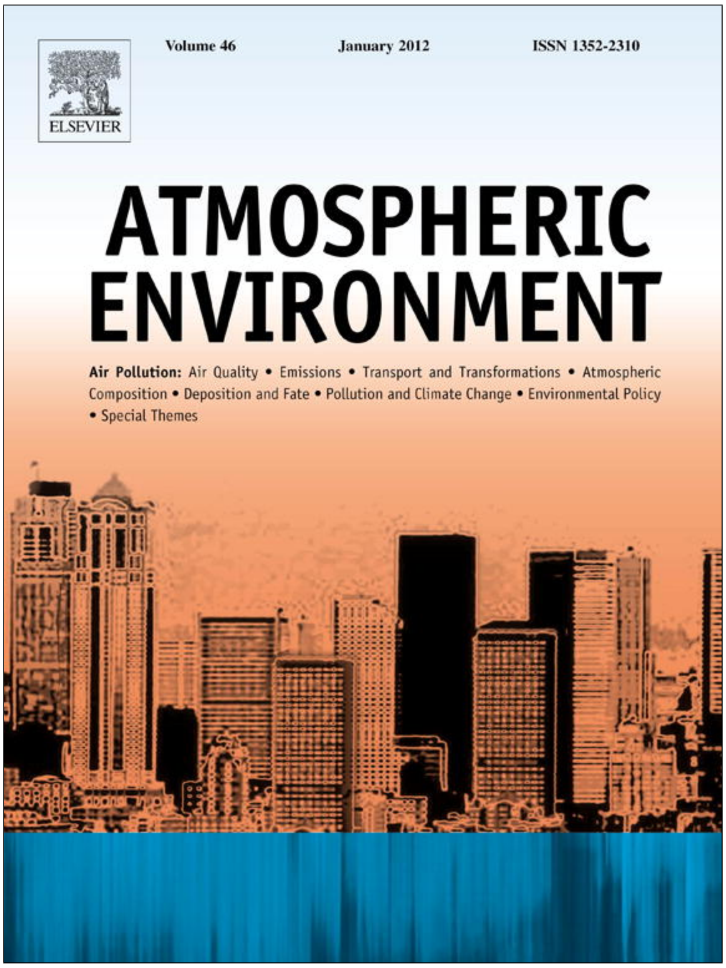
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Long-term analysis of NO, NO_2 and O_3 concentrations in North Rhine-Westphalia, Germany

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HIGHLIGHTS

- ► Long-term pollution data are analysed at different kind of stations in Germany.
- ► The aim is to evaluate the efficiency of legislation norms for the last 2 decades.
- ► Analysis of NO_x and Ozone data has been carried out in urban and rural areas.
- ► Weekly cycles of the pollutants are evaluated in NO_x- and VOC-limited regimes.

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ABSTRACT

Legislative norms developed at the end of the 1970s, structural changes in the economy, and the implementation of filters in both vehicles and industries improved the air quality of North Rhine-Westphalia, the largest western state in Germany in terms of population and economic output. Because these changes occurred unevenly across the state, the main aim of the given study is to analyse the historical development of air pollutants in the various environments (e.g., industrial, traffic or rural background) within the state.

NO, NO_2 and O_3 concentrations observed at six stations (one industrial, two traffic, one urban and two rural background) from 1981 to 2007 have been obtained from the Environmental State Agency for Nature, Environment and Consumer Protection (LANUV NRW). These data have been evaluated to investigate time trends of these pollutants and the impact of weekly cycles on ozone formation in NO_x-limited areas (rural background) and VOC-limited areas (urban areas with traffic network). The relationships between ozone production mechanisms and ozone precursors (NO, NO_2 and their ratio) have also been taken into account.

In contrast to the sharp decrease in NO concentrations (65%), only a moderate, insignificant decrease in NO_2 (10%) was observed because catalytic filters in vehicles support emissions of NO_2 as a primary pollutant. Changes in NO/NO_2 ratio and higher temperature favoured an increase in ozone concentrations (20%), which appears to be the indicator of summer smog. The results showed that, although ozone forming potential is higher at background stations due to higher biogenic VOC and lower NO emissions, time trends were steeper at the industrial stations because of radical changes in NO_x concentrations.

Examination of the weekly and diurnal cycles of NO and NO_2 showed that not only the absolute average values of the pollution levels decreased (with a turning point in 1998) but also the shape of the diurnal cycle (differences between primary and secondary peaks) changed in response to developed legislative norms (Bayerisches Landesamt für Umweltschutz, 2011).

Abbreviations: NRW, North Rhine-Westphalia; NO, nitric monoxide; NO_2, nitric dioxide; O_3, ozone; LANUV, Environmental State Agency for Nature, Environment and Consumer Protection; VOC, volatile organic compounds; NMVOC, non-methane volatile organic compounds; AVOC, anthropogenic volatile organic compounds; BVOC, biogenic volatile organic compounds; Duisburg-Walsum, WALS; Düsseldorf-Mörsenbroich, VDDF; Essen-Ost, Steeler street, VESN; Horn-Bad Meinberg Egge, EGGE; Simmerath Eifel, EIFE; Köln Rodenkirchen, RODE; WDay, weekday; WEnd, weekend.

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1. Introduction

NO_x and O_3 are one of the most important pollutants in urban areas (Moeller, 2010). Investigation on these pollutants has been carried out worldwide examining both their temporal development (Mayer and Schmidt, 1998; Fischer et al., 2006; Pandey et al., 2008; Tan et al., 2009; EPA, 2007) and their interrelations with chemical mechanisms (Sillman, 2003; Jacob and Winner, 2009). Examination of the nitrogen oxides and ozone is of great importance especially in urban-industrialized areas being undergone to economical, structural changes. North Rhine-Westphalia, the largest western state in Germany with area of 32.000 km^2 and 18 million inhabitants, is a good example of this kind of area, where developed legislation norms, structural changes in economy, implementation of filters in cars and industries caused large changes in pollution levels. Six stations in this state having different character (industrial, traffic, urban and rural background) have been chosen from the network of Environmental State Agency for Nature, Environment and Consumer Protection (Landesamt für Natur, Umwelt und Verbraucherschutz Nordrhein-Westphalen, LANUV, NRW, 2007) to analyse the long-terms changes in NO_x and O_3 concentrations (1983–2007).

Not only the impact of legislation norms, but also atmospheric exchange conditions were studied to determine the influence of meteorological parameters on different kinds of pollutants using principal component analysis and correlation matrix.

Another emphasis in this study was given to the estimation of weekly cycles not only to evaluate the impact of emission changes on the pollution levels of different weekdays but also to study the sensitivity of ozone production in NO_x- and VOC-limited areas.

2. Theoretical background

During the process of economic growth, urbanisation, energy consumption, development of dense transport networks and rapid population growth, air pollution became a large problem in many industrialised, urban areas. The relationship between industrialisation and air pollution can be analysed with the so-called Environmental Kuznets curve (Chen and Kan, 2008). As shown in Fig. 1, in a developing industrial economy, less attention is paid to environmental issues; thus, with increasing stage of industrial development, air pollution levels also increase. After attaining a certain standard of living and when environmental pollution is at its maximum, society's focus changes from financial interest to social interest, wherein a clean environment becomes more important, and the trend of environmental pollution is reduced or even reversed from industrialisation. This turning point occurred, for example, in the Ruhr area in 1961, when the former chancellor of the Federal Republic of Germany, Willy Brandt, used the term "Blue sky over Ruhr Area" in his political programme (Nonn, 2009).

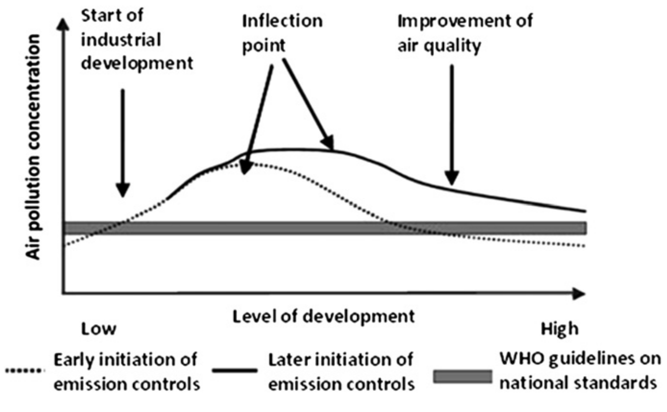

Fig. 1. Environmental Kuznets curve (EKC) showing air pollution concentrations during early (black dotted line) and later (black solid line) initiation of emission controls and WHO guidelines (grey line) (Source: Chen and Kan, 2008).

