CHEMICAL ENGINEERING TRANSACTIONS
VOL. 54, 2016

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Selena Sironi, Laura Capelli

ISBN 978-88-95608-45-7; **ISSN** 2283-9216
DOI: 10.3303/CET1654043

Evaluation of Ambient Air Odour Quality in Vicinity of Municipal Landfill Using Electronic Nose Technique

Jacek Gębicki*[a], Tomasz Dymerski[b], Jacek Namieśnik[b]

[a]Department of Chemical and Process Engineering, Chemical Faculty, Gdansk University of Technology, 11/12 G. Narutowicza Str., 80-233 Gdańsk, Poland.
[b]Department of Analytical Chemistry, Chemical Faculty, Gdansk University of Technology, 11/12 G. Narutowicza Str., 80-233 Gdańsk, Poland.
jacek.gebicki@pg.gda.pl

The paper presents the results of investigation on ambient air quality evaluation with respect to concentration of odorants in a vicinity of municipal landfill. The investigation was carried out with a prototype of electronic nose and a team of panelists utilizing the Nasal Ranger field olfactometers. The prototype was equipped with a set of six semiconductor sensors by FIGARO Co. and one PID-type sensor. Performed measurements revealed that the prototype of electronic nose could be employed for determination of odorants concentration in ambient air; difference in mean values of odorants concentration obtained with both techniques was statistically insignificant in 75% of cases. The highest mean values of odorants concentration amounted from 12.5 to 36.7 ou/m^3 depending on distance from the emitter, measurement direction and applied measurement technique.

1. Introduction

Unpleasant odours are naturally associated with danger, they create the feeling of discomfort and can be a cause of negative psychosomatic symptoms. That is why emission of the gases polluted with odorous substances constitutes an important environmental problem (Belgiorno et al. 2012, Capelli et al. 2013). Emission of the odours of anthropogenic origin can be divided into three groups: agricultural, municipal and industrial. Intense development of cities and suburban regions results in the fact that the municipal objects including landfills, sewage treatment plants or composting plants are localized too close to the residential areas. Such situation causes deterioration of life quality in these regions and periodical odour nuisance is the major reason of complaints on ambient air quality (Kampa and Castanas 2008, Gębicki et al. 2014, Sówka et al. 2015). One of the main causes of odour nuisance in the Tri-city Agglomeration (Gdańsk, Sopot, Gdynia) is emission of volatile organic compounds characterized by unpleasant odour from the municipal landfill. Emission of these compounds is connected with:
- biological processes of organic matter decay during waste disposal,
- composting,
- biogas production.

The main groups of chemical compounds emitted to the atmosphere include: mercaptans, sulphides, alkyl polysulphides, amines, aldehydes, ketones, aromatic hydrocarbons, aliphatic hydrocarbons or terpenes. A natural sensor detecting odours and allowing ambient air quality evaluation is sense of smell. Particular odorous substances present in gas mixture can cause odour magnification (synergism) or odour attenuation (masking or neutralization), hence evaluation of odour impact on human calls for holistic analysis. Dynamic olfactometry is the measurement technique most frequently utilized for ambient air evaluation as far as odour intensity, hedonic quality or odorants concentration are concerned (Bokowa 2010, Capelli et al. 2012, Guillot 2012). Its popularity is emphasized by the fact that it is the most often proposed technique in the countries, which undertake actions to solve the problems connected with odour nuisance. The main advantage of the technique is normalized measurement of substance/odorous mixture concentration. However, measurement accuracy and reproducibility require these tests to be performed in accredited laboratories equipped with

Please cite this article as: Gebicki J., Dymerski T., Namiesnik J., 2016, Evaluation of ambient air odour quality in vicinity of municipal landfill using electronic nose technique, Chemical Engineering Transactions, 54, 253-258 DOI: 10.3303/CET1654043

appropriate rooms as well as employing qualified personnel constituting the measurement tool. It is possible that short-term episodes of high concentration of odorants on given area are not recorded with dynamic olfactometry due to delay in arrival and sampling performed by the qualified personnel as well as time necessary for samples transport and measurement execution. In such situations the on-line techniques would be more convenient for recording of the short-lasting episodes of high concentration of odorants. A dedicated solution could be the sensor matrixes called the electronic noses. Due to their principle of operation based on holistic analysis the electronic nose instruments can be used for both detection and identification of odour via assigning it to a particular class of reference odours. The measurements utilizing the electronic nose instruments have already found application in many fields of human activity including municipal landfills, sewage treatment plants, waste incineration plants, composting plants (Capelli et al. 2008, Bootsma et al. 2014, Gebicki et al. 2016) .
Information on qualitative differences (possibly also quantitative differences) in composition of odorous mixture is provided thanks to application of suitable sensors comprising the electronic nose and suitable data analysis method (Munoz et al. 2010, Boeker 2014, Gebicki et al. 2015). Nowadays, there are three dominant approaches to electronic nose design:

