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Biomonitoring of arsenic, cadmium, lead, manganese and mercury in urine and hair of children living near mining and industrial areas

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HIGHLIGHTS

- The study was conducted in an area with large industry/mining activities.
- Urine and hair levels of As, Cd, Hg, Mn and Pb were determined in School children.
- The only significant correlation between urine and hair levels was found for Hg.
- Cd and Hg levels were higher than in children from other European countries.
- Urine Cd and Hg levels between 25% and 50% of the children might represent a health risk.

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ABSTRACT

Huelva (South West Spain) and its surrounding municipalities represent one of the most polluted estuaries in the world owing to the discharge of mining and industrial related pollutants in their proximity. A biomonitoring study was conducted to assess exposure to arsenic and some trace metals (cadmium, mercury, manganese and lead) in urine and scalp hair from a representative sample of children aged 6–9 years ($n = 261$). This is the only study simultaneously analyzing those five metal elements in children urine and hair. The potential contribution of gender, water consumption, residence area and body mass index on urinary and hair metal concentrations was also studied. Urine levels of cadmium and total mercury in a proportion (25–50%) of our children population living near industrial/mining areas might have an impact on health, likely due to environmental exposure to metal pollution. The only significant correlation between urine and hair levels was found for mercury. Children living near agriculture areas showed increased levels of cadmium and manganese (in urine) and arsenic (in hair). In contrast, decreased urine Hg concentrations were observed in children living near mining areas. Girls exhibited significantly higher trace metal concentrations in hair than boys. The greatest urine arsenic concentrations were found in children drinking well/spring water. Although human hair can be a useful tool for biomonitoring temporal changes in metal concentrations, levels are not correlated with those found in urine except for total mercury, thus providing additional information.

1. Introduction

Trace metal contamination is a cause for concern because of its potential accumulation in both the environment and living organisms, because of their accumulative capacity and potential neurotoxic effects (Gil and Hernández, 2009). Low-dose exposure to environmental pollutants, including trace metals, in non-occupational settings is becoming a serious problem, especially for pregnant women and children as they are considered as the most vulnerable subgroups of population (Rodríguez-Barranco et al., 2013).

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Huelva (South-West Spain) and its surrounding municipalities represent one of the most polluted estuaries in the world as a consequence of the discharge of smelters plumes and mining related pollutants to air and rivers, with the industrial activity influencing the trace element composition of particulate matter (Aguilera et al., 2010).

Thus, exposure of the population living in this area to environmental pollutants raises potential health concerns. In addition, the higher mortality ratios in Huelva province as compared to the rest of Spain has contributed to an increased concern of the population about the potential adverse health effects posed by environmental pollution (Benach et al., 2004).

Environmental exposures, including trace metals, can threaten children's health *in utero* exposure and the mobilization of various toxic compounds from maternal tissues during pregnancy, and at later stages through breast feeding (Massart et al., 2008). Exposure continues during childhood through food and water intake, inhalation and/or dermal absorption of metal elements (Rodríguez-Barranco et al., 2013). Moreover, children are more susceptible than adults to environmental contaminants as they present striking differences in terms of exposure (Landrigan et al., 2004). First, children show immature detoxification mechanisms and their heightened vulnerability is related to physical features (high surface area), nutritional aspects (children drink more water and eat more food per unit of body weight than adults) and behavioral patterns (direct contact with the ground, tendency to put everything into their mouths, etc.). This situation has prioritized children as a target group for studying exposure to environmental pollutants. In this regard, subtle cognitive and neurobehavioral changes have been reported in children exposed to low doses of trace metals, even below concentrations considered safe for most people (Callan et al., 2012).

Blood and urine samples are the most widely accepted matrices for biomonitoring trace metal exposure. As metal cations bind to the sulfur atoms of the keratin present in hair matrix, this tissue appears to be an attractive choice for environmental health surveys (Bencko, 1995). Advantages of human hair include being a stable matrix, a simple collection and transportation and lack of changes during storage. In contrast to blood and urine concentrations, which reflect recent exposure (with the exception of urine Cd, which represents chronic exposure – body burden), hair levels reflect past exposure, providing an average of the growth period (Bermejo-Barrera et al., 1998).

