

# Analysis of Surface Ozone Variations Based on the Long-Term Measurement Series in Kraków (1854–1878), (2005–2013) and Belsk (1995–2012)

Izabela Pawlak and Janusz Jarosławski

**Abstract** One of the first long-term ozone measurement series in the world, as described in the chapter, was made in Poland (Kraków) during the period 1854–1878. The data obtained by the method of Schönbein papers reveal that annually averaged concentrations of ground level ozone in the second half of nineteenth century ranged between 11 and 24 ppb. For comparison, this chapter presents the results of contemporary measurements performed at rural background station in Belsk (1995–2012) and at urban background station in Kraków (2005–2013). Nowadays, annually averaged surface ozone values ranged between 22 and 31 ppb in Belsk and between 12 and 17 ppb in Kraków. Seasonal variation of nineteenth century Kraków series exhibited the highest surface ozone concentration during spring and early summer and the lowest in late autumn and winter. Current data present similar shape of distribution, although the sharp spring peak of high values has been replaced by a broad spring-summer maximum. Long-range averages of surface ozone concentration in rural areas are significantly higher than in urban areas (reaching 26 and 15 ppb, respectively).

**Keywords** Surface ozone · Schönbein paper · Linvill's chart

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## 1 Discovery of Ozone, First Measurements and Speculations About its Origin

In 1839, German chemist Christian Friedrich Schönbein during his experiments on the electrolysis of water smelled a characteristic odor. Initially, due to oxidizing capacity of the newly discovered substance, he thought that it is chlorine or any of its variations, but soon changed his mind realizing that it is a variety of oxygen and proposed the new term “ozone”. Finally he stated that it is a natural component of air created as a result of chemical reactions or through the electrical activity in the atmosphere (Wierzbicki 1882). Andrews (1874) demonstrated that ozone is an allotropic variety of oxygen, most likely consisting of three atoms of oxygen. Furthermore, he confirmed Schönbein’s hypothesis that ozone is present in the air but it is also rapidly destroyed by smoke and other contaminations existing in the air of large towns. In his opinion, ozone is more abundant in rural than in urban regions, and in mountain areas than in the lowlands (Andrews 1874).

Those scientists, who believed in the existence of ozone tried to establish its potential sources. There existed numerous theories about the origin of ozone. The most widespread were associated with: (1) atmospheric electricity, (2) emission of ozone-rich-air by plants, (3) evaporation of water, and (4) action of sunlight on the leaves of green plants; in other theories it was supposed that ozone concentration is closely linked with species and height of the clouds (Wierzbicki 1882). Molecular formula of ozone was defined in 1865 by Soret and subsequently confirmed by him in 1867 (Rubin 2001).

The first measurements of ozone were made by its discoverer Christian Friedrich Schönbein. He exploited the fact that the compounds of iodide with potassium decompose under the influence of ozone. His method involved blotting paper dipped in starch glue with a leaven of potassium iodide. Dried “Schönbein paper” was exposed to ozone present in the air for several hours. Iodine, isolated due to decomposition of potassium iodide, acting on a starch changes its color to blue. More intense color meant more ozone in the air. Then the test-paper was compared with chromatic 10-grades scale and the result was used as a relative concentration of ozone in the atmospheric air. Number 0 means absence of ozone, while number 10 means very high amounts of ozone in the air. Schönbein’s method quickly turned out to be easily applicable and sensitive even if the concentration of ozone is very low (Wierzbicki 1882).

In the mid-1850s, about 300 measuring stations operated by medical doctors, pharmacists and university professors were located in Australia, Europe and North America, where only in the State of Michigan there were about 35 of such stations. Unfortunately, many series of measurements were not performed continuously and usually lasted for a short time (Bojkov 1986).

Despite the fact that Schönbein’s method was widespread around the world, it had also several disadvantages: (1) excretion of iodide in the first hours of exposure is more intense than later on, (2) subjective estimation of intensity of blue colour depending on the observer, and (3) strong dependency of this method on relative

humidity (Wierzbicki 1882). At low relative humidity, the colour has a little intensity even when ozone concentration was high and, vice versa, at high relative humidity the colour was intense even when ozone concentration was low. Also the presence of other gases influenced the colour of test-paper, and that is why measuring points were usually located away from potential sources, especially those of sulphurous acid (Linville et al. 1980). The influence of relative humidity variations was a serious problem until 1980 when Linville, Hooker and Olson proposed a conversion chart constructed to allow the conversion of Schönbein's data into units of ozone concentration used today (ppb). This chart was prepared based on measurements of ozone concentration within the chamber by a Dasibi ozone analyzer (Linville et al. 1980).

Beside the qualitative method of ozone measurements discovered by Schönbein, also a quantitative method for the determination of ozone in the air was used. It is worth mentioning that the long-term measuring series performed by French chemist Albert Levy in the Meteorological Observatory of Montsouris, southern Paris, from 1876 to 1910. This method involved a process of arsenite oxidation. The basic element of the apparatus was a bottle filled with 20 cm<sup>3</sup> of  $5 \times 10^{-4}$  molar potassium arsenite (K<sub>3</sub>AsO<sub>3</sub>) and 2 cm<sup>3</sup> of a 3 % potassium iodide (KI) solution through which the atmospheric air was sucked. The ozone present in the air transformed arsenite into arsenate. The amounts of transformed arsenite were a basis for determining the ozone in the air (Volz and Kley 1988; Bojkov 1986). Volz and Kley decided to rebuild measuring apparatus to compare the obtained data with a modern UV-photometer. They proved that the uncertainty of Montsouris series is about 3 %. Their assessment is that the 30 year average of ozone concentration is about 11 ppb, in a range from 5 to 15 ppb (Kley 1994).

At the beginning of the twentieth century the interest in tropospheric ozone significantly decreased. According to Crutzen (1988) this was probably caused by poor quality of measurements, which made it difficult to determine reliable spatial and temporal patterns of ozone concentration. A big break-through came in the second decade of the twentieth century with the development optical techniques. Furthermore, by the end of the third decade the well-known chemical techniques based on conversion of potassium iodide (KI) to iodine (I<sub>2</sub>) were improved. Measurements of this kind were commonly used in Europe in the half of twentieth century and their quality was regarded to be good. Because of the abundance of observations, in this chapter we mention only about two series of measurements performed on the territory of today's Poland. The first one was carried out by H. Cauer from June to October between 1934 and 1936 in the Tatra Mountains. Measurement points were located at different altitudes between 400 and 1000 m. a.s.l. According to these observations, the surface ozone concentration during day ranged from less than 10 to 25 ppbv. The second series of measurements using the same method was performed by H. Tichy between February and April in 1937 and 1938 in Schreiberhau (today: Szklarska Poręba, Poland) at 700 m altitude. The well-known diurnal cycle with maximum in the early afternoon hours was noticed. Tichy explained this fact by the correlation between surface ozone concentration and intensity of ultraviolet radiation. An average of early afternoon surface ozone concentration was generally in the range 10–15 ppbv (Crutzen 1988).

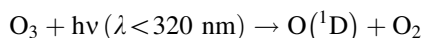
## 2 Theoretical Background

Ozone is a natural constituent of the atmosphere. About 90 % is located in the stratosphere where it is produced through the photolysis of molecular oxygen. The remaining 10 % is present in the troposphere where it is formed as a result of different chemical processes.

