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The effect of anthropogenic activity on BTEX, NO_2, SO_2, and CO concentrations in urban air of the spa city of Sopot and medium-industrialized city of Tczew located in North Poland

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Abstract

The major goal of the present study is to compare the air quality of two urban locations situated in Northern Poland – the spa City of Sopot and the medium-industrialized city of Tczew using chemometric methods. As a criterion for the assessment of atmospheric air quality, measurements of benzene, toluene, ethylbenzene and total xylenes were used (collected from atmospheric air using diffusion-type passive samplers) as well as measurements of inorganic compounds - CO, NO_2 and SO_2, which were subject to routine control and determined by means of automatic analysers. Studies related to determination of defined chemical compounds in the urban air in the monitored area were performed from January 2013 to December 2014. By interpreting the results obtained and using basic multivariate statistical tools (cluster analysis and principal components analysis), major sources of emissions of determined pollutants in the air in urbanized areas were defined. The study also shows the potential influence of the sea breeze on concentrations of chemical compounds in the atmospheric air in the spa city of Sopot.

Keywords: BTEX; inorganic compounds; urban air quality; Hierarchical Cluster Analysis; Principal Components Analysis.

1. Introduction

Progressive urbanization of ever larger areas needs to be treated as a serious hazard to the environment. It is estimated that currently about 75% of the population of Europe lives in urban areas, and by 2020, this proportion will increase to 80% (EEA Raport, 2006). As a result, urban expansion has a huge impact on the environment, and also acts directly on the quality of life of citizens.

The problems with urban air quality are related to at least two key trends: (i) the dramatic increase in traffic in urban areas and the corresponding increase in traffic / transport-related emissions and (ii) the mounting evidence that air pollution has significant effects on health.

Transport-related emissions have become the dominant component of air pollution in the recent years. Vehicles with petrol- and diesel-engines emit a wide variety of air pollutants, such as: CO, NO_2, SO_2, (Wu et al., 2011; Ghozikali et al., 2016) volatile organic compounds (VOCs) (Batterman et al., 2007), polycyclic aromatic hydrocarbons (PAHs) (Oros et al., 2007) and particulate matter (PM) (Bosco et al., 2005) which have an increasing impact on urban air quality. The rapid growth in vehicular traffic means that air pollution might continue to rise in the future.

Volatile organic compounds (VOCs) are an important class of air pollutants found in any urban and industrial region. It is estimated that volatile organic compound (VOC) emissions from transport-related sources account for ~35% of all VOC emissions to the atmosphere. In most EU countries emissions per vehicle have been falling, but the gains have been offset by the continuously increasing number of vehicles. Some VOCs are toxic (e.g. benzene, 1,3-butadiene) while many participate in complex photochemical reactions in the presence of sunlight. The products of VOCs photo-chemical reactions lead to an increase in the formation of airborne toxic chemicals, to production of tropospheric ozone (Shao et al., 2009; Derwent et al., 2003; Finlayson-Pitts and Pitts Jr, 1997) and secondary organic aerosol (SOA) (Hallquist et al., 2009; Carlton et al., 2009).

Nitrogen dioxide (NO_2) is a pollutant gas involved in many different chemical processes in the atmosphere. In the troposphere, it acts as a photocatalyst in a series of oxidation reactions of VOCs, generating ozone and low molecular weight aldehydes (Hallquist et al., 2009). In addition, NO_2 is a precursor in the formation of nitric acid, which participates in the formation of aerosols that can affect human health and modify cloud formation processes (Filho et al., 2015).

In urban environments ozone production is often under a VOC-limited regime. Hence, management of VOC levels is very important for the development of an efficient air pollution abatement strategy and is the key for meeting the ozone concentration standards. Management of ambient concentrations of VOCs and NO_x is essential for maintaining low ozone levels in urban areas (Stranger et al., 2008; Zalel et al., 2008).

The aim of presented research was to assess the air quality in urban areas of the spa city of Sopot and a medium-industrialized city of Tczew in relation to the air components such as, BTEX compounds (benzene, toluene, ethylbenzene and sum of xylenes) as well as measurements of inorganic compounds - CO, NO_2 and SO_2; to determine the relationships between the concentrations of these pollutants and to estimate the influence of anthropogenic emission sources on the concentration of measured organic and inorganic compounds in the urban air using multivariate statistics. The monitoring of the concentration of CO, SO_2 and NO_2 in urban air has been performed by using automated analyzers, which are an integral part of monitoring stations located in the monitored area. The use of automated analyzers allows obtaining information on the monitored substances in real time at one-hour intervals. The BTEX compounds monitoring was performed based on passive sampling technique applying diffusion-type Radiello® passive samplers.

2. Materials and Methods

2.1 Description, location and meteorological conditions in monitoring areas.

Measurements of the BTEX compounds and selected inorganic compounds - CO, NO_2 and SO_2, were conducted using measuring techniques and devices installed at automatic monitoring stations. The monitoring stations are located in North Poland in two medium-sized cities - Sopot (54°26′31″N; 18°33′35″E) which belongs to the Tri-city agglomerations (metropolitan area in northern Poland consisting of three cities: Gdańsk, Gdynia and Sopot) and Tczew (54°05′31,89″N; 18°46′38,39″E) situated approx. 40 km away from this agglomeration. Sopot is a main spa resort, which is visited by many tourists in the summer seasons. Sopot is situated on the Gdańsk Bay with the population of 38 thousand and the surface area of 17.3 km^2. Tczew, on the other hand, is a medium-size medium-industrialized city situated on the Vistula River with the population of approx. 61 thousand and the surface area of 22.3 km^2. The locations of the automatic monitoring stations in these cities are

presented in Figure 1. Both stations are owned and administrated by the ARMAAG Foundation (Agency of Regional Air Quality Monitoring in the Gdańsk Metropolitan Area).
To properly interpret data obtained (BTEX and CO, NO_2, SO_2, concentrations) it is very important to have clear information about weather conditions including air temperature, humidity, atmospheric pressure, wind speed and direction, insolation and precipitation but also detailed descriptions of sampling locations with the indications of potential emission sources. Detailed information about sampling locations and weather conditions in Sopot and in Tczew in the monitored period (from January 2013 to December 2014), including the influence of seasonal breeze circulation on the quality of atmospheric air in Sopot, wind roses determined for areas under monitoring, area are presented in Supplementary Files (Supplementary Information, Supplementary Table 1, Supplementary Figure 1).

2.2 Analytical procedure used for determination of BTEX compounds in urban air

2.2.1 BTEX sampling technique

Diffusion-type Radiello® passive samplers (Fondazione Salvatore Maugeri, Padova, Italy) were used for analytes samples collection from the air. This sampling device consists of a cylindrical adsorbing cartridge housed coaxially inside a cylindrical diffusive body of polycarbonate and microporous polyethylene (diffusion zone length 150 mm; porosity 10 ± 2 μm). The analyte passes across a microporous diffusive body/membrane before reaching an inner stainless steel net cylinder containing graphitized charcoal Carbograph 4 (300 ± 10 mg; 35-50 mesh) as the adsorbent. More detailed information on the design and application of Radiello® passive samplers in the monitoring of atmospheric air quality were described in (Plaisance et al., 2008; Woolfenden, 2010, Król et al., 2012; Marć et al., 2015).
During monitoring campaign, two diffusion-type Radiello® passive samplers were placed in specially designed stainless steel shelters, 20 cm apart at each monitoring station. The stainless steel shelters protect Radiello® passive samplers from the harmful influence of atmospheric conditions (precipitation and wind). The shelters were located at a height of 3 m above ground level. The exposure time of passive samplers was 14 days. After the defined exposure time, the stainless steel net cylinder containing adsorbent was removed from diffusion body and placed in a sealed glass container. Next, the new cylindrical containers filled with a clean sorption bed were placed inside the diffusive membranes. Glass containers with the sorption medium were then transported to the analytical laboratory.

During the entire period of the studies (the years 2013-2014), 96 samples were collected - 48 samples a year for each monitoring station.

