CHANGES IN ATMOSPHERIC CH$_4$, O$_3$, NO$_2$, SO$_2$ CONCENTRATION DYNAMICS IN LUBLIN IN THE YEARS 2007-2009

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Abstract. Changes in atmospheric concentrations of gases including CH$_4$, O$_3$, NO$_2$, SO$_2$ are one of the most current issues, due to the observed global warming. The concentration of atmospheric gases is being monitored by satellite measurements and also by tropospheric air monitoring stations located at various geographical latitudes. Polish law and EU Directives determine the limit values of concentrations of air pollutants established for the protection of human health: sulphur dioxide, nitrogen dioxide, benzene, carbon monoxide, ozone, PM10, lead, arsenic, cadmium, nickel and benzo(a)pyrene. The basic equipment of monitoring stations does not include methane analysers. Our monitoring station is one of two stations in Poland with a CH$_4$ analyser. The sampling intake of the KUL monitoring station is located on the wall oriented perpendicularly to the Lublin-Krakow road, c.a. 41.5 m from this very frequently used road. The research, conducted for three years beginning from 2007 until 2009, showed significant variations in greenhouse gases (GHG) concentrations. The increase in mean annual methane concentration noted at the KUL station was 1.4 % for the years 2007-2008 and 1.7% for 2008-2009. The growth rate of ozone mixing ratio was 29% in the period of 2007-2009. Annual mean values of NO$_2$ concentration in 2007 were 50.3% higher than in 2009. The growth rate of SO$_2$ mixing ratio exceeded 65% between 2007 and 2008. The concentration levels of pollutants in the air were related directly with the emission of pollutants to the atmosphere and with the meteorological conditions.

Keywords: greenhouses gases, global warming, monitoring of air pollutants

LIST OF SYMBOLS USED

GHG – greenhouse gases,
KUL – the John Paul II Catholic University of Lublin station,
KASLAB – Kasprowy Wierch station,
PMS – National Environmental Monitoring System,
INTRODUCTION

Total GHG emissions, without Land Use, Land-Use Change and Forestry (LULUCF) in the EU-27 decreased by 17.4% between 1990 and 2009 (974 million tonnes of CO₂-equivalents). Emission decreased by 7.1% (355 million tons of CO₂-equivalents) between 2008 and 2009 (EEA 2011). In Europe, policies and actions at all levels have greatly reduced anthropogenic emissions and exposure, but some air pollutants still harm human health.

In 2007 year the Intergovernmental Panel on Climate Change (IPCC) concluded that climate change is, without doubt, occurring and that the Earth is warming. Moreover the IPCC concluded that there is over 90% probability that this global warming is primarily caused by human activities (IPCC 2007). Climate changes will be increasingly manifested in important and tangible ways, such as changes in extremes of temperature and precipitation, decreases in seasonal and perennial snow and ice extent, and sea level rise. Anthropogenic climate change is now likely to continue for many centuries.

The governments establish primary air quality standards to protect public health. For example, in the United States, emissions standards are managed by the Environmental Protection Agency (EPA); in the case of Poland the office for air monitoring under the National Environmental Monitoring System (PMS) is the Chief Inspectorate of Environmental Protection (GIOS). Within each region the body responsible for monitoring and evaluation of air quality is the Voivodship Inspectorate for Environmental Protection (WIOS). The local laws have set national air quality standards for eleven common air pollutants: sulphur dioxide, nitrogen dioxide, benzene, carbon monoxide, ozone, PM10, lead, arsenic, cadmium, nickel and benzo(a)pyrene. The above mentioned include the major green-
house gases, i.e. sulphur dioxide, nitrogen dioxide, benzene, carbon monoxide, ozone, PM10. However, one can note the lack of monitoring and limit values for methane. According to our knowledge, the only methane monitoring systems in Poland are working at the stations of Kasprowy Wierch (KASLAB) and of the Department of Biochemistry and Environmental Chemistry at the John Paul II Catholic University of Lublin (KUL).

Atmospheric concentration of methane is, after carbon dioxide (CO₂), one of the major factors determining global climate change. Following water vapour and CO₂, methane is the most abundant greenhouse gas in the troposphere. It was shown that, both on a molecule and a mass basis, additional methane is actually much more effective as a greenhouse gas than additional CO₂. Methane is also the most abundant reactive trace gas in the troposphere and its reactivity is important to both tropospheric and stratospheric chemistry.

