COMPREHENSIVE ANALYSIS OF ORGANIC MICRO-POLLUTANTS IN AMBIENT AIR PARTICULATE MATTER IN HANOI

Hanh Thi Duong[1], Kiwao Kadokami[2], Ha Thu Trinh[3]

[1] Institute of Environmental Technology, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet Street, Cau Giay District, Hanoi, Viet Nam
[2] The University of Kitakyushu, 1-1 Hibikino, Wakamatsu, Kitakyushu, Fukuoka 808-0135, Japan
[3] Institute of Chemistry, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet Street, Cau Giay District, Hanoi, Viet Nam

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Background

❖**Sources of ambient air particulate matters in Vietnam:** traffic, construction, industrial, especially in big cities.

❖**PM_{10}, PM $_{2,5}$ and fine particulate matters:** adversely affects the respiratory system, increases death-rate due to heart and lung-related diseases.

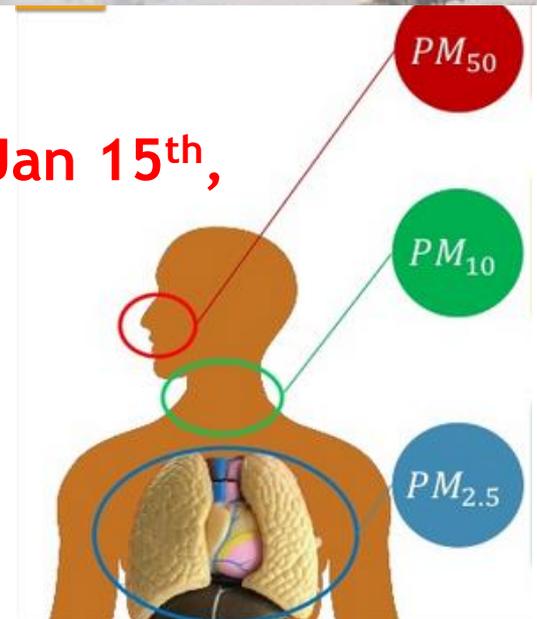**Real-time Air Quality Index (AQI) at 15:00, Jan 15th, 2020:**

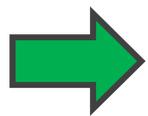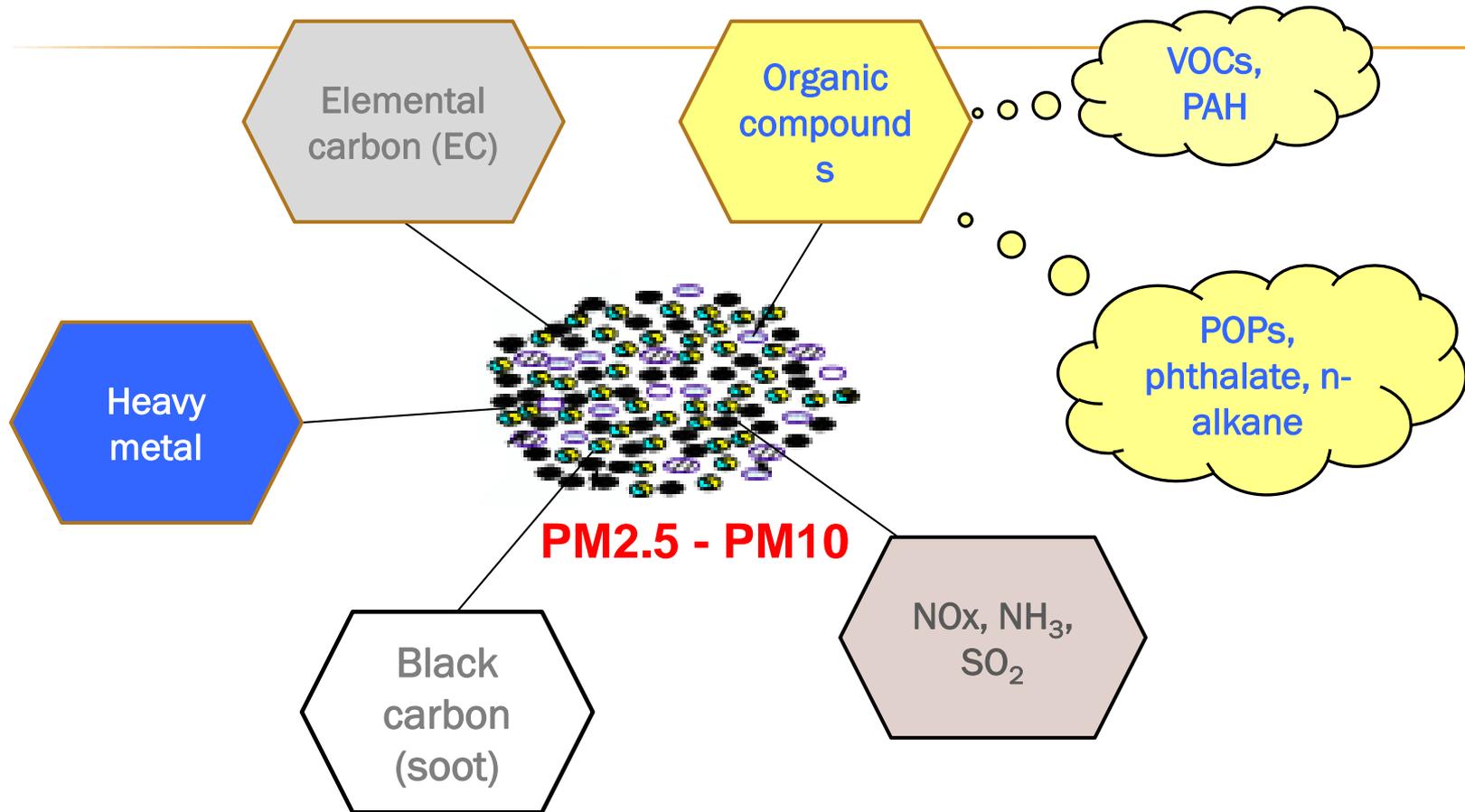❑ **Hà Nội: AQI: 244 (very unhealthy)**

