

## Intercalibration of selected anthropogenic radionuclides for the GEOTRACES Program

Timothy C. Kenna<sup>1\*</sup>, Pere Masqué<sup>2</sup>, José Luís Mas<sup>2</sup>, Patricia Camara-Mor<sup>2</sup>, Elena Chamizo<sup>2</sup>, Jan Scholten<sup>3</sup>, Mats Eriksson<sup>3</sup>, Joan-Albert Sanchez-Cabeza<sup>3</sup>, Janine Gastaud<sup>3†</sup>, Isabelle Levy<sup>3</sup>, Jürgen Herrmann<sup>4</sup>, Patric Lindahl<sup>5</sup>, Gi-Hoon Hong<sup>5</sup>, and Sven Nielsen<sup>6</sup>

<sup>1</sup>Lamont-Doherty Earth Observatory, Palisades, NY, 10964, USA

<sup>2</sup>Universitat Autònoma de Barcelona, 08193, Bellaterra, Spain

<sup>3</sup>Marine Environment Laboratories, International Atomic Energy Agency, MC 98000 Monaco

<sup>4</sup>Bundesamt für Seeschifffahrt und Hydrographie, 22589 Hamburg, Germany

<sup>5</sup>Korea Ocean Research and Development Institute, Ansan 426-744, Republic of Korea

<sup>6</sup>Risoe National Laboratory, 4000 Roskilde, Denmark

### Abstract

As part of the GEOTRACES Program, six laboratories participated in an intercalibration exercise on several anthropogenic radionuclides of interest. The effort was successful for <sup>239,240</sup>Pu activity, <sup>240</sup>Pu/<sup>239</sup>Pu isotope ratio, and <sup>137</sup>Cs activity measured in filtered seawater samples from the Bermuda Atlantic Time Series station (BATS) and a site on the continental slope of the Northeastern U.S. A limited number of analyses were reported for <sup>237</sup>Np, <sup>241</sup>Am, <sup>90</sup>Sr, and <sup>238</sup>Pu in filtered seawater. Intercalibration of any of the isotopes of interest in filtered particulate matter was unsuccessful due to insufficient size of the samples distributed. Methods used were based on traditional radio-counting techniques and inductively coupled plasma mass spectrometry (ICP-MS). Although the majority of analyses were performed on samples ≥ 60 L, one lab demonstrated the ability to analyze several of the anthropogenic radionuclides on 10-20 L sample volumes using ICP-MS.

GEOTRACES is a global study of the marine biogeochemical cycles of trace elements and their isotopes (TEIs). Given that the program will span many years and include scientists from numerous participating countries, the GEOTRACES intercalibration initiative was designed to ensure that different methods used by different laboratories produce results that are as accurate, precise, and internally consistent as possible (GEOTRACES Planning Group 2006). Here we report activities and results related to the intercalibration of selected anthropogenic radionuclides of interest (ARs) including <sup>239</sup>Pu ( $t_{1/2} = 24,110$  y), <sup>240</sup>Pu ( $t_{1/2} = 6563$  y), <sup>137</sup>Cs ( $t_{1/2} = 30.07$  y), <sup>237</sup>Np ( $t_{1/2} = 2,144,000$  y), <sup>241</sup>Am ( $t_{1/2} = 432.2$  y), <sup>90</sup>Sr ( $t_{1/2} = 28.79$  y), and <sup>238</sup>Pu ( $t_{1/2} = 87.7$  y) in seawater and filtered particulate material. Although the ARs are not listed as key parameters in the GEOTRACES program, they are used as removal, source, and contaminant tracers; gaining a better understanding of

these processes is listed as an anticipated benefit of the program. During the GEOSECS expeditions in the early 1970s (Bowen et al. 1980; Craig and Turekian 1976; Livingston et al. 1985), a large-scale effort was led to systematically map the vertical and horizontal distribution of selected ARs in the ocean (i.e., <sup>137</sup>Cs, <sup>90</sup>Sr, and <sup>239,240</sup>Pu). More recently, <sup>137</sup>Cs and <sup>239,240</sup>Pu have been extensively mapped in the Southern Hemisphere during the SHOTS (Southern Hemisphere Ocean Tracers Study) project (Aoyama et al. 2011a, 2011b; Gastaud et al. 2011; Hirose et al. 2011; Levy et al. 2011; Povinec et al. 2011; Sanchez-Cabeza et al. 2011).

The ARs have been introduced to the oceans primarily as a result of atmospheric and surface testing of nuclear weapons in the late 1950s and early 1960s (UNSCEAR 2000). Whereas the main source of these nuclides has been global stratospheric fallout, close-in fallout from equatorial Pacific test sites has also contributed (mainly in the early 1950s) as well as other inputs from nuclear fuel reprocessing facilities (e.g., Sellafield) and accidents (e.g., Chernobyl). This last point is made more relevant in light of the recent events involving releases from reactors in Fukushima, Japan in March, 2011. Improving our knowledge of the fate, transport, and distribution of these nuclides is important for the assessment of environmental and

\*Corresponding author: E-mail: tkenna@LDEO.columbia.edu

†Deceased.

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human health impacts as well as the assessment of future accidental or intentional releases. Further, their absence in the environment at appreciable levels before ~1950, accurate knowledge regarding the different sources, release histories, and in the case of plutonium isotopes, the ability to identify and resolve inputs from different sources make these isotopes extremely useful as tracers of marine geochemical, biological, and sedimentary processes. Numerous studies have applied these man-made tracers to study processes such as ocean currents and mixing, particle association transport and fate, sediment and porewater dynamics as well as biological processes (see review articles by Hong et al. 2011; Livingston and Povinec 2002; Sholkovitz 1983).

Although proximity to a source of contamination may result in elevated levels of a particular nuclide, the concentrations of many ARs in seawater are extremely low and accurate analysis typically requires large volume (10-100s of liters) samples. In addition, some isotopes have relatively short half-lives (~days-few years). These issues are common for many naturally occurring radionuclides (e.g., long-lived primary radionuclides and daughters, cosmogenic radionuclides; see NRC (2002) for a more detailed discussion). Further, the ARs are operationally grouped together because they are derived from nuclear industrial activities, but as individuals, they exhibit a wide range of geochemical behaviors leading to differential distributions with depth and/or between phases (i.e., dissolved and particulate). Quantitation of the ARs as a group requires complex separation schemes and a variety of different instrumentation; in some cases, a particular radionuclide may be measured by one of several different techniques, each with potentially different detection limits and sample volume requirements. These factors combine making intercalibration exercises as well as the production, storage, and distribution of true seawater reference materials for typical levels of ARs a significant challenge.

These issues notwithstanding, the Marine Environment Laboratories at the International Atomic Energy Agency (IAEA-MEL) in Monaco has been active for decades in the area of interlaboratory comparison exercises and production of reference materials and certified reference materials (C/RM) for radionuclides pertaining to the marine environment, which were based on International Organization for Standardization (ISO) and International Union of Pure and Applied Physics (IUPAC) recommendations and served to guide to the current interlaboratory comparison exercise (Ballestra et al. 1993; Cofino and Wells 1994; Baskaran et al. 2009; ISO 2006; ISO/IEC 1997a, 1997b; Pham et al. 2006, 2008, 2010a, 2010b, 2011; Povinec et al. 2002, 2007; Sanchez-Cabeza et al. 2008; Thompson et al. 2006). Of particular interest are RMs based on surface water collected from Irish Sea (i.e., IAEA-381 and IAEA-443), which include information on the ARs of interest, albeit at significantly elevated levels over open ocean values due to the discharges from the Sellafield reprocessing plant.

The choice to develop Irish Sea water as a C/RM overcomes the sample volume limitations, and the availability of such a C/RM is invaluable for method development, improving data quality and providing traceability. However, problems such as C/RM commutability (i.e., adequacy or match to a sample under analysis), a finite number of laboratories with adequate technical capabilities, and a limited number of laboratories willing to participate in the intercalibration are not solved and remain particularly relevant to the GEOTRACES Program (Bowen 1978; Bowen and Volchok 1980; Dvorkin 2004; Kuselman and Fajgelj 2010), which will focus mainly on seawater collected along open ocean transects with relatively lower AR concentrations.

This intercalibration exercise should be seen as a first step toward the establishment of baseline stations and cruise cross-over requirements that shall provide the opportunity for additional interlaboratory comparisons as well as the opportunity to collect additional water for new arrivals to the program. Although necessary, the decision to ship large volumes of seawater to participants was expensive and ultimately limited the type and number of samples included in the intercalibration. Participating laboratories (Table 1 and 2) had different analytical capabilities and volume requirements and typically measured a subset of the ARs of interest.

#### Objectives

The main objective was to have participants perform an intercalibration on as many of the ARs as possible as well as the  $^{240}\text{Pu}/^{239}\text{Pu}$  isotope ratio in both dissolved and particulate seawater samples at levels expected in open ocean samples. Four of the seven labs planned to analyze samples for  $^{137}\text{Cs}$ . One or more labs also expressed an interest in analyzing other radionuclides, such as  $^{237}\text{Np}$ ,  $^{241}\text{Am}$ ,  $^{90}\text{Sr}$ , and  $^{238}\text{Pu}$ .

A second and equally important goal was to optimize current methods to decrease required sample volume; much of the published AR data are based on large volume (~hundreds of liters) samples. To fully participate in the GEOTRACES program, where sample volume comes at a premium, the ability to analyze smaller samples will be required. In the planning stage, it was agreed that decreasing sample volume requirements to ~20 L might be possible for several of the participating labs with the caveat of method optimization.

