



# **Assessment of VOCs Emission Inventory in Seoul Through Spatiotemporal Observations Using Passive and Online PAMS Measurements**

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# Methods for analyzing VOCs



TD(Thermo Desorption)-Gas Chromatography (GC)/FID (Flame Ionization Detector)

TD-GC/MS (Mass Spectrometry)



PTR-MS(Proton Transfer Reaction Mass Spectrometry )

# Methods for sampling VOCs



Canister



Passive tube Sampler



Active tube Sampler with vacuum pump

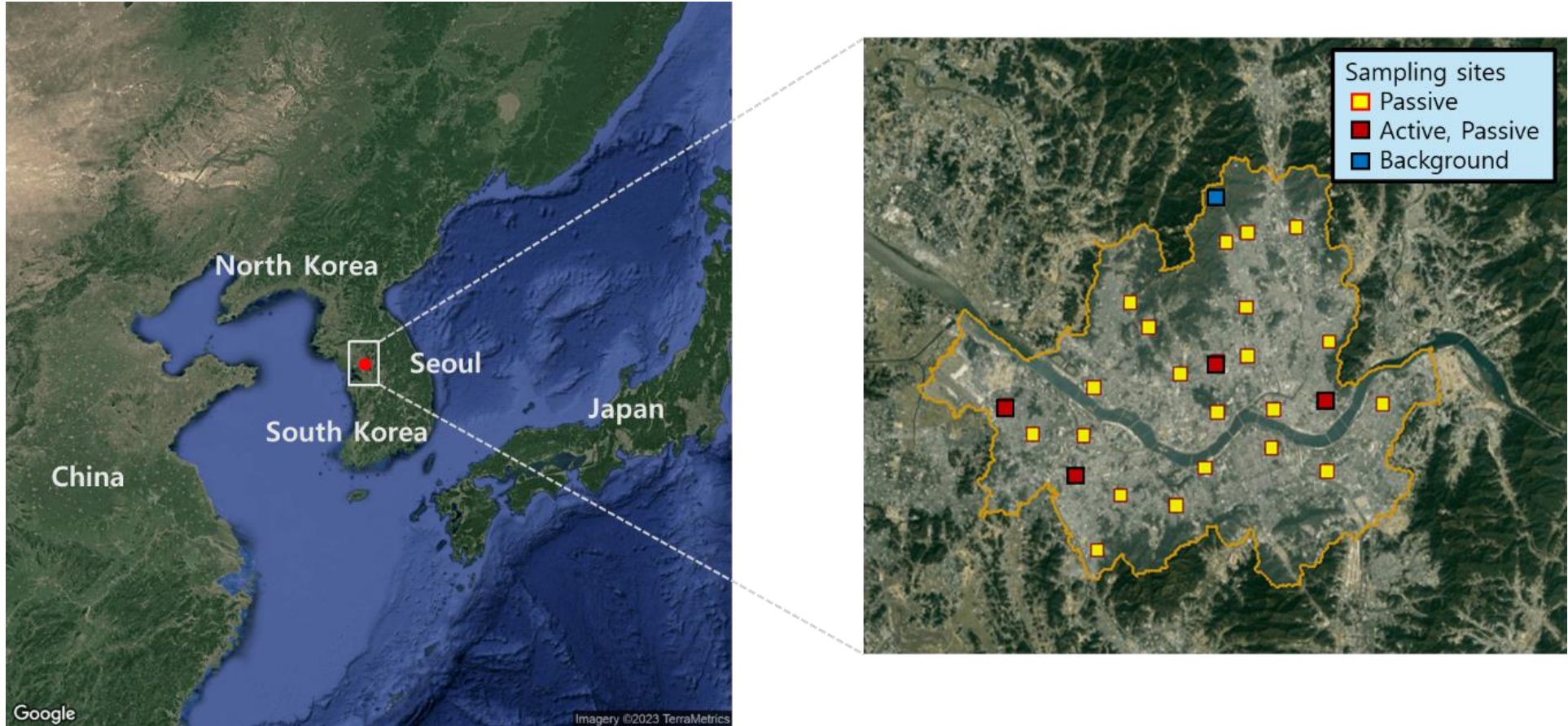
# Passive and active sampling

- Installed passive air samplers (PAS, FLM Carbopack deactivated (Supelco, USA)) at 25 location in Seoul's urban air monitoring network to collect samples.
- Analyzed **56 PAMS VOCs** (Ozone Precursor Mixture, EPA PAMS Target compounds) using TD-GC/FID (TD: Perkin elmer turbo350 matrix , GC/FID: Agilent 7890A).
- 56 VOCs have been monitored hourly at Photochemical Assessment Monitoring Station network(PAMS) operated by the Seoul Metropolitan Institute of Health and Environment using an online Thermal desorption Gas chromatograph/Flame ionization detector(TD-GC/FID) during 2022.05-2023.05.

**Table 1) Sampling duration and number of samples**

Sampling period	Number of sampling sites	Number of samples
Sep 16 - Oct 7, 2022	25	50
Feb 2 - Feb 23, 2023	26	52
May 25 - June 25, 2023	26	51

# Locations of passive and active air sampling sites (25 urban air monitoring network) in Seoul, Korea



## Passive sampling



Passive air sampler(PAS)

analysis



TD-GC/FID

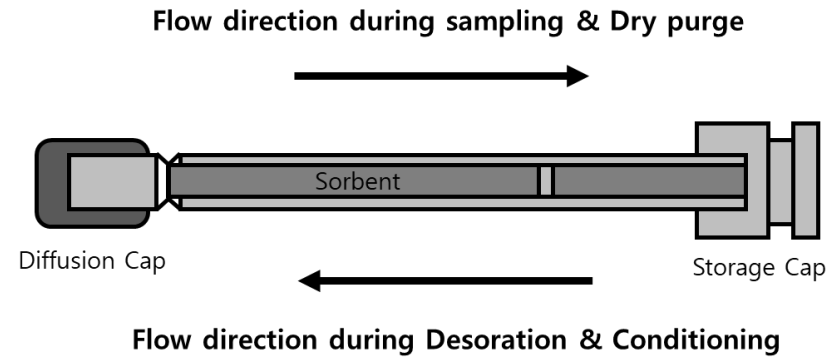
- Ease of installation
- Cost-effectiveness
- Suitable for long-term and large scale monitoring