- the first type, where the measurement system is comprised of the chemical sensors of one type only,
- the second type, where the measurement system consists of the chemical sensors of different types,
- the third type, where the measurement system employs chromatographic detectors and appropriately selected chromatographic columns differing in polarity of a stationary phase.

In most convenient arrangement the electronic nose should be composed of the sensors possessing non-identical measurement characteristics since differences in sensitivity and selectivity of particular sensors enhance versatility of information contained in measurement data.
The authors of this paper want to present the results of investigation on ambient air quality with respect to odorants concentration performed with the electronic nose prototype of the second type. The electronic nose was built from commercial semiconductor sensors by FIGARO Co. and photoionization sensor of PID-type. Additional aim of the investigation was verification of usability of the electronic nose prototype as an alternative tool for the field olfactometers of Nasal Ranger type. The object under investigation was ambient air collected in a vicinity of the municipal landfill.

2. Experimental

2.1 Measurement set-up

In case of the investigations conducted using the prototype of electronic nose the measurement set-up consisted of a Tedlar bag, a Tecfluid flow meter, the prototype of electronic nose, a suction pump and a PC class computer. Volumetric flow rate of the air sucked from the Tedlar bag was 1 dm^3/min. The prototype consisted of a set of six commercial semiconductor sensors (Metal Oxide Semiconductor) by FIGARO Co. (TGS 823, TGS 826, TGS 832, TGS 2600, TGS 2602, TGS 2603) and one photoionization sensor of PID-type (PPB MiniPID). All internal elements of the prototype were thermostated in order to provide stable measurement conditions. Dedicated miniaturized electronic circuit processed the output signal from the sensor set of the prototype. Its task was to convert changes of sensor resistance into voltage signal measurable by analogue-to-digital converter (ADC). This step yielded a voltage signal, the changes of which within full measurement range of the converter corresponded to complete range of changes of the sensor resistance. The voltage obtained was converted into digital form in the range from 0 to 16 bits. The measurement data were collected, archived and pre-processed using a dedicated, self-created, basic software. The values of particular sensor signal taken for data analysis originated from the range, where the sensor signal attained steady value (steady state). Four persons took part in the investigations carried out with the field olfactometers Nasal Ranger (St. Croix Sensory, USA). These persons (a team of panelists) were selected from a group of 12 people following a standard procedure elaborated by the St. Croix Sensory, Inc. (St. Croix Sensory 2006). Application of this procedure made it possible to determine individual threshold of odour sensing of the test participants. Selected team of panelists was trained with respect to sensory analysis and their knowledge of the rules governing the sensory analysis was verified one week before the actual investigations. The panelists were non-smokers and their psycho-physical condition was evaluated as very good. For one hour before each analysis they did not eat or drink in order to avoid any interference between foreign odours and investigated odorous substances. Individual odour concentration Z_{ITE} at a given measurement point was calculated based on D/T value (dilution to sensing threshold) using the following Eq(1):

$$Z_{ITE} = \sqrt{Z_{NO} \times Z_{YES}} \quad [\text{ou/m}^3] \qquad (1)$$

where:
Z_{NO}=D/T+1 - D/T value, where odour is imperceptible, prior to the D/T value, where odour is perceptible,

Z_{YES}=D/T+1- D/T value, where odour is perceptible, following to the D/T value, where odour is imperceptible.

The value of odour concentration c_{od} [ou/m^3] was calculated as a geometrical mean of the n set of all individual odour concentrations (Z_{ITE}) for a given measurement point using the Eq(2):

$$c_{od} = \sqrt[n]{Z_{ITE1} \times Z_{ITE2} \times Z_{ITE3} \times \ldots\ldots Z_{ITEn}} \quad [\text{ou/m}^3] \qquad (2)$$

where: Z_{ITEn} is the individual odour concentration provided by the panelist.

