IJBPAS, October, 2016, 5(10): 2623-2628

ISSN: 2277–4998

International Journal of Biology, Pharmacy and Allied Sciences (IJBPAS)

'A Bridge Between Laboratory and Reader'

www.ijbpas.com

APPLICATION OF X-RAY FLUORESCENCE METHOD FOR ASSESSING THE POLLUTION OF SNOW COVER

ONDAR, U. V*, CHAMBAL, I.V., OCHUR-OOL, A.O., CHERTEK, CH.O AND SMAGUNOVA, A.N.

Federal State-Funded Educational Institution of Higher Education «Tuva State University», Kyzyl, Russia

***Corresponding Author: Urana Ondar**

Received 10th July 2016; Revised 28th July 2016; Accepted 30th August 2016; Available online 1st Oct. 2016

ABSTRACT

The method of X-ray fluorescence analysis has showed that the concentration of some heavy metals (V, Cr, Cu, As) in the snow cover does not exceed the maximum permissible concentration.

Zinc has been detected in some samples of snow. It has been found that the concentration of lead is above the maximum permissible concentration in almost all samples; it indicates that the contamination of the snow cover is mainly caused by motor vehicles.

Key words: pollution of snow cover, X-ray fluorescence method, heavy metals, maximum permissible concentration

1. INTRODUCTION

The condition of air in urbanized areas directly influences human health. Snow cover is a convenient natural object suitable for assessing air pollution in the areas where snow persists over long time periods. Snow cover accumulates contaminators adsorbed as crystals on its surface and serves as an air pollution indicator. Dust aerosols are accumulated in snow cover and remain there until snowmelt, providing significant seasonal geochemical information. Because of both dry and wet ablation, the concentration of dust aerosols in snow is 2-3 times higher than it is in air [1-4]. Therefore, changes in the concentration of these substances can be measured by relatively simple but highly reliable methods.

The city of Kyzyl (the Tuva Republic) is known to have a high level of

air contamination during winter periods [5] due to the city's location in an intermountain basin, climatic factors (low temperatures, lack of wind in winter periods) and usage of solid fuel – coal for heating. Thus, Kyzyl was chosen as a base station for background measurements.

The X-ray fluorescence analysis is convenient for the control of snow cover pollution as it is a multi-element and simple express-method for conducting operation analysis.

Therefore, our work aims at assessing the rate of snow cover pollution in Kyzyl by the X-ray fluorescence method.

2. Experimental part

According to the Guide [6], two parallel samples were taken at each of ten different places of Kyzyl in February 2014. Two parallel samples were picked nearby from each other. The sampling area was 1 × 2 m; the sampling depth was the entire depth of the snow pit except the pre-soil layer. The samples were placed in plastic bags.

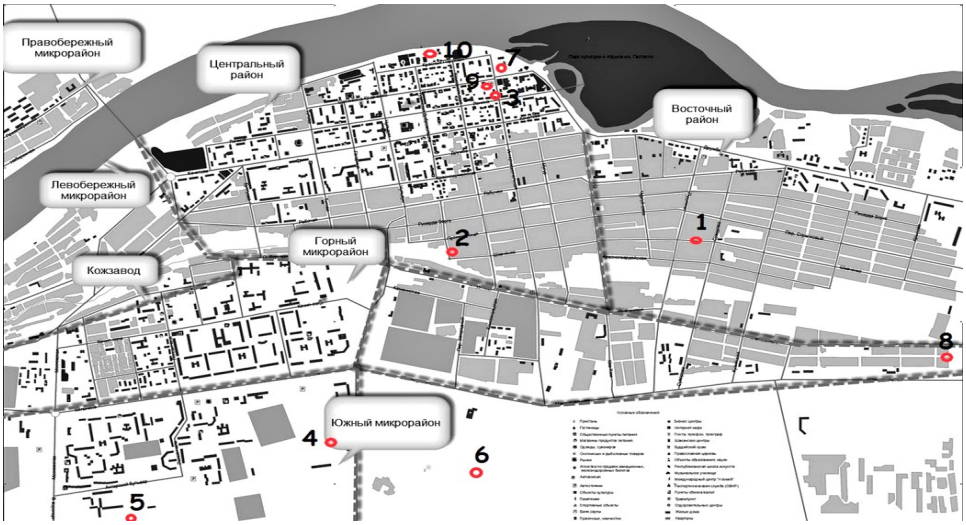

Figure 1: Kyzyl city map with the sampling scheme

In environmental research, the sampling error significantly affects the total error [7]. Thus, to assess the sampling-to-analysis errors ratio, the experiment was conducted by means of variance analysis.

$$S^2_{total} = S^2_{s-ing} + S^2_{s/p} + S^2_r, \quad \ldots(1)$$

where S^2_{total} - is the total error; S^2_{s-ing} - the error of sampling; $S^2_{s/p}$ – the error of samples preparation (preparation of emitters); S^2_r - the error of reproducibility.