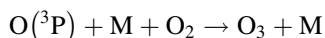
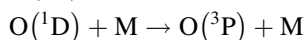
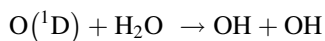
Until about 40 years ago, the dominant theory was that all ozone in the troposphere was previously created in the stratosphere. On the contrary to the common thinking, it is now proven that a significant part of ozone is formed and destroyed in the troposphere through numerous chemical reactions (Crutzen et al. 1998).

Surface ozone is a secondary air pollutant and its concentration is controlled by emission of the ozone precursors, the pollutants: nitrogen oxides (NO<sub>x</sub>), volatile organic compounds (VOCs) and carbon monoxide (CO) (Logan 1985). Interaction between O<sub>3</sub> and its precursors are often complex and nonlinear (Monks 2005).

The key chemical component that controls tropospheric chemistry (including the processes of ozone formation and destruction) is OH radicals, which are created from the photolysis of ozone itself:



Excited oxygen atom (O(<sup>1</sup>D)) can either react with water vapour to produce OH radicals or form ozone following the collision with the other molecule “M” (predominantly O<sub>2</sub> or N<sub>2</sub>).



where O(<sup>3</sup>P) is the oxygen atom in ground state, O(<sup>1</sup>D) the oxygen atom in excited state.

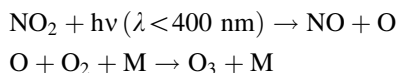
Hydroxyl radicals are responsible for processes of oxidation of different atmospheric pollutants, mainly CH<sub>4</sub> and CO, thereby initiating a series of reactions that produce or destroy ozone. Whether the above processes of oxidation lead to the ozone production is strongly dependent on the concentration of nitrogen oxides, NO<sub>x</sub> (NO + NO<sub>2</sub>) (Crutzen et al. 1998). Non-linear relationship between O<sub>3</sub> and NO<sub>x</sub> is manifested by the fact that, depending on whether we are in the area of high or low NO<sub>x</sub>, an increase of NO<sub>x</sub> emission can promote or reduce the ozone formation. The area of high or low NO<sub>x</sub> is defined by a relative efficiency of radicals (S) production and NO<sub>x</sub> emission:

- When  $S > \text{NO}_x \text{ emission}$  = low NO<sub>x</sub> area, then the concentration of O<sub>3</sub> increases with decreasing amounts of NO<sub>x</sub> and almost does not depend on the amount of VOC.

- When  $S < \text{NO}_x$  emission = high  $\text{NO}_x$  area, then the concentration of  $\text{O}_3$  decreases with increasing amount of  $\text{NO}_x$  and increases with increasing amounts of VOC.

It can be concluded that an increase of concentration of VOCs generally promotes the ozone formation while an increase of  $\text{NO}_x$  emission can either promote or limit the ozone production.

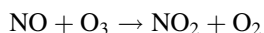
Meteorological conditions, beside the presence ozone precursors, are another factor that plays a crucial role in surface ozone formation. High ozone concentrations are usually associated with intense solar radiation, high temperature, low wind speed and low relative humidity (Pulikesi et al. 2006). Numerous observations have revealed that an increase of temperature and intensity of solar radiation on the cloudless days significantly affect the increase of ozone concentration (Pudasainee et al. 2006). Solar radiation is essential for the initiation of photochemical processes leading to ozone production. The only known method of ozone formation is the reaction of oxygen atom (O) with oxygen molecule ( $\text{O}_2$ ). The main source of O near the Earth's surface is a process of photodissociation of  $\text{NO}_2$  initiated by quantum of solar radiation at a wavelength below 400 nm:



Also the influence of temperature on the surface ozone content is not insignificant. High temperature enhances the rate of some chemical reactions (Science Policy Report 15/08 2008). Biogenic sources emit more VOCs at high temperature; especially the isoprene, due to its high reactivity plays a significant role in surface ozone production (Bell and Ellis 2004). Moreover, during daytime due to convective heating the processes of vertical mixing and simultaneously downward transport of ozone are most efficient (Lal et al. 2000).

The ozone concentration varies diurnally and seasonally, reaching its maximum during summer afternoon hours, when photochemical formation is most efficient. A secondary maximum during spring afternoons is additionally enhanced by the stratospheric-tropospheric exchange (Bloomer et al. 2010).

Analyzing the spatial variability of surface ozone concentration, the kind of study area turns out to be a very important factor. Distinction between rural and urban areas allows us to note that rural regions are often characterized by higher ozone concentration. The lower ozone amount in urban areas is generally connected with high concentration of  $\text{NO}_x$  and direct destruction of  $\text{O}_3$  through the process:



During night, the lack of solar radiation hinders the process of photodissociation of  $\text{NO}_2$  (to create O) and consequently makes ozone formation impossible.

Diurnal variations at high-altitude stations are quite different and do not show signs of daytime photochemical build-up characteristic of rural or urban areas. Relatively low values of daily ozone concentration are usually noticed at clear, elevated locations deprived of the influence of potential sources of pollutants (Oltmans and Levy 1994; Naja et al. 2003).

### 3 Objective of the Chapter

The main objective of this chapter is to present, known from the literature, ground-level ozone measurement series performed in the area of contemporary Poland. In this chapter we decided to use one of the first long-ranged ozone measurements series performed in Kraków in the second half of 19th century by Wierzbicki using Schönbein papers. Despite the poor uniformity of Schönbein method, already noted by Wierzbicki, we appreciate this extremely valuable series and used it to compare those data with current ozone observations. For this purpose we used Linvill's chart to convert Schönbein numbers into ppb units. Such an attempt has been already made by Degórska et al. (1996), who used data from Kraków to compare them with modern tropospheric ozone data from Belsk (Poland) and from Hohenpeissenberg (Germany).

In this work we present the results of the surface ozone measurements performed in Kraków (1854–1878) and Belsk (1995–2012). The analysis focuses on the daily (with the division into day and night) as well as the monthly, seasonal and annual variations of surface ozone concentration. The main objective of this work is to describe the surface ozone distribution observed in 19th century Kraków and contemporary Kraków and Belsk and determine the conditions governing the processes of surface ozone formation and destruction.

### 4 Experimental Details

One of the first long series of ground-level ozone measurements was performed by Wierzbicki in 1854–1878 in Kraków. Observations were carried out 2 times per day: at 6 am and 10 pm, thus the exposition time lasted 16 h during day and 8 h during night. The terms day and night used in the text refer to the above-mentioned time intervals. Daily average values were calculated as an average value over the day and night. Ozone papers were situated on the second floor of the Astronomical Observatory at a height of 11.7 m for the first 16 years (1854–1868) on the north-west, and then (1869–1878) on the south-west side of the building. For most of the time, until the beginning of 1875, measurements were carried out using papers prepared in trustful compliance with the original Schönbein's recipe using 10 point scale but later using papers produced in a factory of Lenz and Lender using 14 point scale. Shortly after the end of the measurements, the obtained results were

standardized and statistically compiled by Wierzbicki, and published by the Academy of Arts and Sciences in 1882.

