Tomasz OLSZOWSKI

GASEOUS POLLUTANTS – A CASE STUDY OF LAND-USE CHANGE “BEFORE-AFTER” ON THE EXAMPLE OF A NEW ROAD WITH MEDIUM TRAFFIC. PART II*

Abstract: The article showed the continuation of tests on the impact of road traffic on the air quality. The paper presents results of studies on the concentration of light hydrocarbons (BTEX) and SO₂, as well as NO₂ in the vicinity of a medium traffic road. The presented approach differs from the previous ones with the method of obtaining results for the reference state, which previously were set out in the same sites, in which later were investigated the effect of motor traffic on the qualities of the air. As absorbents – BTEX and SO₂, as well as NO₂, passive samplers, respectively with activated carbon and a triethanolamine-impregnated filter were used in the research study. The samplers were exposed twice at the same area for a period of 30 days, in April 2004 (an area without human intervention) and in 2012 (an area of operation). The study was conducted on the area of 3.5 km of the current section of the northern ring road of Opole (PL). Qualitative and quantitative indications were performed using gas chromatography. It was shown that the change of land-use, which is the exploitation of new road, will increase concentrations of BTEX and NO₂ in the air. It was found that the road transport plays a marginal role as a source of SO₂. It was indicated that the speed of vehicles is one of the key factors influencing the degree of air degradation.

Keywords: outdoor air pollutants; road traffic; NO₂, SO₂, BTEX; passive samplers

Introduction

Emissions from road traffic play a key role for the impact on entering several types of pollutants into the air, causing that the troposphere depends on the intensity and type of the transport [1]. The research works on the impact of road traffic comprise mainly urban areas, which due to the high density of population is fully justified [2–4]. The studies on the impact of the road traffic are carried out not only in urban areas, but also

in rural areas, [5], in road tunnels and canyons, [6] as well as at motorways [7]. Furthermore, huge impact in the research play also projects related with verification of dispersion models of road traffic pollutants [8]. The critical assessment of the model assumptions and recommendations, as well as the necessity of further research studies was presented in [9].

Road traffic plays an important role in producing, inter alia NO\textsubscript{x} and volatile organic compounds, particularly the volatile aromatic hydrocarbons (BTEX) [10–12]. The estimated share of the total of NO\textsubscript{2} and VOC’s emissions, is at the level of approximately 29–35 % [13, 14]. Studies on the estimation of concentration of those pollutants in the air are very often carried out, due to their high toxicity and ability to create secondary substances [3, 5, 7, 15]. Many authors have focused their attention on the impact of sulphur, nitrogen, and hydrocarbons on the human health [16–18], while indicating the need for further research and monitoring.

Gaseous pollutants, such as NO\textsubscript{2}, SO\textsubscript{2} and the representative of BTEX – C\textsubscript{6}H\textsubscript{6} are seen as benchmarks for air quality [16], and due to the toxic effects, the value of their permissible concentrations in the atmosphere are regulated by law [19]. Nitrogen dioxide and sulphur dioxide have a negative impact on the respiratory and circulatory system [20]. Benzene is a strongly carcinogenic compound [21]. Carcinogenic and/or mutagenic effects have also the ethylbenzene [22]. In addition, the volatile aromatic hydrocarbons (BTEX) may have negative effect on the nervous, respiratory and circulatory system [22, 23]. Single-ring hydrocarbons, except its toxic properties, are characterized by high potential to create tropospheric ozone (ground level ozone), and also are present (toluene, ethylbenzene, xylenes) in formation of secondary organic aerosols that are harmful to humans and ecosystems [24]. The above-mentioned properties determine the on-going research and actions, especially those from the dominant emission source which is transportation.

