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Molecular size distribution of Pu in the presence of humic substances in river and groundwaters

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Key wards: Plutonium, humic substances, organic complexes, molecular size distribution, aquatic environments

Abstract

The association properties of Pu with aquatic humic substances in a 0.01M $NaClO_4$ solution at pH 6-8 were studied on the basis of molecular size distribution. Seven humic substances were isolated from river and groundwaters by the XAD extraction technique, and were used for comparing their effects on the association of Pu. In the presence of humic acid, dominant molecular size of Pu was 100k-30k Da. The Pu in the presence of fulvic acid has three dominant molecular size of 30k-10k Da,30k-5k Da and less than 5k Da. The association of Pu-humus complexes may be controlled by the molecular size distribution of humic substances, and their characteristics of each size fraction.

Introduction

Macromolecular components of dissolved organic materials such as humic substances (humic and fulvic acids) are widely recognized as important complexing ligands towards trace elements and radionuclides in aquatic environments. Humic substances are polymeric, brown or black complex organic acids with a wide range of molecular weight. These substances are the largest fraction of organics in natural waters[1] and have high complexation affinity for actinide ions.[2-4] Some parts of actinides and lanthanides in natural waters are associated with anionic organic materials, especially humic substances (humic and fulvic acids) in the different molecular size fractions.[5-10] The authors have reported the complexation properties of humic substances with actinides-lanthanides such as Eu, Am and Pu[11-14]. These molecular size effects of humic substances on the complexation affinity and the sorption ability may significantly affect the migration behavior of actinides.

This study reports the association properties of Pu with aquatic humic substances having different origin on the basis of molecular size distribution. The aquatic humic substances were isolated from two river waters, surface lake water and two groundwaters, and then used for comparing their effects on the association of Pu.

Experimental

Humic substances

Humic (HA) and fulvic acids (FA) isolated from two river waters (Yodo and Suwannee Rivers) and a Norwegian surface water with different environmental conditions were used in this study. The Yodo River is a major river running through the Kinki region, where is most the heavily populated urban developments, in Japan. The river water is originated from Lake Biwa in Shiga Prefecture, and supplied from the lake at a rate of 40 m^3/sec. The Suwannee River flows through South Georgia and north Florida. Most of the Okefennokee Swamp drain into the Suwannee River. Color of the waters from the Suwannee and Nordic is brownish. The groundwater humic substances from Glass Block site (GB) and Wallace Point (WP) in the Chalk River Laboratories of Atomic Energy of Canada Limited were also used in this study. The GB site is located in the recharge area for a shallow sand aquifer. The recharge area is a seasonal wetland and the subsurface residence time for the groundwater is an order of one year. The WP is located in the discharge zone of an overburden flow system. The physico-chemical properties of water samples are given in Table 1.[15-17]

The Yodo humic substances were isolated from a 140 –l of river water sample collected at a site of the downstream of Yodo River. 20000-l and 10000-l of shallow groundwaters were collected from the GB and the WP sites, respectively. The isolation and purification of humic substances were carried out by the column method using XAD-8 or DAX-8 resin.[18] The amounts of humic substances were 0.04 g for the Yodo, 18.2 g for the GB and 9.3g for the WP. Suwannee River HA and FA isolated by the XAD-8 extraction procedure were purchased from the International Humic Substances Society (IHSS). Nordic HA and FA from the IHSS were also used in this study.

Stock solution of the humic substances was prepared by dissolving 10 mg of the purified humic substances in a dilute NaOH solution, and then the solution was made up to 100 ml of 0.01M $NaClO_4$. The pH of the solution was adjusted to pH 8 by adding dilute $HClO_4$. All humus stock solutions were stored in a refrigerator at 4°C.

