

# ICP-MS Studies of Plutonium in the Environment

**Plutonium is distributed globally in the Earth's surface environment as a result of atmospheric weapons tests, nuclear accidents, and nuclear fuel reprocessing. Mass spectrometry (MS), in particular, sector field ICP-MS, now is used widely to determine Pu activities and isotope ratios;  $^{240}\text{Pu}/^{239}\text{Pu}$  is very useful in determining Pu origin. Determination of Pu by ICP-MS involves dissolution, column separation, and the MS determination; detection limits are 0.1–10 fg for each isotope. Applications of the determination of sector field ICP-MS to studies of environmental Pu include discerning sources of contamination near the Chernobyl reactor, and chronology of recent aquatic sediments.**

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## Origins of Environmental Plutonium

Produced through successive neutron capture processes in a reactor or bomb that initially begin with  $^{235}\text{U}$  or  $^{238}\text{U}$ , plutonium (Pu) has become widely distributed in the Earth's surface environment as a result of human activities during the last six decades. With minor exceptions, Pu in the environment is entirely of anthropogenic origin. Plutonium in the Earth's surface environment consists principally of five isotopes:  $^{238}\text{Pu}$  ( $t_{1/2} = 87.74$  y),  $^{239}\text{Pu}$  ( $t_{1/2} = 24110$  y),  $^{240}\text{Pu}$  ( $t_{1/2} = 6563$  y),  $^{241}\text{Pu}$  ( $t_{1/2} = 14.4$  y), and  $^{242}\text{Pu}$  ( $t_{1/2} = 373,000$  y). The isotopes  $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ , and  $^{242}\text{Pu}$  all decay by emission of  $\alpha$  particles, while  $^{241}\text{Pu}$  undergoes  $\beta$  decay to produce  $^{241}\text{Am}$ . The uppermost 30 cm of undisturbed Earth's

crust has  $^{239}\text{Pu}$  concentrations:  $\sim 10^4$ – $10^5$  times greater than natural (neutron capture-produced) concentrations. No evidence to date has identified nonanthropogenic sources for the isotopes  $^{240}\text{Pu}$ ,  $^{241}\text{Pu}$ , and  $^{242}\text{Pu}$ . Approximately 6000 kg of  $^{239}\text{Pu}$ , along with smaller masses of  $^{240}\text{Pu}$ ,  $^{241}\text{Pu}$ , and  $^{242}\text{Pu}$ , has been deposited onto the Earth's surface, mainly as a result of atmospheric weapons tests conducted in the 1950s and 1960s.

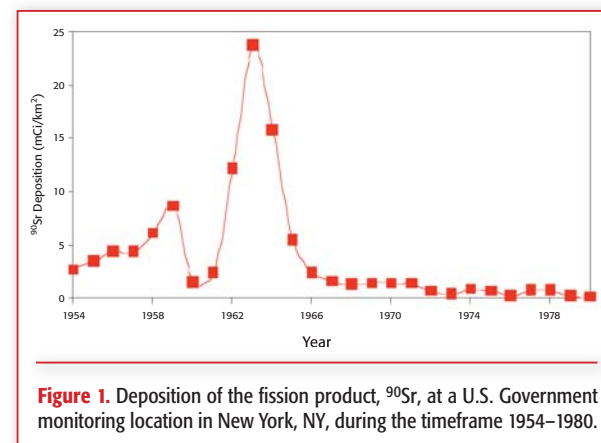
The U.S. conducted low-yield above-ground tests at the Nevada Test Site (NTS) from 1951 to 1962, and high-yield tests were conducted between 1952 and 1962 at the Pacific Proving Grounds. Atmospheric deposition of Pu and associated fission products such as  $^{90}\text{Sr}$  was pronounced

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in the 1950s and 1960s, with a pronounced and well known maximum in the 1963–1964 timeframe, followed by a sharp decrease in deposition. The decrease in deposition coincided with the 1963 Limited Test Ban Treaty, signed by the U.S., former Soviet Union, and

