

**Article**

# Environmental behavior of plutonium isotopes studied in the area affected by the Chernobyl accident

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## Abstract

The environmental behavior of Chernobyl-derived plutonium was reviewed in soil and aquatic environments in the affected areas of Ukraine. Dissolution of the released fuel particles marked the beginning of the migration in the environment for the Chernobyl-derived plutonium. Once dissolved, the plutonium distributed over the surface soil layer with low infiltration capacity. This relative immobility of plutonium in the soil environment is attributed to its affinity for soil organics, as suggested by previous studies of chemical partitioning. The relative immobility of plutonium was also seen in its fluvial transport along the Dnieper River. Dissolved organic matter, most probably humic substances, helped stabilize dissolved plutonium in the lake waters. Dissolved organic matter and purified humic substances in the area have been characterized for the fluorescence properties, molecular size distribution, functionality, and sources. Further analyses of the phase and chemical speciation of plutonium, taking into account the characterizations of matrices including humic substances, are needed to more fully understand the behavior of Chernobyl-derived plutonium, and to contribute to predict the migration of plutonium in other circumstances.

## Introduction

Over twenty years have passed since the nuclear accident at the Chernobyl Power Plant in 1986. On this memorial occasion, two international authorities from IAEA and WHO released reports containing the latest analyses of the influence of the accident including its environmental, radiological, and social aspects (IAEA, 2006a; IAEA, 2006b; WHO, 2006). These reports stated that the radiological effects on people are mostly attributable to radionuclides of iodine, cesium and strontium. However, the accident area was also contaminated with plutonium isotopes.

The stock of civil plutonium is clearly increasing in the world as a result of nuclear power generation. According to Albright et al. (1997), the total discharge of civil plutonium from nuclear power reactors in the world became 850 tons (1 ton = 1000 kilograms) at the end of 1993 and was estimated to be “a little over 2100 tons” by the end of 2010, increasing at a rate of approx. 70 tons annually. Thus, we

need a better understanding of the behavior of plutonium in the environment to prevent further detriment to our ecosystems in order to ensure stable and reliable nuclear energy supply.

One useful approach to this objective is a field investigation of actual Pu contamination. Contamination in the case of the Chernobyl accident has the unique characteristic that it occurred over a short period of time, a little over 10 days. The period of the accident, when the accidental Pu started to react in the environment, was clearly identified. Thus, it affords a unique opportunity to study the dynamics of Pu contamination. An investigation comparing plutonium isotopes with other important radionuclides such as <sup>137</sup>Cs and <sup>90</sup>Sr is also possible.

Nevertheless, there has been limited information about the behavior of plutonium in the Chernobyl accident area. This paucity of information is attributed to two aspects: i) the health influence of the accident is dominated by radionuclides other than plutonium (WHO, 2006); and ii) a great deal of la-

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laboratory preparation and equipment is required for radiochemical analysis and speciation of plutonium (Runde et al., Lucey et al., 2007).

Humic substances, "the products of the decomposition of primarily plant material by microbes" (Drever, 1997), consist of a major part of natural organic matter in soil and water. In surface water, more than half of the dissolved organic compounds are fluvic acids and humic acids both of which belong to humic substances (Drever, 1997). The total concentration of dissolved organic matter (DOM) in water is often evaluated by the content of dissolved organic carbon (DOC) analytically. It is known that DOC in natural waters mostly originates from dissolved fluvic and humic acids. Humic substances and their components (fluvic and humic acids, and some others), which cover various individual compounds, have a large number of functional groups that might bind some kind of trace elements and radionuclides. Therefore, humic substances have been recognized as decisive material in affecting plutonium behavior in the environment.

A number of laboratory experiments have been carried out on this subject using model compounds or purified humic/fluvic acids from humic substances (e.g., Mudge et al, 1988; Warwick et al., 2000). However, studies in contaminated environment with plutonium have been relatively limited. Here, we review studies dealing with the environmental behaviors of Chernobyl-derived plutonium in the soil and the aquatic environment, with an emphasis on the relation between environmental plutonium behavior and the presence of humic substances.

## Radioactive contamination in the Chernobyl accident area

### The Accident

The Chernobyl accident occurred during a test of emergency preparedness for a loss of offsite power, in the early morning of April 26, 1986. Detailed descrip-

tions of the accident are typically given by IAEA(1991, 2006a), UNSCEAR(2000), Vargo (2000), OECD/NEA (2002), Andoh and Hirano (2002), and Smith and Beresford (2005). Briefly, nuclear reactions in the reactor increased markedly as a combined result of improper operation and technical deficiencies of the reactor itself. The resultant thermal energy overheated the coolant water, producing water vapor which further increased the reactor power due to the nature of nuclear reaction and the design of this reactor. This sequence of events occurred within 3 minutes (Smith and Beresford, 2005), and resulted in a steam pressure induced-explosion. Hydrogen may have been also involved in the explosion (Andoh and Hirano, 2002). A part of the nuclear fuel contained in zirconium metal tubes was broken down into fine particles of several hundred microns in diameter, or was melted into super-heated hot debris. Because the explosion damaged the reactor building, radionuclides liberated from the nuclear fuel were released into the open

**Table 1.** Inventory and released radionuclides in the Chernobyl accident (modified from UNSCEAR, 2000)

Radionuclide	Half-life d: days y: years	Inventory* (PBq, 10 <sup>15</sup> Bq) (Sich et al., 1994)	Activity Released (PBq, 10 <sup>15</sup> Bq) (Kruger et al., 1996)	Fraction Released (%)
[Group 1 : Noble Gas and volatile elements of short half-lives]				
<sup>133</sup> Xe	5.25 d	6510	6500	100
<sup>131</sup> I	8.04 d	3080	1800	58
[Group 2 : Refractory elements of short half-lives]				
<sup>95</sup> Zr	64 d	5850	140	2.4
<sup>144</sup> Ce	284 d	3920	90	2.3
[Group 3: Elements of intermediately long half-lives, other than transuranics]				
<sup>134</sup> Cs	2.06 y	170	50	29
<sup>137</sup> Cs	30.0 y	260	86	33
<sup>90</sup> Sr	29.12 y	230	8	3.5
[Group 4: Transuranics]				
<sup>238</sup> Pu	87.7 y	1.3	0.033	3.5
<sup>239</sup> Pu	24110 y	0.95	0.0334	3.5
<sup>240</sup> Pu	6564 y	1.5	0.053	3.5
<sup>241</sup> Pu	14.35 y	180	6.3	3.5
<sup>241</sup> Am	432.2 y	0.17	(0.06)**	(3.5)**
<sup>244</sup> Cm	18.10 y	0.43	(0.015)**	(3.5)**

Several radionuclides are excluded from this table for the sake of legibility.

\* Decay corrected to 26 April 1986.

\*\* Released activity was estimated by the present author by assuming the released fraction to be 3.5 %.

**Table 2.** Isotopic concentrations of plutonium of different origins

Radionuclide	Chernobyl*	PWR (33 000 MWd/t)	Global Fallout	Weapon Grade
$^{238}\text{Pu}$	0.3	1.3		
$^{239}\text{Pu}$	64.0	56.6	83.6	93.0
$^{240}\text{Pu}$	28.8	23.2	15.4	6.5
$^{241}\text{Pu}$	6.9	13.9	1.0	0.5
$^{242}\text{Pu}$	n.a.	4.7		

\* Based on data on Table 1.  $^{242}\text{Pu}$  was excluded due to lack of data.