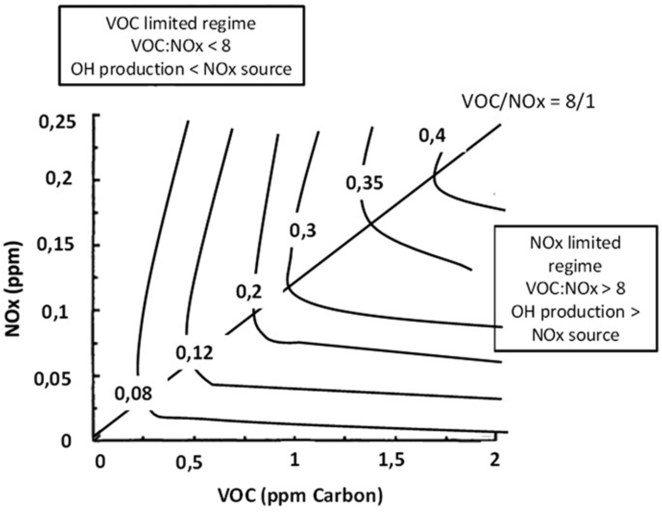

Fig. 2. Ozone isopleths as a function of the average concentrations for NO_x and VOC (Source: Röth, 2002, based on Sillman, 1999, modified).

Due to the combustion of fossil fuels, transport (not only through roads, but also water) contributes the main source of NO_x (56%) in Germany. The other important sources are industrial entities, especially energy-producing sources (18%) (data from Umweltbundesamt for 1990–2007). As highly reactive gases, NO_x are very important because nitrogen oxides, together with CO, methane and non-methane volatile organic compounds (NMVOCs), favour ozone production in the presence of sunlight and high temperatures (Sillman, 2003; Jacob and Winner, 2009).

The relationship between O_3 and both of its precursors, NO_x and VOC, can be observed in the counter diagram (Fig. 2) (Röth, 2002), showing O_3 peak values as a function of NO_x and VOC mixing ratios. Here, NO_x-sensitive and VOC-sensitive regimes are shown separately. In the NO_x-sensitive regime, in which NO_x is relatively low

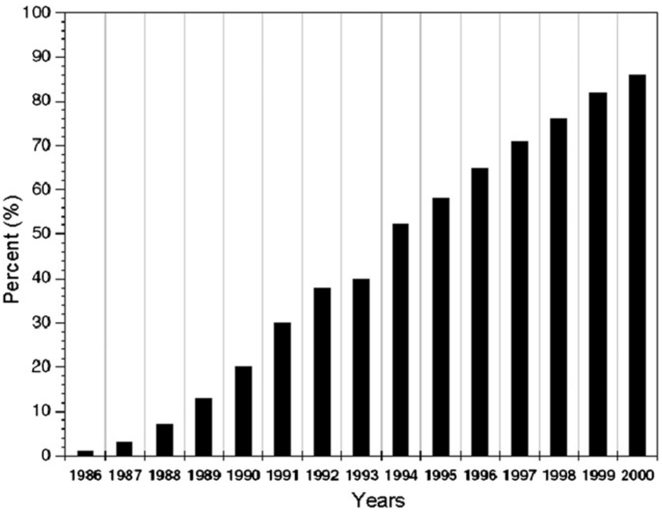

Fig. 3. The trend in the percentage of cars with three-way catalytic filters in Germany (Source: Fischer et al., 2006).

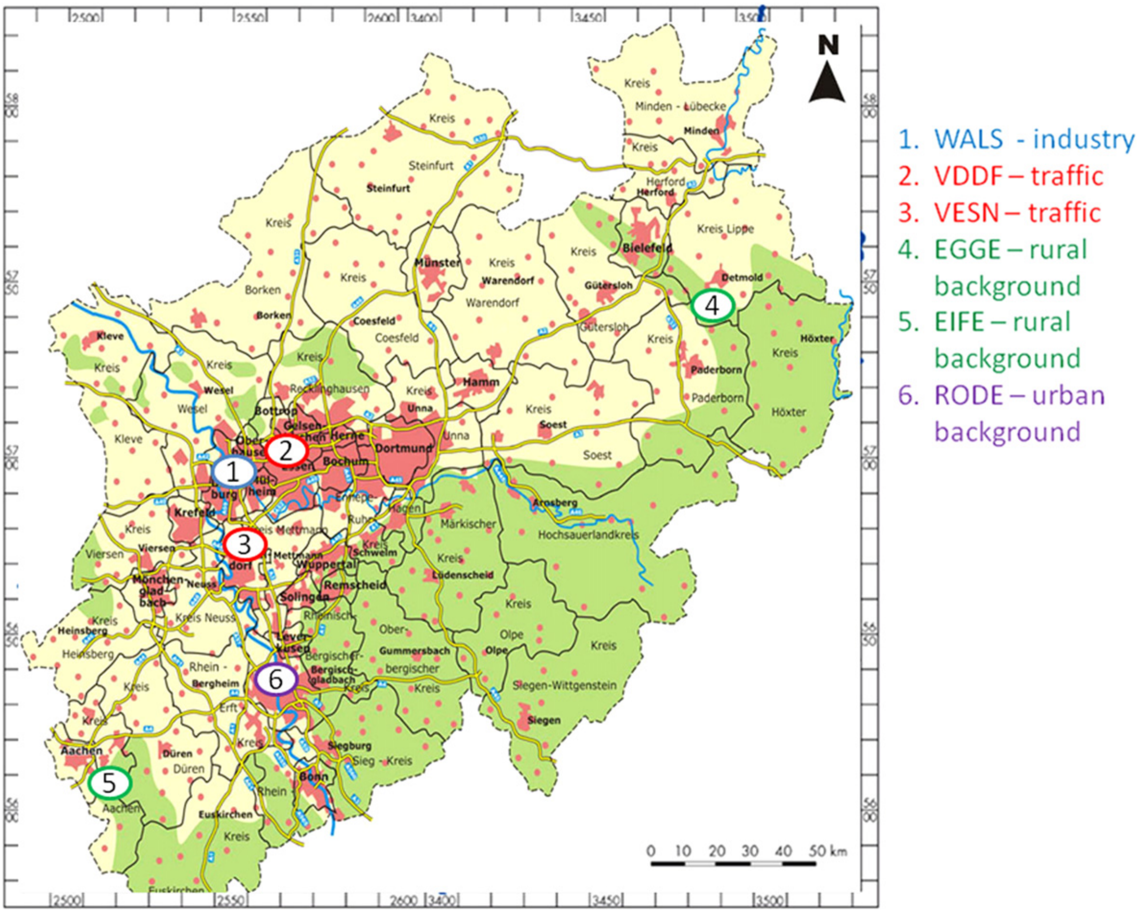

Fig. 4. Measurement stations for air quality in North Rhine-Westphalia (Source: LANUV, NRW, 2007).

and BVOC is high (as is typical of remote forest regions), O_3 levels are getting higher with increasing NO_x and changes little with respect to VOC. The VOC-sensitive regime exhibits the opposite behaviour. Thus, it can be concluded that ozone pollution events are not limited to the rural areas but occur in the cities as well, harming the health of the population.

To avoid the negative impacts of increased population and urbanisation, legislative norms have been implemented worldwide to mitigate and reduce pollution concentrations. To decrease pollution concentrations, the implementation of filters (catalytic filters) in both cars and industrial factories has largely been realised. Filters implemented in cars are called catalytic converters. These devices reduce the toxicity of certain kinds of emissions from the internal combustion engine by providing an environment for a chemical reaction wherein toxic combustion by-products are converted into less toxic substances. Three-way catalytic filters have three functions: a) reduction of nitrogen oxides into nitrogen and oxygen, b) oxidation of carbon monoxide into carbon dioxide, and c) oxidation of unburned hydrocarbons to carbon dioxide and water. The trend in the percentage of cars with three-way catalytic filters in Germany is shown in Fig. 3.

