Assessment of total human exposure to lead and cadmium

Maja Blanuša Department of Mineral Metabolism, Institute for Medical Research and Occupational Health, Zagreb, Croatia

Introduction

Higher concentrations of lead and cadmium in the environment deserve attention due to their impact on health and human longevity. To make a full assessment of the pollution process and effects, the sequence of events from emission of the pollutant, transport and transformation in the environment, to human exposure and impact on human health must be considered.

Monitoring of environmental pollution relates mainly to identification of sources and assessment of pollution levels. This approach is very often connected with studies of transport pathways and impact on various organisms to assess human risk. The purpose of biological monitoring is to identify and prevent adverse health effects. These two aspects are very closely connected. The control and surveillance of environmental exposure to toxic elements are necessary to prevent hazardous absorption levels. Achieving this goal by collection of specimens for biological monitoring has become an important supplement. Besides surveillance-type assays of human blood, dietary or other environmental samples and measurement of enzyme or metabolite levels may occasionally be substituted as specific indicators of metal concentrations in the body[1].

Indirect methods of human exposure assessment involve daily activities and food consumption. From air pollution and food contamination data, mathematical modelling of daily intake of toxic elements through air and food is possible. The direct method of human exposure assessment to pollutant involves highly motivated volunteers to carry out personal sampling of air and collection of duplicate diets. Such studies are difficult to carry out on large population groups due to problems in obtaining an adequate number of motivated subjects. However, studies on small population groups carried out as a pilot project could possibly give insight into the level of human exposure through different media.

Biological indicators of exposure, complementary to exposure assessment methods, include sampling and analysis of body fluids (blood, urine, sweat, milk), hair, nails and/or deciduous teeth. Post-mortem human organ sampling and analysis is also a way of assessing normal population exposure level and its health impact. By analysing quantity of toxic metal in a target organ, i.e. body, life exposure of a pollutant can be estimated. From these records, the range of human exposure in a population can be analysed to calculate the numbers at risk and identify any sections of the community in particular danger.

Croatia, as a developing country, has a specific position among other European countries because of its very slow and difficult adaptation to the use of unleaded gasoline. Due to high urban traffic density lead in the air is higher compared to other western European cities. Air lead as well as lead in food and drinks are the main source of Croatian population normal exposure to lead. Cadmium intake originates mainly from food and from cigarette smoke in the smoking population. Moreover, Croatia has had several regions devastated during the Serbian aggression of 1991. The impact of many shelling and ammunition stockpile explosions on heavy-metal pollution of environment are still unknown. This aspect of environmental pollution and its impact on human health remains to be explored.

Analytical methods and quality control (QC)

The most common and widespread method for lead and cadmium quantitative analysis in various biological samples is flame atomic absorption spectrometry (FAAS) or electrothermal atomic absorption spectrometry (ETAAS). Different procedures for sample pretreatments are needed according to the type of sample. For environmental food items, whole meals or duplicate diet samples, the most adequate method of mineralization is the dry ashing method. Recently introduced microwave oven destruction methods seem to be adequate. Only whole meals or duplicate diet samples need to be homogenized before sample ashing. Food items can be fresh weighed without homogenization. One to five grams of sample should be sufficient for analysis if dissolved (after ashing) and adjusted to 10 ml of 2-10 per cent nitric acid. Measurements of
lead and cadmium carried out either by FAAS or ETAAS should be done by correction of non-atomic absorption (deuterium or Zeeman).

One of the most important parts of analytical procedure is quality assurance, which shows the degree of reliability and accuracy of the applied method. If the method meets certain criteria, its results can be reliably compared with results done in other laboratories and/or countries. The reference material results from a specific laboratory are compared with international reference values by a statistical test. The test compares regression plots of reference and laboratory results and indicates the maximum acceptable deviation from the reference regression. To illustrate the necessity of the quality control, an example of possible error introduction in the analytical procedure of lead determination is described in reference [2]. The analysis of lead in a duplicate diet by ETAAS was done in reference samples after ashing in porcelain and in quartz crucibles. Results obtained were related to reference values. Lead results were not within the acceptable interval when samples were ashed in porcelain. However, cadmium concentrations found in the same food samples yielded acceptable results after ashing in porcelain. Cadmium and lead in faecal samples after ashing in porcelain gave acceptable results. The difference in lead reaction with porcelain crucible between two biological matrices, food and faeces, shows that the concentration of lead in the biological sample, chemical form, and probably also the concentration of other components of the matrix should be considered in analysing metal content in biological material.

A reliable system for maintaining a high quality of analytical performance is essential. Therefore, the procedures used to ensure quality control, along with estimates of accuracy and the precision of data, should be included when reporting results.

**Environmental monitoring**

Environmental monitoring is generally considered as the monitoring of air or atmosphere. When lead and cadmium are studied, food is equally as important as air, since these are two main environmental media through which lead and cadmium enters into the body.