Based on the information being presented in the quoted works, in general it can be stated that:

– despite the significant decrease in the growth rate, the road traffic still generates a significant amounts of pollution and is the major anthropogenic NO\textsubscript{2} and VOC emission source,

– the highest concentrations of pollutants occur horizontally within 10–30 m from the road and 2–5 m vertically, and with the distance are decreasing,

– the traffic intensity, the age of vehicles and the quota of its various types have considerable influence on the amount of the emitted pollutants,

– previous studies on establishing the impact of the road traffic on the air quality were carried out by comparing the obtained results to the quality results for areas that were not directly affected by transportation and situated on other areas.

So far no comparative studies for the area, where selected qualitative and quantitative parameters for the air would be specified before and during the exploitation of the communication thread, were held*. The main objective of this study was to analyse and

* Research results of air quality before and after the change in the road traffic density were presented in [2]. The change was the result of execution of road works on the reconstruction of one of the main arteries of the city Antwerp (Belgium).
evaluate the changes in the volume of atmospheric immission that are typical gaseous pollutions generated by the road traffic. Similar as dust deposition research, the scope of the examination consisted of carrying out two medium-term measurement campaigns in the same area, ie in its original state (before the road was constructed) and during the stabilized exploitation. The second part of the article presents the results of gaseous pollutants, such as NO₂, SO₂ and BTEX.

**Materials and methods**

Measurement site and monitoring period, weather conditions and exploitation parameters of beltway set out in article describing the impact of the road on particulate emissions [25].

**The methodology of sampling and analysis**

To determine the content of SO₂, NO₂ and BTEX [benzene (B), toluene (T), ethylbenzene (E), meta- and para-xylene (m+p-X) and ortho-xylene (o-X)] in the atmospheric aerosol the modified Amaya badge-type permeation passive samplers [26] were used. Similar measures and methods for the determination were already used many times [2, 7, 27]. They are widely used in Poland by the national stations for monitoring atmospheric aerosol pollutants. In the case of sulphur and nitrogen dioxides, the method is based on the technique of analyte adsorption on a filter soaked in a triethanolamine solution. In case of BTEX, the method is based on the adsorption of analytes on the activated carbon. The determined compounds are transferred from the air into the sampler due to the free diffusion. After exposition of the samplers during the period from 01 to 30 April 2004 and 2012, the substances were desorbed and determined using the chromatographic method. BTEX was desorbed quantitatively by thermal elution with carbon disulphide and determined by the gas chromatograph method with FID detector (Carlo Ebra). The procedure of probes and reagents preparation for determining SO₂, NO₂ and BTEX was carried out in line with the Author’s recommendations [26], and the procedures of desorption, chromatographic analysis, calibration and calculations for – benzene, based on the manual [28] and for SO₂ and NO₂ on the guidelines [26]. Concentrations of SO₂ and NO₂ were determined with the use of Dionex DX-120.

Concentrations of SO₂, NO₂ and BTEX in the atmospheric aerosol were calculated according to the formula:

\[ c_i = 1.44 \cdot 10^5 \cdot \frac{m_i}{P_i \cdot t} \]  \hspace{1cm} (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, less the mass of the substance \( i \) in the blind sample [\( \mu g \)],  
\( t \) – exposition time [min];  
\( P \) – empirical conversion factor, characteristic for the substance \( i \) [28].
The Method Detection Limit (MDL) and Method Quantification Limit (MQL), precision (RSD), method accuracy (MA) and expanded measurement uncertainty (U) for individual compounds were presented in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>SO₂</th>
<th>NO₂</th>
<th>Benzene</th>
<th>Toluene</th>
<th>Ethylbenzene</th>
<th>m+p-Xylene</th>
<th>o-Xylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDL</td>
<td>0.1</td>
<td>0.1</td>
<td>0.25</td>
<td>0.25</td>
<td>0.3</td>
<td>0.37</td>
<td>0.32</td>
</tr>
<tr>
<td>MQL</td>
<td>0.7</td>
<td>0.5</td>
<td>0.5</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>RSD (%)</td>
<td>14</td>
<td>6</td>
<td>6</td>
<td>7</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>MA (%)</td>
<td>15</td>
<td>30</td>
<td>5</td>
<td>15</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>U (%)</td>
<td>12</td>
<td>10</td>
<td>17</td>
<td>20</td>
<td>29</td>
<td>29</td>
<td>29</td>
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</table>

