Fluvial Transport of Chernobyl Plutonium (Pu) to the Black Sea: Evidence from $^{240}Pu/^{239}Pu$ Atom Ratios in Danube Delta Sediments

Michael E. Ketterer[*,1], Sergei B. Gulin[2], Gary D. MacLellan[1] and Wendy J. Hartsock[1]

[1]*Department of Chemistry and Biochemistry, Box 5698, Northern Arizona University, Flagstaff, AZ 86011-5698, USA*

[2]*Institute of Biology of the Southern Seas, 2 Nakhimov Av., IBSS, Sevastopol UA-335011, Ukraine*

Abstract: Sector field ICP-MS has been used to determine $^{239+240}Pu$ activity and $^{240}Pu/^{239}Pu$ atom ratio profiles in a sediment core obtained in 1997 from the Danube Delta region of the Black Sea. The $^{239+240}Pu$ activity profile reveals the presence of a 1963 stratospheric fallout peak, along with two more recent peaks stemming from fluvial transport of Chernobyl Pu through the Danube watershed into the Black Sea. The two recent peaks occur in the early 1990's and are associated with $^{240}Pu/^{239}Pu$ atom ratios as high as 0.307, significantly exceeding the established range of stratospheric fallout ($^{240}Pu/^{239}Pu$ = 0.180 ± 0.014). The Chernobyl-derived $^{240}Pu/^{239}Pu$ features in the core are also associated with elevated ^{238}Pu activities (determined by alpha spectrometry), and $^{238}Pu/^{239+240}Pu$ activity ratios of 0.08-0.10 in excess of the stratospheric fallout signature ($^{238}Pu/^{239+240}Pu$ = 0.04).

Keywords: Black Sea, Danube River, plutonium, isotope ratios, chernobyl, sediments.

1. INTRODUCTION

The Black Sea is one of the most contaminated marine basins in the Northern Hemisphere; since the 26 April 1986 Chernobyl disaster, the Black Sea has been a sink for Chernobyl-associated radionuclides. It has been estimated that ~ 2 PBq of ^{137}Cs were directly deposited by the atmosphere onto the water surface of the Black Sea [1]. Two major rivers, the Danube and Dnieper, account for 75% of the total runoff entering the Black Sea; in the northwestern Black Sea, these two systems account for ~ 95% of the entering fluvial input. The Danube basin generally received lower Chernobyl fallout than other basins such as the Dnieper and Don; however, with a vast catchment area of 817,000 km^2, the Danube represents the largest source of dissolved and particle-associated nuclides that are still being transported into the Black Sea. Between 1986 and 1994, the estimated delivery of ^{137}Cs *via* the Danube was approximately 25 TBq [2].

Most previous papers investigating fluvial transport of Chernobyl debris into the Black Sea have focused on ^{137}Cs and ^{90}Sr [3-5]. Also associated with direct atmospheric fallout as well as fluvial transport, however, are nonvolatile radionuclides from fuel particles, including transuranium elements (Np, Pu, Am, Cm). In a 2002 study, Gulin *et al*. [2] investigated the ^{137}Cs, ^{238}Pu, $^{239+240}Pu$, and ^{241}Am activity profiles in sediments collected from the Danube and Dnieper Deltas. In surface sediments (0-5 cm), a distinct enhancement of ^{137}Cs was evident in the vicinities of the river mouths, with activities diminishing *vs* distance; ^{137}Cs inventories were 1-2 orders of magnitude higher in the deltas *vs* remote locations. Gulin *et al*.'s Danube core [2] revealed a ^{137}Cs activity peak associated with 1963 stratospheric fallout, as well as a more recent, higher-activity peak associated with Chernobyl. The ^{238}Pu and $^{239+240}Pu$ activity profiles exhibited similiar features, dated as 1991 and 1993 from hydrologic data. The presence of high ^{241}Am activities, $^{241}Am/^{239+240}Pu$ activity ratios of ~ 1, and $^{238}Pu/^{239+240}Pu$ exceeding stratospheric fallout ratios all supported the finding that Chernobyl-derived Pu was being transported in an episodic fashion into the Black Sea.