**Table 1.** GEOTRACES anthropogenic radionuclide intercalibration participating laboratories.

Organization	Country
Lamont-Doherty Earth Observatory	USA
Marine Environment Laboratories (IAEA)	Monaco
Autonomous University of Barcelona*	Spain
Federal Maritime and Hydrographic Agency (BSH)	Germany
Korea Ocean Research and Development Institute (KORDI)	Korea
Risø National Laboratory	Denmark

\*Pu measurements were made at Centro Nacional de Aceleradores (CNA), Sevilla, Spain

**Table 2.** Anthropogenic radionuclides (ARs) analyzed and methods by Lab ID number.

Lab number	ARs reported	Method codes*
1	$^{239}\text{Pu}$ , $^{240}\text{Pu}$ , $^{240}\text{Pu}/^{239}\text{Pu}$ , $^{237}\text{Np}$ , $^{137}\text{Cs}$	ID1, ID2, ID5, S1, S3, D, I, MS1, G
2	$^{239,240}\text{Pu}$ , $^{137}\text{Cs}$	ID1, ID5, S2, S1, S3, I, A, G
3	$^{239,240}\text{Pu}$ , $^{137}\text{Cs}$ , $^{241}\text{Am}$ , $^{90}\text{Sr}$ , $^{238}\text{Pu}$	ID1, ID4, ID5, S1, S3, I, A, G, B
4	$^{239}\text{Pu}$ , $^{240}\text{Pu}$ , $^{240}\text{Pu}/^{239}\text{Pu}$ , $^{237}\text{Np}$ , $^{137}\text{Cs}$ , $^{241}\text{Am}$ , $^{90}\text{Sr}$ , $^{238}\text{Pu}$	ID1, ID4, ID5, S1, S3, MS1, A, G, B
5	$^{239}\text{Pu}$ , $^{240}\text{Pu}$ , $^{240}\text{Pu}/^{239}\text{Pu}$	ID1, S1, D, I, MS2
6	$^{239}\text{Pu}$ , $^{240}\text{Pu}$ , $^{240}\text{Pu}/^{239}\text{Pu}$	ID1, S2, I, MS1

\*Method codes (Aoyama et al. 2000; Ballestra and Fukai 1983; Chamizo et al. 2008; Chen et al. 2001a, 2001b, 2002b; Holm and Fukai 1976; Kenna 2002; La Rosa et al. 2001; Lindahl et al. 2010; Murray and Statham 1976):

A – Electrodeposition, $\alpha$ spectroscopy	ID1 – $^{242}\text{Pu}$	MS1 – ICP-MS
B – $\beta$ -counting of Y-90 after ingrowth	ID2 – $^{236}\text{Np}$	MS2 – AMS
D – digestion/treatment	ID3 – $^{239}\text{Np}$	S1- $\text{Fe}(\text{OH})_3$ coprecipitation
G – High resolution $\gamma$ spectroscopy	ID4 – $^{243}\text{Am}$	S2- $\text{MnO}_2$ coprecipitation
I – ion exchange	ID5 – $^{134}\text{Cs}$	S3 – AMP sorption

## Background

As mentioned above, the GEOSECS program was among the first to map the distribution of  $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$ , and  $^{239,240}\text{Pu}$  in the world oceans, which typically entailed the analysis of 60-L seawater samples. Sample handling and processing varied somewhat between participating labs but generally entailed the acidification of samples at sea or upon return to the lab, addition of recovery standards, separations via coprecipitation, sorption, and ion exchange (Livingston et al. 1974, 1975; Noshkin et al. 1976; Wong et al. 1970, 1978). During GEOSECS,  $\alpha$  spectrometry was employed extensively to measure  $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$ , and  $^{240}\text{Pu}$ . Because  $\alpha$  spectrometric techniques cannot resolve the individual  $\alpha$  energies of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ , their combined concentrations are usually reported as  $^{239,240}\text{Pu}$ .

As part of the GEOSECS program, measurement accuracy, blanks, and analytical precision were carefully considered, with participating laboratories providing various quality control data. Specific strategies included 1) the analysis of “blind” knowns (i.e., a QA-QC sample that resembles real unknowns and is not identified to the analyst, duplicates, and environmental and reagent blanks; 2) depth profiles from individual stations were often split between participating laboratories to elucidate any systematic offsets; and 3) laboratories participating in GEOSECS also engaged in interlaboratory analytical comparison exercises organized by various agencies (Bowen 1978; Bowen et al. 1980; Bowen and Volchok 1980; Volchok et al. 1980).

During the time period of GEOSECS, interlaboratory analytical comparison exercises for seawater were organized by IAEA and Environmental Measurements Laboratory and consisted of both spiked sample and natural matrix standards exhibiting concentrations ranging from those expected in the open ocean to several orders of magnitude higher. For the spiked sample standards (BERLI-1/SW-1; 14 laboratories participating), the expected values were 3.63 and 218 mBq/m<sup>3</sup> and the average difference from the expected values were 11% and 34% for  $^{239,240}\text{Pu}$  and  $^{137}\text{Cs}$ , respectively (Watters 1978). Beasley et al. (1981) reported results that agreed with predicted

values to within 10% to 20% for BERLI-1, but they noted that agreement between laboratories for large volume natural matrix seawater samples was less satisfactory. Bowen and Volchok (1980) observed that performance on knowns at relative high concentrations was not a good predictor of performance on knowns or samples of much lower concentrations, and stressed that the range of concentrations available must correspond approximately to that encountered among the unknowns to be analyzed.

Since the GEOSECS program, measurement capabilities for several ARs in various laboratories around the world have improved—in some cases dramatically (improvements in detection limits and reduction in sample size)—the main advances in radioanalytical techniques for determining short- and medium-lived radionuclides have been the development of larger volume Ge detectors and the construction of underground  $\gamma$  counting facilities. Whereas adequate shielding and ventilation and the use of low background materials can largely remove the background contributions from ambient radioactivity in the laboratory, radon and daughter products, and the shield and detector itself, the primary means to reduce the background contributions from cosmic rays is to perform measurements underground (Baudis et al. 2011; Finnerty et al. 2011; Hult et al. 2006; Pellicciari et al. 2005; Povinec et al. 2001, 2004). For example, Japanese researchers working at an ultra-low background  $\gamma$  counting facility located ~235 m below ground in a former copper mine report  $^{137}\text{Cs}$  activities ~0.2 Bq/m<sup>3</sup> measured in 10 L deep ocean samples and activities ~1 Bq/m<sup>3</sup> measured in as little as 250 mL of archived seawater (Hirose et al. 2005; Hirose et al. 2008; Komura and Hamajima 2004).

For longer-lived radionuclides, mass spectrometry offers many advantages. In what may be considered the “gold standard,” Pu and Np isotopic data generated from thermal ionization mass spectrometry (TIMS) have been published for seawater samples as small as 4 L and not only include the  $^{240}\text{Pu}/^{239}\text{Pu}$  ratio, but the minor ratios  $^{241}\text{Pu}/^{239}\text{Pu}$ , and  $^{242}\text{Pu}/^{239}\text{Pu}$  as well (Beasley et al. 1998; Buesseler and Halverson 1987). It should be noted, however, that the generation of

such data can be traced to specialized and custom TIMS machines owned and operated by the US DOE national laboratories (Lagergren and Stoffels 1970). Bürger et al (2009) demonstrated sub fg detection limits using a heavily modified commercially available TIMS located at another US DOE lab but did not analyze seawater. In general, access to these machines is limited and cost-prohibitive within the scope of GEOTRACES. More recently published Pu data generated by unmodified TIMS do not exhibit the same sensitivity nor have they included the analysis of seawater (Elliot et al. 2006; Jakopic et al. 2009).

These advances aside, it is not uncommon for modern-day studies to publish data generated from large volume seawater samples using traditional  $\gamma$  and  $\alpha$  counting. Other techniques for Pu analysis developed since GEOSECS that have resulted in improved detection limits, better precision, and the separate quantitation of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  include Resonance Ionization mass spectrometry (RIMS), Accelerator mass spectrometry (AMS), and ICP-MS (e.g., Eroglu et al. 1998; Fifield et al. 1996; Kenna 2002; Kershaw et al. 1995; Ketterer and Szechenyi 2008; Ketterer et al. 2002; Kim and Kim 2002; Ruster et al. 1989; Taylor et al. 2001). With respect to Pu isotope analysis, use of ICP-MS based techniques have become widespread, largely replacing  $\alpha$  spectrometry, although measurements of  $^{238}\text{Pu}$  still requires  $\alpha$  spectrometry due to low environmental levels and isobaric interference from  $^{238}\text{U}$  when ICP-MS is employed (Hong et al. 2011).

## Materials and procedures

### Intercalibration samples

We collected and distributed seawater and particulate samples from the Leg 2 of the First GEOTRACES Intercalibration Cruise (KN193-06; June/July 2008) to participating laboratories. We collected both large (55 L) and small (20 L) intercalibration samples. Seawater samples for the AR intercalibration were collected at three different sites: 1) The BATS Station (Bermuda Atlantic Time Series) ( $31^\circ 45.93' \text{ N} \times 64^\circ 07.52' \text{ W}$ ); 2) A site on the continental slope near Norfolk Canyon ( $37^\circ 01.45' \text{ N} \times 74^\circ 24.56' \text{ W}$ ); and 3) A site on the continental shelf near Chesapeake Bay ( $36^\circ 57.71' \text{ N} \times 76^\circ 1.99' \text{ W}$ ). Water samples were collected using different systems. Specifications regarding filter cut-off and final pH were different between systems. These were based on the collective needs of different intercalibration groups or the collection system owners. It was generally agreed by the AR intercalibration participants that the noted differences between systems would have negligible impact on our results. Additional sampling details are presented below.

#### *Bats shallow 1 (BS1)*

Samples were collected using the ship's intake (~10 m). Water was filtered through a 1.0 micron cartridge filter into a 1250 L tank (Charette et al. 2012). The water was homogenized for several hours using an internal pump before sampling. Flow meters were available for this system, and flow

in/out values were noted to estimate sample volume. However, participants were encouraged to weigh samples in their home laboratories. Seawater was drained directly from the tank into the sample containers provided by the participants, rinsing each container at least two times with water from the tank before filling it. Once sample containers were full, samples were acidified to pH of ~1.7 using Fisher brand trace-metal grade hydrochloric acid. All participating labs received between 165 and 180 L sample water, with the idea of performing triplicate analysis on samples that were between 50 and 60 L each.

