Long – term analysis of NO, NO_2 and O_3 weekly cycles in the Rhine – Ruhr area, Germany

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Introduction

In this paper temporal cycles of the air pollutants NO, NO_2 and O_3 have been examined on the basis of the data from 16 stations (Fig. 1) classified in four groups (industrial, traffic, urban background and rural background) in North Rhine – Westphalia for the time period of 1981 – 2007. The results of Fourier transformation showed clearly defined 7 – day cycles for industrial, traffic and urban background stations making 36 % difference (t-test: 99.2 %) between weekday – weekend NO concentrations, and 20 % (t-test: 99 %) for NO_2. This was not the case for the far remote background stations.

Ozone concentrations were higher by 21 % on weekends in comparison to those on working days at the industrial stations, whereas the difference was only 4 % at the remote background stations, though concentration levels were in absolute average 80 % higher at the background stations (t-test: 99 %).

Pollution levels are not only dependent on the emission levels, but also on meteorological factors that influence the pollution distribution, dispersion, photochemical transformation and transport towards areas far away from the pollution sources (Mayer, 1999; Elansky et al., 2007). Significant correlation on the one hand between ozone and humidity, and on the other hand between NO_x and wind speed made it important to examine ozone weekly cycles for different humidity values, and the amplitude of NO_x weekly cycles for different wind speeds.

