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Inhalation - Route of EDC exposure in seabirds (*Larus argentatus*) from the Southern Baltic

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ABSTRACT

Despite the presence of endocrine disrupting mercury, PAHs, alkylphenols and bisphenol A in inhaled air, scientific literature lacks information on their penetration into the lungs. Large lung capacity in birds makes this route of penetration more significant than in other animals.

The studies were conducted on lungs of herring gulls found in the Gulf of Gdansk area. The results were juxtaposed with other tissues, including the intestines, which reflect the main, alimentary penetration route of harmful substances into the organism. It was determined that the capacity of bird's lungs, affects the efficiency with which mercury is absorbed from the air. Birds found to have high mercury concentrations in lungs had low PAHs concentrations, what was determined by the fact that the birds foraged in two different areas, as well as on different trophic levels. The alimentary route of phenol derivatives into the organism was of greater significance than inhalation.

1. Introduction

The air in industrialised and urbanised areas is usually described as polluted, particularly in comparison with non-urbanised, forest or seaside areas. This condition of the environment results from human activity. The most dangerous, toxic, carcinogenic and endocrine disrupting substances penetrate into the air as a result of combustion. Industrial emissions (heavy industries, coal plants, heat and energy plants), transport emissions (burning petrol, diesel fuels, the abrasion of tarmac surfaces and tyres), low emissions, uncontrolled fires, burning wood and grasses are of great significance locally, but often also regionally (Bojakowska, 2003; Oren et al., 2006; Lewandowska et al., 2012).

The middle of the previous century saw an expansion of dangerous substances into the atmosphere, driven by technological progress related to the production of solvents, detergents, pesticides, paint additives, textiles, cosmetics and even medicines. The groups of toxic substances included, e.g. mercury, polycyclic aromatic hydrocarbons (PAHs) as well as alkylphenols (APs) - (4-tert-octylphenol- OP and 4-nonylphenol- NP) and bisphenol A (BPA). These compounds are the focus of the authors' interest here, as they are on the list of priority pollutants, drawn up by the US Environmental Protection Agency (US EPA) and by the International Agency for Research on Cancer (IARC). PAHs afflict mainly the activity of the immune, reproductive and hormonal systems, and can also initiate a cancer process (Xue and Warshawsky, 2005). According to an assessment by the European Environmental Agency, Poland is the country with the highest pollution levels of benzo(a)pyrene (EEA, 2014), which is considered to be the most toxic, carcinogenic and mutagenic for humans and animals. Mercury is the strongest neurotoxin with mutagenic influence, disruptive for the circulatory system and the central nervous system (Rutkiewicz et al., 2011; Falkowska, 2016). In the EU Framework Water Directive of 2000, 4-tert-octylphenol, 4-nonylphenol and bisphenol A are on the list of high risk substances. In 2011, alkylphenols were flagged up by the European Chemical Agency (ECHA), as compounds which raise particularly great worries.

The main source of mercury, PAHs and phenol derivatives in birds is food. When food is consumed, xenobiotics penetrate through the intestinal barrier into the circulatory system and are distributed with blood to all organs and tissues, where they can then be accumulated (Burgess et al., 2013; Kim et al., 2003; Kannan and Perrotta, 2008; Sturve et al., 2006). Lungs are a less significant route of penetration (Chmielnicka, 1994; Chmielnicka, 2006; Gehle, 2009). Nevertheless, a bird's respiratory system is the largest area of the organism's interaction with air, and probably the most important route of penetration for inorganic mercury. Little is known about the content of PAHs or phenol derivatives in bird organisms, and particularly about their respiratory exposure. The emission of PAHs and phenol derivatives from landfills, as pointed out by the Health Protection Agency, can increase the risk of low weight of birds foraging in such areas (HPA, 2011).

The authors of the present paper wanted to determine if the exposure to mercury, PAH and phenol derivatives in the seaside air is

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reflected in bird lungs, and what factors condition the xenobiotic burden in the lungs. By comparing results from two different routes of introduction: alimentary and respiratory, an attempt was made to determine the level of exposure for the herring gull (*Larus argentatus*) and to indicate the significance of food from various trophic levels, as well as potential sources of xenobiotics in the inhaled air. The authors put forward a hypothesis that gulls which limit their foraging area to the coastal zone of the sea, assimilate mercury compounds via two routes (inhalatory and alimentary) to a higher degree than specimens which search for food further away from the sea, the latter being more exposed to organic compounds, chlorine and phenol derivatives.

The results of studies on seabirds may constitute important information for humans, who breathe in the same air. In the Pomerania region, >1.5 million people are in danger of developing health problems. What is more, in recent years the incidence of cancers and mortality rates have been observed to be higher in this region when compared to those with heavily contaminated area in Poland (Bartosińska et al., 2005).

2. Sampling area

The million-strong agglomeration of the Tri-city (Gdansk, Sopot, Gdynia) is located in the coastal zone of the Southern Baltic, on the Gulf of Gdansk. It is a highly urbanised area with population density exceeding 15,000 people per km^2. Tri-city inhabitants are exposed to the emission of toxic substances originating from e.g. car traffic, heat and energy plants, refineries, shipbuilding and harbour industry, domestic stoves/fireplaces or landfills. The monitoring of air quality in the Tri-city has indicated exceedances of limits, e.g. mean daily norms of PM10 concentrations in the winter season, but in Gdynia also in summer ($>50\ \mu g \cdot m^{-3}$) and of mean 8-h ozone concentrations in summer ($>120\ \mu g \cdot m^{-3}$) (ARMAAG, 2015). According to the EEA (2014), over the Gulf of Gdansk during the summer of 2014 there were 1–15 days on which ozone concentrations exceeded the long-term objective for the protection of health. In addition, Tri-City is located in the vicinity of the Kashubian region characterised by high levels of low emissions. Western winds, which dominates in this region are responsible for transport of particles with adsorbed PAHs to Gulf of Gdansk region (Lewandowska et al., 2012).

