



Evaluation of correlated Pandora column NO₂ and in situ surface NO₂ measurements during GMAP campaign

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Abstract. To validate the Geostationary Environment Monitoring Spectrometer (GEMS), the GEMS Map of Air Pollution (GMAP) campaign was conducted during 2020–2021 by integrating Pandora Asia Network, aircraft, and in situ measurements. In the present study, GMAP-2020 measurements were applied to evaluate urban air quality and explore the synergy of Pandora column (PC) NO₂ measurements and surface in situ (SI) NO₂ measurements for Seosan, South Korea, where large point source (LPS) emissions are densely clustered. Due to the difficulty of interpreting the effects of LPS emissions on air quality downwind of Seosan using SI monitoring networks alone, we explored the combined analysis of both PC-NO₂ and SI-NO₂ measurements. Agglomerative hierarchical clustering using vertical meteorological variables combined with PC-NO₂ and SI-NO₂ yielded three distinct conditions: synoptic wind-dominant (SD), mixed (MD), and local wind-dominant (LD). These results suggest meteorology-dependent correlations between PC-NO₂ and SI-NO₂. Overall, yearly daytime mean (11:00–17:00 KST) PC-NO₂ and SI-NO₂ statistical data showed good linear correlations ($R \approx 0.73$); however, the differences in correlations were largely attributed to meteorological conditions. SD conditions characterized by higher wind speeds and advected marine boundary layer heights suppressed fluctuations in both PC-NO₂ and SI-NO₂, driving a uniform vertical NO₂ structure with higher correlations, whereas under LD conditions, LPS plumes were decoupled from the surface or were transported from nearby cities, weakening correlations through anomalous vertical NO₂ gradients. The discrepancies suggest that using either PC-NO₂ or SI-NO₂ observations alone involves a higher possibility of uncertainty under LD conditions or prevailing transport processes. However, under MD conditions, both pollution ventilation due to high surface wind speeds and daytime photochemical NO₂ loss contributed to stronger correlations through a decline in both PC-NO₂ and SI-NO₂ towards noon. Thus, Pandora Asia Network observations collected over 13 Asian countries since 2021 can be utilized for detailed investigation of the vertical complexity of air quality, and the conclusions can be also applied when performing GEMS observation interpretation in combination with SI measurements.

1 Introduction

Rapid developments in environmental remote sensing have led to a new era of air quality observations, and recent hyperspectral data retrieval technologies have allowed for routine and accurate monitoring of air pollutants at high spatial and temporal resolution. In particular, the Geostationary Environment Monitoring Spectrometer (GEMS), which was launched on 18 February 2020, measures the total and tropospheric air pollutant columns hourly at spatial resolutions of 7 km × 8 km for gas and 3.5 km × 8 km for aerosols (Kim et al., 2020), facilitating the tracking of pollution transport from local to synoptic scales.

Recent studies have revealed the potential of satellite observations to evaluate surface air quality, particularly in regions with sparse air quality-monitoring networks. The main approach is to convert column density to surface concentrations using a shape factor of the ratio of the partial column (Ω_{z_0}) within the lowest layer (z_0) to the total column (Ω_{total}) (Zhao et al., 2019), as follows:

$$S = \frac{\Omega_{z_0}}{\Omega_{\text{total}}} \times \frac{C}{\Delta z_0}, \quad (1)$$

where S , C , and Δz_0 are the surface concentration, column density, and lowest layer thickness, respectively. Acquiring accurate profile shape information is critical for determining the relationship between the column amount and surface concentration because the shape factor is spatiotemporally variable. Considering this, numerous studies have obtained close relationships using chemical transport model simulations, aircraft in situ measurements, and satellite observations with high correlation coefficients (R) of 0.7 or more, and used them to scale up surface NO₂ to column NO₂ (Wang and Christopher, 2003; Boersma et al., 2009; Lamsal et al., 2010). This strong correlation can be explained by the generally uniform planetary boundary layer height (PBLH), and by aerosol type and abundance, which is also the case for trace gases.

By contrast, the implications of weak correlations between column and surface measurements remain unclear. Engel-Cox et al. (2004) found a negative correlation of aerosol optical depth (AOD) and surface PM_{2.5} in northwestern USA, and explained it based on elevated haze decoupled from the surface. Thompson et al. (2019) examined weak correlations between Pandora column (PC) measurements and surface in situ (SI) observations of NO₂ over the Yellow Sea during the Korea–US air quality (KORUS-AQ) field study, and suggested, as a possible reason, the transported non-uniform plumes originated in China and Seoul hundreds of meters above the ground from the surface layer. The estimated surface PM_{2.5} concentration was weakly correlated ($R = 0.4\text{--}0.49$) with observed PM_{2.5} concentrations in Seoul because only PBLH was added to the multi-linear regression model to correlate AOD to surface PM_{2.5} (Kim et al., 2021). This effect may be related to the significant impact of long-range

transport on PM_{2.5}, with a contribution of up to 39 % in Seoul (Lee et al., 2021). Thus, the wide variability in the degree of correlation between PC–PM and SI–PM is closely related to vertical profile variability (Flynn et al., 2016).

It appears highly probable that several factors are responsible for the correlations between PC–NO₂ and SI–NO₂; therefore, it is necessary to improve our understanding of the degree of correlation through detailed measurements, including column concentration. In this study, we focused on the impact of meteorology and chemistry on correlation variability using PC, SI and aircraft measurements, and meteorological observations. Understanding vertical profile variability is also useful for evaluating the effects of various emissions on urban air quality, particularly in areas neighboring active large point source (LPS) emissions sites. Quantifying the impact of LPS emissions on downwind cities remains challenging due to the lack of three-dimensional (3D) measurements. Accurate vertical profile data are also useful for improving remote sensing retrieval algorithms because the profile shape contributes to the conversion of slant column density into vertical column density as part of the air mass factor.

In mid-2019, the Pandonia Global Network (PGN; <https://pandonia-global-network.org>, last access: 22 August 2022) was launched, with support from the National Aeronautics and Space Administration (NASA) and European Space Agency (ESA), to facilitate the validation and verification of low-orbit or geostationary environmental satellites. This network is attempting to expand air quality monitoring through integration with existing long-term air quality monitoring stations. Since 2020, the National Institute of Environmental Research, Economic and Social Commission for Asia and the Pacific, and Korea Environment Corporation have been extending the Pandora Asia Network to include 13 Asian countries, with support from the Korea International Cooperation Agency. The Pandora Asia Network is expected to be widely used to study urban air quality in Asia, which is increasingly deteriorating due to rapid economic growth.

As part of the GEMS Map of Air Pollution (GMAP) campaign, a suite of Pandora instruments was deployed in Seosan, a South Korean coastal city, from November 2020 to January 2021 (GMAP-2020), and we applied GMAP-2020 measurements to explore the synergy of PC observations when evaluating air quality over Seosan. Further results from this research project are also reported in this special issue, including GEMS validation and urban air quality evaluations based on Pandora, aircraft, surface flux, and in situ surface chemical measurements conducted during GMAP-2020.

2 GMAP-2020 campaign

GEMS was launched on 19 February 2020; it is the first instrument to observe air quality from a geostationary Earth orbit. GEMS provides hourly air quality data on aerosols and gases at a spatial resolution of 7 km × 8 km. It is a scanning

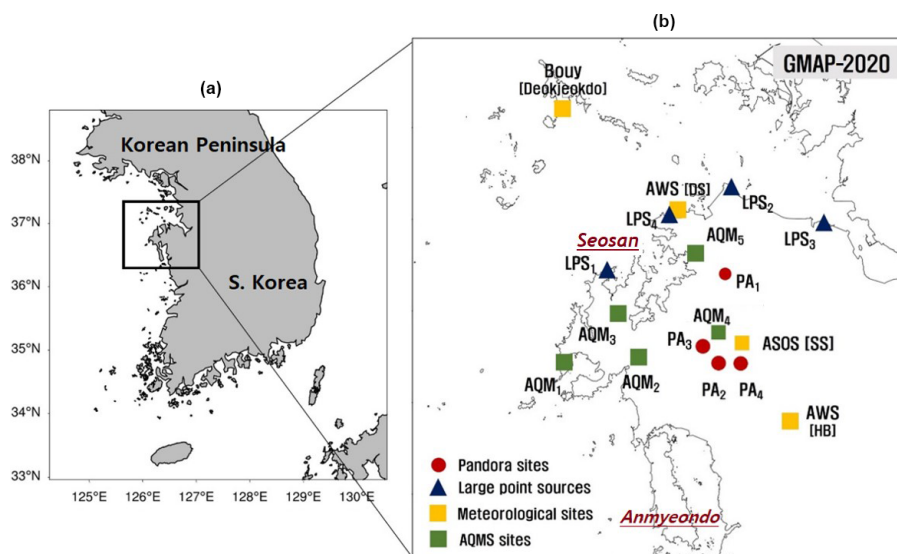


Figure 1. Map of sites used for Geostationary Environment Monitoring Spectrometer (GEMS) Map of Air Pollution (GMAP) campaigns conducted in (a) Seosan, South Korea in November 2020 to January 2021 (GMAP-2020), and (b) the Seoul metropolitan area from October 2021 to November 2021 (GMAP-2021). (a) Measurement sites around Seosan, the study area for the GMAP-2020 campaign. Red circles indicate Pandora column measurement sites including (b) Seosan Daehoji (PA₁), Seosan Dongmun (PA₂), Seosan city council (PA₃), and Seosan super site (PA₄). Blue triangles indicate large point sources (LPSs) including the Taean and Dangjin thermal power stations (LPS₁ and LPS₂, respectively), Hyundai steelworks (LPS₃), and Daesan petrochemical complex (LPS₄). Yellow squares indicate Automated Synoptic Observing System meteorological sites in Seosan (Met₁), AWS (Met₂), and buoy (Met₃). Green squares indicate air quality monitoring (AQM) network stations including Padori (AQM₁), Leewon (AQM₂), Taean (AQM₃), Daesan (AQM₄), Seongyeon (AQM₅), and Dongmoon (AQM₆). In the right panel, the black line indicates the route used for car-based differential optical absorption spectroscopy (CarDOAS) measurements and the blue dotted line indicates the horizontal domain of Geostationary Coastal and Air Pollution Events (GEOCAPE) airborne simulator (GCAS) measurements taken during the GMAP-2021 campaign.

ultraviolet (UV)–visible spectrometer that observes key atmospheric constituents including O₃, NO₂, CO, SO₂, CH₂O, CHOCHO, aerosols, clouds, and UV indices. This mission heralded a new era of satellite air quality monitoring and will be joined by NASA’s Tropospheric Emissions: Monitoring of Pollution (TEMPO) and ESA’s Sentinel-4 to form the GEO Air Quality Constellation in ~ 3 years, to cover the most polluted region in the Northern Hemisphere.