2.2.2 Analytes liberation technique

The sorption media of the diffusion-type Radiello® passive samplers were removed from the sealed glass tubes and placed inside stainless-steel tubes (89 mm x 6.4 mm o.d.), which were then loaded into the thermal desorber (Omnisfera, Poland). In the first step, a tube was heated to 280°C and held at this temperature for 20 min with pure helium gas passing through it at a flow rate 40 ml/min to desorb the analytes and focus them in a cold trap kept at 1°C. The cold trap was packed with Tenax TA (37 mg) and Carbotrap (27 mg). The entire analyte mass desorbed from the Radiello sorption medium was transferred into the cold trap. In the second step, cold trap desorption, the cold trap's helium flow was inverted and the trap was heated rapidly to 300°C. The analytes were quickly desorbed from the trap and transferred into the chromatographic column (DB-1 (J&W), 30 m × 0.32 mm × 5 μm).
Detailed information about two-stage thermal desorption system, used for BTEX liberation , has been described elsewhere (Przyk et al., 2003; Zabiegała et al., 2007).

Gas chromatography analysis and final determination stage

The gas chromatography technique (Hewlett-Packard 5890 GC Series II) with a flame ionization detector (FID) was applied. The GC oven temperature program was initially set to 40°C for 1 min, then raised at a rate of 15°C/min up to 120°C, then increased at a rate of 10°C/min up to 220°C, and finally maintained for 5 min at 220°C. The temperature of the transfer line connecting the thermal desorber with a gas chromatograph was 150°C, while the temperature of the FID operation was 280°C. The GC carrier gas flow rate (high-purity helium) was 2.2 ml/min.
The external standard calibration method (ESTD) was performed using a volatile calibration mix containing 13 VOCs (containing BTEX compounds) in the methanol solution in which the concentration of each organic compound was 2000 μg/ml (VOC Mix 2, Supelco, Bellefonte, PA, USA). Two five-point calibration curves were created for two concentration ranges, 50 to 400 μg/ml and 400 to 2000 μg/ml.
Detailed characteristics of conducting the calibration of the TD-GC-FID system based on the external standard method together with the used devices were described in former papers

(Zabiegała et al., 2011; Marć et al., 2014b). Based on the obtained equations of calibration curves the limit of quantification of the analytical procedure used (MQL) were calculated, which ranged from 0.020 μg/m^3 for p, m-xylene to 0.050 μg/m^3 for benzene (Marć et al., 2014a).

The time weighted average (TWA) concentrations of BTEX compounds were calculated based on the knowledge of the exposure time of the samplers, masses of the analytes trapped by the sorption medium (determined chromatographically), and analyte sampling rates (SR). The uptake rate values (Q), supplied by the manufacturer of diffusion-type Radiello® passive samplers, were determined at 25^{o}C and 1013 hPa in a controlled atmosphere; consequently, they had to be adjusted for the actual mean sampling temperature (Fondelli et al., 2008; Dumanoglu et al., 2014). The uncertainty of the uptake rate values (Q) of BTEX compounds was also supplied by the manufacturer. These values fall within the range from 7.5% for benzene to 11.3% for p, m-xylene.

2.3 On-line analysers used for determination of selected inorganic compounds in urban air

Taking into account the requirements presented in Directive EU 2008/50/EC, monitoring stations situated in Tczew and Sopot which are administered by ARMAAG foundation are equipped with appropriate automatic analysers. At the monitoring station which is located in Tczew, the following automatic analysers were used to determine sulphur dioxide, nitrogen oxides and carbon monoxides: Thermo Environmental 43 C (SO_2), Teledyne T200 (NO-NO_2-NO_x) and Thermo Environmental 48 C (CO), respectively. At the monitoring station which is located in Sopot, the following automatic analysers were used: Thermo Environmental 43 C (SO_2), Thermo Environmental 42 C (NO-NO_2-NO_x) and Thermo Environmental 48 C (CO), respectively.

Information about the content of the determined inorganic compound in the atmospheric air is published on the ARMAAG foundation website on a continuous basis (www.armaag.gda.pl). Information about concentrations of inorganic compounds in the atmospheric air in the studied area is provided every hour. The operation of the aforementioned devices is monitored remotely and by periodic on-site service inspections by the personnel. The extended uncertainty of measurements obtained by means of automatic analysers at the monitoring stations was 15%.

2.4 Multivariate statistical methods

The chemometric methods used in the present study are already classical approach in many cases of classification, modelling and interpretation of environmental monitoring data. Cluster analysis (CA) and principal components analysis (PCA) were applied for intelligent data analysis. Both methods are well documented in scientific work presented by Vandeginste et al., 1998. In principle, hierarchical CA is used as a classification tool and PCA as a typical display method. It enables revealing the "hidden" structure of the data set. Interpretation of the results of PCA is usually carried out by visualization of the component scores and loadings. The software package used for calculations was STATISTICA 7.0 (StatSoft®, Poland)

3. Results and Discussion

3.1 Concentrations of the BTEX compounds in the atmospheric air in Tczew and Sopot

In accordance with information contained in Directive 2008/50/EC, the legislator recommends that studies related to the quality of atmospheric air in urbanized areas should include the monitoring of the content of 31 organic compounds classified as potential precursors for the formation of tropospheric ozone (O_3), which includes, amongst other things, compounds from the BTEX group and from the trimethylbenzene group. The aforementioned Directive, places special emphasis only on the monitoring of the benzene content whose average annual concentration in the atmospheric air must not exceed 5 $\mu g/m^3$ in the urbanized area. According to literature reports and the report by the International Agency for Research on Cancer, benzene is classified in Group I as a chemical compound with carcinogenic properties (I.A.R.C., 1982). Excessive and long-term exposure of the human body to the harmful effects of benzene may be the cause of plastic anaemia and acute myeloid leukaemia (Pariselli et al., 2009; Schiavon et al., 2015). For this reason, in all monitoring tests related to the atmospheric air quality in urbanized areas, benzene contents are considered on an individual basis as opposed to other organic compounds from the BTEX group.

Interpretation of results of the research on the quality of atmospheric air in Tczew and Sopot conducted in the years 2013-2014 did not reveal exceeding of the limit value of annual average concentrations of benzene (<5 $\mu g/m^3$) in the studied air in the monitored area. In

2013, the average time-weighted concentrations of benzene in atmospheric air in Tczew amounted to 0.75±0.55 μg/m^3, while in Sopot it amounted to 0.53±0.43 μg/m^3. For research performed in 2014, the average time-weighted concentrations of benzene in atmospheric air in Tczew amounted to 1.4±1.1 μg/m^3, while in Sopot it amounted to 1.07±0.97 μg/m^3. In 2013, the highest average monthly time-weighted benzene concentration in the atmospheric air in Tczew was recorded in March (1.75 μg/m^3), while the lowest in August (0.10 μg/m^3). For research conducted in the same year in Sopot, the highest average monthly time-weighted benzene concentration in the atmospheric air was recorded in December (1.21 μg/m^3), while the lowest in August where the determined average monthly time-weighted concentration was similar to the numerical value of MQL (0.050 μg/m^3). As regards the research conducted in the area in which atmospheric air was monitored in 2014, the highest average monthly time-weighted benzene concentration in the atmospheric air in Tczew was recorded in February (3.48 μg/m^3), while the lowest in June (0.25 μg/m^3). As regards to the quality of atmospheric air in Sopot, the highest average monthly time-weighted concentration of benzene was recorded in February (2.92 μg/m^3), while the lowest was recorded in June (0.16 μg/m^3).

Temperature is a significant meteorological factor which needs to be considered in the interpretation of research results related to the benzene content in the atmospheric air. Figure 2 presents graphically the relationship between the temperature and the average monthly time-weighted benzene concentration determined in the atmospheric air in the monitored area (the Tczew and Sopot city) in the years 2013-2014. As regards the data presented in Figure 2, it can be noticed that both in Tczew and in Sopot, there is a moderate relationship between the temperature and the benzene content. This can lead to the conclusion that a decrease in the atmospheric air temperature in the urbanized area may influence the benzene content. To confirm this thesis, the period of research including a given calendar year should be divided into two basic seasons: the heating season which lasts from the beginning of October to the end of April in Poland (7 months); the summer season which includes the period from the beginning of May to the end of September (5 months). As regards the research conducted in Tczew in the years 2013 and 2014, the values of time-weighted average benzene concentration determined in the atmospheric air in the heating season were: 1.13±0.36 μg/m^3 and 2.0±1.1 μg/m^3, respectively, while in the summer season it were: 0.201±0.090 μg/m^3 and 0.49±0.24 μg/m^3, respectively. The temperature of the atmospheric air in Tczew in the years 2013 and 2014 in the heating season was 3.2^{o}C and 4.8^{o}C, respectively and in the summer season: 16.8^{o}C and 17.1^{o}C, respectively. A comparison of the heating and summers seasons in

the years 2013 and 2014 in Tczew revealed that the average time-weighted benzene concentrations determined in the atmospheric air in the heating season were over 4 (year 2013) and over 5 (year 2014) times higher than in the summer season. Similarly, while analysing information obtained from monitoring research conducted in Sopot area in the year 2013 and 2014, the values of time-weighted average benzene concentration determined in the atmospheric air in the heating season were: 0.84±0.27 μg/m^3 and 1.58±0.98 μg/m^3, respectively, while in the summer season it were: 0.096±0.064 μg/m^3 and 0.36±0.21 μg/m^3, respectively. The temperature of the atmospheric air in Sopot in the heating season in the years 2013 and 2014 was: 4.2^{o}C and 5.5^{o}C, respectively and in the summer season: 15.8^{o}C and 16.1^{o}C, respectively. A comparison of information about the quality of atmospheric air in the heating season and the summer season in Sopot revealed that the concentrations of benzene determined in the atmospheric air in the heating season was nearly 9 times higher in 2013 and over 4 times higher in 2014 as compared to the summer season.

