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Plutonium isotopes as tracers for ocean processes: A review

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Abstract

Since the first nuclear weapons tests in the 1940s, pulsed inputs of plutonium isotopes have served as excellent tracers for understanding sources, pathways, dynamics and the fate of pollutants and particles in the marine environment. Due to the well-defined spatial and temporal inputs of Pu, the long half-lives of ²⁴⁰Pu and ²³⁹Pu and its unique chemical properties, Pu is a potential tracer for various physical and biogeochemical ocean processes, including circulation, sedimentation and biological productivity, and hence a means of assessing the impacts of global climate change. Due to the source dependency of the Pu isotopic signature, plutonium isotopes are beginning to be exploited as tools for the evaluation and improvement of regional and global ocean models that will enhance understanding of past and future changes in the oceans. This paper addresses the major sources of Pu and the physical and biogeochemical behaviour in the marine environment. Finally, the use of Pu isotopes as tracers for various oceanic processes (e.g. water mass transport, particle export, and sedimentation) is considered.

Keywords: plutonium; isotopic ratio; inventory; source term, marine environment; marine tracer; water; sediment; biota

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1. Introduction

The World Ocean plays a critical role in regulating the earth's climate and reliable tracers are required to predict water mass movement and elucidate ocean processes. Anthropogenic radionuclides play important roles as tracers for ocean processes (Dahlgaard, 1995; Livingston and Povinec, 2002) and can be used to reconstruct past environmental conditions and therefore enhance our knowledge about past and future climate change. In addition, the distribution of anthropogenic radionuclides can be modelled to derive rates of ocean transport on timescales not attainable by direct measurement. Since the input histories of anthropogenic radionuclides to the environment are well known, it enables us to trace small-scale (near shore) and large-scale oceanic processes (circulation, sedimentation and biological productivity) and predict future climate change processes and their impact on the marine environment.

Plutonium has been released into the marine environment since the first nuclear weapons test in 1945. Plutonium isotopes are mainly produced by neutron irradiation of uranium, and the isotopic composition of Pu is characteristic of the source, as it depends on the neutron intensity and the duration of irradiation. Plutonium concentrations in the marine environment are continuously changing due to marine processes such as ocean currents, sedimentation, remobilisation and biological uptake. The well-defined spatial and temporal source terms and high particle affinity of Pu provide a powerful tool for studying a variety of processes in the marine environment such as water mass transport (advection and convection), particle fluxes and scavenging, and validating various global circulation and biogeochemical ocean models. The most frequently studied Pu isotopes in the marine environment are ^{238}Pu ($T_{1/2} = 87.74$ a), ^{239}Pu ($T_{1/2} = 24\,100$ a), ^{240}Pu ($T_{1/2} = 6\,561$ a), ^{241}Pu ($T_{1/2} = 14.33$ a) and ^{242}Pu ($T_{1/2} = 373\,000$ a) with ^{239}Pu and ^{240}Pu as the most abundant in the marine environment.

Recent advances in analytical procedures and Inductively Coupled Plasma Mass

Spectrometry (ICP-MS) have improved the determination of low concentrations of Pu and provide precise isotopic ratios with reasonable costs (Kim et al., 2007; Ketterer and Szechenyi, 2008; Qiao et al., 2009). Previously, Pu analysis in marine samples was mainly performed by conventional alpha spectrometry, with the disadvantage of long measurement times and no resolution between ^{239}Pu and ^{240}Pu , due to similar alpha energies.

Comprehensive studies on the distribution and behaviour of Pu in the marine environment have been summarised in several review papers (e.g. Sholkovitz, 1983; Baxter et al., 1995; Livingston and Povinec, 2000; Livingston et al., 2001; Livingston and Povinec, 2002; Hamilton, 2005; León Vintó et al., 2005).

The specific aim of this paper is to provide an overview of the use of Pu isotopes as tracers for various processes in the marine environment. First, the major Pu sources to the marine environment and their isotopic composition are summarised. This is followed by an overview of the geochemical and biogeochemical processes affecting the behaviour and distribution of Pu isotopes in the marine environment. Finally, the utility of Pu isotopes as tracers for various marine processes is considered, with an emphasis on the use of specific Pu isotopic composition (e.g. $^{240}\text{Pu}/^{239}\text{Pu}$ ratio).

2. Sources of Pu in the oceans

The majority of Pu in the environment is derived from man-made sources with only trace amounts from natural sources (Taylor, 2001). The main sources of Pu isotopes in the World Ocean are fallout from atmospheric nuclear weapons testing and liquid discharges from nuclear reprocessing plants (León Vintó et al., 2005). Other sources that have impacted on Pu levels in the marine environment at the local and/or regional scale are the Chernobyl accident, aircraft accidents involving nuclear weapons, burn-up of nuclear powered satellites and, to a

lesser extent, dumping of radioactive wastes and the loss of nuclear submarines. The composition of Pu isotopes from different sources in the marine environment varies significantly due to the characteristic isotopic composition corresponding to the means of production (see Table 1). Reactor-grade Pu typically contains more than 35 % ^{239}Pu with a $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio of 0.2 - 1.0 after fuel burn-up (Yamana et al., 2001). The $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio in weapon-grade Pu is much lower (0.02 - 0.06) because burn-up is kept low to minimise the production of higher Pu isotopes (Mark, 1993).

