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The Evolution of the Seasonal Variation and the Summer Diurnal Variation of Primary and Secondary Photochemical Air Pollution in Athens †

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Abstract: The city of Athens has faced air pollution problems over the last few decades due to the high population density associated with an intense emission load constrained by the local topography causing poor ventilation. In addition, the high levels of solar irradiation, in combination with emissions of nitrogen oxides and hydrocarbons, have led to the formation of photochemical pollutants, especially ozone. In this study, the evolution of the seasonal variation of primary and secondary photochemical urban air pollution in Athens was examined for the 2001–2021 period. For this purpose, the monthly NO_x ($NO+NO_2$), ozone, and O_x (O_3+NO_2) averages for the Athens air pollution monitoring stations of Geoponiki, Liossia, Ag. Paraskevi, and Thrakomakedones in the selected periods of 2001–2004, 2010–2013, 2016–2019, and 2020–2021 were plotted. In addition, summer diurnal NO_x, ozone, and O_x variations were examined. There was a clear reduction in NO_x levels at all four examined stations, especially at the urban background site of Geoponiki, as well as at the most polluted peripheral site of Liossia, following a reduction in urban emissions, mainly from car traffic during the examined period. The ozone and O_x curves did not show the same patterns due to the complicated nature of local ozone photochemical production, in combination with the rural surface ozone background, which was particularly high over the area.

Keywords: Athens; urban air pollution; ozone; nitrogen oxides

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1. Introduction

Over the last few decades, the high air pollution levels in Athens, Greece, have become a priority issue for the authorities and have been the subject of many research studies. Scientists at the Research Centre for Atmospheric Physics and Climatology of the Academy of Athens actively participated in studies on urban photochemical pollution [1–9], regional rural surface ozone background [10–13], and vertical tropospheric ozone distribution [14–20].

In this study, the evolution of the interannual and seasonal variation of primary and secondary photochemical urban air pollution in Athens has been examined for the 2001–2021 period. For this purpose, the annual and monthly NO_x ($NO+NO_2$), ozone, and O_x (O_3+NO_2) averages for the urban background station of Geoponiki, as well as for the peripheral stations of Geoponiki, Liossia, Ag. Paraskevi, and Thrakomakedones, during the selected periods of 2001–2004, 2010–2013, 2016–2019, and 2020–2021 were plotted.

2. Results and Discussion

Figure 1 shows the average annual ozone and NO_x concentrations at the stations of the Athens air pollution monitoring network, as approximately located at the NW-NE axis of the basin for the 2001–2021 period. The most polluted stations, specifically regarding primary pollution, were Patission (PAT), Athinas (ATH), and Peireas (PEI), while they showed the lowest ozone mean values. At the same time, the O_x concentrations were comparable at all stations, expectedly due to NO titration by ozone [7]. From the 11 presented stations, the peripheral stations of Liossia (LIO), Ag. Paraskevi (AGP), and Thrakomakedones (THR), as well as the urban background station of Geoponiki (GEO), were selected for further analysis.

