

## Inter-element interactions in human hair

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### Abstract

The concentrations of 33 elements: Ca, Mg, Na, U, Cu, Zn, P, Fe, Mn, Cr, Se, B, Co, Mo, Si, V, Ni, Be, Hg, Cd, Al, Pb, As, Ba, Au, Pt, Ag, Sr, Sn, Ti, W, Sb and Zr in hair were determined by inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma-atomic emission spectrometry (ICP-AES). Hair samples ( $n = 83$ ) were collected between 1996 and 2003 from inhabitants of city of Wrocław, located in Lower Silesia, south-west Poland (urbanized and industrialized region). Inter-element interactions were studied by evaluation of correlation coefficients between two elements, as well as by multiple regression analysis. The strongest relations found between the elements in the hair were as follows: Mg and Ca, Mn and Ca, Sr and Ca, Sr and Mg, U and Na, Ni and Zn, Mn and Sr, Cd and Ni, Sb and Pt. We obtained also the following essential linear multiple dependences ( $p < 0.05$ ):  $Al = f(U, P, Mn)$ ,  $As = f(Zn, Fe)$  (Zn is negatively correlated,  $\beta < 0$ ),  $Cu = f(V)$ ,  $Fe = f(Mn, As)$ ,  $Mg = f(Ca)$ ,  $Ca = f(Mg, Ba)$ ,  $Ni = f(Zn, Cd)$ ,  $Sb = f(Pt, Sn, W)$  and  $Ti = f(Fe, Co)$ . These relations can be useful in the explanation of relationships among the elements in man.

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### 1. Introduction

Elements enter the organism via different routes; they are transferred from air, water, foods, drugs through skin, respiratory tract and GI tract. Further, they are transported and distributed through blood into organs (i.e. liver, kidney) and removed from the organism through the following excretory pathways: sweat, hair, urine and feces (Apostoli, 2002; Lee et al., 2000). Thus, human hair is an excretory system for trace metals and can act as an accumulating tissue and thus metal content can reflect (“freeze”) the body status for a long period, including exposure in time (Sera et al., 2002), recording the history of personal exposure to metals in time (Almeida et al., 1999; Apostoli, 2002; Teresa et al., 1997). The high affinity of hair to metals is mainly due to the presence of cystine, which makes up approximately 14% of human hair (Morton et al., 2000). The investigation of trace elements in human hair has

been correlated with the diagnosis of various diseases (i.e. cancer) (Wang et al., 1995), as well as in forensic science to demonstrate poisoning states. Hair are also indicators of deficiency states in nutrition (Apostoli, 2002). According to the Environmental Protection Agency (EPA), human hair is one of the most important biological materials for worldwide environmental monitoring (Morton et al., 2000).

Human hair is a reliable and convenient biological indicator of environmental pollution (Miekeley et al., 1998; Leko-uch et al., 1999; Bencko, 1995). The analysis of human hair is used to study environmental and occupational exposure as well as to assess nutritional and bodily status of several metals—essential (Ca, Cr, Cu, K, Mg, Mn, Na and Zn) and toxic (Ag, Al, Cd, Ni and Pb) (Ashraf et al., 1995; Ashraf and Jaffar, 1997; Bermejo-Barrera et al., 2002). Hair, unlike blood or organs, can be collected easily and painlessly, is easy to transport and store (Hać et al., 1997). The elemental composition of hair (unlike blood or urine) reflects long-term exposure to these metals, since hair is an indicator of past changes in metabolism and environmental exposure (Ashraf and Jaf-

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far, 1997). Hair content depends also on age, sex, anatomic location (Hać et al., 1997), hair color, ethnic and geographic origin, dietary habits (Miekeley et al., 1998) and exposure (associated with urbanization and industrialization) (Ashraf and Jaffar, 1997). There are also several problems related with hair analysis, including differentiation between endogenous and exogenous deposition (Rodushkin and Axelsson, 2000) or with metabolic status of a given subject.

Usually, the elemental composition of hair is compared with normal concentration ranges, elaborated for unexposed population (Table 1). Except for a few elements, large variations are common in established normal concentration ranges for hair. This diversity reflects variation of factors affecting element content, such as dietary habits, lifestyle, geochemical environment, age sex, hair color and smoking habits (Rodushkin and Axelsson, 2000).

Lately, increasing interest was directed towards inter-element interactions (antagonistic or synergistic effects), in particular in establishing whether combined exposure to metals, not toxic by themselves, may induce damage to health.

Such interactions have been found in animal experiments (Apostoli, 2002), but have not been clearly confirmed in human.

