Surface ozone measurements in mountain forested areas using diffusive samplers

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Abstract

The surface ozone levels were measured in the forested mountain areas of the Czech Republic in vegetation periods of 2004 and 2005 using the diffusive samplers. Commercially available Ogawa samplers, using filters coated with a nitrite-based solution, were applied. The ambient ozone oxidises the nitrite to nitrate, which after the exposure, is analysed by ion chromatography. The object of this study was to characterize a spatial and temporal distribution of ozone aiming to indicate within the mountain forested regions the risk areas as to the potential surface ozone impacts. Three research areas were established in forested regions adjacent to the country border. All of these areas are very important with regard to territorial landscape protection and tourism. They are forested, unpolluted with few minor emission sources located on their territory, mostly influenced by the long-range transport of pollutants (either of surface ozone or its precursors). The study has not yet been completed, and some preliminary results are presented here. The precision of replicate samples in both years was very good. The 2-week average concentrations for the Orlicke hory Mts. in 2004 were relatively high with the maximum of 70 ppb between July and August. The difference in the ambient ozone concentrations, calculated using the theoretical or empirical uptake rate, ranges between 2.3–3.9. This results in substantial underestimation of ambient ozone level if using the theoretical uptake rate, *ca* by a factor of 2–4. The diffusive samplers proved to be a very good tool for environmental studies in rural areas with complex terrain.
Keywords: surface ozone, passive samplers, Ogawa, Czech Republic, 2004–2005.


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1 Introduction

Ozone plays a vital role in global atmospheric chemistry. The surface ozone is a secondary pollutant formed from the precursors NO_x and VOCs, both emitted from natural and antropogenic sources, during the photochemical reactions as described by e.g. Seinfeld and Pandis [1] and Warneck [2]. The surface ozone levels show significant temporal and spatial variability as a result of a number of factors such as geographical position, altitude, site location, period of the year and synoptic situation [3]. The meteorological situation is very important for the ozone concentration levels. The hot sunny stabile weather is conducive for surface ozone formation. The high temperature, high intensity of solar irradiance, low wind speed, low relative humidity and the absence of precipitation are the factors recognized widely as ideal meteorological conditions for photochemical formation of ozone.

The surface ozone is a pollutant of major concern due to its impacts on receptors at current ambient levels in many regions of the world [4]. It is a phytotoxic pollutant and its effects on vegetation at different levels – biochemical, cell and physiological are known [5].

Related to the studies aimed at revealing the surface ozone impacts on forests, increasingly more attention is paid to the assessment of temporal and spatial variability of ozone levels in mountain regions. The relatively low-cost method of diffusive (or passive) samplers can be used. The interest in use of diffusive samplers for quantifying ambient, gaseous air pollutant concentrations, particularly in remote and wilderness areas, is growing among the scientists studying the links of air pollution and vegetation [6].

A diffusive sampler has been defined by the European Committee for Standardization as "a device capable of taking samples of gases or vapours from the atmosphere at a rate controlled by a physical process such as gaseous diffusion through a static air layer or a porous material and/or permeation through a membrane, but which does not involve active movement of air through the device." The driving force is the difference between the pollutant ambient air concentration and the concentration at the sorbent, which should be negligible, compared to the ambient level. Diffusive sampling is based on the principles of the Fick's first law of diffusion.

Diffusive sampling dates back at least to the 1930s, when qualitative devices were described for use in occupational environment. The first serious attempt to apply science to quantitative diffusive sampling was in 1973, when Palmes and Gunnison described a tube-form diffusive sampler for SO_2. The use of diffusive samplers for monitoring in non-industrial environment, however, is relatively recent [7]. Currently many devices are commercially available for measuring different ambient gases.

The diffusive samplers in environmental studies are used for different purposes such as for the increase in the spatial resolution of measurements, in screening studies to evaluate the monitoring site, as indicative measurements, etc. In the context we are discussing, the diffusive samplers were used e.g. for ozone measurements in the U.S. National Parks where they have been shown to

be useful in extending the continuous monitoring networks and for exploratory studies [8]. The development of low cost robust diffusive monitors has enabled affordable landscape studies of air pollution patterns in remote areas. The study in the U.S. Sierra Nevada was among the first combining the new diffusive samplers with existing continuous monitors, and foliar surveys to study relationship between ozone and tree health status [9]. In Europe the diffusive samplers were used extensively e.g. in the international cooperative project on distribution of ozone in the Carpathian Mountains in 1997–1999 [10].