Analyses of air trapped in polar ice show that over at least the past 450,000 years methane mixing ratio, while correlating strongly with temperature, has not exceeded 700 ppb (Delmotte et al. 2004). It was also documented that atmospheric methane concentration over the period of 1010-1700 AD was relatively stable and at the level of 693 ± 10 ppb (Etheridge et al. 1998). Since that time methane mixing ratio has been rising, reaching 1774 ppb in 2005 (IPCC 2007). In past decades the growth rate of atmospheric methane was variable. Atmospheric methane (CH₄) increased during the past century, with a decline in the growth rate in the 90’s. Since 1998, methane abundances have been roughly constant, however, following almost a decade with little change in global atmospheric methane, renewed growth started near the beginning of 2007 (Rigby et al. 2008).

The observed increase in atmospheric methane concentration is a result of an imbalance between its sources and the two majors sinks – photochemical and microbial oxidation. It is widely accepted that human activities such as landfilling, agriculture and fossil fuel burning play a predominant role in increasing atmospheric methane burden, contributing in ca. 70% to total global emissions of that potent greenhouse gas. However, there is still much uncertainty about the global methane budget, including estimates of the strength of particular sources. Further research into climate change and the development of remedial environmental policies requires a reliable assessment of the long-term growth rate in the atmospheric methane load. This can only be done based on an appropriate amount of data. The purpose of this paper is to deliver data on the trends in the concentration of CH₄, O₃, NO₂, SO₂ in the city of Lublin, with particular emphasis on methane concentration original data.
MATERIALS AND METHODS

The ambient air quality was monitored in respect to CH₄, SO₂, NO₂, O₃ over three years period automatically and continuously. The air monitoring station is located in the building of the Catholic University of Lublin at Kraśnicka Avenue (the national road No. 19), the main driveway leading from the South-Western direction to the centre of Lublin (354 000 inhabitants), a city located in the south-east part of Poland (N: 510, E: 220; Fig. 1), with heavy traffic of 1400-1800 car/h in rush hours (Stępniewska and Szafranek 2003).

![Fig. 1. Location of the monitoring site](image)

Lublin has a temperate continental climate. Average air temperature in 2009 was 8.2°C, annual rainfall 681mm, wind speed 2.8 m s⁻¹ and cloud cover 5.3. The southern part, especially the Lublin Upland, is characterised by abundant sunshine (WIOŚ Lublin, 2010). Air sampling was performed at a location situated c.a. 20 m from the road, at the height of 5 m.

Concentrations of greenhouse gases were measured using flow gas analysers for SO₂ – APSA-350, O₃ - APOA-350E, CH₄ - APHA-370 and NOₓ - Environment AC 31M. Parallel with the gases, air temperature was monitored and gathered in the Server. An important element of all analysers used was a detector which converts the chemical signal in the analytical signal, and an electronic circuit converts the results into an electrical signal. The automatic analysers were based on the classical methods of instrumental chemical analysis.
The data set has been analysed with the aim of studying the annual and inter-annual variability using Kruskal-Wallis one-way analysis of variance test. The adopted significance level was 0.05. The analyses, taking into account the correlation according to Spearman's rank correlation coefficient (Rs), were performed for the average 3-year data. Statistical analysis was performed using STATISTICA 10.0 software.

RESULTS AND DISCUSSION

Significant (p<0.05) year-to-year variability of atmospheric gases (CH4, O3, NO2, SO2) was analysed in the period 2007-2009 and is presented and discussed below.

CH4

Annually the level of CH4 increased from 1328 ± 61 µg m⁻³ in 2007 to 1347 ± 63 µg m⁻³ in 2008 and to 1940 ± 54 µg m⁻³ in 2009, which means that the growth rate of methane mixing ratio was 1.4% (19.1 µg m⁻³) in the 2007-2008 time period and 1.7% (23.3 µg m⁻³) in the years 2008-2009. This trend only partially corresponds with global methane mixing ratio changes described by Fiore and co-workers (2006) who investigated the same time period and calculated methane mixing ratio growth rate at the level of 8 and 4 µg m⁻³ in years 2007 and 2008, respectively.

Seasonal changes in methane mixing ratio were also detected and were similar in every year under investigation. Monthly means of CH4 mixing ratios were much higher from September to March compared to the warmer spring or summer months (Fig. 2). The seasonal methane cycle is generally determined by the reaction of CH4 and OH radicals that are photochemically produced in reactions induced by UV radiation. The reactions are strongly dependent on temperature and seem to play a predominant role in regulating methane concentration in Lublin atmosphere as the observed CH4 concentrations were significantly correlated with temperature (Rs = −0.52; p = 0.05, n = 1037), and similar correlations of those parameters were found worldwide (Artuso et al. 2007).

