Ozone Monitoring in the Krakow Province, Southern Poland[1]

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Abstract

From June to mid-October in 1995, the concentration of tropospheric ozone in 18 localities in the Krakow Province of southern Poland was measured by using ultraviolet monitors and Ogawa passive samplers. At three active monitoring stations, tropospheric ozone was recorded in the downtown and western part of Krakow and in Szarow, 30 km to the east. The passive method was applied in a dozen or so localities distributed within and outside Krakow's city limits. In these locations two varieties of tobacco (Nicotiana tabacum *L.*), *Bel-W3 and Bel-B, were exposed. In the Krakow Province the mean 24-hour ozone concentration (from active monitors) was higher than 30 μg/m*^{3} *(24-hour Polish standard) in June through July and part of September. The highest concentration was recorded in early afternoons and the lowest between midnight and sunrise. The maximum 30-minute concentration of 205 μg/m*^{3} *occurred in August. However, great diversity of the tropospheric ozone concentration (measured with passive samplers) was recorded in all locations. The lowest average concentration was recorded in Krakow and areas located west, northwest and east of the city, whereas the highest average concentration was recorded in the north, northeastern, southeastern, and southwestern parts of the Province. The highest average concentration of 100 μg/m*^{3} *for a 2-week period of filter exposure was recorded in July and August from the sites Ratanica, located 40 km south, and Goszcza, 25 km north of Krakow. The amount of damage to the leaves of the ozone-sensitive variety of tobacco (Bel-W3) exposed at all sites was correlated (coefficient 0.69, p<0.000) with concentration results obtained with passive samplers. Greater damage was recorded in the sites located outside the city than elsewhere, whereas the damage that occurred within Krakow was markedly smaller.*

Introduction

Tropospheric ozone is believed to be an important phytotoxic air pollutant (Fuhrer and Achermann 1994, Guderian 1985, Stanners and Bourdeau 1995). Ozone levels recorded in western Europe, such as France (Proyou and others 1991), Switzerland (Ballaman 1993), or Austria (Dovland 1987), exceed the permissible concentrations for that pollutant. In the countries located in northeastern Europe, such as Finland (Laurila and Lattila 1993) or Lithuania (Girgzdiene 1991), concentrations of ozone are relatively lower than in central Europe (Simpson 1993). Southern Poland is among the most polluted areas of central Europe. The high input of sulphur, nitrogen oxides, and heavy metals has originated from local and remote sources (Nowicki 1993). Recent studies performed in southern Poland (Upper Silesia Region, Beskidy Mountains, Krakow Region) have shown that during the summer season a single 1-hour average ozone concentration may reach 120 ppb (Bytnerowicz and others 1993, Godzik and others 1994).

In the Krakow agglomeration, the main sources of pollution are a huge steel mill, a cement factory, an electric power station, privately-owned coal stoves and also rapidly increasing car traffic (Turzanski 1994). The highest concentration of air pollutants in the Krakow Province occurs centrally in the city of Krakow (Turzanski 1996).

This paper reports a study of ozone concentrations within the city of Krakow in southern Poland and outside its limits; identifies which areas have the highest ozone levels; and evaluates phytotoxic effects of ozone on the basis of responses of bioindicator tobacco (*Nicotiana tabacum* L.) plants.

Study Area and Methods

The Krakow Province covers an area of 3,254 km^2. In 1995 measurements of the ozone concentration were made at 18 sites: 7 among them were located within the

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city limits, 11 were evenly distributed in the Krakow Province *(fig. 1)*. Two sites located within the city (Balice, Wieza Ratuszowa) and the one in Szarow (30 km east of the city) were equipped with continuously working monitors (Thermo Environmental Model 49 UV-photometric ambient O_3 analyzer, Franklin, MA).[3] In two stations within the city measurements were performed by the Voivodship Inspectorate for Environmental Protection in Krakow. The correlation coefficient for the conversion of ppb to µg/m^3 were 1.93 for T=20 °C. All sites were furnished with the Ogawa passive samplers (Ogawa and Company, Pompano Beach, FL) (Koutrakis and others 1993). Passive sampler exposure was done from early June to mid-October in 2- or 3-week intervals. The O_3 concentration in the Krakow Province was mapped by using Surfer 5.0 program. Isolines were made following the kriging method for the parameters: component 1 = linear, scale C = 133, length A = 40.7. Graphic description was made in CorelDraw 3.0 program.