It is estimated that 80-90 per cent of lead in ambient air derives from the combustion of leaded petrol. Baseline levels of lead in the atmosphere before the industrial age are estimated to be in the range of $5 \times 10^{-5}$ $\mu g/ m^3$. Human activities have raised this concentration in the air considerably. In urban areas, lead pollution from combustion of leaded petrol differs from country to country depending on motor vehicle density and the efficiency of efforts to reduce the lead content of petrol. In non-urban sites, located near urban areas, air lead levels average around 0.5 $\mu g/ m^3$, while in rural areas, levels between 0.1 and 0.3 $\mu g/ m^3$ are found. In most European cities annual means are in the range of 0.5 to 3.0 $\mu g/ m^3$. However, owing to decreases in the lead content of petrol, there is a trend towards lower air lead values. The city of Zagreb's general population exposure study carried out during 1972 gave values of 1.0 to 2.6 $\mu g/ m^3$. Another study performed in Zagreb in the winter of 1987 by direct personal measurements of the breathing zone air resulted in concentrations of 0.140-0.840 $\mu g/ m^3$ as shown in Table I. However, within the same study, the concentrations of lead obtained in the Stockholm breathing zone air were 0.042-0.094 $\mu g/ m^3$. These significantly lower values compared to those in Zagreb could be explained by the higher use of unleaded petrol in Stockholm vehicles.

The mining and smelting of lead ores create pollution of the surrounding air and soil. Pollution depends on the amount of lead emitted, the height of the stack, topography and other local conditions. Measurements of air lead concentrations performed in the lead smeltery in Meža valley (Republic of Slovenia) in 1972 showed high air lead pollution, between 14 and 26 $\mu g/ m^3$ (Table I). After that period, an efficient pollution control was performed by introducing an electrostatic filter in the same smeltery. In 1988 the air lead concentration was lowered to 0.17-1.97 in the summer and 0.38-2.76 $\mu g/ m^3$ in the winter period [5].

Food contaminated with lead originates from high-density centres, particularly those located near to lead smelters and heat- or power-generating plants. High lead levels in soil, vegetables and in meals were found in lead smeltery regions even ten years after the reduction of smeltery lead air pollution [6]. Concentrations of lead in different foodstuffs (vegetables) collected in Croatia's uncontaminated rural regions were within the range of 6-129 $\mu g/ kg$ fresh weight [7]. Daily intake of lead obtained by duplicate diet and faecal elimination method was 6.1-37 $\mu g/ day$ and 8.8-112 per person. Vegetables grown in local gardens near the lead smelter area were found to have much higher lead concentrations than those grown in the control area. The range of lead concentration was 27-24,163 $\mu g/ kg$ fresh weight depending on the proximity from the smeltery [6] as shown in Figures 1.
Assessment of total human exposure to lead and cadmium

Cadmium in air originates mainly from the steel industry, waste incineration, volcanic action and zinc production. Concentrations reported in European rural air ranged from <1 to 5 ng/m³, in urban areas 5-15 ng/m³ and 15-50 ng/m³ in industrial areas[3]. The range of values, obtained by measurements of breathing zone air in Zagreb in 1987, was 1.7-9.9 ng/m³. In the lead smeltery area the lowest cadmium value in summer and the highest in winter 1988 was 2.0 and 18.9 ng/m³ respectively (Table I).

The direct input of cadmium into arable soils originates mainly from phosphate fertilizers or municipal sewage sludge[9]. The daily intake of cadmium via food is much higher than by air. In European countries and in North America the average intake of 10-30 µg/day is reported[3]. In the Croatian rural control region a range of cadmium concentrations in vegetables of 3-283 µg/kg fresh weight was obtained[7]. In lead smeltery areas it was 37-440 µg/kg[6] (Figures 1 and 2). In the Zagreb area values of cadmium daily intake between 3.5-18.6 µg/day were obtained by duplicate diet method and values of between 5.0-25 µg/day by faecal elimination method[7]. In the lead smeltery area daily intake of cadmium obtained by the duplicate diet sampling method was 3.6-22.8 µg/day[8], this being within the same range as in the Zagreb urban area.

| Table I |
| Air lead and cadmium exposure monitoring of different population groups (data from [5]) |

<table>
<thead>
<tr>
<th>Pollutant (µg/m³)</th>
<th>Number of subjects</th>
<th>Range (µg/m³)</th>
<th>Method, year of measurement, area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>17</td>
<td>1.0-2.6</td>
<td>Population exposure, 1972 Zagreb</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>0.14-0.84 (w)</td>
<td>Personal exposure*, 1987 Zagreb</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>0.26</td>
<td>Population exposure, 1972 lead smeltery</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0.38-2.76 (w)</td>
<td>Individual exposure*, 1988 lead smeltery</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.17-1.97 (s)</td>
<td>Individual exposure*, 1988 lead smeltery</td>
</tr>
<tr>
<td>Cd (ng/m³)</td>
<td>17</td>
<td>1.7-9.9</td>
<td>Personal exposure*, 1987 Zagreb</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>3.7-18.9 (w)</td>
<td>Individual exposure*, 1988 lead smeltery</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>2.0 - 11.2 (s)</td>
<td>Individual exposure*, 1988 lead smeltery</td>
</tr>
</tbody>
</table>