#### *Bats shallow 2 (BS2)*

Samples were collected with a towed fish from a depth of ~15 m to produce a homogenous 1000-L sample using the trace metal-clean SAFE tanks (Johnson et al. 2007; Cutter and Bruland 2012). Sample water was filtered using an Osmonics cartridge and a 0.2 micron pore diameter filter, and then acidified to a pH of ~1.9 with Fisher Optima hydrochloric acid. Water was drained directly from the SAFE tanks into the sample containers that were provided by the participants, rinsing each container at least two times with water from the tank before filling it. Each lab that requested small volume samples also received a ~60 L sample with the plan of performing triplicate analysis on samples that were ~20 L each. Flow meters were not available for the SAFE system, and sample volumes/weights were determined by each participant. Not all labs received BS2 samples.

#### *Bats deep (BD)*

Samples were collected following the same protocols as those used for BS2 samples with the exception that water was collected using the trace-metal clean GEOTRACES rosette from a depth of 2000 m and composited in the SAFE tanks. BD samples were analyzed by Lab 1 only.

#### *Slope (SL)*

Samples were collected using the system and procedure as the BS1 samples (i.e., shipboard intake). All participating labs received ~165 L sample water with the aim of performing triplicate analysis on ~20 L samples and a single analysis on one ~60 L sample.

#### *Shelf (SH)*

A limited number of ~60 and ~20 L samples were collected using the system and procedure as the BS1 and SL samples (i.e., shipboard intake), with the exception that were not homogenized in the 1250 L tank. SH samples were analyzed by Lab 1 only.

Particulate samples for intercalibration of ARs were collected using McLane pump systems equipped with 142 mm diameter Supor polyethersulfone filters (0.45 micron pore size) (Buesseler et al. 2005; Maiti et al. in press). To provide samples as similar as possible in expected concentrations of particulate material, eight McLane pumps were hung on a carousel and operated at the same depth and for the same time interval. Pump casts were programmed so that each pump would filter approximately 600 L; however, in most cases the volume fil-

tered was slightly less than this. Each filter was cut into quarters using a ceramic “pie cutter” template. Each participant received one quarter filter samples (~150 L) and dip blanks (i.e., one of the McLane pumps was deployed with the same set up as the others but not energized) from two out of the three stations. Each participating lab received subsamples from two of three different locations: 1) BATS Shallow (80 m water depth), 2) BATS deep (2000 m water depth, corresponding to the depth of the seawater intercalibration samples for other groups), and 3) Continental Slope: A site over the continental slope off the mouth of Chesapeake Bay in 1200 m water depth was sampled at a depth of 80 m to provide samples with a higher concentration of particulate material than at the BATS site.

Filter sub-samples (90 mm punch-aliquots) representing significantly larger sample volumes collected on QMA filters were obtained at both the BATS and SLOPE sites from the MULVFS sampling system (Bishop et al. 1985). MULVFS samples were analyzed by Lab 1 only.

#### <sup>242</sup>Pu spike intercalibration

Since all participating labs use <sup>242</sup>Pu as a yield monitor, each was invited to submit aliquots of their spike to Lab 1 for analysis. Spike aliquots were diluted with Optima grade HNO<sub>3</sub> and 18 MΩ water to working levels (~5 × 10<sup>9</sup> atoms <sup>242</sup>Pu/g in 1N HNO<sub>3</sub>). All spike, acid, and water amounts were determined gravimetrically. A double internal standard comprised of well-characterized NIST-traceable <sup>239</sup>Pu (SRM-4330a) and <sup>240</sup>Pu (SRM-4338a) solutions was added to aliquots of the working spikes, and the <sup>242</sup>Pu/<sup>239</sup>Pu and <sup>242</sup>Pu/<sup>240</sup>Pu atom ratios were determined using a VG Axiom single collector sector field ICP-MS equipped with an S-option interface pump and an Aridus desolvating nebulizer system (Cetac). Based on the known amounts of <sup>239</sup>Pu and <sup>240</sup>Pu added to each spike and the measured ratios, the <sup>242</sup>Pu concentration of each lab’s spike was calculated and compared to the stated concentration.

#### Analytical protocols

In an attempt to maintain participant anonymity, each participant was assigned an ID number. Given the rather small pool of participants, we decided to reference all methods but generalize the protocols and analytical techniques used with but assign method codes to the assigned lab number, rather than identify a specific method with a specific lab (Table 2).

#### Data treatment

To compare data between labs, average values and associated uncertainties were computed from individual results. If more than two results were available, the arithmetic mean and uncertainty was computed; in the case of only two results, the weighted mean and uncertainty was computed. If a lab submitted only a single result, the reported value and uncertainty were used in subsequent calculations. Once representative values for each lab were available, outliers were identified using the box and whisker plot method and the median value was computed from the remaining values (McGill et al. 1978; Tukey 1977). For a given sample size (N), nonparametric two-

sided confidence intervals (95%) were computed for the median; in the case of N < 9, this amounted to the minimum and maximum of accepted values. The median was taken as the consensus value. Given the relatively small number of participating laboratories (i.e., N ≤ 6), we did not calculate z-scores as a means to assess individual laboratory performance; we did, however, note if a particular lab’s value was identified as an outlier.

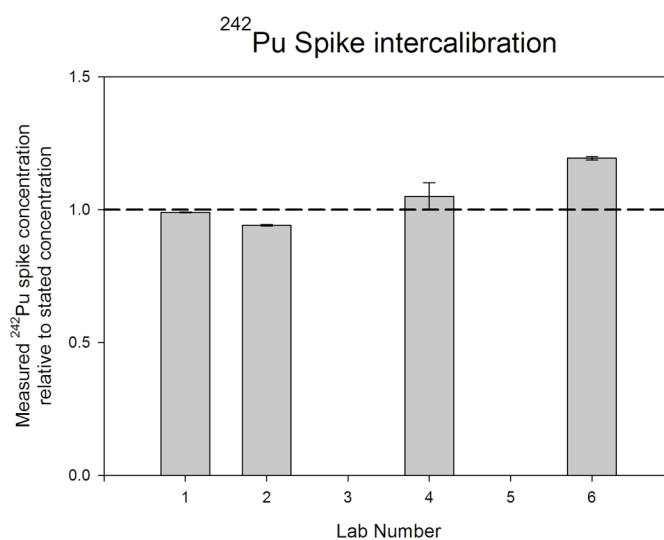
## Results

### Spike intercalibration results

Four of six labs that received intercalibration samples sent an aliquot of their <sup>242</sup>Pu spike for intercomparison. The <sup>242</sup>Pu spike intercalibration (Fig. 1) indicated that Labs 1, 2, and 4 were within ~5% of their stated spike concentrations. Lab 6 was within ~20%.

### Intercalibration results—filtered seawater

Six laboratories reported the activities of up to seven ARs of interest on a volumetric basis. Four labs also reported the <sup>240</sup>Pu/<sup>239</sup>Pu atom ratio. Uncertainties are given as ± 1 sd, which indicates uncertainty based on an attempt to account for sources of random error influencing the measurement. Volumes analyzed ranged from 10 to 180 L; some laboratories reported replicate measurements for a given sample/AR, while other laboratories pooled individual samples (originally designed as replicates) and reported a single value and uncertainty for a particular AR for water from the different intercalibration sample groups (i.e., BS1, BS2, and SL). All reported results are tabulated in Web Appendix A along with additional sample details. Representative laboratory values are given in Table 3, and consensus values for BS1, BS2, and SL are given in Table 4.



**Fig. 1.** Results of <sup>242</sup>Pu spike intercalibration (4 labs participating). The dashed line indicates a value of 1 (i.e., measured concentration = stated concentration).

**Table 3.** Representative laboratory values for BS1, BS2, and SL.

Measurement	Location	Lab nr.	Vol range (L)	Nr of results.	Value	± 1 s	rel. uncert
$^{240}\text{Pu}/^{239}\text{Pu}$ (atom ratio)	BS1	1	55-62	3	0.21	0.02	7%
		4	165	1	0.19	0.03	14%
		5	60, 60	2	0.24	0.02	13%
		6	18-105	3	0.20	0.01	3%
$^{239,240}\text{Pu}$ (mBq/m <sup>3</sup> )	BS1	1	55-62	3	1.7	0.0	1%
		2	180	1	1.9	0.2	8%
		3	165	1	2.4	0.4	15%
		4	165	1	3.1*	0.6	19%
		5	60, 60	2	1.8	0.1	7%
		6	18-105	3	1.7	0.3	20%
$^{239}\text{Pu}$ (mBq/m <sup>3</sup> )	BS1	1	55-62	3	1.0	0.0	4%
		4	165	1	1.6*	0.1	7%
		5	60-60	3	1.0	0.1	5%
$^{240}\text{Pu}$ (mBq/m <sup>3</sup> )	BS1	6	18-105	3	1.0	0.2	21%
		1	55-62	3	0.7	0.02	3%
		4	165	1	1.1	0.13	12%
$^{237}\text{Np}$ (mBq/m <sup>3</sup> )	BS1	5	60, 60	2	0.8	0.07	12%
		6	18-105	3	0.7	0.13	18%
		1	55-62	3	0.12	0.004	3%
$^{137}\text{Cs}$ (Bq/m <sup>3</sup> )	BS1	4	165	1	0.07	0.004	6%
		1	55- 62	3	1.3	0.2	16%
$^{90}\text{Sr}$ (Bq/m <sup>3</sup> )	BS1	2	180	1	1.2	0.04	3%
		3	165	1	1.1	0.1	8%
		4	165	1	1.1	0.2	22%
		3	165	1	0.8	0.04	5%
$^{238}\text{Pu}$ (mBq/m <sup>3</sup> )	BS1	4	165	1	0.9	0.09	10%
		3	165	1	0.2	0.08	32%
$^{241}\text{Am}$ (mBq/m <sup>3</sup> )	BS1	4	165	0	< 0.6	—	—
		3	165	1	1.3	0.2	13%
$^{240}\text{Pu}/^{239}\text{Pu}$ (atom ratio)	BS2	4	165	1	0.6	0.3	41%
		1	21, 20	2	0.22†	0.005	2%
$^{239,240}\text{Pu}$ (mBq/m <sup>3</sup> )	BS2	6	66	1	0.16	0.02	13%
		1	10-21	4	2.1	0.11	6%
		2	60	1	2.5	0.3	12%
$^{239}\text{Pu}$ (mBq/m <sup>3</sup> )	BS2	6	66	1	1.7	0.09	5%
		1	10-21	4	1.07	0.14	13%
		5	60	1	1.4	0.14	10%
$^{240}\text{Pu}$ (mBq/m <sup>3</sup> )	BS2	6	66	1	1.06	0.14	13%
		1	10-21	4	1.0	0.13	13%
$^{237}\text{Np}$ (mBq/m <sup>3</sup> )	BS2	6	66	1	0.6	0.08	13%
		1	10-21	4	0.12	0.003	2%
$^{137}\text{Cs}$ (Bq/m <sup>3</sup> )	BS2	1	10-21	4	1.1	0.24	23%
		2	60	1	1.2	0.07	6%
$^{240}\text{Pu}/^{239}\text{Pu}$ (atom ratio)	SL	1	18-60	4	0.21	0.01	3%
		4	165	1	0.15	0.02	11%
		5	60	1	0.18	0.03	17%
		6	112	1	0.19	0.01	5%