In every monitoring site four plants of the Bel-W3 and four plants of the Bel-B tobacco *(Nicotiana tabacum* L.*)* varieties were exposed during two periods (07/20-08/08 and 08/11-09/06). Damage to leaves was measured at 1-week intervals according to procedures described by Manning and Feder (1980). Four leaves on each plant were evaluated for injury by the sum of percentage area showing symptoms on each leaf. The correlation between percentage of leaf damage and ozone concentration was analyzed by Spearman rank test.

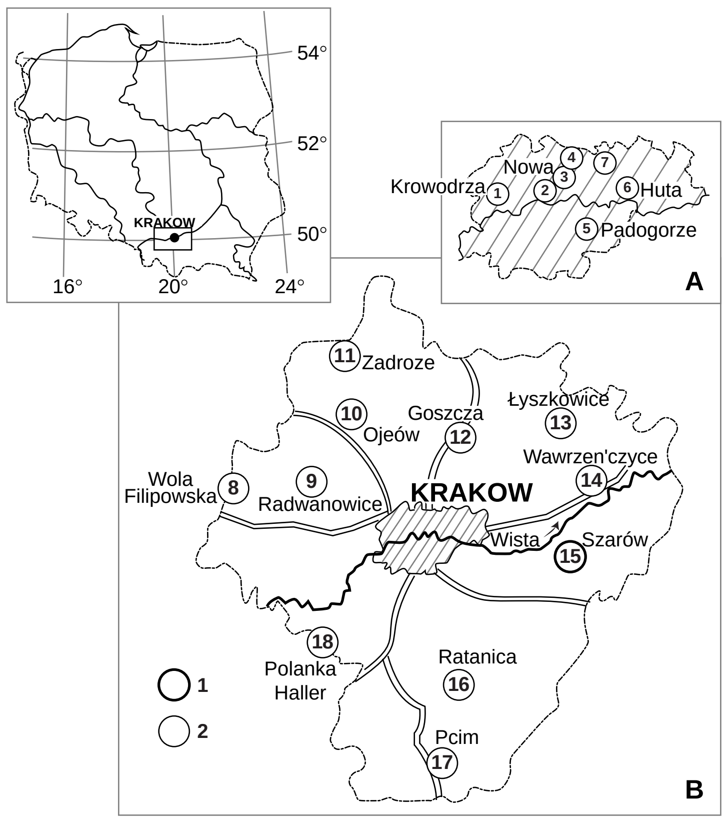

Figure 1 — Distribution of ozone-monitoring sites in the Krakow city (A) and the Krakow Province (B). 1—stations equipped with monitor and passive samplers, 2—stations equipped with passive samplers.

Results

Thirty-minute average concentrations of ozone measured with continuous monitors varied predictably during a 24-hour period (especially in July and August) and between months in all sites. The ozone concentration at night decreased to several µg/m^3, and it increased to 160 µg/m^3 during the day *(fig. 2)*. According to the Polish standard, the 30-minute concentration should not be greater than 100 µg/m^3. About 100 hours in June and July and more than 200 hours in August showed concentrations higher than the standard. In September excessive ozone concentrations occurred less frequently *(fig. 3)*.

[3] Mention of trade names or products is for information only and does not imply endorsement by the U.S. Department of Agriculture.

