



OZONE CONCENTRATION VARIATIONS NEAR HIGH-VOLTAGE TRANSMISSION LINES

Vaida Valuntaitė¹, Vaida Šerevičienė², Raselė Girgždienė³

*Dept of Physics, Vilnius Gediminas Technical University,
Saulėtekio al. 11, LT-10223 Vilnius, Lithuania*

E-mail: ¹Vaida.Valuntaite@fm.vgtu.lt; ²vaida.sereviciene@ap.vgtu.lt;

³Rasele.Girgzdiene@fm.vgtu.lt

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Abstract. Changes and distribution of ozone concentration in the area of high-voltage transmission lines were investigated. The investigation on ozone concentration changes was performed with application of two methods: by using an ozone analyser and by passive samplers. The role of an accumulating element was performed by a glass-fiber filter installed in a passive sampler. It was impregnated with a 1.2-di(4-pyridyl)ethylene and acetate acid solution. The impact of meteorological parameters on the passive sampler efficiency and ozone concentration variation is discussed. These parameters can increase or decrease the real concentration value in comparison with the concentration obtained by co-located continuously running ozone analyser. Ozone concentration near high-voltage lines varied from 10 to 51 ppb, and “background” ozone concentration changed from 3 to 50 ppb during the investigation period. The average concentrations were 28.1 and 27.5 ppb near the lines and “background” during the whole experiment period. The wind direction from “background” location to the high-voltage lines prevailed during the experiment. The obtained results by different methods demonstrated good agreement; the difference between ozone concentrations was from 1 to 24% for individual cases.

Keywords: high-voltage lines, ozone concentration, passive sampler, meteorological parameters, wind speed and direction, temperature, relative humidity.

1. Introduction

Ozone is classified as a principal atmospheric pollutant and is an object of the global system of environmental monitoring (WMO 1994).

Ozone has a dominant role in the photochemistry of the troposphere. The ground-level ozone has two major sources, namely, transport from the stratosphere and photochemical formation in the troposphere as a result of reactions between nitrogen oxides, hydrocarbons, and some other organic substances (Zhang and Liou 1994). However, there are some other sources that can have significant input in the local ozone concentration level. They could be natural as lightning, or manmade as some technological process with corona effect.

Ozone is relatively stable molecule; only at high ozone concentrations and/or elevated temperatures it decomposes to oxygen at a significant rate (Weschler 2000).

In Lithuania hourly ozone concentration in ambient air varies in a wide range from 5 to 220 $\mu\text{g}/\text{m}^3$. Long-term investigation shows that only for about 9% of time it exceeded 100 $\mu\text{g}/\text{m}^3$ (Girgždienė 1991). The surface ozone has a seasonal course with the maximum concentration in summer. The amplitude of diurnal ozone variation is very changeable, and the maximum concentrations are observed mostly in the afternoon (Bakas *et al.* 1995). Measures to reduce ozone concentrations are complicated

by the fact that ozone is a secondary pollutant, not directly emitted but formed within the atmosphere by photochemical reactions involving, primary, oxygen, nitrogen monoxide, nitrogen dioxide, volatile organic compounds and sunlight (Derwent *et al.* 2003).

Meteorology plays an important role in air pollutant formation, dispersion, transport and dilution (Bimbaitė and Girgždienė 2007). Therefore, variations in local meteorological conditions, such as wind direction, wind speed, temperature and relative humidity, can affect temporal variations in O_3 and its precursors (Dueñas *et al.* 2002, Elminir 2005, Satsagi *et al.* 2004).

It is shown (Еланский и Невраев 1999) that high-voltage lines (HVLs) can be a significant source of ozone. Ozone forms as a result of interaction between molecular and atomic oxygen. Atomic oxygen forms at corona discharges. HVLs can also generate active radicals, such as OH, and thus can promote oxidation of volatile organic compounds (VOCs) and change the air composition in their vicinity.

