Fluoride in the urine, hair, and nails of phosphate fertiliser workers

W Czarnowski, J Krechniak

Abstract

The fluoride content in the urine, hair, and nails of 106 workers employed in a phosphate fertiliser plant was significantly raised above the control level. Positive correlations were found between the group means for concentrations of fluorides in urine and hair (r = 0.77), urine and nails (r = 0.99), and hair and nails (r = 0.70). Individual values in the whole population gave significant correlations between concentrations in urine and nails (r = 0.73). The obtained results indicate that the fluoride content in hair and nails may be used as an indicator of occupational exposure to fluorides.

Fluorapatites and phosphorites are used in manufacturing phosphate fertilisers. About 3% or 4% of these raw materials is fluoride. During the preparation of soluble phosphates, treatment with sulphuric acid releases about half the fluoride in gaseous form, mostly as hydrogen fluoride (HF). The reaction of hydrofluoric acid with silica present in the rock also produces silicon tetrafluoride. During the whole procedure workers are exposed to fluoride gases and dusts. Also, the finished phosphates contain some fluoride and are potentially dangerous. The exposure to fluoride compounds may be evaluated by air analyses.

It is generally accepted, however, that a better index of exposure is urinary excretion. Continuous fluoride inhalation at low concentrations creates a steady state in fluoride balance.

At steady state fluoride concentration in air correlates with the average urine concentration of fluoride in samples collected during the shifts and in the 24 hour urine samples. The best correlation occurred when postshift urine samples were evaluated.12

More recently hair analyses were used also to evaluate exposure. It is not a routine procedure but it is gaining importance especially in the evaluation of environmental exposure. Raised hair concentrations of different elements (arsenic, cadmium, and mercury) reflect industrial and environmental exposure from air pollution and the contamination of drinking water and food.34 Balazova ascertained increased fluoride concentrations in the urine, hair, and nails of children exposed to gaseous fluoride compounds emitted from an aluminium smelter.6 One of us (JK) found a positive correlation between the duration of exposure of welders and the fluoride level in hair.7 Also the fluoride content in the hair of rats was increased by sodium fluoride in drinking water.8

The aim of the present study was to evaluate the exposure of fertiliser plant workers employed on different posts and exposed to fluorine compounds. The exposure may be crudely graded into three levels. High exposure was at workplaces where superfos- phate, fluorosilicate, and phosphoric acid were produced (mean HF concentrations 0.5–3.0 mg/m³). Median exposure was in groups 2 and 7 (table 1), where mean HF concentrations were below 0.5 mg/m³. Low exposure was in units located in the vicinity of the plant (laboratory, office, production of sulphuric acid). The employees are exposed mostly on gaseous fluoride compounds. The level of particulate fluorides is only about 1% of the HF concentrations. The fluoride concentrations in workshop air changed irregularly during the workshift. As no personal dosimeters were available, the exposure was estimated by analyses of workers’ urine, hair, and nails.

Materials and methods

Fluoride concentrations in the urine, hair, and nails of 106 employees (88 men and 18 women) of a phosphate fertiliser plant were determined. The mean age of the examined group was 39.7 years (range 22–61) and the mean period of employment was 14.9 years (range 1–35). Samples of urine were collected during the workshift and immediately thereafter. Samples of hair (minimal length 1.5 cm) and nails were taken on the same day. The control group consisted of workers not exposed occupation-
ally to fluorine compounds (mean age 38-3 years, range 21-57). The concentration of fluorides in drinking water in the investigated region ranges from 0.5 to 1.0 mg/l.

Fluoride in urine was determined by a fluoride specific electrode and an Ag/AgCl reference electrode with a double jacket. Before measurement samples were diluted with equal amounts of (pH = 7.0) citrate buffer. The accuracy of measurements was tested with "Lananorm Metals 2" controls. Determined values in controls were within the assigned confidence range.

Samples of hair and nails were brushed and then rinsed on a fritted glass filter with acetone, detergent, 2N sulphuric acid, and redistilled water. After drying 100 mg aliquots were placed into test tubes, treated with concentrated sodium hydroxide solution, and heated in a boiling water bath until complete solution (hair—30 minutes; nails—60 minutes). Cooled and neutralised samples made up with water to 4 ml were diluted with equal volumes of citrate buffer. Fluoride concentrations were measured by a fluoride specific electrode. Calculations were based on a response factor from a standard curve prepared daily. Recovery of F⁻ from hair and nails amounted to 100 ± 8%. The coefficient of variation in 10 samples of hair obtained from the same person amounted to 9.2%.

**Results**

The fluoride contents in urine, hair, and nails of workers employed in a phosphate fertiliser plant were higher than in controls (table 1). The differences were significant in nails for all groups of employees (2-8), in urine and hair only in workers employed at the production and dispatch of superphosphate, production of fluorosilicate, and phosphoric acid (2-5).

Positive correlations were found between group means for fluoride concentrations between urine and hair (r = 0.77), hair and nails (r = 0.70), as well as urine and nails (r = 0.99). Individual values in the total population gave a positive correlation only for concentrations in urine and nails (r = 0.73). No correlation was found between the period of employment and the fluoride content in indicator media.