<Table 1 here>

2.1. Atmospheric nuclear weapon tests

Between 1945 and 1980, 543 atmospheric nuclear weapons tests (440 Mt total yield) were carried out worldwide with the most intense periods in 1952 - 1958 and in 1961 - 1962 (UNSCEAR, 2000a). Figure 1 shows the total annual yields (Mt per year) from atmospheric nuclear weapons tests together with the activity of ^{90}Sr deposited in the northern and southern hemispheres. The ^{90}Sr global fallout pattern is similar to that of Pu isotopes, with an average $^{239+240}\text{Pu}/^{90}\text{Sr}$ activity ratio in global fallout of about 0.025 (decay corrected to 2000) based on the normalised production rate for ^{90}Sr and Pu isotopes in nuclear explosions (UNSCEAR, 2000a; Aarkrog, 2003).

The low-yield fission weapons tests up to 1951 produced mainly tropospheric fallout that was deposited around the latitude band of the test sites (close-in fallout). From 1952 until the early 1960s, high-yield thermonuclear devices were tested and the fallout was spread worldwide (global fallout). Due to the distribution of the weapons tests locations the majority (ca. 76 %) of the fallout debris was deposited in the northern hemisphere (Fig. 1) with the highest deposition density between the 40 and 50 °N latitudes (UNSCEAR, 2000a).

<Figure 1 here>

It has been estimated that 12 PBq of $^{239+240}\text{Pu}$ was deposited in the World Ocean from atmospheric nuclear weapons tests (Hamilton, 2005) and the resulting Pu isotope inventory is shown in Table 2. The Pu isotopic composition in the debris from nuclear detonations varies considerably and depends on the explosive yield, test site location and weapon type (Perkins and Thomas, 1980). The Pu isotopic composition in atmospheric fallout debris has changed over time due to changes in weapon design and yield, as demonstrated by $^{240}\text{Pu}/^{239}\text{Pu}$ time series analysis of samples from around the world (Koide et al., 1985; Leifer and Chan, 1997; Warneke et al., 2002; Olivier et al., 2004). The overall integrated $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio in global fallout debris is characterised by a ratio of 0.178 ± 0.023 (2 SD; 95 % confidence level) (Kelley et al., 1999).

<Table 2 here>

More than 70 % of the global input of Pu from atmospheric nuclear weapons testing was from Novaya Zemlya (Russia) and the Marshall Islands (North Pacific). The Novaya Zemlya testing grounds were used mainly for large-scale atmospheric tests, with most of the debris injected into the stratosphere, and hence contributed mainly to the global fallout with only minor local marine contamination (Osvath et al., 1999; Oughton et al., 2004). However, a series of surface and underwater tests contributed significantly to elevated Pu levels in Chernaya Bay, off the southern coast of Novaya Zemlya. Approximately 11 TBq of $^{239+240}\text{Pu}$ from the tests remains in Chernaya Bay sediments and still acts as a source to the Barents Sea, with an average $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio of about 0.03, equivalent to low-yield nuclear detonations (Smith et al., 1995; Smith et al., 2000b). Most of the Marshall Islands tests were conducted near the surface, resulting in significant local and regional inputs of Pu to the marine environment (Buesseler, 1997; Robison and Noshkin, 1999). Debris from the first high-yield (Ivy Mike test, 15 Mt) thermonuclear detonation in 1952 at the Enewetak Atoll had

a $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio of 0.363 ± 0.004 (Diamond et al., 1960). It has been estimated that debris from this detonation contributed about 5.1 PBq of $^{239+240}\text{Pu}$ to the local marine environment (Hamilton, 2005). Close-in fallout from the highest yield (Bravo test, 15 Mt) detonation performed at the Bikini Island in 1954 had a $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio of 0.33 ± 0.06 (Muramatsu et al., 2001). The main Pu contamination from these sites is buried in lagoon sediments (*ca.* 90 TBq $^{239+240}\text{Pu}$ in 2000) which still act as a Pu source in the Pacific Ocean with an estimated annual $^{239+240}\text{Pu}$ export of about 0.2 TBq a^{-1} to the open ocean (Noshkin et al., 1987; Hamilton et al., 1996; Donaldson et al., 1997; Robison and Noshkin, 1999; Hamilton, 2005).

Other locations with significant input to the global or local marine environment include the Johnston Atoll and the Christmas Island (North Pacific), the Lop Nor site (China), the Mururoa and the Fangataufa Atolls (South Pacific), and the Semipalatinsk site (Kazakhstan). Contributions from other tests were very small or negligible (Livingston and Povinec, 2000). Overall, about 85 % of the Pu injected into the atmosphere has been deposited globally and 15 % locally or regionally (UNSCEAR, 2000a).

2.2. Discharges from the nuclear industry

When spent nuclear fuel is treated in nuclear reprocessing facilities low-level liquid radioactive wastes containing variable quantities of Pu are released into the marine environment. The nuclear reprocessing facilities in Sellafield (UK) and La Hague (France) in the North East Atlantic region are the most prominent sources. In the Arctic Ocean, a potential Pu source is run off from contaminated sediment in the Ob and Yenisey river system connected to the Mayak, Krasnoyarsk and Tomsk nuclear facilities and the Seimpalatinsk test site (Lind et al., 2006). Recent Pu analyses of sediment cores from the Ob and Yenisey estuaries showed $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios of about 0.11 and 0.18, respectively, indicating

contributions from both global fallout and the nuclear industry in the outflow to the Kara Sea (Skipperud et al., 2009).

Plutonium releases from other installations that may have influenced local Pu levels include Hanford plutonium production facility into the North East Pacific (Beasley and Jennings, 1984), Oak Ridge and Savannah River production plants into the West Atlantic (Carlton et al., 1996), Marcoule reprocessing plant in the Northwestern Mediterranean Sea (Miralles et al., 2004; Lansard et al., 2007), Rokkasho and Tokaimura nuclear reprocessing plants on the west coast of Japan (Yamada and Zheng, 2008), and Trombay and Tarapur nuclear reprocessing plants on the west coast of India. Other nuclear facilities that discharge liquid radioactive waste into the oceans, directly or indirectly, have made a less significant contribution to Pu contamination of the marine environment.

