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DISTRIBUTION OF SOME TRACE ELEMENTS IN BIOSUBSTRATES OF WORKERS OCCUPIED IN THE PRODUCTION OF MINERAL NITROGENOUS PHOSPHATE FERTILIZERS

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Распределение некоторых микроэлементов в биосубстратах
рабочего персонала, занятого в производстве минеральных
азотно-фосфорных удобрений

Приведены данные по содержанию некоторых микроэлементов, характерных для производства азотно-фосфорных минеральных удобрений (F, Sr, РЗЭ), а также тяжелых и токсичных металлов в промпродуктах, воздухе рабочей зоны, питьевой воде и биосубстратах (моча, волосы) рабочего персонала предприятия. Показана взаимосвязь между содержанием F в моче и волосах рабочих; между уровнем содержания F в моче, рабочим стажем и возрастом работника. Оценена корреляционная зависимость между содержанием в биосубстратах F и ряда характерных для данного типа производства микроэлементов. Проведено сравнение уровня и характера заболеваемости рабочих предприятия и населения, не имеющего контакта с производством.

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Distribution of Some Trace Elements in Biosubstrates
of Workers Occupied in the Production of Mineral
Nitrogenous Phosphate Fertilizers

The data on the content of some trace elements typical for the production of nitrogenous phosphate fertilizers (F, Sr, rare-earth elements), as well as heavy and toxic metals in industrial products, occupational air, drinking water and biosubstrates (urine, hair) of the factory workers are presented. The correlations between the content of fluorine in urine and hair of workers and between the content of fluorine, length of service and age, have been shown. The correlation dependence between the content of F in biosubstrates and a number of trace elements typical for the given type of production has been evaluated. The comparison of the morbidity and character of diseases of the factory workers and of the local residents unoccupied in the production has been made.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR, and at the Geological Institute of RAS, Moscow.

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INTRODUCTION

Workers of unhealthy trades occupied in the production of mineral phosphate fertilizers constantly or periodically contact with a number of toxic substances, among which inorganic compounds of fluorine (anhydrous hydrogen fluoride, sodium fluoride, cryolite, sodium silicofluoride) are the most significant.

Fluorine enters the human body via the respiratory organs and the digestive tract. On inhaling, anhydrous hydrogen fluoride is completely absorbed in blood, where it circulates in a complex with serum albumin. Bones and, to a significantly lesser degree, teeth and hair are a deposition medium for the absorbed fluorine.

Fluoride compounds are cleared from the body very slowly, mainly with urine. On entry of fluorine into the body, a toxic fluoride-ion is formed being a protoplasmic and enzymatic toxin of multiple action. It is responsible for imbalance in oxidation-reduction processes and mineral metabolism (especially calcium and phosphoric metabolism). As a result, poorly soluble calcium fluoride is formed in the body, making calcium biologically inert. In principle, fluorine adversely affects all systems of an organism, but its pathologic effect on bone, excretory, immune and endocrine systems, on respiratory apparatus and organs of vision, is especially detrimental. The effect of fluorine on nervous system and the development of allergic reactions are considered to be secondary.

The biomarker of the fluoride effect is the fluoride-ion itself [1, 2]. In most cases to diagnose its effect, urine is analyzed and the obtained data are compared with the physiological, allowable and critical levels of fluorine accepted for a human organism. For diagnostics of fluorine intoxication at early stages in the medical and sanitary-hygienic literature the following levels of fluorine in urine are indicated: physiological — 1.5 mg/l, allowable — 2 mg/l, critical — 4 mg/l. In the literature it is pointed out that hair is a deposition biomaterial for fluorine [3]. A clear dependence of the fluorine content in hair on its concentration in the occupational air has been revealed. It has been found out that the concentration level of fluorine in hair of people who have no occupational contact to fluorine, but live in the plant impact area, is 80–100 μg/g, and the fluorine content in hair of people unexposed to its action does not exceed 10 μg/g [4].

Apart from fluorine, the production of phosphate fertilizers is characterized by the presence of some other trace elements in raw materials and technological products [5–8]. The behavior of these trace elements in biosubstrates of workers exposed to harmful action of fluorine is practically unexplored. A study of the relation between fluorine and other trace elements in biosubstrates is of interest: this relation may reflect an integrated occupational impact on workers' health.

The aim of the present study is to determine the level of fluorine impact on the manufacturing personnel occupied in the production of mineral phosphate fertilizers, to search for the relation between the fluoride impact and microelement composition of workers' biomaterials, to evaluate the level of fluorine impact on the disease incidence of the manufacturing personnel. The plant «Voskresensk mineral fertilizers» in the town of Voskresensk in the Moscow Region has been chosen to be a subject of investigation.

In the framework of this study the following tasks were to be fulfilled:

• Determination of the concentration range of fluorine and other characteristic trace elements in diagnostic biosubstrates of the factory workers;

• Determination of statistically significant dependencies between concentrations of fluoride-ions and other trace elements in diagnostic biosubstrates of the factory workers (urine, hair);

• Evaluation of the relation between the specific character of production, the length of service in the factory, worker's age and the specificity of fluorine distribution in the factory workers' biosubstrates;

• Evaluation of the level and specificity of sickness rate of the factory workers as compared to the population unoccupied in the production.

EXPERIMENTAL PROCEDURE

The plant «Voskresensk mineral fertilizers» is located in the southeast suburb of the town of Voskresensk and occupies a territory of more than 10 km^2. At present, seven shops of the plant are in service: shops of phosphoric acid extraction (PAE-1, 3, 4); shops of ammophos production (A-1, 2); shop of precipitation of fluorine salts (PFS); shop of fluorine salt production (FSP).

In the shops of phosphoric acid extraction, raw apatite is treated with sulfuric acid with the resulting formation of pulp consisting of phosphogypsum and phosphoric acid with an admixture of a significant amount of hydrofluoric acid. In the shops of ammophos production the ammonation (interaction of phosphoric acid with ammonia), granulation and drying of the finished products are carried out. Hydrofluoric acid obtained as a by-product in the shops PAE-1, 3, 4 and A-1, 2 is used to produce fluorine salts in the shops PFS and FSP. Since raw apatite contains up to 3 % of fluorine and ammophos contains up to 1–1.5 % of fluorine, at various stages of the manufacturing process the problem of its disposal and reduction of its emissions into the ventilation system arises.