Because of the aforementioned three functions of catalytic converters and the fact that NO_x originate mainly from the transport sector, the successful implementation of catalytic filters together with the Petrol Lead Norm (adopted in 05.08.1971 in Germany, aiming to reduce lead in gasoline) produced large decreases not only in absolute NO concentrations but also in the NO/NO_2 ratio, particularly in regions which are defined by dense transport networks. In contrast, it is known that cars using these filters emit NO_2 as a primary pollutant (starting from the 1990s)

Table 1
Characteristics of the stations; Source (LANUV, 2010).

Station Name	Duisburg-Walsum	Essen-Ost, Steeler Str	Düsseldorf-Mörsenbroich	Horn-Bad Meinberg Egge	Simmerath Eifel	Köln-Rodenkirchen
Short name	WALS	VESN	VDDF	EGGE	EIFE	RODE
Area type	Urban area	Urban area	Urban area	Rural area	Rural area	Suburban area
Measurement start	1/5/1979	1/1/1989	4/4/1989	1/10/1983	1/9/1983	1/12/1980
Measurement end	–	–	2/1/1984	2/1/2008	–	–
Height above sea level	28 m	100 m	38 m	430 m	572 m	45 m
Longitude	6° 44′ 56″	7° 1′ 51″	6° 48′ 6″	8° 57′ 5″	6° 16′ 54″	6° 59′ 9″
Latitude	51° 31′ 31″	51° 27′ 8″	51° 15′ 7″	51° 49′ 56″	50° 39′ 16″	50° 53′ 27″

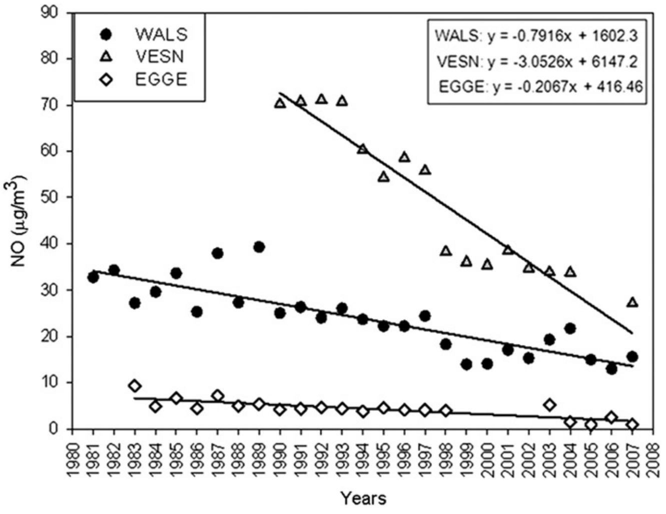

Fig. 5. Annual mean concentrations of NO at the industrial (WALS), traffic (VESN) and rural background (EGGE) stations for the period 1981–2007 (Source: Melkonyan, 2011, modified).

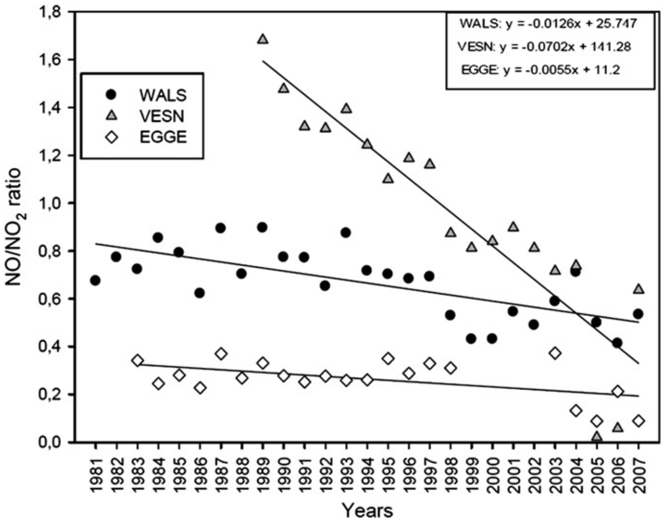

Fig. 7. NO/NO_2 ratio on the basis of annual mean concentrations of NO and NO_2 at the industrial (WALS), traffic (VESN) and rural background (EGGE) stations for the period 1981–2007 (Source: Melkonyan, 2011, modified).

such that the trend of NO_2 cannot be clearly recognised. Thus, the trend of NO_x emissions exhibits both increases and decreases over European countries. It is also not easy to define a clear increase in ozone trends (Mol et al., 2009).

In addition to emission levels, meteorological parameters also highly influence the pollution levels by their transport or transmission (Mayer, 1999; Teixeira et al., 2009); temperature and radiation favour the photochemical production of ozone (Richter et al., 2005; Sillman, 2003; Solberg et al., 2005; Elansky et al., 2007; Jacob and Winner, 2009).

Weekly cycles have been largely used worldwide to investigate anthropogenic effects on pollution levels. Mayer (1999) showed that there are differences in weekday vs. weekend concentration levels for NO, NO_2, O_3, and O_x. Bäumer et al. (2008) have found that pollution concentrations (SO_2, NO_x, and PM_{10}) are nearly constant from Monday to Friday and that they are 40–60% lower on Saturday and Sunday for south-western Germany. Shutters and Balling (2006) have analysed the weekly cycles of NO_x in Phoenix, Arizona related to traffic density, temperature range, and average wind speed, concluding that traffic density is the driving factor of weekly periodicity in climate variables.

In contrast to the other pollutants, ozone exhibits a contrary behaviour by reaching higher values on weekends than on weekdays. This phenomenon is referred to as the 'weekend ozone effect' or 'Sunday effect' (Graedel et al., 1977). Several hypotheses have been proposed to explain this paradox: (a) a nonlinear relationship between O_3 and its precursors NO_x and VOC, together with lower NO_x values on the weekends, cause ozone production in NO_x-saturated areas (Sillman, 2003; Murphy et al., 2006); (b) a negative correlation between O_3 and its precursors NO_x and VOC, which tend to increase on working days (Bäumer and Vogel, 2007; Mayer, 1999); (c) a reduction of aerosols on weekends, which, in turn, initiates more UV radiation and thus faster ozone production (Murphy et al., 2006); (d) the occurrence of weekend traffic

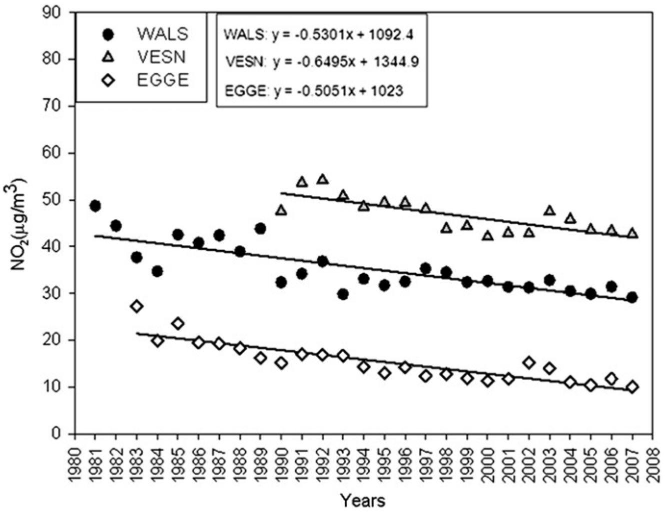

Fig. 6. Annual mean concentrations of NO_2 at the industrial (WALS), traffic (VESN) and rural background (EGGE) stations for the period 1981–2007 (Source: Melkonyan, 2011, modified).