During GMAP-2020, Pandora instruments (PA₁–PA₄) were deployed near large point sources (LPS₁–LPS₄) in Seosan; in situ surface air quality monitoring systems (AQM₁–AQM₆) and meteorological observations (Met₁–Met₃) were also used in this study (see their locations in Fig. 1). Aircraft measurements were also used to validate GEMS and diagnose LPSs located in industrial areas surrounding Seosan. We explored the synergy of Pandora observations and SI measurements, based on measurements collected during GMAP-2020, by evaluating air quality in industrial Seosan (where LPSs are densely clustered). We particularly investigated the impacts of vertical profile and sub-pixel variability for trace gases and aerosols, for further GEMS validation. All measurement sites for both GMAP-2020 campaigns are indicated in Fig. 1.

3 Methods

3.1 Study area

Seosan, the target area of the GMAP-2020 campaign, is a small city with a population of 174 780 in 2017; it is accessed via three expressways to the east and four national highways cross the city. It is located in midwestern South Korea, and is affected by > 300 emissions point sources including LPSs. Coal-fired power plants including Taean, Dangjin, the Hyundai Dangjin steelworks, and the Daesan petrochemistry industrial complex (LPS₁–LPS₄, respectively, in Fig. 1) have the highest emissions rates in South Korea. The Hyundai Dangjin steelworks (LPS₃) and Taean and Dangjin power plants (LPS₁ and LPS₂) emit 10.5, 11, and 8.8 Gg of NO_x per year, respectively. Although Seosan accounts for only 1.8 % of the population of Seoul, its NO_x emissions (10.2 Gg yr^{−1}) account for 13.2 % of its total NO_x emissions. The transportation sector of Seosan is a far greater NO_x source than the industrial sector of Seoul (ratio of 99 : 1); however, within Seosan, the industrial sector is on par with the transport sector (52 : 48; <https://www.air.go.kr/en-main.do>, last access: 22 August 2022).

During the past decade, the annual mean NO₂ level in Seosan has been 17 ppb, which is approximately half of that

in Seoul (31.2 ppb). NO₂ exhibits strong seasonal variation, reaching a minimum in summer and maximum in winter, due to meteorological factors and greater energy use during winter (Kim and Kim, 2020). Therefore, the timing of the GMAP-2020 campaign was well suited to tracking pollution.

3.2 Pandora measurements

Pandora measures the UV and visible wavelengths (280–525 nm) of direct sunlight with a spectral resolution of 0.6 nm, to determine the vertical column density of NO₂, O₃, and HCHO (Herman et al., 2009). For measurements in Dobson units (DU; 1 DU = 26.9 Pmol cm⁻²), column NO₂ has a very high signal-to-noise ratio (700 : 1) and very high precision (0.01 DU) for clear skies (Herman et al., 2009). The vertical column density of NO₂ can be determined using DOAS software (Van Roozendaal and Fayt, 2001). Pandora direct-sun measurements are advantageous in that the air mass factor is simplified, and therefore is dependent only on the geography for a known solar zenith angle.

From retrieved Pandora measurements, tropospheric and total (= tropospheric + stratospheric) vertical column densities are both available. However, it should be noted that appreciable uncertainties cannot be neglected in the tropospheric NO₂ profiles obtained from Pandora instruments, particularly for the high aerosol-loading areas such as East Asia. In this background, we used total vertical column densities in the present study, and also confirmed that they have a high correlation with the tropospheric column densities observed in our study period, with little change in stratospheric column density in space and time at the local scale.

Four Pandora instruments were installed at sites to the south of LPSs (Fig. 1) during the GMAP-2020 campaign, i.e., at Seosan Daehoji, Seosan Dongmun, Seosan city council, and Seosan super site (PA₁–PA₄ in Fig. 1). The presence of clouds reduces vertical column density precision by decreasing the number of photons arriving at Pandora instruments within a fixed integration time. Therefore, the retrieved Pandora measurements were cloud-screened using an observed cloud cover of 0.6. Cloud cover was provided by the Korea Meteorological Administration (KMA), and the precision improvement afforded by cloud screening was verified by comparing each Pandora-derived vertical column density with the median vertical column density, with and without cloud screening within the inter-comparison period.

At PA₄, the operating period was extended to cover almost the entire year (12 November 2020–30 October 2021) including the GMAP-2020 campaign period, and the Pandora spectra were processed into vertical column density data for trace gases using the standard NO₂ algorithm in BlickP software provided by PGN (Cede, 2019). The resultant PC-NO₂ data were obtained from the PGN website (<https://pandonia-global-network.org>, last access: 22 August 2022) for the 1-year period from 12 November 2020 to 30 Octo-

ber 2021, and were also used as PC-NO₂ statistics for PA₄, in this study.

3.3 Surface and airborne chemical measurements

Hourly average data for SI-NO₂ over a period of 1 year were obtained from Ministry of Environment AQM network stations in Seosan: Pandori, Leewon, Taean, Dongmoon, Seongyeon, and Daesan (AQM₁–AQM₆, respectively, in Fig. 1). The Seosan super site (PA₄/AQM₁) provided hourly data for NO and NO_y via an NO-DIF-NO_y analyzer (42i-Y; Thermo Scientific, Waltham, MA, USA), and for PM_{2.5} chemical species using an ambient ion monitor (AIM; URG 9000D, URG Corp., Chapel Hill, NC, USA). Weekly zero and span checks were conducted for NO_y calibration to ensure that differences between checks remained < 3%. Water-soluble ions in aerosol and gaseous species were measured hourly using an AIM, and ion mass balance was used to ensure data quality under the quality control procedures of the AQM network installation and operation guidelines (NIER, 2021).

Aircraft measurements were conducted during the GMAP-2020 campaign period, and nine flights were conducted on 8 d (26, 27, and 28 November and 1, 6, 8, 9, and 12 December 2020). The horizontal and vertical distributions of NO₂ and O₃ over Seosan were measured during GMAP-2020 using an NO₂ monitor (T500U; Teledyne, Thousand Oaks, CA, USA) and an O₃ analyzer (TEI49C; Thermo Scientific) onboard the Cessna Grand Caravan 208 B. These instruments had response times of < 40 and < 20 s, and detection limits of 40 ppt and 1 ppb, respectively. The flight paths included a raster mode over all of Seosan at a height of 500–700 m and a profiling mode from 500 m to 1.5 km over PA₁ and PA₄ (Fig. 2).

3.4 Meteorological measurements

Ground-based hourly observation data for meteorological variables were obtained from Seosan Automated Synoptic Observing System (ASOS) stations maintained by the KMA, and wind and temperature profile data were obtained twice daily (00:00 and 12:00 UTC) via a rawinsonde instrument at the Osan World Meteorological Organization upper air measurement station (47122) near Seosan. Due to time constraints of the sonde measurements, information on PBLH variation was obtained from Unified Model (UM) simulation results provided on the KMA website (<https://afso.kma.go.kr>, last access: 22 August 2022).

During the GMAP-2020 campaign, a 3D sonic anemometer (CPEC200; Campbell Scientific, Logan, UT, USA) was also installed on the rooftop at PA₄ for turbulent flux measurements at the city–atmosphere interface (Hong et al., 2019). All wind components and sonic temperatures were measured at a 10 Hz sampling rate, and ground-level sensitive heat flux was measured directly using a 30 min averag-

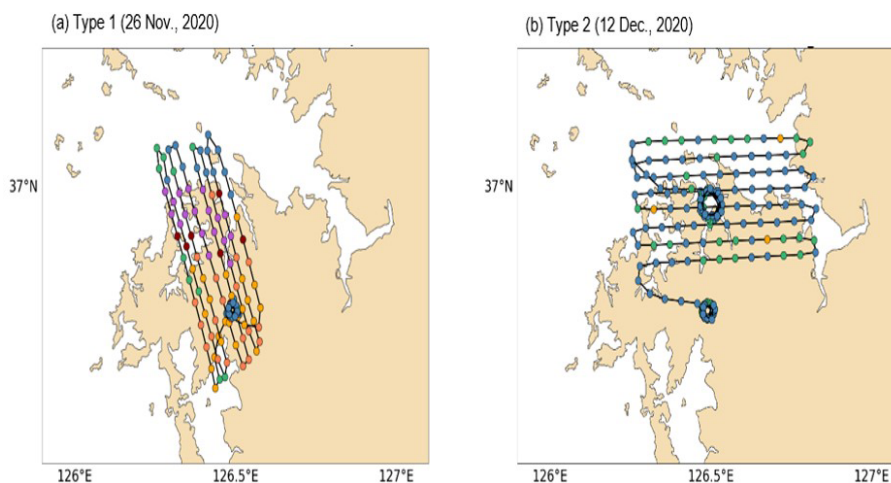


Figure 2. Flight tracks for two Cessna Grand Caravan 208 B aircraft over Pandora sites (a) PA₄ and (b) PA₁ during the GMAP-2020 campaign. Colored circles indicate airborne NO₂ concentration observations. Stacked circles indicate spiral flights conducted over two sites.

ing period. Quality controls such as double rotation, spike removal, and outlier filtering were also applied.

3.5 Correlation analyses

We examined the synergy of PC and SI data obtained during the GMAP-2020 campaign, and combined these measurement data to evaluate air quality in Seosan, South Korea. We attempted to interpret the meteorological and photochemistry data measured during GMAP-2020, and to demonstrate that caution is required when attempting to study the vertical structure of air pollutants using either surface observations or satellite data only, particularly in industrial areas.