**Discussion**

Normal values for urinary fluoride depend mostly on the fluoride concentration in drinking water. It is generally accepted that in regions without excessive fluoride in water the normal concentration in urine is about 0.4-2.0 mg/l. Fewer data are available on fluoride in hair and nails. Values presented by different authors range from 1 to 30 μg/g and 5 to 200 μg/g respectively. Some differences in published data may be caused by using various methods. In this study the mean fluoride values in controls were estimated as: 1.32 mg/l and 1.16 mg/g creatinine for urine, 5.4 μg/g for hair, and 8.8 μg/g for nails.

In workers employed in the production units of the plant (groups 2-5) where hydrogen fluoride concent-

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**Table 1**  Fluoride content in urine, hair, and nails

<table>
<thead>
<tr>
<th>No</th>
<th>Workplace</th>
<th>Urine (μg Fr/l)</th>
<th>Urine (μg Fr/g creatinine)</th>
<th>Hair (μg Fr/g)</th>
<th>Nails (μg Fr/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No</td>
<td>Mean ± SD</td>
<td>p</td>
<td>No</td>
<td>Mean ± SD</td>
</tr>
<tr>
<td>1</td>
<td>Controls</td>
<td>19 1.32 ± 0.53</td>
<td>&lt;0.001</td>
<td>19 1.16 ± 0.40</td>
<td>36 5.4 ± 1.7</td>
</tr>
<tr>
<td>2</td>
<td>Superphosphate production</td>
<td>21 3.79 ± 1.99</td>
<td>&lt;0.001</td>
<td>24 3.52 ± 2.69</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>3</td>
<td>Superphosphate dispatch</td>
<td>11 2.65 ± 0.79</td>
<td>&lt;0.001</td>
<td>11 2.06 ± 0.67</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>4</td>
<td>Fluorosilicate production</td>
<td>7 11.43 ± 7.42</td>
<td>&lt;0.001</td>
<td>7 8.50 ± 5.12</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>5</td>
<td>Phosphoric acid production</td>
<td>18 3.42 ± 2.14</td>
<td>&lt;0.001</td>
<td>18 3.07 ± 1.63</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>6</td>
<td>Sulphuric acid production</td>
<td>5 1.48 ± 0.46</td>
<td>&lt;0.001</td>
<td>5 1.98 ± 1.00</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>7</td>
<td>Division of chief engineer</td>
<td>7 3.40 ± 3.48</td>
<td>&lt;0.001</td>
<td>7 2.06 ± 1.51</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>8</td>
<td>Laboratory</td>
<td>7 2.10 ± 0.88</td>
<td>&lt;0.001</td>
<td>7 1.86 ± 0.95</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>9</td>
<td>Office</td>
<td>15 2.23 ± 1.02</td>
<td>&lt;0.001</td>
<td>15 1.80 ± 0.92</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

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**Table 2**  Correlation coefficients (r) of fluoride contents in urine, hair, and nails. (Numbers in parentheses give the number of comparisons)

<table>
<thead>
<tr>
<th>Workplace</th>
<th>r(Urine/hair)</th>
<th>r(Urine/nails)</th>
<th>r(Hair/nails)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Controls</td>
<td>+0.07 (18)</td>
<td>-0.29 (19)</td>
<td>+0.71 (19)</td>
</tr>
<tr>
<td>2 Superphosphate production</td>
<td>+0.02 (24)</td>
<td>-0.13 (17)</td>
<td>+0.26 (17)</td>
</tr>
<tr>
<td>3 Superphosphate dispatch</td>
<td>+0.75 (8)</td>
<td>+0.41 (9)</td>
<td>+0.71 (8)</td>
</tr>
<tr>
<td>4 Fluorosilicate production</td>
<td>+0.01 (7)</td>
<td>+0.69 (6)</td>
<td>+0.17 (6)</td>
</tr>
<tr>
<td>5 Phosphoric acid production</td>
<td>-0.03 (18)</td>
<td>+0.32 (17)</td>
<td>+0.65 (17)</td>
</tr>
<tr>
<td>6 Sulphuric acid production</td>
<td>-0.33 (5)</td>
<td>-0.52 (5)</td>
<td>+0.51 (7)</td>
</tr>
<tr>
<td>7 Division of chief engineer</td>
<td>+0.84 (7)</td>
<td>+0.94 (7)</td>
<td>+0.97 (7)</td>
</tr>
<tr>
<td>8 Laboratory</td>
<td>+0.92 (6)</td>
<td>+0.17 (7)</td>
<td>+0.90 (6)</td>
</tr>
<tr>
<td>9 Office</td>
<td>+0.49 (14)</td>
<td>-0.02 (13)</td>
<td>+0.08 (12)</td>
</tr>
<tr>
<td>All categories</td>
<td>+0.28 (87)</td>
<td>+0.73 (79)</td>
<td>+0.38 (79)</td>
</tr>
</tbody>
</table>
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Fluoride in the urine, hair, and nails of phosphate fertiliser workers. In conclusion, our results seem to indicate that a considerable increase in fluoride content in all text materials occurred in each group of employees in the fertiliser plant. The increase depended on the degree of occupational exposure. By far the highest increment was noticed in the hair. Taking into account the availability of this material, hair may be regarded as a useful material in evaluating prolonged exposure to fluoride compounds.

8 Krechniak J. Fluorides in drinking water and hair. Fluoride 1975;8:38-40.

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