Redox interactions of Pu(V) in solutions containing different humic substances

Oxana Blinova *, Alexandr Novikov, Irina Perminova,
Tatyana Goryachenkova, Richard Haire

*A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Department of Radiochemistry,
Leninsky Prospekt, 31, 119991 Moscow, Russia*

Abstract

Humic substances play an important role in the speciation of actinides in the environment due to complexing, redox and sorptive interactions. This work is devoted to plutonium(V) reduction studies in solutions containing different humic substances, eluted from Mollisol and Sod-podzolic soil samples, as compared to real Pu distribution is contaminated soils. On the basis of kinetic curve slopes, the reducing ability is increased in the order: HA < FA ∼ low molecular weight fraction. The data obtained show that the different humic compounds play different roles in Pu(V) migration ability due to differing reducing and complexing properties.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Humic substances; Plutonium speciations; Actinide migration

1. Introduction

The migration ability of Pu in the environment depends on its speciation. Pu in the environment is mostly present as Pu(V) and Pu (IV). Pu(V) shows high migration ability and, on the contrary, Pu (IV) appears more immobile due to its high affinity to mineral surfaces, although, it can be very mobile when bounded with colloidal particles, that can be particularly presented by colloidal humic substances (HS). HS are complex mixtures of natural macromolecules and smaller molecules and ions which occur throughout the environment, including deep anoxic underground systems. They can be generally separated into humic acids, fulvic acids and humie.

In fact, the formation of actual Pu species depends on the complex of actual geochemical conditions, particularly the presence of reducing agents that can be metal ions and organic chemicals. Humic substances comprise from 50 to 80% of the organic carbon pool content in soils and waters and are the most widely distributed natural organic matter [1–4]. Furthermore, HS have high reducing ability towards Pu [5]. Therefore, redox interac-

tions of humic substances are important for estimation of Pu mobility in aqueous systems.

The aim of the current study is to define the role of different humic substances in Pu(V) reduction in aqueous system. For this purpose kinetics of Pu(V) reduction by natural occurring HS was studied and comparison of the results obtained with real Pu distribution among humic fractions in contaminated soils is presented.

2. Experimental

The humic acid sample was purchased from Aldrich (AHA) and purified by several precipitations and ion exchange according to the procedure described in reference [6].

Contaminated and non-contaminated soil samples were collected. Contaminated Mollisol and Sod-podzolic soil samples were collected under birch wood and coniferous-birch wood in the territory of the East Ural Radioactive Trace. Non-contaminated Mollisol samples were collected in Kursk District and non-contaminated Sod-podzolic soil was sampled in the Moscow region from the well-characterized location of the Moscow State University biological station.

Both soils can be classified as loamy soil according to their particle-size composition and are characterized with a similar content of organic carbon, exchangeable Ca^{2+}, Mg^{2+} as well as with similar pH values. The properties of the soil samples were determined and summarized in Table 1.

From non-contaminated soil samples humic and fulvic acids were isolated and purified using the procedures described below (Section 2.1). Contaminated

* Corresponding author.
E-mail address: artist_oks@mail.ru (O. Blinova).

Table 1
The chemical and physical characteristics of the collected soil samples

Soil	C (%)	pH	Exchangeable cations (cmol$_c$ kg^{-1})				Particle-size composition (%)		
			Ca^{2+}	Mg^{2+}	K$^+$	Na$^+$	>0.01 mm	0.01–0.001 mm	<0.001 mm
Non-contaminated soil									
Sod-podzolic	3.8	4.7	3.1	1.2	0.3	–	71	15	14
Mollisol	5.8	6.6	30.8	6.9	0.5	0.4	59	19	22
Contaminarted soil									
Sod-podzolic	2.0	5.7	–	8.0	–	–	50	25	25
Mollisol	4.1	6.2	20.0	9.0	–	–	53	14	33

soils were treated for fractionation of organic matter (OM) depending on their nature (HA or FA), solubility and affinity to mineral part of soil (Section 2.1). The Pu content was determined in the OM fractions obtained. The soil properties given in Table 1 suggests, that the humic materials isolated from the pairs of non-contaminated and contaminated soils possess the similar properties.

The kinetics of Pu(V) by the obtained HS was studied.