Association experiments

The association experiments were carried out in a medium of 0.01M $NaClO_4$ solution at the humus concentration of 10 mg/l and pH 6-8. Nitrate solution of ^{238}Pu was used for the experiments. Stock solution containing ^{238}Pu was prepared by diluting with deionized water. The pH of the stock solution was adjusted to 4 with NaOH solution. Valence of ^{238}Pu in the stock solution was confirmed to be Pu(IV) by the TTA-xylene extraction method. 100 μl of ^{238}Pu solution was added to 10 ml of humus solution in a teflon centrifugation tube. The initial concentration of Pu was $(3.0\sim 7.6)\text{x}10^{-6}$ M. After 7 days under shaking in an oven at 25°C, the solution was filtered with 450 nm filters and measured for pH.

Ultrafiltration technique was used to size-fractionate Pu in the humus solutions because of a non-destructive and reagent-free method. The sample solution was sequentially ultrafiltered with simple ultrafiltration filters (Millipore Ultrafree CL filters) having nominal cut-off molecular weight of 100,000, 30,000 (polyethersulfone membrane filters), 10,000 and 5,000 Da (regenerated cellulose membrane filters). The radioactivities of ^{238}Pu were measured for each molecular size fraction by liquid scintillation counting. The percentage of Pu in each molecular size range was calculated from the radioactive concentration in each molecular size fraction. The molecular size distribution of the humic substances was measured by high-performance size exclusion chromatography according to the method given elsewhere.[19]

Results and discussion

Effect of humus concentration

The molecular size distribution of Pu in the absence and presence of the Yodo fulvic acid (FA) is shown in Fig. 1. In the absence of FA, 74% and 25% of Pu were found in the molecular size above 450 nm (particulate forms) and less than 5k Da (dissolved forms) at pH 6-7, respectively because of the polymerization and/or precipitation on the basis of kinetic estimation. The percentage of particulate Pu decreases with increasing the FA concentration. This indicates the complexation of Pu with the Yodo FA.

In the presence of FA, 0.7-11 % and 0-3.6% of Pu is found in the size fraction of 450 nm-100k Da and 100k-30k Da, respectively. As shown in this figure, the percentage of Pu in the size fraction of 100k-10K Da increases with the FA concentration. On the other hand, the variation in Pu is not significant for the size fraction less than 5k Da and nearly equal to that at the blank experiment. Pu appears to be complexed with FA having specific molecular size fractions.

Existent forms of Pu in the presence of humic substances with different origin

The molecular size distribution of Pu in the presence of humic substances with different origin is shown in Fig. 2. In the presence of Suwannee and Nordic HA, the dominant size fraction of Pu is 100k-30k Da (46-57%). On the other hand, major part of Pu in the presence of FA is found in smaller molecular size than the Pu-HA experimental systems. The dominant size fractions of Pu are less than 5k Da for the GB humic substances (46%) and 30k-10k Da for the Suwannee and Nordic FA (57-64%). However, 25% of Pu at the blank experiment is found in size fraction less than 5k Da. Percentage of Pu complexed with FA in the lowest size fraction is calculated as 10% for the Yodo FA, 18% for the WP and 41% for the GB. Therefore, the patterns of Pu size distribution can be divided into three groups as follows: 1) Pu-GB humic substances, 2) Pu-Yodo FA and WP humic substances, and 3) Pu-Suwannee and Nordic FA.

The molecular size distribution of humic substances is shown in Fig. 3. Dominant size of the HA is 100k-30k Da for the Suwannee and the Nordic samples. The FA has the dominant size fractions with 30k-10k Da for the Nordic sample, and less than 5k Da for the Suwannee and the Yodo FA and the groundwater humic substances. There is a discrepancy in molecular size distribution between Pu in the presence of humic substances and humic substances themselves.

Relation in characteristics between Pu-humus complexes and humic substances

In order to understand the humus complexation properties for Pu in detail, the percentage of Pu in each size fraction is plotted as a function of that of humic substances (Fig. 4). Data plotted in Fig. 4 is the results from the association experiments for the humic substances as shown in Fig. 2. There is a positive correlation (r=0.84) between Pu and humic substances with molecular size of 100k-5k Da except for the Suwanne and Nordic with 30k-10k Da. This size fraction has relatively high complexation affinity for Pu rather than the Yodo FA and groundwater humus fractions. The lowest size fractions of humic substances have lower complexation ability and/or lower competitive reaction than the high molecular size fractions.

