VERSITA DOI: 10.2478/eces-2013-0050 ECOL CHEM ENG S. 2013;20(4):719-732

Tomasz OLSZOWSKI[1]

SEASONAL VALUES OF THE GASEOUS CONCENTRATIONS OF AIR QUALITY RATINGS IN A RURAL AREA

SEZONOWE WARTOŚCI STĘŻEŃ GAZOWYCH WSKAŹNIKÓW JAKOŚCI POWIETRZA NA OBSZARZE WIEJSKIM

Abstract: This study presents the quantities of immission of the selected gas pollutions in the area of a compact development village. Within a range of a one-year research project (2012), the yearly average, seasonal and daily profiles of concentrations of the gas compounds in the air had been determined (SO_2, NO_2 and BTEX). Measures were executed in the area of a rural development and in the areas adjacent to the administrative village periphery. In the seasonal researches a passive method and a GC analytic technique had been used along with an automatic analyser to determine daily NO_2 concentrations. It was found out that an air quality in a rural area is determined by the influence of the local sources (unstructured emission from domestic and farm buildings as well as a communication emission) and a toxicants' quantity, enriching environment, depends on cyclic weather states, characteristic for a moderate climate. It has been proved that the maximum concentrations of the tested compounds occur in the center of a village development. It has been proved that it was winter emission that influenced the value of a yearly average concentration of pollutions in the air in a most significant manner. Theory concerning parity of a natural and anthropogenic sources affecting the aerosanitary parameters of rural compact settlement area, has been questioned. It has been proposed to introduce an obligatory, temporary indicator monitoring of a compound, which might prove be a nitrogen dioxide.

Keywords: immission, NO_2, SO_2, BTEX, passive samplers, rural area

Introduction

Publications dealing with the issue of air pollution are mainly focused on presenting data on air quality in densely populated areas [1-3]. The literature sporadically presents results of researches focusing on aerosanitary conditions in the rural areas [4, 5], are occasionally presented. However, toxic influence of the pollution significantly influences village inhabitants as well [6, 7]. This problem concerns particularly rural households located in the moderate and subpolar climate, and results *ia* from the necessity of a longterm, intensive exploitation of the heating energy sources [8]. Apart from aerosols, enriched with *ia* heavy metals and WWA [9, 10], the following gas pollutants are generated into the rural troposphere: NO_2, SO_2, O_3, C_6H_6. According to the guidelines [11], the latter

[1] Department of Thermal Engineering and Industrial Facilities, Faculty of Mechanical Engineering, Opole University of Technology, ul. S. Mikołajczyka 5, 45-271 Opole, Poland, phone +48 77 449 84 57, fax +48 77 449 99 24, email: t.olszowski@po.opole.pl

are considered to be a reference factor for an air quality [12, 13]. Nitrogen dioxide and sulphur dioxide have a negative impact on the respiratory and circulatory system [14]. Benzene is a strongly carcinogenic compound [15]. Carcinogenic and/or mutagenic effects have also the ethylbenzene [16]. In addition, the volatile aromatic hydrocarbons (BTEX) may have negative effect on the nervous, respiratory and circulatory system [14, 17]. Single-ring hydrocarbons, except its toxic properties, are characterized by high potential to create tropospheric ozone (ground level ozone), and also are present (toluene, ethyl-benzene, xylenes) in formation of secondary organic aerosols that are harmful to humans and ecosystems [18-21]. The above mentioned properties determine the on-going research and actions, especially those from the dominant anthropogenic emission sources and the necessity of measuring the above is unquestionable from the perspective of human health [22].

In Poland there are practically no studies on air quality in rural areas. Incidental works of a scientific nature concern researches; mainly those carried out in order to check the measuring devices [23], testing influence of a particular external centre on the physicochemical parameters of a rural troposphere [24], testing range of influence of an anthropogenic rural emission [8], on the estimation of the utility values and possibilities of an area development [25]. Noteworthy is a publication presenting influence and level of a mercury contents in the air in the rural area [26]. Unfortunately, the situation of the national air monitoring stations is similar, i.e. the stations carry out their statutory tasks mainly in towns and cities. As demonstrated in the paper under the supervision of Hlawiczka [27], the overall nationwide share of non-urban measuring stations amounts to 8% (21/253). Due to the evident lack of rural measurement stations, the air quality is established solely on the basis of mathematical modelling results. Nevertheless, it should be remembered that the modelling serves to complement the practice. It is the practical and not the theoretical study of air pollution that plays the decisive role in formulating and improving the strategy of control and negative effects prevention [28]. Taking into account the key factors like: lack of long-term measurements of the rural background, small number of publications on the quality of air in the Polish countryside, social inclination to downplay threats and local authorities' passiveness in pollution monitoring, steps have been taken in order to analyse seasonal changes of the air quality in non-industrialised rural areas.

The main purpose of this study was to present a yearly average and seasonal quantities of the classical immission of gas pollution in a rural area. The complementary objectives concerned the following: determination of a prevailing emission source, determination of a daily profile of concentration variability, finding correlation between tested pollution and determination of the potential indicatory pollution, determination of a spational pollution typical for a period of the year in question.

The research hypotheses assumed that: values of concentrations of the individual pollution in the air do not depend on intensity of use of the classical emission sources, use of which is forced by the meteorological conditions typical for the season of a year in question (A); distribution of a pollution in the area of a village compact development does not depend on main emission sources' location (B).

This paper presents the results and conclusions of long-term measurements of selected pollutants in immission phase, conducted in the typical Polish countryside with compact settlement.

Materials and methods

Tests on a quantitative assessment of a nitric and sulphur oxides as well as BTEX had been carried out in the village of Dylaki (Fig. 1). The village is located in south-western Poland at the Silesian Valley (Opole Voivodship, Opole district, 50°43'57"N, 18°11'12"E). The nearest town (Ozimek 9.7 thousand inhabitants) is located 10 km in the south-east direction, and a capital of the region - Opole (128 thousand inhabitants) is located about 30 km westwards. Dylaki represents type of a compact development village. Within the village limits there are 140 buildings used by about 1.5 thousand of inhabitants. Currently, the village is a typical habitat locality.

