Bull. Environ. Contam. Toxicol. (2003) 70:343–350
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DOI: 10.1007/s00128-002-0197-0

Bulletin of Environmental Contamination and Toxicology

Comparison of Active and Passive Measurement of Ozone in Zagreb Air

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Received: 2 April 2002/Accepted: 27 November 2002

The Ordinance on Recommended and Limit Air Quality Values based on the Croatian Law on Air Quality Protection defines the following values for ozone:

Monitoring period	Recommended value of 98th percentile (RV_{98})	Limit value of 98th percentile (LV_{98})	Average time
1 year	110 $\mu g\ m^{-3}$	150 $\mu g\ m^{-3}$	24 hr
		180 $\mu g\ m^{-3}$	1 hr

The RV_{98} and LV_{98} values are used to categorize the air quality of the area with respect to ozone:
1st category - clean air (concentration values are below RV_{98})
2nd category - moderately polluted air (concentration values are above RV_{98} but below LV_{98})
3rd category - polluted air (concentration values are above LV_{98})

There are several methods to measure ozone concentrations in ambient air, including automatic devices, classical passive and active methods and bioindicators. Automatic devices are based on UV absorption and are used often because they are accurate and precise. They enable continuous monitoring and can provide averages of ozone concentrations on hourly basis. However, classical active and passive methods of sampling and analysis are often used instead (NIOSH 1977; Monn and Hangartner 1990; UNEP/WHO 1994, Koutrakis et al. 1993, Hangartner et al. 1996; Zhou and Smith 1997). Those methods are usually simple and less expensive. In ambient air measurements passive sampling methods based on free diffusion or permeation through a membrane can provide weekly or monthly averages only, whereas air protection laws and guidelines are usually expressed in daily and hourly averages.

The purpose of our study was to test passive and active sampling methods for ozone determination and to find an appropriate method for comparison

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of ozone results with Croatian regulations in order to categorize the air quality of the area.

MATERIALS AND METHODS

Preliminary measurements of ozone concentrations were carried out in 1998 by the automatic device based on UV absorption at 254 nm (Ansyco Environnement s.a. O3M41) on three sites in Zagreb: the north (1 Feb - 30 May), the center (10 Jun - 16 Sep) and the south (18 Sep - 31 Dec). The instrument was maintained and serviced regularly, and its accuracy was tested at the intercomparison workshop organised by World Health Organization.

Plastic passive samplers for ozone were designed by the Environmental Hygiene Unit of the Institute for Medical Research and Occupational Health. They consisted of three rings and a net against the wind. The sampler was 4.7 cm long with an adsorption area of 7.07 cm^2. Air samples were taken on glass-fiber filters (Ø 37 mm) impregnated with the solution of 0.5% $NaNO_2$, 0.5% K_2CO_3 and 2% glycerol in water (Koutrakis et al.1993, Zhou and Smith 1997). Nitrite ion reacts with ozone forming nitrate. After the sampling, filters were sonicated for 15 minutes in 15 mL of water and then centrifuged for 10 minutes. The nitrate ion was analysed using Dionex DX-120 ion chromatographer. Anions were separated on AS14 analytical column and AG14 guard column, with 3.5 m*M* Na_2CO_3/1.0 m*M* $NaHCO_3$ mixture as an eluent and a conductivity detector.

The passive method, first described by Koutrakis et al. (1993), was modified into the active sampling method in our measurements. Samples were collected by sucking the air in glass bubblers or impingers through a central tube with sinter plate. Bubblers or impingers were filled with 25 mL or 15 mL of the absorption solution, respectively, containing 50 mg L^{-1} $NaNO_2$ and Na_2CO_3. The flow through the absorption solution was 0.2-0.5 L min^{-1} After the sampling, the nitrate ion was measured by ion chromatography, as described above for passive samplers.

The results obtained by passive and active sampling in the northern part of the city were compared with the results obtained by automatic measurement. The statistical analysis included the calculation of linear correlation coefficient and paired t-test.

In 2000, ozone concentrations were measured at four sites in Zagreb using the active method described above:
- North - residential part, with modest traffic and small population density
- South - densely populated residential part of the town
- West - industrial part of the town
- Center - densely populated area with dense traffic

Figure 1 represents the location of measurement sites in Zagreb.