2.2 Methodology of investigation

Investigation of air quality with respect to odorants concentration carried out with the electronic nose prototype was performed for the air samples collected around the municipal landfill in Gdańsk. The samples were collected at 8 control points located within 1- and 2-kilometre distances from the landfill. Localization and distribution of the air sampling points around the landfill is illustrated in Figure 1.

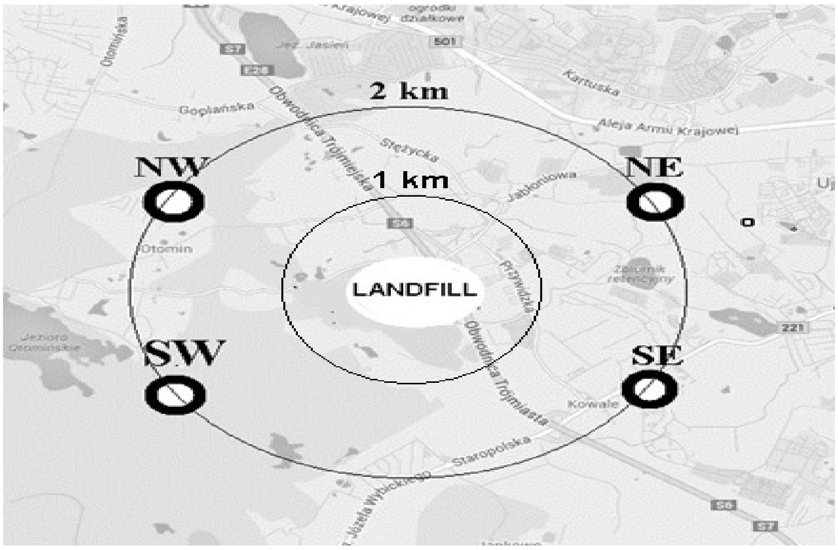

Figure 1: Map of the municipal landfill with the points of atmospheric air samples collection

8 samples were collected on a daily basis for 2 months during the winter season from the aforementioned directions and within the aforementioned distance from the landfill. There was no atmospheric precipitation during the sampling operation. The samples were collected into the Tedlar bags (SKC Inc., USA) of 5 dm^3 volume using a device called Lung sampler, which was designed and built in the Department of Analytical Chemistry of the Gdańsk University of Technology. Prior to sampling the bags were blown with nitrogen (in laboratory) and conditioned – blown with the air from the place of the actual samples collection, which were aimed at minimization of changes in the sample composition due to adsorption. The total of 120 atmospheric air samples were collected around the landfill and analysed. Calibration of the electronic nose prototype with respect to particular concentrations of the odorants involved the reference aqueous solutions of five odour markers (toluene, ethyl acetate, d-limonene, 2-methylbutane, hexane) present in the air samples collected around the landfill and characterized by the highest values of S/N (signal-to-noise) ratio determined via chromatographic investigations. The reference solutions were prepared using deionized water in such a concentration range, which in gas phase provided the summary concentration range from 50 ppb v/v to 1.6 ppm v/v for the respective ratio 1:1:1:1:1 (ethyl acetate, toluene, d-limonene, 2-methylbutane, hexane). Concentration of the aforementioned markers in gas phase was estimated using the Eq(3) and Eq(4). All measurements were performed in laboratory at 20°C.

$$H = \frac{c_r}{p_g} \qquad (3)$$

$$\frac{c_r}{c_g} = \frac{HRT}{101.325} \qquad (4)$$

where: H – Henry's constant [mol×m^{-3}×Pa^{-1}], p_g – vapour pressure of given substance in gas phase [Pa] , c_r – concentration of given substance in deionized water [mol×m^{-3}], c_g - concentration of given substance in gas phase [mol×m^{-3}] , R- gas constant [J×mol^{-1}×K^{-1}], T- temperature [K].

Analysis of the data obtained with the electronic nose prototype was performed employing free R software being a part of Free Software Foundation (Free Software Foundation, Boston, MA, USA).
Air quality investigations with respect to odorants concentration performed with the Nasal Ranger field olfactometers were carried out at the same time and in the same control points, where the air was sampled into the Tedlar bags. The total of 480 measurements were performed with the Nasal Ranger field olfactometers.

