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NEUTRON ACTIVATION ANALYSIS FOR MONITORING NORTHERN TERRESTRIAL ECOSYSTEMS

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New experimental data have been obtained on heavy metal and rare-earth element concentrations in environmental objects, namely pine needles and soils, caused by atmospheric pollution in different regions of the Kola Peninsula. The investigation was performed with the use of epithermal neutron activation analysis at the IBR-2 fast pulsed reactor. Analysis of nearly 40 element distributions in pine-needles and solids from the studied geographical points testifies of a strong contamination source — the nickel smelting complex in Monchegorsk. The contamination levels for Ni, Co, Cr, Se, and other are also high and may be hazardous for this region population because some of these elements are carcinogenic.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

Применение активационного анализа для мониторинга северных земных экосистем

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Получены новые экспериментальные данные по концентрациям тяжелых металлов и редкоземельных элементов в экологических образцах — хвое сосны и почве с Кольского полуострова. Исследования выполнены с помощью нейтронного активационного анализа на тепловых и резонансных нейтронах на реакторе ИБР-2. Анализ распределений концентраций примерно 40 элементов в зависимости от географии точек отбора проб почв и хвой свидетельствует о наличии сильного источника загрязнения — комбината по выплавке никеля в Мончегорске. Уровни загрязнения по Ni, Co, Cr, Se и т.д. высоки и могут представлять опасность для местного населения, поскольку некоторые из этих элементов являются канцерогенами.

Работа выполнена в Лаборатории нейтронной физики им И.М.Франка ОИЯИ.

All industrial production, as is well known, is connected with risk to the environment and human health. The significant increase in the industrial production of the world during the last decades caused further deterioration of the ecological situation in some regions of the globe. Investigations in the field of environmental protection are presently being performed in many countries by different physical-chemical and nuclear-related methods. The objective of this investigation, achieved jointly with ecologists from the Kola Science Centre of the Institute of North Industrial Ecology Problems (Apatity, Russia), was to obtain data on the concentrations of different chemical elements in soils and pine-needles in several industrial regions of the Kola Peninsula (Murmansk region) with the use of neutron activation analysis (NAA).

Several large mining and colour metallurgy concerns are situated in the Murmansk region, where extraction, recovery, and enrichment of copper-nickel, ferriferous, and apatite-nepheline ores are being done. Colour metals, such as Ni, Co, Cu, and Al, are produced in Monchegorsk, Nikel and Kandalaksha. As a result of this long and intensive production, the environment near these industrial cities is contaminated with different chemical elements and their compounds. For example, in extracted nickel-sulfide ores, besides Ni, Co, and Cu, amounts of S, Se, Te, Rh, Pd, Pt, Au, etc., are also present. In ferriferous ores, Fe, Cr, P, Mn, Zn, and As are present. Smelting of Ni, Co, and Cu leads to the pollution of atmospheric air by these and other elements, and also by such toxic combinations as SO_2 , CO, $\text{Ni}(\text{CO})_4$ (tetracarbonyl), and often As_2O_3 . During the process of mica extraction, which is also being done in the Murmansk region, mainly by surface extraction methods, the environment is contaminated by Na, Ca, Ba, Rb, Cs, Be, B, Sn, Nb, Ta, Ti, Mo, W, U, Th, Y, and Bi contained in the ores.

1. Experimental

Samples of pine-needles and soils were received from the Kola Science Centre. They were collected in the autumn of 1992 at 15 geographical points in the Murmansk region (Kola Peninsula, Russia): in Monchegorsk and in the suburbs of Nikel (points 1—2 and 7—14, respectively) in which large mining industry and colour metallurgy concerns are situated. These points correspond to the more contaminated regions of the Kola Peninsula. In order to have the possibility of making a comparison with cleaner regions, some of the samples were selected in less contaminated regions, namely, to the south-west of Monchegorsk, near Eno and Kovdor (points 3—6). At each point approximately 6—15 samples of pine-needles and soil were selected. All genetic horizons in each soil profile were selected separately. But in this work, we will discuss only the results obtained for superficial soils and for year-old pine needles. The sample preparation procedure is described in detail in book [1].