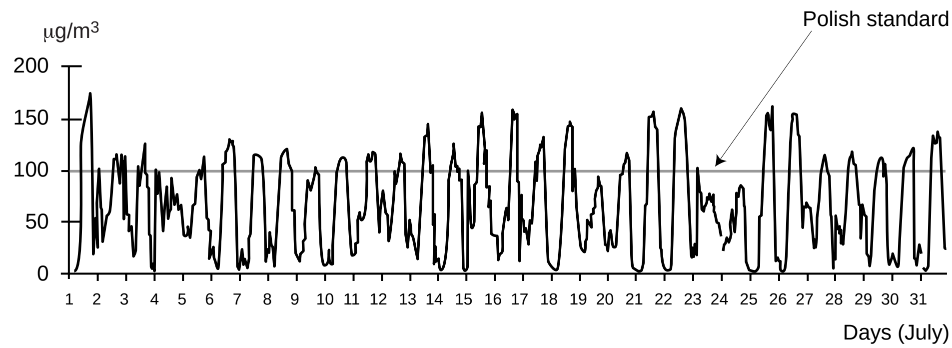

Figure 2 — Diurnal pattern of ozone concentration (µg/m³) in July 1995 at the Balice monitoring station (western part of the city). (1µg/m³ O_3= 0.51 ppb O_3 at 25ºC, 760 mm of Hg.)

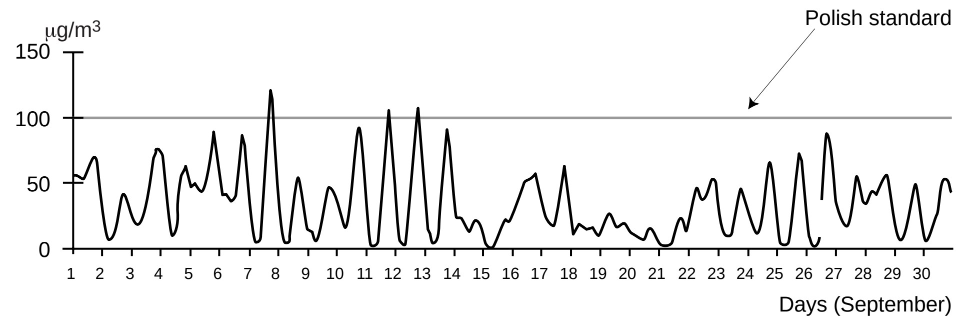

Figure 3 — Diurnal pattern of ozone concentration (µg/m³) in September 1995 at the Balice monitoring station (western part of the city).

Table 1 *— Highest 30-minute ozone concentration (µg/m³) at three sites in southern Poland, by month of measurement.*

	June	July	August	September
Balice	152	177	[1]159	120
Wieza Ratuszowa	148	189	205	126
Szarow	-	-	180	129

[1] *Data incomplete for a whole period*

The maximum 30-minute ozone concentration for subsequent months occurred in August *(table 1)*. The highest ozone concentration occurred in August. The lowest concentration was recorded between midnight and sunrise and the highest in early afternoons *(fig. 4)*.

In July and August the maximum mean 24-hour concentrations at the Balice research station were higher than in June. These values were markedly lower in September than in the previous months *(table 2)*. The mean 24-hour concentrations of ozone at the Wieza Ratuszowa station were similar in subsequent months to the concentrations recorded in the Balice station. In general, however, the minimum values for subsequent months were lower and the maximum values were higher than the ones recorded from the Balice station *(table 2)*. The mean 24-hour permissible ozone concentration, which follows the Polish standard, should not be higher than 30 µg/m^3. In June, July, August, and part of September the mean 24-hour concentration in Krakow was markedly higher than the Polish standard.

During the period of measurements from June through September, the mean monthly concentrations measured by active monitor were higher at the Balice station (western part of the city) than at the Wieza Ratuszowa station (center of the city). The highest mean monthly value for August was recorded from the Szarow station (30 km east of Krakow) *(table 2)*.

Figure 4 — Monthly averages of diurnal dynamics of ozone concentrations (µg/m³) at the Balice monitoring station.

