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ORIGINAL ARTICLE

Polycyclic Aromatic Hydrocarbons (PAHs) in the atmosphere of the Baltic Sea Region

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Abstract *– The paper presents a review of publications on the concentrations of polycyclic aromatic hydrocarbons (PAHs) in the atmosphere of the Baltic Sea Region (BSR). It indicates the main emission sources of these substances, related to anthropogenic activity. These include incomplete combustion of fuels in engines on land and from marine transportation, as well as the burning of coal in the community sector. High PAH concentrations in the air are also related to increased industrial activity in urban areas. In the Baltic Sea Region, Germany and Poland have been determined to be responsible for the greatest proportion of PAH emissions. However, the highest number of exceedances of the accepted annual norm for benzo(a)pyrene concentrations was recorded in Poland.*

Keywords *- Atmospheric pollution, Polycyclic aromatic hydrocarbons (PAHs), Baltic Sea Region*

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Introduction

The atmosphere is a participant in the global circulation system of carbon in the nature, and an important factor influencing changes in the chemical composition of the atmosphere is human activity. Technological development and rapid growth of the global population since the beginning of the industrial age, coupled with the consumptive lifestyles of many people, are effecting a rise in environmental pollution. This concerns the atmosphere among other components of the environment. Global industry is largely based on natural energy resources, such as fossil fuels. They are the basis for the development of energetic industry, enabling the mechanization and automation of work. Apart from that, the significance of fossil fuels is also enormous for transportation and the community sector. In developed countries, the burning of fossil fuels is the main source of pollution in the atmosphere and it causes, among other things, a rise in the concentration of greenhouse gases (i.e. carbon dioxide, methane and carbon oxide). At the beginning of the industrial era, in 1850, the concentration of CO_2 in the air was about 280 ppm. It has been growing continuously since then, reaching over 401 ppm in December 2015 (www.esrl.noaa.gov).

Carbon compounds present in aerosols can also be found in the atmosphere along with the above-mentioned gases. In the coastal zone of the southern Baltic Sea organic carbon may make up more than 50% of aerosols mass (Lewandowska and Falkowska 2013). Among these, polycyclic aromatic hydrocarbons (PAHs) have attracted the most attention in recent years, having been recognized as toxic and harmful for human health by such international organizations as the World Health Organization (WHO), the Helsinki Convention (HELCOM) or the United States Environmental Protection Agency (US EPA). From among over 100 polycyclic aromatic hydrocarbons (PAHs) the most toxic are: acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(e)pyrene, benzo(b)fluoranthene, benzo(j)fluoranthene, chrysene, benzo(k)fluoranthene, benzo(g,h,i)perylene, dibenzo(a,h)anthracene, fluoranthene, fluorene, phenathrene, pyrene, indeno-(1,2,3-cd)pyrene (Papageorgopoulou et al. 1999). Polycyclic aromatic hydrocarbons never occur singly in the environment, but always in a mixture. The presence of one in the air indicates the presence of other PAHs. In the atmosphere, under the influence of solar radiation and in the presence of ozone, nitric oxides and sulphur oxides, PAHs undergo transformations into even more toxic peroxides, quinones, or sulfur and nitric derivatives. (Papageorgopoulou et al. 1999; Chetwittayachan et al. 2002). It is estimated that between 60% and 95% of PAHs are adsorbed onto aerosol particles that measure between 1 and 2 µm, which are then inhaled by humans (Zhong 2005). Epidemiological studies confirm the relationship between the concentration of aerosols rich in toxic substances and an increase in incidence of e.g. lung cancer (Chetwittayachan et al. 2002; Halek 2006).

A priority indicator of toxic PAH pollutants is benzo(a)pyrene, which has been classified by the International Agency for Research on Cancer (IRAC) as a compound which is likely to have a carcinogenic effect on humans (group 2A). B(a)P, an indicator of air pollution with PAHs, is being included into air monitoring schemes in most countries in Europe and globally. In order to achieve improvement of air quality, it is important to recognize the variability of carbon compounds in different spatial and temporal ranges and to determine the nature and size of emissions from anthropogenic sources. As the content of toxic substances in the atmospheric air increases, it is also important to devise models of carbon circulation, not only on a global scale, but also regionally.

Characteristics of the Baltic Sea Region

The *Baltic Sea Region* (BSR) is characterized by diverse social, geographic and political conditions and a variety of natural resources. The industry of the 9 countries surrounding the Baltic (Denmark, Sweden, Finland, Russia, Estonia, Latvia, Lithuania, Poland and Germany (Fig. 1)) is based on the sea's resources. (Baltic Maritime Outlook 2006). Indirectly, the BSR also includes Norway, owing to its communication routes being part of the transportation system of the Baltic.

