Ozone Air Pollution in the Ukrainian Carpathian Mountains and Kiev Region[1]

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Abstract

*Ambient concentrations of ozone (O_3) were measured at five highland forest locations in the Ukrainian Carpathians and in two lowland locations in the Kiev region during August to September 1995 by using O_3 passive samplers. The ozone passive samplers were calibrated against a Thermo Environmental Model 49 ozone monitor located at the Central Botanical Garden in Kiev. The 2-week long average concentrations in August to September at the Carpathian Mountains ranged from 27.4 to 51.8 ppb, and at the lowland forest location (Lutezh, near Kiev) ranged from 29.3 to 32.2 ppb. The 2-week long average concentrations in Kiev (Botanical Garden) ranged from 22.0 to 31.5 ppb. The highest diurnal average concentration in August 1995 in the Botanical Garden was 42.1 ppb while the highest 1-hr average concentration reached 84.4 ppb. Ozone-sensitive Bel-W3 tobacco (*Nicotiana tabacum *L.) plants at the Botanical Garden in Kiev were injured from exposure to ambient concentration of ozone. Ozone injury symptoms were found on native plants (e.g.,* Sambucus racemosa *and* Humulus lupulus*) elsewhere in Kiev and at some of the study sites in the Carpathians.*

Introduction

In general, elevated concentrations of sulfur and nitrogen oxides have been blamed for air pollution-related damage to forest vegetation in central and eastern Europe. However, increasing concentrations of ozone may also play an important role in the observed suite of symptoms of forest decline in that part of Europe. Ozone alone may affect plant health, while the effects of mixtures of ozone with other pollutants, especially with sulfur dioxide, may be synergistic (more than additive) in nature (Guderian 1985).

Recently, ozone concentrations have significantly increased across Europe mainly because of increased production of ozone precursors from combustion of gasoline and other fuels (Derwent and Jenkin 1991). Long range atmospheric transport may also be responsible for elevated concentrations of ozone in various forested areas of the region (Dovland 1987).

In Ukraine the annual atmospheric emissions of gaseous pollutants are: NO_x (nitrogen oxides) — 1.1 million tons; CO (carbon monoxide) — 8 million tons; C_xH_y (hydrocarbons) — 1.4 million tons (National Report 1994). As a result of photochemical transformation of these emissions, the level of surface background concentrations of ozone could theoretically increase two-fold compared to the pre-industrial pollution period (Nikolay Gurevich, personal communication).

Average 24-hour background O_3 concentrations in the unpolluted lower troposphere ranged from 10 to 40 ppb (Logan 1985). It has been estimated that in the countries of the former USSR the background O_3 concentrations ranged from 15 to 40 ppb (Israel 1984). Concentrations of ozone in European countries of higher latitudes, such as Finland (Laurila and Lattila 1993) or Lithuania (Girgzdiene 1991), are relatively low and do not pose a threat to vegetation. However, higher ozone concentrations, potentially phytotoxic, occur in the lower latitudes of western and central Europe (Emberson and others 1996, Semenov and Kouhta 1996).

Still relatively little is known about concentrations of ozone and potential toxic effects of ozone in forests in the former Communist countries of central and eastern Europe, particularly in Ukraine. Levels of ozone in central and western European countries of comparable climatic conditions such as Poland (Bytnerowicz and others 1993, Godzik 1996), Czech Republic (Bytnerowicz and others 1995), Austria

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(Dovland 1987), Switzerland (Ballaman 1993), or France (Proyou and others 1991) often exceed permissible levels for that pollutant. For example, in forested areas of central and southern Poland 1-hour mean ozone concentrations can be as high as 105 ppb (Bytnerowicz and others 1993). During long periods of hot weather and high solar radiation, the highest 1-hour mean ozone concentrations monitored in Katowice (the Upper Silesia Region of Poland) have reached 115 ppb (Godzik and others 1994).

Information about the air pollution status of the Ukrainian Carpathians is essential for a better understanding of environmental stresses that affect valuable forest ecosystems of central Europe. Thus, level of ozone, one of the main components of photochemical smog and a strong phytotoxic agent, is a primary area of study.

Until recently, surface background concentrations of ozone in natural landscapes of Ukraine were not measured, with the exception of O_3 monitoring in the territory of Karadag State Reserve on a coast of the Black Sea of the Crimea. At that site, the 24-hour average O_3 concentrations in the spring-summer period of about 15 ppb and 1-hour average O_3 maximum concentrations of about 105 ppb have been recorded.[5]

This paper discusses results of a pilot study that used ozone-sensitive Bel-W3 tobacco and other plants to measure ozone concentrations in Ukraine.