## Active sampling

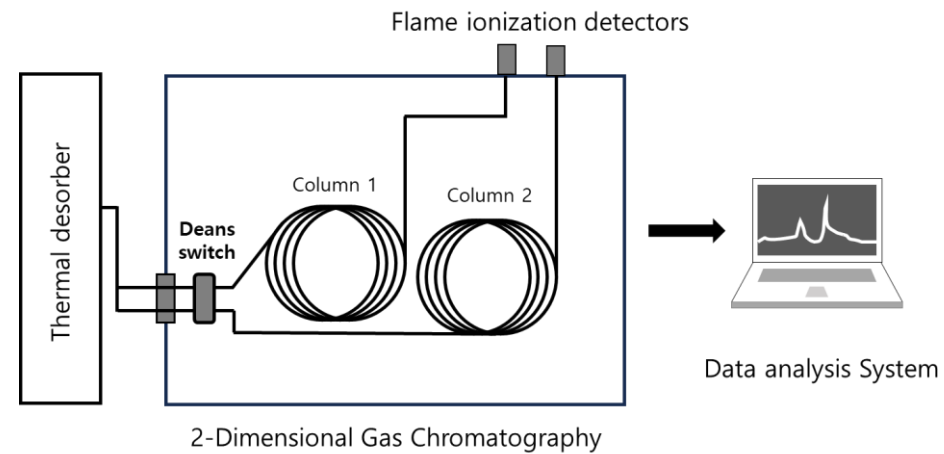


- Captures short-term fluctuations
- Continuous monitoring

# Structure of automated thermal desorption tube passive air sampler (Supelco FLM carbopack X)



## TD-GC/FID instruments for VOCs analysis

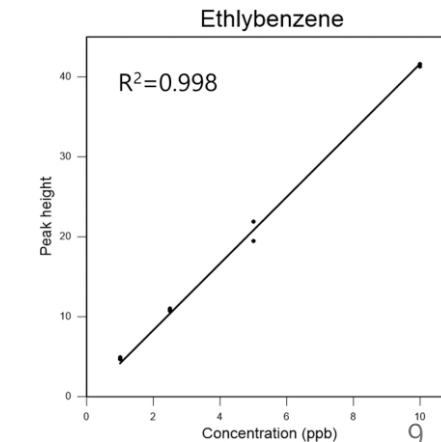
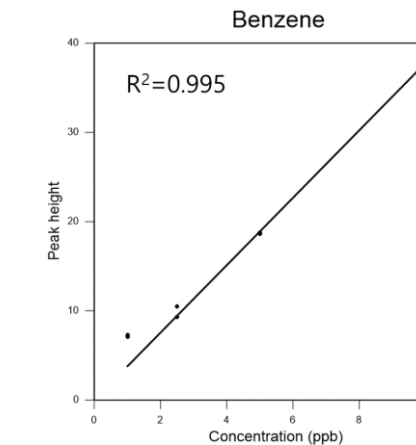
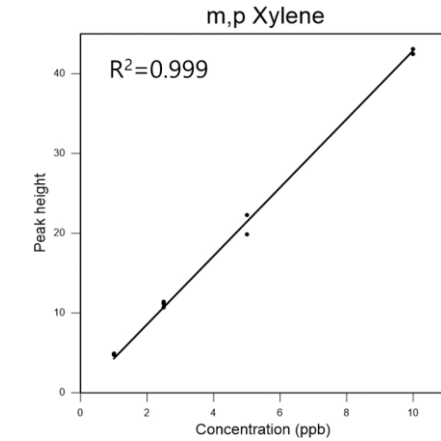
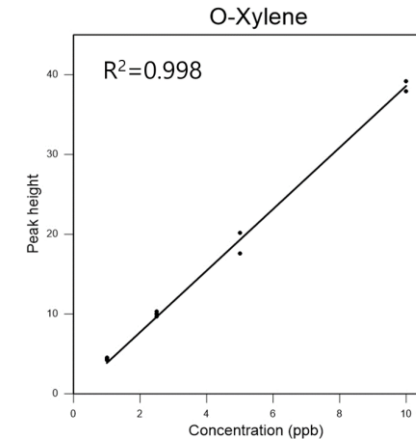
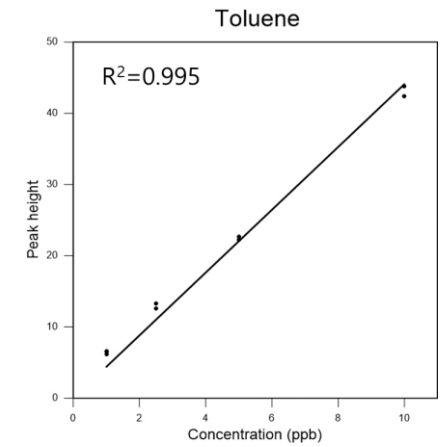
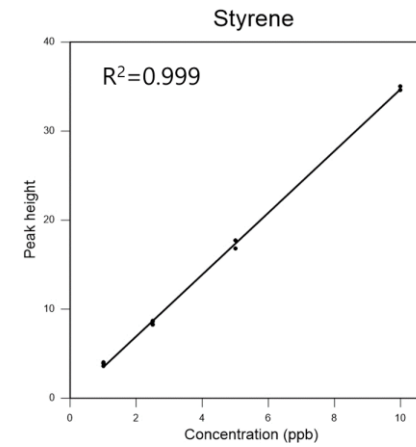


# Analytical conditions for measuring VOCs using PAS and online PAMS methods

	Analytical condition	
	Online PAMS	PAS
<b>column1</b>	AL-PLOT : 50m x 0.32mm x 5µm	AL-PLOT : 50m x 0.32mm x 5µm
<b>column2</b>	BP-1 : 50m x 0.22mm x 1.00µm	CP Sil 5CB : 60m x 0.25mm x 1.00µm
<b>preconcentration</b>	-30 °C	-20 °C
<b>initial temp</b>	46 °C	45 °C
<b>initial time</b>	15 min	10 min
<b>ramp rate</b>	5 °C/min to 170 °C	5 °C/min to 170 °C
<b>Isothermal hold</b>	0 min	0 min
<b>oven temp</b>	15 °C/min	15 °C/min
<b>final temp</b>	200 °C (6 min hold)	200°C (10 min hold)
<b>detector</b>	dual FID, 250°C	dual FID, 300°C

# Calibration standard curves of main VOCs

- VOCs concentrations trapped in passive tubes were quantified with a certified standard gas
  - PAMS 100 ppbv (Rigas, South Korea)
  - Dilution to 1, 3, 5, 10 ppbv



# Different estimates of precision for 23 VOCs measured by passive sampling

$$\text{RMS Precision} = \sqrt{\frac{1}{n} \sum_{i=1}^n D^2} * 100\%$$

$$\text{MAD Precision} = \sqrt{\frac{\pi}{2} \frac{1}{n} \sum_{i=1}^n |D_i|} * 100\%$$

Percentile Precision

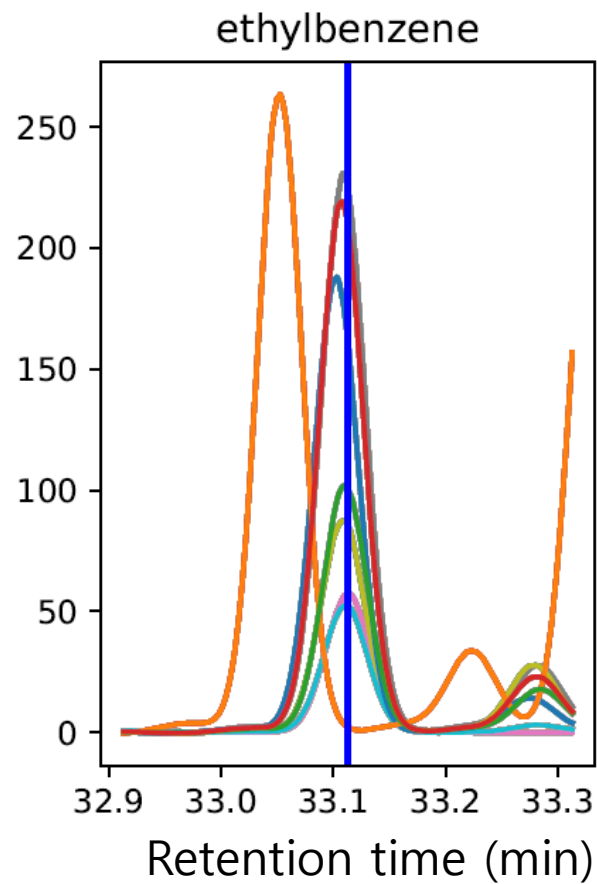
$$= \frac{1}{2} (P_{84}(D_i) - P_{16}(D_i)) * 100\%$$

