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Urinary polycyclic aromatic hydrocarbon metabolites among 3-year-old children from Krakow, Poland

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are widespread in the environment and can adversely affect human health. The aim of the present study is to describe the level of PAHs exposure in children living in Kraków, one of the most polluted cities in Poland, and to determine the relationship of urinary biomarkers with environmental PAHsexposure.

Urinary monohydroxy metabolites (OH-PAHs) of 20 PAHs were assessed in 218 three-year old children, of which only 10 were present in nearly all the samples: monohydroxy metabolites of naphthalene, fluorene, phenantrene and pyrene. Of the metabolites analyzed, hydroxynaphthalenes were predominant and constituted almost 73% of total excreted OH-PAHs, while 1-OH-PYRene was the least abundant (2.3% of total OH-PAHs). All measured urinary OH-PAHs were statistically significantly correlated with each other (R = 0.165–0.880) but the highest correlation coefficients with other individual OH-PAHs and with total OH-PAHs were observed for 2-OH-FLUOR.

Children exposed at home to environmental tobacco smoke (ETS) had higher concentrations of fluorene and pyrene urinary metabolites compared to those without ETS exposure; and those exposed to gas-based appliances used for cooking or heating water had higher levels of fluorene and phenanthrene metabolites than children not exposed. The use of coal, wood or oil for heating was associated with elevated levels of 1-OH-PYRene. Urinary PAHs metabolites only modestly reflect high molecular weight carcinogenic PAHs exposures such as those monitored in air in the present study. None of the measured PAHs metabolites was correlated with airborne $PM_{2.5}$ and only two were slightly correlated with measured higher molecular mass airborne PAHs.

The average concentrations of these specific metabolites in Polish children were much higher than observed in other pediatric populations living in developed countries. Our findings suggest that to capture various sources of PAHs, in addition to 1-OH-PYRene, biomonitoring of PAHs exposure should include 2-OH-NAP and 2-OH-FLUOR.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic compounds composed of at least two aromatic rings that occur naturally in coal, crude oil and tar deposits. Environmental PAHs are produced through the heating or incomplete combustion of organic materials, especially in an oxygen deficient environment; thus one of their major sources in ambient air, besides natural fires, is human activity. Important anthropogenic sources include fossil fuel combustion, incineration of municipal waste, and the release of fumes from manufacturing industries using fossil fuels (Mumtaz and George, 1996; Ramesh et al., 2012). Deposition of PAHs leads to contamination of soil and water. The concentrations of PAHs in the soil can be several fold greater than those in the air, while water usually contains trace

Abbreviations: 1-OH-NAP, 1- hydroxynaphthalene; 2-OH-NAP, 2- hydroxynaphthalene; 2-OH-FLUOR, 2-hydroxyfluorene; 3-OH-FLUOR, 3-hydroxyfluorene; 9-OH-FLUOR, 9-hydroxyfluorene; 1-OH-PHEN, 1-hydroxyphenanthrene; 1-OH-PHEN, 2-hydroxyphenanthrene; 3-OH-PHEN, 3-hydroxyphenanthrene; 4-OH-PHEN, 4-hydroxyphenanthrene; 1-OH-PYR, 1-hydroxypyrene; OH-PAHs, monohydroxy metabolites; CDC, Center for Disease Control and Prevention; ETS, environmental tobacco smoke; LOD, limit of detection; P, percentile; PAHs, polycyclic aromatic hydrocarbons; PM2.5, particulate matter with diameter < 2.5 μm; Q1, 1st quartile; Q3, 3rd quartile

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amounts of PAHs due to their weak solubility (Ramesh et al., 2012). Many PAHs can adversely affect human health, and some are classified as probable or possible human and animal carcinogens or mutagens. They also can have effects such as neurotoxicity, infertility, negative impacts on fetal development and impaired child development (IARC, 2010, 2002). Young children are considered to be at greater risk of harmful effects of environmental toxicants such as PAHs because of their less efficient detoxification ability and higher exposures than adults in relation to their body weight. During early childhood, the bronchial tree is still developing, and the lung epithelium is not fully developed, what results in greater permeability (Pinkerton and Joad, 2000; Schwartz, 2004). Moreover, children have a larger lung surface area per kilogram of body weight than adults and, under normal breathing, breathe 50% more air per kilogram of body weight than adults. They are also usually more physically active, compared to adults, what additionally increase ventilation rates (Schwartz, 2004). Children are also experiencing very rapid growth and development through complex processes that can be disrupted by toxic exposures (Perlroth and Castelo Branco, 2017).

Humans are exposed to PAHs from a variety of sources including occupational exposures, ambient air pollution, behaviors including smoking and consumption of smoked and grilled food (Abdel-Shafy and Mansour, 2015; Hansen et al., 2008; Jacob and Seidel, 2002). For small children the main source of PAHs is indoor air pollution, as small children spend the majority of their time at home. Potential sources of indoor PAHs, in addition to infiltration of outdoor PAHs, include burning coal and biofuels at home for cooking and heating, exposure to environmental tobacco smoke (ETS), and candle and incense burning (Abdel-Shafy and Mansour, 2015; Jacob and Seidel, 2002). Additionally, in our prior research in the same cohort we found a very high correlation between levels of PAHs in indoor and outdoor air ((Choi et al., 2008)).

