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Articles

Plutonium Isotopes Research in the Marine Environment: A synthesis

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Plutonium (Pu) isotopes are one of most important artificial radionuclides. Recent advances in analytical methodology of Pu have enabled Pu to play a vital role in tracing biogenic elements and pollutants transport, sediment deposition/resuspension and other marine process. The various ratios of Pu isotopes (^{238}Pu, ^{239}Pu, ^{240}Pu and ^{241}Pu), which are dependent on the Pu sources, are useful for identifying the contributions from different sources, and these ratios can be utilized to indicate the marine processes. The aim of this manuscript is to provide an overview of the applications of Pu for studying various processes in the marine environment, such as the determination of recent sedimentation rate, to assess sediment transport and deposition/resuspension, water mass transport, etc, based on the knowledge and advances in the analytical methodology and the geochemical behavior of Pu. Furthermore, this work is expected to provide new insights for broadening the application of Pu in the marine environment and to help better understand land-sea interactions and global climate change.

1. Introduction

Plutonium (Pu), mainly derived from thermonuclear bomb testing, nuclear accidents, nuclear reprocessing facilities and nuclear power plants since the 1950s, entered the ocean by global fallout and by direct release and was then transported by ocean current, exchanged, transformed and eventually buried in the ocean. Pu in the marine environment consists mainly of four isotopes, namely, ^{238}Pu ($T_{1/2}$ = 87.7 a), ^{239}Pu ($T_{1/2}$ = 24100 a), ^{240}Pu ($T_{1/2}$ = 6561 a) and ^{241}Pu ($T_{1/2}$ = 14.3 a), in which a very small fraction of ^{239}Pu originates from uranium mineral and most ^{239}Pu comes from anthropogenic activity. Additionally, Pu has two isotopes with extremely low concentrations namely, ^{242}Pu ($T_{1/2}$ = 376000 a) and ^{244}Pu ($T_{1/2}$ = 8.7 $\times 10^7$ a).[1] The distribution of Pu concentration in the marine environment is influenced by ocean current distribution and biogeochemical cycles, and therefore, Pu isotopes are typically utilized to trace water mass exchange, particle scavenging and biogeochemical cycles.[2-4] Compared to ^{90}Sr ($K_{d:}$ 10-10^2 L kg^{-1}) and ^{137}Cs ($K_{d:}$ 10^2-10^3 L kg^{-1}), Pu has a much stronger particle affinity in marine environments ($K_{d:}$ 10^4-10^7 L kg^{-1}) and thus can serve as a better tracer for indicating transport, scavenging and particle deposition.[5-8]

To use Pu as a tracer for environmental process, the geochemical behavior of Pu should be understood and the analytical method for Pu need to be improved. With the development of analytical methods for Pu, the detection limit of Pu in seawater and sediments has continuously decreased,[9-11] which allows increasing numbers of researchers (Figure 1) to focus on the sources, geochemical behaviors, distribution and environmental implications.[12-18] Pu from different sources or incidents has unique atom (or activity) ratios,[19] e.g., ^{240}Pu/^{239}Pu, ^{241}Pu/^{239}Pu and ^{238}Pu/$^{239+240}$Pu, and these ratios can be used to quantitatively evaluate the source of Pu and to study different marine processes along with $^{239+240}$Pu activity concentration. Therefore, this study aims to synthesize the application of Pu to marine processes based on a summary of its sources, geochemical behaviors, distribution and analytical methods.

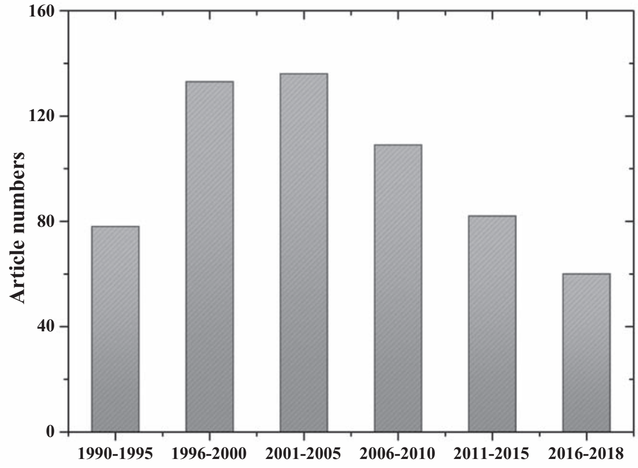

Figure 1. Publication numbers of Pu in the marine environments during 1990 and 2018 (Statistics on Web of Science using “Plutonium” and “sea” as keywords).

2. Sources of Pu isotopes

2.1. Thermonuclear bomb testing. Nuclear testing is the predominant source of Pu isotopes in the marine environment. There were 2055 instances of nuclear testing from 1945 to 2016 (https://www.armscontrol.org/factsheets/nucleartesttally), including 18 tests in 1951 and 178 tests in 1962, which released a total 170 PBq of Pu. The resulting Pu was released into the troposphere and stratosphere and was subsequently deposited on the earth’s surface, thus affect the local and global Pu distribution.[20] In the Northern Hemisphere, Pu entered the troposphere via aerosol and was scavenged via rainfall or natural settling after approximately 71 days.[21] Therefore, two time-markers are used in most marine environment: one marker corresponding to the introduction of Pu to the environment in 1952, and the second marker correspond-

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ing to the peak fallout levels in 1963. The ^{240}Pu/^{239}Pu atom ratios vary depending on the plutonium sources. The fractionation of atmospheric nuclear weapons testing in Novaya Zemlya (Russia) to stratosphere was 78 Mt, which released amount of Pu with ^{240}Pu/^{239}Pu atom ratios of 0.03.[13] Nuclear weapons testing in the Pacific Proving Grounds (PPG) produced a total yield of 26 Mt with ^{240}Pu/^{239}Pu atom ratios of 0.33-0.36.[22] Nuclear weapons testing in these two regions contributed 70% of the global fallout Pu[20] and significantly affected Pu distribution in local regions.[23,24] The Pu with different sources and ^{240}Pu/^{239}Pu atom ratios entered the stratosphere and mixed completely, which led to global fallout with ^{240}Pu/^{239}Pu atom ratio of 0.18.[19] Additionally, at Mururoa and Fangataufa Atolls in French Polynesia, France conducted a series of nuclear weapons tests, and released Pu into the marine environment, with ^{240}Pu/^{239}Pu atom ratios of 0.02-0.05.[25] It is estimated that the total amount of ^{238,239,240}Pu in French Polynesia lagoons is approximately 30 TBq.[26]

