Measuring Pu Isotope Ratios with Mass Spectrometry

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INTRODUCTION

Anthropogenic plutonium has been introduced into the environment over the past 50 years as the result of the detonation of nuclear weapons and operational releases from the nuclear industry. In the Arctic environment, the main source of plutonium is from atmospheric weapons testing, which have resulted in a relatively uniform, underlying global distribution of plutonium. Other releases can give rise to enhanced local or regional concentrations, such as from underwater weapons tests, reactor accidents, and dumped radioactive waste. Nuclear installations discharging waste to marine (e.g., Sellafield) and terrestrial waters (e.g., Mayak, Tomsk-7, Krashnoyarsk) represent an additional long-range source. Plutonium isotope ratios are known to vary with reactor type, nuclear fuel-burn up time, neutron flux, and energy, and for fallout from nuclear detonations, weapon type and yield. Weapons-grade plutonium is characterized by a low content of the ^{240}Pu isotope, with ^{240}Pu/^{239}Pu isotope ratio less than 0.05. In contrast, both global weapons fallout and spent nuclear fuel from civil reactors have higher ^{240}Pu/^{239}Pu isotope ratios (civil nuclear power reactors have ^{240}Pu/^{239}Pu atom ratios of between about 0.2-1). Thus, different sources often exhibit characteristic plutonium isotope ratios and these ratios can be used to identify the origin of contamination, calculate inventories, or follow the migration of contaminated sediments and waters (Oughton et al. 2000; Oughton et al. 2004; Skipperud et al. 2004).

Table 1. Pu isotope ratios in selected sources (UNSCEAR 1993) (Yamamoto et al. 1996) (Clacher 1995) (Kershaw et al. 1995) (Kutkov 1995) (Smith et al. 1995) (ANWAP 1997) (Beasley et al. 1997; Oughton et al. 2000; Oughton et al. 2004) (Salbu et al. 2003) (Skipperud et al. 2004)

Site	Information	^{240}Pu/^{239}Pu (atom ratio)	^{238}Pu/^{239,240}Pu (activity ratio)
Global Fallout – Northern Henisphere		0.175 – 0.19	0.025 – 0.04
Reprocessing Plants			
Sellafield	Surface sediment	0.22	0.19
	Sediment profile	0.05 – 0.25	
La Hague	Effluentg	0.34 ± 0.03	0.36
	Sediment profile	0.26 – 0.30	
Mayak PA			
Upper Tacha	Soil profile	0.012 – 0.024	0.005 – 0.018
EURT	Soil	0.028 ± 0.001	0.008 – 0.023
Weapon test site			
Chernaya Bay		0.030	
Semipalatinsk		0.036 ± 0.001	
Dumped submarine reactors	Abrosimov (PWR, 7-20 % ^{235}U, burn up 1.4 – 3.9 GW_d)	0.13	0.45
	Stepovogo (LMR, 90 % ^{235}U, burn up 0.88 GW_d)	0.0055	0.12
Chernobyl	Fuel particles	0.45 – 0.52	0.48

The measurement of the plutonium-isotope ratios offers both a means of identifying the origin of radionuclide contamination and the influence of the various nuclear installations on inputs

to the environment, as well as a potential method for following the movement of water and sediment loads in the rivers. The present paper presents some results from determination of plutonium isotope ratios in sediment samples collected during various expeditions to the Kara Sea, the Ob and Yenisey estuaries and their river systems and also Pu isotope ratios in the near area of Mayak PA.

MATERIALS AND METHODS

Samples for AMS measurements represent different sites in Ob and Yenisey estuaries. These samples were collected during Norwegian-Russian Karex expedition in 1994 and the Norwegian-Russian expedition in the EU Establish program in 2001 . The sediment samples from Mayak basin used in the study were collected during joint Norwegian-Russian field work in 1994 and 1996 as part of bilateral investigations on sources contributing to radioactive contamination of the Techa River and areas surrounding the Mayak PA (JRNEG 1997). Samples for this study were taken from a cross section of the two reservoirs, intended to represent both the old river bed and the flooded soils.

Sample preparation

Dried, ground and homogenized aliquots of sediments (2-10g) were ashed and/or digested with aqua regia, filtered and extracts taken to dryness. Plutonium isotopes were separated by anion exchange chromatography, using ^{242}Pu as a yield monitor (Clacher 1995). For AMS, the analyte needs to be dispersed in an iron oxide matrix. This is most commonly produced by dissolving the analyte in HNO_3, adding iron nitrate, evaporating to dryness, and baking at 500-800^{o}C to convert the nitrate to oxide. The iron oxide matrix are then mixed with metal powder (which serves as both an electrical and a thermal conductor) and pressed firmly into a suitably designed sample holder (Fifield et al. 1997). Samples solutions analysed by the Inductively Coupled Plasma Mass Spectrometer (ICP-MS) where just dissolved in 10 ml of 0.1M ultra pure HNO_3 and were ready for measurement at the ICP-MS. Standard and certified reference solutions were taken to dryness and diluted directly in 10 ml 0.1 M ultra pure HNO_3 (Skipperud et al. 2005).