\*\* Albright et al. (1997)

environment (Tables 1 and 2). About 3.5% of the total nuclear fuel was also released. This number has been still in discussion. High temperatures due to both fire and nuclear decay heat contributed to the release of radioactive materials over several days after the explosion. A major release of radionuclides continued for about 10 days, and a small-scale release continued for more than 1 month.

#### *Natural environment of the accident area*

The Chernobyl Nuclear Power Plant is located in the northeast region of Ukraine, about 130 km of north of Kiev. In this review, “the accident area” refers to a specific area in the vicinity of the power plant, termed “the Exclusion Zone”, which was highly contaminated and has been controlled by Ukrainian authorities. The area includes the land up to a distance of 10-40 km from the Chernobyl Nuclear Power Plant, covering more than 2044 km<sup>2</sup> (Shestopalov and Poyarkov, 2000). The area includes a lower reach of the Pripyat River, a significant tributary of the Dnieper River. There are also ponds and marshes within this area. The surface soil is comprised of sand derived from glacial till, podzol, and peat (Lukashev, 1993). The Pripyat River enters into the Kiev artificial reservoir about 30 km south of the power plant, thus joining the main stream of the Dnieper River. The Dnieper flows out to the Black Sea after traveling about 540 km from the power plant through several reservoir lakes.

#### *Released radionuclides and field contamination*

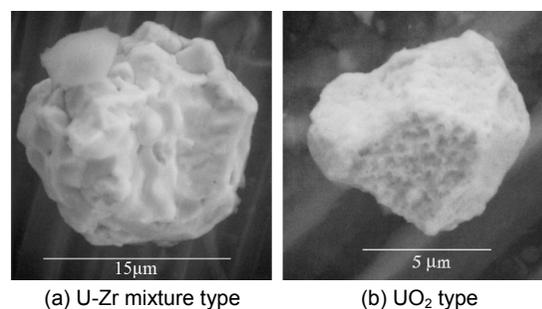
##### *(1) Radioactive plumes*

During the 10 days of the major release, radionuclides were released in plumes that dispersed in various directions determined by wind direction and other meteorological conditions. Also, the composition

and form of the released radionuclides changed over time as the radionuclides of the damaged nuclear fuels underwent continuing physical/chemical fractionation and radioactive disintegration. As a result, in the region several bands of high contamination with different radionuclide compositions were formed (UNSCEAR 2000; Terada et al., 2005). There were several major plumes recorded as described by Shestopalov and Poyarkov (2000). The West Plume produced by the initial explosion, had the highest contamination level. It was narrow (1-5 km wide), relatively short (up to 80 km), and extended to the west of the power plant. Nevertheless, the effects of the West Plume could be observed far to the west more than 300 km away, as seen in elevated concentrations at “hot” radioactive spots. The Northwest Plume, which was released during a fire after the original explosion, was much shorter than the West Plume but contained a high proportion of nuclear fuel particles. During the last several days of the major release, the South Plume was produced, which passed through Kiev, and even through part of Odessa. This plume had the second highest contamination level.

##### *(2) Forms of radionuclide release*

Chernobyl-derived radionuclides have affected a vast area of Europe (De Cort et al., 1998; UNSCEAR, 2000; Terada et al., 2005) and even Asia. In the present article, we focus on the contamination in Ukraine, particularly in the accident area. There were two forms of radionuclide releases in this accident: a gaseous form, which included iodine, xenon, krypton and a part of cesium, and a particulate form, com-



**Figure 1.** Fuel particles found in surface soil layer (0-1 cm) in the forest affected by the “West Plume”. The sample were collected in a forest 6 km west to the Chernobyl Nuclear Power Plant. Reproduced from Yanase et al. (2002) by permission of the Akadémiai Kiadó,

prised of damaged nuclear fuel (hereafter “fuel particles”). Photographs of fuel particles by SEM are shown in Fig. 1 for different types of matrix (Yanase et al., 2002). Refractory nuclides such as  $^{90}\text{Sr}$  and plutonium isotopes ( $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ , and  $^{241}\text{Pu}$ ) were almost entirely (> 90% by radioactivity) contained in the fuel particles (Shestoparov and Poyarkov, 2000).

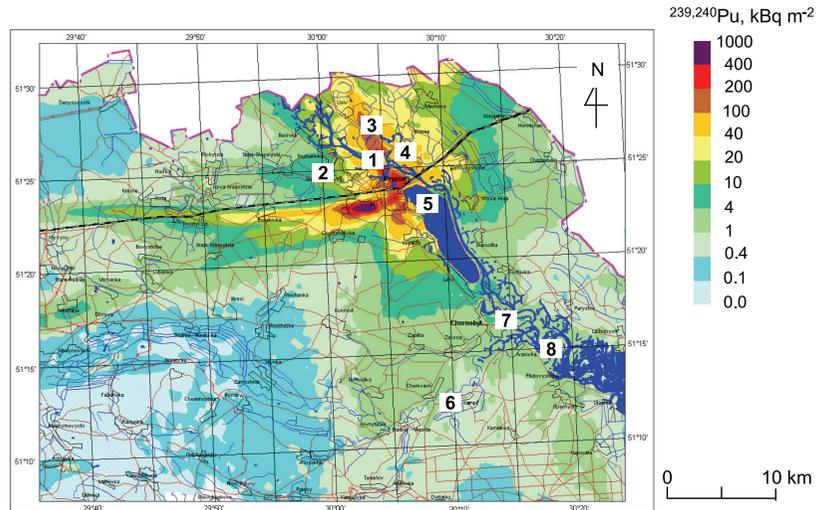
### (3) Field contamination in the accident area

In 1997, the total fallout of  $^{90}\text{Sr}$  and  $^{239,240}\text{Pu}$  in the accident area, except at the damaged reactor site and radioactive waste storage sites, was estimated to be  $2.6 \times 10^{15}$  and  $4.9 \times 10^{13}$  Bq, respectively. The highest density of  $^{239,240}\text{Pu}$  in the area was over  $400 \text{ kBq m}^{-2}$  (Fig. 2a) (Kashparov et al. (2003), which was 4000 times higher than the common baseline level in Europe of radioactivity from nuclear weapon tests in the atmosphere. Cesiums-137 was mostly included in fuel particles in the accident area, 75 % of it detected within 10 km from the power plant. The fraction of  $^{137}\text{Cs}$  in fuel particles decreased with distance from the power plant, associated with an increased contribution of gaseous fallout of  $^{137}\text{Cs}$ . The total activity of  $^{137}\text{Cs}$  in the accident area was estimated to be  $5.6 \times 10^{15}$  Bq in 1997 (Shestopalov and Poyarkov, 2000).