Valuable Pu fingerprinting information can also be ascertained using $^{240}Pu/^{239}Pu$ atom ratios [6]. Since Pu is almost exclusively of synthetic origin, its isotope composition reflects the neutron flux conditions present during its production. The main sources of Pu in the Earth's surface environment have been releases from Pu production reactors (i.e., Hanford), power reactor accidents (e.g., Chernobyl), and fallout from the large-scale atmospheric tests of nuclear weapons that commenced in the early 1950's. Weapons tests released fallout on a local/regional basis from low-yield tests such as those conducted at the Nevada Test Site [7]; however, high-yield, thermonuclear tests injected material into the stratosphere, following which it returned to the Earth's surface and was deposited globally. For stratospheric fallout deposited in the mid-latitude regions, a consistent $^{240}Pu/^{239}Pu$ ratio of 0.180 ± 0.014 (2σ) is observed [8], with other local or regional sources typically having disparate ratios. Unfortunately, discrimination between ^{239}Pu and ^{240}Pu is not possible using conventional alpha spectrometry, as these two isotopes have overlapping energies. Nevertheless, it is now commonplace to use mass spectrometry, particularly inductively coupled plasma mass spectrometry (ICPMS) to distinguish between stratospheric fallout and other sources of Pu in the environment [6, 9].

Compared to stratospheric fallout, Chernobyl debris exhibits much higher $^{240}Pu/^{239}Pu$; Muramatsu *et al*. [10] studied soils from the 30 km exclusion zone near the reactor

*Address correspondence to this author at the Department of Chemistry and Biochemistry, Box 5698, Northern Arizona University Flagstaff, AZ 86011-5698, USA; Tel: +1-928-523-7055; Fax: +1 928-523-8111;
E-mail: Michael.ketterer@nau.edu

1875-0389/10

and found $^{240}Pu/^{239}Pu$ = 0.403 ± 0.009 (1 SD, n=8). Mass spectrometry is an attractive approach for further characterization of the Chernobyl Pu plume in northern and eastern Europe; while some previous Chernobyl-global fallout Pu apportionment studies have examined activity ratios such as $^{238}Pu/^{239+240}Pu$ and $^{241}Pu/^{239+240}Pu$ [11, 12], mass spectrometry can rapidly produce analogous fingerprinting and apportionment information *via* Pu atom compositions. Ketterer *et al.* [13] used sector field ICPMS in a study of Pu atom ratios in soils from Poland; evidence of mixing between global fallout and Chernobyl Pu was found through re-analysis of NdF_3 alpha sources. The atom ratios $^{240}Pu/^{239}Pu$ and $^{241}Pu/^{239}Pu$ both indicated pronounced Chernobyl Pu deposition in northeastern Poland; a sample from one forested location near Plaska (53°54' N, 23°15' E) exhibited $^{240}Pu/^{239}Pu$ = 0.348 ± 0.011, corresponding to a mixture of 81% Chernobyl Pu and 19% stratospheric fallout Pu. This region of northeastern Poland received fallout of non-volatile reactor debris from the first Chernobyl plume that was subsequently detected in Scandinavia. However, Pu in forest soils and peat bogs of southern Poland was dominated by global fallout Pu [13], despite the presence of significant Chernobyl-derived ^{137}Cs in southern Poland. This behavioral difference underscores the differences in the environmental distribution of volatile- *vs* particle-form reactor debris.

In the present work, we have re-analyzed one of Gulin *et al.*'s sediment cores [2] from the Danube Delta. We demonstrate, through use of $^{240}Pu/^{239}Pu$ atom ratios, that recent sediments in the Danube Delta exhibit Chernobyl-derived Pu, and we contrast the fingerprinting information obtained *via* this ICPMS analysis *vs* the existing radiochemical results.

