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Gender as a key factor in trace metal and metalloid content of human scalp hair. A multi-site study

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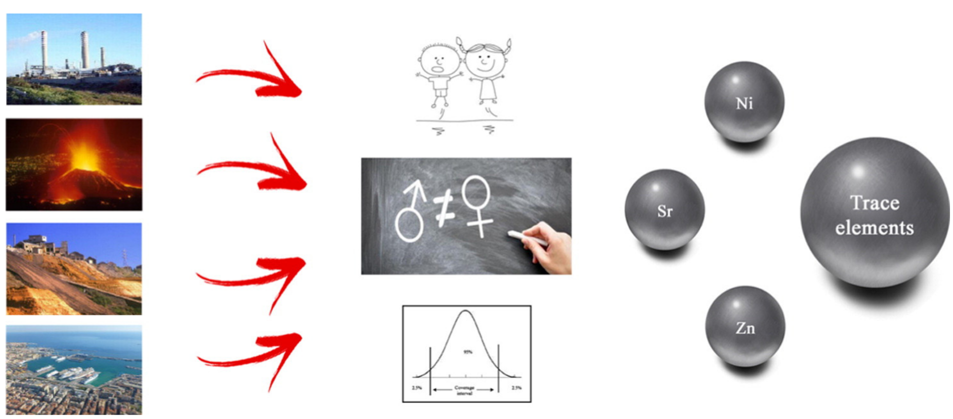
HIGHLIGHTS

- Gender is a confounding factor in the interpretation of metal profiles in human hair.
- Gender effect can significant impact on the application of the common coverage intervals.
- The content of some trace elements in human hair is statistically different between female and male, regardless of the residence site.
- Adolescent girls exhibit significantly higher hair concentrations of Sr, Zn and Ni than boys.

GRAPHICAL ABSTRACT



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ABSTRACT

This multi-site study discusses the content of metals and metalloids (MM) in scalp hair of children, living in different environmental contexts, with the purpose of verifying if hair level of some MM is distinctively gender-specific. A total of 943 hair samples (537 females and 406 males) from adolescents were analyzed for their content of Al, As, Ba, Cd, Co, Cr, Cu, Li, Mn, Mo, Ni, Pb, Rb, Sb, Se, Sr, U, V and Zn. Elemental quantification was performed by ICP-MS. The obtained data identified different metal distributions in adolescent girls which exhibited significantly higher hair concentrations of some trace metals, especially Sr, Zn and Ni, than boys. On the base of the median value, hair of female donors contained 3.8 times more Sr (6.6 μg/g) than males (1.7 μg/g). Highest concentrations of Zn in females were observed in samples from the mining area of Sardinia (587 μg/g). Nickel showed significant differences resulting 2.5-fold higher in female hair. Regardless of the residence site, these elements resulted always significantly different (at $p < 0.01$) between female and male indicating that gender is a confounding factor that has to be more extensively considered for a correct interpretation of metal profiles in human hair.

1. Introduction

Exposure of people to trace metals and metalloids (MM) is an issue that raises many public concerns and debates because of their large-scale use in almost all industrial, agricultural, and technological applications and their potential effects on human health (Combs, 2005; Biggeri et al., 2006; Manno et al., 2006; Tamim et al., 2016). Ingestion of food (vegetables, meat, fish) or water, dust inhalation and also dermal

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contact are the main ways of human exposure to MM (US EPA, 1989, 1996; Islam et al., 2014, 2015, 2016; López-Alonso et al., 2016). Metals and metalloids, even at trace concentration levels, play a variety of essential roles in the human body which employs them, at different extent, to maintain normal yet complex biochemical and physiological functions (Lindh, 2005; Combs, 2005). However, adverse effects on human health may derive from either dietary excess or abnormal exposure (WHO, 1996; Aggett et al., 2015; Nordberg and Nordberg, 2016).

To assess human exposure to potentially toxic elements, human biomonitoring (HBM) is a scientific approach which develops through measurement of chemicals or their metabolites in body fluids and tissues, such as blood (Alimonti et al., 2005; Sanna et al., 2007, 2008, 2011; Gil et al., 2011; Liu et al., 2012; Richmond-Bryant et al., 2013; Coelho et al., 2014), plasma (Vural et al., 2010; Knerr et al., 2013), serum (Alimonti et al., 2005; Klimenko et al., 2016), breast milk (Aquilio et al., 1996; Yamawaki et al., 2005), urine (Berglund et al., 2011; Gil et al., 2011; Sanna et al., 2011; Coelho et al., 2014), lung fluids (Censi et al., 2011a, 2011b), nail (Carneiro et al., 2011a; Coelho et al., 2014) and also hairs (Bencko, 1995; D'Ilio et al., 2000; Violante et al., 2000; Pereira et al., 2004; Amaral et al., 2008; Rodrigues et al., 2008; Sanna et al., 2007, 2008, 2011; Bormann de Souza et al., 2009; Carneiro et al., 2011a, 2011b; Coelho et al., 2014; Mikulewicz et al., 2015). Among these matrices, scalp hair, because of its structure, mainly composed of fibrous keratinocytes, and especially of cystine, the primary amino acid of this protein, constitutes an optimal matrix for HBM due to its ability to accumulate MM in response to dietary intakes and other exposures at a greater extent than other biological matrices and for a longer time frame (ATSDR, 2001; Rodushkin and Axelsson, 2000; Gellein et al., 2008; Rodrigues et al., 2008; Esteban and Castaño, 2009; Abbruzzo et al., 2016).

