processes

MDPI

Review

Progress of the Analytical Methods and Application of Plutonium Isotopes in the Environment

Xidong Liu [1,2], Yang Shao [2,*], Min Luo [2], Lingling Ma [2], Gang Xu [1] and Minghong Wu [1,*]

[1] School of Environmental and Chemical Engineering, Shanghai University, Shanghai 200444, China
[2] Beijing Engineering Research Center of Radiographic Techniques and Equipment, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China
* Correspondence: shaoyang@ihep.ac.cn (Y.S.); mhwu@shu.edu.cn (M.W.)

Abstract: Since the beginning of the use of nuclear energy in the twentieth century, atmospheric nuclear weapons testing, nuclear accidents, and spent fuel reprocessing have released large amounts of radioisotopes into the environment, especially plutonium isotopes. As an important anthropogenic radionuclide, plutonium is mainly produced by neutron irradiation of uranium. Plutonium isotopes and their ratios from different sources have a specific 'fingerprint', which is determined by irradiation time and intensity. Accordingly, several methods have been developed for the analysis of plutonium isotopes. As a popular new tracer in recent years, plutonium isotopes could be used for environmental tracer applications and source identification of regional environmental contamination sources. This paper summarizes and compares the pretreatment of plutonium isotopes in various samples and the detection and analysis methods in recent years. Plutonium isotopes in various environmental samples were enriched by chemical treatments, such as ashing, acid digestion, and alkali fusion. Then it was purified and separated by extraction resins to remove interfering nuclides for the subsequent mass spectrometry. The practical applications of plutonium isotopes and their related ratios in the environment are summarized, such as the determination of plutonium isotopes and their related ratios in the environment near two representative nuclear power plant accidents and the monitoring of the safe operation of nuclear power plants; the establishment of a plutonium isotope database in the vicinity of Chinese waters; and the traceability of plutonium isotopes in environmental regions through the global atmosphere and sand and dust. Finally, the outlook for subsequent research in plutonium isotope detection and applications is presented.

Keywords: plutonium; pretreatment; purification and separation; mass spectrometry analysis; environmental application

Citation: Liu, X.; Shao, Y.; Luo, M.; Ma, L.; Xu, G.; Wu, M. Progress of the Analytical Methods and Application of Plutonium Isotopes in the Environment. *Processes* **2023**, *11*, 1430. https://doi.org/10.3390/pr11051430

Academic Editor: Maria Victoria Lopez-Ramon

Received: 11 April 2023
Revised: 3 May 2023
Accepted: 5 May 2023
Published: 8 May 2023

1. Introduction

As a radioactive isotope, the natural abundance of plutonium isotopes in the environment is extremely low. Only ^{244}Pu and trace amounts of ^{239}Pu are natural products among the plutonium isotopes discovered so far. Plutonium isotopes are mainly produced by neutron irradiation of uranium and are dependent on the intensity and duration of neutron irradiation. However, the large amount of plutonium isotopes present in the environment is mainly due to human activities, such as atmospheric nuclear weapons testing, liquid discharge from nuclear reprocessing plants, nuclear accidents, and satellite disintegration [1,2]. ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu, and ^{244}Pu are important isotopes, and their physical properties are shown in Table 1.

Table 1. Isotopic properties of plutonium.

Plutonium Isotope	Half-Life	Specific Activity (Bq g^{-1})	Principal Decay Mode	Decay Energy (MeV)	Production Method
^{238}Pu	87.7 year	6.338×10^{11}	α	α 5.499 (70.9%) 5.456 (29.0%)	^{242}Cm daughter ^{238}Np daughter
^{239}Pu	2.411×10^4 year	2.296×10^9	α	α 5.157 (70.77%) 5.144 (17.11%) 5.106 (11.94%) γ 0.129	^{239}Np daughter
^{240}Pu	6.561×10^3 year	8.401×10^9	α	α 5.168 (72.8%) 5.124 (27.1%)	Multiple n capture
^{241}Pu	14.35 year	3.825×10^{12}	β^-	α 4.896 (83.2%) 4.853 (12.2%) β^- 0.021 γ 0.149	Multiple n capture
^{242}Pu	3.75×10^5 year	1.458×10^8	α	α 4.902 (76.49%) 4.856 (23.48%)	Multiple n capture
^{244}Pu	8.08×10^7 year	6.710×10^5	α	α 4.589 (81%) 4.546 (19%)	Multiple n capture

The release amounts of ^{239}Pu, ^{240}Pu, and ^{241} Pu are the largest among all of the plutonium isotopes released during human activities. According to the 2000 UNSCEAR (United Nations Scientific Committee on the Effects of Atomic Radiation) report, the release amounts of these three plutonium isotopes from nuclear weapons testing were 6.52 PBq, 4.35 PBq, and 142 PBq, respectively [3]. Due to the long half-life of plutonium isotopes, they can exist in the environment for a long time. Meanwhile, the concentration and isotopic ratio of ^{239}Pu and ^{240}Pu released from different sources are different. Therefore, the ^{240}Pu/^{239}Pu atomic ratio can be used as a special “fingerprint” to monitor the operation of nuclear facilities and investigate the sources of plutonium in the regional environment [4].

Plutonium isotopes can also be applied to environmental tracer studies. The distribution characteristics of plutonium are greatly influenced by different environments, such as atmospheric, terrestrial, and aquatic environments, and the concentration of plutonium isotopes may vary with the location of the site and the transport between and within environmental media [5,6]. The ocean is a dynamic system, and radionuclides can be transported to different regions through ocean currents. The fingerprint characteristics of radionuclides can be helpful in studying ocean circulation and variation. Plutonium, a particle-active radionuclide, is easily adsorbed on the surface of particulate matter and participates in ocean circulation. The ocean currents and sedimentation systems can be studied by analyzing the differences in the concentration and isotope ratios of plutonium in different sea areas where plutonium isotopes are released. At the same time, the distribution of plutonium isotopes in the ocean is relatively uneven, and the concentration in each sea area shows significant differences. Due to their relatively stable physicochemical properties and unique fingerprint characteristics, ^{239}Pu, ^{240}Pu, and their isotope ratios have gradually become new tracers applied in marine environmental research in recent years [7].

Accurate and reliable determination of plutonium isotopes is very important for environmental risk assessment, nuclear industry emergency preparedness, and so on. So far, various methods for determining plutonium isotopes have been developed. For the detection of plutonium isotopes, the traditional detection method is radioactive decay detection, mainly through alpha spectrometry. This method is mature, simple, and low-cost, but the detection time is long and not suitable for emergency use. Moreover, the alpha spectrometer cannot distinguish the characteristic peaks of ^{239}Pu (5.16 MeV) and ^{240}Pu (5.17 MeV) and cannot detect the isotope ratio of ^{240}Pu/^{239}Pu [8]. Mass spectrometry can distinguish different elements and isotopes by mass-to-charge ratios, so it can overcome the deficiency of alpha spectrometry in detecting the isotope ratio of ^{240}Pu/^{239}Pu. So far, techniques such as inductively coupled plasma mass spectrometry (ICP-MS) [9,10], thermal ionization mass spectrometry (TIMS) [11], secondary ion mass spectrometry (SIMS) [12,13], and accelerator mass spectrometry (AMS) [14] have been applied to plutonium isotope detection. Compared with alpha spectrometry, mass spectrometry detection has the advantages of a short detection time, a low detection limit, and high sensitivity, which satisfy the need for rapid results in emergency situations. However, due to the low concentration of plutonium in the environment, it is easy to interfere with during detection. Therefore, sample pretreatment is required before detection, including enrichment and purification separation, to remove interfering elements in the sample matrix.

This article summarizes the pretreatment and detection methods of plutonium isotopes and their applications in the environment. The advantages, disadvantages, and applicable conditions of different mass spectrometry detection methods were compared. In addition, the application of plutonium isotopes as a new tracer in environmental tracing was also presented. Finally, the development of plutonium isotope detection technology and its application were proposed.

2. Plutonium Isotope Pretreatment and Purification Separation

2.1. Sample Pretreatment Techniques

Due to the low concentration of plutonium isotopes in environmental samples, pretreatment is needed to concentrate plutonium from a large amount of environmental matrix and convert it into an acidic solution that can be used for subsequent purification separation. For solid environmental samples, pretreatment methods include ashing, strong acid digestion, and fusion. Before sample digestion, it is necessary to decompose organic matter in the environmental matrix through ashing treatment. Temperature control is crucial during this process. If the temperature is too low, the organic matter in the sample cannot be completely decomposed. If the temperature is too high, refractory particles may be generated, resulting in the loss of target nuclides. Wang et al. [15] studied the effect of different ashing temperatures at 400 to 900 °C on the recovery of plutonium, and the results showed that when the ashing temperature was higher than 600 °C, about 40% of plutonium would be wrapped by refractory substances, resulting in a low recovery of plutonium. It was found that the ashing temperature should be controlled below 500 °C, and the optimal temperature was around 450 °C.

The methods of acid digestion include single acid digestion and mixed acid digestion. Nitric acid digestion is currently the most widely used method, but it is strongly affected by sample ashing and is also time-consuming [15]. For example, Kazi et al. [16] used 10 mL of 16 M nitric acid to digest a 0.5–2 g sample that had been ashed for 16 h, and the recovery of plutonium was more than 90%. However, the digestion process took more than 10 h. Jakopic et al. [17] used 100 mL of nitric acid to digest 1–2 g of sample, and the entire process takes more than 36 h, with the recovery of plutonium only between 42 and 60%. When the sample contains a large number of refractory oxides, such as PuO_2, single nitric acid digestion can lead to a low recovery of plutonium. However, adding hydrofluoric acid can overcome this disadvantage and increase the recovery of plutonium to more than 90% [18,19]. In addition, a mixed acid of nitric acid, hydrofluoric acid, and perchloric acid is often used for plutonium recovery, which can completely dissolve and enrich plutonium from the sample matrix [20,21]. In order to reduce the processing time, increase the recovery rate, and reduce the amount of strong acid used, microwave-assisted digestion has gradually been applied [22]. For example, Varga et al. [23] used microwave digestion to treat 0.5–3 g of soil samples with 10 mL of nitric acid; the entire digestion process can be completed within 30 min, and the recovery rate of plutonium can reach more than 80%. Although microwave digestion reduces the sample preparation time, it is more suitable for digesting milligram level samples. For the detection of plutonium in soil and sediment samples when using 2–5 g, microwave digestion will increase the amount of acid used and increase the processing time in the subsequent solvent exchange process.

The fusion method is another commonly used method. Compared with the acid digestion method, the fusion method is characterized by complete decomposition of the sample, higher recovery of plutonium, and higher treatment efficiency. However, this method usually requires high temperatures. The commonly used fusion mixture is potassium fluoride, potassium bifluoride, and potassium tetrafluoride, or a mixture of potassium fluoride and potassium sulfate. For example, when Sill et al. [24] used potassium fluoride and pyrosulfate as the fusion agents to decompose soil samples, the recovery of plutonium could reach more than 88%. However, this fusion method produced a large amount of hydrogen fluoride and sulfuric acid smoke, which was harmful to the operator's health. For now, lithium borate is the most commonly used reagent in the fusion method [25]. This fusion agent could quickly dissolve most silicates, carbonates, sulfates, and oxides and could quickly determine 700 soil samples within ten weeks [26]. Similarly, Warwick et al. [27] mixed 5 g of the sample with 7 g of lithium tetraborate flux and fused it at 1100 °C. After fusion and acid dissolution, the sample could be directly transferred to TRU resin without additional chemical separation processes. This method obtained a highly reproducible chemical recovery of over 60% for plutonium and a decontamination factor of 10^3–10^4. Luo et al. [28] optimized and established the lithium metaborate fusion method. When the sample size was between 0.5 and 10 g, the optimal ratio of sample:$LiBO_2$:LiI:$Na_2S_2O_8$ was 1:0.5:0.02:0.2; when the sample size was above 10 g, the optimal ratio of sample:$LiBO_2$:LiI:$Na_2S_2O_8$ was 1:1:0.2:0.2. The optimized method obtained a recovery of over 70% for plutonium. The entire experimental process could be completed within 2.5 days, and 12 samples could be analyzed in one week. In addition to using high-melting borates as fluxes, sodium hydroxide is another commonly used reagent. Maxwell et al. [29] developed a series of methods for plutonium analysis in different types of samples using sodium hydroxide. The sample could be completely decomposed within 1–2 h and obtained an average recovery of higher than 90% [30–32]. Although the recovery of plutonium is high, the method mentioned before still needs to be carried out at a temperature higher than 600 °C, and the heating and cooling processes are relatively time-consuming. Therefore, the low-temperature fusion method using NH_4HF_2 and NH_4HSO_4 as fusion reagents has become popular nowadays [33–35]. Wang et al. [36] explored the NH_4HF_2 and NH_4HSO_4 low-temperature fusion methods for the rapid determination of plutonium in soil and sediment samples. The fusion temperature was 250 °C, and the entire fusion process only took about ten minutes. For 0.5 g and 1.0 g samples, the plutonium recovery could reach more than 70% and 90%, respectively, which is comparable to the acid digestion method.