2.2. Nuclear accidents. Accidental releases are important sources of Pu in the marine environment. The Chernobyl accident in April 1986 released 6 PBq of Pu into the environment and the Pu from this event was mainly deposited in the Scandinavian countries and in the Baltic regions.[20,27,28] However, Holm[29] estimated that the Chernobyl accident contributed less than 10% of the total $^{239+240}$Pu in the Baltic Sea. The Fukushima accident released a mass of artificial radionuclides (340-800 PBq)[30] but produced much less Pu; Zheng et al[31] using the Pu isotopic ratios, which was estimated that this Pu release using the Pu isotopic ratios to be less than 0.01% of that the amount released from the Chernobyl accident. Bu et al[32] reported that $^{239+240}$Pu concentrations in the surface sediments near the Fukushima nuclear power plant were 0.01-5.81 Bq kg^{-1} before the accident and 0.48-3.53 Bq kg^{-1} after the accident, and reported ^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu atom ratios of 0.170-0.280 and 0.0012-0.0016 before the accident, respectively, and 0.188-0.255 and 0.0014-0.0016 after the accident, respectively. Zheng et al[31] reported that the Fukushima accident released Pu with ^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu atom ratios of 0.30-0.33 and 0.103-0.135, respectively. Both the $^{239+240}$Pu concentration and ^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu atom ratio after the accident clearly did not increased compared to the levels before the accident and, thus, the contribution from the Fukushima accident to the Pu in the marine environment was negligible.

The SNAP-9A satellites accident released 0.63 PBq of ^{238}Pu into the stratosphere on 21 April 1964, and most of this Pu was deposited in the Southern Hemisphere.[33] Roos et al[34] observed that the ^{238}Pu/$^{239+240}$Pu activity ratios (0.21) in the Antarctic Peninsula area were much higher than those from global fallout (0.019). Lee et al[35] reported that the ^{238}Pu/$^{239+240}$Pu activity ratios in the southern Indian Ocean also showed higher values of 0.08-0.20. In Palomares, Spain (1966), and Thule, Greenland (1968), two aircraft aircrafts crash accidents released 5.5×10^{-5} and 0.01 PBq of $^{239+240}$Pu, respectively, with ^{240}Pu/^{239}Pu atom ratios of 0.05-0.06, which significantly affected the local Pu distribution. For example, the ^{240}Pu/^{239}Pu atom ratios in the soils of Palomares, Spain were clearly below 0.18 and close to 0.05.[36,37] However, most of this Pu was deposited on the land and the contribution to the marine environment was very small.[3]

2.3. Nuclear reprocessing facilities. Effluents from the later part of the nuclear fuel cycle in nuclear reprocessing facilities contain small fraction of Pu; however, due to the large effluent flow quantities, large amounts of Pu have entered the marine environment. The nuclear reprocessing facilities in Sellafield (UK) and La Hague (France) have discharged 22 PBq and 0.14 PBq of Pu into the ocean, respectively, with ^{240}Pu/^{239}Pu atom ratios of 0.06-0.25 and 0.34, respectively.[6,38] It was reported that 0.5-1.4 TBq $^{239+240}$Pu was transported into the Irish Sea through the English Channel, and 99% of this amount was contributed by Sellafield (UK) activities, causing ^{240}Pu/^{239}Pu atom ratios to be lower in the Irish Sea.[6,38-40] In addition, the nuclear reprocessing facilities in Mayak, Krasnoyarsk and Tomsk, Russia, Hanford and Savannah River, USA, Marcoule, France discharged small amounts of Pu into the Kara Sea, eastern Pacific Ocean, the western Atlantic Ocean and the Mediterranean Sea, respectively, with lower ^{240}Pu/^{239}Pu atom ratios of <0.13.[41-44] For example, the Savannah River production plants discharged 140 GBq of Pu into the atmosphere and 23 GBq of Pu into local small rivers and ponds from 1954 and 1989.[45] Due to the effects of the Marcoule reprocessing plant, the sedimentary inventory of $^{239+240}$Pu in the Rhone River and Lions Gulf was reported to be 172 GBq from 1945 and 2000.[46]

The incidents discussed above comprise the main sources of Pu in the marine environment, in which 26 PBq Pu was stored in the ocean as estimated by Aarkrog [47]. Additionally, the USSR Navy nuclear submarine ‘‘Kosmomolets” sank in the Barents Sea, and the dumping of radioactive wastes from the nuclear industry Sea into Northeast Atlantic and the Arctic Oceans are potential sources of oceanic Pu.[47] However, these potential sources might affect the distribution of Pu in marine environments in the future, but the contribution to Pu is currently negligible.

3. Analytical method for Pu isotopes

Since the 1960s, researchers have begun to use alpha spectrometry to measure Pu and there was a report regarding the analysis of Pu using mass spectrometry in 1971; the detection limit improved from 10^{-13} g in 1980s to 10^{-18} g in 2015.[10,48,49] The analytical procedure for Pu usually consists of sample pretreatment, chemical separation and purification, source preparation and instrumental measurement. A total of 2-25 g of solid samples (soil, sediment and biological samples) are first ashed at 400–600°C to decompose organic matter and are spiked with a tracer (generally ^{242}Pu). The residue is then digested using alkali fusion or acid digestion consisting of acid leaching (partial digestion) and total dissolution.[9] Concentrated HNO_3, HCl, HNO_3+HCl, or HNO_3+H_2O_2 are used to leach Pu.[50-53] Some samples containing Pu oxide can be completely dissolved by HF+HCl+$HClO_4$,[54,55] but total dissolution also creates more matrix components/ interfering elements and is further detrimental to subsequent chemical separation and purification. Alkali fusion can completely decompose the samples and completely melt the Pu but could also melt the container, thus producing more interfering elements. Pu is concentrated by coprecipitation using NdF_3, LaF_3, CaF_2, CeF_3, $Ca(OH)_2$, $Mg(OH)_2$, $Fe(OH)_2$, $Fe(OH)_3$, MnO_2, $CaHPO_4$, $Ca_3(PO_4)_2$ or CaC_2O_4, etc. The Pu in water sample is concentrated by using coprecipitation after filtration and the volume of the water samples for determining Pu levels varied varies between 20 and 500 L.[9,11]

The Pu in acid leaching solution usually existed as Pu^{3+}, Pu^{4+}, PuO^{2+} and PuO_2^{2+}, in which the partition coefficient of $Pu(NO_3)_6^{2-}$ in resin is highest in nitric acid systems, and thus the Pu in the sample should remain in IV valence before it is loaded into the column for separation and purification. In the case of acidic condition, Pu can be adjusted to Pu^{3+} using I^-, Fe^{2+}, Ti^{3+}, NH_2OH or N_2H_4 and then be oxidized to Pu^{4+} using H_2O_2, NO_3^- or $NaNO_2$.[9,56] The method for separating and purifying Pu involves solvent extraction, ion exchange chromatography or extraction chromatography. Solvent extraction introduces major organic pollutants and thus is seldom used to analyze Pu in environmental samples; this procedure is mainly utilized for the separation of high-level liquid waste.[57] Ion

