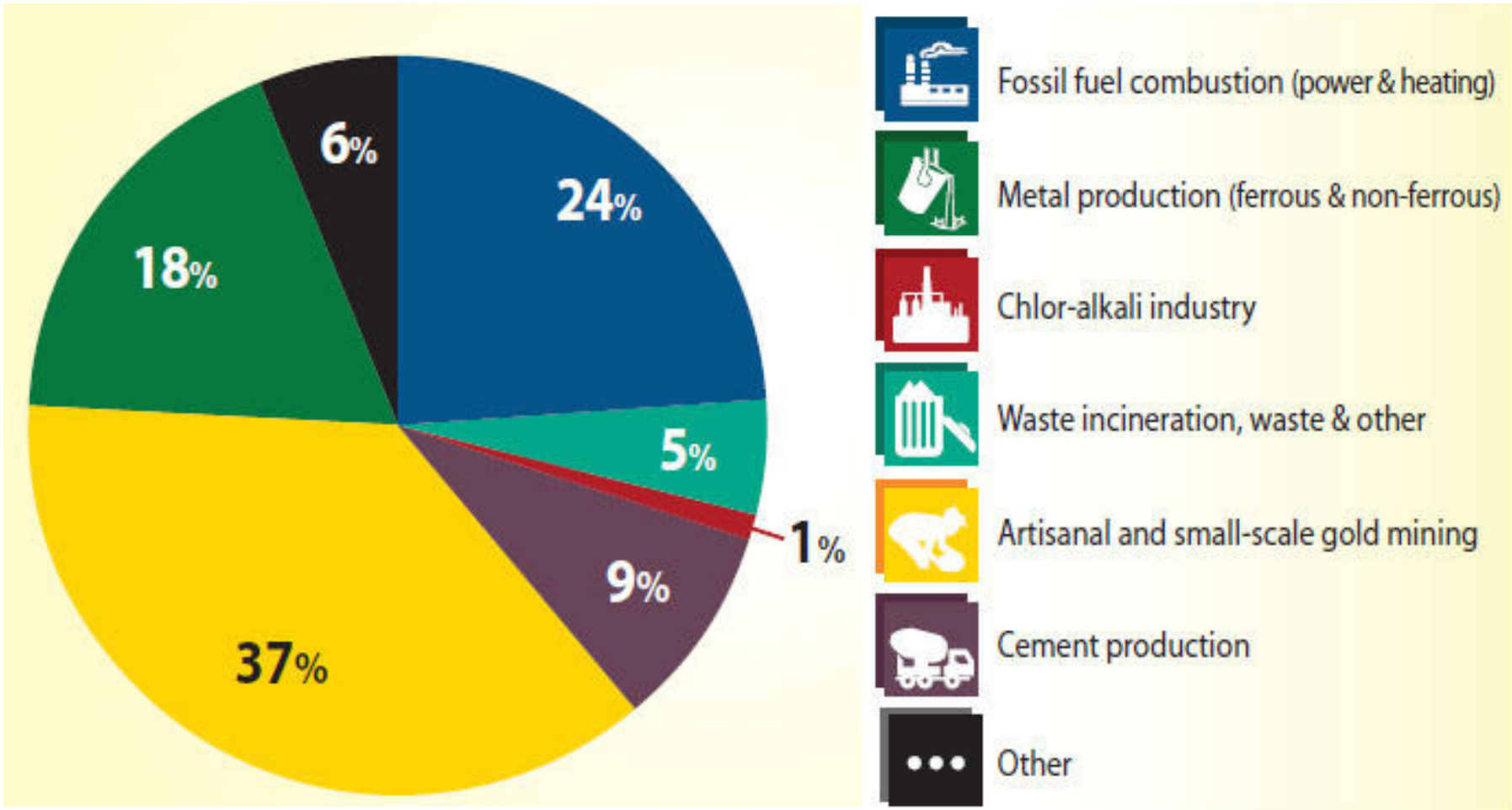


- **Introduction of Hg emission and speciation**
- **Hg speciation and transformation in flue gas**
  - ***Coal combustion***
  - ***Cement production***
  - ***Non-ferrous metal smelting***
  - ***Iron and steel production***
- **Speciated Hg emissions for China**
- **Conclusions**

Introduction of mercury emission and speciation



Global anthropogenic Hg emissions to air



UNEP. Global Mercury Assessment, 2013

Speciation profile of Hg emissions

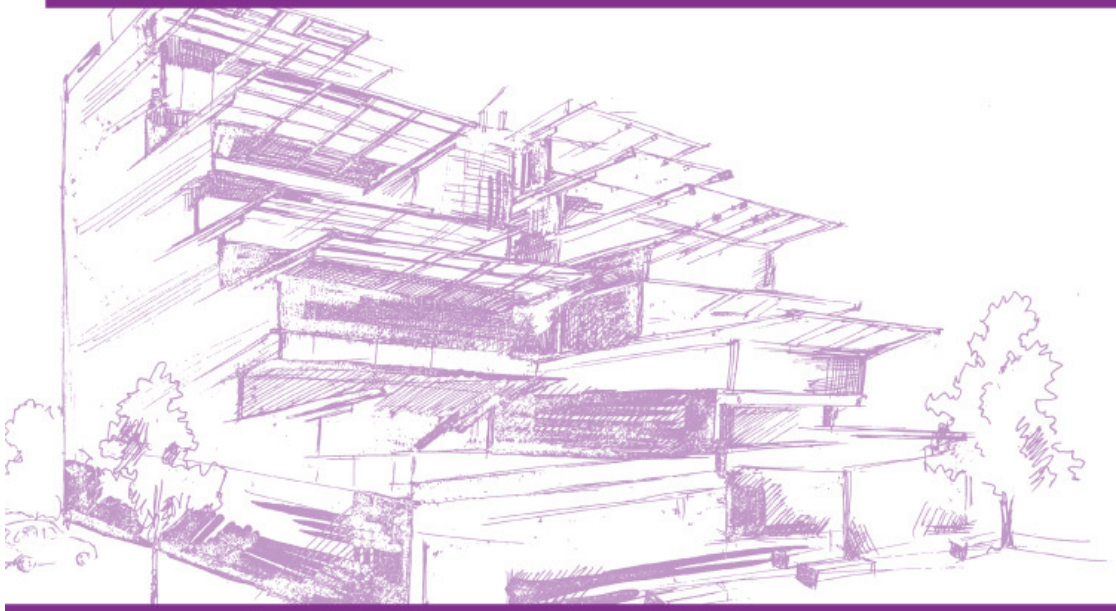


	Source category	Hg^0	Hg^{2+}	Hg^p
1.	Coal combustion[a]			
	Power plants	0.20	0.78	0.02
	Industrial use			
	(a) w/PM control devices	0.20	0.78	0.02
	(b) Stoker, w/o PM control devices	0.09	0.03	0.88
	(c) Cyclone, w/o PM control devices	0.23	0.35	0.42
	(d) Coke production	0.07	0.58	0.35
	(e) Coke/burned, w PM control devices	0.20	0.78	0.02
	(f) Coke/burned, w/o PM control devices	0.07	0.58	0.35
	Residential and other uses	0.09	0.03	0.88
2.	Fuel oil for stationary sources (e.g., power plants, industrial use)[b]	0.50	0.40	0.10
3.	Gasoline, diesel, and kerosene combustion[b]	0.50	0.40	0.10
4.	Biofuel combustion[c]	0.96	0.00	0.04
5.	Grassland/savanna burning[c]	0.96	0.00	0.04
6.	Forest burning[c]	0.96	0.00	0.04
7.	Waste and residue burning[c]	0.96	0.00	0.04
8.	Coal mines spontaneous burning[d]	0.09	0.03	0.88
9.	Cement production[b]	0.80	0.15	0.05
10.	Iron and steel production[b]	0.80	0.15	0.05

The data used is

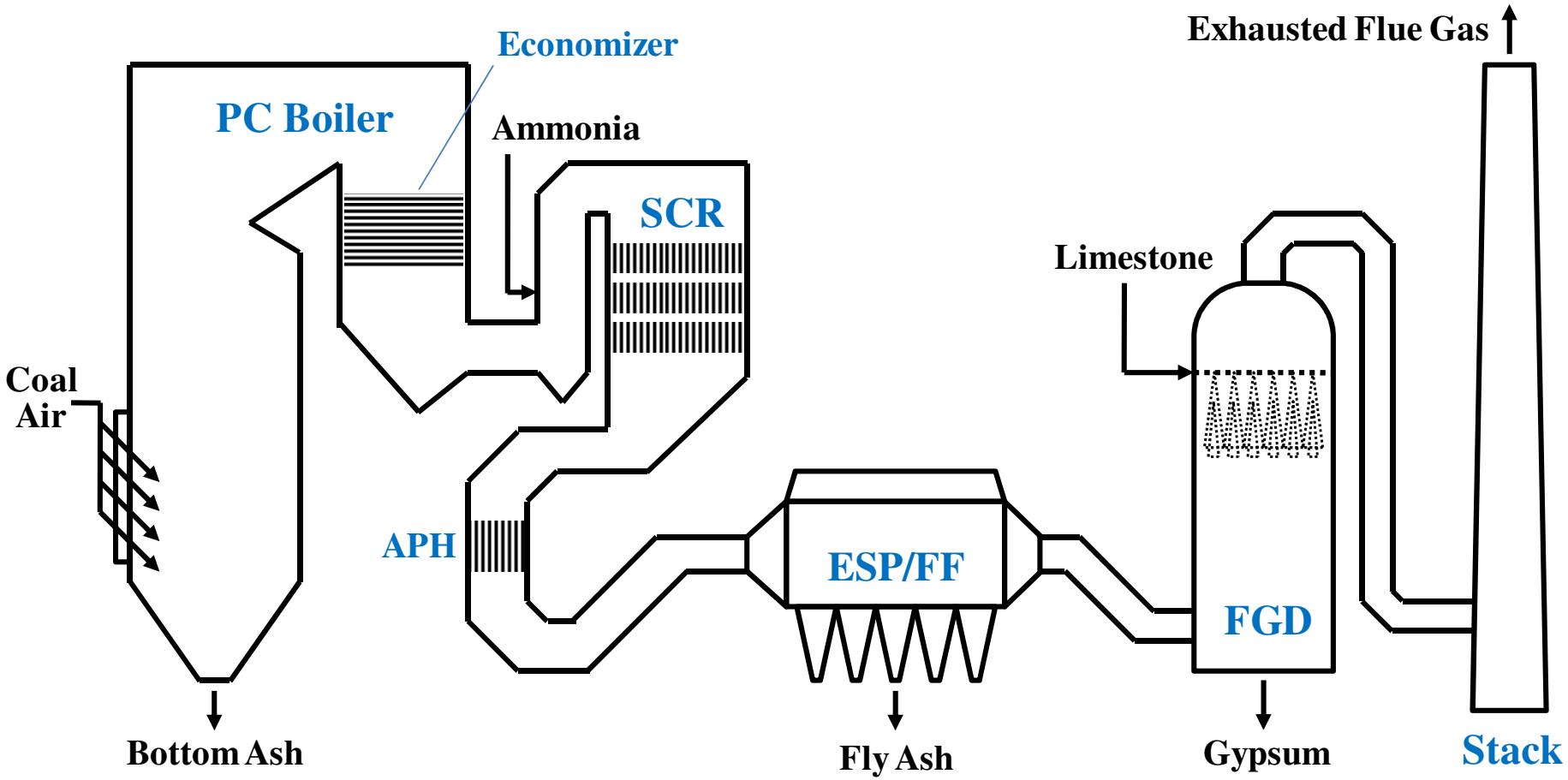
- **for outdated industrial process/air pollution control techniques**
- **not from field tests**