3. Results and discussion

Figure 2 presents dependence between mean odour intensity (*I*) and logarithm of summary concentration of selected odour markers (*c*) in gas phase originating from the reference aqueous solutions. Based on the obtained calibration curve described by the Eq(5):

$$I = 1.04 \log c + 1.57 \quad (5)$$

it was possible to estimate the threshold of odour sensing of the odorants mixture, for which odour intensity was I=0. The estimated value was equal 30 ppb v/v; thanks to the obtained information about the threshold of odour sensing of the odorants mixture, the values of odour concentration of the reference mixtures were estimated and expressed in the units of [ou/m^3]. The concentration range was from 1.7 to 53.3 ou/m^3.

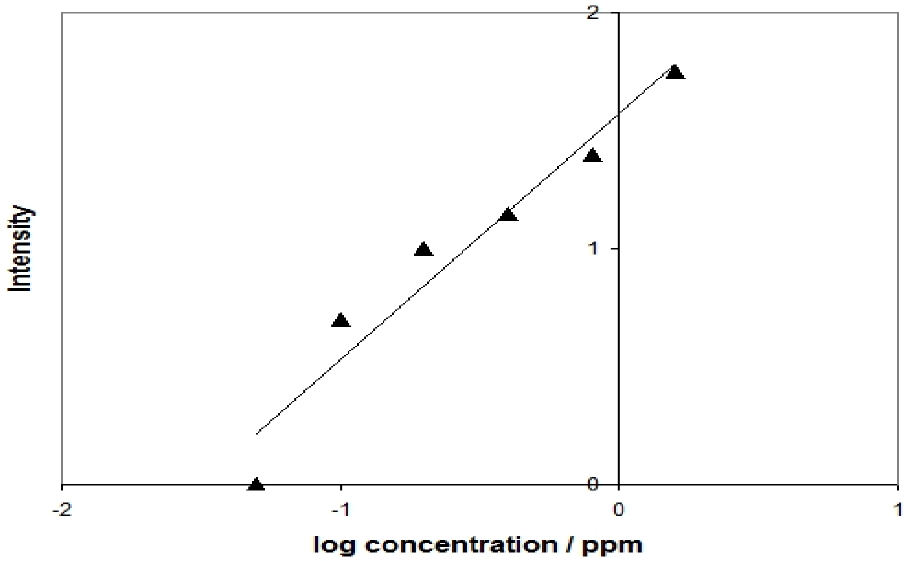

Figure 2: Mean odour intensity versus logarithmic concentration of the sample of reference odorous mixture

Figure 3 shows the PCA results for the samples of mixture of odour markers of the reference solutions. One can notice spatial arrangement of the measurement results on the PC plane. The first principal component contains as much as 99.2% of information about the analysed data set. Considering only the first principal component it can be seen that there is proportionality between the principal component factor and the summary concentration of markers mixture. Figure 4 presents a plot of odour concentration of the markers mixture versus the first principal component factor. This dependence allows determination of the calibration curve described by the Eq(6), which then was used to evaluate odorants concentration in the samples collected in a vicinity of the municipal landfill.

$$c_{od} = 13.1 e^{-0.5PC1} \quad (6)$$

Table 1 gathers mean concentrations of the odorants in the air samples collected from various directions and at different distances from the municipal landfill. There is a comparison between the values of odorants concentration obtained by the team of panelists using the field olfactometers and the ones determined with the electronic nose prototype using the calibration curve (5). The information included in Table 1 reveals that the values of odorants concentration determined by the team of panelists employing the Nasal Ranger olfactometers were higher than the mean values of odorants concentration evaluated with the electronic nose prototype. In two cases it was observed that the differences in mean values of odorants concentration were statistically significant for the significance level α=0.05. Moreover, it was noticed that the values of odorants concentration in the ambient air samples collected along NE direction were higher as compared to the other sampling directions. Discriminated direction corresponded to the actual conditions as there was relatively big number of complaints on odour nuisance from the residents of that area. Of course, these are preliminary tests and the results obtained by means of an electronic nose have yet to be validated. A common man will still be the main sensor determines the intensity and quality of hedonic odor around the emitters.

