Research Square

Preprints are preliminary reports that have not undergone peer review.
They should not be considered conclusive, used to inform clinical practice,
or referenced by the media as validated information.

Evaluation of atmospheric conditions at a quasi-national park adjacent to the downtown of a highly industrialized Japanese city

Momoko Abe
The University of Kitakyushu
Sho Oniwa
The University of Kitakyushu
Hayato Imazu
The University of Kitakyushu
Tetsuhiro Tanaka
City of Kitakyushu
Masahide Aikawa
masahide_aikawa@kitakyu-u.ac.jp
The University of Kitakyushu

Research Article

Keywords: quasi-national park, air pollution, passive sampler, potential ozone

Posted Date: February 7th, 2024

DOI: https://doi.org/10.21203/rs.3.rs-3908227/v1

License: This work is licensed under a Creative Commons Attribution 4.0 International License.
Read Full License

Additional Declarations: No competing interests reported.

Abstract

The atmospheric condition at the quasi-national park adjacent to the downtown of a highly industrialized city was evaluated based on three-site observations (quasi-national park, downtown, and suburbs). The concentrations of NOx, NO, NO_2, O_3, SO_2, and NH_3 were determined. The NOx and NO_2 concentrations at the quasi-national park were lower and higher than those downtown and in the suburbs, respectively. The O_3 concentration at the quasi-national park was higher than that downtown and equivalent to that in the suburbs, indicating that the impact of O_3 air pollution on plants and the forest ecosystem is potentially more severe at the quasi-national park than downtown. Potential ozone (PO), defined as $\mathrm{PO} = \mathrm{O_3} + \mathrm{NO_2} - 0.1 \times \mathrm{NOx}$, showed no statistically significant difference ($p<0.05$) among the three sites, indicating that the nitric oxide titration operated and controlled the O_3 concentration across the entire city. The definite difference in the level among the three sites in the SO_2 concentration strongly implied the large contribution of sulfur supply from stationary emission sources and ships located along the shoreline. Fog events at the quasi-national park could be attributed to the determination of the NH_3 concentration at the quasi-national park, i.e., the effective scavenging of NH_3 from the ambient air by fog water.

1. Introduction

National parks and quasi-national parks are designated by the government and are managed by the national or local government. Quasi-national parks are designated for purposes such as the conservation of nature and the conservation of green spaces near an urban region. In the management of quasi-national parks, the atmospheric environment, i.e., the degree of air pollution, is one of the key elements to be evaluated because quasi-national parks are often designated in the vicinity of urban area.

Exposure to ozone damages plants through ozone-induced stress (e.g., Alvarez et al. 1998; Gravano et al. 2003; Miguel et al. 2022; Saji et al. 2022). Ozone is a critical air pollutant affecting the conservation of plants and the forest ecosystem (Broberg et al. 2015; Chaudhary and Rathore 2022; Wang et al. 2023). Ozone is an air pollutant produced/reduced secondarily via. photochemical reactions involving volatile organic compounds and oxides of nitrogen in ambient air (Seinfeld and Pandis 2016). Nitric oxide titration is a chemical reaction that consumes ozone in ambient air: $\mathrm{O_3} + \mathrm{NO} \rightarrow \mathrm{NO_2} + \mathrm{O_2}$. As can be understood, by this nitric oxide titration, NO is consumed and NO_2 is produced; thereby, in considering the effect of air pollution on ozone, it is necessary to consider not only O_3 itself but also NO and NO_2 simultaneously. Environmental standards are set for SO_2 as well as for NO_2 and O_3. Since many sightseers visit the quasi-national park, it is also inevitable that SO_2 should be observed. In particular, in the target area of this study, the largest contributor (ca. 26%) to air pollution is industrial combustion plus ship emissions (Zhang et al. 2021). An autoanalyzer for the chemical species shown above—O_3, NO, NO_2, and SO_2—has been already developed, and national and local governments have been monitoring the concentration from the viewpoint of protecting the health of citizens. However, the constant observation on an hourly basis has been limited to the area where many people are usually living.

Therefore, information regarding the degree of air pollution in a forested area that includes quasi-national parks is quite inadequate for evaluating the degree of air pollution.

Furthermore, information on air pollutants having no environmental standard is further limited; ambient NH_3 is a typical example. Ambient NH_3 plays an important role not only in air pollution but also in the eutrophication of the environment including fresh water, sea water, and soil (Roy et al. 2021; Manninen et al. 2023). In addition, NH_3 is the most abundant inorganic alkaline gas in the atmosphere, and it contributes to the deacidification of precipitation as a univalent base. However, once NH_3 deposits onto the soil, it works as a bivalent acid by the reaction of $\mathrm{NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+}$, totally working as a univalent acid from the atmosphere to the soil.

Japan's Kitakyushu Quasi-National Park plays an important role in the lives and recreation not only of the inhabitants living in Kitakyushu City but also of tourists. Kitakyushu Quasi-National Park is located in the largest industrialized city: Kitakyushu City. However, there is little information on air pollution, such as the concentrations of air pollutants, even though environmental standards have been set for those items. Therefore, we tried to observe the atmospheric conditions at Kitakyushu Quasi-National Park in this article not only to evaluate the current situation of air pollution there but also to improve and conserve the park in a more comfortable condition for years to come.

2. Material and methods

2.1 Survey sites

The atmospheric environment from the viewpoint of air pollution was studied based on the data set determined at four sites. The locations and attributes of the sites are summarized in Table 1, together with the items to be determined and the methods. The atmospheric environment was evaluated in terms of the site attribute: (1) a quasi-national park adjacently located to the downtown of a highly industrialized area of Kitakyushu City, Japan (Sarakura site), (2) the suburbs (University site and Egawa site), and (3) downtown (Tobata site) of Kitakyushu City.