The same processes play a fundamental role in the determination of the daily methane cycle, which is especially visible in summer months. The daily methane cycle is characterised by night minimum and maximum in the central hours, which results from higher temperature and enhanced OH production. In 2007 self-cleaning processes in the Lublin atmosphere, due to photochemical reactions, were clearly visible. However, in years 2008 and 2009 the daily amplitudes in methane concentration were smaller. This may result from enhanced anthropogenic activity (e.g. road traffic) followed by methane emissions during the day. Evolution of the average daily CH4 cycle in Lublin is presented in Figure 3.
Fig. 2. Calculated monthly means and standard deviation of methane concentration in Lublin in 2007-2009.

Fig. 3. Changes the daily methane mixing ratio cycle in Lublin during the years 2007, 2008 and 2009

The data suggest that methane mixing ratio in Lublin is much higher than the global average. Also the growth rate of annual mean concentration is higher than that described by other authors for this part of Europe (Fiore et al. 2006, Artuso et al. 2007). This suggest there are strong local sources existing in the Lublin area among which we suggest transport and heating as those playing the predominant role.
In the period of 2007–2009 significant differences in ozone concentrations were found in the city of Lublin. The annual average of $O_3$ concentration reached the lowest value of $54.038 \pm 11.622 \, \mu g \, m^{-3}$ in 2008 and $58.245 \pm 19.906 \, \mu g \, m^{-3}$ in 2007, while the highest value of $81.931 \pm 10.285 \, \mu g \, m^{-3}$ was recorded in 2009. Average monthly concentrations of ozone in 2007-2009 did not exceed the limit value of 120 $\mu g \, m^{-3}$ (Fig. 4). However, the average of 8-hour ozone concentrations exceeded the limit many times in the tested period, in 2009 even 59 times. Daily maximum of 8-hour average concentrations higher than 120 $\mu g \, m^{-3}$ were observed in every EU country, in every summer month (EEA 2010).

The concentration values of $O_3$ in 2009 ranged from 77 $\mu g \, m^{-3}$ to 250.8 $\mu g \, m^{-3}$. The growth rate of ozone mixing ratio was almost 29% in the 2007-2009 time period.

As can be seen from the analysis of average daily concentrations of $CH_4$ at the KUL monitoring station, there was no significant correlation between $CH_4$ and $O_3$, as reflected by the low value of the Spearman rank correlation coefficient ($p = -0.067; p = 0.05, n = 1037$). The effect of ozone became apparent during the summer months. It seems that the sunlight plays a key role in the formation of ozone and its concentrations between April and September are the highest. Although the summer ozone production is the most intense, it is then the least stable, largely due to higher temperatures in the ozonosphere. So, high ozone levels are observed in the early spring, and the lowest in late autumn. $O_3$ concentration averaged for the period April-September was higher than the annual average and
amounted to $62.069 \pm 22.349 \, \mu g \, m^{-3}$ in 2007 and $89.992 \pm 7.557 \, \mu g \, m^{-3}$ in 2009, while in 2008 it was only on the level of $47.277 \pm 11.489 \, \mu g \, m^{-3}$.

At the current level of precursor emissions, the year-to-year differences in the occurrence of ozone threshold exceedances are induced substantially by meteorological variations (Solberg and Lindskog 2005). Hot, dry summers with long-lasting periods of high air pressure over large parts of the European continent lead to elevated ozone concentrations and more exceedances of ozone threshold values; the hotter the summers, the higher the number of exceedances.

Ozone is a secondary air pollutant. It is more harmful than the primary pollutants from which it arises. The main sources of ozone are nitrogen oxides and hydrocarbons. Simultaneous emission of nitrogen oxides and hydrocarbons gives rise to increasing ozone concentrations, which probably contributed to the increased ozone level in Lublin over the studied period. The main sectors that emit ozone precursors are road transport, power and heat generation, household, industry, and petrol storage and distribution.

**NO$_2$**

In the period of 2007-2009 a decrease in nitrogen dioxide concentrations in Lublin was noted. The annual average of NO$_2$ concentration reached the highest value of $13.106 \pm 6.566 \, \mu g \, m^{-3}$ in 2007 and $8.015 \pm 2.830 \, \mu g \, m^{-3}$ in 2008, while the lowest value $6.519 \pm 5.035 \, \mu g \, m^{-3}$ was found in 2009. Average monthly concentrations of nitrogen dioxide in 2007-2009 did not exceed the limit value (200 \, \mu g \, m^{-3}; Fig 5.)