Concentrations of elements in dry samples were obtained with the use of thermal and epithermal neutron activation analysis at the IBR-2 reactor of the Joint Institute for Nuclear Research (JINR, Dubna, Russia). For determination of short-lived nuclides, a pneumatic system with a transport time from the irradiation position to the measurement site of 10—15 seconds was used. This kind of analysis was used for determining Al, V, Mn, As, Mo, etc. The main part of the obtained data on heavy metals and rare-earth elements was determined by using middle- and long-lived nuclides. Gamma spectrometry of irradiated samples was performed by using Ge(Li) detectors calibrated with standard gamma-sources. Elemental concentrations were determined by comparison with Standard Reference Materials (SD-M-2/TM) and by absolute calculations. Data were processed by programs developed at JINR. Interferences in the gamma spectrometry were partially avoided during processing by the choice of interference-free photo-peaks. If it was needed, contributions of interfering reactions were accounted for.

2. Results and Discussion

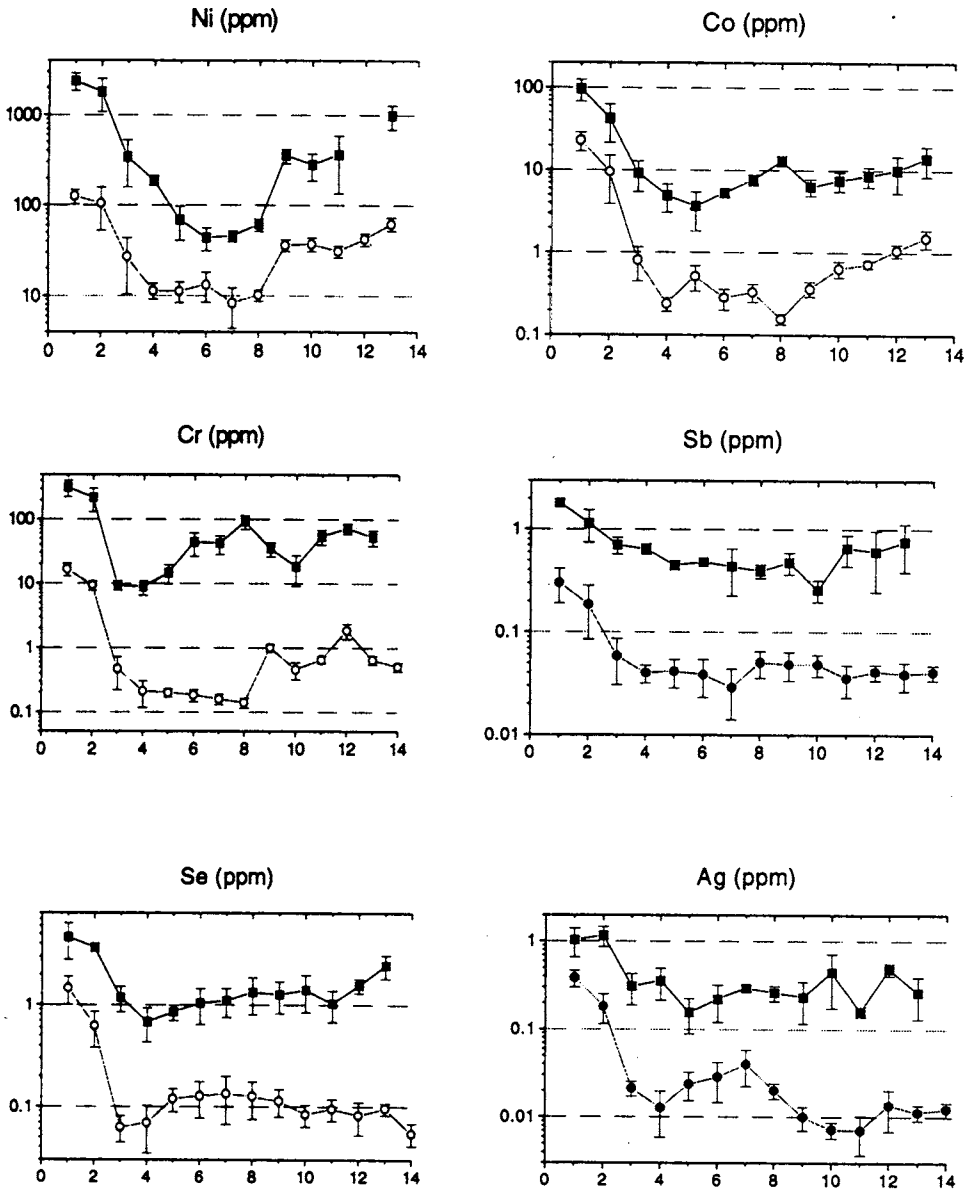
On the basis of the concentrations of elements obtained in individual samples of soils and pine-needles, we calculated the average concentrations of elements and their confidence intervals for each geographical point. We analysed the distributions of the average concentrations for each element in pine-needles and soils versus the number of geographical point where the samples were selected. This procedure allowed us to observe correlations in the behaviour of elemental concentrations between soils and pine-needles and to see where the sources of environmental contamination are situated (see the figure).