Before (2004) [µg/m³]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>SO₂</th>
<th>NO₂</th>
<th>Benzene</th>
<th>Toluene</th>
<th>Ethylbenzene</th>
<th>m+p-Xylene</th>
<th>o-Xylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.3</td>
<td>0.8</td>
<td>&lt; MDL</td>
<td>0.6</td>
<td>&lt; MDL</td>
<td>0.41</td>
<td>&lt; MDL</td>
</tr>
<tr>
<td>Avg</td>
<td>9.28</td>
<td>17.58</td>
<td>1.50</td>
<td>3.04</td>
<td>1.14</td>
<td>1.39</td>
<td>1.19</td>
</tr>
<tr>
<td>Min</td>
<td>7.40</td>
<td>14.00</td>
<td>1.00</td>
<td>1.80</td>
<td>1.00</td>
<td>1.20</td>
<td>1.00</td>
</tr>
<tr>
<td>Max</td>
<td>11.00</td>
<td>21.40</td>
<td>2.00</td>
<td>4.40</td>
<td>1.40</td>
<td>1.80</td>
<td>1.50</td>
</tr>
<tr>
<td>Med.</td>
<td>9.35</td>
<td>17.65</td>
<td>1.50</td>
<td>3.05</td>
<td>1.10</td>
<td>1.35</td>
<td>1.20</td>
</tr>
<tr>
<td>S.D.</td>
<td>1.09</td>
<td>2.48</td>
<td>0.34</td>
<td>0.93</td>
<td>0.12</td>
<td>0.18</td>
<td>0.16</td>
</tr>
</tbody>
</table>

After (2012) [µg/m³]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>SO₂</th>
<th>NO₂</th>
<th>Benzene</th>
<th>Toluene</th>
<th>Ethylbenzene</th>
<th>m+p-Xylene</th>
<th>o-Xylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.4</td>
<td>0.9</td>
<td>0.28</td>
<td>0.5</td>
<td>&lt; MDL</td>
<td>&lt; MDL</td>
<td>&lt; MDL</td>
</tr>
<tr>
<td>Avg</td>
<td>10.14</td>
<td>40.22</td>
<td>3.09</td>
<td>7.67</td>
<td>1.42</td>
<td>3.43</td>
<td>1.42</td>
</tr>
<tr>
<td>Min</td>
<td>8.40</td>
<td>32.90</td>
<td>2.40</td>
<td>6.20</td>
<td>1.10</td>
<td>2.90</td>
<td>1.10</td>
</tr>
<tr>
<td>Max</td>
<td>12.10</td>
<td>50.20</td>
<td>3.80</td>
<td>9.30</td>
<td>1.70</td>
<td>4.20</td>
<td>1.80</td>
</tr>
<tr>
<td>Med.</td>
<td>10.05</td>
<td>41.35</td>
<td>3.10</td>
<td>7.65</td>
<td>1.40</td>
<td>3.40</td>
<td>1.40</td>
</tr>
<tr>
<td>S.D.</td>
<td>1.08</td>
<td>5.43</td>
<td>0.44</td>
<td>1.06</td>
<td>0.16</td>
<td>0.38</td>
<td>0.19</td>
</tr>
</tbody>
</table>

At Point ‘0’ and Point ‘1’, although in 2004 as in 2012, were located 12 samplers (6 for measurement of SO₂ and NO₂ and 6 for assessment of BTEX). Measurement media of gaseous pollutants were installed at both sites at the same height of 2 m in order to minimise secondary emissions from the ground.

Results and discussion

Ambient air gaseous concentration. Before-after relation

Aggregated results of the concentrations of gaseous pollutants, calculated based on the Formula 1, were presented in Table 1.