TABLE 1: Comparison between different methods for detecting Pu isotopes (modified after Qiao et al.[9] and Wang et al.[61])

Method	Measurable isotope	Interfering species	Detection Limit (mBq)	Operation time	Cost
α-spectrometry	^{238}Pu	^{241}Am, ^{210}Po, ^{228}Th	0.01-0.1	Day-weeks	Fair/high
	^{239,240}Pu	^{231}Pa, ^{243}Am	0.01-0.1		
	^{241}Pu	^{210}Po, $^{228\text{Th}}$	0.1-1.0		
LSC	^{241}Pu, ^{238}Pu, ^{239,240}Pu	All beta emitters	5-50	hours	Fair/high
ICP-MS	^{239}Pu	^{238}U^{1}H, ^{208}Pb^{31}P, ^{206}Pb^{33}S, ^{204}Hg^{35}Cl, ^{202}Hg^{37}Cl, ^{199}Hg^{40}Ar, ^{204}Pb^{35}Cl	10^{-4}-10^{-2}	minutes	Fair/low
	^{240}Pu	^{238}U^{2}H, ^{209}Bi^{31}P, ^{207}Pb^{33}S, ^{205}Tl^{35}Cl, ^{204}Pb^{36}Ar, ^{200}Hg^{40}Ar	10^{-4}-10^{-2}		
	^{241}Pu	^{204}Hg^{37}Cl, ^{204}Pb^{37}Cl, ^{206}Pb^{35}Cl	0.36-5		
AMS	^{239}Pu	similar m/z as 239	10^{-4}-10^{-3}	minutes	high
	^{240}Pu	similar m/z as 240	10^{-4}-10^{-3}		
	^{241}Pu	similar m/z as 241	-		
RIMS	^{239}Pu	Matrix elements	0.01-0.1	minutes	high
	^{240}Pu		0.01-0.1		
	^{241}Pu		5-50		
TIMS	^{239}Pu	Matrix elements	10^{-4}-10^{-3}	minutes	high
	^{240}Pu		10^{-4}-10^{-3}		
	^{241}Pu		-		

exchange chromatography and extraction chromatography are the most commonly used method for analyzing Pu.[58] Due to the advantage of simple operating procedures and short operating times, extraction chromatography has attracted increasing attention.[59] Commonly used resins, e.g., AG 1×4, AG 1×8, Bio-Rad AG 1×8, Dowex 1×4, Dowex 1×8, UTEVA+TRU and Chelating+TRU are used singly or are combined, to separate and purify Pu.[50,60,61] TEVA resin with good selectivity for Pu and a high decontamination factor for U and chemical yields, serves as one of most commonly used resins for Pu analysis.[9,11] Since the environmental samples contain large quantities of U, decontaminating the U is very important due to the formation of polyatomic ions (e.g., ^{238}U^{1}H^{+} and ^{238}U^{1}H^{2+}) when measurements are conducted by using inductively coupled plasma mass spectrometry (ICP-MS) (Table 1).

There are several types of detection techniques for the determination of Pu: α-spectrometry, liquid scintillation counting (LSC), ICP-MS, thermal ionization mass spectrometry (TIMS), accelerator mass spectrometry (AMS) and resonance ionization mass spectrometry (RIMS) (Table 1). α-spectrometry, as a traditional counting method, was the most commonly used method in previous years, but this method has a higher detection limit and longer operating times and cannot determine ^{240}Pu/^{239}Pu atom ratios. LSC also has a very high detection limit and cannot determine ^{240}Pu/^{239}Pu atom ratios. AMS has the advantages of high sensitivity and short operating time but is more costly. TIMS and RIMS have high precision and sensitivity with short operating times but requires complex chemical procedures for the separation and purification of Pu. ICP-MS, with the advantages of high sensitivity, reasonable costs and relatively short operating times, presently serves as the most commonly used method for detecting ^{239}Pu and ^{240}Pu. Reports regarding Pu measurement also show that ICP-MS has been widely used to determine Pu in recent years (Figure 2). As discussed above, the major problem in Pu analysis in marine samples using MS is the separation of U at high concentrations due to the high salinity of seawater. Initially, researchers use an anion exchange resin to separate U, but the decontamination factor was not high and the chemical yield of the whole procedure was relatively low (e.g., Zheng and Yamada[62]). Subsequently, researchers began using TEVA resin which has a higher selectivity for Pu to purify Pu samples (e.g., Ketterer and Szechenyi[56]). Recently, researchers have used UTEVA to remove U and have combined TEVA for purifying Pu with SF-ICP-MS detection,[61,63] which showed a very low detection limit (i.e., 10^{-4} mBq for ^{239}Pu, 10^{-4} mBq for ^{240}Pu, and 0.36 mBq for ^{241}Pu).

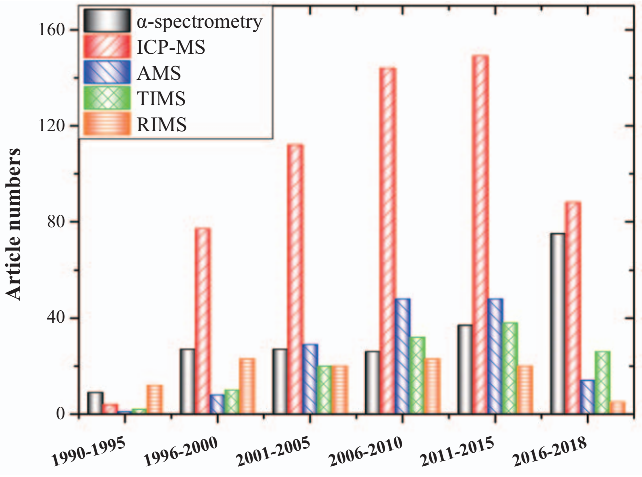

Figure 2. Publication numbers of Pu using different instruments during 1990 and 2018 (Statistics on Web of Science using "Plutonium" and related instrument as keywords).

