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CHANGES IN THE POLLUTION OF LODZ VOIVODSHIP RAINWATER AS A RESULT OF CHANGES IN POLLUTANT IMMISSIONS

Abstract
Increasing urbanization rates, particularly in cities, cause an increase in pollutant emissions into the environment. Immission of pollutants is the amount of particulate or gaseous pollutants that is received by the environment. Natural precipitation, i.e. rainwater, is polluted during the contact with air. As a result of atmospheric precipitation groundwater and soil become polluted. The pollutants also penetrate surface water, causing further contamination. In rainwater that goes to the sewage system, there are pollutants such as hydrocarbons, heavy metals, slurries, plant protection products and many more. This is largely dependent on the type of management of the catchment, its sanitary condition, and the time and intensity of precipitation. Another important factor is the composition of pollutants emitted into the atmospheric air in each area. The work shows changes in the pollution of rainwater in Lodz Voivodship in the years 2010-2016 and presents analysis of the data collected by the Regional Inspectorate for Environmental Protection. The analysis shows that the state of rainwater is steadily deteriorating which is directly related to air quality.

Keywords
air quality, emission, immission, rainwater pollution

Introduction
According to the classical concept, atmospheric air is a colourless and odourless mixture of gases and aerosols forming a heterogeneous layer called the Earth's atmosphere [1]. The composition of dry and clean air is as follows: nitrogen (78.08%); oxygen (20.95%); argon (0.93%); carbon dioxide (ca. 0.036%); noble gases, hydrogen and methane (0.004%); water vapour (in variable amounts).

Any substances introduced into the air and causing changes in its permanent composition are considered as pollutants. They may threaten human and animal health as well as soil and water environment. More and more often, their source are human activities. The main source of anthropogenic emissions of pollutants into the air is the combustion of solid, liquid and gaseous fuels. Depending on the way in which pollutants are emitted into the air, three types of emission sources can be distinguished [2-7]:

- point emission sources – high chimneys in large buildings, from which pollutant plume is raised to a considerable height and dispersed;
- line emission sources – groups of point sources located along straight lines, most often represented by road, rail and water transport, where emissions from individual emitters add up along communication routes;
- surface emission sources – emission sources with a height of several orders lower than the occupied area, which include mainly residential areas with individual heating systems, but also agricultural areas, landfills, mine heaps and open-pit mines.

Pollutants emitted into the atmosphere as a result of wet deposition get to the hydrogeochemical circulation and together with atmospheric precipitation fall to the earth surface penetrating it [8-12]. The chemical composition of atmospheric precipitation depends on pollutants contained in the air and meteorological conditions prevailing in the area [13-17]. The main meteorological factors affecting the spread of pollutants in atmospheric air are temperature, pressure, wind speed, thermodynamic equilibrium of the atmosphere and air humidity [18-22]. Lodz Voivodship is located in central Poland where variable meteorological conditions occur. The inflow of humid maritime polar air mass from the south-west directions dominates. Periodically, the circulation changes, and dry continental air mass from Russia, from the eastern direction, advances into the country. Due to the topography in the area of Lodz Voivodship there are also changeable conditions of pollutant dispersion in the air [23]. Although in the vicinity of Lodz there are mostly uplands, the main city of the region, i.e. Lodz, is not free of smog episodes. During the year, there are about 50 smog days in Lodz, i.e.
the days when permissible concentrations are exceeded – PM10 particulate matter in this case [24-28]. A particular increase in the concentration of this pollutant is observed at low temperatures, low wind speed, low pressure and high air humidity. These are characteristic features of the so-called “Polish smog” [29] which differs significantly from the London smog widely described in the literature.