For large-volume liquid samples, co-precipitation is the commonly used step for plutonium concentration. Commonly used reagents for plutonium co-precipitation include hydroxide [37,38], fluoride [17,23], phosphate [39], oxalate [40], manganese dioxide [41,42], or a mixture of several reagents [43,44]. Among them, bismuth phosphate ($BiPO_4$) was the first co-precipitation reagent used for large-scale processing of plutonium in water samples. Pu (III) and Pu (IV) could be efficiently co-precipitated with $BiPO_4$ under acidic conditions [45]. Currently, NdF_3, LaF_3, and CeF_3 are commonly used co-precipitation reagents for separating Pu (IV). These reagents can reduce the co-precipitation of U (VI), which is beneficial for plutonium analysis. Additionally, prior to purification, the CaF_2 co-precipitation technique is also a commonly used methods for preliminary enrichment of plutonium in large-volume liquid sample. This method obtained a plutonium recovery of above 80%, and sample preparation and measurement could be completed within 6 h [46,47]. For the extraction of plutonium isotopes from a large amount of seawater, co-precipitants such as $Fe(OH)_3$, $Fe(OH)_2$, and MnO_2 are used. For example, Sidhu [43] used MnO_2 and $Fe(OH)_3$ to pre-concentrate plutonium from 200 L of seawater. First, the solution was adjusted to pH 8–9 using NaOH. Under this condition, plutonium co-precipitated with $Mn(OH)_2$ and $Fe(OH)_3$. Then, 4 M HCl was added to adjust the pH to 6, and $Mn(OH)_2$ was dissolved while $Fe(OH)_3$ did not dissolve. Finally, the precipitate was dissolved in 8 M HNO_3, and TRU resin was used for further separation and purification of plutonium.

The results showed that the recovery of plutonium in this method was between 80 and 85%, and the method was simpler and more reliable.

2.2. Purification and Separation Methods for Plutonium Isotopes

Due to the low concentration in environmental samples and instrumental detection limits, plutonium should be thoroughly separated from interfering nuclides before detection. Liquid-liquid extraction, ion exchange, and extraction chromatography, or a combination of multiple methods, are commonly used for the purification and separation of plutonium isotopes. The purification of plutonium is mainly based on Pu (IV), so it is necessary to adjust the oxidation state of plutonium ions in solution to Pu (IV). The nitrite ion plays an important role in adjusting the oxidation state of plutonium ions in solution, which can oxidize Pu (III) to Pu (IV) and reduce Pu (VI) to Pu (IV). Therefore, $NaNO_2$ is often used to adjust plutonium to Pu (IV) in practical processes. In addition, heating or adding other reducing agents such as ferrous ions and ascorbic acid can speed up the reduction reaction [21]. Since Pu (III) is easily oxidized in nitric acid, it is better to carry out the separation in a hydrochloric acid system.

Liquid-liquid extraction is often used for the separation of plutonium in the post-treatment of spent fuel and the treatment of radioactive waste. Commonly used extractants include chelating extractants (such as TTA and HDEHP) [48–50], ion pairing agents (such as TOPO) [51], and amine extractants (such as TOA) [52]. For example, Rameback and Skalberg [48] developed the HDEHP extraction method for the separation of Np, Am, Cm, and Pu. Am and Cm were back-extracted using 5M HNO_3, Np was back-extracted using 1 M HNO_3 containing $NH_2OH \bullet HNO_3$, and Pu was recovered in the last step using 3 M HNO_3 containing Ti (III). The method obtained a decontamination factor of 2800 for uranium and a recovery of 91% for plutonium. Momoshima et al. [53] used TOA-xylene to separate plutonium from the environmental sample matrix. After digesting with 8 M HNO_3, the sample solution was extracted twice with TOA-xylene, and finally, plutonium was back-extracted using 0.1 M NH_4I-8.5 M HCl. The recovery of plutonium was in the range of 59–72%. K. Norisuye et al. [49] used TTA-benzene to extract plutonium from a large volume of seawater. ICP-MS results show that the recovery of plutonium was as high as 96% when using this extractant. The decontamination factor for uranium was 1.7×10^7. Liquid-liquid extraction has a great advantage in plutonium extraction, but it requires multiple extractions to thoroughly separate plutonium from the sample matrix, which is particularly time-consuming and environmentally unfriendly. Therefore, it has been gradually replaced by methods of ion exchange and extraction chromatography.

Due to its high potential and tendency to form anionic complexes, plutonium can be adsorbed on anion exchange resins and exchanged with ions of the same valence on the resin [54]. Dowex-1, AG-1, and AG MP-1 are the commonly used anion exchange resins for plutonium separation [20,55–58]. The separation mechanism relies on the strong adsorption ability of anionic complexes of Pu (IV) and NO_3^- in nitric acid medium on the resin, while other elements in the sample solution will not be adsorbed under this condition. Therefore, the key point for this method is the oxidation state adjustment of plutonium. For example, Huang et al. [59] developed the AG MP-1M resin method to separate plutonium from soil and sediment samples. The resin was pre-washed with 20 mL of 7.2 M HNO_3-0.4 M $NaNO_2$. After the oxidation state of plutonium was adjusted, thorium and uranium were removed with 20 mL concentrated HCl-0.3 mL concentrated HNO_3 and 60 mL of 7.2 M HNO_3, respectively. Finally, plutonium was eluted from the resin using 16 mL concentrated HBr. The recovery of plutonium could reach more than 72%. Wang and Yamada [60] used AG-1 × 8 resin to separate plutonium from sediment samples. First, the sample was dissolved with 8 M HNO_3 and 0.2 g of $NaNO_2$, and the valence state of plutonium in the solution was adjusted. Then, interference elements were removed by washing the resin with 50 mL of 8 M HNO_3 and 50 mL of 10 M HCl, respectively. Finally, 50 mL of 0.1 M NH_4I-12 M HCl was used to elute plutonium. The recovery of plutonium was in the range of 70–88%.

The extraction chromatography method is a technique for extracting and purifying samples on resin columns through continuous multiple extractions. Compared to ion exchange, this method has the advantages of high separation efficiency, good selectivity, less chemical reagent usage, less waste production, and being economical. Commonly used chromatography columns for purifying plutonium include TRU, TEVA, and UTEVA resins. The purification mechanism for plutonium is to use the adsorption coefficient differences of plutonium isotopes and other interference elements in different acid solutions, as well as the effect of plutonium oxidation states on the absorption of plutonium on the resin [40,46,53,61,62]. TEVA resin is widely used for purifying actinide elements in 2–4 M HNO_3 or HCl media. For example, Varga, Z. et al. [46] developed the TEVA method for plutonium analysis in marine sediments. First, the valence state of plutonium in the solution was adjusted to Pu (IV) using $NaNO_2$, and the resin column was pre-washed with 10 mL of 3 M HNO_3. Uranium and thorium were eluted with 20 mL of 3 M HNO_3 and 15 mL of 6 M HCl, respectively. Finally, plutonium was eluted using 20 mL of 0.1 M HNO_3/0.1 M HF. The results showed that the decontamination factors of uranium, thorium, and americium were all above 10^5, and the plutonium recovery was in the range of 72–92%. TRU resin is another extraction resin for plutonium purification. When the nitric acid concentration is greater than 0.5 M, actinide elements with oxidation states III, IV, and VI can be strongly adsorbed on the resin, while most of the matrix components and potential interference elements are not adsorbed under this condition. Finally, the elution of plutonium was based on the mechanism of no adsorption effect of trivalent actinide elements in hydrochloric acid media [63]. For example, Kuwabara and Noguchi [64] developed a rapid analysis method for separating plutonium in urine based on calcium and magnesium phosphate coprecipitation and TRU resin separation. The resin column was eluted with concentrated nitric acid and an 8% hydrochloric acid solution, and then plutonium on the resin column was reduced to Pu (III) and eluted with 10 mL of an 8% hydrochloric acid solution containing 1% diphenyl quinone. The plutonium recovery could reach more than 89%. Furthermore, the sample preparation and analysis could be completed within 12 h, which was suitable for an emergency situation.

Due to the high concentration of uranium and other actinide elements and the trace concentration of plutonium in environmental samples, a single resin column is often insufficient to separate and purify plutonium isotopes. Therefore, further purification steps are needed to remove impurities from plutonium, especially uranium. For example, UTEVA resin and TEVA or TRU resin are often used together. The UTEVA resin is mainly used to remove uranium from the sample. The eluent that has passed through the UTEVA resin is then directly loaded onto another resin for further separation and purification of plutonium. For example, UTEVA and TRU resins were used to separate plutonium from soil and sediment. Plutonium was reduced to Pu (III) using ferrous ions and ascorbic acid, and the sample acidity was adjusted to 3 M HNO_3 before transferring the sample to the resin column. Uranium and thorium were retained on the UTEVA resin, while Pu (III) was retained on the TRU resin. The Pu (III) on the TRU resin was then oxidized to Pu (IV) using 2 M HNO_3-0.1 M $NaNO_3$ and 0.5 M HNO_3, and then the column system was converted to the hydrochloric acid system using 9 M HCl. Finally, the plutonium was eluted using 0.1 M $NH_4HC_2O_4$. The recovery of plutonium could reach more than 80%, and the decontamination factor of uranium was greater than 10^4 [21]. Furthermore, the combination of different resins can also achieve simultaneous separation and purification of various radionuclides from a single sample, such as the simultaneous separation and purification of uranium, thorium, ^{241}Am, ^{237}Np, and other nuclides. The key to achieving this goal lies in the order in which different chromatographic columns are connected and the selection of different elution schemes. Table 2 summarizes the methods used in recent years to separate plutonium and other radionuclides using multiple resin columns in combination. For example, Lopez-Lora et al. [65] used TEVA and UTEVA resins to separate and purify $^{239+240}$Pu, ^{236}U, and ^{237}Np in seawater samples. The results showed that the recovery rates of all three target elements were above 80%. Wang et al. [66] used

UTEVA, DGA, and TEVA resins to simultaneously separate plutonium and americium in soil and sediment samples. First, UTEVA and DGA resins were used to remove most interference elements. In the meantime, plutonium and americium were separated. Then, the TEVA resin was used for further purification of plutonium. The results showed that the decontamination factor of americium is 7.0×10^3, and the recovery of plutonium and americium was 71–91% and 70–80%, respectively. This method could complete the analysis in 14 h. For example, Zapata-Garcia et al. [67] used two different resin column combinations to separate uranium, americium, strontium, and plutonium from soil samples. The first method used UTEVA, TRU, and Sr resins in combination, where UTEVA resin was used to adsorb uranium from the solution, Sr resin was used to adsorb ^{90}Sr, and TRU resin was used to separate plutonium and americium. The second method uses a combination of TEVA, UTEVA, DGA, and Sr resins, where DGA resin was used to separate americium and TEVA resin was used to purify and separate plutonium. The results showed that the recovery rates for plutonium, americium, and strontium were all above 75%. For example, the combination of anion exchange and extraction chromatography is used to separate actinide elements in samples. Luo et al. [68] developed a separation method for actinide elements and Sr in soil and sediment samples greater than 20 g. AG MP-1M, DGA, TEVA, and UTEVA resins were used to elute different elements. This method obtained a high recovery rate (>70%) for plutonium, americium, strontium, and yttrium.

Table 2. Simultaneous purification and separation of Pu isotopes from other radionuclides.

Sample Type	Nuclide	Resin Column	Chemical Yield	Ref.
Natural water	Pu, U, Am, Tc	TEVA, TRU, DOWEX 1 × 8	>70%	[69]
Dust	Pu, U, Am, Sr	UTEVA, DGA, TRU, Sr	>75%	[67]
Seawater	Pu, U, Np	TEVA, UTEVA	>80%	[65]
Soil	Pu, Np	AG MP-1M, TEVA	>72%	[59]
Wipe sample	Pu, U	TEVA, UTEVA	>80%	[70]
Soil	Pu, U	UTEVA, DOWEX 1 × 8	/	[71]
Water	Pu, Sr, Am, U, Th, Np	AnaLig Pu-02/Sr-01, DGA	90%	[72]
Urine	Pu, Am, Sr	AG MP-1M, TEVA, UTEVA	84%	[73]
Wipe sample/Water	Pu, Np, Th, U, Am, Cm, Pm, Y, Sr, Fe	AG MP-1M, TEVA, UTEVA, DGA, Sr, TRU	99.6 ± 4.3%	[74]
Core sediment	Pu, Cs, Am, U	TEVA, UTEVA, DGA	/	[75]
Soil/Sediment	Pu, Am, Sr, Y	AG MP-1M, DGA, TEVA, UTEVA	>75%	[68]
Soil/Sediment	Pu, Am	UTEVA, DGA, TEVA	71–91%	[66]

3. Methods for Detecting Plutonium Isotopes

3.1. Alpha Spectrometry

Alpha spectrometry, as a traditional method of radioactive technology, has been applied to the detection of plutonium isotopes for a long time [17,46,58,76,77]. For example, E. Hrnecek et al. [58] used alpha spectrometry with a silicon detector to analyze plutonium isotopes in environmental samples; a detection limit of 0.4 mBq was achieved for $^{239+240}$Pu and ^{238}Pu by using the NdF_3 micro-precipitation method to prepare the detection source. Alpha spectrometry is widely used for plutonium analysis due to its stability, reliability, simplicity of operation, and low detection cost. However, due to the limitation of energy resolution, it is not possible to detect plutonium isotopes such as the ^{239}Pu/^{240}Pu atom ratio and ^{241}Pu. At the same time, alpha spectrometry requires a counting time of 1–30 days, which cannot be used for emergency situations (within 1 day). In addition, even in very thin absorbers, the high charge (+2) and low velocity of alpha particles will result in significant energy loss, and the spectrum will become degraded with the increase of peak overlap and the decrease of resolution. Therefore, plutonium isotopes must be thoroughly separated from interfering elements in the sample matrix before alpha spectrometry detection.

