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

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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.

Fluoroapatites 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 fluorine compounds may be evaluated by air analyses.

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

At steady state fluorine 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.[1 2]

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.[3 4] Balazova ascertained increased fluoride concentrations in the urine, hair, and nails of children exposed to gaseous fluoride compounds emitted from an aluminium smelter.[5 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 superphosphate, fluorosilicate, and phosphoric acid were produced (mean HF concentrations 0·5–3·0 mg/m^3).

Median exposure was in groups 2 and 7 (table 1), where mean HF concentrations were below 0·5 mg/m^3.

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 fluorine 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-

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Table 1 Fluoride content in urine, hair, and nails

No	Workplace	Urine (mg F/l) No	Mean ± SD	p	Urine (mg F/g) creatinine No	Mean ± SD	p	Hair (μg F/g) No	Mean ± SD	p	Nails (μg F/g) No	Mean ± SD	p
1	Controls	19	1·32 ± 0·53		19	1·16 ± 0·40		36	5·4 ± 1·7		22	8·8 ± 2·7	
2	Superphosphate production	21	3·79 ± 1·99	<0·001	24	3·52 ± 2·69	<0·001	25	1081 ± 988	<0·001	17	124 ± 111	<0
3	Superphosphate dispatch	11	2·65 ± 0·79	<0·001	11	2·06 ± 0·67	<0·001	8	438 ± 450	<0·01	10	60·3 ± 51·2	<0
4	Fluorisilicate production	7	11·43 ± 7·42	<0·01	7	8·50 ± 5·12	<0·001	7	1007 ± 699	<0·001	6	624 ± 577	<0
5	Phosphoric acid production	18	3·42 ± 2·14	<0·001	18	3·07 ± 1·63	<0·001	19	471 ± 389	<0·001	17	119 ± 117	<0
6	Sulphuric acid production	5	1·48 ± 0·46	<0·5	5	1·58 ± 1·00	<0·4	7	25·8 ± 37·2	<0·2	7	24·8 ± 19·2	<0
7	Division of chief engineer	7	3·40 ± 3·48	<0·2	7	2·06 ± 1·51	<0·2	8	77·2 ± 142	<0·2	7	61·9 ± 72·7	<0
8	Laboratory	7	2·10 ± 0·88	<0·05	7	1·86 ± 0·95	<0·1	6	12·4 ± 10·9	<0·2	8	52·7 ± 51·8	<0
9	Office	15	2·23 ± 1·02	<0·01	15	1·80 ± 0·92	<0·02	14	6·1 ± 2·7	<0·4	14	19·2 ± 14·5	<0

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.[9] Before measurement samples were diluted with equal amounts of (pH = 7·0) citrate buffer. The accuracy of measurements was tested with "Lananorm Metals 2" control urine (Behring). 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.[10] 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).[11] 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.[1,2,9,12] 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.[5,6,8,10,13] 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 concen-

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

	Workplace	r (Urine/hair)	r (Urine/nails)	r (Hair/nails
1	Controls	+0·07 (18)	−0·29 (19)	+071 (19)
2	Superphosphate production	+0·02 (24)	−0·13 (17)	+0·26 (17)
3	Superphosphate dispatch	+0·75 (8)	+0·41 (9)	+0·71 (8)
4	Fluorosilicate production	+0·01 (7)	+0·69 (6)	+0·17 (6)
5	Phosphoric acid production	−0·03 (18)	+0·32 (17)	+0·65 (17)
6	Sulphuric acid production	−0·33 (5)	−0·52 (5)	+0·51 (7)
7	Division of chief engineer	+0·84 (7)	+0·94 (7)	+0·97 (7)
8	Laboratory	+0·82 (6)	+0·17 (7)	+0·90 (6)
9	Office	+0·49 (14)	−0·02 (13)	+0·08 (12)
	All categories	+0·28 (87)	+0·73 (79)	+0·38 (79)

tration in air exceeded three to six fold the MAC value in Poland (0·5 mg HF/m^3), mean fluoride concentration in urine, hair, and nails was high, though it exceeded the biological limit value for urine in Poland (3–4 mg/g creatinine) only in workers producing fluorosilicates (group 4) and in 12 members of groups 2 and 5. On the other hand, low fluoride concentrations were found in workers employed in the office, laboratory, and sulphuric acid production, where the exposure is much lower. The estimated urinary fluoride concentrations were comparable to values obtained by different authors in other Polish phosphate fertiliser plants.[13 14]

The highest increase in fluoride content was found in hair. In highly exposed workers the obtained results exceeded even more than a hundredfold the normal value. There is often, however, a large dispersion of results within a group of employees caused most probably by differences in exposure. For example, in the production of superphosphate the highest value was 3650/μg/g and the lowest 10·0 μg/g (an electrician).

An individual variation may be caused by considerable differences in absorption, distribution, and excretion of fluorides or by differences in eating and drinking habits and work practices.

The correlation between fluoride concentration in different index media was not consistent. Within groups the correlation was mostly poor or nonsignificant (table 2). Nevertheless, when group means were used consistent positive correlations were found for fluoride concentrations in urine and hair ($r = 0·77$), urine and nails ($r = 0·99$), and hair and nails ($r = 0·70$). When individual rather than group values were correlated a positive correlation was found only between the concentrations in urine and nails ($r = 0·73$).

For reasons mentioned above no correlations between fluoride concentrations in biological media and air could be established.

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 fluorine compounds.

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