All previously mentioned pieces of information confirm the thesis that the temperature of the atmospheric air in the urbanized area can have a significant influence on the benzene content in the atmospheric air. The traffic of vehicles with internal combustion engines is the main anthropogenic factor causing an increase in benzene concentrations in the atmospheric air in the urbanized area in the autumn-winter period (low temperatures of the atmospheric air). The time necessary for the achievement of the optimal liquid fuel combustion temperature in internal combustion engines is considerably extended, due to, amongst other things, an increase in the fuel density. For this reason, at the initial stage of using a mechanical vehicle, the process of incomplete liquid fuel combustion may occur, which may result in benzene emissions into the atmospheric air. Moreover, internal combustion engines installed in cars use much more liquid fuel in the autumn-winter period, than in the summer season. This is related, amongst other things, to the intensive use of the heating system inside the car and longer use of the external lighting of the vehicle in the autumn-winter period than in the summer season.

Another anthropogenic factor which influences the increase in the benzene content in the atmospheric are in the autumn and winter period in the urbanized area is the heating of flats and houses using low-performance heating systems (e.g. a tiled stoves or furnaces). In such systems, wood or low-quality coal can be used, which, together with the low performance of the system, may cause benzene emissions into the atmospheric air. Together with a decrease in the external temperature, the intensity of the use of heating systems in flats and houses grows to keep the optimal temperature of residential rooms. Low-performance tiled stoves or

furnaces can be usually found in very old houses or flats where the heat-transfer line from the main city power plant was not installed or in small-sized buildings situated in recreational and allotment areas.

Higher benzene concentrations in the atmospheric air in the autumn and winter season than in the summer season in the urbanized areas may also result from lower intensity of physicochemical transformations occurring in the atmosphere. According to information contained in the literature, the phenomenon of reduction in the thickness of the boundary layer and the intensity of air mass mixing/circulation is reduced (Tao et al., 2007; Choi et al., 2011; Zhang et al., 2015). Moreover, as a result of low temperatures of the atmospheric air and considerably limited availability of solar radiation in the layer of the air over the urbanized area, photochemical reactions between benzene and strong oxidiser (tropospheric ozone or hydroxyl radical) are slowed down. As a result, the so-called lifetime of benzene in the atmospheric air is extended (on a standard basis of approx. 9.4 days), which has a significant influence on the content of this compound in the atmospheric air in the urbanized area (Monod et al., 2001).

Through the interpretation of results obtained, it was found that the annual average benzene concentration determined in the atmospheric air in Tczew, both in 2013 and 2014, was higher (by 40% and 28%, respectively) than the concentration of benzene determined in the atmospheric air in Sopot during the same time. A similar phenomenon was observed while comparing the benzene contents determined in atmospheric air in the autumn and winter period. The following factors may have an influence on higher benzene concentrations in the atmospheric air in Tczew, as compared to Sopot, obtained in the research: the location of the station - the monitoring station in Tczew is situated in close vicinity of the main traffic node (Wojska Polskiego Street), the railway node and seasonally used recreational allotments; the smoothness of vehicle traffic – the traffic is very often considerably slowed down or stopped at this traffic node, the age and type of buildings – low-performance tiled stoves or furnaces are still used in some of the buildings and low-quality coal as a solid fuel is used.

Figure 3 presents the results of monitoring tests which were aimed at obtaining analytical information on the levels of toluene, ethylbenzene and total xylenes determined in the atmospheric air in Tczew and Sopot in 2013 and 2014. The average time weighted concentrations of toluene, ethylbenzene and total xylenes determined in the atmospheric air in Tczew in 2013 were: 2.2±1.0 μg/m^3, 0.99±0.76 μg/m^3, 4.4±3.4 μg/m^3, respectively while in 2014: 3.1±2.5 μg/m^3, 1.12±0.56 μg/m^3, 4.5±2.4 μg/m^3, respectively. As regards the average time weighted concentrations of toluene, ethylbenzene and total xylenes which were

determined in the atmospheric air in Sopot in 2013, they amounted to: 1.34±0.72 μg/m^3, 0.23±0.13 μg/m^3, 0.95±0.59 μg/m^3, respectively while in 2014: 1.90±0.52 μg/m^3, 0.44±0.17 μg/m^3, 1.80±0.66 μg/m^3, respectively. It should be noticed that both in Tczew and Sopot, the content of toluene, ethylbenzene and total xylenes determined in the atmospheric air in 2014 was higher than in 2013. Moreover, the average annual time weighted concentrations of organic compounds determined in the atmospheric air were higher in Tczew than in Sopot both in 2013 and 2014.

While interpreting data which is graphically summarized in Figure 3, it can be noticed that there is no clear relationship between the season (the heating season or the summer season) and the average monthly time weighted concentration of the selected organic compound determined in the atmospheric air in the monitored area. This is mostly caused by the fact that, according to the literature data, toluene, ethylbenzene and compounds from the xylenes group are characterized by a very short lifetime in the atmospheric air (from a few to a few dozen hours) in the urbanized area. These compounds which are present in the atmospheric air undergo photochemical reactions more easily with the participation of strong oxidisers, such as hydroxyl radical (·OH) than benzene (Monod et al., 2001). Moreover, in the case of toluene, ethylbenzene and total xylenes, their presence in the atmospheric air may result not only from vehicle traffic or symptoms of the activity of tiled stoves or furnaces for residential buildings (burning low-quality coal) and also the activity of various types of industrial or commercial centres situated in the monitored area, e.g. a company dealing with the collection and management of various types of solid, liquid and electronic waste. The main means of transport used for transporting various types of waste are trucks with diesel engines.

3.2 Variations in the inter-species ratios of B÷T÷E÷X in the monitored area in the period 2013-2014

To perform preliminary comparison of two or more areas which are monitored in terms of the influence of main sources of emissions of the BTEX compounds on the quality of atmospheric air, two analytical approaches are commonly used in the literature. The first is related to the definition of the influence of vehicle traffic on the levels of the BTEX compounds in the atmospheric air and is defined as the ratio of benzene, toluene and total xylenes concentrations to the ethylbenzene concentration determined in the atmospheric air in the monitored area, B÷E, T÷E and X÷E, respectively. Under ideal conditions, where the only

source of emissions of BTEX compounds is vehicle traffic, the numerical values of the B÷T÷E÷X parameter is 3÷4÷1÷5 and B÷E<5, and T÷E<6 (Chiang et al., 1996; Wang et al., 2002; Khoder, 2007). It is possible to obtain similar numerical values of the B÷T÷E÷X parameter only if weather conditions observed in comparable monitored areas are similar, the vehicle traffic has similar intensity, vehicles use the same type of fuel which is characterized by similar quality and the age of mechanical vehicles falls within the same range. Moreover, concentrations of the BTEX compounds may not be influenced by other sources of emissions in any of the monitored areas, such as the activity of local industrial and commercial centres or the location of green areas (Vardoulakis etal., 2011; Lan and Minh, 2013).