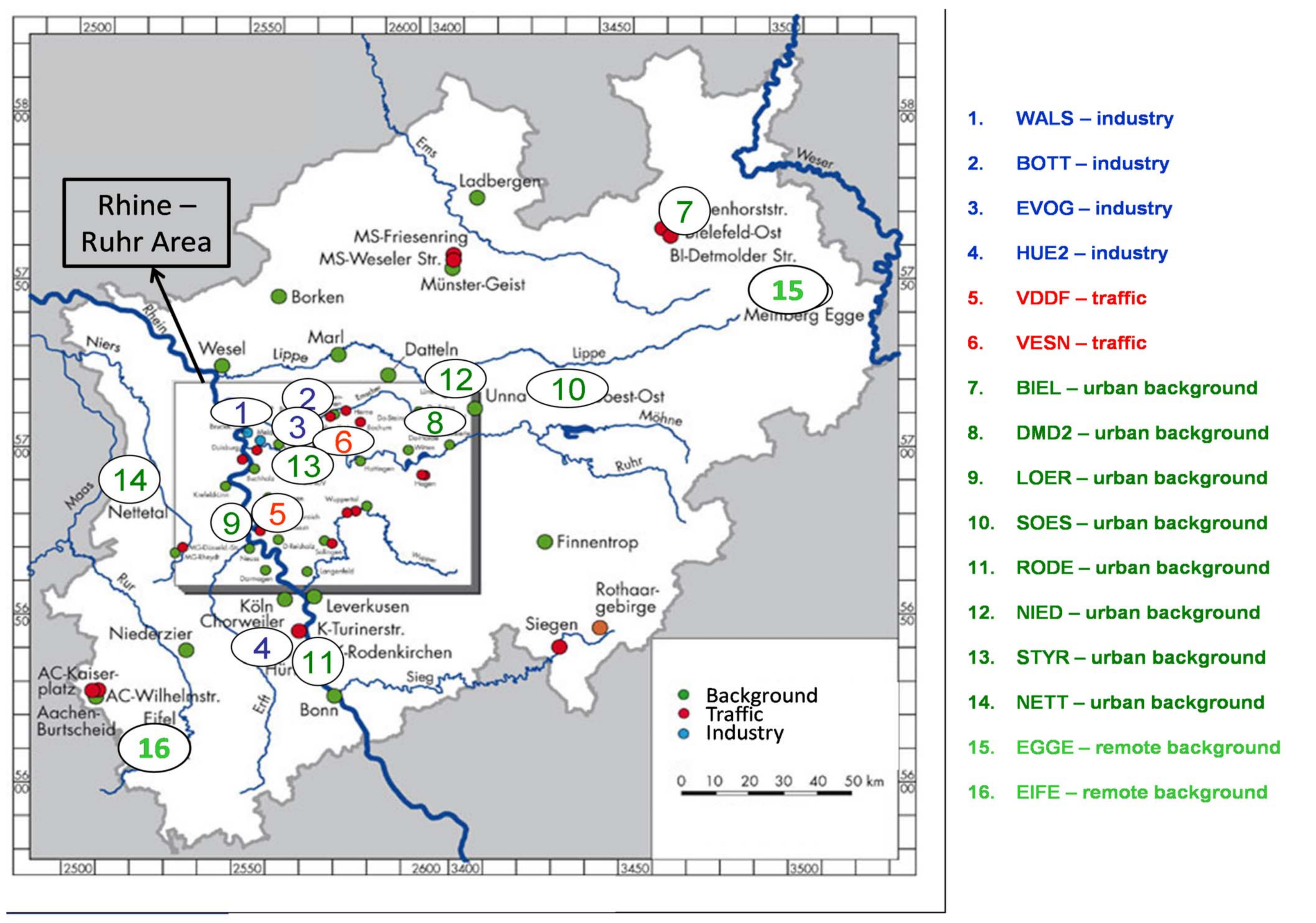


Fig. 1: Map of the stations location: light and dark green colours stand for remote and urban background stations respectively, blue for industrial, and red for traffic stations. Marked 16 stations have been chosen with criteria of the longest available dataset (LANUV NRW, 2011).

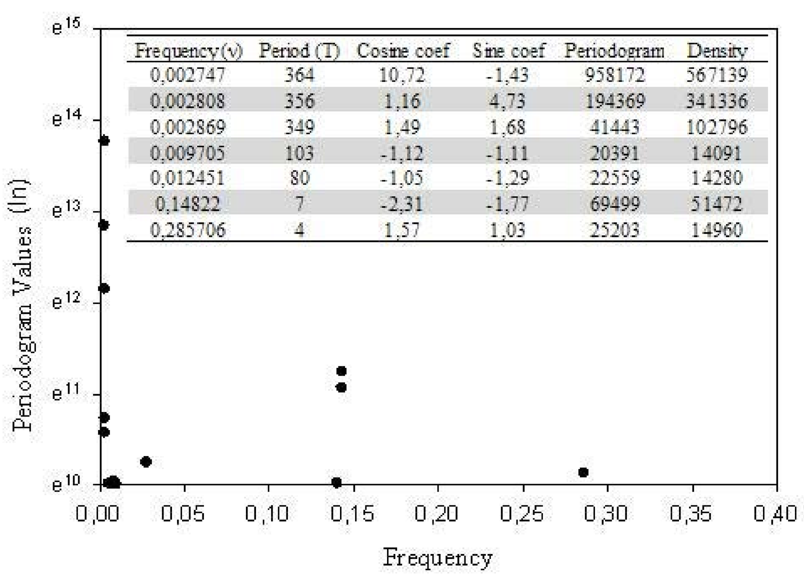
Methods

All the half-an-hour data from 16 stations (10 —background, 4—industry, and 2—traffic stations) for the six kind of pollutants (CO, NO, NO_2, SO_2, O_3, PM_{10}) and meteorology running from 1981 till 2007 have been analysed for the quality having used box plots. Statistically defined outliers were defined tot be extremely high pollution levels because of their systematic bivariate distribution and were remained in datasets for the further investigations.

All the pollutant concentrations at the four groups of stations have been averaged and aggregated on the basis of days of the week firstly to show the absolute average concentration differences and secondly weekday – weekend concentration differences among the different kind of stations. As comparison criteria t-test was used (Shao, 1976). Not only the significance test, but also Fourier (spectral) analysis (Panofsky, 1958) was applied.

Results

Fourier (spectral) transformation has been applied to the air pollutants in order to prove the existence of temporal cycles in air pollution concentration levels at different kind of stations. Periodogram values of hourly NO concentrations at the industrial stations (WALS and BOTT) are exhibited in Table 1 and Fig. 2, where significantly high periodogram values (presented in log natural scale) can be seen for the frequencies of 0.002747 (364),..., and 0.148280 (7 days). This is not the case for the remote background stations (EGGE and EIFE, Fig. 3).