$$D_1 = \frac{(C_{i1} - C_{i2})/\sqrt{2}}{C_1}$$

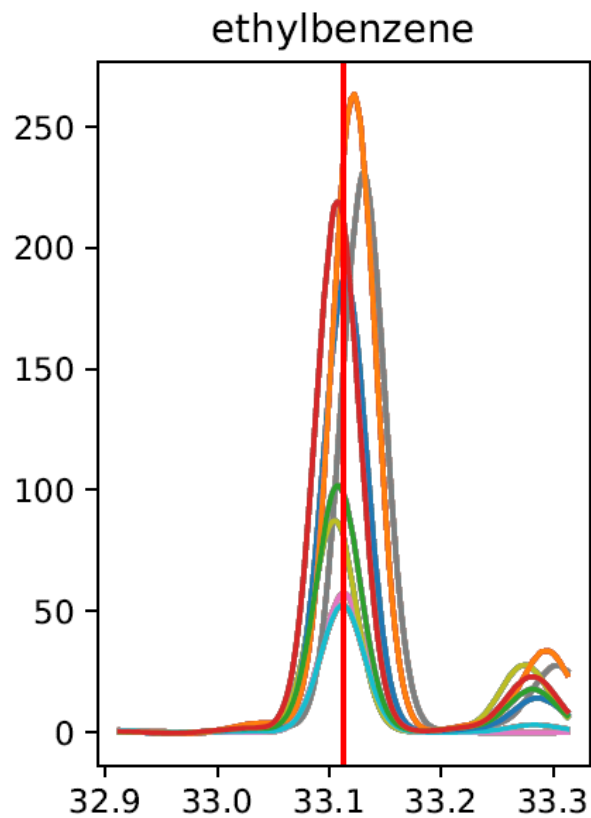
$$\text{Bias} = \frac{1}{n} \sum_{i=1}^n D_i * 100\%$$

Species	RMS Precision	MAD	Percentile Precision	Bias	p-value
Propylene	23.6	24.3	21.3	2.3	0.42
iso-Butane	8.3	6.4	4.6	-1.5	0.27
n-Butane	10.3	7.9	5.7	-0.5	0.68
1-Butene	26.8	26.7	21.5	-5.5	0.27
Cyclopentane	8.7	6.0	4.4	1.6	0.10
iso-Pentane	7.1	6.0	5.0	-0.7	0.41
n-Pentane	5.6	5.8	5.6	0.2	0.91
2-Methyl-pentane	6.9	7.1	4.5	4.6	0.17
Isoprene	16.8	19.3	15.3	7.5	0.48
n-Hexane	11.1	8.6	6.1	3.0	0.12
Methylcyclopentane	5.4	5.9	3.3	2.4	0.16
2,4-Dimethylpentane	5.2	5.4	3.1	1.3	0.31
Cyclohexane	11.5	11.7	11.4	-1.7	0.40
2-Methylhexane	10.9	9.4	7.1	-1.2	0.39
3-Methylhexane	33.1	28.4	21.9	-15.1	0.09
n-Heptane	4.7	4.8	2.0	3.4	0.11
Methylcyclohexane	5.7	5.5	5.5	1.7	0.44
o-Xylene	7.8	8.2	5.7	4.0	0.01
Toluene	11.2	8.3	5.7	-0.6	0.82
Ethylbenzene	10.4	10.6	10.1	5.4	0.00
p,m-Xylene	7.46	7.50	6.28	2.00	0
Styrene	25.86	24.47	22.97	-7.17	0
Benzene	13.5	11.5	8.3	-3.3	0.09

