

Chemical and mineralogical composition of the Mongolian rural soils and their uranium sorption behavior

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ABSTRACT

Distribution of uranium (VI) between soil solids and solutions is a key parameter in assessing the risk to the biosphere of disposing uranium-rich waste products from nuclear plants as well as uranium (U) ore mining. Both of these topics have recently been brought to public attention in Mongolia. Regional background levels of soil elements are an important dataset for accessing the actual environmental situation and monitoring pollution levels. Little information, however, is available on background concentrations of various elements in Mongolian soils. Thirteen rural soils were sampled from six provinces in Mongolia, and the concentrations of macro-, micro- and trace elements were measured. The values obtained served as a reference (baseline) for uncontaminated soils. The soils were characterized with slightly acidic to strongly alkaline pH values. With the exception of the sample from a western province, all the soils investigated contained little organic matter. The content of soil elements did not vary widely among geographical regions. The concentration of most micro elements was within the range of worldwide soil values but the value for Zn tended to be moderately higher. The U (VI) sorption into the soils was investigated using the batch technique and the ²³⁷U radionuclide tracer, produced by the photo fission reaction ²³⁸U(γ, n) ²³⁷U at an electron accelerator. The ²³⁷U distribution coefficient (K_d), derived from the sorption isotherms, was related to solution pH and varying from 9 to 2547 mL g⁻¹ when the pH ranged between 3 and 7.7. The sorption process was interpreted in terms of the formation of different U (VI) species at given concentrations, calculated using the Speciation program with and without carbonate in the system. The U sorption isotherm displayed two general patterns: one where sorption decreased as solution pH increased, showing a maximum at pH 3, and another pattern revealed an adsorption maximum at pH 5 and then decreased up to pH 7.7 (the final solution pH). The observed decrease in K_d when solution pH increased from 6 to 8 was consistent with the increased formation of soluble UO₂(OH)₂ species. A linear negative correlation between lg K_d and the solution pH was observed similarly to that reported for the soils with a pH \geq 6.

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1. Introduction

Uranium is the most common radionuclide contaminant of surface soils (Filipov et al., 2009; Figueiredo et al., 2011). The mining of the U minerals as well as the operation of nuclear power plants and disposal of spent nuclear fuel are potential sources of

radioactive pollution of the environment. Mongolia has 150 billion tons of coal and 63 thousand tons of U, according to the estimated resources, comprising 2.8 and 0.9% of the global coal and uranium reserves, respectively. There has been intensive U ore exploration and investigation in Mongolia since nuclear energy legislation was approved in 2009. Soil and water systems in the vicinity of operative mines and even those near non-exploited deposits could be enriched by radioactive elements.

The energy services (heat and power) of Mongolia rely virtually completely on coal. Direct combustion technology is being used without pretreatment or prior upgrading to increase combustion

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efficiency and concurrently decrease emissions. In addition, coal burning power plants release enormous amounts of toxic and mildly radioactive ash due to concentration of heavy metals and naturally occurring radioactive elements resulting from the weight loss on ignition (Maslov et al., 2010; Papastefanou, 2010). This waste product may be carried by natural winds and deposited some distance away from the point sources.

Safeguarding human populations from exposure to natural and man-made radionuclides, as they move up the soil–plant–animal–animal product food chain, is a present and urgent radioecological issue. This problem needs to be approached by investigating the speciation and dynamics of radionuclides in different environmental compartments over time. Besides being influenced by nuclide species, the interactions of radionuclides with soil is controlled mineralogical composition and soil pH. In the presence of carbonates, for example, U (VI) forms negatively charged carbonate complexes such as $\text{UO}_2(\text{CO}_3)_2^{2-}$ or $\text{UO}_2(\text{CO}_3)_3^{4-}$. Since these species have a lower affinity for soil minerals than uranyl and hydroxyl complexes, the overall sorption of U (VI) dramatically decreases (Ho and Miller, 1986).

In assessing the risk of soil contamination by radionuclides (e.g., uranium) to human health, it is essential to evaluate the natural abundance of these elements in soil. Data are sparse on Mongolian soils and are difficult to access because reports are dated and written in a non-English language.

The present study aims at interpreting the kinetics of U sorption in the Mongolian soils and ascertaining the possibilities of limiting the extent of pollution from an accidental discharge of radioactive elements. For this purpose, the background levels of elements and natural radioactivity in some rural soils from Mongolia were measured along with the mineralogical and chemical properties. Thereafter, U (VI) partitioning was investigated as a function of system pH and with varying concentrations of U, taking the formation of uranyl ions (UO_2^{2+}) as being responsible for the behavior of this radionuclide in soils. Finally, the U species were calculated using a software program in order to ascertain the different species in relation to the solubility and mobility.

2. Materials and methods

2.1. Soil sampling sites

The geography of Mongolia is varied with the Gobi Desert lying in the south, and cold mountainous regions in the north and west.

Average annual precipitation is highest in the north (200–350 mm) and lowest in the south, which receives 100–200 mm. Thirteen sampling sites were selected in the western, central, eastern, and Gobi desert regions. Their names and coordinates are given in Table 1 and Fig. 1. All soil samples were taken from the open countryside and considered to be free from pollutions.

One topsoil (10 cm depth) sample was collected 100 m from Lake Khorgo in Tsengel sum, Bayan-Olgy province. Four surface soils (5 cm depth) were sampled near the Shiveegobi coal mining area about 10 km from Choir city. Two samples were from Tuvshinshree sum, Sukhbaatar province. Surface soils were also sampled from Matad sum in Dornod province and Mandakh sum in Dornogobi province. In addition, four surface soils, including two soils were from Khuld, one from Bayanjargalan and other one from Saintsagaan sum, were sampled from Dundgobi province. Khuld sum is a desert steppe region with an extremely arid climate where the soils are largely sandy.

2.2. Experimental methods

2.2.1. Organic and inorganic soil constituents and natural radioactivity

The collected native soils were air-dried and ground in an agate mortar. All analytic data refer to the fraction of less than 2 mm in diameter. Soil pH value was measured in a soil:water = 1:5 slurry with a pH meter (Sartorius Professional meter PP-50) and soil water content was derived from the weight loss after oven-drying at 105 °C. Total organic carbon (TOC) and total carbon (C) contents were analyzed with an Element analyzer (PE2400 II, USA). TOC was measured after removal of carbonates by treatment with HCL solution. Total organic matter (TOM) was calculated from TOC on the basis that organic matter contains 58% organic C. Inorganic carbon content was estimated by subtracting the TOC content from soil total carbon.