PAHs exposure involves a complex mixture of different PAHs. Moreover, PAHs can enter the body via the respiratory system, gastrointestinal tract or skin; and exposures typically involve more than one route simultaneously. Children have higher respiratory rates than adults and therefore higher exposure to pollutants in air. They may also have high levels of non-dietary PAHs ingestion from hand-to-mouth activities while playing on the floor or outside. As biomarkers of internal dose, monohydroxy PAHs metabolites (OH-PAHs) in human urine can be used to assess recent exposure to PAHs. Advantages of analyzing urinary metabolites are that collection is non-invasive, samples are relatively accessible, and metabolites reflect exposure from multiple routes (Jacob and Seidel, 2002; Strickland and Kang, 1999).

Once PAHs enter the human body, they undergo a multistep detoxification process. In phase one, cytochrome P450 oxygenases induce oxidative activation. In phase two, phenols and dihydrodiols are conjugated to sulphuric acid or glucuronic acid to create a more water soluble form and thus facilitate their excretion. Studies have shown that most PAHs are fairly rapidly excreted via feces and urine within a few days. More specifically, low molecular weight PAHs metabolites are primarily excreted in urine, whereas those with higher molecular mass are eliminated mainly via the bile with feces (Ramesh et al., 2012). Although analytical precision is high, human biomonitoring of PAHs exposure is limited by the number of metabolites that can currently be measured (Angerer et al., 2007; Esteban and Castaño, 2009).

The most often studied PAHs biomarker of environmental sources is 1- hydroxypyrene (1-OH-PYR), the main metabolite of pyrene formed in mammals (Jacob and Seidel, 2002). The advantages of using 1-OH-PYR are its present in PAH-mixtures and correlationship with other PAHs and their metabolites (Campo et al., 2010a; Jongeneelen, 1997; Li et al., 2008). Elevated levels of 1-OH-PYR have been seen primarily in occupational settings in workers exposed to PAHs mixtures. High levels have also been seen in smokers, patients who received coal tar treatment, and subjects consuming charbroiled or smoked food (Strickland and Kang, 1999). Urinary 1-OH-PYR is the preferred measure of both occupational and environmental exposure assessments (Hansen et al., 2008; Jacob and Seidel, 2002; Strickland and Kang, 1999) but is a less adequate biomarker of internal dose for more volatile PAHs (Campo et al., 2010b). Moreover, exposure to PAHs mixtures may modify metabolism or induce synergistic or antagonistic effects (Abdel-Shafy and Mansour, 2015). Therefore a single metabolite is not able to characterize total exposure to PAHs.

The aim of this study in a cohort of three year old Polish children is to describe PAHs exposure measured via urinary monohydroxy metabolites and to determine the relationship of urinary biomarkers with the potential sources of environmental PAHs.

2. Material and methods

This study is part of an ongoing longitudinal investigation of the health impacts of prenatal exposure to outdoor and indoor air pollution on infants and children in Krakow. The prospective cohort study design and detailed selection of the population have been described previously (Jedrychowski et al., 2003). Briefly, nonsmoking, pregnant women aged 18–35, living in Krakow, Poland, who were free from chronic diseases including diabetes and hypertension, were enrolled between 2000 and 2003 during the first or second trimester of pregnancy. Health and exposure questionnaires were administered to the mothers prenatally and every 3 months until the child turned 2 years, then subsequently every 6 months until age 3.

The study was approved by the Jagiellonian University Bioethics Committee and written informed consent was obtained from all study participants.

2.1. Study population and variables describing home environment and potential outdoor sources of PAHs

The present analysis is restricted to 218 children (47.2% were girls), who had urine collected at age three and analysis of PAHs metabolites completed (years 2004–2007). Questionnaires covering the previous 6 month period were used to determine 3 year residential characteristics including: type of residence (block of flats, tenement or family house), place (city center vs. other), socioeconomic status estimated by maternal education (university vs. lower), type of cooking appliances (gas vs. electric), use of gas for water heating (yes vs. no), exposure to ETS, poor residential conditions (defined as presence of at least one of the following conditions: mold, moisture, leaky pipes, paint chips or dust from paint), other combustion sources of PAHs in the home environment (coal and wood burning), and other potential PAHs sources (cleaning substances e.g. floor polish, paint products, solvents, pesticides, herbicides). Exposure to ETS was defined as present if any household member had smoked regularly for at least 6 months during the period of interest. Potential outdoor PAHs sources considered were: living in the vicinity of a cross-road, parking lot or other sources of pollutant exposure (car repair garage, dry cleaning shop, restaurant, bus depot, petrol station, industrial plant) or having windows facing the street (no street, light traffic street, high traffic street). Information on fuel type used for heating (town heating system, gas, electric, coal, wood heating) came from a questionnaire covering the 48 h of indoor air pollution measurement at age 3.

2.2. Airborne indoor exposure to $PM_{2.5}$ and PAHs compounds

At age three years children were monitored for exposure to airborne particulate matter ($PM_{2.5}$) and PAHs. The samplers were placed in the main room of the home and ran over a consecutive 48-hr period. The sampling pump drew air through a personal environmental monitoring sampler (PEM) to measure particle mass as well as a polyurethane sampler (PUF) to measure PAHs concentration. Flow rates were calibrated (with filters in place) prior to monitoring and were checked during the battery pack change on the second day and again at the