Chemical Characteristic of Submicron Particles in the West Sea of Korea Using Airborne Measurements: Focusing on 2019-2023

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INTRODUCTION

❖ Background

- KORUS-AQ concluded the necessity of using medium-sized aircraft for observations during high pollution seasons
- Airborne observations are required to understand the long-range transport of air pollutants and the impact of large pollution sources in the Seoul Metropolitan Area and surrounding regions.

❖ Objectives

- Real-time observation of major components of $PM_{1.0}$ and gases using airborne measurements
- Understanding the characteristics and inflow amount of long-range transported $PM_{1.0}$ and gases
- Identifying the spatial distribution of $PM_{1.0}$ and gases from foreign sources and local (domestic) emissions

❖ Specifics

- Analysis of high $PM_{1.0}$ episode in winter and spring
- Investigation of the spatial distribution of $PM_{1.0}$/precursor over the west and east sea and the Seoul metropolitan area during winter and spring
- Identification of greenhouse gases (such as CO_2, CH_4, CO) distribution according to regional characteristics such as background atmosphere, Seoul metropolitan area, and emission sources
- Identification of the distribution of air pollutants over large point sources in Chungcheong-do and other area
- ➢ Advantages of Airborne Measurements for Air Pollution
  - Equipped with high-performance instrument and based on outstanding mobility/accessibility, observation of air pollutants over a wide area

Method

❖ Aircraft (Beechcraft 1900D)

Figure 1. Aircraft (Beechcraft 1900D)

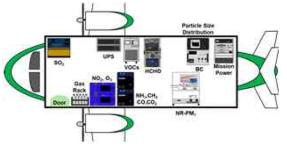

Figure 2. Layout of instruments in aircraft

❖ Configuration and Instruments

Table1. Configuration of instruments and observation species

Category	Instrument	Species
Gases	PTR-ToF-MS	Volatile Organic Carbons
	Off-axis ICOS NH_3	NH_3
	Off-axis ICOS	CO, CO_2, CH_4
	CAPS	NO_2
	Chemiluminescence	Ozone
	TILDAS HCHO	CH_2O
	CIMS	HNO_3, SO_2
Particles	HR-ToF-AMS	$NR\text{-}PM_1$ (O, N, S, Am)*,O:C, H:C etc
	UHSAS, PCAPS	Size distributions
	SP2	rBC
Meteorology and GPS	AIMMS-30 (Air data probe)	Meteorology (T, H, P, WS, WD)**, GPS (Lat, Lon, Alt)***

*O : Organics, N : nitrate, S : sulfate, Am : ammonium
**T : temperature, H : humidity, P : pressure, WS : wind speed, WD : wind direction
***Lat : latitude, Lon : longitude, Alt : altitude

Results

❖ Aircraft Flight path: 2019.11 – 2023.05

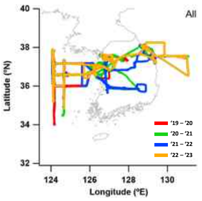

Figure 3. Flight path by year

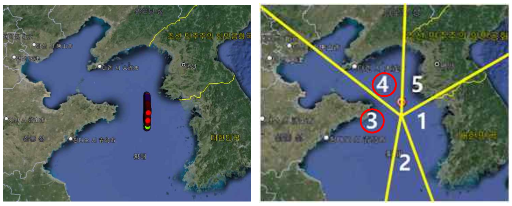

Figure 4. Selection of analysis data over the west sea (left), Classification of the sectors(right)

Table 2. Number of research flights

Target	Number of research flights			
	19-20	20-21	21-22	22-23
West sea	19	17	15	18
Large Point Sources	6	5	2	4
SMA	6	4	6	7
East sea	-	4	7	4
Total (times)	31	30	30	33
Total (hours)	102	100	100	100

Table 3. Number of research flights by classified sector

Sector	Location	Total Case #	19	20	21	22
1	South Korea	1	1			
2	Sea	1		1		
3	**China (include Qingdao)**	**21**	**7**	**4**	**5**	**5**
4	China (exclude Qingdao)	8	1	1		5
5	North Korea	5	2		2	1
	Total	36	11	6	7	11

❖ Pearson correlation coefficient

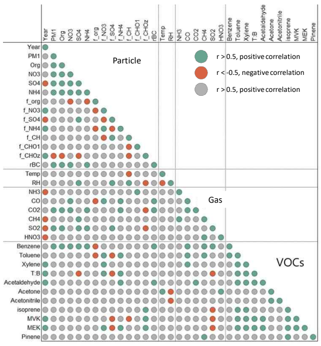

Figure 5. Pearson correlation coefficient

Table 4. Summary of significant correlation coefficient

Correlation	2019 → 2023	PM_1, Org	NO_3^- ($f\_NO_3^-$)	SO_4^{2-} ($f\_SO_4^{2-}$)
+	$f\_NO_3^-$, $f\_NH_4^+$, C_8, T/B, OVOCs	BC, CO_2, SO_2	BC, CO, CO_2 ($f\_NH_4^+$, CO, TOL, C_8)	RH, CH_4, SO_2, Benzene
-	SO_4^{2-}, $f\_SO_4^{2-}$, SO_2, NH_3	f_CHOz	($f\_SO_4^{2-}$, f_CH)	f_CHOz, T/B (Toluene)

- **PM_1, Org**
  - ➢ Impact of relatively nearby sources during long-range transport
- **NO_3^- ($f\_NO_3^-$)**
  - ➢ Correlation with the stable compounds ↑
  - ➢ More impact of secondary formation compared to direct emissions
  - ➢ Increasing lifetime = f_Org → f_NO_3
- **SO_4^{2-} ($f\_SO_4^{2-}$)**
  - ➢ Formation by aqueous phase reaction?
  - ➢ Impact of large point sources?