Contemporary data were obtained from the Central Geophysical Observatory of the Institute of Geophysics, Polish Academy of Sciences at Belsk, which constitutes a background measuring station operating under the Regional Inspectorate of Environmental Protection in Warsaw. Daily average data as well as average day and night values were calculated based on hourly averaged data wherein the day and night values of ozone concentration are representative for the same time intervals as in Kraków (16 and 8 h, respectively). Measurements have been performed by Monitor Labs and Monitor Europe analyzers (model ML8810 and ML9810), operating on the basis of UV absorption by ozone at wavelength 253.7 nm, which is generated by a low pressure mercury lamp. The measurement consists of two parts:

- (1) Measurement of UV light passing through the sample of air without ozone to determine the reference light intensity (removal of ozone from the sample is done using ozone scrubber).
- (2) Measurement of UV light passing through the sample of air with ozone to determine intensity of light after absorption.

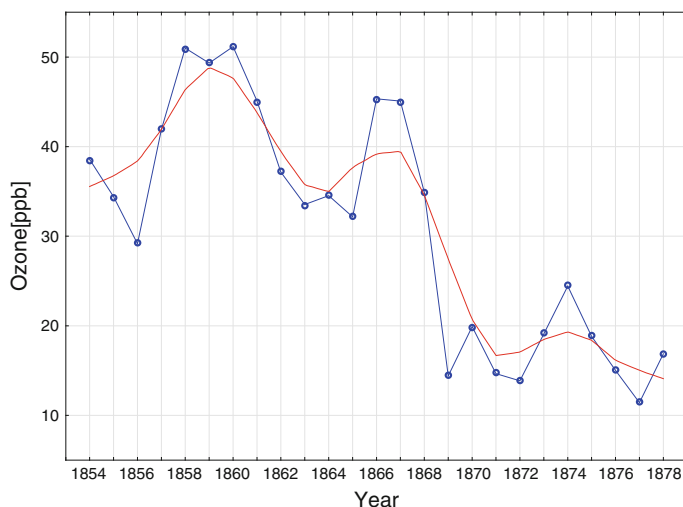
The degree of absorption is proportional to the amount of ozone, and, using Beer-Lambert absorption equation, it is possible to calculate the concentration of ozone in the air. The inlet for trace gas measurements is situated on the roof of the Laboratory building at a height of 7 m above the ground level.

## 5 Results and Discussion

### 5.1 Measurement Series in Kraków (1854–1878)

To describe temporal variability of surface ozone amount in the period 1854–1878 in Kraków, annually averaged concentrations are presented in Fig. 1.

In order to reveal the long-term changes, the annual data have been smoothed using the Locally weighted scatter plot smooth (LOWESS) technique. Analyzing this chart, the most conspicuous are small amounts of ozone in the second half of measurement series (1869–1878) in comparison to the first (1854–1868). The turning point, which occurred between 1868 and 1869, evidently divided 25 years of measurements into two parts. In the first one, the highest annual average was 51 ppb (1860), the lowest being 29 ppb (1856), while in the second one these values were 24 ppb (1874) and 11 ppb (1877), respectively. An average ozone concentration in the first part was more than 40 ppb, while in the second part only less than 17 ppb. Probably this was caused by changing the location of measuring point. Until 1869 the Schönbein papers were exposed from the north-west side of the building, near the street and the yard. It is well-known that such a location might have promoted accumulation of different components of the air, which could



**Fig. 1** Annually averaged concentration for 1854–1878 time series of surface ozone

influence on the color of paper. From 1869 to 1878 the test papers were exposed from the south-west side of the building, near the garden. To explain the influence of the location of measuring point during 22 April–31 May, Wierzbicki decided to perform the same kind of measurements in both places (Table 1).

During forty days of observations performed on North location, the average daily ozone concentrations were significantly higher than those performed on the South. The differences ranged between 20 and 25 ppb. During nights, the situation was similar: average ozone concentrations performed on the North side were higher, although the differences were slightly lower than during day and oscillated between 2 and 23 ppb.

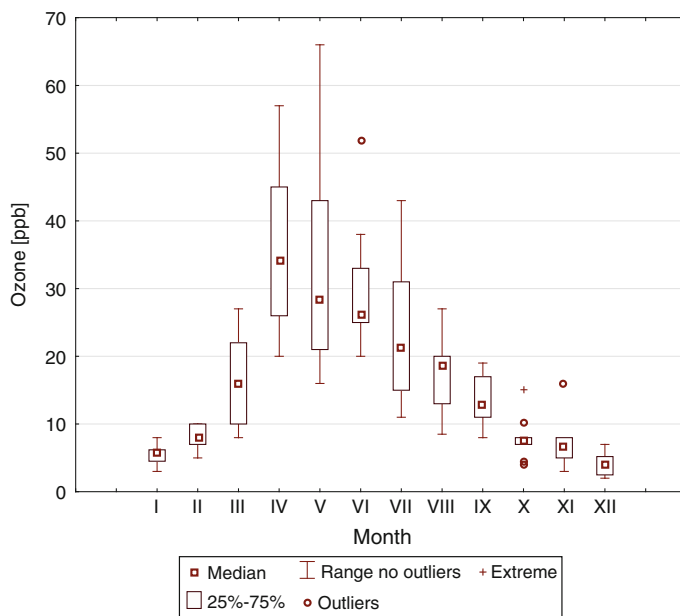
According to the recommendations of a researcher, who has performed these measurements, we decided to use in our chapter only data from 1869–1878 as the most reliable.

Analyzing seasonal variation of surface ozone in 1869–1878 (Fig. 2) it is possible to conclude what was the main mechanism that governed the distribution of ground-level ozone in the second part of 19th century. Very pronounced spring maximum indicates the dominant influence of the tropospheric-stratospheric exchange as the main source of ozone. Gradual decrease of surface ozone values throughout the summer and simultaneously significantly lower concentrations prove that photochemical production of ozone was of secondary importance in ozone budget. It was also found that surface ozone concentration varied in a broad range within a month, especially during spring and summer season. This can be explained by significantly higher potential of ozone production in summer. Based on statistics, the monthly median of surface ozone concentration ranged between 4 (December) and 34 (April) ppb, while the monthly average fluctuated in the range of 4.1 (December) and 35.1 (April) ppb.