AMS

AMS measurements were carried out using the 14UD tandem accelerator at the Australian National University, Canberra; full details of the analytical technique have been reported elsewhere (Fifield et al. 1997). The three plutonium isotopes (mass 242, 240 and 239) were counted sequentially using repeat cycles for each sample (Skipperud et al. 2004).

ICP-MS

In this work samples were analysed using a Perkin Elmer SCIEX (Norwalk CT, USA) ELAN 6000 ICP-MS. The sample introduction systems used were an ultrasonic nebulizer (USN) with membrane desolvator, because this gave better detection levels than the more normally used cross-flow nebulizer.

RESULTS AND DISCUSSION

Ob and Yenisey Estuaries

The Ob and Yenisey Rivers both have a number of weapon-grade plutonium sources in their catchments area, including the Russian plutonium production and reprocessing plants at Mayak, Tomsk-7 and Krasnoyarsk, and the Semipalantinsk nuclear weapons testing site in Kazakhstan. However, most of these installations are situated more than 2000 km from the

estuary. The general low levels of radionuclides in Arctic sediments, often combined with limited sample sizes, necessitate reliable low-level techniques for determination of plutonium isotopes. Accelerator mass spectrometry has proved to be a powerful method for measuring low-level plutonium activity concentrations and plutonium isotope ratios, and the study has shown conclusively that deviation from global fallout ^{240}Pu:^{239}Pu ratios can be identified in sediments from the Yenisey River and Estuary (Table 2).

Table 1. Summary of results of measurements in River Yenisey, Ob and Yenisey Estuaries (Skipperud et al. 2004).

	n	^{239,240}Pu Bq/kg average	^{239,240}Pu Bq/kg range	^{240}Pu:^{239}Pu atom ratio average	^{240}Pu:^{239}Pu atom ratio range
Ob Estuary	7	0.40 ± 0.23	0.16 - 0.75	0.17 ± 0.20	0.16 - 0.18
Yenisey Estuary	8	0.24 ± 0.19	0.003 - 0.61	0.11 ± 0.01	0.09 - 0.13
Yenisey River	5	3.7 ± 4.2	1.0 - 11.0	0.08 ± 0.03	0.05 - 0.12
Kara Sea	7	0.55 ± 0.27	0.14 - 0.96	0.17 ± 0.01	0.15 - 0.18
Global fallout					0.17 - 0.19

An influence from low burn-up or non-civil sources is apparent in the Yenisey Estuary, whereas plutonium in the Ob Estuary is dominated by global fallout. The data suggest that the plutonium-isotope "fingerprint" would be a useful method of following the migration and behaviour of both plutonium and sediments and particle loads in the two rivers, and further investigation will be carried out to obtain more information on the distribution of and mobility of plutonium associated with sediment samples.

Mayak sediments

Determination of Pu-isotope ratios in various Mayak samples has identified the presence of different sources and confirmed recent reports of civil reprocessing at Mayak (Fig.1).

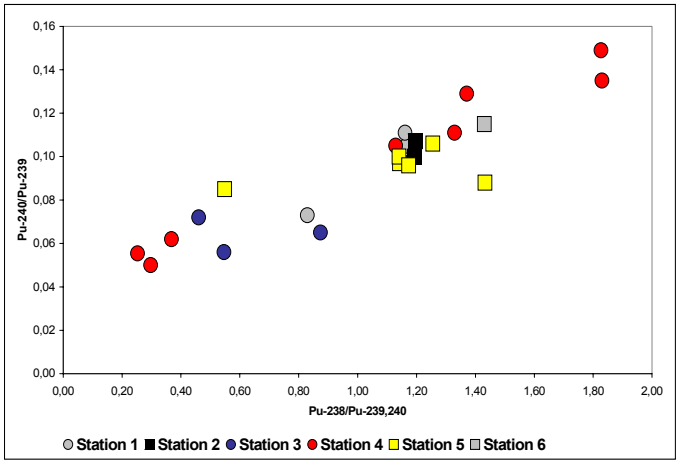

Figure 1 Pu isotope ratio in sediments from Reservoir 10. X-axis: Pu-238/Pu-239,240 (activity ratios), Y-axis: Pu-240/Pu-239 (atom ratios).

Activity levels and isotope ratios in Reservoir sediment samples suggest that up to 50 TBq Pu isotopes could have been released during the early, weapons production operation of the plant, and that the majority of Pu in Reservoir 10 originates from later discharges (Table 3).

Table 3. Plutonium activity ratios and estimated amount from "old" and "new" sources in Mayak Reservoirs (Skipperud et al. 2005).

	Amount	^{240}Pu/^{239}Pu	^{238}Pu/^{239,240}Pu
Old sources	25% (10 TBq)	0.06	0.04
New sources	75% (30 TBq)	Up to 0.60	Up to 1.6

CONCLUSION

Measruing Pu isotope ratios is a good tool for identifying the origin of radionuclide contamination and the influence of the various nuclear installations on inputs to the environment, as well as a potential method for following the movement of water and sediment loads in the rivers. ICP-MS has proven to be a good tool together with traditional α-spectrometry when it comes to determining total plutonium and its isotope ratios in contaminated areas. Accelerator mass spectrometry has proved to be a powerful method for measuring low-level Pu activity concentrations and Pu isotope ratios. Absolute detection limits by AMS of less than 1 fg Pu and can compete with ICP-MS and alpha-spectrometry.

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