<Figure 2 here>

Low-level liquid radioactive discharges from the Sellafield nuclear reprocessing plant on the coast of the Irish Sea in Cumbria, UK have been a major Pu source to the marine environment since 1952 (Kershaw et al., 2001). The total $^{239+240}\text{Pu}$ in liquid discharges (1952 - 2007) from the plant is about 0.6 PBq, with a peak in the early to mid-1970s (Fig. 2). The Pu isotopic composition of Sellafield effluents has varied over the years due to the different plant operations and the fuel reprocessed (Kershaw et al., 1995b). The complex was designed initially for the production of low burn-up weapons-grade Pu but focused later on reprocessing high burn-up spent fuel from commercial power reactors. Studies of dated sediment cores collected in the vicinity of the Sellafield plant showed $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios of 0.06 in the 1960s, corresponding to weapons-grade Pu, increasing to > 0.20 in the 1980s, corresponding mainly to commercial spent fuel reprocessing (Fig. 2) (Kershaw et al., 1995a; Morris et al., 2000). A similar pattern was observed for the $^{238}\text{Pu}/^{239+240}\text{Pu}$ activity ratio, due to greater neutron capture by ^{238}U with longer burn-up times. Plutonium discharges from the

Sellafield site decreased in the early 1980s but the Pu deposited in the Irish Sea sediment continues to act as a source for transport to the North Atlantic and the Arctic Ocean (Hunt and Kershaw, 1990; Cook et al., 1997; Kershaw et al., 1999a; Kershaw et al., 1999b). The estimated $^{239+240}\text{Pu}$ inventory in the seabed of the Irish Sea is in the range 440 - 560 TBq, with annual transport through the North Channel of 0.5 - 1.3 TBq a⁻¹ (Cook et al., 1997; Jones et al., 1999; Kershaw et al., 1999a; Leonard et al., 1999). Recent model predictions support the view that the major Pu source in the Irish Sea is the contaminated sediments resulting from historical Sellafield discharges (Aldridge et al., 2003).

The Pu input from the La Hague site on the north coast of France has been small compared with the Sellafield site (~0.4 %), with a total Pu release of < 0.005 PBq (Kershaw and Baxter, 1995; Kershaw et al., 1995b; Nyffeler et al., 1996; Boust, 1999).

2.3. Accidental releases

The Chernobyl accident and incidents involving aircrafts and satellites have been the main accidental releases of Pu isotopes to the marine environment. The latter generally have local or regional impact but the SNAP-9A satellite incident had a wider footprint.

The Chernobyl accident in April 1986 has been the most serious accident involving a nuclear power reactor, with significant radionuclide fallout in the Northern Hemisphere. The explosions and subsequent fire released about 2.5 PBq $^{239+240}\text{Pu}$ into the air, mostly deposited in the vicinity of the reactor (UNSCEAR, 2000b). The $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio from the Chernobyl fallout is about 0.38 (Table 1), which is considerably higher than the worldwide-integrated fallout ratio of *ca.* 0.18. The Pu input to the marine environment was reasonably small and mostly local, i.e. to the Baltic Sea and the Black Sea (Holm, 1995; Buesseler and Livingston, 1996). About 9 % (1.5 TBq) of the total $^{239+240}\text{Pu}$ inventory in the Baltic Sea can

be attributed to the Chernobyl accident (Holm, 1995).

In addition, Pu has been released into the marine environment from two accidents involving aircraft carrying nuclear weapons; in Palomares, Spain (1966) and in Thule, Greenland (1968) (Mitchell et al., 1997). In Thule, the Pu was dispersed locally after the chemical explosive components detonated on impact. Although an extensive clean-up operation was carried out on the ice around Thule immediately after the accident, the residual $^{239+240}\text{Pu}$ contamination of the marine environment was in the range 5 - 15 TBq (Eriksson, 2002). Most of the Pu released from the Palomares accident was deposited on land and only a small fraction has been transferred to the marine environment, with a maximum estimated input of 1.4 TBq (Papucci et al., 1996; Sanchez-Cabeza et al., 2003). The characteristic $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio from both these sources was around 0.06 (Table 1), which corresponds well with $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio in weapons-grade Pu.

In 1964, about 0.63 PBq of ^{238}Pu was injected in the stratosphere from the burn-up of nuclear-powered SNAP-9A navigational satellite (Krey, 1967). Consequently, about 78 % of the ^{238}Pu debris was deposited in the Southern Hemisphere, with the highest deposition between latitudes 20 °S and 50 °S (Perkins and Thomas, 1980). The accident has contributed to the total inventory of ^{238}Pu in the World Ocean with an estimated input of ^{238}Pu of about 0.32 PBq decay corrected to the year 2000 (Hamilton, 2005). As a result of the SNAP-9A incident the average $^{238}\text{Pu}/^{239+240}\text{Pu}$ activity ratio in global fallout increased from 0.019 ± 0.003 to 0.029 ± 0.005 in the Northern hemisphere and 0.14 ± 0.04 in the Southern hemisphere (values are decay corrected to 2000) (Perkins and Thomas, 1980).

2.4. Other potential Pu inputs to the marine environment

Nuclear-powered submarines lost at sea may be potential Pu sources to the marine

environment. For example, the USSR Navy nuclear submarine “Kosmomolets” sank to a depth of 1700 m in the Barents Sea in 1989 with an estimated ^{239}Pu inventory of 21 TBq (Livingston and Povinec, 2000). However, no Pu contamination from the submarine has yet been reported (Nies et al., 1999). Other potential accidental Pu sources include nuclear powered generators from the interplanetary station “Mars’ 96” (0.17 PBq of ^{238}Pu) and Apollo 13 (1.6 PBq of ^{238}Pu and 1.2 TBq of ^{239}Pu), both of which landed intact in the deep South Pacific Ocean (Dobry Jr, 1980; IAEA, 2001).

