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DETERMINATION OF MAJOR AND MINOR ELEMENTS IN SEDIMENTS OF THE CENTRAL AND NORTHERN MONGOLIAN RIVERS USING INAA

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Гэрбиш Ш. и др. Определение макро- и микроэлементов в осадочных породах центральных и северных рек Монголии методом инструментального нейтронного активационного анализа

Впервые для оценки загрязнения окружающей среды в районе городов Улан-Батор, Дархан и Горно-обогатительного комбината (г. Эрдэнэт) были проведены исследования осадочных пород центральных и северных рек Монголии с помощью метода ИНАА на реакторе ИБР-2. Метод ИНАА с использованием тепловых и резонансных нейтронов позволил определить концентрации 41 элемента (Na, Mg, Cl, K, Ca, Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Sr, Rb, Zr, Nb, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Dy, Tm, Hf, Ta, W, Au, Hg, Th, U) в образцах осадочных пород рек. В результате изучения данных образцов показано, что выбранные образцы осадочных пород рек могут быть использованы для оценки вредного воздействия на окружающую среду городов и Горнообогатительного комбината (г. Эрдэнэт). Проведено сравнение полученных результатов с литературными данными.

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Determination of Major and Minor Elements in Sediments of the Central and Northern Mongolian Rivers Using INAA

The sediment samples from rivers of the central and northern part of Mongolia were studied and the concentration of 41 elements (Na, Mg, Cl, K, Ca, Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Sr, Rb, Zr, Nb, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Dy, Tm, Hf, Ta, W, Au, Hg, Th, U) was determined by instrumental neutron activation analysis using epithermal neutrons (INAA) at the IBR-2 reactor (FLNP, JINR, Dubna). The obtained results of heavy metals and other trace elements in these samples were compared with the reference materials and other clean area data.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR, and at the Nuclear Research Center of National University of Mongolia, Ulan-Bator, Mongolia.

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INTRODUCTION

Many of the sediments in rivers, lakes, and oceans have been contaminated by pollutants and most of the contaminants were released years ago while other contaminants enter our water every day. Some contaminants flow directly from industrial and municipal waste dischargers, while others come from polluted runoff in urban and agricultural areas. Still other contaminants are carried through the air, landing in lakes and streams far from the factories and other facilities that produced them. The samples of sediments were collected from the Selenga inflow rivers, which are mainly contaminated by antropogenic pollutants from industrial, urban and agricultural areas of Mongolia in 2002-2003 years. The sediment analysis of minor and trace elements must be useful to estimate sufficiently the pollution area and river's water. As the rivers flow they are carrying soil, sand, and sediment along with them. The sediments that rivers transport actually play quite an important role in shaping the environment and even in our own lives. When it rains, soil and debris from the surrounding land are eroded and washed into streams. From there, sediment particles ranging from as small as clay to as large as boulders flow along with the water.

1. EXPERIMENTAL PROCEDURE

Monitoring studies of concentration of heavy metals and trace elements in the sediments of the Selenga inflow rivers are important for assessing the effect of contamination by pollutants from industrial, urban and agricultural areas. Sampling points of the sediment have been chosen from the rivers near the most industrial, urban and agricultural areas of the central and northern part of Mongolia (for example, the Tola gol near Ulan-Bator, the Khara gol near Darkhan and Khangal gol near Erdenet) (see Table 1).

After the thermal procedure the sediment powder samples were prepared for irradiation and analyzed at the IBR-2 reactor of FLNP (JINR, Dubna), using thermal and epithermal neutrons. The samples were irradiated in channels of the fast pulsed IBR-2 reactor; the flux parameters of neutrons at irradiation channels: the thermal neutron flux density was $1.1E+12 \text{ cm}^{-2} \cdot \text{s}^{-1}$ and the fast neutron density was $1.4E+12 \text{ cm}^{-2} \cdot \text{s}^{-1}$. For the neutron flux density measurement,