continued...

**Table 3.** continued

Measurement	Location	Lab nr.	Vol range (L)	Nr of results.	Value	± 1 s	rel. uncert
<sup>239,240</sup> Pu (mBq/m <sup>3</sup> )	SL	1	18-60	4	2.4	0.2	7%
		2	120	1	2.9	0.3	9%
		3	165	1	2.5	0.3	10%
		4	165	1	3.1	0.5	17%
		5	60	1	2.3	0.2	8%
		6	112	1	2.0	0.1	4%
<sup>239</sup> Pu (mBq/m <sup>3</sup> )	SL	1	18-60	4	1.4	0.1	7%
		4	165	1	1.9	0.2	9%
		5	60, 60	2	1.5	0.1	10%
		6	112	1	1.2	0.1	6%
<sup>240</sup> Pu (mBq/m <sup>3</sup> )	SL	1	18-60	4	1.0	0.1	7%
		4	165	1	1.1	0.1	7%
		5	60	1	0.9	0.1	14%
		6	112	1	0.8	0.0	6%
<sup>237</sup> Np (mBq/m <sup>3</sup> )	SL	1	18-60	4	0.2	0.004	2%
		4	165	1	0.1	0.01	9%
<sup>137</sup> Cs (Bq/m <sup>3</sup> )	SL	1	18-60	4	1.5	0.2	15%
		2	120	1	1.5	0.1	4%
		3	165	1	1.2*	0.1	7%
		4	165	1	1.7	0.2	15%
<sup>90</sup> Sr (Bq/m <sup>3</sup> )	SL	3	165	1	1.2	0.03	2%
		4	165	1	1.3	0.1	10%
<sup>238</sup> Pu (mBq/m <sup>3</sup> )	SL	3	165	1	0.2	0.07	30%
		4	165	0	< 0.5	—	—
<sup>241</sup> Am (mBq/m <sup>3</sup> )	SL	3	165	1	1.2	0.2	14%
		4	165	1	0.7	0.2	30%

\*Identified as outliers

†Values for 10 L samples excluded from Lab 1 <sup>240</sup>Pu/<sup>239</sup>Pu mean for BS2**<sup>239,240</sup>Pu activity**

Six data sets were received for <sup>239,240</sup>Pu activity; one outlier for BS1 was identified (Fig. 2; Table 3). Analytical methods included  $\alpha$  spectroscopy, ICP-MS, and AMS. Sample volumes ranged from 10 L to 185 L. When replicate samples were analyzed, reported results from individual labs were generally internally consistent. The median concentrations are 1.8 (1.7-2.4), 2.1 (1.7-2.5), and 2.5 (2.0-3.1) mBq m<sup>-3</sup>, for BS1, BS2, and SL samples, respectively. The effect of intercalibrating the <sup>242</sup>Pu spike (hollow squares) is within the uncertainty reported for the initial measurement for all labs that participated (4 of 6 labs). Further examination of the spike-corrected results indicates that the reported results from Lab 4 are consistently higher (BS1 was identified as an outlier); however, this does not appear to be an effect of sample size or analytical method. Although smaller volumes (10-30 L) were not analyzed on the same samples by Labs 1 (BS1) and 6 (BS2), the results agree well with values reported for larger volumes.

**<sup>240</sup>Pu/<sup>239</sup>Pu atom ratio**

Four labs reported results for the Pu isotopic ratio (Fig. 3). The majority of reported values for volumes between 20 and 165 L were not significantly different from the expected

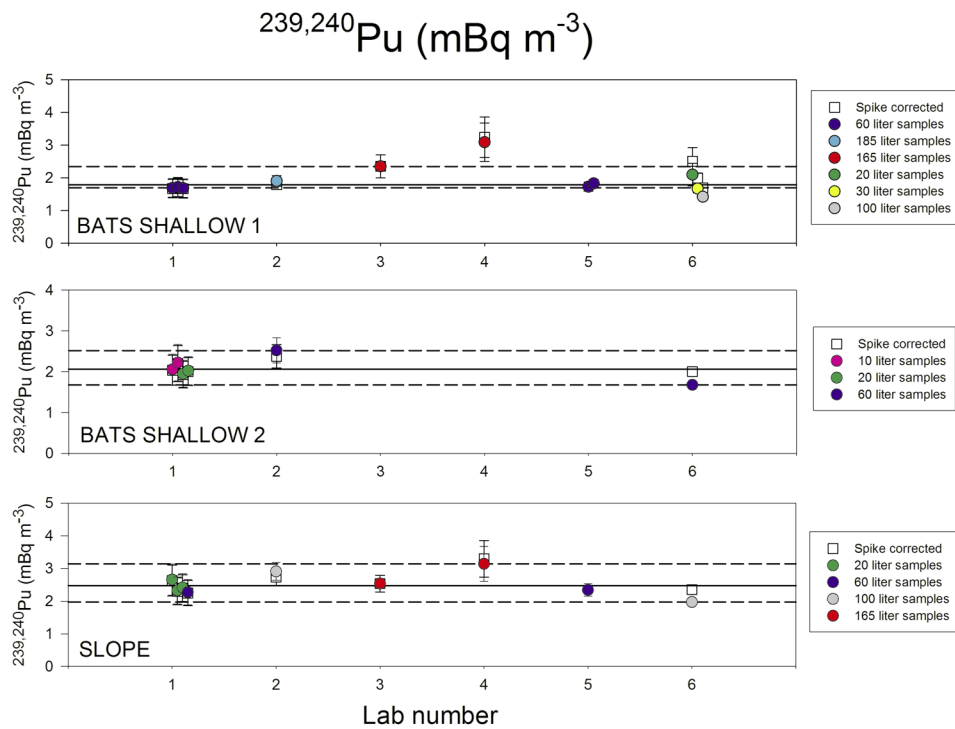
<sup>240</sup>Pu/<sup>239</sup>Pu ratio of  $0.18 \pm 0.014$  (2 s) reported by Kelley et al. (1999). With the exception of BS1 results, the 95% CIs generally include the 2 s range of global fallout, which is likely related to the small sample population. The accurate determination of the <sup>240</sup>Pu/<sup>239</sup>Pu ratio on 10 L samples is challenging due to detection limits of <sup>240</sup>Pu. Additional work is necessary before routinely analyzing samples of this size may be considered. Lab 5 results for BS1 are outside  $\pm 2$  sigma global fallout value, while their results for SL are in good agreement. Whereas Lab 5 results are derived from AMS versus those of the other Labs 1, 4, and 6, which are derived from ICP-MS, additional work is necessary before concluding that the AMS approach is problematic. Although within uncertainty, Lab 1 reported values that were generally higher than the +2 sigma value.

**<sup>137</sup>Cs activity**

Four labs reported results for <sup>137</sup>Cs activity (Fig. 4); one outlier for SL was identified. Although there is some scatter in the data, especially the values reported for 10 and 20 L samples, there does not appear to be a systematic offset between labs for results from both sites. The median concentrations are 1.1 (1.1-1.3), 1.1 (1.1-1.2), and 1.5 (1.5-1.7) Bq m<sup>-3</sup>, for BS1, BS2, and SL samples, respectively.