For most of the elements one can see clearly visible peak (geographical points 1—2) belonging to Monchegorsk, where the Ni and Co production concern is situated. The second source, visible only for some elements such as Ni, Cr, and Co, corresponds to Nikel (points 8—14) where the concern for enrichment of nickel-sulfide ores and on the re-smelting of metallic Ni is situated. We do not see a clearly visible peak at points 8—14 for these elements. We observe only an increase of concentration levels, because points 8—14 correspond to the suburbs of Nikel and are disposed close to one another. The concentrations of Ni, Cr, and Co at these points are higher in comparison with the less contaminated geographical points 3—7 (situated south-west of Monchegorsk) where a clearly visible minimum is seen.

Monchegorsk is seen as a source of Ni, Co, Fe, Cr, Sc, Ag, Sb, Sn, Mo, Se, etc., contamination. Ratios of maximal (points 1—2) to minimal (points 3—7) concentrations for some elements in soils are close to a factor of 10 or more. Obvious correlations in the distributions of Ni, Co, Cr, Ag, Sb, Se, Fe, and Mo concentrations versus the geographical point number in pine-needles and soils reliably confirm the fact we actually see as the sources of environmental contamination. It would be interesting to concentrate our further analysis of the obtained data in order to get an answer to the question: are the visible concentrations of elements in the vicinity of Monchegorsk sufficiently hazardous for the environment and the health of the neighbouring population. In trying to get answer to this question, we are faced with the difficulty caused by the following circumstance. The form of our samples (pine-needle and soils) does not allow us to directly connect the obtained data with any control or critical levels of elements in the human organism. Therefore, we can make only an indirect estimate of possible hazards of the actual elemental concentrations to the environment and human health.

Literary data on the averaged concentrations of different elements in superficial soils [2—6] are presented in the first column of Table 1. We compare them with concentrations of elements in Kola soils. Maximal and minimal concentrations of elements with their confidence intervals in percents are presented in columns 2 and 3. Ratios of maximal to minimal concentrations of elements in Kola soil and ratios of maximal concentrations in Kola soil to literary data for soils are also shown in columns 4 and 5. Ratios significantly exceeding the unit for Ni, Co, Cr, Se, Mo, Ag, Sn, etc., may be considered as an indication of technogenic contamination of the superficial soils.

The natural abundances of some elements in soils are high. Therefore, technogenic additions to them in soils may be barely visible in comparison with their natural abundances. In these cases, data on elemental concentrations in pine-needles are especially important. It is also favourable to use some additional data for pine-needles from another clean region of Russia to compare with data on Kola pine-needles. Such data for pine-needles from the Tver region (close to Moscow) we obtained ourselves. Elemental concentrations with confidence intervals in percents for the Tver pine-needles are presented



Distributions of elemental concentrations for Kola soil and pine-needle samples (upper and lower curves, respectively) versus the number of the geographical point

in column 1 of Table 2. Analysis of maximal elemental concentrations in Kola pine-needles (column 2) has shown that higher concentrations of Sc, Cr, Fe, Co, Ni, Se, As, Sr, Mo, Ag, Cd, Sn, Sb, Ba, Cs, La, Ce, Sm, Tb, Ta, and W are observed as compared with Tver pine-needles.