No.	Name of rivers	Location
1	Tola	Ulan-Bator (south part)
2	Dundgol	Peace bridge, Ulan-Bator
3	Selbe	Lion bridge, Ulan-Bator (central part)
4	Uliastai	Uliastai bridge, Ulan-Bator (east part)
5	Govil	Erdenet town
6	Soil	Erdenet town (central part)
7	Shariingol	Bridge, Selenga aimak
8	Kharaagol	Darkhan bridge, Darkhan
9	Khangal	Ulaantolgoi, Erdenet
10	Khangal	Erdenet bridge, Erdenet (central part)
11	Tola	Zaamar bridge, Central aimak
12	Tola	Ovoot bridge, Central aimak
13	Tola	Gachurt bridge, Ulan-Bator (east)
14	Tola	Altan Dornot, Zaamar, Central aimak

Table 1. Sampling places of the sediment samples

the gold foil was used [1–3]. Two kinds of analysis were performed: the long irradiation (for 100 h) in channel (Ch.1) was used to determine the elements associated with long-lived radionuclides of elements (As, Cd, Ba, Br, Ce, Cs, Eu, Fe, Ni, La, Rb, Sb, Sc, Se, Sm, Th, U, Zn) and the short irradiation (for 20 min) in channel (Ch.2) was used for short-lived radionuclides of elements (Al, Ca, Cl, I, K, Na, Mg, Mn, V, Cu).

Gamma-ray spectra were recorded 4–5 times using the gamma spectrometers with HPGe detector. The cooling times of 5 and 10 min were chosen after the decay periods following the short irradiation and those of 5, 13, and 20 d for the long irradiation.

2. DISCUSSION AND CONCLUSION

Out of 41 determined elements biogenic or essential macroelements (Na, K, Mg, Ca, Cl) were found; biogenic or essential microelements (Fe, Cu, Zn, Mn, Cr, Se, Co, V, Ti, Ni, As); non-biogenic or other elements (Hg, Sb, Ba, Sr, Cs, Al, Rb, Zr, Nb, Au, Br, Sc, La, Tm, Hf, Ta, W, Th, U and some REE: such as Ce, Nd, Sm, Eu, Tb, Dy) were determined by INAA and shown in Tables 2 and 3.

Accumulation of heavy metals and trace elements in sediments of central and northern rivers has been collected from polluted industrial, urban and agricultural areas. The results of our study are important for assessing the effect of contamination pollutants and confirmed by the conclusions.