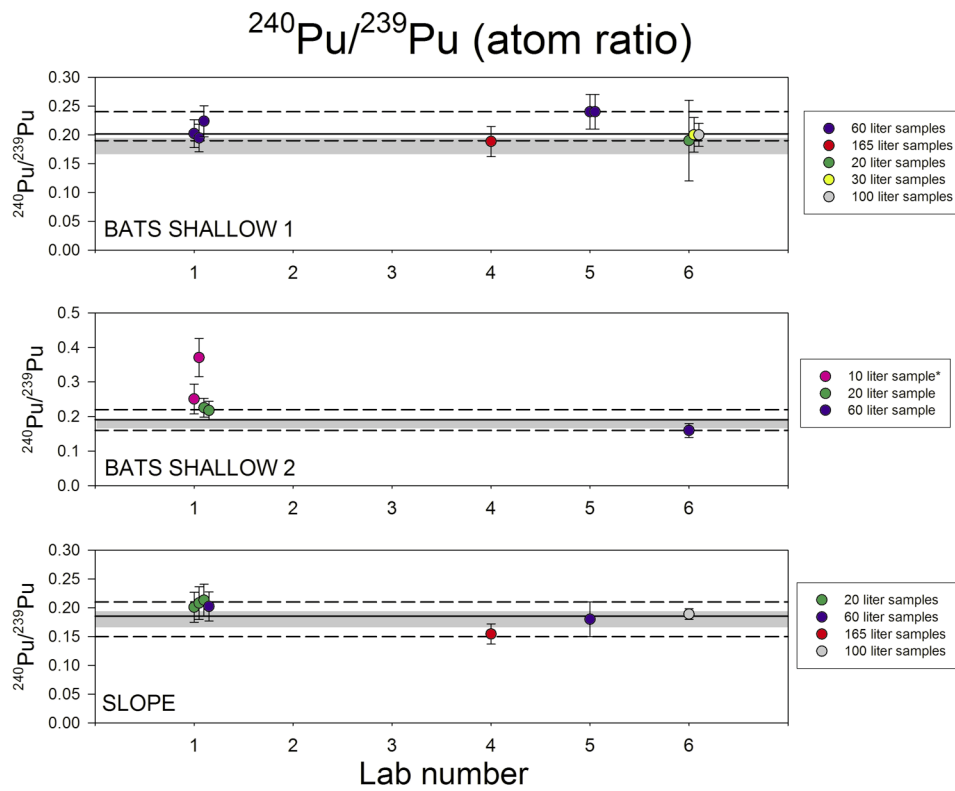
**Table 4.** Consensus values for BS1, BS2, and SL.

Sample	Measurement	Mean	±1 s	Median	C.I. (α = 0.05)	Lab means	
						Reported	Accepted
BS1	<sup>240</sup> Pu/ <sup>239</sup> Pu (atom ratio)	0.21	0.02	0.20	0.19-0.24	4	4
	<sup>239,240</sup> Pu (mBq/m <sup>3</sup> )	1.9	0.3	1.8	1.7-2.4	6	5
	<sup>239</sup> Pu (mBq/m <sup>3</sup> )	1.0	0.0	1.0	0.96-1.01	4	3
	<sup>240</sup> Pu (mBq/m <sup>3</sup> )	0.8	0.2	0.8	0.7-1.1	4	4
	<sup>237</sup> Np (mBq/m <sup>3</sup> )	0.09	0.03	0.09	0.07-0.12	2	2
	<sup>137</sup> Cs (Bq/m <sup>3</sup> )	1.1	0.1	1.1	1.1-1.3	4	4
	<sup>90</sup> Sr (Bq/m <sup>3</sup> )	0.9	0.1	0.9	0.8-0.9	2	2
	<sup>238</sup> Pu (mBq/m <sup>3</sup> )	0.2	0.1	—	—	1	1
BS2	<sup>240</sup> Pu/ <sup>239</sup> Pu (atom ratio)	0.19	0.04	0.19	0.16-0.22	2	2
	<sup>239,240</sup> Pu (mBq/m <sup>3</sup> )	2.1	0.4	2.06	1.7-2.5	3	3
	<sup>239</sup> Pu (mBq/m <sup>3</sup> )	1.2	0.2	1.07	1.1-1.4	3	3
	<sup>240</sup> Pu (mBq/m <sup>3</sup> )	0.8	0.3	0.81	0.6-1.0	2	2
	<sup>237</sup> Np (mBq/m <sup>3</sup> )	0.7	0.4	0.81	0.1-1.1	4	4
	<sup>137</sup> Cs (Bq/m <sup>3</sup> )	1.1	0.1	1.11	1.1-1.2	2	2
SL	<sup>240</sup> Pu/ <sup>239</sup> Pu (atom ratio)	0.18	0.02	0.18	0.15-0.21	4	4
	<sup>239,240</sup> Pu (mBq/m <sup>3</sup> )	2.6	0.4	2.5	2.0-3.1	6	6
	<sup>239</sup> Pu (mBq/m <sup>3</sup> )	1.5	0.3	1.5	1.2-1.9	4	4
	<sup>240</sup> Pu (mBq/m <sup>3</sup> )	1.0	0.1	1.0	0.8-1.1	4	4
	<sup>237</sup> Np (mBq/m <sup>3</sup> )	0.5	0.4	0.5	0.1-1.0	4	4
	<sup>137</sup> Cs (Bq/m <sup>3</sup> )	1.5	0.1	1.5	1.5-1.7	4	3
	<sup>90</sup> Sr (Bq/m <sup>3</sup> )	1.2	0.0	1.2	1.2-1.3	2	2
	<sup>238</sup> Pu (mBq/m <sup>3</sup> )	0.2	0.1	—	—	1	1
<sup>241</sup> Am (mBq/m <sup>3</sup> )	0.9	0.4	0.9	0.7-1.2	2	2	

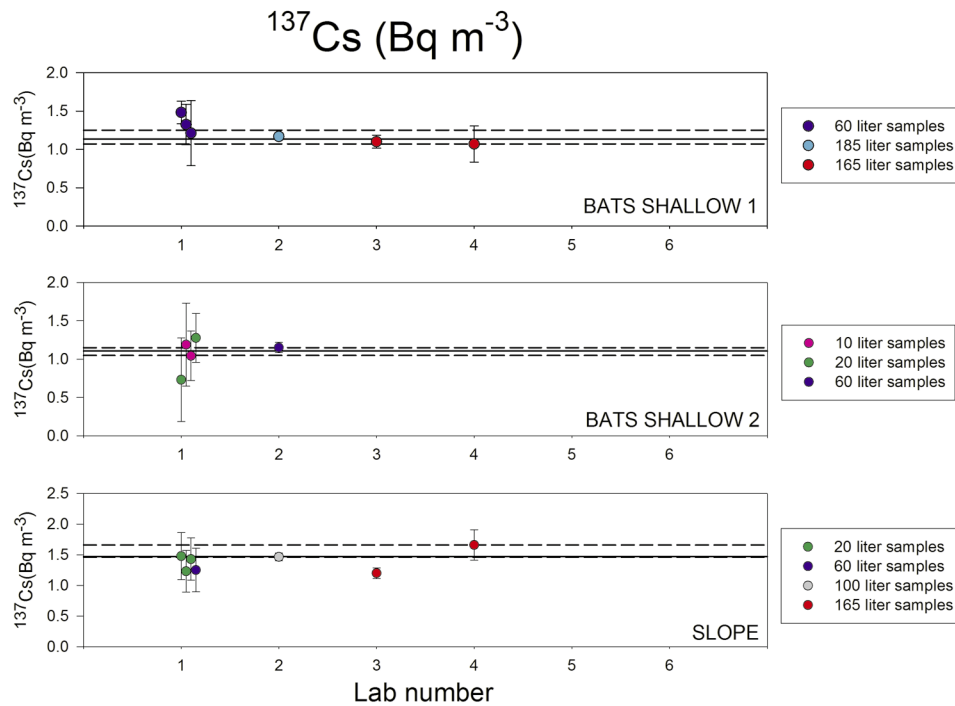


**Fig. 2.** Plutonium intercalibration results for BS1, BS2, and SL (6 labs participating). Results reported as <sup>239,240</sup>Pu activity (the combined activity of <sup>240</sup>Pu and <sup>239</sup>Pu in units of mBq m<sup>-3</sup>). Hollow squares show the effect of <sup>242</sup>Pu spike intercalibration on reported activity. Solid and dashed lines are the median and 95% CI, respectively, of the lab means after outlier removal. Individual lab results for different volumes are shown.





**Fig. 3.** Intercalibration results for  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratio for BS1, BS2, and SL samples (4 labs participating). Solid and dashed lines are the median and 95% CI, respectively, of the lab means after outlier removal. Individual lab results for different volumes are shown. The gray region represents the  $\pm 2$  sigma value for global fallout reported by Kelley et al. (1999).



**Fig. 4.** Cesium-137 intercalibration results for BATS shallow and Slope sites; 4 labs participating. Solid and dashed lines are the median and 95% CI, respectively, of the lab means after outlier removal. Individual lab results for different volumes are shown.

**Intercalibration results—<sup>237</sup>Np, <sup>241</sup>Am, <sup>90</sup>Sr, and <sup>238</sup>Pu**

In some cases, results were submitted by only two labs and were not in good agreement (Table 3 and summarized below). With the exception of <sup>237</sup>Np, the other ARs were analyzed by laboratories requiring large volumes (>100 L) for analysis. Labs 1 and 4 reported <sup>237</sup>Np results. Lab 1 results were internally consistent over a range of volumes (10-60 L). Lab 4 analyzed a single 165 L sample at BS1 and SL sites. Lab 4 and Lab 1 results were systematically different by a factor of 1.5–2 at both sites. Labs 3 and 4 reported <sup>241</sup>Am results for large volume (165 L) samples, which were significantly different (~factor of 2) at both at BS1 and SL sites. Labs 3 and 4 reported <sup>90</sup>Sr results for large (165 L) liter samples, and both labs were in good agreement. Labs 3 and 4 reported <sup>238</sup>Pu results for large (165 L) liter samples, although Lab 4 results were below detection limits at both sites.

Due to limited intercalibration resources and the desire to focus on decreasing sample volumes, we did not pursue additional intercalibration efforts. We expect that some of these issues can be dealt with as part of the analysis of samples from cross-over stations, which is included in the general design of GEOTRACES cruises.

**Intercalibration results—particulate material from large volume filtration**

Lab 1 reported results for the particulate samples. Pu and Np levels in the representative 150 L samples and dip blanks were at or below detection limits, and larger samples on the order of several hundreds of liters will likely be necessary to obtain acceptable results. Although not collected as part of the intercalibration, selected filter sub-samples from MULVFS, representing significantly larger sample volumes, were analyzed by Lab 1 at both the BATS and SLOPE sites.