$PM_{2.5}$ = 278 μg m^{-3}

❑ **Hồ Chí Minh: AQI: 158 (unhealthy)**

$PM_{2.5}$: 179 μg/m^3

(QCVN: 50 μg/m^3 and WHO: 25 μg/m^3- 24 hours mean)

Pollutants in particulate matters

Elemental carbon (EC)

Organic compounds

VOCs, PAH

POPs, phthalate, n-alkane

Heavy metal

PM2.5 - PM10

Black carbon (soot)

NOx, NH$_3$, SO$_2$

➡ **Particulate matters from different pollution sources carries different pollutant components**

Pope III et.al., 2002. J. Am. Med. Assoc. 287, 1132–41
Raaschou-Nielsen et.al., 2011. Environ. Health Perspect. 119, 860–5.
Fontal et.al., 2015. J Chromatogr A. 1404, 28-38.

Research on pollutants in particulate matters

❖ **In Vietnam:** PAHs, flame retardants, … in point sources

❖ **Global:**

   o Polar and semi-polar organic pollutants, PAHs, OCPs, PCBs,…

   o Bioassay assessment.

❖ **Ambient air quality standard in Vietnam (QCVN-06/BTNMT; QCVN-05/BTNMT, 2013) is regulated only for 44 substances which is not enough to evaluate the overall status of ambient air quality**

Objectives

☐ **Screening over 1000 organic micro-pollutants contain in air particulate matter sample in Hanoi** using the automatic identification and quantitation database system **(AIQS-GC (TIM, SIM, SRM), AIQS-LC) for GC/MS and LCQ-TOF/MS-SWATH.**

☐ Clarify occurrence of OMPs in ambient air particulate matter in Hanoi

☐ Elucidate **pollution characteristic** of contaminants and find the pollution sources.

What is the Automated Identification and Quantification database System AIQS-GC

> identify and quantify nearly 1000 organic chemicals without the use of standards

> Database consists of GC retention times, calibration curves and mass spectra of 940 chemicals

> Set and tune a GC-MS to the same conditions as those at the time of construction of the database → **to obtain reliable results**

> Retention times can be predicted using PTRI

> **The database allows the addition of new substances →** more compounds can be measured

$y = 1.4532x$
$R^2 = 0.9999$

Calibration Curves

Mass spectra

Retention times

AIQS-DB

Sep. 25, 2012
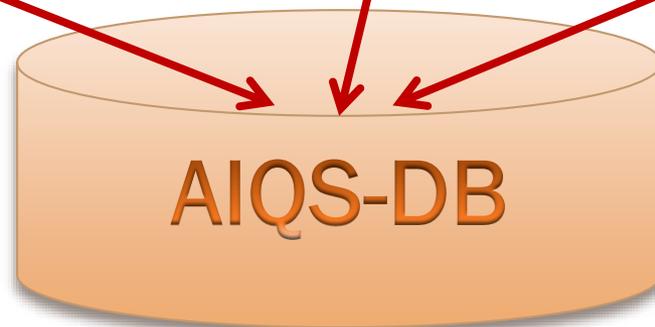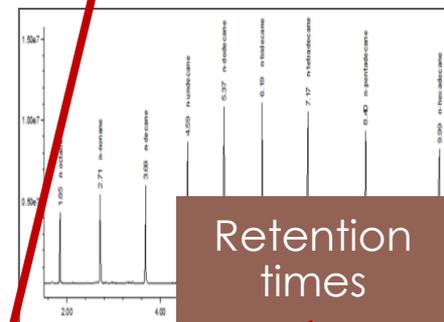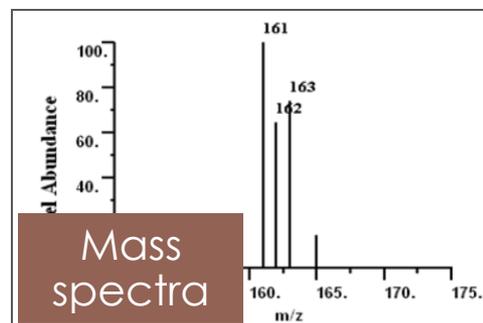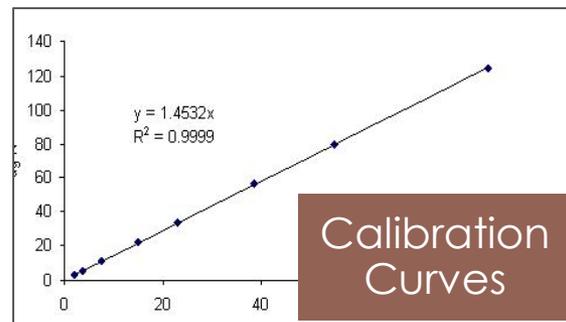
Physico-chemical Properties of Chemicals and Analytical Instruments

	Volatile	Semi-volatile	Non-volatile
Polar			**LC-QTOF/MS**
Semi-polar	**Objectives** **GC/MS** We have developed an analytical method that can target screen 1000 SVOCs by using Automated Identification and Quantification System with a database (AIQS-GC*).		We have developed another quantitative target screening method for 500 polar substances in environmental samples.
Non-polar	*K. Kadokami, *J. Chromatogr A*, 2005		
	Low MW	Medium MW	Large MW

Substances Registered in AIQS-GC

Substance classification		Number
Compound contains CH	Aliphatic hydrocarbons, Polycyclic aromatic hydrocarbons, PCBs, etc.	190
Acid-containing compounds	Phenols, etc.	160
Asphyxiant compounds	Aromatic amines, etc.	113
Pesticides	Insecticide, herbicide, etc.	453
Others	PPCPs, Lin compounds, etc.	56
	Total	972

Substances Registered in AIQS-LC

Class	Number	Example
Pesticides	298	Insecticide, Herbicide, etc.
Pharmaceutical and Personal Care Products (PPCPs)	162	Antibiotic, Analgesic, UV filter, etc.
Industrial chemical	8	
Others	21	
Total	489	

Sampling locations

Sampling site: 2 sites in Hanoi

AP1: heavily traffic transposition

AP2: highly populated residential area (fresh noodle industry)

Sampling method: HV model -120H Kimoto with Quartz fiber filter (203 x 254mm).

