Emissions of **Condensable Particulate Matter** from stationary combustion sources

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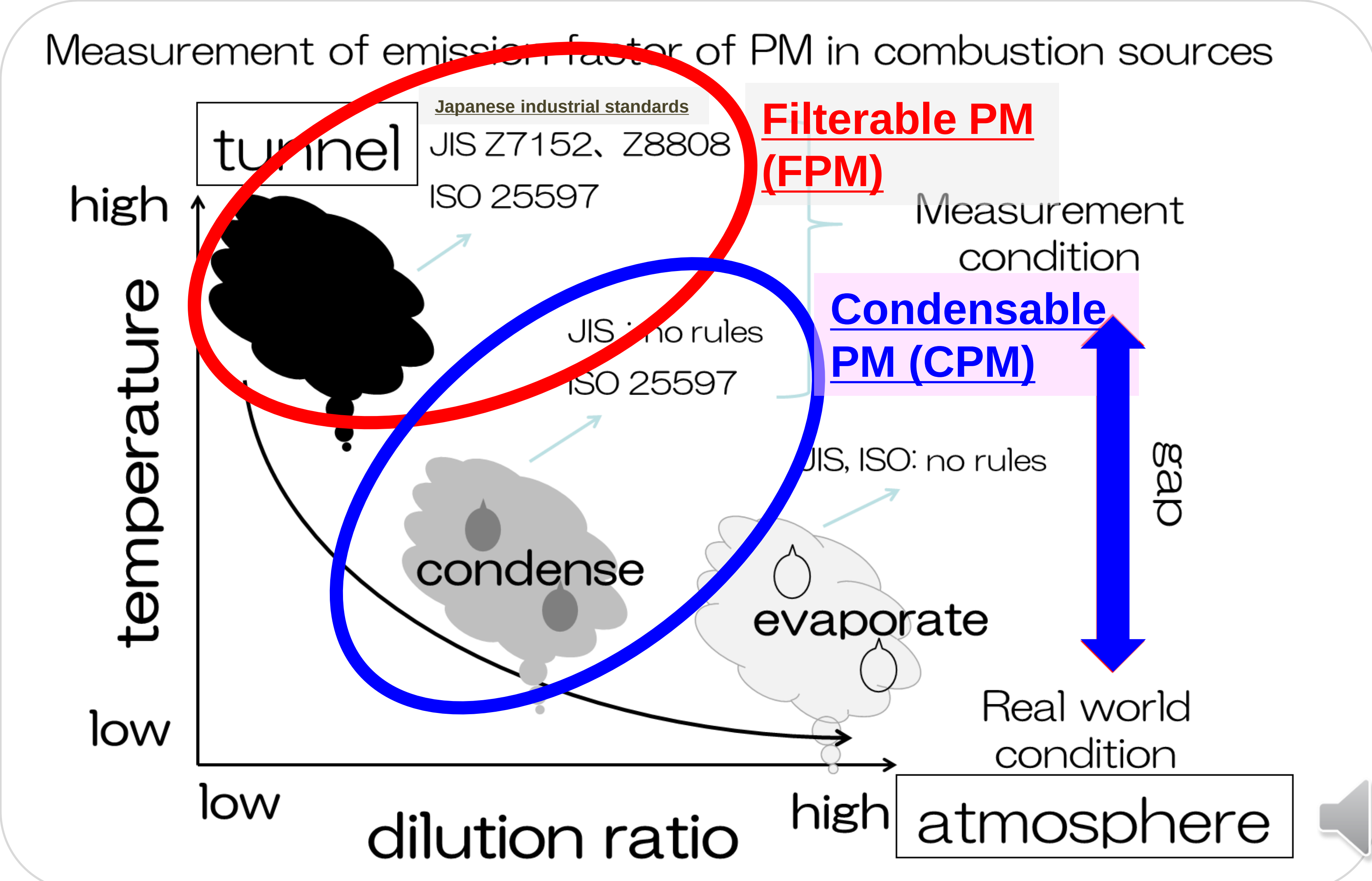
Condensable particulate matter

- **In the gas phase** under stack conditions
- **Condense into PM** immediately after discharge from the stack