Kitakyushu City is one of Japan's highly industrialized cities, being located in the northern part of Kyushu Island. Kyushu Island is situated in the western part of Japan, and Japan is on the eastern edge of East Asia (Fig. 1). Due to its geographical location, Kitakyushu City is influenced by outflow from the Asian continent in the spring, autumn, and winter seasons; in contrast, Kitakyushu City rarely suffers outflow from the Asian continent in the summer season because the air mass formed over the Pacific Ocean covers Japan, and the southern wind is dominant in the summer (Aikawa et al. 2010; Zhang et al. 2021). The largest contribution (ca. 26%) to air pollution is industrial combustion plus ship emissions (Zhang et al. 2021).

2.2 Items to be determined, method, sampling frequency, and target period to study

Items to be measured are NOx (= NO + NO_2), NO, NO_2, SO_2, O_3, and NH_3. The survey at Sarakura was carried out with a passive method (Ogawa 2022) due to the limited power supply. NH_3 was measured by a passive method at all sites. Measurements by autoanalyzer were organized and controlled by the local government of Kitakyushu City (City of Kitakyushu). SO_2 at University was determined by a five-stage filter pack (Aikawa et al. 2005; Network Center of EANET 2013).

The chemical analysis except by autoanalyzer followed the manuals for each item (Ogawa 2022) and EANET manuals for filter packs (Network Center of EANET 2013). The devices of UV–VIS spectrophotometer (UV-1280, Shimadzu, Kyoto, Japan) for NOx and NO_2 and ion chromatography system (Thermo Fisher Scientific™ Dionex™ Integrion, Thermo Fisher Scientific Inc., Chelmsford, MA, USA) for SO_2 and NH_3 were used to determine the extract of each filter paper.

Sampling at Sarakura was biweekly. Samplings by a passive method at University and Tobata and a filter-pack method were basically weekly (Monday to the next Monday). The determination by autoanalyzer was on an hourly basis; therefore, in the comparison among items, a weekly mean was calculated from the hourly data for the results by autoanalyzer. In the time series (Figs. 2–5), the data at Sarakura was doubly used. The two-year data set from June 2020 to May 2022 was set as the target period studied in this article.

Table 1
Survey sites, items to be determined and method to determine

Site	Attribute	Latitude	Longitude	Elevation / m a.s.l.	Items to be determined	Method to determine
Sarakura	Quasi-National Park	33.8452	130.7946	550	NOx[*1], NO_2, SO_2, O_3, NH_3, (NO)[*2]	Passive
University	Suburbs	33.8899	130.7118	29	SO_2	Filter pack
					NH_3	Passive
Egawa		33.8933	130.6929	26	NOx, NO, O_3, (NO_2)[*3]	Autoanalyzer
Tobata	Downtown	33.8952	130.8293	12	NOx, NO, SO_2, O_3, (NO_2)[*3]	Autoanalyzer
					NH_3	Passive

*1: NOx is the sum of NO and NO_2. *2: NO is determined as the difference between NOx and NO_2. *3: NO_2 is determined as the difference between NOx and NO.

3. Results and discussion

3.1 Temporal variation of the concentration

3.1.1 NOx, NO_2, and NO

Figure 2(a)–(c) shows the time series of the concentrations of NOx (a), NO_2 (b), and NO (c), respectively at Tobata (downtown), Egawa (suburbs), and Sarakura (quasi-national park). The comparison below among the sites was tested by ANOVA and Tukey's test.

The NOx concentration at Tobata (mean: 15.1 ppb) was higher than those of Sarakura (mean: 11.5 ppb) and Egawa (mean: 8.7 ppb) with a statistical significance ($p < 0.05$), and the NOx concentration at Sarakura (mean: 11.5 ppb) was higher than that of Egawa (mean: 8.7 ppb) with a statistical significance ($p < 0.05$). It is noteworthy that the NOx concentration was higher at the quasi-national park (Sarakura) than in the suburbs (Egawa). This would be attributable to its location in the vicinity of the downtown even though the site is established in a mountainous area and the elevation (550 m a.s.l.) is high.

A difference among the sites similar to the case of the NOx concentration was observed in the NO_2 concentration: Tobata (mean: 13.2 ppb) > Sarakura (mean: 9.4 ppb) > Egawa (mean: 7.5 ppb), with a statistical significance ($p < 0.05$). Since NO_2 is deeply related to an oxidizing chemical reaction of NO by O_3, the comparison among the sites would not be as simple as the case of NOx; nonetheless, it is also noteworthy that the NO_2 concentration was higher at the quasi-national park (Sarakura) than in the suburbs (Egawa).

The magnitude correlation in the case of NO was different from those of NOx and NO_2. The NO concentrations at Tobata (mean: 1.96 ppb) and Sarakura (mean: 1.63 ppb) were higher than that of Egawa (mean: 1.22 ppb) with a statistical significance ($p < 0.05$); in the meantime, no statistically significant difference ($p > 0.05$) was observed between Tobata and Sarakura. This will be discussed in greater detail in section 3.1.2, as it relates to O_3 and PO.

3.1.2 O_3 and potential ozone (PO)

Figure 3(a) and (b) shows the time series of the concentrations of O_3 (a) and PO (b), respectively, at Tobata (downtown), Egawa (suburbs), and Sarakura (quasi-national park). Potential ozone is defined by the following formula: $\mathrm{PO} = \mathrm{O_3} + \mathrm{NO_2} - 0.1 \times \mathrm{NOx}$; here, NOx is the sum of NO and NO_2 (NOx = NO + NO_2). The concept of PO is based on the facts that (1) NO_2 in ambient air has been produced by the oxidation of NO by O_3: $\mathrm{O_3} + \mathrm{NO} \rightarrow \mathrm{NO_2} + \mathrm{O_2}$, and (2) NO_2 and NO account for 10% and 90% of the primary emissions of NOx, respectively.