### (4) Field contamination by Chernobyl-derived Pu in far field

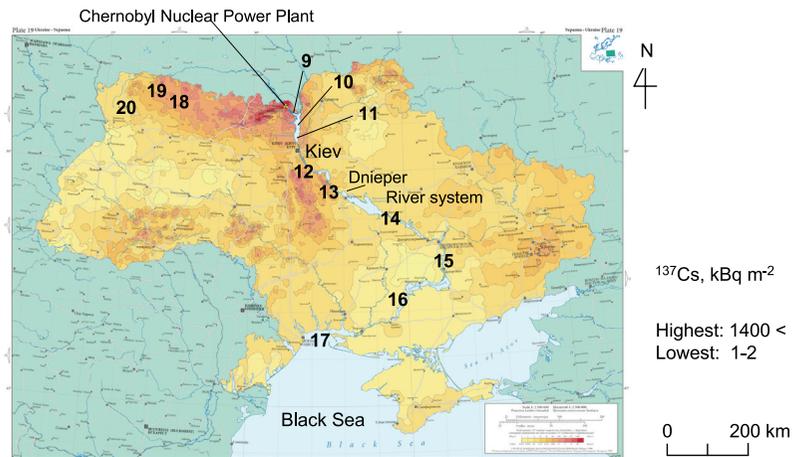
Although there is very little data on Chernobyl-derived Pu outside the accident

area, the density of  $^{239,240}\text{Pu}$  in all areas in Ukraine has been determined by the Ukrainian Institute of Agricultural Radiology (UIAR) (Kashparov et al., 2003). The result is depicted in Fig. 2a (Kashparov et al., 2003). To understand the structure of contamination outside the accident area, vertical profiles and isotopic compositions of plutonium in soil were in-



Coloured map: from the Ukrainian Institute of Agricultural Radiology. Monochrome: Kashparov et al. (2003).

(a) Water sampling locations and  $^{239,240}\text{Pu}$  contamination in the accident area



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(b) Water sampling locations and  $^{137}\text{Cs}$  contamination in Ukraine

**Figure 2.** Contamination map with (a)  $^{239,240}\text{Pu}$  in the Chernobyl accident area on 2000 and (b)  $^{137}\text{Cs}$  in the whole Ukraine (corrected for radioactive decay to 10 May 1986). In Fig.2a, numbered denote studied sites for plutonium concentrations (see Figure 5 and Table 4). The map of Fig. 2a has been reproduced and modified from Kashparov et al. (2003) by permission of the Elsevier Ltd. and UIAR. The map of Fig. 2b is from De Cort et al. (1998), prepared by H. Terada, by permission. Copyright also belongs to EC/IGCE. Water sampling locations and some names have been placed by the present authors.

**Table 3.** Surface soil contamination with  $^{239,240}\text{Pu}$  in Ukraine outside the Exclusion Zone (MEXT, 1999-2003)

No.	Region	Distance from ChNPP (km)	Type of farmland; Type of soil	Note	Pu-239,240 (Bq/m <sup>2</sup> )		Chernobyl Contribution (%)
					Density	Standard Deviation	
1p*	Kyiv	47	Meadow; Soddy-podzolic sandy-loam	Western trace	141	12	46
3p	Zhitomyr	94	Meadow near the forest; Meadow light loamy	Western trace	58	6	25
5p	Zhitomyr	126	Pasture; Soddy sandy-loam	Western trace	74	7	27
7p	Zhitomyr	168	Pasture; Soddy sandy-loam	Western trace	148	21	30
9p	Rivne	239	Pasture; Meadow light loamy	Western trace	86	9	19
14p	Kyiv	30	Meadow near the forest; Soddy-podzolic	Southern trace	1500	450	83
15p	Kyiv	52	Pasture; Peaty	Southern trace	620	170	70
16p	Kyiv	75	Pasture; Peaty	Southern trace	500	55	39
17	Kyiv	84	Arable land; Soddy-podzolic	Southern trace	150	14	61
18	Kyiv	105	Meadow; Peaty	Southern trace	233	10	70
19	Chernigiv	62	Meadow; Soddy light-loamy carbonate	Eastern direction	69	4	44
20	Chernigiv	75	Meadow; Soddy-podzolic	Eastern direction	80	4	34
21	Chernigiv	98	Meadow; Soddy-podzolic	Eastern direction	95	9	40

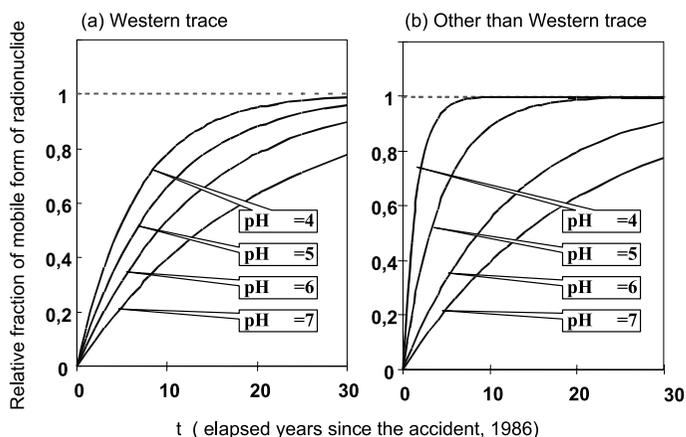
investigated in several locations in the western and southern areas in Ukraine by the project of MEXT (Japan Ministry of Education, Culture, Science, and Technology, 1999-2003). Both areas correspond to major radioactive plumes or their traces. Table 3 presents the project's findings. In the western locations, the spatial densities of  $^{239,240}\text{Pu}$  were 60-150 Bq m<sup>-2</sup>, which is equivalent or slightly higher than those for mid Europe (60 Bq m<sup>-2</sup>) due to the nuclear weapon tests in 1950-60's. In the southern locations, densities of  $^{239,240}\text{Pu}$  were 150-1500 Bq m<sup>-2</sup>. The contribution of Chernobyl-derived Pu in the ground of Ukraine was determined based on the ratio of the radioactivity of  $^{238}\text{Pu}$  to that of  $^{239,240}\text{Pu}$ . The contribution of Chernobyl  $^{239,240}\text{Pu}$  to the total  $^{239,240}\text{Pu}$  was comparative to that of the weapon test-derived Pu in the western locations (19-46%), and was found to be higher in the southern locations (39-83%). However,

it should be noted that the number of sampling sites was limited and that the heterogeneity of the Chernobyl fallout was high.

### Behavior of Chernobyl-derived Pu in the environment

#### *Dissolution of fuel particles in soil*

Because Pu isotopes were released in the form of fuel particles in the accident, it is important to understand the dissolution of fuel particles in soil for our analysis of the behavior of plutonium. Kashparov et al. (2004) investigated the dissolution process of the fuel particles by examining i) the properties of hot particles and ii) the properties of soil. Two types of fuel particles were produced at the time of the accident: "non-oxidized fuel particles" and "oxidized fuel particles." The former were formed by the me-



**Figure 3.** Dynamics of relative increase of radionuclides in mobile form from the fuel particles matrix depending on the soil acidity (pH, H<sub>2</sub>O) for the different traces of the Chernobyl fallout. Reproduced and modified from Kashparov et al. (2004) by permission of the Elsevier Ltd.

chanical destruction of nuclear fuel (UO<sub>2</sub>), and they were mainly released on the first day of the accident by an explosion, and contributed to the west plume of contamination. The latter were formed during the subsequent reactor fire. As a result, mechanically damaged particles in the reactor were oxidized to UO<sub>2+x</sub> with relatively large excess of oxygen atoms. They were released in the days following the accident after annealing in the reactor and contributed to the northern and southern plumes (Kashparov et al., 2004). Generally, plutonium in irradiated nuclear fuel in a nuclear reactor of water coolant is considered to be in a tetravalent state, forming solid solution with uranium dioxide as (Pu, U)O<sub>2+x</sub> with a limited excess of oxygen atoms (Arai, private communication; Olander, 1976). However, there is no reported direct evidence about oxidation state of Pu in the two types of fuel particles released in the Chernobyl accident.