Concentrations of major elements were determined using an Axios PW4400 X-Ray Fluorescence (XRF) spectrometer (Panalytic, Netherlands), calibrated against 21 geological standards and reference materials. Micro- and trace elements were measured by ICP-OES (CCD Simultaneous ICP-OES, Vista-MPX) and ICP-MS (Platform ICP, Micromass Instruments Corporation) after an acid bomb digestion. Microanalytical accuracy and precision were estimated by analyzing Certified Reference Materials (soil GBW-07408 and sediment GBW-07305) and performing duplicate analyses of each sample. Recovery was 78–110% for all the

Table 1
Sampling sites in different regions of Mongolia and some properties of the soils sampled.

Sampling sites and sample designation	Coordinates	Water content, %	TOM ^a , g kg ⁻¹	C _{inorg} ^b , %	pH _{water}
<i>Western region</i>					
Bayan-Olgy	N48°36'27"; E88°25'24"	2.22	119.25	1.92	5.90
<i>Central region</i>					
Gobisumber 3	N46°15'46"; E108°27'17"	2.64	16.72	0.62	8.07
Gobisumber 28	N46°15'28"; E108°27'17"	1.38	12.33	0.13	7.37
Gobisumber 41	N46°15'18"; E108°27'15"	0.00	11.76	0.00	7.83
Gobisumber 52	N46°15'09"; E108°27'19"	1.23	9.25	0.97	8.60
<i>Eastern region</i>					
Sukhbaatar 1	N46°34'59"; E111°48'27"	5.69	24.15	0.20	6.94
Sukhbaatar 2	N46°33'01"; E111°48'31"	4.78	24.73	0.26	6.25
Dornod	N47°37'48"; E117°00'48"	0.61	17.60	0.38	6.85
<i>Gobi Desert region</i>					
Dornogobi	N43°53'28"; E108°23'76"	0.76	2.93	0.20	8.95
Dundgobi 1	N45°58'39"; E106°08'52"	0.96	13.55	0.18	6.65
Dundgobi 2		3.31	11.59	0.36	7.88
Dundgobi 3	N45°02'26"; E105°47'05"	0.94	1.69	0.25	8.69
Dundgobi 4	N44°51'50"; E105°53'23"	2.47	0.88	0.22	8.90

^a TOM-total organic matter.

^b C_{inorg}-carbonate carbon.

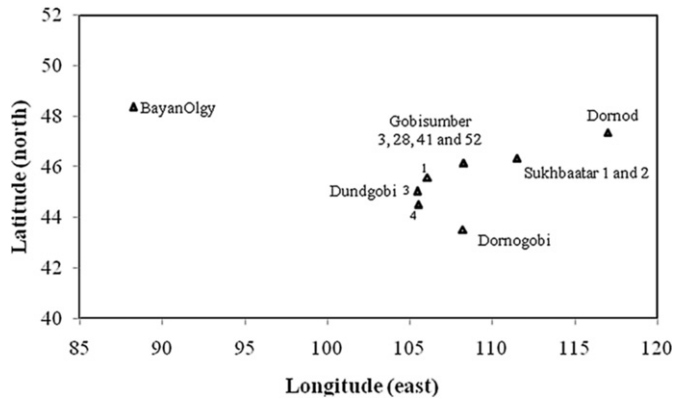


Fig. 1. Geographical locations of the sampling sites.

elements determined, more specifically 78–84% for Zr, 99–100% for Pb and 90% for Ti.

The mineralogical composition of the soils was determined by X-ray diffraction (XRD) using a D/Max2200 diffractometer (Japan), and nickel filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.54178\text{\AA}$). The XRD patterns were recorded in the 2θ range of $3\text{--}60^\circ$, using a step-scanning mode with a step size of 0.04° , and a counting time of 5 s per step. Amorphous and crystalline mineral phases were identified, and their contents were calculated using the JADE 5 software. The crystalline phases in the samples were determined by comparing their XRD patterns with those of various mineral standards. The K-value method (Meng et al., 2012) was employed to determine quantities of soil minerals.

Natural radioactivity was evaluated with a multichannel amplitude pulse analyzer equipped with a HPGe detector with a resolution of 1.5 keV on the ^{60}Co line at 1.33 MeV and gamma spectra were acquired for 24 h. The radioactivity concentrations of thorium (Th) and U were determined by means of the measured γ -photopeaks, emitted by specific radionuclides in the ^{232}Th and ^{238}U decay series; respectively ^{212}Pb and ^{228}Ac , and ^{214}Pb and ^{214}Bi decay products. The concentrations of ^{40}K and ^{137}Cs were measured directly. An empty vessel was measured for the same counting time and this background counting was subtracted from that of the samples. The specific activity (in Bq kg^{-1}), A , is calculated by the following equation (1) (Junior et al., 2006):

$$A = \frac{N}{\epsilon_\gamma \cdot \tau \cdot I_\gamma \cdot M} \text{ Bq/Kg} \quad (1)$$

Where N is the area of the considered peak (after subtracting background)

- M is the mass of the sample, kg
- I_γ is the emission probability of the specific energy peak
- ϵ_γ is the absolute efficiency of the detector
- τ is the counting lifetime, sec.

2.2.2. Sorption experiments

The kinetics of U(VI) sorption by all 13 soils was studied using oven-dry (105°C) samples with a particle size of less than 100 mesh (0.15 mm) and the ^{237}U tracer [$T_{1/2} = 6.75$ days, $E_\gamma = 59.54$ keV (34.5%), 208.00 keV (21.2%)], which was produced by the reaction $^{238}\text{U}(\gamma, n)^{237}\text{U}$ on the MT-25 microtron electron accelerator at the Flerov Laboratory of Nuclear Reaction of Joint Institute for Nuclear Research, Russia (Gustova et al., 2005). The ^{238}U , in the form of uranyl nitrate, was dissolved in deionized water after irradiation. The concentration of U after irradiation was calculated using a formula given by Vasylyeva et al. (2000), was $0.3 \cdot 10^{-8} \text{ mol L}^{-1}$.