The O_3 concentrations at Egawa (mean: 35.2 ppb) and Sarakura (mean: 33.9 ppb) were higher than that of Tobata (mean: 29.8 ppb) with a statistical significance ($p < 0.05$); in the meantime, no statistically

significant difference ($p > 0.05$) was observed between Egawa and Sarakura (Fig. 3(a)). This indicates that the impact by the O_3 air pollution is potentially more severe in the quasi-national park (Sarakura) and the suburbs (Egawa) than in the downtown (Tobata), suggesting that considerable attention should be paid to O_3 air pollution from the viewpoint of ensuring the preservation of plants and forest ecosystems as well as protecting human health. Meanwhile, the concentrations of PO at three sites: Tobata (41.5 ppb), Sarakura (42.6 ppb), and Egawa (41.8 ppb) had no statistically significant difference ($p > 0.05$). As shown in section 3.1.1, the concentrations of both NOx and NO_2 at Tobata (downtown) were significantly higher than those at the other two sites, and the NO concentration at Tobata was statistically higher than that at Egawa (suburbs) and was not statistically different from that at Sarakura (quasi-national park). Taking the definition of PO and the reaction of $\mathrm{O_3 + NO \rightarrow NO_2 + O_2}$ into account, the O_3 air pollution at Tobata (downtown) was presumably mitigated by NO through nitric oxide titration ($\mathrm{O_3 + NO \rightarrow NO_2 + O_2}$) in ambient air. However, since the PO concentrations at three sites were at an equivalent level, the potential risk arising from the O_3 air pollution should be studied comprehensively in a wider scale across all of Kitakyushu City.

3.1.3 SO_2

Figure 4 shows the time series of the SO_2 concentration at Tobata (downtown), University (suburbs), and Sarakura (quasi-national park). The spatial distribution of air pollution by SO_2 was definitely different from those by NOx, NO, NO_2, O_3, and PO. The SO_2 concentration at Sarakura (mean: 0.17 ppb) was ca. one-fifth (20%) those at Tobata (0.88 ppb) and University (mean: 0.77 ppb); in the meantime, no statistically significant difference ($p > 0.05$) was observed between Tobata and University. The NOx concentration at Sarakura (11.5 ppb) was also lower than that at Tobata (15.1 ppb); however, that is just 76% (= 11.5/15.1). This difference between NOx and SO_2 would be attributable to difference in their emission sources and their location/distance from emission sources. The dominant contributor to NOx air pollution in Japan is mobile emission like automobile; in contrast, the dominant emission sources of SO_2 are stationary emissions and ships. Most stationary emission sources are located near the shoreline, and Kitakyushu City is facing an enclosed water area, the Seto Inland Sea. The large contribution of sulfur from ships running in the Seto Inland Sea has been shown in previous studies (Nakatsubo et al. 2020; Wang et al. 2021; Zhang et al. 2021; Kondo et al. 2023). We simply estimated the dilution coefficient due to the differences in SO_2 and NOx under some assumptions, as given below:

1. The horizontal distance of Sarakura from the nearest shoreline and main road is ca. 4 km and ca. 2 km, respectively, and the elevation of the Sarakura site is 0.55 km.
2. The stationary emission sources of SO_2 are located on the shoreline, and the ships run along the shoreline.
3. The dominant emission of NOx is attributable to automobiles, and the direction of the advection of NOx is same as that of SO_2 from the stationary source.
4. The concentration of air pollutants is diluted in the plume flow from the emission sources.

$$Dilution coefficient due to differences in SO_2 and NO_x$$

$$= \frac{dilution\ factor\ of\ SO_2}{dilution\ factor\ of\ NO_x} = \frac{1/\sqrt{4^2 + 0.55^2}}{1/\sqrt{2^2 + 0.55^2}} = 0.51.$$

The estimation of 0.51 is not small enough to explain the difference in SO_2 (20%) and NOx (76%); 0.2/0.76 = 0.26. The biggest factor responsible for this gap is presumed to be an error in the assumption that the advection of NOx was in the same direction as SO_2, although the emission source of NOx is a non-point source.

Assuming that the three-dimensional dilution is by diffusion and not by advection, the dilution of 0.14 would be expected as seen below:

$$1/(\frac{\sqrt{4^2+0.55^2}^3}{\sqrt{2^2+0.55^2}^3}) = 0.14.$$

Further, it is worth noting that no statistically significant difference ($p > 0.05$) was observed between Tobata (downtown) and University (suburbs), although the NOx concentration at Tobata (mean: 15.1 ppb) was higher than that of Egawa (suburbs) (mean: 8.7 ppb) with a statistical significance ($p < 0.05$). Both Tobata and University are located in areas similarly far from the shoreline; on the other hand, Tobata is located in the vicinity of the downtown where stationary sources are concentratedly established, whereas there are few large stationary sources on the shoreline where University is located. This result is consistent with the emission source of SO_2 being stationary sources and ships; in addition, the larger contribution of ships is strongly suggested.

In this section, the difference in the concentrations of NOx and SO_2 observed at Sarakura could be conclusively attributable to the difference in NOx and SO_2 emission sources and the location/distance of the emission sources; in addition, a large contribution from ships is also strongly implied.

3.1.4 NH_3

Figure 5 shows the time series of the NH_3 concentration at Tobata (downtown), University (suburbs), and Sarakura (quasi-national park). The NH_3 concentration at Tobata (mean: 5.18 ppb) was higher than those of Sarakura (mean: 2.31 ppb) and University (mean: 2.49 ppb) with a statistical significance ($p < 0.05$); however, no statistically significant difference ($p > 0.05$) was observed between Sarakura and University. The NH_3 concentrations at Sarakura and University were within the range of the NH_3 concentrations in Japan (Japan Environmental Laboratories Association 2018; Yokoyama et al. 2019). On the other hand, the NH_3 concentration at Tobata was equivalent to the maximum level of Japan (Yokoyama et al., 2019); however, the NH_3 concentration at Tobata in this target period seemed to be higher than that during another period (Nguyen et al. 2020), indicating that the NH_3 concentration should continue to be monitored, taking the trend into account. Since emissions from automobiles would be a dominant