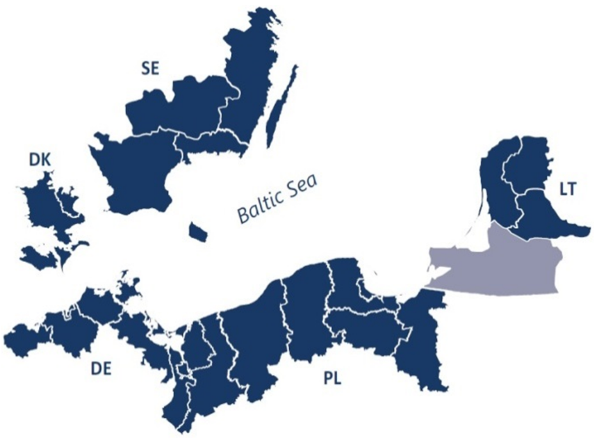

Figure 1. The Southern Baltic Region (Griekere 2014).

The drainage area of the Baltic Sea stretches from the Carpathian Mountains and the Sudetes to regions located beyond the Arctic Circle. Its area is 1,650,000 km² and is four times greater than the surface area of the sea itself. The drainage area is inhabited by 80 million people, which results in a high level of pollution of the Baltic Sea (EEA 2002). Lands such as Sweden, Denmark, the north of Germany, the north of Poland, and Lithuania are mainly rural but they nevertheless include some large urban centres, which are currently experiencing significant social-economic development. In the Baltic Sea Region, port and shipbuilding centers, as well as land and sea transportation, exert significant influence on the quality of air and its pollution with PAH compounds. The largest ports within the BSCR are those located in Rotterdam, Hamburg, Aarthus, Goetteborg, Swinoujscie, Gdynia, Gdansk and Klaipeda. The annual transshipment level taking place at these ports ranges from 18 million tonnes (Gdynia) to 442 million tonnes (Rotterdam) (Grzybowski 2013).

Yet another important route of pollutant introduction into the atmosphere is the industry developing in the Baltic Sea Region. There are factories producing e.g. phosphoric and nitric fertilizers (Denmark, Poland, Estonia), refineries and heat and energy plants (Poland, Denmark), iron ore, copper and zinc mining industries (Sweden) or pulp and paper industries (Sweden, Finland). Norwegian industry, on the other hand, is mainly based on the mining and processing of petroleum and gas and the production of ammonium and chlorine. The Baltic European Region is thus a significant area in terms of exportation and importation, with numerous trade routes.

Such industrial diversity in Baltic Europe introduces a number of pollutants into the atmosphere, including PAHs. For this reason, the Baltic countries have undertaken the monitoring of atmospheric quality also with respect to these compounds. The present article outlines selected results of studies into PAHs in the Baltic Sea Region.

The contamination of the atmosphere in the Baltic Sea Region with PAH compounds

Evidence for anthropogenic contamination of the air is to be seen in the fact that it contains various substances originating directly from human activity. The concentration of such substances is usually higher than under natural conditions, and the pollutants can be harmful to the environment, even threatening the health and life of humans inhabiting a given area. Among such substances are polycyclic aromatic hydrocarbons. Their emission into the atmosphere happens as a result of natural biomass burning processes, forest fires and volcanic eruptions. However, their main source of origin is related to anthropogenic activity, particularly to incomplete burning of fossil fuels in engines, communal heating systems, waste incineration plants and industrial processes (Nielsen 2014).

In EU law there are no regulations regarding PAH emission limits, either nationally or from particular production processes. The European Parliament and Council Directive 2001/81/WE of 23rd October 2001 on national emission levels for certain types of air pollutants does not include national limits of PAH emission. The provisions of the European Parliament and Council Directive 2010/75/UE of 24th November 2010 on industrial emissions (integrated prevention and control of pollution) also do not concern PAH emission. Taking into account the AirBase database, run by the European Environment Agency (EEA), and using the reports compliant with Decision 2004/461/EC found on the EEA's Central Data Repository website, it was possible to determine that in 2013 the combined emission of the four basic PAHs (benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene) into the European atmosphere was 1063 Mg/year (EEA 2015). Poland is considered to be one of the largest emitters of

PAHs into the atmosphere in Europe. In the years 1990-2013, the national yearly emission of PAHs into the air from Poland was between 132 and 211 Mg/year. In 2013 Poland's emission of the four above mentioned PAHs amounted to about 15% of EU emission, reaching 155.2 Mg/year. In the Baltic Sea Region, only Germany emitted more than Poland (16.2 Mg) (EEA 2015).