**Table 1** Average 10-days surface ozone values in Kraków

| Ten days | Average daily ozone concentration (ppb) |       |            | Average night ozone concentration (ppb) |       |            |
|----------|---|-------|------------|---|-------|------------|
|          | North                                   | South | Difference | North                                   | South | Difference |
| I        | 76                                      | 56    | 20         | 62                                      | 44    | 18         |
| II       | 56                                      | 31    | 25         | 49                                      | 38    | 11         |
| III      | 77                                      | 55    | 22         | 26                                      | 24    | 2          |
| IV       | 98                                      | 78    | 20         | 94                                      | 71    | 23         |

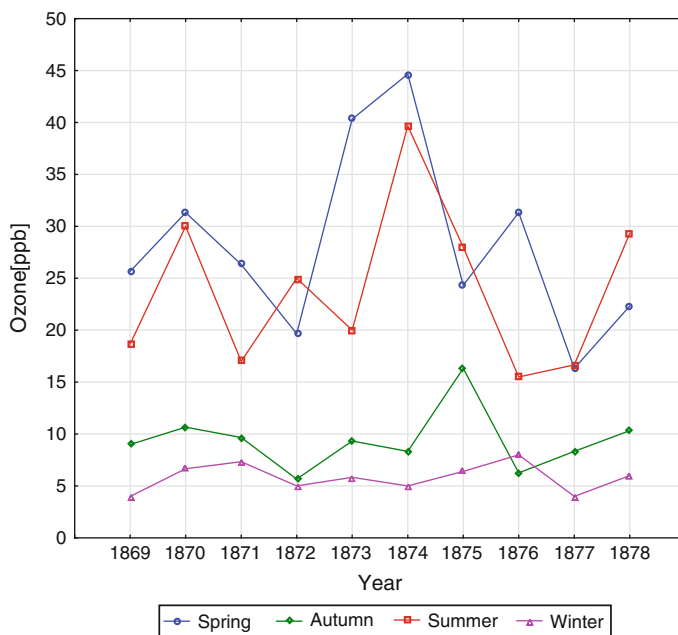


**Fig. 2** Seasonal variations of surface ozone concentration for 1869–1878 time series

Analyzing the chart depicted in Fig. 3 we can further delve into the subject of seasonal variations of surface ozone concentration and notice again that the seasonal maximum of surface ozone concentration in each year occurred in spring. Slightly smaller values were noticed in summer, significantly lower values were observed during autumn, and the lowest during winter. The average values of seasonal surface ozone concentration for the period 1869–1878 were: 28 ppb in spring, 24 ppb in summer, 9 ppb in autumn, and—6 ppb in winter.

Looking at Table 2 we can state that in the years 1869–1873 the monthly maximum occurred in April (with the exception of 1869, when the maximum, amounting to 27 ppb, occurred in March).

The highest values varied from year to year and ranged between 26 and 57 ppb. In the subsequent years (1874–1878) the monthly maximum occurred alternately in May (1874—66 ppb, 1876—43 ppb) in June (1875—33 ppb, 1877—26 ppb) or



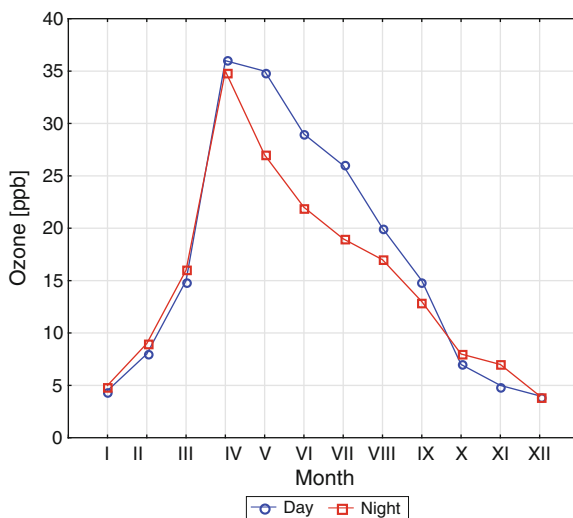
**Fig. 3** Seasonal variations of surface ozone concentration for 1869–1878 time series divided into seasons

**Table 2** Monthly averaged concentration of surface ozone (ppb) for 1869–1878 time series

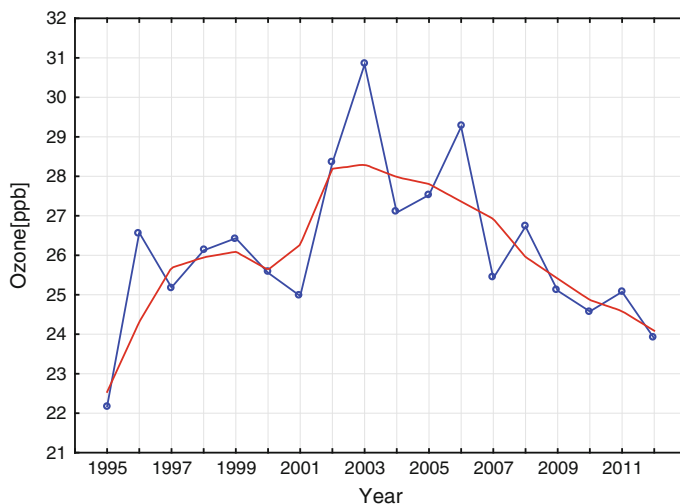
| Year/Month | I   | II | III | IV | V  | VI | VII | VIII | IX | X   | XI  | XII |
|------------|-----|----|-----|----|----|----|-----|------|----|-----|-----|-----|
| 1869       | 4.5 | 5  | 27  | 26 | 24 | 20 | 18  | 18   | 11 | 8   | 8   | 4   |
| 1870       | 6   | 10 | 23  | 45 | 26 | 38 | 25  | 27   | 19 | 7   | 6.5 | 7   |
| 1871       | 7   | 8  | 10  | 35 | 34 | 25 | 15  | 11   | 11 | 10  | 8   | 2   |
| 1872       | 5   | 8  | 8   | 35 | 16 | 27 | 29  | 19   | 10 | 4   | 3   | 2.3 |
| 1873       | 5.2 | 10 | 15  | 57 | 49 | 26 | 17  | 17   | 14 | 7   | 7   | 5   |
| 1874       | 3   | 7  | 17  | 47 | 66 | 52 | 40  | 27   | 12 | 8   | 5   | 5.2 |
| 1875       | 6.2 | 8  | 14  | 28 | 31 | 33 | 31  | 20   | 18 | 15  | 16  | 6   |
| 1876       | 8   | 10 | 18  | 33 | 43 | 24 | 14  | 8.5  | 8  | 4.3 | 6.5 | 3   |
| 1877       | 4.2 | 5  | 8   | 20 | 21 | 26 | 11  | 13   | 14 | 7   | 4.2 | 4   |
| 1878       | 6   | 8  | 22  | 25 | 20 | 25 | 43  | 20   | 17 | 8   | 6   | 2.5 |

in July (43 ppb). Predominantly lowest monthly averaged values were in December (2–6 ppb) and in 2 years in January (1870—6 ppb, 1874—3 ppb). The highest values of surface ozone concentration may indicate a dominant role of stratospheric-tropospheric exchange as a main source of surface ozone (Volz and Kley 1988). Monthly averaged values of ground level ozone with division into day and night for the period 1869–1878 are presented in Fig. 4.

**Fig. 4** Monthly averaged concentration of surface ozone with division into day and night for 1869–1878 time series



It is clearly seen that during months from April to September the ozone concentrations during day were higher than during night. The highest differences occurred in May, June and July and reached 8, 7 and 7 ppb, respectively. At this time, the potential of photochemical ozone production due to intensive solar radiation is the biggest. Opposite situation was noticed from October to March. In this case, differences were not so high and oscillated in a narrow range—up to 2 ppb. In the 19th century, the chemistry of atmosphere was dominated mainly by emission of  $\text{SO}_2$ ,  $\text{CO}$  and  $\text{CO}_2$  as by-products of coal combustion. The absence of developed road transport was the reason why the  $\text{NO}_x$  concentration level was significantly lower. In this case, it is especially important because during nighttime,  $\text{NO}_x$  act as ozone destroyers ( $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ ). In effect, locations distinguished by low concentration of  $\text{NO}_x$  (even today) are characterized by relatively high surface ozone amounts during night. Furthermore, advection of frozen, fresh air from north and north-west directions during winter is generally responsible for the high ozone values. Most Arctic stations are characterized by the highest ozone concentrations in winter time (December–May) due to the weakness of ozone sinks during the dark period (Helmig et al. 2007). In winter months, photochemical production of ozone due to weak solar activity could be significantly smaller (as it is observed nowadays). We can suggest that air pollution associated for example with intensive domestic heating additionally limited the solar radiation. The poor efficiency of photochemical ozone formation under these conditions during day and reduced ozone titration processes at night resulted in similar values of surface ozone concentration during whole day (more details about the phenomenon of low ozone concentration during winter days in modern urban areas are contained in Sect. 5.3).