**Lab 1 results—filtered seawater**

The sample volume limitations imposed by the GEOTRACES program are significant, and therefore, method opti-

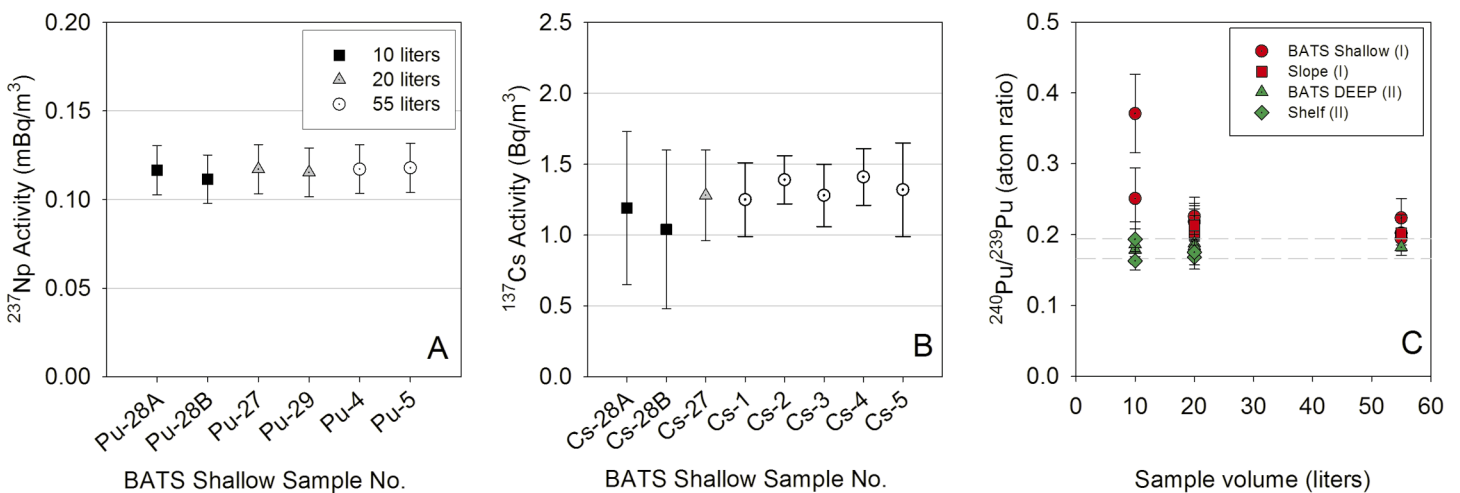
mization for small sample sizes is a goal of this study. Samples analyzed include those collected from the surface at the BATS and SLOPE sites and a second round of samples collected from the BATS Deep site and the Continental Shelf.

As part of the intercalibration exercise, Lab 1 demonstrated the ability to measure <sup>137</sup>Cs on samples ≥ 20 L and <sup>237</sup>Np on samples ≥ 10 L without any systematic offsets (Fig. 5, panels A and B). Uncertainties for <sup>137</sup>Cs in 10 L samples were large (~50%), making these data not very useful. Lab 1 is in the process of evaluating γ counting protocols to determine if uncertainties can be reduced.

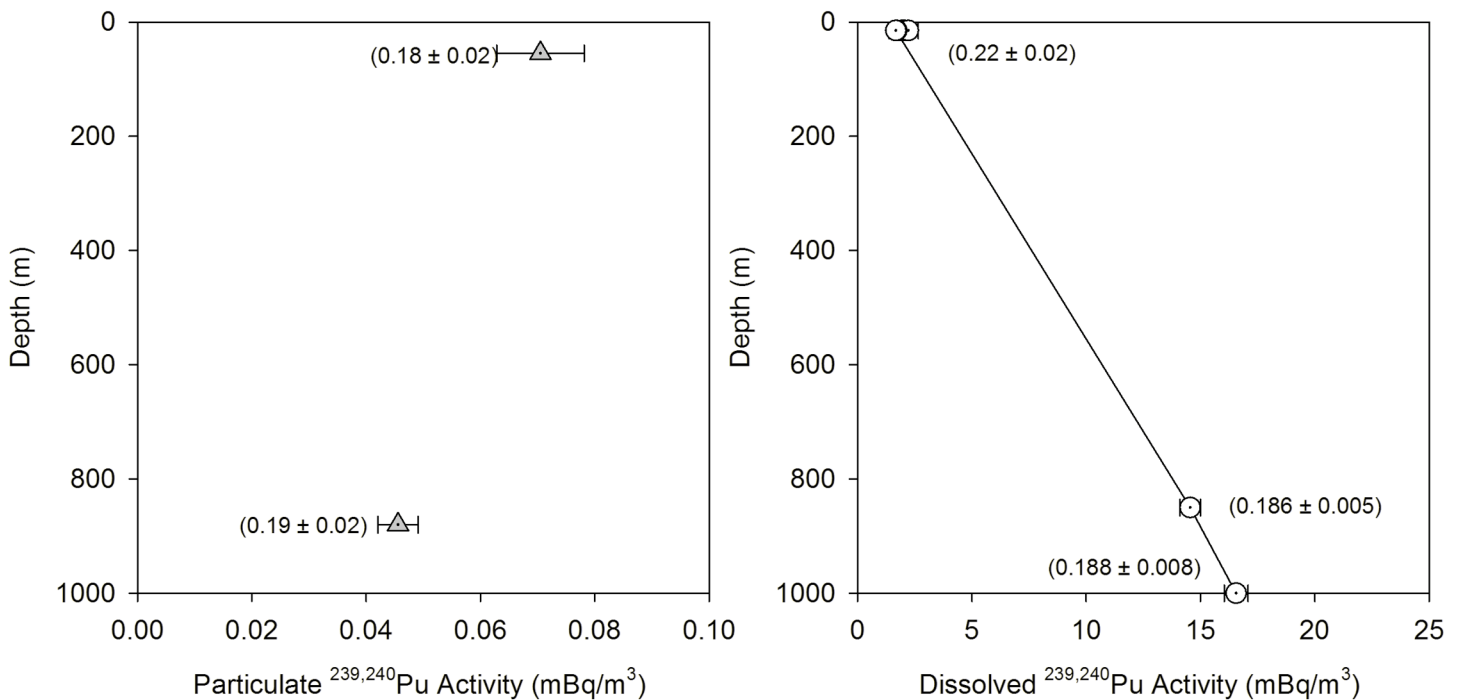
The initial plutonium results from Lab 1 were problematic. The <sup>240</sup>Pu/<sup>239</sup>Pu ratios were higher than the ± 2 sigma value for global fallout, which was expected, and the data showed a clear effect of decreasing sample volumes (Fig. 5, panel C: BATS shallow and Slope data). In the second round of analyses, clear improvements were made by avoiding the addition of <sup>243</sup>Am, which contains contaminant <sup>239</sup>Pu (Panel C; BATS Deep and Shelf data). The <sup>243</sup>Am spike is added both as a yield monitor for <sup>241</sup>Am and as an internal run standard (Kenna 2002). Neither addition is truly necessary for Pu analysis. Whereas this was not a problem for sediments (the original target of the method), the resulting corrections are large relative to seawater sample concentrations.

**Lab 1 results—particulate material from MULVFS samples**

As discussed above the filtered particulate samples distributed as part of the GEOTRACES Intercalibration were too small. As a follow up, Lab 1 also analyzed two filter sub-samples that were obtained from the BATS site from the MULVFS sampling system (Fig. 6; panel A). These represent significantly larger sampling volumes (~400 and ~1600 L) than those sent to intercalibration participants. For both samples, the global fallout <sup>240</sup>Pu/<sup>239</sup>Pu ratio is observed as well as clear dif-



**Fig. 5.** Lab 1 results for <sup>237</sup>Np, <sup>137</sup>Cs from surface waters collected at the BATS site; the x-axes in panels A and B represent samples of different volumes. Panel C shows all Lab 1 <sup>240</sup>Pu/<sup>239</sup>Pu results from samples collected from several locations during the first intercalibration cruise. In panel C, red and green symbols indicate measurements made before and after method changes.

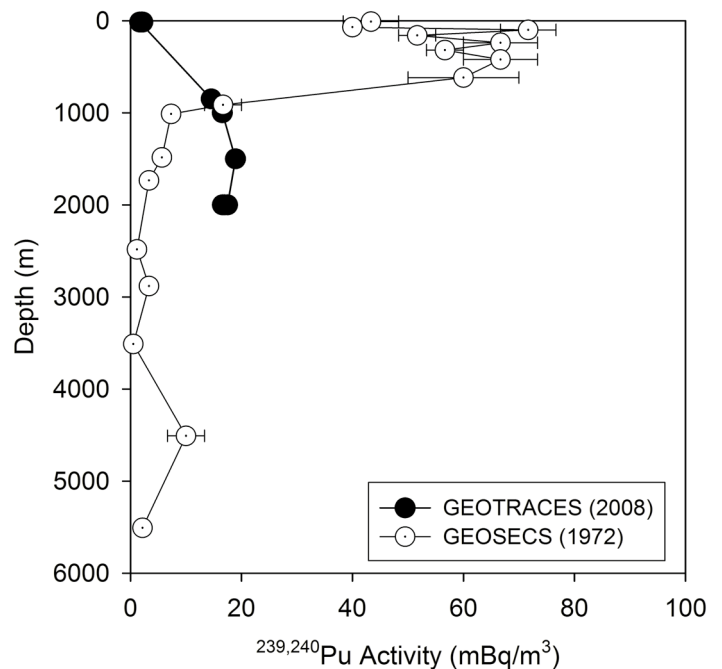


**Fig. 6.** Plutonium activity and isotopic composition determined on 90 mm QMA filter punch aliquots obtained from the MULVFS in situ pumping system (left) at 55 and 877 m. Filtered volumes were ~400 and ~1600 L for the shallow and deep sample, respectively. The measured <sup>240</sup>Pu/<sup>239</sup>Pu atom ratios are shown in parentheses. The right-hand pattern shows plutonium concentrations and atom ratios measured in the dissolved phase for samples collected at depths similar to the particulate samples (15, 850, and 1000 m).