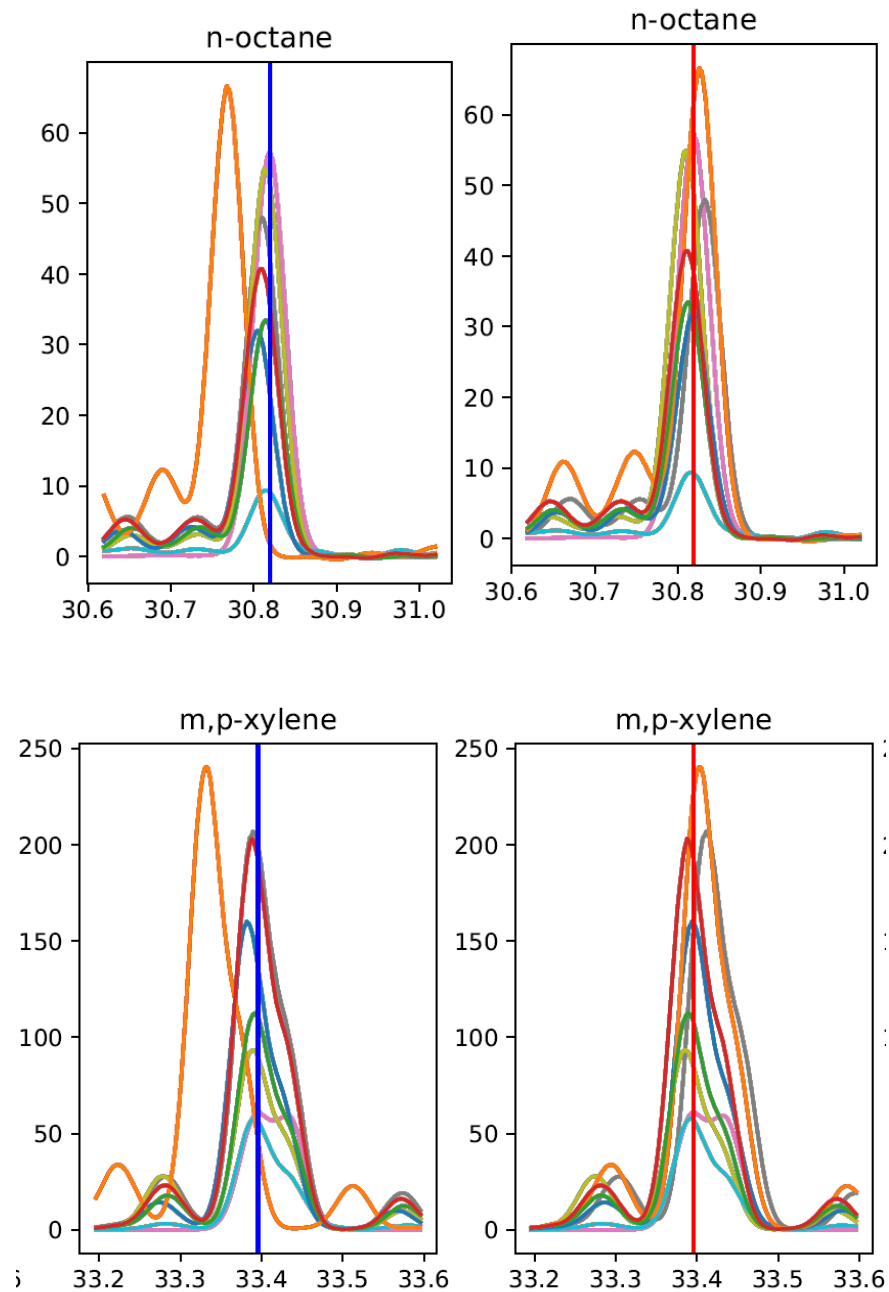
# Peak alignment of GC data



original



aligned



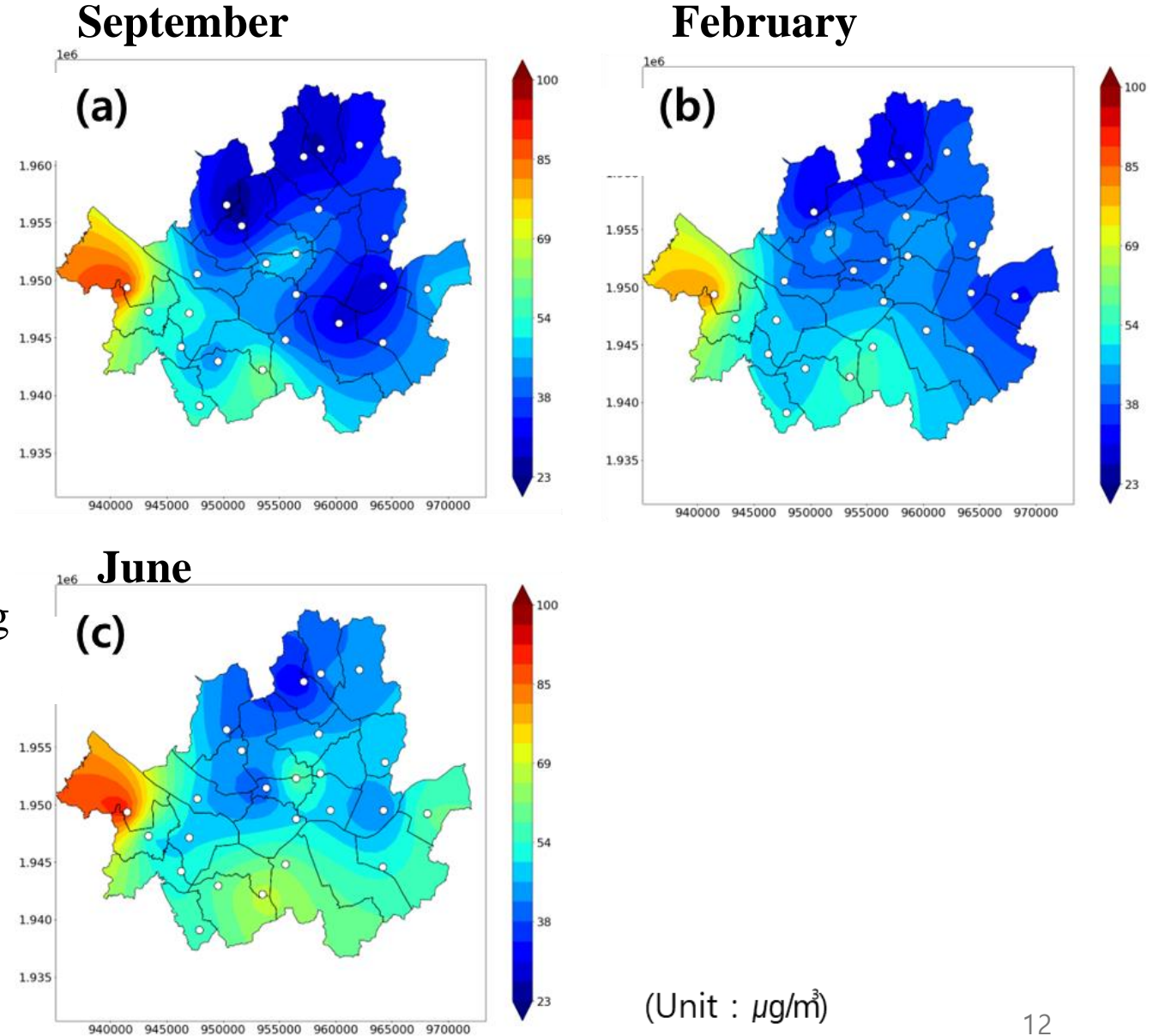
# Seasonal spatial distribution of TVOCs measured by PAS

- Consistent high concentrations in the southwestern region during all three observation periods

- heavy traffic, automobile paint shops

- close to the metropolitan landfill, and the airport

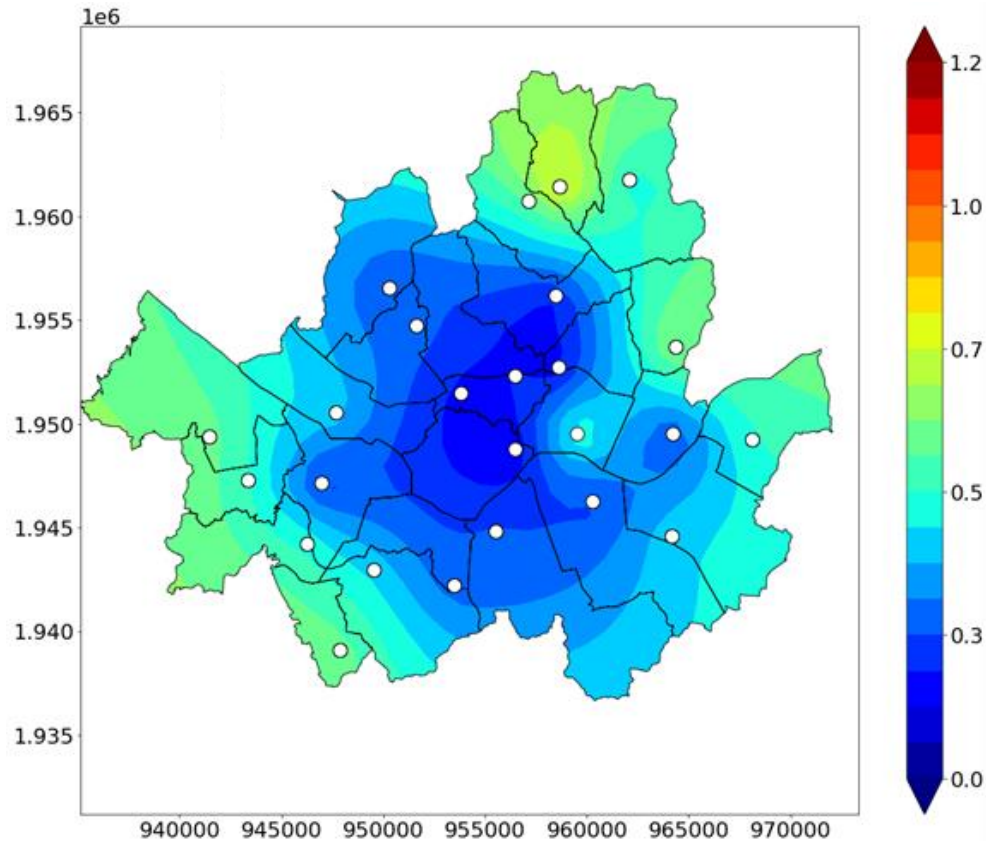
- Higher VOC concentrations in central Seoul during the summer, likely due to increased evaporation of organic solvents by printing business



(Unit :  $\mu\text{g}/\text{m}^3$ )

