

Ozone formation sensitivity based on the secondary formaldehyde-to-nitrogen dioxide ratio (FNR_{sec}) derived from ground-based remote sensing measurements and a chemical transport model

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Abstract. Sensitivity analysis is essential for developing effective ozone (O₃) mitigation strategies. This study aims to extensively investigate the diurnal, seasonal, and vertical chemical sensitivity of O₃ using a photochemical indicator, the secondary formaldehyde (HCHO)-to-nitrogen dioxide (NO₂) ratio (FNR_{sec}) as measured by Pandora remote-sensing spectrometers located across Japan. Region-specific FNR_{sec} thresholds were determined using the GEOS-Chem chemical transport model. Surface concentrations and vertical column amounts of HCHO and NO₂ were obtained from in situ measurements and Pandora spectrometers. The concentrations of HCHO and NO₂ varied with season and altitude. Moreover, external pollution transport affected the vertical profiles and likely contributed to elevated concentrations. During exceedance events, the O₃ sensitivity analysis showed that NO_x-limited conditions were dominant in summer, transitional regimes in spring and fall. Vertically, RO_x-limited conditions typically formed near the surface layers, followed by transitional regimes in the mid-levels, and NO_x-limited regimes aloft. Therefore, O₃ mitigation strategies should target not only the surface level but also elevated altitudes. This study contributes to fostering a comprehensive understanding of O₃ sensitivity in the troposphere using FNR_{sec} retrieved from Pandora measurements.

Keywords: ozone chemical regime, Pandora, FNR_{sec}, GEOS-Chem model.

1. Introduction

Tropospheric ozone (O₃) is a central secondary pollutant formed through photochemical reactions involving its main precursors: nitrogen oxides (NO_x, including NO and NO₂) and volatile organic compounds (VOCs) in the presence of sunlight. Increases in tropospheric O₃ levels negatively affect human health (Liu et al., 2018; Nuvolone et al., 2018), crop productivity (Mahmood et al., 2020; Ramya et al., 2023), and ecosystems (Feng et al., 2021; Grulke and Heath, 2020). Due to its well-known impacts, enormous efforts have been made in many cities and countries to mitigate O₃ pollution (Hu et al., 2024; Chang et al., 2025; Shi et al., 2025a). A major challenge that hinders O₃ pollution mitigation strategy is that O₃ formation results from non-linear photochemical reactions of its precursors, rather than from direct emissions (Mishra et al., 2024; Sadanaga et al., 2017). Internally, O₃ production is initiated by the formation of peroxy radical (RO_x), generated through reactions between VOCs and hydroxyl radical (OH). O₃ is subsequently produced when RO_x radicals (HO₂ or RO₂) react with NO, leading to radical propagation (Kleinman et al., 2001; Sillman and He, 2002). The radical termination proceeds control the O₃ production. These proceeds occur either through the reaction of OH with NO_x to form nitric acid (referred as LNO_x) or through radical-radical reactions (referred as LRO_x) (Schroeder et al., 2017).

40 Sensitivity analysis is of significant importance for developing effective O₃ mitigation strategies. Tropospheric O₃ production is conventionally categorized into three regimes: NO_x-limited (or NO_x-sensitive) regime, transitional regime, and radical-limited (also referred to as VOC-limited, VOC-sensitive, or NO_x-saturated) regime. Depending on the sensitivity regime, controlling either NO_x or VOC emissions can be an effective approach to mitigating O₃ pollution. Sensitivity analyses have been conducted using various approaches, including model-based methods (Thorp et al., 2021), absolute sensitivity analysis (Sakamoto et al., 2019), and photochemical indicators such as the formaldehyde-to-nitrogen dioxide ratio (FNR) (Jung et al., 2022; Qian et al., 2024; Souri et al., 2023b), the robust H₂O₂-to-HNO₃ ratio (Hammer, et al., 2002; Souri et al., 2023a), and the LRO_x/LNO_x ratio (Abdi-Oskouei et al., 2022; Schroeder et al., 2017). O₃ formation sensitivity can be visually represented using empirical kinetics modeling approach (EKMA) that produces curves between NO_x and VOCs (Tonnesen and Dennis, 2000). However, measuring hundreds of VOC species is impractical. Meanwhile, HCHO reflects the VOC oxidation strength and is widely used as a proxy for VOCs reactivity (Irie et al., 2021). It should be noted that only secondary HCHO, produced photochemically from VOCs, accurately reflects the VOC oxidation capacity (Xue et al., 2022). Primary HCHO is directly emitted from anthropogenic activities; therefore, considering primary HCHO may be misleading in the assessment of VOCs reactivity. Previously, the HCHO-to-NO_y ratio was used as an indicator of the chemical sensitivity. NO_y consists of NO_x and NO_z (including HNO₃, HONO, organic nitrates, etc.). The HCHO-to-NO₂ ratio has been proposed as a better indicator because HCHO and NO₂ have similar lifetimes and better represent the competition for OH radicals (Santiago et al., 2021; Tonnesen and Dennis, 2000). The FNR has inherent limitations in representing O₃ chemistry because it does not account for other atmospheric dimensions, such as photolysis rates and water vapor (Souri et al., 2023a, 2026). A wide transition/ambiguous range of FNR values has been reported compared with the more precise LNO_x/LRO_x ratio (Schroeder et al., 2017). Consequently, under certain conditions, especially under low photolysis rates, FNR may misclassify O₃ formation sensitivity. Nonetheless, FNR remains a commonly used indicator because it can be readily obtained. In this study, we discuss the application of FNR under conditions of strong photolysis rates to minimize potential misclassification.

O₃ formation occurs not only at the surface but also at elevated altitudes in the troposphere (Hu et al., 2024). Moreover, due to atmospheric convection, elevated O₃ can be dispersed downward to the near-surface layer (Souri et al., 2021). Indeed, study of O₃ production within the planetary boundary layer (PBL) is more important than at the surface alone. VOCs, such as isoprene emitted from vegetation, can be vertically transported to higher layer, where they produce RO_x radicals and secondarily formed HCHO through photochemical processes. The vertical distributions of HCHO is therefore primarily driven by vertical transport and chemistry, which complicates the vertical formation of tropospheric O₃ (Souri et al., 2023b). To investigate the vertical sensitivity of O₃ formation, previous studies have employed column FNR observed by multi-axis differential optical absorption spectroscopy (MAX-DOAS) (Irie et al., 2021; Zhang et al., 2021; Ryan et al., 2023; Wang et al., 2025). Other studies have applied satellite-based techniques to assess the spatial sensitivity of O₃ formation (Duncan et al., 2010; Jin et al., 2017; Jung et al., 2022). By combining satellite and ground-based remote sensing, column FNR sheds light on the development of spatially and temporally targeted O₃ mitigation strategies.

The Pandora instrument is a passive UV-VIS spectrometer that observes solar photons over the 280–530 nm spectral range (Herman et al., 2009). The Pandonia Global Network (PGN) is a joint project supported by NASA and ESA, providing real-time, standardized, calibrated, and verified air quality data along with associated uncertainty estimates (<https://www.pandonia-global-network.org/>). With more than 200 operational stations worldwide, the PGN has been widely applied in atmospheric research. In particular, due to their high accuracy, Pandora instruments have served as Fiducial Reference Measurement (FRM) for validating satellite observations (Douros et al., 2023; Judd et al., 2020; Kim et al., 2023) and airborne spectrometers (Choo et al., 2023; Judd et al., 2019). Additionally, Pandora observations have successfully highlighted the seasonal and diurnal variations of air pollutants (Herman and Mao, 2024; Liu et al., 2024). Mouat et al. (2024) reported a complex, heterogeneous environment near an airport using Pandora data. With its two viewing geometries, namely direct-sun and sky-scan modes, Pandora quantitatively observes total column amounts and lower tropospheric column amounts of several trace gases,

including NO₂, HCHO, and SO₂ (Cede et al., 2021a, b). Furthermore, the instrument provides both column and vertical distribution information, making it appropriate for investigating the O₃ formation sensitivity. Nevertheless, no studies have employed Pandora to analyze O₃ formation sensitivity.

Increased levels of air pollution not only influence health but also place a burden on socioeconomic costs and healthcare resources (Xu et al., 2025). Japan is facing the problem of an aging population that is more vulnerable to air pollution. A modeling study predicted that 80 % of Japan's population could be exposed to the highest levels of O₃ between 2030 and 2050 if no climate change mitigation policies are implemented (Chen et al., 2024). Looking back on history, the first episode of photochemical air pollution occurred in 1970, leading to the hospitalization of schoolchildren and high school students (Akimoto, 2017). In response, the government has implemented stringent emission controls since the 1980s, leading to a 56 % reduction in NO_x and a 50 % reduction in VOCs emissions from 2000 to 2019 (Chatani et al., 2023). Despite the emission reductions, O₃ level remain unpredictable due to non-linear photochemical processes and an increase in transboundary transport (Akimoto, 2017; Irie et al., 2021). Therefore, extensive studies on O₃ formation are needed to more efficiently mitigate human exposure.

In this study, we first utilized both Pandora direct-sun and sky-scan modes to analyze O₃ formation sensitivity at different altitudes and latitudes across Japan. The Japan Pandora Network (JPN), as part of the PGN, has established more than 10 stations, providing real-time vertical measurements. Because FNR threshold values depend on the study region, meteorological conditions, and emissions, we applied the GEOS-Chem chemical transport model to determine region-specific FNR thresholds for Japan. To improve accuracy, we accounted for secondary HCHO contributions. The findings of this study provide scientific insights into the application of Pandora measurements for mitigating regional O₃ pollution.

2. Methodology

2.1 Surface measurements

To obtain surface concentrations of HCHO and NO₂, we conducted in situ measurements at Tokyo Metropolitan University (Tokyo-TMU) during the summer (July 1–19) and fall (October 17–31) of 2022. NO₂ was measured using a cavity attenuated phase shift (CAPS) analyzer, which directly detects NO₂ by measuring absorption around 450 nm, with a detection limit of less than 0.1 ppb (Choi et al., 2020). Meanwhile, HCHO was obtained using a selected ion flow tube mass spectrometer (SIFT-MS). SIFT-MS utilizes precursor ions such as H₃O⁺, NO⁺, and O₂⁺ for ionization and detection of target substances (Langford et al., 2023; Roberts et al., 2022). This instrument is recommended as an efficient method for the measurement of HCHO in both indoor and outdoor environments (Zogka et al., 2022).

Surface O₃ concentrations were obtained from nearby air monitoring stations using the UV absorption method. These stations are operated by the Atmospheric Environmental Regional Observation System (AEROS) (<https://soramame.env.go.jp/>).

2.2 Tropospheric column amounts and vertical profiles derived from Pandora observations

Pandora spectrometer consists of a head sensor, an optical fiber transmission system, and a charge-coupled device (CCD) used as a spectral detector. The data retrieval begins with the raw measurement spectra (L0). The corrected signal (L1) is obtained by applying complex corrections, such as dark correction, latency correction, etc. Spectral fitting (L2Fit) is performed to derive slant column densities relative to a reference spectrum using the differential optical absorption spectroscopy (DOAS) method. Finally, L2 data is produced by converting slant columns into vertical columns utilizing geometrical air mass factors (AMFs) for the direct-sun mode and analytical methods for the sky-scan mode (Rawat et al., 2025). The direct-sun mode measures total NO₂ column with high precision (2.7×10^{14} molecules cm⁻²) and accuracy (2.7×10^{15} molecules cm⁻²). For total HCHO column, a statistical error of 6 % and a systematic error of 26 % have been reported (Spinei et al., 2018). The bias of the sky-

scan measurement is approximately -0.02×10^{16} molecules cm^{-2} for NO_2 and -0.05×10^{16} molecules cm^{-2} for HCHO (Tirpitz et al., 2021; Verhoelst et al., 2021). In this study, we explored both the tropospheric column FNR and vertical FNR profile by combining the direct-sun and sky-scan modes of Pandora. In the direct-sun mode, the tropospheric columns of NO_2 and HCHO were derived by subtracting the stratospheric contribution. This stratospheric information was derived from the GEOS-Chem model (Sect. 2.3). In addition to column densities in the lower troposphere (up to an altitude of 3 km), the sky-scan measurements provided vertical distributions from the surface up to an altitude of 3 km with several layers of measurements. These profiles are crucial for examining the vertical characteristics of NO_2 and HCHO, as well as O_3 production in the troposphere.