The dumping of radioactive wastes from the nuclear industry has been carried out at deep ocean sites, mainly in the North East Atlantic and the Arctic Oceans (IAEA, 1999), with only minor local Pu contamination (Livingston and Povinec, 2000). An estimated inventory of 8.9 TBq $^{239+240}\text{Pu}$ in marine reactors was dumped in the Kara Sea (IAEA, 1998a) and enhanced levels of $^{239+240}\text{Pu}$ in close proximity to the objects indicates some leakage, but no evidence of any transfer from this site has been reported (Salbu et al., 1997; Nies et al., 1999). Radioactive dumping was also carried out in the western North Pacific Ocean and its marginal seas, but with considerably lower Pu inventories, and there is no evidence of elevated Pu from these sources (Livingston and Povinec, 2000). However, the lack of studies around these dumping sites makes it difficult to predict future Pu releases, especially in the Arctic Ocean (Nies et al., 1999; Osvath et al., 1999; Preller and Cheng, 1999; Skipperud, 2004). Nevertheless, these dumping sites may be potential Pu sources to the marine environment in the future.

3. Behaviour of Pu in the marine environment

The geochemical behaviour of Pu in the marine environment is influenced by: (i) the characteristics of the Pu source, (ii) its physico-chemical properties and (iii) biogeochemical

and physical processes in the ocean.

Plutonium from a specific source may be associated with particles, colloids, pseudo-colloids or low molecular mass species (Salbu, 2001) depending on the source and the environmental conditions. Global Pu fallout is mainly associated with sub-micron iron oxide particles, while Pu fallout from surface tests in the Marshall Islands was mainly attached to calcium hydroxide particles (Buesseler, 1997). In effluents from nuclear reprocessing plants most Pu is associated with particulate material or colloids (Leonard et al., 1995).

<Figure 3 here>

The behaviour of Pu in seawater is influenced by a variety of geochemical processes, e.g. solubilisation, hydrolysis, complexation, sorption and colloid formation (Fig. 3). Microbial processes may also have a significant effect on the long-term behaviour and mobility of Pu (Francis, 2001; Francis et al., 2008). The oxidation state of Pu significantly affects its geochemical behaviour. In marine waters four different oxidation states exist, Pu(III), Pu(IV), Pu(V) and Pu(VI), with Pu(V) and Pu(IV) being the most common (Choppin, 2006). The Pu(IV) form is highly particle reactive and easily scavenged by suspended matter and colloids, while Pu(V) is relatively soluble and can be transported in the dissolved phase over long distances. Field studies in the Irish Sea and the Mediterranean Sea have shown that Pu(V) is the prevailing species in the dissolved phase and that particulate Pu is almost entirely in the reduced Pu(IV) form (Mitchell et al., 1995). In anoxic seawater Pu(III) is the dominant oxidation state (Sanchez et al., 1994). In general, Pu oxidation states in seawater are dependent on pH, E_H and the suspended particle concentration (Choppin, 2006).

Interaction with complexing agents and hydrolysis reactions are generally strongest for Pu(IV) and weakest for Pu(V), which leads to the preferential removal of reduced Pu species from solution by adsorption onto colloidal and suspended material (Nelson and Lovett, 1978; Orlandini et al., 1990; Mitchell et al., 1995). In contrast, oxidised Pu(V) has a high

affinity for adsorption onto carbonate particles, e.g. corals, as surface complexes (Keeney-kennicutt and Morse, 1985; Meece and Benninger, 1993; Gouzy et al., 2005b). Field studies of coastal seawater have shown that colloidal Pu (>1 kDa) is only a minor fraction of the total Pu in seawater (Dai et al., 2001; Mitchell et al., 2001).

In shallow waters with higher particle concentrations, preferential removal of Pu from the water column to the sediment takes place while in surface open ocean waters this process is dependent on biological productivity. Thus, in biologically poor (oligotrophic) regions the main component of the deposited Pu inventory from stratospheric fallout remains in the water column while in coastal waters almost all is removed from the water column to the seabed (León Vintró et al., 2005). Field studies in the oligotrophic western Mediterranean Sea indicate that Pu distribution in the upper water column is controlled by the degree of primary production (Fowler et al., 2000). However, close-in Pu fallout from the surface tests at the Marshall Islands had different physico-chemical characteristics, due to interaction with calcium-rich particles from the surrounding media, which resulted in a faster scavenging rate from surface waters to deep ocean sediment (Buesseler, 1997).

Sediment resuspension and dissolution influence the dispersion of Pu from contaminated sediment (Lansard et al., 2006). Plutonium is remobilised from contaminated sediment mainly in the oxidised forms Pu(V,VI) as observed in the Irish Sea (Leonard et al., 1999; Mitchell et al., 2001). Various environmental factors may influence the remobilisation/uptake process such as pH, temperature, light, bioirrigation, bioturbation and natural and anthropogenic physical mixing (McCubbin et al., 1999; Gouzy et al., 2005a; Kaplan et al., 2006). Laboratory studies suggested that only 0.02 - 1 % of the total Pu in the sediment is available for remobilisation (McCubbin et al., 1999; McDonald et al., 2001). However, recent sequential extraction studies of Irish Sea sediment suggested that Pu is more bioavailable, with a release of at least 10 % of the total Pu (Gouzy et al., 2005a). The study

indicated that Pu is loosely bound to the sediment and is oxidised readily on contact with oxygen-rich waters.