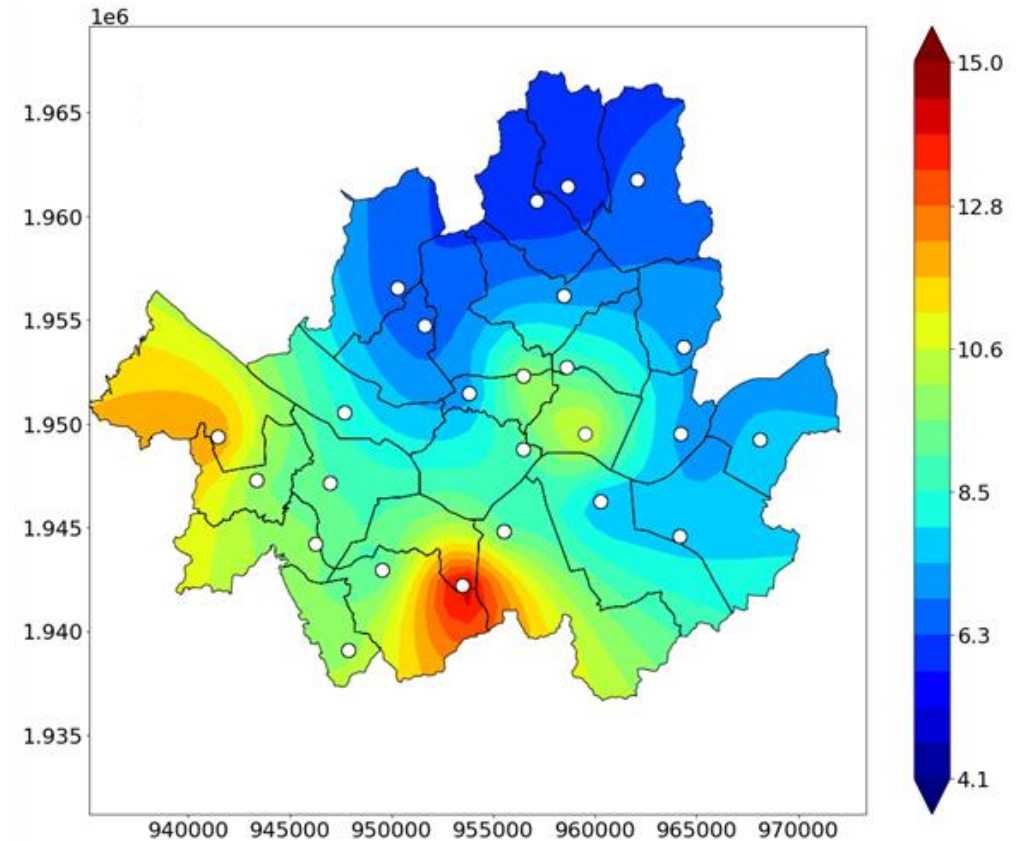
# Spatial distribution of Isoprene and Toluene measured by PAS

## Isoprene



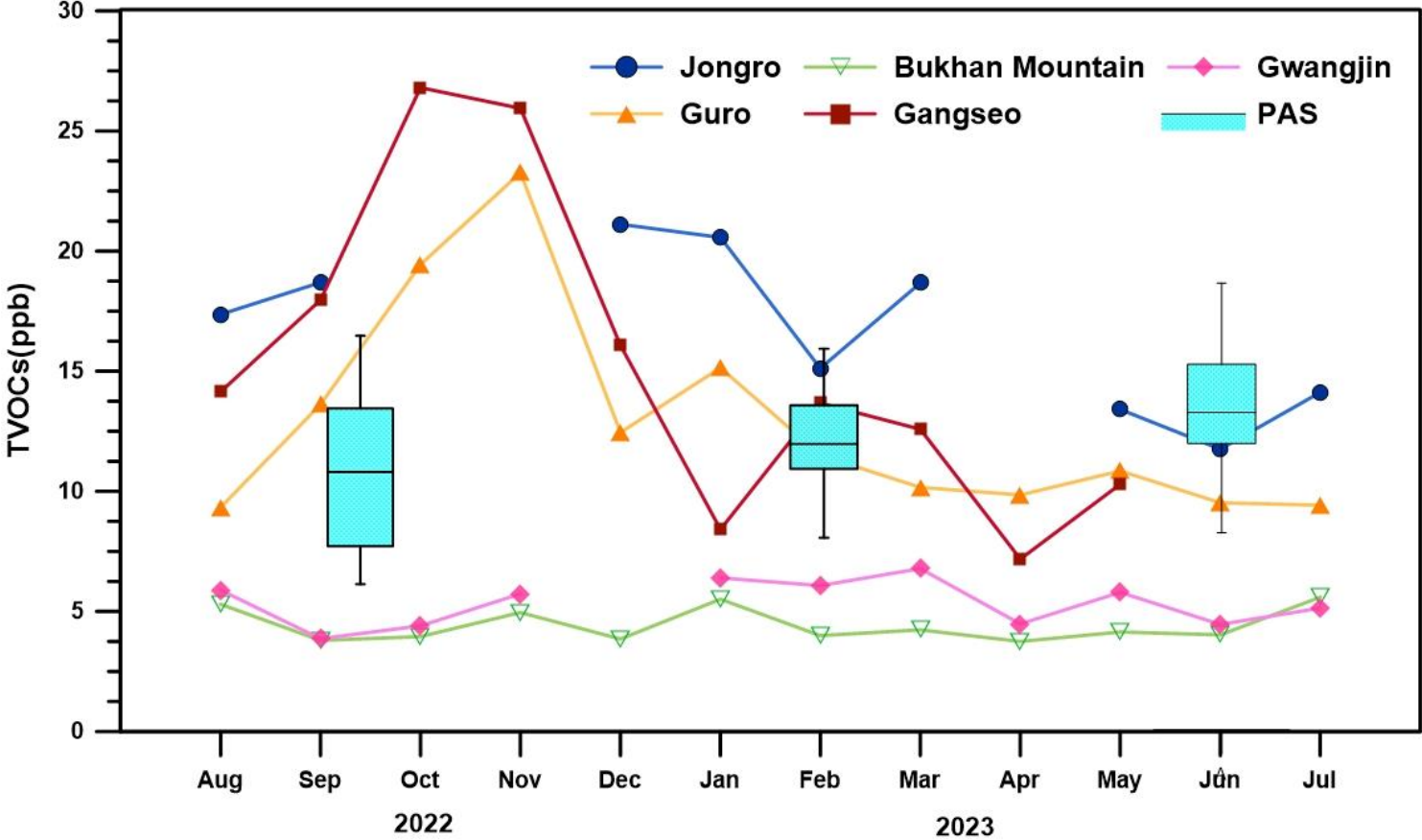
- Isoprene showed high concentrations in forested areas, particularly on the outskirts of Seoul

## Toluene



- Toluene, associated with vehicle emissions and solvent use, showed higher concentrations in central and southwestern Seoul