In a laboratory, snow samples thawed in clean containers; the insoluble precipitates of snow cover (IPSC) were separated from the snow-melted water by filtration with pre-weighted filters (the

«Blue Ribbon» brand). To determine heavy metals in the sample IPSC material, the filters with precipitates were incinerated at a temperature of 450 °C for two hours - according to the methodology, which allowed preventing the loss of components being determined [8]. In an agate pounder with ethanol, the incinerated material was reduced to fragments sized less than 60 μm. Since the crushed sample material resisted pressing, it was suggested to prepare the emitters with addition of an adhesive on a base coat of boric acid.

The X-ray fluorescence analysis (XRF) of the IPSC was conducted using «Spectroscan MAX-GV» spectrometer. The composition of aerosols sampled in the interior of the continent is similar to the composition of soil [1-4]; therefore, the methodology of XPR of the IPSC was gauged in accordance with the state reference standards (SRSs) of soil and bottom sediments. The IPSC samples were analyzed for presence of TiO_2, Fe_2O_3, CaO, Al_2O_3, SiO_2, P_2O_5, K_2O, MgO, MnO, V, Cr, Co, Ni, Cu, Zn, As, Sr, Pb (Tables 1 and 2).

Table 1. Concentration of heavy metals in the IPSC samples (mg / kg)

No.	The concentration of microelements in the samples, mg / kg								
	Sr	V	Cr	MnO	Ni	Cu	Zn	As	Pb
1	866±130	89±9	129±3	820±63	73±16	83±11	927±72	9±1	733±69
2	720±108	82±9	127±3	504±39	59±13	96±13	1123±87	9±1	550±52
3	559±84	13±1	105±2	817±63	31±7	26±4	743±57	9±1	450±42
4	734±111	103±11	120±3	645±50	64±14	86±12	1270±98	9±1	546±51
5	605±91	106±11	123±3	605±47	46±11	77±11	948±73	9±1	491±46
6	1227±185	123±13	82±2	478±37	38±9	124±17	1256±97	8±1	959±91
7	605±91	16±2	87±2	766±59	107±24	116±16	1034±80	9±1	534±50
8	772±117	76±8	87±2	769±59	135±30	213±29	1451±112	9±1	628±59
9	699±105	65±4	89±2	893±69	139±31	234±31	1185±92	10±1	672±64
10	729±110	65±7	106±2	850±66	174±39	177±24	1506±116	10±1	548±52

Table 2. The concentration of macroelements in the IPSC samples (%)

No.	Macroelements' concentration, %							
	K_2O	TiO_2	Fe_2O_3	CaO	Al_2O_3	SiO_2	P_2O_5	MgO
1	1.56±0.05	0.98±0.16	7.81±0.70	4.02±0.09	9.86±0.13	18.49±1.91	0.22±0.06	0.71±0.14
2	1.38±0.04	0.90±0.15	7.53±0.67	3.38±0.08	9.79±0.13	16.91±1.75	0.22±0.06	0.57±0.11
3	1.77±0.06	0.37±0.06	6.22±0.56	5.76±0.13	8.33±0.11	49.56±5.11	0.20±0.05	0.14±0.03
4	1.16±0.04	1.08±0.18	6.41±0.58	2.64±0.06	9.50±0.13	4.50±0.46	0.41±0.12	0.58±0.12
5	1.63±0.05	1.36±0.23	7.04±0.63	3.50±0.08	8.46±0.11	35.54±3.67	0.29±0.07	0.77±0.15
6	1.46±0.05	0.57±0.09	16.70±1.47	5.09±0.11	9.14±0.12	25.77±2.66	0.24±0.07	1.28±0.25
7	1.80±0.06	0.21±0.04	7.57±0.68	5.16±0.12	4.16±0.06	48.98±5.06	0.21±0.06	1.59±0.31
8	1.75±0.06	0.37±0.06	8.96±0.80	3.76±0.08	6.11±0.08	46.14±4.76	0.19±0.06	1.48±0.29
9	1.82±0.06	0.51±0.09	9.58±0.86	4.42±0.10	6.75±0.09	46.41±4.79	0.17±0.04	1.65±0.33
10	1.83±0.06	0.30±0.05	9.26±0.83	6.01±0.13	8.32±0.11	34.59±3.57	0.30±0.08	1.82±0.36

The estimation of variation coefficients that characterize reproducibility of the IPSC XRF, the sampling error, and the error of the emitters preparation demonstrated that the values of these errors were significant for all the elements studied. The reproducibility error varied from 0.74% to 6.6% depending on the element being determined, the sampling error was from 1.18% to 16.11%, and emitters preparation error was 0.57% to 7.84% (Table 3A and 3B). The detection limits were also were assessed, their values appeared to be less or equal to the maximum permissible concentration value ($\leq$ MPC).

