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DYNAMICS OF GROUND-LEVEL OZONE AND NITROGEN OXIDES IN RELATION TO METEOROLOGICAL PARAMETERS IN CONTINENTAL AND COASTAL CROATIA

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INTRODUCTION

Understanding the dynamics of ground-level ozone, a secondary pollutant, and nitrogen oxides (NOx), its primary precursors, is of critical importance for assessing air quality and protecting human health and the environment in urban areas. Ground-level ozone is not emitted directly from anthropogenic sources; rather, it is formed in the troposphere through complex photochemical reactions involving the dissociation of nitrogen dioxide under the influence of solar radiation and elevated air temperatures, a process further accelerated by the presence of volatile organic compounds. Conversely, in urban centers with dense traffic, the phenomenon of photochemical titration frequently occurs, whereby freshly emitted nitrogen monoxide rapidly consumes ambient ozone, leading to localized drops in its concentration near the emission sources. Contemporary climate change and the increasing frequency of extreme meteorological events, such as prolonged summer heatwaves and stable anticyclonic systems, significantly modify the chemical response of the atmosphere. High insolation and extreme temperatures accelerate the kinetics of photochemical ozone production, while the accompanying stagnation of air masses prevents vertical mixing and traps pollutants within the lower layers of the troposphere. However, the ultimate chemical response of the atmosphere is heavily modulated by regional meteorological regimes and local topography. The aim of this study is to analyze and compare the impact of meteorological parameters and air mass movement on the spatiotemporal variations of O_3 and NOx concentrations over a five-year period (from 2019 to 2023) in two geographically and climatically distinct regions of Croatia: Osijek, characterized by a stable continental climate and an open flat terrain favorable for dispersion, and Rijeka, a specific coastal area where complex coastal orography and land-sea breeze circulation (bura or maestral) dominate the transport and accumulation of secondary pollutants.

