WDXRS OF MINOR AND TRACE ELEMENT CONTENTS IN SOILS OF THE KHAMAR-DABAN MOUNTAIN RANGE

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Introduction

With consideration of predominating winds in the region, the Baikal Pulp-and-Paper Complex (BPPC) is likely to be a key source of industrial air emissions on the southern shore of the Baikal Lake to the North-East of the Baikalsk city. Indirect retrospective assessment of the regional pollution level is achievable through a survey focused on environment objects that accumulate chemical elements present in industrial air emissions. Such objects normally include topsoil, mosses, lichens, mushrooms, etc. Topsoil is a more appropriate subject for such surveys. Opposite to other environment components (air, water) where periodic self-treatment processes may occur, soil is an active acceptor of chemical contaminants and virtually has no inherent self-treatment ability. Contaminants are retained in soil for significantly longer time than in other biosphere components (mosses, lichens, mushrooms, etc.) - most likely eternally. Soil serves as a mighty absorber of many chemical elements. It retains them in topsoil, which is the most fertile soil layer. North-western slopes of Khamar-Daban mounts are most representative for regional BPPC impact assessment.

The range of chemical elements emitted to air by solid fuel burning is very diverse. Key air emission contaminants are: Al, As, Ca, Ce, Cl, Co, Cr, Cs, Cu, Eu, F, Fe, Hf, K, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, S, Sb, Sc, Se, Si, Tb, Th, Ti, V, Yb, Zn, etc.[1-4] That is why for properly assessing a region's man-caused degree of pollution it is necessary to maximize the number of chemical elements that can be determined for study. These elements should obviously include top-priority toxicants. The existing Russian environmental standards for soils[5] identify 11 chemical elements, namely As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Sb, V, and Zn.

This research aims at a more detailed examination of the pollution level across the region to the north-east of BPPC caused by some chemical elements of industrial air emissions.

Topsoil samples were taken on the Khamar-Daban mounts to the North-East of BPPC at a height of about 1200 - 1500 m above sea level in two areas located 11 and 84 km away, respectively. The first sampling area (Area 1) is located on the Osinovsky bare mount in upper reaches of the Bolshaya Osinovka River 10 km away from the Baikal shoreline and in 11 km from BPPC. Five topsoil samples were taken in various points of slopes and top of the mount. Investigated samples were classified to mountain-tundra low-capacity soil, cedar elfin woods and reindeer, cowberry-reindeer or grass-reindeer mosses vegetation. The second sampling area (Area 2) is located on the Osinovsky bare mount in upper reaches of the Osinovka River 10 km away from the Baikal shoreline and in 84 km from BPPC. The area is a part of the Baikal nature reservation and is located 3 - 5 km east from the Tankhoi city right opposite the Angara River heads in the West. Four topsoil samples were taken in various points of slopes and top of the mount. Investigated samples were classified to mountain-tundra low-capacity soil, moss and lichen vegetation.

Experimental

Samples. For chemical element analysis soil samples were taken from topsoil 4 cm thick as an average mixed sample by the plastic knife and the plastic scoop. Soil samples were dried in the air in enclosed space at room temperature during a few days. Air-dry scattered soil samples were cleaned from roots, impurities, neoformations and sod, from which soil clods had been carefully shaken off. Then each sample was mixed, homogenized, mechanically ground using the porcelain mortar and sieved to <2 mm using nylon screening. Then a randomized 5 g weight portion of each sample was milled for 5 min using an "IB-micro" mill. This time was enough to reach about 200 mesh dispersion level controlled visually by comparing with the standards. The fine milled soil samples were poured into special dashboard capacities filled up to their edges.

Standards. Quality control of the developed procedure and analytical results was implemented in parallel by examining samples prepared from the IAEA international standard reference material (SRM) - IAEA Soil-7.

Analytical method. Instrumental wave-dispersive X-ray fluorescent analysis (WD-XRF) was used to determine contents of chemical elements. Mass fractions of Mo, Nb, Y, and Zr were measured using an ARF-6 analyzer with an Ag-tube. The same analyzer, but with a Mo-tube was used to determine contents of As, Ba, Br, Pb, Rb, Sr, Th, and U in the samples. Mass fractions of Co, Cr, Cu, Fe, Mn, Ni, Ti, V, and Zn in the soil samples were analyzed using a SPM-25 Quantometer equipped with a Rh-tube. Measurements with the ARF-6 analyzer were carried out twice. The duration of each measurement was 100 s. Measurements of 100 s duration were carried out once using the SPM-25 Quantometer. The $K_{\alpha 1}$-lines were used to register intensities of characteristic X-rays of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Br, Rb, Sr, Y, Zr, Nb, Mo, and Ba, while the $L_{\beta 1}$-lines were used to register intensities of X-rays of Pb, Th, and U. The sample matrix effect was account by noncoherent scattered K_{α}-line of the X-ray tube.

