УДК 621.039.573

EPITHERMAL NEUTRON ACTIVATION ANALYSIS OF MOSS, LICHEN AND PINE NEEDLES IN ATMOSPHERIC DEPOSITION MONITORING

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Experience in the use of epithermal neutron activation analysis (ENAA) in the monitoring atmospheric deposition by means of moss, lichens and pine needles is summarized. It is shown that 45 elements (Mg, K, Ca, Al, Cl, Sc, V, Cr, Mn, Fe, Co, Ni (using (*n, p*)-reaction), Zn, Cu, As, Se, Br, Rb, Sr, Zr, Mo, Ag, Sn, Sb, I, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb, Lu, Hf, Ta, W, Au, Th and U, as well as Ir and Re in pine needles in the presence of anthropogenic pollution by the nickel smelter complex) are reliably determined. Examples of the use of lichens, moss and pine needles as biomonitors of atmospheric deposition in Franz Josef Land, the Kola Peninsula and in the Tver region are given.

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

Эпитепловой нейтронный активационный анализ мхов, лишайников и хвои сосны в мониторинге атмосферных выпадений

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В настоящей работе обобщается опыт эпитеплового нейтронного активационного анализа (ЭНАА) биомониторов (мох, лишайники, хвоя сосны), используемых для мониторинга атмосферных выпадений. Показано, что этим методом могут быть достоверно определены 45 элементов (Mg, K, Ca, Al, Cl, Sc, V, Cr, Mn, Fe, Co, Ni (используя (*n, p*)-реакцию), Zn, Cu, As, Se, Br, Rb, Sr, Zr, Mo, Ag, Sn, Sb, I, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb, Lu, Hf, Ta, W, Au, Th и U, а также Ir и Re в хвое сосны при наличии антропогенных загрязнений окружающей среды никелеплавильным металлургическим комбинатом). Приводятся примеры использования лишайников, мхов и хвои сосны в качестве биомониторов атмосферных выпадений на Земле Франца-Иосифа, Кольском полуострове и Тверской области.

Работа выполнена в Лаборатории нейтронной физики ОИЯИ.

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Introduction

At present, in the practice of biomonitoring of atmospheric deposition of trace elements, moss, lichens, and pine needles are used as biomonitors. The Scandinavian countres, and especially Norway [1—3] have extensive experience in the use of moss for this purpose.

To determine the trace elements content, atomic absorption spectroscopy (AAS) in combination with INAA were frequently used. In the last few years inductively coupled plasma emission spectroscopy (ICP-ES) and inductively coupled plasma mass spectroscopy (ICP-MS) have been the chosen methods [4].

Experience in the use of NAA by means of thermal neutrons [4] shows that INAA of the moss *Hylocomium splendens* allows the determination of only 13 elements.

Our experience with the use of resonance neutrons in INAA of lichens from Franz Josef Land [5] showed that at the IBR-2 reactor 45 elements (Mg, K, Ca, Fe, Na, Cl, Mn, Se, Zn, Cu, V, Zr, Ti, Br, Y, Cr, I, Ni, Ba, Co, Sc, Rb, Sn, W, Mo, Se, As, Hf, Ag, Sb, Ta, Cs, Au, La, Ce, Nd, Sm, Eu, Tb, Ho, Tm, Yb, Lu) were reliably determined.

Thus, to extend the possibilities of using the IBR-2 reactor in analytical applications [6] the present investigations were carried out on the use of resonance neutrons for biomonitoring by means of moss, pine needles and lichens.

In the methodical investigations on the use of INAA for moss, lichens and pine needles analysis, moss samples from Norway [7] and pine needles samples from the Kola Peninsula and Tver region were utilized.

Experiment

Reliable determination of the trace element content in pine needles is based on samples of *Pinus sylvestris L* collected in 11 points of Tver region from five one-year old trees growing in a square of about 100 sq.m. These 11 collection points are situated along the perimeter of approximately 3000 sq.km. In the same points the moss samples *Hylocomium splendens* were collected from the same square. Samples from 5 trees and 5 moss species were used for preparation of one averaged sample respectively to be analysed by INAA. Pine samples of the same type from the Kola Peninsula were collected from 7 trees.

Lichens were collected in the region of the Lunnik glacier on Alexandra Island (Franz Josef Land).