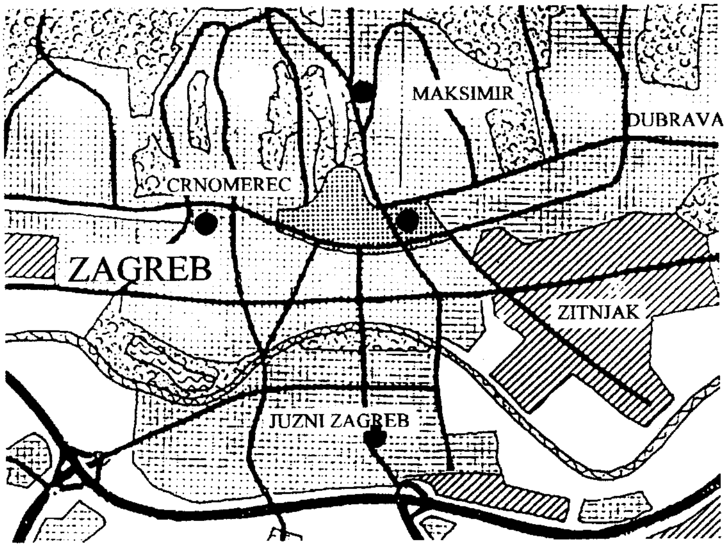

Figure 1. The location of measurement sites in Zagreb

RESULTS AND DISCUSSION

The 1998 automated measurements showed typical daily variations for photochemically originated ozone for all three sites in Zagreb (Figure 2). Ozone concentrations would reach their peak in the early afternoon when the sunlight was the most intense, and would fall over night. Although hourly averages occasionally exceeded the limit of 180 $\mu g\ m^{-3}$ in the summer of 1998, these occurrences kept below the 98th percentile in all three sites.

Unlike automated samplers, passive devices did not meet the demands for precision and detection limit required by 24-hour averages. The results obtained by a 7-day passive sampling in the summer of 2000 in the northern part of the town significantly correlated with automatic device results in 28 coupled samples ($r=0.80$, $P<0.01$). The precision of sampling, expressed as relative standard deviation of 6 concurrently used samplers, was 9.7% for the 7-day period. The limit of detection (γ_{LD}) was calculated according to the formula:

$$\gamma_{LD} = \bar{\gamma}\ (NO_3^-) + 3\ \sigma_\gamma\ (NO_3^-) = 0.021\ mg\ L^{-1} + 3 \times 0.00567\ mg\ L^{-1} = 0.038\ mg\ L^{-1}$$

where $\bar{\gamma}$ is an average of nitrate concentration in 10 blank measurements (unexposed impregnated filters) and σ_γ is the standard deviation of the same measurements. For the 7-day exposure, the nitrate concentration of 0.038 $mg\ L^{-1}$ corresponds to the air ozone concentration of 1.3 $\mu g\ m^{-3}$.