Tanaka et al.[13] have shown that ^{238}Pu was mainly present in the reagent HA fraction of 30k-10k Da at the laboratory studies. Gaffney et al.[7] reported that the molecular size distribution of ^{239,240}Pu was similar with that of dissolved organic carbon (DOC) at Volo Bog at pH4-5. The dominant size fraction was 30k-3k Da. Matsunaga et al.[10] have shown that the major part of dissolved ^{239,240}Pu in the Sakhan River waters from the contaminated Chernobyl area was distributed in high molecular size above than 10k Da (an average value of 70±15%, 49-83%) at pH 7-8. They also have shown that the dominant components were 100k-10k Da in the April sample and 10k-1k and above 100k Da in the September samples. The size-distribution of DOC was distinct from that of Pu. The surface waters from bog and river waters through peat area such as the Sakhan River have high DOC concentration and brownish color, indicating a significant fraction of dissolved organic materials occupied by humic substances.[1] The size selective complexation of humic-like materials with Pu, therefore, occurs in natural environmental systems.

The solution chemistry of humic substances is influenced by functional group heterogeneity and variations in molecular size distribution.[20,21] Molecular size fractions of soil and aquatic HA and FA showed clear differences in chemical composition and functional group content.[7,21-25] Differences in size distribution of Pu in the presence of FA correspond to the groups of size distribution of FA such as the Yodo and the groundwater samples (Figs. 2 and 4). Therefore, one possibility is considered that the amounts of functional groups of molecular size of 100k-30k Da for the HA and 30k-10k Da for the FA, which were isolated from water samples collected at the Suwannee Rivers and the Nordic lake, may be larger than the Yodo FA and groundwater humic substances. These humic substances may be some relationships between the functional group content and percentage of size fractions. Consequently the association properties for Pu-aquatic humus complexes depend on the characteristics of surface water humic substances supplied from the watershed of river systems and the groundwater humic substances in the different recharge area and geologic media.

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Table 1 Characteristics of water samples.

Sample	pH	Conductivity, mS/m	DOC, mg/l	Turbidity, mg/l
Yodo River, Japan[a]	7.4	166	2.1	6
Suwannee River, U.S.A.[b]	3.9	41	37.7	---
Nordic, Norwegian surface water[c]	4.2-6.8	2.2-4.8	3.0-24.0	---
Groundwater Glass Block site	5.7	---	2.3	---
Wallace Point	7.1	---	1.7	---

[a] Water Quality Management Center for Osaka Pref.[13]

[b] Miles et al.[14]

[c] Gjessing et al.[12]