The European Union strongly supports the use of diffusive samplers for ambient air quality measurements. In Council Directive 96/62 EC [11] on Air Quality and Management, a framework is set for preliminary assessment of air quality, station setting, supporting generalisation measurements and evaluation of existing measurements.

The diffusive samplers are simple, inexpensive and their usage does not require the electricity power source. These advantageous properties make them a useful and continuously more popular method for ambient air quality measurement. The major disadvantages of the method are: 1. the fact that we do not obtain the real-time data but time-integrated values for the period between several days – several weeks, and 2. the sensitivity to meteorological conditions. The careful design and resulting reduction of the influence of meteorology on the sample, however, can reduce the uncertainty substantially [12].

The object of this study was to characterize a spatial and temporal distribution of ozone using the diffusive samplers aiming to indicate within the mountain forested regions the risk areas in the Czech Republic as to the potential surface ozone impacts.

2 Methods

2.1 Air pollution monitoring

The surface ozone concentrations were monitored during 2-week long periods in vegetation seasons of 2004 and 2005. Ozone was measured with commercial Ogawa diffusive samplers (Ogawa and Company, USA, Inc.). These samplers use filters coated with a nitrite-based solution. Two parallel filters are mounted on both ends of one badge. The ambient ozone oxidises the nitrite to nitrate, which after the exposure is analysed by ion chromatography to determine the nitrate ion concentration used to calculate the total amount of ozone used in the chemical reaction. The filters are impregnated by nitrite solution by the manufacturer. Nitrate resulting from oxidation of nitrite by ambient ozone was determined with ion chromatography (Dionex Model 4000i instrument) in the laboratory of the Czech Hydrometeorological Institute according to the standard operation procedure published by manufacturer [13].

We used a total of 15 samplers (5 in each studied region) in 2004, in addition 1–2 samplers within each batch were used as the field blanks. In 2005, 3 more samplers were used additionally collocated with the automated stations. We used 2 replicate filters for each sampler (with a few exceptions). Well-trained students

and technical staff changed the samplers in the field. During the transfer between the laboratory and the field, all samples were kept in zip-lock bags and placed in sealed bottles. Most samples were posted, some were delivered by students using public transport.

Ozone concentrations were calculated based on calibration against collocated active ozone monitors at Serlich site (for Area 1) and Hojna Voda (Area 2). These active ozone monitors are part of a nation-wide network (Fig. 1) monitoring continually over the Czech Republic since 1993. The measurements are based on ultraviolet absorption photometry, recognized as a reference method by EC legislation [14].

2.2 Research areas

Three research areas were established in forested regions adjacent to the country border (Fig. 1). Area 1 – the Landscape Protected Area of Orlicke hory Mts. in the Northern part of the country at the Polish border, Area 2 – the Natural Park of Novohradske hory Mts. in the Southern part of the country at the Austrian border, and Area 3 – the National Park of Ceske Svycarsko in the North-western part of the country at the German border, in the "Black Triangle" region (highly industrialized and formerly highly polluted border zone area between southern Saxony in Germany, Silesia in SW Poland and northern Czech Republic). All three regions are important regarding the territorial landscape protection and tourism. They are forested, with few minor emission sources. They are mostly influenced by the long-range transport of pollutants (either of surface ozone or its precursors).