We used the Pandora data at four JPN stations, Sapporo, Tsukuba-NIES, Tokyo-TMU, and Fukuoka. These stations, listed from north to south, were chosen to investigate FNR across different latitude environments. A brief description of these Pandora stations is provided in Table S1 of the Supplementary Information. These Pandora instruments routinely alternate between direct-sun and sky-scan modes on a standard schedule (Cede et al., 2021a). Data processing was performed using the Blick software, which converts L0 (raw measurement spectra) to L2 products (e.g., vertical column densities, profiles, etc.). For FNR calculations, L2 products were employed. To maximize the available scientific data, we applied a new filtering method adopted from Rawat et al. (2025). The cut-off values were defined as the mean plus three standard deviations of the independence uncertainty for data with a high-quality flag. Data with independence uncertainty exceeding the cut-off value was removed. We also excluded data with a solar zenith angle (SZA) $> 75^\circ$ (Mouat et al., 2024). Using this filtering method, the data volume increased significantly by 5–30 % for NO_2 and 20–70 % for HCHO, compared to the filtering method that uses high and medium data quality flags.

2.3 Model simulations and determination of FNR thresholds

To characterize the FNR thresholds, we investigated the response of O_3 to emission perturbations using the GEOS-Chem model. GEOS-Chem is a three-dimensional chemical transport model driven by assimilated meteorological observations from the Goddard Earth Observing System (GEOS) of the NASA Global Modeling and Assimilation Office (GMAO) (<http://www.geos-chem.org>). To simulate O_3 , HCHO, and NO_2 for the year 2022, we used the high-performance GEOS-Chem (GCHP) model, version 14.4.0 (The International GEOS-Chem User Community, 2024). GCHP is described by Eastham et al. (2018). Improved advection, resolution, performance, and community access are described by Martin et al. (2022). In the current study, we configured four model runs.

For Run-1, global anthropogenic emissions were based on the Community Emissions Data System version 2 (CEDSV2) (McDuffie et al., 2020). We used the Regional Emission inventory in ASia version 3.2.1 (REASv3.2.1) (Kurokawa and Ohara, 2020), as the regional anthropogenic emissions override the global anthropogenic emissions for Japan. Biomass burning emissions were taken from the Global Fire Emissions Database version 4 (GFED4) (Van Der Werf et al., 2017). Additionally, dust, sea salt aerosol, soil NO_x , lightning NO_x , and biogenic VOCs emissions were computed offline (Weng et al., 2020). All emissions were configured at run-time using Harmonized Emissions Component (HEMCO, version 3.9.3) (Lin et al., 2021). Table S2 provides a detailed description of the emission inventories used in the model simulation. For meteorology, we used MERRA-2 ($0.5^\circ \times 0.625^\circ$), a global atmospheric reanalysis data product. The full-chem model simulations use chemical mechanism kinetics following JPL/IUPAC recommendations (Bates et al., 2024). Photolysis frequencies for stratospheric and tropospheric chemistry are calculated with Cloud-J v7.7.3 (Prather, 2015). Stratospheric chemistry is represented by a linear chemistry mechanism, the Linoz algorithm (McLinden et al., 2000). The Linoz stratospheric chemistry package is recommended for GEOS-Chem simulations of O_3 . More details on the chemical mechanisms are available at <http://www.geos-chem.org>. In our study, the simulations were run using a 10-minute time step for chemistry and a 5-minute time step for transport. Moreover, we applied the grid-stretching capability to focus on the Japan region. The grid-stretching procedure followed Bindle et al. (2021), with an initial cubed-sphere grid of C90, a target latitude of 37° , a target longitude of 137° , and

165 a stretch factor of 4. This procedure yielded an average horizontal resolution of 27.78 km over Japan. The simulation generated the vertical extent from the surface to approximately 80 km with a 72 vertical-layer grid. Surface concentrations were obtained from the first model layer. The tropospheric column and the stratospheric column were separated using tropopause information. Furthermore, this troposphere-stratosphere distribution was used to derive the tropospheric column from the Pandora direct-sun observations.

170 Run-2 was the same as Run-1 but with all anthropogenic HCHO emissions turned off. Secondary HCHO reflects the VOCs activity through photolysis reactions. Previous studies have highlighted the importance of separating secondary HCHO from anthropogenic HCHO for a more accurate interpretation of the FNR (Hong et al., 2022; Xing et al., 2022; Xue et al., 2022). By comparing Run-1 and Run-2, we determined the contribution of primary HCHO and excluded it from the FNR calculation.

Run-3 and Run-4 were the same as Run-2 but with a 20 % reduction in regional NO_x and VOC emissions, respectively. 175 Ozone concentrations result from both in situ photochemical creation and external transport processes (Hong et al., 2022; Qian et al., 2024). A key advantage of the model-based method is that it allows us to exclude external transport processes, leading to a more precise classification of the O₃ chemical regime. The external O₃ transport influence was eliminated by subtracting Run-3 or Run-4 from Run-2. This step further reflects the response of O₃ to changes in NO_x and VOCs. Figure S1 shows an example of the surface O₃ response to VOC and NO_x emission reductions, resulting from GEOS-Chem simulations. Both 180 negative and positive O₃ changes were observed in response to NO_x emission reduction. In contrast, VOC emission reduction consistently led to decreases in O₃ levels. The Greater Tokyo Metropolitan Area was strongly influenced by these emission perturbations.

Regarding the responses, the O₃ sensitivity regime was categorized following the method of Jin et al. (2017) and Jung et al. (2022). Instead of the term VOC-limited regime, here we used the term “RO_x-limited regime” for more accuracy present 185 for the radical-limited regime. A negative change in O₃ owing to NO_x emission reduction indicates a RO_x-limited regime. A NO_x-limited regime is defined when the positive change in O₃ owing to VOC emission reduction is smaller than that from NO_x emission reduction. The FNR threshold values for RO_x-limited and NO_x-limited regimes were determined as those corresponding to the 95th percentile of the cumulative probability distribution for each regime.

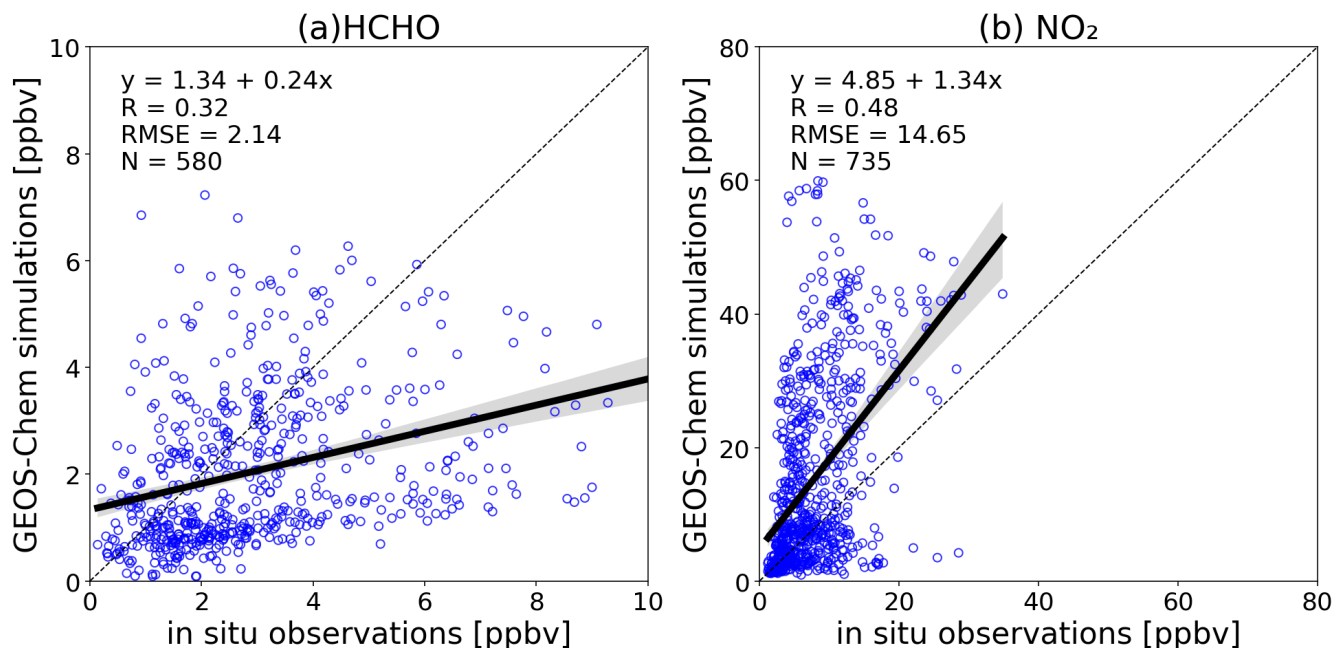
3. Results and discussion

190 3.1 Model simulations of HCHO, NO₂, and O₃

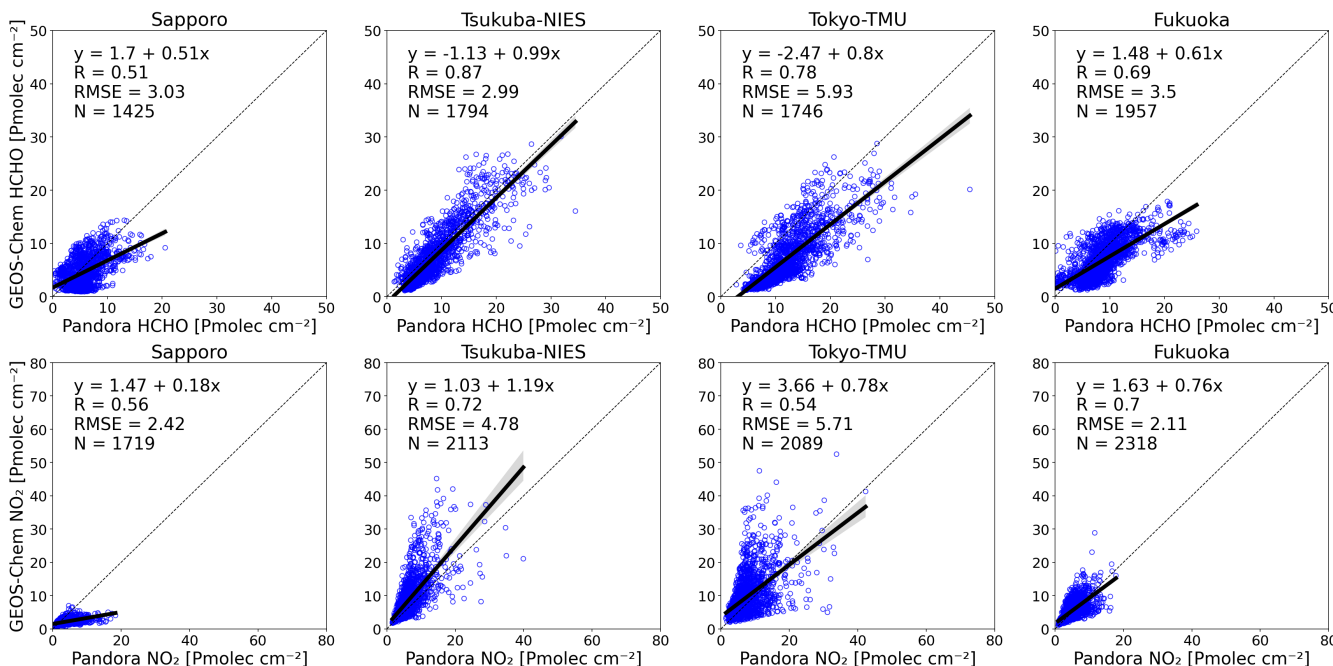
3.1.1 Comparison with in situ and Pandora measurements