Hg speciation and transformation in coal combustion



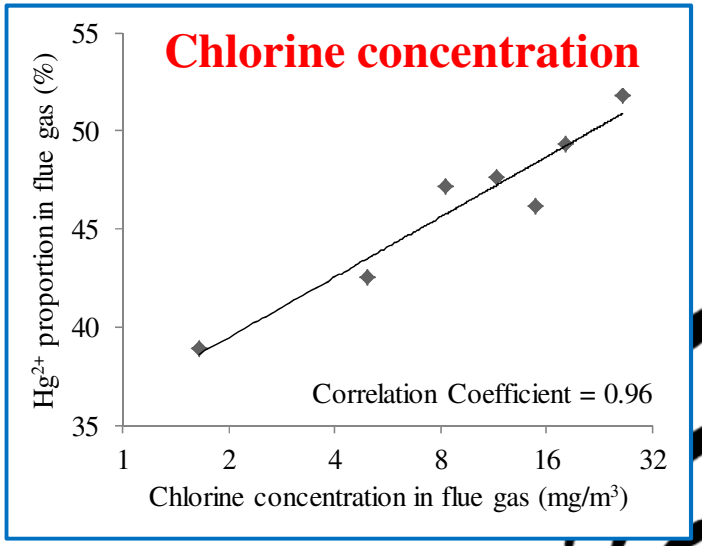
Configuration of coal-fired power plants

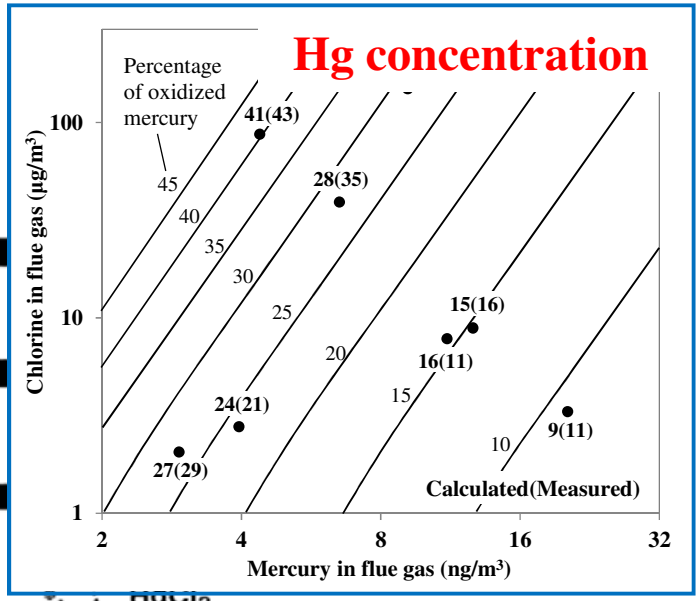


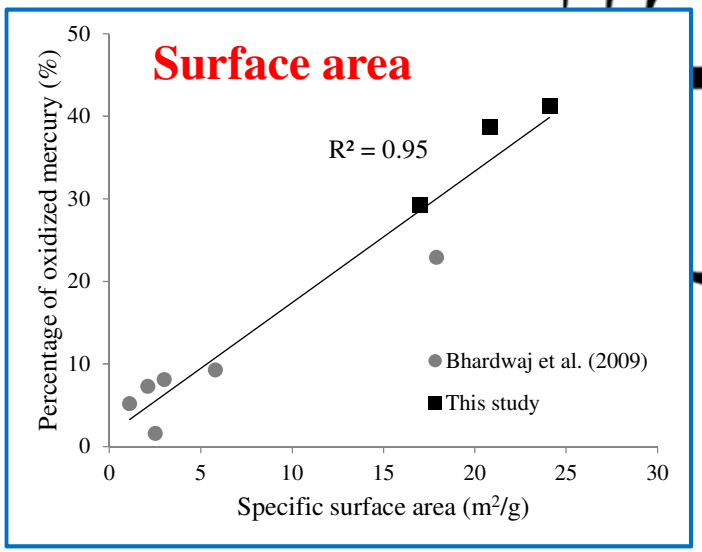


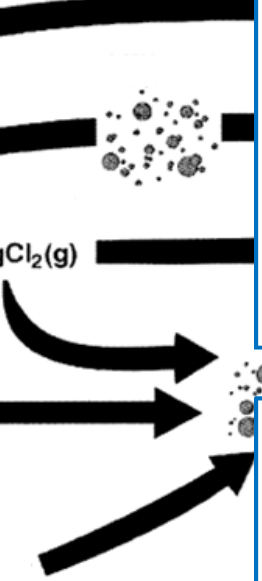
Hg speciation in coal combustion flue gas