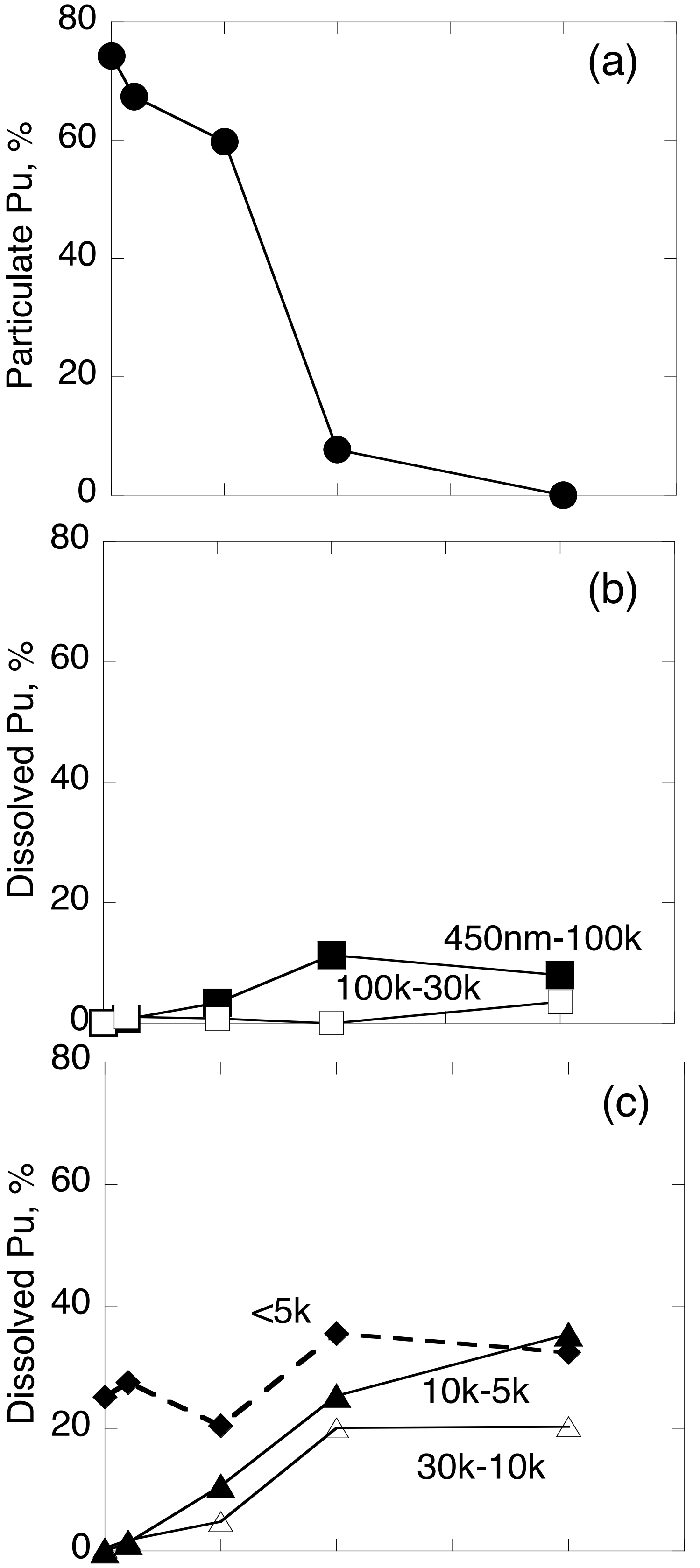
Figure captions

Fig.1. Percentage of Pu in the absence and presence of the Yodo River fulvic acid (FA) as a function of FA concentration.

Fig.2. Molecular size distribution of Pu in the presence of aquatic humic (HA) and fulvic acids (FA) isolated from river waters and groundwater humic substances (HS) with different origin. The pH of the humus solutions in a 0.01M $NaClO_4$ solution was pH 5.5-7.5.

Fig.3. Molecular size distribution of river and groundwater HS in a 0.01M $NaClO_4$ solution at pH 5-7.

Fig.4. Relationship in percentage between Pu in the presence of humic substances and humic substances themselves in each size fraction. Data plotted in this figure was the results from the association experiments as shown in Fig.2. The symbols indicate molecular size fractions as follows: ○ 450nm-100k Da; ▲ 100k-30k Da; ● 30k-10k Da; ■ 10k-5k Da; □ less than 5k Da.