3.2. TIMS

TIMS is one of the best instruments for analyzing uranium and plutonium isotopes, especially low-abundance uranium and plutonium isotopes. Compared to ICP-MS, TIMS has better sensitivity and precision for isotope ratio measurement and is not affected by polyatomic ions. The effect of $^{238}UH^+$ on the detection of ^{239}Pu and ^{240}Pu is relatively small. However, the disadvantage of TIMS is its low ionization efficiency and mass fractionation effect. To improve the ionization efficiency, one of the current research directions is to apply resin bead loading technology and carbon additives such as benzene to enhance the ionization efficiency [78]. For example, using resin bead loading technology, filament carburization, and cavity technology in sample loading could make the total efficiency of measuring plutonium isotopes as high as 0.5–2%, Burger et al. [79]. At the same time, the detection limit of $^{239,240,241,242,244}Pu$ could be less than 0.1 fg by using SEM or MIC. The ionization efficiency could improve by 1–2 orders of magnitude compared to traditional sample preparation techniques. Jakopic et al. [80] applied the benzene gas carburizing technique to improve the total efficiency and stability of the ion beam signal. Under a filament current of 3.5 A and a benzene gas pressure of 1×10^{-3} mbar, the average total efficiency was about 3.1%. Compared with non-carburized filaments, it was increased by 10 times, and the detection limit of plutonium isotope could reach pg level. The continuous heating technique is a new method for measuring isotope ratios in ultra-trace mixed uranium and plutonium samples. The detection mechanism is to utilize the difference in evaporation temperatures of plutonium, uranium, and other actinide elements without additional chemical separation, such as ^{238}Pu and ^{238}U, as well as ^{241}Pu and ^{241}AmLee et al. [81]. When the sample size was at fg level and the detection limit of ^{239}Pu was reduced to 0.006 fg. Compared with other mass spectrometry techniques, TIMS requires a well-trained operator for sample preparation and instrument control.

3.3. AMS

AMS is one of the instruments with the highest sensitivity for measuring trace and ultra-trace long-lived radioactive isotopes in environmental samples. Compared to TIMS and ICP-MS, the main advantage of AMS in detecting plutonium isotopes relies on the interference removal technique. Plutonium can be stripped to a high positive charge state of Pu^{n+} through a tandem accelerator. After acceleration, Pu^{3+} is selected by the analyzing magnet and detected through the detector. During the stripping process, isobaric isotopes and polyatomic ions are suppressed, which results in a lower detection limit and high sensitivity for plutonium [82]. However, due to the limited number of AMS and their cumbersome operation and high cost, they are not suitable for emergency detection [83–85]. Therefore, a new generation of compact AMS devices with smaller accelerator voltages has been developed and applied due to their simple operation and cost-effectiveness. For example, Wacker et al. [86] used a compact AMS system with an acceleration voltage of 300 kV to measure plutonium isotopes in 1–3 g soil samples. After sample pretreatment and purification, the samples were mixed with 3–4 mg of aluminum powder to make AMS targets. The background of plutonium was down to 10^6 atoms for $^{239/240}Pu$, and the atom ratios were all comparable to those of certified values measured by α-spectrometry. The alpha spectroscopy method cannot distinguish between ^{239}Pu and ^{240}Pu, but it can provide the activity of ^{238}Pu. While AMS mass spectrometry can easily detect the atom ratio of $^{239}Pu/^{240}Pu$. Therefore, the combination of the two methods can identify the source of plutonium in environmental samples [87]. For example, Bisinger et al. [88] used compact AMS and alpha spectrometry to measure environmental plutonium from different sources. The results show that the activity of $^{239+240}Pu$ in the environmental samples measured by AMS and alpha spectrometry was very consistent, with $R^2 = 0.99$, and the detection limit of the AMS measurement could reach 10^6 atoms.

3.4. ICP-MS

ICP-MS is currently the most widely used instrument for element analysis, with the advantages of high analytical efficiency and sensitivity, low detection limits, simple operation, and the ability to perform simultaneous multi-nuclide determinations. However, when measuring plutonium using ICP-MS, the low content of plutonium in environmental samples and the large amount of environmental matrix interference result in the difficulty of its application. Moreover, there is a large amount of ^{238}U in the sample, which is more than 10^6 times higher than the plutonium concentration. Therefore, effective radiochemical separation must be performed to remove uranium and sample matrix so that the peak tailing effect caused by $^{238}U^+$ and the isobaric interference caused by the polyatomic ion $^{238}UH^+$ can be reduced [89,90].

To increase instrument sensitivity and lower detection limits, improving sample introduction efficiency is one of the commonly used techniques in ICP-MS applications. For the traditional sample introduction system, most of the sample is discarded as waste liquid, resulting in low sample utilization efficiency. A membrane desolation introduction system has been successfully applied to the detection of ultra-trace plutonium isotopes, with the advantages of reducing the yield of oxides and hydrides and peak tailing effects. For example, Ni et al. [91] developed the ultra-trace plutonium isotope analyzing method using SF-ICP-MS equipped with the Apex-Q sample introduction system. The pretreatment, such as co-precipitation and extraction chromatography, obtained a decontamination factor of 3.8×10^6 for ^{238}U, and the average recovery of ^{242}Pu was $72.7 \pm 5.5\%$. The detection limits of ^{239}Pu, ^{240}Pu, and ^{241}Pu in a 20 mL urine sample were 0.016, 0.016, and 0.019 fg mL^{-1}, respectively, and in a 100 mL urine sample, the detection limits of ^{239}Pu, ^{240}Pu, and ^{241}Pu were 0.003, 0.002, and 0.003 fg mL^{-1}, respectively. Shi et al. [92] used ICP-MS equipped with the Apex-Q sample introduction system and a microflow PFA nebulizer to measure ^{239}Pu in urine samples. The results showed that by controlling the $^{238}U/^{239}Pu$ concentration ratio below 1.2×10^5, the fg level of ^{239}Pu could be accurately analyzed. Bu et al. [93] used the ICP-MS/MS system equipped with the Apex-Ω high-efficiency sample introduction system to detect plutonium isotopes in environmental samples, and the self-suction sample introduction nebulizer TQP-50-A.5 was used. The results showed that the sensitivity was improved by 10 times, and the absolute detection limits of ^{239}Pu and ^{240}Pu were 0.13 fg and 0.08 fg, respectively.

In order to further eliminate the isobaric interferences and tailing effects caused by U^+ and UH^+, collision/reaction cells are one of the most commonly used techniques to remove interferences in ICP-MS. Gases such as He, O_2, N_2O, NH_3, and CO_2 are currently used for collision/reaction cells [94–96]. Different gases and gas combinations have different effects on the elimination of uranium hydride and other polyatomic ion interferences. For example, He could double the sensitivity [10], NH_3 could significantly improve the elimination efficiency of UH^+ [97], and CO_2 as a reaction gas could reduce the ratio of UH^+/U^+ to 10^{-8} [10]. However, the use of a single gas as a reaction gas may also reduce the abundance sensitivity of plutonium isotopes. Therefore, the use of multiple gases in combination is currently a popular solution [98–100]. For example, Shan Xing et al. [97] studied the effect of NH_3/He as the reaction gas on the analysis of plutonium. The results showed that the existence of NH_3 could completely eliminate U^+ and 90% of UH^+, while Pu^+ could not react with NH_3. Compared with the conventional ICP-MS/MS without reaction gas, the sensitivity of ^{239}Pu increased by 1.5 times, and the detection limits of ^{239}Pu and ^{240}Pu in a 3.5 mL sample solution could decrease to 0.55 fg mL^{-1} and 0.092 fg mL^{-1}, respectively. Xu et al. [101] studied the optimal conditions for NH_3/He as the reaction gas, and the results showed that the optimal conditions were 0.4 mL min^{-1} for NH_3 and 6.4 mL min^{-1} for He. Under optimal conditions, UH^+/U^+ was reduced to 2.4×10^{-7}. The detection limits of ^{239}Pu and ^{240}Pu were 0.16 fg g^{-1} and 0.046 fg g^{-1}, respectively. Zhang et al. [95] studied the effect of O_2/He-He as the reaction gas on ultra-trace plutonium analysis. Results showed that $^{238}UHO^{2+}/^{238}UO^{2+}$ was reduced to 4.82×10^{-9}, and the abundance sensitivity of plutonium isotopes was increased by more than six times. For 20 g soil samples, the detection limits of ^{239}Pu and ^{240}Pu were 0.062 fg g^{-1} and 0.055 fg g^{-1}, respectively.

Another commonly used instrument is LA-ICP-MS, which can directly analyze solid samples without dissolution. For example, Boulyga, S. F., et al. [102] developed a LA-ICP-MS method to directly analyze the concentration of plutonium isotopes in soils at the pg g^{-1} level. The uranium hydride ion was significantly suppressed with the application of laser ablation, and a UH^+/U^+ ratio of 1.1×10^{-6} was obtained. At the same time, the application of medium resolution ($m/\Delta m = 4000$) could reduce the tailing effect caused by ^{238}U. This method directly analyzed the ^{239}Pu and ^{240}Pu at a level of 10^{-12}–10^{-11} g g^{-1} in soil and sediment samples. The detection limit for plutonium isotopes reached as low as 3×10^{-13} g g^{-1}. However, LA-ICP-MS requires a sufficiently large sampling area and a high and stable laser ablation rate to avoid the impact of sample inhomogeneity and unstable laser ablation rates on detection accuracy. In summary, more information about the detection methods for plutonium isotopes is shown in Table 3.

3.5. SIMS

Secondary Ion Mass Spectrometry (SIMS) is currently one of the most important instruments for single particle detection. The advantages of SIMS are its high sensitivity and powerful functions such as depth profiles, line scans, elemental mapping, and isotope ratio measurements. When detecting plutonium isotopes, SIMS is also affected by matrix effects and interference from polyatomic ions [12,13,103]. SIMS has been applied to the detection of particles generated in nuclear accidents. For example, in the nuclear forensic field, Betti, M. et al. [12] used SIMS to characterize the fingerprint of plutonium and highly enriched uranium (HEU) particles. Two of the three particles in a sample were identified as plutonium particles based on their $^{239}Pu/^{240}Pu$ ratio, size, and shape. The accuracy and precision of isotope ratio measurement reached 0.5%, and the results were consistent with those obtained by TIMS. By optimizing the parameters of SIMS, the detection limit for plutonium isotopes could reach the ng g^{-1} to pg g^{-1} level. Tamborini and Betti [104] used SIMS to characterize radioactive particles, and the detection limit for plutonium can reach levels of ng g^{-1}. Equipped with a dual-focusing mass spectrometer, it could solve a large number of interference problems at a mass resolution of 2000–10,000. Studies have shown that a mass resolution of 1000 is sufficient to measure plutonium isotopes and achieve the best measurement sensitivity.

Table 3. Comparison of different plutonium isotope detection techniques.