Moss, lichen and pine needle samples were airdried in the air and homogenized. Then 0.5 g samples were chosen and packed in Al cups for long-term irradiation and in polystyrene packs for 3—5 minute irradiation. Samples were irradiated in channels Ch1, Ch3 and Ch4 of the IBR-2 reactor. Densities (n / (cm^2·s)) of thermal (F_{th}), resonance (F_{epi}) and fast (F_{fast}) neutrons in these channels are given in Table 1.

Irradiation time for long-lived isotopes varied from 4 to 7 days in Ch.1 and was 10 days in Ch.3 and Ch.4. Decay time for the first measurement was 4—6 days, for the second one it was 20—30 days. Measuring time varied from 1 to 5 h.

Table 1. Characteristics of the irradiation channels at the IBR-2 reactor

Irradiation site	Neutron flux density (n / (cm^2·s))·10^{12}			T°,C	Chan. diam., mm	Chan. length, mm
	Thermal	Resonance	Fast			
Ch.1	Cg coat	0.23 ± 0.03	1.4 ± 0.16	70	28	260
Ch.2	0.54 ± 0.06	0.12 ± 0.014	0.64 ± 0.04	60	28	260
Ch.3	Gd coat	0.9 ± 0.10	7.0 ± 0.5	30—40	30	400
Ch.4	13.0 ± 0.5	1.25 ± 0.1	7.0 ± 0.5	30—40	30	400
Ch.0	no	< 0.1	150	400	16	180

To determine Cl, V, I, Mg, Cu, Al, and Mn, Ch.1, equipped with a pneumatic system, was used. Irradiation time $T_i = 5$ min., decay time $T_d = 3$—5 min., counting time $T_c =$ 5—8 min.

In the second measurement with $T_d = 15$ h, the concentrations of K and Na were determined from the same samples. Comparison of our results is made with data on moss reference material DK-1 [7].

Gamma spectra were measured using Ge(Li) detectors with a resolution of 2.5 keV for the ^{60}Co 1332.4 keV line, with an efficiency of about 6% compared to 3″ × 3″ NaI detector for the same gamma line. Data processing and element concentration determination was performed on the basis of standard reference materials and comparators, using software developed in FLNP JINR [8].

In irradiations of more than 3 days in Ch.1, a single comparator of Au (10^{-6} g) was used. For 3—5 minutes of irradiation its concentration was (10^{-6} g). For comparison with Ch.3, a comparator of Zr (^{95}Zr and ^{97}Zr) (10 mg) was used. Concentrations of elements which had long-lived isotopes were also determined using standard reference materials SDM, SL-1 (International Atomic Agency, Vienna) and DK-1 [7].

Results and Discussion

Element concentrations for moss reference material DK-1, lichens and pine needles with detection limits for pine needles are given in Tables 2 and 3. Detection limits for lichens and mosses are close to those in pine needles. Detection limits and element concentrations of anthropogenically polluted pine samples (Pechenga-Nickel), irradiated in Ch.1 and Ch.3, are shown in Fig.1.

Detection limits are significantly lower for Ch.3 with the exception of Cl, Cr, Nd, Tm, Gd, W. It can be seen from a comparison of results from Ch.1 and Ch.3 that the detection limits are only noticeably lower for Eu, Sc, Co, Lu, Hg, Cr, Fe, Na and U. This is understandable as these elements are characterized by low I_0 / σ_0 and by the use of Gd coat.

Table 2. Element concentrations in moss samples *Hylocomium splendens*, lichen ones *Usnea sp*, pine needles *Pinus sylvestris L*, and the detection limits for pine needles as measured in irradiation channels 1 and 3