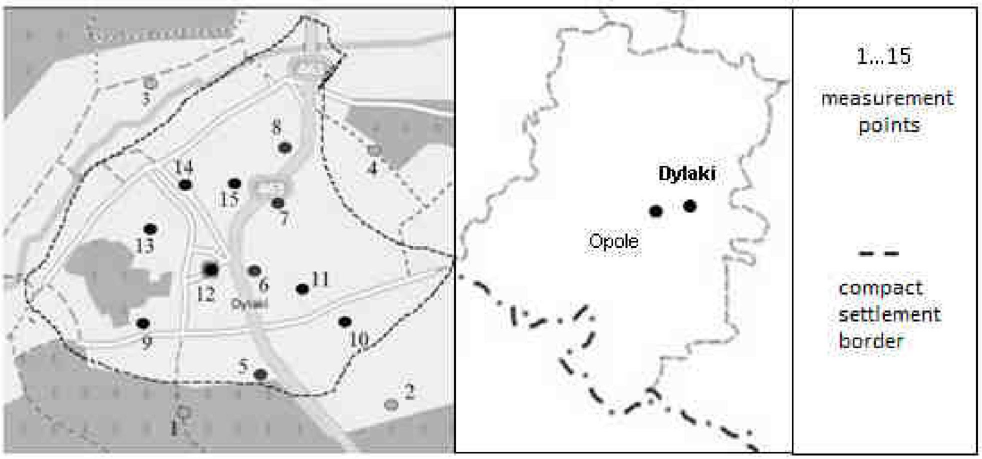


Fig. 1. Map of research area and measure site locations

15 measure points had been selected for tests. Points 1-4 represented an "unurbanised" area, points 5-8 referred to an area of an intensive influence of a road traffic (DW 463 of a concentration approx. 1.8 thousand vehicles/day), while points 9-15 represented an area of a compact development with buildings using an individual heating energy supply system. Measures had been carried out in a quarterly system of 2012 (January, April, July, October) every time during 30 days. The content of SO_2, NO_2 and BTEX in the air was determined with the use of passive samplers. Long-term experience and development of the passive air samples collection techniques cause that the passive measures have been used for years for an air pollution detecting, both by researchers and the national monitoring stations [29, 30]. For the purpose of the study, modified Amaya badge-type permeation passive samplers were used [31]. This choice was also motivated by the fact that national monitoring stations traditionally use this equipment in monitoring air quality in Poland. The method consists in substance adsorption on a filter soaked in a triethanolamine solution (adsorption of SO_2 and NO_2) and on activated carbon (C_6H_6 adsorption). After exposition, the substances are desorbed and analysed with the use of the chromatographic method. Concentrations of SO_2, NO_2 and BTEX in the atmospheric aerosol were calculated according to the formula:

$$C_i = \frac{1.44 \cdot 10^5 \cdot m_i}{P_i \cdot t} \quad (1)$$

where: C_i - concentration of the substance *i* in the air [$\mu g \cdot m^{-3}$], m_i - mass of the substance *i* determined in the probe, reduced by the mass of the substance *i* in the blind sample [μg], *t* - exposition time [min] and *P* - empirical conversion factor, characteristic for the substance *i* [32]. The procedure of probes and reagents preparation for determining SO_2, NO_2 and C_6H_6 was carried out in line with the Authors' recommendations [31], and the procedures of desorption, chromatographic analysis, calibration and calculations for benzene were based on the manual [33] and for SO_2 and NO_2 on the guidelines [31].

Compounds had been determined by a gas chromatography method using a gas chromatograph with FID detector (Carlo Ebra). At the all measure points (15) 3 samplers for the sulphur and nitric oxides interception and 3 samplers for LZO adsorption had been mounted at a height of 2 meters and exposed during a month's period. 3 measurers remained at the laboratory in order to determine the blank test values. In total, 360 samplers had been placed in the area (180 - oxides + 180 - LZO). Table 1 presents validation parameters for a measuring method applied as well as a blank test results.

Table 1

Parameters of the method's validation and blank data

Parameters/ Compound/ Parameter	**NO_2**	**SO_2**	**Benzene**	**Toluene**	**Ethyl-benzene**	***m*+*p*-xylene**	***o*-xylene**
MDL [$\mu g/m^3$]	0.1	0.1	0.25	0.25	0.3	0.37	0.32
MQL [$\mu g/m^3$]	0.5	0.7	0.5	1	1	1	1
RSD [%]	10	8	6	7	10	10	10
MA [%]	30	15	5	15	20	20	20
U [%]	10	12	17	20	29	29	29
Blank [$\mu g/m^3$]	1.9	0.41	< 0.25	1.4	< 0.30	< 0.37	< 0.32

Additionally, in order to estimate the short-term concentration values the size of an NO_2 had been monitored in the centre of Dylaki (point „6") within period from 5th to 10th of an each test month, using an automatic analyzer. For NO_2 detection an AC32M device operating on a basis of a chemiluminescence effect (reference method for NO_2 measure) was used.

During samplers' exposition the basic meteorological parameters were monitored. A portable station LB - 755A had been used for the observation purposes. In order to meet conditions of a proper execution of the meteorological observations, measures were carried out in the vicinity of the point „11". Specification of a meteorological data is presented in the Table 2. During the I research period a significant prevalence of the northern winds (99%) was found, when an average speed of the horizontal air masses did not exceed 0.3 m/s, which considerably limited inflow of pollutions from other areas and, at the same time, was hampering the process of spreading and diluting the indigenous pollutions. During the II, III and IV research stage a significant diversification of wind inflow directions had been observed. Besides, especially in October, its much stronger power was revealed, which influenced possibility of occurrence of the local pollutions' more intense propagation, as well as a possible inflow of the external emissions. The quantity of the precipitation did not favour self-purification of a local troposphere. Excluding January, when a large-scale 46-hours' snowfall took place, a wet deposition effect had the pattern of the short-term convective precipitation.