Sampling time: dry (April) and rainy (Sep.) season in 2017; day and night sampling for 6 consecutive days.

Sample: 48 air particulate matter samples.

Analytical method (AIQS-GC)

PM sample (half of a filter)

↓

 ← Surrogates (100 µL x 10 µg/mL)
 ← 20 ml DCM (3 times)

↓

Ultrasonic bath (15min)

↓

Centrifuge (10 mins, 2000 rpm/min)

↓

Evaporation flask

↓

Dehydrate (Na_2SO_4, preheated at 700^OC, in 6h)

↓

Concentrate (RE, 1 mL)

↓

 ← hexane 5 ml

↓

Concentrate (N_2, 1 ml)

↓

 ← IS (10 µg/mL x 100 µL)

↓

GC- MS (SIM/TIM)

↓

GC/MS-TIM/SIM
 (TIM data is processed by AIQS-DB)

Analytical method (AIQS-LC)

PM sample (half of a filter)

↓
    ← Surrogates (50 µL x 4µg/L)
    ← 20 ml MeOH (and repeated 2 more times with 15ml MeOH)

Ultrasonic bath (15min)

↓

Centrifuge (20 mins, 2000 rpm/min)

↓

Evaporation flask (combine the extract)

↓

Concentrate (RE, 2-3 mL)

↓

Concentrate (N_2, 0,5 ml)

↓
    ← IS (50 µL x 4µg/L)

LC-QTOF-MS-SWATH

Method Detection Limit (MLD)

Compound	LC-QTOF-MS (pg/m³)	GC/MS (ng/m³)	
		GC-MS-TIM *(AIQS-DB)*	GC-MS-MS SRM
Targets	0.3 - 60	≤ 0.5	≤ 0.05

RESULTS & DISCUSSION

Outline of OMPs detected in TSP

➢ **118 OMPs out of 970 in 16 different chemical categories** were detected at least once.

➢ **The total concentration ranged from 200 to 1393 ng/m^3** (median, 346 ng/m^3),

➢ Number of OMP detected per sample ranged from 85 to 103 (median, 92).

➢ **n-alkanes, PAHs, phthalates, sterols, pesticides, and PPCPs were found in over 80% of samples.**

➢ **Little difference in the number of compounds detected** between the two seasons at AP1 and AP2.

PAHs

➢ **23 out of 37 PAHs** were detected.

➢ **PAH were higher in the samples collected at night than those in the day.**
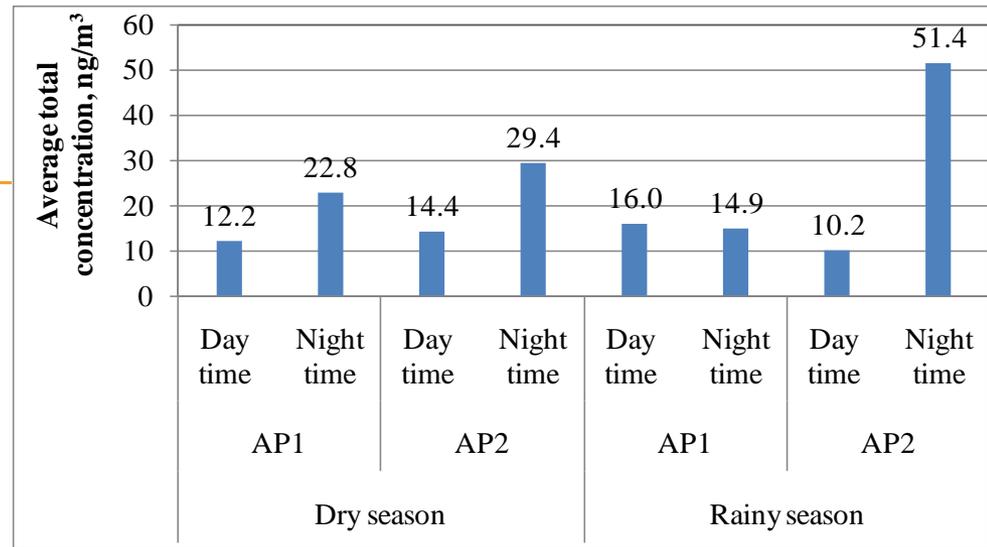
Fig 1. Average total concentration of PAHs in in the rainy and the dry season in AP1 and AP2
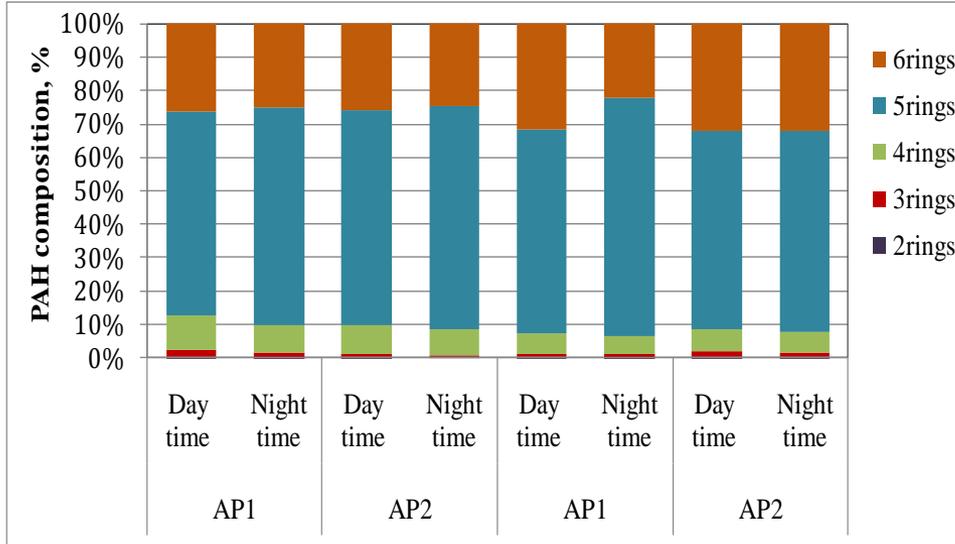