In 1996 and 1998, during the Russian-German experiments TROICA-2 and TROICA-4 (Trans-Siberian Observations of the Chemistry of the Atmosphere) it was found that, in the vicinity of powerful 220- and 500-kV HVLs, the ozone concentration was enhanced relative to the surroundings by about 2 and 3 ppb, respectively. It is about 0.1 % of the total ozone amount forming through-

out the troposphere as a result of photochemical processes. It is evident that a significant effect of HVLs on the global ozone balance is impracticable. However, the calculation made in (Elansky *et al.* 2001) shows that HVLs are able to change significantly the ozone concentration within the atmospheric surface layer over Europe and other regions where the HVL density is rather high.

Ozone at the ground level is an air pollutant with significant detrimental effects to human health, as well as to agriculture and many materials (Blades *et al.* 2000), (Brimblecombe 1988).

Standard ozone monitoring techniques utilize large, heavy and expensive instruments that are not easily adapted for personal or microenvironmental monitoring (Koutrakis *et al.* 1993).

Passive samplers allow the quantification of cumulative exposures, as total or average pollutant concentrations over the sampling time. Some of the advantages of passive samplers are that they do not need power supply, are inexpensive and easy to employ (Sanz *et al.* 2004). The air streams freely around a filter, membrane or other sorbent, which captures pollutants during the period of passive air sampling. It is possible to use polyurethane foam (PUF) for persistent organic pollutant (POPs) sampling (Kohoutek *et al.* 2006).

Development of passive samplers for ozone has progressed over the past two decades. Currently, passive samplers are being used to determine the air quality in a workplace or indoor living environment and an ambient or outdoor environment, including regional-scale air quality (Plaisance *et al.* 2007). The low cost and flexibility of placement for passive sampling systems also make them attractive alternatives for assessing exposures at locations that are difficult to access, such as within the forest canopy. Passive samplers may also be used to identify areas receiving air pollution events, that were previously unknown, and where additional infrastructure for instrumental monitoring may be required (Cox 2003).

Various trapping reagents are used for absorbing ozone like, 1,2-di(4-pyridyl)-ethylene, potassium iodide, nitrite, indigo/indigo carmine compounds, 3-methyl-2-benzothiazolinone acetone azine with 2-phenylphenol and p-acetamidophenol. Only 1,2-di(4-pyridyl)-ethylene and nitrite seems to lead to specific reactions with O_3 , other reagents can cause an interference with other atmospheric oxidants, like NO_x and PAN (Krupa and Legge 2007).

In the work of Cox (2003) it is reported that trapping reagent of sodium nitrite ($NaNO_2$) gives a promising result in being sufficiently sensitive and relatively free of interference problems and provides specific collection for ozone measurement. The sampling technique is based on the oxidation of nitrite (NO_2^-) by ozone to produce nitrate (NO_3^-). The amount of nitrate is determined by ion chromatography (Helaleh *et al.* 2002).

The radial diffusive sampler consists of a micro porous polyethylene cylinder. Two cellulose acetate caps are soldered with an epoxy adhesive to the cylinder ends. An absorbing cartridge is inserted into the cylin-

der. This cartridge is filled with silica gel coated with 1,2-di(4-pyridyl)ethylene (DPE). Ambient ozone diffuses through the porous membrane up to the cartridge where it is trapped by a reaction with DPE. The diffusion of O_3 molecules is controlled by the coefficient of molecular diffusion of ozone in air, the geometry of the sampler, the effective area of the pores in the membrane and the gradient between O_3 concentration in ambient air and at the cartridge area where DPE keeps the ozone concentration close to zero. DPE is light sensitive, so the cartridge is stored in a closed tube in the dark.

During exposure, the opaque diffusive body of Radiello sampler (of a blue colour) protects the cartridge from the light. Due to absorption reaction ozone reacts on DPE and forms an ozonide as intermediate, which upon hydrolysis yields pyridine-4-aldehyde (PA). For analysis, addition of MBTH (3-methyl-2-benzothiazolinone hydrazone) reacting with PA produces a molecule called azine that is measured by a colorimeter. The concentration of pollutant in air is calculated by using an equation derived from the first Fick's law. The absorbance of the extraction solution is measured at 430 nm. The mass of PA in the cartridge is obtained by reference to a linear calibration derived from the spectrophotometric analysis of standard solutions of PA (Plaisance *et al.* 2007).