4. Distribution of Pu in the marine environment

4.1. Distributions of Pu in seawater. Since Pillai et al[64] first reported the activity of ^{238}Pu and ^{239,240}Pu in seawater, there are increasing number of studies focused on the distributions and geochemical behaviors of Pu and the implications for marine processes in the marine environment. Pu distribution in the ocean are affected by global fallout which has a latitude effect (Figure 3). The area with the maximum amount of ^{239,240}Pu from global fallout is distributed between 40 and 50 °N (~80 Bq m^{-2}) and decreases toward north and south. The maximum levels of ^{239,240}Pu in the Southern Hemisphere, 1/4 of those in the North Hemisphere, are distributed between 40 and

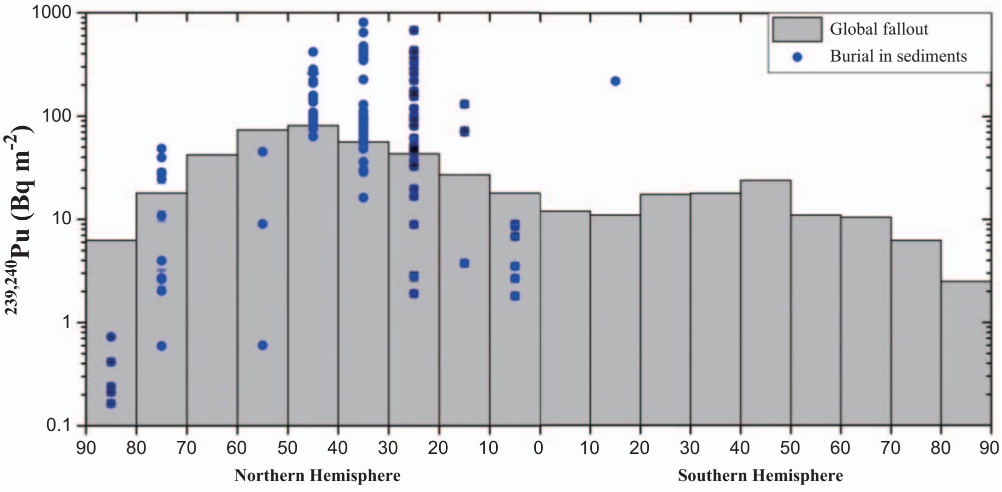

Figure 3. The atmospheric fallout and marine sedimentary deposition of ^{239,240}Pu between different latitudes: The atmospheric fallout ^{239,240}Pu values are estimated by using the activity ratio between ^{239,240}Pu and ^{90}Sr to multiply ^{90}Sr amount in Table 8 in UNSCEAR.[20] The sedimentary deposition is summarized from the literature.[5,15,18,75-90]

TABLE 2: Oceanic inventory (PBq) of Pu isotopes originating from globally dispersed debris, and local deposition from atmospheric nuclear tests (Till to January, 2000, Modified after Aarkrog[47])

Ocean	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu	Total Pu in the Ocean
Arctic Ocean	0.0018	0.050	0.040	0.078	0.000010	0.17
Atlantic Ocean	0.044	1.4	0.89	2.0	0.00030	4.3
North Atlantic	0.035	1.1	0.70	1.6	0.00023	3.4
South Atlantic	0.0088	0.30	0.20	0.41	0.000060	0.91
Indian Ocean	0.018	0.56	0.36	0.80	0.0002	1.7
Pacific Ocean	0.31	4.5	4.0	11	0.0030	20
North Pacific	0.15	2.7	2.3	6.2	0.0015	11
South Pacific	0.062	1.8	1.7	4.8	0.0015	8.4
Total	0.35	6.5	5.4	14	0.0040	26

50°S and decrease toward the north and south, and the minimum levels are observed in the Antarctic.[20] Based on the estimation by Aarkrog[47] (Table 2), most ^{239,240}Pu is stored in the Pacific Ocean (8.45 PBq), accounting for 75% of worldwide total ^{239,240}Pu in the ocean, for which Pu in the North Pacific Ocean accounts for 59% of the total ^{239,240}Pu in the whole Pacific Ocean. Pu in the Atlantic accounts for 17% of total Pu in the ocean, and that in the North Atlantic Ocean accounts for 79% of the total Pu in the Atlantic Ocean. Pu in the Indian and Arctic Oceans only accounts for 6% and 0.5% of Pu, respectively, in the global ocean.

In the 2000s, Aoyama and Hirose[65] found that the maximum ^{239,240}Pu activity was observed in the Irish Sea (>100 mBq m^{-3}) and relatively high values were observed in the North Atlantic, Barents Sea, North Sea, English Channel and the Mediterranean Sea (10-50 mBq m^{-3}); lower ^{239,240}Pu activity was distributed in the Pacific Ocean, South Atlantic Ocean and the Indian Ocean (1-10 mBq m^{-3}); the lowest ^{239,240}Pu activity was found in the Southern Ocean (<0.5 mBq m^{-3}).[65-71] ^{239,240}Pu in the surface seawater of the Pacific ranged from 0.3 to 2.7 mBq m^{-3}, and higher values were observed in the Japan Sea, subarctic Pacific Ocean and the Eastern Pacific Ocean.[72,73] ^{239,240}Pu in the surface water of the Japan Sea decreased in winter due to downward scavenging.[72] ^{239,240}Pu levels in the surface water decreased with time after 1970 due to the influence of water mass transport, biological activity and decrease in global fallout.[74]

^{239,240}Pu activity generally showed maximum values in the subsurface layer (400-900 m) and then gradually decreased with increasing water depth (Figure 4). However, a maximum value for ^{239,240}Pu wasn't observed in the Norwegian Sea and Greenland Sea, which could be related to the remineralization of particulate matter caused by biological activity and water mass transport.[91,92] The shape of the ^{239,240}Pu activity peak is related to the location of the sea area, for example, the peak for the Japan Sea and the Mediterranean Sea are broad, and the peak observed for the northwestern Pacific Ocean is sharp.[93-95] It was estimated that the residence time of ^{239,240}Pu in the subsurface layer is 400-600 years and thus the ^{239,240}Pu stored in the subsurface layer could serve as an important Pu source in adjacent seas.[2]

4.2. Distribution of Pu in marine sediment. As shown in Figure 3, the sedimentary inventory of ^{239,240}Pu is generally greater than the global fallout. From 20-50 °N, the sedimentary inventory of ^{239,240}Pu in the Washington shelf area, Japan Sea, Sagami Bay, northwestern Pacific Ocean, East China Sea, Southern Okinawa Trough and northern South China Sea are 63-417, 59-65, 36-474, 28-30, 2-807, 172-675 and 366 Bq m^{-2}, respectively, which are higher than those of global fallout at the corresponding latitudes.[5,18,76,79-85,87-89] In the Arctic region, Okhotsk Sea and in equatorial waters, the ^{239,240}Pu inventory is small, ranging from 0.16 to 48, from 0.6 to 45 and from 1.8 to 9.0 Bq m^{-2}, respectively, which are close to those of global fallout at the corresponding latitudes.[15,75,78] Report of the sedimentary inventory of ^{239,240}Pu in the Southern Hemisphere indicate lower levels. Pittauer et al[90] reported that the ^{239,240}Pu inventory in the Lombok basin of the India Ocean (10°S) was 219 Bq m^{-2}, which was significantly higher than the global fallout value at this latitude. The distribution of the ^{239,240}Pu