In the process of production of phosphoric acid and ammophos, a gas phase containing fluorine compounds as HF, SiF_4 and ammonia is emitted into the occupational air and sanitary ventilation. During transportation, mechanical processing and warehousing of raw materials and products, a dust fraction is formed that contains fluorine, rare-earth elements and Sr.

In the course of the study, samples of raw materials (apatite), finished products (ammophos) and wastes (phosphogypsum), as well as diagnostic biosubstrates of the production personnel were taken. During the examination the factory workers filled out the questionnaires where they specified their age, length of service (overall and in a shop), occupation, home address. The characteristics of statistical sampling of workers of shops with harmful conditions are given in Table 1. The number of women was 23.6 %.

Table 1. **Data on age and length of service of the examined workers of shops with harmful conditions**

Parameters	PAE-1, 3, 4	A 1, 2	PFS, FSP	Total
Number of people employed	75	42	27	144
Number of women	13	14	7	34
Age, years	44	46	46	45
Length of service, years	23	26	24	24
Length of service in harmful conditions, years	13	15	15	14
Age of entry into the labour activity, years	21	19	22	21

In the polyclinic of the factory the incidence of 25 classes of diseases and specific diseases among the factory workers has been analyzed. The data have been taken from the official annual reports of the factory medical center for 1989–2001.

These data have been compared to the data on other local residents of the town of Voskresensk for the same years. The statistical analysis included diseases, which could be caused by occupational hazards: neoplasms; blood diseases; diseases of musculoskeletal, endocrine and nervous systems; eye and ear diseases; diseases of blood circulation system; of respiratory and digestive organs, of urogenital system; skin diseases, as well as injuries and poisonings.

The analysis of chemical composition of the obtained samples was carried out at the Laboratories of GIN RAS (Moscow) and JINR (Dubna). For determination of chemical composition of the samples the following analytical methods were used: neutron activation analysis (Na, Sc, Cr, Fe, Co, Zn, As, Se, Br, Sb, Cs, La, Ce, Au, Hg, Th), X-ray fluorescence analysis (Ca, Ti, Cu, Zn, Sr, Y, Zr, Nb, Ba, Pb, Th, U), potentiometric analysis (F), atomic absorption analysis (Mn, Fe, Ni, Cu, Zn, Cd, Pb), and inductively coupled plasma mass spectromety (Al, Li, Pr, Nd, Sm, Eu, Tb, Dy), [9–18, 19–22].

The quality of the results has been repeatedly confirmed in the course of intercomparison analytical tests within the framework of programs of cooperation with IAEA [32–34].

Table 2. **Chemical composition of raw materials, finished products and wastes, mg/kg**

Element/Object	Apatite concentrate		Ammophos		Diammophos	Fluoride salts	Phosphogypsum	
Year of production	1997	2001	1997	2001	2001	2001	1997	2001
F, %	2.3 ± 0.3	2.6 ± 0.3	1.2 ± 0.2	1.2 ± 0.2	1.0 ± 0.2	not found	0.14 ± 0.02	0.14 ± 0.02
Water-soluble F, %	not found	not found	not found	0.28 ± 0.02	0.2 ± 0.02	0.1 ± 0.02	not found	0.023 ± 0.003
P_2O_5, %	40.7 ± 1.0	41 ± 1.0	65 ± 1.0	65 ± 1.0	55 ± 1.0	not found	1.4 ± 0.1	1.3 ± 0.1
Ca	30 ± 1.0	40 ± 1.0	0.75 ± 0.01	0.68 ± 0.01	0.72 ± 0.01	< 0.1	39 ± 1.0	40 ± 1.0
Cr	< 5	24 ± 3	< 5	< 5	< 5	21 ± 3	28 ± 3	18 ± 3
Cu	100 ± 10	120 ± 10	50 ± 10	50 ± 10	50 ± 10	< 20	< 20	70 ± 10
Zn	70 ± 10	130 ± 10	50 ± 10	40 ± 10	50 ± 10	10 ± 3	< 10	150 ± 10
As	1.0 ± 0.1	1.5 ± 0.1	< 0.1	< 0.1	0.7 ± 0.1	2.8 ± 0.2	< 0.1	< 0.1
Sr	2.0 ± 0.1	2.5 ± 0.1	0.04 ± 0.001	0.017 ± 0.001	0.023 ± 0.001	0.001 ± 0.000	1.4 ± 0.1	1.5 ± 0.1
Ba	800 ± 50	770 ± 50	40 ± 1.0	20 ± 1.0	30 ± 1.0	< 10	550 ± 50	600 ± 50
La	1900 ± 100	2000 ± 100	110 ± 10	23 ± 3	29 ± 3	1.9 ± 0.3	1000 ± 100	850 ± 100
Ce	3000 ± 100	3200 ± 100	210 ± 10	35 ± 5	60 ± 5	2.5 ± 0.3	1400 ± 100	1800 ± 100
Sb	8.7 ± 1.0	< 0.5	< 1	< 0.5	< 0.5	< 0.5	< 1	< 0.5
Th	23 ± 3	18 ± 3	12 ± 2	6.8 ± 1	6.0 ± 1	< 1	6.0 ± 1	10 ± 1
U	9.4 ± 1.0	1.3 ± 0.2	< 5	< 1	< 1	< 1	10 ± 1	< 1
Pb	1.2 ± 0.3	< 1	< 1	< 1	< 1	< 1	1.0 ± 0.3	< 1

RESULTS AND DISCUSSION

To study the major factors of impact of manufacturing processes on workers of the mineral fertilizers plant, the composition of basic components of the technological production chain (initial apatite raw materials, finished products (ammophos, diammophos, fluoride salts), waste products (phosphogypsum)) has been investigated. The contents of fluorine, phosphorus and trace elements in apatite and technological production of the Voskresensk plant in 1997 [7] and in 2001 are given in Table 2. The raw materials and products practically do not contain toxic elements (As, Sb, U, Th) and heavy metals (Pb, Cr, Cu, Zn). Since 1997 until the present time the reduction of a uranium content in apatite ore and of lanthanides in industrial products and ammophos has been noted. The monitoring of the composition of raw materials and products over a few years has shown the stability of their composition.