The other analytical approach allows preliminary estimation of the so-called photochemical age of air mass ("freshness" of the source of emissions) and determination of the distance from the place with vehicle traffic. It makes it possible to define whether pollutants are transported to the monitored area from sources of emissions situated near the monitoring station or whether they are transported by the movement of air masses from other sources of emissions situated at a considerable distance from the monitoring station. In this case, the numerical values of the following parameters are being set, which depend on concentrations of the BTEX compounds which are determined in atmospheric air in the monitored area: toluene÷benzene (Tol/Benz); (m,p)-xylene÷benzene ((m,p)-Xyl/Benz); o-xylene÷benzene (o-Xyl/Benz); (m,p)-xylene÷ethylbenzene ((m,p)-Xyl/Et.benz). In the analytical practice, two parameters are used for the interpretation of the results obtained and comparison of the quality of atmospheric air in monitored areas, these are toluene÷benzene (Tol/Benz) and (m,p)-xylene÷ethylbenzene ((m,p)-Xyl/Et.benz) (Zhang et al., 2008; Baltrenas et al., 2011; Yurdakul, et al., 2013). If the level of the BTEX compounds in the atmospheric air in urbanized areas is mostly influenced by vehicle traffic, the Tol/Benz content falls within the range from 1.3 up to even 4.3 (Miller et al., 2010; Rad et al., 2014). The higher the value of this parameter, the more distinct the influence of vehicle traffic is on the concentration of the BTEX compounds in the atmospheric air in the monitored area. However, when the source of emissions of organic compounds from the BTEX group is located at a close distance from the measuring/monitoring station (a "fresh" source of emissions), the value of the (m,p)-Xyl/Et.benz parameter is higher than 3.3 (Hsiehet al., 2011; Miller et al., 2011; Cerón-Bretón et al., 2015).

Table 1 presents average numerical values of the B÷T÷E÷X ratio parameters and the toluene÷benzene and (m,p)-xylene÷ethylbenzene parameters determined on the basis of the results obtained in the atmospheric air quality studies in Tczew and Sopot in the years 2013-

2014. While interpreting data summarized in Table 1 as regards the value of the B÷T÷E÷X ratio parameter, it can be noticed that the first additional condition was met both in Tczew and in Sopot, i.e. the B÷E and T÷E parameters were below previously defined values. Such a result may lead to the preliminary conclusion that vehicle traffic is one of the sources of emissions of the BTEX compounds in Tczew and Sopot. In each case, both in 2013 and 2014, the values of the B÷E and T÷E parameter determined for Sopot were much higher than for Tczew. Furthermore, the values of the total B÷T÷E÷X ratio parameter as determined for atmospheric air in Sopot in the years 2013 and 2014 are closer to the reference values (3÷4÷1÷5) than those determined for atmospheric air in Tczew. Such information may lead to the conclusion that in Sopot vehicle traffic was the main source of emissions of the BTEX compounds into atmospheric air throughout the research period. This is confirmed by the fact that Sopot is considered to be one of the most popular Polish resorts and health spas and is visited by a lot of tourists from Poland and abroad. Moreover, there is a lack of large industrial centres or service and commercial concerns in Sopot, which considerably facilitates the interpretation of the research results obtained. The fact that Sopot is situated on the Gdańsk Bay (proximity of the Baltic Sea) also seems significant. For this reason, the final result of determinations may be influenced by the sea breeze and emissions from ships with diesel engines which are stationed near Sopot. Differences between the year 2013 and 2014 in the determined B÷T÷E÷X ratio parameters in Sopot may result from varying intensity of vehicle traffic - not only from cars which are used by the local community but also by tourists which visit this city seasonally. In the case of the total B÷T÷E÷X ratio parameter determined for atmospheric air in Tczew in the year 2013 and 2014, it can be observed that these values significantly diverge from the reference values (3÷4÷1÷5). The occurrence of this phenomenon shows that vehicle traffic is not the only source of emissions of the BTEX compounds into the atmospheric air in the monitored area. The level of the BTEX compounds in the air in Tczew can be influenced by the activity of other factors situated in the monitored area, such as low-performance tiled stoves or furnaces in houses, seasonal use of recreational allotment areas and activity of industrial centres or service and commercial concerns.

Referring to the data contained in Table 1 which is related to the average content of the determined Tol/Benz parameter for atmospheric air in Tczew and Sopot in the years 2013-2014, it was observed that these values fall within the range from 1.3 to 4.3. This shows that vehicle traffic is not the only source of emissions of the BTEX compounds into the atmospheric air in the monitored area. It was noticed that both in 2013 and 2014, higher values of the Tol/Benz coefficient were observed for the atmospheric air in Tczew (2.96 and

2.29, respectively). This results from the fact that the monitoring station in Tczew is located near the main communication node where the vehicle traffic is often slowed down or stopped. Moreover, there is no increased circulation and exchange of air resulting from the vicinity of the Gdańsk Bay (the sea-breeze has no influence on the quality of atmospheric air). For this reason, the activity of the vehicle traffic as a source of emissions, i.e. the vehicle traffic, has a consequential influence on the content of the BTEX compounds in the atmospheric air in Tczew, even it is not the only emission source of BTEX compounds.

Interpretation of parameters presented in Table 1 which are related to the (m,p)-Xyl/Et.benz parameter, whose determination allows preliminary specification of the proximity of the sources of emissions of the BTEX compounds, it was noticed that both in 2013 and in 2014 the greatest values were observed in Tczew (3.04 and 2.74, respectively). This can constitute the basis for drawing a conclusion that an intensive source of emissions of the BTEX compounds , i.e. vehicle traffic, is situated near the monitoring station. Moreover, the BTEX compound levels are influenced by the "fresh" source of emissions, which probably is increased vehicle traffic in the monitored area. In Sopot, the values of the (m,p)-Xyl/Et.benz parameter determined in the year 2013 and 2014 were similar and they amounted to 2.70 and 2.63, respectively. This shows that the source of emissions of the BTEX compounds into the atmospheric air (vehicle traffic) in the monitored area is situated at the same distance from the monitoring station. Moreover, the values of the (m,p)-Xyl/Et.benz parameter which were designated for Sopot may lead to the conclusion that the intensity of the source of emissions of the BTEX compounds (vehicle traffic) is more balanced than in the case of data obtained for Tczew.

3.3 Concentrations of selected inorganic compounds CO, NO_2, SO_2 in the monitored urban areas in the period 2013-2014.

Table 2 presents information about the average annual levels of the content of selected inorganic compounds determined in the atmospheric air in the monitored areas – Tczew and Sopot in 2013-2014. The summary takes into account the division of the research results obtained into two basic time periods: the heating season (autumn-winter) and the summer season. Automatic analysers installed at the monitoring stations which were used in the studies for determining inorganic compounds in the atmospheric air make it possible to obtain information connected with the concentration of a given inorganic compound at one-hour intervals. To better interpret and present the results obtained, Figure 4 presents the levels of

the NO_2, SO_2 and CO content determined in the atmospheric air in the monitored areas in the form of average monthly concentrations.

As regards information summarized in Table 2, it can be noticed that the values of the annual average concentrations of inorganic compounds determined in the atmospheric air in Tczew were higher than in Sopot, virtually throughout the research period. This can be caused by the fact that the monitoring station is situated in close vicinity of the main urban traffic node and a company dealing with a system of waste collection and management, where trucks with diesel engines are used.

The annual average concentration of nitrogen oxides determined in the air is an exception in the areas monitored in 2014, which was higher in Sopot than in Tczew. The occurrence of such a phenomenon can be caused by a higher intensity of use of vehicles powered by combustion engines in close vicinity of the monitoring station in Sopot. Another reason, which results from the fact that Sopot is one of the most popular seaside resorts and spa cities situated in Poland can be a seasonal increase (especially in the summer) in the number of vehicles with internal combustion engines in the monitored area.

While interpreting data presented graphically in Figure 4 and in Table 2, it can be noticed that both in Tczew and in Sopot in the heating season (the autumn and winter period), the average annual concentrations of inorganic compounds determined in the atmospheric air were much higher than in the summer. The process of liquid fuel combustion in internal combustion engines of vehicles is main source of emissions of nitrogen oxides and carbon monoxide into the atmospheric air in urbanized areas. Just as in the previously described phenomenon of benzene emissions into the atmospheric air, also in this case the quantity of determined inorganic compounds (especially carbon monoxide resulting from incomplete combustion of organic compounds) released into the air, is influenced by the optimal temperature of liquid fuel combustion in the engine of a vehicle, an increase in the fuel density resulting from lower air temperatures and the method of using the vehicle in the autumn and winter period. Moreover, the quantity of carbon monoxides in the atmospheric air in the urbanized area is influenced by the use of low-performance tiled stoves or furnaces where the solid fuel (coal) burning process may not be complete. A comparison of the values of carbon monoxide concentrations determined in the atmospheric air in monitored areas reveals a clear difference between the heating season and the summer season. In the case of atmospheric air in Tczew in the period of research, the carbon monoxide concentrations in the summer were on average by 40% lower than in the heating season. The interpretation of data on carbon monoxide

concentrations in the atmospheric air in Sopot shows that carbon monoxide concentrations are on average by 30% lower in the summer than in the heating season.