Fig 2. Profiles of Σ 2- to Σ 6- rings of PAHs in TSP in the rainy and the dry season in AP1 and AP2

➢ **5- and 6-ring PAHs were dominant in all samples.**

➢ **Source of PAH in TSP: petrogenic** (leakage of gasoline, diesel fuel, and fuel oil from vehicles) and **pyrolytic** (vehicle exhaust gases) origin
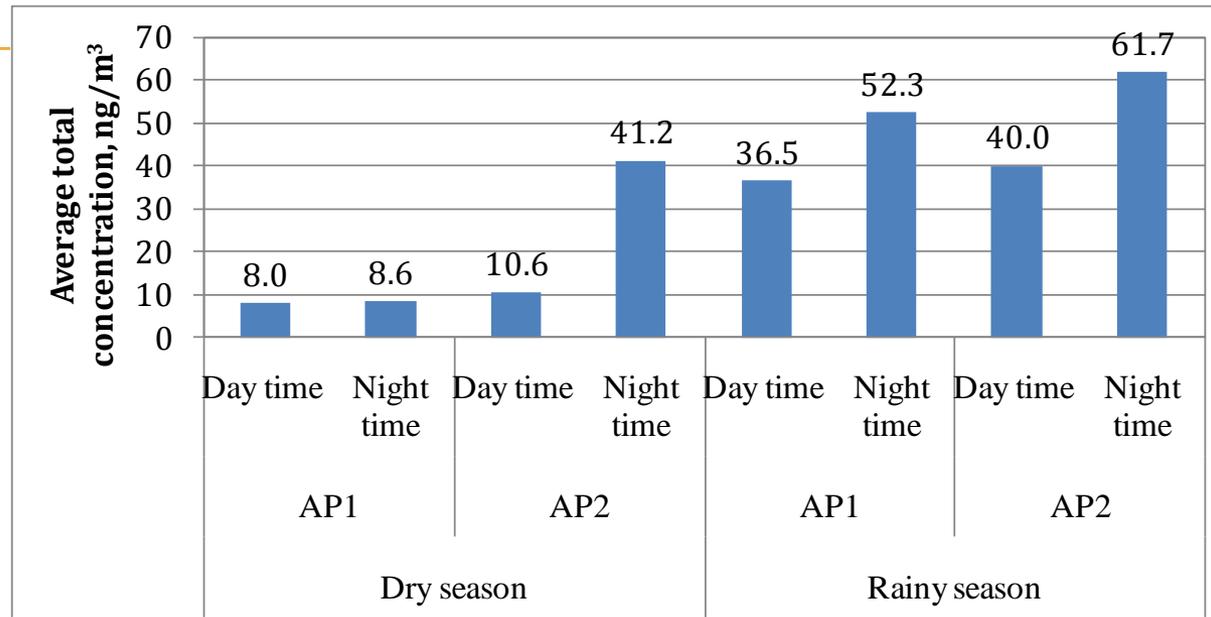
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Pesticides detected in AIQS-GC

Fig. 3. Average total concentration of pesticide in the rainy and the dry season in AP1 and AP2

➤ **18 out of 452 pesticides in AIQS-GC were detected** (12 insecticides, 4 herbicides, and 2 fungicides)

➤ Permethrin-2, carbofuran, fenobucarb, chlorpyrifos, metolachlor were detected in over 70% of samples.

➤ **Prohibited pesticides were detected in TSP**: chlorpyrifos, permethrin, deltamethrin, cypermethrin, carbofuran, atrazine.