The uptake of Pu into marine biota is dependent on the species and the surrounding environment (IAEA, 2004). Sediment-dwelling species play a significant role in the remobilisation process, as they may redistribute deposited Pu in the sediments by mixing and agitation (Ryan, 2002).

In summary, the scavenging rate of Pu in the marine environment depends on (i) the physical and chemical forms of Pu; (ii) the amount of particulate matter; (iii) the settling rate of particles; (iv) mixing processes (e.g. diffusion, resuspension and bioturbation); and (v) biogeochemical processes (e.g. mineralogical transformations, redox reactions and uptake by biota).

4. Use of Pu isotopes for studying marine processes

Because of the unique sources (spatial and temporal) of Pu in the World Ocean and its non-conservative behaviour, the inventory is not uniformly distributed and Pu concentrations show significant variability around the world. The $^{239+240}\text{Pu}$ activity concentration in surface waters varies from a few mBq m^{-3} in the open ocean up to $> 100 \text{ mBq m}^{-3}$ in semi-enclosed waters close to a Pu source (e.g. Irish Sea) (IAEA, 2005).

The main advantage of using Pu isotopes as tracers for marine processes is their well-defined source terms. The $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio from integrated global fallout (~ 0.18) is assumed to be uniformly distributed throughout the marine environment. For the calculation of the contribution of different sources with different Pu isotopic composition in marine samples, simple mixing models can be used (Kelley et al., 1999; Ketterer et al., 2004). In most marine regions Pu contamination consists mainly of contributions from global fallout

and a local/regional source except in some cases such as the Baltic Sea (Holm, 1995) and the Arctic Ocean (Cooper et al., 2000). In general, the measured isotopic ratio, R_S , in a marine sample consists of contribution from n source terms and can be expressed as:

$$R_S = x_1 R_1 + x_2 R_2 + \dots + x_n R_n \quad (1)$$

$$x_1 + x_2 + \dots + x_n = 1 \quad (2)$$

where x_i is the contribution from source term i and R_i is the isotopic ratio of source term i . In the case of two source terms the contribution (x_1) of source term (in %) can be calculated by combining Eqs. (1) and (2) as follows:

$$x_1 = 100 \times (R_m - R_2) / (R_1 - R_2) \quad (3)$$

where R_m is the measured ratio. With the application of Eq. (3), a good estimation of the contribution of a particular source term can be helpful in understanding oceanographic processes, e.g. water mass exchange, in a specific marine region,. This has been applied in a number of marine studies such as estimation of the influence of Chernobyl Pu fallout to the Baltic Sea (Lindahl et al., 2005), the influence of the Pu-contaminated Rhone river input to the Mediterranean Sea (Miralles et al., 2004), the contribution of Pu debris from the Nevada Test Site in deep North West Atlantic waters (Buesseler and Sholkovitz, 1987), determination of the influence of underwater nuclear tests in the Bering Sea on the marine environment (Dasher et al., 2002), determination of the source of radioactivity in the Arctic Ocean (Huh et

al., 1997; Cooper et al., 1999; Cooper et al., 2000), and estimation of the contribution of close-in fallout from the Marshall Islands to the Northwest Pacific Ocean and its marginal seas, and to the Indian Ocean (Zheng and Yamada, 2004; Lee et al., 2005; Wang and Yamada, 2005; Zheng and Yamada, 2005b; Yamada et al., 2006; Oikawa and Yamamoto, 2007; Yamada et al., 2007; Yamada and Zheng, 2008).

4.1. Seawater studies

Plutonium isotopes are effective as indicators for physical and biogeochemical processes in the water column. Plutonium in seawater is usually transported via advection, diffusion and particle scavenging. Many studies carried out in the open ocean water column have shown that Pu concentration depth profiles often show a pronounced sub-surface maximum (León Vintró et al., 2005). As an example, Figure 4 is showing $^{239+240}\text{Pu}$ depth profiles from different sites in the North Pacific Ocean. It has been suggested that this sub-surface maximum is related to vertical fluxes of Pu-bearing particles and subsequent remineralisation by biological activity as well as physical circulation processes (Fowler et al., 2000; Livingston et al., 2001). Enhanced $^{239+240}\text{Pu}$ concentrations in deep bottom waters in the Pacific Ocean have been observed and this may be explained by rapid transport of Pu isotopes attached to large particles through the water column to deep ocean sediments and resuspension by near-bottom currents (Livingston and Anderson, 1983; Yamada and Aono, 2006). In shallow and coastal waters, the concentration of Pu is low as it is removed rapidly from the water column by particulate material.

<Figure 4 here>

Zheng and Yamada (2006b) observed an increase in Pu flux with increased depth in the continental margins of Northwest Pacific by determining Pu concentrations in settling

particles from sediment traps. They also found, from $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio analyses, that dissolved Pu is transported from the open ocean to ocean margins where Pu is removed into the margin sediments by scavenging. Scavenging has also been found to have a profound effect on the net annual outflow of $^{239+240}\text{Pu}$ from the Mediterranean Sea to the Atlantic, which has decreased by about one third from the amount estimated in 1988. This is due to the vertical transport of Pu and the consequent decrease of its concentration at intermediate depths (IAEA, 2005). Sediment trap studies have indicated that particles sinking through deep waters (1 000 - 2 000 m) could account for 26 % to 72 % of the derived annual $^{239+240}\text{Pu}$ loss in the Mediterranean Sea (Fowler et al., 2000). The advection of deep water masses to the south-western part of the Mediterranean Sea from the Levantine Basin in the eastern Mediterranean has also been identified from the depth distributions of $^{239+240}\text{Pu}$ and ^{238}Pu together with ^{137}Cs (Noureddine et al., 2008).