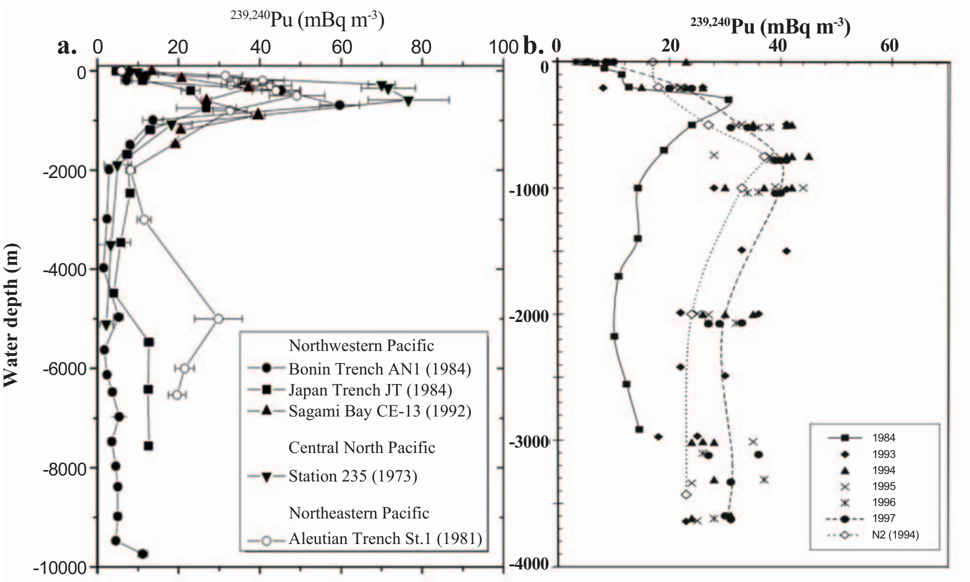

Figure 4. ^{239,240}Pu depth profiles in ocean seawater: (Modified after Lindahl et al.[3] and Hong et al.[95]): a. North Pacific; b. central Northwest Pacific Ocean.

inventory in these regions is related to its geochemical behavior and to different sources (riverine input, atmospheric deposition and advective input from neighboring sea). For example, in the East China Sea, South China Sea, and the marginal seas of the northwestern Pacific, the higher inventory of ^{239,240}Pu relative to global fallout levels is caused by oceanic input from the PPG that is transported via the Kuroshio Current and North Equatorial Current and riverine inputs affected the estuarine regions (inputs from the Changjiang and Pearl River).[18,89] Meanwhile, Pu sediment distribution are also be influenced by ocean currents and by sediment focusing/erosion and transport, which are discussed in detail below.

5. Geochemical behaviors of Pu in marine environment

Pu distributions in the water column are also related to its geochemical behaviors and are affected by the particulate matter density, physico-chemical properties, hydrolysis, inorganic and organic matter complexation, and by high-molecular weight polymer, etc.[92,96] As discussed above, Pu is present as four different oxidation states in the aqueous environment. The low valence state of Pu is stable when the pH is low and the high valence Pu state is stable when the pH is high. The Pu (III, IV) forms exhibit higher reactivity than the Pu (V, VI) form, which are very easily hydrolyzed in aqueous environments and do not readily undergo complexation with organic ligands (e.g., humic acid), leading to extremely low concentrations of the free state Pu (IV) form.[74] The particle concentration in the open ocean are very low, which cause the particulate Pu concentration to also be lower. The K_d value for Pu in the open ocean is lower (i.e., 10^4 L kg^{-1}); for example, particulate ^{239,240}Pu represents only 10% of the total ^{239,240}Pu in the surface water of the Mediterranean Sea and the North Pacific and represents much smaller portion (<2%) in the deep water of the Pacific Ocean.[97-99] The dissolved Pu mainly exists in the Pu (V, VI) forms and is dominated by the Pu (V) form, e.g., the ^{239,240}Pu (V) form accounts for more than 70% of the total dissolved phase in the Irish Sea and Mediterranean Sea.[100,101] In coastal regions Pu is dominated by the Pu (III, IV) form, with K_d values of 10^6-10^7 L kg^{-1}.[2] Due to these higher K_d values and relatively higher particle concentration, the dissolved phase of Pu in these regions (e.g., 46%-92%) are less than those in open ocean (close to 100%).[102,103] The Pu (III, IV) forms are easily adsorbed onto colloids and particles and are scavenged from the water column whereas the Pu (V, VI) forms are preferentially adsorbed onto carbonate particles (e.g., coral).[23,104]

Some studies have reported that Pu is remobilized by physical mixing, biological activity, or changes in redox conditions.[104-106] Sediments in a lagoon in the Marshall Island that was polluted by the PPG contain large amounts of Pu and release Pu at a rate of 0.2 TBq a^{-1} due to the influence of sediment resuspension. [107] ^{239,240}Pu activity increases slightly in the bottom layer of the water column, which should be related to the release from the sediments due to the resuspension process.[15] However, experimental results showed that ^{239,240}Pu in sediment from the Irish Sea was only desorbed by less than 1%.[108] The desorption of ^{239,240}Pu is expected to increase when bioturbation occurs, which suggests that biological activity plays an important role in the mobility of Pu.[109,110] Experimental results have also shown that the K_d values for Pu increased with decrease in organic matter content.[4] Baskaran et al[111] observed that ^{239,240}Pu in sediment in the Florida coastal region that contained high organic matter content (loss on ignition >50%) exhibited pre-depositional mobility phenomena, which caused the activity peak corresponding to 1963 to be broader. This result occurs because the degradation of organic matter enhanced the sediment phase ^{239,240}Pu entry into the porewater resulting in the remobilization of ^{239,240}Pu. However, Pu mobility is much lower relative to ^{137}Cs mobility in most aqueous environments (except for environments with rich organic matters or bioturbation) and can be negligible.[18,112]

6. Implication of Pu isotopes for marine process

As it has been discussed above, Pu is highly particle-reactive in coastal regions (K_d >10^6 L kg^{-1}) and can be used to trace particle/sediment dynamics and biogeochemical processes whereas it is weakly particle-reactive in the open ocean (K_d =10^4 L kg^{-1}) and is useful for tracing water mass exchange.