Materials and Methods

Research Sites

In summer 1995 research sites were established in five forest locations in the Ukrainian Carpathians (*fig. 1*) in the forest complex of the northern Ukraine (Staropetrovskaya Forest Research Station, vil. Lutezh, near Kiev) and at two locations, one the northern and one in the southern part, in the Central Botanical Garden of the National Academy of Sciences in Kiev (50°24'47" N, 30°34'14" E; 190 m a.s.l.).

Forest sites were located at altitude 750-1,000 m a.s.l. along the Carpathian range from the west to south-west: 1 — Uzhoksky Pass (Sjanki village, 850 m a.s.l.); 2 — Synevir (National Park "Synevir," 1,000 m a.s.l.); 3 — Shiroky Lug (Carpathian Biosphere Reserve, Kuzij massif, peak Sokolyne Berdo, 750 m a.s.l.); 4 — Yablunitsa village, Yablunetski Pass (Carpathian National Park, 968 m a.s.l.); 5 — Kryvopilja village (Carpathian National Park, 975 m a.s.l.).

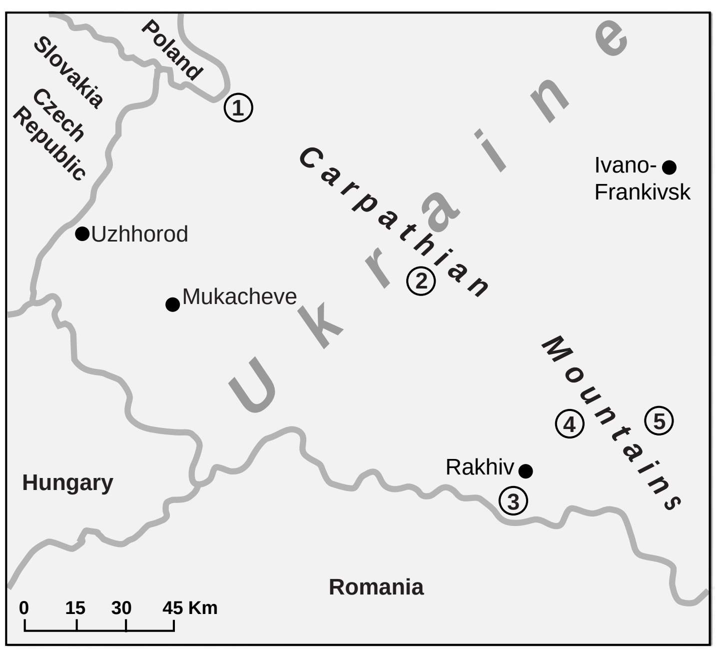

Figure 1 — Ozone monitoring sites in the Carpathian Mountains in Ukraine:
1 — Uzhoksky Pass,
2 — Synevir,
3 — Shiroky Lug,
4 — Yablunitsa,
5 — Kryvopilja.

[5] Unpublished data on file, Gas Institute, National Academy of Sciences of Ukraine

Ozone Monitoring

Average ambient concentrations of O_3 were determined with the Ogawa and Co., Inc., passive ozone samplers[6] (Koutrakis and others 1993). The samplers were exposed to ambient air for a duration of 7 to 14 days. Measurements were carried out in all forest locations from the beginning of August to the end of September.

In the Central Botanical Garden (Kiev) measurements of O_3 with passive samplers were accompanied by continuous monitoring with the Thermo Environmental Model 49 ultraviolet absorption instrument (Cambridge, MA). Results from passive ozone samplers were compared to those obtained from the Thermo Environmental instrument, which had been calibrated before its use.

Ozone Phytotoxicity

Cultivated and native plants were surveyed for symptoms of ozone injury at all five Carpathian forest locations and in Kiev. To determine the phytotoxicity of ambient O_3, two cultivars of tobacco (*Nicotiana tabacum* L.) were used: Bel-W3 (O_3-sensitive), and Bel-B (O_3-tolerant) (Heggestad 1991). Before field exposures, all seedlings were grown in charcoal filtered air to the 4-leaf stage of development in a special growing substrate (pH = 6.5), consisting of peat, perlite, and gypsum (1:1:1 by volume).

The ozone-free air chamber made of transparent plastic (1.1 m^3 volume) was constructed in order to grow tobacco plants. The chamber was located in the laboratory room. Two incandescent lamps (500 W) wrapped with aluminum foil (for darkening) and a thermo-relay kept constant temperature at about 32 - 35 °C. Air entering the chamber was pumped at a flow rate of 30 l/min. through a charcoal filter. Cuvettes with water placed at the bottom of the chamber provided the required humidity for proper growth of the tobacco plants. The plants were grown under natural and luminescent lighting (light/dark regime — 16:8 hours).