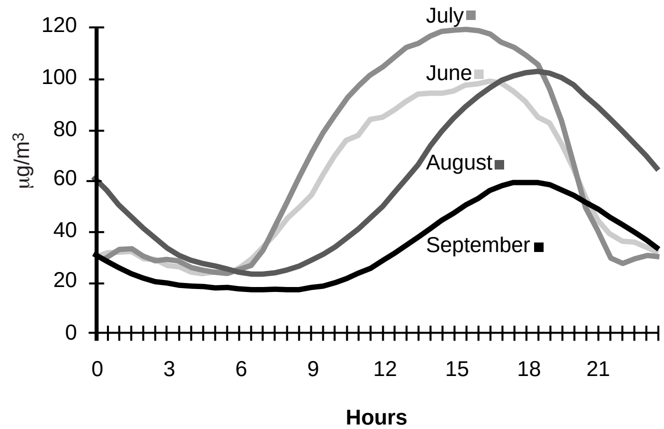

Table 2 — *Average daily minimum (min) and maximum (max) and average monthly (x) ozone concentrations (µg/m³) at the Balice, Wieza Ratuszowa, and Szarow Research Station.*

Month		Balice	Wieza Ratuszowa	Szarow
	min	30.21	25.11	-
June	max	69.71	78.43	-
	x	57.95	55.06	-
	min	46.66	45.57	-
July	max	83.02	87.72	-
	x	66.46	65.28	-
	min	30.13	21.49	28.16
August	max	92.08	98.41	113.96
	x	58.98	53.86	68.68
	min	10.51	5.25	10.28
September	max	58.96	52.65	61.48
	x	34.06	27.64	30.41

In all periods of measurements made with passive samplers, the average ozone concentration was markedly different among selected sites and exposure periods *(table 3)*. In the first two 2-week periods of measurement (including June) and in the last two (September and October) the mean ozone concentration was low (table 3). In July and August it increased dramatically. The maximum values for a 3-week exposure (June, July) were recorded from Goszcza and Ratanica research site (about 100 µg/m³ *(table 3)*. During the same period, a high average ozone concentration occurred also in Szarow, Polanka Haller, and Trzyciąz. In all measurement periods the lowest average concentration of ozone was recorded from the sites located in the city center (Krasinski Avenue, Helclow Street) *(table 3)*. All sequences of measurements yielded a similar pattern of spatial differentiation of the ozone concentration in the Krakow Province. During all exposure periods the lowest average ozone concentration occurred in the center of the Krakow Province (Krakow city and the areas located west, northwest, and east of the city) and in its southern part *(figs. 5, 6, 7)*. The highest concentration was determined in the north, northeastern, southeastern, and southwestern parts of the Krakow Province *(figs. 5, 6, 7)*.

The amount of damage to the leaves of the ozone-sensitive variety of tobacco (Bel-W3) exposed at all sites was correlated with results obtained through passive samplers. This coefficient (=0.69, p<0.000) was statistically significant. During two exposition periods of tobacco *(Nicotiana tabacum* L.*)* the lowest injury to the leaves of the ozone-sensitive (Bel-W3) variety of tobacco was recorded at the sites located in the center of Krakow (Krasinski Avenue, Helclow Street) and at the sites located west of the city (Radwanowice, Ojcow, Wola Filipowska) (*fig. 8*). The most severe injury to the tobacco leaves were noted in sites located in the northern, southeastern, and southwestern parts of the Krakow Province (Trzyciąz, Goszcza, Szarow, Ratanica, Polanka Haller) (*fig. 8*). No leaf injury was observed in the ozone-tolerant tobacco variety (Bel-B) at any of the study sites.

***Table 3** — Average ozone concentrations (µg/m^3) during different exposure periods in the Krakow city and the Krakow Province.*

Station	Exposure periods						
	5/31 -6/13	6/14 -6/27	6/27 -7/17	7/17 -8/7	8/7 -8/30	8/30 -9/21	9/21 -10/17
Krakow city:							
1. Balice	54.5	43.3	72.9	78.5	55.8	32.1	32.2
2. Krasinskiego	-	-	19.3	14.7	17.1	12.7	10.8
3. Helclow	-	4.9	25.7	25.1	23.5	12.7	7.6
4. Strzelcow	-	-	50.2	57.9	45.0	28.5	18.5
5. Wallenroda	-	-	71.5	65.0	46.3	35.3	22.3
6. Zeromskiego	-	43.6	71.1	66.9	48.4	26.6	19.3
7. Zielone	-	-	57.2	49.3	38.7	23.2	17.4
Krakow Province:							
8. Wola Filipowska	44.0	30.3	55.1	49.8	39.1	24.9	19.5
9. Radwanowice	47.7	31.4	49.8	55.8	43.8	24.8	21.7
10. Ojcow	29.8	12.4	32.9	37.9	29.1	19.1	16.8
11. Zadroze	60.7	57.3	86.2	88.0	67.1	45.4	39.3
12. Goszcza	65.0	57.2	100.1	101.5	61.4	48.1	35.3
13. Lyszkowice	54.3	48.1	77.9	81.5	60.8	42.3	29.4
14. Wawrzenczyce	40.3	17.9	50.5	50.0	39.3	31.8	19.8
15. Szarow	58.8	51.1	81.5	89.1	70.5	39.1	45.9
16. Ratanica	69.5	52.6	98.1	107.6	73.3	56.2	32.1
17. Pcim	35.4	50.8	50.0	47.4	35.8	26.5	20.3
18. Polanka Haller	54.3	48.2	86.6	85.9	63.5	44.2	41.4