A sorption test was performed at room temperature ($T = 20 \pm 0.5^\circ\text{C}$) using a batch technique. A 0.5 g portion of soil was placed in a 25 mL plastic test tube to which 20 mL of water solutions with a definite pH value (adjusted with HNO_3 or NaOH) and 50 μL of a solution containing 5.6 k Bq mL^{-1} of ^{237}U were added. Sorption equilibrium was determined on a soil (i.e., from the Bayan-Olgii province) with the highest organic content and the results are shown in Fig. 2. A contact time of 47 h was found to be sufficient to achieve equilibrium. The activity in a 15 mL aliquot of the initial and equilibrium solutions was measured using the multichannel amplitude pulse analyzer equipped with the HPGe detector with a resolution of 1.5 keV on the ^{60}Co line at 1.33 MeV. To determine ^{237}U , we used the line with $E_\gamma = 208.00$ keV (21.2%). The U distribution coefficient between the soil solids and solutions was calculated from the activity of ^{237}U in the solution before and after sorption, using the equation (2):

$$K_d = \frac{(A_0 - A_i)}{A_i m} \cdot V \quad (2)$$

where K_d is the U distribution coefficient, mL g^{-1}

- A_0 the activity of the nuclide in solution before sorption, Bq
- A_i the activity of the nuclide in solution after sorption, Bq
- V the solution volume, mL
- and m the weight of soil, g.

The U speciation in solution was determined using the Speciation program (Academic Software: Sol-Eq). For the calculations, the stability constants for hydroxy-, nitrate- and carbonate complexes of uranyl (Kohler et al., 2004) (Table 2) and the solubility constant ($\log K_s = 5.6$) of the hydroxy complex, $\text{UO}_2(\text{OH})_2$ were used (Omar et al., 2007).

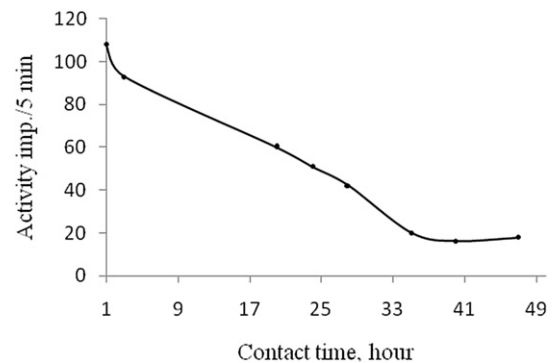


Fig. 2. Kinetics of ^{237}U sorption by the Bayan-Olgii soil at pH 7.

Table 2
Stability constants of uranyl complexes $\log \beta$ (ionic strength $I = 0$) (Kohler et al., 2004).

Complex	$\log \beta$	Complex	$\log \beta$
$\text{UO}_2(\text{OH})^+$	-5.20	$(\text{UO}_2)_4(\text{OH})_7^+$	-21.9
$\text{UO}_2(\text{OH})_2^0(\text{aq})$	-11.5	UO_2NO_3^+	0.3
$\text{UO}_2(\text{OH})_3^-$	-20.0	$\text{UO}_2\text{CO}_3^0(\text{aq})$	9.7
$\text{UO}_2(\text{OH})_4^{2-}$	-33.0	$\text{UO}_2(\text{CO}_3)_2^{2-}$	16.9
$(\text{UO}_2)_2(\text{OH})_3^{3+}$	-2.7	$\text{UO}_2(\text{CO}_3)_3^{4-}$	21.6
$(\text{UO}_2)_2(\text{OH})_2^{2+}$	-5.6	$(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$	54.0
$(\text{UO}_2)_3(\text{OH})_4^{2+}$	-11.9	HCO_3^-	10.3
$(\text{UO}_2)_3(\text{OH})_5^{2+}$	-15.6	$\text{H}_2\text{CO}_3^0(\text{aq})$	16.7
$(\text{UO}_2)_3(\text{OH})_7^-$	-31.0		

Table 3
Radioactivity concentration of some nuclides, Bq kg⁻¹.

Samples	²³⁸ U	²³² Th	⁴⁰ K	¹³⁷ Cs
Bayan-Olgıy	13.2	15.5	419.7	19.9
Gobisumber 28	22.1	11.9	654.6	4.6
Dundgobi 3	10.3	13.1	604.7	0

Table 4
Contents of major elements (oxide form) in Mongolian soils (% w/w).

Sample number	Soil designation	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Na ₂ O	K ₂ O	CaO	MgO
1	Bayan-Olgıy	56.78	11.82	3.89	2.04	2.68	1.8	1.91
2	Gobisumber 3	64.99	13.88	3.70	1.53	3.26	2.05	1.62
3	Gobisumber 28	60.46	14.56	3.22	1.82	3.37	1.25	1.47
4	Gobisumber 41	60.48	14.19	2.89	2.17	3.37	1.41	1.26
5	Gobisumber 52	59.39	13.13	2.75	1.98	3.23	3.27	1.47
6	Dornogobi 1	58.95	12.75	4.04	2.44	2.34	2.63	2.00
7	Dornod 1	71.76	10.52	1.65	1.68	2.94	0.92	0.60
8	Dundgobi 1	62.02	15.58	3.59	2.17	2.90	1.22	1.20
9	Dundgobi 2	62.96	15.34	5.81	1.30	2.85	1.56	1.69
10	Dundgobi 3	73.68	14.31	2.15	1.97	3.35	1.84	0.73
11	Dundgobi 4	72.57	13.43	3.04	1.61	3.14	1.25	0.9
12	Sukhbaatar 1	57.39	14.66	3.90	2.09	3.29	1.59	1.25
13	Sukhbaatar 2	57.74	14.43	3.76	2.17	3.25	1.72	1.32

3. Results and discussion

3.1. Soil characterization and main components

The physical and chemical properties of soils determine biogeochemical cycles of radionuclides in some extent. Some characteristics of the 13 soil samples from the six different provinces in Mongolia are given in Table 1. The observed variation in properties may be ascribed to differences in regional climate and precipitation patterns. The low total organic matter (TOM) content of the samples, ranging from 0.88 to 24.73 g kg⁻¹ (except for the Bayan-Olgıy soil) is typical for soils from arid and semi-arid areas. For the most part, pH values tended to be slight acidic to strongly alkaline, while near neutral pH value (6.25–6.94) was observed for samples from the eastern provinces. The high pH (8.95) of the sandy soils from Gobi provinces is related to surface accumulation of soluble salts due to very low precipitation. One sample from the western province of Bayan-Olgıy had a relatively low pH (5.9) and the highest TOM content (119.25 g kg⁻¹).

The average activities of ²³⁸U, ²²⁶Ra, ²³²Th and ⁴⁰K in soils are 35, 35, 30 and 400 Bq kg⁻¹, respectively (UNSCEAR, 2000). Among

these, ²³⁸U and ²³²Th made the highest contributions to soil total radioactivity due to their great number of decay products (Kannan et al., 2002). Table 3 shows that the activities of ²³⁸U and ²³²Th in the Bayan-Olgıy, Gobisumber 28 and Dundgobi 3 soils were 10.3–22.1 and 11.9–15.5 Bq kg⁻¹, respectively. These values were close to the low end range measured for soil worldwide. The ⁴⁰K activity tended to be at the high end of the global range. The globally distributed artificial radionuclide ¹³⁷Cs was detected in the two soils from western and central regions. The presence of ¹³⁷Cs in soils from eastern Mongolia has also been reported by Kato et al. (2010). On the other hand, we did not find this nuclide in the Dundgobi 3 soil from the Gobi region.