2. EXPERIMENTAL

2.1. Sample Collection and Pre-Processing

A sediment core was collected on May 10, 1997 by IBSS personnel at a location in the Danube Delta (45°12.14'N, 29°50.80 E, 26 meters water depth, 13 km offshore) shown in Fig. (**1**). The sediments were collected with a 30 cm x 30 cm x 60 cm deep box corer; the box core was sub-sampled with a 6.9 cm diameter acrylic tube and sliced into 0.2 – 1.0 cm sections. Each depth interval was dried and ground. ^{238}Pu and $^{239+240}Pu$ were measured previously using alpha spectrometry [2].

2.2. Analytical Measurements

To conserve material, the sediment remaining after the alpha spectrometric analysis was composited from two adjacent 1 cm intervals, producing 2 cm intervals. Samples of 5-8 grams dry sediment were weighed into 180 mL borosilicate glass beakers, and were dry-ashed at 600° C for 16 hours to remove organic matter. After ashing, ^{242}Pu yield tracer (0.007 Bq, prepared from NIST 4334g stock) was added along with 15-20 g potassium pyrosulfate; the sample and flux were thoroughly blended. The mixtures were subsequently fused at 600° C for 3 hours; the cooled, solidified flux was treated with 100 mL of 8 M HNO_3 to dissolve the flux and sample constituents; the remaining residue consisted of white, thoroughly leached SiO_2, which was removed by filtration.

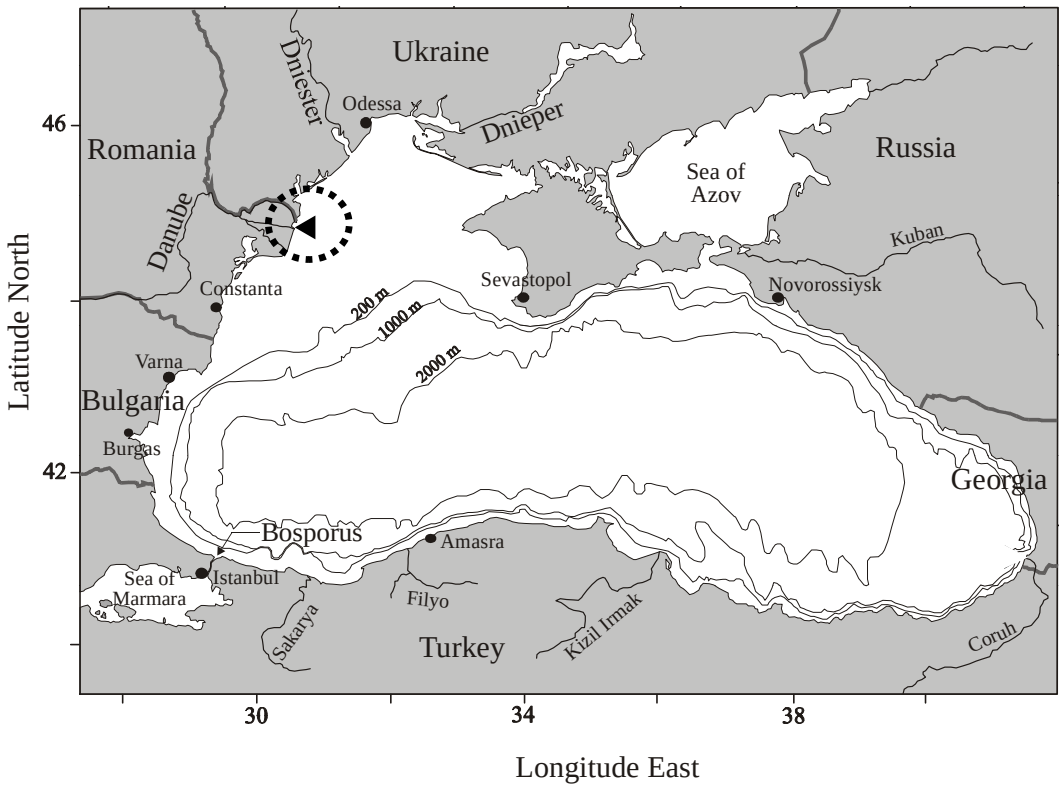

Fig. (1). Map of the Black Sea, depicting the Danube Delta (dotted black circle) and the location where the sediment core was collected in 1997 (black triangle).