First, we examined the combined use of year-long PC-NO₂ and SI-NO₂ measurements, and investigated the factors modulating their correlation. Numerous studies have examined the correlations between chemical species, including aerosols (Thomson et al., 2019; Wang et al., 2019; Kim et al., 2012, 2018; Jo and Kim, 2013; Sanchez et al., 1990). Wang et al. (2019) reported that aerosols moderately correlate with NO₂ due to the frequent occurrence of lifted layers probably related to the transport of pollutants. Jo and Kim (2013) differentiated haze types using the trajectory speed and direction and different synoptic conditions. In this background, we hypothesized that their differences in PC-NO₂ and SI-NO₂ were due to meteorological conditions, and performed *k*-means and agglomerative hierarchical cluster analyses of various meteorological variables. Clustering is the grouping of objects that are alike and are different from the objects belonging to other clusters. As a first step, *k*-means clustering was applied to find smaller clusters until each object was classified in one cluster. Subsequently, agglomerative hierarchical steps are applied to make up for the shortcomings of *k*-means clustering, in which once merging (or splitting) is done, it can never be undone. More

details are found in Venkat Reddy et al. (2017). We used XLSTAT software (Addinsoft, Paris, France) for the cluster analysis with eight meteorological variables representing local and synoptic circulations in the cluster analysis: surface wind speed (Wsfc), 925 hPa temperature (T925), sea level pressure (Psfc), pressure tendency (dPsfc/dt), 850 hPa wind speed (W850) and its north–south and east–west components (NS850 and EW850), and 500 hPa geopotential height (GPH500). We subtracted 30 d moving averages from all data to account for typical seasonal variation. Monthly averages were used for PC-NO₂ analysis due to the limited availability of hourly data.

Correlations between PC-NO₂ and SI-NO₂ were analyzed in each meteorological group and the impact of photochemistry was interpreted based on case-specific features. We also investigated correlations in association with near-surface micrometeorological variables such as PBLH in each meteorological group.

4 Results and discussion

4.1 Correlation analysis results for PC-NO₂ and SI-NO₂

The yearly PC-NO₂ statistics at four Pandora sites (PA₁–PA₄) are summarized in Table 1. The total averaged PC-NO₂ over all sites was 0.45 DU during GMAP-2020, which is well above the typical values (0.1–0.2 DU) for Anmyeondo (the location is shown in Fig. 1), a representative background site (Herman et al., 2018). Although site PA₃ is located in a rural area, it nevertheless exhibited the highest PC-NO₂ amounts, suggesting that plumes were frequently transported from nearby point sources and/or urban areas.

Scatter diagrams of hourly PC-NO₂ and SI-NO₂ measurements from Pandora sites PA₁–PA₃ (GMAP-2020) and PA₄ (yearly measurement; 12 November 2020–30 October 2021)

Table 1. Summary of NO₂ column data from four Pandora (PA) measurement sites.

Site	Site name	Site location		Mean (DU)	SD (DU)	Minimum (DU)	Maximum (DU)	Number of data points	Operating period (days)
		Longitude (° E)	Latitude (DU) (° N)						
PA ₁	Seosan-DHJ	126.502	36.900	0.50	0.22	0.20	1.60	838 (11)	GMAP-2020 campaign
PA ₂	Seosan-DM	126.458	36.778	0.43	0.19	0.18	1.62	1241 (13)	GMAP-2020 campaign
PA ₃	Seosan-CC	126.449	36.785	0.40	0.14	0.18	0.97	1242 (13)	GMAP-2020 campaign
PA ₄	Seosan-SS	127.492	36.777	0.39	0.16	0.17	1.79	8753 (141)*	1 year (12 Nov 2020–30 Oct 2021)

* The Pandonia Global Network (PGN) retrieval algorithm was applied to yearly measurements.

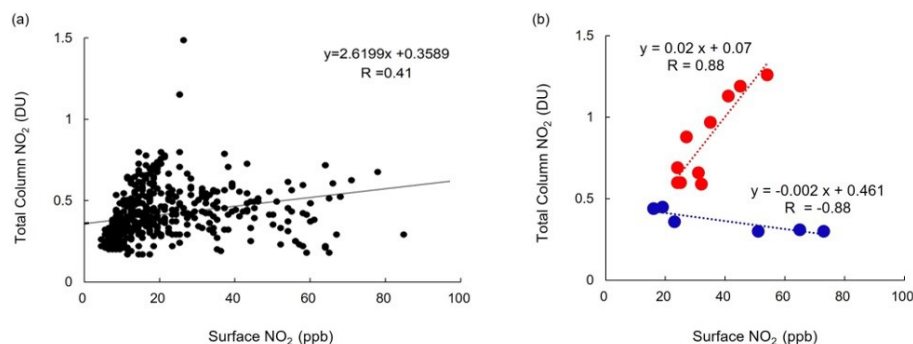


Figure 3. (a) Pandora column (PC) NO₂ measurements as a function of surface in situ (SI) NO₂ observations at Pandora sites PA₁–PA₃ during the GMAP-2020 campaign and PA₄ during a 1-year period. A 1 : 1 linear regression model was used to evaluate the relationship between PC and SI measurements (black line). (b) Sample scatterplots of PC-NO₂ and SI-NO₂ for 24 February (red) and 21 April 2021 (blue).

are shown in Fig. 3a. These hourly data had a fair 1 : 1 linear relationship ($R = 0.41$), implying the overall uniformity of NO₂ profiles, whereas the linear relationship with PC-NO₂ weakened as SI-NO₂ levels increased (Fig. 3a). It appears that the SI-NO₂ has a distinct diurnal change despite the same PC-NO₂, and higher variable surface NO₂ levels may result from the relatively weaker linear relationship between PC-NO₂ and SI-NO₂. To explore these anti-correlation cases further, we selected the lower and upper bounds of the tendencies; these are plotted in Fig. 3b, which shows that PC-NO₂ was positively correlated with SI-NO₂ on 24 February 2021 ($R = 0.88$), while a negative correlation occurred on 21 April 2021 ($R = -0.88$), indicating a wide range of case-specific correlations. The negative correlation on 21 April (Fig. 3b) implied that the nonhomogeneous NO₂ distributions vertically were partially due to the photochemical process. For example, the decrease in PC-NO₂ despite an increase in SI-NO₂ might have occurred because NO₂ is removed by photochemical loss; it can occur more severely in the upper atmosphere with high OH concentrations. Another possible reason is the occurrence of lifted layers related to pollutant transport, yielding sharp changes in vertical concentration from the surface to the upper layer. The case-specific discussion follows.

4.2 Impacts of meteorological conditions on correlations between PC-NO₂ and SI-NO₂

Our *k*-means cluster analysis distinguished three groups with the lowest within-group variance and largest among-group variance. Among the total of 141 cases, 47, 66, and 28 were classified into groups 1–3, respectively. Thus, group 2 had the largest proportion of cases (47 %) and group 3 had the smallest (20 %). The combination of meteorological components in group 1 indicated the end of a high-pressure system ($P_{\text{surf}} > 0$, $dP_{\text{surf}}/dt < 0$), with southerly winds ($NS850 > 0$) bringing warmer air ($T925 > 0$) to the region, leading to stable atmospheric stratification and weak surface winds (Fig. 4). This group 1 meteorological mode appeared to result in very weak NO₂ ventilation, which produced the highest PC-NO₂ and SI-NO₂ values. Group 3 showed the opposite trend, with strong northerly winds bringing colder air into the region, leading to an unstable atmosphere and stronger surface winds, and ultimately decreasing PC-NO₂ and SI-NO₂ to their lowest levels.

SI-NO₂ was approximately twice as high in group 1 than group 3, whereas PC-NO₂ showed no significant difference (Fig. 4a). We hypothesized that PBLH might also differ significantly under these micrometeorological conditions; therefore, we further explored daily maximum PBLH simulated by the Global Forecast System (GFS) and Lagrangian back-

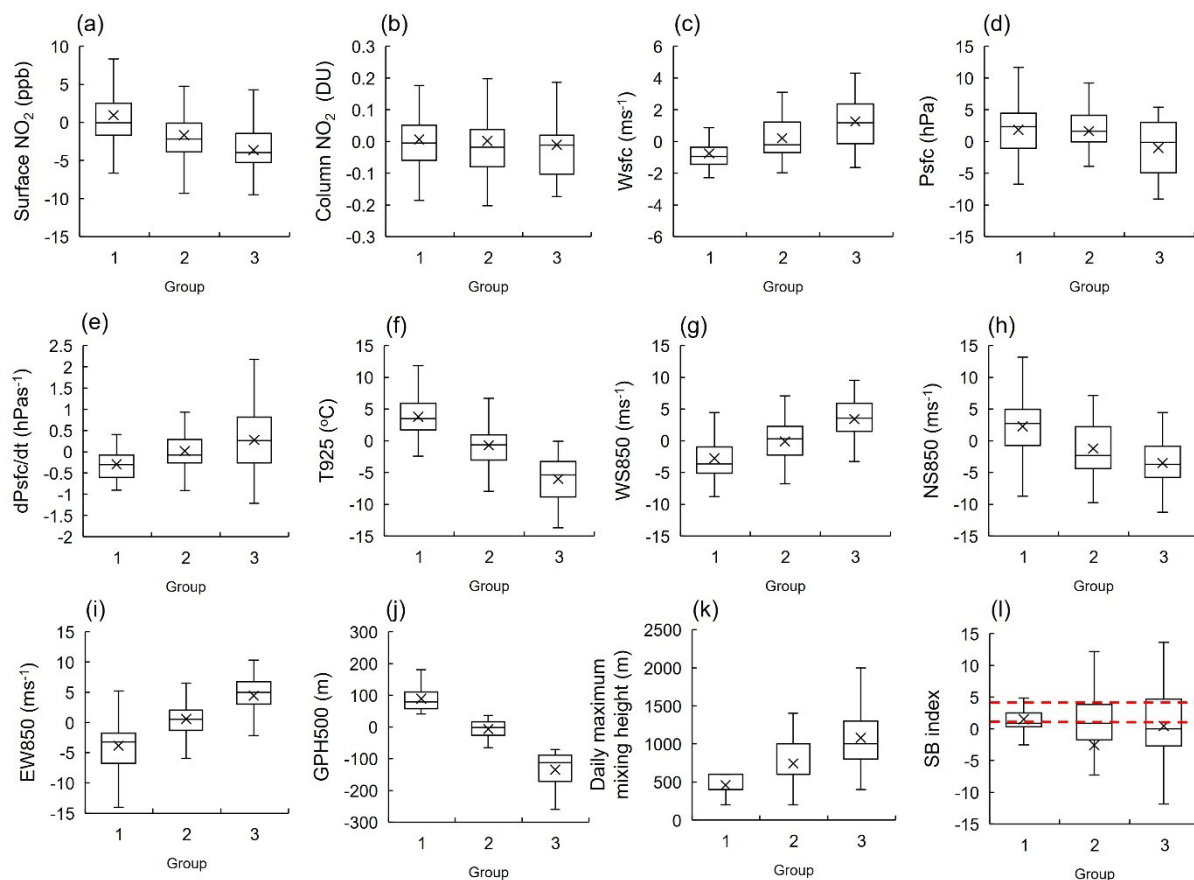


Figure 4. K-means clustering yielded three groups of cases for (a) surface NO₂ and (b) PC-NO₂, associated with eight meteorological variables: (c) surface wind speed (Wsfc), (d) Psfc, (e) Psfc tendency (dPsfc/dt), (f) 925 hPa air temperature (T925), (g) 850 hPa wind speed (W850), (h) 850 hPa north–south wind component (NS850), (i) 850 hPa east–west wind component (EW850), and (j) 500 hPa geopotential height (GPH500). All data were de-seasonalized using the 30 d moving average, except PC-NO₂, for which the monthly average was used. (k) Simulated daily maximum mixing height (not directly clustered). (l) Box and whisker plots of the sea breeze index (SBI) at Seosan for the 1-year period. Red dots indicate the critical SBI (a value of 3), suggested by Biggs and Graves (1962).