The non-oxidized fuel particles were more resistant to weathering dissolution, due to organic acid in soil, than the oxidized particles. This is because oxidation causes superficial cracking of the particles leading to an increased dissolution rate (Kashparov et al., 2000). The regional variability of soil type (or soil acidity) was another factor in dissolution of the fuel particles. The empirical relationships between soil acidity and the dissolution rate of fuel particles are given in Fig. 3 (Kashparov et al., 2004). They observed that the non-oxidized particles in the west plume deposited on peat soils (pH=5.2-5.5) and der-

no-podzolic soils (pH=5.6) were best preserved, more than 70% remaining in 2000, whereas the other particles were dissolved by this time. This fact is significant because the Chernobyl-Pu would not begin to migrate through the ecosystem until dissolution of the fuel particles had begun. From this perspective, the importance of the role of organic acid in controlling the behavior of Chernobyl-derived Pu is quite clear (Kashparov et al., 2000; Kashparov et al., 2004).

### Migration of Pu in soil

#### (1) Vertical profile

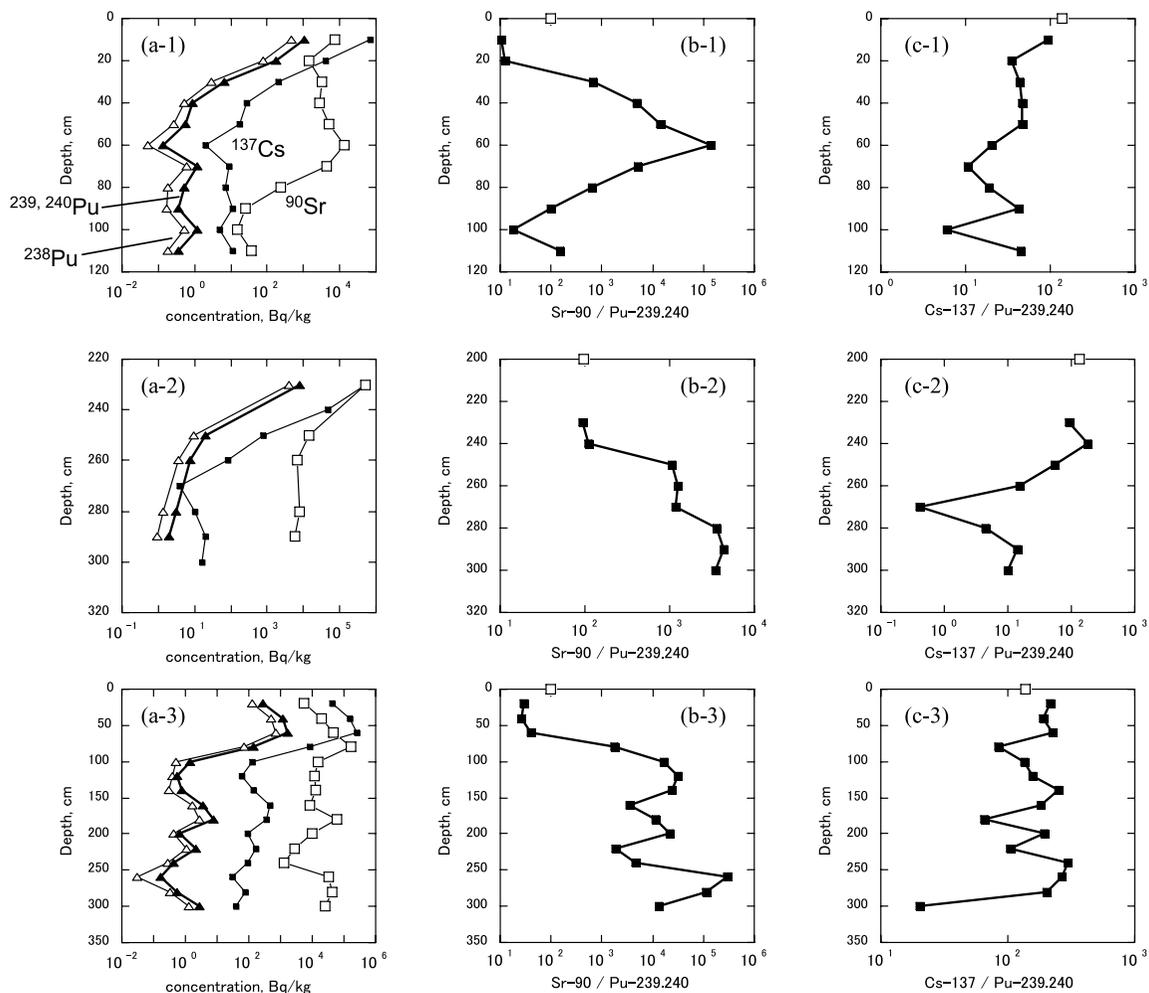
##### Studied sites in the accident area

Figure 4 shows vertical profiles of Chernobyl-derived radionuclides in selected sites in the accident area. The sampling sites can be described as follows (MEXT, 1999-2003). Site 1, located 4 km to the north of the power plant, has non-disturbed sandy soil and turf of high soil acidity. The <sup>239,240</sup>Pu contamination density was 40-100 kBq m<sup>-2</sup>. Sites 2 and 3 were close to each other, 2 km west of the power plant, in an area greatly affected by the West Plume, and which has been called the "Red Forest." At site 2 was soil strata under a trench, in which highly contaminated trees and other wastes (not specified) produced by the accident were buried.

Leaching from those buried materials caused high radioactivity in the deep soil strata. The top layer (0-40 cm) of site 3, as well as other plots in this area, was covered with 'clean' river sand for mitigation of radioactivity after the accident. The soil layer at a depth of 40-80 cm corresponded to the original surface layer, consisting of a humus layer, and it contained the heaviest radioactive fallout attributable to the accident in the vertical sub-samples.

#### Features of vertical profiles

The Chernobyl-derived Pu is predominantly distributed in the upper soil horizons in the case of undisturbed soil (Pavlotskaya et al., 1991; Knatko et al., 1996). Most of the <sup>239,240</sup>Pu was confined within 60 cm of the surface in the studied sites in the Exclusion Zone described above. Specifically, the top soil within about 10 cm of the surface and the litter layer were found to be the most significant Pu-containing strata. Such uneven distribution is commonly found



**Figure 4.** Depth profile of radionuclide concentrations and their relative abundances in selected locations in the Exclusion Zone. Concentrations are shown in sub-plots a. Abundances in sub-plots b and c for  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  normalized for  $^{239,240}\text{Pu}$ . Legends in sub-plots a-2 and a-1 are as those in a-1. In sub-plots b and c, radioactivities have been corrected for disintegrations to the time of the accident (April 26, 1986). In sub-plots b and c, open square denotes abundance in the reactor core inventory at the time of the accident. In notations a-i, i denotes the ID number of sampling sites, and the same for b-i and c-i. See text for the sites. Data from MEXT (1999-2003) by permission.

in the case of weapon tests-derived plutonium (Bunzl et al., 1998a). In a vertical profile in forest soil from southern Germany, more than 72% of the  $^{239,240}\text{Pu}$ , originating from weapon-tests, was concentrated in the litter/humus (decomposed organic matter in soils) layer and the upper 2 cm soil layer. Sequential extraction revealed that 81% of that Pu was in an organically bound form (Bunzl et al., 1998a).