Frequency(v)	Period (T)	Cosine coef	Sine coef	Periodogram	Density
0,002747	364	10,72	-1,43	958172	567139
0,002808	356	1,16	4,73	194369	341336
0,002869	349	1,49	1,68	41443	102796
0,009705	103	-1,12	-1,11	20391	14091
0,012451	80	-1,05	-1,29	22559	14280
0,14822	7	-2,31	-1,77	69499	51472
0,285706	4	1,57	1,03	25203	14960

Fig. 2 and **Table 1**: Results of Fourier analysis for daily mean NO concentrations at the industrial stations (WALS and BOTT) for the period of 1981 – 2007 .

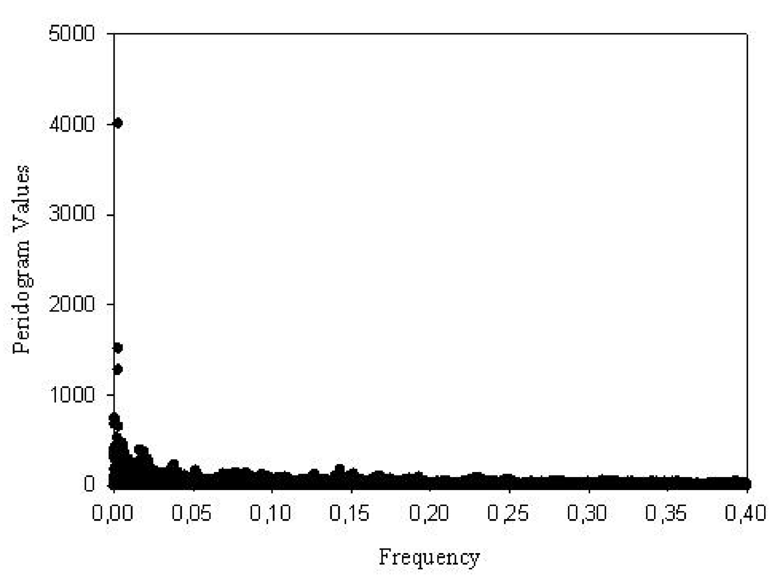


Fig. 3: Periodogram values obtained from Fourier analysis for NO daily mean concentrations at the remote background stations (EGGE and EIFE) for the period of 1981 – 2007.

In Fig. 4 a) NO_x at the industrial station exhibits clearly defined weekly cycles, the diurnal course of NO_x concentrations is double waved with two peaks – one at the morning (6 – 8 a.m.) and the other one at the evening hours (4 – 8 p.m.) during the working days caused by rush – hour traffic. No peaks can be identified on weekends, but it can be seen that concentrations get higher values during afternoon hours (on Saturdays and Sundays), which might be explained with leisure activities of humans.

