11th International Conference on Carbonaceous Particles in the Atmosphere

Investigating the Secondary Organic Aerosols from Biomass Burning Emission Sources

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Introduction - Air Pollution in Hong Kong

- **Local street level air pollution**
- **Regional smog problem**

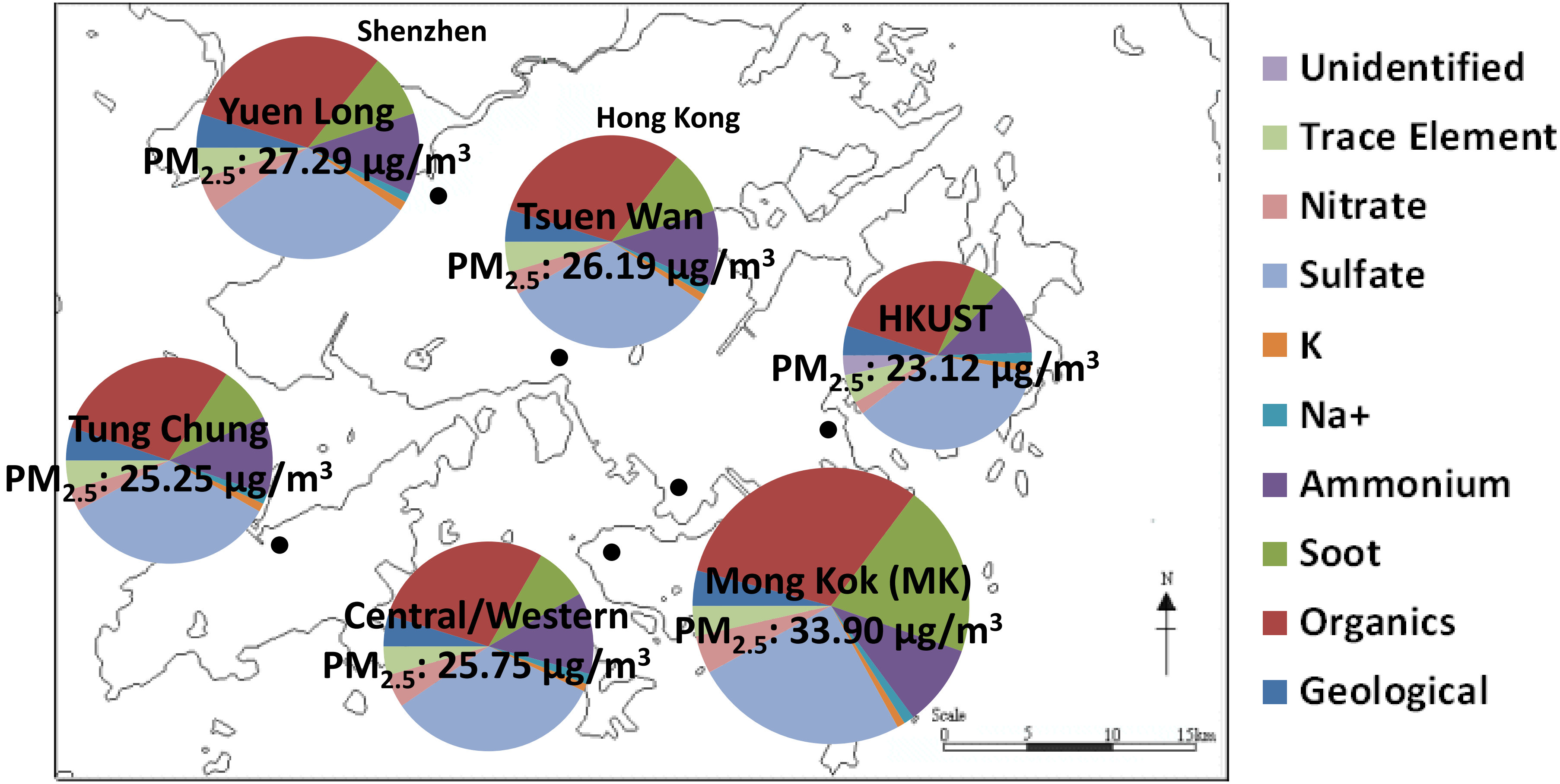
(Source: SCMP)

(Source: Alex Hofford Photography)

(Source: HKEPD)

Introduction - $PM_{2.5}$ Speciation Network in Hong Kong

$PM_{2.5}$ and major chemical composition in Hong Kong (2014)



- On average, sulfate, organics (1.4×OC, 27-32%) and ammonium are more abundant components in $PM_{2.5}$ all over Hong Kong;
- Soot (EC) concentrations exhibited a roadside-urban-suburban gradient pattern.

Introduction - Major $PM_{2.5}$ & OC Source in Hong Kong

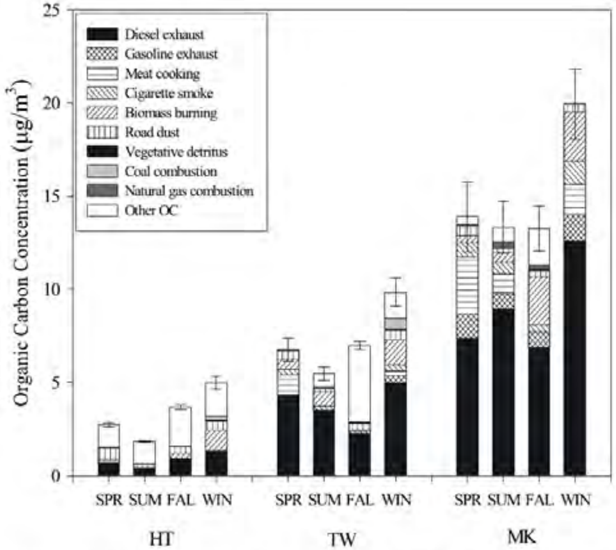


Figure 8. Source contributions to organic carbon in PM2.5. The CMB7.0 model was used to estimate contributions of major sources, and the modeled OC was compared to the measured OC concentrations. The error bar represents the error of modeled OC, which is propagated from the error of each identified source category.