Discussion

Ozone has been recognized as a major phytotoxic constituent of urban and suburban air pollution (Stanners and Bourdeau 1995). Concentrations of ozone at average and high latitudes of the northern hemisphere doubled during the last century (Anfossi and others 1991, Volz and Kley 1988). Over the last decade an increase in ozone concentration has also been observed in the countries of north-eastern Europe. For example, rural Lithuania has been affected by the long-range transport from central Europe (Girgzdiene 1995).

Ozone causes the reduction of yield in crop species in North America and Europe (Fuhrer and Ascherman 1994), and these effects become more apparent as the phytotoxic concentrations of ozone increase in the rural areas (Colbeck and Mackenzie 1994). Ozone is also one of the factors causing recent forest decline on these continents (Ashmore and others 1985, Chevone and Linzon 1988).

Studies made in the Krakow Province found that the concentration of ozone in this area is markedly higher from the levels generally accepted as natural (Guderian 1985). During summer the concentrations of ozone in the area surrounding Krakow are higher than in unpolluted areas of central Europe (Girgzdiene 1991, Hakoala and others 1991), and they are similar to the ozone concentrations recorded from western European countries (Ballaman 1993, Dovland

Figure 5 — Spatial ozone distribution (µg/m^3) obtained from passive samplers in the Krakow Province for the period 27 June to 17 July 1995.

Figure 6 — Spatial ozone distribution (µg/m^3) obtained from passive samplers in the Krakow Province for the period 17 July to 7 August 1995.

Figure 7 — Spatial ozone distribution (µg/m^3) obtained from passive samplers in the Krakow Province for the period 21 September to 16 October 1995.

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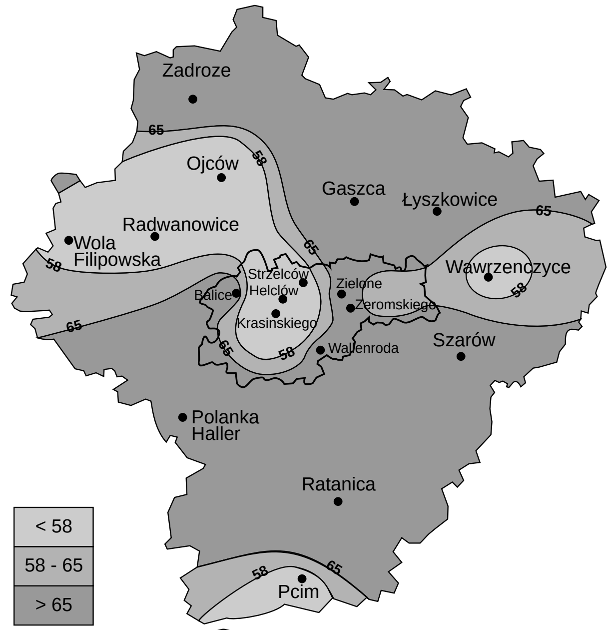