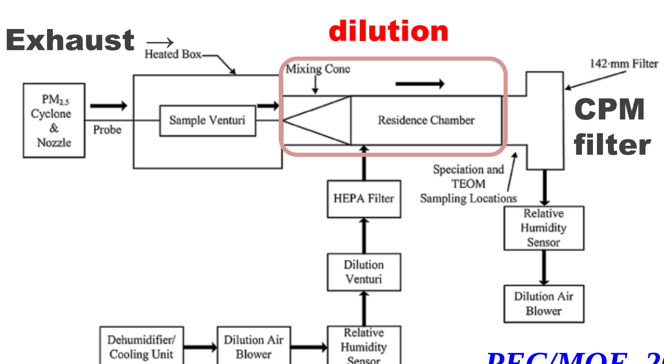
Previous studies on **condensable PM**

Recent measurement of condensable PM from stationary combustion sources in Asia

Organization	Methods	Sources	References
Tokyo Metropolis / MOE, Japan	Dilution	PP, IND, WI, others	Morino et al. (2018, ES&T)
Chaoyang University of Technology, Taiwan	Dry impinger	PP, IND, WI, others	Yang et al. (2014;2015, AAQR, 2016, JAWMA, 2018; 2019, E&F)
Zhejiang University, China	Dry impinger	PP	Li et al. (2017, E&F) Li et al. (2019, ESPR) Song et al. (2020, Chemos)
Zhejiang University, China	Dilution	PP	Zheng et al. (2018, E&F)
Tsinghua University, China	Dry impinger	PP, WI	Wang et al. (2018; 2019, STOTEN)
Tsinghua University, China	Dilution/dry impinger	PP, WI	Wang et al. (2020, ES&T)
Nanjing Normal University, China	Dry impinger	PP	Wang (2020, Fuel)
NIER, Korea	Dry impinger	PP, IND	Gong et al. (2016, JKSAE) Choi et al. (2019, Sustainability)

PP: power plants, IND: industrial facilities, WI: waste incinerators

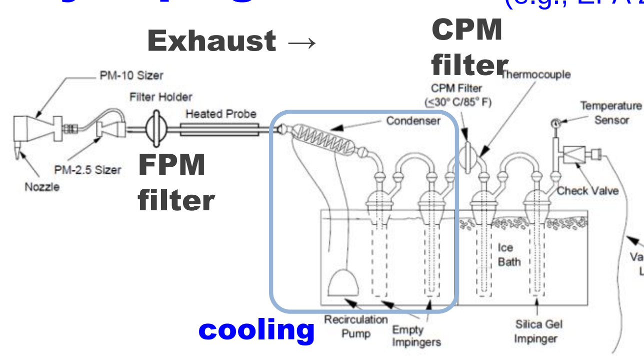
Dilution sampling method (e.g., ISO, CTM-039)



PEC/MOE, 2014

- Sampling of CPM after isothermal dilution.
- Possibility of negative artifacts by SVOC wall loss.

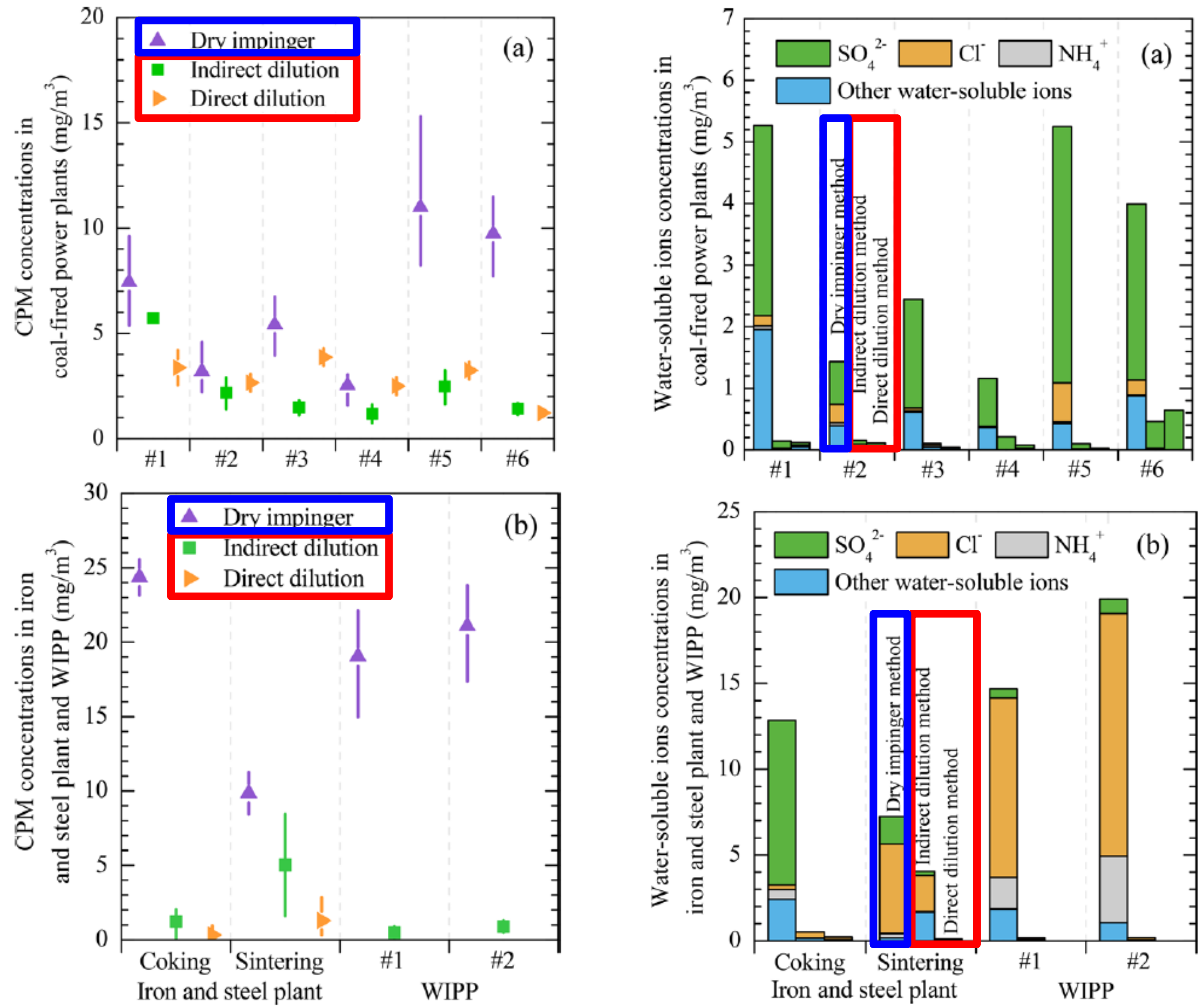
Dry impinger method (e.g., EPA 201A/202)