Element	Element concentrations, pm				$\frac{I_0}{\sigma_0}$
	Moss DK-1	Lichen *Usnea sp*	Pine needles	Concentr. limit	
Na	530(8)	900(5)	121(5)	5.0[1]	0.59
Mg	< 800	8200(10)	2500(15)	600[1]	0.68
Al	480(5)	< 50	750(5)	20[1]	0.74
Cl	328(11)	57(20)	810(20)	100[1]	0.69
K	3300	1800(40)	5000(8)	190	0.97
Ca	1630(3)	5100(46)	2500(35)	340	1.31
Sc	0.16(13)	2.0(8)	0.043(15)	1.0E-3	0.44
V	6.0(10)	17.0(6)	2.2(17)	0.6[1]	0.55
Cr	1.9(8)	3.2(8)	1.9(15)	0.1	0.53
Mn	143(7)	53.0(4)	198(5)	3.5[1]	1.07
Fe	575(9)	2200(8)	194(17)	2.0	1.30
Co	0.26(5)	2.23(7)	6.8(7)	5 OE-3	2.02
Ni	1.58(21)	2.70(15)	190(5)	0.3	(*n*, *p*)
Cu	240(25)	< 20	280(8)	25[1]	1.06
Zn	30.8(13)	21.4(5)	21.0(6)	0.3	1.96
As	0.64(3)	0.12(8)	2.0(8)	4E-2	14.0
Se	0.43(9)	0.22(13)	1.1(13)	6E-3	10.9
Br	13.5(7)	5.8(6)	2.46(6)	3E-2	19.3
Rb	12.9(7)	1.8(9)	24.8(8)	0.5	14.8
Sr	33.0(4)	23.8(17)	3.9(22)	0.8	4.1
Zr	11.0(11)	13.0(15)	< 0.7	0.7	282
Mo	< 1.4	< 0.3	7.3(27)	1.4[1]	53.1
Ru	0.16(25)	< 0.1	< 0.01	0.01	3.63
Ag	0.05(8)	0.02(7)	0.27(12)	3E-3	17.7
Cd	< 0.1	< 0.1	0.15(27)	2E-3	48.0
Sn	2.4(15)	1.7(10)	5.7(18)	2E-3	49.1
Sb	0.37(6)	0.02(7)	0.36(9)	6E-4	28.8
Te	< 0.1	< 0.1	0.11(37)	0.1	1.7

Element	Element concentrations, pm				$\frac{I_0}{\sigma_0}$
	Moss DK-1	Lichen *Usnea sp*	Pine needles	Concentr. limit	
I	3.8(8)	3.0(4)	< 1.0	0.1[1]	24.8
Cs	0.29(7)	0.016(9)	0.046(8)	3E-3	18.5
Ba	18.5(8)	2.5(12)	2.0(46)	0.3	23.5
Hf	0.21(14)	0.12	< 0.002	2E-3	2.52
Ta	0.026(14)	0.016(13)	0.00057(20)	2E-4	33.3
W	0.73(27)	< 0.2	0.34(12)	6E-2[1]	13.7
Re	< 0.001	< 0.001	< 0.0022(23)	1.0E-3	15.3
Ir	< 0.0003	< 0.0002	0.0007(20)	5E-4	5.8
Au	0.00074(20)	0.0008(8)	0.0073(7)	5E-5	15.7
Hg	0.67(10)	< 0.05	< 0.02	2E-2	0.88
Th	0.2(5)	< 0.02	0.0021(9)	1.0E-3	12.0
U	0.19(5)	< 0.02	< 0.015	2.0E-2	102.3

1 — detectrion limit for channel Ch.1.

Table 3. Concentration of REE in moss samples *Hylocomium splendens*, the lichen ones *Usnea sp*, pine needles *Pinus sylvestris L*, and the detection limits for pine needles in channel 3

Element	Element concentrations, ppm				$\frac{I_0}{\sigma_0}$
	Moss DK-1	Lichen	Pine needles	Detect. limit	
La	1.22(7)	1.07(9)	0.13(13)	3.0E-3	1.24
Ce	2.92(8)	2.38(10)	0.16(19)	5.0E-2	0.82
Nd	0.92(26)	2.55(16)	0.56(15)	2.0E-2*	2.35
Sm	0.23(8)	0.46(6)	0.013(8)	1.4E-4[1]	14.4
Eu	0.042(24)	0.060(11)	0.001(29)	5.0E-4[1]	0.67/5.67**
Gd	0.21(14)	< 0.1	0.026(16)	1.0E-2	2.75
Tb	0.022(9)	0.089(8)	0.002(20)	5.0E-4	17.2
Tm	0.015(13)	0.14(6)	0.0019(30)	1.4E-3*	17.9
Yb	0.054(40)	0.012(10)	0.0065(28)	4.0E-3	0.44
Lu	0.028(29)	0.096(8)	< 0.002	2.0E-3	2.26

*without Gd coat
** for ^{152}Eu
1 — detection limit for channel Ch.1.