Passive samplers are generally protected from rain, sun and mechanical damage during field deployment by a shelter of a various design (Cox 2003).

A key parameter related to correct measurement of ozone in air using the passive sampler is its sampling rate. The sampling rate is affected by many factors such as temperature, relative humidity, wind direction, wind speed, sampler structure, collection media, etc. Sampling rates increase with the increase of temperature, wind speed and relative humidity (RH) (Tang and Lau 2000). In the work of Tang and Lau (2000) it is reported that at a temperature of $-18^\circ C$, 19% of relative humidity and 130 cm/sec of face velocity, the measured sampling rate (R_s) was 81 ml/min, but at $31^\circ C$ and 19% of RH, the measured R_s was 100 ml/min. The overall R_s increase from $-18^\circ C$ to $21^\circ C$ was 19 ml/min, which is about a 23% increase. This change is very significant.

The aim of the work was to investigate the peculiarities of the changes in ozone concentration near high-voltage transmission lines with application of different methods (passive samplers and an ozone analyser) as well as to assess the impact of environmental parameters on the change of this pollutant near a manmade ozone source.

2. Investigation methodology

The investigation of ozone concentrations was carried out near Juškėnai village, where two high-voltage transmission lines of 330 kV arranged parallel to each other were the source of ozone emission (Fig. 1). Juškėnai ($55^\circ 33' N$ and $25^\circ 39' E$) is situated near Utena in the eastern part of Lithuania.



Fig. 1. High-voltage transmission lines and sensors of meteorological parameters

Ozone concentrations were measured continuously by commercial ozone analysers at two locations at a distance of 222 m. Ozone concentration near high-voltage lines was measured by RS 1003 and “background” ozone concentration was investigated by ML 9811. The obtained data at a distance of 222 m from high-voltage lines were attributed to “background” ozone concentration, i.e., already without the influence of production from the local source. Operation of analysers is based on the principle of ultraviolet absorption. Concentration of ozone was measured continuously, and the data were presented as a 5-minute average. The data were recorded automatically in a computer. The precision of measurements was $2 \mu\text{g}/\text{m}^3$. Both UV-photometric analysers were calibrated before the experiment against transfer standard – ozone analyser O₃41M, which was calibrated against the standard reference UV photometer SRP17 at Czech Hydrometeorological Institute. After calibration they worked simultaneously for some days by sucking the investigated air from the same tube. The obtained results were compared; the correlation coefficient between the data was 0.997.

Passive samplers were also used for determining ozone concentration. Some amount of persistent organic pollutants are always in the air. The relationship between the amount of POPs captured on PUF filter and their concentrations in sampled air has not been mathematically fully described yet. Due to this reason, only empirical estimated information (for example, based on parallel active and passive measurements) is available for result interpretation (Kohoutek *et al.* 2006). In cooperation with the Lithuanian Forest Research Institute, passive samplers were also used for the measurements based on the methodology, developed by Polish scientists (Serafinavičiūtė 2007). The passive samplers consist of a housing, accumulating element inside it, a supporting ring, membrane, a holder and a cover. A dark polyethylene housing protects the accumulating element from sunrays, while a polypropylene membrane, which covers it, protects it from wind, rain and dust.

The most important requirement regarding the performance of a diffusive sampler, the expanded uncertainty that should be lower than 30%, is in agreement with the requirements of the O₃ European Directive (EN 13528-1: 2002).

The passive samplers (Fig. 2) were displayed in four locations (A, B, C and D) which were at a different distance from the high-voltage lines (Fig. 3): location A was under the high voltage lines at 1.5 m height; B was at 25 m distance to the east with respect to A at 1.5 m height; C was located at 56 m distance to the west with respect to A at 2 m height; D was at 222 m distance to the southeast with respect to A at 2 m height.