Calculations. Standard program for calculations of an arithmetical mean (M), standard deviation (S.D.), and standard deviation of the mean (S.E.) was used for the statistical treatment of the results.

Results and discussion

The accuracy of the obtained results was estimated by determination of the element contents in samples of the IAEA Soil-7 international certified reference material. The Table 1 results show that application of instrumental WD-XRF analysis makes it possible to determine mass fractions of not less than 21 chemical elements in the soil samples. The relative errors of a single measurement of different element mass fractions vary within a rather wide range to be no more than 5% for Fe, Mn, Rb, Sr, Th, and Zr, 6% to 10% for Ba, Br, Co, Cr, Cu, Nb, Ni, Pb, Ti, V, and Zn, and above 10% for As, Mo and U. Coincidence of the WD-XRF mean values of chemical element contents in the IAEA Soil-7 reference material with certificate data in the range of 95% confidential interval was obtained for 17 elements from 21. The only exclusion was the results of Fe (not certified), Mn, V, and U for which the difference between means of mass fraction were +31%, +19%, +48 and –38% respectively. Thus, a systematic error might be available only while determining Mn, V, and U contents by WD-XRF analysis. In general, good coincidence with certificate data indicates high accuracy of the used technique and the correctness of the obtained results.

Table 1. WD-XRF data of some minor and trace elements of the IAEA Soil-7 reference material compared to certified values

No	Element	Certified values			Our results
		Mean	95% confidence interval	Type*	Mean
1	As, mg/kg	13.4	12.5-14.2	C	14
2	Ba, mg/kg	159	131-196	N	184
3	Br, mg/kg	7.0	3.0-10.0	N	8
4	Co, mg/kg	8.9	8.4-10.1	C	9
5	Cr, mg/kg	60	49-74	C	74
6	Cu, mg/kg	11.0	9.0-13.0	C	12
7	Fe, g/kg	25.7	25.2-26.3	N	33.6
8	Mn, mg/kg	631	604-650	C	750
9	Mo, mg/kg	2.5	0.9-5.1	N	3
10	Nb, mg/kg	12	7-17	N	10
11	Ni, mg/kg	26	21-37	N	22
12	Pb, mg/kg	60	55-71	C	55
13	Rb, mg/kg	51	47-56	C	51
14	Sr, mg/kg	108	103-114	C	107
15	Th, mg/kg	8.2	6.5-8.7	C	6.8
16	Ti, g/kg	3.0	2.6-3.7	N	3.4
17	U, mg/kg	2.6	2.2-3.3	C	1.6
18	V, mg/kg	66	59-73	C	98
19	Y, mg/kg	21	15-27	C	26
20	Zn, mg/kg	104	101-113	C	102
21	Zr, mg/kg	185	180-201	C	185

* C - certified values, N - non-certified values

A considerable remoteness of Area 2 from BPPC (84 km), as compared to Area 1 (11 km), allows to assuming it as a checkpoint (background levels) in BPPC air emission impact assessment. The comparison of mean values in topsoil on the Osinovsky slopes in Areas 1 and 2 made for 19 chemical element mass fractions did not reveal any statistically valid increases (Table 2) with Y exclusion only. Moreover in soil of the mount top in Area 2 contents of such elements, as Sr and U, were correspondingly 1.18 and 1.67 times higher (statistically valid) than in Area 1 (Table 2).

The comparison of the obtained results with literature data makes it possible to conclude that mean contents of all 19 elements in Osinovsky topsoil are within the range characteristic of non-polluted soils on the territories of former USSR, CIS and across the world (Table 3).