Zheng et al., J. Geophys. Res., 2006

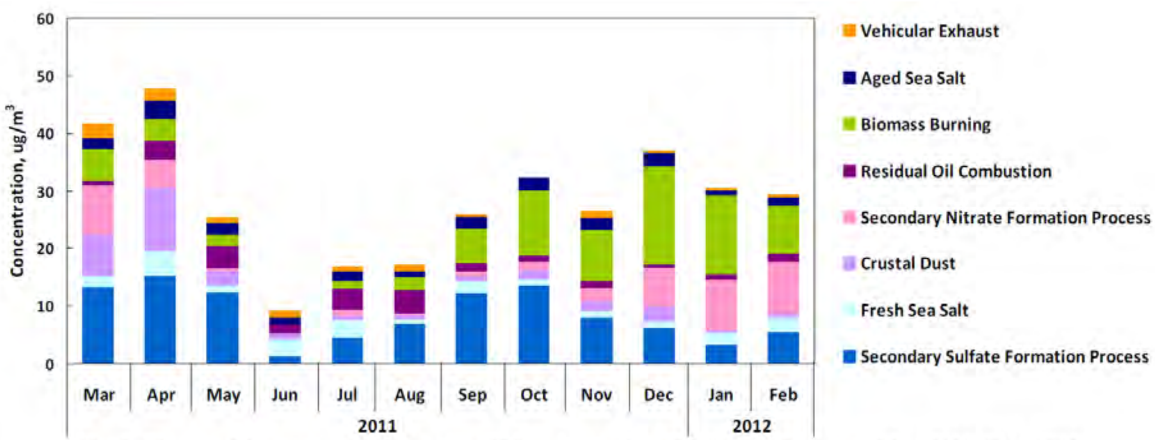


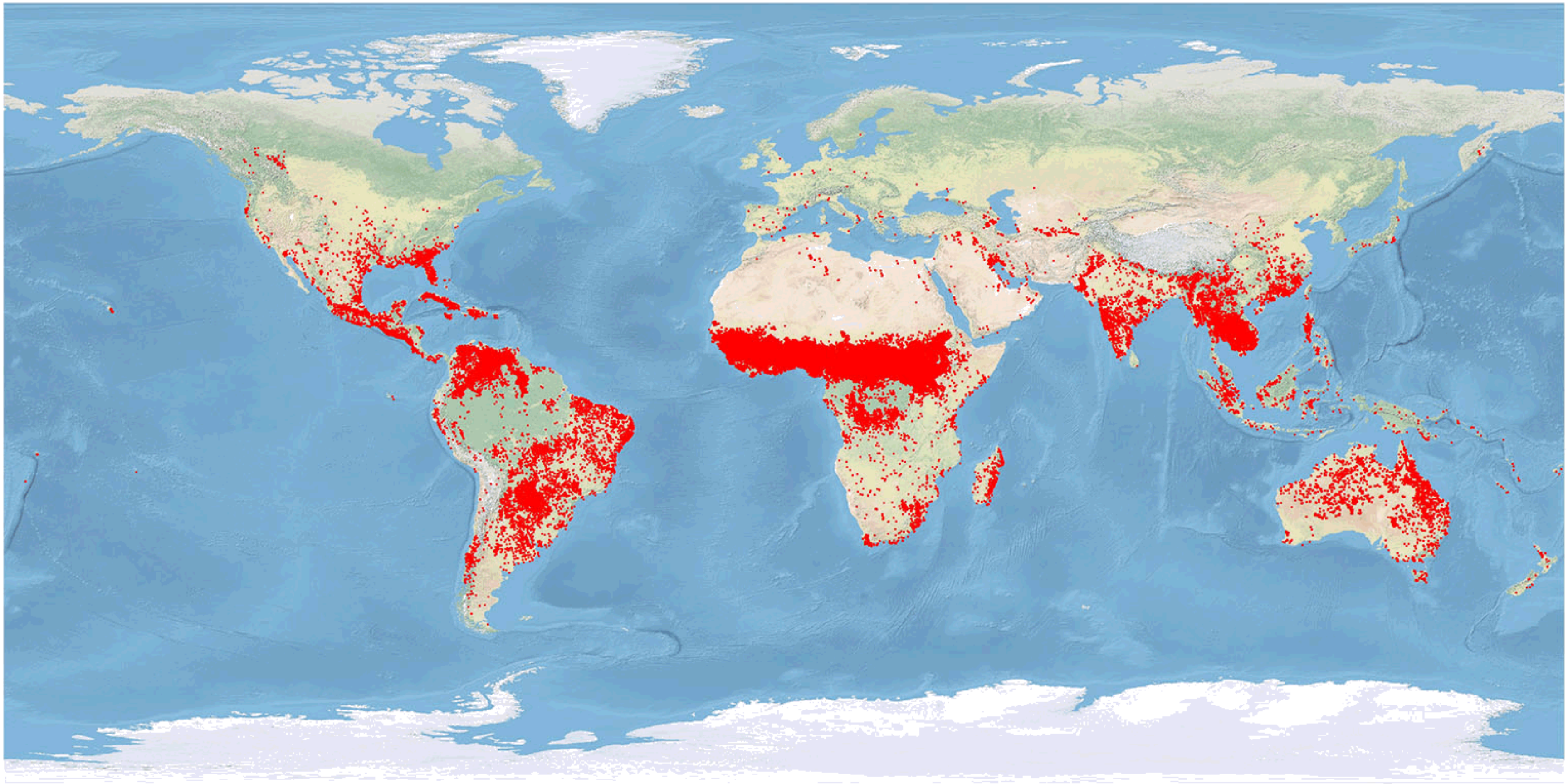
Fig. 9. The monthly source contributions to $PM_{2.5}$ observed at HKUST AQRS during Mar. 2011–Feb. 2012.