The results clearly indicate that exploitation of transport routes significantly affects the degradation of ambient air quality. Because distribution of the measurements results was unknown for comparison of the concentrations the Wilcoxon signed-rank test was utilized. The two-tailed critical confidence level was considered in testing and the...
critical p-value was 0.05. The statistical analysis showed that after changing the way of
land use, only the concentration of SO₂ did not change significantly (p-value = 0.07),
which means that road traffic is not a significant source of emissions of this compound.
Similar findings were made by other authors in their studies; inter alia [1, 3]. For other
compounds, the analysis has confirmed the results obtained by other researchers that
road transport produces significant amounts of NO₂ and BTEX [2, 30]. The measured
concentrations did not exceed the permissible values, this means 5 μg · m⁻³ the average
annual concentration index for C₆H₆ – from the perspective of human health and 20
μg/m³ for SO₂ – for the crop protection). However, it is alarming that the urban
ring-road with medium traffic intensity exceeds the permissible concentration of NO₂
(40 μg/m³) at local sites. Only 20 % higher results were obtained by [31] that were
measured at similar distance on motorways, where the traffic intensity is 6–10 times
higher than the one in the analysed sites. The obtained results may indicate that Polish
vehicle fleet is outdated and vehicles do not have emission control apparatus or it is
faulty. The ratio of NO₂ to SO₂ was 3.96 (1.89 before changes). For comparison, on
motorways in Switzerland it amounted of 2.5 [32], in the Czech Republic capital of
approx. 6.5 [3], while in pristine forests of the Carpathians that are free of anthropo-
genic pollution – approx. 0.5 [33]. Comparing the last result with the ‘automobile’ ones
can be answered the question of how the intensive road-traffic pollutes the air with
nitrogen dioxide. Specific emission factor for road transport is the ration of toluene to
benzene. In the analysed ‘after-before’ cases the ration of T/B was 2.5 and 2.0,
respectively. Vardoulakis et al. [34] has measured on the streets of Paris the ration of
T/B which amounted in the range of 2.9 to 3.4, Hansen and Palmgren [35] obtained 2.2
ratio in Copenhagen, and Khoder [24] 2.45 ratio in Cairo. Research studies carried out
in Asian cities has indicated significantly higher ratio of T/B, whereas was stated that
[36] such state is caused by impact of industrial sources. The ratio of BTEX before and
after the change in land use amounted to 1.31:2.66:1.00:2.26 and 2.8:5.41:1.00:3.42,
respectively. The ratio values received during the road exploitation are similar to those
of urban roads that were obtained by the Authors measuring the BTEX pollution in the
air [2, 24]. The index for BTEX, except xylenes is close to the results observed in suburban areas [15]. Figure 1 shows distribution of the relative increase rates (RIR) of particular pollutants in the air. The high values of RIR (for NO₂ and BTEX) and BTEX ratio values obtained for benzene, toluene and xylenes indicate that transportation is a significant source for anthropogenic pollution of these compounds into the atmosphere. A slight increase of SO₂ in the ambient air is the result of the above given data and the use (commonly in Poland since 2006) of ultra-low-sulfur fuels. The low value of the RIR for ethylbenzene is caused by the fact that it has the lowest concentration in the ‘Total BTEX’ of single-ring aromatic hydrocarbons being released during exploitation of roads and motor vehicles [12, 37].