Richards et al., 2005

- CPM is sampled with a condenser, dry impingers, and a filter.
- Positive artifacts by gas adsorption.

Comparison: methodology for **condensable PM** measurement



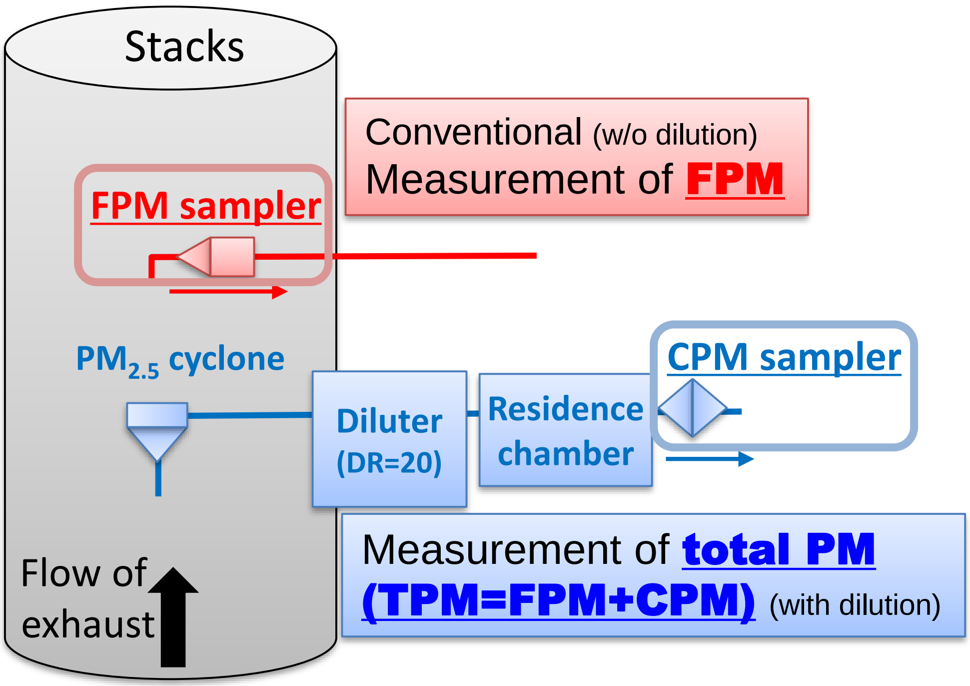
Wang et al., 2020

- The CPM concentrations measured by **the dry impinger method** are much higher than those measured by **the two dilution methods**
- Absorption of the soluble gases (e.g., SO_2, HCl, and NH_3) by the impinger solutions are the main reason for the overestimation

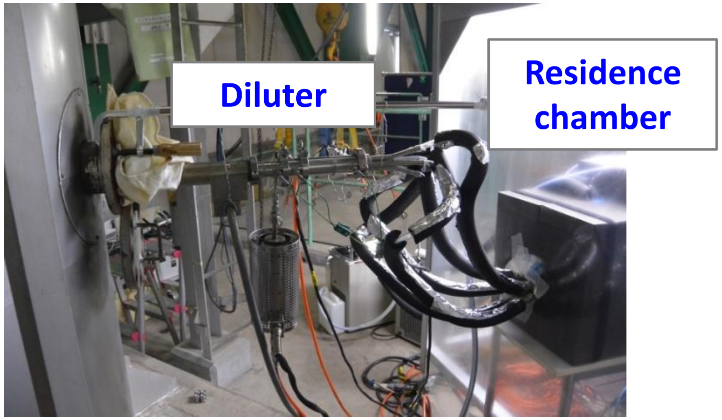
Emission surveys of **filterable and condensable PM**

- ✓ In the conventional emission survey of $PM_{2.5}$, condensable PM was not measured.
- → Exhaust should be sampled after dilution and cooling.