Pu was subsequently isolated by extraction chromatography using TEVA resin. 3.0 g of $NaNO_2$ (s) were added to adjust Pu to the +4 oxidation state; then 0.3 grams of TEVA resin (TE-B25-A, 100-150 μm, EIChrom, Lisle, IL, USA) was added to uptake Pu in a batch mode with gentle stirring for 16 hours. The TEVA resin was collected using a 10 mL pipet tip equipped with a glass wool plug to form a resin column. The column was rinsed 3x with 5 mL of 2 M HNO_3, followed by 2 mL of 8 M HCl; these rinse steps removed the vast majority of Th and U. Pu fractions were eluted using the following sequence: 1 mL water, 2 mL of 0.05 M aqueous ammonium oxalate, and 2 mL water.

Pu fractions were analyzed by sector field ICPMS using a VG Axiom MC system equipped with a CETAC U-5000AT ultrasonic nebulizer. The ICPMS instrument was operated in the single collector, electron multiplier mode. The low-resolution mode ($m/\Delta m \sim 400$ at 10% height) was used. A tuning solution containing 0.05 μg/L U was used to adjust and optimize the experimental conditions before analysis. Solutions were supplied to the ultrasonic nebulizer by means of a peristaltic pump operating at an uptake rate of 400-500 μL/min. Ion intensities were collected at a single point at the summit of each mass spectral peak with a dwell time of 10 ms; ions monitored were $^{238}U^+$, $^{239}Pu^+$, $^{240}Pu^+$, and $^{242}Pu^+$. The E-scan (electrostatic sector scanning) mode was used to cycle repeatedly between these ions for three to five sequential 90 second integrations. A $^{238}U^1H^+/^{238}U^+$ ratio of 0.00003 was measured, and the $^{238}U^+$ intensity was used with this correction factor to subtract the UH^+ contribution on $^{239}Pu^+$, the correction amounting to ≤ 2% of the total m/z 239 signal. Mass discrimination was 0.7-0.8% per m/z, and corrections were performed using a factor determined based upon $^{238}U/^{235}U$ measured externally for a natural U standard ($^{238}U/^{235}U$ = 137.88). The UH^+ and mass-discrimination corrected ICPMS data were used to calculate $^{239+240}Pu$ activities and $^{240}Pu/^{239}Pu$ atom ratios.

The accuracy of the ICPMS-based $^{239+240}Pu$ activity measurements were assessed through preparation and analyses of two standard reference materials produced from the US National Institute of Standards and Technology (NIST). Seven aliquots of 1.0 grams nominal mass were prepared for each of these materials through the course of the study. For NIST 4353 (Rocky Flats Soil-1), a $^{239+240}Pu$ activity of 8.3 ± 1.4 Bq/kg was found; for NIST 4357 (Ocean Sediment), a $^{239+240}Pu$ activity of 10.7 ± 0.9 Bq/kg was obtained. These compare well *vs* the certified activities of 8.03 ± 0.60 and 10.4 ± 0.2 Bq/kg, respectively. Though these materials are not certified for any Pu atom ratios, the $^{240}Pu/^{239}Pu$ results obtained (0.061 ± 0.003 and 0.227 ± 0.010 for 4353 and 4357, respectively) are concordant with expected $^{240}Pu/^{239}Pu$ in materials containing weapons-grade Pu (NIST 4353) and Pu from latter Sellafield discharges (NIST 4357).