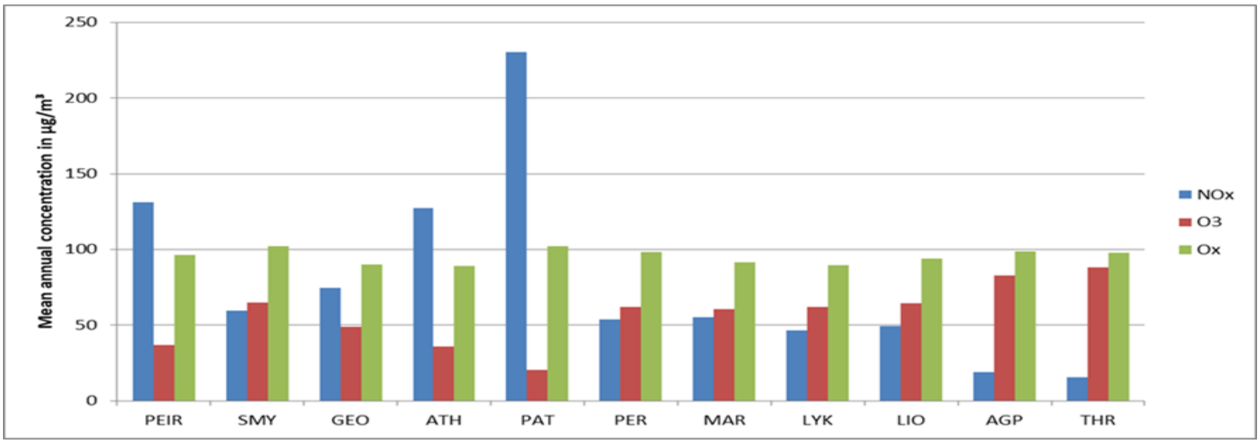

Figure 1. Average annual ozone and NO_x concentrations at Athens air pollution monitoring network stations, as approximately located at the NW-NE axis of the basin for the 2001–2021 period.

In Figure 2, the evolution of annual NO_x, O_3, and O_x pollutant concentrations at the GEO, LIO, AGP, and THR stations of the Athens air pollution monitoring network is presented. There was a significant reduction in NO_x concentrations at GEO and LIO stations during the 2001–2011 period (around 40–50%), while there was an increase in ozone concentrations at the same stations. For the AGP and THR stations, the NO_x reductions and ozone increases were less significant. Finally, the annual O_x concentrations remained relatively stable throughout the examined period.

In Figure 3, seasonal variations in monthly average NO_x concentrations at the stations of GEO, LIO, AGP, and THR during the periods of 2001–2004, 2010–2013, 2016–2019, and and 2020–2021, as well as the corresponding NO_2 concentrations for the same time periods, are presented. Significant reductions in primary NO_x pollution were observed at the urban background station of GEO, as well as at the peripheral station of LIO, located to the north of the basin, especially during the autumn and winter months and between the periods 2001–2004 and 2010–2013. During the summer months, the reductions were less significant, especially during the more recent periods, although an extra reduction was observed during the pandemic period (2020–2021) relatively to the previous period (2016–2019) during both autumn and winter months. Similar NO_2 variations between the examined periods were observed, showing a smoother seasonal variation in summer.

In Figure 4, seasonal variations in monthly average ozone concentrations at the stations of GEO, LIO, AGP, and THR during the periods of 2001–2004, 2010–2013, 2016–2019, and 2020–2021, as well as the corresponding O_x variations for the same time periods, are presented. Significant ozone and O_x reductions were observed at the AGP and THR stations, while at the LIO station, O_x shows the same pattern. On the contrary, significant ozone increases were observed at the GEO station.