![Fig. 5. Calculated monthly means and standard deviation of nitrogen dioxide concentration in Lublin in 2007-2009](image)

In 2007 the minimum concentration of nitrogen dioxide in the atmosphere was 2.6 \, \mu g \, m^{-3} and the maximum 58.4 \, \mu g \, m^{-3}. Accordingly, in subsequent years
the minimum and maximum values were as follows: in 2008 the minimum concentration was 3.5 µg m\(^{-3}\), and the maximum 21.6 µg m\(^{-3}\), in 2009 it varied from 1.6 µg m\(^{-3}\) to 33 µg m\(^{-3}\). Annual mean concentration values of NO\(_2\) in 2007 were two times higher than the average value of nitrogen dioxide concentrations in 2009. Between 2008 and 2009 the 24-hour average concentrations did not show significant changes.

At the present time in the cities of developed countries as well as in Poland, the concentration of nitrogen oxides is mainly increasing. Significant increase of this gas concentration is connected with road traffic, power plants and boilers. At the same time, in the past several years in Poland a downward trend was observed, resulting from decrease in NOx emissions from sources related with the professional power sector (Brechler and Halenka 2003).

Also seasonal changes were observed in NO\(_2\) concentration. In the cool half of the year the conditions for the spreading of pollutants emitted in urban areas are less favourable than in the warm half (April-September). This is due to increased emissions pollution and prevailing anticyclonic weather, which leads to formation of an equilibrium constant in the air layer (Tab.1). Convection air transport is weak and the main pollution of dilution factor is the advection transport. The emission NO\(_2\) involved in car traffic is confirmed by other studies conducted in the world and in Poland (Derwent et al. 1995, Delaney and Dowding 1998, Stepniewska and Szafranek 2002). An indicator of the degree of the impact of transportation in the area may be the value of relative diversity in the concentrations of NO\(_2\) between the cool and the warm half of year.

Table 1. Seasonal changes in the concentration of selected research gases

<table>
<thead>
<tr>
<th>Time (year)</th>
<th>2007</th>
<th>2008</th>
<th>2009</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4) concentration (µg m(^{-3}))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cold half-year</td>
<td>1360</td>
<td>1390</td>
<td>1400</td>
</tr>
<tr>
<td>warm half-year</td>
<td>1310</td>
<td>1330</td>
<td>1350</td>
</tr>
<tr>
<td>NO(_2) concentration (µg m(^{-3}))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cold half-year</td>
<td>12.62</td>
<td>9.66</td>
<td>8.55</td>
</tr>
<tr>
<td>warm half-year</td>
<td>15.26</td>
<td>6.37</td>
<td>7.23</td>
</tr>
<tr>
<td>SO(_2) concentration (µg m(^{-3}))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cold half-year</td>
<td>25.24</td>
<td>39.86</td>
<td>54.86</td>
</tr>
<tr>
<td>warm half-year</td>
<td>14.76</td>
<td>41.83</td>
<td>59.98</td>
</tr>
</tbody>
</table>
SO₂

The acceptable level of sulphur dioxide in the air in Lublin for average 24-hour period, amounting to 125µg m⁻³, was not exceeded. However, the annual average concentration of SO₂ from year to year was higher and higher, in 2007 it was 20.00 ± 7.985 µg m⁻³, in 2008 – 40.844 ±8.746 µg m⁻³ and in 2009 – 57.418 ± 10.138 µg m⁻³.

The level of sulphur dioxide in 2009, compared to 2007, was almost three times higher. In 2007, the minimum concentration of SO₂ in the atmosphere was 5.8 µg m⁻³, and the maximum 55.3 µg m⁻³. Respectively, in the subsequent years the minimum and maximum values were as follows: in 2008 23.3 µg m⁻³ and 70.6 µg m⁻³, in 2009 43 µg m⁻³ and 92.3 µg m⁻³. Average daily concentrations throughout the period showed a large variation. Generally, the lowest concentrations of SO₂ occurred in the first half of the year. In the second half of the year, from June to December, the average daily concentrations for 3 years showed a high variability. Especially in June, August and December, the concentration of sulphur dioxide in atmospheric air was much higher (Fig. 6). Significant correlations were observed for the correlation between SO₂ and temperature (Rₑ = 0.50; p = 0.05, n = 1037).