Fig. 2. The used passive sampler

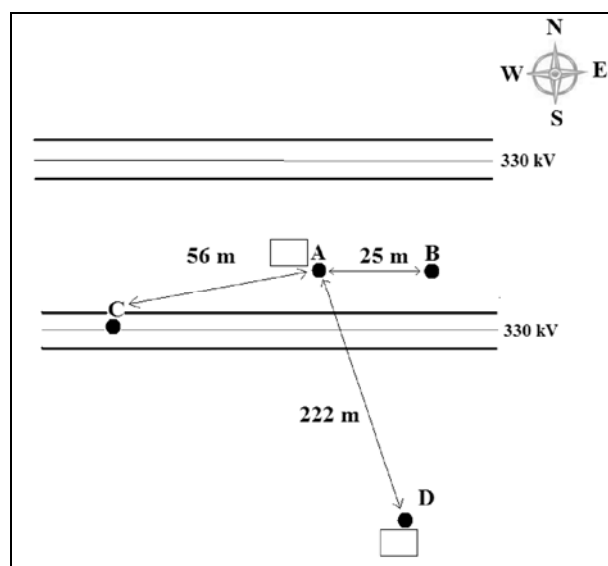


Fig. 3. Scheme of ozone concentration measuring locations: black circles – locations of passive sampler display; squares – ozone analysers; lines – high-voltage lines

The passive samplers were opened before the display. Since organic molecules are sensitive to UV radiation, the collector with the sorbent for determining ozone was protected from direct sunlight. The role of an accumulating element was performed by a glass-fibre filter, which was impregnated with a 1,2-di(4-pyridyl)ethylene and acetate acid solution. Pyridin-4-aldehyd (PA) is the product of a reaction with ozone. After a set display time

the samplers were closed with the cover and sent to the laboratory for chemical analysis.

The meteorological parameters (temperature, relative humidity, wind speed, wind direction) were measured during the experiment by using PC Radio Weather Station. The temperature, relative humidity, wind speed and wind direction sensors were located near high-voltage transmission lines (Fig. 1).

Measurement of the “background” ozone concentration was carried out at 222 m distance south-east from high-voltage lines. Air sample was sucked through Teflon tube. Analogue signal was converted into digital by the converter ADC-16; and this helped to directly with the programs PicoLog and Microsoft Excel.

3. Experimental results

The measurements were carried out continuously on 22–27 September 2007. The courses of the near high-voltage lines and far from the lines, i.e. “background” ozone concentration, are presented in Fig. 4.

The diurnal courses of ozone at both places were very close. The intervals of their amplitude were also close. Ozone concentration near high-voltage lines varied from 10 to 51 ppb, and “background” ozone concentration was in the interval of 3–50 ppb. The largest differences of the concentrations was found during night hours. The average concentrations were 28.1 and 27.5 ppb near the lines and “background” during whole experiment period, respectively.

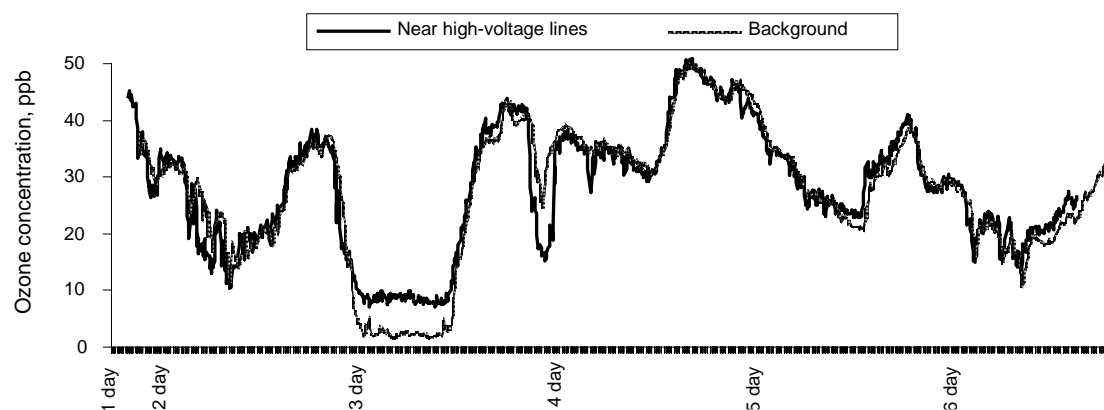


Fig. 4. Variations of “background” and ozone concentration near high-voltage lines, September 22–27, 2007