In 2013, the mean B(a)P concentration value in Poland amounted to 5.0 ng/m^3, and the maximum value was 10.0 ng/m^3. An annual average concentration of benzo(a)pyrene in aerosols in the studied area exceeded the value of 1.0 ng/m^3 acceptable for EU countries (Directive 2004/107/WE (EU 2004) (Fig. 2).

In 2014 the target level of B(a)P in Poland was exceeded at 128 out of 134 stations, including 111 of the 113 urban background stations. At 5% of all urban background stations in Poland the mean annual B(a)P concentration exceeded the target level by over ten-fold (EEA 2015).

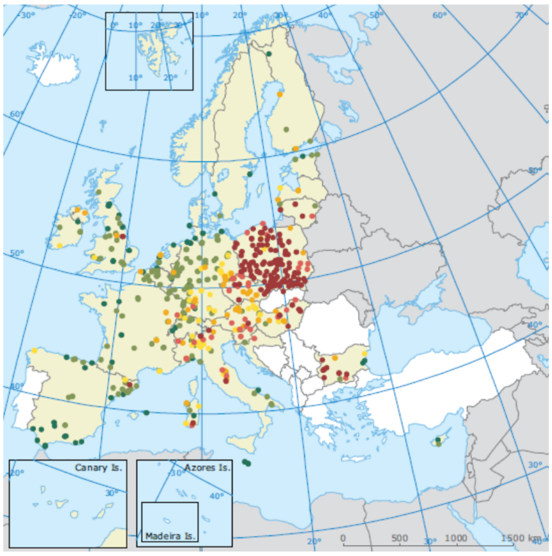

Figure 2. Mean concentrations of B(a)P in PM10 in Europe in 2013. Red dots mark stations where the accepted value of mean annual B(a)P concentration (1 ng/m^3) was exceeded (*EEA 2015).*

PAH concentrations in Poland are much higher than those observed in other European countries (Fig. 2). Another country characterized by B(a)P concentrations over 1.5 ng/m^3 was Lithuania. High concentrations recorded there are related to port activity (Klaipeda port), and the petrochemical, metallurgical and wood industries (EEA 2015). Countries such as Sweden, Estonia, Denmark, Finland or Latvia did not exceed the accepted value of mean annual B(a)P concentration (1 ng/m^3). In all EU countries, the emission of PAHs into the atmosphere was mainly related to the heating of buildings in the community sector and to land and sea transportation. An increase in PAH concentration values was observed in winter, when heating activity increased. In Poland, as much as 87% of total emission was from individual home heating systems (EEA 2015).

More than half of the 8.9 million people inhabiting the direct coastline of the Baltic Sea live in the Polish coastal zone (Griekere 2014). Out of this nearly one million people inhabit the so-called Tri-city agglomeration, which encompasses Gdansk, Gdynia and Sopot, three cities directly adjacent to one another (www.infoeko.pomorskie.pl). The level of air pollution in this region has been growing exponentially since the 20th century (Garrido et al. 2014). Studies into B(a)P in the air of the urbanized coastal zone of the Southern Baltic (Gdynia) were carried out in 2007-2008 by Staniszewska et al. (2013). Based on these studies, it was found that there is a seasonal variability in the concentration of this PAH indicator. The mean B(a)P concentration during the heating season amounted to 2.18 ng/m^3 and was two orders of magnitude higher than in the non-heating season (0.05 ng/m^3) (Staniszewska et al. 2013). An annual average concentration of benzo(a)pyrene in aerosols in the studied area was equal to 1.29 ng/m^3 and exceeded the value (1 ng/m^3) acceptable for EU countries (EU 2004). That was mainly the result of high B(a)P concentrations recorded in winter. Such a tendency is typical, not only in the Southern Baltic coastal zone. Mean B(a)P concentration in 2013 in the whole of Poland exceeded the value of 1.5 ng/m^3, and the emission was mainly related to individual heating of buildings in a period of low air temperature (EEA 2015). Low air temperature favors increased benzo(a)pyrene emission to the atmosphere not only in a direct way (heating), but also decreases the vapor pressure of B(a)P, what increases its affinity to aerosols (Ravindra et al. 2008). Moreover, the low air temperature in winter typically causes lowering of the mixing height which results in increased concentrations of B(a)P in the lower layers of the atmosphere. At the same time precipitation usually decreases the B(a)P concentration in aerosols (Staniszewska et al. 2013).