Huang et al., Aerosol Air Qual. Res., 2014

Identified sources include:

- Vehicle emissions
- Biomass burning
- Marine emissions
- Industrial activities
- SOA

2013 MODIS Active Fire Detections from the Aqua and Terra satellites

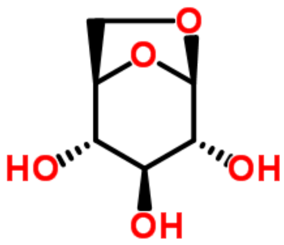


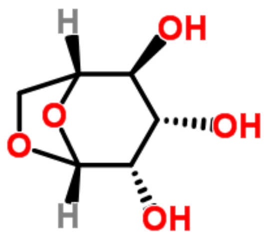
January February March April May June July August September October November December

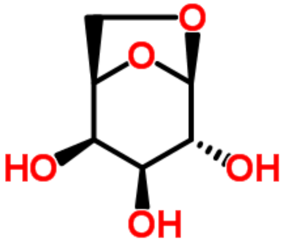
Active fires, shown in red, are detected using MODIS data from the Aqua and Terra satellites.
Source: NASA Fire Information for Resource Management System (FIRMS) https://earthdata.nasa.gov/firms

Tracers for Biomass Burning

- Water-soluble potassium (K^+)
- Levoglucosan and its isomers







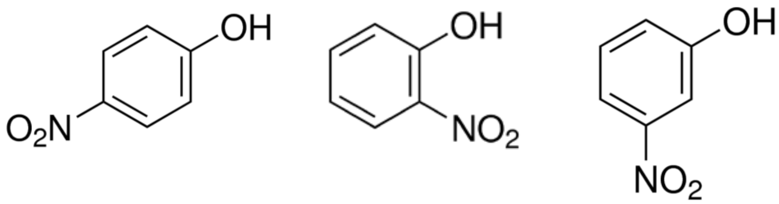
- Nitrocatechols (e.g. Ilnuma et al., 2010; Kitanovski et al., 2012)

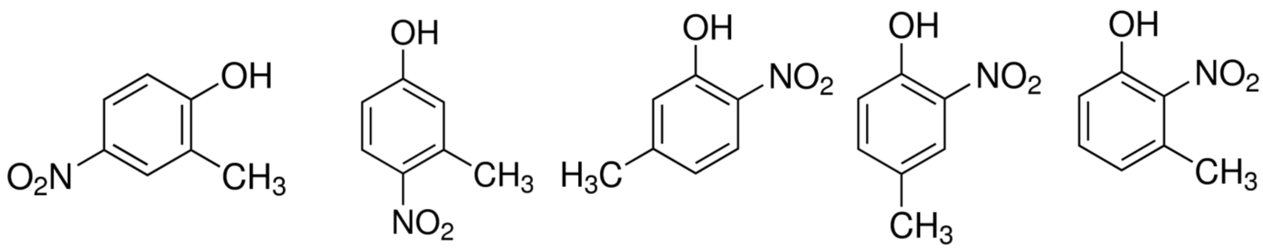


Nitroaromatic Compounds (NACs)

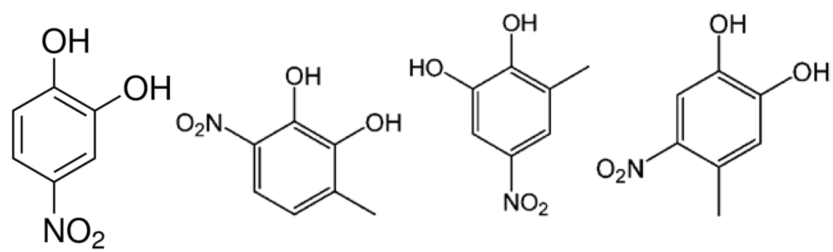
An important light-absorbing portion of BrC