source of NH_3 in the urban area (e.g., Pandolfi et al. 2012; Reche et al. 2015), traffic density would be responsible for the difference between Tobata (downtown) and University (suburbs). The NH_3 concentration at Sarakura (2.31 ppb) was also lower than that at Tobata (5.18 ppb), corresponding to just 45% (= 2.31/5.18). This dilution of the NH_3 concentration was larger than that of the NOx concentration (76%). One of the possibilities peculiar to the Sarakura site that could explain the larger dilution of the NH_3 concentration in the atmosphere is the foggy condition due to the high elevation of the Sarakura site. Abe et al. (2022) showed that air pollutants were highly concentrated in the fog water collected at the same site as this study (Sarakura). A wet deposition process is related with scavenging of ambient NH_3 (Roy et al. 2021). Since NH_3 has a high solubility to water, more frequent fog events at Sarakura than at Tobata could contribute to a more effective scavenging of NH_3 from the ambient air.

4. Conclusions

The atmospheric condition at the quasi-national park was evaluated by comparing it with the atmospheric conditions at not only the downtown but also the suburbs based on the ambient concentrations of NOx, NO, NO_2, O_3, SO_2, and NH_3. The concentrations of potential ozone ($\mathrm{PO} = \mathrm{O_3} + \mathrm{NO_2} - 0.1 \times \mathrm{NOx}$) at three locations were the same with no statistically significant difference ($p>0.05$); on the other hand, the concentration of O_3, which impacts plants and forest ecosystems at the quasi-national park, was higher than that downtown due to less nitric oxide titration in the atmosphere. The SO_2 concentration at the quasi-national park was absolutely lower than those downtown and in the suburbs, which is surely due to the distance from the emission sources, that are ships and stationary sources along the shoreline. The NH_3 concentrations at the quasi-national park and the suburbs were within the range of those in Japan; on the other hand, the NH_3 concentration downtown was at the maximum level in Japan. The scavenging of ambient NH_3 by fog water would be involved in determining the NH_3 concentration at the quasi-national park.

Declarations

Funding: The authors declare that no funds, grants, or other support were received during the preparation of this manuscript.

Competing interests: The authors declare that they have no conflict of interest.

Author Contributions:

Momoko Abe: Sampling at suburbs and quasi-national park sites, Chemical analysis, Statistical analysis, Writing - original draft

Sho Oniwa: Sampling at suburbs and quasi-national park sites, Chemical analysis

Hayato Imazu: Sampling at suburbs and quasi-national park sites, Chemical analysis

Tetsuhiro Tanaka: Sampling at downtown site

Masahide Aikawa: Design, Organization, Methodology, Project administration, Supervision, Validation, Writing - review & editing

All authors read and approved the final manuscript.

Data Availability: Data will be made available on reasonable request.

Ethics approval, Consent to participate and Consent to publish: Not applicable

Acknowledgements

The survey at the quasi-national park was supported by the Mount Sarakura Visitor Center. We greatly appreciate the cooperation of the Mount Sarakura Visitor Center. The data measured by autoanalyzer was supplied by City of Kitakyushu through the Web site. We greatly appreciate the cooperation of City of Kitakyushu.

References

1. Abe M, Oniwa S, Okochi H and Aikawa M (2022) Fog water, throughfall and bulk precipitation chemistry and a newly developed methodology for the estimation of fog water deposition. Water, Air and Soil Pollution (2022) 233:474. https://doi.org/10.1007/s11270-022-05939-5
2. Aikawa M, Hiraki T and Tamaki M (2005) Characteristics in concentration of chemical species in ambient air based on three-year monitoring by filter pack method. Water, Air and Soil Pollution 161, 335–352.
3. Aikawa M, Ohara T, Hiraki T, Oishi O, Tsuji A, Yamagami M, Murano K and Mukai H (2010) Significant geographic gradients in particulate sulfate over Japan determined from multiple site measurements and a chemical transport model: Impacts of transboundary pollution from the Asian continent. Atmospheric Environment 44, 381–391. DOI:10.1016/j.atmosenv.2009.10.025
4. Alvarez D, Laguna G and Rosas I (1998) Macroscopic and microscopic symptoms in *Abies religiosa* exposed to ozone in a forest near Mexico City. Environmental Pollution 103, 251–259.
5. Broberg MC, Feng Z, Xin Y, Pleijel H (2015) Ozone effects on wheat grain quality – A summary. Environmental Pollution 197 (2015) 203–213. http://dx.doi.org/10.1016/j.envpol.2014.12.009
6. Chaudhary IJ, Rathore D (2022) Effects of ambient and elevated ozone on morphophysiology of cotton (Gossypium hirsutum L.) and its correlation with yield traits. Environmental Technology & Innovation 25 (2022) 102146. https://doi.org/10.1016/j.eti.2021.102146
7. Gravano E, Giulietti V, Desotgiu R, Bussotti F, Grossoni P, Gerosa G and Tani C (2003) Foliar response of an *Ailanthus altissima* clone in two sites with different levels of ozone-pollution. Environmental Pollution 121, 137–146.