Injury of the Bel-W3 tobacco plants in the Central Botanical Garden was observed in two locations from early August to early September 1995. At one of the research sites, measurements with O_3 passive samplers and bioindicators were accompanied by photometric monitoring of ambient O_3 concentrations (near Building No. 5, Department of Plant Physiology). At another location, (i.e., the Palmetto Orchard) measurements were done by using only O_3 passive samplers and the bioindicator tobacco plants.

Results and Discussions

Ozone Concentrations

The 2-week long average concentrations in August to September in the Carpathian Mountains sites ranged from 27.4 to 51.8 ppb, while at Lutezh, the lowland forest location near Kiev, they ranged from 29.3 to 32.2 ppb. The 2-week long average concentrations in Kiev (Botanical Garden) ranged from 22.0 to 31.5 ppb (*table 1*). The highest 24-hour average concentration measured with the Thermo Environmental instrument in August 1995 in the Botanical Garden was 46.7 ppb, while the highest 1-hr average concentration reached 84.4 ppb. The lowest 1-hour average concentrations were as low as 7.0 ppb (*fig. 2*).

In Kiev, typically, the lowest O_3 levels occurred in the morning with highest concentrations found in the afternoon. Average concentrations of O_3 at night were about 25 ppb, while the maximum values reached about 47 ppb (*fig. 3*).

In general, O_3 concentrations in the five mountain forested locations in the Ukrainian Carpathians were low or only moderately elevated. The determined concentrations were similar or slightly lower than the values determined in the forested locations of central and southern Poland (Bytnerowicz and others 1993, Godzik 1996) and the Czech Republic (Bytnerowicz and others 1995). Ozone results obtained with the Ogawa passive samplers in areas of low ozone concentrations have about ± 20 percent sampling accuracy (Koutrakis and others 1993).

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

***Table 1** — Concentrations of ozone determined with the Ogawa passive samplers in summer 1995 in the Ukrainian locations (ppb).*

Location	August 6-19	August 19-Sept. 4	September 4-18
1. Uzhoksky Pass	40.9	36.3	34.2
2. Synevir	39.5	38.3	27.4
3. Shiroky Lug	27.4	33.1	51.8
4. Yablumitsa	-	36.1	-
5. Kryvopilja	-	35.8	-
6. Kiev, Palmetto	22	31.5	-
7. Kiev, Bldg. No. 5	30	29.8	25.7
8. Lutezh	29.3	32.2	-

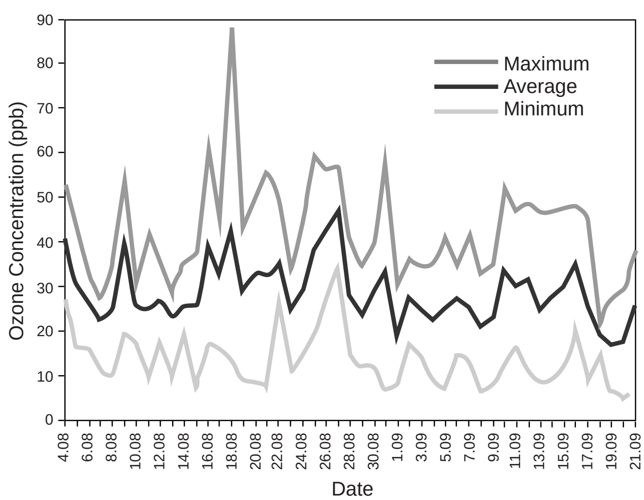

Figure 2 — Results of O_3 monitoring in the Botanical Garden in Kiev during the August 4 to September 21, 1995 period. Results are shown as 24-hour averages, and 1-hour maximum and 1-hour minimum values for every day during the monitoring period (ppb).

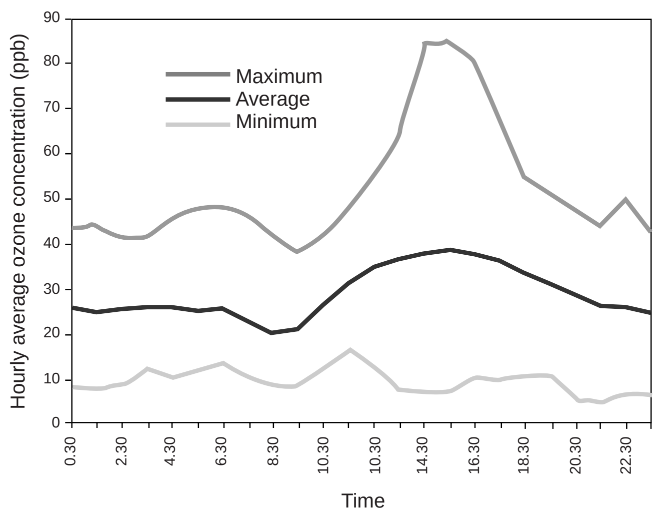

Figure 3 — Diurnal dynamics of O_3 concentrations in the Central Botanical Garden, National Academy of Sciences in Kiev, shown as averages for the August 4 to September 21, 1995 period. Results are shown as mean, maximum, and minimum values for every hour.