Method	Measurable Isotope	Interference	Detection Limit (mBq)	Detect-ion Time	Cost	Advantage	Disadvantage	Ref.
α-spectrometry	^{238}Pu $^{239+240}Pu$ ^{241}Pu	^{241}Am, ^{210}Po, ^{228}Th 229Th, ^{231}Pa, ^{232}U, ^{243}Am ^{210}Po, ^{228}Th	0.01–0.1 0.01–0.1 0.1–1.0	Day–weeks	High	Simple, mature, reliable, low cost, and most used.	Large sample size. Long measurement time.	[8,17,46]
AMS	^{239}Pu ^{240}Pu ^{241}Pu	^{238}U, molecules with the same or similar m/z as ^{239}Pu. Molecules with the same or similar m/z as ^{240}Pu and ^{241}Am. Molecules with the same or similar m/z as ^{241}Pu	10^{-4}–10^{-3} 10^{-4}–10^{-3} /	Hour/min	High	The best detection limits. Possibility to distinguish between ^{239}Pu and ^{240}Pu. Small sample size and short measurement time.	Technically complex and costly.	[14,58,85,87]
TIMS	^{239}Pu ^{240}Pu ^{241}Pu	Matrix elements	10^{-4}–10^{-3} 10^{-4}–10^{-3} /	Hour/min	High	High precision. Good sensitivity.	Complex sample preparation. Large sample volume and difficult operation.	[105]
ICP-MS	^{239}Pu	$^{238}U^{1}H$,$^{208}Pb^{31}P$,$^{206}Pb^{33}S$, $^{204}Hg^{35}Cl$,$^{205}Tl^{34}S$,$^{203}Tl^{36}Ar$, $^{202}Hg^{37}Cl$,$^{199}Hg^{40}Ar$	0.01–0.1	Hour/min	Low	Low detection limit and high measurement accuracy. Can distinguish ^{239}Pu from ^{240}Pu. Small sample size and short measurement time.	Inability to effectively exclude the disturbance of homogeneous isotopes and molecular ions, and high requirements for sample preparation. Difficult to remove the system background, matrix effects.	[91,93,106,107]

4. Plutonium in the Environment

4.1. Plutonium Released by Nuclear Weapon Tests and Spent Fuel Reprocessing Plant

In the history of nuclear weapons tests and the peaceful development and utilization of nuclear energy, a large number of radionuclides have been released into the environment. Plutonium isotopes, due to their relatively long half-lives, have persisted in the environment for a long time. Additionally, because of their highly toxic and potentially internal and external irradiation characteristics, plutonium isotopes have received widespread attention in radiation protection and environmental studies. Moreover, the atom ratio of plutonium isotopes exhibits specific fingerprint characteristics that vary depending on the source. Table 4 summarizes the isotopic ratios of plutonium from different sources. Atmospheric nuclear weapons tests between 1945 and 1980 were the main source of plutonium in the environment, releasing a total of approximately 6.5 PBq of ^{239}Pu and 4.4 PBq of ^{240}Pu into the environment [54]. In addition to atmospheric nuclear weapons tests, spent fuel reprocessing plants are another major release source for the marine environment. The Sellafield spent fuel reprocessing plant in the UK and the La Hague spent fuel reprocessing plant in France are the two most significant sources of emissions. The total amount of $^{239+240}$Pu released by the Sellafield plant between 1952 and 2007 was approximately 0.6 PBq. Studies of sediment cores near the plant have shown that the ^{240}Pu/^{239}Pu atom ratio was 0.06 in the 1960s. Since the 1980s, the data have increased to 0.2. The Sellafield plant has deposited approximately 440–560 TBq of $^{239+240}$Pu in the Irish Sea seabed [108].

Table 4. Different ratios of plutonium isotopes from different sources.

Source	^{238}Pu/$^{239+240}$Pu Activity Ratio	^{241}Pu/$^{239+240}$Pu Activity Ratio	^{240}Pu/^{239}Pu Atomic Ratio	Ref.
Global Settlement	0.03	13–15	0.18	[108–111]
Nuclear Test	<0.01	27–30	0.3	[112–114]
Chernobyl Accident	0.5	85	0.41	[110,115]
Fukushima Nuclear Accident	1.2	108	0.30–33	[116–119]
Sahara Dust	0.028	3.1	0.192	[120]

4.2. Plutonium Released by Nuclear Power Plant Accidents

In the history of human peaceful use of nuclear energy, there have been two serious nuclear accidents, namely the Chernobyl nuclear accident in the former Soviet Union and the Fukushima nuclear accident in Japan. Both accidents released large amounts of radionuclides into the environment. In 1986, a nuclear reactor explosion occurred at the Chernobyl nuclear power plant in Ukraine. According to simulation calculations and statistics, about 70 TBq of $^{239+240}$Pu was released into the atmosphere [3]. Bisinger et al. [88] used α spectrometry and AMS to study the ^{240}Pu/^{239}Pu and ^{238}Pu/^{239}Pu ratios in soil samples near Chernobyl; the results were 0.475 and 0.007, respectively. Similarly, Muramatsu et al. [121] used ICP-MS to detect the concentrations and ratios of ^{239}Pu and ^{240}Pu in forest soil samples within 30 km of the Chernobyl reactor. The results showed that the concentration of $^{239+240}$Pu in samples collected 6 km from the nuclear power plant was 1280 Bq kg^{-1}, while the average concentration of $^{239+240}$Pu in samples collected 26 and 28.5 km from the nuclear power plant was 161 Bq kg^{-1}. However, the average value of ^{240}Pu/^{239}Pu for different locations was 0.408, indicating that the area was contaminated by nuclear materials from the Chernobyl nuclear power plant. For example, the atmospheric particulate samples collected in Finland in 1963 and after the 1986 accident were analyzed. The results showed that the ^{240}Pu/^{239}Pu ratio was between 0.14 and 0.37 before the accident, indicating that global fallout was the only source at that time. After the accident, the ^{240}Pu/^{239}Pu ratio in the collected samples was in the range of 0.33 to 0.53, indicating the Chernobyl nuclear accident's source of plutonium. According to simulation calculations, about 90% of the ^{239}Pu comes from Chernobyl [90]. Lindahl et al. [122] studied the ratio of plutonium isotopes in lichen samples collected from 18 locations in Sweden between 1986 and 1988. The ^{240}Pu/^{239}Pu ratio was detected between 0.16 and 0.44, indicating that plutonium in Swedish lichen samples was affected by both global fallout and the Chernobyl accident. The contribution from the Chernobyl nuclear accident varied from 15% to 70%.

In addition to the Chernobyl nuclear power plant accident, a serious nuclear accident occurred at the Fukushima Daiichi nuclear power plant in Japan in March 2011, which resulted in a large amount of radioactive material leakage. After the accident, a radioactive plume was observed moving in the northwest direction of the nuclear power plant. The activity ratio of ^{238}Pu/$^{239+240}$Pu was detected to be between 0.33 and 2.2, significantly higher than the global fallout activity ratio of 0.03, indicating that the plutonium isotope anomaly in the northwest direction may be related to the Fukushima Daiichi nuclear accident [123]. On 28–29 March 2011, an early radiation survey was conducted on Iitate Village, located 25–45 km from the Fukushima Daiichi nuclear power plant, and five soil samples were collected. The results showed that the activity ratio of ^{238}Pu/$^{239+240}$Pu in the soil samples ranged from 0.110 to 1.324, higher than the global fallout value of 0.03, confirming the release of nuclear fuel into the environment from the Fukushima nuclear accident [124]. The study and analysis of plutonium isotopes in surface soil and litter samples within 20–30 km of the nuclear power plant showed that the atom ratios of ^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu produced by the Fukushima nuclear power plant accident were relatively high, and the ^{241}Pu/$^{239+240}$Pu activity ratio reached 100, which was much higher than that of the Chernobyl accident. The activity ratio of ^{137}Cs/$^{239+240}$Pu was found to be between 10^5 and 10^7, which estimated that the ^{241}Pu released by the Fukushima nuclear accident was approximately 1.1×10^{11}–2.6×10^{11} Bq and the $^{239+240}$Pu released was approximately 1.0×10^9–2.4×10^9 Bq [116]. Three days after the explosion, aerosol samples were collected from Tokaimura, and the ratio of ^{240}Pu/^{239}Pu in the samples was significantly higher than the global fallout observed in Japan. However, it was consistent with the plutonium isotope ratio characteristics of litter near the Fukushima nuclear power plant accident. Combined with the activity ratio of radioactive cesium isotopes and the NOAA-Hysplit model, it was confirmed that the radiation anomaly in that area was caused by the Fukushima nuclear accident [125]. In addition to being released into the atmosphere, a large number of radionuclides were also released into the ocean due to the use of freshwater and seawater to cool the reactors after the explosion and the direct leakage of reactor damage. In the surface sediment of the sea area 30 km away from the Fukushima nuclear power plant, the atom ratio of ^{240}Pu/^{239}Pu was detected to be between 0.216 and 0.255, significantly lower than that of the Fukushima nuclear accident and consistent with the values observed before the accident (0.150–0.281). At the same time, the activity of $^{239+240}$Pu was at the same level before and after the Fukushima nuclear power plant accident, and there was no significant increase after the accident, indicating that there was no observed plutonium contamination in ocean sediment beyond the 30 km area [61]. After the accident, Kim et al. [126] analyzed the activity of $^{239+240}$Pu and the ^{240}Pu/^{239}Pu ratio in seawater samples from 52 sampling sites around the Korean peninsula, and the results show that the ^{240}Pu/^{239}Pu ratio in surface seawater samples was between 0.194 and 0.259, while the ratio in deep-sea samples is between 0.204 and 0.266, consistent with the pre-Fukushima nuclear accident levels. This indicates that the waters near Korea have not been affected by the Fukushima nuclear accident.

4.3. Global Fallout Plutonium for Environmental Application

With the development of the nuclear industry, especially with the development of nuclear power plants in China's coastal areas, the activity and ratio of radionuclides in the marine environment around China have significant implications for monitoring the safe operation of nuclear power plants. Establishing a background database of plutonium activity and ratio in China's surrounding marine environment is particularly important. In recent years, a large number of literature reports have documented the activity and ^{240}Pu/^{239}Pu atom ratio in surface and core sediments in the China Sea, as shown in Figure 1 [127–134]. Huang et al. [135] studied the spatial distribution and sources of ^{239}Pu and ^{240}Pu in surface sediments from 516 locations in the China Sea and adjacent seas. The samples were collected from the Bohai Sea (BS), Yellow Sea (YS), East China Sea (ECS), and South China Sea (SCS). The activity of $^{239+240}$Pu in marine surface sediments ranged from 0.001 to 3.520 mBq g^{-1}, and the ^{240}Pu/^{239}Pu atom ratio was between 0.158 ± 0.022 and 0.310 ± 0.101. The spatial distribution of activity and atom ratio showed a decreasing trend from south to north. The results verified that the existing plutonium in China's marine environment mainly came from global fallout and input from the Pacific Proving Grounds

(PPG). The global fallout source of plutonium had a stable atom ratio of $^{240}Pu/^{239}Pu$. Therefore, the variation in the $^{240}Pu/^{239}Pu$ ratio in surface sediments in China's seas and adjacent areas was controlled by the input from PPG. Wu et al. [136] summarized the proportion of PPG-derived plutonium in China's seas, accounting for 10–76% in seawater and 13–55% in sediments.

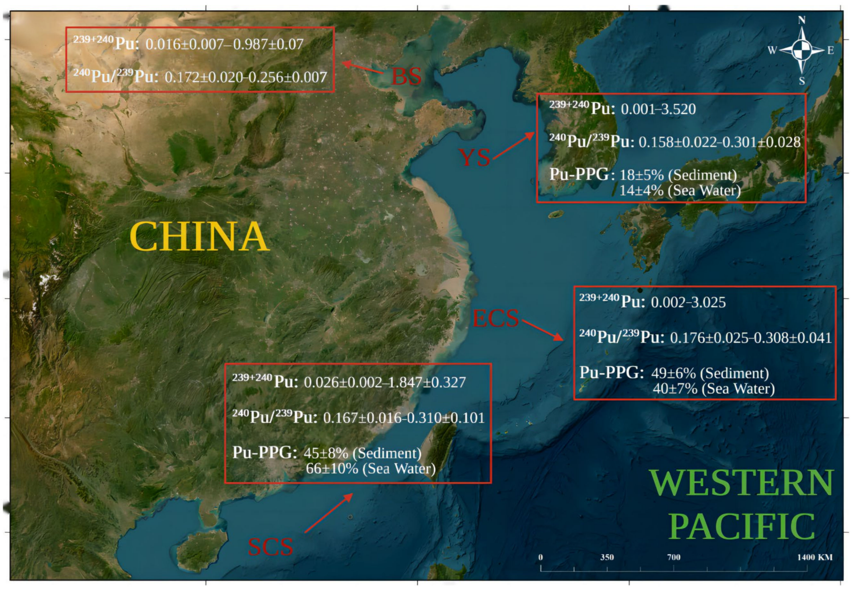

Figure 1. Plutonium isotope activity, atom ratio, and source in Chinese waters ($^{239+240}Pu$: activity, mBq g^{-1}; $^{240}Pu/^{239}Pu$: atom ratio; Pu-PPG: plutonium from the Pacific Nuclear Test Site).