❖ $PM_{1.0}$ concentration

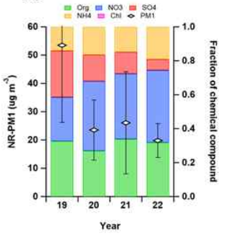

Figure 6. West sea $PM_{1.0}$ concentration (yearly changes)

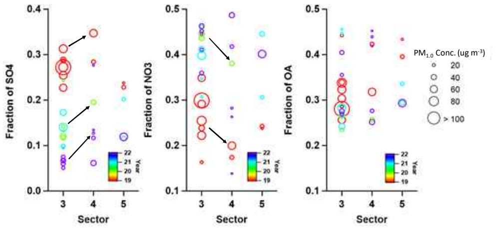

Figure 7. Chemical compositions of the $PM_{1.0}$ by sector

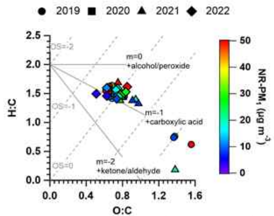

Figure 8. Organics oxidation states (Van Klaveren diagram)

- Decreasing trends of the $PM_{1.0}$
- $f\_SO_4^{2-}$ decrease
- $f\_NO_3^-$ ($f\_NH_4^+$) increase
- Not much difference the organics over 4 years

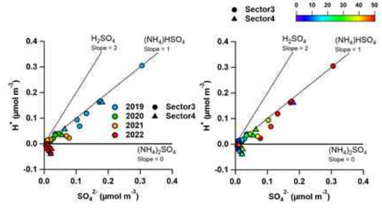

Figure 9. Type of SO_4^{2-} inflow

- $(NH_4)HSO_4$ types are existing : lack of NH_3
- ✓ Chen et al., 2022
  - ➢ NH_3 → contribution to SA formation
  - ➢ NH_3 decrease = PM concentration decrease
  - ➢ Reduction in nitrogen fertilizer usage → NH_3 emission decrease
  - ➢ Reduction in NH_3 emission due to fertilizer
  - ➢ Low fertilizer usage in winter = low NH_3 emission
  - ➢ Influx of unneutralized SO_4^{2-}

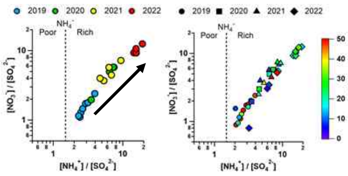

Figure 10. Ammonium nitrate plot

- Lack of NH_3 needed for SO_4^{2-} neutralization. But increasing of AN
  - ➢ When long-range transport occur, Heterogeneous < Homogeneous reaction
  - ➢ Impact simply due to China's emission characteristics

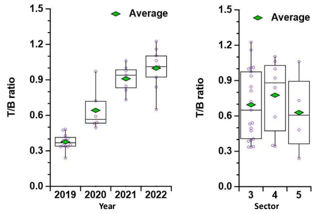

Figure 11. Toluene and Benzene ratio

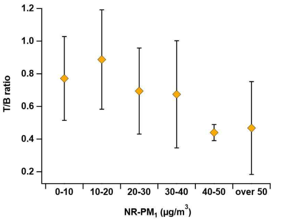

Figure 12. Toluene and Benzene ratio by $PM_{1.0}$ concentration

- Toluene / Benzene ratio increase
  - ➢ changes in emission patterns and impacts
- $PM_{1.0}$ high concentration case, there is a chance to originate from a far location
  - ➢ Lifetime = $Benzene_{(10\ days)}$ > $Toluene_{(2.5\ days)}$ (Sahu et al., 2020)

Summary

1. We conducted winter airborne measurement from November 2019 to May 2023 (124 times, 402 hours).
2. In winter, long-range transport $PM_{1.0}$ concentration keeps decreasing trend.
3. Trends of influx ration from other countries was an increase for NO_3^- and toluene/benzene ratio, and a decrease for SO_4^{2-}. It seems to be the effect of changes in emission characteristics due to China air pollution reduction policies.
4. The concentration of NO_3^- is high when influx from Sector3 and the concentration of SO_4^{2-} is high when influx from Sector4. Therefore, the case of long-range transport episodes, it is important to figure out the influx path or sector.
5. Reduction in NH_3 emission due to China NH_3 reduction policies, SO_4^{2-} is not neutralized and exist as a type of $(NH_4)HSO_4$. There is possibility of increased PM concentration due to additional reaction with NH_3 at inland.
6. Continual increase in toluene/benzene ratio observed every year. The higher the concentration in high concentration cases, the lower the toluene/benzene ratio. This is a result of the short lifetime of toluene, suggesting that originate from a farther location in high concentration cases.

Reference

- Chen, Youfan, et al. "High-resolution ammonia emissions from nitrogen fertilizer application in China during 2005–2020." Atmosphere 13.8 (2022): 1297.
- Sahu, L. K., Ravi Yadav, and Nidhi Tripathi. "Aromatic compounds in a semi-urban site of western India: seasonal variability and emission ratios." Atmospheric Research 246 (2020): 105114.

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