3. RESULTS AND DISCUSSION

Fig. (**2**) depicts core profiles for $^{239+240}Pu$ activities by ICPMS, $^{239+240}Pu$ activities by alpha spectrometry, ^{238}Pu activities (alpha spectrometry), $^{240}Pu/^{239}Pu$ atom ratios, and $^{238}Pu/^{239+240}Pu$ activity ratios. Note that the $^{239+240}Pu$ activity profiles obtained by ICPMS and alpha spectrometry were obtained using separate sub-samples; the alpha spectrometry profile used 1 cm intervals, while the ICPMS profile was obtained using composites of two adjacent 1 cm intervals. Despite this difference in the material analyzed, the two $^{239+240}Pu$ activity profiles are rather similar. In both cases, the 1963 stratospheric fallout deposition maximum is present at a depth of 18-20 cm. Several lines of evidence support the 1963 interpretation of this maximum: i) the Pu ratios in this depth range agrees with the isotopic composition of stratospheric fallout [8]; ii) a ^{238}Pu activity peak is also observed at this depth; iii) the $^{238}Pu/^{239+240}Pu$ activity ratios in this portion of the sediment core are close to the Northern Hemisphere stratospheric fallout activity ratio of 0.04 cited by Mietelski and Was [11]; and iv) the $^{239+240}Pu$ activity peaks also coincide with a ^{137}Cs activity maximum found in earlier studies [2]. The seven ICPMS-analyzed intervals between 14-16 cm and 26-28 cm, inclusive, have $^{240}Pu/^{239}Pu$ = 0.187 ± 0.005 (1 SD), which coincides with the 2σ range of 0.180 ± 0.014 quoted by Kelley *et al*. [8]. In the same depth range of the core, the ten intervals between 14-15 and 24-25 cm analyzed by alpha spectrometry have $^{238}Pu/^{239+240}Pu$ = 0.038 ± 0.005 (1 SD).

The upper portion of the sediment core, commencing at about 12 cm, clearly shows systematic changes stemming from an additional input of non-stratospheric fallout Pu. The vertical profiles of ^{238}Pu and $^{239+240}Pu$ both show double peaks above 12 cm. Associated with these peaks are $^{238}Pu/^{239+240}Pu$ activity ratios and $^{240}Pu/^{239}Pu$ atom ratios that are significantly higher than stratospheric fallout; the highest $^{240}Pu/^{239}Pu$ ratio of 0.307 ± 0.014 was found in the 4-6 cm depth interval. The ^{238}Pu and $^{239+240}Pu$ activity double peaks are also coincident with similar features in the ^{137}Cs and ^{241}Am activity profiles reported previously [2].

It follows that the near-surface double peaks stem from fluvial transport of Chernobyl-associated radionuclides *via* the Danube River, as these peaks exhibit $^{238}Pu/^{239+240}Pu$ and $^{240}Pu/^{239}Pu$ signatures consistent with mixing of Chernobyl debris with stratospheric fallout. As a result of the Chernobyl accident, both volatile fission products (e.g. ^{137}Cs) and non-volatile actinides (U, Pu) were distributed over a widespread area of Eurasia. The non-volatile actinides, along with non-volatile fission products are contained in individual "hot" fuel particles of 1-10 μm aerodynamic diameter [14]; these particles have been previously identified in Poland [11-14] and in Finland [15, 16]. The transport of "hot" fuel particles over distances of up to ~ 1000 km is evident in these previous studies [11-16]. Deposition of non-volatile Chernobyl particles into the Danube watershed occurred during the course of the accident; over subsequent years, material has been eroding from the catchment basin, entering the Danube River, and is thereafter transported towards the Black Sea. The double peak behavior is consistent with annual variations in the Danube's discharge, as has been previously discussed [2].