Table 2

Meteorological data for research periods. Average values

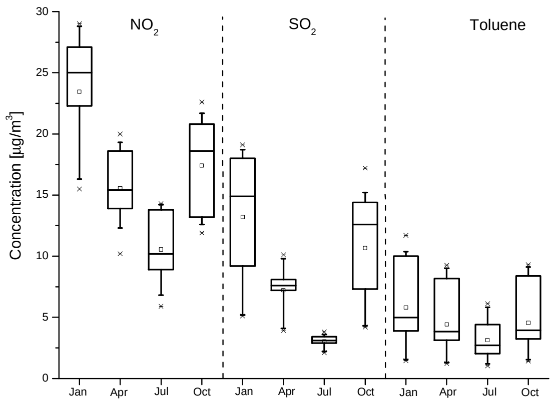
Research period	Temperature [ºC]	Humidity [%]	Pressure [mm Hg]	Wind speed [m/s]	Dominate wind direction [%]	Precipitation [mm/m^2]
January	–7.9	71.1	751	0.3	N (99)	58
April	10.1	62.4	755	2.7	S,SE (39); N,NW (36)	46
July	19.6	71.6	762	2.1	N,NW (49); W (19)	37
October	6.7	86.3	761	5.2	S,SE (41); NW (19)	41

Results and discussion

At the Figure 2 the cumulative specification of an experiment results is presented. A graphic interpretation shows the averaged specification of results obtained in all measure points at the observation stage in question. Values obtained during consecutive representative periods of the classical seasons of a year allowed assessment of the yearly average levels. An average NO_2 concentration value was 16.7 μg/m^3, and SO_2 - 8.5 μg/m^3, which makes ≈ 43% of a value acceptable for a nitric dioxide and the reference value for a sulphur dioxide [34]. Except for the incidental cases for the benzene (in January in 5-8 points), there had not been noted an excess of acceptable value concentrations for considered pollution in respect to the year within an administrative village peripheries.

Nonetheless, it can be stated that within the range of a compact rural development, a significant degradation of an air quality does occur. Comparison of obtained results with data obtained from the national stations of an air monitoring presented in the Table 3, confirms the above statement.

Confronting results obtained in Dylaki against the values included in the Table 3 also shows that it is mainly pollution from the local sources that is responsible for an areosanitary conditions in the area of the considered village. The yearly average concentrations of the standard pointer pollution exceed the background values by 140, 88 and 71% for NO_2, benzene and SO_2 respectively. The air in Dylaki is characterised by a slightly lower nitric dioxide pollution (by 25%) than it occurs in the strongly urbanised area (Opole). Still this level is corresponding to an air quality in the area of the Opole district. At the same time, a ground troposphere of the village is being much more enriched in the sulphur dioxide and benzene (by 30% and 58% respectively) than the city and Opole district themselves. High SO_2 value derives probably from influence of a low emission resulting mainly from the cumulated clausal sources. Additionally, the transport-related emission is responsible for a benzene (and other LZO) levels. Comparing obtained results against results of the over-regional stations, a drastic difference in a troposphere quality becomes evident.



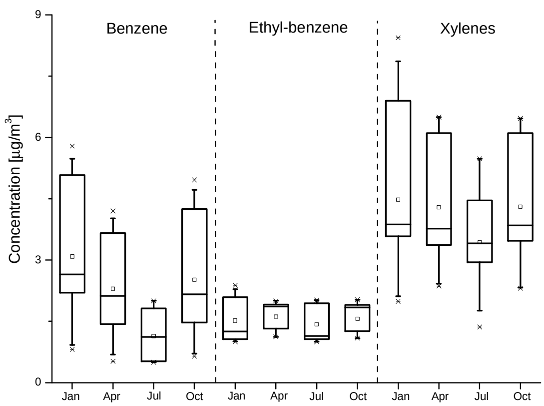


Fig. 2. Results for all research periods. Boxes show the range between the 25th and 75th percentiles. The whiskers extend from the edge of the box to the 5th and 95th percentile of the data. The horizontal line inside indicates the median value. The small square inside indicates the average value

Table 3

Annual average values of SO_2, NO_2 and benzene [µg/m^3]

Mesuring capacity	**NO_2**	**SO_2**	**Benzene**	**Reference**
Opole - city	21.0	6.4	1.3	[35]
Opole - district	17.1	5.4	1.2	[35]
Environmental background (bacground level for Poland)	7.0	5.0	1.3	[36]
Interexchange environmental background (background level for Europe)	1.7	1.1	nd	[36]

A compact urban development and lack of occurrence of the favourable meteorological conditions, intensifying the effect of a gas pollution propagation, contribute to the obviously higher local concentrations of NO_2 and benzene in particular. The yearly average concentrations in the area of the villages with a similar number of households and a street development type were lower by approx. 26% in case of NO_2 and 35% in case of benzene. SO_2 concentration remained the similar level [8]. For villages with a compact development (Dylaki), relation of a yearly average NO_2 concentration to SO_2 was 1.96, which comparing to observations from Szybowice (street type development) NO_2/SO_2 = 1.36, is a value higher by 44%. The above may suggest that if a low rural emission occurs, the sulphur compounds are characterised by significantly lower tendency to propagation.

