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Exposure and risk assessment to arsenic species in Spanish children using biomonitoring

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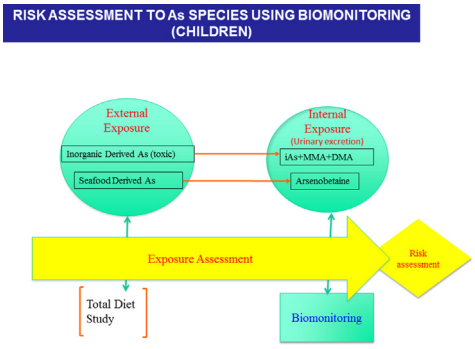
HIGHLIGHTS

- We use biomonitoring of urinary arsenic species in children for risk assessment.
- The average concentration of Arsenobetaine was 15.0 μg/L.
- Geometric mean concentrations for DMA and MMA were 8.32 and 0.27 μg/L, respectively.
- Hazard Quotient for urinary speciated arsenic (USAs = iAs + MMA + DMA) was 0.9.
- 18% of children presented levels of USAs higher than the Biomonitoring Equivalent.

GRAPHICAL ABSTRACT



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ABSTRACT

We present a new approach to arsenic (As) risk assessment using biomonitoring. In this pilot study we determined the levels of total and speciated urinary arsenicin 109 Spanish school children aged between 6 and 11 years, and interpreted these concentrations in a risk assessment context. The geometric mean (GM) for total As (TAs) was 33.82 μ/L. The order of occurrence and average concentrations of the different species was arsenobetaine (AsB) (100%, 15 μg/L), dimethylarsinic (DMA) (97%, 8.32 μg/L), monomethylarsonic (MMA) (26%, 0.27 μg/L) and inorganic As (iAs) (4%, 0.14 μg/L). 18% of children presented exposures to inorganic arsenic (7.52 μg/g creatinine) higher than guidance value for non-cancer risk (8.3 μg/g creatinine). For cancer risk the exposure to inorganic arsenic was much higher than the guidance value. Urinary DMA was positively associated with urinary AsB, suggesting exposure directly to this specie or metabolism of organic arsenicals to this specie, mainly through seafood consumption. Consequently, the exposure to inorganic As needs to be carefully interpreted because it may be overestimated. Our study supports the hypothesis that urinary iAs + MMA is the most reliable biomarker of exposure to inorganic As.

1. Introduction

Arsenic (As) is a ubiquitous natural component of the earth's crust, which is present in more than 200 mineral species, and is widely distributed throughout the environment in the earth soil, water and air (Sarkar

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and Paul, 2016). Human activities such as mining, smelting, fossil-fuel combustion or specific industrial applications, such as agricultural chemicals, the processing of glass or allowing agent can alter the natural presence of As (Chen et al., 2016).

Arsenic occurs as a wide diversity of arsenic compounds, of which inorganic arsenic is the most toxic form. Inorganic arsenic (iAs) has been classified by the International Agency for Research on Cancer in group 1, as carcinogenic to humans (IARC, 2009). In addition to skin cancer, long-term exposure to arsenic may also cause cancer of the bladder and lungs (Jomova et al., 2011). Arsenic is also associated with adverse pregnancy outcomes and infant mortality, with impacts on child health, and there is some evidence of negative impact on cognitive development (Quansah et al., 2015).

The main sources of exposure to As for the general population is food and water. Seafood is the highest contributor to As intake through the diet, where As is present mainly in the form of organic compounds, such as arsenosugars, arsenolipids and arsenobetaine (AsB), the major As form found in most finfish and shellfish, while methylated arsenicals, such as dimethylarsinate (DMA) are minor constituents of seafood (Taylor et al., 2017). Current risk assessment of dietary exposure to As has been established for the inorganic forms (EFSA (European Food Safety Authority), 2014). Chronic dietary exposure to iAs in Europe among infants, toddlers and other children ranged from 0.20 to 1.37 μg/kg b.w. per day, while the 95th percentile dietary-exposure estimates ranged from 0.36 to 2.09 μg/kg b.w. per day (EFSA (European Food Safety Authority), 2014). In general, the largest food commodities contributing to iAs exposure in children (3–10 years of age) are wheat bread and rolls, rice, milk and dairy products, while drinking water represented about 8% of iAs intake.