Nitrophenols

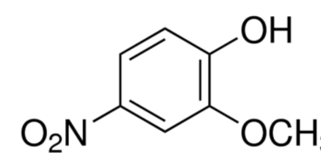




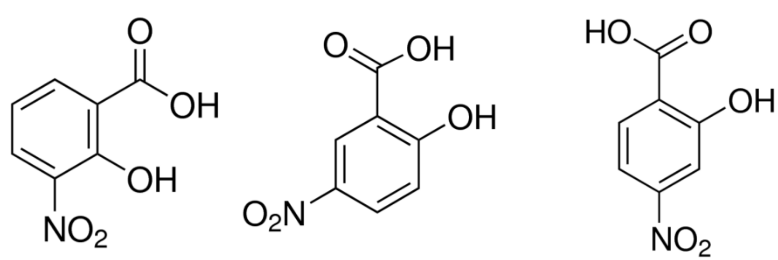
Nitrocatechols

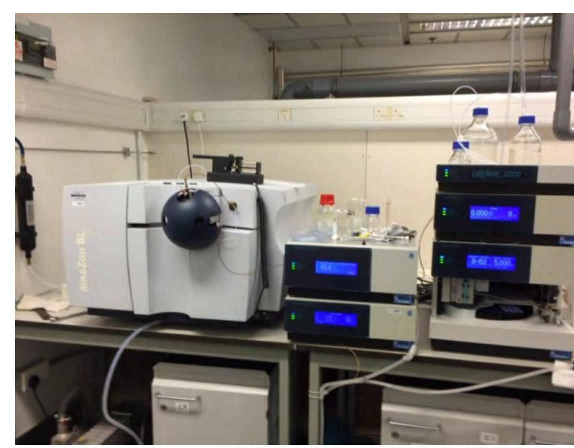


Nitroguaiacol



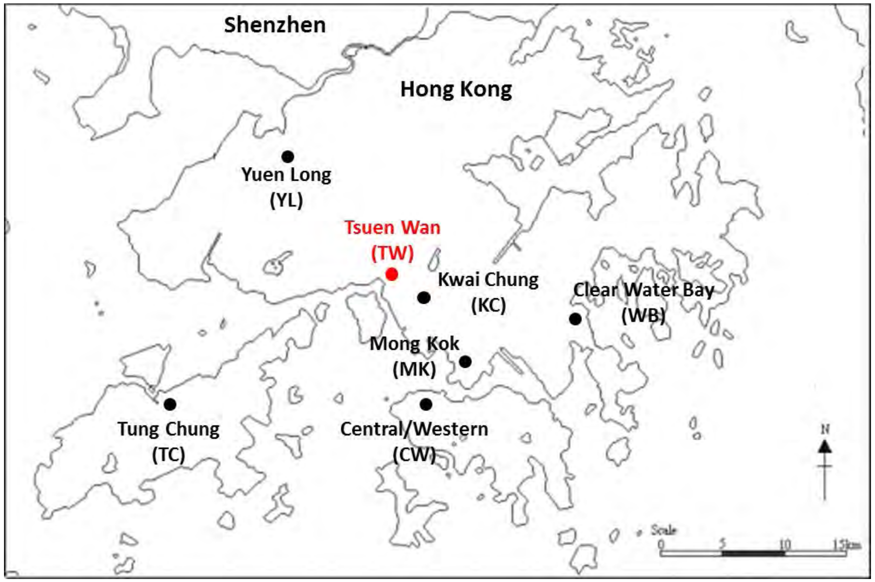
Nitrosalicylic acids

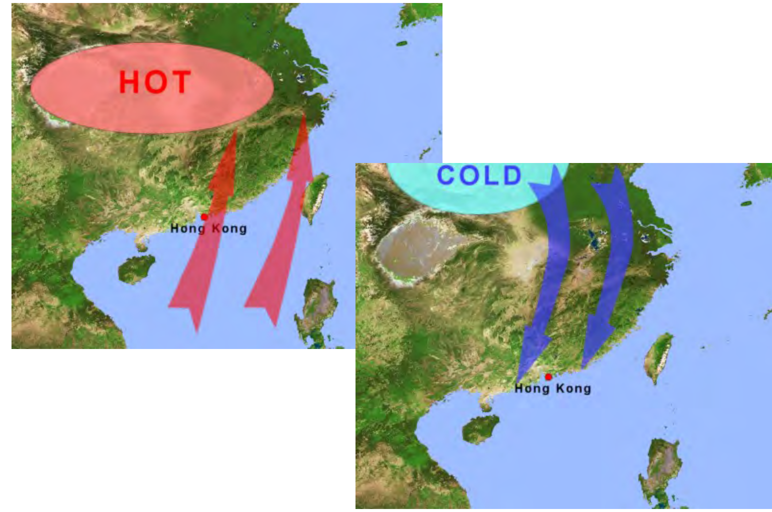




Claeys et al., 2012, Zhang et al., 2013; Desyaterik et al., 2014; Li et al., 2014, etc.

Aerosol Sample Collection





Source: Hong Kong Observatory

Aerosol Sample Collection

- High-Volume $PM_{2.5}$ Samplers (Andersen Instruments Inc.)
  - Filter substrate: 8 × 10” quartz fiber filter
  - Flow rate: 40 CFM (approx. 1.13 m^3/min) w/ mass flow control
- Reference Ambient Air Sampler (RAAS2.5-400, four channels, Andersen Instrument Inc.)

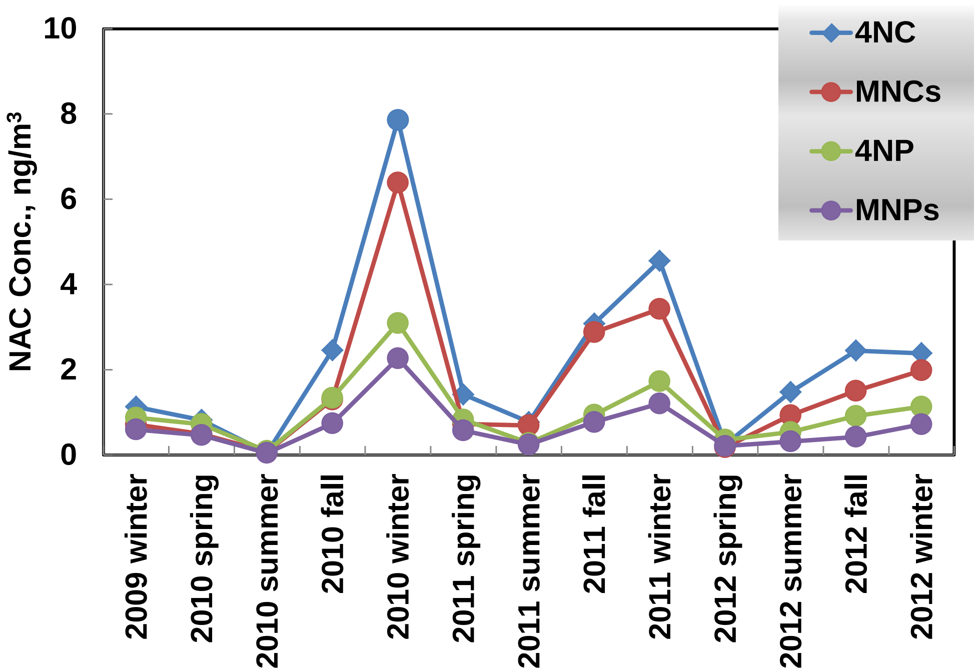
Channel ID	Flow Rate (LPM)	Filter Type
1	16.67	Teflon
2	7.3	Nylon (with Na_2CO_3 denuder)
3	7.3	Quartz
4	16.67	Quartz