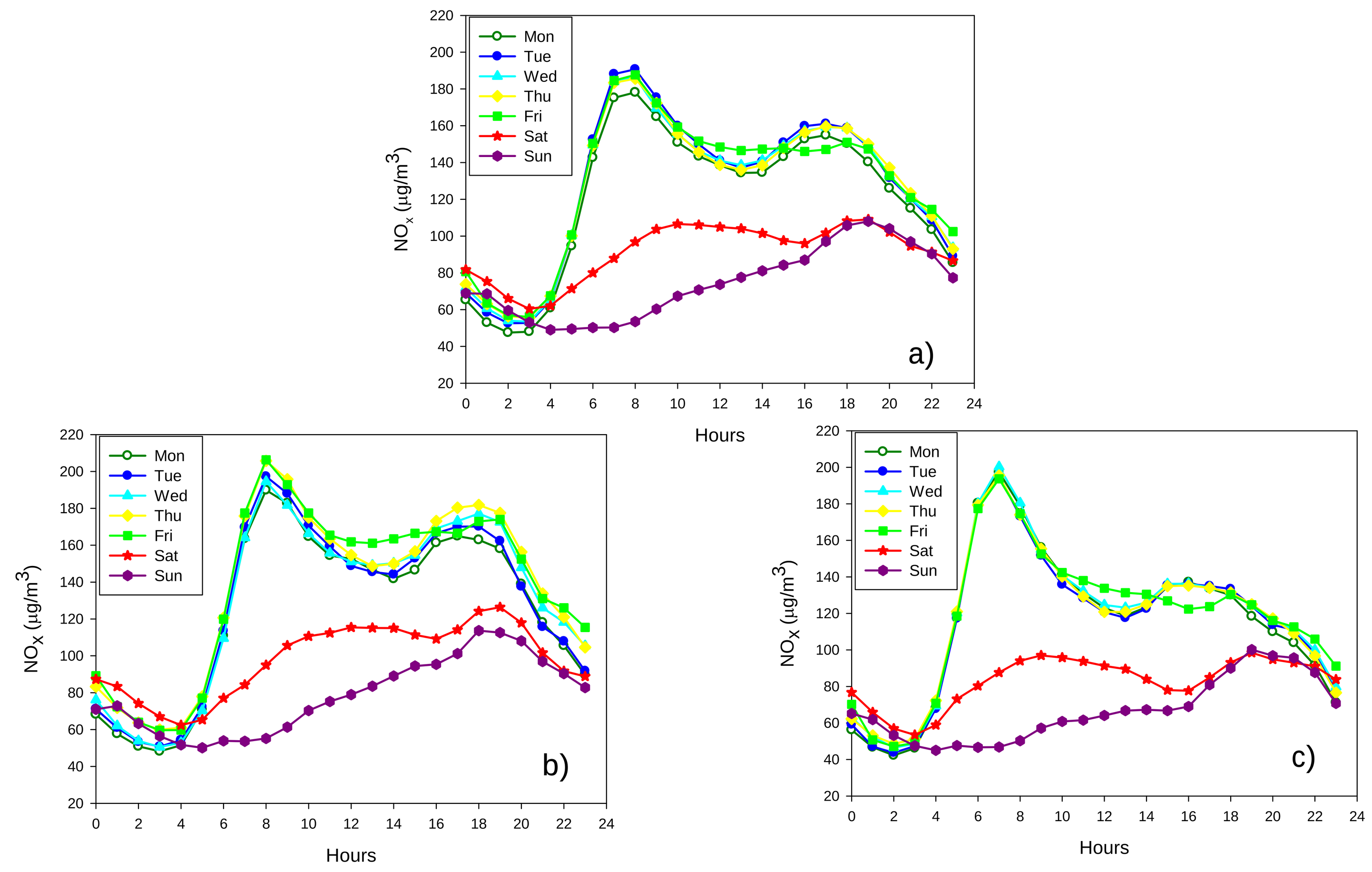


Fig. 4: Weekly and diurnal cycles of NO_x concentrations at the traffic stations (VESN, VDDF) for a) average, b) winter (DJF), and c) summer (JJA) seasons for the period of 1981 – 2005.

Diurnal course of pollution is influenced not only by the anthropogenic effect, e.g. rush – hour traffic, but also by the development of mixing layer in the atmosphere during the daylight hours and frequent inversions in the evening hours (Mayer, 1999).

Seasonal pattern of pollution levels differs in winter (DJF) (Fig 4b) and summer (JJA) (Fig. 4c) seasons. NO_x concentrations are in average by 18 % higher in winter compared to those in summer. If NO_x concentrations are observed to be significantly higher on working days and in winter, it is not the case for ozone (not shown here), which shows a vice versa behavior – called 'Sunday effect' (Cerveny and Balling Jr., 1998).

To examine ozone photochemical production under dry air conditions with high temperature and radiation at different kind of stations, ozone weekly behavior has been estimated once for days with low humidity, and once for days with high humidity (Fig 6a-b). To find out the limit between low and high humidity, the frequency of humidity values has been studied (Fig. 5) for the remote background station EGGE (1984 – 2007). Up till 90 % of relative humidity the trend is linear, and starting from this point the increase of the curve is steep, turning to exponential dependence, hence the limit was set at 90 %.