**Fig. 5** Annually averaged concentration of surface ozone for 1995–2012 time series

## 5.2 Measurement Series in Belsk (1995–2012)

To describe temporal variability of surface ozone at station Belsk, annually averaged concentrations of surface ozone are presented in Fig. 5.

Data were smoothed using the LOWESS technique, which allows to track long-term changes of ozone. Analyzing this chart we can observe specific behavior of ozone concentration: from 1995 surface ozone concentration has been gradually increasing, revealing the maximum around 2003 and was steadily decreasing since that time. Probably such a situation was caused by decreasing emission to the atmosphere of contaminants of air being precursors of ozone. In the period 1990–2010 across the EEA-32 countries, significant decreases of NO<sub>x</sub> (–42 %), NMVOC (–53 %), CH<sub>4</sub> (–32 %) and CO (–61 %) were noticed. In Poland, the values were as follows: NO<sub>x</sub> (–30 %), NMVOC (–20 %), CH<sub>4</sub> (–25 %) and CO (–60 %). This improvement of air quality has been achieved by catalytic converters, which considerably reduced the amount of emission of NO<sub>x</sub> and CO from motor vehicles (EEA 2012).

Figure 6 depicts that minimum values of surface ozone occur in November and the increase in ozone concentration was then noticed, reaching the highest amount in April. Thereafter, through all the months until November, ozone concentrations decrease steadily. Based on statistics, the monthly median of surface ozone concentration ranged between 12.8 ppb (November) and 36.6 ppb (April) while the monthly average fluctuated in range from 13.3 (November) to 36.2 ppb (April).

Seasonally averaged surface ozone concentration presented in Fig. 7 allows to conclude that during the measurement period (1995–2012) the highest amounts of ozone occur in spring (35.11 ppb) and in summer (32.34 ppb). The lowest values

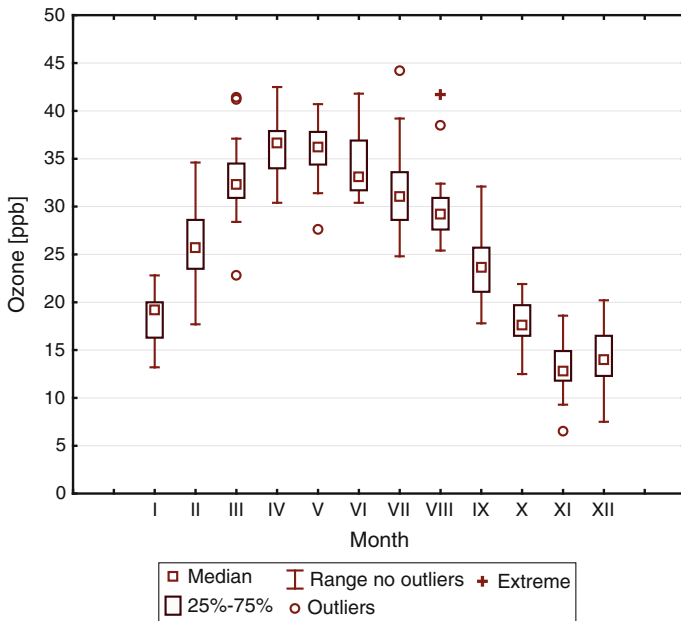
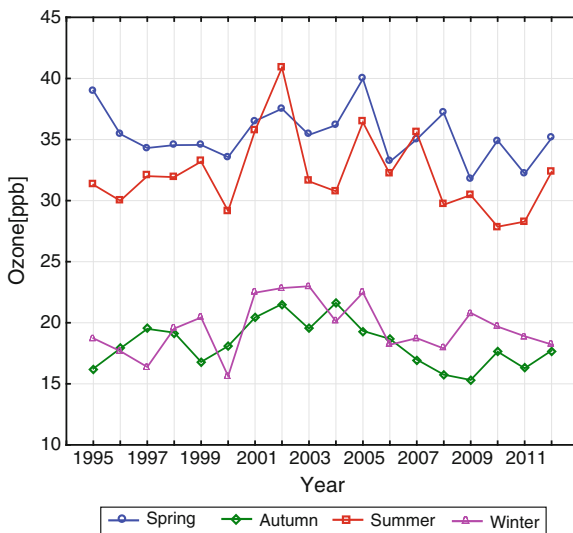


Fig. 6 Seasonal variations of surface ozone concentration for 1995–2012 time series

Fig. 7 Seasonal variations of surface ozone concentration for 1995–2012 time series divided into seasons



of surface ozone concentration occur in autumn (17.72 ppb) and in winter (18.22 ppb). As demonstrated by Volz and Kley (1988), the concentration of surface ozone in Europe in the last century almost doubled. Also the course of seasonal changes has been modified. The currently observed broad spring–summer

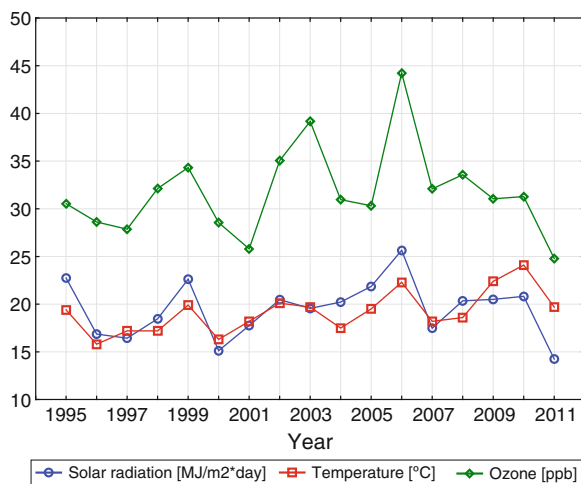
**Table 3** Monthly averaged concentration of surface ozone (ppb) for 1995–2012 time series