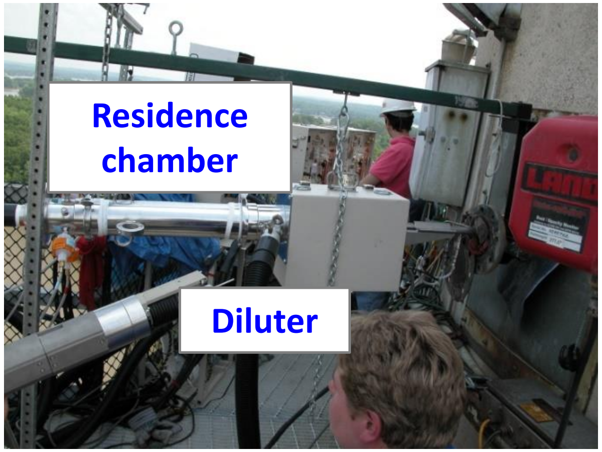
Emission survey of $PM_{2.5}$
(stationary combustion sources)



$PM_{2.5}$ measurement by NIES (dilution sampling)



Emission survey in the US



Preliminary estimates of condensable PM emissions

$$E_{OA}(\mathrm{TPM}) = E_{PM2.5}(\mathrm{FPM}) \times \frac{E_{OA}(\mathrm{TPM})}{E_{PM2.5}(\mathrm{FPM})}$$

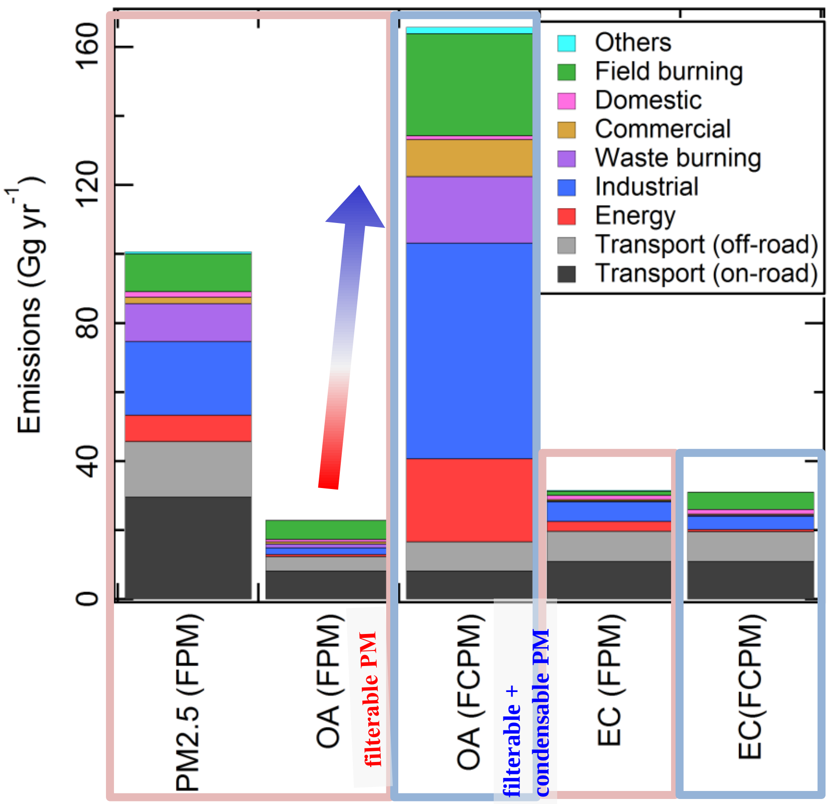
filterable + condensable PM

filterable PM

Summary of Emission Surveys in Japan

	emission sources	number	$E_{OA}(\mathrm{FPM})/E_{PM2.5}(\mathrm{FPM})$ [a]	$E_{OA}(\mathrm{FCPM})/E_{PM2.5}(\mathrm{FPM})$ [b]
1	heavy oil combustion	8	0.08	2.13
2	coal combustion	1	0.01	0.96
3	gas combustion	3	0.37	18.27
4	wood burning	2	0.12	0.77
5	waste burning	5	0.10	1.25
6	waste burning–sewage sludge	5		6.01
7	marine shipping	3	0.29	1.02
8	field burning	2	0.50	2.71