In Table 2 were presented the results of R² correlation coefficient for the analysed pollutants. High linear correlation coefficients between concentrations of the measured analytes could indicate on the common origin of NO₂ and BTEX being determined by road traffic.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>SO₂</th>
<th>NO₂</th>
<th>Benzene</th>
<th>Toluene</th>
<th>Ethylbenzene</th>
<th>m+p-Xylene</th>
<th>o-Xylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂</td>
<td>0.301</td>
<td>0.319</td>
<td>0.466</td>
<td>0.161</td>
<td>0.460</td>
<td>0.014</td>
<td></td>
</tr>
<tr>
<td>NO₂</td>
<td>0.907</td>
<td>0.933</td>
<td>0.940</td>
<td>0.773</td>
<td>0.902</td>
<td>0.902</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>0.276</td>
<td>0.409</td>
<td>0.966</td>
<td>0.875</td>
<td>0.937</td>
<td>0.739</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>0.351</td>
<td>0.493</td>
<td>0.914</td>
<td>0.778</td>
<td>0.918</td>
<td>0.588</td>
<td></td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>−0.113</td>
<td>0.030</td>
<td>0.721</td>
<td>0.677</td>
<td>0.845</td>
<td>0.919</td>
<td></td>
</tr>
<tr>
<td>m+p-Xylene</td>
<td>0.181</td>
<td>0.276</td>
<td>0.887</td>
<td>0.888</td>
<td>0.737</td>
<td>0.750</td>
<td></td>
</tr>
<tr>
<td>o-Xylene</td>
<td>−0.038</td>
<td>0.287</td>
<td>0.835</td>
<td>0.805</td>
<td>0.742</td>
<td>0.824</td>
<td></td>
</tr>
</tbody>
</table>

Correlation is significant at the 0.05 level (two-tailed)

A significant positive correlation was measured between NO₂ and B, T and m+p-Xylene (r > 0.9). When analysing the results, it can be concluded that benzene, as well as NO₂ can be considered as a counter for the simple aromatic hydrocarbons. The lowest value: R² > 0.73 was determined for the linear dependence between B and o-Xylene, the highest value: R² = 0.96 was determined for the linear dependence between B and T. Similar R² values for the analysed compounds were measured by [7, 24, 38]. This leads to the conclusion that during monitoring of road traffic polluting the air quality, data containing the results on concentrations of at least one of the mentioned above compounds should be gathered and analysed. Wherein, the urban monitoring stations at sites of heavy road traffics should measure the concentration level of both pollutants simultaneously. Unfortunately, for example in Poland, such measurements are carried out only in the biggest cities. The results presented in italics apply to the research studies carried out in 2004. In natural environment (with low level of anthropogenic pollutions) the lack of correlation between concentrations of NO₂ and BTEX can be seen. Simultaneously, the correlation between B, T and X (R² > 0.8) and between the classic indicators of the tropospheric air quality (R² > 0.9) can be find.
Ambient air gaseous concentration. Point “1” to “0” relation

Additional objective of this study was to analyse the distribution of volume concentrations in both zones of the road traffic, it means in the braking / accelerating zone (average speed < 30 km/h) – Point ‘0’ and the slow-zone – Point ‘1’ (average speed 80–100 km/h). Many authors, performing examination and theoretical works, provide information that except the type and intensity of the road traffic, the speed of vehicles is also an important factor that directly influences the level of air pollution. As shown by [39], the emission of NO₂ and VOC are 10-times higher at the speed < 25 km/h than at the speed > 60 km/h. In the study [40] was stated that the critical velocity, regarding the emission of benzene, is the speed of 120 and < 50 km/h. Whereas Baldasano et al [41] indicates that the speed of 80 km/h is the most favourable, and maintaining it at this level allows to decrease the total emission of pollutions by 5–7 %.

Figure 2 presents the scatter plot showing the correlation between concentrations being measured in the characterized zones. Results of the model [39] are not supported, but it should be kept in mind that it was prepared for almost two decades ago, when individual protection equipment was rarely used in vehicles and ‘green’ quality requirements for fuels practically did not existed.

![Fig. 2. Correlation (scatter plot) between concentrations being measured in the characterized zones](image)

The results obtained in the presented case indicate that the slow-zone (Point ‘0’), higher concentrations of the measured pollutants are observed. A relative difference in pollutant concentration between the braking / accelerating zone and the slow-zone amounted to: above 26 % for NO₂ and for toluene, > 22 % for benzene and xylenes. The smallest increase was observed for ethylbenzene (≈ 10 %). In general, the results are confirmed by observations made by the authors [40, 41].