2.1. Isolation and purification of organic matter from non-contaminated soil

2.1.1. Isolation of HA from soil

The isolation was carried out in accordance with the IHSS-procedure [7] and was as follows. After removing the plant roots, the dry soil samples were sieved through a 2.0 mm sieve. The pH value was adjusted to 1–2 using 1 M HCl at room temperature. The solution volume was adjusted with 0.1 M HCl to a final *V/m* ratio of 10 mL of liquid per 1 g of dry sample. The suspension was shaken for 1 h and then the supernatant was separated from the residue by decantation. The supernatant (FA 1) was stored for the isolation of FA.

The soil residue was neutralized with 1 M NaOH to pH 7.0 and then 0.1 M NaOH was added to get a final extractant to soil ratio of 10:1. The alkaline suspension was settled overnight. Afterwards, the supernatant was collected by means of decantation. The supernatant was acidified with 6 M HCl with constant stirring to pH 1.0 and then the suspension was left for 12–16 h. The suspension was centrifuged to separate the HA (precipitate) and FA (supernatant—FA 2) fractions. The HA fraction was redissolved by adding a minimum volume of 0.1 M KOH and solid KCl was added to attain a concentration of 0.3 M [K$^+$] and then centrifuged at 6000 rpm to remove the suspended solids. The HA were reprecipitated by adding 6 M HCl with constant stirring to pH 1, centrifuged and the supernatant was discarded. The HA precipitate was suspended in 0.1 M HCl/0.3 M HF solution, shaken overnight and centrifuged. This procedure was repeated four times. Then, HA was purified by dialysis (membrane MEMBRA-CEL-MD-44-4, 14 kD) and freeze dried.

2.1.2. Isolation of soil FA

FA 1 and FA 2 were concentrated using XAD-8 resin. Then, XAD-8 column was back eluted with 1 column volume of 0.1 M NaOH, followed by 3 column volumes of distilled H$_2$O. FA was purified by passing through H$^+$-saturated cation exchange resin (KU-2-8) and freeze dried.

2.2. Isolation and partitioning of organic matter from contaminated soil

2.2.1. Isolation of Fraction 1

For this purpose, 0.1 M NaOH was added to the corresponding samples to obtain a *V/m* ratio of 20:1 The slurry obtained was shaken vigorously and left over night and then centrifuged at 3000 rpm; the supernatant obtained was filtered through a 1 μm lavsan Wattman filter and acidified to pH 1–2 using 6 M HCl for coagulation of HA.

The acidified solution was heated at 70–80 °C for 30 min and centrifuged at 3000 rpm. The supernatant was filtered through a Wattman filter. The HA precipitate was dissolved in hot 0.1 M NaOH. Fraction 1 was presented by free humic and fulvic acids, and those bound to Fe, Mn, Al, etc. hydroxides.

2.2.2. Isolation of Fraction 1a (decalcinate)

To another part of the contaminated samples 0.1 M HCl was added to get a *V/m* value of 10:1. The slurry obtained was left for 12–16 h under continued stirring and then centrifuged at 3000 rpm.

The supernatant obtained was filtered through a 1 μm Wattman filter. The solid phase was repeatedly treated with 0.1 M HCl until a negative calcium test of the filtrate (indicator reaction with murexide). This fraction was presented by free fulvic acids and low molecular weight organic acids and those bound to Fe, Mn, Al, etc. hydroxides.

2.2.3. Isolation of Fractions 1 + 2

To the residual solid after decalcination 0.1 M NaOH was added to get a *V/m* ratio of 10:1. The obtained slurry was vigorously mixed and left for 12–18 h. Then Na$_2$SO$_4$·10H$_2$O was added and mixed until complete dissolution of sulfate to provide a coagulation of mineral colloids. The dark brown solution obtained was centrifuged at 3000 rpm and filtered. The extraction of humic acids was repeated until a slightly colored solution was obtained. For separation of humic and fulvic acids, 6 M HCl was added to the basic filtrate until pH 1 as described above for Fraction 1. The acidic solution containing fulvic acids was collected into a separate vessel. The precipitate of humic acids was dissolved in hot 0.1 M KOH, and then KCl was added. The solution was left until precipitation of mineral colloids which were separated by centrifugation. Humic acids were then precipitated again by addition of 6 M HCl until the pH is 1. The suspension was left for 12–16 h and humic acids were centrifuged and washed sequentially with 0.1 M HCl and distilled water. The precipitate was washed with water until the solution started turning brown. The washings were collected into a separate vessel. Fractions 1 + 2 was free humic and fulvic acids and those bound to Fe, Mn, Al, etc. hydroxides and calcium.