U.K. Figure 1 illustrates the annual deposition of  $^{90}\text{Sr}$  in New York, NY during the time interval 1954–1980 (1). Samples were collected monthly between 1954 and 1976, and quarterly thereafter. Evident in this curve is the small peak in 1959, a “moratorium” in 1960–1961 corresponding to the suspension of U.S. and Soviet testing, and the maximum deposition in 1963. The curve for  $^{90}\text{Sr}$  is a very close approximation of the Pu deposition curve, as both of these species were deposited primarily through the same stratospheric delivery mechanism. A similar deposition chronology is observed at locations worldwide.

While the localized deposition of Pu and fission products was relatively uniform, deposition was highest in the mid-latitude regions of the northern hemisphere, and in regions of highest precipitation, as rain and snow removed fallout radionuclides from the troposphere after their re-entry from the stratosphere. At  $40^\circ$  N, the inventory (cumulative, depth-integrated deposition per unit area) of  $^{239+240}\text{Pu}$  is  $\sim 50$ – $100$  Bq/m<sup>2</sup> and the



**Figure 1.** Deposition of the fission product,  $^{90}\text{Sr}$ , at a U.S. Government monitoring location in New York, NY, during the timeframe 1954–1980.

surface Pu activities are  $\sim 2$  Bq/kg. This activity corresponds to mass concentrations of  $\sim 500$  and  $90$  fg/g for  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ , respectively.

Plutonium isotopic compositions vary according to the mode of production of this element. As examples, “weapons-grade” Pu consists mainly of  $^{239}\text{Pu}$ , and  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratios of  $\sim 0.03$ – $0.07$  are typical. Pu from low-yield fission tests, such as at the NTS, exhibits  $^{240}\text{Pu}/^{239}\text{Pu}$  unaltered from the Pu contained in the original device. The isotopic composition of stratospheric fallout Pu has been compiled by Kelley et al. (2), who used thermal ionization mass spectrometry (TIMS) for measurements of 54 worldwide samples. At  $31$ – $70^\circ$  N, average atom ratios ( $\pm 2$  [[need symbol]]) are:  $^{240}\text{Pu}/^{239}\text{Pu}$ ,  $0.180 \pm 0.014$ ;  $^{241}\text{Pu}/^{239}\text{Pu}$ ,  $0.00194 \pm 0.00028$ ; and  $^{242}\text{Pu}/^{239}\text{Pu}$ ,  $0.00387 \pm 0.00071$ . However, Pu that has been subjected to lengthy neutron activation in power reactors contains relatively larger abundances of the heavier isotopes (3). The Pu isotopic composition, therefore, can provide a “fingerprint” of different sources and is useful

in studies of the movement of a specific point or regional source.

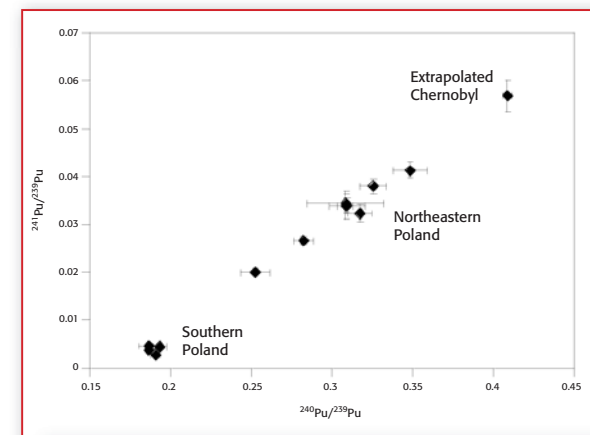
**MS Determination of Pu Activities and Isotope Ratios**

Although counting alpha or beta decay events represents the classical approach that has been used successfully for environmental monitoring studies, determinations of Pu activities and isotopic compositions by MS nonetheless are very attractive. MS is inherently advantageous for determination of long-lived radionuclides; the contrast between MS and decay-counting approaches is detailed elsewhere (4). While determination of <sup>238</sup>Pu in environmental samples by MS generally is precluded by small numbers of atoms and interference from <sup>238</sup>U, MS determinations of <sup>239</sup>Pu, <sup>240</sup>Pu, <sup>241</sup>Pu, and <sup>242</sup>Pu by isotope dilution are all well known. <sup>242</sup>Pu is available readily as a high-purity standard reference material (NIST 4334g), and its use as a spike isotope

is commonplace.