Ozone Phytotoxicity

Ozone injury symptoms were present on both Bel-W3 (ozone sensitive cultivar) and Bel-B (ozone tolerant cultivar) tobacco plants exposed to ambient air in the Botanical Garden (Kiev). The highest amount of O_3 injury was found on the Bel-W3 plants at the Palmetto Orchard and near the Building No. 5 (*table 2*) reaching 62 percent of the foliar area on the first leaf of plants after 14-day exposure. Moderate injury on the Bel-W3 plants (11-20 percent of the leaf area) occurred at the Building No. 5 location after 7-day exposure. Slight O_3 injury was also observed on the Bel-B tobacco plants (ozone tolerant cultivar, 1-4 percent of the leaf area) in the Building No. 5 location after 14-day exposure. Higher degree of injury on the Bel-B plants (up to 13 percent of the leaf area) occurred at the Palmetto Garden location after 14-day exposure.

Table 2 *— Injury of the Bel-W3 and Bel-B tobacco plants at two locations in the Central Botanical Garden, Kiev (percent of leaf area injured presented as means and standard deviation; n=4).*

Location	Leaf No.	7 days of exposure (Aug. 7-14)	14 days of exposure (Aug. 7-21)	7 days of exposure (Aug. 22-29)	14 days of exposure (Aug. 22-Sept. 6)
Bel-W3					
Palmetto Orchard	1	37 ± 9	40 ± 11	30 ± 12	62 ± 1
	2	32 ± 14	35 ± 15	23 ± 8	57 ± 11
	3	7 ± 3	25 ± 5	5 ± 3	11 ± 31
	4	0	4 ± 3	0	2 ± 6
Building No. 5	1	11 ± 5	18 ± 6	19 ± 9	39 ± 16
	2	20 ± 9	27 ± 8	17 ± 7	40 ± 8
	3	2 ± 1	6 ± 4	9 ± 5	18 ± 13
	4	0	1 ± 1	0	0.5 ± 0.9
Bel-B					
Palmetto Orchard	1	0	0	6 ± 2	13 ± 6
	2	0	0	1 ± 1	11 ± 7
	3	0	0	0	0
	4	0	0	0	0
Building No. 5	1	0	0	0	4 ± 2
	2	0	0	0	1 ± 1
	3	0	0	0	0
	4	0	0	0	0

Ozone injury was found on morning glory (*Ipomea purpurea*) leaves at a monastery complex in Kiev (*table 2*). Wild hop (*Humulus lupulus*) and native clematis (*Clematic vita alba*) showed possible ozone injury at the Botanical Garden in Kiev. At Uzoksky Pass, possible ozone injury was observed on leaves of red-fruited elderberry (*Sambucus racemosa*), a common forest inhabitant. At Synevir, elderberry also showed possible ozone injury. At Shiroky Lug, probable ozone injury was observed on blackberry (*Rubus hirtus*), hazelnut (*Corylus avellana*), wild clematis (*Clematis* hyb.), and vincetoxicum (*Vincetoxicum* sp.). At a forestry administration unit near Rakhiv, probable ozone injury was noted on cultivated clematis, wild hop, and elderberry.

Some native plants are potentially excellent detector indicators of ambient ozone in the Carpathian Mountains of Ukraine:

- Actual Injury — Bel-W3 tobacco (*Nicotiana tabacum*), morning glory (*Ipomoea purpurea*).
- Probable Injury — wild hop (*Humulus lupulus*).
- New Species — clematis (*Clematis vita alba*), clematis (*Clematis hyb.*), hazelnut (*Corylus avellana*), Vincetoxicum (*Vincetoxicum sp.*).
- Known Species — blackberry (*Rubus hirtus*), elderberry (*Sambucus racemosa*).

Their response to ozone needs to be verified so that they can be used as bioindicators.

In general, the results of our pilot study indicated that ambient O_3 in Kiev and some forest regions of Ukraine during some summer periods could injure plants. The predicted increase of automobile traffic in Ukraine and the neighboring countries and long-range transport of the air masses contaminated with photochemical smog may cause further increase of O_3 concentrations in the forested areas of the Ukrainian Carpathian Mountains. Continuous monitoring of O_3 concentrations and its phytotoxic effects in the Carpathian forests and other parts of Ukraine is needed in order to signal the potential for deterioration of sensitive plant species in this part of Europe.

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