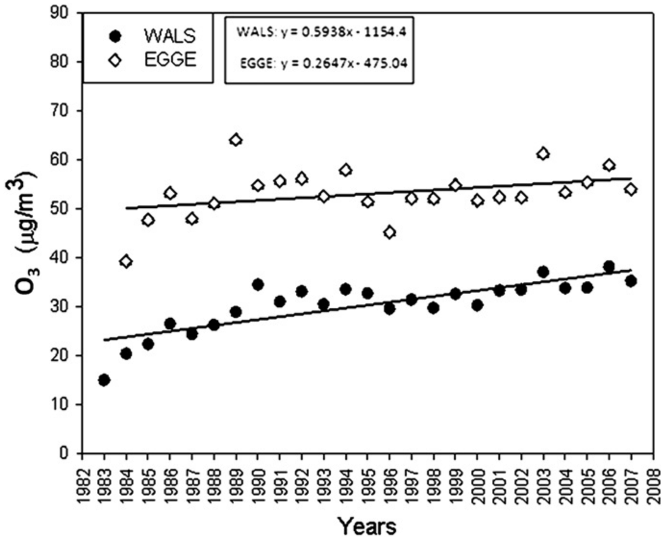

Fig. 8. Annual mean concentrations of O_3 at the industrial (WALS), and rural background (EGGE) stations for the period 1983–2007 (Source: Melkonyan, 2011, modified).

Table 2
Annual mean concentrations of NO, NO_2 and O_3 at the industrial, traffic, urban and rural background stations (1981–2007).

Years	Industrial			Traffic		Rural Background			Urban Background		
	NO	NO_2	O_3	NO	NO_2	NO	NO_2	O_3	NO	NO_2	O_3
1981	32.82	48.72							61.20	52.67	
1982	34.32	44.44							59.03	44.35	
1983	27.26	37.72	14.94			6.75	23.32	31.45	56.94	42.14	20.41
1984	29.65	34.74	20.37			4.76	18.22	43.43	56.54	42.65	14.90
1985	33.70	42.57	22.36			6.39	20.91	47.75	67.20	47.78	
1986	25.37	40.82	26.48			4.53	18.35	55.57	58.64	46.57	19.38
1987	37.88	42.43	24.37			6.33	17.62	49.85	63.83	44.26	18.80
1988	27.34	38.94	26.24			4.61	17.11	50.71	49.62	41.79	26.49
1989	39.27	43.82	28.90			4.46	14.93	59.70	63.13	49.38	23.90
1990	25.03	32.38	34.52	105.37	54.19	3.93	13.81	57.47	45.09	46.31	26.17
1991	26.38	34.20	31.02	104.60	53.66	3.93	17.04	58.17	45.51		26.31
1992	24.04	36.88	33.09	95.91	56.10	4.31	14.50	57.03	40.52	36.59	26.00
1993	26.07	29.85	30.50	91.52	53.71	4.03	14.26	55.46	36.21	36.62	26.36
1994	23.72	33.13	33.57	81.42	51.16	3.62	11.98	60.65	29.64	35.12	29.20
1995	22.28	31.75	32.73	79.19	54.11	4.11	12.10	56.71	32.46	37.46	25.74
1996	22.24	32.56	29.57	76.75	53.11	4.04	13.55	49.72	34.33	36.93	23.86
1997	24.44	35.33	31.41	73.58	51.49	3.88	11.94	54.96	34.50	36.82	26.21
1998	18.29	34.57	29.73	60.39	48.39	3.71	11.29	55.24	25.73	35.29	27.13
1999	13.96	32.43	32.54	50.61	47.78	2.36	10.80	59.09	25.65	33.20	33.32
2000	14.08	32.66	30.28	45.08	44.29	1.29	9.79	54.20	22.71	31.78	31.79
2001	17.12	31.41	33.30	49.01	44.52	1.91	10.63	54.97	26.97	33.42	32.63
2002	15.31	31.29	33.47	44.67	46.30	3.97	11.91	54.85	22.69	33.63	31.08
2003	19.32	32.83	37.07	42.56	52.44	3.24	11.62	63.26	25.13	36.68	37.77
2004	21.69	30.51	33.78	42.36	49.50	1.37	10.00	55.37	24.84	33.46	29.56
2005	14.96	29.93	33.90	25.50	47.90	0.90	8.76	56.31	22.14	34.00	30.05
2006	12.98	31.44	38.18	24.02	47.78	1.91	10.25	60.53	19.63	33.64	35.44
2007	15.58	29.18	35.24	39.20	48.47	0.88	9.33	54.54	21.09	34.32	31.18

patterns later in the day when sunshine is stronger. Debaje and Kakade (2006) found that the weekend ozone effect is more pronounced at urban sites than at rural sites due to the VOC-limited conditions.

In addition to estimating the magnitude of weekday–weekend concentration differences, it is important to analyse time trends of weekly cycles. The annual trends of weekday–weekend pollution concentrations have been investigated by Stephens et al. (2008) for Mexico City for the time period of 1986–2007. Relative weekend reductions in NO_x remained constant, ranging between 40 and 60%. In contrast, the O_3 weekend effect amplitude showed a positive trend, with values ranging from −20 to 0% in the late 1980s and from 0 to +10% over the last few years. An increase of the O_3 weekend effect at the urban site was registered by Debaje and Kakade (2006), whereas no systematic increase was observed at the rural site.

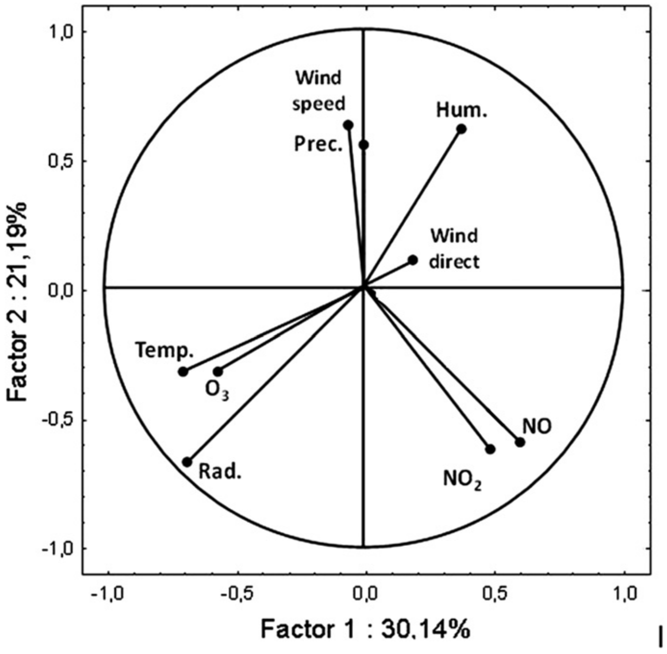

Fig. 9. Principal component analysis for the industrial station WALS, daily mean data for the period of 1986–2005 (Source: Melkonyan, 2011, modified).

3. Research area

The research area covers the state of North Rhine-Westphalia, which is the largest western federal state of Germany in terms of population and economic output. This region contains nearly 18 million inhabitants (Bezirksregierung Düsseldorf, 2010), contributes approximately 22% of Germany's gross domestic product, and comprises a land area of 34.000 km^2 (Die Landesregierung Nordrhein-Westfalen, 2011). It is characterised by a high population and traffic density as well as a high degree of industrialisation concentrated in the Rhine-Ruhr area. The negative impact of these conditions on the region's natural resources has led to intensive and successful efforts aimed at improving environmental

Table 3
Variable correlation with the Factor 1 and 2 for the principal component analysis at the industrial station WALS (1986–2005).

Variables	Factor 1	Factor 2
NO	0.72	−0.50
NO_2	0.61	−0.50535
O_3	−0.63	−0.31
Temp.	−0.72	−0.28
Radiation balance	−0.71	−0.59
Humidity	0.48	0.59
Precipitation	0.01	0.51
Wind speed	−0.02	0.61
Wind direct.	0.24	0.13

Table 4
Correlation matrix of daily mean values of air pollutants and meteorological parameters at the industrial station WALS (1986–2005), the bold values show significance of $p < 0.05$.

	NO	NO_2	O_3	SO_2	Temp.	Rad.	Rel. Hum.	Prec.	Wind speed	Wind direct.
NO	1									
NO_2	0.61	1								
O_3	−0.25	−0.21	1							
Temp.	−0.32	−0.19	**0.47**	−0.36	1					
Rad.	−0.20	−0.11	**0.54**	−0.15	**0.65**	1				
Rel. Hum.	0.13	−0.10	−0.31	−0.13	**−0.39**	−0.70	1			
Prec.	−0.14	−0.12	0.00	−0.10	0.03	−0.20	0.31	1		
Wind speed	−0.36	−0.25	−0.17	0.01	−0.14	−0.28	0.02	0.24	1	
Wind direct.	0.12	0.21	−0.11	−0.04	0.05	−0.20	0.10	0.12	0.21	1

conditions (e.g., air pollution control, water pollution control and soil protection). Over the last several years, the focus of these efforts has undergone a considerable shift from point sources of pollution (industry) to line sources (traffic)". In this paper, six stations (one industrial, two traffic, two rural background and one urban background) were chosen using the criteria of the longest dataset (from 1981 to 2007) and availability of data on both air pollution and meteorological parameters. The locations and characteristics of the stations are given in Fig. 4 and Table 1.