Concentrations of $^{239+240}\text{Pu}$ and ^{137}Cs in surface seawater, coupled with oceanographic parameters, i.e. salinity and nutrient concentrations, have been utilised to demonstrate the exchange of surface water masses between different sea areas in the South Pacific Ocean (Hirose et al., 2007). By comparing the $^{239+240}\text{Pu}/^{137}\text{Cs}$ activity ratios in surface water with the global fallout ratio they found good correlations between $^{239+240}\text{Pu}$ concentrations and particle scavenging rates, which provided additional evidence to support the suggested exchange processes. A similar approach was applied to vertical profiles of the $^{239+240}\text{Pu}/^{137}\text{Cs}$ activity ratios in shallow waters of the North Pacific (Hirose et al., 2009). Depth profiles of $^{239+240}\text{Pu}/^{137}\text{Cs}$ were expressed by a simple exponential function reflecting export and regeneration processes.

In addition, speciation studies have shown that the ratio between oxidised and reduced forms of Pu may be a valuable tracer for lateral water movement processes (Baxter et al., 1995). The $^{238}\text{Pu}/^{239+240}\text{Pu}$ activity ratio and Pu oxidation state ratio in the water column of

two Norwegian Fjords were used as a tracer for water exchange between the fjords and the North Sea (Sanchez et al., 1994).

4.2. Sediment studies

Marine sediments are major repositories of organic matter and pollutants that are embedded in the sediment layers. Understanding the dispersion and fate of these contaminants is of great importance due to their influence on global biogeochemical cycles and marine processes (Hedges and Keil, 1995).

There have been a large number of studies of Pu in marine sediments, including the dynamics of mixing processes and accumulation rates. Sediment studies usually include Pu isotopes in combination with other radionuclides or stable isotopes (e.g. Krishnaswami et al., 1980; Santschi et al., 1980; Benninger and Krishnaswami, 1981; Cochran, 1985; Smith et al., 1986; Carpenter et al., 1987; Lapique et al., 1987; Buffoni et al., 1992; Huh et al., 1997; Huh and Su, 1999; Smith et al., 2000b; Gascó et al., 2002; Su and Huh, 2002; Moon et al., 2003; Garcia-Orellana et al., 2009). Knowledge of particle mixing rates in sediments is essential for deconvoluting different depth-dependent sediment processes that could influence the distribution of chemical pollutants. The various Pu studies in marine sediments have contributed to developing sediment mixing models with constant, continuous, or pulsed Pu inputs (Smith et al., 1995; Smith et al., 2000b; Moon et al., 2003).

The deposition of Pu in shelf or slope environments is controlled by the extent of scavenging in the upper water layers. Hence, the depth distribution of Pu is often a measure of historical Pu-flux in the water column. In areas with negligible mixing compared to sediment accumulation, global fallout $^{239+240}\text{Pu}$ (with distinct peak at around 1964), in combination with the well-established ^{210}Pb dating methodology, in sediment cores can be used to estimate the

past flux of particulate material. For example, high particle flux events were observed in the continental margin of the East China Sea by determining $^{239+240}\text{Pu}$ and natural radionuclides in settling particles and surface sediment (Yamada and Aono, 2002; 2006). These high flux events were attributed to episodic lateral transport of resuspended particles that flow down the continental slope with the nepheloid layer.

Studies of Pu and natural radionuclides association with particulate matter in the ocean have considerably advanced understanding of the ocean carbon cycle and ocean particle mixing (Bacon et al., 1985). The sinking of Pu-bearing particles (Pu-flux) in the upper euphotic zone is closely coupled with the carbon flux (Baxter et al., 1995) and scavenging of trace metals (Hirose et al., 1992). The techniques developed for the study of particle associated Pu in the ocean were used in the Joint Global Ocean Flux Study (JGOFS) (Livingston and Povinec, 2002). Plutonium isotopes have also been used at a seasonal polynia off the northeast coast of Greenland to evaluate the carbon cycle and to improve the estimation of the particulate organic carbon flux. In this study, the $^{239+240}\text{Pu}$ depth distribution in sediment was used as an indicator of particle mixing, with accumulation rates estimated from ^{210}Pb (Roberts et al., 1997).

Distribution and transport of particulate matter in riverine inputs to coastal waters can be estimated by using Pu isotopes in sediments contaminated with various identified sources such as global fallout and nuclear facilities linked to the river (Olsen et al., 1989; Thomas, 1997; Eyrolle et al., 2004; Miralles et al., 2004; Duffa and Renaud, 2005; Lansard et al., 2007). For example, Oktay et al. (2000) found a five-fold decrease in riverine particle discharges into the Gulf of Mexico from the Mississippi River prior to the early 1960, by applying Pu isotopes in combination with excess ^{210}Pb in determination of an ^{129}I chronology record.

Another approach for dating of deep-sea sediments may be the use of ^{241}Pu and

²⁴¹Am concentrations in the sediment layers with the assumption that all ²⁴¹Am is produced from ingrowth of ²⁴¹Pu (Lee et al., 2005).

4.3. Retrospective studies

In research on global climate change, retrospective studies on past ocean conditions are based mainly on isotopic analyses of natural archives in the marine environment, including sediments, corals and other marine biota. These natural archives (proxies) provide information regarding historical chemical and physical conditions in the surrounding seawater. Isotopic analyses of annual bands from corals has provided sensitive time series of past ocean chemistry, ocean circulation and climate (Druffel, 1997). As the Pu isotopic composition differs from each source, retrospective studies of Pu may provide valuable information on past ocean circulation and aid understanding of the biogeochemical cycles of oceanic carbon, particle-reactive nutrients and pollutants.