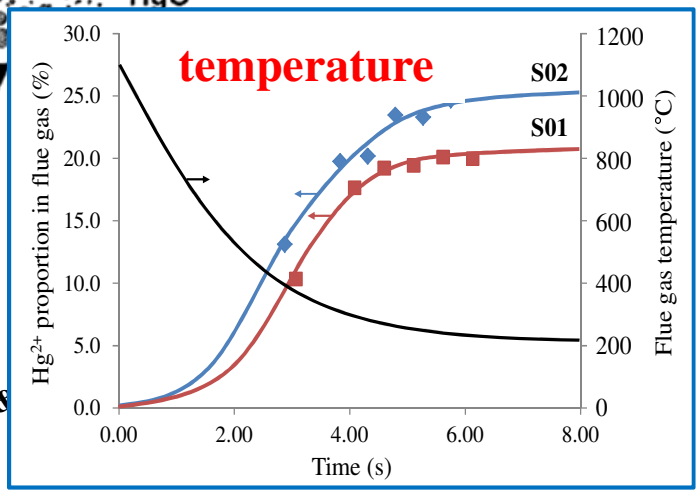








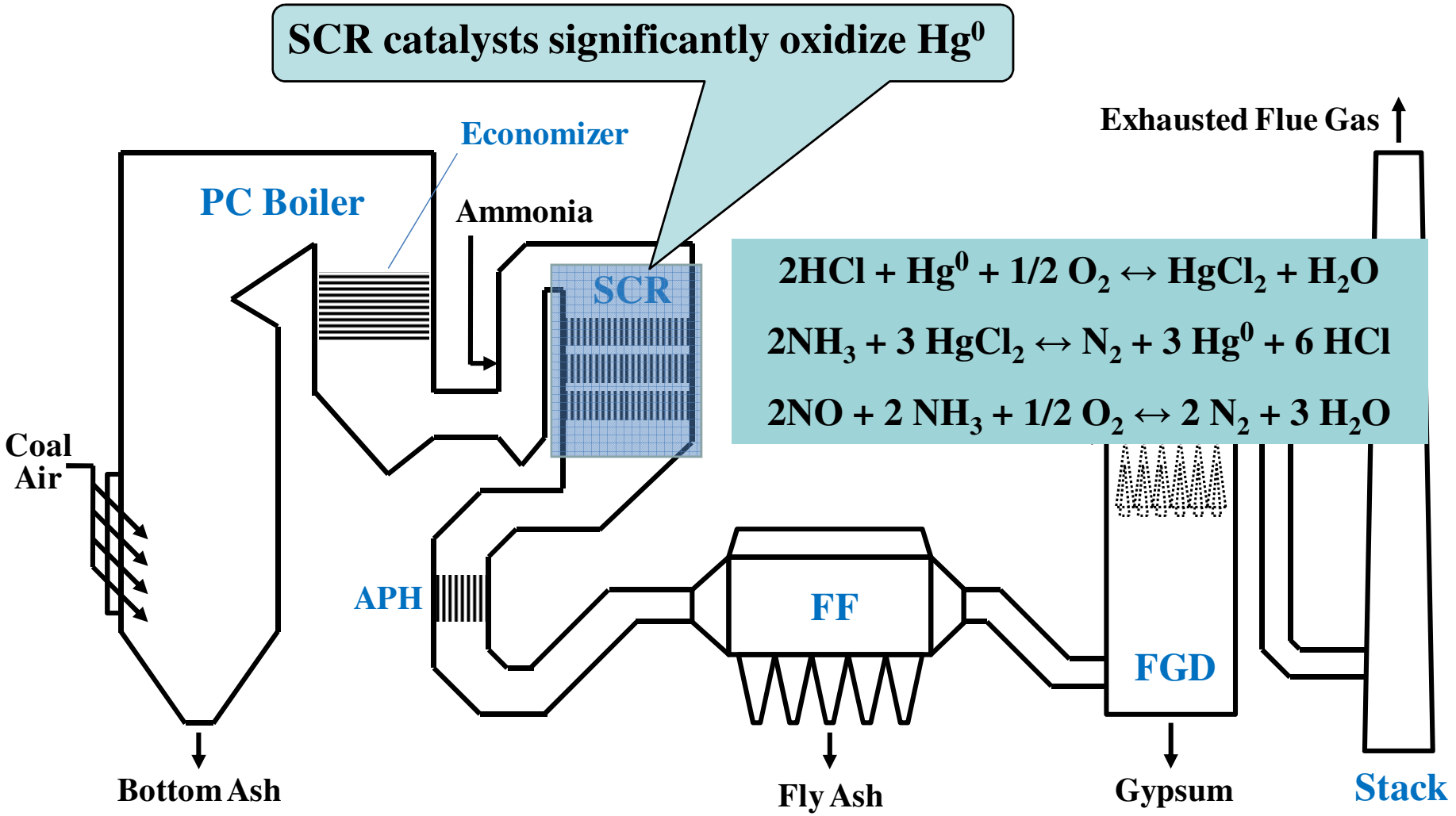




Zhang et al., in preparation

Hg oxidation across SCR



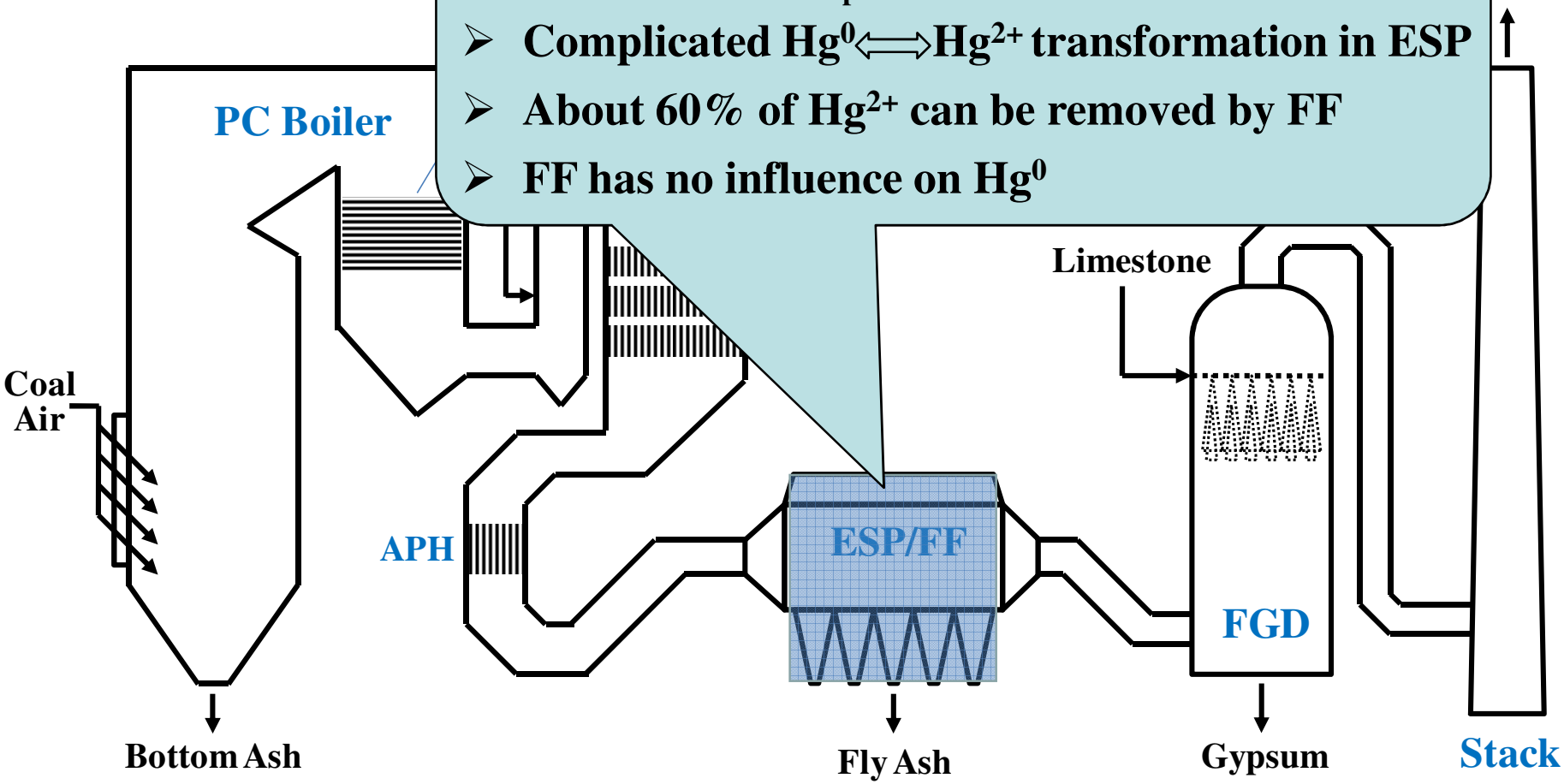


Senior, 2005

Hg transformation across ESP/FF



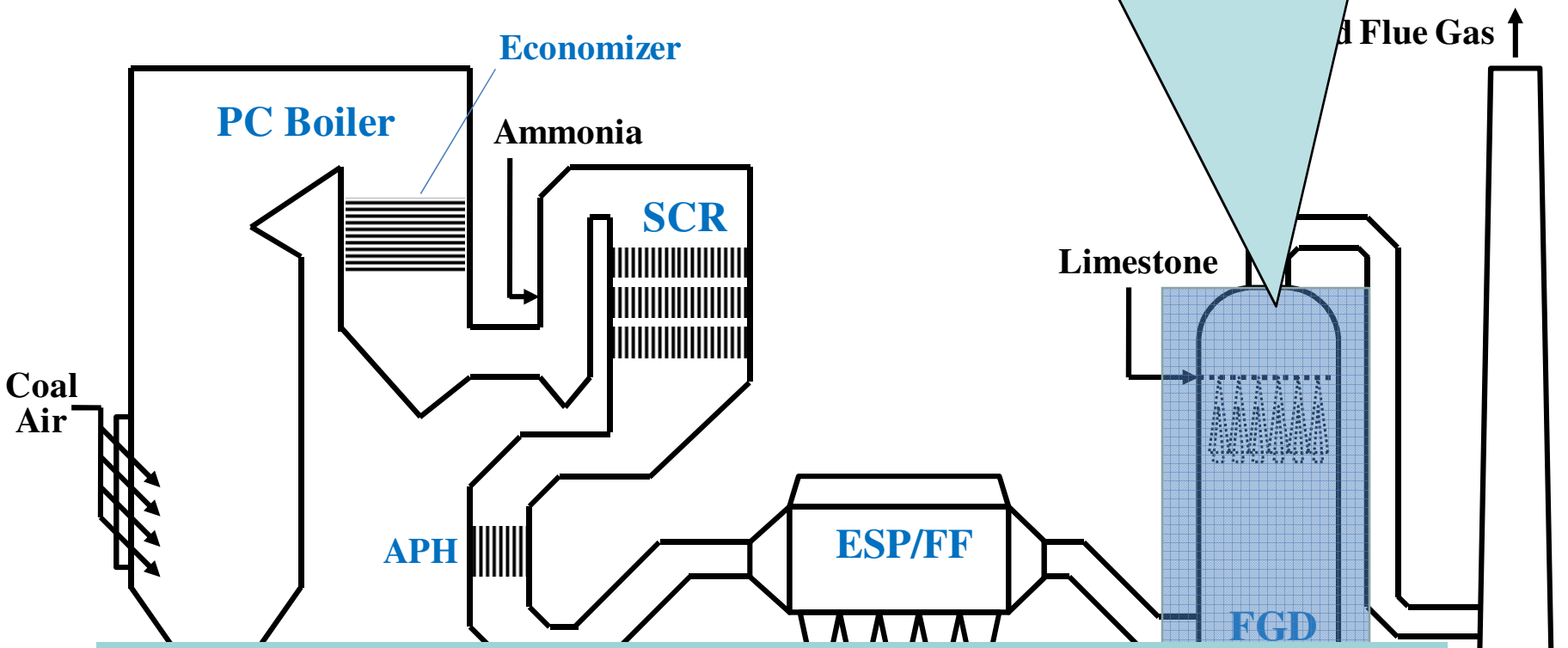
- Over 99% of Hg_p can be removed by ESP/FF
- Complicated $Hg^0 \Longleftrightarrow Hg^{2+}$ transformation in ESP
- About 60% of Hg^{2+} can be removed by FF
- FF has no influence on Hg^0



Hg transformation across WFGD



➢ About 80% of Hg^{2+} can be removed by WFGD



$$HgCl_2(g) \Leftrightarrow HgCl_2(aq)$$

$$HgCl_2(aq) + SO_3^{2-}(aq) + H_2O \Leftrightarrow Hg(g) + SO_4^{2-}(aq) + 2Cl^-(aq) + 2H^+(aq)$$

$$Hg(g) + 2Cl(ads) \Leftrightarrow HgCl_2(g)$$

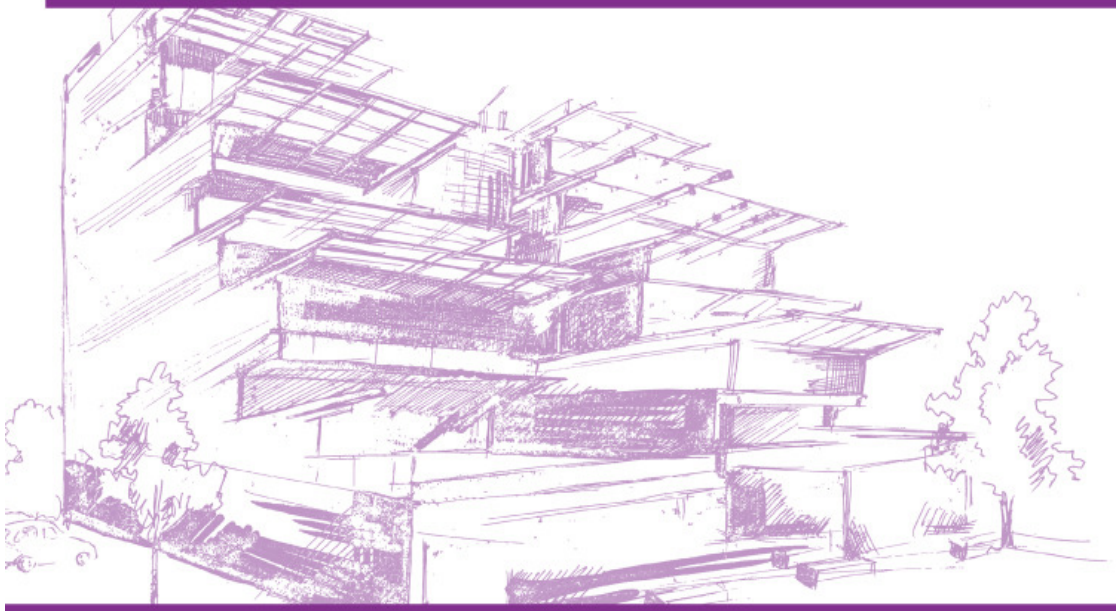
Summary of Hg speciation after APCDs



	Hg^0	Hg^{2+}	Hg_p	No. of tests
None	56 (8-94)	34 (5-82)	10 (1-28)	13
ESP	58 (16-95)	41 (5-84)	1.3 (0.1-10)	31
ESP+WFGD	84 (74-96)	16 (4-25)	0.6 (0.1-1.9)	7
FF	31 (10-58)	58 (34-76)	11 (1-25)	3
WS	65 (39-87)	33 (10-60)	2.0 (0.2-4.5)	6
SCR+ESP+WFGD	73.8 (16-96)	26 (4-84)	0.2 (0.1-0.4)	6
FF+WFGD	78	21	0.9	1
(CFB+)ESP	72	27.4	0.6	1

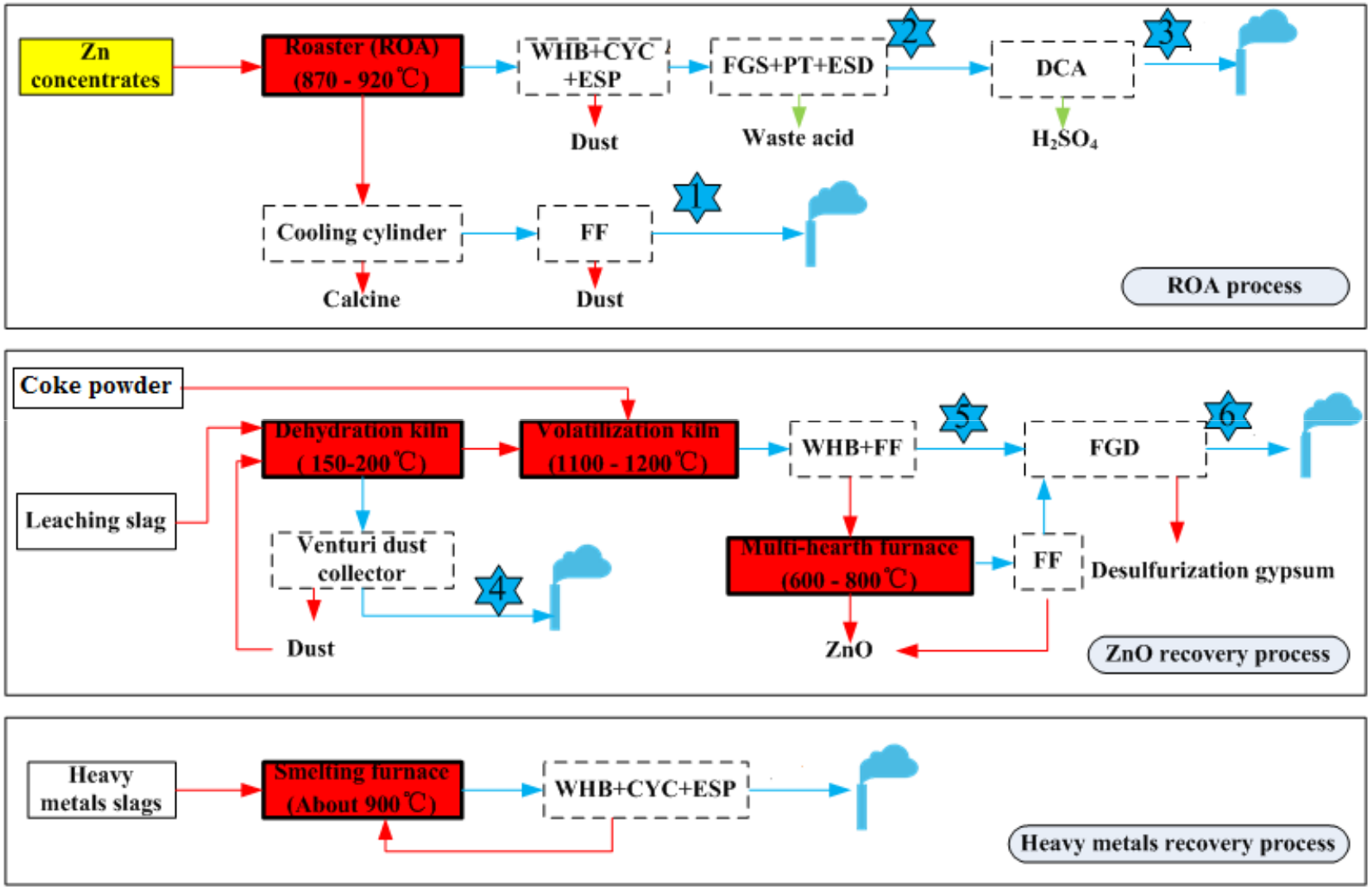
Chen et al., 2007; Zhou et al., 2008; Wang et al., 2008; Yang et al., 2007; Duan et al., 2005; Kellie et al., 2004; Shah et al., 2010; Guo et al., 2004; Tang, 2004; Goodarzi, 2004; Lee et al., 2006; Kim et al., 2009; Wang et al., 2010; Zhang et al., 2012