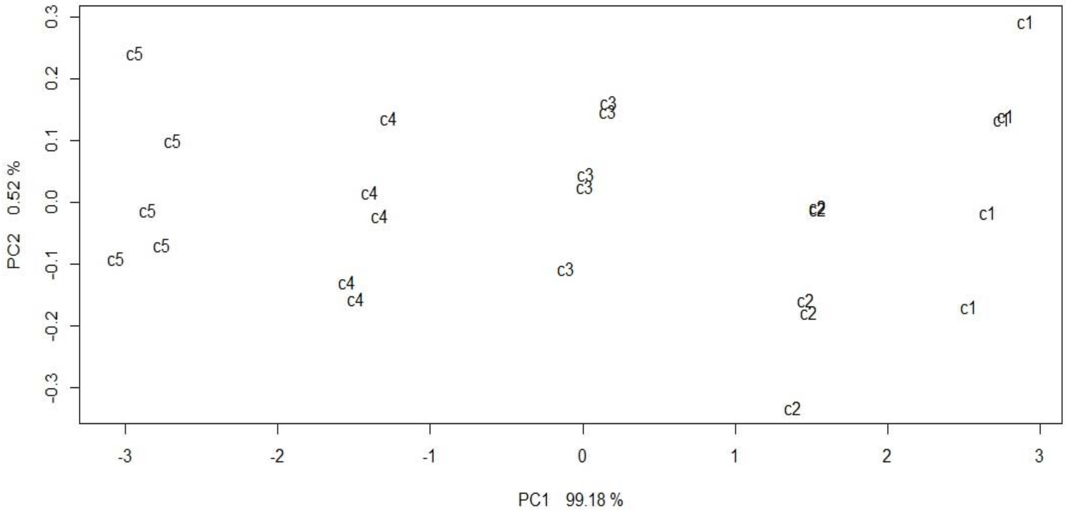

Figure 3: PCA result for the samples of mixture of odour markers of the reference solutions. Measurements were carried out with the electronic nose prototype.

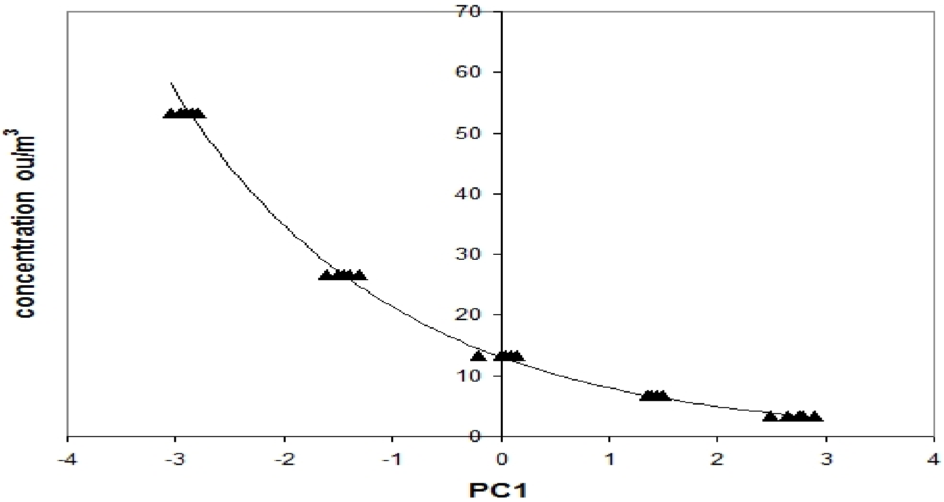

Figure 4: Dependence between odour concentration of odour markers mixture and PC1 component.

Table 1. Comparison of the values of odorants concentration in the ambient air samples collected along different direction around the municipal landfill. Measurements performed with the Nasal Ranger field olfactometers and the electronic nose prototype.

direction of sampling with respect to the municipal landfill	distance from the landfill - 1 km			distance from the landfill - 2 km		
	team of panelists	e-nose prototype	statistical significance	team of panelists	e-nose prototype	statistical significance
NE	36.7	32.5	no	12.5	10.2	no
SE	12.7	10.5	no	2.5	2.0	no
SW	2.6	2.0	no	1.7	1.3	no
NW	3.8	2.8	yes	1.9	1.0	yes