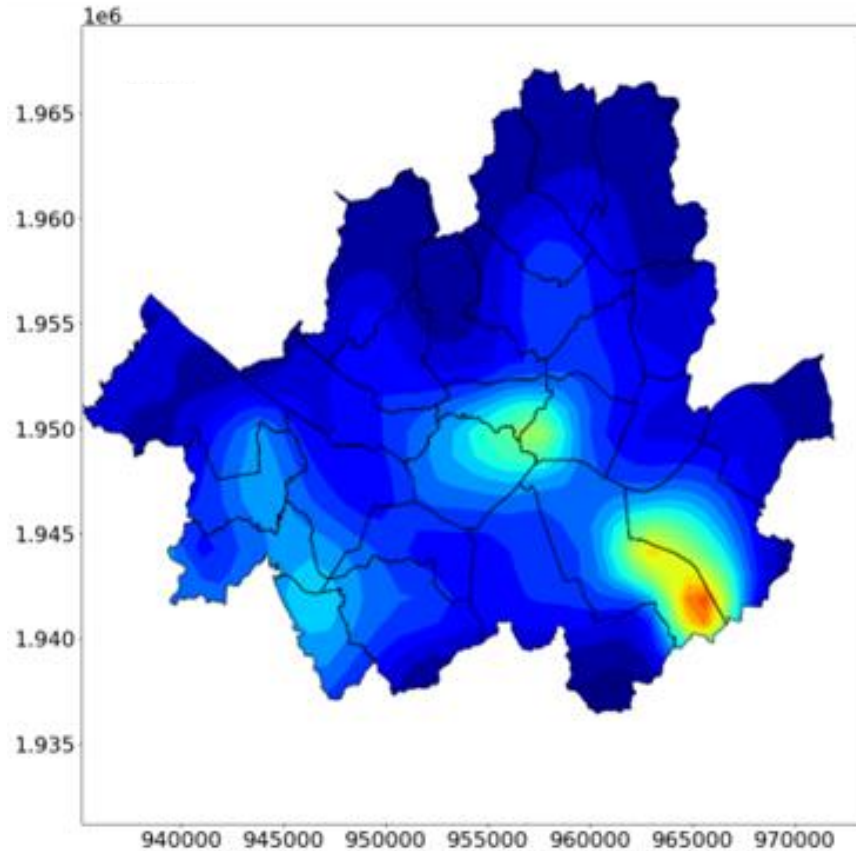
# Comparison of Active vs Passive sampling for VOCs



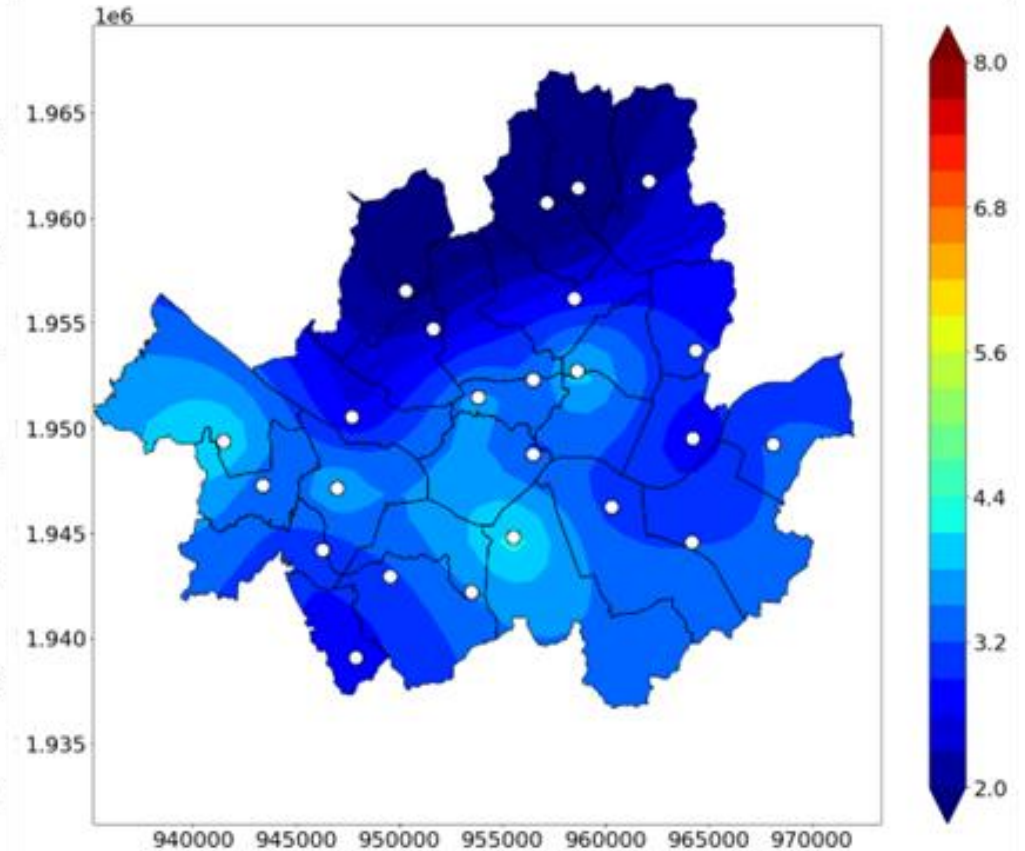
- In general, comparable concentration levels were observed when comparing measurements from active and passive air samplers (PAS)
- active measurements show elevated concentrations in September, while passive measurements show elevated concentrations in June.