The total contents of the major elements are tabulated in Table 4, while concentrations of primary and secondary minerals are shown in Table 5. The common primary minerals in all the soils were quartz and K-feldspar (notably anorthite), the contents of which ranged from 82.13 to 99.99%. Interestingly, the soils designated as Sukhbaatar 1 and 2, Bayan-Olgıy and Gobisumber 3 contained significantly higher amounts of clay minerals than the other samples listed in Table 1. Since secondary minerals, such as montmorillonite (Tsunashima et al., 1981), kaolinite (Garvilescu et al., 2009) and illite, can retard uranyl ion mobility, the above mentioned soils would be able to retain U that enters into these soils. Likewise, clay mineral amendment of sandy (clay-poor) soils can potentially reduce the mobility of U(VI), and hence lower the risk of U contamination of human health.

The abundance of anatase (TiO₂) in soils from Sukhbaatar and Dornogobi provinces was consistent with their Ti content as determined by the ICP-MS analysis (Table 6). The most common carbonate minerals including calcite and dolomite were not detectable, indicating minimal contribution of limestone to the soil formation. Thus, the formation of negatively charged, soluble U(VI) carbonate complexes in these soils would be negligible. Though such complexes may form in the atmospheric levels of CO₂ and this contribution should not be ignored. The Dornod soil has a rather unique mineralogy in that primary minerals make up close to 100% of its mineral composition. The near absence of clay minerals that typically have a good affinity for trace ions, accounts for the low concentration of micro- and trace elements in this soil.

The concentrations of macro-, micro- and trace elements in the 13 Mongolian soils are listed in Table 4 and 6. As Mongolia is a landlocked country, the element content of its soils is not affected by sea sprays. Further, the urban areas are not well populated and fairly undeveloped. The total content of various elements in the 13 soils may, therefore, be considered to represent background values. Indeed, the total amounts of minor and trace

Table 5
Concentrations (% w/w) of primary and secondary minerals in soils from different regions of Mongolia.

Soil sample designation	Quartz	K-feldspar	Anorthite	Illite	Montmorillonite	Hornblende	Anatase	Kaolinite	Fe containing mineral
Bayan-Olgıy	41.83	–	40.30	10.20	3.83	0.89	+	2.93	+
Gobisumber 3	25.03	50.07	19.91	14.42	1.49	–	–	0.64	1.42
Gobisumber 28	27.85	+	71.00	0.60	0.54	+	–	+	–
Gobisumber 41	18.12	+	79.29	1.97	+	+	0.61	–	+
Gobisumber 52	22.66	+	74.92	+	0.78	–	–	0.58	1.05
Dornogobi 1	17.15	–	77.27	1.07	+	0.75	1.07	0.96	1.71
Dornod 1	50.14	+	49.85	–	+	–	–	–	+
Dundgobi 1	17.77	+	72.86	4.27	1.92	+	+	0.60	+
Dundgobi 2	30.92	22.74	36.82	3.41	3.20	1.00	–	0.78	1.13
Dundgobi 3	27.57	38.66	29.41	1.47	1.57	0.73	–	0.57	+
Dundgobi 4	52.71	40.43	+	3.36	1.80	1.68	–	+	+
Sukhbaatar 1	20.87	–	66.96	8.12	+	+	1.73	–	2.31
Sukhbaatar 2	19.76	–	64.95	6.87	3.43	2.40	1.72	0.85	–

Note: "+" = trace amount.
"–" = not detected.

Table 6
Micro- and trace elements in the Mongolian soils ($\mu\text{g g}^{-1}$).