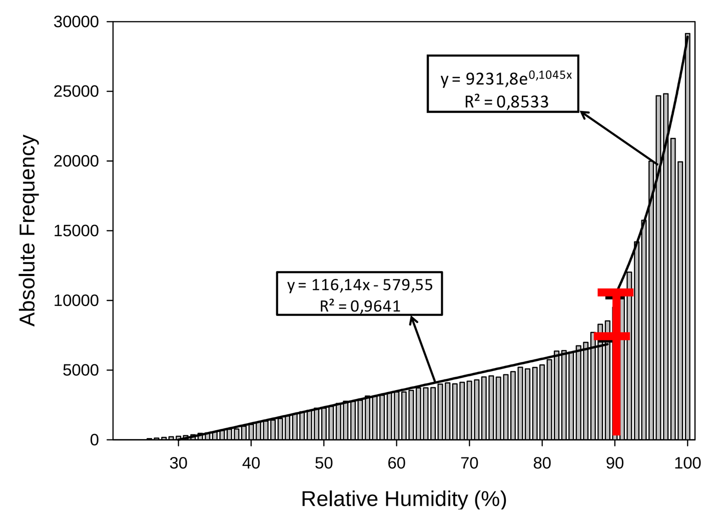


Fig. 5: Frequency distribution of relative humidity at the remote background station EGGE (1984–2007).

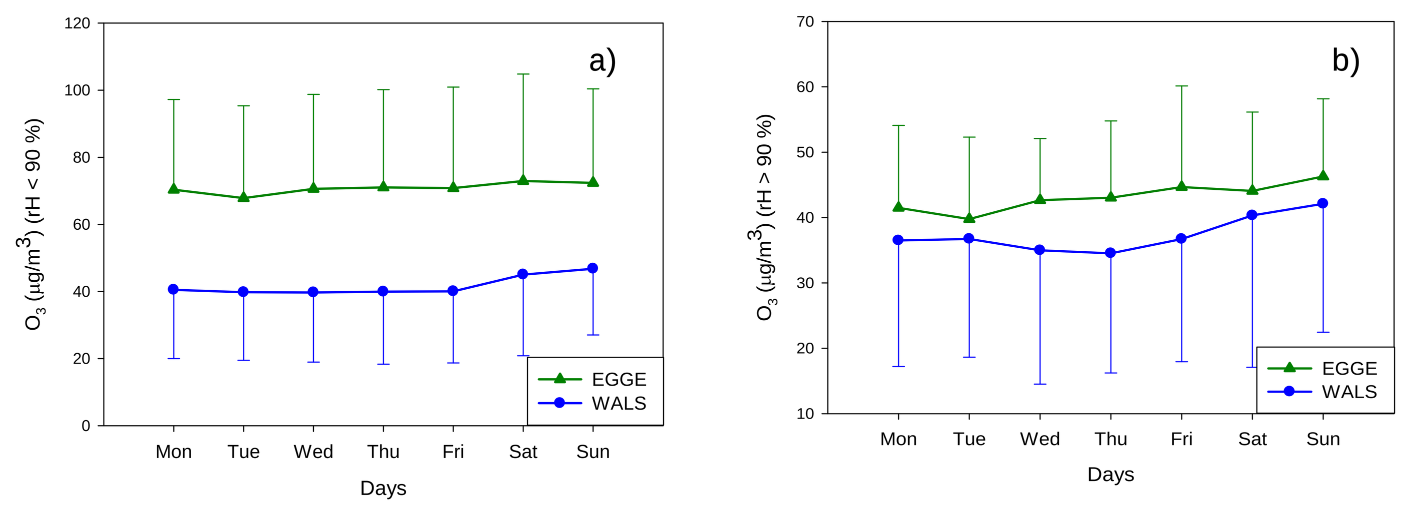


Fig. 6: Weekly cycles of ozone at the remote background (EGGE) and industrial (WALS) stations for a) humidity < 90% and b) humidity > 90 % (1984 – 2007).

Conclusions

Clearly defined weekly cycles could be proved at the traffic, industrial and urban background stations with the help of Fourier (spectral) analysis, which was not the case at the remote background ones. NO_x (NO + NO2) were registered to get 126 µg/m³ (mean for the whole research period), whereas they were 82 µg/m³ on working days, making 35 % difference. On the other hand despite the fact that ozone concentrations were double more at the regional background stations in comparison to the industrial ones during the last two decades, the weekly cycles were significant at the latter ones, making 20 % difference (28 µg/m³ on working days and 34 µg/m³ on weekends), whereas at the remote background stations it was only 2 % (54 µg/m³ on working days and 56 µg/m³ on weekdays).

Temporal cycles are not caused only by anthropogenic effect, meteorology plays also a great role on their strength. Assessment of weekly cycle's amplitude of NO_x for different wind speeds showed that not only absolute average concentrations decrease, but the amplitude does it as well. Relative humidity plays a great role in ozone pattern.

References

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