As it was previously mentioned, the parameter that characterizes the road transport as a source of pollution is the ratio of T/B. The cited Authors define it for the source, which is the road traffic, according to the site and measurement conditions, at the level of 2–5. Figure 3 shows the T/B ratio at various points by monitoring periods.
Generally, after the road is put into service, the increase in the ratio T/B is noted in both measuring sites. At point ‘0’ the increase amounted to > 16 %, and at the point ‘1’ was > 34 %. The relatively high value of T/B for the point ‘0’, received in 2004, is undoubtedly the result of the impact on the environment of the old road that was exploited at that time, to which the analysed section of the ring road was added. Therefore, more reliable are the results obtained at the point ‘1’.

Conclusions

The results of the study are confirmed by long-term monitoring carried out by other authors and indicate that the exploitation of roads and motor vehicles causes intensive emission of NO₂ and BTEX to the air. Currently, transport as a source does not play a significant role in polluting of SO₂ into the atmosphere. In this case, the measured concentration values are lower than those obtained on motorways and roads with heavy traffic. However, the specific corelations between the analysed pollutants that were determined using indicators, are preserved. Therefore, it can be stated that studies carried out using the measurement system at source and comparing the results with the data from distant sites are justified and recommended. There were no significant differences between the ‘classical’ – often being used, and the described method of studying the impact of road traffic on the ambient air. Vehicle speed is a factor, which significantly affects the scale of polluting the air with toxicants. Thus, it is recommended that the new and modernized transport lanes constructed to minimize occurrence of the braking / accelerating zones. It will help to mitigate the adverse effect of vehicle traffic on the environment.

References


Zanieczyszczenia gazowe – Studium przypadku zmiany sposobu użytkowania terenu na przykładzie nowej drogi o średnim natężeniu ruchu. Część II

Katedra Techniki Cieplnej i Aparatury Przemysłowej, Wydział Mechaniczny Politechnika Opolska

Abstract: Artykuł przedstawia kontynuację badań nad wpływem ruchu drogowego na jakość powietrza atmosferycznego. Praca przedstawia wyniki badań dotyczących stężenia lekkich węglowodorów aromatycznych (BTEX) oraz SO₂ i NO₂ w sąsiedztwie drogi o średnim natężeniu ruchu. Zaprezentowane podejście różni się od dotychczasowych sposobem uzyskania wyników dla stanu odniesienia, które wcześniej określono w tych samych miejscach, w których później badano wpływ ruchu pojazdów silnikowych na walory powietrza. Do badań, jako absorber BTEX oraz SO₂ i NO₂, wykorzystano mierniki pasywne, odpowiednio z węglem aktywnym i filtrem nasączone trietanoalaminą. Mierniki ekspонowano dwukrotnie w tym samym terenie przez okres 30 dni w miesiącu kwietniu, w 2004 (teren pozbawiony ingeryncji ludzkiej) i 2012 roku (teren eksploatowany). Badania prowadzono na obszarze 3,5 km obecnego odcinka północnej obwodnicy Opola (PL). Oznaczenia jakościowe i ilościowe wykonano przy użyciu chromatografii gazowej. Wykazano, że zmiana sposobu użytkowania terenu, jakim jest eksploatacja nowej drogi, powoduje przyrost stężeń BTEX i NO₂ w powietrzu. Stwierdzono, że transport drogowy odgrywa marginalną rolę jako źródło SO₂. Wykazano, że prędkość pojazdów jest jednym z kluczowych czynników wpływających na stopień degradacji powietrza.

Słowa kluczowe: zanieczyszczenia powietrza zewnętrznego; ruch drogowy; NO₂, SO₂, BTEX; mierniki pasywne