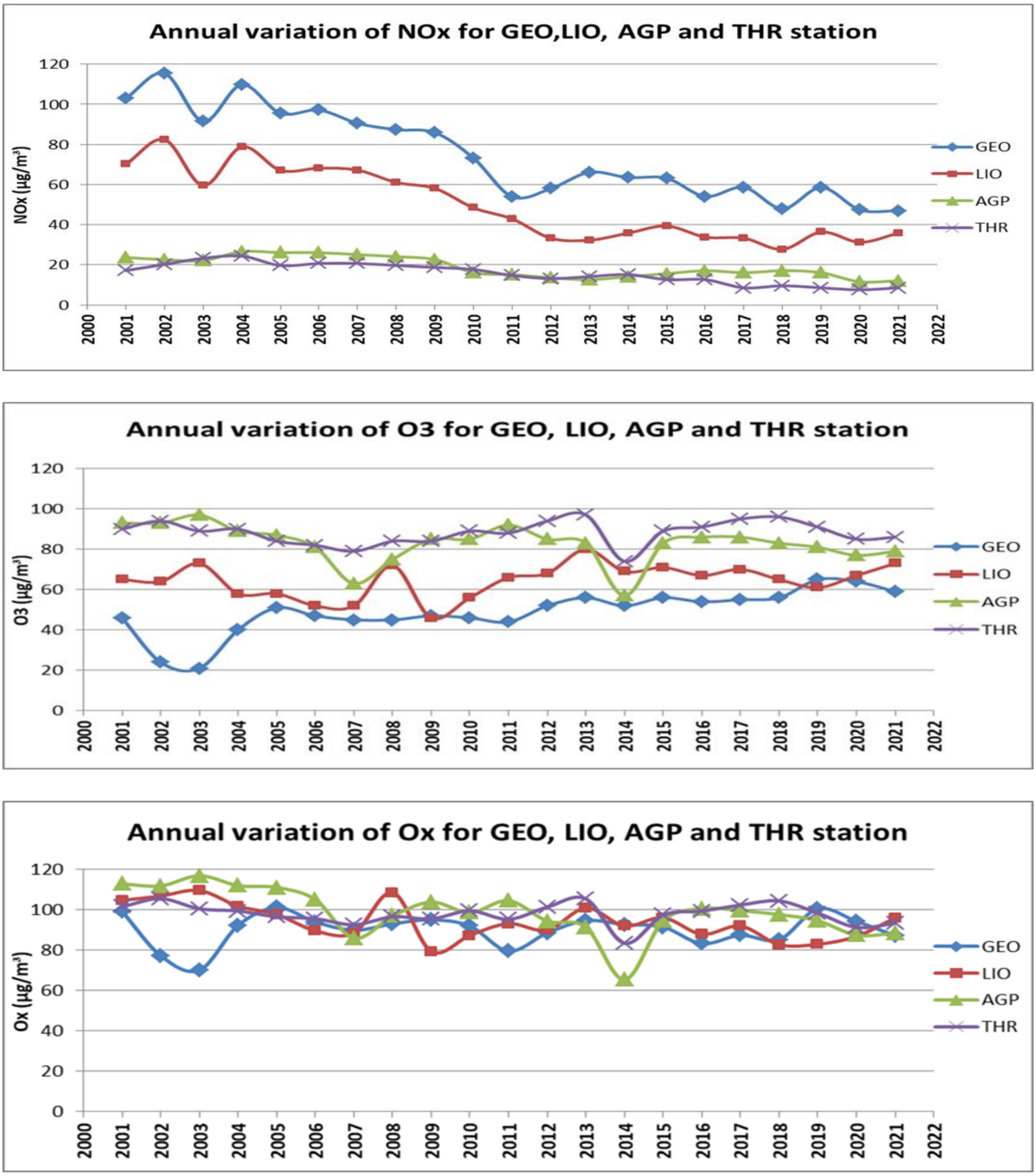

Figure 2. Evolution of annual pollutant concentrations at the GEO, LIO, AGP, and THR stations of the Athens air pollution monitoring network: NO_x (upper panel), O_3 (middle panel), and O_x (lower panel).