# Spatial distributions of area sources

## CAPSS emission inventory



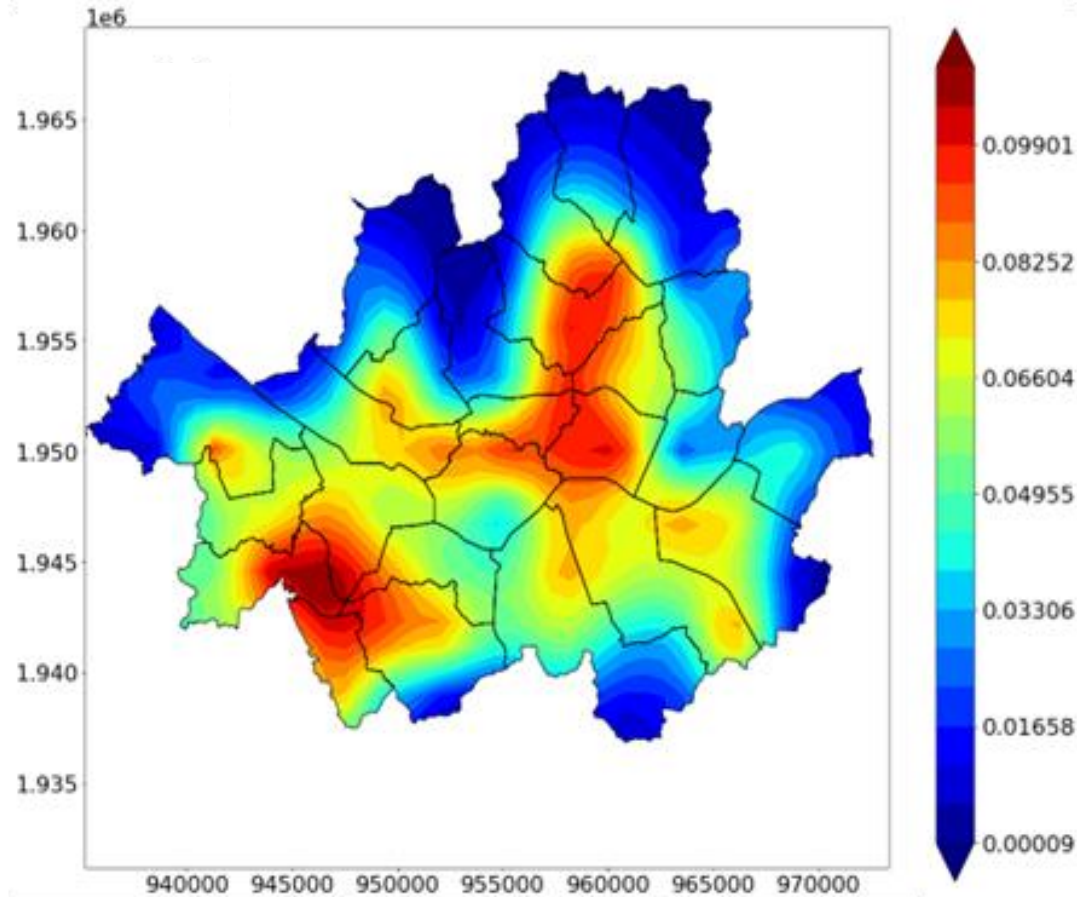
## PAS\_PMF



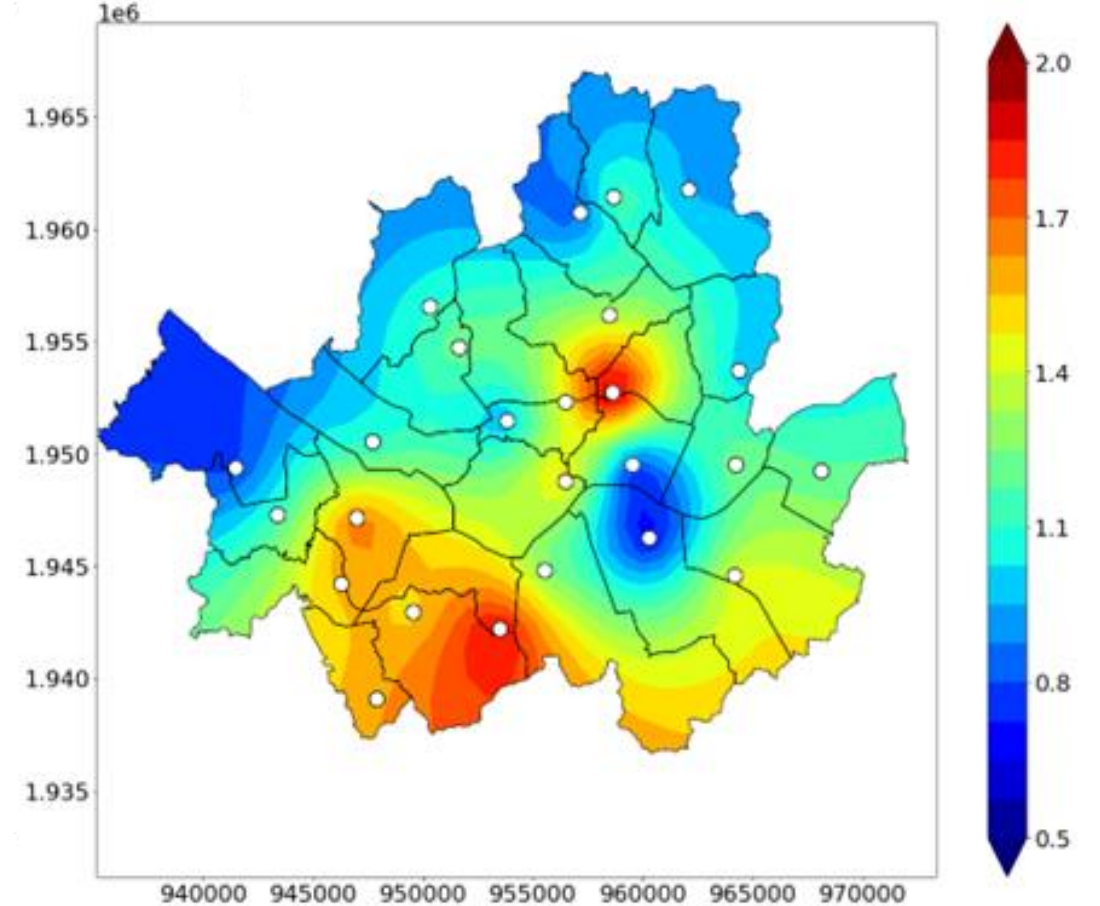
- PMF analysis-derived area sources showed high VOC concentrations in southern and southwestern Seoul, consistent with CAPSS data.
- High emission sources by CAPSS inventory in southeastern Seoul were not identified by PAS/PMF

# Spatial distributions of road sources

emission



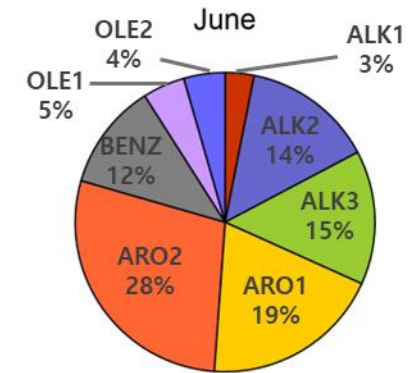
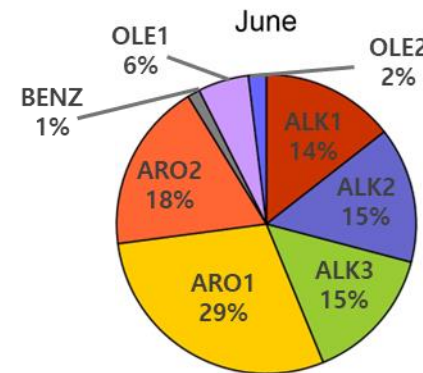
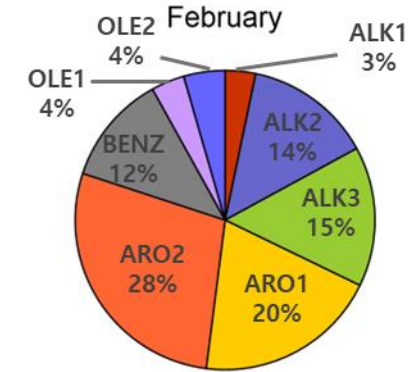
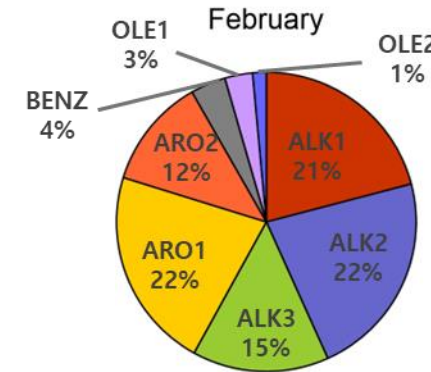
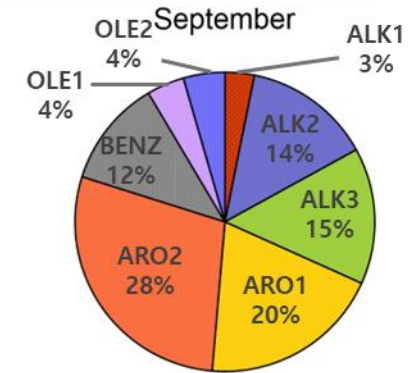
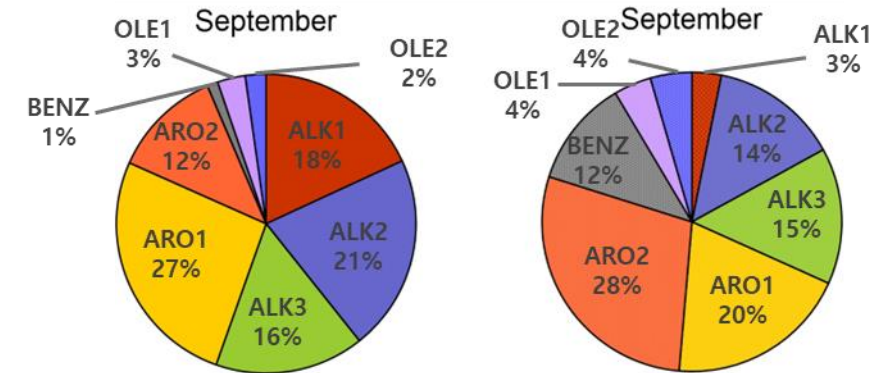
PAS\_PMF



- In case of the road VOCS source, the spatial distribution of road traffic emissions derived from the CAPSS emission inventory largely aligned with the PAS/PMF analysis data.