Ele-	N7 1	N. A	N 0	N. 4	N 10	N7 44	N 10
me-	No. 1	No. 2	No. 3	No. 4	No. 13	No. 11	No. 12
nts	24800 (10)	16000(10)	18200 (10)	18100 (10)	28100 (10)	21400 (10)	21400 (10)
Ma	24800 (10)	10900(10)	18200(10)	18100(10)	28100 (10)	21400 (10)	21400 (10)
Mg	27900 (28)	32000 (28) 80200 (20)	27900 (28)	23700 (13)	22900 (29)	30700 (29)	23000 (29)
AI C1	38900 (20)	80300 (20)	71300 (20)	07400 (20)	3700(20)	70000 (20) 8 86 (22)	74000 (20)
V	3.22 (33)	3.22(33)	3.22(33)	4.91 (33)	3.22 (33)	8.80 (33) 26300 (23)	3.22(33)
К Со	28000 (23)	25300 (23)	27400(23)	23800 (23)	34000(23)	20300 (23)	24200 (23)
Ca	48100(33)	30000(33)	95500 (55)	21000 (33)	21200(33)	30900 (33) 8 51 (12)	32000 (33)
<u>эс</u>	9.98 (15)	12.1(13)	9.00 (13)	3.90 (13)	4.00(13)	8.31 (13)	4.33 (13)
V	4130(41)	$\frac{101}{22}$	4750 (42)	2930 (43)	2800 (42)	4120(42)	4240 (41)
V Cu	114(21)	101(22)	140(20)	03.1(24)	42.9 (29)	93.5 (22)	74.8 (23)
Cr	54.3 (23)	66.7 (24)	60.7 (23)	26.3 (24)	20.8 (20)	29.0 (25)	20.8 (20)
Min	880 (6)	010 (0)	921 (6)	4/3 (6)	576 (6)	8/8 (0)	542 (6)
Fe	26200 (4)	31400 (5)	25200 (4)	18100 (4)	10500(4)	21500 (4)	9460 (4)
Co	11.7 (11)	13.2 (11)	13.6 (11)	5.76 (11)	3.94 (12)	9.20 (11)	3.61 (12)
N1	14.0 (27)	21.8 (23)	22.8 (23)	8.42 (30)	8.26 (28)	17.2 (23)	9.17 (26)
Cu	ND	ND	ND	ND	ND	ND	ND
Zn	97.7 (6)	120 (5)	160 (5)	63.9 (6)	31.5 (8)	57.3 (6)	20.6 (9)
As	14.0 (6)	7.61 (6)	20.7 (6)	7.16 (6)	8.72 (8)	10.2 (6)	3.58 (7)
Se	0.290 (25)	0.016 (14)	0.22 (27)	0.016 (17)	0.23 (23)	0.314 (25)	0.016 (17)
Br	7.06 (25)	6.28 (25)	12.2 (25)	1.96 (25)	6.3 (25)	7.42 (25)	1.62 (27)
Rb	74.1 (9)	102 (9)	72.4 (9)	84.2 (9)	67.1 (9)	63.4 (9)	49.6 (9)
Sr	316 (8)	318 (7)	310 (8)	309 (7)	192 (8)	214 (8)	183 (8)
Zr	315 (7)	345 (7)	176 (11)	203 (8)	181 (8)	227 (8)	248 (7)
Nb	22.3 (21)	23.7 (21)	13.2 (21)	14.7 (22)	10.9 (22)	16.7 (22)	16.4 (21)
Sb	2.38 (13)	2.41 (13)	3.29 (13)	2.06(13)	0.77 (15)	1.06 (14)	0.536 (16)
Cs	5.41 (13)	6.47 (13)	6.12 (13)	3.96 (13)	2.43 (13)	4.03 (13)	1.95 (14)
Ba	502 (8)	677 (8)	523 (9)	629 (8)	405 (9)	383 (8)	347 (8)
La	51.8 (7)	37.0 (7)	47.3 (7)	22.4 (7)	33.4 (7)	44.4 (7)	26.7 (7)
Ce	124 (11)	126 (11)	107 (11)	77.3 (11)	66.2 (11)	94.4 (11)	46.4 (11)
Nd	22.8 (32)	34.0 (19)	17.0 (38)	11.0 (47)	13.8 (37)	17.1 (35)	21.5 (25)
Sm	8.85 (7)	8.01 (7)	8.98 (7)	5.00 (7)	5.51 (7)	8.25 (7)	4.85 (7)
Eu	ND	1.09 (38)	ND	ND	0.588 (35)	0.346 (51)	0.626 (40)
Tb	0.679 (33)	0.828 (33)	0.604 (33)	0.516 (33)	0.380 (33)	0.591 (33)	0.386 (33)
Dy	6.40 (38)	6.37 (39)	9.96 (39)	3.83 (55)	5.67 (39)	5.12 (43)	5.93 (39)
Tm	ND	1.12 (8)	ND	0.601 (9)	ND	ND	0.549 (9)
Hf	8.0 (8)	8.39 (8)	4.06 (9)	5.56 (8)	4.05 (8)	5.02 (8)	5.96 (8)
Та	0.99 (25)	1.17 (25)	0.74 (25)	0.76 (25)	0.51 (25)	0.76 (25)	0.61 (25)
W	11 (13)	9.73 (11)	13.9 (11)	5.40 (13)	4.2 (16)	5.17 (15)	3.94 (15)
Au	ND	0.012 (24)	0.047 (9)	0.003 ± 34	ND	ND	ND
Hg	ND	ND	ND	ND	ND	ND	0.076 (45)
Th	15.5 (10)	17.0 (10)	13.8 (10)	9.27 (10)	10.3(10)	10.9(10)	6.26(10)
U	10.5 (15)	8.13 (15)	12.4 (14)	4.19 (14)	9.98 (14)	7.41 (14)	5.01 (14)

Table 2. Contents (mg/kg) in sediments of the Selenga inflow rivers (Mongolia); (C $\pm\Delta C,~\%)$

Note: ND — nondetected.