Since plutonium has a tendency to adsorb on the surface of particulate matter and migrate in the environment, the use of plutonium as a tracer for atmospheric circulation and the origin of atmospheric particulate matter have been hot research topics in recent years. Hirose and Povinec [6] analyzed the long-term variations of plutonium in the atmospheric stratosphere and troposphere in the Northern Hemisphere from 1964 to 2010. It could be seen from Figure 2 that the occurrence of the highest concentration of $^{239+240}Pu$ in the stratosphere coincided with the time of atmospheric nuclear weapons tests. For example, the highest concentration in 1963 was due to large-scale atmospheric nuclear weapons tests from 1961 to 1962. Overall, the residence time of $^{239+240}Pu$ in the stratosphere is 1.3 ± 0.3 years. The concentration of $^{239+240}Pu$ in surface air has remained stable in the range of 1–10 nBq m^{-3}, indicating that the $^{239+240}Pu$ in surface air is not related to the stratosphere. In the stratosphere, ^{238}Pu mainly came from the SNAP-9A satellite disintegration accident in the United States in 1964. As shown in Figure 3, the concentration of ^{238}Pu in the stratosphere decreased rapidly. Most of ^{238}Pu had settled to the land surface until 1980 [137]. Lujanienė et al. [138] analyzed plutonium isotopes in aerosol samples collected from the Vilnius sampling station in Lithuania from 1994 to 2011. The $^{240}Pu/^{239}Pu$ atom ratio showed a double peak, indicating that there were two sources of plutonium. The ratio of 0.195 indicates that it originated from global fallout, while the ratio of 0.253 indicates that it originated from the resuspension of plutonium in the soil and the Chernobyl accident. Chamizo et al. [139] studied the concentration variations of ^{239}Pu and ^{240}Pu in the ground-level air in Seville in 2001–2002, and the results showed that the concentration of $^{239+240}Pu$ reached its maximum in the summer without rain, ranging from 1 to 20 nBq m^{-3}. The $^{240}Pu/^{239}Pu$ atomic ratio remained constant at 0.18 ± 0.03 during the two year period, consistent with the global fallout value. Atmospheric plutonium also came from the transport of desert dust worldwide, mainly from the Sahara and Asian dust. The characteristics of plutonium isotopes make them a useful tool for studying dust resuspension. For example, Masson O. et al. [120] investigated the plutonium isotopes in French airborne dust that was sourced from the 2004 Sahara dust storm, and the results showed that the activity levels of ^{238}Pu and $^{239+240}$Pu in the transported dust were 0.029 ± 0.002 Bq kg^{-1} and 1.042 ± 0.032 Bq kg^{-1}, respectively, leading to an increase in plutonium isotope concentrations in the atmosphere. Choi et al. [140] analyzed the concentration and corresponding ratios of plutonium in aerosol samples collected during yellow sand events, and the results showed that in the spring, the concentrations of ^{239}Pu and ^{240}Pu were 0.580 μBq m^{-3} and 0.404 μBq m^{-3}, respectively. The ^{240}Pu/^{239}Pu atom ratio was 0.191 ± 0.014, which was close to the global fallout value. There was also a good linear relationship between the concentration of plutonium in aerosol samples and the concentration of aluminum, which is typically the main component of dust, indicating that plutonium is transported along with dust resuspension. It meant that most of the plutonium in the atmosphere came from the resuspension of soil particles.

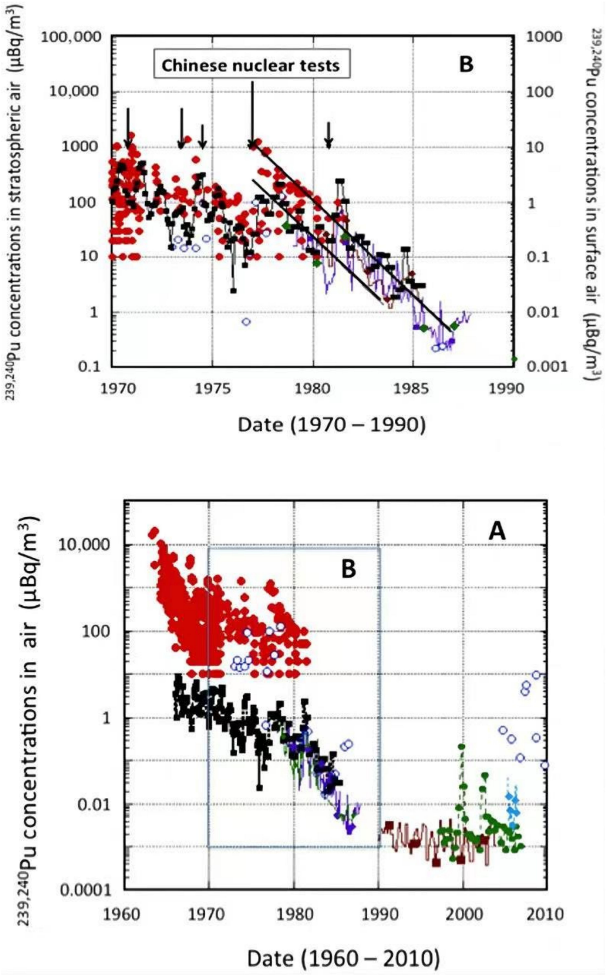

Figure 2. Temporal variations of ^{239,240}Pu concentrations in stratospheric and surface air of the Northern Hemisphere. The black line represents the decreasing trend of ^{239,240}Pu concentration. Closed red circles: the upper stratosphere (20–40 km height); open blue circles: the lower stratosphere (10.1–14.2 km height); closed black squares: the surface air (New York); brown closed rhombic: the surface air (Beaverton Oregon); green closed rhombic: the surface air (Milford Haven); purple squares: the surface air (Tsukuba); brown closed squares: the surface air (Braunschweig); green closed circles: the surface air (Prague); blue closed rhombic: the surface air (Vilnius).Reprinted with permission from (Katsumi Hirose et al., 2015) [6] Copyright (2015), Springer Nature, UK.

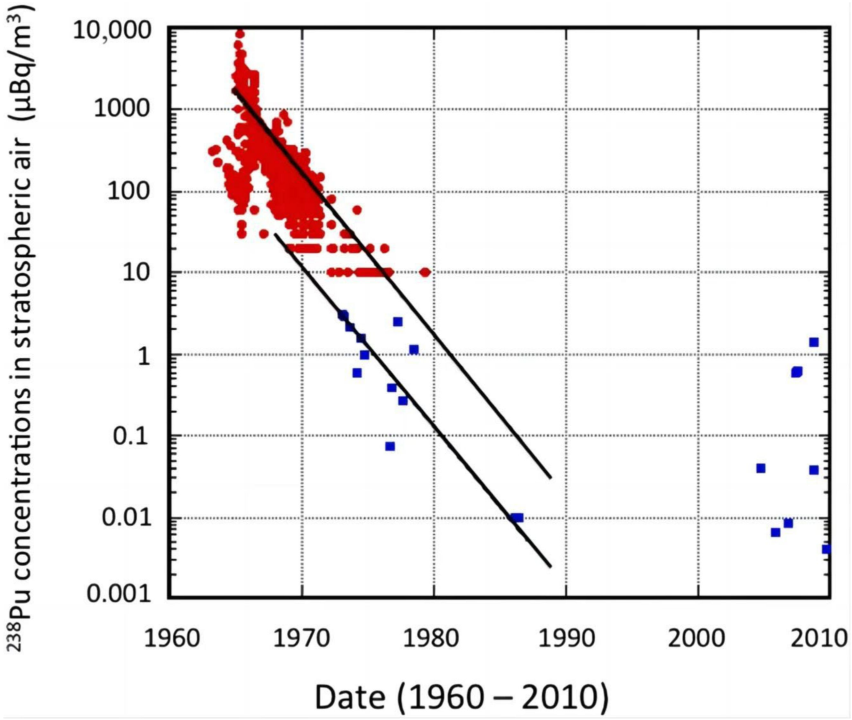

Figure 3. Temporal variations of stratospheric ^{238}Pu concentrations in the Northern Hemisphere. The black line represents the decreasing trend of ^{238}Pu concentration. Closed circles: the upper stratosphere (20–40 km height), closed squares: the lower stratosphere (10.1–14.2 km height). Reprinted with permission from (Katsumi Hirose et al., 2015) [6] Copyright (2015), Springer Nature, UK.

5. Conclusions and Outlook

Different sources of plutonium in the environment have unique "fingerprints", such as isotopic ratios and concentrations, which can be used to trace their sources and investigate regional environmental pollution. Therefore, based on the important role of plutonium in the environment, we summarized the methods for chemical pretreatment, purification, and detection of plutonium isotopes in environmental samples and their applications in recent years. First, pretreatment methods such as ashing, acid digestion, fusion, and co-precipitation for sample pretreatment in the environment were introduced. The advantages and disadvantages of various methods were compared. For the purification of plutonium, liquid-liquid extraction, anion exchange, and extraction chromatography were commonly used methods. The development of plutonium detection methods was then summarized, which focused on the applications, advantages and disadvantages, and detection limits of mass spectrometry methods such as TIMS, AMS, ICP-MS, and SIMS. Finally, the application of plutonium isotopes and their atom and activity ratios in the environment was also summarized.

Due to the unique properties of plutonium, it has been widely used for environmental tracing. In the marine environment, plutonium was applied in environmental behavior research such as water mass movement, particle input, and sedimentary studies. It could also be used in the simulation of pollutants diffusion in the marine environment. In terrestrial environments, ^{137}Cs and plutonium were the most commonly used anthropogenic radionuclides in soil erosion studies. However, due to the relatively short half-life of ^{137}Cs, its application has been limited after decaying for half a century. Its application has been gradually replaced by plutonium isotopes. In other environmental applications, the use of plutonium isotopes is relatively limited, especially in atmospheric particulate matter tracing. It is a new research direction to apply plutonium for the contribution calculation of soil dust sources to atmospheric particulate matter. Furthermore, the establishment of a plutonium database in environmental media is particularly important, as it helps us understand the environmental behavior, migration, and transformation of plutonium and can also provide basic data for nuclear emergency environmental monitoring.

Author Contributions: Conceptualization, X.L. and Y.S.; methodology, Y.S.; validation, X.L., Y.S. and M.W.; investigation, X.L.; resources, M.W. and L.M.; writing—original draft preparation, X.L.; writing—review and editing, Y.S. and M.W.; supervision, G.X. and M.L.; funding acquisition, Y.S. and M.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (Grant/Award Number: 12105311, 12275301) and the Ministry Science and Technology of China (Grant/Award Number: 2022xjkk0300).

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Taylor, D.M. Environmental plutonium—Creation of the universe to twenty-first century mankind. In Proceedings of the 2nd International Symposium on Plutonium in the Environment, Osaka, Japan, 9–12 November 1999; pp. 1–14.
2. Vintró, L.; Mitchell, P.I.; Smith, K.J.; Kershaw, P.J.; Livingston, H.D. Chapter 3 Transuranium nuclides in the world's oceans. *Radioact. Environ.* **2005**, *6*, 79–108.
3. Monty, C. UNSCEAR Report 2000: Sources and Effects of Ionizing Radiation. *J. Radiol. Prot.* **2001**, *21*, 83.
4. Lindahl, P.; Lee, S.H.; Worsfold, P.; Keith-Roach, M. Plutonium isotopes as tracers for ocean processes: A review. *Mar. Environ. Res.* **2010**, *69*, 73–84. [CrossRef]
5. Aarkrog, A. Input of anthropogenic radionuclides into the World Ocean. *Deep. Sea Res. Part II* **2003**, *50*, 2597–2606. [CrossRef]
6. Hirose, K.; Povinec, P.P. Sources of plutonium in the atmosphere and stratosphere-troposphere mixing. *Sci. Rep.* **2015**, *5*, 15707. [CrossRef] [PubMed]
7. Povinec, P.P.; Buesseler, A.A.; Delfanti, K.O.; Hirose, R.; Hong, K.; Ito, G.H.; Livingston, T.; Nies, H.D.; Noshkin, H.; Shima, V.E.; et al. 90Sr, 137Cs and 239,240Pu concentration surface water time series in the Pacific and Indian Oceans—WOMARS results. *J. Environ. Radioact.* **2005**, *81*, 63–87. [CrossRef] [PubMed]
8. Hou, X.L.; Roos, P. Critical comparison of radiometric and mass spectrometric methods for the determination of radionuclides in environmental, biological and nuclear waste samples. *Anal. Chim. Acta* **2008**, *608*, 105–139. [CrossRef]
9. Hattendorf, B.; Gunther, D. Characteristics and capabilities of an ICP-MS with a dynamic reaction cell for dry aerosols and laser ablation. *J. Anal. At. Spectrom.* **2000**, *15*, 1125–1131. [CrossRef]
10. Hou, X.L.; Zhang, W.C.; Wang, Y.Y. Determination of Femtogram-Level Plutonium Isotopes in Environmental and Forensic Samples with High-Level Uranium Using Chemical Separation and ICP-MS/MS Measurement. *Anal. Chem.* **2019**, *91*, 11553–11561. [CrossRef]
11. Wallenius, M.; Mayer, K. Age determination of plutonium material in nuclear forensics by thermal ionisation mass spectrometry. *Fresenius J. Anal. Chem.* **2000**, *366*, 234. [CrossRef]
12. Betti, M.; Tamborini, G.; Koch, L. Use of secondary ion mass spectrometry in nuclear forensic analysis for the characterization of plutonium and highly enriched uranium particles. *Anal. Chem.* **1999**, *71*, 2616–2622. [CrossRef]
13. Portier, S.; Brémier, S.; Walker, C.T. Secondary ion mass spectrometry of irradiated nuclear fuel and cladding: An overview. *Int. J. Mass. Spectrom.* **2007**, *263*, 113–126. [CrossRef]
14. Chamizo, E.; Enamorado, S.M.; Garcia-Leon, M.; Suter, M.; Wacker, L. Plutonium measurements on the 1 MV AMS system at the Centro Nacional de Aceleradores (CNA). *Nucl. Instrum. Methods Phys. Res. B* **2008**, *266*, 4948–4954. [CrossRef]
15. Wang, Z.T.; Yang, G.S.; Zheng, J.; Cao, L.G.; Yu, H.J.; Zhu, Y.; Tagami, K.; Uchida, S. Effect of Ashing Temperature on Accurate Determination of Plutonium in Soil Samples. *Anal. Chem.* **2015**, *87*, 5511–5515. [CrossRef] [PubMed]
16. Kazi, Z.H.; Cornett, J.R.; Zhao, X.L.; Kieser, L. Americium and plutonium separation by extraction chromatography for determination by accelerator mass spectrometry. *Anal. Chim. Acta* **2014**, *829*, 75–80. [CrossRef]
17. Jakopic, R.; Tavcar, P.; Benedik, L. Sequential determination of Pu and Am radioisotopes in environmental samples; a comparison of two separation procedures. *Appl. Radiat. Isot.* **2007**, *65*, 504–511. [CrossRef]
18. Chu, Y.N. Plutonium determination in soil by leaching and ion-exchange separation. *Anal. Chem.* **1971**, *43*, 449–452. [CrossRef]
19. Sill, C.W. Some Problems in Measuring Plutonium in the Environment. *Health Phys.* **1975**, *29*, 619–626. [CrossRef]
20. Lee, S.H.; Gastaud, J.; La Rosa, J.J.; Kwong, L.L.W.; Povinec, P.P.; Wyse, E.; Fifield, L.K.; Hausladen, P.A.; Di Tada, L.M.; Santos, G.M. Analysis of plutonium isotopes in marine samples by radiometric, ICP-MS and AMS techniques. *J. Radioanal. Nucl. Chem.* **2001**, *248*, 757. [CrossRef]
21. Toribio, M.; Garcia, J.F.; Rauret, G.; Pilvio, R.; Bickel, M. Plutonium determination in mineral soils and sediments by a procedure involving microwave digestion and extraction chromatography. *Anal. Chim. Acta* **2001**, *447*, 179–189. [CrossRef]