| Year/Month | I    | II   | III  | IV   | V    | VI   | VII  | VIII | IX   | X    | XI   | XII  |
|------------|------|------|------|------|------|------|------|------|------|------|------|------|
| 1995       | 17.5 | 17.7 | 22.8 | 30.4 | 31.4 | 31.7 | 30.5 | 29.4 | 24.1 | 16.5 | 6.5  | 7.5  |
| 1996       | 18.5 | 30.1 | 41.2 | 41.4 | 34.4 | 38   | 28.6 | 27.3 | 18.2 | 17.7 | 12.8 | 10.5 |
| 1997       | 14.6 | 27.9 | 31.7 | 37.9 | 36.8 | 32.4 | 27.9 | 29.7 | 23.5 | 18.1 | 12.1 | 9.7  |
| 1998       | 16   | 23.5 | 34.5 | 31.7 | 36.8 | 34.9 | 32.1 | 29   | 21.3 | 20.5 | 16.7 | 16.6 |
| 1999       | 14.7 | 27.3 | 31.9 | 34   | 37.8 | 30.5 | 34.3 | 30.9 | 26.3 | 18   | 13.3 | 18.2 |
| 2000       | 19.6 | 23.6 | 29.7 | 34   | 40   | 40.3 | 28.5 | 30.7 | 21.3 | 19.7 | 9.3  | 9.9  |
| 2001       | 13.2 | 23.8 | 30.9 | 32.7 | 37   | 32.8 | 25.8 | 28.9 | 19.1 | 16.7 | 18.6 | 20.2 |
| 2002       | 19.4 | 27.7 | 31.9 | 36.9 | 40.7 | 33.6 | 35   | 38.5 | 26.1 | 20.5 | 14.7 | 14.9 |
| 2003       | 19   | 34.6 | 37.1 | 37.9 | 37.5 | 41.8 | 39.2 | 41.7 | 30   | 21.9 | 12.7 | 16.5 |
| 2004       | 22.8 | 29.6 | 34.4 | 37.7 | 34   | 33.1 | 31   | 30.6 | 25.1 | 16.8 | 16.6 | 13.1 |
| 2005       | 21.7 | 25.6 | 36.7 | 37.3 | 34.5 | 34.5 | 30.3 | 27.5 | 32.1 | 20   | 12.8 | 17.4 |
| 2006       | 19.9 | 30.1 | 41.4 | 38.8 | 39.7 | 36.9 | 44.2 | 28.1 | 25.7 | 18.1 | 14.2 | 13.9 |
| 2007       | 21.3 | 19.4 | 28.4 | 35.9 | 35.2 | 33.1 | 32.1 | 31.4 | 23.3 | 15.3 | 17.3 | 12.3 |
| 2008       | 20.3 | 23.6 | 32.8 | 36.7 | 35.6 | 40.7 | 33.6 | 32.4 | 19.5 | 16.6 | 14.9 | 14.1 |
| 2009       | 16.3 | 23.3 | 30.8 | 42.5 | 38.2 | 30.4 | 31.1 | 27.6 | 23.8 | 12.5 | 11   | 13.9 |
| 2010       | 20   | 28.6 | 32.7 | 34.9 | 27.6 | 31.3 | 31.3 | 28.8 | 17.8 | 15.9 | 12.2 | 13.9 |
| 2011       | 19.4 | 25.8 | 32.7 | 36.6 | 35.5 | 32.9 | 24.8 | 25.9 | 23.8 | 17.5 | 11.6 | 14.4 |
| 2012       | 18.8 | 23.4 | 31   | 33.7 | 31.9 | 30.7 | 28.7 | 25.4 | 21.1 | 15.9 | 11.8 | 14.1 |

ozone maximum is probably a result of presence in the atmosphere of large amounts of ozone precursors, which are an important source of surface ozone during the summer maximum of solar radiation. Looking at Table 3 showing monthly averaged values of surface ozone concentrations for each year, we can notice that until 2004 the annual maximum generally occurred in May or in June.

Since 2004 we observe a shift in the early maximum, and the highest values are usually in April. This kind of annual ozone distribution is connected with two main sources of surface ozone: (1) photochemical reactions are more intense during spring and summer months, when values of temperature and solar radiation are significantly higher than in winter or autumn, (2) fluxes of stratospheric ozone are the most common during early spring months. The situation in recent years can be indicative of an important role of stratosphere-troposphere exchange as a source of surface ozone amount. A specific kind of distribution of ozone was noticed in 2006. This year was unusual in terms of meteorological situation in Europe. During the period 16 June–30 July, unusually high pressure systems settled over Europe, that alternately were connected with continental high from Russia. As a result, Poland was affected by tropical air masses from south-west, south and south-east directions. In this kind of circulation, solar radiation and temperature were very high and significantly exceeded long-term average values (Lorenc et al. 2006). As can be seen in Fig. 8, the surface ozone and solar radiation values in July were the highest during the measurement period (1995–2011) and were higher by 40 and 31 %, respectively, than long-term average values. It can be assumed that such meteorological conditions promoted the rate of reactions and in situ photochemical ozone production. Average temperature in July was also higher

**Fig. 8** Variations of surface ozone concentration, solar radiation and temperature in July for 1995–2011



than the long-term value by 16 %. We can observe good compatibility between surface ozone and the above meteorological parameters. Correlation coefficients between surface ozone and solar radiation and temperature reach 0.72 and 0.43, respectively.

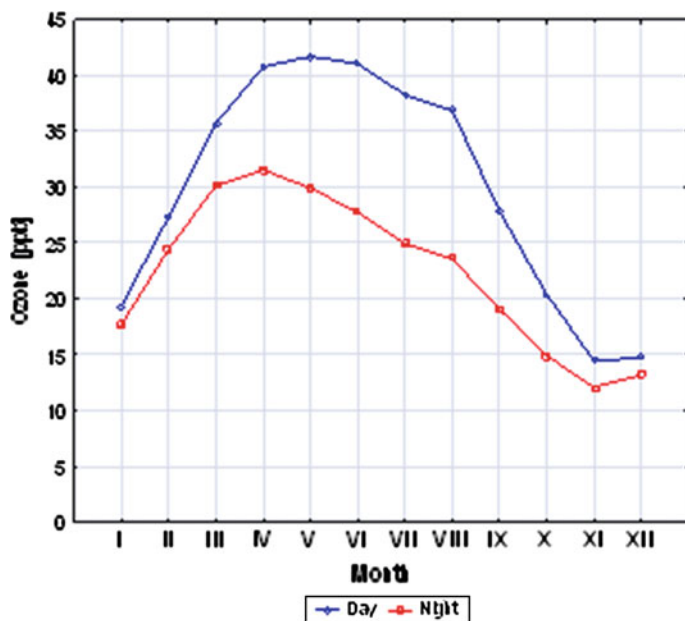
Monthly averaged surface ozone concentrations with division into day and night are presented in Fig. 9.

For each month, higher values during day than during night are observed. Processes of ozone formation during night do not take place. Furthermore, processes of ozone destruction, which are a result of ozone titration by NO ( $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ ), lead to low values of surface ozone at night (Gerasopoulos et al. 2006).

### 5.3 Comparison of Seasonal Distribution of Measurement Series in Kraków (1869–1878) and Belsk (1995–2012)

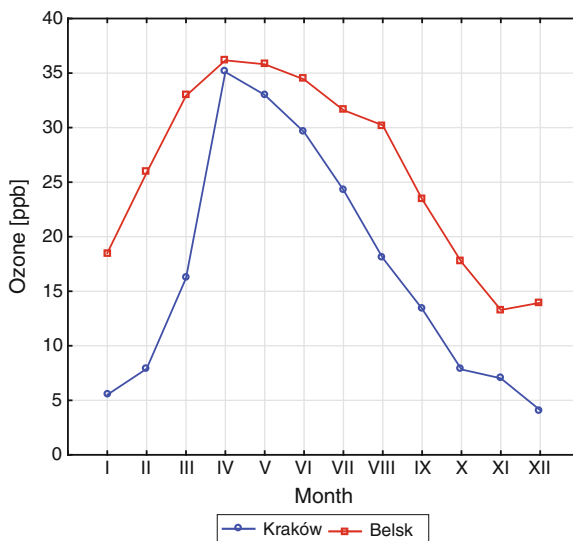
Seasonal variations of surface ozone in Kraków (1869–1878) and Belsk (1995–2012) are presented in Fig. 10.