Hg speciation and transformation in non-ferrous metal smelters



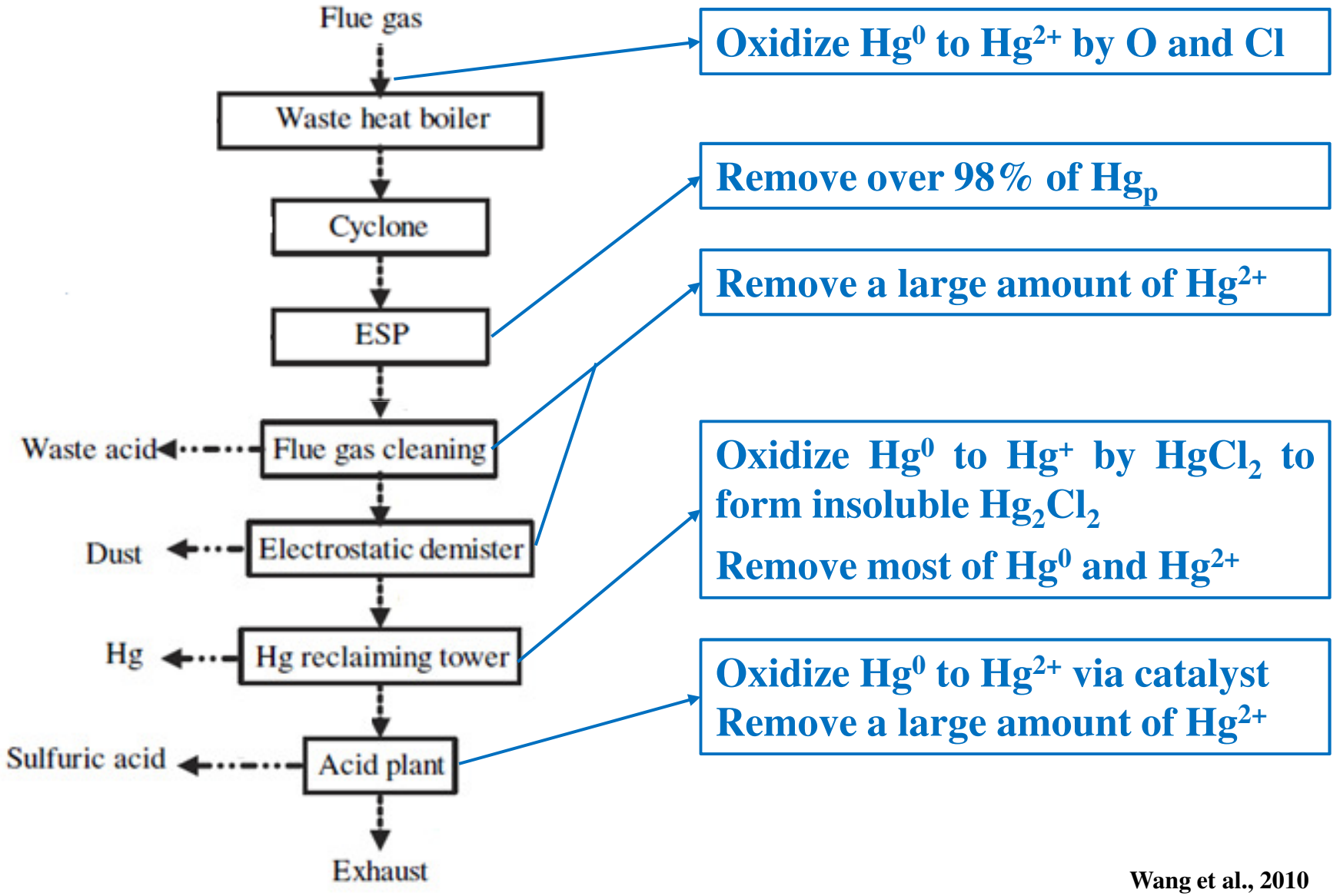
Configuration of non-ferrous metal smelter





Hg transformation across ROA process

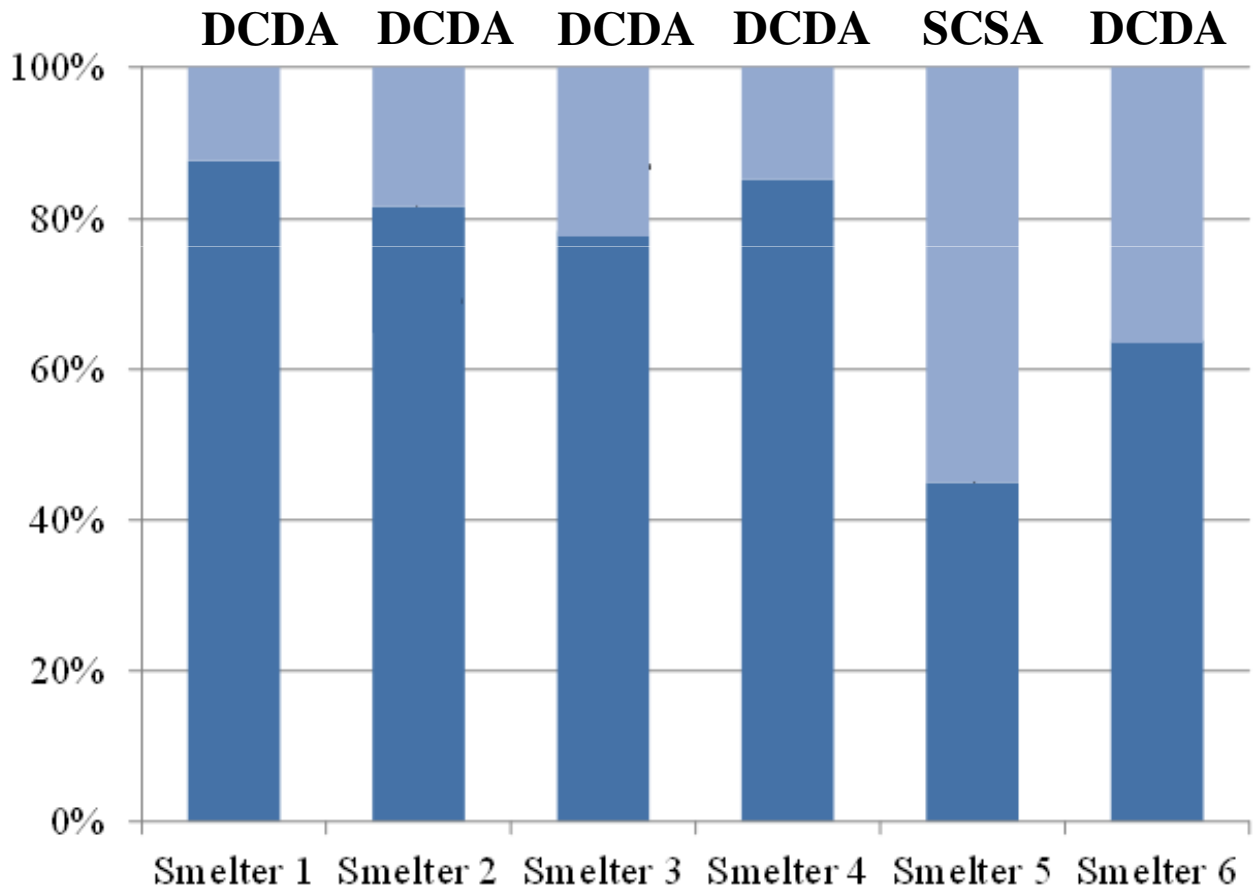




Wang et al., 2010

Hg speciation before and after acid plants

- Conversion and absorption process has significant impact
- DCDA is more effective than SCSA
- Hg^{2+} dominates in flue gas after acid plants



DCDA – double conversion double absorption

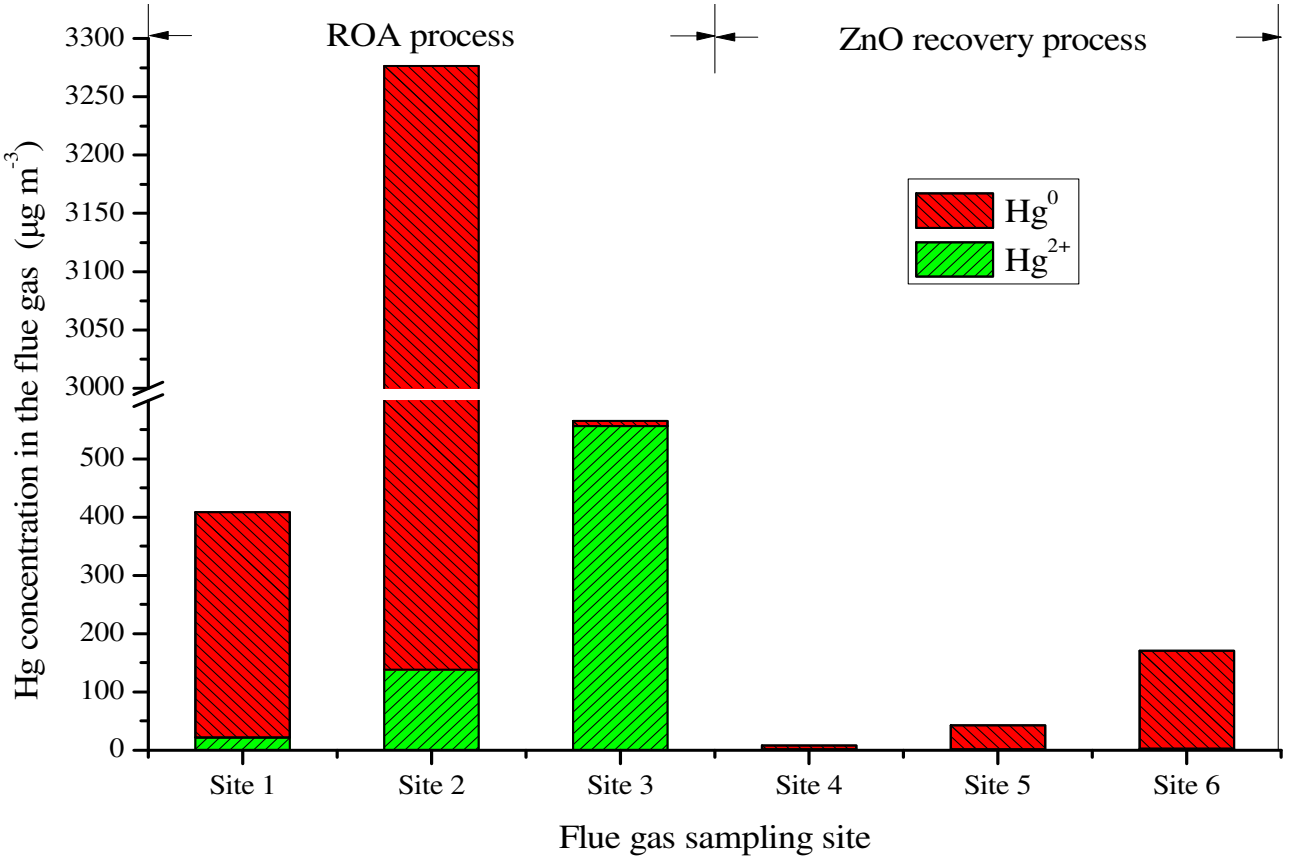
SCSA – single conversion single absorption

Zhang et al., 2012

Hg speciation in flue gas of various kilns



- **Hg^0 is the main chemical form in exhaust gases from cooling cylinder and volatilization kiln, accounting for up to 97.8% of total Hg**



Site 1: Exhaust cooling cylinder gas
Site 2: Roasting flue gas before DCA
Site 3: Exhaust roasting gas
Site 4: Exhaust dehydration gas
Site 5: Volatilization kiln flue gas before FGD
Site 6: Exhaust volatilization kiln gas