Thus, the vertically uneven distribution of Pu of both origins can be attributed to the affinity of plutonium for natural organic matter. In the Chernobyl forest, a large portion of the plutonium was also

found in an organic matrix. In contrast,  $^{90}\text{Sr}$  exhibited a different vertical profile from plutonium, being less concentrated in the upper soil horizons (Fig. 4 b-1, b-2, b-3). In a sample taken from a different site than those of Fig. 4, the sequential extraction findings were consistent with this pattern (Sanada, unpublished data). Soil samples were collected from a forest near Lake Glubokoye, located 6 km north of the power plant. The site received concentrated fallout of fuel particles in the days following the accident. Strontium-90 was found mostly in phases that were “acid soluble” (extractable with  $\text{CH}_3\text{COOH}$ ) and

Fe/Mn (hydr)oxides ( $\text{NH}_2\text{OH} \cdot \text{HCl}$  extractable), while plutonium isotopes were found in the less soluble phases “organic phase” ( $\text{H}_2\text{O}_2$  and  $\text{CH}_3\text{COONH}_4$  extractable) and “residual phase” comprising the decomposed matrix with HCl and HF. Goryachenkova et al. (1991) also reported that an organic component (free humic acids and their compounds with Ca, Fe, Al and others) was the most important fraction for Pu in various types of soil samples including Chernobyl fallout, as well as hydroxides of Fe and Al.

## **(2) Infiltration process**

### **Relative mobility in infiltration**

Although the greater portion of the plutonium remained in the upper soil layers, as described above, a small amount of the plutonium did infiltrate to deeper layers. A concurrent variation in  $^{239,240}\text{Pu}$  and  $^{238}\text{Pu}$  radioactivity concentrations suggests that this infiltrating plutonium was of Chernobyl origin (Fig. 4, a-1, a-2, a-3), because the weapon test-derived Pu contains little  $^{238}\text{Pu}$  (Table 2).

To compare the mobility of different radionuclides (Pu,  $^{137}\text{Cs}$ , and  $^{90}\text{Sr}$ ), we normalized their radioactivity concentrations to that of  $^{239,240}\text{Pu}$ , and compared them with ratios of radionuclides in the nuclear fuel in the Chernobyl nuclear reactor at the time of the accident (hereafter “the fuel ratio”). All locations in the Red Forest, where the data in Fig. 4 were obtained, were exclusively contaminated with fuel particles. Therefore, comparison of Fig. 4 b-1, b-2, and b-3 provides an insight into the relative mobility of the radionuclides after deposition.

The normalized concentration of  $^{90}\text{Sr}$  was lower than the fuel ratio, except in the upper soil layers, indicating that more of the strontium migrated away. In the deeper layers, the normalized concentration of  $^{90}\text{Sr}$  was increased, except in layers far deeper than 60 cm (Fig. 4 b-1), suggesting that  $^{90}\text{Sr}$  has greater infiltration capacity than  $^{239,240}\text{Pu}$ . Dewiere et al. (2004) investigated the mechanisms allowing the large filtration capacity of  $^{90}\text{Sr}$ . In the case of  $^{137}\text{Cs}$ , the normalized concentration was generally comparable to the fuel ratio (Fig. 4 c-1, c-2 and c-3). In these sites, the migration capacity of  $^{137}\text{Cs}$  seemed to be generally comparable to that of  $^{239,240}\text{Pu}$ . However, a more detailed analysis revealed that in some cases the normalized concentration of  $^{137}\text{Cs}$  gradually decreased with depth (Fig. 4 c-1 and c-2).

### **Forms of radionuclide in infiltration**

Using a soil sample collected from a forest soil in the Chernobyl accident area, Hanzawa and others (unpublished data) investigated the role of colloids in the migration of Chernobyl-derived radionuclides in soil by ultrafiltration using extractants with distilled water, which were considered to be mobile in the soil layer. They found that a high proportion of  $^{239,240}\text{Pu}$  was in the form of colloids with a nominal molecular weight of greater than 1000 daltons (98% of the extracted  $^{239,240}\text{Pu}$ ). The colloid proportion was lower for  $^{90}\text{Sr}$  (55%) and even lower for  $^{137}\text{Cs}$  (26%). This field evidence suggests that plutonium preferentially associates with large colloids to a greater extent than do other radionuclides.

Goryachenkov et al. (1991) stated that fast transport of plutonium in soil occurs in a form of soluble complex of Fe and Al with fulvic and small molecular acids. To their perspective, the amount of Pu in these compounds is limited so that migration of soluble Pu in soil is insignificant. However, this question, to quantify plutonium migration facilitated by mobile species such as organic colloids, has long been a subject of study (e.g. Dai et al., 2002; Francis, 2007).

### **Behavior of plutonium in the aquatic environment**

#### **(1) Fluvial environment**

MEXT (1999-2003) conducted an extensive survey of the concentrations of plutonium and strontium-90 in river water along the Dnieper River system from the Chernobyl Nuclear Power Plant to the Black Sea (see the map of Fig. 2b from De Cort et al., 1998), and also in the streams and lakes in western Ukraine (see the map of Fig. 2a from Kashparov et al., 2003). The survey conducted in 2001 and 2002 was carried out by the Ukrainian Institute of Agricultural Radiology (UIAR) under the management of the Nuclear Safety Research Association (NSRA) of Japan and the International Chernobyl Center (ICC) of Ukraine. They found that there still were water bodies highly contaminated with plutonium in the vicinity of the power plant. The relative immobility of plutonium in the soil environment was also noted in the fluvial environment. Along the Dnieper River, the concentration of  $^{239,240}\text{Pu}$  steadily decreased with distance along the river. By contrast, the concentration of  $^{90}\text{Sr}$  showed a limited decrease with distance. Its fluvial transport accounts for 25% of total input for the budget of  $^{90}\text{Sr}$  in the Black Sea in the first 10

years after the accident (Kanivets et al., 1999).

This difference in mobility among the radionuclides is reflected in the form of transportation in the fluvial environment. While  $^{90}\text{Sr}$  is transported exclusively in dissolved form, when  $^{239,240}\text{Pu}$  is transported in river water it is fractionated into a dissolved form and a suspended form (Fig. 5).