Even though hair results do not provide quantitative dose-response relationships and their possible clinical significance they constitute an useful tool for screening procedures of exposure. Moreover, scalp hair sampling and analysis possess a number of important advantages over other matrices, including: non-invasive and painless collection, easy transport, storage and chemical inertness of samples (ATSDR, 2001; Esteban and Castaño, 2009) and small specimen size required for analysis.

Despite these vantages, several researchers argue some drawbacks in the interpretation of readings based on hair mineral analysis. Most of these are related to: (1) the scarce theoretical knowledge of the biochemical mechanisms involved in the uptake of MM (ATSDR, 2001); (2) hair analysis results may not relate to MM levels in blood, urine and other target tissues (ATSDR, 2001; Esteban and Castaño, 2009); (3) no uniform opinions on the standard hair analysis protocol (for example the need to wash the samples before analysis (Kempson and Lombi, 2011); (4) inadequacy of reference intervals estimated without taking into account age, gender and ethnicity (Harkins and Susten, 2003; Barbosa et al., 2005; Dongarrà et al., 2011; Tamburo et al., 2015a). With regard to this last point, may be worth noting that trace elements in human hair may depend on several factors as gender, hair color, eating habits, age and lifestyle (Sturaro et al., 1994; Chojnacka et al., 2006, 2010a, 2010b; Zaichick and Zaichick, 2010; Skalnaya et al., 2015; Pan and Li, 2015; Skalny et al., 2015).

Age-specific reference values for some chemical elements were reported by Vanaelst et al. (2012); Zaichick and Zaichick (2010) and Skalnaya et al. (2015). Site-specific reference values for human hair from urban population may be found in Senofonte et al. (2000); Park et al. (2007); Carneiro et al. (2011b); Dongarrà et al. (2011); Vanaelst et al. (2012); Peña-Fernández et al. (2014) and Skalnaya et al. (2015). Differences in the metal content of hair samples from people living close to mining or volcanic areas as well as in urban and industrialized areas have been also reported (Amaral et al., 2008; Dongarrà et al., 2011, 2012; Barbieri et al., 2011; Varrica et al., 2014a, 2014b; Tamburo et al., 2015a).

To estimate causal relationships between environmental factors, human health and the level of trace elements in hair extensive use of coverage intervals (CI) is made. As recommended by International Union of Pure and Applied Chemistry (IUPAC) (Poulsen et al., 1997), they refer to concentration intervals, generally between the 0.025 and 0.975 fractiles, computed from a well-defined group of individuals reflecting normal and healthy people. A critical point in the efficient use of CI, when used for comparative decision-making processes, forensic and clinic considerations, is constituted by the presence of potential confounding factors as the living site of the study population and the specific characteristics of the participants. In particular, the different behavior of female and male with respect to MM content in human hair is rarely taken into account, although it appears to be a key factor in trace metal and metalloid content of human scalp hair (Chojnacka et al., 2006, 2010a, 2010b; Sanna et al., 2007, 2008, 2011; Vahter et al., 2007; Peña-Fernández et al., 2014; Varrica et al., 2014a, 2014b; Tamburo et al., 2015b). The aim of this paper is to further show, by some examples, that the coverage intervals for some trace elements in human hair may be gender-specific. To this purpose 943 hair samples from adolescents of both genders, living in industrial, urban, volcanic and polymetallic mining areas were taken into account.

2. Material and methods

2.1. Sample collection

A total of 943 hair samples from adolescents, from 11 to 14 years old, were analyzed for their content of Al, As, Ba, Cd, Co, Cr, Cu, Li, Mn, Mo, Ni, Pb, Rb, Sb, Se, Sr, U, V and Zn. Donors were 537 females and 406 males, all of them responding to the following exclusion criteria:

- non-Caucasian ethnicity;
- living in the selected area for <5 years;
- presence of diseases;
- habitual use of cigarettes;
- recent surgery or orthodontic treatment;
- colored hair or recent use of hairstyling products.

The use of mineral supplements was not considered during the sampling as being unlikely. Hair samples were categorized into four groups to which the following labels were assigned:

Samples from industrial areas (IA):

- Pace del Mela, a coastal town near Messina (north-eastern Sicily), is an area at high environmental risk, due to the presence of a large petrochemical plant. Outcropping rocks in the study area are mainly of sedimentary origin, with alternating sandstone, clay, limestone, ivory-white calcareous marl, calcarenite and sand; $N_{total} = 111$ (mean age: 12.6 ± 0.95), $N_{male} = 47$ (mean age: 12.7 ± 0.90), $N_{female} = 64$ (mean age: 12.6 ± 1.0; percentage of girls who reached menarche: 70%);
- Gela, Butera and Niscemi are located in southwestern Sicily and, from a geological point of view, they lie on sedimentary rocks represented by limestone, clay, marly-clay, white or yellow quaternary biocalcarenites and gypsum. The municipalities of Gela, Butera and Niscemi were declared "area at high risk of environmental crisis", since 1986 (Law n. 349/1986) due to the presence of a large oil refinery, together with a number of important chemical and petrochemical industries that led to the definition of "site of national concern for soil remediation" (Law n. 426/1998); $N_{total} = 174$ (mean age: 12.3 ± 0.96), $N_{male} = 81$ (mean age: 12.4 ± 0.89), $N_{female} = 93$(mean age: 12.3 ± 1.03; percentage of girls who reached menarche: 52%);

Samples from polymetallic mining area (PA):

- Iglesias and Sant'Antioco, are located in southwestern Sardinia. The large outcrops of sulfide and oxide ores, as well as the products of