Ele-							
me-	No. 5	No. 9	No. 10	No. 7	No. 8	No. 6	No. 14
nts	10000 (10)	22000 (10)	22400 (10)	20000 (10)	22200 (10)	14000 (10)	(020 (10)
Na	18000 (10)	28000 (10)	22400 (10)	30900 (10)	22300 (10)	14000(10)	6020 (10)
Mg	31800 (29)	27400 (28)	29400 (29)	23500 (13)	27700 (28)	28900 (28)	33800 (28)
Al	75400 (20)	76700 (20)	68200 (20)	61800 (20)	/4/00 (20)	61600 (20)	75200 (20)
CI	13.1 (33)	5.76 (33)	12.1 (33)	3.22 (33)	4.36 (33)	5.00 (33)	3.22 (33)
K	20900 (33)	23600 (33)	21600 (23)	25500± 24	19800 (33)	19400 (33)	19700 (33)
Ca	99600 (33)	58200 (33)	53900 (33)	4/300 (33)	44800 (33)	39500 (33)	33000 (33)
Sc	4.80 (13)	9.64 (13)	6.85 (13)	7.87 (13)	7.80 (13)	11.8 (13)	14.1(13)
11	6510 (41)	7610 (40)	4260 (42)	4530 (41)	4830 (41)	5550 (40)	6240 (41)
V	143 (19)	165 (19)	98.6 (20)	81.8 (22)	88.6 (22)	120 (19)	137 (21)
Cr	32.5 (24)	56.1 (33)	37.7 (33)	20.8 (28)	42.6 (33)	58.1 (22)	20.8 (20)
Mn	900 (6)	831 (6)	611 (6)	628 (6)	684 (6)	839 (6)	863 (6)
Fe	12000 (4)	2/100 (5)	19300 (4)	16300 (4)	16500 (4)	31500 (3)	35200 (3)
Co	5.90 (11)	9.48 (11)	8.76 (11)	5.81 (11)	5.84 (12)	13.0 (11)	15.3 (10)
Ni	13.5 (24)	15.4 (24)	13.9 (24)	9.30 (29)	8.24 (31)	20.7 (22)	41.5 (19)
Cu	1030 (53)	1510 (11)	1630 (28)	ND	ND	ND	ND
Zn	24.9 (11)	50.0 (7)	52.8 (6)	41.0 (7)	27.8 (9)	82.7 (6)	20.6 (9)
As	8.35 (6)	19.1 (6)	16.1 (6)	3.34 (8)	5.50 (7)	9.53 (6)	50.5 (6)
Se	0.249 (33)	1.23 (25)	0.518 (24)	0.249 (24)	0.017 (33)	0.017 (17)	0.023 (21)
Br	9.54 (25)	4.86 (25)	2.68 (26)	3.52 (26)	1.93 (26)	7.02 (25)	0.324 (33)
Rb	27.7 (10)	51.1 (9)	42.9 (9)	49.7 (9)	61.0 (9)	68.3 (9)	71.9 (9)
Sr	176 (8)	385 (7)	351 (7)	283 (7)	291 (7)	371 (7)	125 (8)
Zr	111 (11)	330 (7)	197 (8)	482 (6)	514 (6)	312 (8)	205 (6)
Nb	8.01 (23)	22.4 (21)	14.7 (21)	31.8 (21)	32.9 (21)	16.7 (22)	16.4 (21)
Sb	0.414 (16)	1.85 (13)	2.70 (13)	0.37 (17)	0.66 (16)	1.18 (14)	1.27 (13)
Cs	1.51 (14)	1.90 (14)	1.63 (14)	2.03 (14)	2.35 (14)	3.58 (13)	1.95 (14)
Ba	226 (8)	452 (8)	453 (9)	412 (8)	451 (8)	579 (8)	425 (8)
La	31.2 (7)	35.6 (7)	23.7 (7)	44.8 (7)	30.7 (7)	30.6 (7)	29.6 (7)
Ce	42.9 (12)	81.1 (11)	54.8 (11)	80.8 (11)	83.4 (11)	97.0 (11)	84.8 (11)
Nd	ND	20.1 (33)	11.1 (42)	ND	17.8 (29)	21.2 (31)	25.6 (26)
Sm	7.08 (7)	8.17 (7)	4.91 (7)	8.47 (7)	7.29 (7)	7.13 (7)	7.13 (7)
Eu	ND	0.881 (37)	0.374 (66)	1.02 (32)	0.986 (34)	0.916 (38)	1.14 (26)
Tb	0.283 (33)	0.541 (33)	0.382 (33)	0.626 (33)	0.661 (33)	0.687 (33)	0.622 (33)
Dy	6.89 (40)	6.05 (39)	7.21 (48)	5.99 (39)	3.83 (55)	6.54 (40)	6.48 (40)
Tm	ND	1.14 (8)	0.471 (9)	ND	0.776 (8)	0.771 (8)	0.638 (7)
Hf	2.43 (9)	7.69 (8)	4.97 (8)	11.1 (7)	12.0 (7)	2.43 (9)	4.75 (8)
Та	0.343 (26)	0.787 (25)	0.537 (25)	1.01 (25)	0.922 (25)	0.965 (25)	0.719 (25)
W	3.68 (17)	5.60 (14)	5.46 (14)	3.97 ± 18	4.40 (14)	3.89 (13)	5.61 (12)
Au	ND	ND	0.0083 (27)	ND	0.0033 (48)	ND	0.008 (21)
Hg	ND	ND	ND	ND	0.128 (40)	ND	0.076 (45)
Th	5.11 (10)	7.60 (10)	5.42 (10)	9.71 (10)	9.52 (10)	12.5 (10)	9.67 (10)
U	4.82 (15)	5.63 (15)	3.64 (15)	7.71 (14)	5.16 (14)	4.52 (14)	4.60 (14)