The correlation statistics between the GEOS-Chem simulations (Run-1) and in situ measurements are shown in Fig. 1, and those with Pandora are shown in Fig. 2. The GEOS-Chem simulations underestimated the surface HCHO concentrations, with a slope of 0.37, a correlation coefficient (R) of 0.32, and a root mean square error (RMSE) of 1.56 ppbv. Meanwhile, the 195 GEOS-Chem overestimated the surface NO₂ concentrations, with a slope of 1.34, R = 0.48, and RMSE = 14.65 ppbv. However, the GEOS-Chem simulations aligned better with the Pandora tropospheric column densities. Specifically, the correlation coefficients between GEOS-Chem and Pandora for HCHO and NO₂ were 0.51 and 0.56, respectively, for Sapporo, 0.87 and 0.72 for Tsukuba-NIES, 0.78 and 0.54 for Tokyo-TMU, and 0.69 and 0.70 for Fukuoka. The RMSE varied from 2.99 to 5.93 Pmolec cm⁻² for HCHO and from 2.11 to 5.71 Pmolec cm⁻² for NO₂. The surface conditions are likely more complex compared 200 to the tropospheric column, which could explain why the GEOS-Chem model imperfectly captured the surface characteristics. Additionally, the local emission inventory implemented in the model was based on the year 2015, which might cause a significant bias in the model results. The diurnal cycles of HCHO and NO₂ simulated by the GEOS-Chem model were compared with in situ measurements (Fig. S2) and Pandora (Fig. S3). The GEOS-Chem model successfully reproduced the surface diurnal cycle of HCHO. For surface NO₂, the simulation captured the diurnal cycle in October quite well, but

205 dramatically overestimated NO_2 concentrations in July. Both the Pandora observations and the GEOS-Chem simulations showed a midday decrease in tropospheric NO_2 columns. The GEOS-Chem model also simulated the growth in HCHO from the morning; however, it showed a slight decrease after 2:00 PM. A larger difference between the model and Pandora was observed at Tokyo-TMU, where primary HCHO emissions are significant.



210 **Figure 1: Scatter plots of the surface HCHO (a) and NO_2 (b) comparing in situ measurements with GEOS-Chem model simulation at Tokyo-TMU. The y-axis represents GEOS-Chem simulations, and the x-axis represents in situ observations. The dashed line indicates the 1:1 line.**



215 **Figure 2: Scatter plots of tropospheric vertical column densities of HCHO (top panels) and NO_2 (bottom panels) between the Pandora direct-sun measurements and GEOS-Chem model simulations. The dashed line indicates the 1:1 line.**

For surface O_3 , we compared the GEOS-Chem model performance with in situ measurements from nearby air monitoring stations at the four Pandora locations. The GEOS-Chem simulation was able to reproduce the inverted U-shaped pattern of O_3 but showed positive biases (15–25 ppbv) (Fig. 3). The O_3 depletion during nighttime was not well generated by the GEOS-Chem model, resulting in overestimated concentrations during photochemical periods. The faster nighttime depletion rate of O_3 at Tokyo-TMU and Tsukuba-NIES suggests stronger deposition, which was not reflected by the model simulation. High positive biases in surface O_3 have been reported in the literature (Travis et al., 2016; Travis and Jacob, 2019). The diurnal

variations in mixed-layer dynamics and ozone deposition velocities in the model are one of the key factors contributing to this bias (Travis and Jacob, 2019). However, GEOS-Chem generally captured the observed variations in daytime O₃, such as large fluctuations at Tokyo-TMU and Tsukuba-NIES, and narrower variations at Fukuoka and Sapporo. The agreement between model simulation and in situ measurements was moderate, with an R of 0.56, 0.61, 0.53, and 0.59 for Sapporo, Tsukuba-NIES, Tokyo-TMU, and Fukuoka, respectively. Overall, the GEOS-Chem model could capture O₃ production at the study locations, indicating its suitability for investigating the O₃ sensitivity regime.

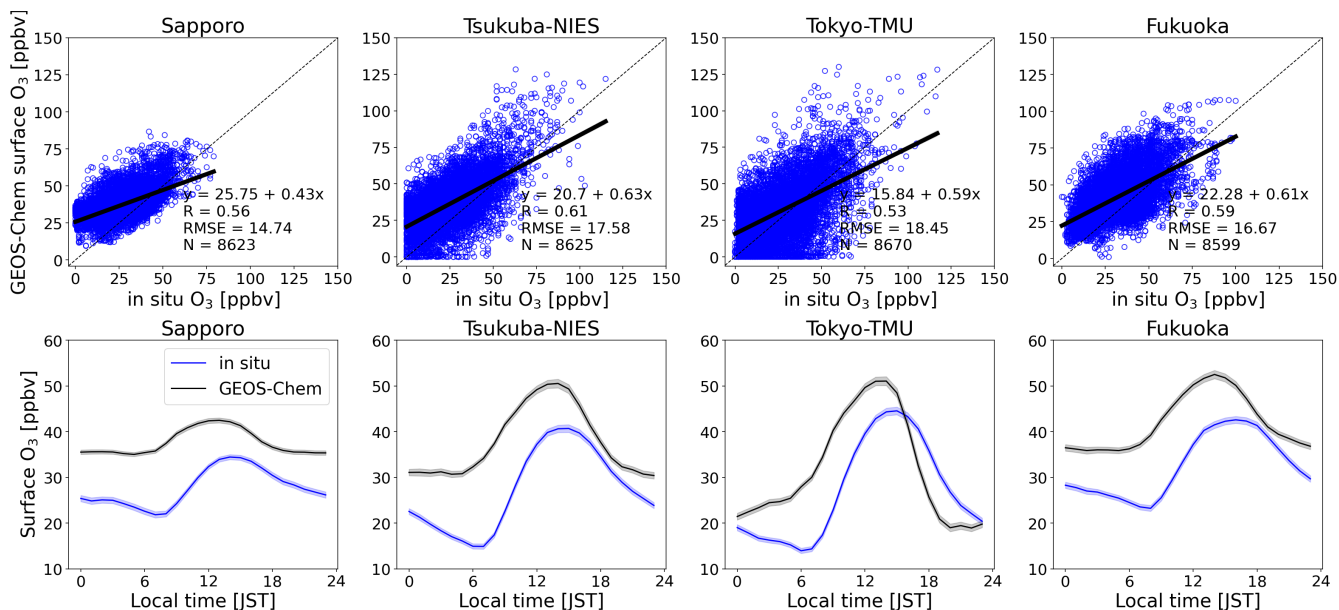


Figure 3: Comparison of hourly surface O₃ between the GEOS-Chem model and in situ measurements at the study locations. The top-row panels show scatterplots with linear regression equations. The bottom-row panels present the diurnal cycles of surface O₃, with shaded error bands indicating ± 1 standard error.

3.1.2 Contribution of secondary HCHO

Table 1 shows the contributions of secondary HCHO at the study locations, derived from the GEOS-Chem simulations. We only considered daytime simulation from 8:00 to 16:00, when photochemical reactions actively occur. Basically, secondary HCHO contributed the majority at the surface level, with values of 86 %, 87 %, 76 %, and 90 % at Sapporo, Tsukuba-NIES, Tokyo-TMU, and Fukuoka, respectively. The contribution of primary HCHO was slightly higher at Tokyo-TMU (24 %). The secondary HCHO contribution increased in summer and decreased in winter. A diurnal variation of the contribution of secondary HCHO was observed, with the highest contribution around noon (not shown). For the tropospheric column, the seasonal contribution of secondary HCHO remained consistent. Additionally, the secondary HCHO contribution increased with altitude (Fig. S4a). The contribution at altitudes above 2 km was almost entirely attributed to secondary formation. This vertical distribution depends on primary emission sources, VOC oxidation, and photolysis rates. The higher photolysis frequency above 2 km compared to surface (Fig. S4b) therefore enhanced VOC oxidation as well as the magnitude of O₃ production. Secondary HCHO effectively represents a proxy for VOC reactivity (Su et al., 2019; Xue et al., 2022). For more accurate FNR calculation, these secondary HCHO contributions from the model simulations were adopted for both in situ and Pandora measurements. The FNR using secondary HCHO is referred to as FNR_{sec}. This approach is particularly important in areas with a high contribution of primary sources of HCHO, for example, urban and industrial areas.

Table 1: Contribution of secondary HCHO (%) at the surface level and in the tropospheric columns, obtained from the GEOS-Chem model simulation at the JPN sites. The statistical values were considered only for 8-hour daytime simulations (8:00 to 16:00).

Location		Spring	Summer	Fall	Winter	Annual average
Sapporo	Surface	89 ± 13	98 ± 1	91 ± 9	65 ± 15	86 ± 17
	Tropospheric column	98 ± 2	99 ± 0	98 ± 2	93 ± 3	97 ± 3

Tsukuba-NIES	Surface	89 ± 11	96 ± 4	91 ± 10	74 ± 16	87 ± 14
	Tropospheric column	96 ± 4	99 ± 1	97 ± 3	90 ± 6	95 ± 5
Tokyo-TMU	Surface	76 ± 16	92 ± 8	77 ± 19	58 ± 22	76 ± 21
	Tropospheric column	91 ± 5	97 ± 2	93 ± 5	85 ± 8	92 ± 7
Fukuoka	Surface	90 ± 9	97 ± 3	92 ± 8	79 ± 13	90 ± 11
	Tropospheric column	97 ± 3	99 ± 0	98 ± 2	94 ± 3	97 ± 3

3.2 Overall levels of HCHO and NO₂

250 3.2.1 Surface levels

The diurnal plots of HCHO and NO₂ obtained from in situ measurements at the Tokyo-TMU site are shown in Fig. S2. Near the surface, HCHO concentrations fluctuated within a narrow range of a few ppbv throughout the day. The minimum occurred at mid night, while the peak was observed around noon (in July) or late afternoon (in October). HCHO concentrations are generally expected to be higher in summer due to enhanced photochemical reactions driven by stronger solar irradiance and increased biogenic VOCs emissions from the local flora (Irie et al., 2021). However, interestingly, we found negligible differences in surface HCHO concentrations between July and October. The mean HCHO concentrations in July and October were 2.77 ± 1.73 and 3.06 ± 2.10 ppbv, respectively.