Table 3A. Estimated variation coefficients of IPSC XRF reproducibility, sampling and sample-preparation errors

	Macroelements' error values, %							
	K2O	TiO2	Fe2O3	CaO	Al2O3	P2O5	MgO	SiO2
S_r	0.02	0.02	0.21	0.04	0.04	0.02	0.05	0.98
S_{s-ing}	2.64	4.50	2.00	1.19	0.04	4.43	1.76	4.23
$S_{s/p}$	0.33	1.59	1.59	0.55	0.28	0.01	0.7	2.42

Table 3B. Estimated variation coefficients of IPSC XRFA reproducibility, sampling and sample-preparation errors

	Microelements' error values, mg/kg								
	Sr	V	Cr	MnO	Ni	Cu	Zn	As	Pb
S_r	31.11	1.71	0.74	15.91	5.70	6.49	18.56	0.35	18.0
S_{s-ing}	16.11	13.05	1.18	6.84	15.17	5.18	2.64	3.22	4.27
$S_{s/p}$	4.48	2.57	0.57	2.71	7.84	6.3	1.22	2.99	1.82

Considering that the normative standards of the IPSC MPC are missing, we converted the elements' concentration to the mg/l type of measurement taking into account the volume of the snowmelt water and the precipitation mass - to compare them with the MPC value for water. Further, we estimated the degrees of pollution with heavy metals for the studied samples of snow (Table 4):

$$H_c = \frac{C}{MPC}. \quad \text{.....(2)}$$

Table 4. Estimated degrees of snow cover pollution with heavy metals, MPC values

Samples	H_c							
	Ni	Zn	Pb	Sr	V	Cr	Cu	As
1	0.24	0.30	2.42	0.04	0.29	0.08	0.03	0.06
2	0.21	0.41	2.03	0.03	0.30	0.09	0.03	0.06
3	0.62	1.48	8.96	0.16	0.25	0.42	0.05	0.38
4	0.12	0.24	1.04	0.02	0.19	0.04	0.01	0.03
5	0.19	0.36	1.89	0.03	0.42	0.09	0.03	0.07
6	0.04	0.13	1.02	0.01	0.13	0.02	0.01	0.02
7	1.02	0.99	5.10	0.08	0.15	0.16	0.11	0.17
8	0.38	0.40	1.71	0.03	0.20	0.05	0.06	0.05
9	0.59	0.51	2.89	0.04	0.28	0.07	0.10	0.08
10	1.16	1.00	3.65	0.07	0.44	0.14	0.11	0.13
MPC, mg/l	0.10	1.00	0.10	7	0.1	0.5	1	0.05

The estimation of the degrees of snow cover pollution with heavy metals showed that the concentration of every element –V, Cr, Cu, As – does not exceed the MPC value for water.

It was revealed that the concentration of some heavy metals (Zn, Pb, Ni) in the studied samples exceeded the MPC value for water (Table 4). The pollution with lead was particularly remarkable in all the samples (Figure 1).

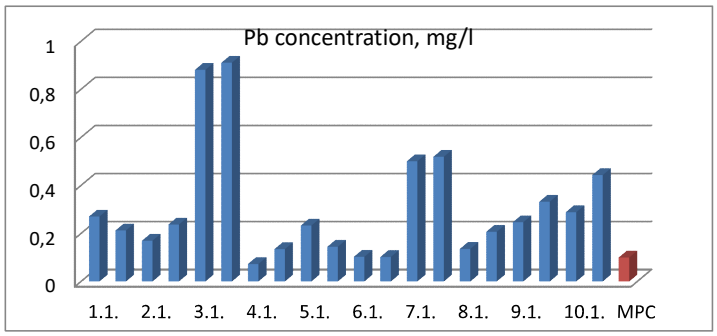

Figure 2. Pb concentration in snow samples compared with the MPC value.

The concentration of Pb in the samples No. 4 and 6 was in agreement with the MPC value, the concentration in the samples No. 1, 2, 5, 8, 9 exceeded the MPC value in 2 times, the concentration of Pb in the samples No. 3, 7, 10 was almost 5 times higher than the permissible one. The increased content of Pb in the snow samples explained the character of the snow cover pollution – it is mostly caused by motor vehicles.

CONCLUSION

Thus, the conducted investigations allowed us to formulate the following conclusions: 1) the estimation of the contribution of chemical analysis, sampling and sample-preparation errors demonstrated the significance of all these summands for the total error: the value of the sampling error reaches 16%, the sample-preparation error does not exceed 7%; that indicates the need to take the sampling error into account when snow cover is chemically analyzed; 2) there is a proposed method of preparing IPSC samples for the XRF procedure: including preliminary filtration of snowmelt water samples, incineration of precipitation samples accumulated on filters, reducing samples to fragments in an agate pounder with alcohol and pressing with added adhesive; 3) the degree of Kyzyl snow cover pollution with heavy metals is studied. The obtained IPSC XRF analysis results showed that the concentrations of heavy metals (V, Cr, Cu, As) in snow cover does not exceed the MPC value. The

concentration of Ni in some samples does not exceed the MPC; in other samples, it corresponds to the established standards. Pollution with zinc is observed only in several snow samples. The Pb concentration exceeds the MPC value in almost all samples. It indicates that snow cover pollution is caused mainly by motor vehicles.

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