A yearly average benzene concentration in the air in the rural area had been assessed at the level of 2.4 $\mu g/m^3$ (48% of an acceptable value). In case of other volatile organic compounds the yearly average concentrations were at the levels of 4.5, 1.5 and 4.2 $\mu g/m^3$, which constituted 45%, 4% and 42% of a reference value for a toluene, ethyl-benzene and xylene. In case of benzene, a similar - though lower - yearly average value had been noted in the only village site of the Opole WIOS (*Voivodship Inspectorate of the Environment Protection*) in a Januszkowice village (1.6 $\mu g/m^3$). Similar results had been obtained for the rural areas in Spain [37] and the suburban zones in Michigan (USA) [38]. Considering results from the angle of a distribution of the average hydrocarbons' concentration for the area of a rural development it can be stated that the maximum values occur in the closest vicinity of the two main emission sources, *ie* a compact development and a transport route (ΣBTEX ≈ 14.8 $\mu g/m^3$). A compact development with occasionally used access roads structure is characterised by an average concentration values nearly half lower (ΣBTEX ≈ 8.1 $\mu g/m^3$). The lowest yearly average concentrations had been observed in the open areas around villages (ΣBTEX ≈ 3.5 $\mu g/m^3$).

The yearly average concentration ratio B: T: E and X, including results from the points assigned to the compact rural development was 1.7 : 3.4: 1.0 and 2.7. A similar result was obtained for the rural areas in Spain: 2.1 : 4.4 : 1.0 and 3.1 [37]. Much more significant differences of the B-T-E-X concentrations ratio had been observed in the USA; 4.2 : 6.1 : 1.0 : 4.0 [39] and China, 5.6 : 10.6 : 1.0 : 2.7 [40], whereas much smaller divergence was found for the rural area in Egypt: 2.3: 3.0 : 1.0 : 2.6 [21]. However, what the cited authors noted, results obtained outside of the European continent had been significantly influenced by other anthropogenic sources (local industry, transport). Obtained coefficients also do not correspond to observations of the authors, who - indicating transport as a main LZO emission source - obtained the values of 1.9 : 5.3 : 1.0 and 4.2. The above may indicate that the obtained results are characteristic for the rural areas in Europe, where transport emission is not a prevalent source of the aromatic hydrocarbons.

Individual hydrocarbons' ratios are implied as indicators of the emission sources. Assessment of the T/B, m+p–X/B and o–X/B ratio is helpful in determining sources influence in the atmosphere quality. Unfortunately, the revised literature indicates solely indices characteristic for the linear emission sources. According to Khoder [21], T/B = 2.7, m,p-X/B = 1.8, o-X/B = 0.9 indices are characteristic for the areas where a road transport is a main source. Obtained average concentration ratio of the mentioned compounds 1.9, 1.2 and 0.7 respectively, may indicate that transport is not a main determinant of enriching local air in LZO. T/B ratio, determined by other authors [21, 37, 39] for a rural area was ranged from 1.29 to 2.17. And the low T/B = 1.29 had been obtained for a rural area in Egypt, where the local VOC emission sources did not occur. Parra [37] found T/B = 2.17 and justified it by an influence of a local road traffic. In Dylaki an average value of 2.16 had been obtained from all measure points, while a transport traffic had an impact on a restricted area (in the points located next to the road the value of T/B = 2.32 was obtained, in the other developed area the result was of 2.18). Thus, we should consider a low emission resulting from the energetic fuels combustion (unfortunately, not always conventional ones used in Poland) in the adjacent boiler-houses as a main B and T source in the village. It confirms observations of Schauer [41] that a mineral coal and wood combustion is a significant source of these compounds in the ambient air.

As anticipated, the highest concentration values of the tested compounds had been obtained during winter season. Except SO_2, the comparable concentration values of individual toxicants had been found during II and IV test periods. And in October these values were generally higher than in April, which was influenced by a lower external temperature during the autumn season and, at the same time, by a necessity of a more intensive use of an individual energetic sources. The obtained results indicate that similarly to the central heating systems (in the cities) an extended - in relation to the year - period of using heating energy devices is also observable in the rural area. A climatic zone and related monthly average air temperature as well as a need to maintain a heating comfort inside the residential houses are imposing an over half of a year exploitation of the individual heating systems. It is confirmed by an analysis of the values of an average concentrations of tested compounds during the individual seasons of a year in relation to the yearly average concentration. Both in a winter month, in the springtime as well as in the autumn, higher values for all pollutions considered here against a yearly average had been observed. In case of the indicatory NO_2 and SO_2 the significant differences had been observed. Concentration ratio January/year exceeded the value of 1.5, and coefficients April/year and October/year oscillated around the value of 1.04. For BTEX concentration ratio January/year, April/year and October/year were at a less differentiated level ranging from 1.3 (winter) to 1.05 (spring, autumn). A clear aerosanitary conditions improvement had been noted in the summer. Concentration ratio July/year for a nitric dioxide was 0.62, for a sulphur dioxide was 0.35, and in case BTEX it was 0.77. Obtained coefficients seem to confirm a thesis that a fuel combustion is a main source of a local air pollution by the gas toxicants. Analysing results from the angle of the intensity of the sources influence we can state that the highest concentrations during each season of a year had been registered at the points representing mixed emission, transport and habitat points (points 5-8). Besides, in case of NO_2 and SO_2, at the points characterising a compact development area and at the same time, a typical punctual emission (9-15), the lower values by only 12%, and in the case of BTEX by 35% had been found.

The implemented tests permitted to carry out an analysis which would let us determine whether there exists indicatory pollution whose concentration value might prove to be a point of reference for other toxicants. Pearson's correlation had been applied. Relations between tested pollutions proved that the strongest correlations were obtained for the benzene as a reference compound (benzene - other toxicants: $R > 0.8$). The significant positive correlation was found also for a nitric dioxide ($R > 0.7$). It makes us incline towards a conclusion that data including concentration results of at least one of the mentioned pollutions should be collected and analysed in the monitoring of an influence of the anthropogenic rural sources at the air quality. In case of a passive method, applied in described researches and recommended by the national authorities for an air monitoring, during benzene determining a difficulty occurs with maintaining a sample stability (short time required between exposition and analysis). Thus, it is suggested that a nitric dioxide became a reference compound.