Table 2. Means (M±S.D.) of chemical elements mass fraction in soils of slopes and tops in areas 1 and 2 (air-dried soil)

Element	Slopes			Tops		
	Areas 1	Areas 2 Reservation	p< *t*–test	Areas 1	Areas 2 Reservation	p< *t*–test
As, mg/kg	<3.0	<3.0-3.1	-	3.6±0.4	4.3±0.1	-
Ba, mg/kg	325±49	355±120	-	395±7	400±14	-
Br, mg/kg	1.9±1.6	2.8±2.7	-	2.6±0.1	3.4±0.6	-
Co, mg/kg	4.0±1.4	12.0±5.7	-	7.5±0.7	7.5±0.7	-
Cr, mg/kg	51±4	52±34	-	86.0±15.6	72.5±0.7	-
Cu, mg/kg	16.5±6.4	38.5±26.2	-	37.0±4.2	37.0±2.8	-
Fe, g/kg	19.3±4.2	36.2±25.2	-	44.0±2.0	43.6±1.1	-
Mn, mg/kg	410±42	580±367	-	715±162	605±7	-
Ni, mg/kg	2.85±0.78	3.50±0.28	-	23.0±1.4	19.0±1.4	-
Pb, mg/kg	4.0±0.1	5.5±3.5	-	7.5±0.7	8.5±0.7	
Rb, mg/kg	54.5±9.2	82.5±14.8	-	67.0±7.1	80.5±0.7	-
Sr, mg/kg	125±35	155±7	-	165±7.1	195±7	0.05
Th, mg/kg	3.25±0.35	3.25±3.18	-	6.35±0.92	6.80±0.14	-
Ti, g/kg	5.75±0.35	4.20±1.27	-	5.75±1.06	6.05±0.07	-
U, mg/kg	<1	<1-2.1	-	1.35±0.07	2.25±0.07	0.01
V, mg/kg	90.5±14,8	79.0±39.6	-	107±6	106±2	-
Y, mg/kg	24.0±1.4	17.5±6.4	-	22.0±1.4	13.0±1.4	0.01
Zn, mg/kg	31±4	32±13	-	22.0±4.2	15.5±0.7	-
Zr, mg/kg	195±7	145±35	-	205±57	215±7	-

The attained results provide evidence that the BPPC air emission total for the overall operation period did not induce any shifts in the chemical composition of soils in the adjacent region that would be beyond background (natural) values. However, this conclusion does not allow to generally rule out any impact from the BPPC operation on the chemical composition of regional soils but just defines a scale of such exposure. It is known that in nature there exist so-called biogeochemical provinces where either a deficit or excess of chemical elements in soils leads to human or animal diseases as well as suppresses plant growth. Development of understandings about "healthy soil" and optimum chemical element contents in soil is a challenging and multi dimensional endeavor. Available scientific literature offers only a few Russian and international references, which provide data on upper and lower limits of optimum chemical element contents in soils accompanied by rather convincing justification.[6,10-12,16,19,20] For 11 chemical elements (As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Sb, V, and Zn) the existing GOST (Russian State Standard) defines maximum permissible level

(MPL) or tentative permissible level (TPL) on the basis of a few soil characteristics (Table 4).[5,21] Among the 19 chemical elements, mass fraction of which were determined in soils of the Osinovsky mount, recommended ("Norm") or regulatory (MPL and TPL) data is available for only 10, namely for As, Co, Cr, Cu, Mn, Ni, Pb, Sr, V and Zn (Table 4). Mean mass fractions of these elements in Osinovsky topsoil fall within the optimum range and do exceed neither MPL nor TPL. Thus, soils of the Osinovsky bare mount are to be characterized as "healthy" and "non-toxic" in terms of chemical element contents.

Table 3. Comparison of the obtained results with the published data on chemical element mass fractions (median and range of means) in soils of the former USSR, CIS and globally (air-dried soil)

Element	Soils of the former USSR and CIS (Russian references[5,6-16]) Range of means	World's soils (Bowen[17]; Ure & Berrow[18] and Russian references[5,6-16]) Median & Range of means	Soils of Osinovsky mountains Range of means
As, mg/kg	1 - 40	11.3 (0.1-194)	<3.0-4.3
Ba, mg/kg	<10 - 30000	568 (<1-10000)	325-400
Br, mg/kg	0.8 - 5.0	42.6 (0.27-850)	1.9-3.4
Co, mg/kg	0.4 - 90	12 (0.3-200)	4.0-12.0
Cr, mg/kg	8.0 - 614	84 (0.9-4000)	51.0-86.0
Cu, mg/kg	< 1.0 - 500	25.8 (<1-390)	16.5-38.5
Fe, g/kg	0.0003 - 3.9	3.2 (0.01-55)	19.3-44.0
Mn, mg/kg	10 - 7400	760 (<1-18300)	410-715
Ni, mg/kg	1.9 - 3000	33.7 (0.1-1520)	2.85-23.0
Pb, mg/kg	<1 - 3000	29,2 (<1-3000)	4.0-8.5
Rb, mg/kg	70 - 194	120 (1.5-1800)	54.5-82.5
Sr, mg/kg	1 - 3500	278 (1-3500)	125-195
Th, mg/kg	0.04 - 22	14 (0.04-72)	3.25-6.80
Ti, g/kg	0.0006 - 1.5	0.51 (0.000017-3.4)	4.20-6.05
U, mg/kg	0.4 - 1.4	2.18 (0.1-14)	<1-2.25
V, mg/kg	3.0 - 700	108 (0.8-1000)	79.0-107
Y, mg/kg	5.8 - 50	27.7 (5-250)	13.0-24.0
Zn, mg/kg	0.5 - 7000	59.8 (1.5-7000)	15.5-32.0
Zr, mg/kg	100 - 870	345 (<10-3000)	145-215