- Sampling duration: 24 hours (starting from 0:00 midnight)
- Sampling frequency: 1-in-6 day
- Sampling period: Jan 2010 – Dec 2012

Laboratory Analysis on Aerosol Samples

Filter Type	Sampler	Target Species	Instrument
47 mm Teflon filter	RAAS	$PM_{2.5}$ mass Elements	Gravimetric ED-XRF
47 mm Nylon filter	RAAS	Major ions	IC
47 mm Quartz filter	RAAS	OC & EC	Carbon analyzer
8 x 10” Quartz filter	High-Volume	Monosaccharides	HPAEC-PAD
8 x 10” Quartz filter	High-Volume	NPOCs	TD-GCMS
8 x 10” Quartz filter	High-Volume	NACs	LC-MS

NAC Levels & Seasonal Variation



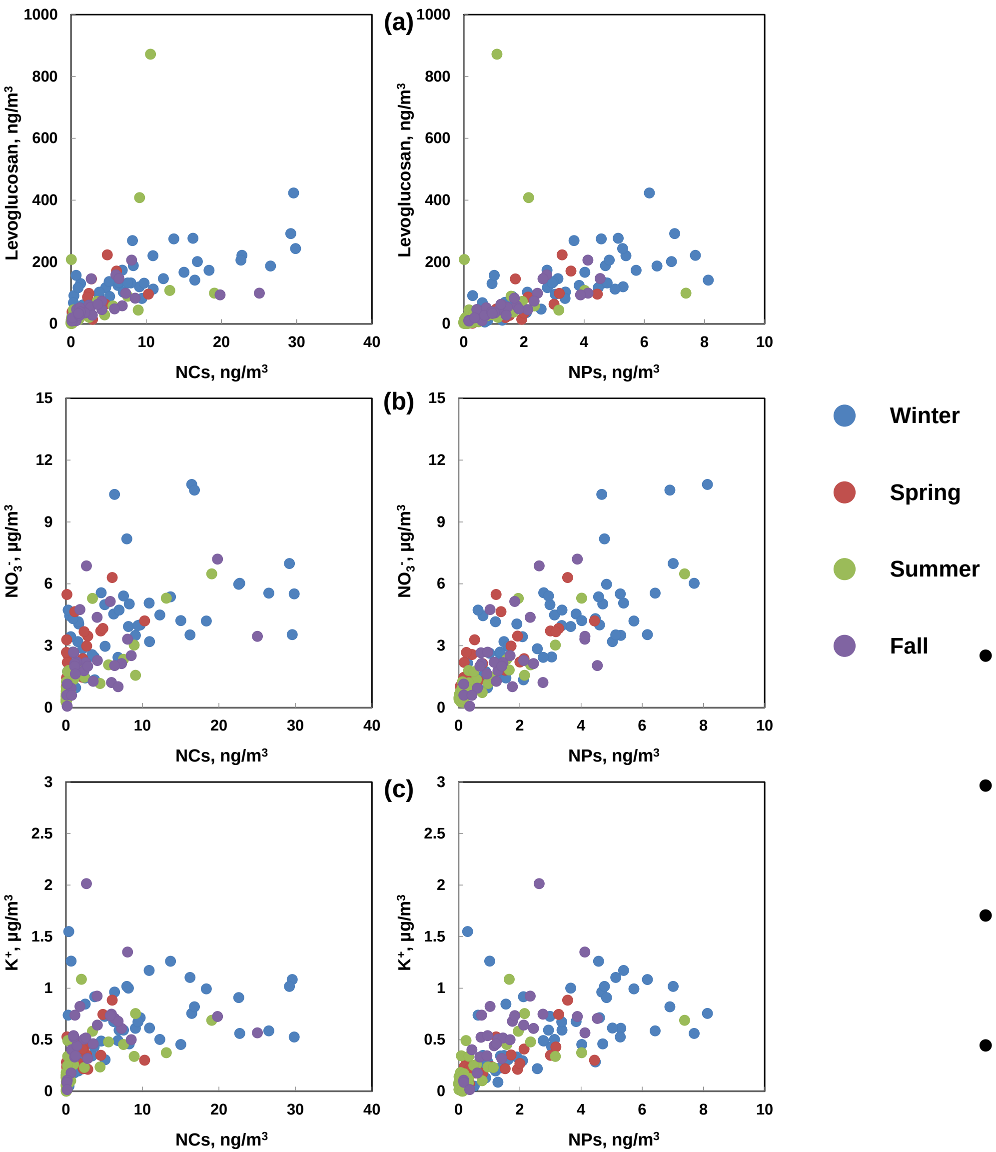
- A total of 15 NACs were consistently detected in ambient $PM_{2.5}$ samples ;
- In general, NAC levels in urban Hong Kong were lower than those found in rural areas in other parts of the world;
- NCs were at higher concentration levels than NPs;
- NACs were observed at highest level in winter (12.2±13.5 ng/m^3) and lowest in summer (2.2±4.9 ng/m^3).

