

On the use of MnO₂ cartridges for the plutonium determination in seawater

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Abstract

To analyze plutonium (Pu) in open ocean waters can be challenging due to the low seawater concentrations. In this study we compared two techniques for Pu determination, one in-situ MnO₂ cartridge system and the more commonly used MnO₂ precipitation technique. During the pre-pilot GEOTRACES cruise ANT XXX-1 (2005) we tested MnO₂ cartridges for the pre-concentration of Pu from seawater at 19 sampling stations on a transect in the southeastern Atlantic Ocean between Vigo (Spain) and Cape Town (South Africa). Our in-situ sampling setup consisted of one particle cartridge followed by three MnO₂ cartridges in a series. Through the system we pumped between 956 - 2700 l of surface seawater with a flow rate between 1.6-5.2 l/min. We found that the adsorption efficiency of a single MnO₂ cartridge to adsorb Pu was rather constant and on average a 58 ± 7 %. The adsorption efficiency was also found to be independent of seawater: temperature in the range of 18.3-29.2 °C, salinity range 34.2 – 37.1 ‰, and conductivity in the range of 46.8 -58.4 mS/cm. In parallel with the in-situ sampling, discrete surface water samples between 259-281 l were taken and Pu was pre-concentrated using the MnO₂ precipitation method. We find a good agreement between the Pu concentrations determined with the two different techniques. The in-situ pre-concentration technique requires more radiochemical work in the laboratory but has the advantage that large seawater volumes

can be sampled without the necessity for radiochemical processing on-board the ship. The much larger volumes sampled with the in-situ technique compared with the precipitation technique, enables accurate determination of Pu-isotopic ratios with a low relative standard deviation. We have shown in this study that in-situ MnO₂ cartridge technique can be used in a reliable way for the determination of dissolved Pu seawater concentration in open ocean waters.

Keywords: *plutonium, in situ, MnO₂ cartridge system, MnO₂ precipitation, seawater, GEOTRACES*

1. Introduction

The interest of studying plutonium in the marine environment to day is mainly because the potential wide use of Pu as tracer in oceanographic and marine geochemistry processes. First studies focused on the radiological consequences of the long-lived radionuclide released to the marine environment. However, it has been shown that in case of local high environmental level Pu contamination the resulting radiation dose to humans are insignificant or very low (Strand et al., 1998). Plutonium is included as a tracer in the GEOTRACES program, which is an international study aiming to improve our understanding of the biogeochemical cycles and the processes controlling the large-scale distribution of trace elements and their isotopes in the marine environment (GEOTRACES, 2018). The advantages of using Pu as a marine tracer is that the input functions are well described (both in time and the spatial distribution). In addition, the nuclear fingerprint (i.e. the Pu isotopic composition) can be used to estimate Pu contributions from different sources, e.g. fallout from the nuclear atmospheric test programs, effluents from reprocessing plants, accidental releases like the Chernobyl, Fukushima, Thule and Palomares, and the satellite reentry of SNAP 9A. From the global nuclear test fallout, which is that major contributor of Pu released to the environment, about 6.5 PBq (or ~2800 kg) of ²³⁹Pu has entered the oceans (Aarkrog, 2003, Hamilton, 2005). In the open ocean, Pu in its +IV oxidation state is rapidly scavenged into deeper water masses. Typical Pu water-column profiles show relatively low surface concentrations and a sub-surface maximum between 500-1500 meters water depth. The sub-surface maximum has been attributed to biogeochemical processes re-mineralizing sinking particle and elements bound to them (León Vitró et al., 2005, Hirose et al., 2011, Gastaud et al., 2011). Assuming that all the released Pu has accumulated uniformly in water depths down to 1500 m, that would result in a global mean seawater concentration in this layer to be ~ 9 µBq/l ($4 \cdot 10^{-18}$ kg/l or 0.016 fmol/l) of ²³⁹Pu. This is equal to a concentration of about 10 million atoms of ²³⁹Pu per liter of seawater. This low

concentration is among the lowest compared to all other elements, means that Pu is one of the less abundant elements in the oceans. Plutonium can be expected to be associated with several different carriers/complexes as Pu can be present in multiple oxidation state in natural waters. However, some studies have shown that the dissolved Pu is dominantly in its higher oxidation states (V, VI) in open ocean surface waters (Lindahl et al., 2010, Choppin, 2006, Choppin and Kobachi, 1990), i.e. Pu in its most soluble state.