Rather high concentrations of gross (bulk) and water-soluble fluorine are observed in all kinds of production and waste products of the plant. The share of readily available water-soluble fluorine is fairly large and amounts to approximately 20 % of its total content. This fact is of considerable significance for evaluating the impact of fluorine on the natural environment and workers' health.

The key parameters controlled in the occupational air according to the current sanitary code and regulations are the contents of HF and dust fraction [23, 24]. The occupational air monitoring points are located in the immediate vicinity of workplaces in the shops. The characteristics of the occupational air pollution indices monitored in the plant are given in Table 3. The data on the content of HF and dust burden in the shops are presented in terms of values averaged over an appreciable length of time (10 months of 2001).

Table 3. **Content of HF and dust in the occupational air**

Shop	HF, mg/m^3			Dust, mg/m^3			Balance
	C(F)	Median	Min/Max	C(dust) average	Median	Min/Max	HF/dust, %
PAE-1	0.22	0.2	0.03-0.45	1.2	1.3	0.1-1.8	15/85
PAE-3	0.17	0.15	0.01–0.55	3	3.2	0.8–4.8	5/95
PAE-4	0.16	0.14	0.01–0.46	2.9	3.2	0.4–5.2	5/95
A-1	0.2	0.19	0.01–0.47	2.1	2.2	0.5–5.2	9/91
A-2	0.19	0.17	0.03–0.33	1.3	1	0.3–3.2	16/84
FSP	0.11	0.11	0.01–0.32	0.7	0.6	0.1–1.9	14/86
PFS	1.9	2.1	0.6–2.9	0.7	0.7	0.3–1.0	73/27
Maximum allowable conc. (MAC)	0.5			10			

Table 4. **Composition of trace elements in the occupational air, ng/m^3**

Shop	Sc	Cr	Fe, μg/g	Co	As	Br	Sr	Sb	Cs	La	Ce	W	Hg	Au	Th	Pb
PAE-1	< 0.1	140	8	5	< 0.5	50	65000	4.5	< 1	600	990	< 5	< 5	1.2	< 1	< 20
PAE-3	0.9	90	48	20	< 0.5	30	2700	< 1	< 1	12800	21900	< 5	< 5	1.4	120	< 20
PAE-4	0.2	20	9	5	< 0.5	< 10	530	6.8	< 1	2000	3470	0.3	23	0.3	23	6.8
A-1 Site 1	1	190	24	15	< 0.5	60	310	4.9	< 1	440	760	0.4	66	0.4	66	4.9
Site 2	0.3	20	17	10	< 0.5	15	380	15	< 1	200	310	0.6	30	0.6	30	15
A-2 Site 1	0.4	< 10	1	12	< 0.5	9200	240	12	< 1	250	420	1.8	8	1.8	8	12
Site 2	< 0.1	< 10	< 1	6	< 0.5	860	300	3.2	< 1	20	35	2.2	4.3	2.2	4.3	3.2
PFS Site 1	< 0.1	200	7	15	< 0.5	60	1400	2.5	< 1	100	180	47	60	1.1	4.2	< 20
Site 2	3.3	60	22	13	< 0.5	60	210	4.5	< 1	160	310	14	10	0.7	5.9	< 20
FSP	< 0.1	< 10	< 1.0	5	< 0.5	4600	240	140	< 1	30	66	< 5	200	2.5	< 1	< 20
MAC	—	$1 \cdot 10^6$	—	$5 \cdot 10^5$	3000	$5 \cdot 10^5$	—	—	—	—	—	$6 \cdot 10^5$	5000	—	$5 \cdot 10^4$	7000

Table 5. **Content of fluorine and trace elements in drinking water supplied to the plant, μg/l**

Shop	F, mg/l	Cu	Fe	Co	Ni	Cr	Mn	Pb	Zn	Cd	Sr, mg/l
A-1	0.62	3	45	< 0.7	5.6	< 0.7	80	< 0.7	5	< 0.06	0.7
A-2	0.6	6	46	< 0.7	5.9	< 0.7	81	< 0.7	7.4	< 0.06	0.73
FSP	0.61	0.4	47	< 0.7	5.8	< 0.7	79	< 0.7	< 2	< 0.06	0.63
PFS	0.59	2.6	100	< 0.7	5.5	< 0.7	59	1.3	4.6	< 0.06	0.75
PAE-1	0.76	0.3	17	< 0.6	6.1	< 0.6	78	< 0.6	1.2	< 0.06	0.71
PAE-4	0.66	1.2	10	< 0.7	6	< 0.7	83	< 0.7	< 2	< 0.06	0.7
Canteen	0.69	0.7	57	< 0.7	5.3	< 0.7	78	< 0.7	< 2	< 0.06	0.61
MAC	1.5	1000	300	100	100	50	100	30	5000	1	7

The average level of the controlled indices in the shops, with the exception of the shop of precipitation of fluorine salts, does not exceed the maximum allowable limits. At the same time, up to 5 % of individual analyses exceed these limits.

The trace element composition of dust fraction is presented in Table 4. As can be seen from the table, it is characterized by significant variations of concentration of individual elements with prevailing Fe (1–48 (μg/g), Sr (0.2–65 (μg/m^3), La (0.02–13 (μg/m^3), Ce (0.03–22 (μg/m^3), i.e. the main trace components contained in the processed raw materials and finished products. Their concentrations in the occupational air do not exceed the maximum allowable limits [23, 25, 26]. The concentration of heavy and toxic metals is also low and does not constitute a hazard to human health.

Drinking water in the water supply system of the plant is another factor that can have an immediate impact on workers' health. The trace element composition of the drinking water supplied to the plant from the city water intake facilities and distribution system is shown in Table 5. It is characterized by low concentrations of toxic elements and heavy metals. Concentrations of trace elements do not exceed maximum allowable limits for drinking water [27].