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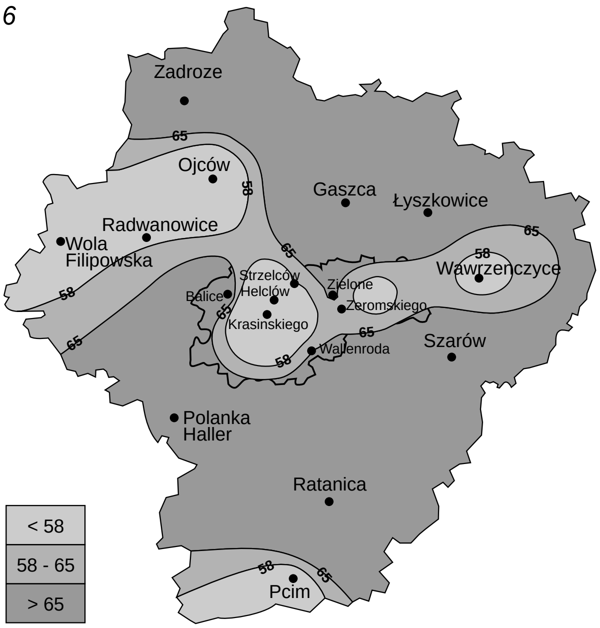

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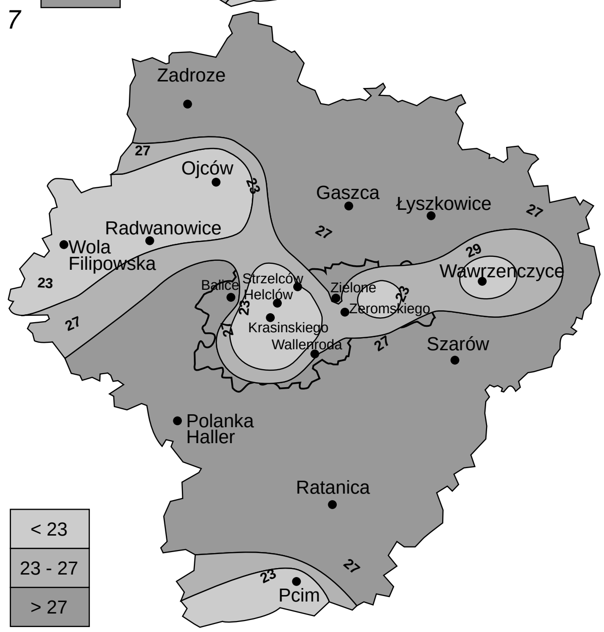

1987, Proyou and others 1991). The highest monthly ozone concentration in southern Poland occurred in July and in the beginning of August. In Upper Silesia (80 km west of Krakow) the ozone concentration recorded in 1994 was similar to the values recorded in Krakow and were higher than the values recorded from these areas in 1995 (Godzik and others 1994, Godzik and Grodzinska 1996). Although the highest concentration of ozone occurred in the city of Katowice, a high concentration was not recorded at that time in other sites in Silesia. This was probably caused by the presence of appropriately high concentrations of ozone precursors in the air (Godzik and others 1995). Ozone concentrations within the Krakow Province differed: higher concentrations were recorded in the northern and southern sites that are at higher elevations. In these localities, in contrast to the urban areas, small changes in the ozone concentration over 24 hours have been observed (absence of zero ozone concentration in the night) (Godzik and others 1995). It is impossible to give definite reasons for the occurrence of the highest ozone concentration in the northern and southern parts of the Krakow Province because data are not available on the proportion of nitrogen oxides and hydrocarbon or sun exposure regimes for the study sites.