Wu et al., submitted

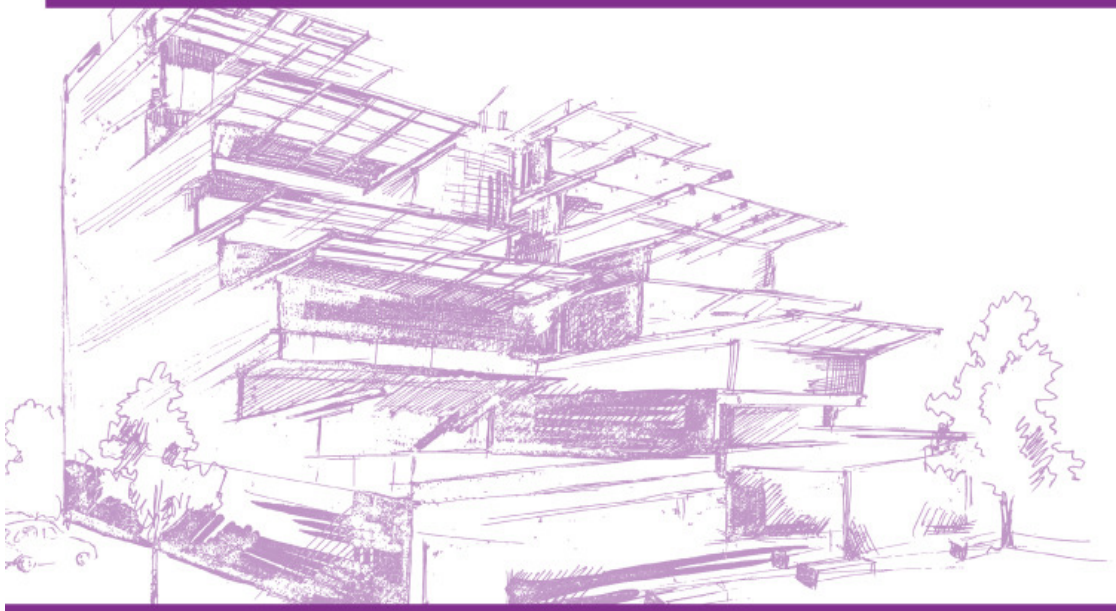
Summary of Hg speciation after APCDs



	Hg^0	Hg^{2+}	Hg_p
DC+FGS+ESD+DCDA	46	49	5
DC+FGS+ESD+MRT+DCDA	6	90	4
DC+FGS+ESD+SCSA	57	38	5
DC+FGS	41	54	5
DC	33	62	5
FGS	65	33	2
None	56	34	10

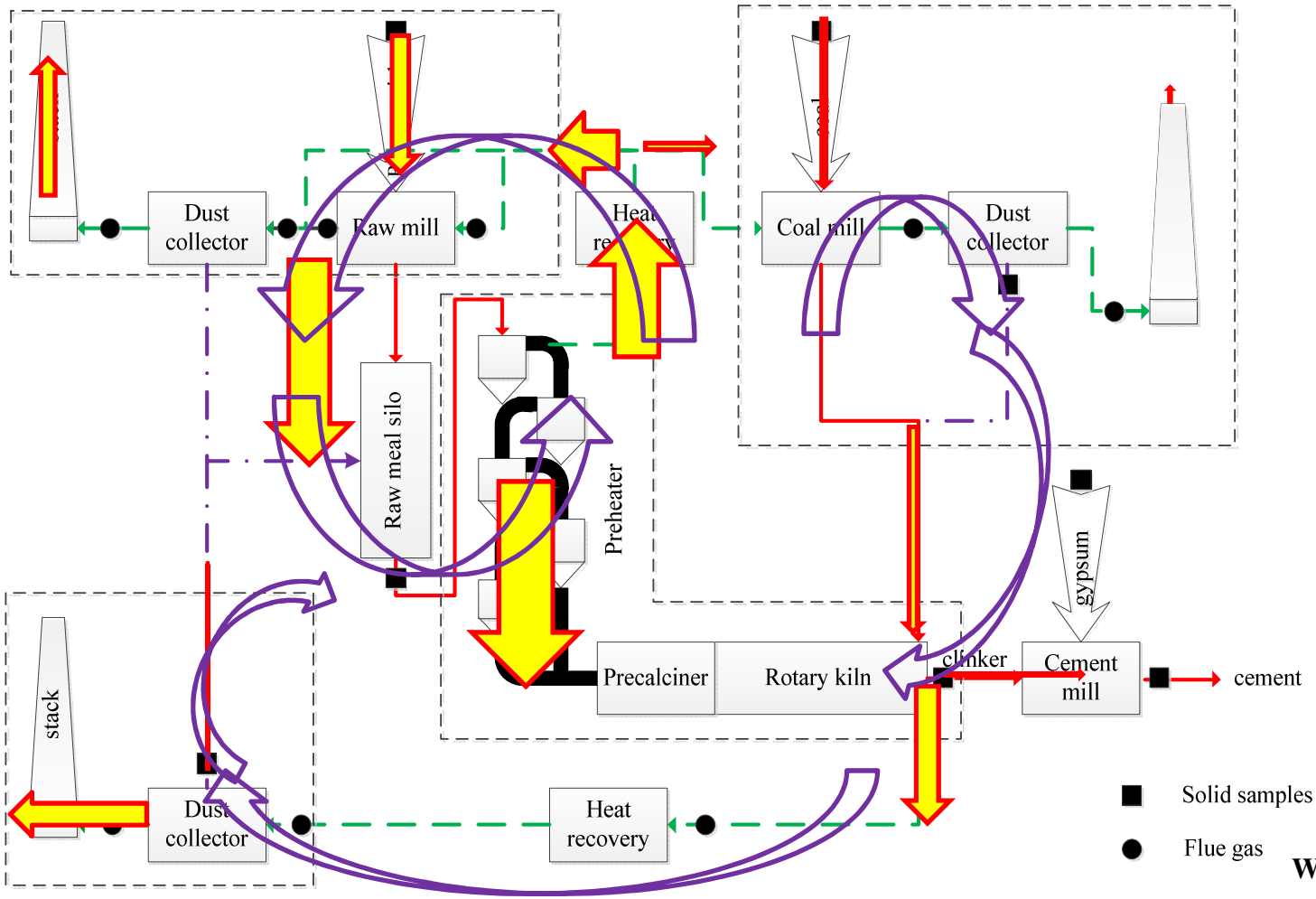
Wang et al., 2010; Li et al., 2010; Zhang et al., 2012; Wu et al., 2012

Hg speciation and transformation in cement plants



Hg flow during cement production

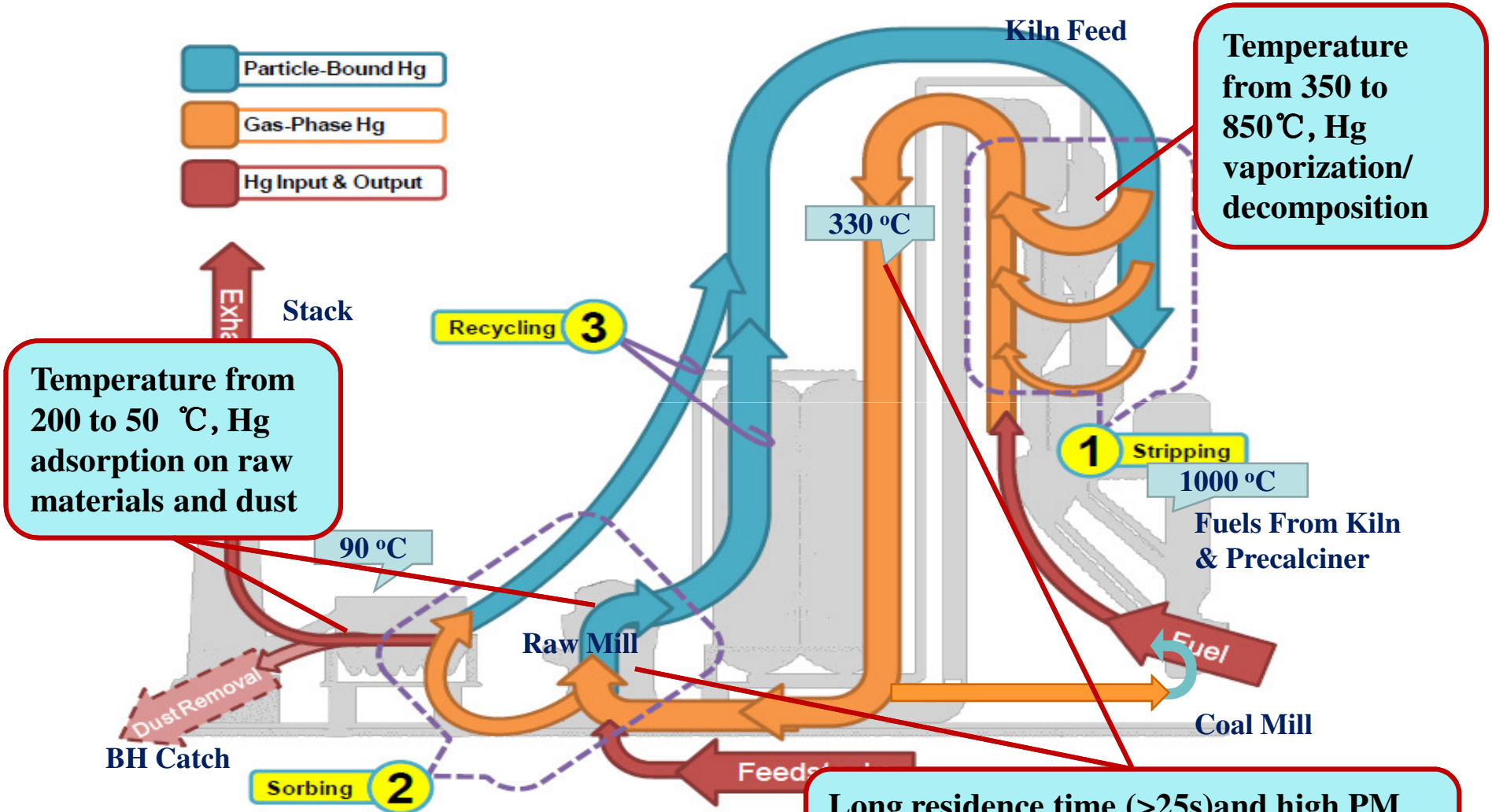
- **Precalciner process is the predominant cement production process worldwide**
- **The recycling of collected dust from FFs/ESPs and the preheat of raw materials/coal cause mercury cycling in cement production**