22. Donard, O.F.X.; Bruneau, F.; Moldovan, M.; Garraud, H.; Epov, V.N.; Boust, D. Multi-isotopic determination of plutonium (Pu-239, Pu-240, Pu-241 and Pu-242) in marine sediments using sector-field inductively coupled plasma mass spectrometry. *Anal. Chim. Acta* **2007**, *587*, 170–179. [CrossRef] [PubMed]
23. Varga, Z.; Suranyi, G.; Vajda, N.; Stefanka, Z. Determination of plutonium and americium in environmental samples by inductively coupled plasma sector field mass spectrometry and alpha spectrometry. *Microchem. J.* **2007**, *85*, 39–45. [CrossRef]
24. Sill, C.W.; Puphal, K.W.; Hindman, F.D. Simultaneous Determination of Alpha-Emitting Nuclides of Radium through Californium in Soil. *Anal. Chem.* **1974**, *46*, 1725–1737. [CrossRef] [PubMed]
25. Xing, S.; Luo, M.Y.; Yuan, N.; Liu, D.Q.; Yang, Y.; Dai, X.X.; Zhang, W.C.; Chen, N. Accurate Determination of Plutonium in Soil by Tandem Quadrupole ICP-MS with Different Sample Preparation Methods. *At. Spectrosc.* **2021**, *42*, 62–70. [CrossRef]
26. Croudace, I.; Warwick, P.; Taylor, R.N.; Dee, S. Rapid procedure for plutonium and uranium determination in soils using a borate fusion followed by ion-exchange and extraction chromatography. *Anal. Chim. Acta* **1998**, *371*, 217–225. [CrossRef]
27. Warwick, P.; Croudace, I.; Oh, J.-S. Radiochemical determination of 241Am and Pu (α) in environmental materials. *Anal. Chem.* **2001**, *73*, 3410–3416. [CrossRef]
28. Luo, M.Y.; Xing, S.; Yang, Y.G.; Song, L.J.; Ma, Y.; Wang, Y.D.; Dai, X.X.; Happel, S. Sequential analyses of actinides in large-size soil and sediment samples with total sample dissolution. *J. Environ. Radioact.* **2018**, *187*, 73–80. [CrossRef]
29. Maxwell, S.L.; Culligan, B.K.; Hutchison, J.B. Rapid fusion method for determination of plutonium isotopes in large rice samples. *J. Radioanal. Nucl. Chem.* **2013**, *298*, 1367–1374. [CrossRef]
30. Maxwell, S.L.; Culligan, B.K.; Jones, V.D.; Nichols, S.T.; Bernard, M.A.; Noyes, G.W. Determination of 237Np and Pu isotopes in large soil samples by inductively coupled plasma mass spectrometry. *Anal. Chim. Acta* **2010**, *682*, 130–136. [CrossRef]
31. Maxwell, S.L.; Culligan, B.K.; Hutchison, J.B.; Spencer, R.B. Rapid fusion method for determination of actinides in fecal samples. *J. Radioanal. Nucl. Chem.* **2013**, *298*, 1533–1542. [CrossRef]
32. Maxwell, S.L.; Culligan, B.; Hutchison, J.B.; Mcalister, D.R. Rapid fusion method for the determination of Pu, Np, and Am in large soil samples. *J. Radioanal. Nucl. Chem.* **2015**, *305*, 599–608. [CrossRef]
33. Hubley, N.; Brown, J.W.N.; Guthrie, J.; Robertson, J.D.; Brockman, J.D. Development of ammonium bifluoride fusion method for rapid dissolution of trinitite samples and analysis by ICP-MS. *J. Radioanal. Nucl. Chem.* **2016**, *307*, 1777–1780. [CrossRef]
34. Hubley, N.T.; Brockman, J.D.; Robertson, J.D. Evaluation of ammonium bifluoride fusion for rapid dissolution in post-detonation nuclear forensic analysis. *Radiochim. Acta* **2017**, *105*, 629–635. [CrossRef]
35. Yang, G.S.; Zheng, J.; Kim, E.; Zhang, S.; Seno, H.; Kowatari, M.; Aono, T.; Kurihara, O. Rapid analysis of Np-237 and Pu isotopes in small volume urine by SF- ICP-MS and ICP-MS/MS. *Anal. Chim. Acta* **2021**, *1158*, 338431. [CrossRef]
36. Wang, H.; Ni, Y.; Zheng, J.; Huang, Z.; Xiao, D.; Aono, T. Low-temperature fusion using NH4HSO4 and NH4HF2 for rapid determination of Pu in soil and sediment samples. *Anal. Chim. Acta* **2019**, *1050*, 71–79. [CrossRef] [PubMed]
37. Michel, H.; Barci-Funel, G.; Dalmasso, J.; Ardisson, G. One step ion exchange process for the radiochemical separation of americium, plutonium and neptunium in sediments. *J. Radioanal. Nucl. Chem.* **1999**, *240*, 467–470. [CrossRef]
38. Zheng, J.; Yamada, M. Precise determination of Pu isotopes in a seawater reference material using ID-SF-ICP-MS combined with two-stage anion-exchange chromatography. *Anal. Sci.* **2007**, *23*, 611–615. [CrossRef]
39. Zoriy, M.V.; Pickhardt, C.; Ostapczuk, P.; Hille, R.; Becker, J.S. Determination of Pu in urine at ultratrace level by sector field inductively coupled plasma mass spectrometry. *Int. J. Mass Spectrom.* **2004**, *232*, 217–224. [CrossRef]
40. Michel, H.; Levent, D.; Barci, V.; Barci-Funel, G.; Hurel, C. Soil and sediment sample analysis for the sequential determination of natural and anthropogenic radionuclides. *Talanta* **2008**, *74*, 1527–1533. [CrossRef]
41. La Rosa, J.J.; Burnett, W.; Lee, S.H.; Levy, I.; Gastaud, J.; Povinec, P.P. Separation of actinides, cesium and strontium from marine samples using extraction chromatography and sorbents. *J. Radioanal. Nucl. Chem.* **2001**, *248*, 765. [CrossRef]
42. La Rosa, J.; Gastaud, J.; Lagan, L.; Lee, S.H.; Levy-Palomo, I.; Povinec, P.P.; Wyse, E. Recent developments in the analysis of transuranics (Np, Pu, Am) in seawater. *J. Radioanal. Nucl. Chem.* **2005**, *263*, 427–436. [CrossRef]
43. Sidhu, R.S. A robust procedure for the determination of plutonium and americium in seawater. *J. Radioanal. Nucl. Chem.* **2003**, *256*, 501–504. [CrossRef]
44. Ageyev, V.A.; Odintsov, O.O.; Sajeniouk, A.D. Routine radiochemical method for the determination of 90 Sr, 238 Pu, 239+240 Pu, 241 Am and 244 Cm in environmental samples. *J. Radioanal. Nucl. Chem.* **2005**, *264*, 337–342.
45. Kimura, T. Simultaneous Determination of Neptunium, Plutonium, Americium and Curium Using Coprecipitation with Bismuth Phosphate. *JJ. Radioanal. Nucl. Chem. Ar.* **1990**, *139*, 297–305. [CrossRef]
46. Varga, Z.; Suranyi, G.; Vajda, N.; Stefanka, Z. Improved sample preparation method for environmental plutonium analysis by ICP-SFMS and alpha-spectrometry. *J. Radioanal. Nucl. Chem.* **2007**, *274*, 87–94. [CrossRef]
47. Varga, Z.; Suranyi, G.; Vajda, N.; Stefanka, Z. Rapid sequential determination of americium and plutonium in sediment and soil samples by ICP-SFMS and alpha-spectrometry. *Radiochim. Acta* **2007**, *95*, 81–87. [CrossRef]
48. Rameback, H.; Skalberg, M. Separation of neptunium, plutonium, americium and curium from uranium with di-(2-ethylhexyl)-phosphoric acid (HDEHP) for radiometric and ICP-MS analysis. *J. Radioanal. Nucl. Chem.* **1998**, *235*, 229–233. [CrossRef]
49. Norisuye, K.; Okamura, K.; Sohrin, Y.; Hasegawa, H.; Nakanishi, T. Large volume preconcentration and purification for determining the Pu-240/Pu-239 isotopic ratio and Pu-238/Pu239+240 alpha-activity ratio in seawater. *J. Radioanal. Nucl. Chem.* **2006**, *267*, 183–193. [CrossRef]