Adjacent to the industrial station (WALS) there are coking plants, coal mining, steel, paper proceeding, chemical factories, and brown coal industries. The traffic stations (VDDF, VESN) are located on streets and highways with dense traffic (>90.000 vehicles per day) (Ministerium für Bauen und Verkehr des Landes Nordrhein-Westfalen, Straßenverkehrszählung, 2005). The urban background station (RODE) is located within a residential area, whereas the rural background stations (EGGE, EIFE) are in forested areas.

4. Data and methods

Data on air pollutants and meteorological parameters used in this investigation have been provided by the North Rhine-Westphalia State Agency for Nature, Environment, and Consumer (LANUV, NRW, Essen). The measurement height at all stations is 3.5 m agl (above the ground).

All the data represent 30-min averages. Before starting the analysis, all data were checked for quality using box–whisker diagrams (Tukey, 1977), with outliers defined as values exceeding 1.5 times the inter-quartile range (25th–75th percentiles). These outliers may be the result of a data entry error, poor measurement or simply extreme high values of pollution concentrations. In air pollution and climate investigations, these outliers must be explored before excluding them from the dataset because they could have occurred during unfavourable weather conditions (e.g., ozone concentrations during the heat wave periods in 2003 and 2006 or the other pollutants during winter, when stagnant weather conditions are more frequent) or during rush-hour traffic. To avoid eliminating the data, which play a great role in investigating the air quality in the region, all the statistically defined outliers were aggregated based on hour of day and season. Systematic appearance of these values implies that they are not statistically defined outliers but extreme high values of pollution concentrations being influenced by different parameters; in such cases, this extreme high values remained in the datasets (Melkonyan, 2011).

Pollutant concentrations at the six stations have been averaged and aggregated based on days of the week to show both the absolute average concentration differences and weekday–weekend concentration differences among the different kinds of stations. As a criterion for comparison, Student's *t*-test was used. Principal component analysis and a correlation matrix have been used to assess the interrelationships between air pollutants and meteorological parameters.

5. Results

The results are presented in four parts. The first part concentrates on emission changes and their impact on pollution levels within the last two decades at different kinds of stations in North Rhine-Westphalia, Germany. The second part is devoted to interrelationships between meteorological parameters and pollutants. Diurnal and weekly cycles of ozone, NO_x and the time trends of weekly cycles are analysed in the last two parts.

a. Time trends of NO_x and ozone

The largest western state of Germany, North Rhine-Westphalia was famous for coal mining, metal processing, textile producing, tobacco manufacturing, machine and steam machine producing industrial factories (Bleidick, 2009). The high level of industrialisation and the growing population made it necessary to develop a densely loaded traffic network, with a large effect on air pollution in the state. Air quality control was implemented in 1962 and included regular measurements of the main air pollutants, i.e., SO_2 (starting in 1964), NO and benzene (since the early 1980s), technical innovations in industries, reduction of environmental endangering constituents and wastes, systematic filtration of effluents and exhaust gases (Nonn, 2009), and implementation of catalytic filters in vehicles. Thus, one of the aims of this paper is to understand the effects of the changes in policy on the pollution concentrations.

Levels of NO, which is emitted from both industrial and transport sectors, are shown for 1981–2007 in Fig. 5. It can be observed that a sharp 65% decrease of NO concentrations occurred at the traffic station due to the implementation of filters in vehicles, although these concentrations remained at a higher level than those at the industrial and rural background stations. Whereas catalytic filters had a large impact on the decrease in NO concentrations, there was practically no significant change in the concentration of NO_2 because primary nitrogen dioxide continued to be emitted after the implementation of the filters (Kourtidis et al., 2002) (Fig. 6).

Before looking closely at the annual trends of ozone, it is important to recognise that ozone production is highly dependent not only on temperature and radiation but also on the ozone's precursors – biogenic and anthropogenic volatile organic compounds (BVOC and AVOC, respectively) (not discussed here due to the lack of data), NO and NO_2. Of particular importance is the ratio of NO/NO_2. NO and NO_2 enhance ozone's dissociation and production, respectively. Thus, if the NO/NO_2 ratio decreases, ozone concentrations increase.

So, to understand the ozone trend, the behaviour of the NO/NO_2 ratio must be analysed. In Fig. 7, the NO/NO_2 ratio for the period 1981–2007 at the industrial (WALS), traffic (VESN) and background (EGGE) stations is presented.

A decrease of NO/NO_2 occurred during the last two decades, which was especially steep at the traffic station VESN and relatively modest at the other two stations. This result can be explained by the sharp decrease of NO and relatively slight decrease in NO_2 concentrations at the traffic station VESN. These results are in very good accordance with those obtained by Fischer et al. (2006).

The decrease of NO/NO_2 ratio at the industrial (WALS) and background (EGGE) stations favoured the annual increase of O_3 concentrations (Fig. 8) (ozone data are not available at the traffic stations). As shown in Fig. 8, a small increase in annual mean ozone concentrations was registered at both stations. Fischer et al. (2006) explain the high ozone concentrations and decreased NO/NO_2 ratio over the 1984–2004 period as a consequence of global climate change. Namely, high-pressure weather conditions in the summer are related to low cloud coverage and therefore to intensive incoming short-wave radiation. Thus, the increase in the frequency of these conditions has an indirect impact on high ozone values.

Time trends on NO_x and ozone concentrations for different station groups are given in Table 2.

b. The impact of meteorological factors on pollution levels

High pollution levels are not only induced by the emission levels but also by meteorological factors that influence the pollution's dispersion, photochemical transformation and transport. The best way to identify multivariate relationships between the pollutants and meteorological factors is to employ principal component analysis. In this analysis, the daily mean pollution concentrations and meteorological parameters have been used as the input data vectors. For example, Fig. 9 and Table 3 show the principal component analysis for the industrial station (WALS; 1986–2005). Factor 1, which comprises NO, NO_2, O_3, air temperature and radiation balance, explains 30.14% of the variance of the overall dataset, whereas Factor 2, which comprises humidity, precipitation and wind speed, explains 21.17% of the variance of the entire dataset.

As shown in Fig. 9, the pollutants NO and NO_2 are well correlated with one another, as they are in the same group. Another group of variables is composed of temperature, radiation balance and ozone. The strong correlation of ozone with temperature and radiation balance is explained by the photochemical production of ozone under high temperature and radiation. In contrast, temperature and radiation balance are negatively correlated with humidity because these variables are located in opposite sectors. No relationships can be detected among precipitation, wind speed and wind direction. The same conclusions are described in detail in Table 4, which presents the results of the correlation analysis of the same variables.

c. Diurnal and weekly cycles of NO_x and ozone

Weekly cycles of NO_x assume high concentration levels on working days compared with those on weekends and public holidays; moreover, this difference is highly significant (*t*-test shows significance at the 95% confidence level). The diurnal course of NO_x concentrations exhibits two peaks during weekdays: one in the morning hours (6–8 a.m.) and the other in the evening hours (4–8 p.m.), which are both caused by rush-hour traffic (Fig. 10). No peaks can be identified on the weekends, but it can be observed that concentrations reach higher values during the afternoon hours (on Saturdays and Sundays), which might be explained by people's leisure activities (Fig. 10a).