4. Conclusions

Municipal landfills emit relatively big amount of the odorants characterized by various hedonic quality and odour concentration. Additionally, meteorological conditions (temperature, wind velocity and direction) influence on spreading and distribution of the odorous pollutants. The episodes of high concentration of the odorants cannot be recorded via the olfactometric measurements. That is why it becomes justified to apply on-line monitoring employing the electronic nose instruments. Presented concept of odorants concentration measurement in a vicinity of the municipal landfill using the electronic nose prototype comprised of the semiconductor sensors and the PID-type sensor seems quite promising. Mean values of odorants concentration obtained with the electronic nose prototype were compared with the values provided with the Nasal Ranger field olfactometers. The results from the electronic nose prototype confirmed the possibility of application of this technique to measurement of odorants concentration in ambient air. Difference in the mean values of odorants concentration obtained with both techniques was statistically insignificant in 75% of cases. The highest values of odorants concentration originated from the air samples collected along the north-east direction. They were from 12.5 to 36.7 ou/m^3. It should be emphasized that these are very high concentrations. However, they are episodic and are the cause of complaints of people living around the city municipal landfill (in previous studies recorded concentrations sometimes even at 50 ou/ m^3). It was also observed that the mean values of odorants concentration determined using the electronic nose were always lower than the mean odorants concentrations obtained with the Nasal Ranger field olfactometers. It stemmed from the fact that the electronic nose was calibrated with respect to five odour markers, while field tests engulfed broader spectrum of odorous compounds present in ambient air. Accordingly, the values of odorants concentration estimated using the calibration equation (6) were underrated as compared to the odorants concentration determined by the team of panelists utilizing the field olfactometers. Summarizing, the electronic nose technique can be a supplementary tool for the odour analysis methods employing the olfactometric techniques.

Acknowledgments

The authors acknowledge the financial support for this study by the Grant No PBSII/B9/24/2013 from National Centre for Research and Development of Poland

References

Belgiorno V., Naddeo V., Zarra T., 2012, Odour Impact Assessment Handbook. John Wiley and Sons, Inc., Hoboken, USA.

Boeker P., 2014, On ‘Electronic Nose’ methodology, Sens. Actuator B-Chem. 204, 2-17.

Bokowa A.H., 2010, Review of odour legislation, Chemical Engineering Transactions, 23, 31-36.

Bootsma S., Leuwerink T., Bilsen I., 2014, Online air monitoring with enoses at the tata steel plant in the Netherlands, Chemical Engineering Transactions, 40, 79-84.

Capelli L., Sironi S., Centola P., Del Rosso R., Il Grande M., 2008, Electronic noses for the continuous monitoring of odours from a wastewater treatment plant at specific receptors: Focus on training methods, Sens. Actuator B-Chem. 131, 53–62.

Capelli L., Sironi S., Barczak R., Il Grande M., Del Rosso R., 2012, Validation of a method for odor sampling on solid area sources, Water Sci. Technol. 66, 1607–1613.

Capelli L., Sironi S., Del Rosso R., Guillot J.M., 2013, Measuring odours in the environment vs. dispersion modelling: A review., Atmos. Environ. 79, 731–743.

Gebicki J., Szulczyński B., M. Kamiński M., 2015, Determination of authenticity of brand perfume using electronic nose prototypes, Meas. Sci. Technol. 26(12), 125103.

Gebicki J., Byliński H., Namieśnik J., 2016, Measurement techniques for assessing the olfactory impact of municipal sewage treatment plants, Environ. Monit. Assess. 188 (1), 32.

Gębicki J., Dymerski T., Namiesnik J., 2014, Monitoring of Odour Nuisance from Landfill Using Electronic Nose, Chemical Engineering Transactions, 40, 85-90.

Guillot J.M., 2012, Odour Measurement: Focus on Main Remaining Limits Due to Sampling, Chemical Engineering Transactions, 30, 295-300.

Kampa M., Castanas E., 2008, Human health effects of air pollution, Environ. Pollut. 151, 362–367.

Munoz, R., Sivret, E.C., Parcsi, G., Lebrero, R., Wang, X., Suffet, I.H., Stuetz, R.M., 2010, Monitoring techniques for odour abatement assessment, Water Res. 44, 5129–5149.

Sówka I., Sobczyński P., Miller U., 2015, Impact of Seasonal Variation of Odour Emission from Passive Area Sources on Odour Impact Range of Selected WWTP, Rocz. Ochr. Sr., 17, 1339-1349.