6.1. Implication of Pu isotopes for sediment dynamics.

1) Dating recent sediments: Some Pu isotopes have long half-lives (e.g., ^{239}Pu and ^{240}Pu) and are highly particle-reactive in coastal regions and thus can be used to trace sediment dynamics (Figure 5) ^{239,240}Pu shares similar sources with ^{137}Cs and can be used to date recent sediments by using two common time markers “1952” and “1963” corresponding to the introduction of Pu to the environment and to peak fallout levels. In addition, ^{240}Pu/^{239}Pu atom ratios can also be used to date recent

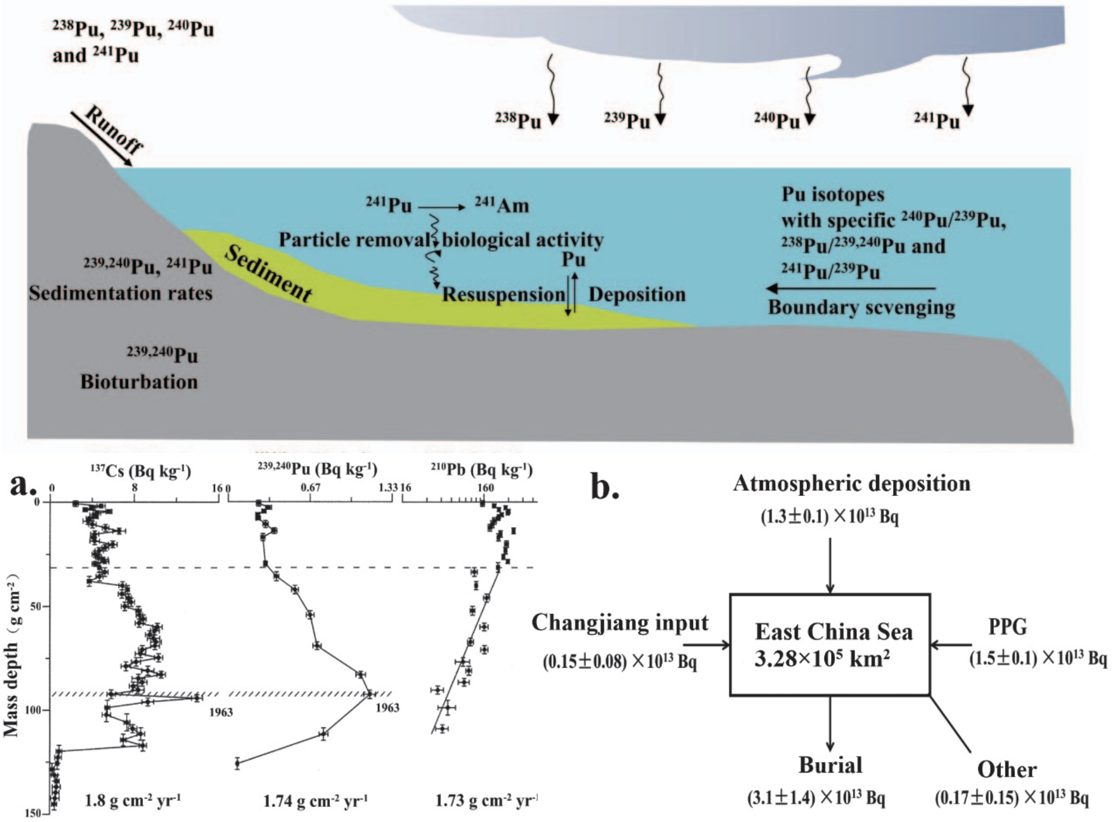

Figure 5. Application of Pu isotopes in the marine process tracing research: a. Dating in the ECS sediment (core OR499-16, modified after Su and Huh[81]; b. The mass balance of $^{239+240}$Pu in the ECS sediment (modified after Wang et al.[18]).

sediments, for example, in the marginal seas of the Northwestern Pacific, the atom ratios were high in the 1950s and can be used as a time marker. Recently, increasing numbers of studies have used Pu for sediment dating (Figure 5).[85-89] Wang et al[18] compared the dating results using ^{210}Pb, ^{137}Cs and ^{239,240}Pu in sediments in the East China Sea and found that the dating results between ^{210}Pb and ^{239,240}Pu agreed well in both shallow and deep waters. However, an activity peak for ^{137}Cs was not observed, which was probably caused by its very weak particle affinity and the relatively strong mobility of ^{137}Cs in marine environment.[113-115] ^{137}Cs has a shorter half-life (30.2 a, 75% of peak fallout of ^{137}Cs has decayed away in 2019) and relatively higher mobility, whereas Pu isotopes (^{239}Pu and ^{240}Pu) have longer half-lives and stronger particle affinities, and thus, Pu would play a more important role in dating marine sediments in the future compared to ^{137}Cs. Pu can also be used to date corals. Corals have a strong affinity for dissolved Pu in ocean waters, and Pu could be packed into coral skeleton and accumulate with coral growth; therefore, the signal of Pu in the neighboring waters could be reconstructed by coral.[23,116] Lindahl et al[23] found that the ^{240}Pu/^{239}Pu atom ratios in corals near Guam corresponded to the period of nuclear testing in the PPG. Froehlich et al[117] also found a similar phenomenon in corals from the Marshall Islands, suggesting that ^{240}Pu/^{239}Pu atom ratios could be used to date corals. The historical record of Sr/Ca ratio in coral could reflect climate changes and seawater temperature change,[118,119] and Pu isotopes could provide the chronology for Sr/Ca ratios in coral that is useful in the study of global climate change.

2) Indicating the source of artificial radionuclides associated with adsorbed particles: The atom ratios (R_s) vary depending on their differing sources, and the contribution from n source terms can be estimated by following equation:[19,120]

$$R_s = \chi_1 R_1 + \chi_2 R_2 + \ldots + \chi_n R_n \quad (1)$$

$$\chi_1 + \chi_2 + \ldots + \chi_n = 1 \quad (2)$$

where R_i is the contribution from source term I, and χ_i is the contribution from source term i. It should be noted that this equation is only suitable for stable isotopes or for long-lived radionuclides (e.g., ^{239}Pu and ^{237}Np). Assuming that Pu isotopes (^{239}Pu and ^{240}Pu) have two sources, equation (1) and (2) can be combined to form:

$$\chi_1\ (\%) = 100 \times (R_m - R_2)/(R_1 - R_2) \quad (3)$$

where R_m is the measured ^{240}Pu/^{239}Pu atom ratio. In the East China Sea, the ^{240}Pu/^{239}Pu atom ratios were 0.18-0.31,[18] which lies in the Changjiang input/global fallout range (0.18) and in the PPG input range (0.33-0.36). Using equation (3), it is estimated that the PPG contribution dominate the Pu source(~60%), and the mas balance of Pu in the East China Sea sediments is then obtained (Figure 5b). Zheng and Yamada[15] found that the particulate flux of ^{239,240}Pu near the Okinawa Trough increased with increasing water depth, suggesting that the PPG derived Pu could enter the East China Sea by boundary scavenging. Near the Changjiang Estuary, the ^{240}Pu/^{239}Pu atom ratios were 0.18, which indicate that the Pu source in this region is mainly dominated by riverine inputs.[18,87] Combined with other isotopes-indicated results, it can be concluded that these sediments are from the Changjiang inputs.[81,114,121]