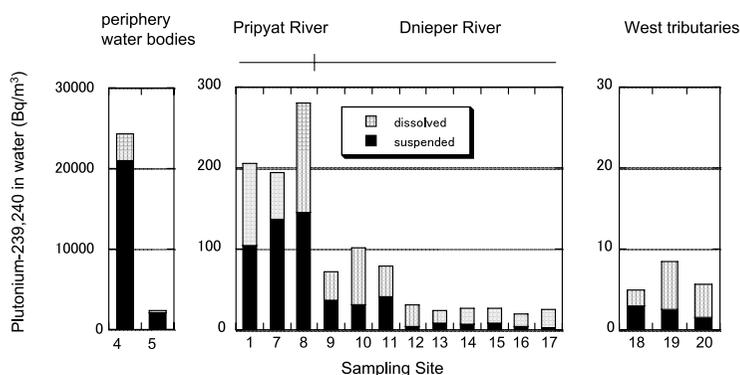
It was found that the fraction associated with suspended material varied along a river course largely (Fig. 5). This variation may be due to i) a supply of  $^{239,240}\text{Pu}$  in suspended material from the contaminated ground in localized source areas ("hot spots"), and ii) a decrease in the concentration of suspended material due to sedimentation. Suspended material held more than half (50-90%) of the total  $^{239,240}\text{Pu}$  in river water in periphery water bodies (Sites #4 and 5) and in rivers in the accident area (#1, 7, and 8). In the Kiev Reservoir (#9-11), the fraction became lower (40-60%), probably because of sedimentation. The concentration of the suspended material decreased to 1-3 mg l<sup>-1</sup> in the reservoir, while it was in a range of 8-20 mg l<sup>-1</sup> in the precedent river water (#1, 7, and 8). Interestingly, a specific radioactivity of  $^{239,240}\text{Pu}$  per unit weight of suspended sediment was higher at several sites in the reservoir than that in precedent river water. This may have been caused by segregation of finer suspended particles during sedimentation. Another possibility is the contribution of phytoplankton in the reservoir that can adsorb plutonium (S.E. Levchuk, private communication; MEXT, 1999-2003).

In the distant reach of the Dnieper River from the accident area, the fraction of  $^{239,240}\text{Pu}$  associated with suspended material gradually went down (15-35%, #12-16; note that #17 was in saline water condition). This was associated with a decrease of the specific radioactivity of suspended  $^{239,240}\text{Pu}$  and an increase of the concentration of suspended material. On the other hand, the concentration of dissolved  $^{239,240}\text{Pu}$  was almost unchanged in the reach. These observations suggest that sorption of dissolved  $^{239,240}\text{Pu}$  onto newly supplied 'clean' suspended

matter did not occur distinctly. This is an instance that dissolved  $^{239,240}\text{Pu}$  becomes important in a fluvial transport over a long distance. Further experimental results are required to consider whether this phenomenon is related to irreversibility of sorption of suspended  $^{239,240}\text{Pu}$  and/or stability of dissolved  $^{239,240}\text{Pu}$  due to complexation with humic substances.

In research unrelated to the Chernobyl accident, Eyrolle et al. (2004a) also reported a significant role of suspended material in fluvial transport of plutonium. They showed that 80 % of the plutonium isotopes in the Rhône River, which originated from both the weapon tests in the atmosphere and from the discharge from a nuclear fuel reprocessing plant, were bound to the suspended material.

High affinity for solid phase of plutonium was similarly reported in the fresh water sediment. In bottom sediment collected from the Pripyat River in 1999 in the vicinity of the power plant, a large depletion (~70%) relative to the "fuel ratio" was found for  $^{90}\text{Sr}$  in terms of the inventory of radionuclides in the sediment core sample (Sanada et al., 2002). The sequential extraction for the sediment core sample



**Figure 5.** Concentration of  $^{239,240}\text{Pu}$  in the Pripyat River and the Dnieper River system. Dissolved components were filtrate by 0.45 mm pore filter, suspended components were residue on the filter. Samples were collected and analyzed in 2001. Note differences in the scale of the vertical axis. A figure in km denotes distance from the Chernobyl Nuclear Power Plant along stream (negative: upstream of the power plant; positive: downstream). Site numbers correspond to following points shown in Figs. 2a and 2b: 4. Left bank stream (-3.5km), 5. Cooling Pond (-), 1. Pripyat(-4 km), 7. Chernobyl(16 km), 8. Ivanika (19 km), 9. Entry into Kiev Reservoir (31.4 km), 10. Northern Kiev Reservoir (59 km), 11. Mid of Kiev Reservoir (68 km), 12. Entry into Kanev Reservoir (169km), 13. Entry into Kremenchuk Reservoir (242 km), 14. Dniprodzerzhinsk Reservoir (380 km), 15. Dni-provske Reservoir (398 km), 16. Kakhovske Reservoir (515 km), 17. Coast of the Black Sea (545 km), 18. Selets (the Goryn River,-243 km), 19. Za-richya (The Styr River, -277 km), 20. Turijsk (The Turiya River, -387 km). Data from MEXT (1999-2003) by permission.

showed that 90 % of  $^{239,240}\text{Pu}$  was present in the least soluble phase, and its 2% in the most soluble phase. In the case of  $^{90}\text{Sr}$ , the fractions were 37% and 15%, respectively.

## (2) Lacustrine environment

MEXT (1999-2003) also conducted a survey of the  $^{239,240}\text{Pu}$  concentrations in several lakes in western Ukraine, in cooperation with UIAR and NSRA. This area was affected by the Western Plume on the day of the accident. In the following, an apparent distribution coefficient means a following concentration ratio:

$$K_d = C_{ss}/C_w,$$

where,

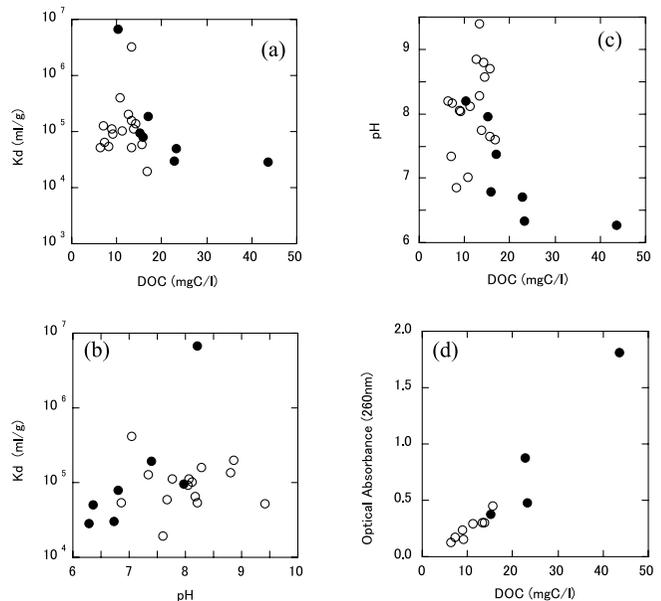
$K_d$ , apparent distribution coefficient (ml/g)

$C_{ss}$ , radioactivity concentration of a radionuclide of interest in suspended solids (Bq/g)

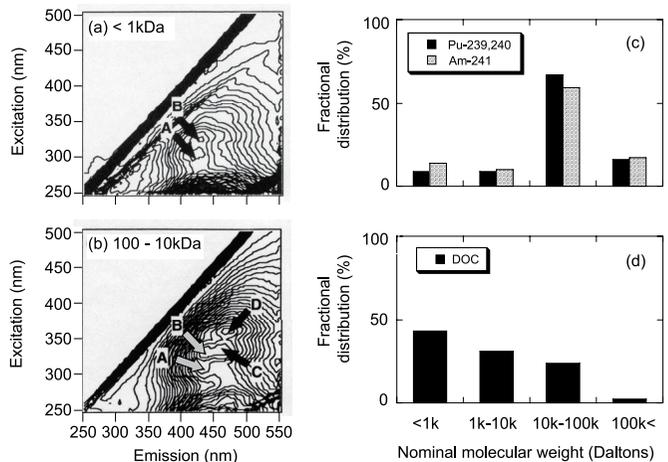
$C_w$ , radioactivity concentration of a radionuclide of interest in filtrated water (Bq/ml).