Inter-NAC Species Correlations

	4NC	4M5NC	3M6NC	3M5NC	4NP	3M4NP	2M4NP	2,6D4NP
4NC	1.00							
4M5NC	0.94	1.00						
3M6NC	0.84	0.91	1.00					
3M5NC	0.94	0.95	0.89	1.00				
4NP	0.87	0.75	0.67	0.74	1.00			
3M4NP	0.85	0.82	0.77	0.75	0.91	1.00		
2M4NP	0.89	0.84	0.77	0.84	0.93	0.93	1.00	
2,6D4NP	0.54	0.59	0.53	0.51	0.57	0.66	0.64	1.00

- NACs are highly correlated, suggesting similar sources or formation processes;
- Correlations within each subgroups (NCs and NPs) are stronger than those between the subgroups;
- Possible reasons:
  - Semi-volatile characteristics of NPs → temperature-dependent GP partitioning
  - Multiple sources of NPs (automobiles, coal combustion, industrial processing, etc.)

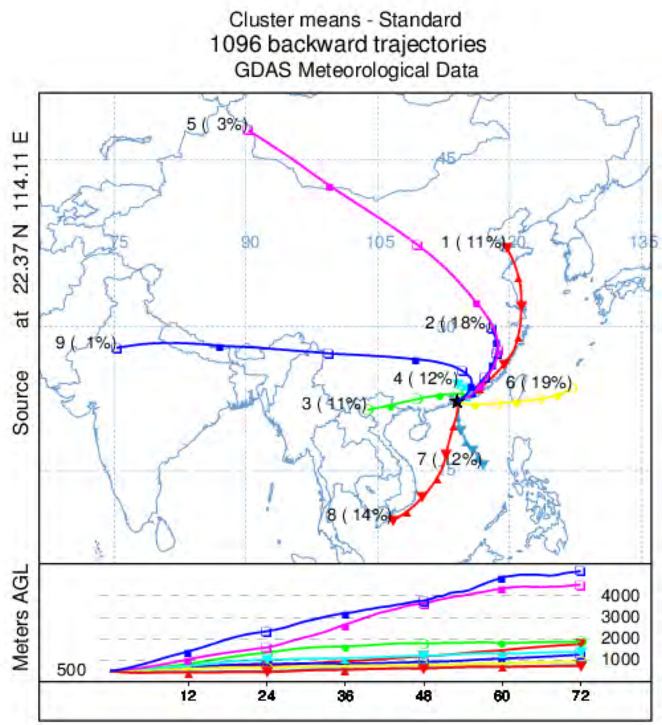
Inter-species Correlation Analysis

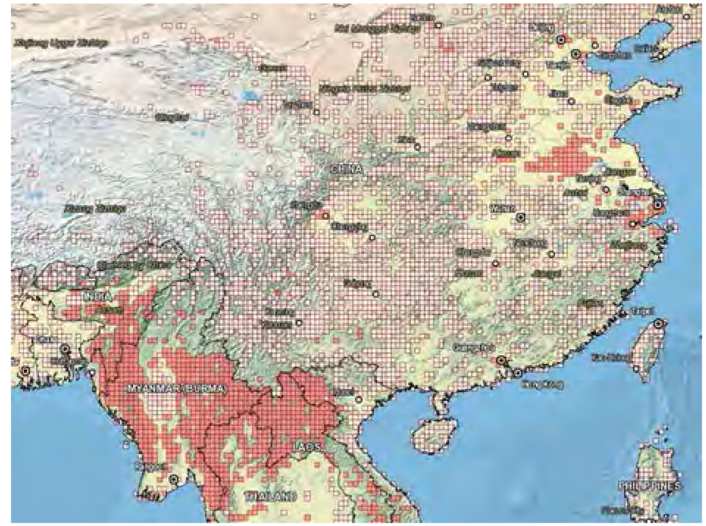


	Winter	Spring	Summer	Fall
NPs vs. levoglucosan	0.77	0.80	0.45	0.85
NCs vs. levoglucosan	0.83	0.71	0.57	0.48
NPs vs. NO_3^-	0.76	0.74	0.90	0.51
NCs vs. NO_3^-	0.55	0.61	0.85	0.45
NPs vs. K^+	0.48	0.72	0.66	0.58
NCs vs. K^+	0.45	0.56	0.61	0.22

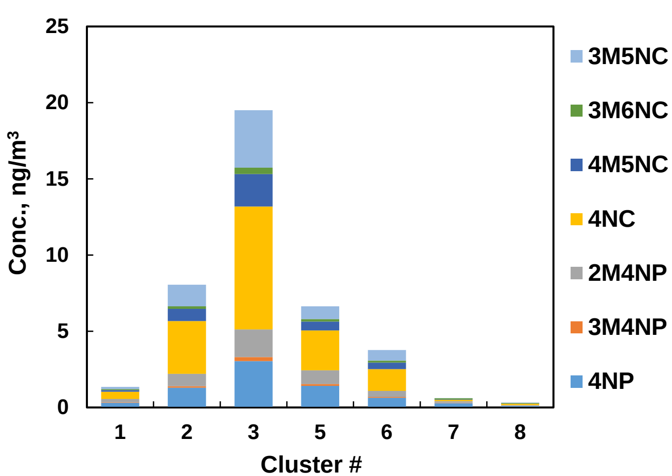
- NACs vs. levoglucosan: good correlations; better in winter, fall, and spring
- NACs vs. NO_3^-: good correlations; better in summer
- NACs vs. K^+: moderate correlations; better in summer
- NACs are more associated with aged aerosols originated from biomass burning