The distribution of concentrations of sulphur compounds in the atmosphere depends on the vertical temperature gradients, which may cause going up of pollutions on high altitude or accumulation in the lower troposphere. Winter is less conducive to the spreading and transformation of SO₂ into other compounds, than the summer (Avila and Alarcon 1999). In the summer SO₂ can easily connect to the alkaline dust particles and oxidize by physicochemical factors. Concentrations of SO₂ take high values when a large emission source occurs under conditions of
low temperature and high humidity (Kupich and Hoffman 2002). But not always the greatest concentration values occur only in winter. The mechanism of spread of SO₂ in the air is very complex. Emissions from point sources are conditioned by many factors, such as climate, topography of the area, height and design of chimneys, residential buildings, etc. (Rogalski and Lenart 2004). It requires, therefore, continuity and thoroughness of research and observation.

CONCLUSIONS

This study demonstrated changes in atmospheric CH₄, O₃, NO₂, SO₂ concentration dynamics in Lublin in the years 2007-2009. The following conclusions summarise our findings:

1. In the period of 2007-2009 there was an increase in CH₄, O₃, SO₂ concentration in Lublin and a decrease of NO₂ concentration. Detection of changes in methane concentration is novel issue because the KUL station is one of two CH₄ monitoring stations in Poland.

2. The growth rate of methane mixing ratio was 1.4% in the 2007-2008 time period and 1.7% in the years 2008-2009.

3. The change in the concentration of O₃ between 2007 and 2009 was 28.9%.

4. Annual mean concentration values of NO₂ in 2007 were two times higher than the average value of nitrogen dioxide concentrations in 2009.

5. The growth rate of SO₂ mixing ratio was 65.2% between 2007 and 2008.

6. Average monthly concentrations of researched pollutants in 2007-2009 did not exceed the limit values.

7. Air concentrations of pollutants in urban areas are controlled by a balance between those factors which lead to pollutant accumulation and those which lead to pollutant dispersal. The processes of emission and vertical dispersion are subject to influences on a wide range of temporal and spatial scales.

8. The concentration of researched gases in the atmosphere depends largely on air temperature and is also determined by other factors, including meteorological and environmental elements, especially transport (1400-1800 car h⁻¹ in rush hours) and heating.

9. Significant correlations were observed caused by the impact of temperature on CH₄ and SO₂ concentrations.

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DYNAMIKA ZMIANY STĘŻENIA ATMOSFERYCZNEGO CH₄, O₃, NO₂, SO₂ W LUBLINIE W LATACH 2007-2009

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Streszczenie. Zmiany stężenia gazów takich jak: CH₄, O₃, NO₂, SO₂ są jednym z najbardziej aktualnych problemów ze względu na obserwowane globalne ocieplenie. Stężenie tych gazów w atmosferze monitorowane jest satelitarnie lub poprzez stacje monitoringu powietrza troposferycznego zlokalizowane na różnych szerokościach geograficznych. Ustawodawstwo polskie i dyrektywy Unii Europejskiej określają wartości dopuszczalne stężenia zanieczyszczeń powietrza określone w celu ochrony ludzkiego zdrowia: dinitrenik siarki, dinitrenik azotu, benzen, tlenek węgla, ozon, PM10, ołów, arsen, kadm, nikiel i benzo(a)piren. Podstawowe wyposażenie stacji monitoringu nie zawiera analizatorów metanu. Stacja KUL jest jedną z dwóch stacji w Polsce posiadającą analizator CH₄. Czerpnia prób gazowych w stacji monitoringu KUL zlokalizowana jest w odległości około 41,5 m od drogi krajowej Lublin-Kraków. Badania prowadzone przez trzy lata począwszy od 2007 do 2009 roku wykazują znaczne różnice w stężeniu analizowanych gazów cieplarnianych (GHG). Odnoszą w stacji monitoringu KUL wzrost średniej rocznej wartości stężenia metanu wynosił w latach 2007-2008 1,4%, w latach 2008-2009 1,7%. Wzrost stężenia ozonu w analizowanym okresie czasu utrzymywał się na poziomie 29%. Średnie roczne wartości stężenia NO₂ w roku 2007 były o 50% wyższe niż w roku 2009. Dynamika zmian stężenia SO₂ w latach 2007 i 2008 przekroczyła 65%. Poziom stężenia badanych zanieczyszczeń wynikał bezpośrednio z ich emisji do atmosfery oraz z warunków meteorologicznych.

Słowa kluczowe: gazy cieplarniane, globalne ocieplenie, monitoring zanieczyszczeń powietrza