The graphic picture of an NO_2 concentration variability in Dylaki, representative for the individual research periods, is presented in the Figure 3. Measure data interpolation had been done with a SADA programme, using affinity between results from the adjacent points and at the second stage - a spherical model. Ratio $NO_2 : SO_2 : B : T : E : X$ equal to 1 : 2.3 : 7.6 : 3.7 : 10.9 : 3.8 was stable in the period of all experiment stages (max SD 18%). Thereby, we can state that obtained results of a spatial distribution of a nitric dioxide for the individual seasons of a year convey also the horizontal distribution of concentration of other pollutions, while maintaining appropriate proportions of the concentrations value. In general, the highest NO_2 concentrations (as well as of the other compounds) had been observed within the range of a compact development and in the vicinity of a voivodship road. Outside of the town centre concentration of pollutants decline significantly, which confirms a local provenience of pollutions. The compact development as well as routes with the relatively intense traffic (a voivodship road in particular) serve neither good ventilation nor dilution as an increased area roughness related to a dense urban development influences wind deceleration.

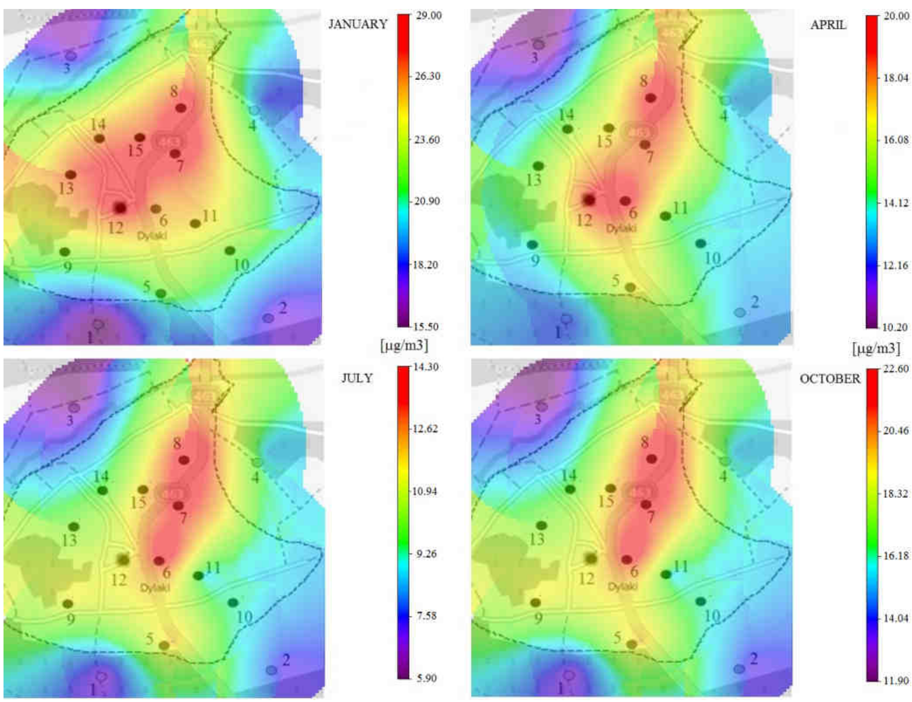


Fig. 3. Spatial distribution of NO_2 in Dylaki area

Observations of the short-term concentrations of a nitric dioxide had been carried out using a reference measure method. The Figure 4 presents the exemplary histograms displaying distribution of NO_2 concentrations in individual measure periods, depending on a time of a day. The graphic interpretation indicates that, with the exception of July, the highest concentrations had been noted in the evening and at night (18-23), which undoubtedly was related to the increased exploitation of the house furnaces, taking place at this time of a day.

Maximum values had been also noted during morning hours which had been influenced by the above as well as by the transitions occurring in the atmosphere (nitric dioxides in particular). The results of daily observations showed that under extremely unfavourable meteorological conditions (January), an air quality is subject to a significant degradation, which results in the catastrophic aerosanitary conditions. Unfortunately, this is a permanent state. The high values of daily concentrations at the level of (> 40 $\mu g/m^3$ for NO_2) are much more hazardous for people than the short-time 1 h lasting exposure for the five times higher concentrations [13, 42].

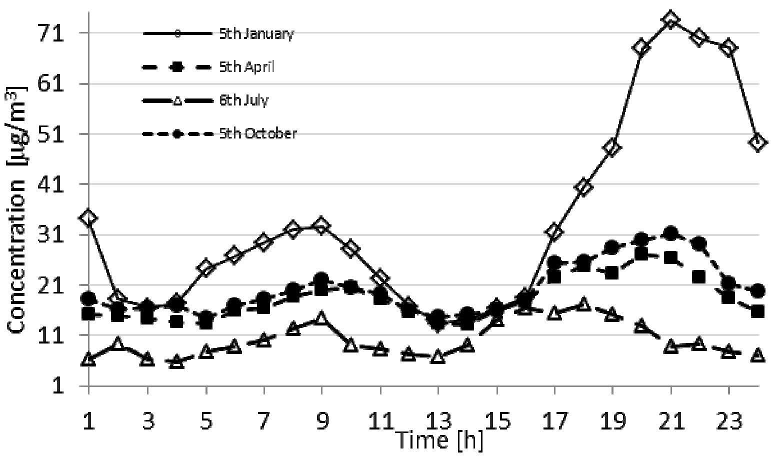


Fig. 4. Exemplary hourly values of NO_2 for several research periods

Table 4 contains specification of results of the Wilcoxon test which served for checking research hypotheses. This non-parametric statistical hypothesis test was used for assessing whether one of two samples of independent observations (results of concentration measurements) tends to have larger values than the other. The two-tailed critical confidence level was considered in testing and the critical p-value was 0.05.