# VOCs compositions in Passive samples vs Emission inventory

- Agreement in compositions
  - Aromatics components are more than 50 % of TVOCs
  - Major compositions are ARO1, ALK2, ALK3
- Disagreement
  - In the most dominant species : as ARO1 in PAS, but ARO2 in CAPSS
  - benzene levels were 4% in the winter with PAS, while CAPSS consistently 12% year-round
  - Alk 1 is much higher in PAS measurement



obtained from PAS measurements

modeled by CAPSS.

# Simulated ambient concentrations using emission data

- Box model with continuity equation :  $(C - C_b) = \frac{\Delta x \cdot Q_a}{u \cdot z_i}$

Source

Change due to Horizontal advection

Change due to Mixing layer growth and vertical advection

$$\Delta x \cdot \Delta y \cdot z_i \frac{\partial C}{\partial t} = \Delta x \cdot \Delta y \cdot Q_a + u \cdot \Delta y \cdot z_i (C - C_b) + \Delta x \cdot \Delta y \frac{\partial z_i}{\partial t} (C_a - C)$$

- Gaussian plume model for area source :  $(C - C_b) = \left(\frac{2}{\pi}\right)^{1/2} \frac{\Delta x \cdot \bar{Q}_a}{u \cdot \sigma_z}$

$$(C - C_b) = \int_0^\infty \int_{-\infty}^\infty \left[ \frac{Q_a}{\pi \cdot u \cdot \sigma_y \cdot \sigma_z} \cdot e^{-\frac{y^2}{2\sigma_y^2}} \right] dy dx$$

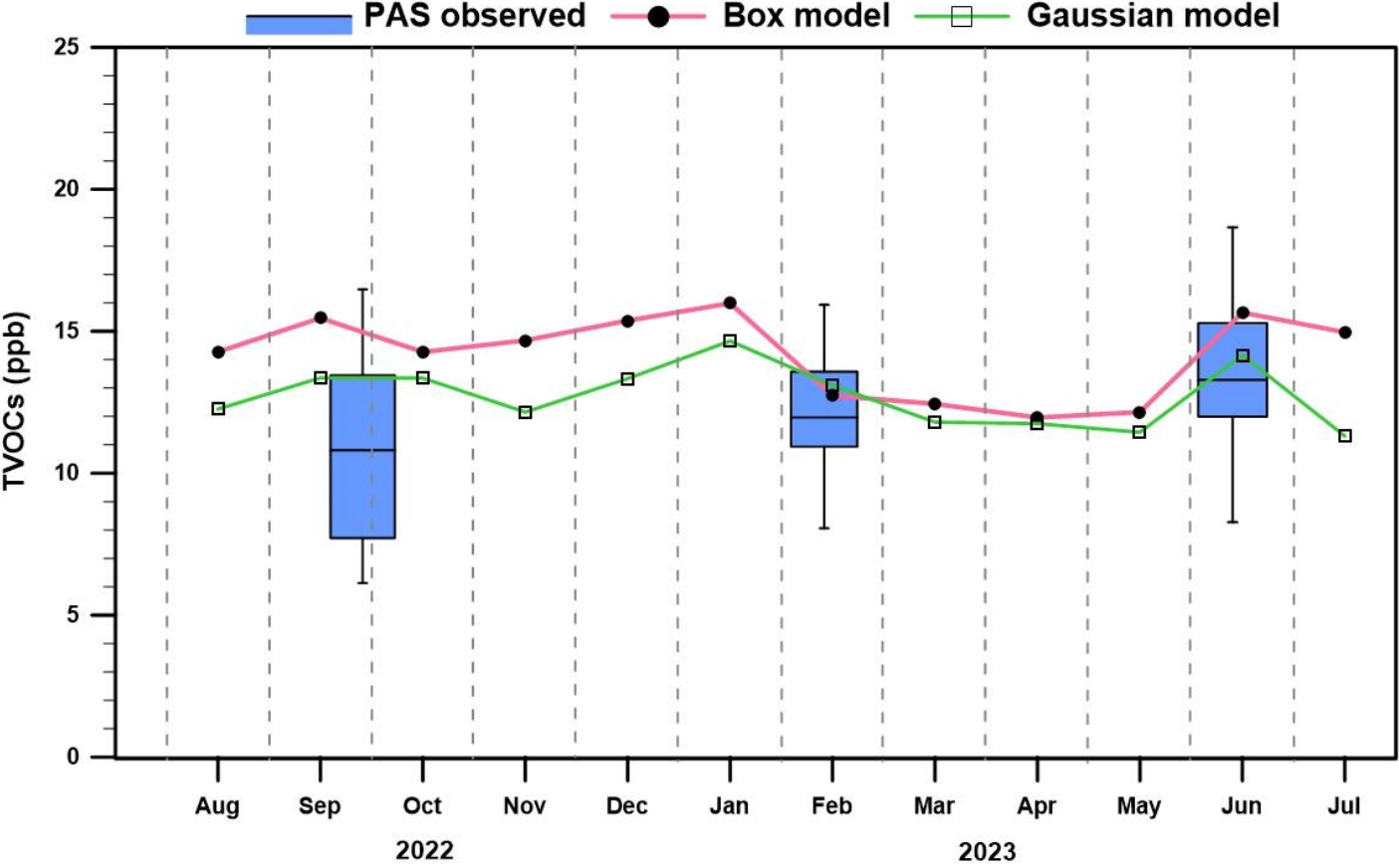
$$(C - C_b) = \int_0^\infty \left[ \left(\frac{2}{\pi}\right)^{1/2} \frac{Q_a}{u \cdot \sigma_z} \right] dx$$

Handbook on Atmospheric diffusion, Hana et al., 1982

	February	June	September
Emissions (moles/s)	41.06	45.07	43.82
*Wind speed (kph)	14.9	11.1	11.7
**PBL height(m)	1167	1319	1240
$\sigma_z$ (m)	900	1200	1200

\*Korea Meteorological Administration \*\*Choi et al. (1998)

# Comparison of calculated TVOCs concentrations by CAPSS emission inventory with the observed one by passive method



- TVOCs concentrations from PAS measurements ranged from 11 to 13 ppbv,
- model estimates based on CAPSS data ranged from 12 to 15 ppbv
- good consistency between PAS observations and modelled values
- potential underestimation by the CAPSS inventory especially in summer

## Conclusion

- Assessed VOCs in Seoul using Passive Air Sampling (PAS) and active sampling at five PAMS stations
- Spatial analysis using PAS showed high observations in the southwestern region of Seoul, which closely aligned with CAPSS emission data.
- The PMF model results using PAS data showed overall agreement with the CAPSS data, but discrepancies were found in southeastern Seoul.
- Underestimation by CAPSS inventory especially in summer.

# Lecture summary

- Various methods for analyzing and sampling VOCs  
:Gas Chromatography (GC), paired with FID or MS, PTR-MS, canister sampling, passive/active air sampler.
- PAS is cost-effective and allows for long-term monitoring but provides average concentrations without capturing short-term fluctuations.
- Required for GC analysis : Calibration , QA/QC procedure, Peak alignment