The term "Polish smog" is a neologism, because until now such a concept in professional literature has not been used. It was created to distinguish the phenomenon appearing more and more often in Polish cities, from the well-known in the literature and repeatedly described acid smog and photochemical smog [30-34]. The "Polish smog" differs mainly from those mentioned earlier – it consists primarily of particulate particles – both PM10 and PM2.5, as well as PM1 and numerous polycyclic aromatic hydrocarbons, including benzo(a)pyrene. So, another term – "dust smog" can also be used. These pollutants are typical for the combustion of solid fuels in low-efficiency furnaces, in the absence of exhaust gas cleaning systems, in other words, household furnaces. Using a broader definition, the basic cause of poor air quality in Polish cities is called "low emission", i.e. emissions from household heating systems fired by solid fuels and from traffic, in particular vehicles operated without catalysts. If we add to this inversion phenomena relatively frequent in Poland during the winter period (e.g. after frost and eastern circulation of the West warmer polar sea masses, or weather periods with high pressure, lack of cloudiness and low wind), it appears that in many areas of the country there are excellent conditions for the formation of smog, above all "dusty", but sometimes also acid smog. The characteristic feature of the "Polish smog" is its formation at high-altitude weather and negative air temperatures. In winter, this is often associated with cloudless weather, causing significant temperature drops and inversions at night. In addition, at low temperatures there is a growing demand for heat, hence the increased emissions of pollutants from individual heating systems. A result is dust concentration in the lower part of the atmosphere, repeatedly exceeding the permitted levels or "dust smog". An interesting fact is that most often it is not accompanied by exceeding the permissible concentrations of SO2 or CO, typical for acid smog.

However, not only the "low emission" is a source of air pollution in Poland. The largest coal-fired power plant in Europe (and the largest brown-coal power plant in the world) is located in the Lodz Voivodship, the third in the world in terms of installed capacity in coal-fired power plants. Annually, its emitters bring into the air approximately 30 000 Mg SO2, 27 800 Mg NOx, 21 400 Mg CO and about 780 Mg dust. Apart from the power station in Belchatów, the major sources of emissions of the above mentioned pollutants are plants in Lodz (approximately 4 100 Mg SO2) as well as in Piotrków Trybunalski, Zgierz, Sieradz, Pabianice, Zduńska Wola and Skierniewice emitting annually from 280 to 420 Mg SO2. These objects also have a significant impact on the state of air pollution in the province, and most likely also on the chemistry of atmospheric precipitation.

The study presents analysis of the data collected by the Regional Inspectorate for Environmental Protection in Lodz in the years 2006-2016 regarding emissions and immission of sulphur dioxide SO2 and nitrogen oxides NOx (NO and NO2). The amount of atmospheric precipitation and its chemical composition were also analyzed. Particular attention was paid to four substances: sulphates, chlorides, nitrates and nitrates as the expected effects of acidification of precipitation by SO2 and NOx emissions.

Research and results
In Lodz Voivodship the Regional Inspectorate for Environmental Protection carries out continuous measurements of air quality at 9 automatic stations and 19 manual stations. The following substances are measured: sulphur dioxide, nitrogen oxides, carbon monoxide, ozone, benzene, benzo(a)pyrene and particulate matter PM10 and PM2.5. The main components of the “Polish smog” are dust in various forms: suspended particulate matter with a particle diameter below 10 µm, respirable dust with a particle diameter below 2.5 µm and soot particles with a diameter below 1 µm. Additionally, in cooperation with the Institute of Meteorology and Water Management at the monitoring station in Sulejów, measurements of rainwater quality are carried out. On the basis of the collected air quality data, the Regional Inspectorate for Environmental Protection in Lodz runs an air quality portal where residents can obtain information about the current air quality. It is graded on a 6-point scale from very bad to very good. On the basis of the collected data, an annual assessment of air quality in the Voivodship is also prepared. In Figures 1 and 2 below, the location of air quality monitoring stations in the Lodz region is presented.

In Lodz Voivodship the meteorological data were analyzed in two stations: Lodz and Sulejow. The wind rose for these stations is shown in Fig. 3 and 4.
The measuring station in Lodz is equipped with analyzers for continuous measurement of such pollutants as PM10, SO$_2$, NO, NO$_2$, O$_3$ and CO and benzene, NO$_x$ and PM2.5. All measurements are based on reference methods recognized by the European Commission [37]:

- for PM10 this is the weakening of beta radiation (the method equivalent to the reference method);
- for SO$_2$, this is ultraviolet fluorescence conforming to the PN-EN 14212:2013-02 (EN 1412:2012) method [38];
- for NO and NO$_2$, this is chemiluminescence, according to the PN-EN 14211:2013-02 (EN 14211:2012) method [39];
- for O$_3$, this is ultraviolet photometry, according to the PN-EN 14625:2013-02 (EN 14625:2012) method [40];
- for CO this is non-dispersive infrared spectroscopy, according to the PN-EN 1426:2013-02 (EN 14626:2012) method [41].