Table 1. Concentrations of elements (ppm) in soils of the Kola Peninsula

| | Literary data (ppm) | Kola Maximal (ppm) | Kola Minimal (ppm) | Ratio (2/3) | Ratio (2/1) | Toxic for plants (ppm) | Contaminated soils (ppm) |
|----|---------------------|--------------------|--------------------|-------------|-------------|------------------------|--------------------------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| Na | 17700[6] | 18700 (20) | 4810 (54) | 3.9 | 1.1 | | |
| Mg | 8600[6] | 51400 (17) | 3560 (68) | 14 | 6 | | |
| Al | 71100[2] | 67120 (31) | 6480 (67) | 10 | 0.95 | | |
| Cl | 166[6] | 1850 (25) | 313 (38) | 6 | 11 | | |
| K | 26200[6] | 16200 (15) | 6310 (27) | 2.6 | 0.6 | | |
| Sc | 9.1[3] | 18.8 (28) | 0.76 (16) | 25 | 2.1 | | |
| Ti | 35000[3] | 46800 (55) | 2730 (90) | 17 | 1.4 | | |
| V | 90[2] | 155 (29) | 23 (44) | 6.7 | 1.7 | 50—100 | |
| Cr | 70[2] | 316 (29) | 8.7 (26) | 3.6 | 4.5 | 60—600 | |
| Mn | 1000[2] | 1034 (28) | 204 (15) | 5 | 1 | > 2200 | |
| Fe | 25100[3] | 45000 (21) | 2750 (21) | 18 | 1.8 | | |
| Co | 8[2] | 96.6 (49) | 3.6 (50) | 27 | 12.1 | | 10—500 |
| Ni | 50[2] | 2380 (22) | 43.6 (28) | 55 | 48 | | 26—5000 |
| Zn | 90[2] | 114 (43) | 44.7 (15) | 2.6 | 1.3 | | 150—4500 |
| Se | 0.37[3] | 4.6 (50) | 0.7 (38) | 6.8 | 12.4 | | |
| As | 8.3[3] | 13.1 (21) | 1.2 (25) | 11 | 1.6 | 15—1000 | 10—20000 |
| Rb | 50-98[4] | 24.5 (30) | 4.6 (74) | 5.4 | < 0.5 | | |
| Sr | 250[2] | 415 (41) | 60 (18) | 7 | 1.7 | | |
| Zr | 224[3] | 336 (46) | 24.2 (16) | 14 | 1.5 | | |
| Mo | 1.0[2] | 7.9 (50) | 0.64 (20) | 12.3 | 7.9 | | |
| Ag | 0.05[2] | 1.16 (30) | 0.16 (44) | 7.4 | 23 | | |
| Sn | 4[2] | 437 (26) | 4.4 (74) | 100 | 110 | > 60 | |
| Sb | 1[2] | 1.8 (10) | 0.26 (24) | 7 | 1.8 | | 2—200 |
| Ba | 220[3] | 324 (23) | 67.6 (20) | 4.8 | 1.5 | | |
| Cs | 0.3-5[3] | 1.85 (72) | 0.35 (65) | 5.4 | < 6.2 | | |
| La | 2.8[5] | 16.6 (49) | 2 (27) | 8.5 | 5.9 | | |
| Ce | 5.5[5] | 44.7 (54) | 4.9 (45) | 9 | 8 | | |
| Nd | 2.4[5] | 30 (28) | 2.4 (20) | 12.5 | 12.5 | | |
| Sm | 0.43[5] | 1.24 (62) | 0.6 (38) | 2.1 | 2.9 | | |
| Eu | 0.083[5] | 0.52 (23) | 0.08 (20) | 6.4 | 6.3 | | |

| | Literary data (ppm) | Kola Maximal (ppm) | Kola Minimal (ppm) | Ratio (2/3) | Ratio (2/1) | Toxic for plants (ppm) | Contaminated soils (ppm) |
|----|---------------------|--------------------|--------------------|-------------|-------------|------------------------|--------------------------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| Tb | 0.08[5] | 0.24 (59) | 0.037 (45) | 6.5 | 3 | | |
| Yb | 0.2[5] | 0.83 (40) | 0.09 (35) | 8.9 | 4.2 | | |
| Hf | | 2.4 (37) | 0.35 (10) | 6.9 | | | |
| Ta | | 3.45 (45) | 0.07 (25) | 48 | | | |
| W | 0.7—3[3] | 6.3 (10) | 1.5 (22) | 4.3 | < 9 | | |
| Ir | | 0.024 (32) | 0.001 (44) | 20 | | | |
| Th | 3—10[3] | 5.5 (74) | 0.28 (10) | 19 | < 1.8 | | 0.4—21 |
| U | 2.0[2] | 1.9 (23) | 0.13 (15) | 15.5 | 1 | | 0.1—11 |