8. Japan Environmental Laboratories Association (2018) Acid deposition survey in Japan, phase 6 (2016). Journal of Environmental Laboratories Association 43(3), 2–42 (in Japanese).
9. Kondo M, Ishida A, Hiramoto T, Nakazono A, Ono S, Nakatsubo R, Futamura A, Oshita Y, Zhang X and Aikawa M (2023) Sudden decrease of airborne sulfates in summer at sites in western Japan prior to the enforcement of the MARPOL Treaty. Atmospheric Environment 295 (2023) 119571. https://doi.org/10.1016/j.atmosenv.2022.119571
10. Manninen S, Jääskeläinen K, Stephens A, Iwanicka A, Tang S, van Dijk N (2023) NH_3 concentrations below the current critical level affect the epiphytic microlichen communities – Evidence from a Northern European City. Science of the Total Environment 877 (2023) 162877. http://dx.doi.org/10.1016/j.scitotenv.2023.162877
11. Miguel GBJ, Aurora RHE and Guillermo LH (2022) Structural and ultrastructural injuries in leaves of *Baccharis conferta* and *Buddleja cordata* broad-leaved species of a forest impacted with ozone. Flora 291, (2022)152075. https://doi.org/10.1016/j.flora.2022.152075
12. Nakatsubo R, Oshita Y, Aikawa M, Takimoto M, Kubo T, Matsumura C, Takaishi Y, Hiraki T (2020) Influence of marine vessel emissions on the atmospheric $PM_{2.5}$ in Japan's around the congested sea areas, Science of the Total Environment, 702, https://doi.org/10.1016/j.scitotenv.2019.134744
13. Nguyen DV, Sato H, Hamada H, Yamaguchi S, Hiraki T, Nakatsubo R, Murano K and Aikawa M (2021) Symbolic seasonal variation newly found in atmospheric ammonia concentration in urban area of Japan. Atmospheric Environment 244, 117943. https://doi.org/10.1016/j.atmosenv.2020.117943
14. Network Center of EANET (2013) Technical Manual for Air Concentration Monitoring in East Asia, https://www.eanet.asia/wp-content/uploads/2019/04/techacm.pdf (last access; Aug. 13th, 2022)
15. Ogawa (2022) http://ogawajapan.com/measurment.html (last access; Oct. 8th, 2022)
16. Pandolfi M, Amato F, Reche C, Alastuey A, Otjes RP, Blom MJ, Querol X (2012) Summer ammonia measurements in a densely populated Mediterranean city. Atmospheric Chemistry and Physics 12 (16), 7557–7575. https://doi.org/10.5194/acp-12-7557-2012.
17. Reche C, Viana M, Karanasiou A, Cusack M, Alastuey A, Artiñano B, Revuelta MA, López-Mahía P, Blanco-Heras G, Rodríguez S (2015) Urban NH_3 levels and sources in six major Spanish cities. Chemosphere 119: 769–777. http://dx.doi.org/10.1016/j.chemosphere.2014.07.097
18. Roy EL, Walters WW, Joyce EE, Hastings MG (2021) Sources of ammonium in seasonal wet deposition at a coastal New England city. Atmospheric Environment 260 (2021) 118557. https://doi.org/10.1016/j.atmosenv.2021.118557
19. Saji S, Saji H, Sage-Ono K, Ono M, Nakajima N, Aono M (2022). Phytocyanin-encoding genes confer enhanced ozone tolerance in Arabidopsis thaliana. Scientific Reports (2022) 12:21204. https://doi.org/10.1038/s41598-022-25706-0
20. Seinfeld JH and Pandis SN (2016) Atmospheric Chemistry and Physics from Air Pollution to Climate Change Third Edition, p. 47, John Wiley & Sons, Inc., New Jersey
21. Wang X, Yi W, Lv Z, Deng F, Zheng S, Xu H, Zhao J, Liu H, He K (2021) Ship emissions around China under gradually promoted control policies from 2016 to 2019. Atmospheric Chemistry and Physics.

21, 13835–13853. https://doi.org/10.5194/acp-21-13835-2021

22. Wang Y, Wang Y, Feng Z, Yuan X, Zhao Y (2023) The impacts of ambient ozone pollution on China's wheat yield and forest production from 2010 to 2021. Environmental Pollution 330(2023)121726. https://doi.org/10.1016/j.envpol.2023.121726
23. Yokoyama S, Yamaguchi T, Aikawa M and Mukai H (2019) Trends in atmospheric ammonia and particulate ammonium concentrations in Japan. Journal of Japan Society for Atmospheric Environment 54(2), 75–83. (In Japanese with English abstract)
24. Zhang X, Murakami T, Wang J, and Aikawa M (2021) Sources, species and secondary formation of atmospheric aerosols and gaseous precursors in the suburb of Kitakyushu, Japan. Science of the Total Environment, 763, 143001. https://doi.org/10.1016/j.scitotenv.2020.143001