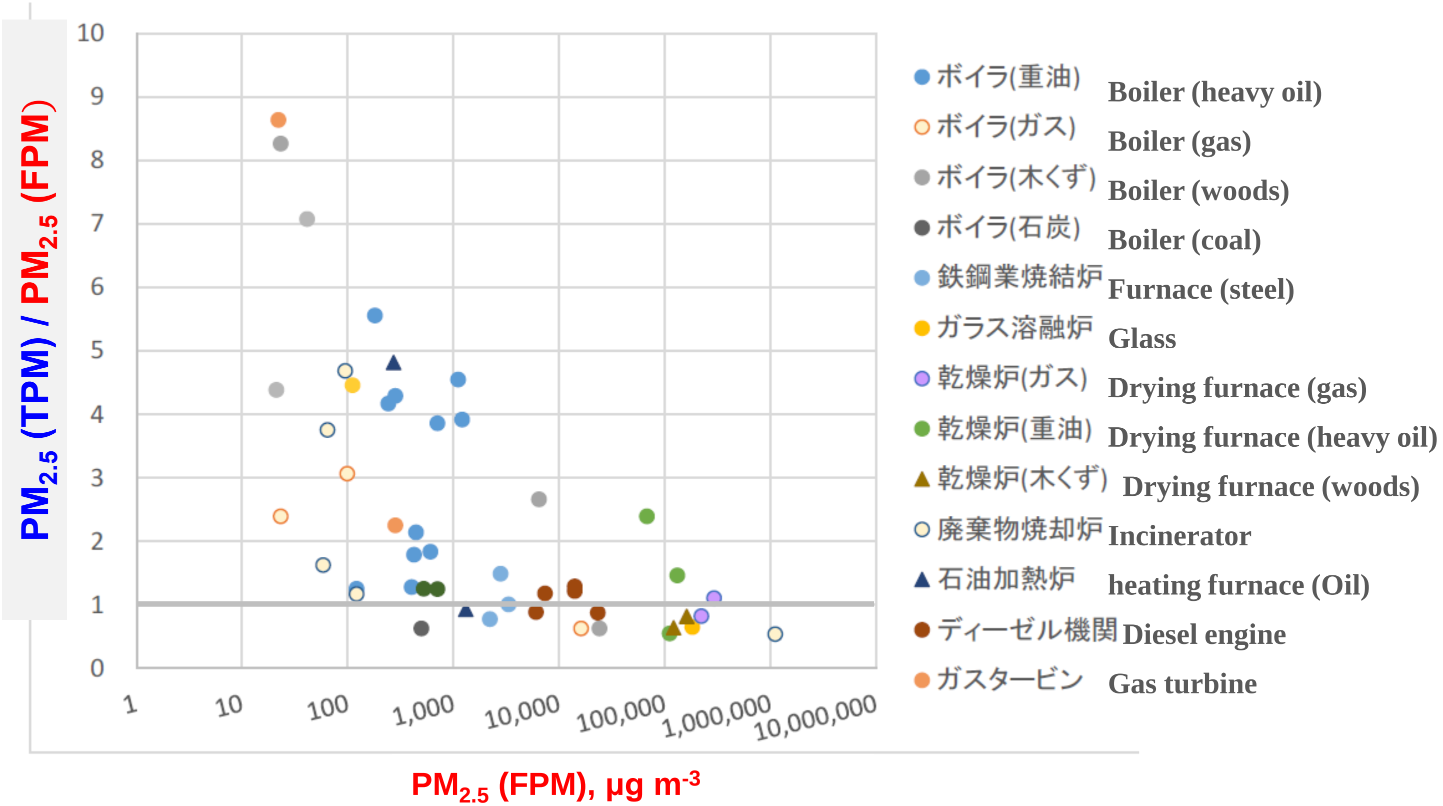
Emissions from Japan in 2012



- **OA emissions increased by a factor of seven** after correction for condensable PM
- EC emissions did not largely change even after correction for condensable PM

Morino et al., ES&T, 2018;