Wang et al., 2014

Hg transformation within cement plants



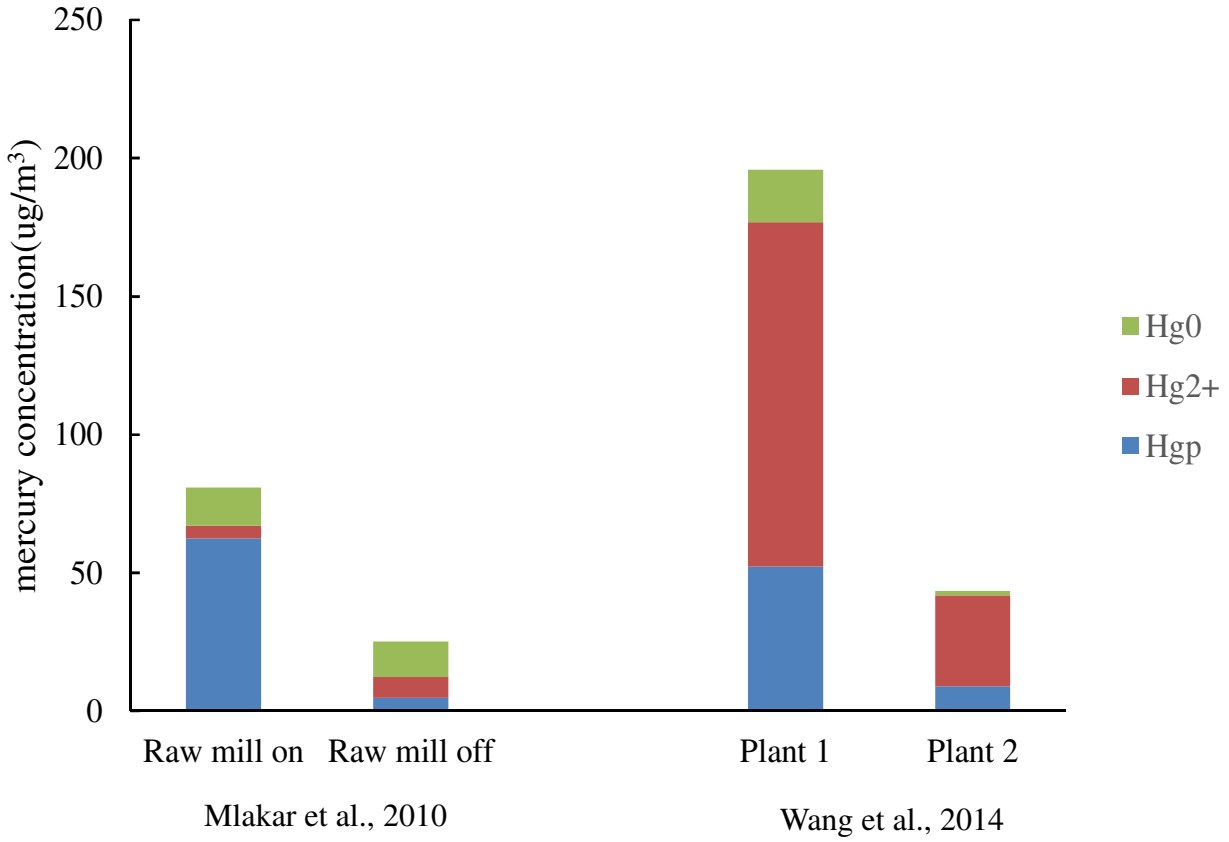


Sikkema et al., 2011

Hg species at the outlet of kiln system



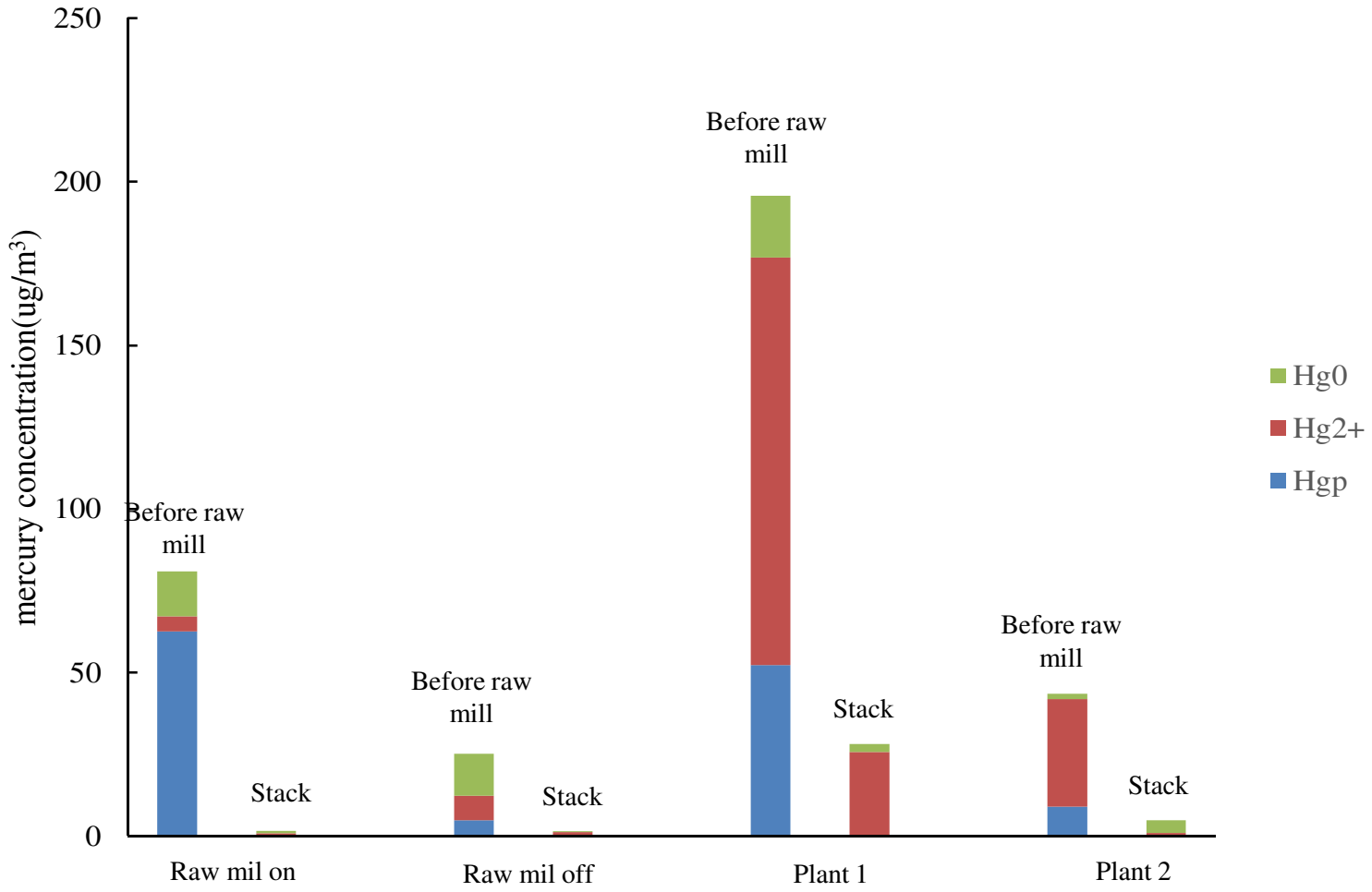
- **The mercury species measured at the outlet of the kiln system is predominantly oxidized mercury and particle-bound mercury**
- **The kinetically-limited mercury oxidation in the flue gas is promoted compared with power plants**



Hg transformation in raw mill and FF



- **The removal efficiencies of raw mill+FF are more than 90%**



Mlakar et al., 2010

Wang et al., 2014

Summary of Hg speciation profiles



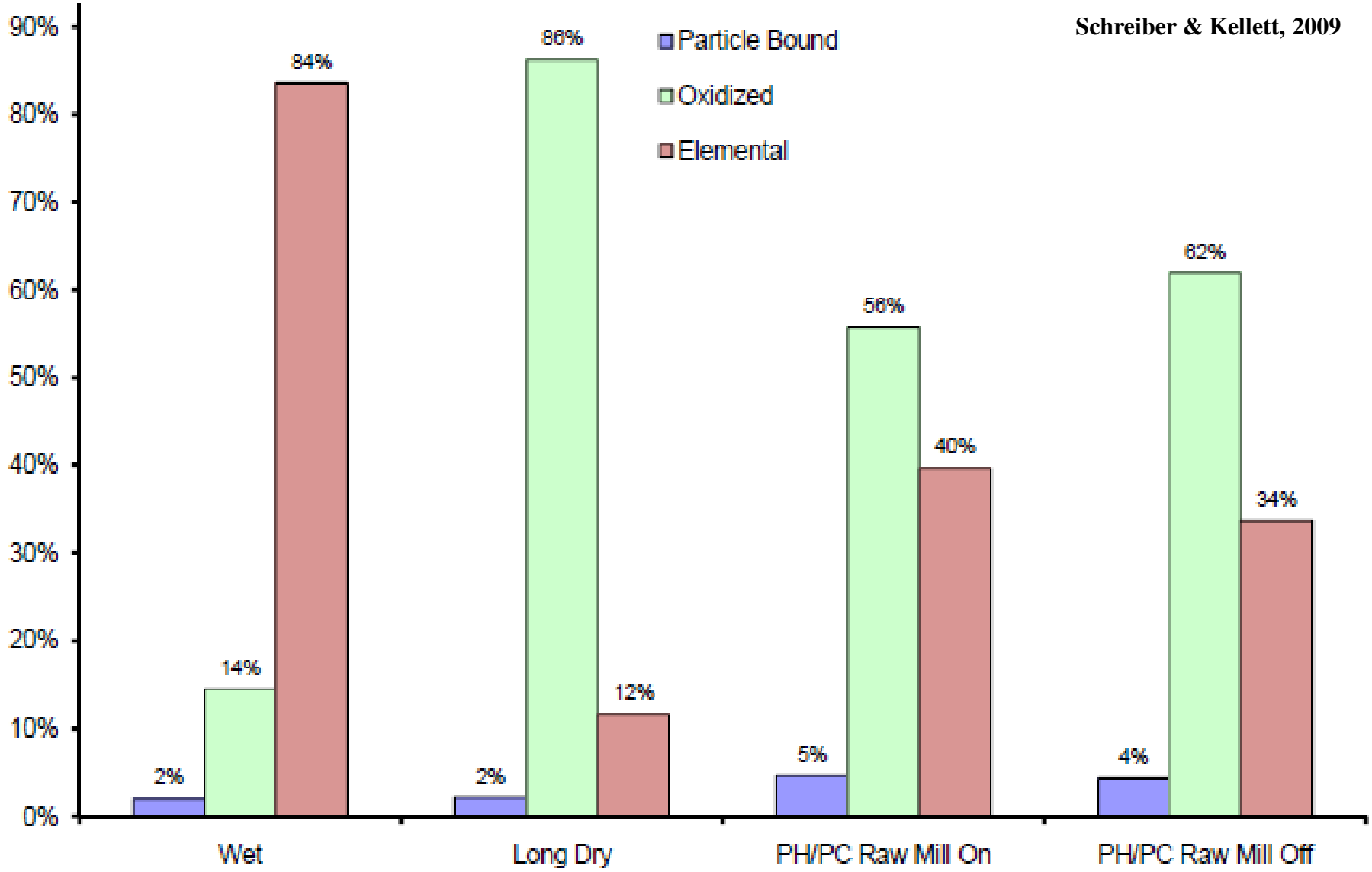
- The mercury emission profile used in previous inventories: 80% Hg^0, 15% Hg^{2+} and 5% Hg^p
- Recent tests indicate that the mercury emitted from cement plant is mainly in oxidized form, accounting for 61.3-90.8%

Proportions of emitted mercury species (%)		Hg^0	Hg^{2+}	Hg^p
Streets et al., 2005	Cement production	80	15	5
Mlakar et al., 2010	Raw mill off	16	75.7	8.3
	Raw mill on	43.1	45.5	11.4
Wang et al., 2014	Plant 1	9.2	90.8	0
	Plant 2	38.7	61.3	0
	Plant 3	23.4	75.1	1.6