ward trajectories obtained from Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) and GFS system for the 141 cases. The mean simulated PBLH in Seosan, our study area, was 942.1 ± 405.3 m for 2020, which was similar to the annual mean daily maximum PBLH (1013.6 m) in Osan (Lee et al., 2013). However, the simulated PBLH differed significantly among the three groups (767.0 ± 304.8 , 923.2 ± 335.3 , and 1280.6 ± 501.2 m for groups 1–3, respectively). The PBLH for group 3 was 1.7-fold higher than that for group 1 (Fig. 4k). We also detected significant differences among the three groups in synoptic components of the lower troposphere including W850, and in local meteorological parameters such as the sea breeze index (SBI) suggested by Biggs and Graves (1962), which is defined as, $SBI = \frac{U^2}{C_p \Delta T}$, where U is Wsfc (Fig. 4c), C_p is specific heat, and ΔT is the temperature difference between T925 and the sea surface temperature. Thus, the SBI represents the ratio between inertial ($\rho U^2/2$) and buoyancy forces ($\rho g c_p \Delta T$), where ρ is

air density and g is gravity, and its value provides an indication of the likelihood of local circulation events such as sea breezes; at higher SBIs (i.e., $SBI > 3$), sea breezes cannot overcome the prevailing wind, whereas lower SBIs (i.e., $0 < SBI < 3$) can indicate strong sea breezes.

In the example shown in Fig. 4l, the SBI for groups 1–3 was 0.1 ± 4.5 , 0.1 ± 9.2 , and -0.2 ± 12.5 , respectively. Most SBIs in group 1 ranged from 0 to 3, indicating that group 1 corresponded to the dominant local circulation (LD), whereas the SBIs in group 3 had the lowest frequencies comparing 1 and 3, which corresponded to a dominant synoptic-scale circulation (SD). Group 2 can be considered a mixture of local and synoptic-scale circulation (MD). These results indicate that Seosan may experience frequent LD conditions (with sun on 1/3 of the days of the year), with infrequent SD conditions (1/5 of all days).

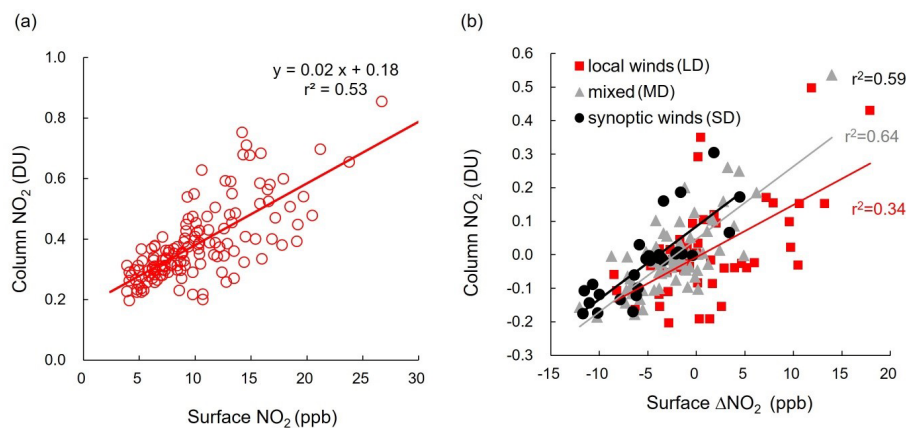


Figure 5. (a) Scatterplots of daytime measurements at site PA₄ (a) PC-NO₂ vs. SI-NO₂ under all meteorological conditions and (b) PC-NO₂ vs. surface NO₂ in each meteorological condition over a 1-year period (12 November 2020–30 October 2021). Here surface NO₂ = SI-NO₂ – (30 d moving average) SI-NO₂.

4.2.1 Relationship between daily mean PC-NO₂ and SI-NO₂ under LD, MD, and SD conditions

Scatter diagrams of daytime mean PC-NO₂ and SI-NO₂ measurements at Seosan over the entire 1-year period are shown in Fig. 5. Based on the 141 cases, daytime mean values averaged between 11:00 and 17:00 KST were used to reduce the effect of nocturnal PBLH variation. Other data selection criteria included concurrent PC-NO₂ and SI-NO₂ measurements, with data acquisition rates of > 80 % per day. Overall, PC-NO₂ and SI-NO₂ were strongly correlated ($R = 0.73$; Fig. 5), suggesting that the vertical profiles were generally uniform in the PBL throughout all four seasons. The slope of the linear regression curve shown in Fig. 5a was 0.02 DU ppb^{-1} ($= 0.53 \times 10^{15} \text{ molec. cm}^{-2} \text{ ppb}^{-1}$), which is comparable to values ($0.3\text{--}0.59 \times 10^{15} \text{ molec. cm}^{-2} \text{ ppb}^{-1}$) obtained previously in a study of surface and OMI-NO₂ measurements downwind of strong point sources in Israeli cities (Boersma et al., 2009). The intercept (0.17 DU) was within the range of previous Anmyeondo Pandora measurements, suggesting that intercepts of 0.15–0.2 DU may represent the local background PC-NO₂ amount (including the stratospheric NO₂), rather than the influence of local anthropogenic NO₂ emissions.

We classified daily averaged PC-NO₂ and SI-NO₂ data according to the three meteorological conditions (LD, MD, and SD) and detected a weak correlation under LD conditions (Fig. 5b); the lowest coefficient of determination for the LD condition ($R^2 = 0.34$) was approximately half of those for the MD (0.359) and SD (0.64) conditions, suggesting that NO₂ vertical profiles were more complex under LD conditions, with anomalous layers.

4.2.2 Diurnal variation in column-surface NO₂ under LD, MD, and SD conditions

Diurnal patterns of PC-NO₂, SI-NO₂, and O₃ under SD, MD, and LD conditions are shown in Fig. 6. Under LD conditions, PC-NO₂ increased from morning to afternoon (Fig. 6a), whereas under SD conditions, it had a weak morning peak and subsequent decrease until late afternoon (Fig. 6c). Under MD conditions, PC-NO₂ had one large peak in the morning and a shoulder peak in the late afternoon (Fig. 6b). However, SI-NO₂ showed nearly identical diurnal patterns among the three meteorological conditions, with an early morning peak followed by a second peak in the late afternoon (Fig. 6d–f). Diurnal patterns of O₃ were strongly associated with O₃-NO₂ photochemical reactions under both LD and MD conditions (Fig. 6g and h), whereas no particular photochemical effects were detected under SD conditions (Fig. 6i).

A simple linear regression was applied to daytime average (11:00–17:00 LST) measurements of both PC-NO₂ and SI-NO₂ under the three meteorological conditions, and yielded correlation coefficients (R) of 0.51 and 0.41 for SD and MD conditions, respectively; however, LD conditions produced a significantly lower R (0.27). Thus, under SD conditions, strong synoptic winds suppressed PC-NO₂ and SI-NO₂ diurnal fluctuations, rendering them similar to each other. Strong winds also inhibited local effects of O₃ formation on the diurnal variation in PC-NO₂, and the smaller impact of chemical conversion from local NO₂ to O₃ lowered R values during the day. Under MD conditions, both PC-NO₂ and SI-NO₂ exhibited distinctive peaks in the morning with a degree of time lag; both subsequently declined toward noon, and showed higher R values than those obtained under SD conditions. By contrast, under MD conditions, correlations were enhanced due to a minimum around 15:00 KST for both PC-NO₂ and SI-NO₂, despite time lags in both peaks in the morning and afternoon.