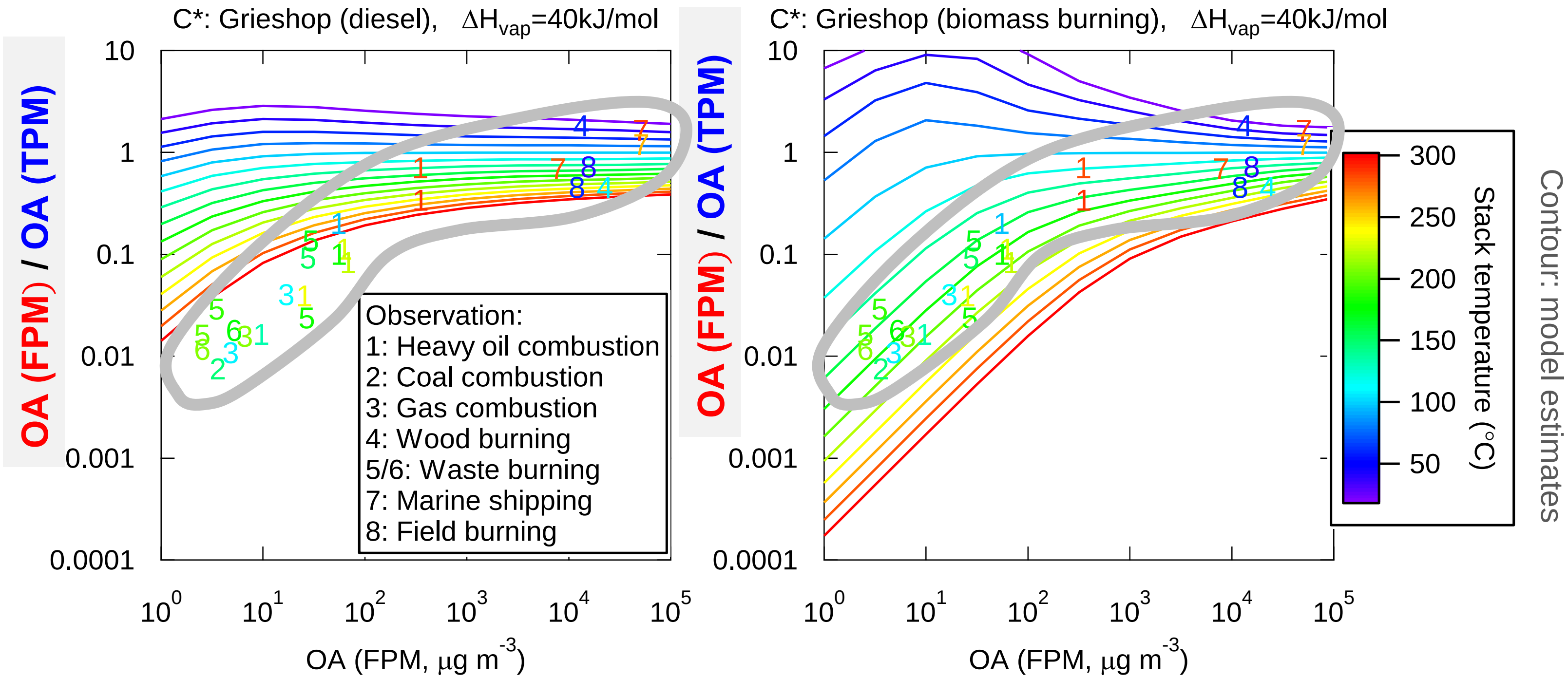
Data from Emission Surveys in Japan



- Fraction of **condensable PM** was higher at lower FPM concentration:
  → Correction for CPM was particularly significant for sources with lower PM emissions
  → Without the consideration of this relationship, correction for CPM could be overestimated.

Characteristics of **condensable PM** emissions (2) Sensitivity to stack temperature

Data from Emission Surveys in Japan



- **The observed temperature dependence of** $\frac{C_{OA}(FPM)}{C_{OA}(TPM)}$ **was small** in the emission survey data.

→ **Inconsistent with the estimates of thermodynamic model**.

Objectives of this study

- **Estimate of CPM emissions** with/without consideration of the relationship between **CPM/FPM ratio** and **FPM concentration or stack temperature**

Estimate of **condensable PM** emissions **with 3 methods**

		Dependence of TPM/FPM ratio on FPM conc.	Dependence of TPM/FPM ratio on Temperature
Method 1	*Uniform CPM/FPM ratio*	×	×
Method 2	*Relationship between CPM/FPM ratio and FPM conc.*	○	×
Method 3	*Thermodynamic model*	○	○

Method 1:

$\frac{E_{OA}(\mathrm{TPM})}{E_{PM2.5}(\mathrm{FPM})}$ ratio from emission survey

$$E_{OA}(\mathrm{TPM}) = E_{PM2.5}(\mathrm{FPM}) \times \frac{E_{OA}(\mathrm{TPM})}{E_{PM2.5}(\mathrm{FPM})}$$

	emission sources	number	$E_{OA}(\mathrm{FPM})/E_{PM2.5}(\mathrm{FPM})$[a]	$E_{OA}(\mathrm{FCPM})/E_{PM2.5}(\mathrm{FPM})$[b]
1	heavy oil combustion	8	0.08	2.13
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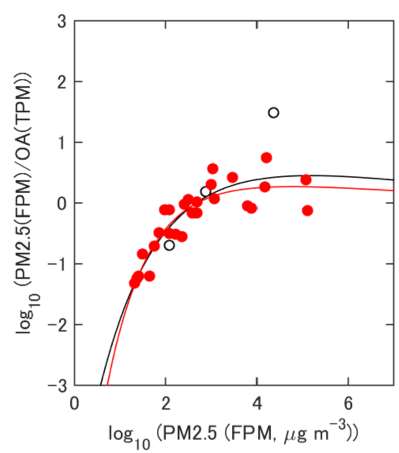
5	waste burning	5	0.10	1.25
6	waste burning–sewage sludge	5		6.01
7	marine shipping	3	0.29	1.02
8	field burning	2	0.50	2.71