In very rare cases in urbanized areas, vehicles can also be a source of SO_2 emissions. However, the condition must be met that the fuel used in vehicles is contaminated with sulphur compounds. Interpretation of data summarized in Table 2 shows that sulphur dioxide concentration in the atmospheric air in Tczew and Sopot is very low. This can result from the fact that high-quality liquid fuels are used in vehicles, which are virtually free from sulphur compounds. The presence of sulphur compounds in the atmospheric air in urbanized areas can also result from burning low-quality coal contaminated with sulphur compounds. Such fuels can be used for heating houses or flats using low-performance tiled stoves or furnaces. Due to the fact that such buildings are situated in close vicinity of the monitoring station in Tczew, the average annual concentrations of SO_2 in atmospheric air are higher than in Sopot. This thesis is also confirmed by higher concentration of SO_2 in the atmospheric air in Tczew than in Sopot also in the heating season (the autumn and winter period).

3.4 Multivariate statistical data mining to detect relationships between measured chemical compounds and identification of potential emission sources in the monitored urban area

As already mentioned to determine potential anthropogenic sources of emissions of chemical compounds determined in the atmospheric air in the monitored areas, Hierarchical Cluster Analysis (HCA) was applied. This multivariate statistical analysis involving the grouping of variables or objects described by the variables (obtained from research results) made it possible to obtain information on the occurrence of relationships between the results obtained from the two monitored areas situated at a considerable distance from each other and differing in topography of the area around the monitoring station.

In the first case, Hierarchical Cluster Analysis was separately performed on the input data sets from Tczew and Sopot. The goal was to find links between variables (values of chemical compound concentrations determined). The output of the clustering aimed to interpret potential sources of emissions of chemical compounds determined in the atmospheric air in both monitored areas. Figure 6 presents graphically the clustering results for variables in Sopot and in Tczew in the years 2013-2014. The information presented in Figure 5 shows that 2 main clusters have been formed. Cluster 1 includes the chemical features toluene, ethylbenzene, o-xylene, p, m-xylene and sum of xylenes and, additionally, the temperature

being rather an outlier that member of cluster K1; Cluster 2 (K2) consists of the chemical variables benzene, NO_2, SO_2, CO. It could be concluded that there is a clear separation between organic pollutant sources (combustion sources – wood and coal or activity of local industrial centres) and inorganic pollutant sources (transport vehicles, soil and road dust). The inclusion of benzene into the group of inorganic pollutant sources results from the fact that vehicle traffic and the use of low-performance tiled stoves or furnaces in old buildings belong to main sources of emissions of this compounds. Moreover, this can lead to the conclusion that a potential increase in the activity of sources of emission of inorganic compounds into the atmospheric air may also influence an increase in the benzene content.

In order to confirm the results discussed above PCA was additionally carried out. Table 3 presents the results of the analysis for all data obtained from the monitoring tests in Sopot and Tczew from 2013 to 2014 (factor loadings table). The results listed in the Table 3 clearly indicate the role of 3 latent factors (PCs) which explain almost 90% of the total variance: PC1 – organic factor containing ethylbenzene, o-xylene, p, m-xylene and sum of xylenes, PC2 – inorganic factor reversely correlated to the temperature containing NO_2, SO_2, CO and as it was presented earlier benzene, PC3 – toluene factor with a separate impact.

For the PC2, the occurrence of the inverse relation between the content in the atmospheric air of chemical compounds (benzene, NO_2, SO_2, CO) and the air temperature, confirms, in principle, the output of the cluster analysis that a decrease in the temperature causes an increase in the intensity of sources of emissions of benzene, NO_2, SO_2 and CO into the atmospheric air. As it was mentioned before, these anthropogenic sources of emissions whose intensity depends on the season of the year (heating season) include, amongst other things, vehicle traffic (with internal combustion engines) and the low operational efficiency of the heating system in closed rooms where poor quality coal can be used as the fuel. Identification of a separate factor related only to the toluene content (PC3) in the atmospheric air in the monitored area may result from the fact that this compound comes probably from many sources of emission characterized by a varying degree of intensity, such as: activity of industrial centres situated near the monitoring stations, commercial plants, vehicle traffic involving cars with internal combustion engines, the use of low-performance tiled stoves or furnaces, petrol stations, rail traffic - diesel engines. Moreover, toluene is also commonly used in various branches of industry as a basic solvent at many production stages.

Next step in multivariate statistical data mining was clustering of the objects of observation (measuring points in different sampling seasons). Figure 6 presents graphically the results of hierarchical clustering of the individual periods of sample collection in the years 2013-2014.

It is clearly seen that two major clusters are formed for significance level 2/3 D_{max} and three clusters – for significance level 1/3 D_{max}. In both situations there is distinct separation between winter samples (C1, C2, C3, C12, C13, C14, C15, C24 – all events from January, February, March and December for both years of observation) which form one of the clusters and summer samples (which include also autumn and spring observations). Special exception is November – November 2014 (C_23) belongs to the typical winter cluster while November 2013 – to the summer grouping (C_11). This separation is traditional for studies where seasonal properties are sought. In the case of the Tczew area a very well defined winter cluster is formed. As for the cluster created for the Sopot area, again two major sub-clusters are formed. In this location, however, the well expressed group of winter samples (C1, C2, C3, C4, C12, C13, C14, C15, C16, C24) also includes autumn events (C10, C11, C22, C23). For this location the seasonal pattern "winter" involved also months from late autumn. The second cluster consists of the remaining sampling events from summer and spring.

In general, the seasonal separation at both locations is very similar but, probably, due to meteorological and geographical conditions there is a slight difference in the grouping patterns. The major conclusion is that winter – summer seasonal separation is observed and proven. The winter – summer patterns are, in general, kept. There is also a relatively well expressed spatial separation between both locations – the Tczew and Sopot areas.

4. Conclusions

Result of determination of BTEX and CO, NO_2, SO_2 in the period from January 2013 to December 2014, to assess the quality of atmospheric air in two cities situated in northern Poland - Tczew and Sopot, were compared. The interpretation of the results of the monitoring research obtained and the use of basic statistical and parametric tools allowed preliminary identification of potential sources of emissions of pollutants into the atmospheric air in the monitored areas. The use of basic statistical tools made it possible to conclude that the pollutants determined in the atmospheric air (both in Tczew and in Sopot) can be classified in two main groups: the so-called inorganic group including concentrations of NO_2, CO, SO_2 and benzene and the so-called organic group including the concentrations of toluene, ethylbenzene and xylenes.

For Tczew, a medium-industrialized city, vehicle traffic involving cars with internal combustion engines has the main influence on the concentrations of benzene, ethylbenzene, xylenes, CO and NO_2. This results from the fact that the monitoring stations is located in very

close vicinity of the main urban traffic node where the traffic is very often slowed down or stopped. Furthermore, as a result of the research, it was found that the level of the benzene and SO_2 content in the atmospheric air in Tczew can be significantly influenced by low-performance tiled stoves or furnaces in old residential buildings which use low-quality coal. Additionally, the very close location of recreational allotments and a plant dealing with the collection and management of different types of solid waste may also influence an increase in concentrations of the BTEX compounds, CO, SO_2 and NO_2 in the atmospheric air in the Tczew. Based on the interpretation of the results of statistical analysis, it was also concluded that the level of toluene in the atmospheric air can be influenced by other, additional sources of emissions such as rail traffic (diesel engines), the activity of industrial plants or commercial plants.