Source Origins of NACs





- 72-hour back trajectories were derived by HYSPLIT4 and assigned to 9 clusters;
- Higher levels of NACs were found to be from the continent;
- Highest NACs from the west: might be due to the large scale biomass burning in Southeast Asia



Source Analysis

- Input Data

Major species (x9)	
Na^+	Cl^-
NH_4^+	NO_3^-
Mg^{2+}	SO_4^{2-}
	$C_2O_4^{2-}$
OC	EC

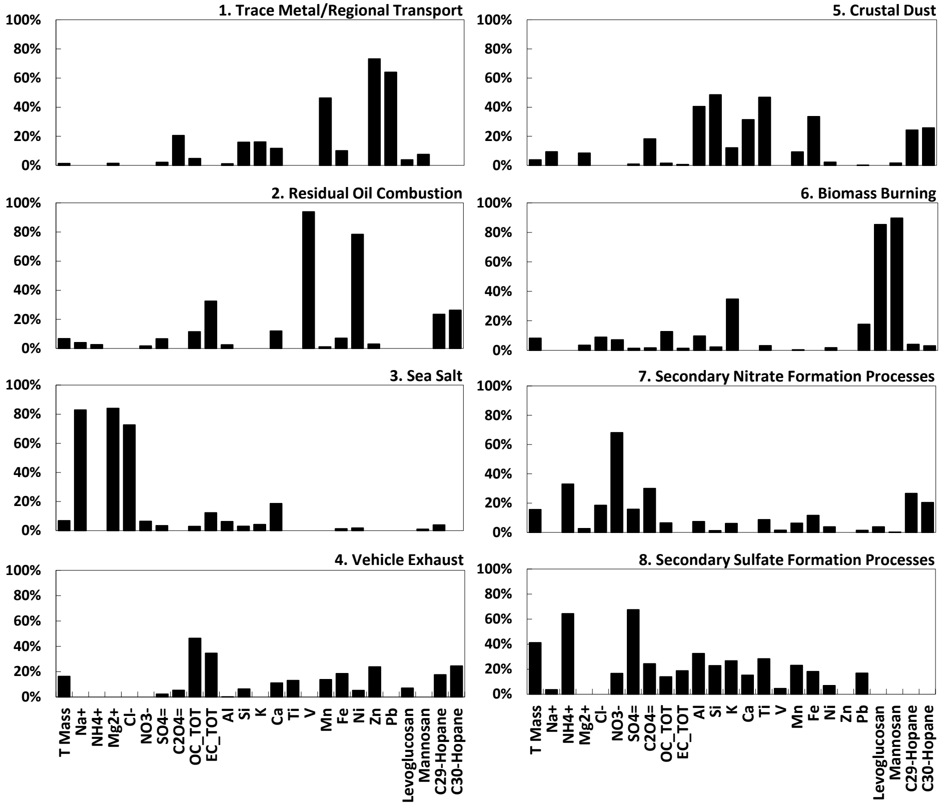
Elements (x11)	
Al	Mn
Si	Fe
K	Ni
Ca	Zn
Ti	Pb
V	

Organic compounds	
Hopanes	αβ-norhopane αβ-hopane
Anhydrosugars	Levoglucosan
	Mannosan
NACs	4-nitrophenol 2-methyl-4-nitrophenol 4-nitrocatechol 4-methyl-5-nitrocatechol