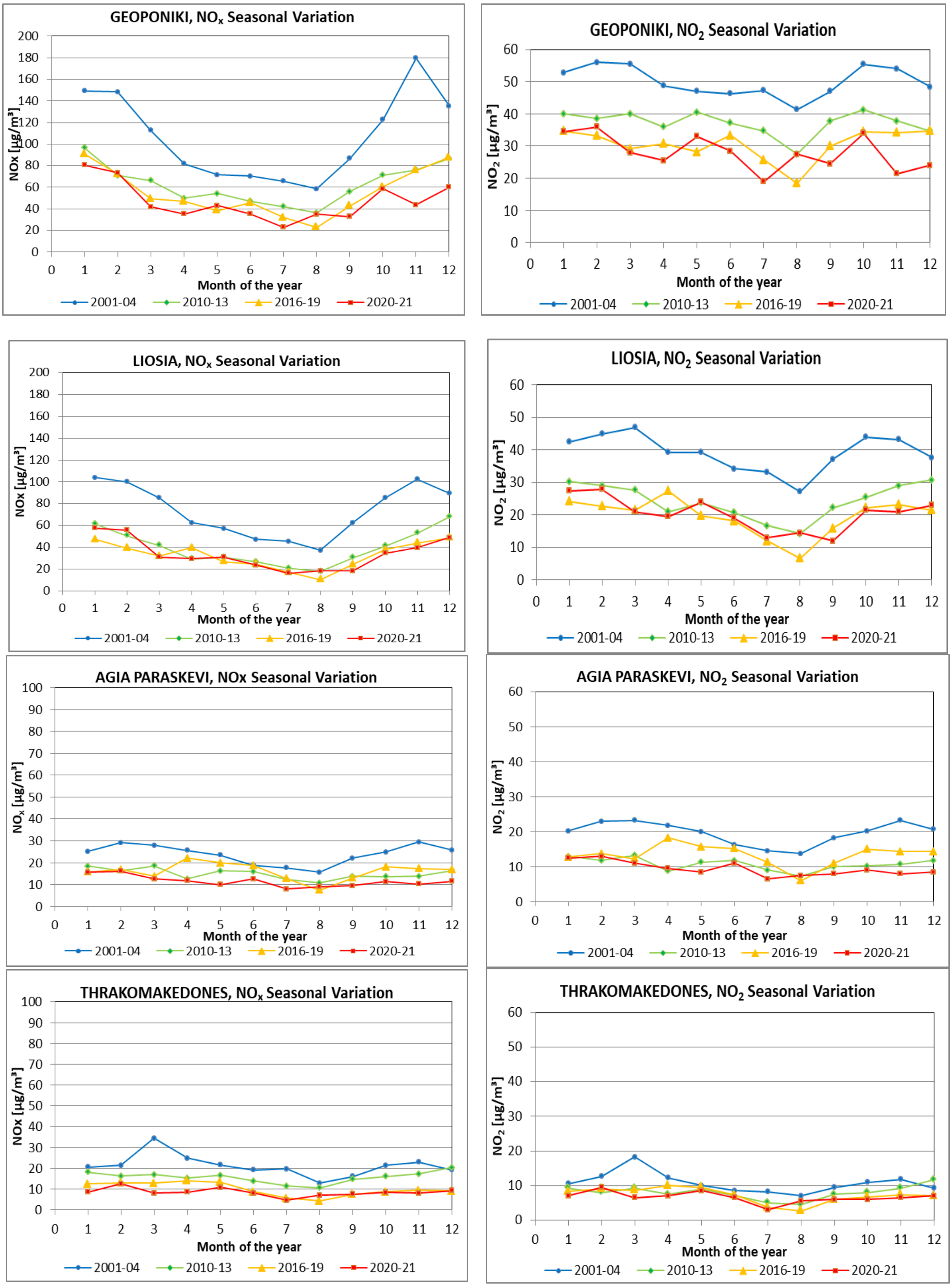

Figure 3. Seasonal variations in monthly NO_x (left column) and NO_2 (right column) averages at GEO, LIO, AGP, and THR for 2001–2004, 2010–2013, 2016–2019, and 2020–2021.