As regards, the atmospheric air quality in the resort city of Sopot, the traffic of vehicles with internal combustion engines is the main source of emissions of the BTEX compounds and NO_2, CO and SO_2. However, according to the research conducted and interpretations of the results obtained, it can be concluded that the intensity of the influence of mechanical vehicles on the quality of atmospheric air in Sopot is lower than in Tczew. This can result from the fact that the measuring station in Sopot is not located in close vicinity of the city's main traffic node. Moreover, during the interpretation of the results of the research, it can be concluded that the influence of the activity of low performance individual heating systems in old buildings or apartments (tiled stoves or furnaces), or large industrial centres on the atmospheric air quality in Sopot is negligible. Additionally, lower levels of the content of chemical compounds determined in Sopot than those determined in the atmospheric air in Tczew are result from the close vicinity of the Baltic Sea. This is probably related to the influence of the sea breeze on the type and quantity of pollutants in the atmospheric air. Despite the fact that Sopot is one of the most popular resorts and spa cities in Poland and it is visited by lots of tourists from Poland and abroad (who very often use cars), it does not have a significant influence on the quality of atmospheric air in terms of the level of the content of the BTEX compounds and NO_2, SO_2 and CO.

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Conflict of interest

The authors have declared no conflict of interest.

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7. Figure captions

Figure 1. Location of the air quality monitoring stations AM6 in Sopot and (AM7) in Tczew, Poland.

Figure 2. The average monthly time-weighted benzene concentration determined in the atmospheric air in the period 2013-2014 in the Tczew and Sopot area.

Figure 3. The average monthly time-weighted toluene, ethylbenzene and sum of xylenes concentration determined in the atmospheric air in the period 2013-2014 in the Tczew and Sopot area.

Figure 4. The monthly average concentrations of inorganic compounds – NO_2, SO_2 and CO determined in the atmospheric air in the period 2013-2014 in the Tczew and Sopot area.

Figure 5. Clustering of variables for Sopot and Tczew data obtained in the period 2013-2014.

Figure 6. Clustering of sampling events from Sopot and Tczew data obtained in the period 2013-2014 where: C_1 is January 2013, C_2 – February 2013 and so on till C-24 – December 2014.

Supplementary Figure 1. Annual wind rose in Sopot and Tczew area in the period 2013-2014.

Table 1. The average BTEX inter-species concentration ratios in the monitoring urban area (Tczew and Sopot) in the period 2013-2014

The average BTEX inter-species ratios in the monitoring area in 2013				
Sampling area	**Benzene**	**Toluene**	**Ethylbenzene**	**Sum of Xylenes**
Tczew	0.76	2.24	1	4.48
Sopot	2.30	5.88	1	4.20
Sampling area	***Tol/Benz***	***(m,p)-Xyl/Benz***	***o-Xyl/Benz***	***(m,p)-Xyl/Ethylbenz***
Tczew	2.96	4.02	1.90	3.04
Sopot	2.56	1.17	0.65	2.70
The average BTEX inter-species ratios in the monitoring area in 2014				
Sampling area	**Benzene**	**Toluene**	**Ethylbenzene**	**Sum of Xylenes**
Tczew	1.23	2.82	1	3.98
Sopot	2.42	4.29	1	4.07
Sampling area	***Tol/Benz***	***(m,p)-Xyl/Benz***	***o-Xyl/Benz***	***(m,p)-Xyl/Ethylbenz***
Tczew	2.29	2.22	1.01	2.74
Sopot	1.77	1.08	0.59	2.63

Table 2

Table 2. Annual average concentration of measured inorganic compounds in atmospheric air over the monitoring urban area in the period 2013-2014.

Concentration of measured inorganic compounds in atmospheric air in 2013						
Parameter	**NO_2 [μg/m^3]**		**SO_2 [μg/m^3]**		**CO [μg/m^3]**	
	Tczew	**Sopot**	**Tczew**	**Sopot**	**Tczew**	**Sopot**
Average ± SD	14.1 ± 2.6	12.2 ± 2.9	6.0 ±2 .1	5.2 ± 1.8	385 ± 108	299 ± 57
Median	13.8	12.5	5.4	4.6	365	285
Max	18.8	17.0	10.0	9.3	582	376
Min	9.4	8.0	3.8	3.4	256	212
Average heating season ± SD	15.6 ± 2.1	14.2 ± 1.8	7.3 ± 1.9	6.3 ± 1.6	458 ± 80	336 ± 42
Average summer season ± SD	12.0 ± 1.6	9.4 ± 1.2	4.3 ± 0.5	3.7 ± 0.3	282 ± 15	248 ± 25
Concentration of measured inorganic compounds in atmospheric air in 2014						
Parameter	**NO_2 [μg/m^3]**		**SO_2 [μg/m^3]**		**CO [μg/m^3]**	
	Tczew	**Sopot**	**Tczew**	**Sopot**	**Tczew**	**Sopot**
Average ± SD	13.0 ± 3.1	13.8 ± 4.9	4.9 ± 1.2	4.8 ± 2.0	330 ± 114	317 ± 93
Median	13.8	13.5	4.9	4.6	330	301
Max	17.1	25.4	7.6	8.9	541	528
Min	8.1	8.3	3.3	2.3	168	215
Average heating season ± SD	15.4 ± 1.4	16.5 ± 4.5	5.7± 1.0	5.7 ± 2.0	405 ± 80	367 ± 91
Average summer season ± SD	10.3 ± 2.0	10.0 ± 1.9	3.9± 0.6	3.6 ± 1.1	225 ± 47	247 ± 31

SD – standard deviation

Table 3. Factor loadings for all data combined from Tczew and Sopot area (marked loadings are statistically significant)

	Factor - 1	Factor - 2	Factor - 3
Benzene	0.057	**0.725**	0.556
Toluene	0.225	0.071	**0.923**
Etylbeznene	**0.973**	-0.005	0.158
o-Xylene	**0.970**	-0.072	0.099
P,m-Xylene	**0.993**	-0.034	0.074
Sum of Xylenes	**0.995**	-0.046	0.083
NO_2	0.015	**0.882**	0.159
SO_2	-0.120	**0.891**	-0.217
CO	0.032	**0.912**	0.179
Temperature	0.127	**-0.897**	-0.007
Expl.Var	3.949	3.747	1.312
Prp.Totl	39.5%	37.5%	13.1%

* only statistically significant loadings are marked by bold

Figure 1

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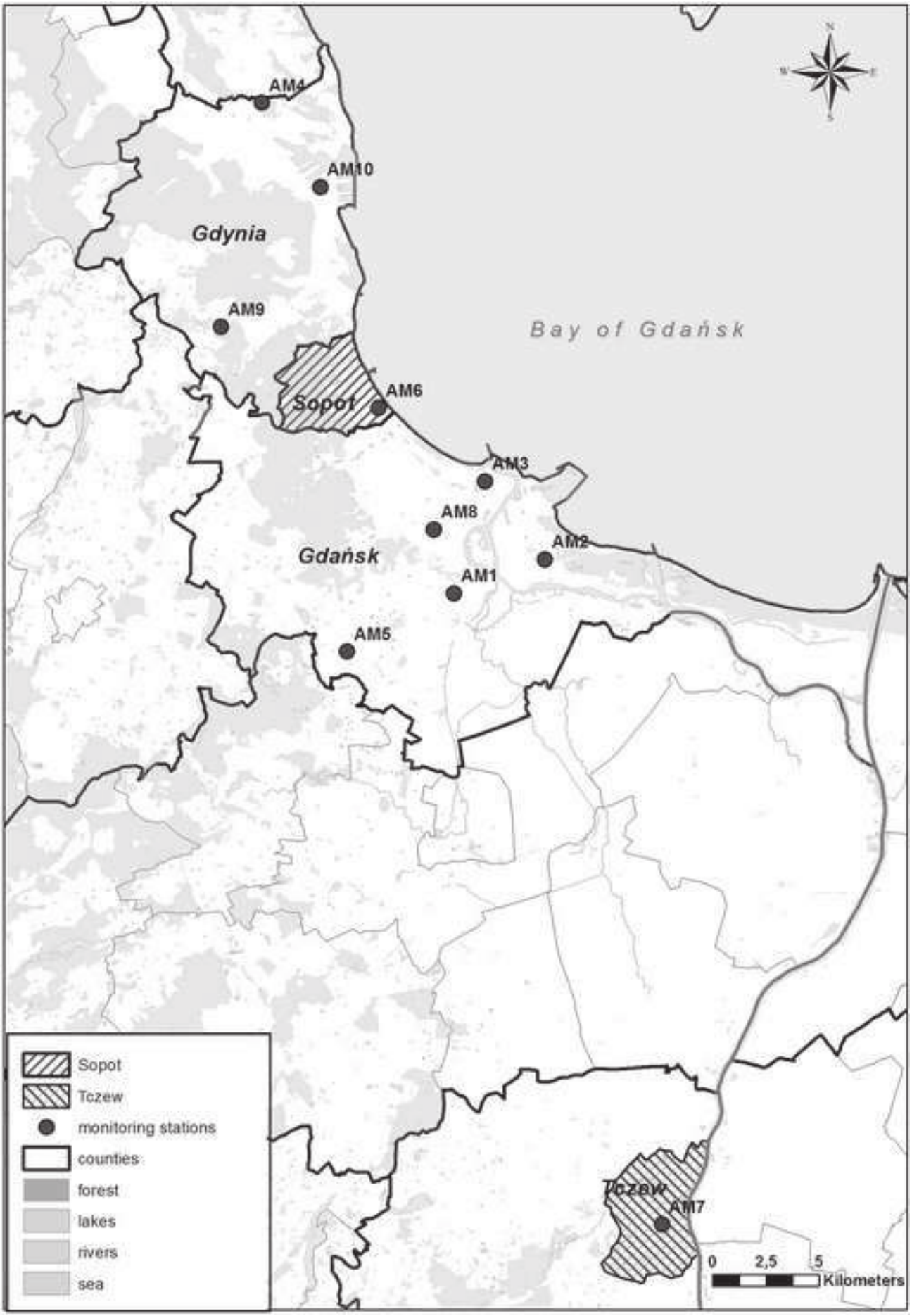