Comparing both curves, a significant difference in their shape is evident. Distribution in Kraków is characterized by a rapid growth of surface ozone concentration from January to April and then equally rapid decrease until December. Such a sharp peak in spring months indicates stratospheric fluxes of air rich in ozone as a main source of ground-level ozone. Distribution in Belsk is characterized by broad spring-summer surface ozone maximum. From March to August we can notice high ozone values and then gradual decrease of ozone values until winter months. This kind of distribution indicates troposphere-stratosphere exchange as a source of ozone near the ground but also (even more importantly) in situ photochemical ozone



**Fig. 9** Monthly averaged concentration of surface ozone with division into day and night for 1995–2012 time series

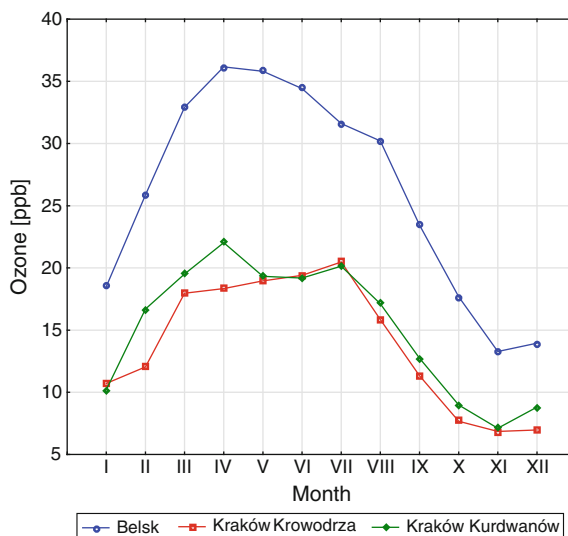
**Fig. 10** Seasonal variations of surface ozone concentration in Kraków (1869–1878) and Belsk (1995–2012)



production. We suspect that an increase in photochemical ozone formation has been possible due to increased content of ozone precursors in the air. It is worth noting about the differences in average values of surface ozone concentration in these two



**Fig. 11** Seasonal variations of surface ozone concentration in Kraków (2005–2013) and Belsk (2005–2013)



analyzed series. Average values in Belsk fluctuated between 13 and 36 ppb while in Kraków ranged from 4 to 35. The highest differences were during winter months (up to 18 ppb in February) and in March (17 ppb).

#### ***5.4 Comparison of Diurnal and Seasonal Distribution of Surface Ozone at Contemporary Rural (Belsk) and Urban (Kraków) Stations***

The 9-year record (2005–2013) of the surface ozone data in Kraków and 18-year record (1995–2013) in Belsk were investigated to determine possible diurnal and seasonal distributions at 2 stations situated at different environments.

The surface ozone data set used in this study for Kraków were taken from the website of The Regional Inspectorate of Environmental Protection in Kraków. From January 1995 to February 2010 data were recorded in station Kraków-Krowodrza (north–west Kraków), from April 2010 to December 2013 in station Kraków-Kurdwanów (south Kraków). Both stations are urban background stations located at a distance of about 9 km.

Hourly averaged values were used to analyze variability during day and night. Monthly means were calculated based on daily values to study the seasonal cycle.

The seasonal variations of surface ozone in Kraków (urban stations) and Belsk (rural station), presented in Fig. 11, show a strong, characteristic variations with rural values of concentration being almost doubled compared to urban stations. The minimum values are observed in autumn (October, November) and winter (December, January) months. At the rural station, the values were reaching about

13–17 ppb and 13–18 ppb, respectively, whereas at the urban stations they were 7–9 ppb and 7–11 ppb, respectively. Broad spring-summer maximum at Belsk with the highest value in May and gradually decreasing during summer is replaced at urban stations by broad spring-summer maximum with 2 peaks during April and July. The first one is connected with stratospheric intrusions of air that was rich in ozone and the initiation of intensive photochemical ozone production, and the second one with photochemical ozone production with the participation of solar radiation and high temperature. The average ozone concentration is higher at rural site than at the urban, which can be associated with smaller number of sinks of ozone in the rural area and transport of precursors from mid or long distances (Saitanis 2003).

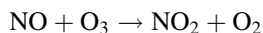
To better understand the big difference between surface ozone concentrations at rural and urban sites, diurnal variation of ozone in the form of day and night averages are presented in Fig. 12.

Diurnal variation of surface ozone is necessary to recognize and understand the different processes responsible for ozone production and destruction at a given area (Elampari and Chithambarathanu 2011). Diurnal ozone concentration is a result of both chemical processes (e.g., occurring with the participation of sunlight) and dynamic processes (e.g., advection of polluted air masses).

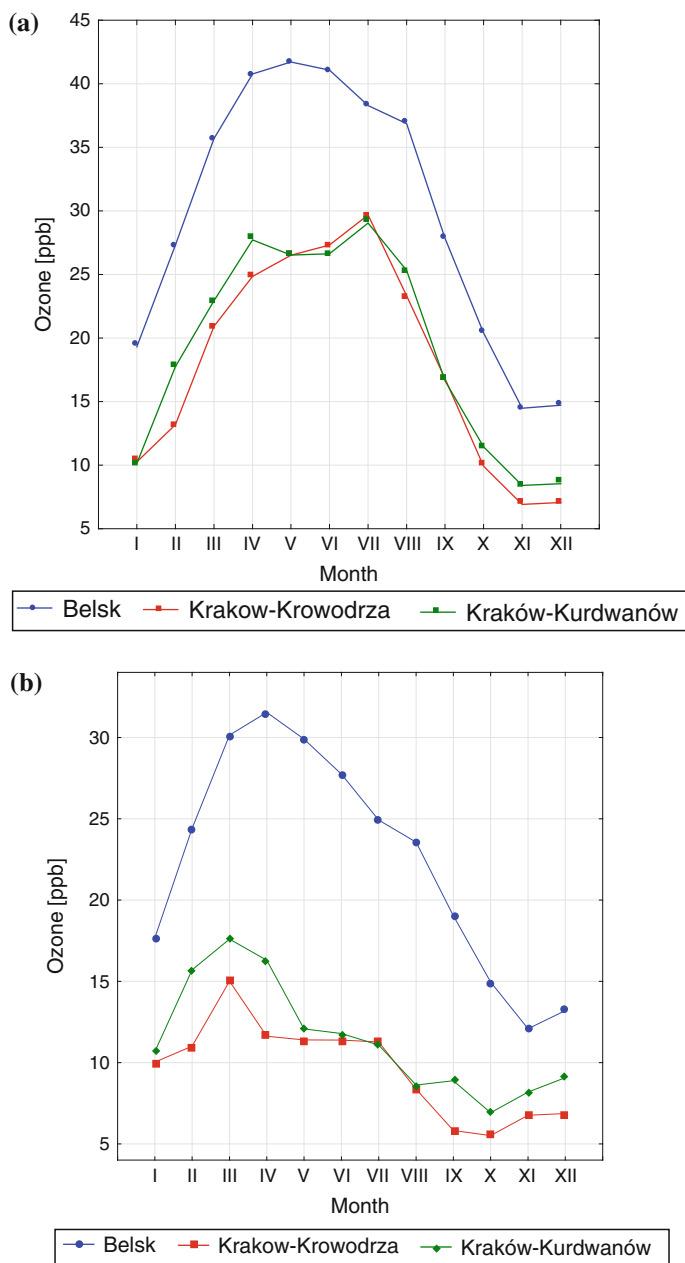
Higher concentration of surface ozone during day is evident at stations of both kinds. It is attributed to the photochemical reactions between ozone precursors and downward transport of air rich in ozone by the vertical mixing due to convective heating during the day (Lal et al. 2000). However, analyzing the ozone concentration at urban stations during November, December and January we can notice that values during nighttime are comparable with daytime. To explain this phenomenon we have to investigate surface ozone distribution during winter and summer months (Fig. 13).