In Table 6 the statistical data on the content of fluorine in urine and hair of the examined workers of the shops with harmful conditions depending on the technological peculiarities of the shops, as well as the average content of fluorine in urine and hair of men and women (workers of these shops) are given. The greatest average concentrations of fluorine are typical for PAE-1, 3, 4 shops. It is likely that this may be due to the maximum levels of the total load (HF + dust) in the occupational air in these shops.

Table 6. **The content of fluorine in urine and hair of factory workers**

Shop	Urine, mg/l		Hair, μg/g	
	C(F) average	Number of workers	C(F) average	Number of workers
EPA-1	2.1 ± 1.1	10	1200 ± 1100	7
EPA-3	3.6 ± 2.4	30	1300 ± 1200	18
EPA-4	4.9 ± 4.2	33	2700 ± 2300	19
A-1	2.1 ± 1.4	16	180 ± 150	12
A-2	2.1 ± 1.7	24	90 ± 75	10
PFS	3.1 ± 1.9	12	60 ± 40	9
FSP	2.4 ± 0.8	14	130 ± 100	10
Women	2.5 ± 1.9	24	330 ± 800	21
Men	3.4 ± 2.2	115	1400 ± 1700	64
Physiological level	1.6		—	
Permissible level	2		—	
Critical level	4		—	

There is a general tendency for a decrease of average concentrations of fluorine in biomaterials of workers of the shops of ammophos production, the shops of precipitation and production of fluorine salts.

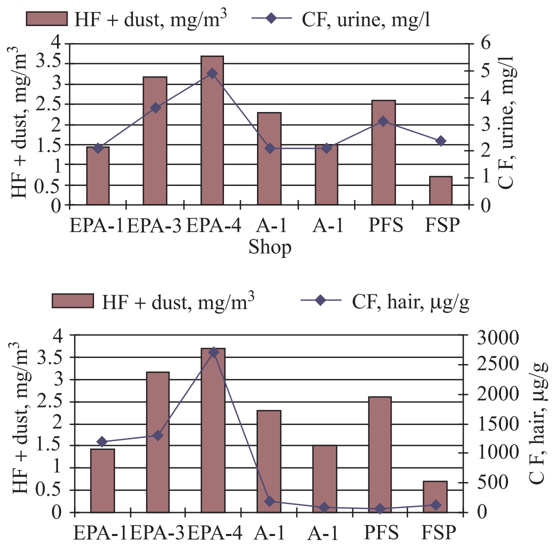

Fig. 1. Distribution of general occupational air pollution and average concentrations of F in urine and hair of workers of various shops

The exception is the content of fluorine in urine of workers of the shop of precipitation of fluorine salts (PFS). The graphs of the distribution of general occupational air pollution and average concentrations of F in urine and hair of workers of various shops are presented in Fig. 1. Noteworthy is a considerable difference in the accumulation of F in urine and hair of workers of the PFS shop. In this shop the gas component in the air pollution (Table 3) is prevailing. Consequently, it may be concluded that the content of gaseous HF in the air has a dominant role for accumulation of fluorine in urine, and the content of dust fraction plays a leading role for accumulation of F in hair. The excess of the critical level of an average content of fluorine in urine of the EPA-4 shop workers should be noted. The excess of the critical level of fluorine in urine of some EPA-3 workers has been found as well. In other shops the critical level of fluorine in urine is not exceeded.

The average content of fluorine in urine of men is approximately 1.3 times higher than that of women. In principle, this difference is small and within the limits of statistical error. The average content of fluorine in hair of men is 4.2 times as great as that of women. As noted above, the concentration of fluorine in hair is determined to a greater extent by the dust component in the occupational air. In this plant men are occupied for the most part in those kinds of work where dust air pollution prevails (unloading of apatite concentrate, loading and transportation of phosphogypsum, etc.). This fact may account for higher concentrations of fluorine in their hair.

The obtained data on the fluorine content in hair of practically all factory workers exceed the level of fluorine content in hair of unexposed population by a factor of 5–100.

The scatter in the data on fluorine concentration in hair of workers from one shop may amount to two orders. The greatest average and maximum concentrations of fluorine have been found in the hair of workers of the EPA-4 shop. This may be connected with poor efficiency of air purification systems in this shop (information of the factory representatives).

The dependence of fluorine concentration in workers' urine and hair on the length of service in this plant and age is illustrated in Fig. 2. The estimate of distribution of the average content of fluorine in workers' urine and hair depending

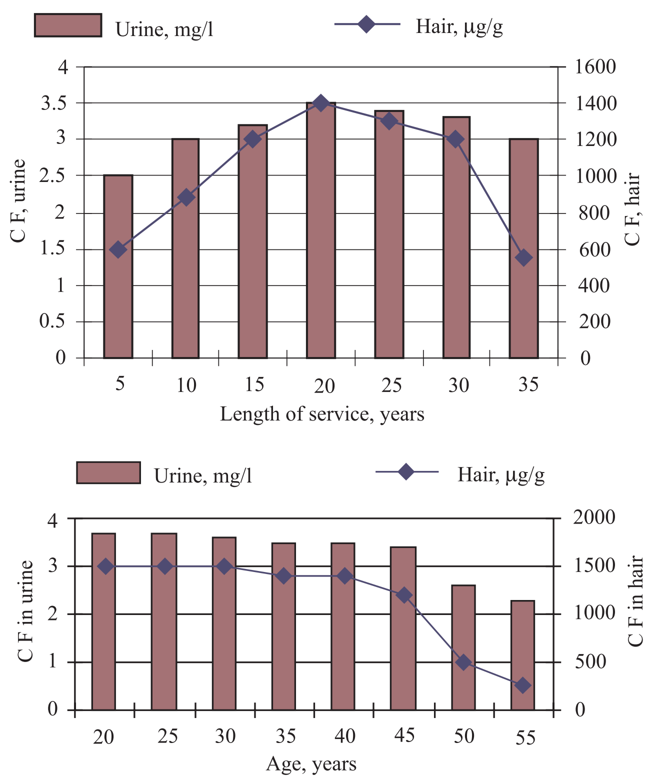

Fig. 2. Dependence of fluorine concentration in workers' urine and hair on the length of service and age

on the length of service has demonstrated an inverse dependence with maximum concentrations of fluorine cleared from the body with urine for the workers with the length of service of 15–25 years.