Based on the collected data, the values of sulphur dioxide emission in the discussed period were analyzed. Figure 5 shows the distribution of point, surface and line emissions in the years 2009-2016. It is easy to notice that the line emission in the analyzed period was practically constant, its average value in the analyzed period was about 750 Mg/year. In the case of surface emissions in 2005 and 2006, there was a slight increase. The
The highest emission values were recorded for point emission, which in 2016 drastically decreased to around 130,000 Mg/year.

Changes in nitrogen oxide emissions in 2006-2016 were also analyzed (Fig. 6). As in the case of sulphur dioxide emissions, the highest values were recorded for point emissions, which started to decrease since 2014. A similar trend was observed for surface and line emissions, which also decreased at the end of the analyzed period.

The next stage of the analysis is the comparison of immission data for sulphur dioxide and nitrogen oxides. For sulphur dioxide, a large decrease in the value of recorded concentrations was noted. In the initial period, the average concentration of this pollutant was about 20 µg/m$^3$ (Fig. 7), and in the final one 6 µg/m$^3$. Nitrogen oxides showed a stable tendency and their concentration was about 20 µg/m$^3$ (Fig. 8).

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**Fig. 5.** SO$_2$ emission in the years 2006-2016 in Lodz Voivodship
*Source: Author’s*

**Fig. 6.** NO$_x$ emission in the years 2006-2016 in Lodz Voivodship
*Source: Author’s*

**Fig. 7.** SO$_2$ immission in the years 2006-2016 in Lodz Voivodship
*Source: Author’s*

**Fig. 8.** NO$_x$ immission in the years 2006-2016 in Lodz Voivodship
*Source: Author’s*

**Fig. 9.** Chemical composition of rainwater in the years 2006-2016 in Lodz Voivodship
*Source: Author’s*
Figure 9 shows chemical composition of atmospheric precipitation. In the analyzed period, the concentrations of chlorides, nitrites and nitrates remained at a constant level and did not exceed 1.5 mg/dm$^3$. The concentration of sulphates was more than twice as high as other pollutants, although since 2009 it has been falling.

In the analyzed period, the pH value systematically increased from approximately 4.80 up to 5.80 (Fig. 10). This value indicates a decreasing, but still occurring acidity of atmospheric precipitation, which may cause soil degradation and, consequently, a decrease in soil sorption properties and its fertility. The pH value of rainwater was not related to the annual precipitation total (Fig. 11). The highest annual precipitation total was recorded in 2014. During this time, the pH value decreased, compared to previous years.

**Summary and conclusions**

The Lodz Voivodship is not one of the most polluted areas in Poland, although the largest point source of pollutant emissions in Poland is located in the region – the Belchatów power plant. As part of this work, it was decided to analyse changes in both the point as well as linear and surface emissions of pollutants from 2009-2016 and to check whether emission changes had an impact on the chemistry of atmospheric precipitation recorded during the analysed period. The subject of analysis were the data of the Regional Inspectorate for Environmental Protection and Institute of Meteorology and Water Management monitoring station in Sulejów for the above-mentioned period.

The analysis showed that in the discussed period of 2009-2016, the point emission of sulphur dioxide and nitrogen oxide in Lodz Voivodship decreased. In the case of sulphur dioxide, surface and line emissions remained on a similar level, while for nitrogen oxides there was a significant increase in the line emission. However, this did not affect this pollutant immission which remained constant. The values of pollutant emissions and immissions are reflected by the chemical composition of rainwater. The concentrations of sulphates decreased in the analyzed period, while those of chlorides, nitrites and nitrates changed only slightly.

Based on these data, it can be concluded that main pollutants emitted to the atmosphere that have an impact on the chemical composition of atmospheric precipitation in the Lodz Voivodship, are sulphur dioxide and other sulphur compounds. The total reduction of emissions of acid gases such as SO$_2$ and NO$_x$ results in a decrease in acidity (i.e. increase in pH) of atmospheric precipitation. Therefore, it is confirmed that there is a causal relationship between the emission and immission of these pollutants as well as the chemical composition (and in particular the pH values) of atmospheric precipitation.

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