ferences in plutonium concentrations between samples collected from different depths. These data serve to demonstrate the ability to analyze filtered particulate samples of sufficient volume. Although dissolved and particulate concentrations were measured on samples from slightly different depths, we obtain a particulate to dissolved ratio of 0.31% at ~850 m. Whereas there are no BATS data for comparison, available data from Hirose et al. (2003) for the Pacific report values ranging between 0.38 and 1.13% for depths between 600 and 1200 m, which suggests that our results are reasonable. As expected, the <sup>237</sup>Np was below detection in both samples, and the surface sample was initially γ counted to determine the presence or absence of <sup>137</sup>Cs, which was also below detection; both results are consistent with Cs and Np being present as soluble species in seawater (Brewer et al. 1972; Keeney-Kennicutt and Morse 1984, 1985)

**GEOTRACES intercalibration <sup>239,240</sup>Pu results compared to GEOSECS data**

Samples obtained during the GEOTRACES intercalibration cruise in 2008 allow a partial water column profile of dissolved <sup>239,240</sup>Pu to be obtained (Fig. 7). When compared with data collected 36 years earlier as part of the GEOSECS program (Livingston et al. 1985), the contrast is striking and serves as an example of how this key AR has continued to be redistributed in the oceans by processes that control the distributions of key trace elements and isotopes in the ocean.



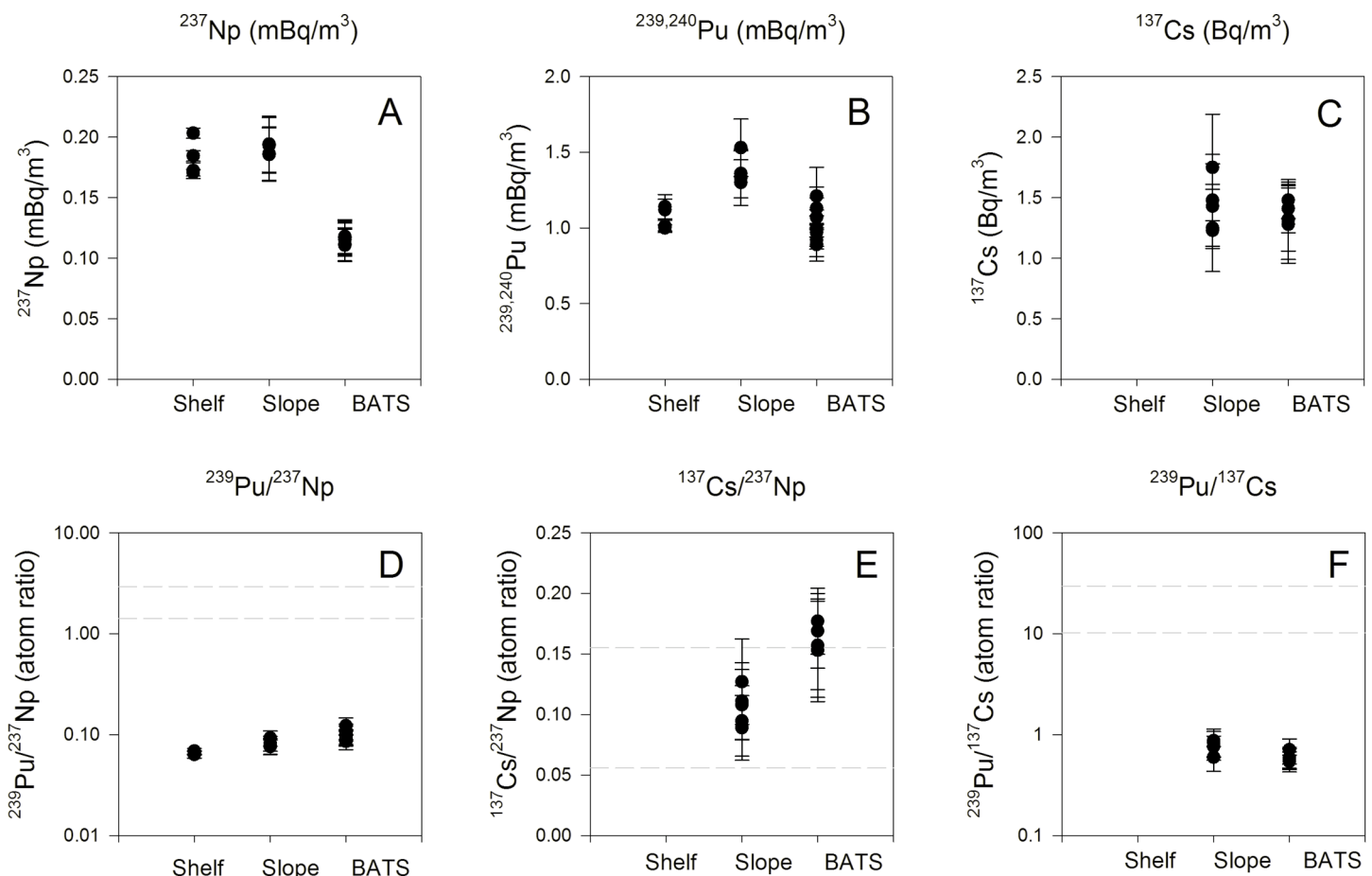
**Fig. 7.** A comparison of dissolved <sup>239,240</sup>Pu distributions between the BATS site measured during the 2008 intercalibration (solid symbols) and GEOSECS Station GX-31 (27° 0.0' N × 53° 31.0' W) measured in 1972 (open symbols).

Although the 2008 data are limited, the elevated levels in the upper water column observed in 1972 are not apparent, and it appears that the  $^{239,240}\text{Pu}$  has been exported to deeper waters (>1000 m). This reduction  $^{239,240}\text{Pu}$  content in the surface water is variable depending upon location. For example, a majority of  $^{239,240}\text{Pu}$  remains above 1000 m in the Pacific (Livingston and Povinec 2002). It has been postulated that this sub-surface maximum is related to vertical fluxes of Pu-bearing particles and subsequent remineralization by biological activity as well as physical circulation processes (Fowler et al. 2000; Livingston and Povinec 2002). Additional isotopic data and water column inventories will allow a better understanding of the decadal scale processes at work and whether we are observing net removal of plutonium or redistribution in the water column between the Atlantic and Pacific Oceans for the last several decades.

#### AR concentrations and isotopic composition measured in surface waters from the northeastern US continental shelf and slope and BATS

Although limited, surface water data collected as part of the first GEOTRACES intercalibration cruise allows us to

examine AR concentrations and isotope ratios at 3 different locations (Fig. 8). An examination of the radionuclide concentrations (panels A-C) indicates that  $^{237}\text{Np}$  is enriched in shelf and slope waters compared with the BATS site, plutonium appears to be variable with the highest concentrations being observed in the slope samples, and although  $^{137}\text{Cs}$  data are not available for the shelf samples, there does not appear to be a significant difference between concentrations measured in the slope and BATS samples. The isotopic ratios when compared with global fallout compositions tell a clearer story (panels D-E). The  $^{239}\text{Pu}/^{237}\text{Np}$  ratio (panel D) is significantly lower than global fallout at all three locations indicating in general excess  $^{237}\text{Np}$ . A seaward trend toward the global fallout ratio is also apparent, suggesting less removal of Pu as one heads offshore. The  $^{137}\text{Cs}/^{237}\text{Np}$  ratios (panel E) in the surface waters of the slope and BATS site are similar to global fallout indicating a behavior that is fairly conservative. Similar to the  $^{239}\text{Pu}/^{237}\text{Np}$  ratios, the  $^{239}\text{Pu}/^{137}\text{Cs}$  ratios are also significantly lower than global fallout, further suggesting a loss of Pu; the offshore trend similar to the one observed in the  $^{239}\text{Pu}/^{237}\text{Np}$  ratio is not apparent.



**Fig. 8.** Dissolved surface water concentration of  $^{237}\text{Np}$ ,  $^{239,240}\text{Pu}$ , and  $^{137}\text{Cs}$  measured in samples collected in shelf and slope waters as well as the BATS site (panels A, B, and C, respectively). Also shown are selected atom ratios,  $^{239}\text{Pu}/^{237}\text{Np}$ ,  $^{137}\text{Cs}/^{237}\text{Np}$ , and  $^{239}\text{Pu}/^{137}\text{Cs}$ . The dashed lines indicate the corresponding  $\pm 2$  sigma value for global fallout (Kelley et al. 1999, Kenna unpubl. data).

## Summary

As part of the GEOTRACES Program, six laboratories participated in an intercalibration exercise on several anthropogenic radionuclides of interest. The effort was successful for  $^{239,240}\text{Pu}$  activity,  $^{240}\text{Pu}/^{239}\text{Pu}$  isotope ratio, and  $^{137}\text{Cs}$  activity measured in filtered seawater samples from the Bermuda Atlantic Time Series station (BATS) and a site on the continental slope of the Northeastern U.S. A limited number of analyses were reported for  $^{237}\text{Np}$ ,  $^{241}\text{Am}$ ,  $^{90}\text{Sr}$ , and  $^{238}\text{Pu}$  in filtered seawater. Intercalibration of any of the isotopes of interest in filtered particulate matter was unsuccessful due to insufficient size of the samples distributed.

Although replicate analyses and optimization of methods was discussed at length before the intercalibration exercise and planned as part of it, the majority of participants did not participate in these aspects of the exercise. This may be due to a combination of factors, such as analytical costs, detection limitations, and/or large volumes required for some of the analytical approaches. It was clear from the beginning that some of the labs would not pursue this aspect of the intercalibration.