Workers under 50 years of age exhibit stable and rather high average content of fluorine both in urine and hair. For workers over 50 years its content in both biomaterials drops sharply.

It is likely to be connected with the peculiarities of physiological reaction of an organism to the action of elements in question, as well as with a decrease in the fluorine clearance rate as a consequence of hypometabolism of the old [28]. According to the research data over 50 years of age fluorine accumulates mainly in bone tissues [29].

The results of the present work do not make it possible to characterize differences in fluorine concentration in urine and hair for workers of various occupations. This is due to the fact that the assessment of real time of exposure of workers of various occupations to harmful factors presents some difficulties. Workers frequently combine and change occupations, even the majority of executives have worked in shops over many years.

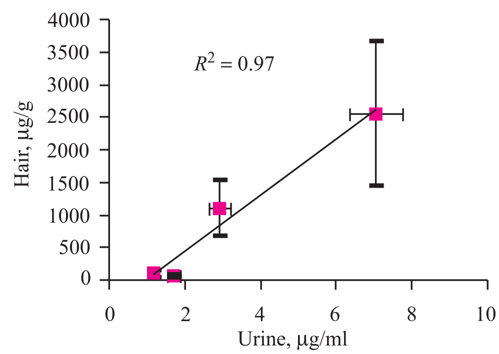

Fig. 3. Correlation dependence between the contents of fluorine in urine and hair of the factory workers

Figure 3 illustrates the degree of correlation between the average content of fluorine in urine and the corresponding average content of fluorine in hair. A high degree of correlation ($R^2 = 0.924$) lends support to the validity and efficiency of use of medium-interval concentrations of fluorine in urine and hair for evaluation of fluorine impact on workers occupied in harmful production. The study also aimed at searching for trace elements connected with fluorine and reflecting the response of worker's organism to injurious effects.

First of all this concerns Sr, La and Ce that are constantly present in increased concentrations in the dust fraction of occupational air in shops.

The content of trace elements in urine of the factory workers is given in Table 7.

Table 7. **Content of trace elements in urine of the factory workers, μg/l**

Shop	Ca, mg/l	Co	Cu	Zn	Rb	Sr	Ag	Cd	Cs	Ba
PAE-3 ($n = 13$)	140 ± 70	0.64 ± 0.35	14 ± 5.8	260 ± 290	1300 ± 570	1200 ± 1400	0.17 ± 0.11	0.66 ± 0.70	5.2 ± 2.1	5.4 ± 9.5
PAE-4 ($n = 15$)	69 ± 30	0.76 ± 0.58	18 ± 16	310 ± 280	1200 ± 620	780 ± 550	0.15 ± 0.07	0.74 ± 0.70	4.6 ± 2.6	< 3
A-1 ($n = 2$)	120 ± 23	0.66 ± 0.20	15 ± 2.5	250 ± 280	1400 ± 420	690 ± 100	< 0.1	0.37 ± 0.3	3.8 ± 2.0	8.6 ± 6.23
A-2 ($n = 8$)	71 ± 26	0.37 ± 0.17	10 ± 5.6	140 ± 150	1000 ± 320	720 ± 500	0.14 ± 0.17	0.43 ± 0.2	3.4 ± 1.3	7.0 ± 5.3
PFS + FSP ($n = 3$)	60 ± 46	0.24 ± 0.08	15 ± 9.0	580 ± 650	1200 ± 600	1200 ± 1100	< 0.1	0.23 ± 0.12	2.8 ± 0.3	19 ± 30
Average conc. ($n = 41$)	93	0.6	15	280	1200	920	0.14	0.59	4.4	14
Median	77	0.5	13	190	1100	650	0.13	0.34	3.7	13
Max	240	1.9	61	1300	3100	5400	0.54	2.58	14	84
Min	27	0.1	< 5	< 100	520	220	< 0.1	< 0.1	1.1	< 3
Background	80–250 [10]	0.46 [28]	11.7 [28]	50–1000 [10]	1900 [26]	200–500 [26]		0.38 [28]	9 [26]	50 [26]

Table 8. **Dependence of the content of trace elements in urine of the factory workers on the length of service, μg/l**

Length of service, years	Ca, mg/l	Co	Cu	Zn	Rb	Sr	Ag	Cd	Cs	Ba
$< 10\,(n=3)$	98 ± 59	0.86 ± 0.76	18 ± 5.9	660 ± 560	1260 ± 400	2000 ± 880	0.22 ± 0.11	0.24 ± 0.06	4.5 ± 1.2	53 ± 31
$11{-}20\,(n=13)$	83 ± 49	0.46 ± 0.16	16 ± 15	330 ± 320	1410 ± 660	940 ± 1350	0.16 ± 0.08	0.43 ± 0.40	5.0 ± 2.8	12 ± 8.9
$21{-}30\,(n=13)$	100 ± 61	0.72 ± 0.51	12 ± 5.3	270 ± 220	1110 ± 540	890 ± 530	0.12 ± 0.09	0.69 ± 0.74	3.8 ± 1.2	8.8 ± 7.3
$> 30\,(n=12)$	95 ± 61	0.57 ± 0.46	16 ± 10	250 ± 230	1050 ± 340	676 ± 380	0.14 ± 0.15	0.71 ± 0.67	4.2 ± 2.5	12 ± 12

Table 9. **Dependence of the content of trace elements in urine of the factory workers on age, μg/l**