The Southern Baltic Region is characterized by a high level of activity in the port and shipbuilding sector. There are seven shipbuilding companies operating here, two large ports with numerous container terminals serviced by many firms. In 2012, 81.3 Mg/year of PAHs was emitted by shipbuilding companies alone (infoekopomorskie.pl). The industrial sector has been experiencing dynamic growth for many years. Sea transportation also plays an important role for PAH emission into the atmosphere. Since 2005, as part of the implementation of the HELCOM Convention of 1992, ship traffic has been monitored using the technique of automatic identification (AIS) (Fig. 3) (HELCOM, 2010). This has helped to observe a successive growing trend in ship traffic in the Baltic Sea. In 2013, 57,567 ships crossed the Skagerrack Strait alone and that constituted 10% more vessels than in 2005 (HELCOM 2005, HELCOM 2014). The transportation within the

Baltic Sea region is characterized by trade exchange between the neighboring countries. The number of trade ships recorded on the Baltic Sea in 2013 was 350,392, out of which as many as 52% were cargo ships, and 17% were tankers (HELCOM 2014).

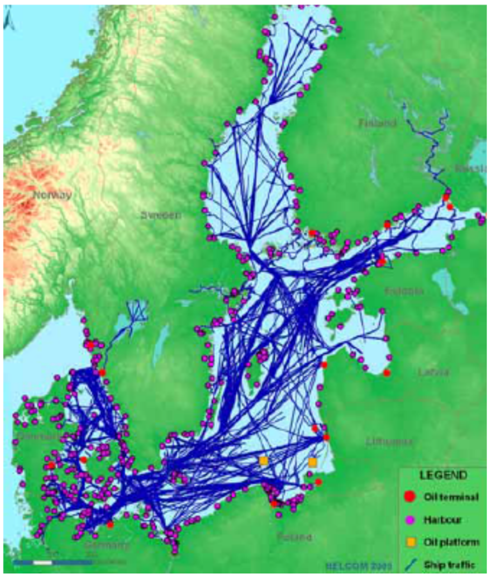

Figure 3. Ship traffic on the Baltic Sea in 2013 (HELCOM AIS, 2014).

In the Southern Baltic Region a dynamic increase can also be observed in the importance of container ports located in the southern part of the Baltic, i.e. ports in Gdynia and Gdansk. These ports introduce PAHs into the atmosphere not only through emission from ships, but also from port activity related to transshipment and further distribution of cargo via land transportation. Besides the community sector and port activity, land transportation also has an effect on the contamination of the air with PAH compounds in the Baltic European region. In all European countries, the level of motorization has been growing for many years. In 2012, the number of cars per 1000 inhabitants amounted to 560 in Finland, 530 in Germany, 486 in Poland, 456 in Estonia, and 305 in Lithuania. On average this number grows by 5% every year (World Bank 2013). In the Tri-city agglomeration, located in the coastal zone of the southern part of the Baltic Sea, the total number of registered cars was 288,796 in 2015. This means about 412 cars per 1,000 inhabitants (www.infoekopomorskie.pl). It is estimated that emission from cars is nearly 5% of total B(a)P emission in Poland, and about 2% of the combined emission of four PAHs (benzo(a)pyrene), benzo(b)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene) (EEA 2015).

Conclusions

Significant sources of anthropogenic PAHs in the atmosphere of the Southern Baltic are the communal and public utility sector and sea and land transportation. The atmospheric environment constantly affects human health and can result in its deterioration. In recent decades, the Southern Baltic region has been characterized by a rise in cancer incidence. Scientists are looking for an answer to this problem in environmental contamination, including atmospheric pollution. Suspended particulate matter measuring under 10 μm has a toxic effect on the upper respiratory tract, with particles measuring below 2.5 μm penetrating into the trachea and the bronchi. The most dangerous, however, are the smallest particles, below 1 μm in diameter, which penetrate into the lungs and the circulation system. Daily an adult inhales about 12.3 m^3 (i.e. 16 kg) of air, which is a mixture of gases, miniature droplets and solid particles (Mahajan 2006). Therefore every component of the inhaled mixture has an effect on the functioning of the human organism, even those occurring in small concentrations. PAHs which adsorb onto aerosols penetrate into the organism, irritating the airways, causing heart attacks, chronic heart diseases, allergies or asthma. PAHs are characterized by increased toxicity when the organism is exposed to them for a long period of time.

Bearing in mind the results of studies into PAHs described in the present article, which indicate significant problems maintaining B(a)P concentrations below the accepted EU norm, it follows that the regional monitoring of air quality in the Southern Baltic region should be continued and that corrective schemes ought to be implemented. An improvement in air quality can be achieved by e.g. undertaking activities to limit PAH emission from individual or local heating of buildings. Such activities involve the development of urban heating systems, replacing heating from solid fuels by gas, oil or electricity in individual installations, using heat pumps or solar panels. It is also necessary to thermo-modernize buildings, replacing old furnaces with new, highly efficient ones, and to introduce a ban on the use and distribution of low quality solid fuels.

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