(a)
Particulate Pu, %
80
60
40
20
0
(b)
Dissolved Pu, %
80
60
40
20
0
450nm-100k
100k-30k
(c)
Dissolved Pu, %
80
60
40
20
0
<5k
10k-5k
30k-10k
0
5
10
15
20
25
Fulvic acid, mg/l

Fig.1

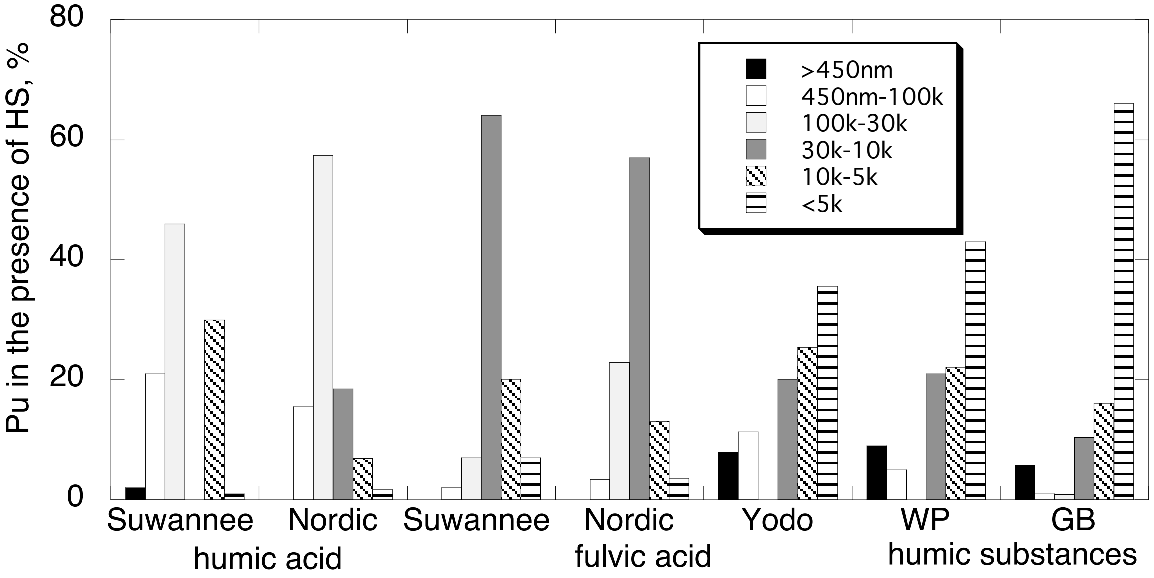

Pu in the presence of HS, %
80
60
40
20
0
>450nm
450nm-100k
100k-30k
30k-10k
10k-5k
<5k
Suwannee
Nordic
humic acid
Suwannee
Nordic
fulvic acid
Yodo
WP
GB
humic substances