Arsenic is excreted in urine in several chemical forms. Ingested iAs is largely metabolised and excreted in urine with a short half-time of a few hours to two days, including arsenous (As^{III}) and arsenic (As^{V}) acids (together, iAs), MMA, and DMA, with typical ratios of 10–30% iAs, 10–20% MMA, and 60–80% DMA (EFSA (European Food Safety Authority), 2009). Urinary Speciated Arsenic (USAs), defined as the sum of iAs, DMA and MMA, is commonly used as a biomarker of short-term exposure to iAs (when non-dietary sources of exposure are negligible). However, USAs could be affected by the ingestion of DMA present in foods or the metabolism of arsenosugars and arsenolipids (Cubadda et al., 2017; Taylor et al., 2017).

The conventional assessment of dietary exposure to harmful chemicals in the food chain, includes determining the concentration of specific forms of the elements in the diet, and their combination with the data from consumption of the different categories of foods that make up the staple diet of the general population or of specific subgroups (Dorne et al., 2009). To assess the concentration of As and of other substances in foods, various methods have been used, including Total Diet Studies (TDS) or monitoring and surveillance programmes. The application of human biomonitoring data for exposure assessment and risk characterisation has attracted major interest in recent years (St-Amand et al., 2014). To use biomonitoring for risk assessment, some epidemiological information supporting the link between human exposures and human health outcomes needs to be available, as well as sufficient toxicology data on the relationship between the biomarker of exposure and a known health effect. These values could be derived from the existing health-based exposure guidance, such as the Biomonitoring Equivalents (BE) or epidemiologically-based values, such as the health-related human biomonitoring values (HBM-I, HBM-II) (Angerer et al., 2011). Fig. 1 shows a diagram of these (external and internal) exposure and risk assessment approaches.

Results from a recent TDS conducted in the Valencian Region (Spain) for exposure and risk assessment to metals (Marín et al., 2017), showed that between 10 and 13% of children (6–15 years of age) exceeded critical limits of iAs intake, attributed mainly to cereal, pulses, tubers and nuts. This prompted us to obtain preliminary data on urinary speciated arsenic in a children population of the Valencian Region.

The objective of the present study was to estimate the exposure and risk assessment to arsenic species in a children population using biomonitoring. To achieve this aim, we i) determined the urinary concentration of the different species and compared the results with other populations, ii) evaluated socio-demographic and food related determinants and iii) performed both non-cancer and cancer risk assessment.

2. Materials and methods

2.1. Study design, population, and sample collection

The study design and population recruitment were previously described in detail (Roca et al., 2014). Briefly, 120 children aged between 6 and 11 were randomly selected from two primary schools, one from an urban area (Valencia) and another one from a rural area (Alzira). First-spot morning urine samples were collected for each participant, aliquoted and properly stored at −80 °C, until analysis, in the Biobank for Biomedical Research and Public Health of the Valencian Community (Spain). Urine specimens were only obtained from 109 children.

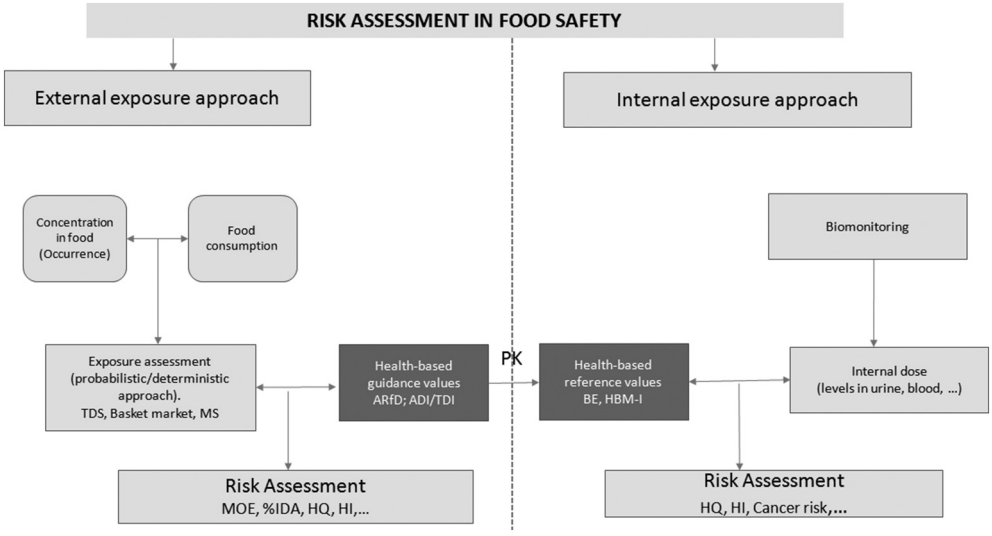

Fig. 1. Framework for risk assessment of metals in the human population combining exposure assessment (external and internal) with toxicological effects (PK: toxicokinetics; MS: Monitoring programs; HQ: hazard quotient; HI: hazard index; BE: biomonitoring equivalents).