Several MS techniques have been used for the determination of environmental Pu: TIMS, accelerator MS (AMS), resonance ionization MS (RIMS), and inductively coupled plasma MS (ICP-MS). Compared with the aforementioned MS techniques, ICP-MS offers reasonable cost, simple introduction of aqueous solutions, and relatively straightforward operation. Original developments in ICP-MS utilized quadrupole mass analyzers; sector field (SF) mass analyzers applications have become more important in the past 10 years or so. The merits of ICP-MS in radionuclide analysis have long been recognized (5). Arguably, because of its widespread availability, ease of use, relatively low capital cost, and high throughput, ICP-MS is the best-suited MS technique for performing large numbers of Pu determinations in environmental samples.

Applications of ICP-MS in Pu analy-



**Figure 3.** Mixing plot of <sup>241</sup>Pu/<sup>239</sup>Pu versus <sup>240</sup>Pu/<sup>239</sup>Pu for Polish forest soils; error bars are ± one standard deviation.

sis have been expanding rapidly; one major reason is the increasing availability of SF-ICP-MS. For Pu analysis, SF-ICP-MS is superior to quadrupole ICP-MS in three major respects. SF-ICP-MS generally exhibits much better atom-counting efficiencies, on the order of 0.05–0.1% for SF-ICP-MS, versus ≤ 0.01 % for quadrupole ICP-MS. This efficiency improvement enables the analysis of smaller bulk samples containing smaller absolute amounts of Pu. SF-ICP-MS also exhibits a low background signal of <1 cps, as opposed to backgrounds of a few cps typical of quadrupole ICP-MS. Third, with most SF-ICP-MS devices, it is possible to use medium- or high-resolution conditions to check for many interfering polyatomic ions.

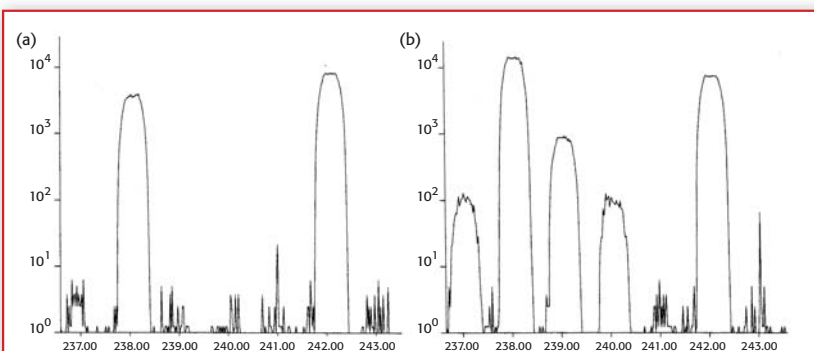
**Sample Preparation and Analytical Considerations**

The determination of Pu by SF-ICP-MS typically involves dissolution or leaching; separation–preconcentration;

fused particles from the Nevada Test Site (6) and from fire-produced PuO<sub>2</sub> particles. Kenna (7) described a procedure for total dissolution with HF-containing acid mixtures, followed by determination of Pu activities and isotopic compositions by SF-ICP-MS. Nygren et al. (8) described the use of a lithium borate for determination of refractory Pu in soils and sediments.