50. Rim, J.H.; Gonzales, E.R.; Armenta, C.E.; Unlu, K.; Peterson, D.S. Developing and evaluating di(2-ethylhexyl) orthophosphoric acid (HDEHP) based polymer ligand film (PLF) for plutonium extraction. *J. Radioanal. Nucl. Chem.* **2013**, *296*, 1099–1103. [CrossRef]
51. Kalmykov, S.N.; Aliev, R.A.; Sapozhnikov, D.Y.; Sapozhnikov, Y.A.; Afinogenov, A.M. Determination of Np-237 by radiochemical neutron activation analysis combined with extraction chromatography. *Appl. Radiat. Isot.* **2004**, *60*, 595–599. [CrossRef]
52. Tonouchi, S.; Habuki, H.; Katoh, K.; Yamazaki, K.; Hashimoto, T. Determination of plutonium by inductively coupled plasma mass spectrometry (ICP-MS). *J. Radioanal. Nucl. Chem.* **2002**, *252*, 367–371. [CrossRef]
53. Momoshima, N.; Kakiuchi, H.; Maeda, Y.; Hirai, E.; Ono, T. Identification of the contamination source of plutonium in environmental samples with isotopic ratios determined by inductively coupled plasma mass spectrometry and alpha-spectrometry. *J. Radioanal. Nucl. Chem.* **1997**, *221*, 213–217. [CrossRef]
54. Qiao, J.X.; Hou, X.L.; Miro, M.; Roos, P. Determination of plutonium isotopes in waters and environmental solids: A review. *Anal. Chim. Acta* **2009**, *652*, 66. [CrossRef] [PubMed]
55. Chen, Q.; Aarkrog, A.; Nielsen, S.P.; Dahlgaard, H.; Nies, H.; Yixua, Y.; Mandrup, K. Determination of plutonium in environmental samples by controlled valence in anion exchange. *J. Radioanal. Nucl. Chem.* **1993**, *172*, 281–288. [CrossRef]
56. Moreno, J.; Vajda, N.; Danesi, P.R.; Larosa, J.J.; Zeiller, E.; Sinojmeri, M. Combined procedure for the determination of90Sr,241Am and Pu radionuclides in soil samples. *J. Radioanal. Nucl. Chem.* **1997**, *226*, 279–284. [CrossRef]
57. Stu¨rup, S.; Henning, D.; Steffen, C.N. High resolution inductively coupled plasma mass spectrometry for the trace determination of plutonium isotopes and isotope ratios in environmental samples. *J. Anal. At. Spectrom.* **1998**, *13*, 1321–1326. [CrossRef]
58. Hrnecek, E.; Steier, P.; Wallner, A. Determination of plutonium in environmental samples by AMS and alpha spectrometry. *Appl. Radiat. Isot.* **2005**, *63*, 633–638. [CrossRef]
59. Huang, Z.; Ni, Y.; Wang, H.; Zheng, J.; Yamazaki, S.; Sakaguchi, A.; Long, X.; Uchida, S. Simultaneous determination of ultra-trace level 237Np and Pu isotopes in soil and sediment samples by SF-ICP-MS with a single column chromatographic separation. *Microchem. J.* **2019**, *148*, 597–604. [CrossRef]
60. Wang, Z.L.; Yamada, M. Plutonium activities and Pu-240/Pu-239 atom ratios in sediment cores from the East China Sea and Okinawa Trough: Sources and inventories. *Earth Planet. Sci. Lett.* **2005**, *233*, 441–453. [CrossRef]
61. Nunnemann, M.; Erdmann, N.; Hasse, H.U.; Huber, G.; Kratz, J.V.; Kunz, P.; Mansel, A.; Passler, G.; Stetzer, O.; Trautmann, N.; et al. Trace analysis of plutonium in environmental samples by resonance ionization mass spectroscopy (RIMS). *J. Alloys Compd.* **1998**, *271*, 45–48. [CrossRef]
62. Ketterer, M.E.; Hafer, K.M.; Mietelski, J.W. Resolving Chernobyl vs. global fallout contributions in soils from Poland using Plutonium atom ratios measured by inductively coupled plasma mass spectrometry. *J. Environ. Radioact.* **2004**, *73*, 183–201. [CrossRef] [PubMed]
63. Kaye, J.H.; Strebin, R.S.; Orr, R.D. Rapid, Quantitative-Analysis of Americium, Curium and Plutonium Isotopes in Hanford Samples Using Extraction Chromatography and Precipitation Plating. *J. Radioanal. Nucl. Chem.* **1995**, *194*, 191–196. [CrossRef]
64. Kuwabara, J.; Noguchi, H. Development of rapid bioassay method for plutonium. *J. Radioanal. Nucl. Chem.* **2002**, *252*, 273–276. [CrossRef]
65. Lopez-Lora, M.; Levy, I.; Chamizo, E. Simple and fast method for the analysis of (236)U, (237)Np, (239)Pu and (240)Pu from seawater samples by Accelerator Mass Spectrometry. *Talanta* **2019**, *200*, 22–30. [CrossRef]
66. Wang, Z.T.; Xie, Y.; Lin, J.X.; Li, Z.J.; Tan, Z.Y. Rapid method for sequential determination of Pu and Am in soil and sediment samples by sector-field inductively coupled plasma mass spectrometry. *J. Radioanal. Nucl. Chem.* **2021**, *328*, 137–147. [CrossRef]
67. Zapata-Garcia, D.; Wershofen, H.; Seferinoglu, M.; Dirican, A.; Aslan, N.; Ozcayan, G.; Yucel, U. Comparison of two methods for the rapid radiochemical analysis of air dust samples in emergency situations. *Appl. Radiat. Isot.* **2019**, *150*, 120–126. [CrossRef]
68. Luo, M.Y.; Liu, D.Q.; Yang, Y.; Dai, X.X.; Wu, Y.; Shi, K.L. Simultaneous determination of actinides and Sr-90 in large-size soil and sediment samples. *J. Environ. Radioact.* **2022**, *247*, 106854. [CrossRef]
69. Rozhkova, A.K.; Kuzmenkova, N.V.; Sibirtsev, A.M.; Petrov, V.G.; Shi, K.L.; Hou, X.L.; Kalmykov, S.N. Simultaneous separation of actinides and technetium from large volumes of natural water for their determination. *J. Radioanal. Nucl. Chem.* **2022**, *331*, 2037–2044. [CrossRef]
70. Metzger, S.C.; Ticknor, B.W.; Rogers, K.T.; Bostick, D.A.; McBay, E.H.; Hexel, C.R. Automated Separation of Uranium and Plutonium from Environmental Swipe Samples for Multiple Collector Inductively Coupled Plasma Mass Spectrometry. *Anal. Chem.* **2018**, *90*, 9441–9448. [CrossRef]
71. Shibahara, Y.; Kubota, T.; Fujii, T.; Fukutani, S.; Takamiya, K.; Konno, M.; Mizuno, S.; Yamana, H. Determination of isotopic ratios of plutonium and uranium in soil samples by thermal ionization mass spectrometry. *J. Radioanal. Nucl. Chem.* **2016**, *307*, 2281–2287. [CrossRef]
72. Habibi, A.; Boulet, B.; Gleizes, M.; Lariviere, D.; Cote, G. Rapid determination of actinides and (90)Sr in river water. *Anal. Chim. Acta* **2015**, *883*, 109–116. [CrossRef] [PubMed]
73. Dulanská, S.; Bilohuščin, J.; Remenec, B.; Galanda, D.; Mátel, L.u. Determination of 239Pu, 241Am and 90Sr in urine using pre-filter material and combined sorbents AnaLig® Pu-02, AnaLig® Sr-01, DGA® Resin. *J. Radioanal. Nucl. Chem.* **2015**, *304*, 127–132. [CrossRef]
74. Dai, X.; Kramer-Tremblay, S. Five-column chromatography separation for simultaneous determination of hard-to-detect radionuclides in water and swipe samples. *Anal. Chem.* **2014**, *86*, 5441–5447. [CrossRef] [PubMed]

75. Rollin, S.; Corcho-Alvarado, J.A.; Sahli, H.; Putyrskaya, V.; Klemt, E. High-resolution records of cesium, plutonium, americium, and uranium isotopes in sediment cores from Swiss lakes. *Environ. Sci. Pollut. R* **2022**, *29*, 85777–85788. [CrossRef] [PubMed]
76. Aggarwal, S.K.; Saxena, M.K.; Jain, H.C. Determination of Plutonium by Alpha Spectrometry. *J. Radioanal. Nucl. Chem.* **1992**, *156*, 111–118. [CrossRef]
77. Zhang, H.-T.; Zhu, F.R.; Xu, J.; Dai, Y.H.; Li, D.M.; Yi, X.W.; Zhang, L.X.; Zhao, Y.G. Age determination of plutonium material by alpha spectrometry and thermal ionization mass spectrometry. *Radiochim. Acta* **2008**, *96*, 327–331. [CrossRef]
78. Maassen, J.; Inglis, J.D.; Wende, A.; Kayzar-Boggs, T.M.; Steiner, R.E.; Kara, A. Analysis of sub-picogram quantities of 238Pu by thermal ionization mass spectrometry. *J. Radioanal. Nucl. Chem.* **2019**, *321*, 1073–1080. [CrossRef]
79. Burger, S.; Riciputi, L.R.; Bostick, D.A.; Turgeon, S.; McBay, E.H.; Lavelle, M. Isotope ratio analysis of actinides, fission products, and geolocators by high-efficiency multi-collector thermal ionization mass spectrometry. *Int. J. Mass Spectrom.* **2009**, *286*, 70–82. [CrossRef]
80. Jakopic, R.; Richter, S.; Kuhn, H.; Benedik, L.; Pihlar, B.; Aregbe, Y. Isotope ratio measurements of pg-size plutonium samples using TIMS in combination with "multiple ion counting" and filament carburization. *Int. J. Mass Spectrom.* **2009**, *279*, 87–92. [CrossRef]
81. Lee, C.G.; Suzuki, D.; Esaka, F.; Magara, M.; Song, K. Ultra-trace analysis of plutonium by thermal ionization mass spectrometry with a continuous heating technique without chemical separation. *Talanta* **2015**, *141*, 92–96. [CrossRef]
82. Chamizo, E.; Christl, M.; Fifield, L.K. Measurement of U-236 on the 1 MV AMS system at the Centro Nacional de Aceleradores (CNA). *Nucl. Instrum. Methods Phys. Res. Sect. B* **2015**, *358*, 45–51. [CrossRef]
83. Brown, T.A.; Marchetti, A.A.; Martinelli, R.E.; Cox, C.C.; Knezovich, J.P.; Hamilton, T.F. Actinide measurements by accelerator mass spectrometry at Lawrence Livermore National Laboratory. *Nucl. Instrum. Meth. Phys. Res. B* **2004**, *223*, 788–795. [CrossRef]
84. Winkler, S.; Ahmad, I.; Golser, R.; Kutschera, W.; Orlandini, K.A.; Paul, M.; Priller, A.; Steier, P.; Valenta, A.; Vockenhuber, C. Developing a detection method of environmental Pu-244. *Nucl. Instrum. Meth. Phys. Res. B* **2004**, *223*, 817–822. [CrossRef]
85. Pacesila, D.; Bishop, S.; Stanciu, I.; Enachescu, M.; Petre, A.R.; Virgolici, M.; Iancu, D.; Tugulan, L.; Done, L.; Petraglia, A.; et al. Ultrasensitive detection of Pu-244 in environmental samples by accelerator mass spectrometry. *J. Anal. At. Spectrom.* **2022**, *37*, 2581–2588. [CrossRef]
86. Wacker, L.; Chamizo, E.; Fifield, L.K.; Stocker, M.; Suter, A.; Synal, H.A. Measurement of actinides on a compact AMS system working at 300 kV. *Nucl. Instrum. Meth. Phys. Res. B* **2005**, *240*, 452–457. [CrossRef]
87. Kierepko, R.; Mietelski, J.W.; Ustrnul, Z.; Anczkiewicz, R.; Wershofen, H.; Holgye, Z.; Kapala, J.; Isajenko, K. Plutonium isotopes in the atmosphere of Central Europe: Isotopic composition and time evolution vs. circulation factors. *Sci. Total Environ.* **2016**, *569*, 937–947. [CrossRef] [PubMed]
88. Bisinger, T.; Hippler, S.; Michel, R.; Wacker, L.; Synal, H.A. Determination of plutonium from different sources in environmental samples using alpha-spectrometry and AMS. *Nucl. Instrum. Methods Phys. Res. Sect. B* **2010**, *268*, 1269–1272. [CrossRef]
89. Kim, C.S.; Kim, C.K.; Lee, J.I.; Lee, K.J. Rapid determination of Pu isotopes and atom ratios in small amounts of environmental samples by an on-line sample pre-treatment system and isotope dilution high resolution inductively coupled plasma mass spectrometry. *J. Anal. At. Spectrom.* **2000**, *15*, 247–255. [CrossRef]
90. Salminen-Paatero, S.; Nygren, U.; Paatero, J. Pu-240/Pu-239 mass ratio in environmental samples in Finland. *J. Environ. Radioact.* **2012**, *113*, 163–170. [CrossRef]
91. Ni, Y.Y.; Zheng, J.; Guo, Q.J.; Men, W.; Tagami, K.; Uchida, S. Rapid determination of ultra-trace plutonium isotopes (Pu-239, Pu-240 and Pu-241) in small-volume human urine bioassay using sector-field inductively coupled plasma mass spectrometry. *Anal. Chim. Acta* **2018**, *1000*, 85–92. [CrossRef]
92. Shi, Y.; Collins, R.; Broome, C. Determination of uranium, thorium and plutonium isotopes by ICP-MS. *J. Radioanal. Nucl. Chem.* **2013**, *296*, 509–515. [CrossRef]
93. Bu, W.T.; Gu, M.; Ding, X.T.; Ni, Y.Y.; Shao, X.P.; Liu, X.M.; Yang, C.T.; Hu, S. Exploring the ability of triple quadrupole inductively coupled plasma mass spectrometry for the determination of Pu isotopes in environmental samples. *J. Anal. At. Spectrom.* **2021**, *36*, 2330–2337. [CrossRef]
94. Gao, R.Q.; Hou, X.L.; Zhang, L.Y.; Zhang, W.C.; Zhang, M.T. Determination of Ultra-Low Level Plutonium Isotopes in Large Volume Environmental Water Samples. *Chin. J. Anal. Chem.* **2020**, *48*, 765–773. [CrossRef]
95. Zhang, W.C.; Lin, J.F.; Fang, S.; Li, C.; Yi, X.W.; Hou, X.L.; Chen, N.; Zhang, H.T.; Xu, Y.H.; Dang, H.J.; et al. Determination of ultra-trace level plutonium isotopes in soil samples by triple-quadrupole inductively coupled plasma-mass spectrometry with mass-shift mode combined with UTEVA chromatographic separation. *Talanta* **2021**, *234*, 122652. [CrossRef] [PubMed]
96. Matsueda, M.; Kawakami, T.; Koarai, K.; Terashima, M.; Fujiwara, K.; Iijima, K.; Furukawa, M.; Takagai, Y. Using CO2 Reactions to Achieve Mass-spectrometric Discrimination in Simultaneous Plutonium-isotope Speciation with Inductively Coupled Plasma-Tandem Mass Spectrometry. *Chem. Lett.* **2022**, *51*, 678–682. [CrossRef]
97. Xing, S.; Zhang, W.; Qiao, J.; Hou, X. Determination of ultra-low level plutonium isotopes (Pu-239,(240)pu) in environmental samples with high uranium. *Talanta* **2018**, *187*, 357–364. [CrossRef] [PubMed]
98. Santos, M.; Marcalo, J.; de Matos, A.P.; Gibson, J.K.; Haire, R.G. Gas-phase oxidation reactions of neptunium and plutonium ions investigated via Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *J. Phys. Chem. A* **2002**, *106*, 7190–7194. [CrossRef]