Studies that accompanied the monitoring showed the air over the Gulf of Gdansk to be characterised by a relatively low concentration of total gaseous mercury ($TGM \leq 3.0\ ng \cdot m^{-3}$), but in the warm season the increase in the temperature of surface seawater and biological activity influences an increase in the emission of mercury from water into the air. At such times, the level of TMG can increase 6 $ng \cdot m^{-3}$ (Bełdowska et al., 2008). Having been emitted into the atmosphere, elemental mercury can become oxidated and undergo conversion. Sea water can also be a source of organic Hg compounds in the air (Schroeder and Munthe, 1998).

In the air over the Gulf of Gdansk, the concentration of mercury in aerosols is characterised by high seasonal variability (Hg_{TPM}). Increased combustion of fossil fuels (greater demand for heat and electricity) can effect a rise of as much as 100-fold in Hg_{TPM} in winter ($1963.9\ pg \cdot m^{-3}$) as opposed to summer (Bełdowska et al., 2007). In winter in the coastal zone of the sea the emission of PAHs also increased: the concentrations of benzo(a)pyrene grew 40-fold on average (in extreme cases even 500-fold). In the winter of 2007/2008 maximum concentrations of B(a)P were observed in Gdynia, reaching 25.02 $ng \cdot m^{-3}$ (Staniszewska et al., 2013). It was shown that it is an area with an exceeded norm of mean annual bezo(a)pyrene concentration in PM10 ($>1\ ng \cdot m^{-3}$) (WIOŚ, 2009). The latest studies estimate that as much as 60–96% of PAHs in the heating season are adsorbed onto very small aerosol particles, measuring under 1–2 μm in diameter, inhaled through respiration. Studies so far have shown that in the air over Gdynia mean BPA, OP and NP concentrations in small aerosol fractions PM < 2.5 were within the range of 0.1 to 1.2 $ng \cdot m^{-3}$. For all the compounds, higher concentrations were observed in the heating season and were between 2 and 6 times higher than in the warm season. The highest elevation of concentrations in the heating season was observed for BPA (Lewandowska et al., 2012).

In addition to atmospheric pollution, the study area is characterised by the presence of endocrine disrupting compounds in the water and sediments of the Gulf of Gdansk. However, mercury concentrations in water and surface sediments did not exceed the limit values considered to be safe for organisms (Murawiec et al., 2007; Jędruch et al., 2015). PAH concentrations also did not exceed Predicted Non-Effect Concentration, although according to Staniszewska et al. (2011), some congeners could have occurred in higher concentrations, particularly in the sediments in the water track for ships entering the ports in Gdynia and Gdansk.

The latest research has indicated that only 3% of BPA, OP and NP concentration results were higher than the PNEC guidelines (Koniecko et al., 2014). On the other hand, the results for phenol derivative concentrations in the surface microlayer of the sea were higher (56% - BPA), 69% - OP, 3% - NP) than the limit values determined by PNEC (Staniszewska et al., 2015).

3. Characterisation of the studied species

The herring gull (*Larus argentatus*) is widespread in Northern Europe. These birds inhabit seaside areas, islands, sand bars in river estuaries, but also in the vicinity of in-land water basins. The gulls breeding on the Polish coast are mainly resident, particularly the mature birds. Juvenile birds are also partially resident, and some of them migrate to the west (no further than Germany). In winter, gulls come over to the Polish coast from the eastern part of Scandinavia and the western part of Russia. The herring gull is one of the largest birds and the most numerous species found on the Polish coast in wintertime (Meissner et al., 2007). Herring gulls live on organisms from various trophic levels and their diet may include: fish, invertebrate, shellfish, small amphibians, eggs and chicks of other gulls, as well as offal and communal waste. The latter, supplementary food source is found by gulls on landfills near the Gdansk agglomeration. The total number of gulls there ranges between a few and over 30,000 specimens.

4. Materials and methods

4.1. Biological material for analyses

The tests were conducted on 53 dead herring gulls found around the Gulf of Gdansk in all seasons between 2010 and 2012. Most of the birds came from the fishing port area in Wladyslawowo (n = 29) and from the Mewia Lacha bird sanctuary located in the Vistula estuary (n = 15). The remaining birds (n = 9) were found within the Tri-city agglomeration. The age of each bird was determined on the basis of its plumage and three age categories were distinguished between: juvenile specimens (chicks and birds in their first plumage), immature specimens (in their second and third plumage) and mature birds (in the fourth and final plumage). Gender was determined on the basis of DNA using the method of polymerase chain reaction – PCR.

The cause of death was not determined, but the cachetic condition of each bird was assessed. 10% of the birds were found to be emaciated, including one male with suspected peritonitis (Falkowska, 2016). All the birds underwent dissection, during which the following were collected: muscles (to assay $\delta^{13}C$, $\delta^{15}N$, Hg_{TOT}, Hg_{ORG}), lungs (Hg_{TOT}, Hg_{ORG}, WWA, BPA, OP, NP), kidneys (Hg_{TOT}, Hg_{ORG}), liver (Hg_{TOT}, Hg_{ORG}), brain (Hg_{TOT}, Hg_{ORG}) and intestines (Hg_{TOT}, Hg_{ORG}, WWA, BPA, OP, NP) (Table 1). Collecting a full set of tissues and organs from each bird was not possible, and sometimes low weight of samples (e.g. brain) made it impossible to carry out all of the assays. The collected material was stored in a freezer (−20 °C). Material preparation included lyophilisation and