2.2.4. Isolation of Fraction 3

After isolation of Fractions 1 + 2 the residual solid was treated with 0.02 M NaOH (the *V/m* ratio was 10:1) by heating in a water bath (80 °C) for 6 h. After the suspension settled, it was centrifuged and filtered through lavsan Wattman filter (1 μm pore size). Humic and fulvic acids were separated as described above. Fraction 3 was humic and fulvic acids strongly bound to hydroxides and mineral components of the sample. The residue of the subsample after separation was ashed at 500 °C and then was dissolved in 7.5 M HNO$_3$. The non-soluble residue was filtered and the Pu concentration was determined in the filtrate.

2.3. Preparation of the ^{239,240}Pu(V) stock solution

Two ml of 0.074 M solution of ^{239,240}Pu in 1–3 M HNO$_3$ was combined with 350 μg KBrO$_3$, and heated in a water bath (80 °C) for 3 h. Twenty microliters of the solution obtained was added to 20 ml of distilled water to obtain a Pu concentration of 7.4×10^{-5} M. To the solution obtained, 0.22 mL of 0.1 M H$_2$O$_2$ was added and kept at room temperature for 1 h.

Then ^{239,240}Pu(V) was extracted from 2 mL of Pu solution using 1 mL of 0.01 M HDEHP in octane. The aqueous phase, after phases separation and containing Pu(V), was used for kinetic experiments. Ten percent of Pu reduction was observed during 3 months of keeping the stock solution in a plastic vial at room temperature and in sunlight.

2.4. Kinetic experiments

A stock solution of humic matter (AHA, purified HS or OM fractions) was diluted in 0.01 M NH$_4$ClO$_4$ to adjust the necessary organic carbon (OC) concentration (which varied from 0.2 to 20 mg/L) and neutralized to pH 6.0. The final volume of the solution taken for the experiment was about 7 mL, to which an aliquot of ^{239,240}Pu(V) was added. A concentration of ^{239,240}Pu(V) was maintained in the range of from 4×10^{-8} to 1×10^{-7} M. The kinetics of Pu(V) reduction to Pu(IV) in solution was studied by liquid extraction of Pu(IV) with di-2-ethyl-hexyl-phophoric acid (HDEHP). The error of the Pu determination was about 6%.

For redox speciation determination of Pu, 200 μL of initially prepared solution were sampled and acidified using 100 μm of 4 M HCl adjusting to pH 0 to destroy possible Pu–humate complexes. Then 20 μL of this solution was used for determination of the initial concentration of Pu. Then 150 μL of HDEHP solution in decane was added to the residual volume of 280 μL. The extraction was performed for 2 min. After separation of the organic phase, 20 μL aliquot of aqueous phase was plated on a steel disk and the ^{239,240}Pu alpha-activity was measured using a semiconductor detector.

Determination of Pu in the organic phase after extraction was not performed because of incomplete destruction of HDEHP during preparation of the sample for measurements. It is also impossible to provide a 100% re-extraction of Pu from the actual system. Although in each case, Pu activities were measured in the aqueous phase before and after extraction. Formation of Pu colloidal-bounded species was taken into account since a decrease of total Pu concentration in the initial solution with time was observed.

3. Results and discussion

3.1. Kinetics of Pu(V) reduction by purified HS

Kinetic curves obtained for the reduction of Pu(V) by AHA and natural HA at pH 6, an organic carbon concentration of 10 mg/L and an initial Pu(V) activity of 5×10^{-8} M are presented in Fig. 1.

The curves obtained for natural FA at pH 6, with an organic carbon concentration of 10 mg/L and an initial Pu activity 4×10^{-8} M are presented in Fig. 2.

As can be seen from Figs. 1 and 2, the rate of Pu(V) reduction by humic and fulvic acids and the Pu(V) quasi-equilibrium

Fig. 2. Kinetics of Pu(V) reduction by purified fulvic acids isolated from Millisol and Sod-podzolic soils at pH 6, organic carbon concentration of 10 mg/L and initial Pu(V) concentration of 4×10^{-8} M.

concentration under the same conditions does not depend on the type of soil from which the actual HS was extracted.