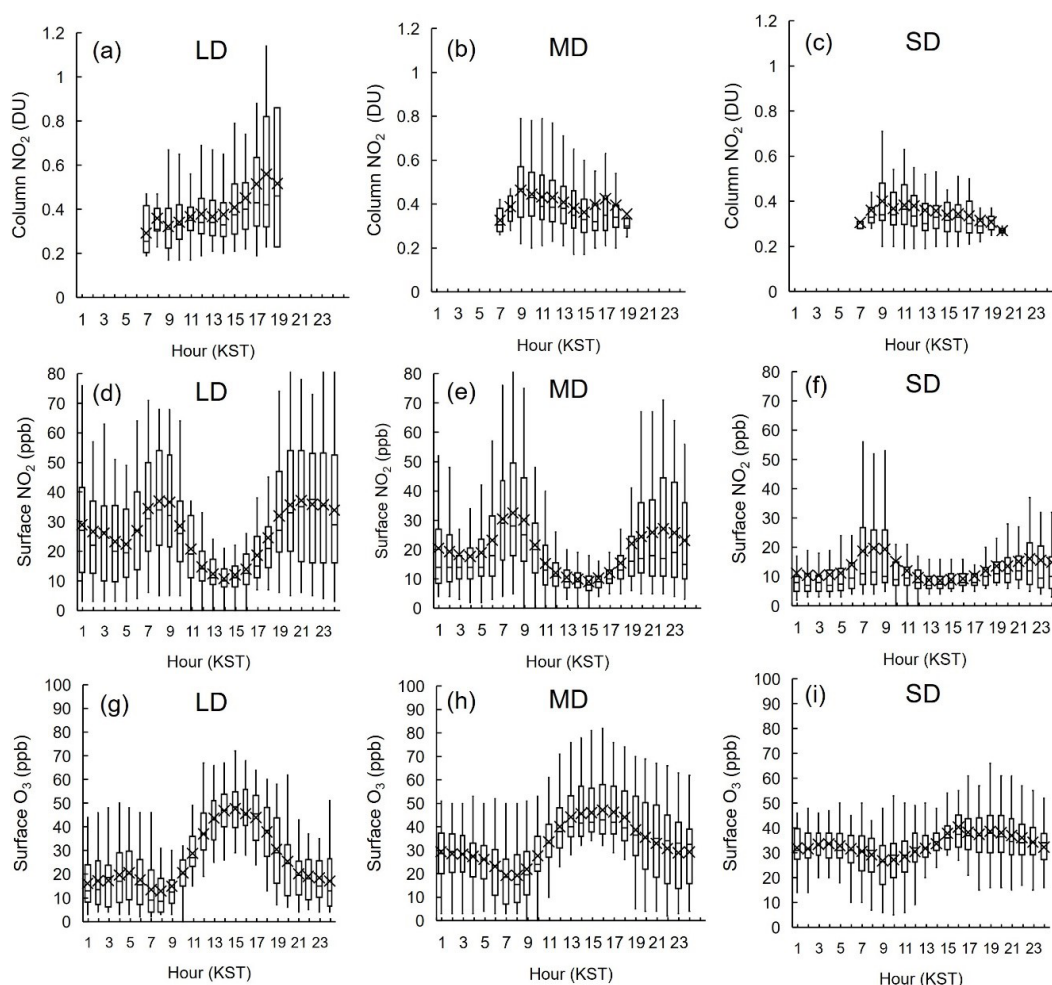


Figure 6. Box and whisker plots of diurnal variation in (a–c) PC-NO₂, (d–f) SI-NO₂, and (g–i) surface O₃ under synoptic wind-dominant (SD), mixed (MD), and local wind-dominant (LD) conditions in Seosan during a 1-year period (12 November 2020–30 October 2021).

Previous studies of the Megacity Air Pollution Seoul (MAPS-Seoul) and KORUS-AQ campaigns reported a typical pattern of continuously increasing PC-NO₂ over the Seoul metropolitan area (Chong et al., 2018; Herman et al., 2018). However, in the current campaign, we found similar results only under LD conditions. The diurnal patterns reported in previous studies were mainly caused by the dominance of NO₂ emissions sources over NO₂ losses (Chong et al., 2018; Herman et al., 2018) among several processes associated with NO₂ photochemical loss, including transport and deposition, which were also investigated in specific cases in the current study.

In this study, we extended the correlation analysis and investigated the correlation between hourly PC-NO₂ and SI-NO₂ data. The results show a lower correlation in the morning and a higher correlation in the afternoon (Fig. S1 in the Supplement). The respective median correlation coefficients for the LD, MD, and SD meteorological condi-

tions were -0.71 , 0.18 , and 0.22 in the morning (09:00–12:00 LST), and 0.84 , 0.77 , and 0.79 in the afternoon (12:00–14:00 LST). These values may reflect PBL development. SI-NO₂ decreases in the morning due to the rapid growth of the PBL, while PC-NO₂ increases due to the accumulation of NO₂ in the atmosphere, deriving a lower correlation. However, there is very little change in the PBL in the afternoon, and PC-NO₂ and SI-NO₂ show similar changes, yielding a positive correlation between them during the GMAP-2020 campaign.

4.3 Aircraft measurements collected during GMAP-2020

Data collected via aircraft during GMAP-2020 are summarized in Table 2. A total of nine aircraft measurements were conducted during the campaign period (12 November 2020–20 January 2021). Four of nine flights were conducted under LD conditions, and the remaining flights (except that on 27 November 2020) were conducted under MD conditions.

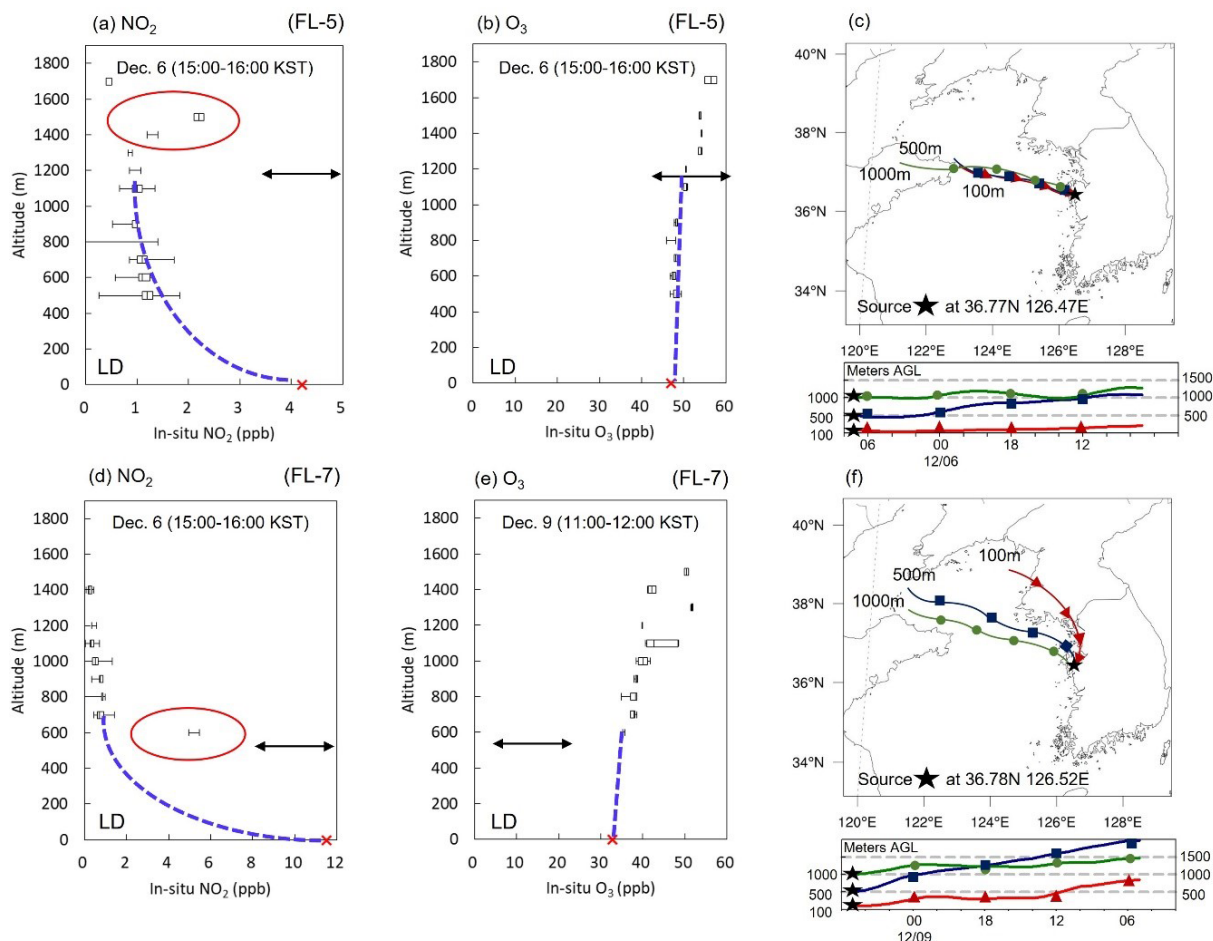


Figure 7. Box and whisker plots of the vertical NO₂ and O₃ profiles measured by GMAP aircraft superposed with in situ AQMS₁ measurements during flights (a, b) FL-5 (6 December) and (d, e) FL-7 (6 and 9 December). Blue dashed lines are linear regression lines fitted to NO₂ and O₃ profiles within the planetary boundary layer (PBL). Black arrows indicate the simulated PBL height (PBLH) obtained from the Korea Meteorological Administration (KMA). HYSPLIT 24 h backward trajectories in Seosan are shown at altitudes of 100, 500, and 1000 m, starting at 16:00 KST on 26 November and 12:00 KST on 12 December.

No aircraft measurements were consistent with SD conditions during the GMAP-2020 campaign.

We examined spiral segments from each flight over Seosan during 11:00–17:00 KST to exclude marginal effects of diurnal variation in NO₂ (Fig. 2). The overall results indicated that the vertical O₃ profiles were relatively constant in the PBL, whereas NO₂ profiles appeared to be highly dependent on meteorological conditions. We compared data collected during flights conducted under LD (one flight) and MD conditions (two flights) during the GMAP-2020 campaign, to examine differences in the vertical structures of the PA and SI observations.