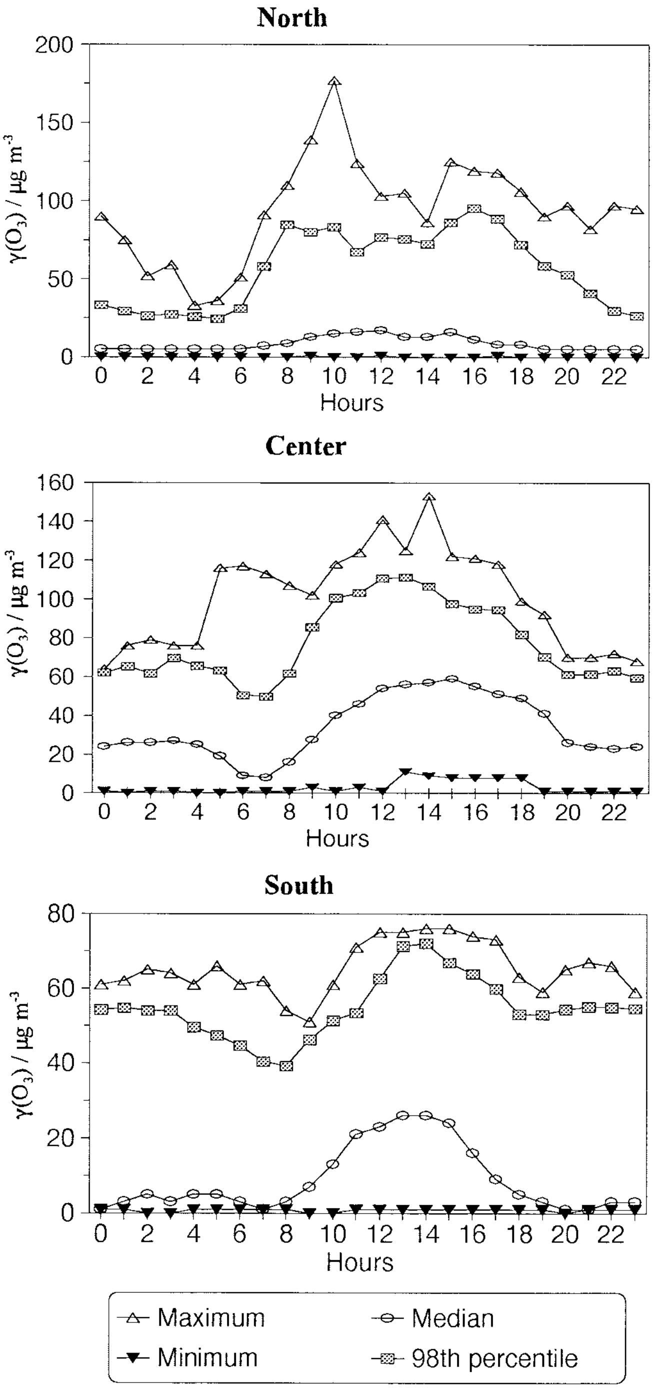

Figure 2. Daily variations of ozone mass concentrations (μg m^{-3}) in Zagreb

Active sampling method was also tested for accuracy, precision, stability and limit of detection in field conditions in the northern part of Zagreb. This test involved concurrent measurements using the described active method and the automatic device for 18 months (May 1999 - Dec 2000). These measurements produced 374 pairs of samples for comparison (Table 1). The results did not show statistically significant differences ($P > 0.05$). The linear correlation coefficient was 0.944, $P < 0.001$ (Figure 3). The sampling precision was tested by parallel sampling with two active devices (Table 2). The results did not significantly differ ($P>0.05$). The detection limit was calculated according to the same formula as for the passive samplers using 10 measurements of nitrate in blank (absorption solution):

$$\gamma_{LD} = \bar{\gamma}\,(NO_3^-) + 3\,\sigma_\gamma\,(NO_3^-) = 0.00167\ mg\ L^{-1} + 3 \times 0.00577\ mg\ L^{-1} = 0.019\ mg\ L^{-1}$$

In 24-hour sampling using the absorption solution volume of 15 mL and the airflow 0.2 L min^{-1}, this nitrate concentration corresponds to the air ozone concentration of 0.5 $\mu g\ m^{-3}$.

Table 1. Comparison of 24-hour averages of ozone mass concentrations ($\mu g\ m^{-3}$) obtained by automatic device and by active sampling method in the northern part of Zagreb between 10 Jun 1999 and 31 December 2000

Statistical parameter	Automatic device	Active sampling method
N	374	374
$\gamma_{min.}$	1.0	4.3
$\gamma_{max.}$	130.0	126.3
$\bar{\gamma}$	32.5	32.4
σ_γ	22.85	21.38
Δ_γ	0.1	
$\sigma_{\bar{\gamma}}$	0.39	
t	0.2937	
P	0.7692	

N - number of samplers
$\gamma_{min.}$ - the smallest value
$\gamma_{max.}$ - the largest value
$\bar{\gamma}$ - the arithmetic mean of values
σ_γ - standard deviation
Δ_γ - arithmetic mean of the difference
$\sigma_{\bar{\gamma}}$ - standard deviation of means
t - Student´s coefficient
P - probability

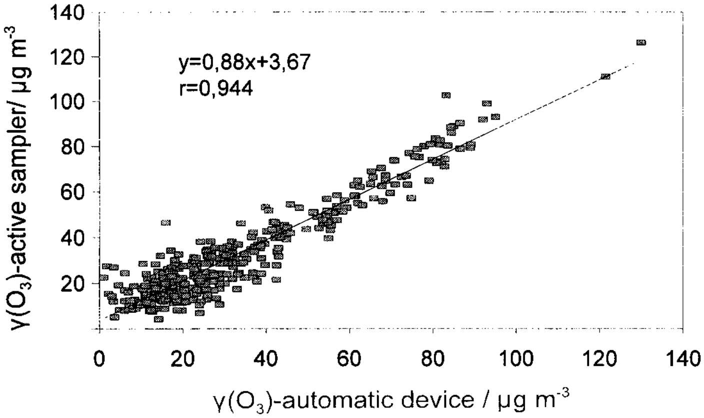

Figure 3. Correlation between ozone mass concentrations (µgm^{-3}) obtained by the automatic UV-device and by active sampler

Table 2. Precision of active sampling in measuring ozone (µg m^{-3}) tested by the use of two parallel active sampling devices (P1 and P2)

	N	γ_{min}	γ_{max}	$\bar{\gamma}$	σ_{γ}	Δ_{γ}	$\sigma_{\bar{\gamma}}$	t	P
P1	40	1.8	32.4	9.7	7.38	0.352	0.470	0.748	0.438
P2	40	2.2	31.6	10.0	7.30				

N - number of samplers
γ_{min}. - the smallest value
γ_{max}. - the largest value
$\bar{\gamma}$ - the arithmetic mean of values
σ_{γ} - standard deviation