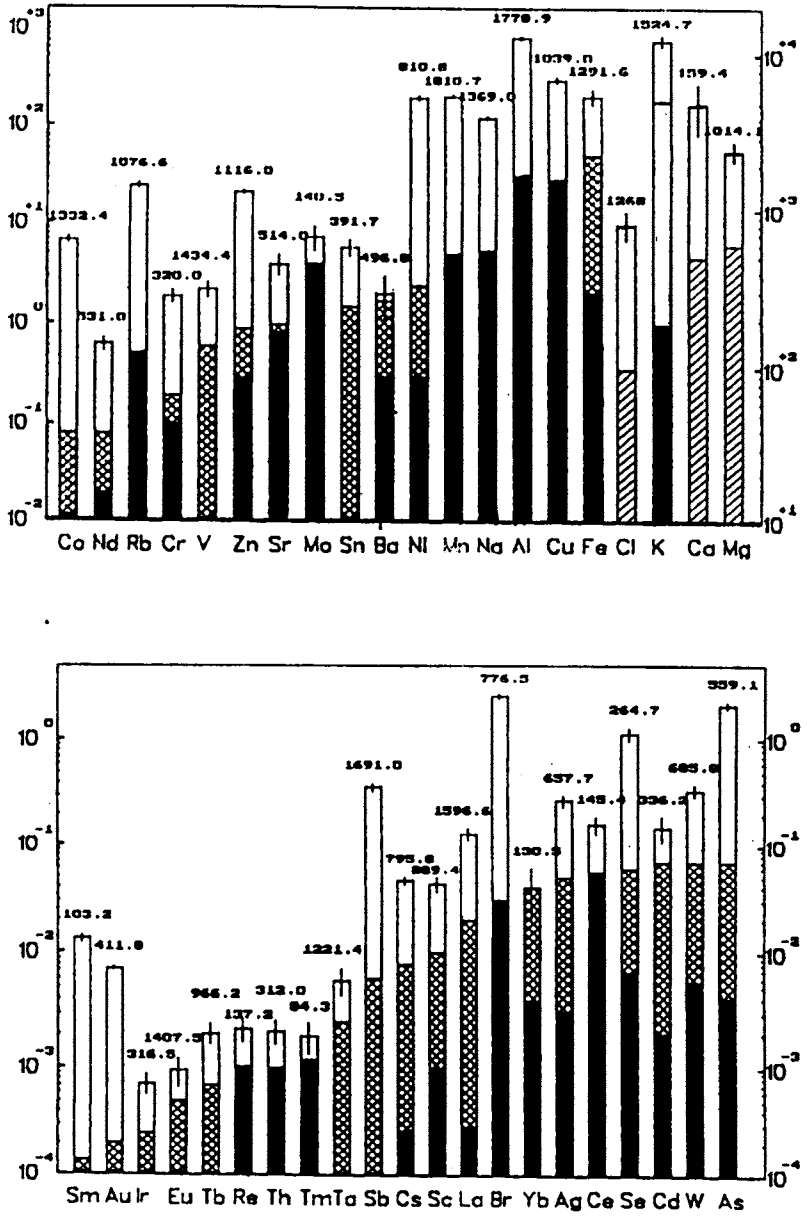

Fig.1. Element concentrations (undashed columns) and detection limits for pine needles (Pechenga-Nickel) irradiated in Ch.1 (light-dashed columns) and Ch.3 (dark-dashed columns)

But at the same time, the Compton gamma quanta registered (especially in the case of Sc, Co and Fe) strongly «shadow» the peaks of other elements, thus lowering the detection limits.

Fast neutrons were used to determine concentrations of Ni from the $^{58}Ni\ (n, p)\ ^{58}Co$ reaction. It works well for INAA. But, on the other hand, density of fast neutrons on both channels of the IBR-2 reactor leads to the interference effect when the concentration of Al, Na, Mn, and Cr, is affected by the $^{31}P\ (n, \alpha)\ ^{28}Al$, $^{28}Si\ (n, p)\ ^{28}Al$, $^{27}Al\ (n, \alpha)\ ^{24}Na$, $^{54}Fe\ (n, \alpha)\ ^{51}Cr$ and reactions $^{56}Fe\ (n, p)\ ^{56}Mn$, respectively.