Fig.2

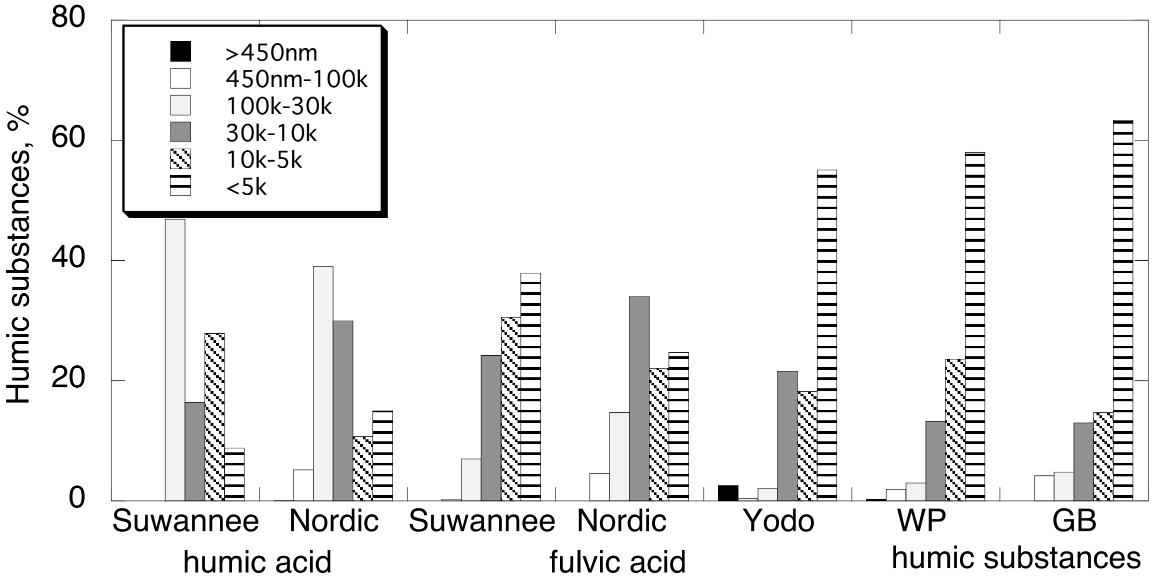

80
60
40
20
0
Humic substances, %
■ >450nm
□ 450nm-100k
□ 100k-30k
■ 30k-10k
▨ 10k-5k
▤ <5k
Suwannee
Nordic
Suwannee
Nordic
Yodo
WP
GB
humic acid
fulvic acid
humic substances

Fig.3

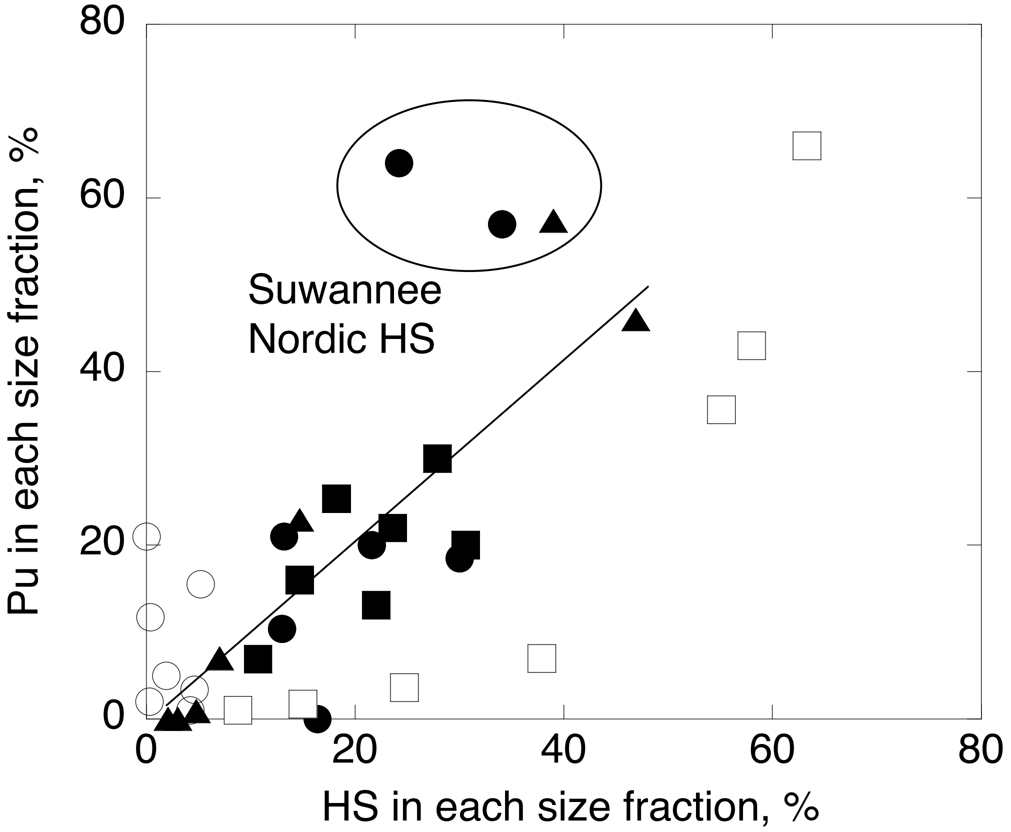

80
60
40
20
0
Pu in each size fraction, %
0
20
40
60
80
HS in each size fraction, %
Suwannee
Nordic HS

Fig. 4