99. Tanner, S.D.; Li, C.S.; Vais, V.; Baranov, V.I.; Bandura, D.R. Chemical resolution of Pu(+) from U(+) and Am(+) using a band-pass reaction cell inductively coupled plasma mass spectrometer. *Anal. Chem.* **2004**, *76*, 3042–3048. [CrossRef]
100. Gourgiotis, A.; Granet, M.; Isnard, H.; Nonell, A.; Gautier, C.; Stadelmann, G.; Aubert, M.; Durand, D.; Legand, S.; Chartier, F. Simultaneous uranium/plutonium separation and direct isotope ratio measurements by using CO_2 as the gas in a collision/reaction cell based MC-ICPMS. *J. Anal. At. Spectrom.* **2010**, *25*, 1939–1945. [CrossRef]
101. Xu, Y.H.; Li, C.; Yu, H.P.; Fang, F.M.; Hou, X.L.; Zhang, C.; Li, X.F.; Xing, S. Rapid determination of plutonium isotopes in small samples using single anion exchange separation and ICP-MS/MS measurement in NH3-He mode for sediment dating. *Talanta* **2022**, *240*, 123152. [CrossRef]
102. Boulyga, S.F.; Tibi, M.; Heumann, K.G. Application of isotope-dilution laser ablation ICP-MS for direct determination of Pu concentrations in soils at pg g^{-1} levels. *Anal. Bioanal. Chem.* **2004**, *378*, 342–347. [PubMed]
103. Wallenius, M.; Lutzenkirchen, K.; Mayer, K.; Ray, I.; Heras, L.A.I.D.L.; Betti, M.; Cromboom, O.; Hild, M.; Lynch, B.; Nicholl, A.; et al. Nuclear forensic investigations with a focus on plutonium. *J. Alloy Compd.* **2007**, *444*, 57–62. [CrossRef]
104. Tamborini, G.; Betti, M. Characterisation of radioactive particles by SIMS. *Microchim. Acta* **2000**, *132*, 411–417. [CrossRef]
105. Efurd, D.W.; Steiner, R.E.; Roensch, F.R.; Glover, S.E.; Musgrave, J.A. Determination of the Pu-240/Pu-239 atom ratio in global fallout at two locations in the Northern Hemisphere. *J. Radioanal. Nucl. Chem.* **2005**, *263*, 387–391. [CrossRef]
106. Kim, C.S.; Kim, C.K.; Martin, P.; Sansone, U. Determination of Pu isotope concentrations and isotope ratio by inductively coupled plasma mass spectrometry: A review of analytical methodology. *J. Anal. Atom Spectrom.* **2007**, *22*, 827–841. [CrossRef]
107. Truscott, J.B.; Jones, P.; Fairman, B.E.; Evans, E.H. Determination of actinide elements at femtogram per gram levels in environmental samples by on-line solid phase extraction and sector-field-inductively coupled plasma-mass spectrometry. *Anal. Chim. Acta* **2001**, *433*, 245–253. [CrossRef]
108. Yamamoto, M.; Yamauchi, Y.; Chatani, K.; Igarashi, S.; Komura, K.; Ueno, K.; Sakanoue, M. Distribution of Global Fallout 237np, Pu Isotopes, and 241am in Lake and Sea Sediments. *J. Radioanal. Nucl. Chem.* **1991**, *147*, 165–176. [CrossRef]
109. Livingston, H.D.; Schneider, D.L.; Bowen, V.T. 241Pu in the marine environment by a radiochemical procedure. *Earth Planet. Sci. Lett.* **1975**, *25*, 361–367. [CrossRef]
110. Holm, E.; Rioseco, J.; Pettersson, H. Fallout of Transuranium Elements Following the Chernobyl Accident. *J. Radioanal. Nucl. Chem.* **1992**, *156*, 183. [CrossRef]
111. Kelley, J.M.; Bond, L.A.; Beasley, T.M. Global distribution of Pu isotopes and Np-237. *Sci. Total Environ.* **1999**, *238*, 483–500. [CrossRef]
112. Hisamatsu, S.I.; Sakanoue, M. Determination of Transuranium Elements in a So-called "Bikini Ash" Sample and in Marine Sediment Samples Collected Near Bikini Atoll. *Health Phys.* **1978**, *35*, 301–307. [CrossRef] [PubMed]
113. Koide, M.; Bertine, K.K.; Chow, T.J.; Goldberg, E.D. The 240Pu/239Pu ratio, a potential geochronometer. *Earth Planet. Sci. Lett.* **1985**, *72*, 1–8. [CrossRef]
114. Muramatsu, Y.; Hamilton, T.; Uchida, S.; Tagami, K.; Yoshida, S.; Robison, W. Measurement of 240Pu/239Pu isotopic ratios in soils from the Marshall Islands using ICP-MS. *Sci. Total Environ.* **2001**, *278*, 151–159. [CrossRef] [PubMed]
115. Lujaniene, G.; Aninkevicius, V.; Lujanas, V. Artificial radionuclides in the atmosphere over Lithuania. *J. Environ. Radioactiv.* **2009**, *100*, 108–119. [CrossRef] [PubMed]
116. Zheng, J.; Tagami, K.; Watanabe, Y.; Uchida, S.; Aono, T.; Ishii, N.; Yoshida, S.; Kubota, Y.; Fuma, S.; Ihara, S. Isotopic evidence of plutonium release into the environment from the Fukushima DNPP accident. *Sci. Rep.* **2012**, *2*, 304. [CrossRef] [PubMed]
117. Kim, S.H.; Lee, S.H.; Lee, H.M.; Hong, G.H. Distribution of 239,240Pu in marine products from the seas around the Korean Peninsula after the Fukushima nuclear power plant accident. *J. Environ. Radioact.* **2020**, *217*, 106191. [CrossRef] [PubMed]
118. Johansen, M.P.; Anderson, D.; Child, D.; Hotchkis, M.A.C.; Tsukada, H.; Okuda, K.; Hinton, T.G. Differentiating Fukushima and Nagasaki plutonium from global fallout using Pu-241/Pu-239 atom ratios: Pu vs. Cs uptake and dose to biota. *Sci. Total Environ.* **2021**, *754*, 141890. [CrossRef]
119. Yamada, M.; Oikawa, S.; Shirotani, Y.; Kusakabe, M.; Shindo, K. Transuranic nuclides Pu, Am and Cm isotopes, and Sr-90 in seafloor sediments off the Fukushima Daiichi Nuclear Power Plant during the period from 2012 to 2019. *J. Environ. Radioact.* **2021**, *227*, 106459. [CrossRef]
120. Masson, O.; Piga, D.; Gurriaran, R.; D'Amico, D. Impact of an exceptional Saharan dust outbreak in France: PM10 and artificial radionuclides concentrations in air and in dust deposit. *Atmos. Environ.* **2010**, *44*, 2478–2486. [CrossRef]
121. Muramatsu, Y.; Ruhm, W.; Yoshida, S.; Tagami, K.; Uchida, S.; Wirth, E. Concentrations of Pu-239 and Pu-240 and their isotopic ratios determined by ICP-MS in soils collected from the Chernobyl 30-km zone. *Environ. Sci. Technol.* **2000**, *34*, 2913–2917. [CrossRef]
122. Lindahl, P.; Roos, P.; Eriksson, M.; Holm, E. Distribution of Np and Pu in Swedish lichen samples (*Cladonia stellaris*) contaminated by atmospheric fallout. *J. Environ. Radioact.* **2004**, *73*, 73–85. [CrossRef] [PubMed]
123. Zheng, J.; Tagami, K.; Uchida, S. Release of Plutonium Isotopes into the Environment from the Fukushima Daiichi Nuclear Power Plant Accident: What Is Known and What Needs to Be Known. *Environ. Sci. Technol.* **2013**, *47*, 9584–9595. [CrossRef] [PubMed]
124. Imanaka, T.; Endo, S.; Sugai, M.; Ozawa, S.; Shizuma, K.; Yamamoto, M. Early radiation survey of Iitate village, which was heavily contaminated by the Fukushima Daiichi accident, conducted on 28 and 29 March 2011. *Health Phys.* **2012**, *102*, 680–686. [CrossRef] [PubMed]

125. Shinonaga, T.; Steier, P.; Lagos, M.; Ohkura, T. Airborne Plutonium and non-natural Uranium from the Fukushima DNPP found at 120 km distance a few days after reactor hydrogen explosions. *Environ. Sci. Technol.* **2014**, *48*, 3808–3814. [CrossRef] [PubMed]
126. Kim, C.K.; Byun, J.I.; Chae, J.S.; Choi, H.Y.; Choi, S.W.; Kim, D.J.; Kim, Y.J.; Lee, D.M.; Park, W.J.; Yim, S.A.; et al. Radiological impact in Korea following the Fukushima nuclear accident. *J. Environ. Radioact.* **2012**, *111*, 70–82. [CrossRef] [PubMed]
127. Hao, Y.P.; Xu, Y.H.; Pan, S.M.; Song, X.W.; Zhang, K.X.; Guo, H.T.; Gu, Z. Sources of plutonium isotopes and Cs-137 in coastal seawaters of Liaodong Bay and Bohai Strait, China and its environmental implications. *Mar. Pollut. Bull.* **2018**, *130*, 240–248. [CrossRef]
128. Wang, R.R.; Lei, L.; Li, G.; Liu, Z.Y. Identification of the Distribution and Sources of Pu in the Northern South China Sea: Influences of Provenance and Scavenging. *ACS Earth Space Chem.* **2019**, *3*, 2684–2694. [CrossRef]
129. Zhuang, Q.; Li, G.; Wang, F.; Tian, L.; Jiang, X.; Zhang, K.; Liu, G.; Pan, S.; Liu, Z. 137Cs and 239+ 240Pu in the Bohai Sea of China: Comparison in distribution and source identification between the inner bay and the tidal flat. *Mar. Pollut. Bull.* **2019**, *138*, 604–617. [CrossRef]
130. Wang, J.; Du, J.; Zheng, J.; Bi, Q.; Ke, Y.; Qu, J. Plutonium in Southern Yellow Sea sediments and its implications for the quantification of oceanic-derived mercury and zinc. *Environ. Pollut.* **2020**, *266*, 115262. [CrossRef]
131. Zhang, R.; Wang, R.; Liu, Z.; Zhang, F.; Li, T.; Guan, M.; Han, Q. Distribution and transport of plutonium in the sediments of the Yangtze River estuary and the adjacent East China Sea. *Appl. Geochem.* **2020**, *115*, 104532. [CrossRef]
132. Wang, J.L.; Du, J.Z.; Qu, J.G.; Bi, Q.Q. Distribution of Pu isotopes and Pb-210 in the Bohai Sea and Yellow Sea: Implications for provenance and transportation. *Chemosphere* **2021**, *263*, 127896. [CrossRef] [PubMed]
133. Wang, R.R.; Zhu, Y.W.; Hu, F.F.; Xu, X.Y.; Sun, Z.Y.; Liu, Z.Y. Distribution and source identification of Pu in the tidal flat wetlands of northern Jiangsu Province and radial sand ridge of southern Yellow Sea-An explanation of "land-sea interaction". *Catena* **2021**, *206*, 105506. [CrossRef]
134. Wang, R.; Fu, Y.; Lei, L.; Li, G.; Liu, Z.J.A.o. Distribution and source identification of Pu in river basins in southern China. *ACS Omega* **2019**, *4*, 22646–22656. [CrossRef]
135. Huang, Y.A.; Sun, X.M.; Zhang, W. Spatio-temporal distribution of Pu239+240 in sediments of the China sea and adjacent waters. *J. Environ. Radioactiv.* **2022**, *253*, 107010. [CrossRef] [PubMed]
136. Wu, J.; Sun, J.; Xiao, X. An overview of current knowledge concerning the inventory and sources of plutonium in the China Seas. *Mar. Pollut. Bull.* **2020**, *150*, 110599. [CrossRef] [PubMed]
137. Hirose, K.; Aoyama, M.; Katsuragi, Y.; Sugimura, Y. Annual Deposition of Sr-90, Cs-137 and Pu-239, 240 from the 1961–1980 Nuclear Explosions: A Simple Model. *J. Meteorol. Soc. Jpn.* **2007**, *65*, 259–277. [CrossRef]
138. Lujanienė, G.; Valiulis, D.; Byčenkienė, S.; Šakalys, J.; Povinec, P.P. Plutonium isotopes and 241Am in the atmosphere of Lithuania: A comparison of different source terms. *Atmos. Environ.* **2012**, *61*, 419–427. [CrossRef]
139. Chamizo, E.; García-León, M.; Enamorado, S.M.; Jiménez-Ramos, M.C.; Wacker, L. Measurement of plutonium isotopes, ^{239}Pu and 240Pu, in air-filter samples from Seville (2001–2002). *Atmos. Environ.* **2010**, *44*, 1851–1858. [CrossRef]
140. Choi, M.S.; Lee, D.S.; Choi, J.C.; Cha, H.J.; Yi, H.I. $^{239+240}$Pu concentration and isotope ratio (^{240}Pu/^{239}Pu) in aerosols during high dust (Yellow Sand) period, Korea. *Sci. Total Environ.* **2006**, *370*, 262–270. [CrossRef]