260 Surface NO₂ concentrations were twice as high in October compared to July. In July, the NO₂ mixing ratio ranged from 0.90 to 21.10 ppbv, with an average of 5.98 ppbv. In October, the surface NO₂ ranged from 1.24 to 39.13 ppbv, with an average of 9.91 ppbv. Peaks in July were not clearly defined. In contrast, October showed a small peak in the morning and a larger one around 18:00, exhibiting traffic emissions, while minimum concentrations occurred at noon due to photochemical loss. The finding that the diurnal trend of NO₂ was opposite to that of HCHO can be explained by photochemical reactions. These diurnal cycles have been well documented in previous studies (Irie et al., 2011; Itahashi and Irie, 2022).

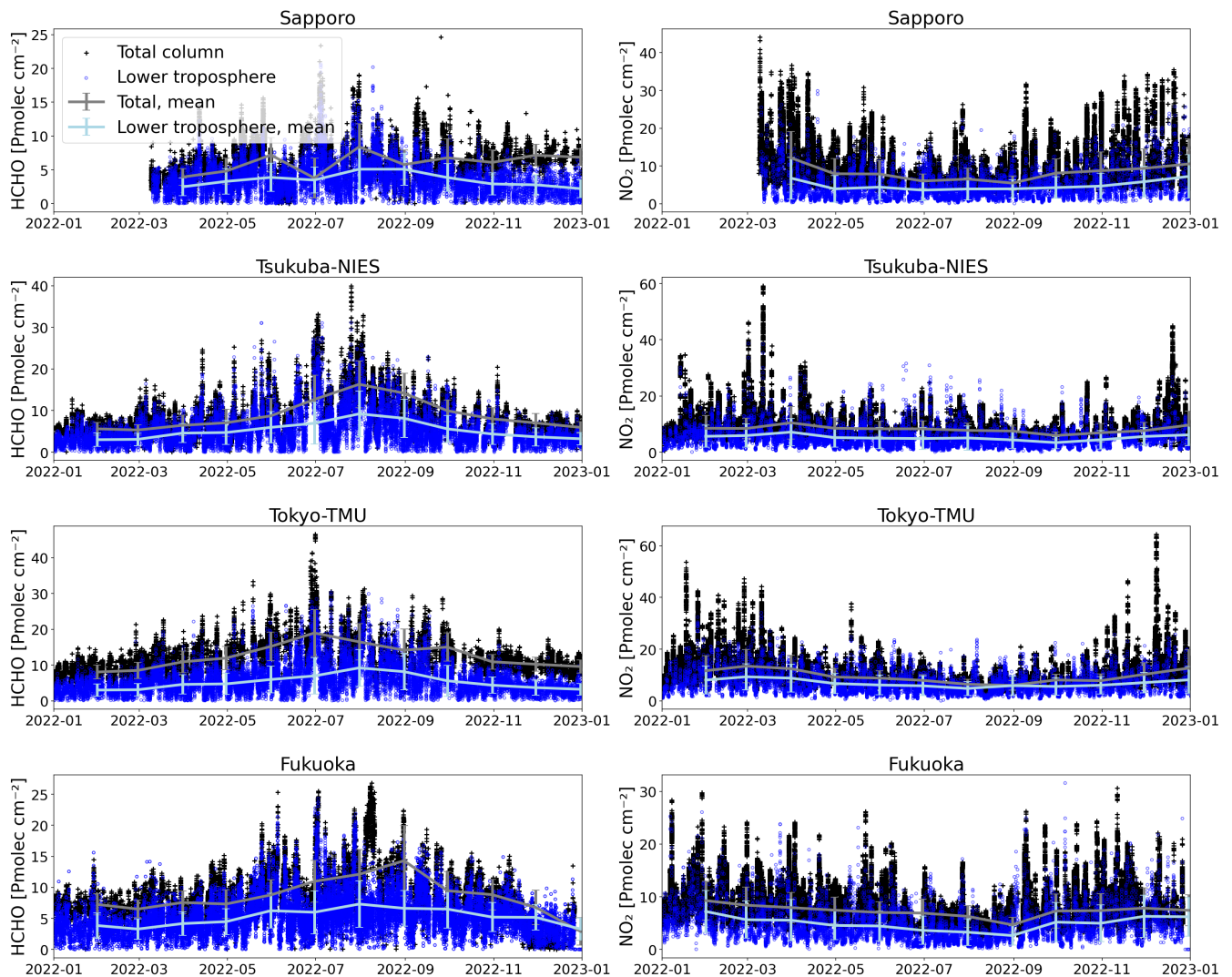
3.2.2 Vertical column amounts

265 Figure 4 shows the variation in vertical column density (VCD) of HCHO measured by the Pandora spectrometer in 2022 at the study sites. The highest total VCD was observed at Tokyo-TMU, with a mean value of 12.30 ± 4.99 Pmolec cm⁻². The levels at Sapporo, Tsukuba-NIES, and Fukuoka were 6.01 ± 2.84 , 8.97 ± 5.05 , and 9.05 ± 4.02 Pmolec cm⁻², respectively. According to the GEOS-Chem simulations, the contribution of primary HCHO at Tokyo-TMU was higher than that at the other study sites (Table 1), indicating that the elevated column amount at Tokyo-TMU was largely influenced by local emission of anthropogenic sources. Clearly, the HCHO column amounts tended to be higher in summer and lower in winter. As discussed in Sect. 3.2.1, the difference in surface HCHO concentrations between July and October at Tokyo-TMU was not statistically significant. However, the total HCHO VCD measured by Pandora in July (16.47 ± 5.05 Pmolec cm⁻²) was 1.5 times higher than that in October (10.90 ± 2.05 Pmolec cm⁻²). Additionally, we found a strong relationship between column densities and surface concentrations, with a correlation of 0.7 for HCHO (Fig. S5). The correlation slope was about three times higher in July than in October, likely due to enhanced HCHO production at higher altitudes during summer. This suggests that column information is essential and complement to surface measurements for fully representing atmospheric HCHO.

275 The lower tropospheric column (up to an altitude of 3 km) of HCHO (obtained from the sky-scan mode) accounted for 59.14 ± 18.83 % at Sapporo, 65.86 ± 14.84 % at Tsukuba-NIES, 49.04 ± 16.76 % at Tokyo-TMU, and 62.27 ± 16.66 % at Fukuoka, relative to the total column amount (obtained from the direct-sun mode). This lower tropospheric contribution was dominant in summer, ranging from 61.27 % to 71.65 %, and decreased in winter, varying from 32.92 % to 54.93 %. However, it should be noted the error budget in Pandora direct-sun HCHO (Spinei et al., 2018). This error budget can overestimate the total column density. The diurnal cycle of the tropospheric HCHO column is shown in Fig. S3. The tropospheric column

measured by Pandora exhibited a continuous increase from the morning to the afternoon. The accumulation of HCHO and the decreasing rate of photolysis in the afternoon can explain this daily cycle of HCHO (Souri et al., 2023b; Zhang et al., 2021).

285 In contrast to the HCHO trend, the NO₂ column amounts reached their minimum in summer (Fig. 4). Tokyo-TMU was also polluted with NO₂, with an average of 9.73 ± 4.99 Pmolec cm⁻² (12.55 ± 6.52 Pmolec cm⁻² in winter and 6.80 ± 2.17 Pmolec cm⁻² in summer), followed by Tsukuba-NIES with an average of 8.33 ± 3.88 Pmolec cm⁻² (8.83 ± 4.42 Pmolec cm⁻² in winter and 7.84 ± 2.50 Pmolec cm⁻² in summer). The total NO₂ VCDs at Sapporo and Fukuoka were 7.92 ± 4.45 Pmolec cm⁻² and 7.22 ± 3.01 Pmolec cm⁻², respectively. The lower tropospheric column contributed 51.38 ± 20.86 %, 53.95 ± 18.06 %
290 %, 59.55 ± 16.79 %, and 56.29 ± 18.83 % to the total column at Sapporo, Tsukuba-NIES, Tokyo-TMU, and Fukuoka, respectively. We also found good agreement for NO₂ between lower tropospheric column densities and surface concentrations, with a correlation of 0.6 (Fig. S5). The slope was similar in July and October, reflecting that NO₂ is mainly concentrated near the surface.



295 **Figure 4:** Time series plots of vertical column densities of HCHO (left column) and NO₂ (right column) at the study locations in 2022. Black plus signs represent total column densities derived from the Pandora direct-sun mode, whereas blue dots indicate lower tropospheric columns (up to an altitude of 3 km) derived from the Pandora sky-scan mode. Solid lines show monthly means, and error bars represent standard deviation. (1 Pmolec cm⁻² = 1×10¹⁵ molecules cm⁻²).

300 3.2.3 Vertical profiles

The Pandora sky-scan mode measures scattered sunlight at several angles, yielding the vertical profiles. The resolution of the vertical profiles depends on the number of scanning angles, referred to as elevation scan routines (i.e., detailed elevation scan

and quick elevation scan). Here, we used detailed elevation scans around noon to investigate the vertical distribution of HCHO and NO₂. The detailed elevation scan routine observes 14 angles without using filter and 12 angles using the U340 filter, respectively (Rawat et al., 2025). We converted these partial vertical columns to mixing ratios, assuming well-mixed conditions in each layer and the ideal gas law. To obtain the seasonal vertical distributions of HCHO and NO₂, after extrapolating into 0.1 km bins, the profiles were averaged by altitude. Since the altitudes of these four Pandora stations ranged from 45 to 135 m, and the maximum vertical sensitivity of the sky-scan mode was generally within 2 km, we only considered the vertical profile from 0.2 to 2 km. Figures 5 and 6 present the seasonal and time-series vertical profiles of HCHO and NO₂, respectively.