An initial study of the Chernobyl disaster and its environmental effects was conducted in 1988 by the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) [17]. The USCEAR report depicts the behavior of the plumes released during the course of the accident, which is summarized in Fig. (**3**). It is evident that Plume A traveled in a northwesterly direction from the reactor site and was responsible for the actinides detected in

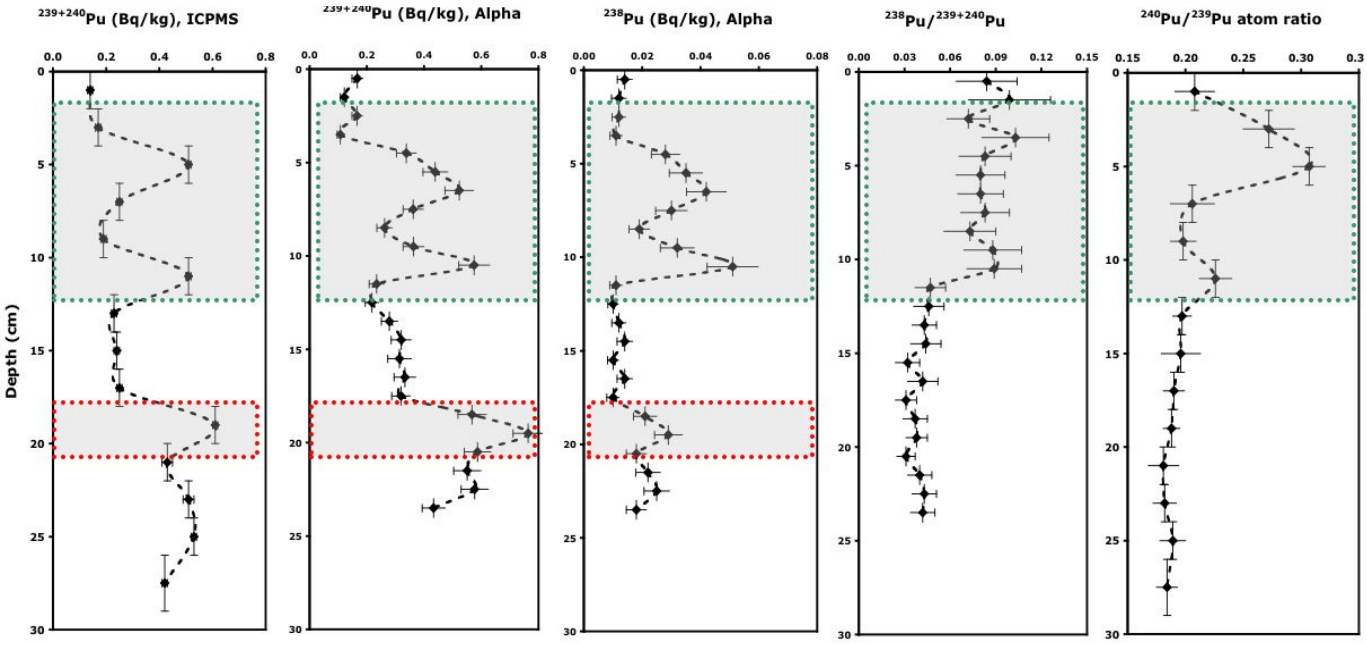

Fig. (2). Depth profiles in the Danube Delta sediment core, for $^{239+240}$Pu activity (ICPMS); $^{239+240}$Pu activity (alpha spectrometry); ^{238}Pu activity (alpha spectrometry); ^{238}Pu/$^{239+240}$Pu activity ratio; and ^{240}Pu/^{239}Pu atom ratio. Activities are reported on a dry-mass basis. The red-bordered gray-shaded region notes the location of the 1963 stratospheric fallout activity maximum, and the green-bordered gray-shaded region depicts the portion of the sediment core exhibiting Chernobyl influence.