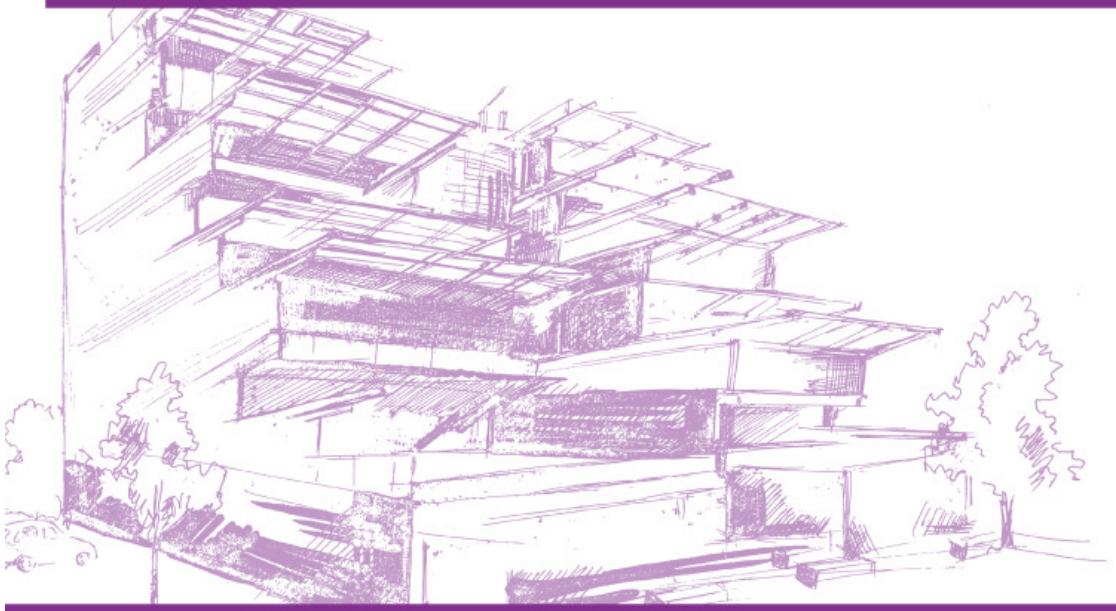
Summary of Hg speciation profiles



Schreiber & Kellett, 2009

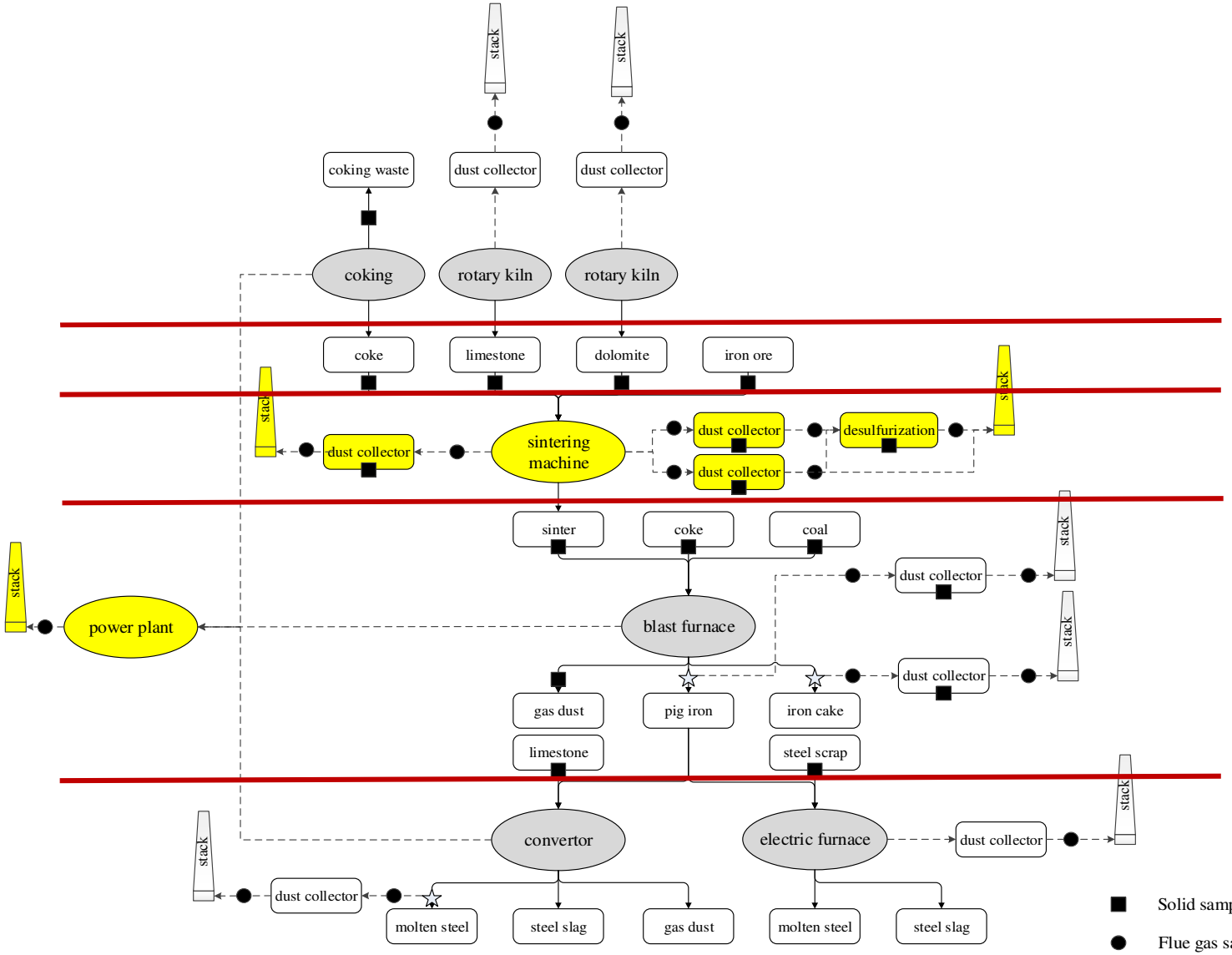


Hg speciation and transformation in iron and steel production



Iron and steel production process





Fukuda et al., 2011

Wang et al., in preparation

Hg transformation in iron & steel plants



- Mercury is vaporized into the flue gas as Hg^0 (>1000°C)
- The predominant species before ESPs is Hg^{2+}, possibly caused by the Fe_2O_3-containing particles in the flue gas
- The Hg removal of ESPs and FGD are correlated with the proportion of Hg^p and Hg^{2+} in the flue gas before the facility

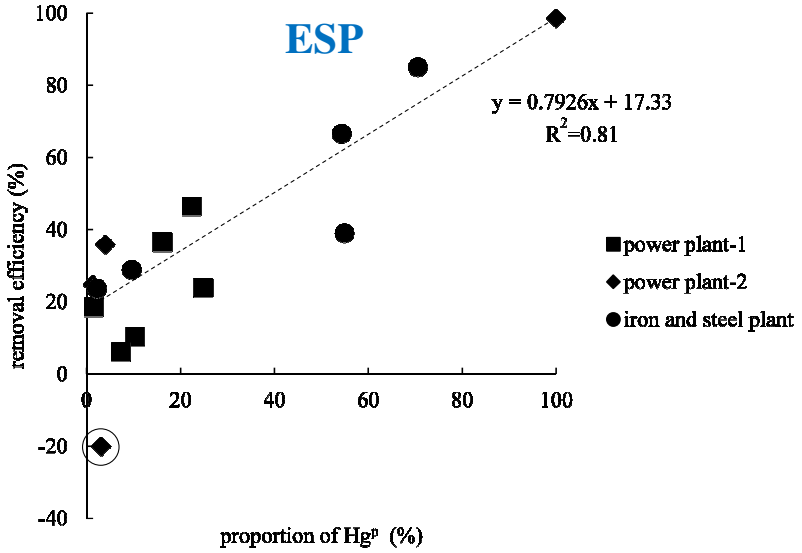


Figure 1 the correlation between the proportion of Hg^p in the flue gas before ESP and the removal efficiency of ESP

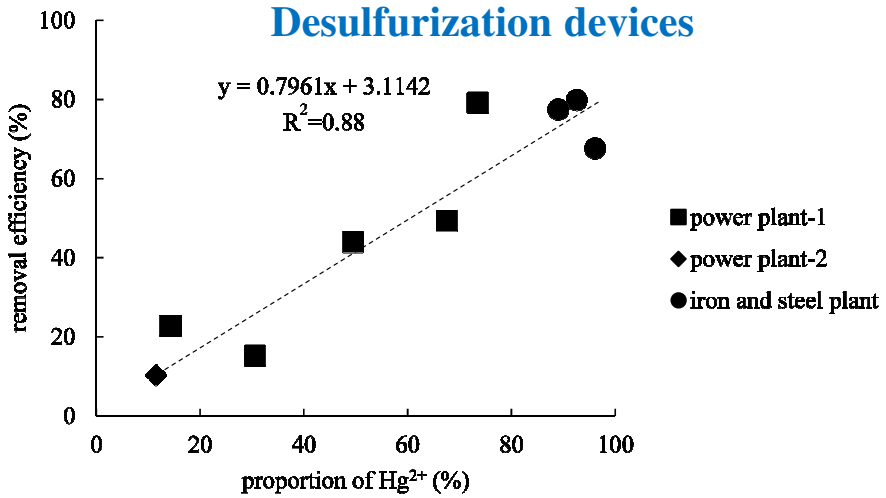


Figure 1 The correlation between the proportion of Hg^{2+} in the flue gas before the flue gas desulfurization devices and the removal efficiencies of flue gas desulfurization devices

Wang et al., in preparation

Summary of Hg speciation profiles

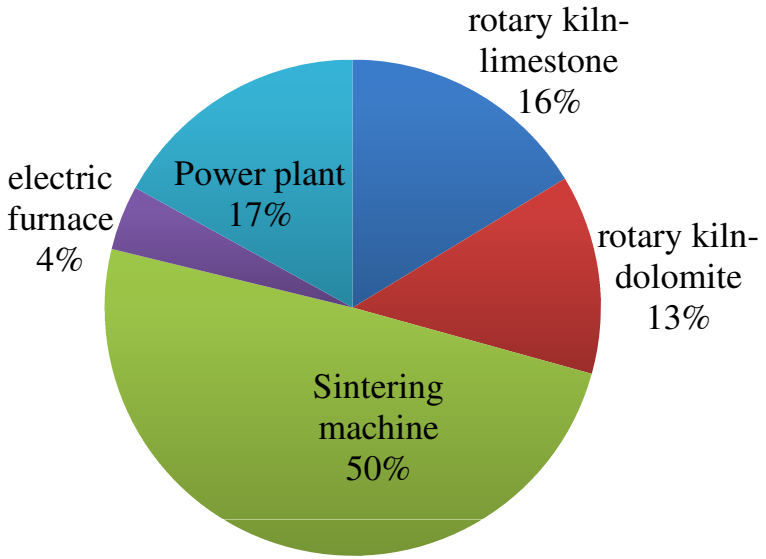


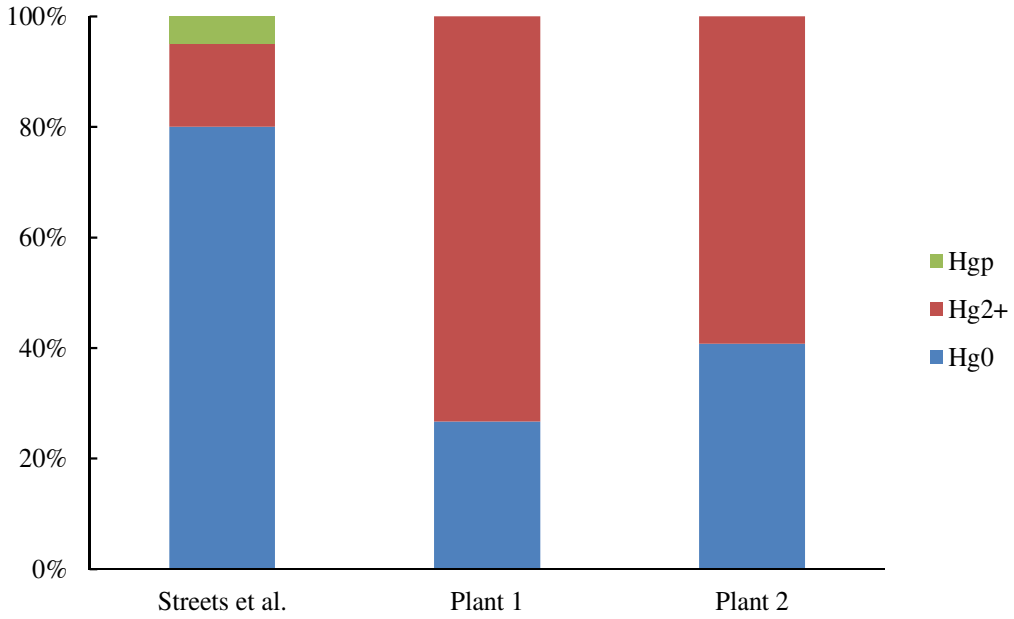
- The mercury species emitted into atmosphere depend on mercury speciation of each stack, and mercury emissions from each stack

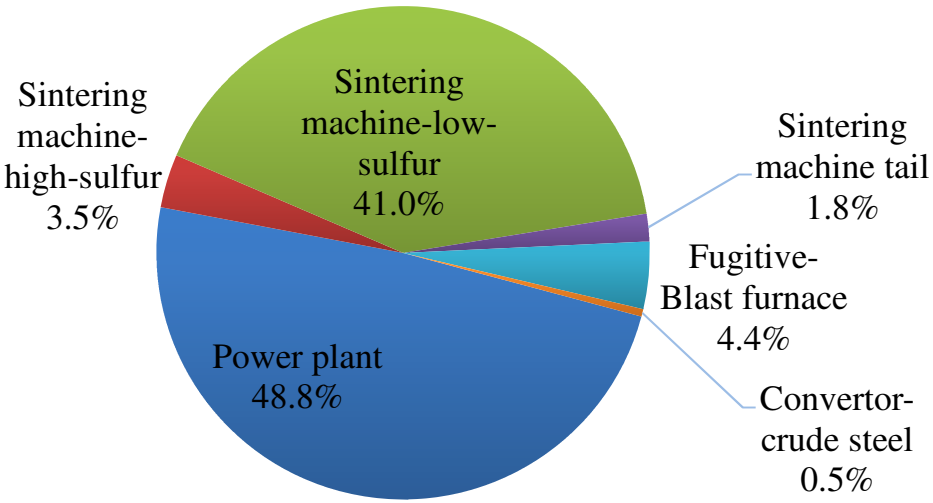
Proportions of emitted mercury species (%)		Hg^0	Hg^{2+}	Hg^p
Streets et al., 2005	Iron and steel production	80	15	5
Wang et al., 2014 Plant 1	rotary kiln for limestone	20.8	79.2	0.0
	rotary kiln for dolomite	8.1	91.9	0.0
	Sintering machine	32.1	67.9	0.0
	electric furnace	92.1	7.9	0.0
	Power plant	15.0	85.0	0.0
Wang et al., 2014 Plant 2	Sintering machine-high-sulfur	0.0	100.0	0.0
	Sintering machine-low-sulfur	0.8	99.2	0.0
	Sintering machine tail	14.3	85.7	0.0
	Blast furnace-pig iron	38.0	62.0	0.0
	Blast furnace-iron scrap	50.0	48.6	0.0
	Convertor-crude steel	53.3	46.7	0.0
	Power plant	77.7	22.3	0.0