Aluminium determination from the $^{27}Al\ (n, \gamma)\ ^{28}Al$ reaction is essentially influenced by the interfering reaction in moss. Up to 50—60% of $^{27}Al\ (n, \gamma)\ ^{28}Al$ is produced by ^{31}P and ^{28}Si. Thus, the real concentrations of Al given in Table 2 have a higher percentage of errors, because the concentration of P was not determined. In all other cases mentioned above, contribution of interfering reactions is insignificant: for Na it is 1%; for Mn, 0,1%; and 0,5% for Cr.

Data on confidence intervals for trace elements and REE are given in Tables 4 and 5. Element concentrations with their confidence intervals in moss and pine needles normalized to DK-1 values are shown in Fig.2. Data on lichens are listed in Table 3.

Table 4. Elements concentrations and confidence interval, μ

Element	Tver region (Dubna)				Kola Peninsula	
	Moss, ppm	μ, %	Pine needles, ppm	μ, %	Pine needles, ppm	μ,
Na	1190	36	56	53		
Mg	1780	31	1370	25		
Al	517	35	193	24		
Cl	1050	23	376	18		
K	9160	18	4300	18		
Ca	7800	40	6050	16	3180	25
Sc	0.066	60	0.018	68	0.11	30
V	1.52	55				
Cr	1.26	26			0.46	28
Mn	290	43	340	44		
Fe	306	39	57	76	132	25
Co	0.46	33	0.17	47	0.73	19
Ni	1.6	26	2.0	60	85	34
Cu	12.4	30	6.3	35		
Zn	39.3	31	35	34	31.6	27
As	0.25	73	3.1	35	0.72	52
Se	0.14	40	3.9	57	0.083	24
Br	3.1	30	1.8	42	4.7	21
Rb	66.1	32	24.7	48	33	16
Sr	27.0	30	11.4	40	11.7	64

Element	Tver region (Dubna)				Kola Peninsula	
	Moss, ppm	μ, %	Pine needles, ppm	μ, %	Pine needles, ppm	μ,
Zr	5.3					
Mo	0.44	57			1.14	42
Ag	3.5E-2	20	1.9E-2	34	0.0072	19
Cd	0.28	115			0.067	21
Sn					2.37	19
Sb	0.16	28	0.04	60	0.047	26
I	1.50	41				
Cs	0.22	37	4.4E-2	53	0.22	55
Ba	15.3	38	0.54	61	1.8	31
Hf	9.0	53	0.23	92	0.034	90
Ta	6.3E-3	54	1.2E-3	71	5.3E-4	49
W	1.9	44	0.96	80	0.46	50
Au	10.2E-3	70	1.9E-3	47	1.2E-3	8
Th	7.9E-2	66	9.4E-3	21	8.1E-3	11
U	0.052	85			6.8E-3	54

$\mu = \frac{SD}{n^{0.5}} t$, t — student's factor for significance level 0.05,

SD — standard deviation, n — number of samples

Table 5. Concentrations of REE (ppm) and confidence interval, μ

Element	Tver region				Kola Peninsula	
	Moss, ppm	μ, %	Pine needles	μ, %	Pine needles	μ, %
La	0.41	55	0.031	58	0.023	30
Ce	1.00	100	1.02	100	0.21	11
Nd	—	—	—	—	0.6	17
Sm	0.042	52	0.0048	32	0.0104	14
Eu	0.0036	51	0.024	48	0.007	53
Gd	0.11	100	1.3	66	0.13	15
Tb	0.015	27	—	—	0.0029	41
Tm	0.028	28	—	—	0.011	34
Yb	0.024	50	0.013	64	0.0043	47
Lu	—	—	—	—	0.00046	41