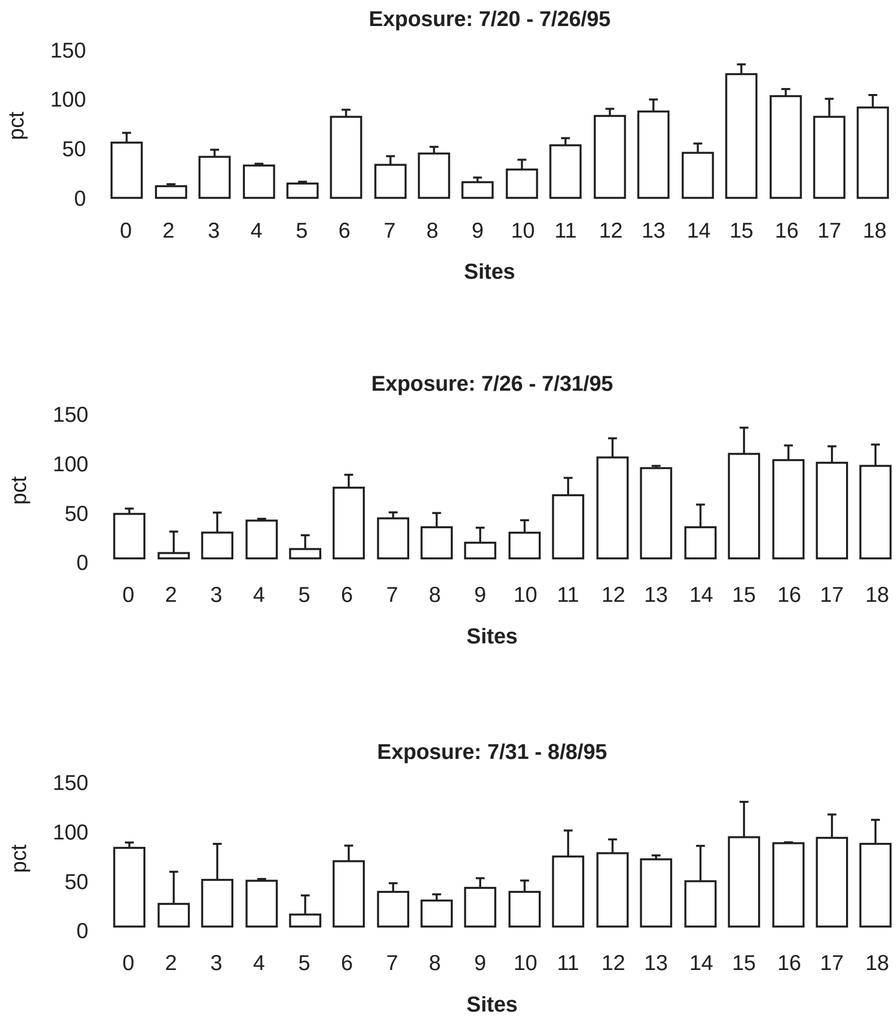

Figure 8 — Leaf injury to bioindicator plants (Bel-W3 cultivar of tobacco) exposed in Krakow (sites 1-7) and outside the city (sites 8-18) in the period 07/20-08/08/1995.The amount of injury is presented as the mean sum for four evaluated leaves from each of the four plants; data accumulated for subsequent exposition weeks. Research sites have been labelled as in *table 3*.

The ozone concentrations in the Krakow Province were high enough to cause leaf injury of the ozone-sensitive variety of tobacco (Bytnerowicz and others 1993, Spellerberg 1991). Similar concentrations in such amounts may also cause injuries in other plant species (Chappelka and Chevone 1992, Runeckles and Chevone 1992).

In the Krakow Province the levels of other pollutants are high, including sulfur dioxide, particulate pollution heavily contaminated with heavy metals, etc. These pollutants originate either from the local sources or from the transboundary transport (Nowicki 1993). Synergistic effects of these compounds and ozone may result higher damage of plants than by single pollutants (Guderian 1985). The results of ozone measurement concentration in southern Poland (Upper Silesia, Krakow region) and evaluation injury of the test-plants have shown that the co-occurence of elevated ozone concentration and high physiological potential of native plants can cause their injury. Ozone injury to native plants in Beskid Śląski of southern Poland has been observed but has not been verified in controlled ozone exposures (Godzik and others 1995). Similarly, the occurrence of ozone injury described in the literature has been recorded in the area surrounding Krakow. Among the affected species are: *Ulmus scabra, Ulmus laevis, Sambucus racemosa, Rubus hirtus*.[4] However, the above observations need to be confirmed in the controlled ozone exposures.

The number of motor vehicles has rapidly increased since 1990 in the Krakow region (Turzanski 1994) and has resulted in increased emission of nitrogen oxides and hydrocarbon. These compounds, known as ozone precursors, can cause further increase in ozone concentrations in the future.

4 Unpublished data on file at the Polish Academy of Sciences.

Acknowledgments

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