Aircraft measurements of vertical NO₂ and O₃ profiles for flights FL-5 (6 December) and FL-6 (8 December) under LD conditions are shown in Fig. 7, along with 24 h backward trajectories starting at different altitudes (100, 500, and 1000 m). All observed NO₂ profiles shown in Fig. 7 ap-

peared to have generally exponential curves, with anomalous features at higher altitudes. For example, when vertical turbulent mixing prevailed within the PBL (O₃ profile, Fig. 7b), the data were fitted with an exponential vertical curve, and the anomalous NO₂ layer aloft was found to have a height of 1.5 km, which was higher than the estimated PBLH of 1.2 km. HYSPLIT 24 h backward trajectories starting at 12:00 KST showed that all air mass from the surface to the lower free atmosphere was transported over the Yellow Sea via the Shandong Peninsula (Fig. 7c). This finding suggests that the anomalous NO₂ layer aloft was not produced locally (i.e., from local LPS emissions), but instead traveled via long-range regional-scale transport. This transport of NO₂ across the region was also discussed and might be particularly high during the winter when the NO_x lifetime is relatively longer (Stohl et al., 2002; Wenig et al., 2003; Lee et al., 2013). According to Anmyeondo lidar measure-

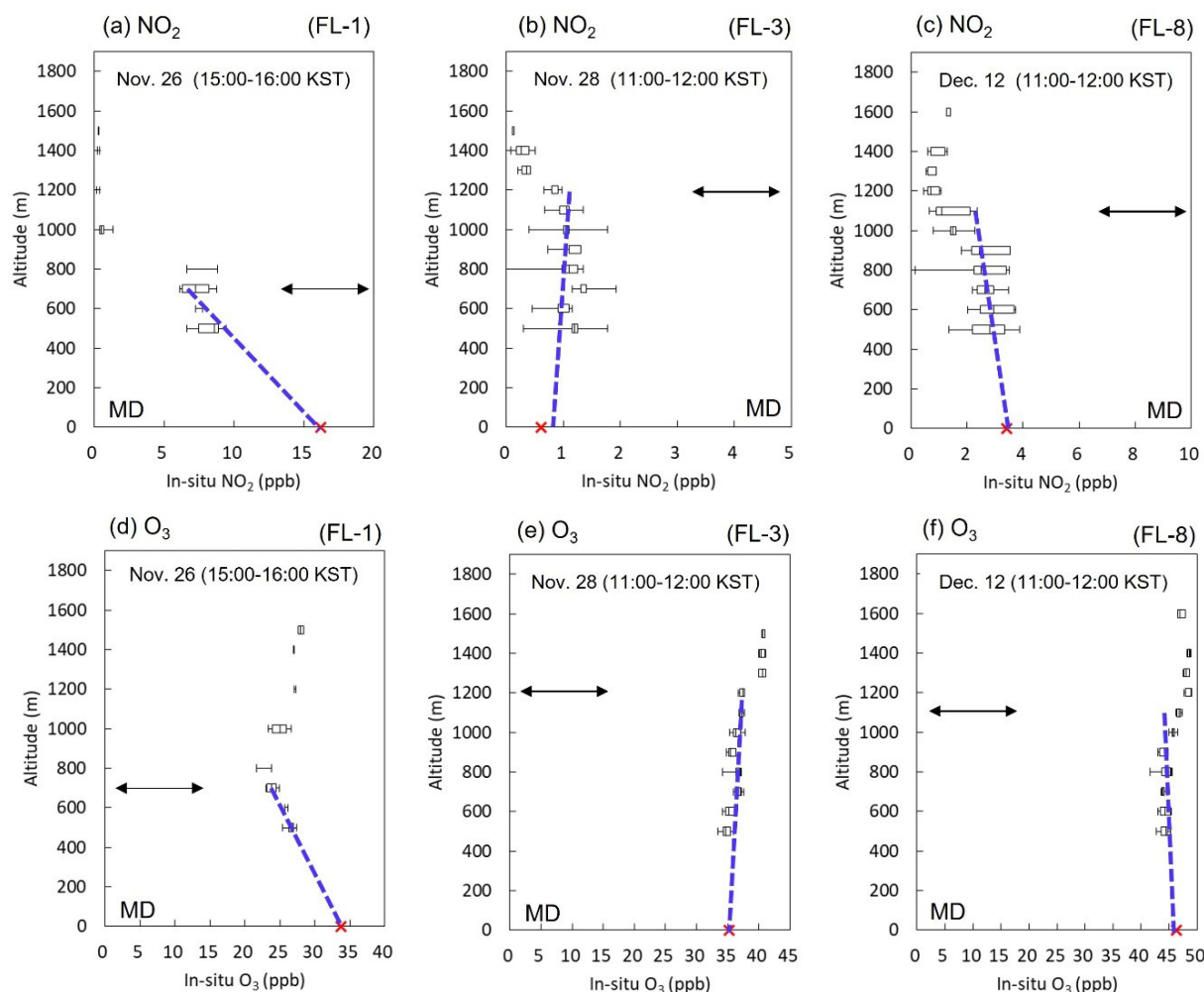


Figure 8. Box and whisker plots of vertical profiles obtained from GMAP aircraft superposed with in situ AQMS measurements for (1) NO₂ and (2) O₃ for flights (a) FL-1 (26 November), (b) FL-3 (28 November), and (c) FL-8 (12 December). Blue dashed lines are linear regression lines fitted to NO₂ and O₃ in the PBL. Black arrows indicate PBLH simulated by the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) Global Forecast System (GFS).

ments for 6 December (<http://kalion.kr>, last access: 22 August 2022), the anomalous NO₂ layer aloft corresponded well to an aerosol layer that appeared at ~ 1.0 km at approximately 12:00 KST, persisting until 2200 KST. However, based on a cross-comparison of our data, high surface levels of SI-NO₂ (> 4 ppb; Fig. 7a) were influenced more by local LPS than by that in the atmosphere aloft due to long-range transport (Fig. 7a).

Aircraft measurements for flight FL-7 (9 December) under LD conditions are shown in Fig. 7b. The NO₂ vertical profile exhibited an exponential curve, with an anomalous peak at ~ 600 m immediately above the top of the simulated PBL. HYSPLIT backward trajectory data starting at 12:00 KST showed that the non-surface air had a different origin from the surface air (Fig. 6d), indicating that the anomalous NO₂ plume likely traveled from coal-fired power plants in a nearby industrial city (Taean) northwest

of Seosan. This finding indicates a distinct vertical structure of higher NO₂ at the surface due to strong local emissions, whereas lower NO₂ levels were observed at higher altitudes, with anomalously high NO₂ levels in some layers aloft due to medium-range transport from nearby areas. Thus, despite the limited number of aircraft measurements, the elevated anomalous NO₂ structure that was observed intermittently led to a negative correlation between PA-NO₂ and SI-NO₂. The discrepancies imply that vertical profile distribution study should proceed cautiously when only surface measurements are obtained under LD meteorological conditions.

Aircraft measurements were conducted under MD conditions on flights FL-1 (26 November), FL-3 (28 November), and FL-8 (12 December) (Fig. 8). We applied several regression models (linear, exponential, and polynomial) to three vertical structures, and obtained two distinct NO₂

Table 2. Summary of aircraft measurements collected during the Geostationary Environment Monitoring Spectrometer (GEMS) Map of Air Pollution (GMAP)-2020 campaign period (12 November 2020–20 January 2021).

Flight no.	Date	Meteorological classification
FL-1	26 Nov 2020	MD ¹
FL-2	27 Nov 2020	No Pandora measurements
FL-3	28 Nov 2020	MD
FL-4	1 Dec 2020	LD ²
FL-5	6 Dec 2020	LD
FL-6	8 Dec 2020	LD
FL-7	9 Dec 2020	LD
FL-8	12 Dec 2020 (a.m.)	MD
FL-9	12 Dec 2020 (p.m.)	MD

¹ LD: local wind-dominant conditions; ² MD: mixed conditions.

vertical profile patterns from the surface to the PBLH: decreasing linearly for FL-1 and FL-8 (Fig. 8), and constant with altitude for FL-3 (Fig. 8b). None of the three cases showed anomalous layers above the PBLH, similar to the exponentially declining profiles obtained under LD conditions (Fig. 7). These vertical structures observed under MD conditions may have been induced by strong vertical mixing within the PBL, supplemented by prominent surface photochemical losses at the same time. The vertical O₃ profile during FL-1 showed a decoupled structure, with different patterns within and above the PBL (Fig. 8d); however, the other 2 d showed uniform distributions, with no particular anomalous features between the upper PBL and surface atmosphere (Fig. 8b, c, e, and f). The observed daily maximum sensible heat fluxes measured at Seosan (Fig. S3) were much higher for FL-3 (175.9 W m⁻²) than FL-1 and FL-8 (118.9 and 102.0 W m⁻²), suggesting that vertical turbulent mixing was much more prominent during FL-3. These chemical and physical characteristics are all related to MD conditions. Thus, the higher coefficient of determination ($R^2 = 0.64$) obtained under MD conditions (Fig. 5b) has an important bearing on the absence of irregular or anomalous layers aloft, with little variation regardless of the shape of the curve (Figs. 7 and 8).

4.4 Analyses of column–surface relationships for specific GMAP-2020 cases

Figure 9 shows examples of PC-NO₂ and SI-NO₂ diurnal variation under LD (FL-5 and FL-7) and MD (FL-1 and FL-8) conditions, and Fig. 10 shows latitudinal mean distributions for FL-5 and FL-7, based on the aircraft measurement data shown in Figs. 7 and 8. PC-NO₂ was decoupled from SI-NO₂ on 2 d, FL-5 and FL-7, which were both classified as having LD conditions (Fig. 9a and b), whereas good vertical mixing and uniform NO₂ distribution were observed on the

remaining 2 d, FL-1 and FL-8, which showed MD conditions (Fig. 9c and d). According to our analysis of the aircraft measurements (Fig. 7), the poor correlations between PC-NO₂ and SI-NO₂ captured by FL-5 and FL-7 were mainly due to an NO₂ polluted layer transported aloft, as described in Sect. 4.3.

4.4.1 LD conditions

Several cases showed poor correlations between PC-NO₂ and SI-NO₂ under LD conditions within the study period. When we examined the results of previous studies (Thompson et al., 2019; Chong et al., 2018; Herman et al., 2018; Kim et al., 2021), we first considered the possibility that LPS emissions influenced downwind regions under LD conditions because the increase in PC-NO₂, but not SI-NO₂, may have required an additional source of NO₂ apart from early afternoon traffic emissions. The FL-5 data for December 6 represent an example of this, showing a poor correlation between PC-NO₂ and SI-NO₂ ($R^2 = 0.06$; Fig. 9a). On the same day, Anmyeondo lidar detected two elevated aerosol layers at 12:00 and 16:00–22:00 KST (<http://kalion.kr>, last access: 22 August 2022); the first aerosol layer may reflect a PC-NO₂ peak, as shown in Fig. 9a. The HYSPLIT backward trajectories, starting at different altitudes from the surface to the lower troposphere, revealed that all air parcels moved eastward from China to Anmyeondo and Seosan (Fig. 1); thus, other NO₂ plumes may have begun to pass over Seosan at 16:00 KST (Fig. 7c). Longitudinal SI-NO₂ distributions (Fig. 10) exhibited 5.2 ppb at 126.1° E, 8.1 ppb at 126.3° E, and 7.3 ppb at 126.4° E, averaged between 13:00 and 16:00 KST by longitude (Table S1 in the Supplement), whereas they were nearly constant at a height of 500–600 m on 6 December. Therefore, westerly winds advected cleaner air from Padori (AQM₁) to Seosan at the surface, but not at a height of 500–600 m, contributing to low SI-NO₂ levels in the afternoon (Fig. 9a).