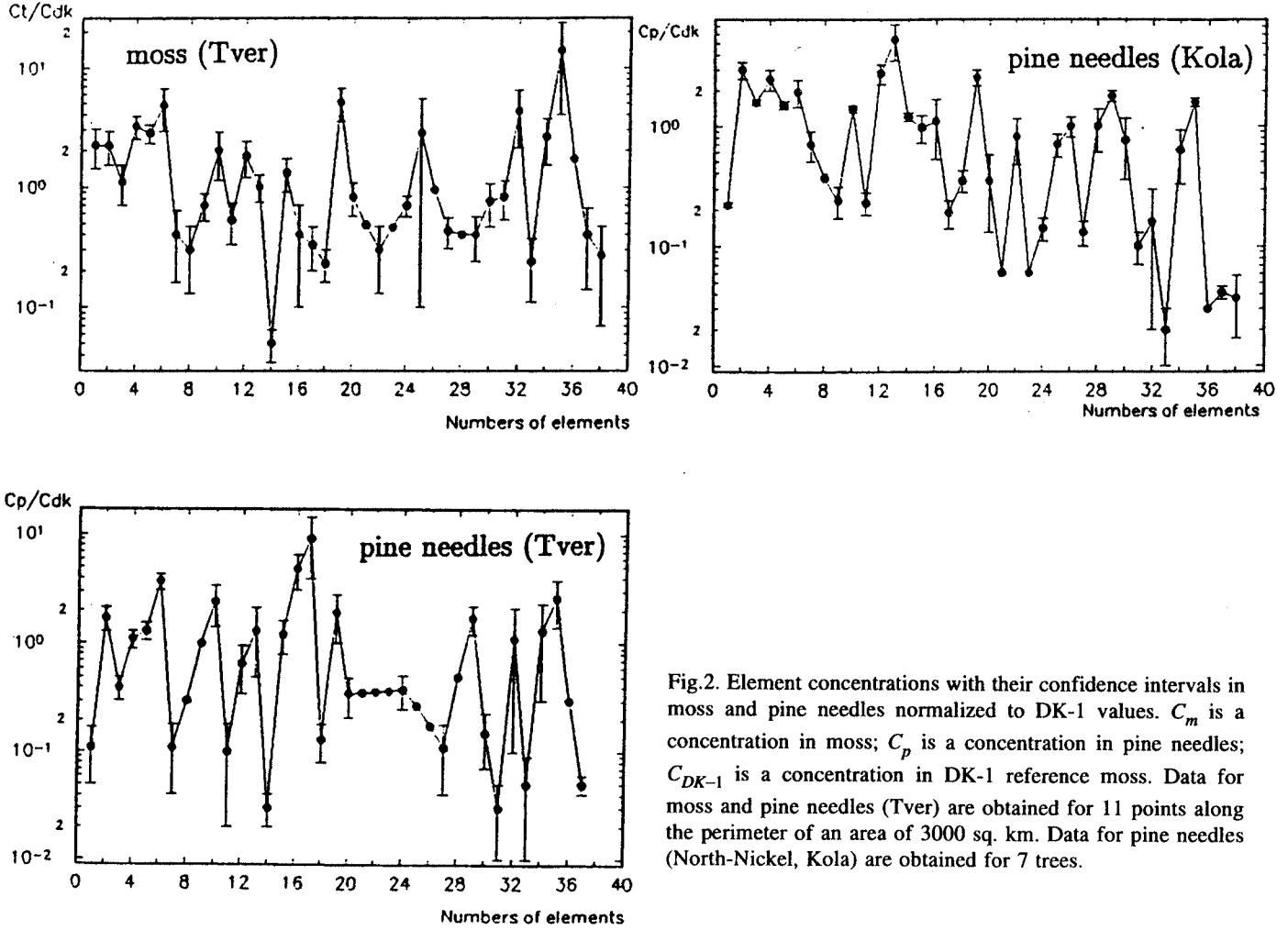

Fig.2. Element concentrations with their confidence intervals in moss and pine needles normalized to DK-1 values. C_m is a concentration in moss; C_p is a concentration in pine needles; C_{DK-1} is a concentration in DK-1 reference moss. Data for moss and pine needles (Tver) are obtained for 11 points along the perimeter of an area of 3000 sq. km. Data for pine needles (North-Nickel, Kola) are obtained for 7 trees.

Conclusion

Potentialities of the use of resonance neutrons for monitoring atmospheric deposition of heavy metals, including REE and a set of nonmetallic elements are demonstrated.

Data obtained for pine needles from Tver region and the Kola Peninsula are similar within the confidence intervals and are not very large. Confidence intervals for pine needles from the Kola Peninsula are lower, but samples from Tver region in the vicinity of Dubna were collected from the significantly smaller squares, along the perimeter of an area of 3000 sq.km.

Concentration values for pine needles for many elements are lower than those for moss samples. Concentrations of REE and some other elements in investigated pine needles are lower than those in DK-1. That is why to determine these concentrations we also used Gd-coated channel Ch.3.

In conclusion, authors express their deep gratitude to Prof. E.Steinnes for providing us with the reference material DK-1 for our investigations, and to Mrs. L.P.Strelkova for help in the preparation of this manuscript.

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Received on January 13, 1995.