Δ_{γ} - arithmetic mean of the difference
$\sigma_{\bar{\gamma}}$ - standard deviation of means
t - Student's coefficient
P - probability

The storage stability of samples was tested using three groups of samples, each consisting of three blank and three non-blank samples. The first group was left on light at room temperature (20-25 °C), the second in the dark at room temperature, and the third in the refrigerator (4 °C). Figure 4 shows the increase in nitrate ions in blanks (absorption solution). Non-blank samples showed similar behavior during storage. After 14 days of exposure to light at room temperature, both blank and non-blank samples became utterly unstable and were not considered valid. In the dark, however, either at room temperature or in the refrigerator, the samples remained stable for up to one month.

The described active method met the demands related to 24-hour averages, and was used to measure ozone concentrations at four sites in Zagreb. Table 3 summarizes the results for the year 2000.

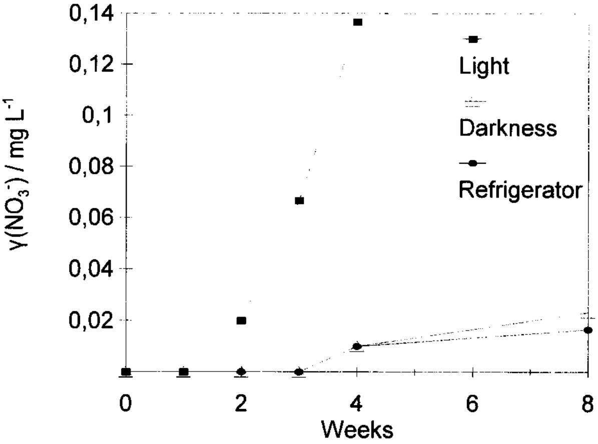

Figure 4. Stability of blanks (absorption solution) in different storage conditions

Table 3. The summary of 24-hour ozone averages (μg m^{-3}) for 1 January 2000 - 31 December 2000 measured at the north, center, west and south

	N	γ_{min}	γ_{max}	$\bar{\gamma}$	γ_{50}	γ_{98}	N>110	N>110 %
North	264	1	126	34	18	87	2	0.8
Center	305	2	194	32	20	94	4	1.3
West	299	0	85	16	6	72	-	-
South	311	0	110	7	3	49	-	-

N - number of samplers
γ_{min}. - the smallest value
γ_{max}. - the largest value
$\bar{\gamma}$ - the arithmetic mean of values
γ_{50} - median
γ_{98} - 98th percentile
N>110 - number of days with 24-hour averages of ozone concentrations higher than 110 μg m^{-3}

Quite expectedly, ozone concentrations were higher in the summer months. In the southern and the western parts of the town seasonal variations were less expressed. Figure 5 shows the average month ozone concentrations at all 4 sites in Zagreb. In 2000, the recommended value of 110 μg m^{-3} was not exceeded in the west and south site. Excess was recorded on two occasions (21 Jun 2000 - 126 μg m^{-3} and 22

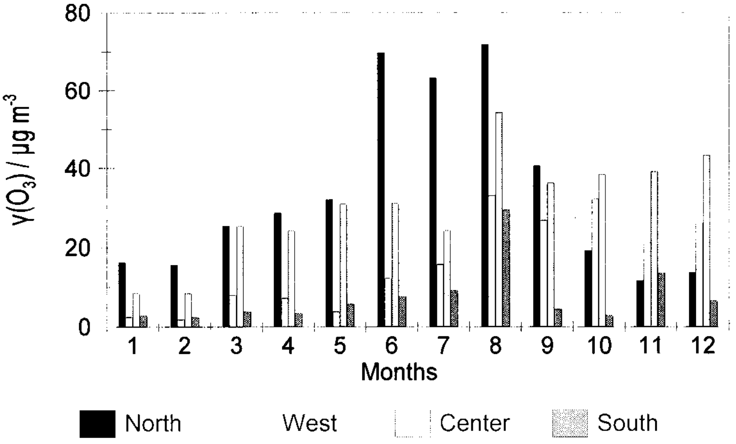

Figure 5. Average ozone monthly cuncentrations (μg m^{-3}) during 2000 at four sites in Zagreb

Jun 2000 - 111 μg m^{-3}) in the northern part of the city. The highest concentrations were recorded in the center in August 2000, when the limit value of 150 μg m^{-3} was also exceeded on two occasions (24 August - 194 μg m^{-3} and 28 August - 175 μg m^{-3}). Regardless of these isolated examples, the air in all four sites was clean in the year 2000 with respect to ozone, that is, it was of the 1st category according to the recommended values for the 98th percentile.

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