Element	Central region					Gobi desert region													
	Bayan-Olgii		Gobisumber			Sukhbaatar 1		Sukhbaatar 2		Dornod 1		Dundgobi 1		Dundgobi 2		Dundgobi 3		Dundgobi 4	
	Gobisumber 3	Gobisumber 28	Gobisumber 41	Gobisumber 52	Sukhbaatar 1	Sukhbaatar 2	Dornod 1	Dornogobi 1	Dundgobi 1	Dundgobi 2	Dundgobi 3	Dundgobi 4							
Cs	3.77 ± 0.07	7.47 ± 0.28	4.93 ± 0.51	5.93 ± 0.34	3.50 ± 0.44	2.74 ± 0.28	2.26 ± 0.03	1.70 ± 0.09	2.50 ± 0.09	6.28 ± 0.54	1.94 ± 0.30	2.84 ± 0.53							
V	59.45 ± 0.64	53.57 ± 1.26	46.95 ± 2.48	48.88 ± 0.29	77.5 ± 1.84	67.15 ± 7.43	26.95 ± 1.34	91.37 ± 5.87	62 ± 0.7	88.8 ± 2.7	65.35 ± 4.3	38 ± 0.7							
Cr	74.85 ± 2.48	59.8	29.45 ± 1.91	34.48 ± 1.91	51.7 ± 11.74	36.35 ± 4.74	22.6 ± 1.84	52.77 ± 0.78	43.3 ± 7.6	61.4 ± 10.1	19.05 ± 0.50	20.4 ± 5.2							
Co	9.39 ± 0.12	7.75 ± 0.03	6.05 ± 0.31	6.61 ± 0.11	9.52 ± 0.06	8.44 ± 1.21	3.86 ± 0.24	9.40 ± 0.52	7.91 ± 0.12	10.83 ± 0.15	7.68 ± 0.93	5.57 ± 0.06							
Cu	21.8 ± 1	22.37 ± 0.64	17.1 ± 1.84	15.43 ± 0.39	26.7 ± 4.53	21.55 ± 7.14	10.21 ± 0.70	32.47 ± 2.51	19.9 ± 0.71	25.4 ± 1.14	20.7 ± 3.8	27.3 ± 0.42							
Zn	104 ± 7	161	98 ± 3	167 ± 4	105 ± 9	109 ± 13	82 ± 0.4	105 ± 16	104 ± 8	132 ± 19	142 ± 52	82 ± 11							
Mn	749 ± 24	994 ± 27	706	1001 ± 55	553 ± 46	568 ± 27	271 ± 11	683 ± 12	571	1010 ± 2	463	422 ± 21							
Ce	16.05 ± 0.64	18.53 ± 1.17	13.33	20.7	28.75	13.25 ± 0.35	5.09	15.47 ± 0.58	14.50 ± 2.26	28.17	5.52 ± 0.73	16 ± 86							
Sr	95 ± 5	131 ± 4	143 ± 2	167 ± 4	130 ± 7	144 ± 22	106	170 ± 32	155 ± 14	179 ± 5	127	136 ± 15							
Y	10.25 ± 0.07	7.45 ± 0.03	5.61	8.66 ± 1.96	11.46 ± 4.72	5.52 ± 0.02	1.30 ± 0.02	8.63 ± 1.36	6.33 ± 0.80	12.7 ± 2.4	2.28 ± 0.03	4.74							
Zr	102 ± 10	153.67 ± 5.13	261 ± 35	220 ± 56	242 ± 56	212.5 ± 6.4	118.5 ± 3.54	207 ± 3	157 ± 28	222.67 ± 33.23	115.5 ± 12.02	121.5 ± 2.1							
Nb	9.41 ± 0.57	11.33 ± 0.70	13.20 ± 1.77	12.98 ± 0.91	21.72 ± 3.6	17.26 ± 0.57	5.41 ± 0.42	10.47 ± 0.73	11.37 ± 0.95	15.25 ± 0.27	5.34 ± 0.31	5.89 ± 0.64							
Mo	0.77 ± 0.01	0.87 ± 0.19	0.57 ± 0.08	0.64 ± 0.05	0.86 ± 0.02	0.72 ± 0.06	1.25 ± 0.22	0.45 ± 0.01	0.62 ± 0.01	1.68 ± 0.05	1.04 ± 0.12	1.56 ± 0.05							
Cd	0.36 ± 0.02	0.27 ± 0.02	0.23 ± 0.04	0.24 ± 0.02	0.23 ± 0.01	0.24 ± 0.01	0.32 ± 0.01	0.18 ± 0.02	0.25 ± 0.06	0.39 ± 0.03	0.19 ± 0.01	0.13 ± 0.01							
Sn	2.63 ± 0.19	2.58 ± 0.06	2.28 ± 0.04	2.43 ± 0.07	3.0 ± 0.08	2.54 ± 0.36	7.28 ± 0.84	1.94 ± 0.05	2.96 ± 0.38	3.67 ± 0.17	1.73 ± 0.11	1.82 ± 0.02							
Ba	169 ± 1	331.67 ± 17.16	585 ± 55	508.75 ± 33.87	478.5 ± 64.35	446.5 ± 4.9	407 ± 32	468 ± 95	500 ± 5.7	448.67 ± 61.51	481 ± 64	714.5 ± 10.6							
Ta	0.68 ± 0.03	0.67 ± 0.14	0.78 ± 0.08	0.78 ± 0.09	1.52 ± 0.29	1.21 ± 0.16	0.20 ± 0.02	0.75 ± 0.10	0.89 ± 0.20	0.83 ± 0.02	0.282 ± 0.02	0.32 ± 0.07							
W	2.38 ± 0.16	2.36 ± 0.02	2.10 ± 0.36	2.22 ± 0.10	2.20 ± 0.13	2.8 ± 0.4	0.79 ± 0.01	0.91 ± 0.07	1.32 ± 0.01	2.98 ± 0.13	1.19 ± 0.06	1.25 ± 0.08							
Tl	0.42 ± 0.01	0.74 ± 0.02	0.77 ± 0.01	0.77 ± 0.02	0.68 ± 0.01	0.70 ± 0.07	0.53 ± 0.02	0.42 ± 0.04	0.49 ± 0.02	0.78 ± 0.04	0.61 ± 0.06	0.59 ± 0.03							
Pb	19.15 ± 0.50	26.3 ± 0.7	24.7 ± 1.13	25.35 ± 0.33	23 ± 1	22.1 ± 1.4	15.5 ± 0.28	17.13 ± 0.46	19.35 ± 1.34	32.03 ± 0.21	18.55	19 ± 2							
Th	3.8 ± 0.13	5.7 ± 0.05	2.92	5.31 ± 0.51	5.92	3.32 ± 0.23	0.81	2.95 ± 0.23	2.65 ± 0.06	7.07 ± 1.78	1.75	2.65							
U	2.26 ± 0.06	1.79 ± 0.06	2.47 ± 0.50	1.89 ± 0.18	3.07 ± 0.64	2.89 ± 0.02	1.13 ± 0.05	1.73 ± 0.08	2.21 ± 0.10	3.52 ± 0.57	2.05	2.31 ± 0.18							
Ti	3030 ± 110	3402 ± 67	3786 ± 288	3906 ± 46	5727 ± 148	5028 ± 432	2190 ± 128	4202 ± 339	1932	2250 ± 85	3768 ± 195	4526 ± 190							

elements were similar across the country with little variation being observed from one region to another. As already remarked on, only the soil from the Dornod province appeared to have a lower concentration of micro- and trace elements in comparison to the other 12 soils (Table 6). In general, considering the characterizations of soils in semiarid and arid climates as well as soil texture and organic poor composition, the amounts of the following elements were within the range of worldwide soil values, expressed in $\mu\text{g g}^{-1}$: 1.7–7.5 for Cs, 95–179 for Sr, 169–714 for Ba, 4.7–12.7 for Y (except for the Dornod soil with $1.3 \mu\text{g g}^{-1}$), 0.13–0.39 for Cd, 19.05–74.85 for Cr, 10.21–32.47 for Cu, 15.5–32.03 for Pb, 0.57–1.68 for Mo, 102–261 for Zr, 0.81–7.07 for Th and 1.13–3.52 for U. The arithmetic means were 11.62 for Y, 0.74 for Ta, 2.5 for Sn (except for one high content $7.28 \mu\text{g g}^{-1}$), 0.63 for Tl, 1.9 for W and were analogous to the worldwide averages for the corresponding elements. The quantities of Zn ($82\text{--}167 \mu\text{g g}^{-1}$) were moderately high. It was also found by Markwitz et al. (2008); indeed, the concentration of Zn in some rural soils of Mongolia was reported to be as high as $259 \mu\text{g g}^{-1}$. No enrichment by any metals, however, was observed in our case.