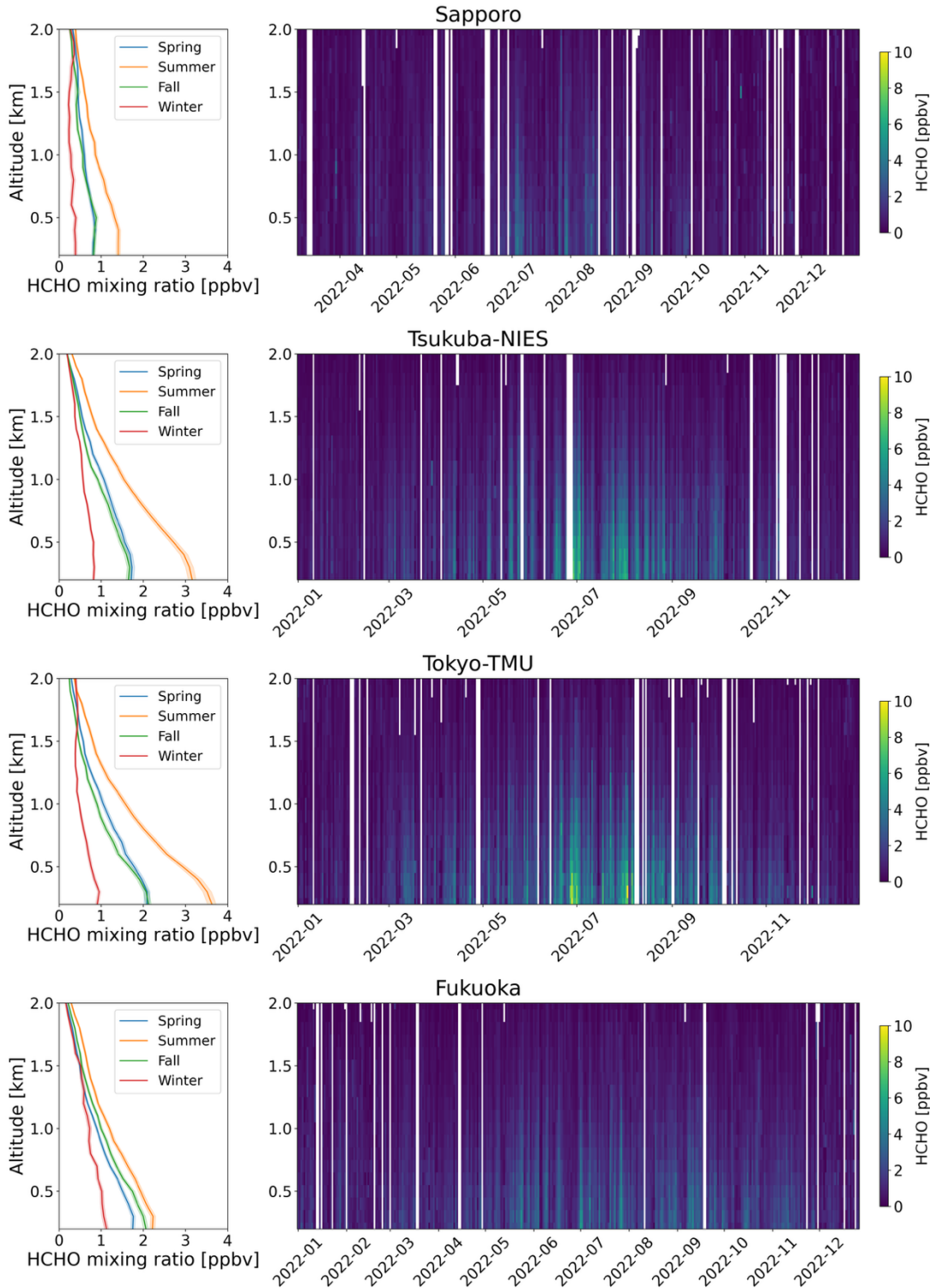
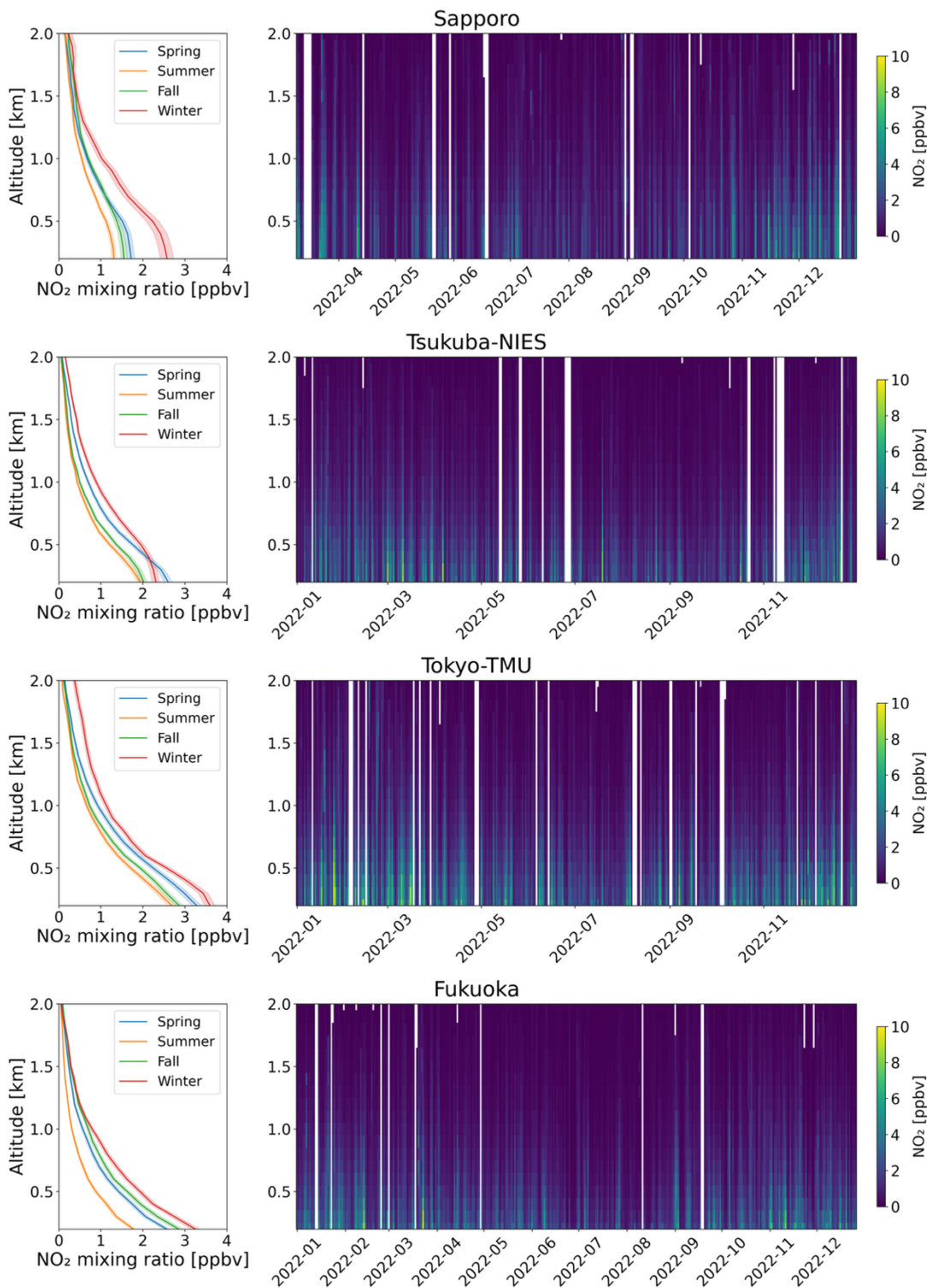


Figure 5: Seasonal (first column) and time series (second column) vertical profiles of HCHO derived from the Pandora sky-scan observations around noon ($12:00 \pm 2:00$). The seasonal vertical profiles are shaded with error bands indicating ± 1 standard error. Color bars exhibit HCHO mixing ratio.



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Figure 6: Seasonal (first column) and time series (second column) vertical profiles of NO₂ derived from the Pandora sky-scan observations around noon (12:00 ± 2:00). The seasonal vertical profiles are shaded with error bands indicating ±1 standard error. Color bars exhibit NO₂ mixing ratio.

The HCHO productions were significantly enhanced during summer due to stronger solar intensity and increased biogenic VOCs emissions such as isoprene. Secondary HCHO is associated with isoprene emitted from vegetation (Ryan et al., 2023). Isoprene emissions exhibit a markedly positive exponential relationship with temperature (Ryan et al., 2023; Wang et al., 2024). At higher temperatures in summer, more isoprene is emitted, which triggers the formation of secondary HCHO. The higher HCHO production at Tsukuba-NIES and Tokyo-TMU compared to Fukuoka suggests that, in addition to biogenic VOCs, anthropogenic VOCs play an important role in HCHO production (Fig. S6). Anthropogenic VOC emission accounted for 20 % of the total emission at the two locations. The summertime increase in anthropogenic VOCs emissions is likely driven by enhanced evaporation processes (Wu et al., 2024). The vertical variation of HCHO appeared to be relatively heterogeneous

in winter. However, we found less significant changes in the seasonal profiles at the highest latitude site (Sapporo). Vertically, HCHO formation was observed up to 2 km, which is consistent with previous studies (Lin et al., 2022; Shi et al., 2025b). HCHO extended to higher altitudes could be attributed to vertical and horizontal transport and chemistry (Souri et al., 2023c).
330 For a more accurate FNR analysis, it is essential to consider not only surface but also elevated measurements (Souri et al., 2025).

The NO₂ distributions more rapidly decreased with increasing altitude compared to HCHO. Unlike HCHO, the bulk of NO₂ was generally concentrated below 1 km because NO_x emissions are mainly near the surface (i.e., traffic). Normally, the vertical NO₂ profile was enhanced in winter. However, we also observed several spikes of NO₂ during summer at Tsukuba-
335 NIES. Generally, NO₂ concentrations are low in summer because of photochemical loss. The enhanced NO₂ profiles observed at Tsukuba-NIES during summer could be attributed to the transport of emissions from surrounding regions. Irie et al. (2021) reported that summertime air masses passing over Tokyo Bay area and reaching Tsukuba lead to a greater O₃ concentrations at this site.

To investigate whether any external transport affected the vertical profiles, we applied the Hybrid Single-Particle
340 Lagrangian Integrated Trajectory (HYSPPLIT) model for the Tsukuba-NIES case. The model, developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resources Laboratory (ARL), has been widely used for atmospheric trajectory and dispersion calculations (Stein et al., 2015). We simulated 48-hour backward trajectories for the year 2022, with endpoints at 13:00 local time (JST) at Tsukuba-NIES, as a case study. The backward trajectories were assigned into four clusters: c1, c2, c3, and c4. The number of clusters was optimized using total spatial variance (TSV) analysis. The cluster
345 frequencies were 15 %, 40 %, 36 %, and 9 % for c1, c2, c3, and c4, respectively (Fig. S7). Figure S8 shows the vertical profiles of NO₂ at Tsukuba-NIES during summer as a function of air mass clusters. During summer, cluster c1 occurred on only one day, clusters c2, c3, and c4 occurred on 34, 33, and 24 days, respectively. Thus, we observed elevated in NO₂ profiles during cluster c4, in which air masses passed through urban Tokyo and industrial areas, transporting anthropogenic pollutants to the Tsukuba-NIES site. This suggests that external pollution transport affected the vertical distributions of NO₂, and consequently,
350 O₃ production.

3.3 Identification of the O₃ sensitivity regime

The O₃, HCHO, and NO₂ outputs from the GEOS-Chem model simulations were utilized to identify the O₃ sensitivity regime (Fig. 7). From the scatter plots, the responses of surface O₃ to NO_x and VOC emission reductions at Sapporo and Fukuoka were within 5 ppbv, which were less pronounced than those at Tsukuba-NIES and Tokyo-TMU (within 10 ppbv). A positive
355 O₃ difference indicates that the emission reduction results in a decrease in surface O₃. Conversely, a negative difference means that the emission reduction enhances surface O₃ concentrations. In our study, generally, VOC emission reductions led to a decrease in surface O₃ concentrations. NO_x emission reductions could either decrease O₃ through photochemical reaction or increase it due to reduced LNO_x processes.

The FNR_{sec} threshold values were determined using both surface and column information (Fig. 7, cumulative graphs).
360 Based on surface FNR_{sec}, the RO_x-limited conditions were distinguished with thresholds of FNR_{sec} <0.2 for Sapporo, <0.29 for Tsukuba-NIES, <0.28 for Tokyo-TMU, and <0.18 for Fukuoka. The NO_x-limited regimes were associated with FNR_{sec} > 0.36 for Sapporo, and >0.91, >0.75, and >0.72 for Tsukuba-NIES, Tokyo-TMU, and Fukuoka, respectively. The surface FNR_{sec} thresholds were generally lower than the column FNR_{sec}. The finding of higher column FNR is consistent with previous studies (Jin et al., 2017; Souri et al., 2023a). The column FNR_{sec} thresholds for the RO_x-limited regimes and NO_x-limited
365 regimes at the Sapporo site were <0.86 and >1.52, respectively. The corresponding column FNR_{sec} threshold ranges for Tsukuba-NIES, Tokyo-TMU, and Fukuoka were 0.74–1.7, 0.62–1.53, and 0.43–1.73, respectively. The transitional regime seemed to occur over a wider range of column FNR_{sec} values at lower latitudes (e.g., Fukuoka) compared to higher latitudes (e.g., Sapporo). The differences between surface and tropospheric column FNR_{sec} could be attributed to the vertical

characteristics of HCHO and NO₂. NO₂ molecules were concentrated near the surface, while HCHO was present in the higher layers. As a result, surface FNR_{sec} did not account for HCHO at higher layers, leading to lower threshold values. The surface and column FNR_{sec} thresholds identified in this study are consistent with those reported by Jin et al. (2017) for East Asia (Table 2).