Conversely, hair has several limitations such as its potential for external contamination that needs be completely removed by different washing procedures (Olmedo et al., 2010). Another disadvantage is the lack of sufficient information to define reference ranges for trace metals, because metal hair concentrations vary significantly according to age, sex and racial/ethnic factors (Esteban and Castaño, 2009). Thus, further studies are needed for hair testing to become a reliable exposure biomarker and to broaden the database for trace metal levels in hair that supports the establishment of normal ranges.

This study was aimed at assessing levels of certain metals (Cd, Hg, Mn, Pb) and metalloid (As) in children living near a industrialized region from the Southwestern coast of Spain (Huelva). Trace elements were selected because of their involvement in environmental pollution in the Ria of Huelva and their potential for adverse health effects in humans. The contribution of some determinants of the variability of metal levels in urine and hair (age, gender, health-related lifestyle, diet habits, residence area…) was also studied. To the best of our knowledge, this is the first study carried out so far in which five trace elements are simultaneously determined in two different matrices from a children population.

2. Materials and methods

2.1. Design, study areas and selection of participants

A cross-sectional study was conducted between January–March 2012 in Huelva (Andalusia, Southwestern Spain). Thirteen schools were selected which includes the capital city of Huelva and six municipalities also located close to industrial and mining areas.

A total of 261 children aged 6–9 years who had been living for at least one year continuously in any of the study areas were eligible. Children with pre-and peri-natal problems were excluded. Children's parents gave informed and written consent to participate in the study and the study protocol was approved by the Biomedical Research Ethics Committee of Granada.

Two questionnaires (one self-administrated and another by phone interview) were applied to the mother, father or guardian to obtain information about demographic and socioeconomic characteristics, environmental and home exposures, parent's occupational history, children's diet and body mass index among other variables.

2.2. Urine sample collection

A first morning urine sample was collected from each participant in a sterile polyethylene container pre-treated with HNO_3 (20%) and rinsed twice with MilliQ water. Samples were then stored at −20 °C until analyzed within 3 months, time period that lasted sample collection.

2.3. Hair samples

Human hair was cut from the back of the head as close as possible to the scalp. Hair samples were kept in acid pre-cleaned polyethylene containers. Hair was then washed by ultrasonic cleaning in a non-ionic detergent and then with an ethanol solution. The cleaned hair was dried at room temperature and digested in a microwave oven (for more details, see Olmedo et al., 2010).

2.4. Determination of arsenic and trace metals

The validation of analytical procedures used for the determination of metal compounds in urine and hair samples has been reported elsewhere (Gil et al., 2006; Olmedo et al., 2010). The analytical method was controlled by using external certified reference materials (CRM). Reference sample for urine (ref. 201205) was supplied by Seronorm (Billingstad, Norway) and reference material NIES No. 5 for hair was obtained from the National Institute for Environmental Studies, Japan Environment Agency. In addition, we were enrolled in an external Quality Control for Pb and Hg in urine organized by the Instituto Nacional de Seguridad e Higiene en el Trabajo, Ministry of Labour, Spain. Atomic Absorption Spectrometry-furnace technique was used for metal ions determination with the exception of arsenic and mercury, which were measured through a hydride generation system. Appropriate matrix modifiers were used for Cd [0.3 g L^{-1} of $Mg(NO_3)_2$ + 0.33 g L^{-1} of $Pd(NO_3)_2$], Pb [10 g L^{-1} of $NH_4H_2PO_4$] and Mn [1 g L^{-1} of $Mg(NO_3)_2$] and prepared in 0.2% (v/v) nitric acid and 0.1% Triton X-100. Urinary creatinine levels were determined by the method of Jaffe using a Hitachi 917 auto-analyzer. Limit of detections (LOD) for urine (μg L^{-1}) and hair (μg g^{-1}) were: 0.030 and 0.0033 for As and Cd, 0.002 and 0.00022 for Hg, 0.120 and 0.0132 for Mn, 0.830 and 0.0913 for Pb. Limits of quantifications (LOQ) for urine (μg L^{-1}) and hair (μg g^{-1}) were: 0.100 and 0.010 for As, 0.090 and 0.010 for Cd, 0.007 and 0.0007 for Hg, 0.390 and 0.040 for