Test results show that the (A) hypothesis works out fully only in case of Ethylobenzenes and Xylenes. Such a result can be surprising, especially when compared to the test results for January and July. Due to a significant difference in case of other pollutions we cannot unambiguously confirm that it is the influence of a dispersed alluvial emission or emission from the natural sources which is responsible for this situation. Still it can suggest that E-benzene and Xylenes are not compounds, whose main source is an anthropogenic activity in the rural area. Significant is also a fact that the statistically important differences in the concentration of pollutions which occur during season of the year characterised by the average temperatures below 10°C, had not been observed. At the same time we should reject the hypothesis as if the emission from the natural sources were responsible for this status quo, since otherwise the significant differences in distributions of concentrations of the pollutions at the points 1-4 and 5-15 would not be found. Test results enable us to accept, to a limited degree, a (B) hypothesis. Except for a warm period (July) test results do not show the statistical differences. Result for SO_2 seems to be interesting in July, *ie* at the time when the prevailing source (apart from the possible natural emission) is a land transport. This result illustrates, and at the same time, confirms the statement that the sulphur dioxide is not a significant compound emitted in effect of fuel combustion in the road vehicles [43, 44].

Table 4

Wilcoxon test results. Ithalic - bold values showed realization of the test conditions

(A) Compound	**Jan-Apr**	**Jan-Jul**	**Jan - Oct**	**Apr-Jul**	**Apr-Oct**	**Jul-Oct**
NO_2	0.002	< 0.001	0.03	<0.001	**0.17**	< 0.001
SO_2	0.004	< 0.001	**0.09**	<0.001	**0.06**	< 0.001
Benzne	**0.17**	< 0.003	**0.24**	0.01	**0.64**	0.01
Toluene	**0.07**	0.01	**0.11**	0.04	**0.66**	0.03
E-benzene	**0.68**	**0.14**	**0.58**	**0.38**	**0.80**	**0.34**
Xylenes	**0.55**	**0.27**	**0.59**	**0.26**	**0.97**	**0.23**
(B) Period/Compound	**NO_2**	**SO_2**	**Benzne**	**Toluene**	**E-benzene**	**Xylenes**
	CS - R	CS - R	CS - R	CS - R	CS - R	CS - R
January	**0.79**	**0.89**	**0.13**	**0.66**	**0.19**	**0.30**
April	**0.34**	**0.95**	**0.12**	**0.32**	**0.05**	**0.13**
July	0.03	**0.39**	0.01	0.04	0.03	0.04
October	**0.24**	**0.66**	**0.05**	**0.16**	0.04	**0.12**
CS - compact settlement (points 9-15), R - main road (points 5-8)						

Conclusions

Despite the fact that the yearly average concentrations of the analysed gas pollutions do not exceed acceptable levels, we can concede that the ground troposphere for the rural areas is significantly enriched with the sulphur and nitrite compounds as well as with the light aromatic hydrocarbons. Above all, it is a disorganised low emission coming from the stationary (boiler rooms) and mobile sources (transport traffic) that is responsible for emission of the gas pollutions. Regardless of a season of a year, the maximum concentration of the gas pollutions, in case of localities with a compact urban development occur at the urban centre of a village. Obtained results as well as results of a statistical analysis challenge the statement maintaining that within a scale of a calendar year a parity occurred regarding participation of the natural and artificial sources in creating an air quality in the rural areas. However, the well-grounding of this thesis requires execution of further research activities. It is noticeable that a winter season has the biggest influence on a size of the emission and, thereby, on a value of a yearly average concentrations. A daily immission profile is not even. The biggest concentrations of determined analytes occur between 6.00 pm and 11.00 pm. It is justifiable, especially in the period when the low temperatures occur (in the winter), to minimalise time of people's staying in the open area within this time period. Due to comparable immission values in the rural area with the concentration levels in permanently monitored urban centres it is recommended to introduce a requirement to implement periodic measures in villages of at least an indicatory compound which could be the nitric dioxide.

Acknowledgements

The Author would like to express his sincere gratitude towards the Authorities of a Mechanical Department of the Opole University of Technology for the financial support without which the execution of this research project would not be possible. Special thanks to Mr Mariusz Lyp for supervising the measure continuity and for comprehensive coordination assistance offered during the field investigations implementation in Dylaki.

References

[1] Sharma RK, Agrawal M, Marshall MF. Atmospheric deposition of heavy metals (Cu, Zn, Cd and Pb) in Varanasi City, India. Environ Monit Assess 2008;142:269-278. DOI: 10.1007/s10661-007-9924-7.

[2] Menezes H, Amorim LCA, Cardeal ZL. Sampling of benzene in environmental and exhaled air by solid-phase microextraction and analysis by gas chromatography-mass spectrometry. Analit Bioanal Chem. 2009;395:2583-2589. DOI: 10.1007/s00216-009-3206-x.

[3] Mijić Z, Stojić A, Perišić M, Rajsić S, Tasić M, Radenković M, et al. Seasonal variability and source apportionment of metals in the atmospheric deposition in Belgrade. Atmos Environ. 2010;44:3630-3637. DOI:10.1016/j.atmosenv.2010.06.045.

[4] Bari MA, Baumbach G, Kuch B, Scheffknecht G. Particle-phase concentrations of polycyclic aromatic hydrocarbons in ambient air of rural residential areas in southern Germany. Air Qual Atmos Health. 2010;3:103-116. DOI: 10.1007/s11869-009-0057-8.

[5] Reisen F, Meyer CP, McCaw L, Powell JC, Tolhurst K, Keywood MD, et al. Impact of smoke from biomass burning on air quality in rural communities in southern Australia. Atmos Environ. 2011;45:3944-3953. DOI:10.1016/j.atmosenv.2011.04.060.