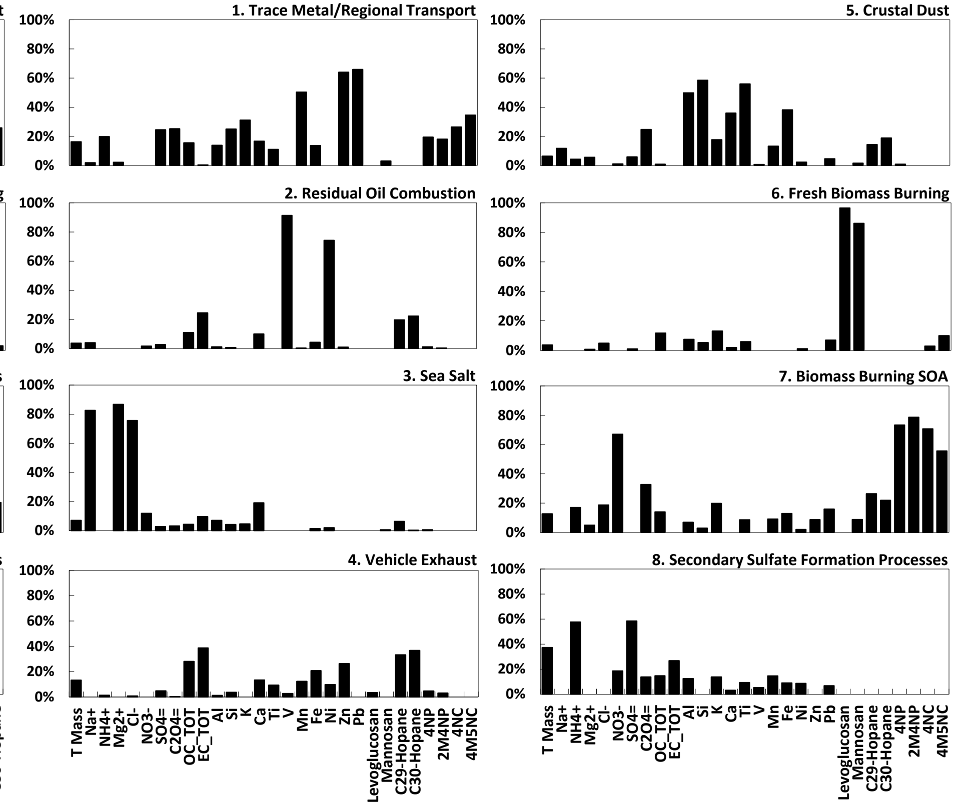
- Receptor modeling: USEPA PMF 5.0

PMF Analysis with Biomass Burning Tracers

A: Major Components + Hopane + Sugar

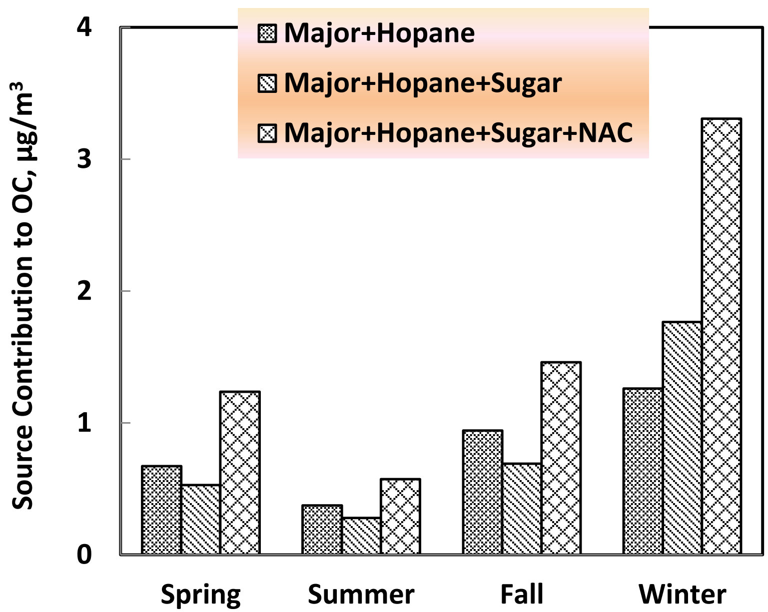


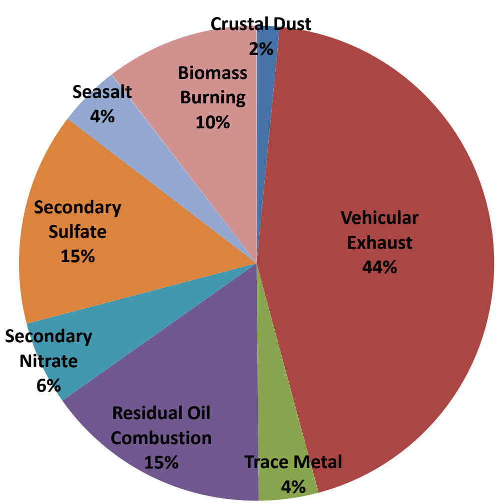
B: Major Components + Hopane + Sugar + NACs



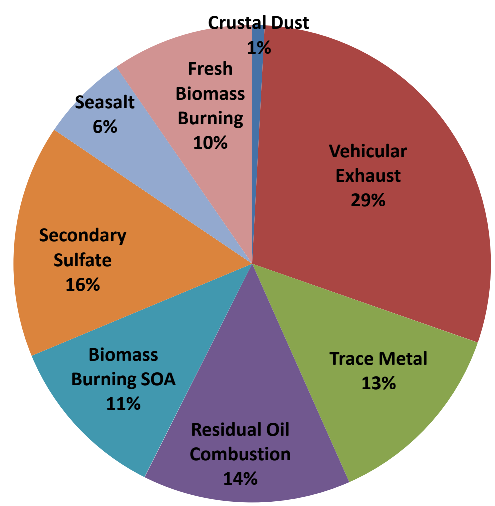
- 8-factor solution is chosen for the third run;
- Profile changes observed in SOA-associated factors (1, 6, 7, & 8);
- NACs appear in factors 1 & 7;
- The nitrate-abundant factor → aged biomass burning?

PMF Analysis with Biomass Burning Tracers





Major+Hopane+Sugar



Major+Hopane+Sugar+NAC

- Fairly stable SCEs: dust; sea salt; marine emissions; and secondary sulfate formation processes.
- NACs help to identify an aged biomass burning source from the nitrate-abundant factor.
- VE SCE to OC ↓
- Industrial Metal Processing/Regional transport SCE to OC ↑
- BB SCE to OC: 10% → 21%, up to 40% in winter
- More SOA tracers → more specified secondary sources (e.g. SOA from VE, VOCs)

Summary

- An analytical approach was established to identify a group of nitroaromatic compounds (NACs) in ambient $PM_{2.5}$ samples;
- The inter-species correlation analysis and case study showed evidences for secondary formation of NACs in the study region;
- The inclusion of NACs in PMF analysis enabled the identification of two biomass burning sources (primary and secondary);
- The two biomass burning sources attributed up to 40% of the observed OC in winter when biomass burning activities were strong in the surrounding area;
- SOA from biomass burning made significant contributions to organic aerosols in this region;
- More effort is needed in identifying specific SOA sources.

Thank you!

Q&A