Semiarid and arid soils tend to be enriched in Co (Nasseem and Abdulla, 2003), but the Co concentration in the studied soil was slightly lower than the mean global value and ranged 3.86–10.83 $\mu\text{g g}^{-1}$. The concentrations of Cu and Zn in soils around Ulaanbaatar, the capital city of Mongolia, reported by Batjargal et al. (2010), were comparable with the values that we obtained. On the other hand, the Cd and Pb concentrations in the urban soils were appreciably higher than the corresponding values for the rural soils investigated here. These authors have suggested that metal pollution is not a serious problem in Ulaanbaatar although elevated levels of As (due to coal burning power plants) and Pb (from vehicle emission) are of concern. In sandy soils, such as those from Dornogobi and Dundgobi provinces, metal ions would tend to leach to the subsurface. The concentrations of metals in these soils, however, were comparable with those found in the other soil samples, probably because these two regions received little precipitation.

3.2. Uranium sorption kinetics by Mongolian soils

Table 7 shows that the U distribution coefficient (K_d) for the 13 Mongolian rural soils varied from 9 to 2547 mL g^{-1} within the pH range of 3–7.7. This finding reflects differences in soil mineralogy and the effect of pH on U(VI) speciation. Interestingly, soils from same province can display different U sorption characteristics. For instance, the K_d values for the two soils from Dundgobi province (numbers 3 and 4) were low ($9\text{--}50 \text{ mL g}^{-1}$), while those for the

Table 7
Uranium distribution coefficient in Mongolian soils, mL g^{-1} .

Soil specimen	pH				
	3	4	5	7	7.7
Bayan-Olgii	1730	1080	903	804	647
Dornod 1	1490	1400	1416	736	638
Dornogobi 1	45	40	47	37	–
Dundgobi 1	1835	1572	2514	1089	1107
Dundgobi 2	1386	603	551	434	–
Dundgobi 3	9	45	50	28	–
Dundgobi 4	21	44	49	32	14
Gobisumber 3	112	120	157	91	118
Gobisumber 28	1309	754	1168	679	544
Gobisumber 41	1723	1405	824	744	187
Gobisumber 52	39	55	66	55	23
Sukhbaatar 1	2547	1914	1669	1138	911
Sukhbaatar 2	2298	1258	2321	706	696

Dundgobi 1 and 2 samples were much higher (434–1835 mL g⁻¹). In general, soils with little affinity for U(VI) showed little variability in K_d as solution pH changes.

The U(VI) sorption was not correlated with the TOM content of the soils investigated. The Sukhbaatar 1 and 2 soils, for example, had the highest K_d values amounting to 911–2547 and 698–2321 mL g⁻¹, respectively; while their TOM content was relatively low (24.15–24.73 g kg⁻¹). By comparison, K_d values of 647–1730 mL g⁻¹ were measured for the Bayan-Olgy soil with a TOM content of 119.25 g kg⁻¹. The relatively low K_d for the soil from Bayan-Olgy may be due to its lower pH than that was found in the Sukhbaatar soils. However, low K_d values were also observed for the Dornogobi, Dundgobi 4 and Gobidumber 52 soils that had fairly low TOM contents.

Fig. 3 shows the relationship between U(VI) sorption, as indicated by the K_d and solution pH. Sorption maxima were observed either at pH 3 or at pH 5 for all the soils studied. The K_d continuously decreased with increasing pH when the adsorption maximum appeared at pH 3 (for the soils Bayan-Olgy, Sukhbaatar 1, Dornod 1, Gobisumber 28 and 41, Dundgobi 2). On the other hand, for the Dornogobi 1, Dundgobi 1 and 4, Sukhbaatar 2 soils, the U sorption decreased when the solution pH increased from 3 to 4, rose to a maximum at pH 5, and then decreased up to pH 7.7 (the final solution pH). The two different maxima (at pH 3 or pH 5) were observed for samples taken in nearby locations, as exemplified by two soils from the Sukhbaatar province that had similar organic matter content and other properties but were different in mineralogical composition (Table 5).

Echevarria et al. (2001) have observed a linear correlation between the U distribution coefficient and soil pH for soils with pH ≥ 6 . We have verified this point by plotting $\lg K_d$ against soil pH for all 13 soil samples whose pH values ranged from 5.9 to 8.9. The K_d values, measured in solutions with pH 5 and 7, were used in plotting Fig. 4. Data showed a reasonably good negative correlation between $\lg K_d$ and soil pH for the Mongolian soils, giving a correlation coefficient of 0.77–0.82. Hence in Mongolian soils, pH value could be the potential measure in determining site-specific U partitioning between soil solids and solutions.

Besides being influenced by pH, the chemical speciation of U and its mobility are strongly dependent on solution concentration. Many studies on U sorption have been performed at low U concentrations (1–300 ppm) in order to simulate natural conditions. The present calculations on the U species, therefore, were

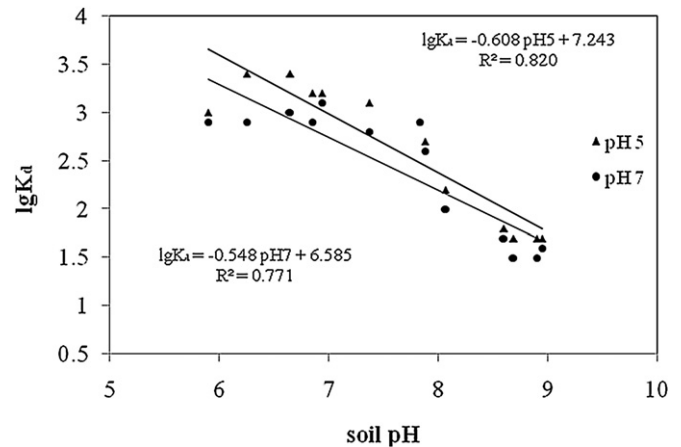


Fig. 4. Correlation between $\lg K_d$ (U distribution coefficient measured in solution at pH 5 and 7) and soil pH values.

conducted at concentrations (C_U) of $1 \cdot 10^{-8}$ mol L⁻¹ and $1 \cdot 10^{-3}$ mol L⁻¹. The former value was of the same order of magnitude as the U concentration used in the sorption experiments (i.e., $C_U = 0.3 \cdot 10^{-8}$ mol L⁻¹). The latter concentration ($C_U = 1 \cdot 10^{-3}$ mol L⁻¹) was selected as an example of a high input of U onto soils, and as a means of predicting the mobility of uranyl ion species that form at high U concentrations.