Water chemistry seems to act as a modification factor in the fractionation of Pu in the lacustrine environment. The apparent distribution coefficient ( $K_d$ ) of suspended and dissolved  $^{239,240}\text{Pu}$  in the studied lakes exhibited lower values with higher dissolved organic carbon (DOC) concentrations and with lower pH (Fig. 6a, 6b, closed circles). A decrease in pH with increased DOC in lakes was also found (Fig. 6c, closed circles), and there was a good correlation between the DOC concentration and optical absorbance at a wavelength of 260 nm (Fig. 6d, closed circles), this absorbance generally indicating dissolved humic substances (Stevenson, 1982). These results suggest that dissolved organic matter, most probably humic substances, helped stabilize dissolved plutonium in the lake waters. Further support for this comes from the findings by Matsunaga et al. (2004) using ultrafiltration. They showed that more than 50% of dissolved plutonium was associated with dissolved organic matter in lakes and streams (Fig. 7c) in the accident area.

Comparing to the data from river waters (MEXT, 1999-2003), the fractionated amount of  $^{239,240}\text{Pu}$  into the dissolved and suspended forms in lakes was very different. Namely,



**Figure 6.** Relationship between apparent distribution coefficient of  $^{239,240}\text{Pu}$  and water quality in the aquatic environment in western Ukraine, the accident area, the Pripjat River, and the Dnieper River. Closed circles : lake locations. Open circles: stream locations. Data from MEXT (1999-2003) by permission.



**Figure 7.** Three-dimensional fluorescence spectra and distribution of dissolved  $^{239,240}\text{Pu}$  and  $^{241}\text{Am}$  for colloids of different molecular size components in stream water from the accident area (the Sahan River, 6 km west of the power plant). The retentate solution of 10-100 kDa (b), that includes dissolved Pu and Am mostly (c), had peak positions at different wave lengths (C, D) besides to those (A, B) of the smallest size fraction (a). In the right hand subplots (c and d), fractional distribution means a fraction of each component to the sum of radioactivities found in dissolved phase filtrated by  $0.2 \mu\text{m}$  pore filter. Reproduced and modified from Matsunaga et al. (2004) by permission from a publisher.

relatively higher dissolved amounts were found in the lacustrine environment. However, the apparent distribution coefficient of  $^{239,240}\text{Pu}$  of the dissolved and suspended components in lakes and in streams did not differ greatly (Fig. 6a and 6b, comparison of closed (lakes) and open (river) circles) with a few exceptions. Thus, the affinity of plutonium for suspended solid did not vary widely by lakes and rivers. Low concentrations of suspended solid (0.8-1.1 mg/l) (MEXT, 199-2003) in the studied lakes seem to be related to a fractionation biased towards the dissolved form.

Looking at other instances of a dissolved phase of plutonium in freshwater, a prominent colloidal component appears to be common. In the case of  $^{239,240}\text{Pu}$  in the River Rhône, colloidal compounds (2-450 nm) accounted for 60 % of the dissolved (<450 nm) plutonium in the river water (Eyrolle et al., 2004b).

### Characterization of natural organic matter in the accident area

Efforts have been made to characterize the dissolved organic matter in surface water in the Chernobyl accident area in terms of the fluorescence properties (Suzuki et al., 1997), its molecular size distribution (Nagao et al., 1997a), its functionality (Nagao et al., 2004), and its sources (Nagao et al., 2004). Here, we briefly review the findings from these investigations.

#### Water chemistry

Table 4 lists key parameters of the water chemistry for the Pripjat River, its tributaries (the Sahan River and the Uzh River), a periphery lake, and a downstream reservoir (Fig. 2a, 2b). These data were derived from field observations made between 1995 and 1999 (Matsunaga et al., 1998; Ueno et al., 2003;

Matsunaga, unpublished data). The pH values of surface waters were between 6.8 and 9.4. The DOC concentration ranged from 7 to 18 mgC l<sup>-1</sup>. A higher concentration of 36 mgC l<sup>-1</sup> was recorded at the Sahan River, in the spring of 1998. This high value may be related to snow melts. In the streams, no apparent relation between pH and DOC was observed. Based on a limited number of observations, high concentrations of DOC were associated with low pH values in conditions of stagnant or low flow rates, e.g., in the lake and in the reservoir (see also Fig. 6c). The ionic strength was generally as low as 0.002-0.004. The most abundant cation and anion dissolved in water in terms of the equivalent concentrations were Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup>, respectively. Each accounted for about 65% of the total concentrations of cations and anions, respectively.

#### Fluorescence properties and Functionality

Recently, the fluorescence properties of HS can be studied by means of three-dimensional spectroscopy (Nagao et al., 1997b). By applying this method to stream waters from the Chernobyl area, Suzuki et al. (1997) found that the samples can be characterized by two fluorescence maxima: 225-240 nm (excitation wavelength)/430-440 nm (emission) and Ex.295-300 nm/Em.430-435 nm. They reported that these positions were similar to those of isolated soil fulvic acid. Their study with ultrafiltrated samples suggested that fluorophores of the peaks mostly consisted of a component less than 5000 daltons.

Gel permeation chromatograms derived from the fluorescence detection at excitation 320 nm and emission 430 nm of the Chernobyl aquatic humic substances after ultrafiltration suggested that the fraction having a nominal molecular size of less than 5000 daltons is dominant (58-74%) in several streams at different seasons (April and September) (Nagao et al., 1997a). In each river system studied, the peak height ratios of each molecular size fraction correlated with each other. However, the peak height ratios were different between the river systems, along with the fluorescence intensities and DOM concentrations. A similar phenomenon was found in the study of Japanese streams (Nagao et al., 1997c).

Nagao et al. (2004) obtained information about functional moieties of aquatic humic substances from the Chernobyl area (the Pripjat River and the Sahan River). In the

**Table 4.** Selected parameters of water quality in surface waters on the Chernobyl accident area

Site No.	Water body	pH	DOC (mgC l <sup>-1</sup> )	Ionic strength
7	Pripjat River	7.3-8.9	7-18	0.004-0.008
2	Sahan River	6.9-7.6	8-36	0.002-0.004
6	Uzh River	7.7-9.4	8-14	0.003-0.004
3	Glubokoye Lake	6.8-8.3	14-17	0.002-0.003
10	Kiev Reservoir	8.4-8.8	9-13	0.004-0.005

Site No. corresponds to the site number shown in Figure 2.

$^{13}\text{C}$ -NMR spectra for the humic acids, peaks attributable to aromatic and carboxylic carbons were predominant. This observation is quite similar to those for aquatic humic substances from other areas, such as from a river in a marsh in Scotland. Moreover, they found that the content of the aromatic carbons for the Chernobyl humic acids (35-39%) was lower than that for IHSS standard humic acids (45%).