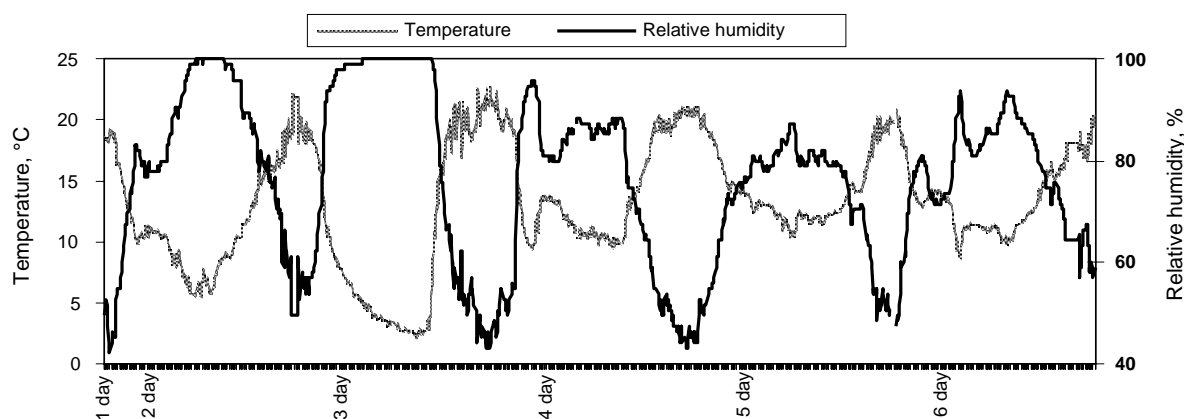


Fig. 5. Variations of temperature and relative humidity, September 22–27, 2007

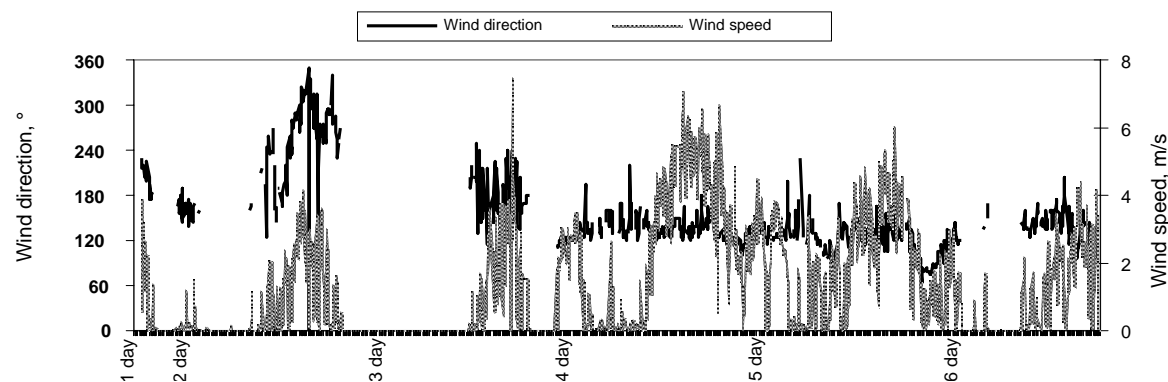


Fig. 6. Variations of wind speed and direction, September 22–27, 2007

The analysis of meteorological parameters (temperature, relative humidity, wind speed, wind direction) was performed for the assessment of ozone dispersion peculiarities near high-voltage lines. The changes of meteorological parameters near high-voltage lines are presented in Figs. 5, 6.

During the experiment the temperature changed from 2 to 22 °C, the relative humidity changed from 40% to 100%. The maximum relative humidity was determined before the sunrise when the lowest air temperature was recorded.

The wind speed and direction were changeable during the period of experiment: calm conditions were observed since 5 PM of 23 Sept. to 10 AM of 24 Sept., while at 3:35 PM on 24 Sept. wind speed reached 7.4 m/s. The south-eastern and southern wind direction prevailed even 50% of the time during the experiment. Any north-eastern wind was determined during the experiment, and northern and north-western wind prevailed only 2% of the time.