Under the same conditions fulvic acids cause faster kinetics of Pu(V) reduction (average specific rate $k = 0.77$ h^{-1}) when compared to humic acids ($k = 0.27$ h^{-1}). The quasi-equilibrium concentration of Pu(V) (at 500 h) in all cases was about 8–12%.

Data obtained for Pu(V) reduction under different concentrations of HA and FA show that the Pu(V) reduction rate increases with increasing organic carbon concentration. The quasi-equilibrium concentration of Pu(V) was reached more rapidly in solutions containing high OC concentrations, as is shown in Fig. 3 for AHA at different concentrations.

3.2. Kinetics of Pu(V) reduction in solutions of different OM fractions isolated from soils

The reduction of Pu(V) by different OM fractions (Section 2.2), isolated from Sod-podzolic and Mollisol samples, was studied. The data obtained has shown similar Pu redox kinet-
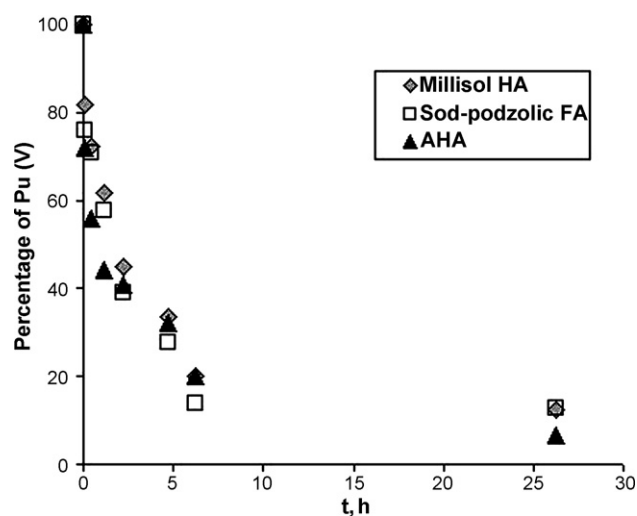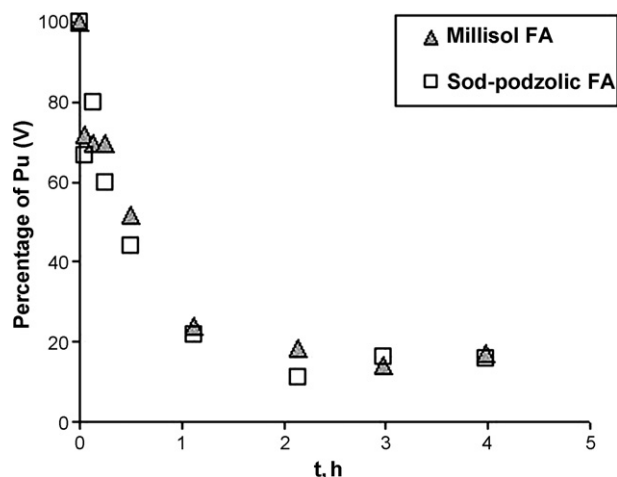

Fig. 1. Kinetics of Pu(V) reduction by Aldrich humic acid (AHA) and purified humic acids isolated from Millisol and Sod-podzolic soils at pH 6, organic carbon concentration of 10 mg/L and initial Pu(V) concentration of 5×10^{-8} M.
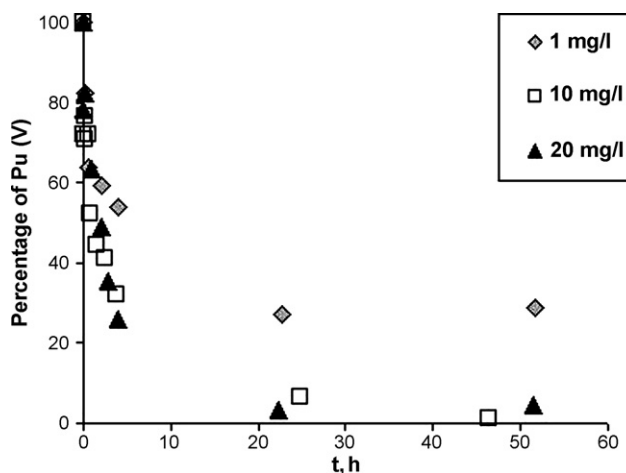