A large number of U species were predicted to form at $C_U = 1 \cdot 10^{-3}$ mol L⁻¹ than at $C_U = 1 \cdot 10^{-8}$ mol L⁻¹. For instance, $(\text{UO}_2)_2(\text{OH})_2^{2+}$ and $\text{UO}_2(\text{OH})_3^{3+}$ were occurred in an acidic media and also significant amount of $(\text{UO}_2)_3(\text{OH})_5^{2+}$ and $(\text{UO}_2)_4(\text{OH})_7^{+}$ would exist at pH 5. On the other hand, at $C_U = 1 \cdot 10^{-8}$ mol L⁻¹ (Fig. 5, left diagram), the UO_2^{2+} , UO_2OH^+ and UO_2NO_3^+ species were dominant in acidic media. Thus, the large U sorption at pH 3 and 5 by the experimental soils (Fig. 3) may partly be explained in terms of a cation exchange mechanism. Similarly, the decrease in sorption at pH > 5 might be related to the increased formation of soluble U(VI) species, notably $\text{UO}_2(\text{OH})_2^0$. Indeed, uncharged $\text{UO}_2(\text{OH})_2^0$ species predominated at pH 7 and 8 (74.9%). At the high U(VI) concentration (Fig. 5, right diagram), the solid form of $\text{UO}_2(\text{OH})_2$ was dominantly present at pH = 6–8, making up to 99.58% at pH 8. At both $1 \cdot 10^{-8}$ mol L⁻¹ and $1 \cdot 10^{-3}$ mol L⁻¹ concentrations, UO_2^{2+} and UO_2NO_3^+ were the major forms in acidic media (pH 3–4).

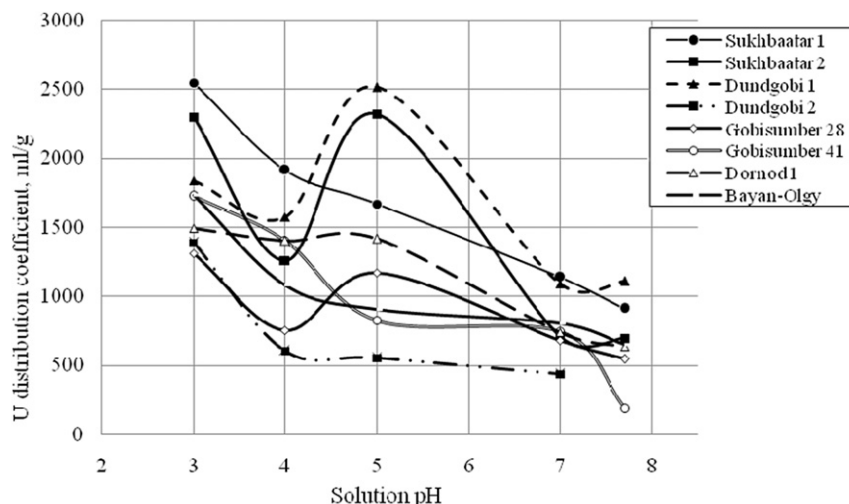


Fig. 3. Variation of U distribution coefficient with solution pH, determined at $C_U = 0.3 \cdot 10^{-8}$ mol L⁻¹

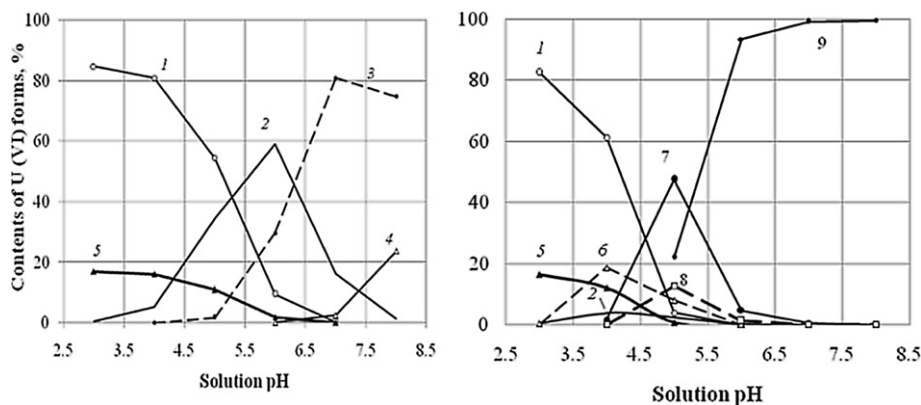


Fig. 5. Main forms of U(VI) in solution: at two different concentrations in function of pH. Left diagram: $C_U = 1 \cdot 10^{-8} \text{ mol L}^{-1}$. Right diagram: $C_U = 1 \cdot 10^{-3} \text{ mol L}^{-1}$. 1- UO_2^{2+} ; 2- UO_2OH^+ ; 3- $\text{UO}_2(\text{OH})_2^0$; 4- $\text{UO}_2(\text{OH})_3^-$; 5- UO_2NO_3^- ; 6- $\text{UO}_2(\text{OH})_2^{2+}$; 7- $(\text{UO}_2)_3(\text{OH})_5^-$; 8- $(\text{UO}_2)_4(\text{OH})_7^-$; 9- $\text{UO}_2(\text{OH})_2^{\text{solid}}$

Table 8

U(VI) speciation at $C_U = 1 \cdot 10^{-8} \text{ mol L}^{-1}$ concentration in the presence of carbonates ($C = 1 \cdot 10^{-4} \text{ mol L}^{-1}$).

U(VI) forms	Contents of U(VI) forms, %						
	pH 3	pH 4	pH 5	pH 6	pH 7	pH 8	pH 9
UO_2^{2+}	82.9	92.2	56.9	5.8	0.2	—	—
UO_2OH^+	0.5	5.8	35.9	36.3	9.1	1.0	0.1
$\text{UO}_2(\text{OH})_2^0$	—	—	1.8	18.2	45.4	50.3	20.7
$\text{UO}_2(\text{OH})_3^-$	—	—	—	0.1	1.4	15.9	65.4
UO_2NO_3^-	16.6	1.8	0.1	—	—	—	—
UO_2CO_3^0	—	0.1	5.3	38.7	25.7	3.4	0.1
$\text{UO}_2(\text{CO}_3)_2^{2-}$	—	—	—	1.1	18.3	28.8	11.4
$\text{UO}_2(\text{CO}_3)_3^{4-}$	—	—	—	—	—	0.6	2.3

In this batch experiment (Table 7), the U sorption was determined under atmospheric CO_2 condition; therefore, calculation of the U speciation was extended to pH 9 in the presence of carbonates. Table 8 shows that the formation of carbonate complexes of U would be facilitated under alkaline conditions due to the increased availability of carbonate ions. U speciation at a concentration of $1 \cdot 10^{-8} \text{ mol L}^{-1}$, however, does not predict strong differences in sorption behavior in the presence or absence of carbonate (Table 8 and Fig. 5, left diagram). Uranyl-carbonate complexes occurred in significant amount only at $\text{pH} > 5$. In addition, the formation of UO_2CO_3^0 , $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ species would cause U sorption to decrease (Ho and Miller, 1986), in line with the experimentally derived sorption isotherm.