Summary of Hg speciation profiles



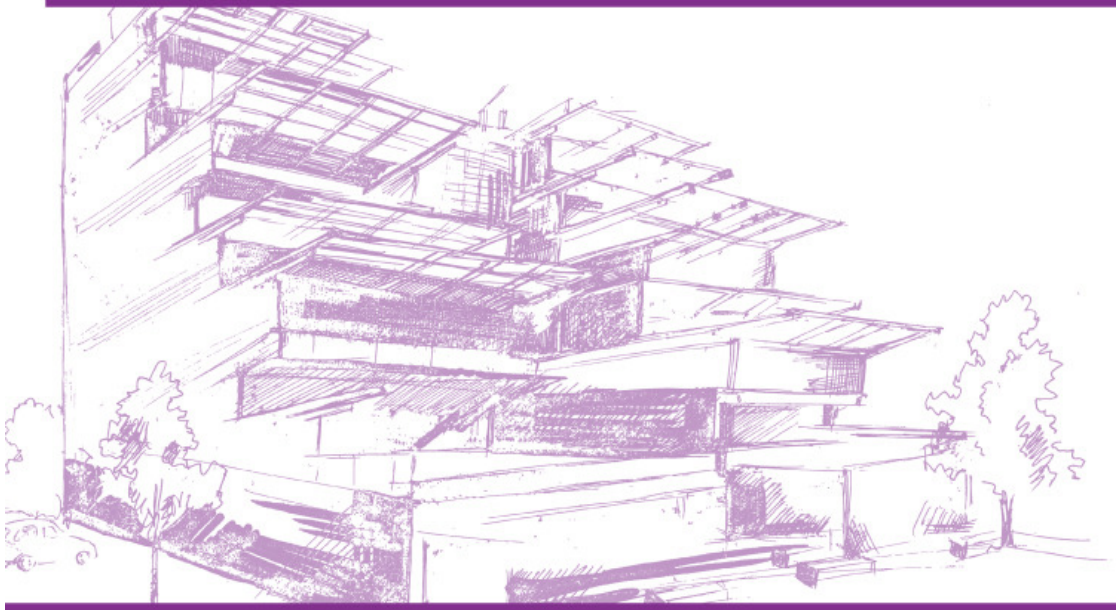






- **Sintering and power plants are predominant emission sources**
- **Hg^{2+} accounts for 59-73% of total Hg in flue gas emitted to air**
- **Speciation profile used in previous study is: 80% Hg^{0}, 15% Hg^{2+} and 5% Hg^{p}**

Speciated Hg emissions for China

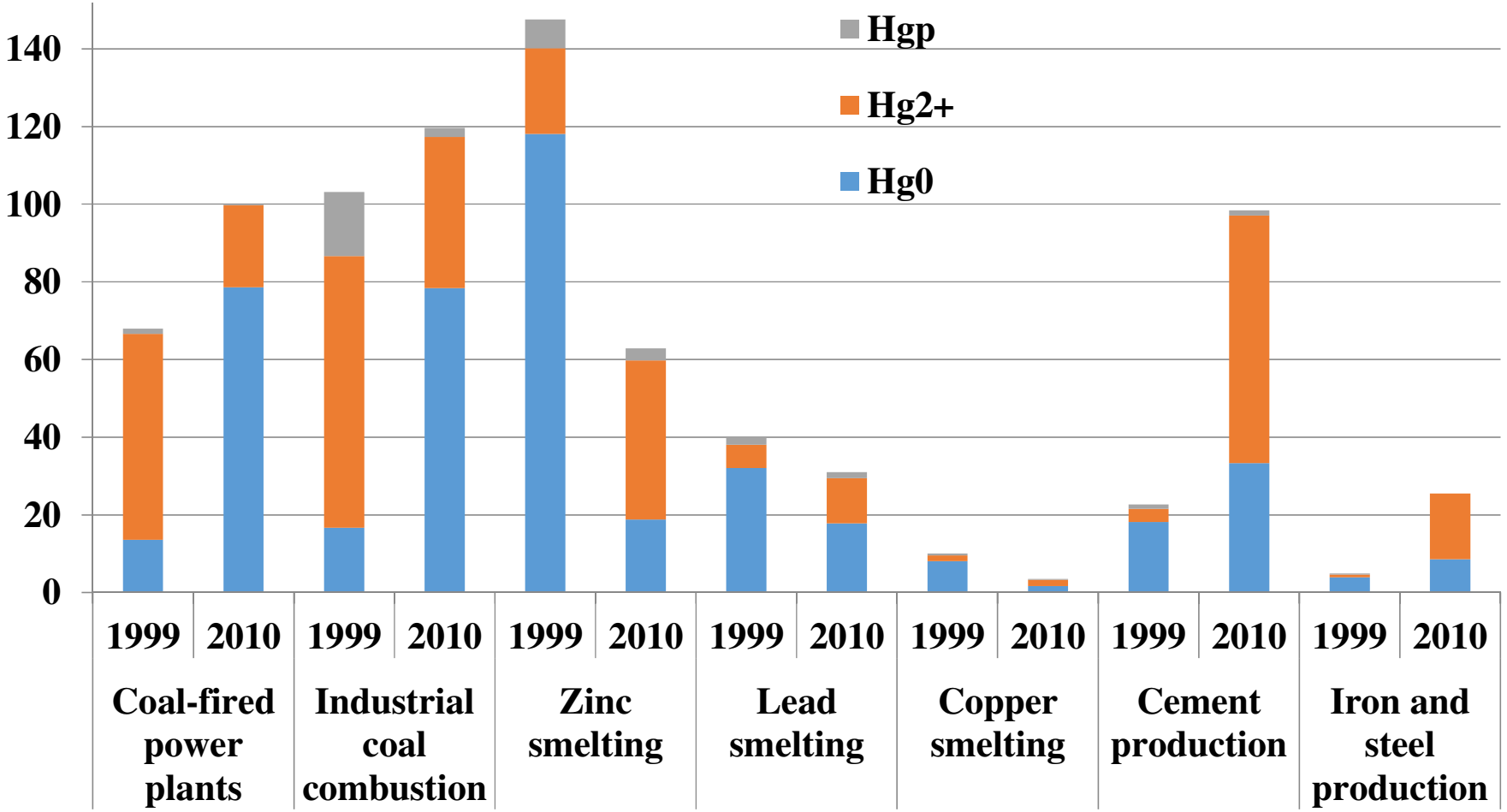


Updated speciation profile of Hg emissions



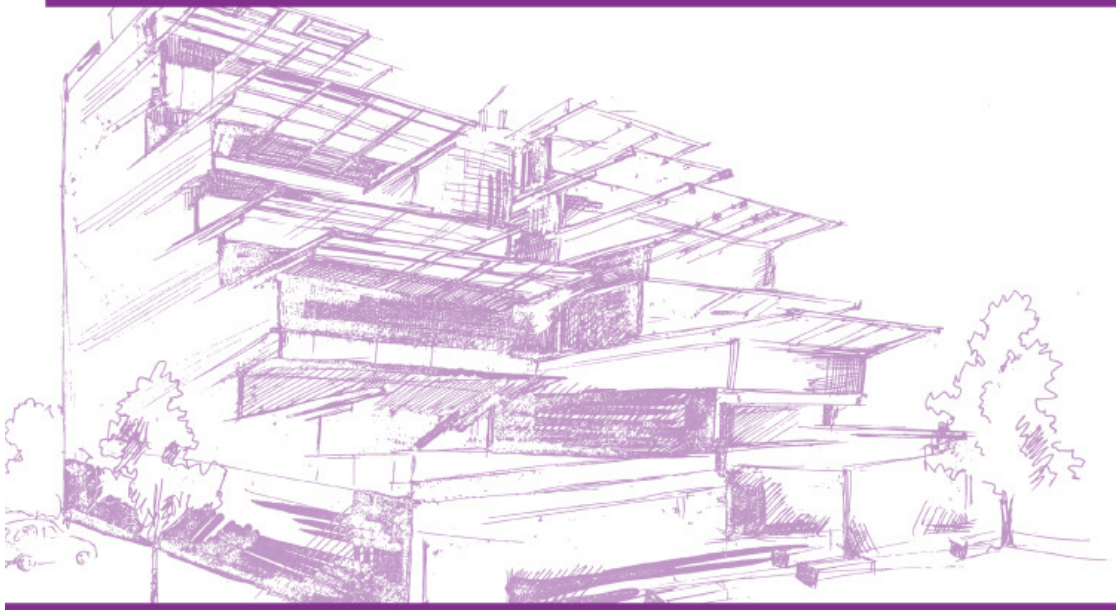
Sub-category	Updated			Streets et al. (2005)		
	Hg^0	Hg^{2+}	Hg_p	Hg^0	Hg^{2+}	Hg_p
Coal-fired power plants	0.79	0.21	0.00	0.20	0.78	0.02
Industrial coal combustion	0.66	0.32	0.02	0.20	0.78	0.02
Residential coal combustion	0.59	0.33	0.07	0.09	0.03	0.88
Other coal combustion	0.66	0.32	0.02	0.09	0.03	0.88
Stationary oil combustion	0.50	0.40	0.10	0.50	0.40	0.10
Mobile oil combustion	0.50	0.40	0.10	0.50	0.40	0.10
Biomass fuel combustion	0.74	0.05	0.21	0.96	0.00	0.04
Waste incineration	0.96	0.00	0.04	0.96	0.00	0.04
Cremation	0.96	0.00	0.04	0.96	0.00	0.04
Zinc smelting	0.30	0.65	0.05	0.80	0.15	0.05
Lead smelting	0.57	0.38	0.05	0.80	0.15	0.05
Copper smelting	0.47	0.48	0.05	0.80	0.15	0.05
Gold production	0.80	0.15	0.05	0.80	0.15	0.05
Mercury production	0.80	0.15	0.05	0.80	0.15	0.05
Cement production	0.34	0.65	0.01	0.80	0.15	0.05
Iron and steel production	0.34	0.66	0.00	0.80	0.15	0.05
Aluminum production	0.80	0.15	0.05	0.80	0.15	0.05

Speciated Hg emissions for China



	HgT	Hg0	Hg2+	Hgp
1999 emission (Streets et al., 2005)	535.8	299.2	171.9	64.7
2010 emissions (Wang et al., 2013)	531.1	302.5	214.4	14.1

Conclusions



Conclusions



- **Homogeneous process at high temperature (400-750°C) and heterogeneous process at low temperature (200-400°C) have equivalent influence on Hg speciation**
- **Composition of fuels or raw materials affects composition of flue gas (e.g. halogen) and properties of fly ash (e.g. SSA), resulting in different Hg speciation**
- **Conventional air pollution control devices have co-benefit removal efficiencies on different Hg species and contribute to Hg transformation**
- **Recent field tests have provided new knowledge and more reliable Hg speciation profile for emission inventories**
- **The speciated Hg emissions have changed significantly and will have substantial impacts on atmospheric Hg transports**

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SCHOOL OF ENVIRONMENT, TSINGHUA UNIVERSITY

Thanks for your attention!

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Email: shxwang@tsinghua.edu.cn