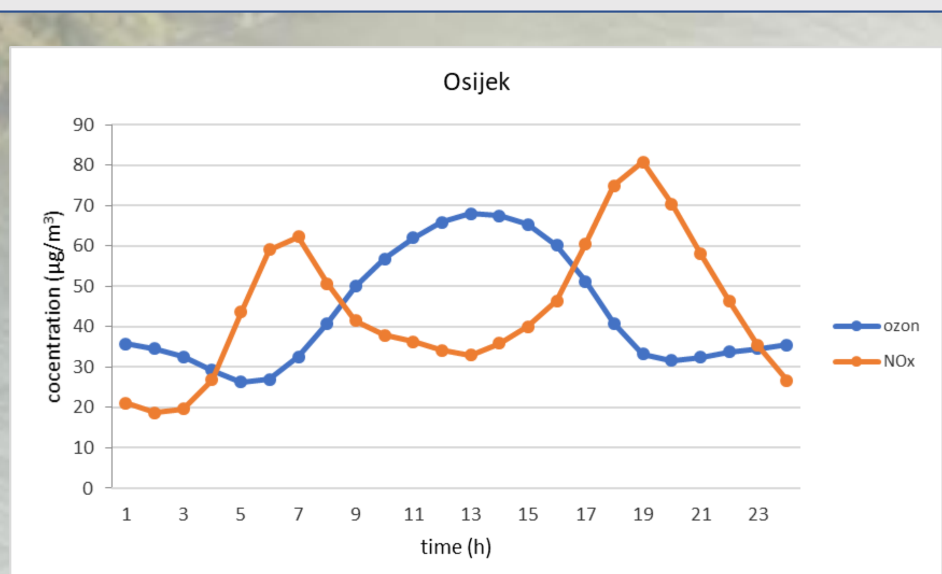

Fig. 1. Daily trend in Osijek

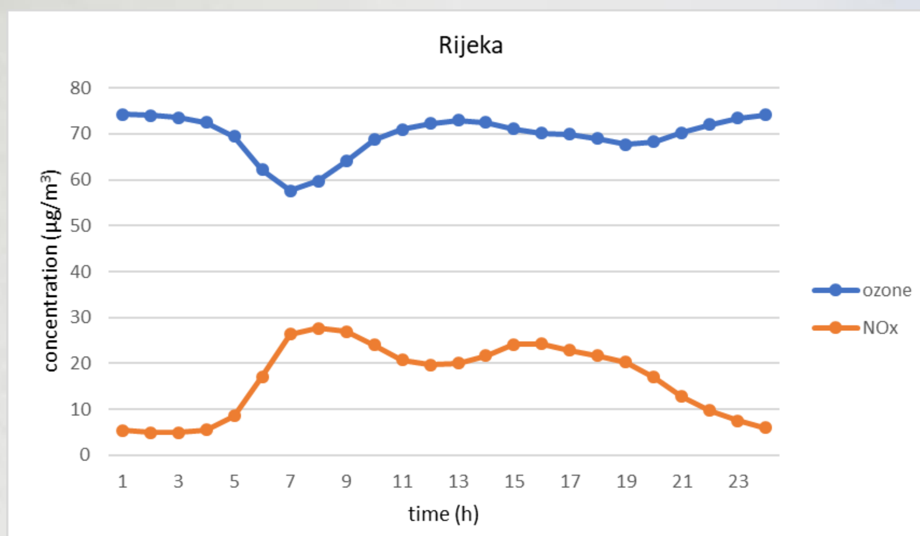

Fig. 2. Daily trend in Rijeka

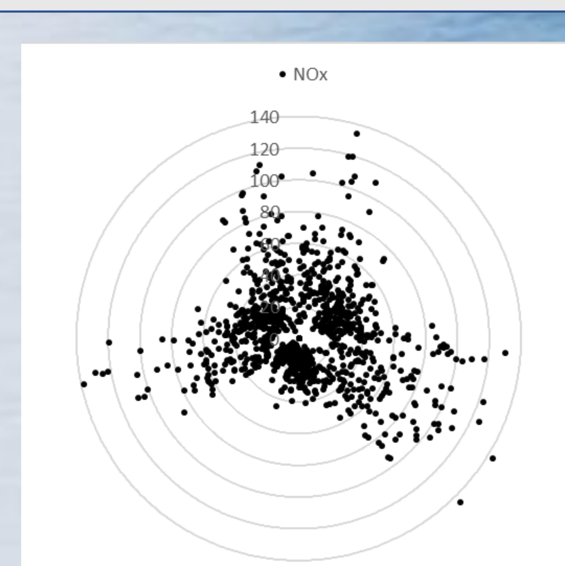

Fig. 3. Polar plot NOx, Osijek

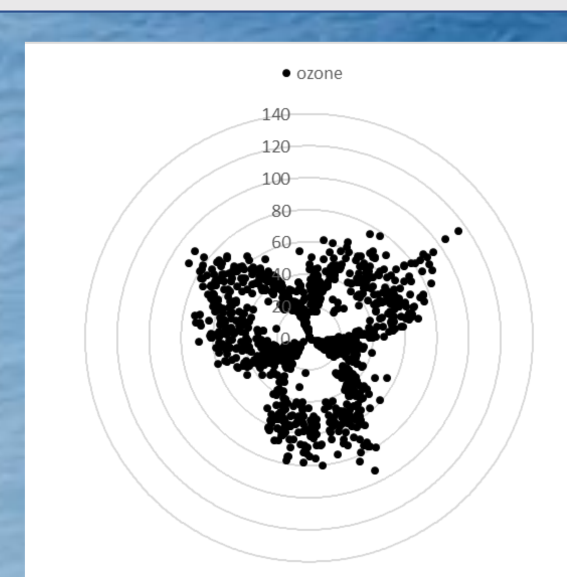

Fig. 4. Polar plot ozone, Osijek

RESULTS

Statistical processing and visualization of the data collected over the period from 2019 to 2023 revealed clear patterns in the diurnal variation and spatial distribution of pollutants as a function of meteorological parameters and air mass movement, indicating significant differences between the two monitored areas. In Osijek (Fig. 1), the nitrogen oxides profile exhibits a classic bimodal character with distinct peaks in the morning and evening, which is directly linked to the intensity of urban traffic as the primary source of precursor emissions. The ground-level ozone curve in Osijek displays a regular bell-shaped pattern with a maximum in the early afternoon, confirming stable continental dynamics and a high correlation of ozone formation with the diurnal cycles of insolation and temperature. Principal Component Analysis for Osijek (Fig. 7) further chemometrically validates this link, as the O_3 and temperature (*T*) variables are located close to each other on the PC1 axis. The open flat terrain of the continental interior allows wind speed (*BV*) to primarily favor the dispersion and dilution of primary pollutants; this is clearly observed in the NOx polar plot (Fig. 3), where the highest concentrations are scattered along the dominant traffic routes, whereas the three-pronged polar plot for ozone (Fig. 4) is more uniform and records lower maximum values (80 µg/m³).