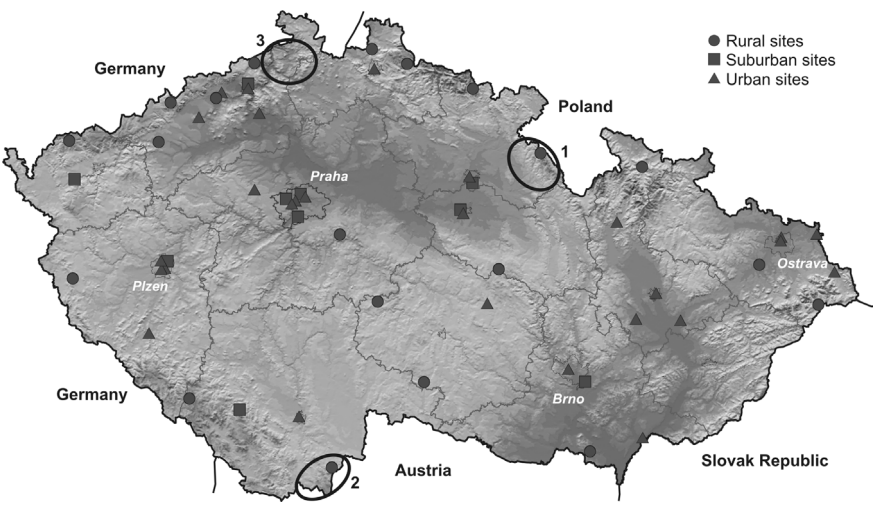

Figure 1: The surface ozone-monitoring network with location of areas using diffusive samplers, the Czech Republic, 2005.

The diffusive samplers were placed in forest clearings at 1.5 – 2 m above the ground at all sampling sites. The clearings differed in character substantially in the regions studied. While in the Orlicke hory Mts. we measured in reforested area with very low young spruce trees, in Ceske Svycarsko the clearings in old spruce stands available for sampling were *ca* 20 x 30 m and in the Novohradske hory Mts. the clearings were even smaller. In the field, the samplers were shielded with a special white opaque PVC cup provided by the manufacturer to protect the samplers from the disturbing meteorological factors.

3 Results

As the results for the entire study have not been completed yet, we hereby present some preliminary results: the precision for replicate filters for both years and the ambient ozone concentrations for the Orlicke hory Mts. area.

We used replicate samples as much as possible. During some periods, however, only a single filter per sampler was used at some sites. The precision of replicate samples is presented at Fig. 2 (year 2004) and at Fig. 3 (year 2005). The precision is expressed for amount of nitrates formed per filter by a reaction of nitrite coating with ozone. It is obvious that precision in both years observed is very good. In 2005, however, a few potential outliers appear in the plot. These were most probably caused by extreme meteorological conditions such as rain and strong wind, resulting in wetting the filters below the PVC cover. Water in the filters may block the chemical reaction, leading to nitrate formation. In 2005 some filters were wet after the exposition, which had not been observed in 2004 when the weather in the vegetation season was standard.

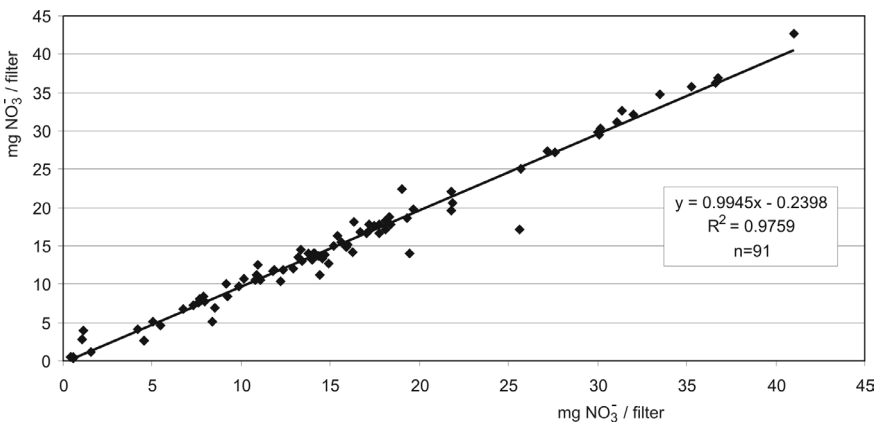

Figure 2: The precision of replicate samples for all sites, 2004.

Fig. 4 presents the results from Orlicke hory Mts. for 2004. Earlier deforested mountain ridge, currently reforested with young low spruce trees represented by two sites (ZAKL – 1026 m a.s.l. and HOMO – 975 m a.s.l.) recorded the highest ozone concentrations. The site SERL – 1011 m a.s.l., where the continuous

method is routinely run, measured significantly lower ozone levels and the LOUS – 875 m a.s.l., site in the valley observed the lowest concentrations throughout the season. The highest 2-week mean concentration equal to 70 ppb was recorded at the HOMO site between July and August. The results are relatively high considering that these are 2-week averages.