Table 2. Connections of elements in pine-needles (ppm) of the Kola Peninsula

| | Tver Average (ppm) | Kola Maximal (ppm) | Kola Minimal (ppm) | Ratio (2/3) | Ratio (2/1) | Normal in Plants (ppm) | Toxic in Plants (ppm) | Cereal Grains (ppm) |
|----|--------------------|--------------------|--------------------|-------------|-------------|------------------------|-----------------------|---------------------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Na | 14 (64) | 325 (19) | 71 (25) | 4.6 | 23 | | | |
| Mg | 785 (19) | 1850 (15) | 870 (14) | 2 | 2.4 | | | |
| Al | 148 (46) | 284 (50) | 58 (33) | 5 | 2 | | | |
| Cl | 177 (28) | 590 (16) | 180 (26) | 3 | 3 | | | |
| K | 2830 (33) | 12900 (15) | 6220 (29) | 2 | 4.6 | | | |
| Sc | 0.013 (30) | 0.25 (40) | 0.035 (60) | 7 | 19 | 0.005—0.7 | | |
| Cr | < 0.1 | 16.5 (23) | 0.14 (18) | 118 | > 160 | 0.002—0.5 | 4—30 | |
| V | < 1 | 3.8 (44) | 0.65 (75) | 6 | > 3.8 | | | |
| Mn | 234 (51) | 760 (10) | 210 (27) | 3.6 | 3.2 | | | |
| Fe | 55 (43) | 1270 (59) | 36 (20) | 35 | 23 | 18—1000 | | 25—80 |
| Co | 0.039 (89) | 22.7 (26) | 0.16 (15) | 140 | 580 | 0.1—20 | 20—50 | 4—20 |
| Ni | 2.4 (70) | 126 (18) | 8.3 (48) | 15 | 53 | 0.1—5 | 10—100 | 0.2—0.6 |
| Zn | 33 (36) | 44 (20) | 19 (12) | 2 | 1.3 | 1—70 | 70—400 | 22—33 |
| Se | < 0.02 | 1.46 (33) | 0.063 (30) | 23 | > 70 | 0.01—0.5 | 0.8—22 | 0.02—0.5 |
| As | < 0.01 | 16 (38) | 0.7 (56) | 23 | > 1600 | 0.01—1.7 | 2—20 | 0.05 |

| | Tver Average (ppm) | Kola Maximal (ppm) | Kola Minimal (ppm) | Ratio (2/3) | Ratio (2/1) | Normal in Plants (ppm) | Toxic in Plants (ppm) | Cereal Grains (ppm) |
|----|--------------------------|--------------------------|--------------------------|----------------|----------------|------------------------------|--------------------------|---------------------------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Rb | 21 (76) | 74 (31) | 17 (40) | 4.4 | 3.5 | 2—50 | | 4 |
| Sr | 3.4 (12) | 25 (29) | 6.1 (24) | 4 | 7.3 | 1—150 | > 600 | 0.5—2 |
| Mo | < 0.4 | 5.4 (33) | 0.72 (49) | 7.5 | > 13 | 0.3—2 | 2—10 | 0.2—0.6 |
| Ag | 0.03 (23) | 0.38 (22) | 0.007 (47) | 54 | 12 | < 0.5 | 5—10 | |
| Cd | < 0.03 | 0.17 (37) | 0.039 (52) | 4.4 | > 5.6 | 0.01—0.3 | 5—30 | 0.01—0.2 |
| Sn | < 0.7 | 25 (31) | 1.8 (17) | 14 | > 35 | 0.2—60 | | 5—8 |
| Sb | 0.033 (42) | 0.3 (37) | 0.041 (67) | 7.3 | 9 | < 0.05 | > 0.15 | 0.002 |
| Ba | 1.2 (58) | 13 (38) | 1.1 (44) | 12 | 11 | 1—75 | > 500 | 4—6 |
| Cs | 0.08 (91) | 1.1 (51) | 0.039 (37) | 28 | 14 | 0.06—0.2 | | |
| La | < 0.01 | 0.73 (20) | 0.017 (28) | 43 | > 70 | 0.003—15 | | |
| Ce | < 0.09 | 0.8 (18) | 0.029 (49) | 28 | > 9 | 0.002—16 | | |
| Nd | < 0.2 | 0.54 (23) | 0.063 (86) | 8.6 | > 2.7 | 0.01—3 | | |
| Sm | < 0.001 | 0.086 (48) | 0.0034 (30) | 25 | > 86 | 0.002—0.8 | | |
| Eu | 0.024 (66) | 0.033 (23) | 0.0012 (33) | 28 | 1.4 | < 0.17 | | |
| Tb | < 0.003 | 0.014 (32) | 0.0012 (47) | 12 | > 4.6 | < 0.12 | | |
| Yb | 0.03 (60) | 0.011 (35) | 0.0032 (40) | 2.9 | 0.36 | 0.001—0.9 | | |
| Hf | 0.34 (67) | 0.047 (15) | 0.0038 (80) | 12 | 0.14 | 0.01—0.4 | | |
| Ta | 0.0015 (40) | 0.032 (72) | 0.0084 (24) | 4 | 21 | < 0.006 | | |
| W | < 0.02 | 5.2 (19) | 0.34 (18) | 15 | > 260 | < 0.35 | > 3 | |
| Ir | < 0.001 | 0.0036 (37) | 0.0014 (33) | 2.6 | > 3.6 | < 0.02 | | |
| Th | 0.07 (12) | 0.064 (41) | 0.028 (54) | 2.3 | 0.87 | < 0.02 | | |
| U | < 0.004 | 0.01 (24) | 0.0057 (38) | 1.8 | > 2.5 | < 0.07 | | |