Fig. 7 presents frequency distribution of the wind speed, i.e. how many times during the experiment the wind speed reoccurred in a certain interval of values. On 22–27 September a low wind speed prevailed, while events with higher than 5 m/s made only 3%. Calm conditions were registered at night, and it made 38% of the time.

The data, presented in Figs. 4, 5 and 6, demonstrate that the lowest ozone concentration at both measuring points were determined at night when there was no wind, i.e. it was calm. During this period the relative humidity reached 100%, while the temperature was low (about 4 °C). During the day, when the wind speed increased to 7 m/s (1 PM of day 4), ozone concentration reached 48 ± 2 ppb, air temperature reached 20 °C, however, a low relative humidity of 53% was observed and south-eastern wind prevailed.

In order to find the meteorological factors influencing ozone concentration and to assess them in the order of importance, a regression analysis was carried out. It was established that temperature, wind speed and relative humidity were the most important meteorological factors influencing variations in ozone level. Analogical results were found in Dueñas *et al.* (2002) work.

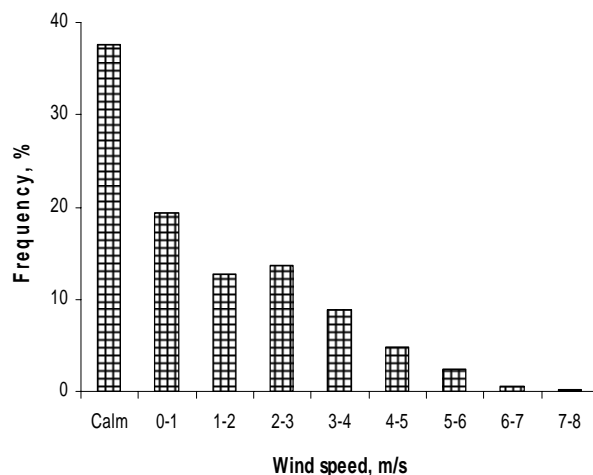


Fig. 7. Frequency distribution of the wind speed during the experiment

In order to investigate a possible error in measuring the average ozone concentration with passive samplers, as already mentioned earlier, the passive sampler results were compared with the results of a co-located continuous O₃ analyser. The description of the passive sampler location conditions is presented in Table 1.

The average ozone concentrations, obtained by different methods, were close (Fig. 8), except sample 10, when the determined ozone concentration was twice above the mean of ozone concentration values, obtained by continuous measuring with an analyser.

This passive sampler was displayed during the whole time, i.e. it was displayed for 122 hours while the reliability of these passive samplers was decreasing with increase in exposition time.

Insignificant difference of ozone concentration values was found between passive sample 5 and the ozone values, obtained by the analyser for the same period. During this period the southern wind was clearly prevailing, and the high-voltage lines did not have any effect on the “background” ozone concentration level. Sample 4 was displayed in the same location as the analyser, however, during this period at night high values of relative humidity were registered; they reached 100%. Relative humidity may have an effect on the sensitivity of a passive sampler

Table 1. Conditions of passive sampler exposition

Sample number	Sampling time interval		Distance and location (in Fig. 2)
	Start	End	
1	22 09 2007 2:00 PM	25 09 2007 12:00 AM	To the east L = 25 m , H = 1.5 m) (B)
2	25 09 2007 12:00 PM	27 09 2007 5:00 PM	
3	27 09 2007 5:00 PM	30 09 2007 2:00 PM	
4	22 09 2007 2:00 PM	25 09 2007 12:00 AM	To the south L = 222, H = 2 m) (D)
5	25 09 2007 12:00 PM	27 09 2007 5:00 PM	
6	27 09 2007 5:00 PM	30 09 2007 2:00 PM	
7	22 09 2007 2:00 PM	25 09 2007 12:00 AM	To the west L = 56 m , H = 2.0 m) (C)
8	25 09 2007 12:00 PM	27 09 2007 5:00 PM	
9	27 09 2007 5:00 PM	30 09 2007 2:00 PM	
10	22 09 2007 2:00 PM	27 09 2007 5:00 PM	Near ozone analyser (H = 1.5 m) (A)