In Rijeka, a considerably more complex situation was recorded, conditioned by coastal circulation and complex orography. The diurnal variation in Rijeka (Fig. 2) reveals a much higher baseline (night-time) ozone level (> 70 µg/m³) , alongside a sharp decline in concentrations during the morning hours that exactly coincides with a sudden spike in NOx emissions. This trend graphically demonstrates the frequent occurrence of photochemical ozone titration within the urban canyon in close proximity to the emission sources themselves. The impact of local meteorological regimes is most clearly illustrated by the polar plots for Rijeka; while elevated NOx concentrations (Fig. 5) are tightly accumulated around the source under weak air movement, the ozone plot (Fig. 6) displays a specific "wing-like" shape (east-west orientation) with a complete absence of data in the north and south directions. This proves that the highest ozone concentrations in the coastal region (> 100 µg/m³) are directly associated with the regional transport of air masses from the sea surface, channeled by the mountainous hinterland and the dynamic land-sea breeze exchange (bura or maestral). The PCA plot for Rijeka (Fig. 8) confirms this dynamic system, where ozone shows a strong association with wind speed (*BV*) and relative humidity (*RV*) on the PC1 axis, whereas temperature is dislocated. Synergy with extreme conditions, such as heatwaves, indicates that stable anticyclones in the continental interior potentiate local photochemical production due to air stagnation, whereas in the coastal system, wind advection and the transport of secondary pollutants remain the dominant factors modifying the atmospheric response.