Age, years	Ca, mg/l	Co	Cu	Zn	Rb	Sr	Ag	Cd	Cs	Ba
$19{-}30\,(n=3)$	120 ± 23	0.89 ± 0.72	11.6 ± 5.5	250 ± 200	1000 ± 100	1400 ± 100	0.20 ± 0.12	0.19 ± 0.10	4.5 ± 1.2	35 ± 43
$31{-}40\,(n=12)$	80 ± 48	0.47 ± 0.16	15.1 ± 16	220 ± 160	1400 ± 720	1100 ± 140	0.15 ± 0.08	0.45 ± 0.35	4.7 ± 3.0	12.0 ± 8.1
$41{-}50\,(n=19)$	97 ± 65	0.71 ± 0.53	16.0 ± 9.0	310 ± 390	1200 ± 480	850 ± 630	0.14 ± 0.1	0.71 ± 0.65	4.3 ± 1.7	14.2 ± 14
$> 50\,(n=7)$	92 ± 51	0.41 ± 0.25	11.6 ± 6.8	310 ± 260	1100 ± 420	660 ± 370	0.13 ± 0.18	0.66 ± 0.86	3.9 ± 2.3	8.1 ± 11

Compared to the content of trace elements in urine of the population unoccupied in the production of mineral fertilizers (background), the workers of all shops exhibit higher average content of strontium with its maximum content (3000 μg/l) found for a worker (shift electrician) of the PAE-3 shop. The content of other elements is at the level of background values.

The distributions of average contents of trace elements in urine of workers depending on the length of service and age are given in Tables 8 and 9. Noteworthy is the presence of rather complex regularities in the distribution of trace elements in urine of the production personnel. For example, the distribution of Ca and Rb depending on the length of service on the whole repeats the distribution of F. The distribution of Zn, Sr and Ba has a clear tendency to the lowering of concentrations with an increase in the length of service, while the content of Cd in urine increases almost three times. It is significant that for the maximum fluorine concentration in urine at the length of service of 11–20 years and age of 31–40 years the minimum calcium concentration is observed. It should be pointed out that there is a general tendency to the lowering of Ca, Sr and Ba concentrations in urine and more than a three-fold increase in Cd concentration with age. For other trace elements no obvious tendencies in their distribution in urine of the production personnel have been observed.

The distribution of average content of rare-earth elements, U and Th in urine of workers of different shops is given in Fig. 4. A significantly increased content of fluorine and rare-earth elements has been observed for the workers of shops of phosphoric acid extraction. This may be connected with the manufacturing processes wherein raw materials (apatite) are processed and waste products (phosphogypsum) enriched with lanthanides are obtained (Table 2). No differences in the content of U and Th have been found.

Basing on the obtained medium-interval contents of fluorine in urine, its relation with trace elements has been evaluated. The content of strontium in workers' urine considerably exceeds the background level and could serve as a

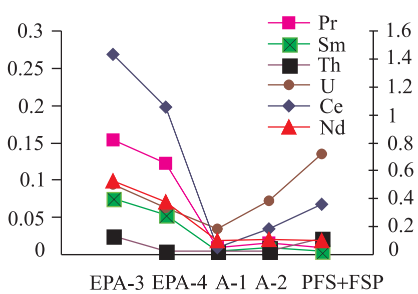

Fig. 4. Distribution of contents of rare-earth elements, Th and U in urine of the factory workers of various shops, μg/l

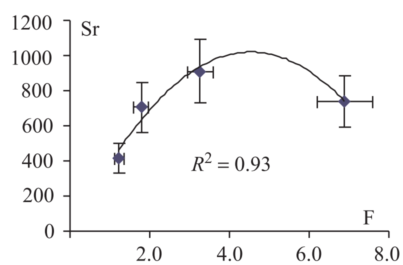

Fig. 5. Distribution of Sr concentration on urine depending on F concentration, mg/l

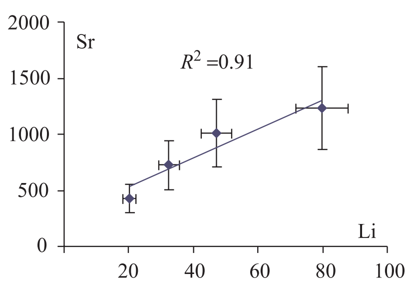

Fig. 6. Correlation between average contents of Li and Sr in urine, mg/l

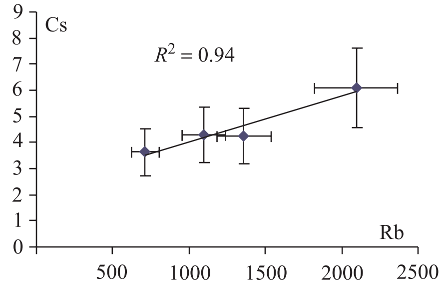

Fig. 7. Correlation between average contents of Rb and Cs in urine, μg/ml

biomarker of impact. An inverse dependence of Sr concentration on fluorine content has been established (Fig. 5). The origin of this dependence is likely to be connected with a mineralizing effect of fluorides [28–30].

Figures 6 and 7 illustrate the correlation dependencies between the content of various trace elements in urine. For Li and Sr, Cs and Rb, as well as for a group of rare-earth elements high values of pair correlations ($R^2 = 0.91{-}0.94$) have been determined. Statistical data on the content of trace elements in the hair of workers of various shops and of the factory as a whole are presented in Table 10. A significant excess of average levels over background levels is observed for Fe, Sr, La.

From these data it can be seen that the distribution of average content of trace elements in hair for different shops is similar to the distribution of fluorine. For the most part this concerns those trace elements that abound in raw materials and waste products — Ca Sc, Mn, Sr, La, Th. No clear-cut distinctions in the average content of trace elements in workers' hair depending on the length of service and age have been revealed.

In hair high values of pair correlations between contents of Ca and F, of Th and Al, of Th and La (Figs. 8 and 9) have been determined. All these elements are present in increased concentrations in industrial goods and waste products.