Fig. 3. Kinetics of Pu(V) reduction by Aldrich humic acid (AHA) at different organic carbon concentrations; initial Pu concentration 8×10^{-8} M and at pH 6.
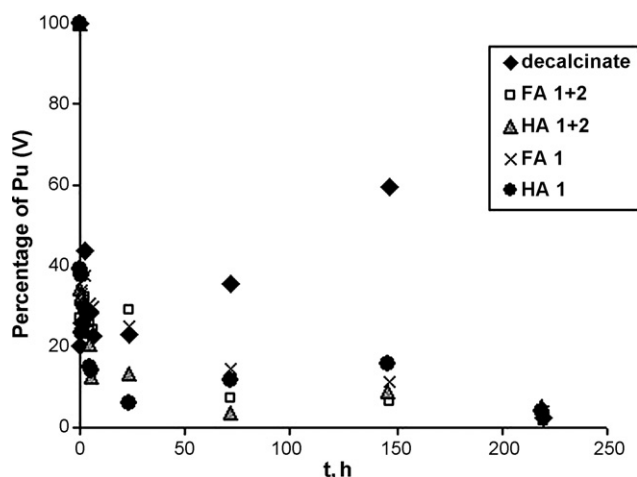
Fig. 4. Kinetics of Pu(V) reduction by different fractions of HS isolated from Sod-Podzolic soil at pH 6 and an initial Pu concentration 1×10^{-7} M.
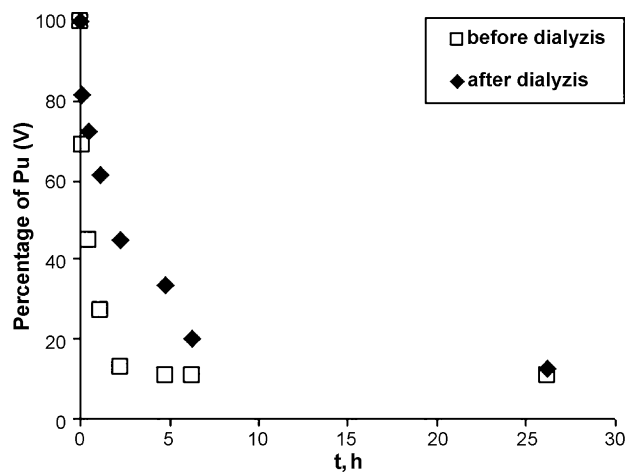

Fig. 5. Kinetics of Pu(V) reduction by HA; Fraction 1 before and after dialysis at pH 6 and initial Pu concentration of 1×10^{-7} M.

ics behavior in OM fractions, extracted from Sod-podzolic and Millisol soils. In Fig. 4, kinetic curves obtained for Sod-Podzolic HS are presented. The fractions studied and corresponding concentrations of OM used for the experiment are presented in Table 2.

As seen in Fig. 4., the initial part of kinetic curves can be separated into two sections. The first section is characterized by a sharp decrease of the Pu(V) concentration, up to 20–30% in the first few minutes. Since all OM obtained by the method presented in Section 2.2, were not purified from the mineral part of the soil, they contained dissolved metal ions and/or metal–organic complexes, that can play the role of redox agents and could cause very high reducing rates during the first few minutes.

The next section of kinetic curves can be approximated by an exponential function and most likely corresponds to Pu(V) reduction directly by HS.

The subsequent increase of the Pu(V) concentration is observed in the case of the decalcinate solution. Although, it could also be another species that was not extracted by HDEHP under the experimental conditions (e.g., formation of colloidal or pseudo-colloidal forms of Pu(IV)).

Table 2
Content of dissolved organic carbon in the solutions of different OM fractions isolated from Sod-podzolic soil

Fraction	Content of organic carbon (mg/L)
1 FA	1.5
1 HA	35
1a (decalcinate)	9.5
(1 + 2) FA	31
(1 + 2) HA	26

This observation indicates the complex interaction patterns of Pu with the actual OM fractions, a rich variety of mineral compounds, as well as with fulvic acids and low molecular weight organic compounds.

To estimate the influence of the low molecular fraction and the mineral component of the sample on Pu(V) reduction, OM fractions were purified by dialysis (membrane MEMBRA-CEL-MD-44-4, 14 kD pore size).

Comparison of Pu(V) reducing rates by the HA 1 Fraction before and after dialysis is presented in Fig. 5. This shows a decrease of the reducing rate after separation of dissolved ions and the low molecular weight fraction. The kinetic curves character obtained is very close to that of Pu(V) reduction by pure HA (i.e., AHA).