4. Conclusions

Soil samples from rural areas in six different provinces in Mongolia were studied for their chemical and mineralogical compositions. The TOM content of soils from the western and eastern provinces tended to be higher than that of samples from the central and southern provinces. The soils from Gobi region have the highest pH. No metal (Cd, Cr, Cu, Pb and Zn) contamination was detected although the average content of Zn ($115 \mu\text{g g}^{-1}$) was almost twice the world average ($60 \mu\text{g g}^{-1}$). Clay mineral phases were greater in the Bayan-Olgii, Gobisumber 3, Sukhbaatar 1 and 2 soils compared with other soils investigated, and none of the soils contained carbonate minerals. Activity concentrations for naturally occurring radionuclides showed normal background levels; however, the presence of ^{137}Cs in some soils would indicate that Mongolia is affected by the worldwide radioactive contamination.

The U sorption kinetics by the soils from Mongolia were studied in pH range of 3–7.7 using a batch technique and ^{237}U as a tracer. The distribution coefficient, K_d , varied from 9 to 2550 mL g^{-1} and a negative linear correlation between $\lg K_d$ and soil pH was observed. Similar results were obtained with soils whose pH was greater than, or equal to 6. Enhanced U availability in solutions with a U concentration of $1 \cdot 10^{-8} \text{ mol L}^{-1}$, was ascribed to the increased formation of soluble species (i.e., $\text{UO}_2(\text{OH})_2^0$) as solution pH increased. However, the Speciation program indicated a different sorption pattern for greater U amounts in solutions. Our data may be used to predict the mobility and migration behavior of U in the Mongolian soils. The amendment of coarse-textured soils with clay minerals could potentially retard U mobility at a local scale.

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References

- Academic Software: Sol-Eq, A.S., <http://acadsoft.co.uk/>.
- Batjargal, T., Otgonjargal, E., Baek, K., Yamg, J.-S., 2010. Assessment of metals contamination of soils in Ulaanbaatar, Mongolia. *J. Hazard. Mater.* 184, 872–876.
- Echevarria, G., Sheppard, M.J., Morel, J.L., 2001. Effect of pH on the sorption of uranium in soils. *J. Environ. Radioactiv.* 53, 257–264.
- Figueiredo, M.O., Silva, T.P., Batista, M.J., Leote, J., Ferreira, M.L., Limpo, V., 2011. Uranium in surface soils: an easy-and-quick assay combining X-ray diffraction and X-ray fluorescence qualitative data. *J. Geochem. Explor.* 109, 134–138.
- Filipov, M.F., Maslov, O.D., Bozhikov, G.A., Tserenpil, S., Gustova, M.V., Milanov, M.V., 2009. Sorption of U(VI) with soil from the region of location of the Novi Khan radioactive waste repository in Bulgaria. *Radiochemistry* 51, 77–79.
- Garvilescu, M., Pavel, L.V., Cretescu, I., 2009. Characterization and remediation of soils contaminated with uranium. *J. Hazard. Mater.* 163, 475–510.
- Gustova, M.V., Dmitriev, S.N., Maslov, O.D., 2005. Method to obtain the radioisotope of ^{237}U . RF Patent 2262759, *Byull. Izobret.* 29.
- Ho, C.H., Miller, N.H., 1986. Adsorption of uranyl species from bicarbonate solution onto hematite particles. *J. Colloid Interf. Sci.* 110, 165–171.
- Junior, J.A.S., Cardoso, J.J.R.F., Siva, C.M., Silveira, S.V., Amaral, R.S., 2006. Determination of radionuclides in the environment using gamma-spectrometry. *J. Radioanal. Nucl. Chem.* 269, 451–455.
- Kannan, M., Rajan, M.P., Iyengar, M.A.R., Ramesh, R., 2002. Distribution of natural and anthropogenic radionuclides in soil and beach sand samples of Kalpakkam (India) using hyper pure germanium (HPG) gamma ray spectrometry. *Appl. Radiat. Isot.* 57, 109–119.
- Kato, H., Onda, Y., Tanaka, Y., 2010. Using ^{137}Cs and $^{210}\text{Pb}_{\text{ex}}$ measurements to estimate soil redistribution rates on semi-arid grassland in Mongolia. *Geomorphol* 114, 508–519.

- Kohler, M., Curtis, G.P., Meece, D.E., Davis, J.A., 2004. Methods for estimating absorbed uranium(VI) and distribution coefficients of contaminated sediments. *Environ. Sci. Technol.* 38, 240–247.
- Markwitz, A., Barry, B., Shagjamba, D., 2008. PIXE analysis of sand and soil from Ulaanbaatar and Karakurum, Mongolia. *Nucl. Instrum. Methods Phys. Res.* 266, 4010–4019.
- Maslov, O.D., Tserenpil, S., Norov, N., Gustova, M.V., Filipov, M.F., 2010. Uranium recovery from coal ash dumps of Mongolia. *Solid Fuel Chem.* 44, 433–438.
- Meng, Y., Gong, G., Wu, Z., Yin, Z., Xie, Y., Liu, S., 2012. Fabrication and microstructure investigation of ultra-high-strength porcelain insulator. *J. Europ. Ceram. Soc.* 32, 3043–3049.
- Nasseem, M.G., Abdulla, Y.H., 2003. Cobalt status in the North Western coast soils of Egypt in relation to cobalt content of barley for ruminants. In: 16th International Symposium on Environmental Biogeochemistry. Edinburgh.
- Omar, H.A., Aziz, M., Shakir, K., 2007. Adsorption of U(VI) from dilute aqueous solutions onto peat moss. *Radiochim. Acta* 95, 17–24.
- Papastefanou, C., 2010. Escaping radioactivity from coal-fired power plants (CPPs) due to coal burning and the associated hazards: a review. *J. Environ. Radioactiv.* 101, 191–200.
- Tsunashima, A., Brindley, G.W., Bastovanov, M., 1981. Adsorption of uranium from solutions by montmorillonite; compositions and properties of uranyl montmorillonites. *Clay Clay Miner.* 29, 10–16.
- UNSCEAR, 2000. United nations scientific committee on the effects of atomic radiation. In: *Sources and Effects of Ionizing Radiation*, vol. I. United Nations, New York.
- Vasylyeva, H.V., Strelko, V.V., Osypenko, A.P., 2000. Influence of solution acidity on the sorption of fission radionuclides by titanium phosphate. *Phys. Chem. Solid State* 11, 195–198.