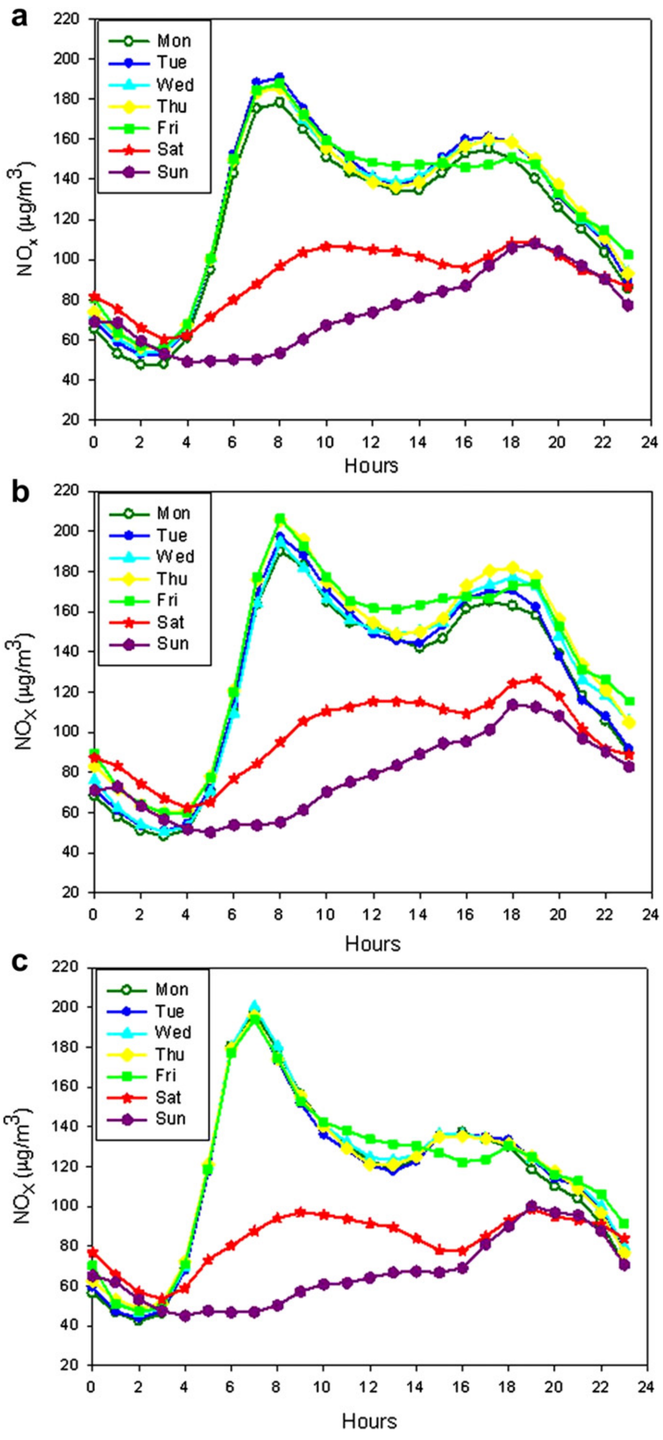

Fig. 10. Weekly and diurnal cycles of NO_x concentrations for a) average, b) winter, and c) summer at the rural background stations (EGGE, EIFE) for the period of 1984–2007 (Source: Melkonyan, 2011, modified).

The diurnal course of pollution is influenced not only by the anthropogenic effect, e.g., rush-hour traffic, but also by the development of the atmospheric mixing layer during the daylight hours (Mayer, 1999). Thus, the seasonal pattern of pollution levels differs between winter (DJF) (Fig. 10b) and summer (JJA) (Fig. 10c). NO_x concentrations are, on average, 18% higher in the winter than in the summer. In particular, evening peaks in NO_x concentrations are 33% higher in the winter than in the summer. This difference might be explained not only by unfavourable weather conditions in winter,

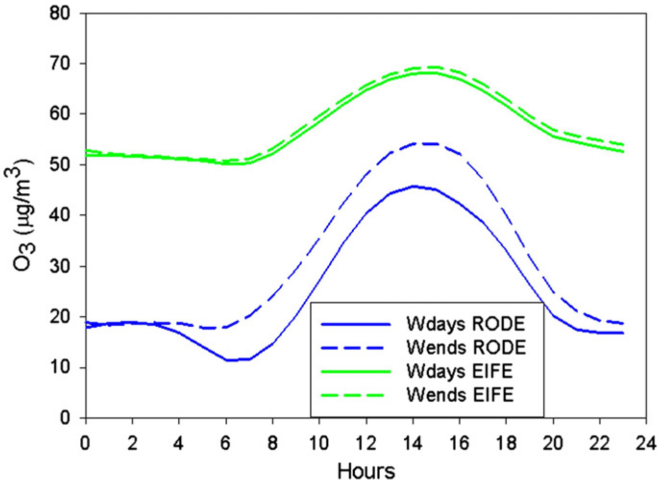

Fig. 11. Diurnal and weekly cycles of O_3 at the urban background (RODE) and rural (EIFE) background stations (1984–2007).

e.g., low mixing layer height and frequent temperature inversions, but also by residential heating.

Ozone shows the reverse behaviour, reaching higher concentration levels on weekends than on working days (‘Sunday effect’ (Graedel et al., 1977)). To clarify the differences in ozone temporal cycles among the different kinds of stations, an urban (RODE) and a rural (EIFE) background station have been chosen for analysis of ozone weekly cycles at NO_x- and VOC-limited regimes (Fig. 11).

Four types of differences can be observed: a) Absolute average ozone concentrations at the rural background station are twice as high (60 µg m^{-3}) as those at the urban background station (30 µg m^{-3}), which can be explained by lower NO concentrations in rural areas, preventing ozone titration. b) There are no weekday–weekend ozone concentration differences at the rural background station due to the low levels and low weekly variability of NO_x. c) In contrast to the rural station, ozone exhibits a secondary maximum at the urban background station in the early night hours (1–3 a.m.). Strassburger and Kuttler (1998) and Reitebuch et al. (2000) explained the secondary ozone maximum with O_3 vertical transport from urban residual layer, enhanced by increased turbulence after the development of a nocturnal low level jet. d) Ozone building begins at 7 a.m. and reaches the peak value at 3 p.m. at both stations, but, as shown in Fig. 11 and Table 5, the slope ((maximum concentration at 3 p.m. − minimum concentration at 7 a.m.)/number of hours when this change occurred – 8 h) is much steeper at the urban than at the rural background station both on working days and weekends. This difference can be explained with ozone formation differences in NO_x- and VOC-limited regimes.

For a better understanding of ozone and NO_x interrelationships at the different kinds of stations, NO, NO_2, NO_x ($NO + NO_2$) and O_x (the sum of O_3 and NO_2) have been presented on diurnal basis in Fig. 12 at the urban (a) and rural background (b) stations. O_x has also been considered to be unaffected by the short-term changes due to titration; thus, O_x represents the ozone potential included in NO_2.

Table 5
Maximum and minimum weekday (WDays) and weekend (WEnds) concentrations of O_3 at the urban (RODE) and rural (EIFE) background stations (1984–2007).

	WDays		WEnds	
	RODE	EIFE	RODE	EIFE
Max	45.73	68.18	54.18	69.36
Min	11.48	50.29	17.81	50.74
Tangens	4.28	2.26	3.64	2.07

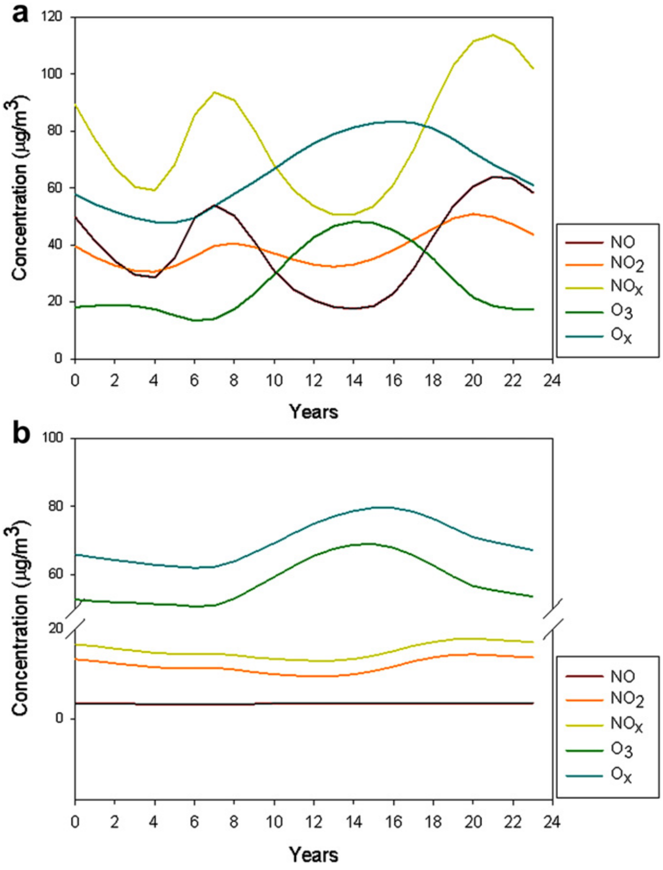

Fig. 12. Diurnal cycles of NO, NO_2, NO_x, O_3 and O_x at the a) urban background and b) rural background stations (1984–2007).