The studies on inter-element interactions in hair are scarce. Rodushkin and Axelsson (2000) reported synergistic interactions between Hf–Zr, Pb–K, Cs–Rb, Sr–Mg, Nb–Th, K–Na and Tl–Fe. They grouped elements, according to their similarity of properties as well as co-occurrence in nature (alkali and alkali-earth elements: Zr–Hf, Sc–REE and Al–Ga) or common exposure sources (Pt–Au, Hg and Ag). The authors found no significant correlations for essential elements (S, P, Zn, Cu and Se) and potentially toxic (Cd, Pb, As and Tl).

The aim of the present work was to study inter-element interactions in human hair sampled from population group living in urbanized and industrialized region of south-west Poland (Wrocław): to determine, whether the concentration of a given metal in hair was correlated with the concentration of another metal, thus indicating a common origin, a linear correlation study was conducted. Also, linear multiple regression analysis was carried out to study the influence of the pres-

Table 1

Normal concentration ranges for human hair (Miekeley et al., 1998) and descriptive statistics for element concentrations in hair for 266 subjects living in non-industrialized region of south Poland (Silesian Beskid Śląski) (Nowak, 1998), for 114 subjects from an urban population group living in north-east Sweden (Rodushkin and Axelsson, 2000) and for 1091 subjects of Rio de Janeiro city (Miekeley et al., 1998)

| Element | Normal concentration ranges | Poland       |      | Sweden       |         | Rio de Janeiro city |       |
|---------|-----------------------------|--------------|------|--------------|---------|---------------------|-------|
|         |                             | Mean (mg/kg) | S.D. | Mean (mg/kg) | S.D.    | Mean (mg/kg)        | S.D.  |
| Ag      | <0.7                        |              |      | 0.231        | 0.298   | 1.19                | 0.04  |
| Al      | <12                         |              |      | 8.2          | 4.8     | 8.3                 | 0.9   |
| As      | <7                          |              |      | 0.085        | 0.054   | <0.04               |       |
| Au      | 0.002–0.75                  |              |      | 0.03         | 0.028   | 0.01                | 0.01  |
| B       | 1.0–3.0                     |              |      | 0.670        | 0.620   |                     |       |
| Ba      | 0.3–3.5                     |              |      | 0.64         | 0.49    | 6.9                 | 0.7   |
| Be      |                             |              |      | 0.0013       | 0.0009  |                     |       |
| Ca      | 350–860                     | 826          | 880  | 750          | 660     | 802                 | 37    |
| Cd      | <1.0                        | 0.61         | 1.13 | 0.058        | 0.056   | 0.59                | 0.05  |
| Co      | 0.26–0.47                   | 0.44         | 0.72 | 0.013        | 0.011   | 0.13                | 0.01  |
| Cr      | 0.78–1.0                    | 0.60         | 1.13 | 0.167        | 0.118   | <0.3                |       |
| Cu      | 13–35                       | 7.96         | 9.12 | 25           | 21      | 44.1                | 3.5   |
| Fe      | 6.0–15                      | 45.7         | 37.7 | 9.6          | 4.4     | 20.8                | 2.2   |
| Hg      | <1.2                        |              |      | 0.261        | 0.145   | 0.62                | 0.002 |
| Mg      | 40–110                      |              |      | 46           | 38      | 43.9                | 1.0   |
| Mn      | 0.26–0.75                   | 2.41         | 2.24 | 0.560        | 0.550   | 5                   | 0.5   |
| Mo      | 0.21–0.44                   |              |      | 0.042        | 0.020   | 0.05                | 0.01  |
| Na      | 18–87                       | 242          | 147  | 147          | 149     | 87.7                | 2.0   |
| Ni      | <1.6                        | 0.75         | 1.15 | 0.430        | 0.400   | 0.7                 | 0.1   |
| P       | 120–180                     |              |      | 133          | 17      | 119                 | 4.1   |
| Pb      | <6.0                        | 4.99         | 3.90 | 0.960        | 0.850   | 12.5                | 0.7   |
| Pt      |                             |              |      | 0.00015      | 0.00017 |                     |       |
| Sb      | <1.8                        |              |      | 0.022        | 0.017   | 0.02                | 0.005 |
| Se      | 0.38–0.7                    |              |      | 0.830        | 0.280   | 129                 | 5.9   |
| Si      |                             |              |      | 33           | 31      |                     |       |
| Sn      | <3.0                        |              |      | 0.320        | 0.390   | 0.13                | 0.02  |
| Sr      | 1.0–7.6                     |              |      | 1.20         | 1.00    | 5.1                 | 0.4   |
| Ti      |                             |              |      | 0.830        | 0.680   |                     |       |
| U       |                             |              |      | 0.057        | 0.065   |                     |       |
| V       | 0.35–0.80                   |              |      | 0.027        | 0.024   | 0.07                | 0.02  |
| W       |                             |              |      | 0.0053       | 0.0049  |                     |       |
| Zn      | 125–165                     | 129          | 60.2 | 142          | 29      | 156                 | 6     |
| Zr      |                             |              |      | 0.155        | 0.237   |                     |       |

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