Dated coral cores have been used to retrieve historical records of Pu isotopes from global and close-in fallout in the surrounding seawater and thereby provide information about source terms, water mass movement, and the geochemical behaviour of Pu in the marine environment (Noshkin et al., 1975; Benninger and Dodge, 1986; Purdy et al., 1989; Buesseler, 1997). Plutonium concentrations in accumulating corals are in equilibrium with surrounding water and the determination of Pu in corals provides a better annual resolution than sediment due to better accumulation rates with distinct seasonal features and negligible mixing between the growth layers.

In the Pacific Ocean, the North Equatorial Current (NEC) and the Kuroshio Current are important currents that supply the Northwest Pacific with warm surface water from the Equatorial Pacific. The Marshall Islands, located in the path of NEC, continuously releases

about 0.2 TBq of $^{239+240}\text{Pu}$ annually from contaminated sediment into the open ocean (see Section 2.1). By determining $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios in sediment and seawater it has been suggested that Pu from the Marshall Islands is transported by the westward-flowing NEC and onwards by the Kuroshio Current up to the Northwest Pacific Ocean and its marginal seas (Kim et al., 2004; Zheng and Yamada, 2004; Lee et al., 2005; Wang and Yamada, 2005; Zheng and Yamada, 2005b; Zheng and Yamada, 2006a; Yamada et al., 2007; Yamada and Zheng, 2008). This hypothesis was recently proposed from elevated $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios in squid liver samples collected from the western and eastern coastal areas of Japan (Kishimoto et al., 2002; Oikawa and Yamamoto, 2007). The high $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios (> 0.20) observed in these studies indicate a contribution from the Marshall Islands source since the tropospheric Pu fallout from the Marshall Islands tests can be assumed to be negligible in these waters (Huh, 1997; Zheng and Yamada, 2005a). Figure 5 shows a time series of $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios in sediment and coral from three sites in the Pacific Ocean. There are indications that the flow of the Kuroshio Current has been disrupted due to global climate change (Sato et al., 2006). Therefore, by tracking the distinct Pu signal from the Marshall Islands in this area, past current flows can be retrospectively studied and the potential coupling with recent climate change can be elucidated.

<Figure 5 here>

The surface current transit time from the Marshall Islands to the marginal areas of the Northwest Pacific was estimated to be six years by analysing $^{239+240}\text{Pu}$ and the $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio in sediments from the Southern Okinawa Trough (Lee et al., 2004). From this estimation, the mean velocity of NEC was calculated to be $\sim 0.022 \text{ m s}^{-1}$, which corresponds well with the annual mean velocity, which is in the range $0.02 - 0.06 \text{ m s}^{-1}$.

Another potential proxy for historical Pu records is the use of dated mollusc shells that contain calcium carbonate. For example, Baskaran et al. (2005) used archived bivalve

shells for reconstructing historical global fallout of ^{90}Sr levels in shallow coastal waters.

Plutonium isotopes and ^{129}I in archived marine algae have been utilised as historical indicators for the transport of seawater contaminated with radioactive waste from nuclear fuel reprocessing plants to the North Atlantic and Arctic Ocean (Cooper et al., 1998).

4.4. Other applications of Pu isotopes in the marine environment

Sea ice transport is an important factor for the long range dispersal of contaminants in the Arctic Ocean and into the North Atlantic because melting releases contaminants from the ice (Pfirman et al., 1995). Plutonium isotopes (^{239}Pu and ^{240}Pu), together with other natural and anthropogenic radionuclides, have been used to track sea ice transport through the Arctic Ocean and to estimate transit times from the source to the removal area (Landa et al., 1998; Masqué et al., 2003; Masqué et al., 2007).

Atmospheric inputs of mineral aerosol into the ocean affect biogeochemical processes in the water column. A method for estimating the mineral aerosol flux to the Pacific Ocean using $^{239+240}\text{Pu}$ as a tracer was developed by utilising $^{239+240}\text{Pu}$ concentrations in surface waters and airborne dust together with Pu residence time and mixed layer depth (Nakanishi et al., 1995).

There is an increasing demand for validated regional and global marine ecosystem models, as well as ocean circulation models for the prediction of future global environmental changes, and the unique chemical properties of Pu, together with its well-defined source terms, will provide important information for the evaluation and improvement of these models.

6. Conclusions

The overall input of Pu to the World Ocean has declined significantly in the last four decades, mainly due to the cessation of atmospheric weapons tests. However, due to the long half-life and unique chemical properties of Pu, it will persist in the marine environment for a long time. Due to the well-defined source terms, Pu isotopes can be utilised in marine research for the study of oceanic processes such as water mass movement, particle export and sediment mixing and accumulation rates. Plutonium isotope data can be used for calibrating and validating numerical models for pollutant dispersion in the marine environment and ocean current circulation (Smith et al., 2000a; Nakano and Povinec, 2003; Tsumune et al., 2003). In view of the increasing concerns relating to global climate change and its impact on the marine environment, the historical Pu signal in natural archives (e.g. sediments and biota) will enhance our understanding of important biogeochemical and physical processes in the ocean. Reconstructed Pu signatures in natural archive marine samples will also provide valuable information on the impact of past climate change on ocean mixing and support the validation and calibration of ocean circulation models.