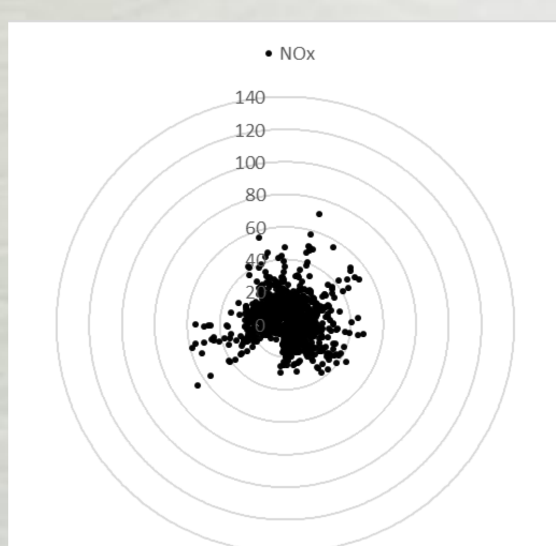

Fig. 5. Polar plot NOx, Rijeka

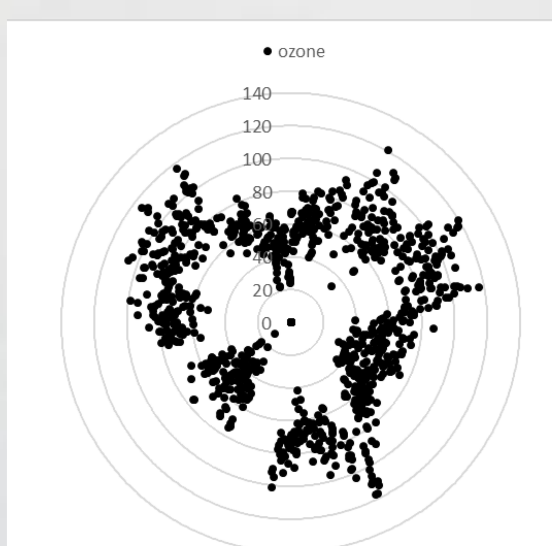

Fig. 6. Polar plot ozone, Rijeka

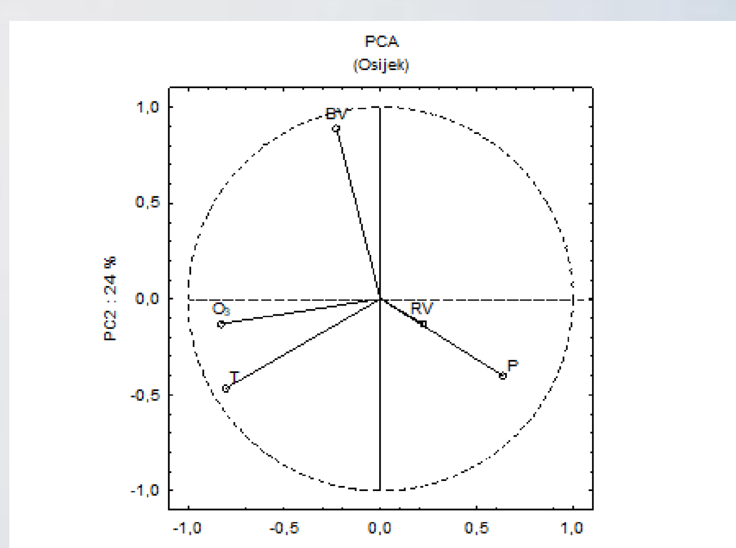

Fig. 7. Factor loadings plot (variables), Osijek

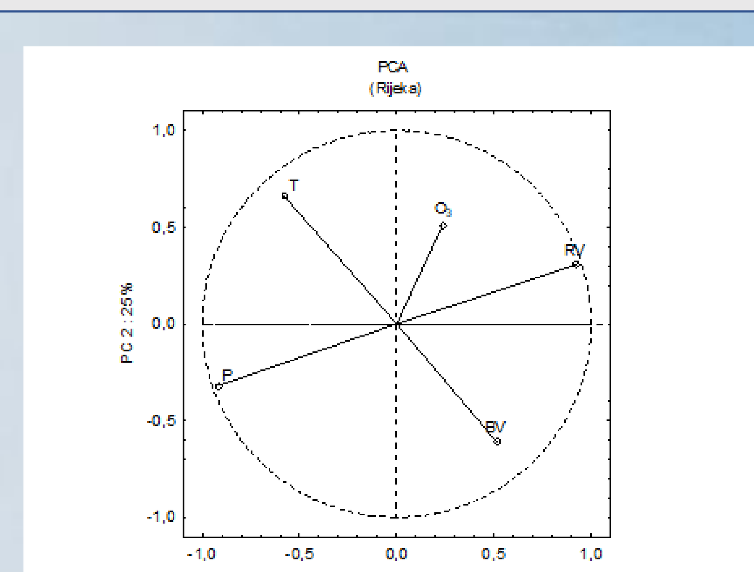

Fig. 8. Factor loadings plot (variables), Rijeka

CONCLUSIONS

The five-year study (2019–2023) confirmed that geographical location and meteorological regimes crucially modify the dynamics of ground-level O_3 and NOx. In the continental region (Osijek), a regular photochemical dynamic driven by diurnal cycles of insolation and temperature was identified, with the open terrain and wind speed primarily favoring the dispersion and dilution of primary pollutants. Conversely, the coastal region (Rijeka) exhibited a more complex system heavily influenced by coastal orography and land-sea breeze circulation (bura or maestral). The high baseline night-time ozone levels in Rijeka and sharp morning photochemical titration clearly demonstrate the impact of the urban canyon on localized ozone consumption. Polar plots and PCA diagrams unambiguously prove that highest ozone concentrations in the coastal area are directly linked to the regional transport of air masses from the sea surface, whereas in the continental interior, extreme conditions such as heatwaves potentiate local photochemical production due to air stagnation. These findings highlight the necessity of implementing regionally tailored air quality management strategies.

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