Another example of a weak correlation was obtained by flight FL-7 (9 December), as shown in Fig. 9b. Time series PC-NO₂ data exhibited several peaks during 12:00–14:00 KST (Fig. 9b), whereas SI-NO₂ showed less temporal variation, resulting in a weak correlation ($R = -0.24$) compared to the overall daytime (11:00–17:00 KST) correlation ($R^2 = 0.53$; Fig. 5a). Latitudinal NO₂ levels at high altitudes of ~ 600 m (Fig. 10b) gradually increased northward, whereas surface NO₂ was minimal at the midpoint. For example, at high altitudes, the latitudinal mean NO₂ levels were 1.4 ppb (36.8° N), 4.1 ppb (36.9° N), and 5.1 ppb (37.0° N), whereas the SI-NO₂ levels at the same sites were 18.0 ppb (36.8° N), 14.3 ppb (36.9° N), and 16.8 ppb (37.0° N), respectively, averaged during 12:00–14:00 KST by latitude (Table S1). This finding is attributable to a prevailing north wind that transported NO₂ southward at high altitudes, while simultaneously ventilating SI-NO₂ toward outer Seosan, re-

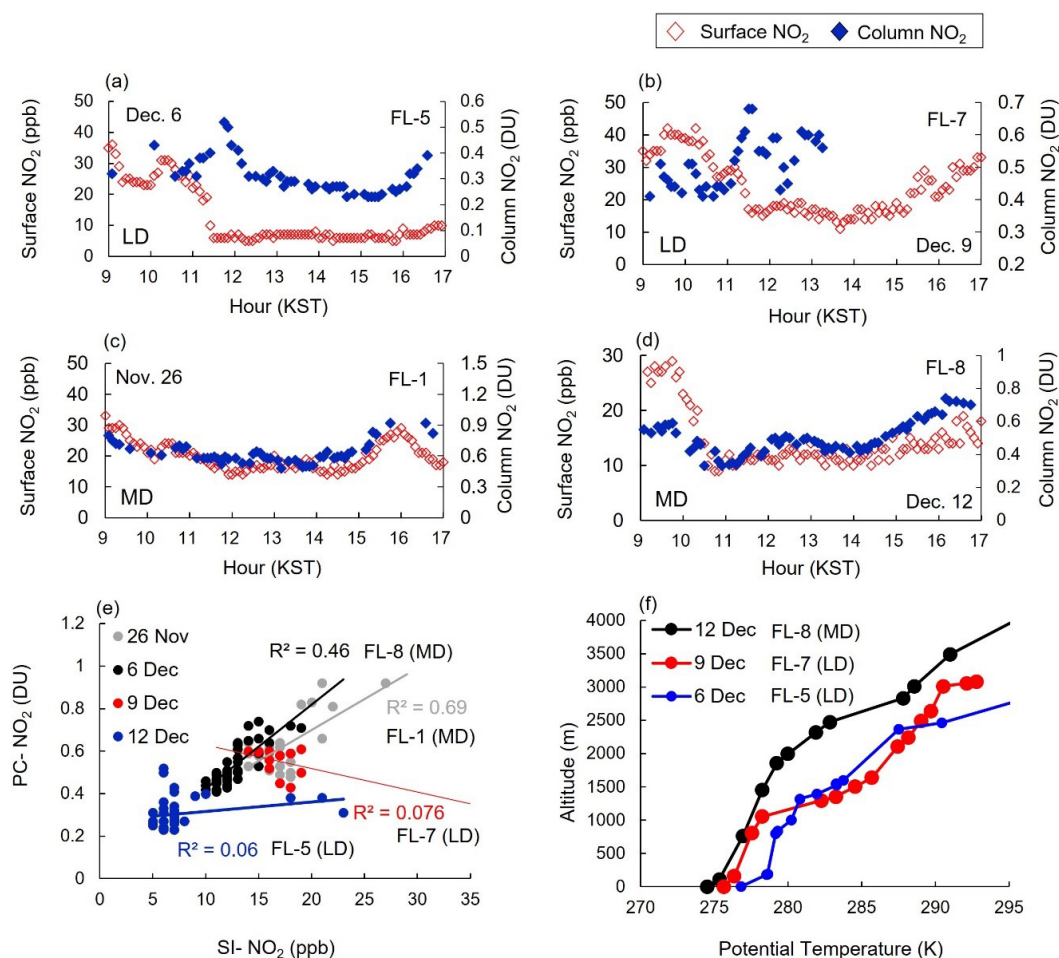


Figure 9. Time series and scatterplots of PC-NO₂ and SI-NO₂ at PA₂ on (a) 6 December, (b) 9 December, (c) 26 November, and (d) 12 December. (e) Scatterplot of PC-NO₂ and SI-NO₂ on 6 December (blue), 9 December (red), 26 November (gray), and 12 December (black). (f) Vertical potential temperature profiles on 6, 9, and 12 December 2020. Radiosonde data for 26 November 2020 are missing.

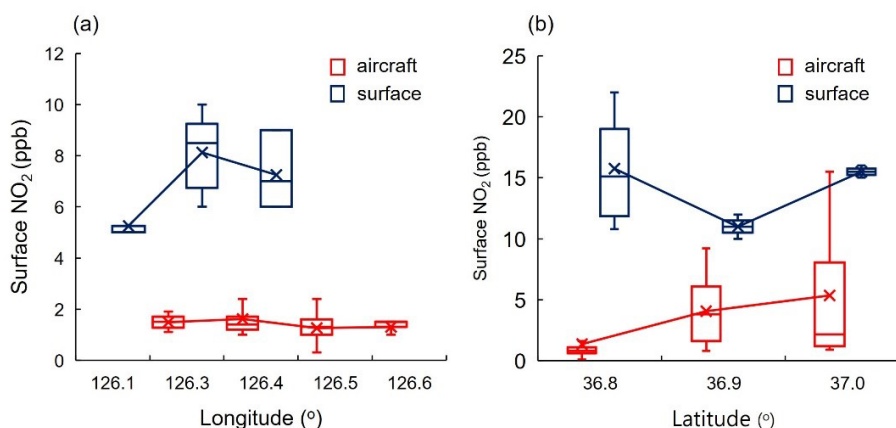


Figure 10. Latitudinal NO₂ distribution at the surface and 600 m over PA₄ (Seosan super site), averaged during (a) 13:00–16:00 KST on 6 December (FL-5) by longitude and (b) 12:00–14:00 KST on 9 December (FL-7) by latitude, obtained from airborne (blue) and surface measurements (red).

sulting in the development of several PC-NO₂ peaks. By contrast, SI-NO₂ decreased slowly (Figs. 9b and 10b).

4.4.2 MD and SD conditions

We obtained higher PC–SI correlation coefficients under MD and SD conditions than LD conditions (Figs. 5b, and 9c and d). Under MD and SD conditions, diurnal variation in PC-NO₂ and SI-NO₂ showed simultaneous declines from early morning until noon (Fig. 6). Notably, PC-NO₂ showed a continuously decreasing trend, particularly during the morning hours, in the period of approximately 09:00–12:00 KST under both MD and SD conditions (Fig. 6b and c). These diurnal patterns of decreasing PC-NO₂ in the study area were opposite to those reported in previous studies (Chong et al., 2018; Herman et al., 2018) that observed increasing PC-NO₂ in large urban areas during the daytime, caused by higher NO₂ emissions even during photochemical NO₂ losses to form O₃.

We hypothesized that decreasing PC-NO₂ can occur due to photochemical loss and surface wind transport, which both intensify with increasing solar radiation in the morning. Photochemically, NO₂ is converted into photochemical oxidants such as PAN, HNO₃, and nitrate under sunlight, thereby disrupting the NO_x–VOC–O₃ cycle. Concurrently, W_{sf}c intensified due to thermal turbulence transport of NO₂ emissions away from Seosan during the day. Thus, PC-NO₂ decreases under MD conditions as a result of ventilation effects caused by stronger wind speeds. There are two possible mechanisms for this: sea breeze penetration (because the study area is adjacent to the northern coast of the Taean Peninsula; Fig. 1), and vigorous turbulent mixing (which leads to vertical mixing of surface NO₂ during PBL growth; Sun et al., 2013). We investigated these factors in detail for specific cases.

Figure 11 shows the diurnal variation in selected meteorological and chemical variables measured under MD (25 November) and SD conditions (14 December). Under MD conditions (Fig. 11a–c), declines in PC-NO₂ and SI-NO₂ were observed toward noon. In particular, decreasing PC-NO₂ was accompanied by increased W_{sf}c (Fig. 11b); therefore, we examined GMAP-2020 campaign measurements of sea breeze penetration. Figure S2a shows diurnal variation in observed air temperatures at site Met₁ and measured sea surface temperatures at nearby site Met₂ (37.14° N, 126.01° E), located 55 km from PA₄. The thermal meteorological observations were used to calculate SBI (+0.37), which was greater than +3 (the threshold for sea breeze occurrence; Brigges and Graves, 1962). Sea breeze disturbances with a sharp decrease (increase) in temperature (humidity) were observed at site Met₃ (Fig. S3b), which is located on the northern coastline of Taean Peninsula (Fig. 1). However, sea breezes did not progress inland at the Met₁ Seosan Meteorological Automated Surface Observing System (ASOS) site, which is closer to the Pandora sites; sea

breezes did not correlate with NO₂ ventilation to offset its high emission.

We further detected a strong positive correlation between wind speed and sensible heat flux (Fig. 11b). We speculated that thermal and momentum turbulences caused by a vertical temperature gradient and surface friction entrained surface turbulence, thus increasing momentum in the free atmosphere downward to the surface due to strong turbulent mixing within the PBL, in turn leading to a uniform vertical NO₂ profile with a positive correlation between PC-NO₂ and SI-NO₂. Figure S3 shows a comparison of daily maximum sensible heat and momentum fluxes under LD, MD, and SD conditions during the GMAP-2020 campaign. SD conditions showed the highest mean heat flux, followed by MD and LD, indicating that downward momentum transport led by both heat and momentum fluxes plays a greater role in W_{sf}c enhancement under MD than LD conditions within the PBL.