3) Implications for sediment transport, mixing and erosion: The spatial distribution of the Pu inventory is useful for indicating sediment transport. The sedimentary inventories of ^{239,240}Pu and ^{137}Cs decrease from the coast to offshore, suggesting that these radionuclides can be transported offshore associated with other particles.[18,114,122] Ketterer et al[123] reported that the transport of drainage particles from the Danube Delta to the Black Sea was indicated by using the spatial distribution of ^{240}Pu/^{239}Pu atom ratios. Tims et al[124] also reported sediment transport in the Herbert River by using ^{239}Pu and ^{137}Cs as tracers. Buffoni et al[125] evaluated the mixing depth and sedimentation rate by observing the vertical profile of ^{239,240}Pu in

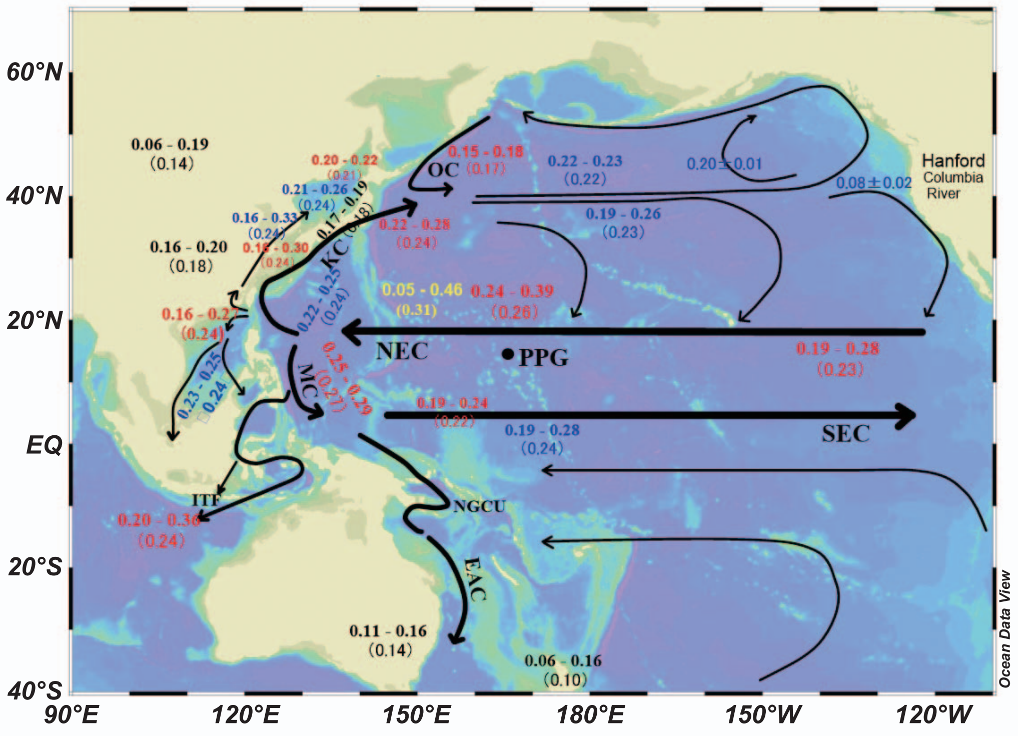

Figure 6. The synthesis of ^{240}Pu/^{239}Pu atom ratios in the areas surrounding the Pacific: Soil (black color),[32,139,140,142-145] sediment (red color),[18,22,83-90,130,140,146-148] seawater (blue color)[149-157] and a coral (yellow color).[23,117,129] NEC: North Equatorial Current; SEC: South Equatorial Current; KC: Kuroshio Current; OC: Oyashio Current; MC: Mindanao Current; NGCU: New Guinea Coastal Undercurrent; EAC: East Australian Current; ITF: Indonesian Throughflow.

sediments. Huh and Su[122] observed the vertical profiles of ^{210}Pb, ^{137}Cs and ^{239,240}Pu and estimated that the average sediment mixing rate in the coastal regions and outer shel were 20 and 0.03-0.3 cm^2 a^{-1}, respectively. Additionally, the temporal distribution of ^{239,240}Pu inventories could indicate sediment erosion. Wang et al[18] observed that the ^{239,240}Pu inventory of three sediment cores collected in same region in 1997, 2006 and 2013 decreased with increasing time, and they inferred that this phenomenon was related to sediment erosion or channel improvement. Livingston and Bowen[126] found that in the shallow waters sediment along the northeast coast of the USA, ^{239,240}Pu/^{137}Cs activity ratios decreased with increasing, depth but the ^{238}Pu/^{239,240}Pu activity ratios didn't change, which indicate that these radionuclides migrated downward due to bioturbation. Santschi et al[127] observed that ^{137}Cs and ^{239,240}Pu in the sediments of the Palos Verdes Shelf showed positive correlation with organic matter content and used the distribution of radionuclides to indicate the source and transport of organic carbon. Due to the distinct ^{240}Pu/^{239}Pu atom ratios arising from different sources, Wang et al[18] proposed that ^{240}Pu/^{239}Pu atom ratios are useful for tracing the transport of particle-reactive species, including radionuclides (^{210}Pb, ^{231}Pa and ^{230}Th, etc) and organic/inorganic matter (Fe, P, etc) from the open ocean to the coastal region. Therefore, it is necessary to strengthen this research to provide technical support for understanding the scientific difficulties of oceanography.

6.2. Implication of Pu isotopes for water mass transport.

1) The Pu signature in water masses: Zheng and Yamada[141] studied the sedimentary profile of Pu isotopes in Sagami Bay and found that the ^{239,240}Pu inventory (mean: ~191 Bq m^{-2})[80] was significantly higher than that from global fallout (42 Bq m^{-2})[128] and the ^{240}Pu/^{239}Pu atom ratio was higher than that from global fallout (0.18) and was close to that from PPG (0.33-0.36). These authors inferred that these Pu isotope ratios were mostly due to long-range transport from the PPG. Since then, there has been increasing research on the distribution of ^{240}Pu/^{239}Pu atom ratios in the Pacific, which corresponds to water mass exchange and further confirms the presence of long-range Pu transport in the Pacific (Figure 6). Wang et al[18] synthesized the transport of PPG-derived Pu in marginal seas (e.g., South China Sea, East China Sea, East Sea and east coasts of Japan); it was reported that the PPG-derived Pu could be transported to the Bering Sea, but the ^{240}Pu/^{239}Pu atom ratio was 0.15-0.18 and was influenced by input from the Arctic Ocean that were transported via the Oyashio Current.[129] The ^{240}Pu/^{239}Pu atom ratio of the bottom waters on the west coast of North America near Washington state were determined to be 0.08 due to the influences from the Pu releases from the Hanford site.[129] Pittauer et al[90] examined the sedimentary profiles of ^{241}Am/^{239}Pu activity ratios and ^{240}Pu/^{239}Pu atom ratios in the Eastern Lombok Basin and found that the PPG-derived artificial radionuclides could be transported to the India Ocean. The ^{240}Pu/^{239}Pu atom ratios in the sediments of the southeast coast of Australia showed lower values (0.11-0.16) caused by nuclear testing by the UK.[130] However, report on the ^{240}Pu/^{239}Pu atom ratios in the South Pacific are still lacking. Though a number of studies have reported the long-range transport of Pu in the Western Pacific and its marginal seas, their conclusions were only indirect speculation based on the ^{240}Pu/^{239}Pu atom ratios. Therefore, more investigations are needed to determine the compositions of the different species Pu isotopes (especially colloidal Pu) to understand the scavenging mechanism for Pu entering shallow waters.