➤ **Sources: heavy use of pesticides for disease vector control during the study period.**
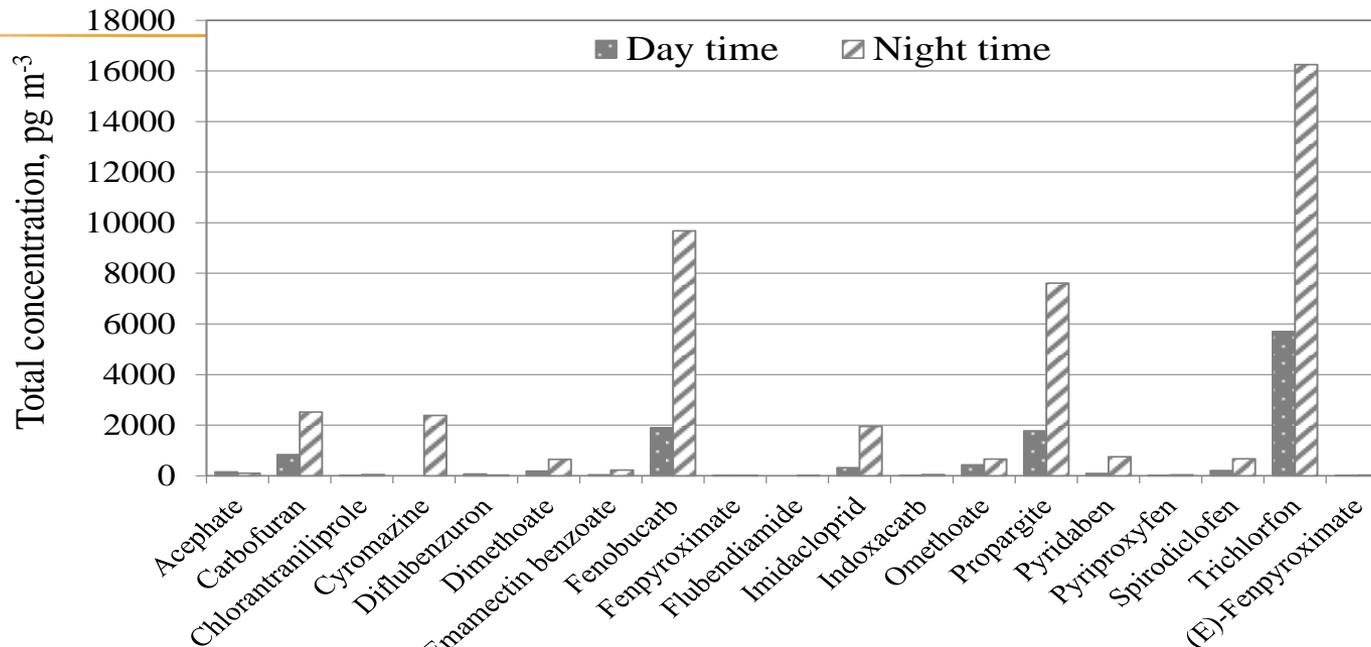
Insecticides detected in AIQS-LC

Fig. 4. Total concentration of each insecticide at in the daytime and nighttime.

> **19 current use insecticides out of 107 insecticides screened were detected.**

> **16 substances are reported for the first time in the literature.**

> Sum conc. of insecticide in sample at night were higher than those in the day of both seasons.

> **Sum conc. of insecticide at AP2 was higher than that at AP1, due to their usage for the control pests during preventive dengue fever campaign.**

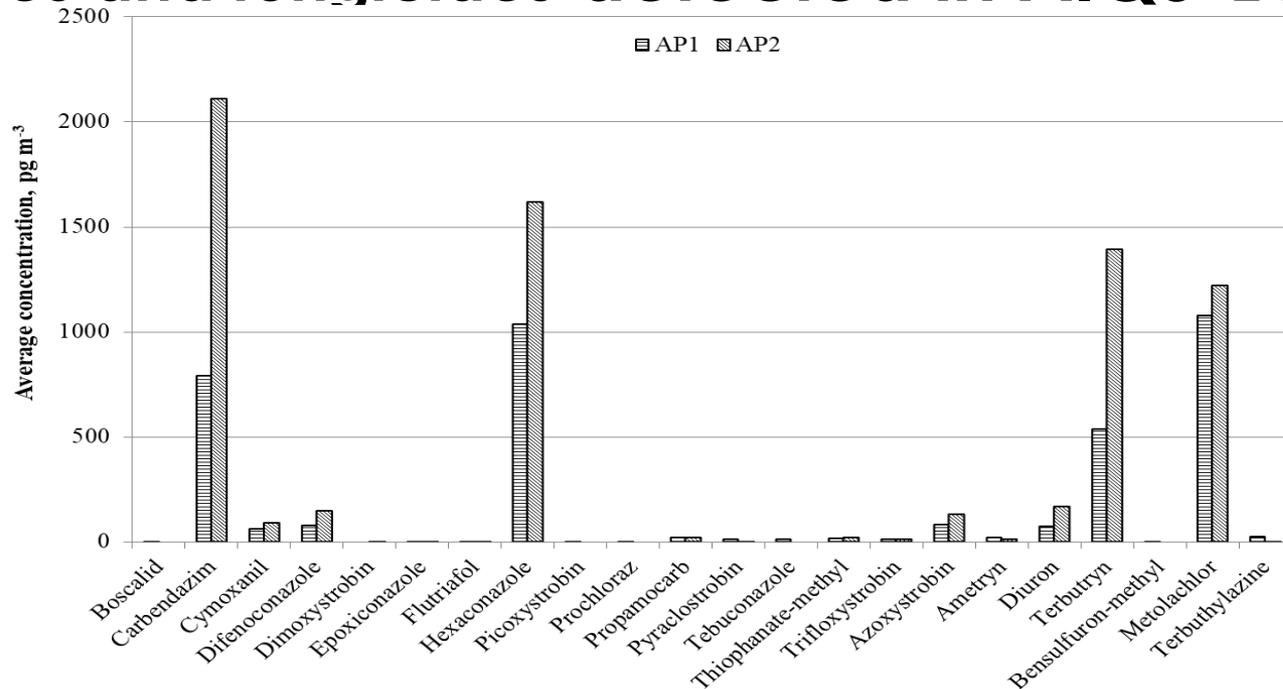# Herbicides and fungicides detected in AIQS-LC

Fig. 5. Concentration of fungicides and herbicides at AP1 and AP2

- 16 fungicides and 6 herbicides were detected at least once in the TSP
- 19 herbicides and fungicides were detected for the first time in TSP Hanoi, Vietnam.

➢ The number of the detected insecticides using LC-QTOF-MSSWATH was higher than those using GC/MS due to their polar and low or nonvolatile characteristics.

