SCIENCE OF THE TOTAL ENVIRONMENT 405 (2008) 370–376

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Evaluation of the use of human hair for biomonitoring the deficiency of essential and exposure to toxic elements

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A R T I C L E I N F O

Article history:
Received 27 March 2008
Received in revised form 4 June 2008
Accepted 6 June 2008
Available online 15 July 2008

Keywords:
Hair
ICP-MS
Trace metals
Biomarkers
Nutrition
Blood
Exposure

A B S T R A C T

Monitoring the nutritional status of essential elements and assessing exposure of individuals to toxic elements is of great importance for human health. Thus, the appropriate selection and measurement of biomarkers of internal dose is of critical importance. Due to their many advantages, hair samples have been widely used to assess human exposure to different contaminants. However, the validity of this biomarker in evaluating the level of trace elements in the human body is debatable. In the present study, we evaluated the relationship between levels of trace elements in hair and whole blood or plasma in a Brazilian population. Hair, blood and plasma were collected from 280 adult volunteers for metal determination. An ICP-MS was used for sample analysis. Manganese, copper, lead and strontium levels in blood varied from 5.1 to 14.7, from 494.8 to 2383.8, from 5.9 to 330.1 and from 11.6 to 87.3 μg/L, respectively. Corresponding levels in hair varied from 0.05 to 6.71, from 0.02 to 37.59, from 0.02 to 30.63 and from 0.9 to 12.6 μg/g. Trace element levels in plasma varied from 0.07 to 8.62, from 118.2 to 1577.7 and from 2.31 to 34.2 μg/L for Mn, Cu and Sr, respectively. There was a weak correlation (r=0.22, p<0.001) between lead levels in hair and blood. Moreover, copper and strontium levels in blood correlate with those levels in plasma (r=0.64 , p<0.001 for Cu) and (r=0.22, p<0.05 for Sr). However, for Cu, Mn and Sr there was no correlation between levels in hair and blood. Our findings suggest that while the idea of measuring trace elements in hair is attractive, hair is not an appropriate biomarker for evaluating Cu, Mn and Sr deficiency or Pb exposure.

1. Introduction

Dietary habits and environmental conditions may partly affect trace element levels in both tissues and biological fluids, and consequently their participation in numerous biochemical mechanisms (Dona et al., 2006). Essential elements are those that are required by an organism to maintain its normal physiological function. Without the essential elements, the organism cannot complete its normal life cycle or achieve normal healthy growth; many such elements are key components of metalloenzymes or are involved in crucial biological functions, such as oxygen transport, free radical scavenging, or hormonal activity (Parsons and Barbosa, 2007). On the other hand, many nonessential elements are so ubiquitous in the environment that they are easily detected in human body tissues and fluids. Some are relatively benign, but others, such as Pb, Cd, Hg and As, are quite toxic even at concentrations considered trace (Barbosa et al., 2006a,b; Parsons and Barbosa, 2007). Monitoring the nutritional status of essential elements and assessing exposure of individuals to toxic elements are of critical importance in human health. Today, the assessment of human exposure to background levels of trace elements in

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doi:10.1016/j.scitotenv.2008.06.002

the environment through measurement of those chemicals or their metabolites in human specimens is termed biomonitoring (Angerer et al., 2007; Parsons and Barbosa, 2007). Most clinical methods used to diagnose trace element deficiencies or to assess environmental or occupational exposure to toxic elements rely on the analysis of blood, serum/ plasma, and/or urine specimens. However, the choice of the appropriate specimen depends on several factors, such as toxicokinetics (time of appearance and residence time of the biological parameter), the convenience or invasiveness of the specimen collection procedure, and the potential for specimen contamination. Thus, the appropriate selection and measurement of biomarkers is of critical importance for health care management purposes, public health decision making, and primary prevention activities.