Morino et al., ES&T, 2018;

Method 2:

Relationship between $\mathrm{PM_{TPM}}$ (or $\mathrm{OA_{TPM}}$) and $\mathrm{PM_{FPM}}$

$$\mathrm{OA_{TPM}} = f_{2B}\left(\mathrm{PM_{FPM}}(\mathrm{EMIS})\right)$$



Method 3:

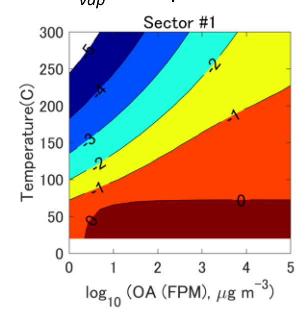
Estimate using thermodynamic model

$$\mathrm{OA_{TPM}} = f_{3A}\left(\mathrm{OA_{FPM}}, \Delta H_{vap}, f_i\right)$$
$$C_{OA} = C_{tot} \sum \left\{ f_i / \left(1 + \frac{C_i^*}{C_{OA}}\right)\right\},$$
$$C_i^*(T) = C_i^*(T_0)\frac{T_0}{T}\exp\left(\frac{\Delta H_{vap,i}}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right).$$

Heavy oil combustion

C^*: Grieshop et al. (2009)

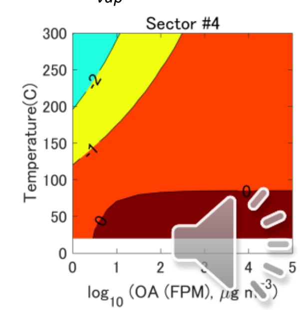
ΔH_{vap}: 56 kJ/mol



Wood combustion

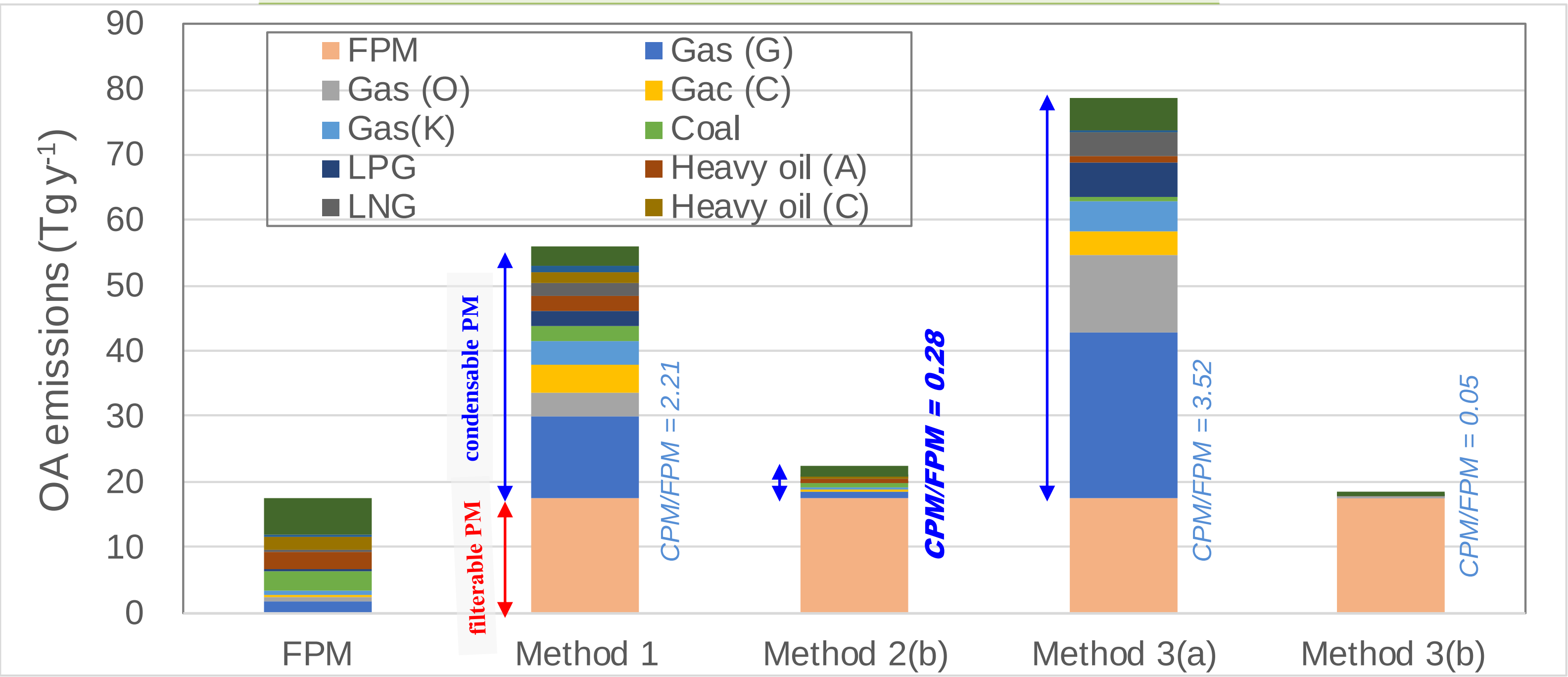
C^*: May et al. (2013)