At some stations in the Northwest Atlantic, the ^{240}Pu/^{239}Pu atom ratios in the deep waters were less than 0.18 due to the influence of nuclear testing at the Nevada Test Site.[131,132] In the Irish Sea, which was affected by the discharges from Sellafield, the ^{240}Pu/^{239}Pu atom ratios of sediments were 0.06 during the 1960s and were greater than 0.20 after the 1980s.[6] This Sellafield derived Pu was transported northward along the west coast of Northern Europe via the North Atlantic Warm Current and the Norwegian Warm Current. This Atlantic derived Pu could enter the Arctic Ocean and affect the distribution of Pu in the Arctic Ocean with other sources. For example, some Pu released from nuclear testing site and nuclear reprocessing facilities could be transported to the Kara Sea via the Ob and Yenisei rivers.[133-136] The transport of Chernobyl-derived Pu in the Baltic and Black seas was observed from the distribution of the ^{240}Pu/^{239}Pu atom ratios.[137,138] In conclusion, the ^{240}Pu/^{239}Pu atom ratios are very useful for tracing water mass transport, but more investigations are needed to confirm the distributions of Pu isotopes in the South Pacific, South Atlantic and the Indian Ocean to better understand the transport of Pu as well as marine process.

2) Indicating the vertical mixing of seawater: At one station in the eastern North Pacific (31.38 N, 150.03 W), the ^{239,240}Pu activity in the subsurface in 1973 was 4 times higher than that in 2000, but ^{239,240}Pu activity was unchanged below 1,000 m.[74] A similar variation trend was also found in the mid-latitude areas of northwestern Pacific (Figure 4a). The decrease in the ^{239,240}Pu maximum in the subsurface layer was not caused by downward settling of particles because the ^{239,240}Pu values below 1,000 m showed no increase. Instead, advective transport should be the main reason for such a phenomenon. The subsurface maxima for ^{239,240}Pu were 70-80, 40-60 and 20-30 mBq m^{-3} in the St. 235 near the PPG, Bonin Trench and Japan Trench, respectively (Figure 4a).[3,140] This decreasing trend from east to west could be related to the westward transport of the North Equatorial Current associated with Pu. The water depth of the subsurface maximum of ^{239,240}Pu in the central Northwestern Pacific varied from 300 m in 1984 to 900 m in 1997 (Figure 4b). This variation is because in this region, bioactivity is strong and particle concentrations are relatively high, leading to settling down of the associated particles.[95] Therefore, the ^{239,240}Pu activity in the water column increases with increasing water depth above the subsurface maximum layer (500-800 m), whereas ^{137}Cs activity exponentially decrease with increasing water depth in the upper 1,000 m. Hirose et al[74] studied the vertical profiles of ^{239,240}Pu/^{137}Cs activity ratios in the subsurface layer in the upwelling region and found that the upwelling depths in the eutrophic Subarctic Pacific were significantly higher than those in the subtropical North Pacific. Hirose et al (2011) found that the ^{239,240}Pu/^{137}Cs activity ratios exponentially increased from the surface to the 1,500 m layer and estimated that the upwelling depths were between those in the subarctic Pacific and subtropical North Pacific. Although there have been many studies of ^{239,240}Pu profiles, Pu behavior in marine environments is complex, and more investigations are needed to understand the temporal variation in the subsurface Pu maxima (peak position and shape) and to better understand marine processes using Pu as a tracer.

7. Conclusions and perspectives

The main areas of progress related to the study of Pu isotopes are the following. 1) The method for determining Pu in the sediment has been well developed and a 1-2 g sample is sufficient for conducting measurement. ICP-MS, with economical cost and efficiency advantages, can determine the isotope ratios and is widely applied for measuring Pu; however, AMS has high sensitivity for Pu measurement but is not widely utilized due to its higher costs. 2) Research on the Pu isotopes distribution in seawater and sediment has mainly been focused on the North Pacific, North Atlantic and Arctic Ocean, but research in the Southern Hemisphere is lacking, especially for the Pu isotope compositions. 3) studies on Pu species in seawater are relatively limited and have mainly focused locally on the Irish Sea and Mediterranean Sea with higher ^{239,240}Pu, whereas studies in the Pacific and Indian Oceans are lacking. 4) In the coastal regions, Pu isotopes have been used to date sediments and to trace sediment transport, focusing and erosion; in the open ocean, Pu is used to indicate water mass transport and vertical mixing. However, studies on Pu isotope compositions in the water column are still lacking, which not only limits the study of Pu geochemical behavior but also restricts the study of the implication of Pu for marine processes.

More studies on Pu isotopes in marine environment worthwhile in the future: 1) It is important to optimize the analytical method for measuring Pu in seawater. The minimum volume for measuring Pu in seawater is currently at least 20 L, which causes difficulty when collecting samples from thousands to ten thousands meter water layers. Thus, further development of the analytical method of Pu is required to reduce sample volume of less than 5 L. 2) The study of Pu geochemical behavior in field observations or laboratory experiments is very easily influenced by external condition. Therefore, stricter experimental conditions are needed for the study of the porewater chemistry of Pu and the influence of colloids and organic matter on Pu behavior. Based on this, the mechanism of Pu transport and setting needs further clarification. 3) Using the unique isotope ratios of Pu with different sources as tracers, e.g., ^{240}Pu/^{239}Pu atom ratios, the long-range transport of oceanic biogenic elements from the open ocean to coastal regions and the upwelling transport are worthy of further study. 4) The mobility of Pu in sediment requires further study to assess its suitability for dating marine sediment. 5) In addition to ^{240}Pu/^{239}Pu, combinations of other artificial radionuclides, e.g., ^{237}Np/^{239}Pu and ^{241}Am/^{239}Pu, to study radionuclides source and marine processes are recommended. Additionally, some particle-reactive natural radionuclides, e.g., ^{210}Pb/^{239}Pu and ^{232}Th/^{239}Pu, can also be combined and used to trace marine processes.

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