Starting with NO concentrations, it can be observed that the diurnal averages remain negligible (less than 5 µg m^{-3}) at the rural station, showing absolutely no variation throughout the day (Fig. 12b). In contrast, NO at the urban station showed a clearly defined bimodal shape, with two peaks related to traffic (55 µg m^{-3} at 7 a.m. and 60 µg m^{-3} at 9 p.m.) (Fig. 12a). NO_2 concentrations are also very low at the rural station, exhibiting a slight diurnal pattern in contrast to the urban station. Thus, NO_x largely follows the pattern of NO and NO_2 at both stations, with the same differences. In contrast, O_x exhibits little difference in absolute average value between the rural (67 µg m^{-3}) and urban (65 µg m^{-3}) stations, which is due to the opposing behaviours of NO_2 and O_3 at these stations.

d. Weekly cycles – time trends

Due to changes in legislative norms, a decrease of 60% in NO concentrations both on working days and on weekends has been registered over the period 1981–2007 at the traffic station VDDF (with the sharpest decline in 1999) (Fig. 13a), whereas NO_2 concentrations show no change on working days and only a slight, insignificant decrease on weekends (Fig. 13b). This constant behaviour of NO_2 might be explained by the fact that, starting in the 1990s, NO_2 is emitted as a primary pollutant because of the implementation of three-way catalytic filters (Kourtidis et al., 2002). To analyse the impact of different legislative norms on diurnal and weekly cycles of NO_x in detail, patterns have been examined for two different time periods (1990–1998 and 1999–2007) and compared with the mean diurnal cycle for the entire period. The boundary between the two periods was not chosen arbitrarily; as shown in Fig. 14, there is a large change in the year 1999.

Three regulatory norms in environmental legislation could cause this sharp decrease in 1999. When guideline 98/70/EG was accepted on 13.10.1998 in the European Union, increased emphasis was placed on conventional fuels (diesel, gas, oil), adding features such as corrosion inhibitors, cleaning additives, and ageing stabilisers.

The second norm, 1999/30/EG, adopted on 22.04.1999, accepted new limit values for the pollutants, for example, NO_2 measuring 400 μg m^{-3} over three consecutive hours at locations representative of air quality over at least 100 km^2 or an entire zone or agglomeration, whichever was smaller.

The third and the most important change was the ecological tax revision in Germany in 1999. Over many steps, the tax per litre of fuel rose from 3.07 cents to 15.3 cents. Since then, fuel sales have decreased sharply, declining by 3.8 million tonnes (6.8%) from 1999 to 2003 (Umweltbundesamt, 2011).

For comparison with the results of the traffic station, trend analysis was also performed for the industrial station WALS (Fig. 15). On average, NO_x concentrations are two times lower at the industrial station than at the traffic station. The decrease of NO concentrations at the industrial station was approximately 50% both on weekdays and weekends, and the trend was more or less homogeneous without drastic changes in 1999 (Fig. 15a), unlike the traffic station. This finding might be explained by the fact that all the legislative norms adopted in the late 1990s (mentioned above) affected merely the transport sector. Similar to NO, NO_2 concentrations also decreased by 50% both on weekdays and on weekends at the industrial station, in contrast to the lack of change in these values at the traffic station (Fig. 15b).

Because of the sharp decrease in 1999, the changes in weekly and diurnal cycles have been assessed for two time periods (mentioned above): 1990–1998 and 1999–2007 (Fig. 16). The results show that there was a significant difference in absolute average NO_x concentrations between these relatively short time periods, decreasing from 165 μg m^{-3} during the period 1990–1998 to 105 μg m^{-3} during the period 1999–2007. In addition, although the bimodal shape of the diurnal cycles is the same for both periods, the relative sizes of the two peaks changed from the first period to the second. During the first period, the primary maximum is 277 μg m^{-3} at 7 a.m., and the secondary maximum is 221 μg m^{-3} at 4 p.m., with a difference of 56 μg m^{-3}. During the second period,

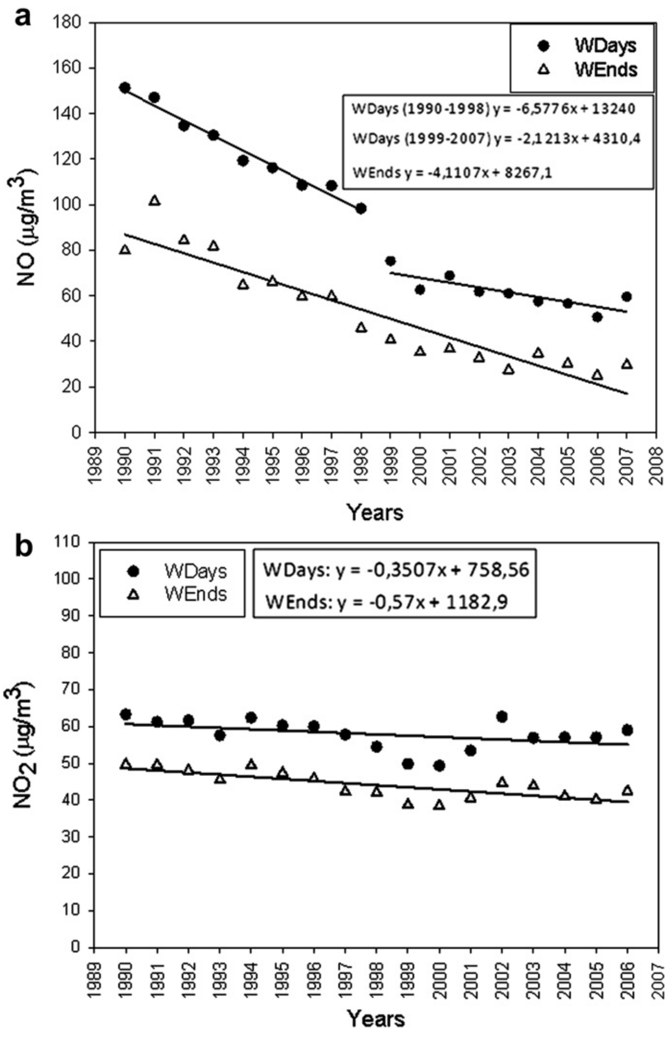

Fig. 13. Annual a) NO and b) NO_2 concentrations on weekdays and weekends at the traffic station (VDDF) (1990–2007) (Source: Melkonyan, 2011, modified).

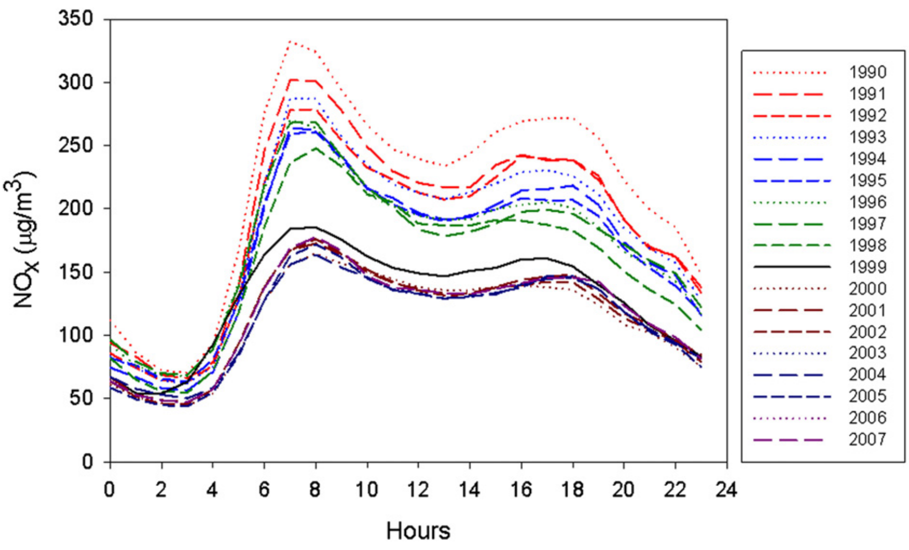

Fig. 14. Diurnal NO_x concentrations on weekdays at the traffic station (VDDF) (1990–2007).