The diurnal variation of surface ozone during July (Fig. 13a) is characterized by high concentration (up to 47 ppb for Belsk, up to 42 ppb for Kraków) during daytime and low concentration (down to 22 ppb for Belsk, down to 8 ppb for Kraków) during morning and evening.

The minimum ozone concentration is observed during the early morning hours. Since this moment, values start increasing rapidly and uniformly, coinciding with solar radiation reaching maximum during afternoon hours. From 17:00, together with less intense solar activity, ozone concentration gradually decreases, maintaining low values during evening and night hours. The nighttime minimum is more pronounced at the polluted urban area, associated with processes of ozone titration by NO expressed in the reaction:

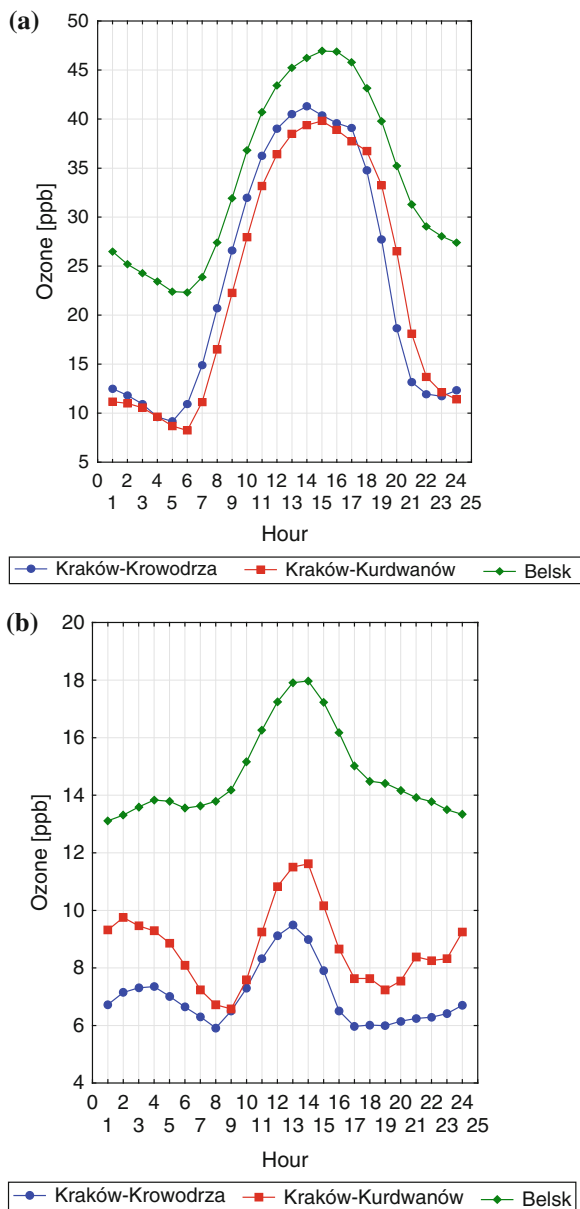


Fresh NO emission in urban area contributes to removal of ozone and production of NO<sub>2</sub> and O<sub>2</sub>. Titration processes are remarkably visible during nighttime hours when the lack of solar radiation prevents the ozone formation (despite



**Fig. 12** Variations of surface ozone concentration in Kraków (2005–2013) and Belsk (2005–2013) in the form of average day (a) and night (b) values

**Fig. 13** Diurnal variations of surface ozone concentration in July (a) and December (b) (2005–2013)



the production of  $\text{NO}_2$ ). Indication of titration during daytime could be hidden by ozone production with the participation of solar radiation.

The variation of surface ozone during December (Fig. 13b) at urban stations is disrupted by deep ozone decreases during morning and evening hours, associated with rush hours and intensified emission of ozone precursors (e.g.,  $\text{NO}_x$ ). During

winter this effect together with limited photochemical ozone production are responsible for low surface ozone concentration. Less intense solar radiation during winter is not able to produce significant amounts of ozone during day to compensate for morning and evening declines and makes the net ozone concentration during day to be significantly higher than during night (like in spring and summer months).

## 6 Conclusions

Systematic measurements of surface ozone performed at Kraków Observatory from 1869 to 1878 have been compared with measurements of surface ozone carried out at Belsk Observatory from 1995 through 2012. Data were investigated in terms of annual, seasonal and diurnal cycles. Annually averaged surface ozone concentrations in the second half of the nineteenth century in Kraków ranged between 11 and 24 ppb. The highest values were noticed during spring and early summer months (April, May, June); in turn, the lowest were during late autumn and winter months (November, December, January). From April to September, concentrations of surface ozone during day were higher than during night by up to 8 ppb. From October to March, concentrations of surface ozone during night were higher than during day by up to 2 ppb. Annually averaged surface ozone concentration in recent years (1995–2012) at rural station ranged from 22 to 31 ppb. During whole measurement series we can distinguish the following stages: (1) gradual increase from 1995 to 2003, and (2) continuous decrease from 2004 to 2012. Annually averaged surface ozone concentrations in the last years (2005–2013) at urban station ranged between 12 and 17 ppb and were similar to those of nineteenth century Kraków. High number of sinks of ozone in the urban area is responsible for lower ozone concentration compared to rural places. An analysis of seasonal, contemporary concentrations of surface ozone revealed a distribution similar to that in the 19th century, with maximum in spring and summer and minimum in autumn and winter.

From the analysis performed in this chapter we may draw the following basic conclusions:

- (1) Urban places exposed to continuous emission of NO<sub>x</sub> are characterized, on the average, by a low surface ozone concentration, comparable to that in the 19th century Kraków.
- (2) Rural sites, where emission of NO<sub>x</sub> is significantly limited (due to low vehicle traffic) are characterized by significantly higher values of surface ozone concentration than those occurring in Kraków almost 150 years ago.
- (3) Since 2003, the background rural station in Belsk is characterized by gradual downward tendency of surface ozone concentration.

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