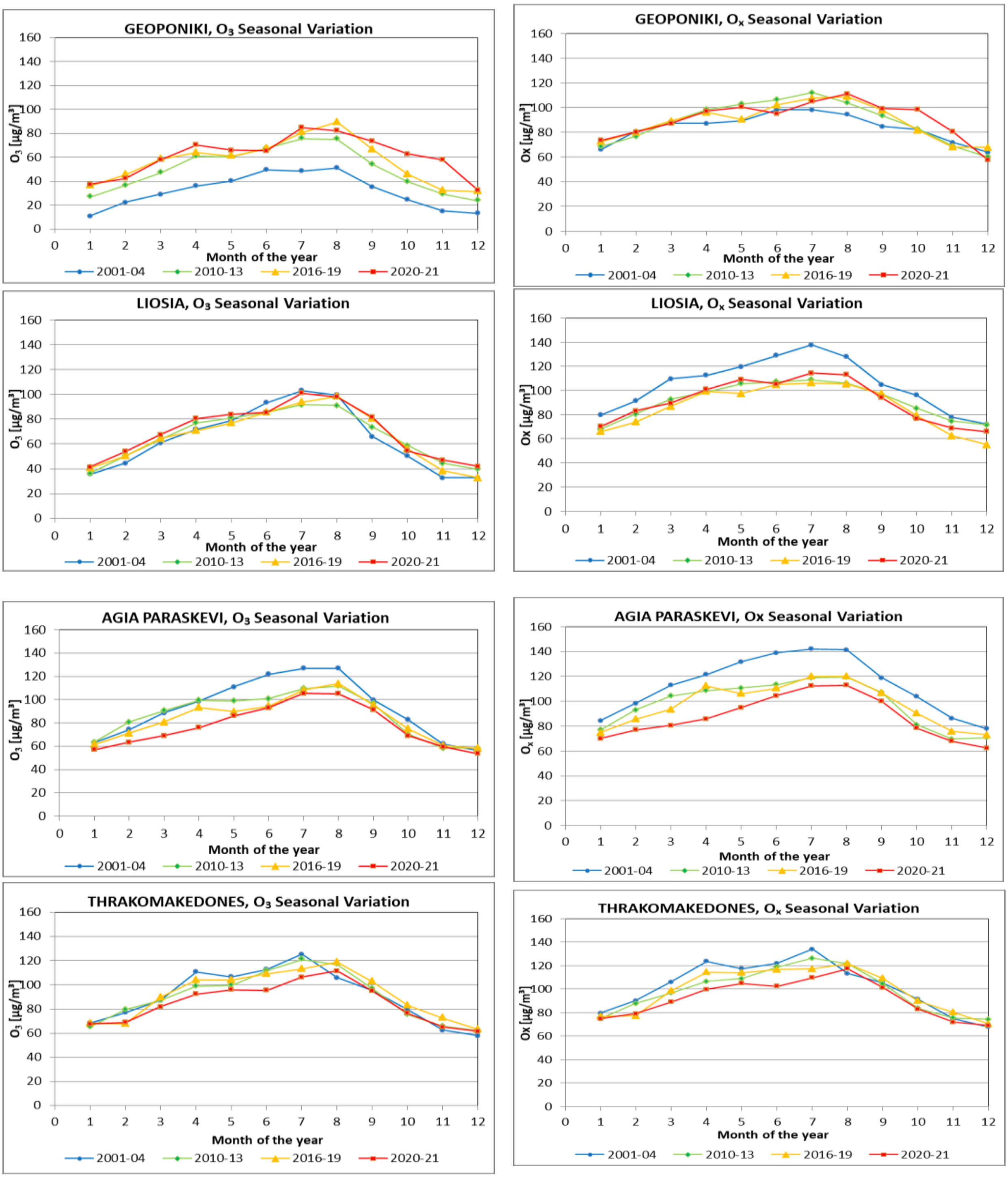

Figure 4. Seasonal variations in monthly O_3 (left column) and O_x (right column) averages at GEO, LIO, AGP, and THR for 2001–2004, 2010–2013, 2016–2019, and 2020–2021.

3. Conclusions

Substantial reductions in NO_x pollution levels (about 50%) occurred at the stations of GEO and LIO during the last two decades and weaker reductions in the stations of AGP and THR, which were even enhanced during the pandemic period, especially during the autumn and winter months. Consequently, ozone levels increased at GEO and LIO stations due to the reduced NO titration effect. On the other hand, at the peripheral stations of AGP and THR, ozone average levels showed a clear decrease, especially during the spring and summer months, indicating a corresponding decrease in regional ozone background levels. Nevertheless, there were still exceedances of air quality standards in some stations of the Athens air quality monitoring network, specifically regarding the photochemical NO_2 and ozone pollutants.