Notes:
- a = direct measurement:
- b = calculation from microenvironmental data performed one week in winter (w) and in summer (s)

Systematic sampling and analysis of human or other biological specimens may help greatly in understanding the relationship between exposure to toxic elements and health hazards. Biological monitoring can establish reference baselines of pollutant concentrations in human beings and provide early warning of increasing levels. In addition, biological monitoring can make existing environmental (physical and chemical) monitoring systems more cost effective by establishing direct or indirect links to humans. Pollutant concentrations found in human beings can be related to sources of environmental contamination, and the population risk can be defined. The effectiveness of control measures may be assessed through periodical biological monitoring that will detect changes in levels of pollutants in man. A lead level is very easily deposited in calcified tissues, but lead level is a representative and reliable indicator of cumulative long-term exposure to lead. Therefore, monitoring of lead in teeth, together with other biological parameters, would give insight into lead body burden and health effects. Since children present a high-risk population group in respect to lead exposure, an international study on "Biological indicators of lead neurotoxicity in children" was sponsored by WHO/CEC in 1985. Within this study lead in deciduous teeth was determined in children residing near lead smeltery in the Republic of Slovenia. Ranges of concentrations obtained were 3.5-12.5 mg/kg (n = 9) in the control area and 5.0-85.1 (n = 40) in the smeltery area. Lead body burden depended on the home distance from the smeltery. By relating several parameters (zinc, copper, iron, residence, ash and age) in factor analysis, lead concentration in deciduous teeth was closely related with concentration of zinc and residential distance[10]. These results indicated that deciduous teeth might be a good indicator of environmental exposure to several trace elements.

During the 1980s monitoring of cadmium in human kidney cortex in Zagreb was performed within the UNEP/WHO Project on "Assessment of Human Exposure to Pollutants through Biological Monitoring". In 50 samples of post-mortem kidney samples from the Zagreb area, a geometric mean of 24.2 mg Cd/kg wet weight of kidney cortex was obtained. Within the same study performed...
in eight different countries, the lowest value of 9.0 mg/kg (n = 42) was reported in India and the highest 56.2 mg/kg (n = 50) in Japan[11]. Concentrations of cadmium in the kidney cortex of non-smokers and smokers in Zagreb were 12.9 (n = 20) and 39.5 (n = 31), respectively[12]. Cadmium, together with other parameters such as zinc and copper concentrations, histopathology, smoking habits and age, were statistically related by means of factor analysis. The results showed that smoking habits, and cadmium and zinc levels, were clearly associated in one factor, showing the possible health-related impact of enhanced cadmium body burden.

**Exposure assessment – personal sampling method**

The method of assessment of total human exposure to lead and cadmium through air and food is described to illustrate a model of direct human exposure evaluation. The study was carried out within the WHO/UNDP pilot programme performed simultaneously in several other countries[4]. The purpose of the programme was to improve the reliability of data obtained in different countries and to provide the basic data enabling exposures in a given population to be determined. The first phase of the project consisted of analytical...
training and the second consisted of a pilot exposure monitoring study for Pb and Cd including an extensive quality control component. The experience gained in the quality control programme showed that good analytical performance for one type of medium was no guarantee of good analytical results with other types of media. Exposure monitoring was carried out in 1988 on a small group of 17 nonsmoking women in Zagreb. The monitoring included measurement of the intake of the two metals via air and diet during a period of seven days. Duplicate daily diets and air filter samples were collected by personal sampling method for analysis of lead and cadmium. To check the intake of lead and cadmium with the daily diet, faeces was collected and analysed. The mean gastrointestinal absorption was estimated to be 4.9 μg/day for lead and 0.75 μg/day for cadmium. These values were derived from faecal data assumed to be more reliable. The daily absorption through inhalation estimated on the basis of air was 2.7 μg for lead and 0.03 μg for cadmium[13].

A slightly modified method of exposure assessment to lead and cadmium was applied in the lead smeltery area[8]. Lead and cadmium intake and absorption data were calculated from micro-environmental air measurements and from duplicate diets over one week.
in winter and one in summer. Mean absorption of lead through air in subjects from the smeltery area was 6.8 μg/day (range 1.7-19.7) and from food and beverages 10.9 μg/day (range 1.3-57.2). Although within wide ranges, relative contribution of lead intake through food (and beverages) was considerable. The calculated mean absorption for cadmium through inhalation and ingestion was 0.04 (range 0.02-0.12) and 0.52 μg/day (range 0.18-1.14), respectively. The results show that people living in this area, particularly those who prepared and consumed meals with vegetables grown in their gardens, may have had higher lead intake than the Provisional Tolerable Weekly Intake (PTWI) defined by WHO (3.0 mg/person).

In conclusion, both populations (urban and lead smeltery area) studied showed that 61-64 percent of absorbed lead and 92-96 percent of absorbed cadmium originates from ingested food.

Therefore, such a "total exposure assessment" approach seems to be justified because it pointed out the importance of lead and cadmium intake through food in these population groups.

References