Comparison of higher elemental concentrations in pine-needles with normal and toxic concentrations in plants (columns 6, 7) shows that the maximal concentrations of Cr, Co, Ni, Se, As, Mo, Sb, and W are inside the interval of toxicity in plants. It is appropriate to compare the concentrations of these elements with their concentrations in an important food product — cereal grains (Table 2, column 8). In this case, we also see that concentrations of Fe, Ni, As, Rb, Mo, and Sb are significantly higher. The high concentration of some elements in pine-needles and in soils testifies indirectly about the level of the concentrations in the atmospheric air. Some of these elements and their combinations are toxic and

carcinogenic. We do not discuss here the negative role of such chemical combinations as CO, SO₂, and As₂O₃ that can also be released into the air during the production of colour metals. We will note here the peculiarities of the influence of only two hazardous elements on the human organism.

Nickel. Its maximal concentration in investigated Kola pine-needles (≈ 130 ppm) is approximately 25 times higher than the upper level (5 ppm) of the interval for normal concentrations of Ni in plants. Possibly in this region, Ni (a strong carcinogen and allergen) transfers partially as air-borne, highly toxic tetracarbonyl, because Ni is produced using the process of carbonylization. As is known, tetracarbonyl is easily absorbed by the lungs and breaks down their defensive mechanisms, causing lung diseases and also cancer of the nose cavity and lungs.

Chromium. The maximal observed concentration of Cr in pine-needles (≈ 17 ppm) is approximately 30 times higher than the upper level of the interval for normal concentrations in plants. Chromium is also a toxic and carcinogenic element. Its abundance causes nephritis and adverse effects of the respiratory system — from changes in lung dynamics to cancer.

3. Conclusions

From the above, it is clear that the excess abundance of toxic and carcinogenic elements, such as Ni and Cr, creates a premise for the increase in serious illnesses. Concentration levels of some elements in Kola pine-needles are significantly higher than those, for example, in the Tver region. This allows one to speak about the ill-disposed ecological situation for the population living near the power smelting plants in Monchegorsk and Nikel.

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References

1. Nikonov V.V., Lukina N.V. — «Forests Biochemical Functions on the Northern Free Line», Russian Academy of Sciences, Kola Science Centre, Institute of North Industrial Ecology Problems, Apatity, 1994.
2. Sigel A., Sigel H. — «Metal Ions in Biological Systems», vol.20, «Concept on Metal on Toxicity», University of Basel, Switzerland, Marcel Dekker Inc., New York and Basel, 1986.
3. Kabata-Pendias A., Pendias A. — «Trace Elements in Solids and Plants», CRC Press, Boca Raton, Florida, 1984.
4. Filov V.A. — «Harmful Chemical Essences. Inorganic Combinations of Group 1—4 Elements», Leningrad, Chemistry, 1988.
5. Bernd M., Zhang D.L. — The Scien. of the Tot. Environ., 1991, v.103, p.27—35.
6. Puling L., Jervis R.E. — Journ. of Radioanal. Chem., 1992, vol.161, N1, p.215—225.