ΔH_{vap}: 47 kJ/mol



Estimate of **condensable PM** emissions **with 3 methods**

		Dependence of TPM/FPM ratio on FPM conc.	Dependence of TPM/FPM ratio on Temperature
Method 1	*Uniform CPM/FPM ratio*	×	×
Method 2	*Relationship between CPM/FPM ratio and FPM conc.*	○	×
Method 3	*Thermodynamic model*	○	○



- If **the relationship between CPM/FPM ratio and FPM conc is reliable**, **the estimate by Method 2** is presumably the best-available estimate.
- Contribution of CPM emissions in Method 2 is much smaller than that in Method 1 (Morino et al., 2018): **OA emissions increased by 28%** by including CPM emissions in Method 2.

Summary

Methodology of CPM measurement

→ For the emission surveys of condensable PM, both **dilution sampling method** and **dry impinger method** have been used. Recent studies clearly indicated that **CPM concentrations measured by the dry impinger method were significantly overestimated**.

Estimate of CPM emissions

→ Japanese emission surveys' data showed that **fraction of condensable PM was higher at lower FPM concentrations**: thus, **CPM emissions estimated assuming uniform CPM/FPM ratio for each source type overestimate the CPM emissions**.

→ **OA emissions increased by 28%** by including CPM emissions with the best-available method.

Remaining issue

→ **Thermodynamic properties of CPM** (including relationship between **CPM fraction** and **FPM concentration**) should be further investigated.

(SI) Estimation of CPM emissions

		Dependence of TPM/FPM ratio on FPM conc.	on Temperature
Method 1	*Uniform CPM/FPM ratio*	×	×
Method 2	*Relationship between CPM/FPM ratio and FPM conc.*	○	×
Method 3	*Thermodynamic model*	○	○

	Equations	Speciation (OA/PM)
1	$\mathrm{OA_{TPM}} = \mathrm{PM_{FPM}(MAP)} \times \frac{\mathrm{OA_{TPM}}}{PM_{\mathrm{FPM}}}\mathrm{(JAP\_ES)}$	
2A	$\mathrm{OA_{FPM}} = \mathrm{PM2.5_{FPM}(MAP)} \times \frac{\mathrm{OA_{FPM}}}{\mathrm{PM2.5_{FPM}}}\mathrm{(SPECIATE)}$ $\mathrm{OA_{TPM}} = f_{2A}(\mathrm{OA_{FPM}})$	FPM
2B	$\mathrm{OA_{TPM}} = f_{2B}\left(\mathrm{PM2.5_{FPM}}(MAP)\right)$	-
2C	$\mathrm{PM_{TPM}} = f_{2C}\left(\mathrm{PM2.5_{FPM}}(MAP)\right)$ $\mathrm{OA_{TPM}} = \mathrm{PM2.5_{TPM}} \times \frac{\mathrm{OA_{TPM}}}{\mathrm{PM2.5_{TPM}}}\mathrm{(SPECIATE)}$	TPM
3A	$\mathrm{OA_{FPM}} = \mathrm{PM2.5_{FPM}(MAP)} \times \frac{\mathrm{OA_{FPM}}}{\mathrm{PM2.5_{FPM}}}\mathrm{(SPECIATE)}$ $\mathrm{OA_{TPM}} = f_{3A}\left(\mathrm{OA_{FPM}}, \Delta H_{vap}, f_i\right)$	FPM
3B	$\mathrm{OA_{TPM}} = f_{3B}\left(\mathrm{PM2.5_{FPM}}(MAP), \frac{\mathrm{OA_{TPM}}}{\mathrm{PM2.5_{TPM}}}\mathrm{(SPECIATE)}, \Delta H_{vap}, f_i\right)$	TPM