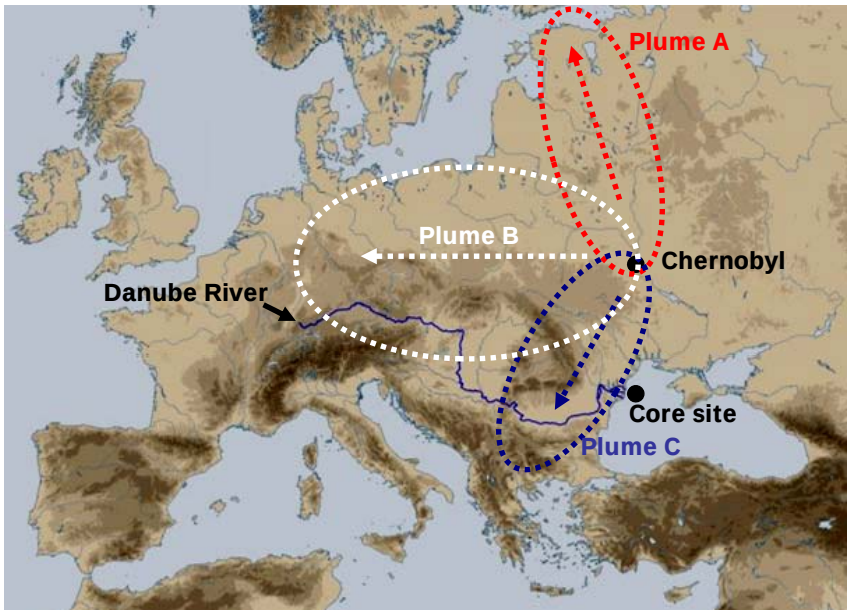

Fig. (3). Map of Europe depicting the direction of travel for Plumes 1, 2, and 3 from the Chernobyl accident. Plume 1 was first detected in Finland and Sweden on April 27, 1986, the day following the accident, and is responsible for the Chernobyl Pu detected in northeastern Poland and Finland [11-16]. Plumes 2 and 3 deposited material into the Danube catchment basin, and are inferred to be responsible for the Pu detected in the Danube Delta sediments in the present study.

northeastern Poland and Finland [11-16]; however, subsequently released Plumes B and C were transported into regions containing the upper and lower portions of the Danube watershed, respectively. We infer that deposition in the Danube watershed from Plumes B and C (Fig. **3**) is responsible for the Chernobyl-derived peaks evident in the Danube Delta core (Fig. **2**).

4. CONCLUSIONS

We have demonstrated using ^{240}Pu/^{239}Pu atom ratios measured by SF-ICPMS, that Chernobyl-derived Pu is present in the Black Sea's Danube Delta sediments. The ^{240}Pu/^{239}Pu ratios in the upper portions of a core collected in 1997 indicate mixing between stratospheric fallout (^{240}Pu/^{239}Pu = 0.180) and Chernobyl debris (^{240}Pu/^{239}Pu =

0.403). The elevated $^{240}Pu/^{239}Pu$ ratios are observed in two early 1990's pulses that coincide with similar features in ^{238}Pu, ^{241}Am, ^{137}Cs, and $^{238}Pu/^{239+240}Pu$ profiles reported previously [2]. The Chernobyl-derived Pu in the Danube Delta sediments evidently originates from non-volatile actinides deposited into the Danube catchment basin during April-May 1986, followed by erosion and fluvial transport to the Black Sea.

ACKNOWLEDGEMENTS

MEK acknowledges support for this work from the US National Science Foundation (EAR-0125934 and CHE-0116804). SBG acknowledges support of the European Commission Programmes EROS-2000 and EROS 21, and the captain and crew of the RV *Professor Vodyanitsky* during the field sampling.

REFERENCES

[1] Egorov, V.N.; Povinec, P.P.; Polikarpov, G.G.; Stokozov, N.A.; Gulin, S.B.; Kulebakina, L.G.; Osvath, I. ^{90}Sr and ^{137}Cs in the Black Sea after the Chernobyl NPP accident: inventories, balance and tracer applications. *J. Environ. Radioact*., **1999**, *43*, 137.

[2] Gulin, S.B.; Polikarpov, G.G.; Egorov, V.N.; Martin, J.M.; Korotkov, A.A.; Stokozov, N.A. Radioactive contamination of the North-western Black Sea sediments. *Estuar. Coast. Shelf Sci.,* **2002**, *54*, 541.