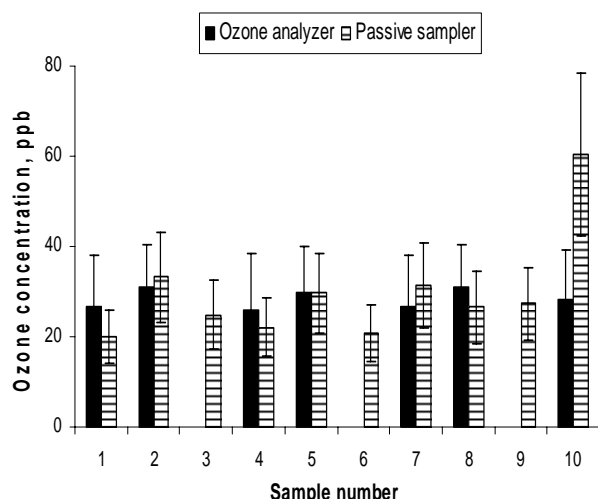


Fig. 8. Comparison of average ozone concentration with application of different methods. Error bars show \pm standard error

(Murad *et al.* 2002; Serafinavičiūtė 2007). This is partially confirmed by sample 1 which also showed lower ozone values than the analyser. However, sample 7 was displayed at the same time, and the ozone concentration measured by it was higher than the average ozone value measured by the analyser. These results indicate that other factors may also have an effect. However, the difference was not significant. These samplers were exposed from 22 day till 25. Passive sampler 7 was hanging on the pole directly under the high-voltage lines, therefore, the ozone concentration there could be higher, because during this period more than half of the time it was calm, and ozone did not transport. Higher ozone values were obtained by passive samplers 2 and 7 in comparison with the analyser data during 25–27 September. This can be related to a few reasons. At that time the wind speed was higher, the calm prevailed only 20% of the time, while during the first study period it prevailed even 52% of the time. Also, the air temperature during these days and nights varied between 10 and 20 °C, whereas during 22–25 September it dropped to 0 °C. Meanwhile, the humidity was on average 81% during 90% of time in the first part of the experiment, and it was only 67% during 90% of time of the second period. Different ozone concentrations could be explained by the fact that the above mentioned meteorological parameters had an effect on different passive sampling rates. However, the differences between the results obtained by both methods did not exceed 24.5% for individual samplers. Our results are close to those of other authors who have analysed the effect of the meteorological conditions state and determined that sampling rates increase with the increase of temperature, wind speed and relative humidity (Plaisance *et al.* 2007; Tang and Lau 2000).

4. Conclusions

1. The experiment results showed that the ozone concentration near high-voltage lines changed from 10 to 51 ppb or the “background” ozone concentration changed

from 3 to 50 ppb. This demonstrates that the average ozone concentration near high-voltage lines was on average by 2% higher than the “background” ozone concentration.

2. The most significant impact on different levels of near high-voltage lines and the “background” ozone concentrations result from temperature, wind speed and relative humidity. It was established that correlation coefficients between ozone concentration and meteorological parameters (temperature, wind speed and relative humidity) were +0.84; +0.65; –0.81, respectively.

3. The data showed a good agreement between ozone concentrations measured by different methods: by a passive sampler and ozone analyser. The differences of average concentrations varied from 1 to 24%. This difference could be explained by the influence of different meteorological conditions.

4. Insufficient results of measured ozone concentration by a passive sampler and analyser were obtained by a long-term exposition of a passive sampler. The difference in average ozone concentration could exceed 100%.