#### **Sources of humic substances in surface water**

In the studies mentioned above, they analyzed the carbon isotope ratios ( $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$ ) of aquatic humic substances from the two streams in the Chernobyl accident area after purification into humic (HA) and fulvic acids (FA) (Nagao et al., 2004). The ecosystem in the area received a pulse input of  $^{14}\text{C}$  at the time of accident (Kovaliuikh and Skripkin, 1998), and the accident increased the radiocarbon content in the litter and the surface soil by one order of magnitude compared with a non-contaminated area. This situation provided an insight into the sources and cycling of aquatic humic substances in the area. The  $\delta^{13}\text{C}$  for HA and FA ranged from -28.0‰ to -28.7‰, which were comparable to those reported in similar watersheds consisting of peaty soils and bogs. In spite of the accidental input of  $^{14}\text{C}$ , the relative abundances of radiocarbon ( $\Delta^{14}\text{C}$ ) in the Chernobyl samples were much lower than those of humic substances from the Amazon and the Suwannee Rivers. The latter samples are considered to be influenced by the 'bomb' carbon due to a fast humification rate. Thus, Nagao et al. (2004) estimated that the aquatic humic substances in Chernobyl surface water may be largely derived from aged groundwater humic substances.

#### **Linkage between HS properties and Pu behavior**

It has been a difficult task in field research to link properties of humic substances to actinide behavior in the aquatic and the terrestrial environment. Following two instances strongly suggest that a research of the interaction of actinides with humic substances in field must be accompanied by characterization of humic substances, not simply by its presence.

In the previous study of the association of dissolved Pu and Am with aquatic humic substances of different sized components, estimates were made regarding the possible relation to the associated fluorescence peaks (Matsunaga et al., 2004). This esti-

mation was based on a combined examination of 3-D fluorescence spectra for different colloidal size fractions and a radiochemical analysis of plutonium distribution over the fractions. Characteristic fluorescence peaks were found for size components larger than 10 kilo-daltons of nominal molecular weight (Fig. 7a, b). Plutonium and americium were preferentially found in a component of 10k-100k daltons (Fig. 7c). This suggests a possibility that those peaks may be responsible in part for the association of actinides with humic substances. As another interest, the component (10k-100k daltons) was not the most distributed one with respect to DOM (Fig. 7d). Similarly, in the soil solution system, the most important colloidal fractions for  $^{239,240}\text{Pu}$  (10k-100k and 1k-10k daltons) held only the half of DOC (Hanzawa et al., unpublished data).

In a recent study on experimental Pu association with aquatic humic substances of various origins, Nagao et al. (2007) reported inconsistency of the size distribution between complexed Pu and the amount of humic substances therein. The size distribution of the aquatic humic substances themselves, including isolated fulvic and humic acids, differed each other depending on recharge areas and geologic media. They found a general, positive relationship between Pu and humic substances with molecular size of 5k-100k daltons. On the contrary, humus from the Suwannee and Nordic rivers did not follow that relation. They estimated that this exceptional response stems from a regional difference in the amounts of functional groups responsible for Pu complexation.

The migration of actinide nuclides in natural environment has been of special concern for a long time (Silva and Nitsche, 2002; Choppin, 2007). Important reactions to determine actinide solubility in natural water are redox reactions, complexation and sorption to mineral surfaces (Banik et al., 2007). The controlling parameters (pH, Eh, inorganic and organic complexants, colloids, etc.) in these reactions are interrelated, and particularly so in the case of plutonium. The nuclide may exist in multiple oxidation states (III, IV, V, VI) and its solubility is markedly altered by the oxidation state (Silva and Nitsche, 2002; Choppin, 2007). Furthermore, humic substances, which are ubiquitous organic complexants for the nuclide, can play a role in redox reactions as an electron donor (André and Choppin, 2000).

Various methods of phase speciation (adsorbed, ionic, colloidal forms) and oxidation state speciation

(Choppin, 2007) have been employed. For instance, in a study of plutonium and americium leaked from solid waste deposits, the dominant colloidal phase was determined by ultrafiltration and the oxidation state of colloidal Pu was evaluated by isoelectric point measurement of an associated colloidal matrix (Santschi et al., 2002).

In the environment affected by the Chernobyl accident, several phase speciation studies have been conducted for the soil solution (Agapkina et al., 1995; Bunzl et al., 1998b; Hanzawa, unpublished), and for the surface water (Matsunaga et al., 2004). However, as long as the authors have accessed, the only published study of the oxidation state of Pu in the accident area dealt only with speciation modeling (Matsunaga et al., 2004) so far. While several properties of aquatic humic substances have been discussed, there still remains a great lack in analysis that integrates these property data with the migration of plutonium derived from the accident area. Further studies, which incorporate phase and chemical speciation with matrix characterizations, are needed to more fully understand the behavior of Chernobyl-derived plutonium, and to contribute to predict the migration of plutonium in other circumstances.

## Conclusions

The environmental behavior of Chernobyl-derived plutonium in soil and aquatic environments has been reviewed. Following characteristics are revealed by various studies.

1) Released plutonium isotopes were almost entirely contained in fuel particles produced by this accident. Thus, one key element in the migration of Pu was the dissolution of those fuel particles in the environment.

2) The total fallout of  $^{239,240}\text{Pu}$  in 1997 in the open field of the accident area ("Exclusion Zone") was estimated to be  $4.9 \times 10^{13}$  Bq, with the highest density over 4000 times higher than the common baseline level in Europe due to nuclear weapon tests.

3) The contribution of the accident to the total ground Pu contamination was comparable to that of the weapon test-derived Pu in the western locations (19-46% of the total) up to about 400 km from the Chernobyl Nuclear Power Plant, and was found to be relatively high in the southern locations (39-83%) up to about 100 km.

4) The dissolution rate of the fuel particles in soil

was found to be accelerated by soil acidity. In this context, the importance of the role of organic acid in controlling the behavior of Chernobyl-derived Pu has become clear.

5) The Chernobyl Pu distributed over organics-rich surface soil layers has persisted since the accident. Further, the vertical mobility of the Pu in soil was much less than that of the Chernobyl  $^{90}\text{Sr}$ . This relative immobility of plutonium in the soil environment is attributable to its affinity for soil organics, as found in chemical partitioning investigations.

6) The relative immobility of plutonium was also seen in its fluvial transport along the Dnieper River. Dissolved organic matter, most probably humic substances, helped stabilize dissolved plutonium in the lake waters.

7) Aquatic humic substances from the accident area have been characterized by their size distribution, functionality, fluorescence properties, and genesis.

To summarize, limited mobility and solubility of Pu were observed in the studied environment. Humic substances seem to be involved in this limitation in mobility and may be important for its modification. Further researches of phase and chemical speciation tied with matrix characterizations are needed for the Chernobyl accident environment.

## Acknowledgement

The authors are indebted to the Ukrainian Institute of Agricultural Radiology (UIAR), the International Chernobyl Center (ICC), the Nuclear Safety Research Association (NSRA), and the Ministry of Education, Culture, Sports, Science and Technology (MEXT) for their providing the results of their long-term research projects on the behavior of plutonium in the affected area by the Chernobyl accident in Ukraine. Invaluable information about the radiology of Chernobyl-derived plutonium from Dr. S.E. Levchuk and Dr. V.A. Kashparov of UIAR is greatly appreciated. We are grateful to Dr. Y. Hanzawa (JAEA) for providing unpublished data. Dr. Y. Arai of JAEA kindly provided information about the status of Pu in irradiated nuclear fuel. Use of a map of cesium contamination in Ukraine, prepared by Dr. H. Terada of JAEA, has been kindly permitted by Dr. De Cort. We thank for the Elsevier Ltd., the Akadémiai Kiadó, and related authors for giving us permission to reproduce published materials.

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