Figures

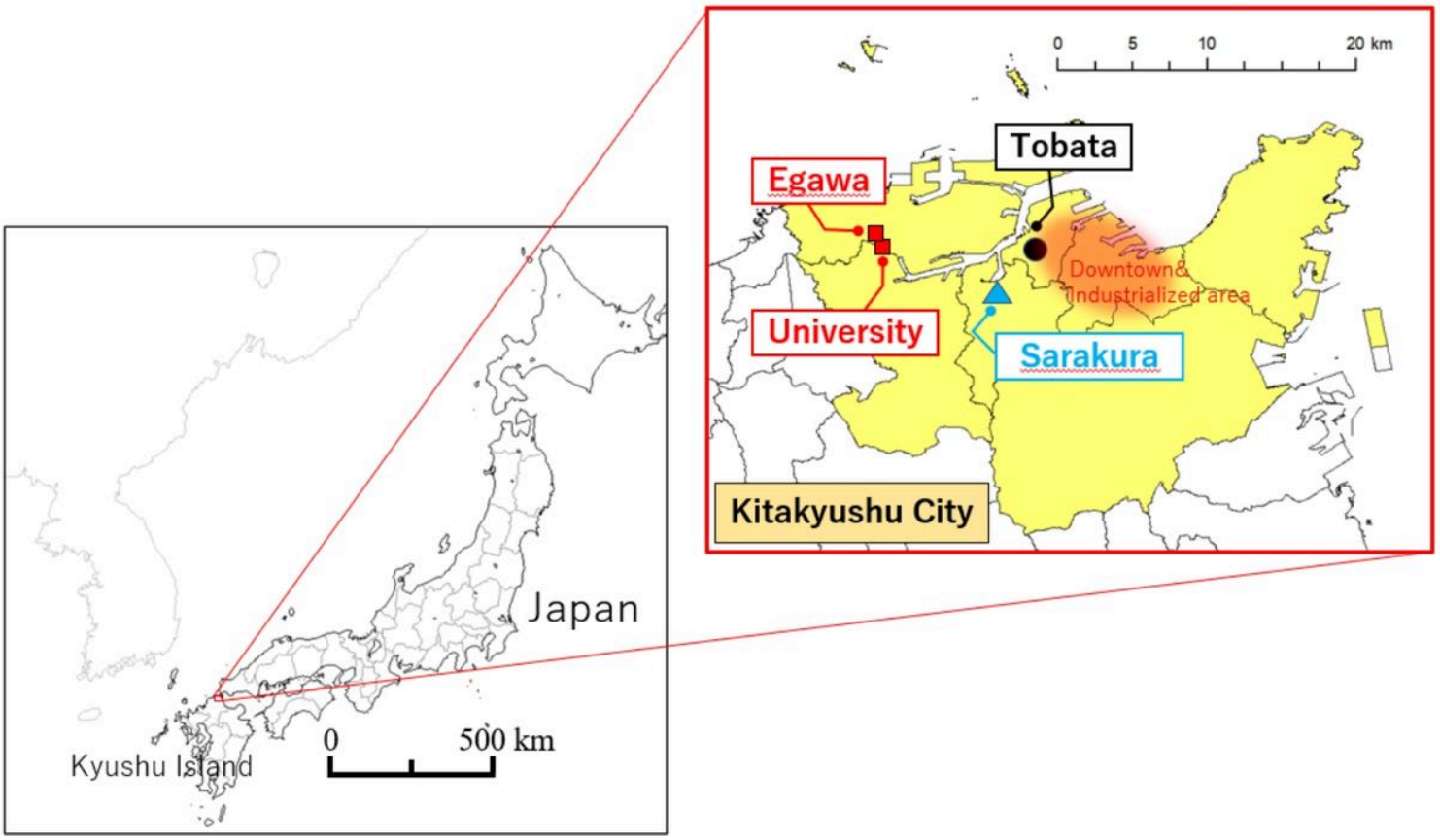

Figure 1

Location of survey sites: Sarakura site (quasi-national park), University site and Egawa site (suburbs), Tobata site (downtown)

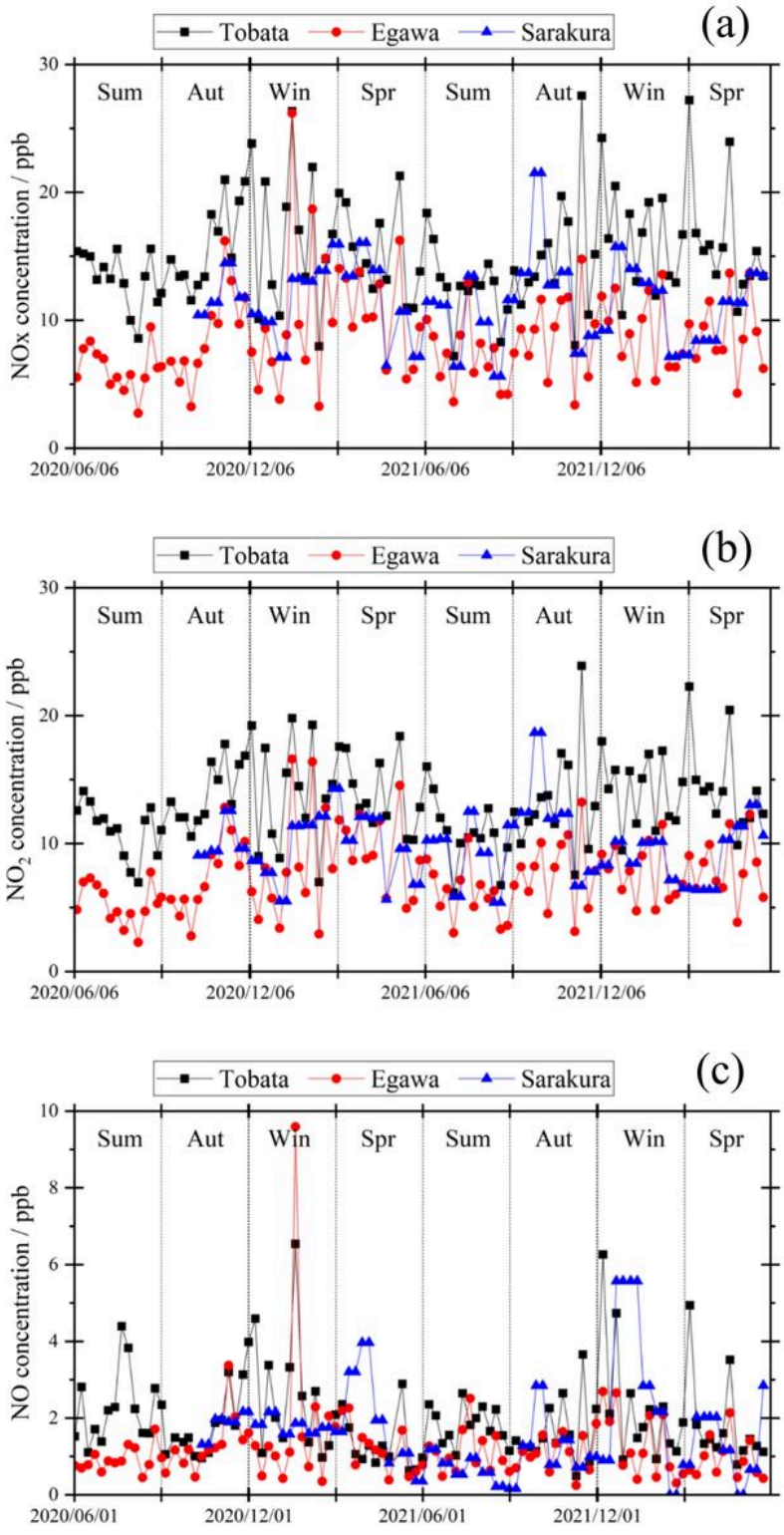

Figure 2

Time series of the concentrations of NOx (a), NO_2 (b) and NO (c), respectively at Tobata (downtown; black solid square) and , Egawa (suburbs; red solid circle) and Sarakura (quasi-national park; blue solid triangle). Indication of Sum, Aut, Win and Spr shows the summer, autumn, winter and spring seasons, respectively.