Conclusion

1. It was shown that the instrumental WD-XRF analysis allowed determining with high accuracy mass fractions up to 21 chemical elements such as As, Ba, Br, Co, Cr, Cu, Fe, Mn, Mo, Nb, Ni, Pb, Rb, Sr, Th, Ti, V, U, Y, Zn, and Zr in the air-dried soil samples even at the natural (uncontaminated) levels. This method is non-destructive, i.e. non-utilizing a sample under study. To prepare a sample for the analysis, it should only be dried and mill. The

method is very express (only 1 to 2 min is required for an element determination) combined with high enough sensitivity, reproducibility, and accuracy of the results. The whole process of the analysis can be partially or even fully automated. The equipment required for the analysis is comparatively cheap, fully autonomous and compact.

Table 4. Comparison of mean mass fractions of chemical elements in Osinovsky mounts soils with maximum permissible and tentative permissible levels (MPL and TPL) adopted for soils in Russia and existing limits for "normal" soil (air-dried soil)

Element	"Norm"*			MPL & TPL[5,21] (1;2;3)**	Soils of Osinovsky mountains
	Kovalsky[11]	Thornton[19]	Ilin[20]		
As, mg/kg	-	<5-40	<15 - 20	2.0 (2, 5, 10)	<3.0-4.3
Ba, mg/kg	-	-	-	-	325-400
Br, mg/kg	-	-	-	-	1.9-3.4
Co, mg/kg	7 - 30	-	7 - 20	-	4.0-12.0
Cr, mg/kg	-	15 - 300	<200	100	51.0-86.0
Cu, mg/kg	15 - 60	2 - 60	<25	55 (33, 66, 132)	16.5-38.5
Fe, g/kg	-	-	-	-	19.3-44.0
Mn, mg/kg	400 - 3000	-	400 - 800	1500	410-715
Ni, mg/kg		2 - 100	<40	85 (20, 40, 80)	2.85-23.0
Pb, , mg/kg		10 - 150	<50	32(32, 65, 130)	4.0-8.5
Rb, mg/kg	-	-	-	-	54.5-82.5
Sr, mg/kg	<600	-	<600 - 1000	-	125-195
Th, mg/kg	-	-	-	-	3.25-6.80
Ti, g/kg	-	-	-	-	4.20-6.05
U, mg/kg	-	-	-	-	<1-2.25
V, mg/kg	-	-	<200	150	79.0-107
Y, mg/kg	-	-	-	-	13.0-24.0
Zn, mg/kg	30 - 70	25 - 200	10 - 70	100(55, 110, 220)	15.5-32.0
Zr, mg/kg	-	-	-	-	145-215

* - normal levels of "health soil"

** - MPL & TPL (1;2;3) – maximum permissible limit (MPL) or tentative permissible limit (TPL) of sand and subsand (1), acid (2), loam and clay (3) soils respectively

2. The attained results evidence that the BPPC air emission total for the overall operation period did not induce any shifts in the mean contents of 19 elements of soils in the adjacent region that would be beyond background (natural) values.

3. Soils of the Osinovsky bare mount are to be characterized as "healthy" and "non-toxic" in terms of chemical element contents.

4. The results of expert assessment do not fully rule out the availability of any impact of the BPPC on the regional soils but just define a scale of such exposure. For high precision evaluation of the impact of BPPC on region's soils, a series of researches on regular-basis

with 2 -3 year frequency are needed. Such researches are in plan of the Institute of Environmental Toxicology as the issue of BPPC shutdown still remains open and the Complex continues its operation.

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