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Human risk assessment of pesticides

Pesticides	Adults		Children		Infants	
	DI_{air}	HQ	DI_{air}	HQ	DI_{air}	HQ
Total DI_{air}	**8.17E-06**		**2.06E-05**		**2.45E-05**	
Hazard Index of fungicides and herbicides		7.27E-04		18.4E-04		2.18E-03
Hazard Index of insecticides		2.51E-03		6.33E-03		7.52E-03
Hazard Index of pesticides (insecticides, fungicides, and herbicides)		3.24E-03		8.17E-03		9.70E-03

The **daily intake via inhalation, the Hazard Quotients of pesticides were less than 1** for three population groups (adults, children, and infants), indicating a negligible exposure risk.

Sterols

➢ **Total 7 of the 13 sterols in the AIQS –GC were detected**
➢ **Cholesterol had the highest detection frequency (98%), followed by β-sitosterol (94%) and coprostanol (77%).**
➢ **Source of cholesterol and β-sitosterol: related to the cooking and noodle production activities of the residents of the study sites.**

➢ **2 samples had ratio > 21**

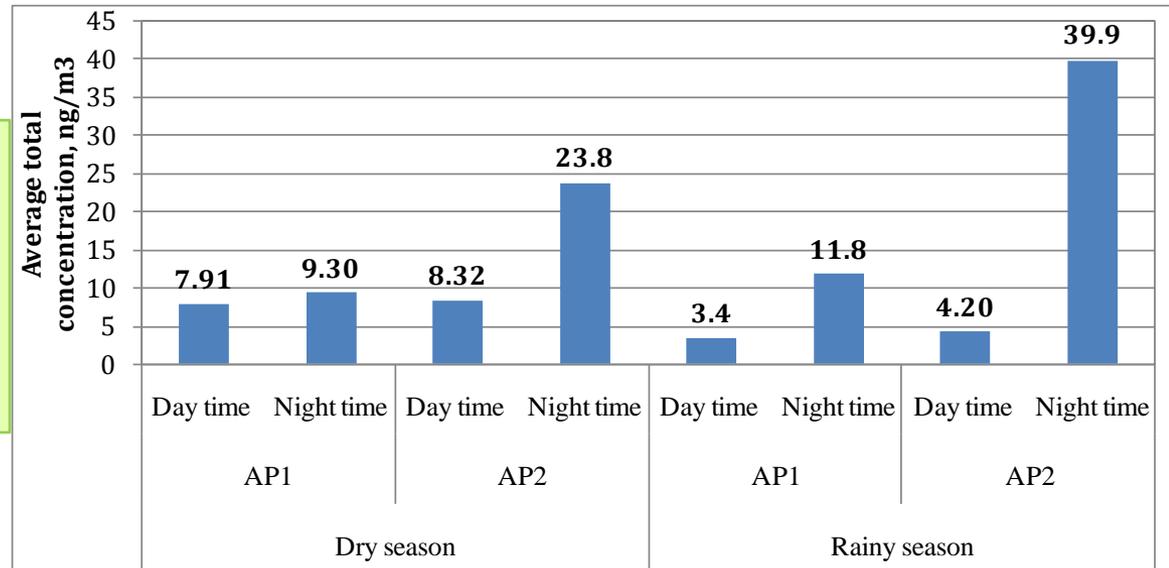➢ **3 samples had ratios from 0.22 to 0.24**

Fig. 6. Average total concentration of sterols in the rainy and the dry season in AP1 and AP2

➢ Coprostanol/cholesterol > 0.2 → sewage origin (*Grimalt et al., 1990*)
➢ Coprostanol/cholesterol > 0.3 → human feces origin (*Glassmeyer et al., 2005*)

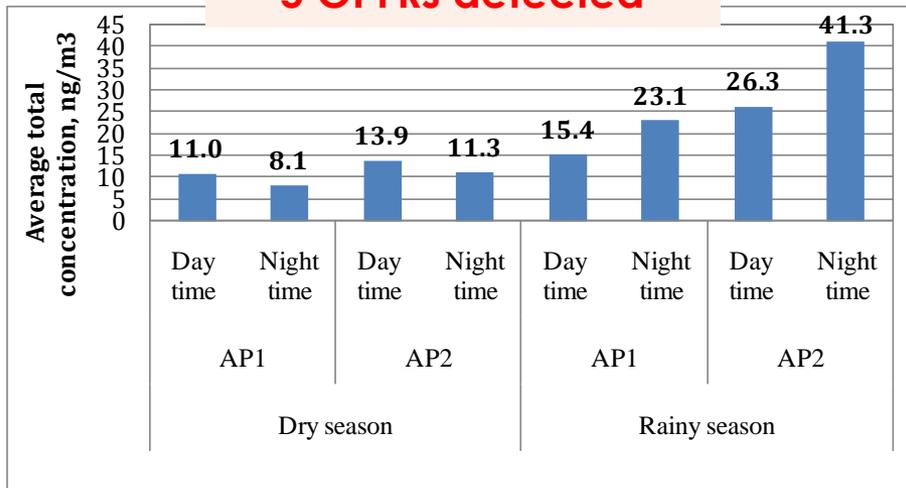# Organophosphorus flame retardants and plasticizers