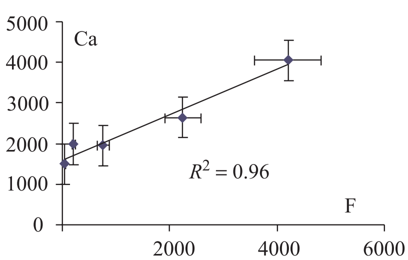

Fig. 8. Correlation between concentrations on fluorine and Ca in hair, μg/g

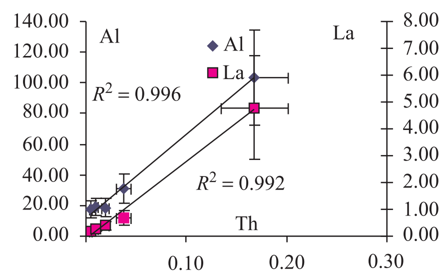

Fig. 9. Correlation between average contents of Th, Al and La in hair, μg/g

Table 10. **Content of trace elements in hair of the factory workers, μg/g**

Shop	Na	Al	Ca	Sc	Mn	Fe	Ni	Co	Cu
PAE-1 ($n = 13$)	38 ± 27	17 ± 12	1900 ± 1020	0.011 ± 0.01	2.2 ± 1.4	50 ± 18	1.3 ± 1.2	0.093 ± 0.095	18 ± 7.1
PAE-3 ($n = 31$)	40 ± 28	37 ± 45	2400 ± 2270	0.023 ± 0.02	2.6 ± 2.2	52 ± 34	0.61 ± 0.73	0.076 ± 0.022	17 ± 5.4
PAE-4 ($n = 27$)	48 ± 38	42 ± 71	3000 ± 2640	0.023 ± 0.01	3.6 ± 3.7	78 ± 76	0.73 ± 0.70	0.098 ± 0.095	20 ± 12.
A-1 ($n = 17$)	50 ± 22	24 ± 14	1800 ± 930	0.014 ± 0.00	2.7 ± 1.6	53 ± 45	2.1 ± 1.1	0.092 ± 0.10	20 ± 8.7
A-2 ($n = 21$)	17 ± 15	11 ± 6.0	1600 ± 1500	0.011 ± 0.01	2.3 ± 1.8	27 ± 20	1.4 ± 2.3	0.073 ± 0.038	22 ± 9.6
PFS ($n = 13$)	44 ± 14	15 ± 8.4	1300 ± 900	0.007 ± 0.00	1.9 ± 1.2	48 ± 30	1.4 ± 0.78	0.094 ± 0.055	18 ± 4.8
FSP ($n = 12$)	31 ± 12	35 ± 39	720 ± 860	0.012 ± 0.00	1.4 ± 2.1	31 ± 38	1.0 ± 0.72	0.070 ± 0.080	14 ± 6.6
Average conc.	39	28	2000	0.016	2.6	51	1.1	0.085	19
Median	33	16	1600	0.01	1.8	37	1	0.07	18
Max	150	360	11000	0.13	18	300	11	0.5	62
Min	7	1	140	0.002	0.25	7	0.11	0.0065	7
Background [21]	17–670		113–2890	0.002–0.13	0.08–2.41	4.9–23	0.11–1.6	0.002–0.063	8.5–96

Shop	Zn	As	Se	Br	Sr	Sb	La	Hg
PAE-1 ($n = 13$)	180 ± 34	0.04 ± 0.03	0.6 ± 0.2	0.9 ± 0.4	25 ± 14	0.11 ± 0.22	0.41 ± 0.62	0.59 ± 0.30
PAE-3 ($n = 31$)	130 ± 39	0.12 ± 0.22	0.5 ± 0.1	1.7 ± 1.9	42 ± 57	0.066 ± 0.15	1.45 ± 2.2	0.69 ± 0.36
PAE-4 ($n = 27$)	160 ± 29	0.09 ± 0.07	0.6 ± 0.1	1.2 ± 1.1	52 ± 50	0.098 ± 0.19	1.59 ± 3.3	0.62 ± 0.44
A-1 ($n = 17$)	160 ± 56	0.07 ± 0.05	0.5 ± 0.2	1.0 ± 0.76	18 ± 8	0.054 ± 0.054	0.17 ± 0.13	0.40 ± 0.23
A-2 ($n = 21$)	160 ± 36	0.08 ± 0.07	0.5 ± 0.2	1.5 ± 1.4	27 ± 44	0.035 ± 0.036	0.09 ± 0.07	0.52 ± 0.33
PFS ($n = 13$)	150 ± 41	0.03 ± 0.03	0.5 ± 0.2	1.2 ± 1	22 ± 25	0.11 ± 0.13	0.16 ± 0.23	0.48 ± 0.37
FSP ($n = 12$)	170 ± 28	0.12 ± 0.08	0.6 ± 0.1	1.9 ± 1.2	13 ± 13	0.031 ± 0.021	0.07 ± 0.05	0.72 ± 0.39
Average conc.	150	0.085	0.55	1.4	32	0.071	0.75	0.58
Median	150	0.063	0.55	0.98	21	0.033	0.19	0.53
Max	340	1.2	0.94	9.9	300	0.88	16	1.8
Min	67	< 0.05	0.17	0.18	1.8	0.0067	< 0.10	< 0.10
Background [21]	68–198	0.034–0.319	0.48–1.84	5.6–221	0.14–5.54	0.007–0.122	0.0046–0.106	0.053–0.927

Evaluation of Disease Incidence of the Factory Workers. The town of Voskresensk is a center of the Voskresensk district of the Moscow Region. There live three fourths of the district population (on the average from 76.1 % in 1989–1990 to 75.9 % in 1999–2000). The number of children and teenagers in the specified decade has decreased from 26 % (rather favorable demographic index) to 21 % (unfavorable demographic index); in the region — from 24.2 % to 19.5 % (unfavorable level). As of the end of 2000 the number of women of childbearing age was 28.2 % of all population (on the average in the region — 26.9 %).

Nevertheless, the population movement indices in the district for the last decade have got worse than in the region (Table 11).

Table 11. **Population movement coefficients (V — Voskresensk district, A — average indices for the region per 1000 of population)**

Years		Birth-rate	Overall death-rate	Natural population growth	Infant mortality
1989–1990	V	11.1	11.85	–0.75	17.4
	A	9.55	12.25	–2.75	14.75
1999–2000	V	7.65	17.85	–10.25	23.25
	A	7.05	17	–9.95	14.65

The birth-rate in the Voskresensk district fell and the overall death-rate rose with greater intensity than on the average in the Moscow Region. The infant death-rate (number of deaths of children under the age of one year per 1000 babies born in a given year) practically unchanged on the average in the region, has increased by a factor of 1.34 in the Voskresensk district. As a result, the natural population loss has increased 12 times in the district and only 3.7 times in the region.