Figure 2

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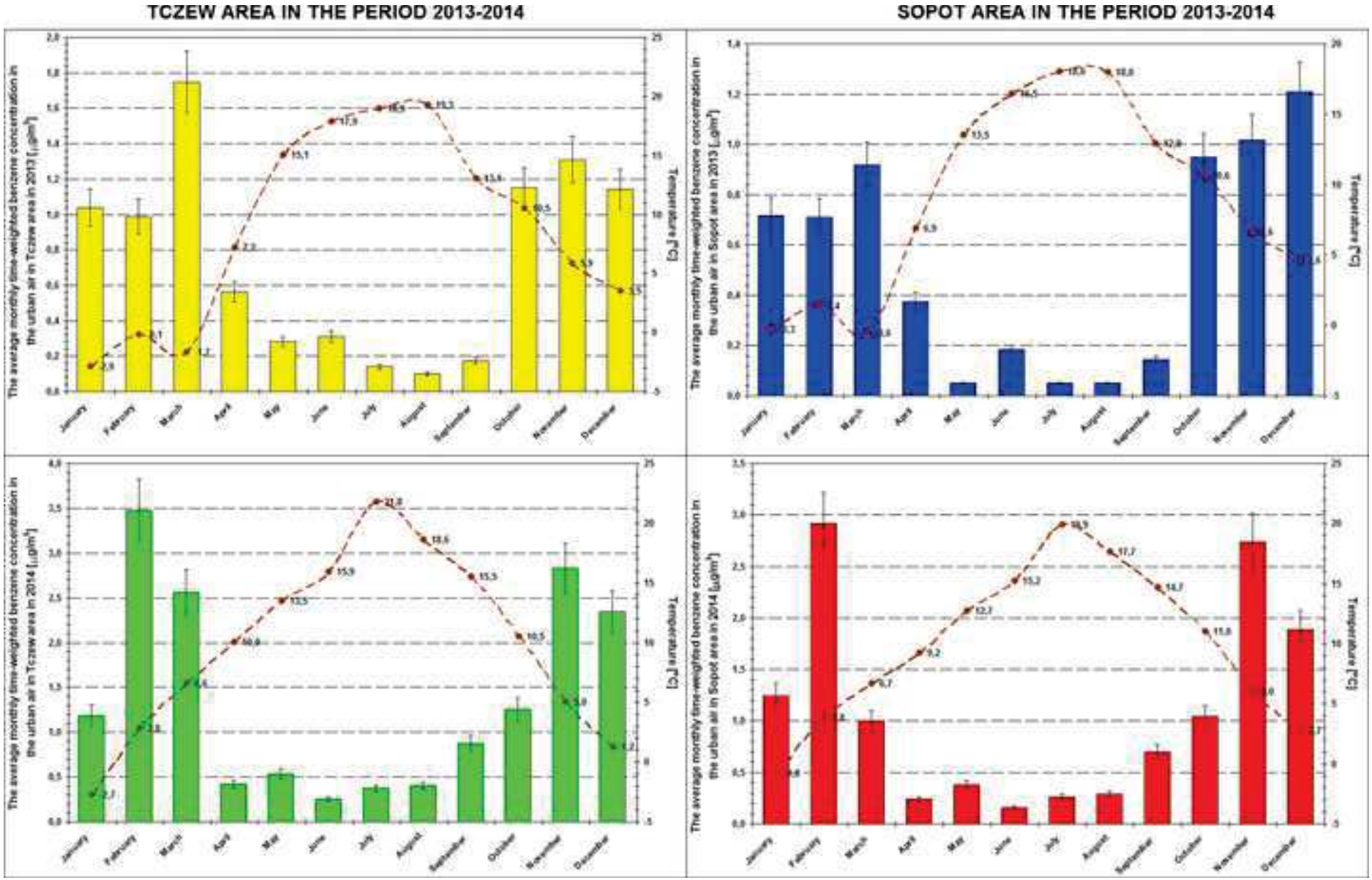

Figure 3

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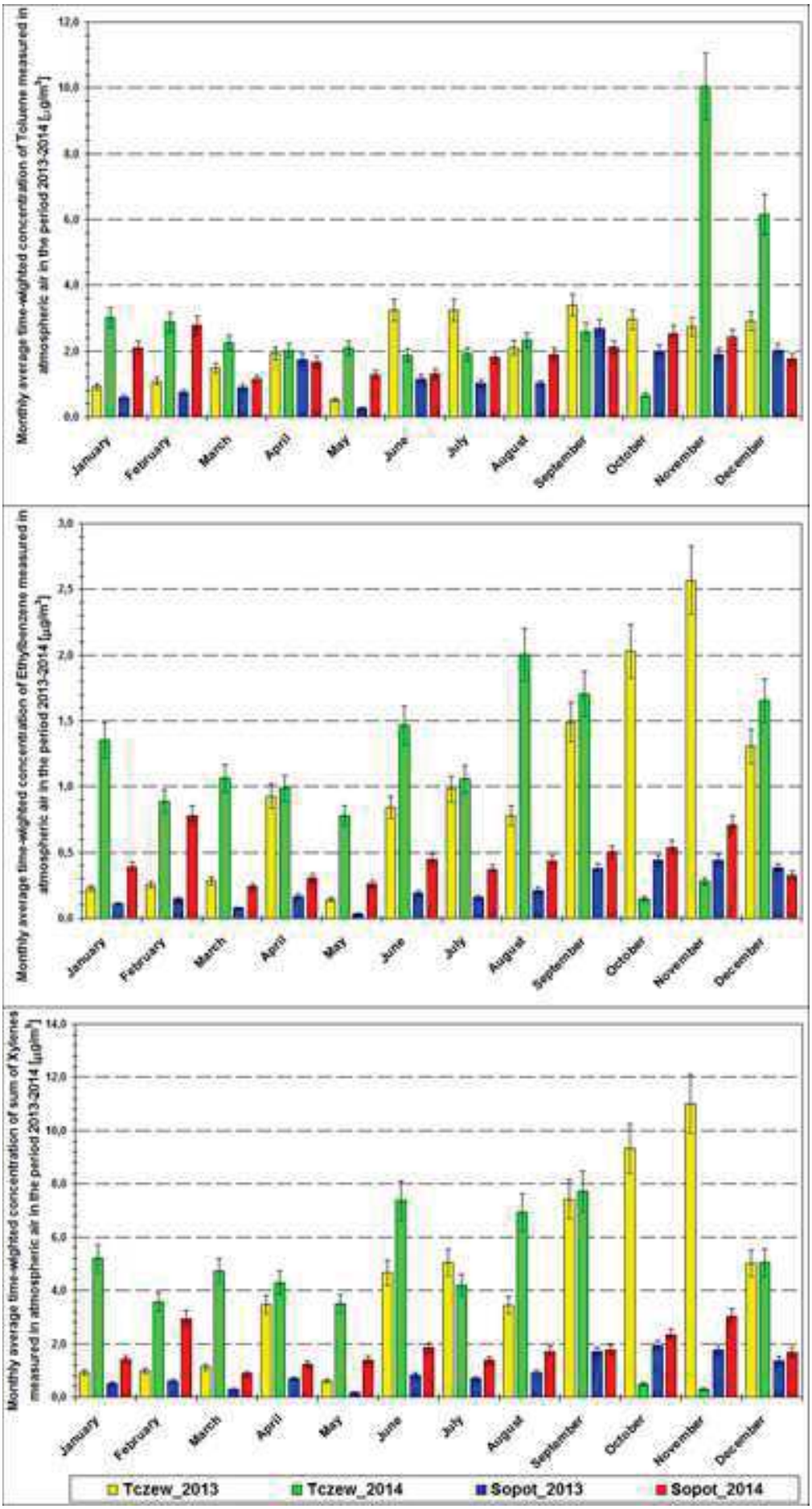