For the column, the transition range for Sapporo was defined as 0.86–1.52 where the cumulative probability of NO_x-limited and RO_x-limited condition reached 95 %, corresponding to a 5 % probability of misclassification. Consequently, 15 % of NO_x-limited and 15 % of RO_x-limited conditions were incorrectly classified as transitional (Fig. 7). Similarly, the probabilities of misclassifying NO_x-limited and RO_x-limited conditions as transitional were 20 % and 25 %, respectively, for Tsukuba-NIES, 35 % and 25 % for Tokyo-TMU, and 15 % and 60 % for Fukuoka. Notably, the probability of misclassification of RO_x-limited condition at Fukuoka was higher than at the other locations. Because we simulated for the year 2022, this uncertainty could be reduced by extending the model simulations to longer time periods.

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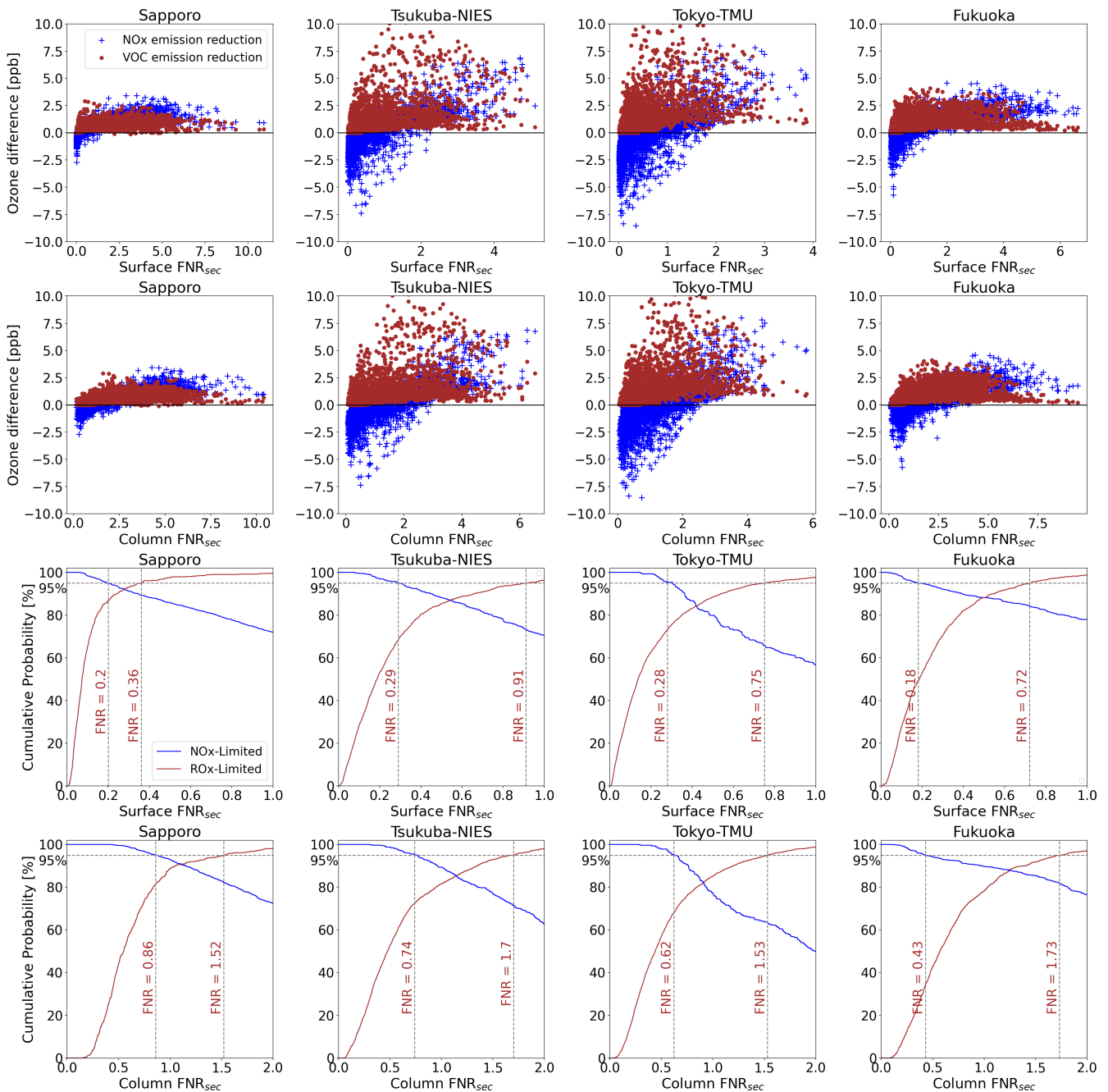


Figure 7: Response of surface O₃ to NO_x and VOC emission perturbations resulting from the GEOS-Chem simulations. The scatter plots depict the O₃ difference between GEOS-Chem Run-2 and Run-3 (blue), and between Run-2 and Run-4 (brown), as a function of surface FNR_{sec} (first row) and tropospheric column FNR_{sec} (second row). The VOC-limited regime was associated with negative

385 change in O₃ due to NO_x emission reduction. The NO_x-limited regime was identified when the positive change in O₃ due to VOC
 emission reductions was smaller than that from NO_x emission reductions. Line plots show the cumulative probability of NO_x-limited
 (blue) and VOC-limited (brown) conditions as a function of surface FNR_{sec} (third row) and tropospheric column FNR_{sec} (fourth
 row). The FNR_{sec} threshold values (vertical dashed lines) for VOC-limited and NO_x-limited regimes were determined as those
 corresponding to the 95th percentile (horizontal dashed lines) of the cumulative probability distribution for each regime.

390 Table 2 presents the column FNR regime thresholds related to surface O₃ sensitivity from previous studies. These threshold
 values vary depending on the methodology, geographic region, and atmospheric conditions. The FNR thresholds using both
 primary and secondary HCHO (FNR_{total}) are higher than those using only secondary HCHO (FNR_{sec}). The transitional regimes
 are reported for a column FNR_{total} of 2.5–4.0 in Guangzhou, China (Hong et al., 2022), and 1.6–2.6 in United States (Jung et
 al., 2022), whereas the column FNR_{sec} thresholds identified in our study were lower than 2. Column FNR regime threshold
 395 values are useful for examining global O₃ production, as both satellite and ground-based remote sensing techniques offer
 extensive spatial coverage (Inoue et al., 2019; Ryan et al., 2023; Santiago et al., 2021).

Table 2: Comparison of column FNR threshold values for O₃ sensitivity in previous studies using different methods.

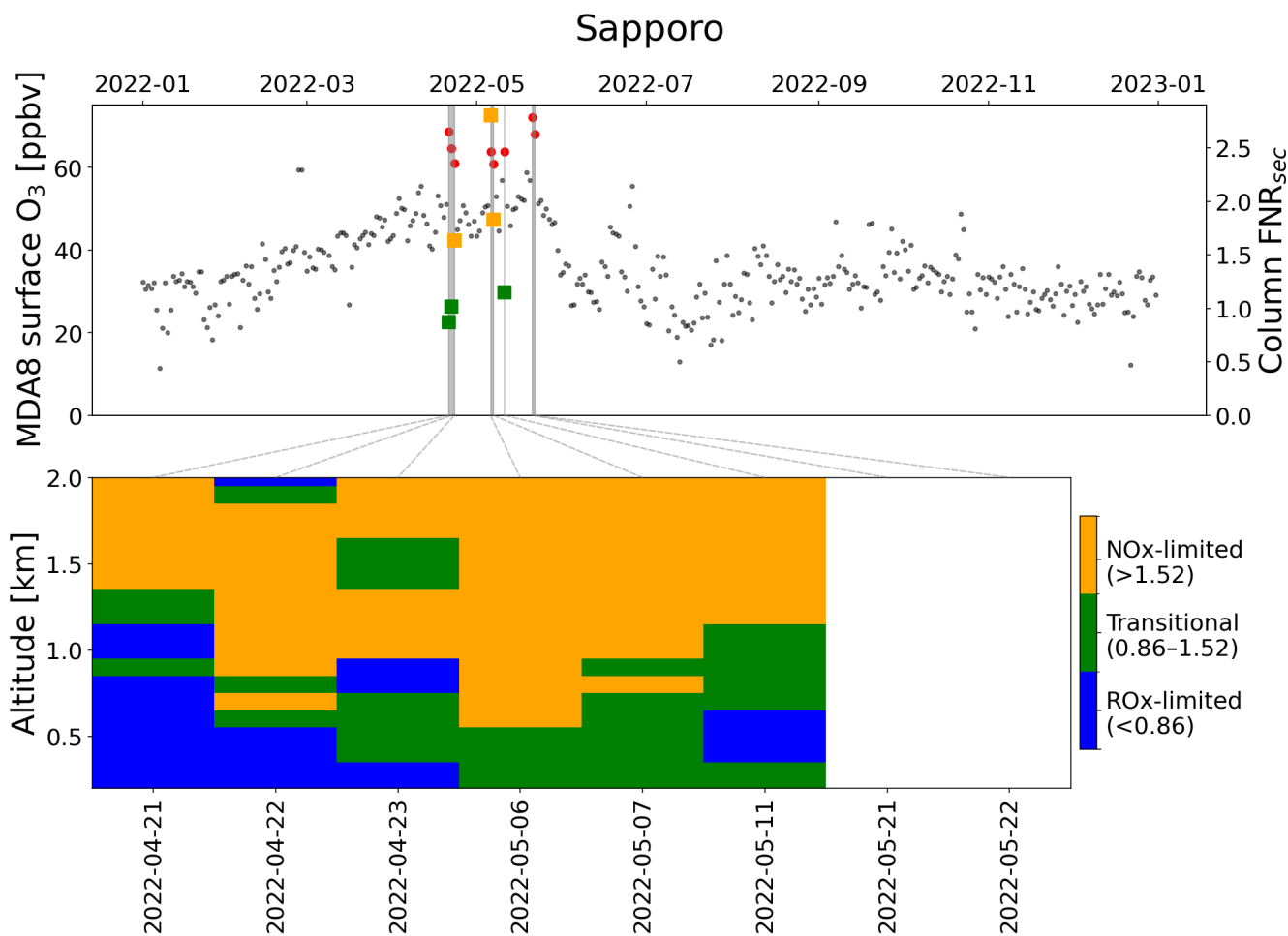
Study area	Indicator	Method	FNR _{total} threshold	FNR _{sec} threshold	Reference
			values	values	
North America	Column FNR _{total}	GEOS-Chem model	0.9–1.4	-	(Jin et al., 2017)
Europe	Column FNR _{total}	GEOS-Chem model	0.9–1.2	-	(Jin et al., 2017)
East Asia	Column FNR _{total}	GEOS-Chem mode	0.9–1.6	-	(Jin et al., 2017)
United States	Column FNR _{total}	CMAQ model	1.6–2.6	-	(Jung et al., 2022)
Guangzhou, China	Column FNR _{total}	Polynomial fit of O ₃	2.5–4.0	-	(Hong et al., 2022)
Sapporo	Column FNR _{sec}	GEOS-Chem model	-	0.86–1.52	This study
Tsukuba-NIES	Column FNR _{sec}	GEOS-Chem model	-	0.74–1.70	This study
Tokyo-TMU	Column FNR _{sec}	GEOS-Chem model	-	0.62–1.53	This study
Fukuoka	Column FNR _{sec}	GEOS-Chem model	-	0.43–1.73	This study

3.4 O₃ sensitivity during exceedance events

The diurnal and seasonal cycles of surface and column FNR are shown in Figs. S9 and S10. Surface FNR_{sec} developed in the
 400 early morning and decreased in the afternoon. During the 8-hour daytime period (8:00 to 16:00), the average surface FNR_{sec}
 was 0.99 ± 0.46 in July and 0.72 ± 0.64 in October. Using tropospheric vertical column densities derived from Pandora sky-
 scan observations, the column FNR_{sec} exhibited a higher value compared to those from surface measurements. Like surface
 FNR_{sec}, the tropospheric column FNR_{sec} grew during the morning. The highest column FNR_{sec} values were found during the
 summer months (JJA). In contrast, these values were normally below 1 in winter (DJF).