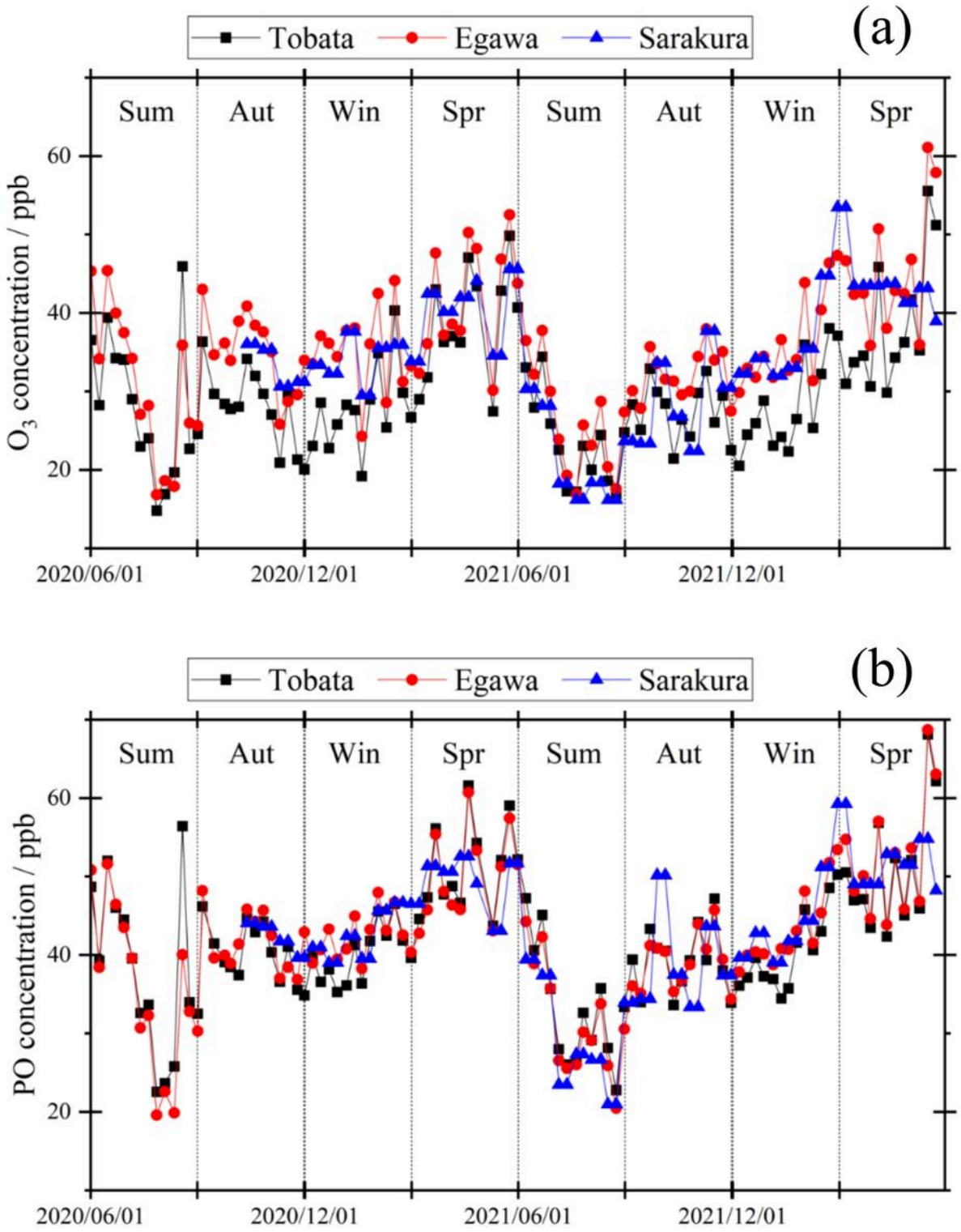

Figure 3

Time series of the concentrations of O_3 (a) and potential ozone (PO) (b) respectively at Tobata (downtown; black solid square) and , Egawa (suburbs; red solid circle) and Sarakura (quasi-national park; blue solid triangle). Indication of Sum, Aut, Win and Spr shows the summer, autumn, winter and spring seasons, respectively.