Photolytic NO₂ loss was detected as temporal variation in NO₂, NO₃[−], and CO at PA₄. Because no NO₂ analyzer was installed at PA₄, NO₂^{*} (=NO_y–NO) was used instead of NO₂ under the assumption that NO_z is negligible in winter. Figure 11c shows the diurnal variation in NO₂, O₃, and NO₃[−] under MD conditions, normalized by CO to reduce the effect of PBL evolution. The results showed that NO₂/CO decreased after the morning peak; however, NO₃[−]/CO and O₃/CO increased toward midday, indicating that photolytic activity also contributed considerably to the concurrent decline of SI-NO₂ and PC-NO₂ (Fig. 11a). In turn, this indicated that photochemistry can contribute to higher correlation coefficients under MD conditions.

Under SD conditions (Fig. 11d–f), PA-NO₂ and SI-NO₂ exhibited weak diurnal variability compared to LD and MD conditions. SD conditions on 14 December produced significantly stronger winds (i.e., wind speed > 6 m s^{−1} at 13:00 KST), with generally higher PBLHs (Fig. 11e). Meteorological features, such as strong wind at both 850 hPa (18.0 m s^{−1}) and 10 m height (4.26 m s^{−1}), suppressed both PC-NO₂ and SI-NO₂ (7.3 ppb and 0.31 DU, respectively) to below the average, producing a strong correlation ($R = 0.9$ at AQM₅) and nearly flattening their temporal curves during the day (Fig. 11d). Thus, under SD conditions, wind speed and turbulent fluxes such as sensible heat flux had larger values, and NO₂ and NO₃[−] decreased or increased at the same time during the day (Fig. 11f), indicating that the transport effect was much greater than that of local photochemical loss over the study area.

In conclusion, in this case-specific study, we assessed the correlations between PC-NO₂ and SI-NO₂, and explored their mechanisms by investigating the impact of meteorological and photochemical conditions. A weak correlation between PC-NO₂ and SI-NO₂ occurred when anomalously high concentrations remained, with ragged fragments of NO₂ plumes in the upper or middle layers. We also found that a negative correlation occurred intermittently under LD con-

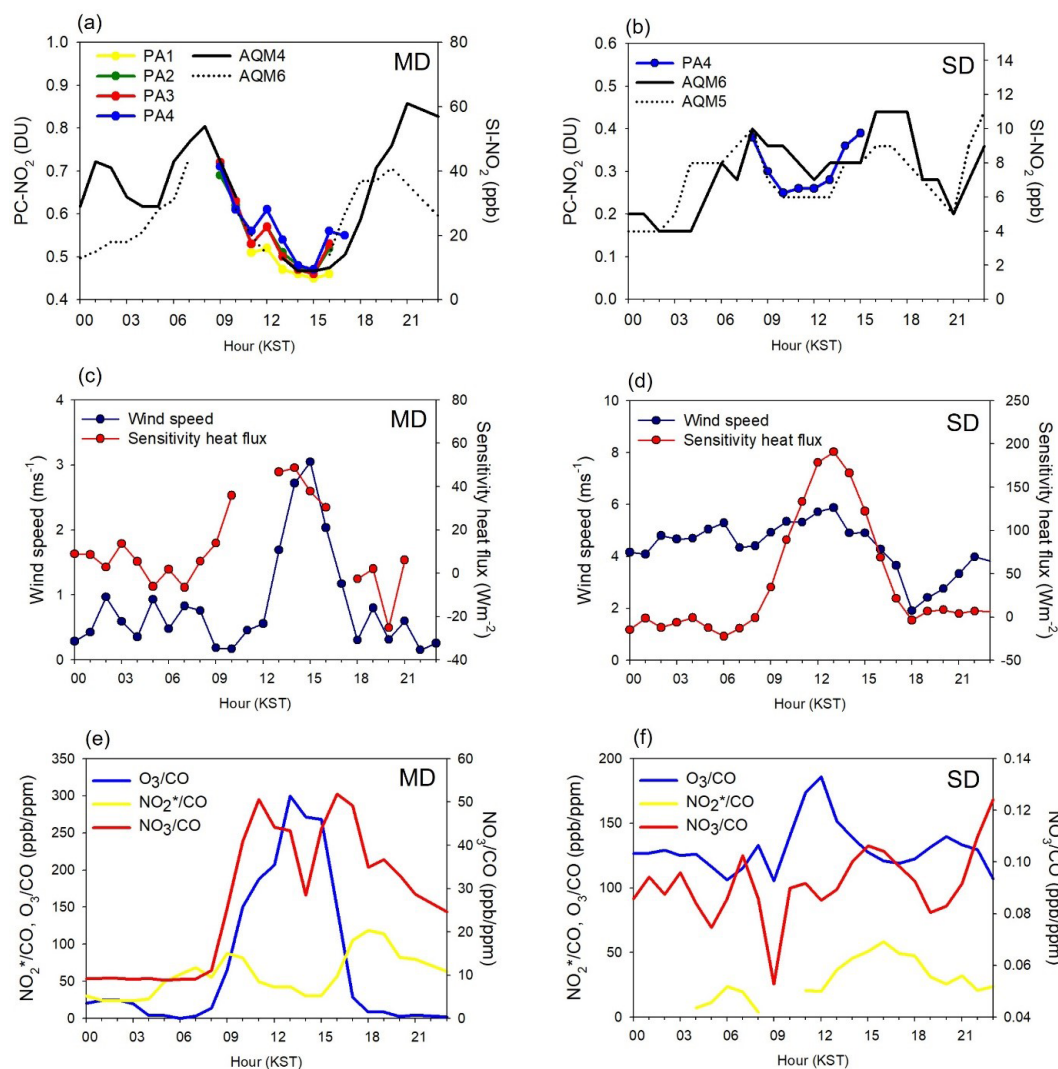


Figure 11. Examples of the diurnal variation on 25 November (a, c, e) and 14 December (b, d, f). (a, b) Column NO₂ at sites PA₁–PA₄, and surface NO₂ at air quality monitoring sites AQM₄ and AQM₆. (c, d) Sensible heat fluxes and surface wind speed at PA₄. (e, f) Diurnal variation in NO₂, NO₂⁻, and O₃ normalized by CO. Figure 1 shows the locations of the measurement sites.

ditions, with generally lower PBLH. In particular, elevated pollutant levels due to regional-scale transport or decoupled NO₂ plumes advected within the PBL may have also caused the weak correlation between PC-NO₂ vs. SI-NO₂. These phenomena were detected only from the PA–SI coupled measurements in this study. Thus, when either PC or SI observations are applied alone for understanding the vertical structure of air pollutants, undetected bias can occur under LD conditions, particularly where transport processes prevail, and these results can be also applicable to GEMS observations analysis.

5 Conclusion

We explored the potential applicability of combined PC-NO₂ and SI-NO₂ measurements collected at Seosan during the GMAP-2020 campaign. We characterized the correlation between PC-NO₂ and SI-NO₂ under various conditions to understand the complex air quality of Seosan, which appears to be vulnerable to LPS emissions from surrounding areas. We hypothesize that correlations between PC-NO₂ and SI-NO₂ are closely related to NO₂ vertical profiles, which also depend on meteorological conditions. We performed statistical analyses of a year-long PC-NO₂ dataset (12 November 2020–30 October 2021) combined with meteorological data, in situ ground data, and airborne chemical data measured during the GMAP-2020 campaign in the same period.

Our results show that hourly PC-NO₂ and SI-NO₂ over the 1-year period exhibited a linear relationship with a fair correlation ($R = 0.41$), and daily mean PC-NO₂ vs. SI-NO₂ exhibited a good linear correlation ($R = 0.73$), supporting the overall uniformity of NO₂ profiles in the PBL over Seosan despite the continuous impact of LPS emissions.

The impact of meteorological conditions on the relationship between PC-NO₂ and SI-NO₂ was investigated through agglomerative hierarchical clustering, which indicated three meteorological conditions: LD, MD, and SD. Under LD conditions, southerly winds advect warm air under the upper ridge, forming stable and short PBLs and weak surface winds. By contrast, under SD conditions, cold northerly winds induce unstable and high PBLs with strong surface winds. The correlations between daily mean PC-NO₂ and SI-NO₂ levels, and their variation during 11:00–17:00 KST, weakened under LD conditions, suggesting that the shape of the NO₂ profile typically deviates from a uniform profile under SD and MD conditions. Aircraft measurements under LD conditions demonstrated NO₂ plumes aloft, with anomalous vertical structures and different horizontal (latitudinal) gradients of surface NO₂ at higher altitudes, such as 600 m over Seosan.

Thus, the relationship between PC-NO₂ and SI-NO₂ depends on the presence of NO₂ plumes aloft under LD conditions, which provide a favorable environment for LPS plumes decoupled from the surface at Seosan. Our findings suggest that the correlation between PC-NO₂ and SI-NO₂ may serve as an indicator of the degree of complexity of urban air quality. This correlation can be optimally applied for air quality evaluation and vertical analysis by combining the Pandora Asia Network with AQM networks, and the results can be also applied to environmental GEMS observation analysis in combination with SI observations. More detailed studies on urban air pollution evaluation will be undertaken based on PC, DOAS, aircraft, SI air quality, and surface turbulence observation data, as well as modeling studies of data collected during the GMAP-2021 campaign.

Code availability. As a cluster analysis, *k*-means clustering and hierarchical analysis have been conducted using paid software code, XLSTAT software (<https://www.xlstat.com/en/>; Addinsoft, 2022), and a trial version of XLSTAT can be available at the same URL. All input data including Pandora measurement and surface measurements related to this paper are available from the corresponding author on reasonable request.

Data availability. The measurements can be accessed by contacting the corresponding authors.

Supplement. The supplement related to this article is available online at: <https://doi.org/10.5194/acp-22-10703-2022-supplement>.

Author contributions. LSC designed the research and managed the paper. DK, HH, DRK, JAY, KL, HL, DK, and JH conducted the experiments and provided data curation. HJY and DK contributed to formal analysis and visualization. CHK co-managed and substantially contributed to the discussion of the results.

Competing interests. The contact author has declared that none of the authors has any competing interests.

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