Several alternative, i.e., non-traditional, specimen matrices including saliva, hair, and nails (Wilhelm et al., 1994; Nowak and Chmielnicka, 2000; Wilhelm et al., 2002; Pereira et al., 2004; Barbosa et al., 2006a,b; Slotnick and Nriagu, 2006) that permit non-invasive collection procedures have been explored, Hair is a biological specimen that is easily and noninvasively collected, inexpensive, and easily stored and transported to the laboratory for analysis. These attributes make hair an attractive biomonitoring substrate, at least superficially (Barbosa et al., 2005). These advantages have led to the widespread use of trace element analysis of hair samples to assess wildlife and human exposure to different contaminants present in the environment (Schuhmacher et al., 1991; Wilhelm et al., 1994; Schuhmacher et al., 1996; Sen and Chaudhuri, 1996) or at the workplace (Ashraf et al., 1994). However, hair analysis is subject to certain limitations, such as the occurrence of exogenous contamination. This contributes to a differential increase in the total contents of different contaminants (Bencze, 1990; Miekeley et al., 1998; ATSDR, 2001; Frisch and Schwartz, 2002). The main sources of exogenous contaminants are deposits of sebum, sweat, polluted air residues or residues of cosmetic or pharmaceutical products. Some other constraints on the use of hair analysis have also been pointed out (Bozsai, 1992; ATSDR, 2001; Seidel et al., 2001; Harkins and Susten, 2003) These constraints include the lack of scientific knowledge about the kinetics of trace element incorporation in hair and the insufficiency of epidemiological data to support predictions concerning the health effects, of a specific concentration of each element in hair. Moreover, given the growing use of hair analyses in health studies, an assessment of the biomarker validation criteria, which include the correlation of the levels found in this specimen with those found in blood or plasma, is called for.

The aim of this paper was to evaluate the use of hair as a biomarker of Sr, Zn and Cu deficiency and/or Pb exposure. Thus, the relationship between the level of these elements in hair with their levels in whole blood or plasma was obtained in an adult Brazilian population.

2. Materials and methods

2.1. *Population*

We studied 280 healthy adults (47% women and 53% men) between 18 and 60 years of age from 3 different Brazilian states (São Paulo, Minas Gerais and Pará). Ethical approval was obtained from the Ethics Committee of the University of São Paulo at Ribeirão Preto (Brazil).

2.2. *Sample collection*

2.2.1. *Blood and hair collection*

A trained Brazilian nurse collected a 4-mL blood sample from each participant. Blood samples were collected in trace-metal-free evacuated tubes (BD Vacutainer®) containing heparin as an anticoagulant. Two mL of blood was then pippeted into an eppendorf tube (2 mL volume) previously cleaned in a 100 clean room and immediately frozen at −20 degrees Celsius before analysis. For plasma separation, 2 mL of blood samples were centrifuged (1000 ×*g* for 6 min). The plasma fraction was then pipetted into an eppendorf tube (2 mL volume) previously cleaned in a 100 clean room and was immediately frozen at −20 °C before analysis.

On the same day as blood collection, hair samples were taken from the occipital area of the head, close to the scalp. The lock of hair was stapled at the base and stored in labeled Ziploc bags. Hair samples were cut into 1 cm lengths and washed before analysis. From each 1-cm hair sample collected, 20 mg was weighed for trace element determination.

2.2.2. *Hair washing*

Hair was washed according to the method proposed by Ohmori (1984), with acetone, water and acetone. After washing, samples were dried in a class — 100 laminar flow hood before analysis.

2.3. *Sample analysis*

2.3.1. *Reagents*

All reagents used were of analytical-reagent grade except HNO_3, which was previously purified in a quartz sub-boiling still (Kürner) before use. A clean laboratory and laminar-flow hood capable of producing class 100 were used for preparing solutions. High purity de-ionized water (resistivity 18.2 MΩ cm) obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA) was used throughout. All solutions were stored in high-density polyethylene bottles. Plastic bottles and glassware were cleaned by soaking in 10% (v/v) HNO_3 for 24 h, rinsed five times with Milli-Q water and dried in a class 100 laminar flow hood before use. All operations were performed on a clean bench.

2.3.2. *Instrumentation*

All measurements were made with an ICP-MS (Elan DRC II PerkinElmer, Norwalk, CT) with high-purity argon (99.999%, White Martins, Brazil). A Meinhard concentric nebulizer (Spectron/Glass Expansion, Ventura, CA, USA) connected to a cyclonic spray chamber was used. A radiofrequency (rf) with 1100 watts of power was selected in pulse mode with autolens one. Sample data were acquired by using 20 sweeps/reading, 1 reading/replicate and a dwell time of 50 ms. Argon nebulizer gas flow rate was optimized daily from 0.5 to 0.9 L min^{-1}. Data were acquired in counts per second (cps). The following isotopes were selected: ^{63}Cu, ^{55}Mn, ^{208}Pb, ^{88}Sr.