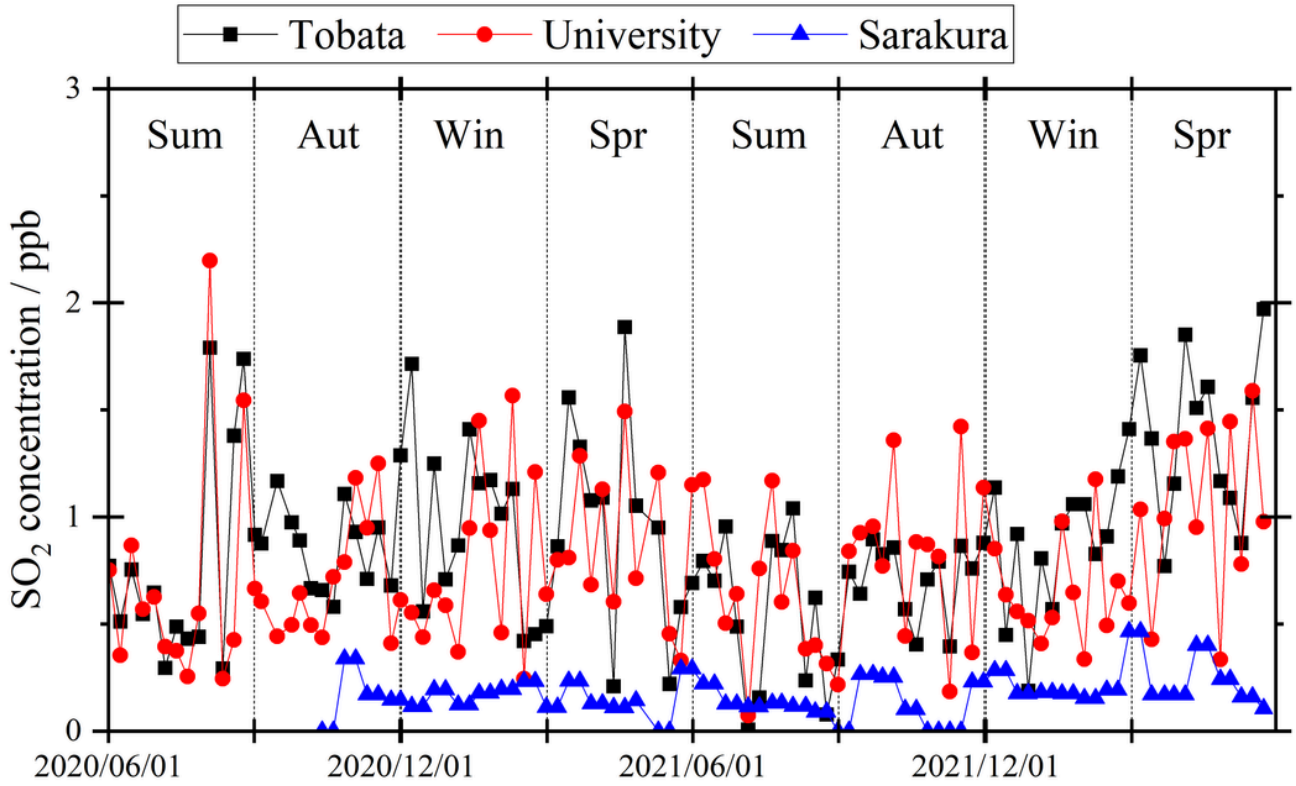

Figure 4

Time series of the SO_2 concentration at Tobata (downtown; black solid square) and, University (suburbs; red solid circle) and Sarakura (quasi-national park; blue solid triangle). Indication of Sum, Aut, Win and Spr shows the summer, autumn, winter and spring seasons, respectively.

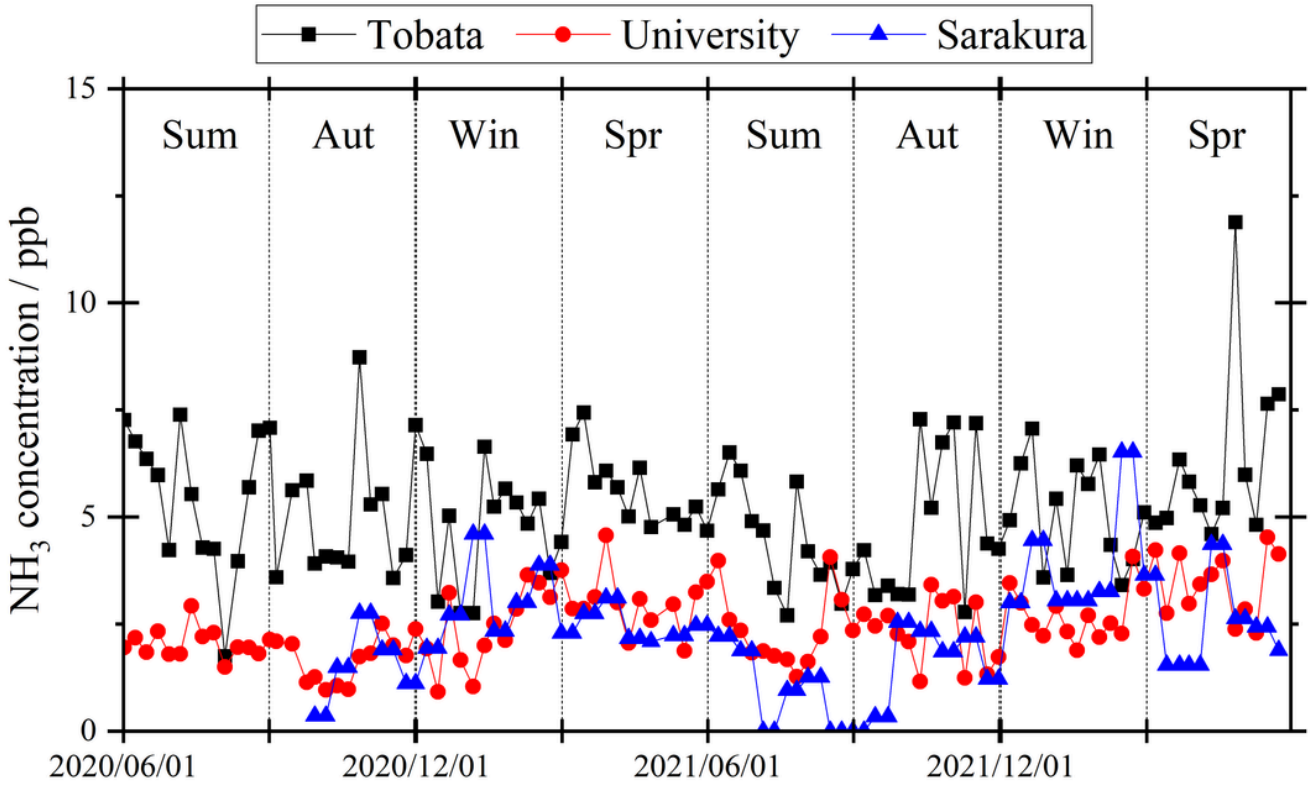

Figure 5

Time series of the NH_3 concentration at Tobata (downtown; black solid square), University (suburbs; red solid circle) and Sarakura (quasi-national park; blue solid triangle). Indication of Sum, Aut, Win and Spr shows the summer, autumn, winter and spring seasons, respectively.