[6] Robinson DL, Monro JM, Campbell EA. Spatial variability and population exposure to PM2.5 pollution from woodsmoke in a New South Wales country town. Atmos Environ. 2007;41:5464-5478. DOI: 10.1016/j.atmosenv.2007.01.059.

[7] Nam KM, Selin NE, Reilly JM, Paltsev S. Measuring welfare loss caused by air pollution in Europe: ACGE analysis. Energy Policy. 2010;38;5059-5071. DOI: 10.1016/j.enpol.2010.04.034.

[8] Olszowski T, Tomaszewska B, Góralna-Włodarczyk K. Air quality in non-industrialised area in the typical Polish countryside based on measurements of selected pollutants in immission and deposition phase. Atmos Environ. 2012;50:139-147. DOI: 10.1016/j.atmosenv.2011.12.049.

[9] Yang W, Omaye ST. Air pollutants, oxidative stress and human health. Mut Res Gen Tox. 2009;674:45-54. DOI: 10.1016/j.mrgentox.2008.10.005.

[10] Anderson HR. Air pollution and mortality: A history. Atmos Environ. 2009;43:142-152. DOI:10.1016/j.atmosenv.2008.09.026.

[11] European Commission; Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe. 2008.

[12] Gaudry A, Moskura M, Mariet C, Ayrault S, Denayer F, Bernard N. Inorganic pollution in PM10 particles collected over three French sites under various influences: rural conditions, traffic and industry. Water Air Soil Pollut. 2008;193:91-106. DOI: 10.1007/s11270-008-9670-7.

[13] Kan H, Wong CM, Vichit-Vadakan N, Qian Z. Short-term association between sulfur dioxide and daily mortality: The Public Health and Air Pollution in Asia (PAPA) study. Environ Res 2010;110:258-264. DOI: 10.1016/j.envres.2010.01.006.

[14] Office of Environmental Health Hazard Assessment; Toxicity criteria database, 2009. http://www.oehha.ca.gov.

[15] International Agency for Research on Cancer (IARC); Overall evaluations of carcinogenicity to humans. IARC Monographs 2004;1-88.

[16] Kyle AD, Wright CC, Caldwell JC, Buffler PA, Woodruff TJ. Evaluating the health significance of hazardous air pollutants using monitoring data. Pub Health Rep. 2001;116:32-44. PubMed ID: 11571406.

[17] Chen CS, Hseu YC, Liang SH, Kuo JY, Chen SC. Assessment of genotoxicity of methyl-*tert*-butyl ether, benzene, toluene, ethylbenzene, and xylene to human lymphocytes using comet assay. J Hazar Mat. 2008;153:351-356. DOI: 10.1016/j.jhazmat.2007.08.053.

[18] Griffin RJ, Dabdub D, Seinfield JH. Secondary organic aerosol. 1. Atmospheric chemical mechanisms for production of molecular constituents. J Geophys Res D. 2002;107:3-26. DOI: 10.1029/2001JD000541.

[19] Rappengluck B, Fabian P, Kalabokas P, Viras LG, Ziomas I. Quasi-continuous measurements of non-methane hydrocarbons (NMHC) in the greater Athens area during MEDCAPHOT-TRACE. Atmos Environ. 1998;32:2103-2121. DOI: 10.1016/S1352-2310(97)00430-5.
[20] Atkinson R. Atmospheric chemistry of VOCs and NOx. Atmos Environ. 2000;34:2063-2101. DOI: 10.1016/S1352-2310(99)00460-4.
[21] Khoder MI. Ambient levels of volatile organic compounds in the atmosphere of Greater Cairo. Atmos Environ. 2007;41:554-566. DOI:10.1016/j.atmosenv.2006.08.051.
[22] Samoli E, Aga E, Touloumi G, Nislotis K, Forsberg B, Lefranc A et al. Short-term effects of nitrogen dioxide on mortality: an analysis within the APHEA project. Europ Resp J. 2006;27:1129-37. DOI: 10.1183/09031936.06.00143905.
[23] Krochmal D, Kalina A. Measurements of nitrogen dioxide and sulphur dioxide concentrations in urban and rural areas using a passive sampling method. Environ Pollut. 1997;96:401-407. PII: S0269-7491(97)-00038-9.
[24] Konarski P, Hałuszka J, Ćwil M. Comparison of urban and rural particulate air pollution characteristics obtained by SIMS and SSMS. App Surf Sc.i 2006;252:7010-7013. DOI: 10.1016/j.apsusc.2006.02.224.
[25] Karnia M, Miczyński J, Zuśka Z. Badania stanu zanieczyszczenia powietrza w gminie Pleśna na potrzeby bonitacji i zagospodarowania terenu. Acta Sci Pol, Formatio Circumiectus. 2007;6(3):43-52.
[26] Zielonka U, Hławiczka S, Fudala J, Wangberg I, Munthe J. Seasonal mercury concentrations measured in rural air in Southern Poland. Contribution from local and regional coal combustion. Atmos Environ. 2005;39:7580-7586. DOI: 10.1016/j.atmosenv.2005.08.003.
[27] Hławiczka S., 2008. Analysis of air pollution and pm2.5 pm10 dust address the chemical composition of dust, including heavy metals and PAHs. Chief Inspectorate of Environmental Protection. Source - internet /in Polish/ http://www.gios.gov.pl/zalaczniki/artykuly/analiza_stanu_zanieczyszczenia_PM10_2_5.pdf
[28] So KL, Guo H, Li YS. Long-term variation of PM2.5 levels and composition at rural, urban, and roadside sites in Hong Kong: Increasing impact of regional air pollution. Atmos Environ. 2007;41:9427-9434. DOI: 10.1016/j.atmosenv.2007.08.053.
[29] Kot-Wasik A, Zabiegała B, Urbanowicz M, Dominiak E, Wasik A, Namieśnik J. Advances in passive sampling in environmental studies. Anal Chim Acta. 2007;602:141-163. DOI: 10.1016/j.aca.2007.09.013.
[30] Salem AA, Soliman AA, El-Haty IA. Determination of nitrogen dioxide, sulfur dioxide, ozone, and ammonia in ambient air using the passive sampling method associated with ion chromatographic and potentiometric analyses. Air Qual Atmos Health. 2009;2:133-145. DOI: 10.1007/s11869-009-0040-4.
[31] Krochmal D, Kalina A. A method of nitrogen oxide and sulphur dioxide determination in ambient air by use of passive samplers and ion chromatography. Atmos Environ. 1997;31:3473-3479. P II S1352-2310(97)00154-4.
[32] Kalina A. Aromatic hydrocarbons - determination with passive sampling sorbent desorption method. Principles and Methods of Assessing of Working Environment. 2000;3(25)149-158 (in Polish).
[33] Begerow J, Jermann E, Keles T, Koch T, Dunemann L. Screening method for the determination of 28 volatile organic compounds in indoor and outdoor air at environmental concentrations using dual-column capillary gas chromatography with tandem electron-capture-flame ionization detection. J Chrom A. 1996;749:181-191. DOI: 10.1016/0021-9673(96)00443-8.
[34] Regulation of a Minister of the Environment Protection dated 13th September 2012 regarding making assessment of the level of substances in the air (Dz. U. 2012, pos. 1032).
[35] http://www.opole.pios.gov.pl/wms/Pliki/2013/Wyniki_pomiarow_jakosci_powietrza_2012.pdf /in Polish/.
[36] http://powietrze.gios.gov.pl/gios/site/measuringstation/E /in Polish/.
[37] Parra M, González L, Elustondo D, Garrigó J, Bermejo R, Santamaría J. Spatial and temporal trends of volatile organic compounds (VOC) in a rural area of northern Spain. Sci Total Environ. 2006;370:157-167. DOI: 10.1016/scitotenv.2006.06.022.
[38] Jia C, Batterman S, Godwin C. VOCs in industrial, urban and suburban neighborhoods, Part 1: Indoor and outdoor concentrations, variation, and risk drivers. Atmos Environ. 2008;42:2083-2100. DOI:10.1016/j.atmosenv.2007.11.005.
[39] Pankow JF, Luo W, Bender M, et al. Concentrations and co-occurrence correlations of 88 volatile organic compounds (VOCs) in the ambient air of 13 semirural to urban locations in the United States., Atmos Environ. 2003;37:5023-5046. DOI: 10.1016/j.atmosenv.2003.08.006.
[40] Guo H, Wang A, Simpson IJ, Blake DR, Yu XM, Kwoka YH, et al. Source contributions to ambient VOCs and CO at a rural site in eastern China. Atmos Environ. 2004;38:4551-4560. DOI:10.1016/j.atmosenv.2004.05.004.