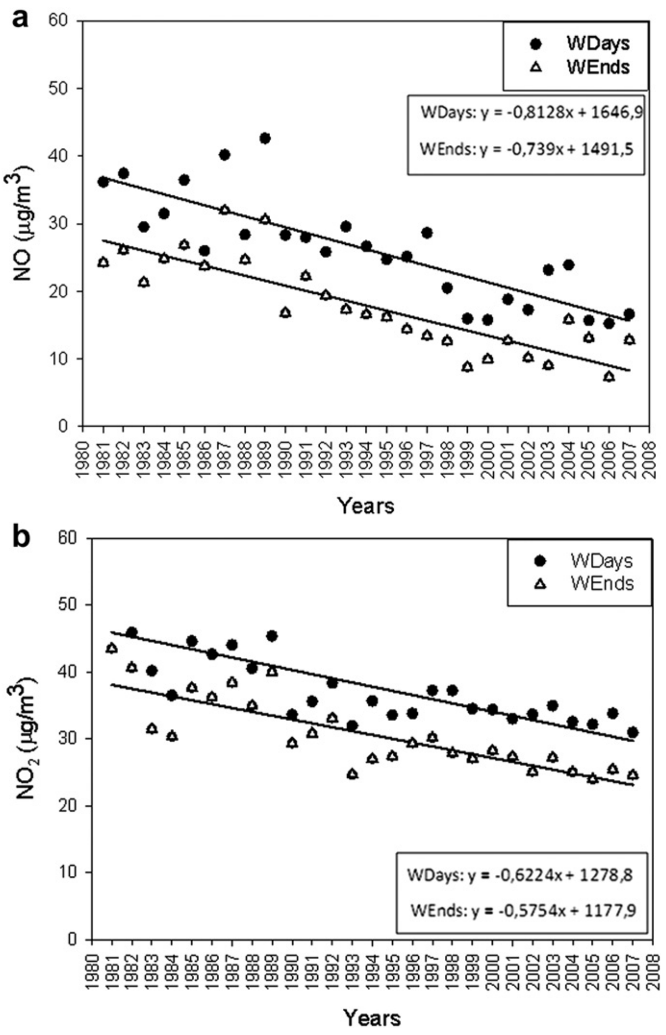

Fig. 15. Annual a) NO and b) NO_2 concentrations on weekdays and weekends at the industrial station (WALS) (1981–2007) (Source: Melkonyan, 2011, modified).

the first maximum is 174 μg m^{-3} at 8 a.m., and the second maximum is 146 μg m^{-3} at 5 p.m., making a difference of only 28 μg m^{-3}. Normalising these differences with the diurnal mean values yields a relative difference between the two peaks of 31% during the first time period and 24% during the second period. This phenomenon might be explained by higher vehicle use in recent years, causing traffic jams, especially in the morning rush hours. Considering that NO_x emissions are lower at lower driving speeds (Bayerisches Landesamt für Umweltschutz), the morning peak concentrations became more moderate during the second research period.

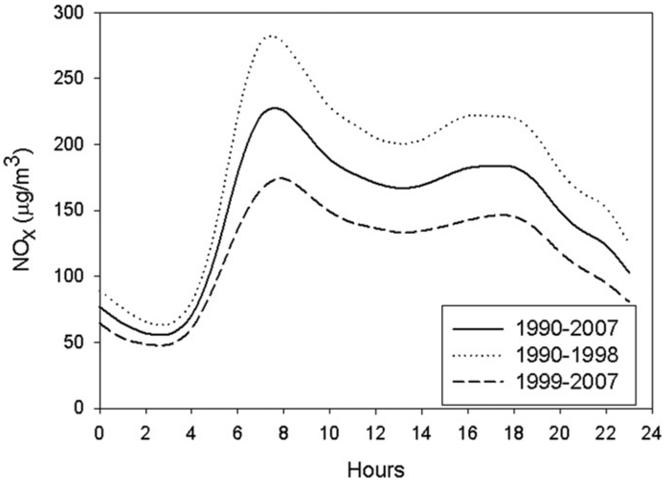

Fig. 16. Diurnal cycles of NO_x concentrations on working days at the traffic stations (VESN, VDDF) (1990–2007).

6.. Conclusions and discussion

Investigation of the long-term air pollution data (1981–2007) within the state of North Rhine-Westphalia showed that annual NO concentrations decreased by 65%, 50% and 80% at the traffic, industrial and background stations, respectively, with the sharpest decrease occurring at the end of 1990s. During the period 1981–1995, decreases of only 35% have been registered in NRW, 44% in Stuttgart-Bad Cannstatt (Mayer, 1999), 40% in Berlin (Berlin Digital Environmental Atlas, 2005) and 25% in the whole Germany (Gauger and Anshelm, 2000).

In contrast to an obvious and significant decrease in NO concentrations, no clear trend has been observed for NO_2, especially for the last decade. Whereas NO_2 levels decreased by 7% and 14% at the industrial and background stations, respectively, changes in NO_2 levels were not significant (0.5%) at the traffic stations (NRW) during the years 1981–2007. Other stations throughout Germany showed a non-significant decrease or even an increase. The following increasing trends were recorded: 33% in Bavaria (at Trostberg, an industrial station) and 26% at Hamburg (at Stresemannstrasse, a traffic station) (Umweltbundesamt, 2007). In contrast with the overall trend in Germany, a 46% decrease in NO_2 levels has been registered over a similar period (1980–2008) at 75 measuring sites in the USA (EPA, 2007). A 30% increase in NO_2 has been observed in Seoul, Korea, which can be explained by the population growth, increased urbanisation, a larger number of vehicles and increased traffic (Pandey et al., 2008), whereas a decrease of 29% has been observed in Taiwan, explained by the implementation of a successful air pollution control policy and the fact that this pollutant remains in the atmosphere for a relatively short time period and thus cannot be transported from another region (Tan et al., 2009).

The simultaneous NO decrease and insignificant changes in NO_2 (resulting NO/NO_2 decrease), the increased frequency of high-pressure global circulation regimes (Mayer and Schmidt, 1998; Fischer et al., 2006) and increased temperatures as a consequence of global climate change (Beniston, 2004; Jacob and Winner, 2009) favoured ozone formation over the last two decades. It has been calculated that ozone increased by 25% and 50% at the background and industrial stations, respectively, in NRW. A corresponding increase of 30% has been observed at the background station Hohenpeissenberg (Mayer and Schmidt, 1998). In contrast to Germany, a rapid growth of 84% of the ozone levels has been registered in Taiwan (Tan et al., 2009), whereas a decrease of 14% has been observed in the USA based on 547 measuring sites (EPA, 2007). This relatively abrupt change in ozone levels coincides with the large NO_x emission reductions induced by the implementation of the NO_x State Implementation Plan (SIP) Call rule, which began in 2003 and was fully implemented in 2004.

After the weekly and diurnal patterns of the pollutants at the urban and rural background stations were estimated, the impact of inter-annual changes in concentration levels on the magnitude and shape of the diurnal cycles has been investigated. Not only have absolute average values of NO_x decreased, but the structure of the diurnal cycle has also changed over the last decade. Namely, the difference between the diurnal peak values of NO_x concentrations became smaller during the last decade due to greater emission reductions, especially within the morning rush-hour traffic. Weekly and diurnal cycles of NO, NO_2, NO_x, O_3 and O_x were used to better understand the interrelationships among these parameters in the NO_x- and VOC-limited regimes, showing that although ozone precursors (NO_x) occur at lower levels at the rural stations, ozone forming potential still remains very high in these regions.

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