Fig. 7. Average total concentration of FRs in the rainy and the dry season in AP1 and AP2
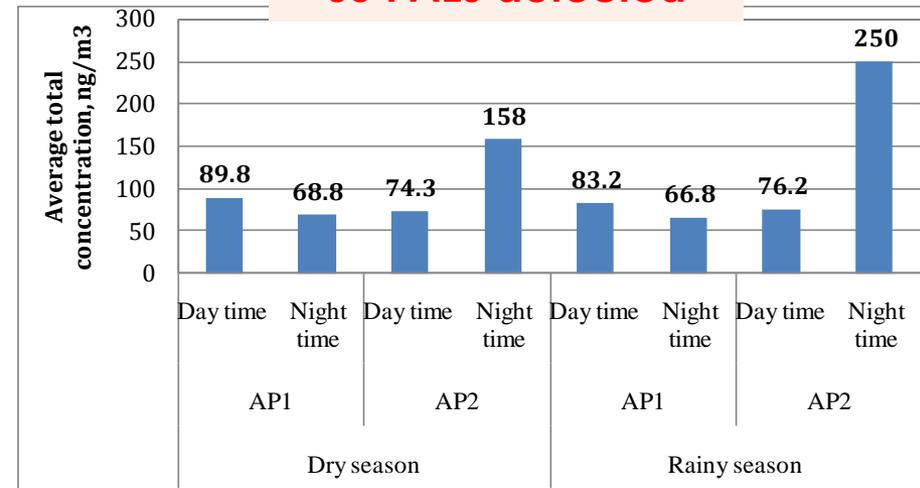

Fig. 8. Average total concentration of phthalates in the rainy and the dry season in AP1 and AP2

➢ Three non-chlorinated chemicals (**TEP, TPP, and TBP**) and two chlorinated isomers (**TCPP1 and -2**) were detected.

➢ TCPP contributed 53% to 94% of the total concentration of OPFRs.

➢ Out of 5 PAEs detected, **DEHP, DBP, and DiBP were found in 100% samples and accounting for over 90% of the $\sum$PAE**s

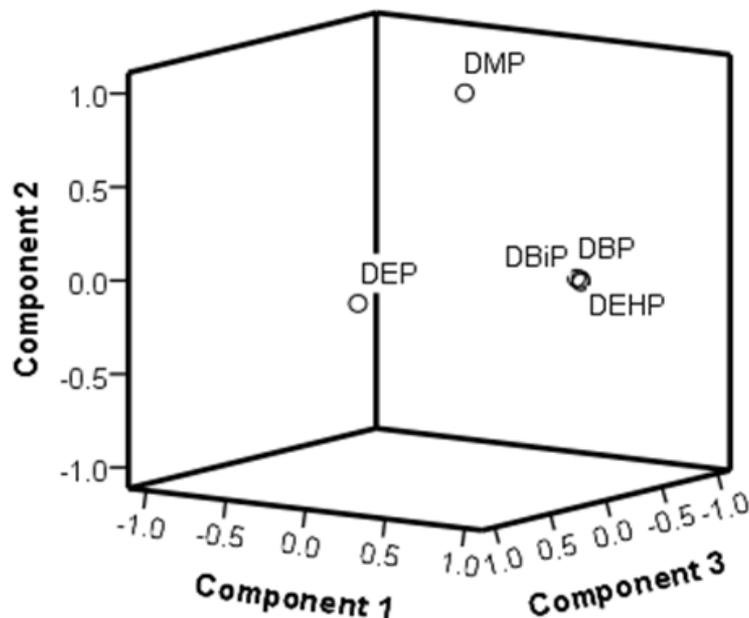# Organophosphorus flame retardants and plasticizers

Fig. 9. Principal component analysis of 48 samples using normanized concentration of 5 detected PAEs

➢ **Significant positive correlations for DiBP, DBP, and DEHP with high loading values (>0.99)** and explained 60.9% of the total variance → **emission from municipal solid waste landfills, waste stacks, or sewage**
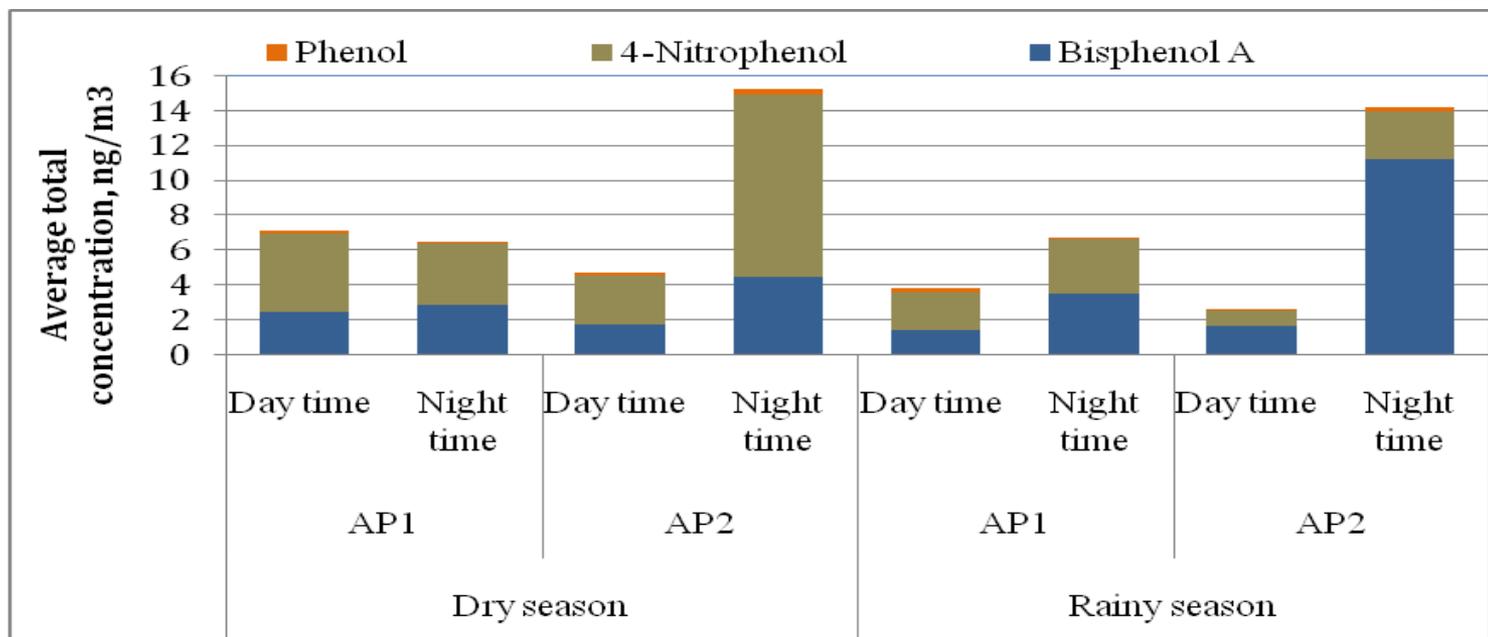
Emerging chemicals