[41] Schauer JJ, Kleeman MJ, Cass GR. Measurement of emission from air pollution sources. 3. C1-C29 organic compounds from fireplace combustion of wood. Environ Sci Technol. 2001;35(9):1716-1728. DOI: 10.1021/es001331e.
[42] Latza U, Gerdes S, Baur X. Effects of nitrogen dioxide on human health: systematic review of experimental and epidemiological studies conducted between 2002 and 2006. Int J Hyg Environ Health. 2009;212:271-87. DOI: 10.1016/j.ijheh.2008.06.003.
[43] Branis M. Air quality of Prague: traffic as a main pollution source. Environ Monit Assess. 2009;156:377-390. DOI: 10.1007/s10661-008-0491-3.
[44] Uherek E, Halenka T, Borken-Kleefeld J, Balkanski Y, Berntsen T, Borrego C, et al. Transport impacts on atmosphere and climate: Land transport. Atmos Environ. 2010;44:4772-4816. DOI: 10.1016/j.atmosenv.2010.01.002.

SEZONOWE WARTOŚCI STĘŻEŃ GAZOWYCH WSKAŹNIKÓW JAKOŚCI POWIETRZA NA OBSZARZE WIEJSKIM

Katedra Techniki Cieplnej i Aparatury Przemysłowej, Politechnika Opolska

Abstrakt: W pracy przedstawiono wielkości imisji wybranych zanieczyszczeń gazowych występujących na obszarze wsi o zwartej zabudowie. W ramach jednorocznego projektu badawczego (2012) określono średnioroczne, sezonowe i dobowe profile stężeń związków gazowych w powietrzu (SO_2, NO_2 i BTEX). Pomiary realizowano na obszarze zabudowy wiejskiej oraz na terenach sąsiadujących z administracyjną granicą wsi. W badaniach sezonowych wykorzystano metodę pasywną i technikę analityczną GC oraz dodatkowo w przypadku ustalania dobowych stężeń NO_2 analizator automatyczny. Stwierdzono, że jakość powietrza na obszarze wiejskim determinowana jest oddziaływaniem źródeł lokalnych (głównie niezorganizowaną emisją z zabudowań mieszkalnych i gospodarczych oraz emisją komunikacyjną), a ilość toksykantów wzbogacających środowisko zależy od cyklicznych okresów stanów pogodowych, charakterystycznych dla klimatu umiarkowanego. Wykazano, że maksymalne stężenia badanych związków występują w centrum zabudowy wsi. Udowodniono, że na wartość średniorocznego stężenia zanieczyszczeń w powietrzu najistotniejszy wpływ ma emisja zimowa. Podważono twierdzenie o parytecie udziału źródeł naturalnych i antropogennych wpływających na parametry areosanitarne obszarów wiejskich o zwartej zabudowie. Zaproponowano wprowadzenie na obszarach wiejskich obligatoryjnego, okresowego monitoringu wskaźnikowego związku, jakim może być ditlenek azotu.

Słowa kluczowe: imisja, NO_2, SO_2, BTEX, mierniki pasywne, obszar wiejski