Figure 4

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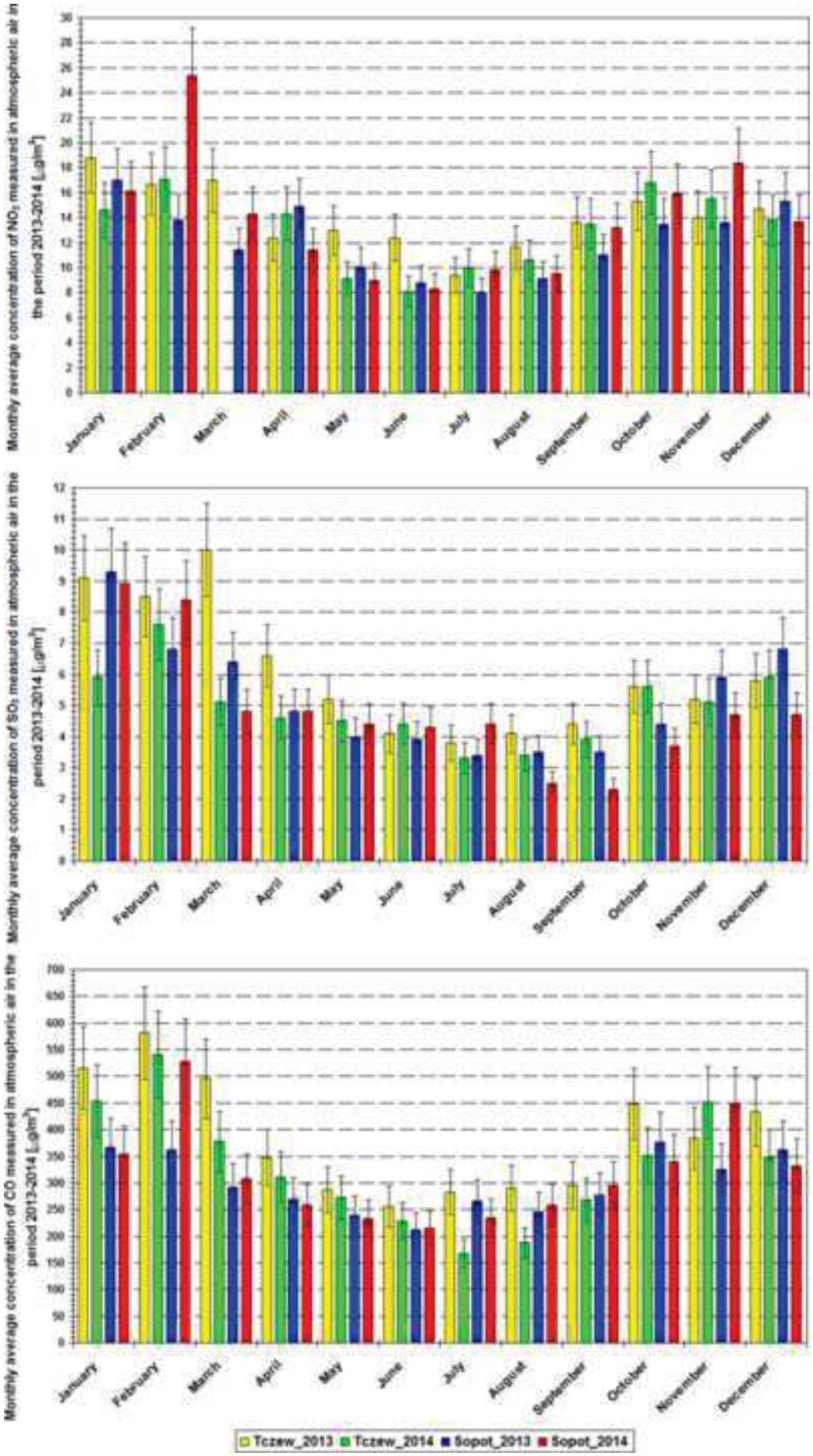

Figure 5
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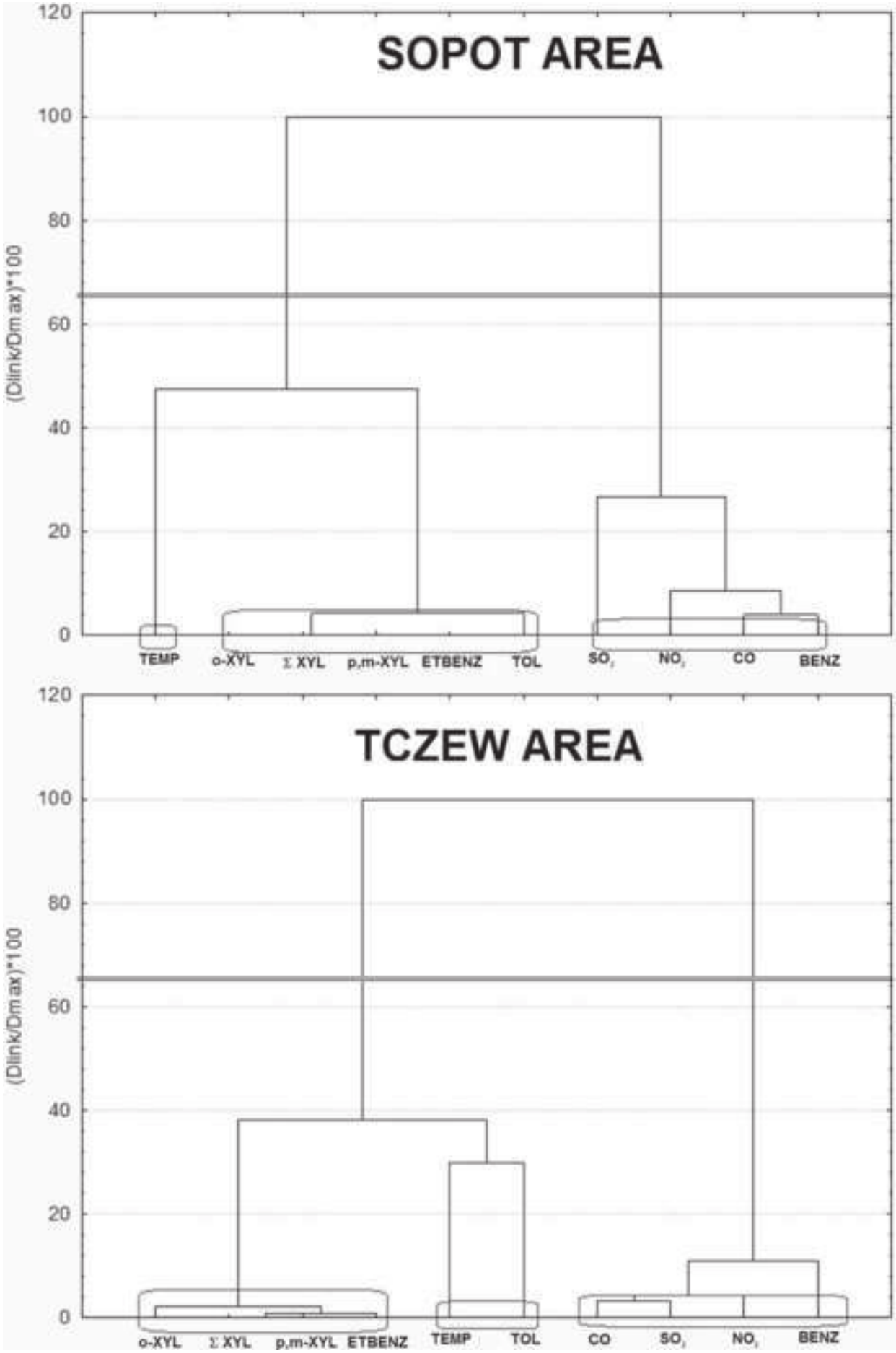

Figure 6
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