Fig. 10. Average total concentration of Phenol, 4-NP and BPA in the rainy and the dry season in AP1 and AP2

➢ **BPA, 4-NP, and phenol were detected in over 90% of the samples**

➢ **4-NP was detected in 45 of the 48 samples, accounting >50% of the total concentration of 31 samples**

  ➢ **4-NP are probably originated from the exhaust gas from vehicles**
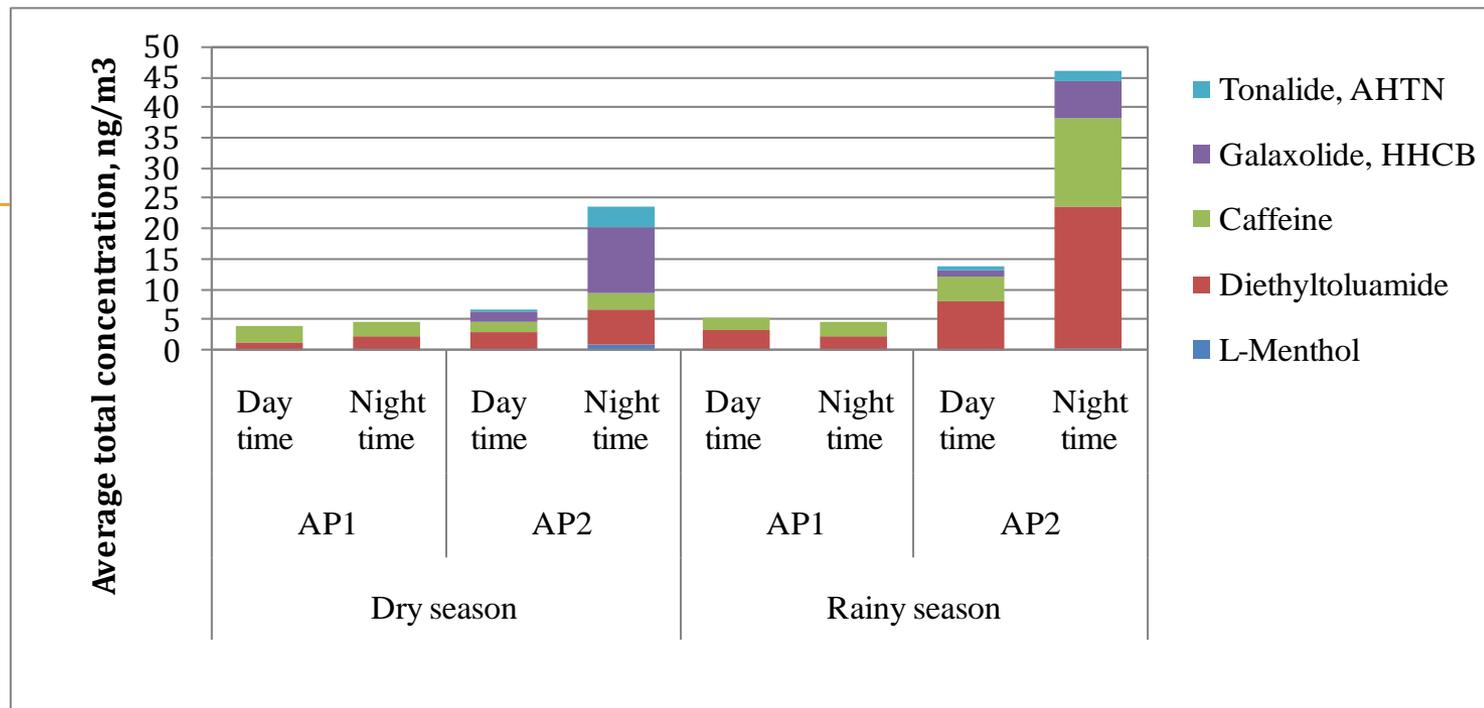
PPCPs

Fig. 11. Average total concentration of PPCPs in the rainy and the dry season in AP1 and AP2

➢ **Diethyltoluamide detected in 100% of the samples, caffeine (90%), galaxolide (48%), tonalide (40%), and L-menthol (17%).**

➢ **DEET is widely used in personal insect repellents that are applied to uncovered human skin or to clothing (Directive 98/8/EC, 2010)**

→ **DEET detected in this study is probably related to the use of insect repellents for disease vector control during the sampling period.**

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Conclusions

➢ **This is the first comprehensive study of OMPs adsorbed on atmospheric particulate matter in Vietnam**

➢ **A total of 118 target compounds were detected.**

➢ The concentrations of PAHs were higher in samples collected at night than in those collected in the day.

➢ Pesticide detected in this study is probably due to their use for **disease vector control during the study period.**

➢ **Seven sterols were detected**, we hypothesize that these compounds originated from discharges of untreated wastewater from residences or small-scale pig farms near the study sites.

➢ **TCPP and DEET were respectively the most abundant OPFRs and PPCPs detected.**

➢ **DEHP, DBP, and DiBP detected in all samples** with high levels, probably have adverse effects in humans.

➢ **Endocrine-disrupting chemicals (BPA and 4-NP) were detected in over 90% of samples.**

Acknowledgments