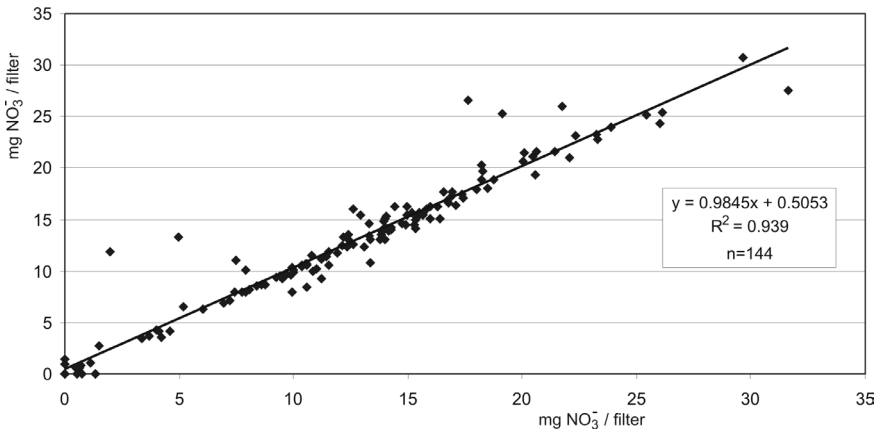

Figure 3: The precision of replicate samples for all sites, 2005.

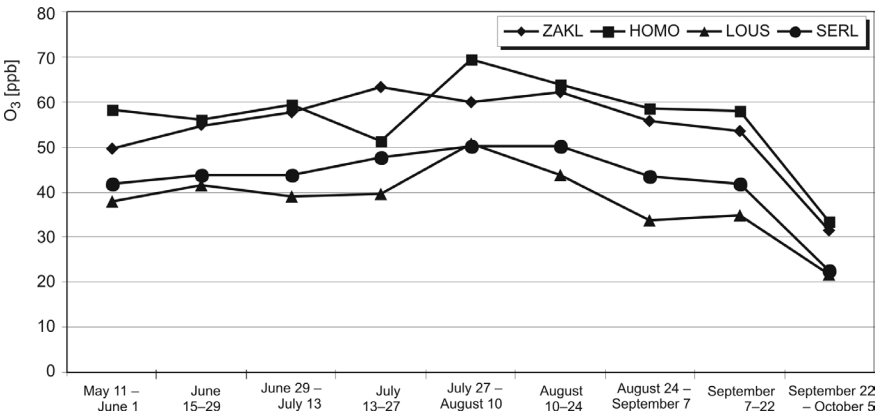

Figure 4: Surface ozone concentrations measured with diffusive samplers expressed as 2-week means, Orlicke hory Mts., 2004.

The concentrations presented at Fig. 4 are calculated using the empirical uptake rate. Fig. 5 presents the difference between the concentrations calculated with the empirical uptake rate obtained from collocated measurement of diffusive samplers and continuous method at the Serlich site (SERL) and the theoretical uptake rate as suggested by the manufacturer [12]. The ratio between the results ranges between 2.3–3.9, which means that if we use the theoretical

uptake rate we underestimate the ambient concentration in the Orlicke hory Mts. in 2004 *ca* by the factor of 2–4.

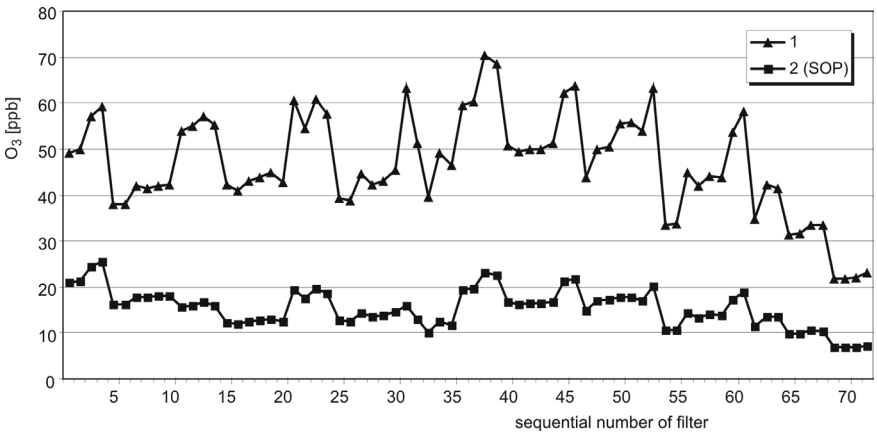

Figure 5: Surface ozone concentrations calculated with the empirical uptake rate (1) and the theoretical uptake rate (2), Orlicke hory Mts., 2004.