For separation and preconcentration, several different column systems have been used; the procedures based upon anion-exchange resins such as Dowex 1-X8 are based upon the classical alpha spectrometric procedures used for the past several decades by radiochemists. Many recent workers use extraction chromatographic resins such as TEVA (9), which consists of a quaternary ammonium ion immobilized on an inert polymer. The Dowex 1-X8 and TEVA separations initially retain Pu from aqueous HNO<sub>3</sub> as anionic [Pu<sup>IV</sup>(NO<sub>3</sub>)<sub>6</sub>]<sup>2-</sup>; U and matrix elements pass unretained through the first col-

and MS measurement. The first two steps strongly resemble those used in classical radiochemical analysis. The analysis commences with dry-ashing, spike isotope addition, and acid leaching with HNO<sub>3</sub> or HCl. However, acid leaching fails to recover insoluble, “refractory” forms of Pu, which have been identified in



**Figure 2.** Mass spectral scans of (a) an acid leach blank and (b) a recent sediment sample containing atmospherically deposited Pu. Peaks present in the blank consist of <sup>238</sup>U (reagent-derived) and <sup>242</sup>Pu (isotope dilution spike, ~50 pg); the recent sediment sample (2 g) exhibits peaks from <sup>237</sup>Np, <sup>239</sup>Pu, and <sup>240</sup>Pu. Note the logarithmic y-scale.

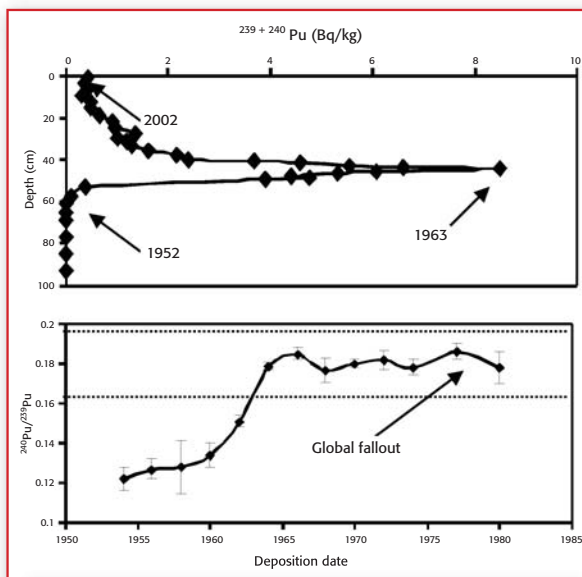
umn stage. In SF-ICP-MS, it is critical to remove the matrix elements U and Th from the sample; U will produce isobaric  $^{238}\text{U}^{1}\text{H}^+$ , and excessive amounts of Th can produce elevated background resulting from  $^{232}\text{Th}^+$  and  $^{232}\text{Th}^{16}\text{O}^+$  peak tails. Column washes with  $\text{HNO}_3$  and  $\text{HCl}$  are used to remove U and Th, respectively. Pu subsequently is removed from the column by reduction to Pu(III) or with a complexing agent such as

oxalate. As is commonly the case with ICP-MS work, the sample preparation is far more time-consuming than are the actual MS determination steps. The determination step typically requires only a few minutes counting time. Sample throughput is 3–10 samples/h and, depending upon the instrument and sample introduction system, detection limits range from  $\sim 0.1$  to 10 fg for each isotope. One major advantage of ICP-MS is the ability to obtain a mass spectrum in approximately 1 min (Figure 2). These spectra quickly confirm the presence of individual isotopes such as  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ , and indicate the suitability of the solution for further peak-jump quantitative analysis.

### Applications

Several prominent areas of interest have emerged for studies of environmental Pu: 1) evaluating local/regional Pu sources and measuring their significance versus global fallout; 2) understanding the sources, distribution, and geochemistry of Pu in the marine environment; 3) nuclear forensics; and 4) using fallout Pu as a tracer of earth/environmental processes. ICP-MS has been applied to all of these areas; in this article, some brief examples from the author's work will be given for topics 1 and 4.