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Table 1. Principal sources in the marine environment and their specific Pu isotopic composition expressed as $^{240}\text{Pu}/^{239}\text{Pu}$ atom and $^{238}\text{Pu}/^{239+240}\text{Pu}$ activity ratios. Uncertainties are expressed as ± 2 SD (95 % confidence level).

| Main sources | $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio | $^{238}\text{Pu}/^{239+240}\text{Pu}$ activity ratio* | References |
|--|---|--|---|
| <u>Atmospheric weapons testing, 1945-1980</u> | | | |
| Integrated global fallout | 0.178 ± 0.023 | 0.019 ± 0.006 | (Perkins and Thomas, 1980; Kelley et al., 1999) |
| <u>Specific test sites</u> | | | |
| Marshall Islands | 0.29 ± 0.04 | | (Muramatsu et al., 2001) |
| Johnston Atoll | ~ 0.06 | | (Wolf et al., 1997) |
| French Polynesia | $0.02 - 0.05$ | $0.1 - 0.4$ | (IAEA, 1998b; Chiappini et al., 1999; Mulsow et al., 1999; Danesi et al., 2002; Hrnccek et al., 2005) |
| Nevada Test Site | 0.032 ± 0.006 | | (Hicks and Barr, 1984) |
| Semipalatinsk | 0.038 ± 0.016 | 0.037 ± 0.002 | (Beasley et al., 1998; Yamamoto et al., 2004) |
| Chernaya Bay, underwater nuclear tests | 0.0320 ± 0.0024 | 0.023 ± 0.009 | (Smith et al., 1995; Smith et al., 2000b) |
| <u>Releases from the nuclear industry</u> | | | |
| Sellafield (up to 1996) | $0.06 - 0.25$ | $0.03 - 0.4$ | (Kershaw et al., 1990; Kershaw et al., 1995a; Morris et al., 2000) |
| La Hague effluent, 1996 | 0.34 ± 0.06 | | (Oughton et al., 1999) |
| Russian river discharges from nuclear reprocessing plants at Krasnoyarsk, Mayak, Tomsk | $0.05 - 0.30$ | | (Oughton et al., 2000; Skipperud et al., 2004; Børretzen et al., 2005; Lind et al., 2006; Gauthier-Lafaye et al., 2008; Skipperud et al., 2009) |
| <u>Accidental releases</u> | | | |
| Chernobyl accident, 1986 | 0.38 ± 0.07 | 0.42 ± 0.04 | (Boulyga et al., 1997; Wendt et al., 1999; Muramatsu et al., 2000; Boulyga and Becker, 2002) |
| Thule accident, 1968 | 0.055 ± 0.008 | 0.0161 ± 0.0010 | (Lind et al., 2005; Eriksson et al., 2008) |
| Palomares accident, 1966 | 0.063 ± 0.006 | 0.015 ± 0.004 | (Chamizo et al., 2006; Pöllänen et al., 2006; Jiménez-Ramos et al., 2007) |
| SNAP-9A, 1964 | | | |
| N Hemisphere | - | 0.010 ± 0.005 | (Perkins and Thomas, 1980) |
| S Hemisphere | - | 0.12 ± 0.07 | |
| <u>Dumping sites</u> | | | |
| Kara Sea | ~ 0.44 | ~ 0.18 | (IAEA, 1998a) |
| Sunken submarine reactors | $0.005 - 0.13$ | $0.12 - 0.45$ | (Oughton et al., 2004) |

* Decay corrected to the year 2000.

Table 2. Estimated Pu isotope inventory (PBq) in the world's oceans originating from atmospheric nuclear weapons tests, 1945 - 1980 (Aarkrog, 2003; Hamilton, 2005).

| | $^{238}\text{Pu}^a$ | ^{239}Pu | ^{240}Pu | $^{241}\text{Pu}^a$ | ^{242}Pu |
|----------------------------------|---------------------|-------------------|-------------------|---------------------|-------------------|
| Arctic Ocean | 0.002 | 0.05 | 0.04 | 0.17 | 0.00001 |
| Atlantic Ocean | 0.05 | 1.38 | 0.89 | 4.24 | 0.0003 |
| North Atlantic | 0.04 | 1.1 | 0.7 | 3.4 | 0.00023 |
| South Atlantic | 0.01 | 0.3 | 0.2 | 0.9 | 0.00006 |
| Indian Ocean | 0.02 | 0.56 | 0.36 | 1.73 | 0.0002 |
| Pacific Ocean^b | 0.35 | 4.47 | 3.98 | 23.89 | 0.003 |
| North Pacific | 0.17 | 2.7 | 2.3 | 13.5 | 0.0015 |
| South Pacific | 0.07 | 1.8 | 1.7 | 10.4 | 0.0015 |
| Southern Ocean | 0.005 | 0.07 | 0.05 | 0.24 | 0.00006 |
| All Oceans | 0.4 | 6.5 | 5.4 | 30 | 0.004 |

^a Decay corrected to 1 January 2000.

^b The Mike shot assumed evenly distributed between North and South Pacific.

Figure captions

Figure 1. Total annual yield energies (Mt per year) and annual fallout debris deposition (from ^{90}Sr deposition, PBq per year) in the northern and southern hemispheres produced from atmospheric nuclear tests, 1945-1980 (UNSCEAR, 2000a).

Figure 2. $^{239+240}\text{Pu}$ discharges from the Sellafield reprocessing plant, 1952 - 2007 (Gray et al., 1995; BNFL, 2002; 2007) and $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios from dated sediment cores collected in the vicinity of the Sellafield plant (Kershaw et al., 1995a; Morris et al., 2000).

Figure 3. Biogeochemical cycle of Pu in the marine environment. Adapted from Choppin and Morgenstern (2001).

Figure 4. $^{239+240}\text{Pu}$ depth profiles in seawater from various stations in the North Pacific Ocean (Bowen et al., 1980; Nelson et al., 1984; Nozaki et al., 1998; Yamada et al., 2007).

Figure 5. Time series of $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio in three sites in the Pacific Ocean (Buesseler, 1997; Lee et al., 2004; Zheng and Yamada, 2004). The sedimentation rate for the Sagami Bay site was estimated from the global fallout $^{239+240}\text{Pu}$ peak.