[3] Sansone, U.; Belli, M.; Voitsekovitch, O.V.; Kanivets, V.V. ^{137}Cs and ^{90}Sr in water and suspended particulate matter of the Dnieper River-Reservoirs System (Ukraine). *Sci. Total Environ.*, **1996**, *186*, 257.

[4] Margvelashvily, N.; Maderich, V.; Zheleznyak, M. Simulation of radionuclide fluxes from the Dnieper-Bug Estuary into the Black Sea. *J. Environ. Radioact.*,. **1999**, *43*, 157.

[5] Matishov, G.G.; Matishov, D.G.; Namjatov, A.A.; Carroll, J.; Dahle, S. Artificial radionuclides in sediments of the Don River Estuary and Azov Sea. *J. Environ. Radioact*., **2002**, *59*, 309.

[6] Ketterer, M.E.; Szechenyi, S.C. Determination of plutonium and other transuranic elements by inductively coupled plasma mass spectrometry: A historical perspective and new frontiers in the environmental sciences. *Spectrochim. Acta B,* **2008**, *63*, 719.

[7] Cizdziel, J.V.; Ketterer, M.E.; Farmer, D.; Faller, S.H.; Hodge, V.F. $^{239,240,241}Pu$ fingerprinting of plutonium in western US soils using ICPMS: solution and laser ablation measurements. *Anal. Bioanal. Chem*., **2008**, *390*, 521.

[8] Kelley, J.M.; Bond, L.A.; Beasley, T.M. Global distribution of Pu isotopes and ^{237}Np. *Sci. Total Environ*., **1999**, *237/238*, 483.

[9] Kim, C.S.; Kim, C.K.; Martin, P.; Sansone, U. Determination of plutonium concentrations and isotope ratio by inductively coupled plasma mass spectrometry: a review of analytical methodology. *J. Anal. Atom. Spectrom*., **2007**, *22*, 827.

[10] Muramatsu, Y.; Rühm, W.; Yoshida, S.; Tagami, K.; Uchida, S.; Wirth, E. Concentrations of ^{239}Pu and ^{240}Pu and their isotopic ratios determined by ICP-MS in soils collected from the Chernobyl 30-km Zone, *Environ. Sci. Technol*., **2000**, *34*, 2913.

[11] Mietelski, J.W; Was, B. Plutonium from Chernobyl in Poland. *Appl. Radiat. Isot*., **1995**, *46*, 1203.

[12] Mietelski, J.W.; Dorda, J.; Was, B. Pu-241 in samples of forest soil from Poland. *Appl. Radiat. Isot*., **1999**, *51*, 435.

[13] Ketterer, M.E.; Hafer, K.M.; Mietelski, J.W. Resolving Chernobyl *vs* global fallout contributions in soils from Poland using Plutonium atom ratios measured by inductively coupled plasma mass spectrometry, *J. Environ. Radioact*., **2004**, *73*, 183.

[14] Broda, R.; Kubica, B.; Szeglowski, Z.; Zuber, K. Alpha emitters in Chernobyl hot particles. *Radiochim. Acta*, **1989**, *48*, 89.

[15] Reponen, A.; Jantunen, M.; Paatero, J.; Jaakkola, T. Plutonium fallout in southern Finland after the Chernobyl accident. *J. Environ. Radioact*., **1993**, *21*, 119.

[16] Paatero, J.; Jaakkola, T.; Ikäheimonen, T.K. Regional distribution of Chernobyl-derived plutonium deposition in Finland. *J. Radioanal. Nucl. Chem*., **2002**, *252*, 407.

[17] United Nations Scientific Committee on the Effects of Atomic Radiation. Sources, effects, and risks of ionizing radiation. Annex D, *Exposures from the Chernobyl Accident*. United Nations: New York, **1988**.

Received: June 10, 2010 Revised: July 13, 2010 Accepted: July 14, 2010