The 1986 nuclear power plant accident at Chernobyl released an estimated  $8.7 \times 10^{13}$  Bq of  $^{239+240}\text{Pu}$  into the environment (10); although this is



**Figure 4.**  $^{239+240}\text{Pu}$  activity and  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratio profiles from a sediment core obtained from Lake Erie's Eastern Basin; inferred dates are 1952 (Pu first detected), 1963 (maximum Pu activity), and 2002 (sampling date). The global fallout  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratio range is from Kelley et al. (2).

much less than global releases of weapons-testing fallout, the Chernobyl plume is regionally very significant. Ketterer et al. (11) used sector ICP-MS in a study of Pu atom ratios in soils from Poland; mixing between global fallout and Chernobyl Pu was found through analysis of archived  $\text{NdF}_3$  alpha sources. The atom ratios  $^{240}\text{Pu}/^{239}\text{Pu}$  and  $^{241}\text{Pu}/^{239}\text{Pu}$  for northeastern Poland samples were both elevated compared with global fallout Pu; a well-defined mixing line was observed (Figure 3). It is believed that northeastern Poland received fallout of nonvolatile debris from the first Chernobyl plume that subsequently was detected in Scandinavia. However, Pu in forest soils and peat bogs of southern Poland was dominated by global fallout Pu.

Dating of recent sediments frequently is determined via atmospherically deposited radionuclides such as  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$ . The basis of  $^{137}\text{Cs}$  dating is that an onset of detection is observed circa 1952, with activity maxima in 1963 (stratospheric fallout) and 1986 (Chernobyl, observed mainly in Europe). The determination of  $^{137}\text{Cs}$  is made by gamma spectrometry; although nondestructive, this determination is often time-consuming. An alternative is  $^{239+240}\text{Pu}$ ; however, the impediment to previous  $^{239+240}\text{Pu}$  chronology studies has been the analytical throughput constraints of alpha spectrometry. Because ICP-MS-based  $^{239+240}\text{Pu}$  activity measurements can be made rapidly and relatively cheaply, there is considerable potential for the routine use of this method in sediment studies (12).

In addition to providing informa-

tion about chronology via interpretation of the  $^{239+240}\text{Pu}$  activity profile, additional information about the provenance of Pu is possible through  $^{240}\text{Pu}/^{239}\text{Pu}$ . One recent study conducted by the author and collaborators determined the sediment chronology in a sediment core from Lake Erie's Eastern Basin (Figure 4). 1.0-g sediment aliquots were prepared by fusion with potassium pyrosulfate (13). The  $^{239+240}\text{Pu}$  activity is first detectable at 60 cm depth, reaches a peak at about 45 cm, and then diminishes sharply to the present. Inferred dates are as shown in Figure 4. The  $^{239+240}\text{Pu}$  activity profile coincides precisely with the  $^{137}\text{Cs}$  profile. Moreover, the  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratios in the five sediment intervals immediately preceding the 1963  $^{239+240}\text{Pu}$  activity maximum all are systematically lower than stratospheric fallout ratios (2). The lower  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratios most likely result from mixing between stratospheric fallout and tropospheric fallout from the NTS.

### Conclusion

Even a brief glimpse of the literature reveals that ICP-MS now has a strong presence in the field of environmental radioactivity and specifically, in its use for measuring activities and isotopic compositions of Pu. In this latter application, the use of SF-ICP-MS is expanding rapidly. The scope of most publications now is shifting from analytical methods development into using SF-ICP-MS data in real-world applications. It is reasonably certain that SF-ICP-MS has sufficient sensitivity to determine Pu activities and isotope ratios in reasonable size samples of fallout-containing material. In this

respect, SF-ICP-MS is superior to traditional alpha spectrometric procedures, which are much more time-consuming. It is difficult to imagine that SF-ICP-MS or other MS techniques eventually will replace alpha spectrometry in all laboratories worldwide completely. However, the present trend of interest in SF-ICP-MS is expected to increase. SF-ICP-MS offers advantages of cost, ease of analysis, and access at many laboratories that cannot be equaled by other MS techniques with similar (or better) capabilities for Pu determination; it would be an unexpected development to see many more AMS facilities or TIMS systems used for Pu analysis in upcoming years.

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