4 Discussion

The successful practical application of diffusive sampling to ambient air requires an understanding of the principles of diffusive sampling. We also have to account for the environmental factors (e.g. wind speed and wind direction, temperature, etc.), which may obviously affect the sampler performance. These factors are frequently much more variable and severe than in indoor applications [7].

The chemical method used by Ogawa samplers to measure ozone is elegant, straightforward and relatively easy to apply. According to the results of Koutrakis et al. [15], who validated the Ogawa sampler, the relative humidity (ranging from 10 to 80 %) and temperature (ranging from 0 to 40 °C) at typical ambient ozone levels (40–100 ppb) do not influence the sampler performance.

The pitfall, however, seems to be the calculation of the surface ozone concentration from the mass of nitrates formed on the filter. The manufacturer presents a calculation with a theoretical uptake rate of 21.8 $ml.min^{-1}$ [13]. We found the surface ozone concentrations calculated using the above uptake rate unrealistic and strongly underestimated.

Diffusive samplers are used widely and many papers on their use and results obtained exist in peer-reviewed literature. Many authors regretfully do not specify the method used for calculating the ambient pollutant concentrations from the diffusive samplers. Some authors emphasize the necessity of using the theoretical uptake rate, others use the empirical uptake rate obtained from calibration with collocated automated sampler.

We calculate the ozone concentrations based on a calibration with continuous monitoring method as is often used in works of US authors, e.g. [16]. Frequently,

authors state that diffusive samplers could function with high accuracy and precision under a variety of ambient conditions as e.g. Brace and Peterson [17]. Our results prove that the precision based on comparison of nitrate mass formed from nitrite coating by oxidation of ambient ozone on parallel filters is very good. We believe, however, that this method does not allow for presenting the accuracy independently, as the ozone concentrations from diffusive samplers are calculated using the ozone concentrations from continuous monitoring.

Using the empirical uptake rate seems to be more relevant. The constant is not appropriate for describing highly variable environmental conditions, since temperature, relative humidity, atmospheric pressure, and other factors can affect the collection rate of samples. This, however, makes the process of obtaining the results much slower than using the theoretical constant uptake rate. The constant expressing the theoretical uptake (dependent on the sampler geometry and diffusion coefficient of the measured pollutant) is known for the diffusive sampler. Thus the concentration of pollutant can be calculated immediately after the chemical analysis of the sample. In contrast, if we use the empirical uptake rate calculated from the collocated measurement of diffusive sampler and continuous method, we can calculate the ozone concentrations as late as the process of the continuous ozone data validation and verification in the nation-wide database is finished. This results in some 5 months delay.

The precision of the measurements calculated from replicate samples was very good for both vegetation seasons. In 2005, however, we encountered some problems with the wetting of sampling filters. The reason was the extreme meteorological conditions of the 2005 vegetation period with the high variability of daily temperatures and frequent heavy rains. The rainy summer with high wind speeds resulted in some filters becoming wet during the exposure, which was never observed in 2004.

The final report and evaluation of the entire measuring campaign applying the diffusive samplers in vegetation seasons of 2 years is not yet ready. The preliminary results, however, are very promising. The diffusive samplers provide an appropriate extension of current Czech monitoring network. This monitoring network provides an excellent data for the Czech nation-wide surface ozone load map [18]. The results of diffusive samplers, however, enable us to prepare the maps with much higher resolution, suitable e.g. for indicating the risk areas within one mountain region.

5 Conclusions

The results of our study indicate that diffusive samplers are very useful for measurements in forested areas. Their advantages far exceed their drawbacks. The measurements obtained by diffusive samplers may be used for extending the current monitoring networks. This is of special interest in a complex forested mountainous terrain. Thus diffusive samplers, if used correctly, can contribute significantly to our knowledge of spatial patterns of surface ozone levels.

Acknowledgements

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