Table 3. Contents (mg/kg) in sediments of the Selenga inflow rivers (Mongolia); (C $\pm\Delta C,\%)$

Note: ND - nondetected.

• We concluded that sediments of rivers are suitable and useful indicators for monitoring studies of environmental pollution of rivers.

• The Nuclear Analytical (INAA) Technique has the sensitivity and accuracy method for the heavy metals and trace element studies of the environments.

• From Tables 2 and 3 one can see that contents of the elements Cr, Ti, V, Cu, As, Se and Sb are higher than in crust rocks [4].

• From Figs. 1 and 2 one can conclude that the accumulation of biogenic elements such as Na, Mg, Cl, K, Ca and Fe are higher in sediments Nos. 5, 9, and 10. Also, the abundances of microelements: Ti, V, Cu, Sb and Se have been found higher than others in samples of these sediments.



Fig. 1. Histogramm of distribution for macroelements in sediments



Fig. 2. Histogramm of distribution for some microelements in sediments

• It is shown that the main pathway of these (Ti, V, Cu, Se and Sb) elements to sediments Nos. 5, 9 and 10 is from the polluted area and the waste water of the rivers Khangal and Govil near the storage of Slag-heap tail [5].

• From Fig. 1 one can conclude that the accumulation of U and Th are higher in sediments Nos. 1, 2, 3, 13 and 7 near Ulan-Bator than in other samples of sediments and it means that the mean pollution sources of these elements are burning brown coal in power plants and heating systems.

• Results of studies of such a kind will be important to determine biogenic or essential macro, micro and non-biogenic or other elements in sediment samples of rivers to determine the pollution sources.

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