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OZONO KONCENTRACIJOS KITIMAS TIES AUKŠTOSIOS ĮTAMPOS TIEKIMO LINIJOMIS

V. Valuntaitė, V. Šerevičienė, R. Girgždienė

Santrauka

Tirta ozono koncentracijos kitimas ir pasiskirstymas ties aukštosios įtampos perdavimo linijomis. Ozono koncentracija matuota dviem metodais – ozono analizatoriumi ir pasyviaisiais kaupikliais. Pasyviajame kaupiklyje kaip kaupiantysis elementas buvo naudojamas stiklo pluošto filtras, impregnuotas 1,2-di(4-pyridil)etileno ir acetatinės rūgšties tirpalu. Vėjo greitis, vėjo kryptis, UV spinduliuotė, temperatūra ir santykinė oro drėgmė gali turėti įtakos pasyviųjų kaupiklių efektyvumui bei ozono koncentracijos pasiskirstymui, todėl kartu tirti ir meteorologiniai parametrai (temperatūra, santykinė oro drėgmė, vėjo greitis ir kryptis). Tyrimo laikotarpiu ozono koncentracija ties aukštosios įtampos tiekimo linijomis kito nuo 10 iki 51 ppb, o nutolusioje per 222 m vietovėje, kuri buvo traktuojama kaip foninė, – nuo 3 iki 50 ppb. Išmatuota vidutinė ozono koncentracija foninėje vietoje buvo 27,5 ppb, o ties linijomis – 28,1 ppb. Eksperimento metu vyravo pietryčių krypties vėjas, t. y. nuo foninės vietos – aukštosios įtampos tiekimo linijų link. Nustatant ozono koncentraciją skirtingais metodais duomenys pakankamai sutapo, pavieniais atvejais nesutapimas svyravo nuo 1 iki 24 %.

Reikšminiai žodžiai: aukštosios įtampos tiekimo linijos, ozono koncentracija, pasyvisis kaupiklis, meteorologiniai parametrai, vėjo greitis, vėjo kryptis, temperatūra, santykinė drėgmė.

ИЗМЕНЕНИЯ КОНЦЕНТРАЦИИ ОЗОНА ВБЛИЗИ ВЫСОКОВОЛЬТНЫХ ЛИНИЙ ЭЛЕКТРОПЕРЕДАЧ

В. Валунтайте, В. Шерявичене, Р. Гиргжене

Резюме

Исследовалось изменение и распределение концентрации озона в районе высоковольтных линий электропередач. Концентрация озона измерялась двумя методами: анализаторами озона УФ-поглощения непрерывного действия и с использованием пассивных сорбентов. В качестве сорбента использовался фильтр из стекловолна, пропитанный 1,2-ди(4-пиридил)этиленом и уксусной кислотой. Параллельно непрерывно измерялась температура и относительная влажность воздуха, скорость и направление ветра. Исследования показали, что концентрация озона в течение эксперимента изменялась в интервале от 10 до 51 ppb у линии и от 3 до 50 ppb на «фоновой» точке, удаленной от линий электропередач на расстояние 222 м. В течение эксперимента почти половину времени преобладал боковой ветер по отношению к высоковольтным линиям со стороны фоновой точки. Средние измеренные концентрации озона составляли 27,5 ppb на «фоновой» точке и 28,1 ppb – у линий. Результаты измерения концентрации озона как анализаторами непрерывного действия, так и по методике с использованием пассивных сорбентов показали хорошее совпадение: разница составляла 2–15% и лишь в отдельных случаях 24%.

Ключевые слова: высоковольтные линии электропередач, концентрация озона, пассивные сорбенты, метеорологические параметры, скорость и направление ветра, температура и относительная влажность воздуха.

Vaida VALUNTAITĖ. Doctoral student, Dept of Physics, Vilnius Gediminas Technical University (VGTU). Doctoral student (environmental protection) (2005), Master of Science (technosphere ecology) (2004), Bachelor of Science (environmental engineering) (2002), VGTU. Research interests: ecology, environmental protection.

Vaida ŠEREVIČIENĖ. Doctoral student, Dept of Environmental Protection, Vilnius Gediminas Technical University (VGTU). Doctoral student (environmental protection)(2008). Master of Science (technosphere ecology) (2008), Bachelor of Science (bioengineering) (2006), VGTU. Research interests: ecology, environmental protection, environmental chemistry.

Rasėlė GIRGŽDIENĖ. Dr, Dept of Physics, Vilnius Gediminas Technical University (VGTU). Doctor of Science (environmental physics), 1986. Publications: more than 60 scientific publications. Research interests: air quality, pollutants transport and transformation, indoors and outdoors problems, monitoring, ozone problems, environmental assessment.