At the main industrial plant of the town — the Voskresensk mineral fertilizers plant — the production volume has been considerably cut back, resulting in the reduction in the number of employed by more than half (approximately from 15000 down to 5800). This factor should be considered as a severe stress situation of socio-economic character for the whole town, which plays a leading role in the totality of reasons for the negative demographic indices.

We have analyzed the incidence of 25 classes of diseases and specific diseases among the factory workers on the basis of the official annual reports of the factory medical center for 1989–2001 and compared these data with the data on other local residents of the town of Voskresensk for the same years (Table 12). This analysis has shown that for the last few years the sickness rate (reasoning from the medical aid appealability to the town clinics and the factory medical center) was stable and the disease incidence among the factory workers in general was even lower than that of the other population of the town. Cases of fluorosis have not been noted either for the factory workers or for the population of the town. Noteworthy is the increased incidence (by a factor of 2–2.5) of chronic pharyngitis, sinusitis and arthrosis among the factory workers, as well as higher rate of injuries.

CONCLUSIONS

In the process of carrying out of the given work, we have developed a combined approach for evaluation of the environmental impact and health effect of the production of nitrogenous phosphate mineral fertilizers. This approach consists of several stages and includes the determination of a group of polluting elements, evaluation of their impact on the transporting and depositional natural environments, as well as on the population living in the plant impact areas (including analysis of biosubstrates and comparative analysis of medical statistics) and biota, the analysis of the health effect on the factory personnel specifying high risk groups. We have published some results of application of this approach earlier [5–7]. We consider this approach to be sufficiently universal to study the environmental impact and health effect of production with any technological peculiarities. Certain parts of this approach have been applied and are being used now to evaluate lead pollution of the environment and its effect on health of children of various cities in central regions of Russia. In the present work the results on the health effect of the given type of production obtained at the final stage of realization of our method are presented.

From the results of the present work we can draw the following conclusions:

1. The analysis of the occupational air in the shops has revealed that on the whole the average level of HF concentration does not exceed the allowable limits. However, the data on the shop of precipitation of fluorine salts and about 5 % of individual analyses in other shops exceed the maximum concentration limit.

2. Concentrations of heavy metals in the occupational air in the shops do not exceed the norm.

3. In drinking water in the plant the concentration of F and heavy metals does not exceed the maximum concentration limit.

4. The supporting evidence for a harmful effect of fluorine — one of the basic impurity elements in the raw material used for the production of mineral fertilizers (apatite) — has been obtained. In the case of the factory workers, the main path of fluorine intake is through the respiratory tract, on inhaling hydrogen fluoride and fluorine-containing dust present in the occupational air in increased concentrations. An average fluorine content in urine and hair of workers of an individual shop is a reflection of the condition of the occupational air (total load of hydrogen fluoride and dust) in this shop.

Table 12. **Average indices of disease incidence among adult population of the town of Voskresensk and the factory workers for 1989–2001 per 1000 of population**

Classes of diseases and specific diseases	Disease incidence (average for 1989–2001), number of morbid events	
	Adult population of Voskresensk	Factory workers
Total	**842.6**	**666**
Neoplasms	34.2	10.5
Blood diseases	4.1	3.5
Endocrine diseases	27	12.9
Nervous system diseases	33.5	29
Eye diseases	35.2	17.1
Ear diseases	18.7	23.3
Blood circulation system diseases	102.8	63.3
Respiratory apparatus diseases	252.3	272.9
Among them:		
Chronic bronchitis and pneumonia	16.2	7.9
Chronic pharyngitis, sinusitis	4.7	11.2
Digestive system diseases	53.5	33.8
Skin diseases	50	8.9
Musculoskeletal system diseases	62.4	79.5
Among them:		
Arthrosis	5.9	13.8
Urogenital system diseases	50.6	21.2
Injuries and poisonings	36.6	60.6

5. Data on fluorine content in workers' urine and hair have proved to be very informative to study harmful factors of production. The level of fluorine in urine of more than half of the examined workers exceeds the allowable level for the population unoccupied in the production; 10 % are in a risk group. A high degree of correlation between the contents of fluorine in workers' urine and hair has been established. The possibility and efficiency of use of medium-interval estimates of fluorine contents in biosubstrates to study its harmful effect on workers occupied in the production of phosphate fertilizers have been substantiated.

6. The age dependence of fluorine clearing from humans has been revealed and it has been found that at the age of fifty the F clearance rate drops sharply.

7. The trace element composition of workers' biosubstrates (urine, hair) has been investigated. A potential biomarker of impact of the production of phosphate fertilizers on workers' health — strontium — has been found. It has been revealed that its content in urine of workers of all shops considerably exceeds the level for the population unoccupied in the production. The maximum obtained value is 10 times greater than the background value.

8. The increased contents of rare-earth elements in urine and of Ca, Sr, La, Th in hair of workers involved in raw material processing at the beginning of the technological production chain have been found. The content of these elements in the corresponding biosubstrates of workers of shops that are the continuation of the technological production chain decreases sharply. The distribution of average contents of Ca, Sr, rare-earth elements and Th in hair of workers of different shops is similar to the distribution of fluorine. In urine, as in the case of fluorine, a reduction in the contents of some trace elements (Sr, Ba) with age and length of service is observed.

9. For trace elements the correlations between Li and Sr, Cs and Cu, Cs and Rb in urine and between Th and Al, Th and La in hair with high values of reliability of approximation R^2 (0.7–0.99) have been found.

10. The incidence of fluorosis has not been noted either for the factory workers or for the population of the town. However, the increased incidence of chronic pharyngitis, sinusitis and arthrosis among the factory workers has been observed. In other classes of diseases the sickness rate among the factory workers is either the same or even lower than that of the other population of the town.

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