3.3. Partitioning of Pu between different OM fractions isolated from contaminated soils

The partitioning of plutonium among different fractions of organic matter was carried out in an effort to reveal the correlation between Pu binding with OM and the reducing capability of the corresponding fraction. The results obtained are presented in Table 3.

A value of 44.6% of the total Pu is bound with humic materials for Mollisol and 61% for Sod-podzolic soil. As shown in Table 3, the major part of the Pu is bound to humic acids, and the small part to fulvic acids. The residual soil contains almost half of the plutonium and this indicates predominant binding of the Pu to low solubility components of Mollisol. Also, a significant quantity of Pu is bound to Fraction HA 2, which is particularly represented by low mobility Ca humates.

Table 3
The distribution of plutonium among OM fractions of the contaminated soils under study (in percent of the total Pu content)

Soil sample	Bound to humic acid fractions				Bound to fulvic acid fractions					Residue
	1	2	3	Sum	1a	1	2	3	Sum	
Mollisol	6.8	21.5	8.5	36.8	0.4	1.2	2.7	3.5	7.8	55.4
Sod-podzolic	17.3	12.7	8.0	38.0	3.7	8.4	3.4	7.5	23.0	39.0

Upon separation and reprecipitation of humic acids and upon washing by 0.1 M HCl and distilled water, the washing solutions contain 1.1% of Pu. This indicates strong binding of plutonium to Ca humates.

For Sod-podzolic soil, the fraction of plutonium bound to mobile fractions of HS (Fractions 1 and 1a) was substantially higher than that for Mollisol. On one hand, the portion of plutonium bound to low mobility Ca humates in Sod-podzolic soil is lower than that in Mollisol. On the other hand, in the Sod-podzolic soil, the plutonium content is 9 times higher in the fraction of mobile fulvic acids (Fraction 1a) when compared to that in the Mollisol. This indicates a higher migration ability of plutonium in Sod-podzolic soil compared to the Mollisol.

4. Conclusions

The kinetics of Pu(V) reduction in solutions containing purified natural HS was studied. On the basis of curve slope analysis, reducing rates at given conditions ($I = 0.01$ M, $c(OC) = 0.2$–20 mg/L) an increase in the order: HA < FA ∼ low molecular weight fraction and does not depend on nature of soil from which the HS was extracted.

The lower reducing rates of Pu(V) in HA solutions might be explained by stereochemistry considerations.

The study of Pu behavior in real solutions containing OM fractions and dissolved mineral compounds has shown the complex influence patterns of various kinds of humics.

The data obtained for real contaminated soils indicate the dual influence of natural organic matter on Pu distribution among different OM fractions. On the one hand, because of the formation of soluble complexes of Pu(IV) with low molecular weight and mobile fulvic acids, the migration of plutonium in the environment is possible and must not be disregarded. On the other hand, the formation of low solubility humates and their polymeric complexes with Fe, Mn and other hydroxides, favor binding of plutonium with immobile fractions and subsequent accumulation of Pu in humic layer of soils.

In summary, it can be concluded from the results of this study that fulvic acids and low-molecular weight organic fraction preferably reduce Pu due to faster kinetics. Mobile Pu species can be preferentially formed with FA due to the strong interaction of Pu(IV).

Acknowledgements

References

[1] G.R. Aiken, D.M. McKnight, R.L. Wershaw (Eds.), Humic Substances in Soil, Sediment and Water, Wiley, New York, 1985.
[2] D.S. Orlov, Soil Humic Acids and General Theory of Humification, State University Publisher, Moscow, 1990 (In Russian).
[3] E.M. Thurman, Organic Geochemistry of Natural Waters, Martinus Nijhof/Dr. W. Junk Publishers, Dordrecht, The Netherlands, 1985.
[4] K.R. Czerwinski, G. Buckau, F. Scherbaum, J.I. Kim, Radiochim. Acta 65 (1994) 111–119.
[5] C. Andre, G.R. Choppin, Radiochim. Acta 88 (2000) 613–619.
[6] M. Schnitzer, S.U. Khan, Soil Organic Matter, Elsevier Scientific Publishing Co., 1978.
[7] R.S. Swift, in: D.L. Sparks (Ed.), Methods of Soil Analysis, Part 3: Chemical Methods, SSSA Book Series No. 5, SSSA and ASA, Madison, WI, 1996, pp. 1011–1069.