405 In this section, we analyze the O₃ formation sensitivity focusing on polluted days when the maximum daily 8-hour averaged
 surface O₃ (MDA8) exceeded 60 ppbv. We identified 8, 30, 38, and 43 exceedance events in 2022 at Sapporo, Tsukuba-NIES,
 Tokyo-TMU, and Fukuoka, respectively. During O₃ exceedance events, photochemical reactions were typically strong,
 allowing us to determine the sensitive regime with minimum biases. Because the model simulations did not reproduce surface
 NO₂ and HCHO as well as the column densities, we will focus only on column FNR. Although Pandora direct-sun mode
 410 provides highly accurate NO₂ measurements, the HCHO retrieval attains non-negligible error budget, which can cause more
 uncertainty and bias in the FNR. In contrast, Pandora sky-scan mode provides lower tropospheric columns of NO₂ and HCHO
 and yields lower uncertainty in the HCHO data product. Additionally, the sensitivity diagnosis within the boundary layer is
 better represent tropospheric O₃ production processes. Therefore, we discuss instead the column FNR_{sec} derived from Pandora
 sky-scan observations which is sensitive to the boundary layer. We averaged available sky-scan observations around noon
 415 ($12:00 \pm 2:00$), when photolysis rates are highest. Figures 8-11 present column FNR_{sec} during O₃ polluted events at Sapporo,
 Tsukuba-NIES, Tokyo-TMU, and Fukuoka, respectively. The advantage of Pandora observations is the ability to examine

daily O₃ production in greater detail and investigate specific periods such as exceedance events. Based on the analysis of these events, policy strategies could be proposed to help mitigate O₃ pollution.



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Figure 8: Sensitivity analysis of O₃ during MDA8 exceedance events at Sapporo. The top panel presents MDA8 surface O₃, with non-exceedance days indicated by black dots and exceedance days shown as red points with grey shadows. Squares depict the column FNR_{sec} derived from Pandora sky-scan measurements around local noon (12:00 ± 2:00). The bottom panel illustrates the vertical formation sensitivity of O₃ corresponding to exceedance events. The squares and color bars are colored according to FNR_{sec} threshold values determined from the GEOS-Chem model.

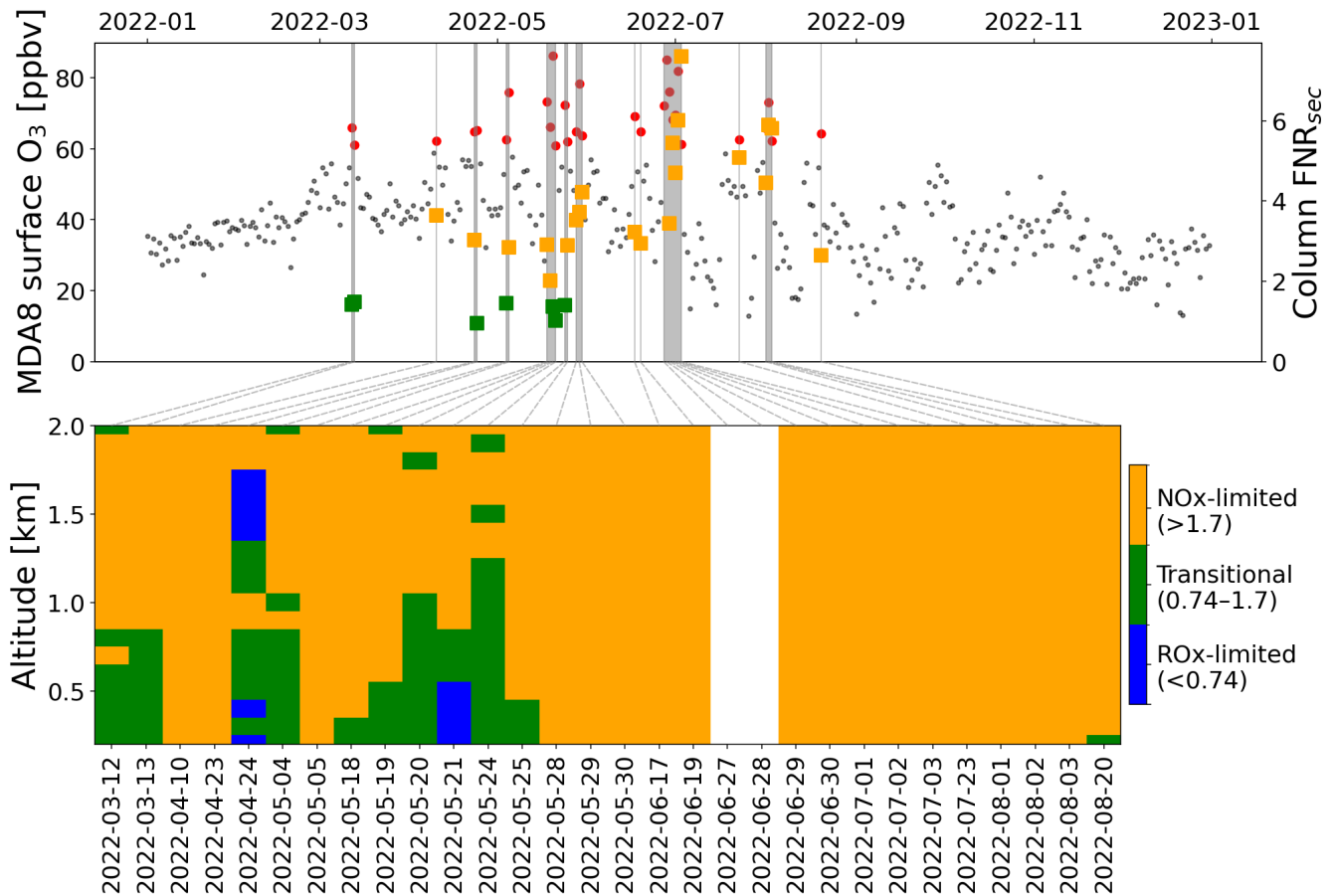
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At Sapporo, the O₃ concentrations increased during spring (Fig. 8). All eight events with MDA8 O₃ exceeding 60 ppbv occurred in April and May 2022. Pandora observations were unavailable on 21 and 22 May 2022. Given the transition range determined at Sapporo ($0.86 < \text{FNR}_{\text{sec}} < 1.52$), the column FNR_{sec} exhibited O₃ sensitivity in transitional and NO_x-limited regime. Therefore, reducing NO_x emission would be the optimal strategy for mitigating O₃ levels. The vertical sensitivity indicated that the RO_x-limited regime was typically confined to the near surface layer during events classified as transitional using column FNR_{sec}. Concurrently, the NO_x-limited regime frequently formed aloft, whereas the transitional regime formed in the mid-levels. Figure S11 in the SI illustrates the corresponding HCHO and NO₂ profiles for these exceedance events. Higher concentration of NO₂ on 21 and 22 April, concentrated below 0.5 km, led to a RO_x-limited regime within this layer. For events categorized as NO_x-limited (6-7 May) according to the column FNR_{sec}, the NO_x-limited regime dominated at higher altitudes and expanded downward to the surface, while the RO_x-limited regime retreated. Even during periods of high MDA8, the vertical profiles of both NO₂ and HCHO on 23 April and 6 May were low, suggesting that O₃ could be influenced by regional or vertical transport. This influence could be recognized using Pandora HCHO and NO₂ observations; however, further studies are needed to distinguish these events from local photochemical O₃ production.

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Tsukuba-NIES

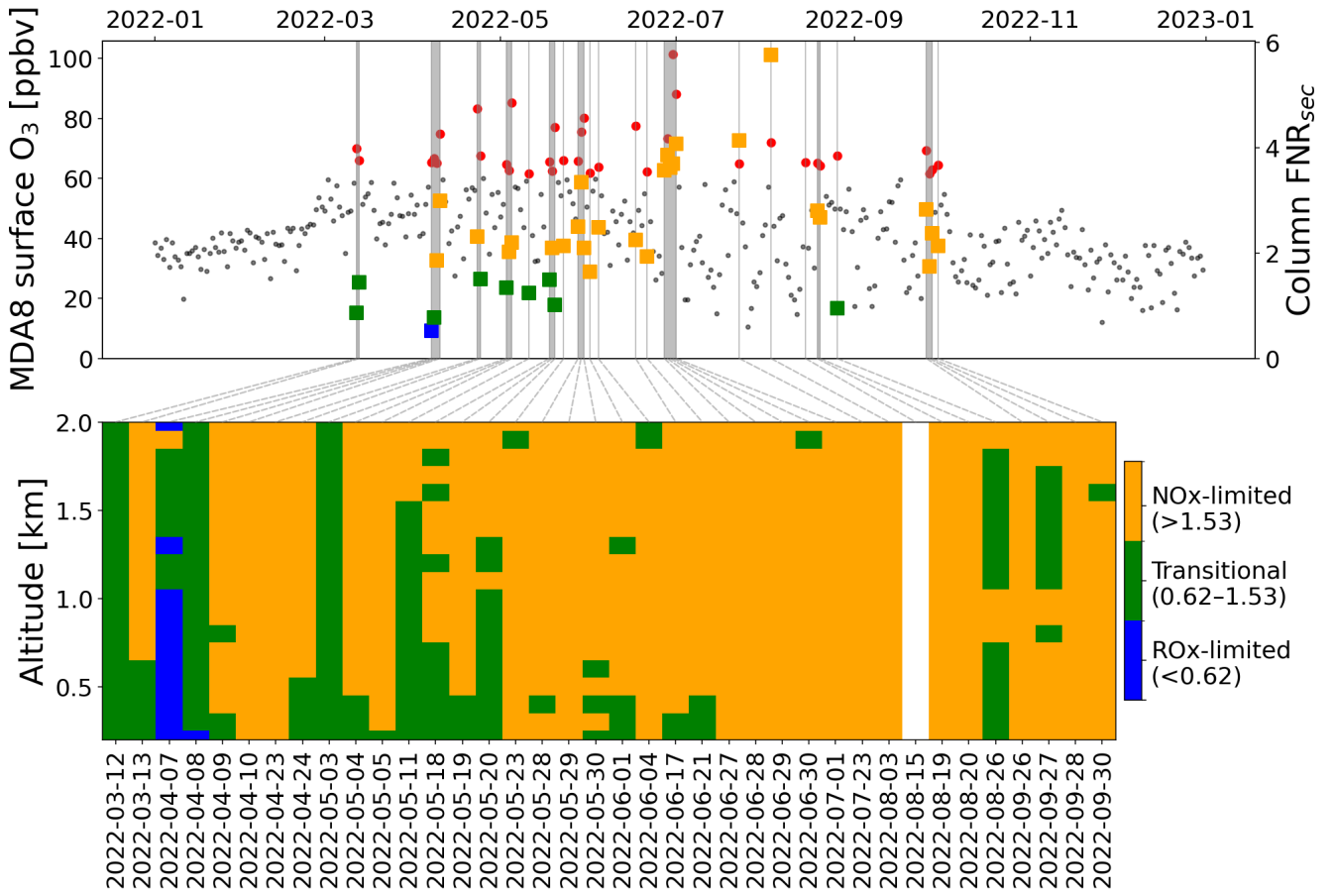


440 **Figure 9: Sensitivity analysis of O₃ during MDA8 exceedance events at Tsukuba-NIES. The top panel presents MDA8 surface O₃, with non-exceedance days indicated by black dots and exceedance days shown as red points with grey shadows. Squares depict the column FNR_{sec} derived from Pandora sky-scan measurements around local noon (12:00 ± 2:00). The bottom panel illustrates the vertical formation sensitivity of O₃ corresponding to exceedance events. The squares and color bars are colored according to FNR_{sec} threshold values determined from the GEOS-Chem model.**