One of the goals/strengths of the intercalibration exercise was to develop the capacity to share samples between and/or directly compare results from different labs. Since the intercalibration, at least two of the participating labs have begun collaborating in this fashion on GEOTRACES cruises in the Atlantic. One item that needs to be addressed is how other researchers interested in the anthropogenic radionuclides can/will join GEOTRACES post-intercalibration. Maintaining a ready supply of high-quality intercalibration samples as some of the groups measuring other TEIs have been able to do is both a great service to the community and a significant amount of work. In the case of the low level TEIs that require large volumes, the collection, storage, and shipping of additional intercalibration samples is made more difficult. In a limited fashion, the collection of additional samples from BATS or other crossover stations may be possible. Following the example of the Th group (Anderson et al. 2012), we have started to work with an internal Pu laboratory standard that is designed to simulate the level and isotopic compositions found in seawater—this has been very useful in method optimization and instrument evaluation and may be part of the solution for adding new participants.

A new CRM for ARs in seawater from the Irish Sea (IAEA-443) has recently been produced and could be a valuable resource (Pham et al. 2011). Including the analysis of this CRM as part of a GEOTRACES AR QA-QC protocol has merit. For example, this higher activity CRM could be analyzed or diluted and analyzed at the appropriate levels, however the practice relying solely on knowns at or in excess of the expected high end of the concentration range for quality control can be problematic, leading to a false sense of proficiency on lower level samples (see discussions Bowen 1978; Bowen

and Volchok 1980). Bowen and Volchok (1980) suggest a rule of thumb that both qualifying analyses and routine quality control analyses should be made, at a minimum, on samples of two “known” series, one close to the maximum concentration to be reported, and one about five times the minimum concentration to be reported. The authors suggested that good performance on both these standard series would be a reasonable indicator of proficiency over the expected range.

## Recommendations

1. We do not recommend a specific sampling or processing for the anthropogenic radionuclides. Although the collection and analysis of separate dissolved and particulate phases would be ideal for some of the radionuclides (e.g., Pu isotopes,  $^{241}\text{Am}$ ), the large volumes required (hundreds to thousands of liters) to analyze these isotopes in the particulate phase and specialized equipment (i.e., large volume in-situ pumps) may or may not be available. Therefore, total analysis (i.e., unfiltered samples) may also be considered. If accessible, ICP-MS analysis is preferred over  $\alpha$  spectrometry, primarily for its lower detection limits and ability to determine the  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratio. We recommend that a target precision of  $< 10\%$  be adopted for the  $^{239}\text{Pu}/^{240}\text{Pu}$  ratio.

2. Due to the significant volume requirements, dedicated hydrocasts will likely be necessary. Collection with a standard rosette system is adequate. Although not prone to contamination, we recommend that sampling containers for the non-contamination prone TEIs in a similar fashion (i.e., acid-cleaned high or low density polyethylene [HDPE or LDPE] containers) to allow for the possibility of method development allowing other constituents to be measured on the same sample. Proper cleaning also allows for the removal of catalysts, release agents used in the production process that could conceivably interfere with chemical recoveries or other problems such as isobaric interference during the ICP-MS measurement. Note that vertical concentration gradients may be large, so cross contamination is possible. If seawater samples are to be analyzed for total concentrations, they may be simply drawn, unfiltered from the Niskin bottles. If separate collection of the dissolved phase is planned, gravity filtration using an acceptable cartridge filter (e.g., Acropak 500 filter cartridges were used in this study) is recommended.

3. Acidification in the field is not strictly necessary, although we did not evaluate this particular aspect of sample processing. However, many methods do call for the acidification of samples and both hydrochloric and nitric acids are suitable for this purpose. On a practical note, samples acidified to  $\text{pH} = 2$  with hydrochloric acid have less shipping restrictions than those acidified with nitric acid. Trace metal grade acid is sufficient, unless sample processing is driven by more contamination-prone element. For safety, if the decision is made to acidify at sea, we recommend working with 6N hydrochloric acid rather than full strength. Samples appear to be stable after acidification.

4. Samples may be spiked and preconcentrated at sea or acidified at sea and shipped to the home laboratory for spiking and preconcentration. Given the large volumes, “at sea” processing is often the method of choice if sufficient personnel and shipboard space are available. Processing at sea avoids the necessity of shipping large quantities of seawater to the home laboratory. It does however require handling of radioisotopes at sea as well as more shipboard space and personnel.

5. The isotope dilution method should be employed for accurate measurements using well-characterized spikes. In general, spikes should be carefully characterized and maintained to preserve integrity. If possible, a spike intercalibration should be performed among participating laboratories with agreement on a primary isotope standard. If spike intercalibration cannot be completed prior to the work, aliquots of the spikes used in should be archived for future intercalibrations. In general, spikes should be added gravimetrically. If processing of samples at sea is planned, it is recommended that spikes be preweighed on land and carefully transferred at sea. If samples are spiked volumetrically (on land or at sea), extreme care should be taken to properly calibrate the pipettor that is used. If quantification of  $^{134}\text{Cs}$  is desired along with  $^{137}\text{Cs}$ , it may be achieved by using stable Cs as the yield monitor as established earlier.

6. A variety of approaches have been used to record sample weight and/or volume, and the literature should be consulted for the best one to use in a particular cruise. Since the majority of separations involve a coprecipitation step, the necessity to weigh samples at sea may be determined by the decision to spike and coprecipitate at sea or ship samples back to the laboratory for analysis.

7. The required volumes for particles are large and almost certainly require an in situ filtration approach. These include MULVFS, McLane, and Challenger pumps. QMA filters (quartz fiber  $\sim 1\ \mu\text{m}$ ) are recommended for in-situ pumping, specifically for their high loading and ease in digesting. QMA material does not appear to present a blank issue for the anthropogenic radionuclides.

Items 8-10 identify three areas that serve to limit the determination of ARs and encourage a discussion within the community.

8. *Lack of a CRM with typical open ocean AR levels to address issues of commutability*—This issue was discussed during GEOSECS and still remains problematic. One approach would be to perform initial processing (i.e., volume reduction) and then develop CRMs. For example, one could perform a large volume seawater coprecipitation, followed an AMP sorption on the remaining liquid. Both the coprecipitate and the AMP could then be developed as CRMs. This approach would 1) circumvent the problem of storing and shipping large volumes of seawater, 2) contain ARs at the requisite levels, 3) contain the proper AR/seawater matrix for various sample volumes required by different laboratories/techniques, 4) likely be stable (acidic solution).

9. Lack of a commercially available thermal ionization mass spectrometer (TIMS) capable of low-level Pu/Np mea-

surements (off-the-shelf)—TIMS offers excellent sensitivity and low detection limits for  $^{237}\text{Np}$ ,  $^{239}\text{Pu}$ , and  $^{240}\text{Pu}$  of  $<5 \times 10^5$ ,  $<7 \times 10^4$ , and  $<3 \times 10^4$  atoms  $\text{kg}^{-1}$ , respectively. Pu and Np isotopic data generated from TIMS have been published for seawater samples as small as 4 L and not only include the  $^{240}\text{Pu}/^{239}\text{Pu}$  ratio, but the ratios  $^{241}\text{Pu}/^{239}\text{Pu}$ , and  $^{242}\text{Pu}/^{239}\text{Pu}$  as well (Beasley et al. 1998; Buesseler and Halverson 1987). Note, however, that the generation of such data can be traced to specialized and custom TIMS machines owned and operated by the US DOE national laboratories (Lagergren and Stoffels 1970). Bürger et al (2009) demonstrated sub fg detection limits using a commercially available, albeit heavily modified, TIMS located at another US DOE lab but did not analyze seawater. In general, access to these machines is limited and cost-prohibitive within the scope of GEOTRACES. More recently published Pu data generated by unmodified TIMS do not exhibit the same sensitivity nor have they included the analysis of seawater (Elliot et al. 2006; Jakopic et al. 2009).

10. *Lack of a commercially available long-lived yield tracer for neptunium*—Whereas  $^{237}\text{Np}$  analysis is fairly straightforward using ICP-MS, an important limitation on many labs with ICP-MS capabilities is the lack of available commercial solutions providing a long-lived neptunium isotope (i.e.,  $^{236}\text{Np}$ ) that could be used as chemical yield tracer (Efurd et al. 1991). Without such a yield monitor, researchers have used  $^{239}\text{Np}$  ( $t_{1/2} = 2.36$  days) or  $^{242}\text{Pu}$  as a yield monitor, or standard addition of  $^{237}\text{Np}$ , each of which presents challenges (Chen et al. 2002a; Chen et al. 2001b; Holm et al. 1987; La Rosa et al. 2005; Qiao et al. 2011). Production of a pure  $^{236}\text{Np}$  spike that is available to the community would be a dramatic improvement.

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Among the strengths of GEOTRACES are the measurement of multiple TEIs, the inclusion of several specialized sampling systems, and the assembly of a critical mass of knowledge and expertise regarding marine biogeochemical processes on a single cruise. This approach can provide important insights and allow questions to be addressed that would be difficult if not impossible on a single project cruise. The work presented herein has certainly benefited from this synergy and would not have been possible without contributions from numerous individuals. We would especially like to thank Greg Cutter, who has led the intercalibration effort from its inception, through logistically complex sampling cruises as chief scientist, and ultimately to the publication of this special volume. The authors would like to gratefully acknowledge the captain and crew of the R/V *Knorr* (KN193-6), and co-chief scientists Ken Bruland and Rob Sherrell. We would like to thank Matthew Charette, Willard Moore, Henrieta Dulaiova, Ken Bruland, and Geoff Smith for water samples provided from their onboard collection systems. Samples of particulate material collected by in situ filtration were provided by two groups. We thank Ken Buesseler, Kanchan Maiti, and Steve Pike for providing the intercalibration samples collected from the



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