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References

1. Mantis, H.T.; Repapis, C.C.; Zerefos, C.; Ziomas, I. Assessment of the potential for photochemical air pollution in Athens: A comparison of emissions and air-pollutant levels in Athens with those in Los Angeles. *J. Appl. Meteor.* **1992**, *31*, 1467–1476. [CrossRef]
2. Ziomas, I.; Suppan, P.; Rappengluck, B.; Balis, D.; Tzoumaka, P.; Melas, D.; Papayannis, A.; Fabian, P.; Zerefos, C. A contribution to the study of the photochemical smog in the greater Athens area. *Beit. Phys. Atmos.* **1995**, *68*, 191–203.
3. Rappenglück, B.; Fabian, P.; Kalabokas, P.; Viras, L.G.; Ziomas, I.C. Quasi-continuous measurements of non-methane hydrocarbons (NMHC) in the greater Athens area during MEDCAPHOT-TRACE. *Atmos. Environ.* **1998**, *32*, 2103–2121. [CrossRef]
4. Ziomas, I.C. The mediterranean campaign of photochemical tracers-transport and chemical evolution (MEDCAPHOT-TRACE): An outline. *Atmos. Environ.* **1998**, *32*, 2045–2054. [CrossRef]
5. Kalabokas, P.D.; Viras, L.G.; Repapis, C.C.; Bartzis, J.G. Analysis of the 11-year record (1987–1997) of air pollution measurements in Athens; Greece. Part II: Photochemical pollutants. *Glob. Nest Int. J.* **1999**, *1*, 169–176.
6. Kalabokas, P.D.; Viras, L.G.; Repapis, C.C. Analysis of the 11-year record (1987–1997) of air pollution measurements in Athens; Greece. Part I: Primary air pollutants. *Glob. Nest Int. J.* **1999**, *1*, 157–168.
7. Kalabokas, P.D.; Viras, L.G.; Bartzis, J.G.; Repapis, C.C. Mediterranean rural ozone characteristics around the urban area of Athens. *Atmos. Environ.* **2000**, *34*, 5199–5208. [CrossRef]
8. Kalabokas, P.D.; Repapis, C.C. A climatological study of rural surface ozone in central Greece. *Atmos. Chem. Phys.* **2004**, *4*, 1139–1147. [CrossRef]
9. Kalabokas, P.; Repapis, C.C.; Mantis, H. A field study on the origins of surface ozone at the periphery of the urban area of Athens. *Fresenius Environ. Bull.* **2006**, *8*, 878–882.
10. Zerefos, C.S.; Kourtidis, K.A.; Melas, D.; Balis, D.; Zanis, P.; Katsaros, L.; Mantis, H.T.; Repapis, C.; Isaksen, I.; Calpini, B.; et al. Photo-chemical Activity and Solar Ultraviolet Radiation (PAUR) Modulation factors: An overview of the project. *J. Geophys. Res.* **2002**, *107*, 8134. [CrossRef]
11. Kourtidis, K.; Zerefos, C.; Rapsomanikis, S.; Simeonov, V.; Balis, D.; Perros, P.E.; Thompson, A.M.; Witte, J.; Calpini, B.; Sharobiem, W.M.; et al. Regional levels of ozone in the troposphere over Eastern Mediterranean. *J. Geophys. Res.* **2002**, *107*, 8140. [CrossRef]
12. Kalabokas, P.D.; Mihalopoulos, N.; Ellul, R.; Kleanthous, S.; Repapis, C.C. An investigation of the meteorological and photochemical factors influencing the background rural and marine surface ozone levels in the Central and Eastern Mediterranean. *Atmos. Environ.* **2008**, *42*, 7894–7906. [CrossRef]
13. Poupkou, A.; Melas, D.; Ziomas, I.C.; Symeonidis, P.; Lisaridis, I.; Gerasopoulos, E.; Zerefos, C. Simulated summertime regional ground-level ozone concentrations over Greece. *Water Air Soil. Pollut.* **2009**, *196*, 169–181. [CrossRef]
14. Mariolopoulos, E.; Zerefos, C.S.; Bloutsos, A.; Repapis, C. Ozone and temperature balloon measurements during the annular solar eclipse of 29 April 1976. *Proc. Acad. Athens* **1977**, *51*, 636–645.
15. Varotsos, C.; Kalabokas, P.; Chronopoulos, G. Atmospheric ozone concentration at Athens, Greece. Part II: Vertical ozone distribution in the troposphere. *Atmos. Res.* **1993**, *30*, 151–155. [CrossRef]
16. Kalabokas, P.D.; Chronopoulos, G.; Varotsos, C.; Zerefos, C.; Repapis, C.C. Vertical tropospheric ozone characteristics over Athens, Greece. In Proceedings of the XX Quadrennial Ozone Symposium, Kos, Greece, 1–8 June 2004; pp. 191–192.
17. Papayannis, A.; Balis, D.; Zanis, P.; Galani, E.; Wernli, H.; Zerefos, C.; Stohl, A.; Eckhardt, S.; Amiridis, V. Sampling of an STT event over the Eastern Mediterranean region by lidar and electrochemical sonde. *Ann. Geophys.* **2005**, *23*, 2039–2050. [CrossRef]

18. Kalabokas, P.D.; Volz-Thomas, A.; Brioude, J.; Thouret, V.; Cammas, J.P.; Repapis, C.C. Vertical ozone measurements in the troposphere over the Eastern Mediterranean and comparison with Central Europe. *Atmos. Chem. Phys.* **2007**, *7*, 3783–3790. [CrossRef]
19. Kalabokas, P.D.; Papayannis, A.D.; Tsaknakis, G.; Ziomas, I. Study on the atmospheric concentrations of primary and secondary air pollutants in the Athens basin performed by DOAS and DIAL measuring techniques. *Sci. Total Environ.* **2012**, *414*, 556–563. [CrossRef]
20. Kalabokas, P.D.; Cammas, J.-P.; Thouret, V.; Volz-Thomas, A.; Boulanger, D.; Repapis, C.C. Examination of the atmospheric conditions associated with high and low summer ozone levels in the lower troposphere over the eastern Mediterranean. *Atmos. Chem. Phys.* **2013**, *13*, 10339–10352. [CrossRef]