445 Figure 9 is similar to Figure 8, but for Tsukuba-NIES. Compare with Sapporo, more O₃ exceedance events were found at Tsukuba-NIES, with 30 events in 2022. These events primarily took place during spring and summer. Like the results at Sapporo, the column FNR_{sec} exhibited transitional and NO_x-limited conditions during spring events, whereas O₃ chemistry was almost entirely NO_x-limited during summer events, likely due to substantial enhancement in HCHO production (Fig. S11). Regarding vertical sensitivity, we determined a lower probability of RO_x-limited regime during the spring events. During

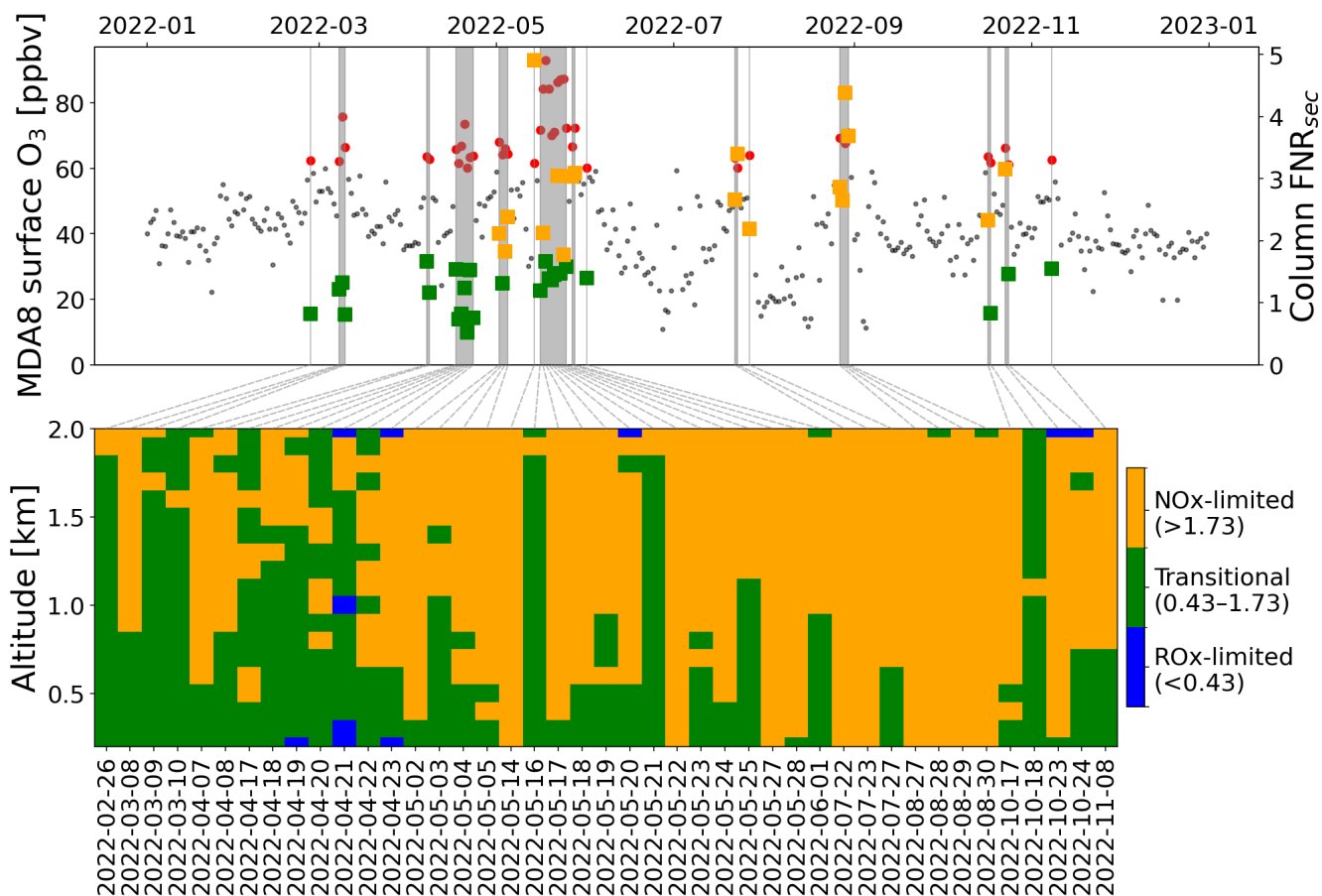
450 summer events, O₃ formation sensitivity throughout the lower troposphere was consistently NO_x-limited, consistent with the column FNR_{sec} classification. Thus, emission policies focusing on continued reductions in NO_x would effectively improve tropospheric O₃ pollution during summer.

Tokyo-TMU



455 **Figure 10: Sensitivity analysis of O₃ during MDA8 exceedance events at Tokyo-TMU. The top panel presents MDA8 surface O₃, with non-exceedance days indicated by black dots and exceedance days shown as red points with grey shadows. Squares depict the column FNR_{sec} derived from Pandora sky-scan measurements around local noon (12:00 ± 2:00). The bottom panel illustrates the vertical formation sensitivity of O₃ corresponding to exceedance events. The squares and color bars are colored according to FNR_{sec} threshold values determined from the GEOS-Chem model.**

Fukuoka



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Figure 11: Sensitivity analysis of O₃ during MDA8 exceedance events at Fukuoka. The top panel presents MDA8 surface O₃, with non-exceedance days indicated by black dots and exceedance days shown as red points with grey shadows. Squares depict the column FNR_{sec} derived from Pandora sky-scan measurements around local noon (12:00 ± 2:00). The bottom panel illustrates the vertical formation sensitivity of O₃ corresponding to exceedance events. The squares and color bars are colored according to FNR_{sec} threshold values determined from the GEOS-Chem model.

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The exceedance events of O₃ spanned a broad period from spring through fall at both Tokyo-TMU and Fukuoka (Figs. 10 and 11). The column FNR_{sec} were higher during summer leading to a dominant classification in the NO_x-limited regime. Transitional conditions were observed more frequently during spring and fall. At Tokyo-TMU, only one exceedance event (7 April) was found to be sensitive to RO_x radicals. The locally elevated NO_x emissions on that event shifted the chemical environment downward to lower FNR_{sec} values (Fig. S12). Vertical sensitivity profiles showed a RO_x-limited regime within the lower 1 km on 7-8 April. For Fukuoka, the transitional condition occurred more frequently during the exceedance events, emphasizing the need for simultaneous control strategies targeting both NO_x and VOCs in this region.

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Limitations and future scopes

The use of FNR indicator with satellite and ground-based observations can be readily implemented. However, FNR has inherent limitations in inferring the complex interactions among O₃ production, its precursors, photolysis rates, and water vapor (Jin et al., 2025; Schroeder et al., 2017; Souri et al., 2026; Yang et al., 2026). For example, during the early morning and late afternoon, weak light intensity can lead to large biases in the interpretation of FNR because O₃ production is less sensitive to its precursors under low photolysis conditions. In this study, we minimized the potential biases in predicting O₃ chemistry by using Pandora data under conditions of strong photolysis rates. This may underutilize the rich hourly observations provided by Pandora and geostationary satellites. Lin et al. (2025) developed an approach to link the FNR with O₃ chemistry using a steady-state O₃-NO_x-VOC model combined with GOES-CF simulations, and applied it to TEMPO observations.

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Additionally, Souri et al. (2026) optimized the OMI and TROPOMI data to investigate the daily mapping of net O₃ production using a deep neural network approach. A similar approach could also be applied to Pandora data to derive accurate hourly net O₃ production estimates.

485 **Conclusions**

This study demonstrates the use of Pandora measurements to investigate O₃ sensitivity. Pandora provides vertical column densities and profiles of NO₂ and HCHO, which are valuable for a comprehensive understanding of O₃ production in the lower to mid-troposphere. Additionally, with the aid of the GEOS-Chem chemical transport model, we identified the region-specific thresholds to improve sensitivity analysis.

490 By applying the grid-stretching capability of the high-performance GEOS-Chem model, the diurnal cycles of NO₂, HCHO, and O₃ were generally well reproduced. The correlation coefficients between the model and in situ surface measurements were 0.48 for NO₂ and 0.32 for HCHO, and from 0.53 to 0.61 for O₃. For the tropospheric columns, the correlations between GEOS-Chem and Pandora ranged from 0.54 to 0.72 for NO₂, and from 0.51 to 0.87 for HCHO.

According to the GEOS-Chem simulations, secondary HCHO was the dominant contributor to total HCHO, with its
495 contribution increasing with altitude. Furthermore, the region-specific thresholds for the O₃ sensitivity regime were identified. The surface FNR_{sec} values tended to be lower compared to the column FNR_{sec}. The column FNR_{sec} threshold ranges were 0.86–1.52 in Sapporo, 0.74–1.7 in Tsukuba-NIES, 0.62–1.53 in Tokyo-TMU, and 0.43–1.73 in Fukuoka.

Using the tropospheric column FNR_{sec} during high O₃ episodes, the formation regime was found to be mainly NO_x-limited during summer, due to increasing VOCs emissions and strong photochemical activity. The vertical distribution of O₃ sensitivity
500 regimes was also obtained from the Pandora vertical profile. The diagnostics could assist regulators in reducing the frequency of O₃ exceedance events.

To mitigate O₃ exposure, particularly for sensitive groups, policymakers should prioritize VOC emission controls near the surface layers in higher-latitude locations. During summertime, greater attention should be paid to controlling local NO_x emissions. Moreover, regional transport of NO_x from large emission sources can contribute to elevated NO_x, where the NO_x-
505 limited regime is dominant, thereby enhancing O₃ production.

The FNR indicator can be readily obtained from both satellite and ground-based observations, enabling quick assessment of O₃ chemistry. However, the FNR indicator lacks consideration of other factors, such as photolysis rates and water vapor. For more precise interpretation, future studies should incorporate these indicators and others atmospheric dimensions. The combination of both modeling and machine learning could also be beneficial for the interpretation.

510 **Data availability**

The Pandora data are available at the PGN website (<https://www.pandonia-global-network.org>).

Author contributions

NC: Conceptualization, Formal analysis, Writing (original draft preparation). HT: Conceptualization, Supervision, Writing (review and editing). SI: Conceptualization, Writing (review and editing). TF, MF, SK, and HT: Data curation, Writing (review and editing). KI, YD, AM and RU: Writing (review and editing).
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Competing interests

The authors declare that they have no conflict of interest.

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