The low concentrations in seawater is often the limitation of using Pu as a tracer as its detection requires large water volumes to get a measurable amount of decays or atoms. The most common technique for pre-concentration of Pu from seawater is co-precipitation. Typically water volumes from a few liters up to 300 liters are sampled with this technique. Pu can be co-precipitated with a mix of calcium and magnesium hydroxide precipitate (Ballestra et al., 1978, Holm et al., 1987) or with ferrous hydroxide (Wong, 1971, 14. Qingjiang et al., 2001), ferric hydroxide (Holm and Fukai, 1976, Martin and Thomas, 1990), calcium oxalate (Ristic et al., 2002), bismuth phosphate (Pillai, 1975), neodymium or lanthanum fluoride (Fukai et al., 1987) and manganese dioxide (Wong et al, 1978, La Rosa et al., 2001). Such co-precipitation of Pu onboard a moving vessel can be a difficult task due to the large water volumes (typically in the order of several hundred liters of seawater) and the amount of hazardous chemicals handled. Alternative, *in-situ* pre-concentration methods for Pu determination in seawater have been tested with various results, e.g. *in-situ* Pu adsorption techniques using MnO₂ cartridge (Mann et al. 1984, Livingston and Cochran, 1987) and Al₂O₃ sorption bed (Mitchell et al., 1995). The advantages of using in-situ pre-concentration are that it requires less handling and chemical onboard the ship and that large water volumes can be sampled (several cubic meters of water) enabling accurate activity determination in low level contaminated waters like the south Atlantic.

In order to test the reliability of the *in-situ* MnO₂ cartridge system we have compared this technique with the more commonly used MnO₂ co-precipitation technique. These tests were performed using surface seawater sampled on an ocean transect in the Southeast Atlantic, an area known to have ultralow Pu concentration (Gastaud et al., 2011). The transect passed different water masses, upwelling areas off the West Africa, areas influenced by Saharan dust input and the oligotrophic Angola basin. This water masses have different physical and chemical properties as temperature, salinity, conductivity and suspended particle load that might alter the absorption properties of the MnO₂ cartridge.

2. Material and Methods

The MnO₂ cartridge technique was tested on a pre-GEOTRACES cruise ANT XXX-1 (Rutgers van der Loeff, 2007) in the Southeast Atlantic between Vigo (Spain) and Cape Town (South Africa). On this transect, 19 stations were sampled (Figure 1) with the MnO₂ cartridge system (three MnO₂ cartridges in a series), by passing between 956-2700 l (mean = 1450 l) surface water at a flow rate between 1.6 – 5.2 l/min (mean = 2.7 l/min) through the system. In Table 1. the sampling information can be found. The sampling was conducted during ship transport and on average one station covered a distance of ~200 km. The Pu activity concentrations gained from the cartridge system would then represent the average Pu concentration during the sampling station. For all stations, additional discrete surface water samples between 259-281 l were taken and Pu was pre-concentrated using the MnO₂ precipitation method (Table 2). These samples were taken about halfway into the station, not necessarily representing the average Pu activity concentrations calculated from the cartridge system. As we didn't anticipate large variations in Pu concentration, these results were used to evaluate the total efficiency and performance of the MnO₂ cartridge system.

All chemicals used in this study were of pro analysis grade or higher. Solutions, unless otherwise noted, were prepared before analyses and stored in clean polyethylene bottles at room temperature covered from excess light. We used between 8 and 32 mBq of a certified ²⁴²Pu standard, traceable to National Physics Laboratory (NPL) UK, as chemical yield determinant in our radiochemical analysis. The impurity levels of the ²³⁸Pu, ²³⁹Pu and ²⁴⁰Pu were less than $4.3 \cdot 10^{-5}$ Bq per Bq of ²⁴²Pu in the tracer solution.

The MnO₂ impregnated cartridges were obtained from Woods Hole Oceanographic Institution (Massachusetts, USA). Details on the impregnation method can be found elsewhere (Buesseler et al., 1992, Hartman and Buesseler, 1994). Briefly, 25 cm long thermally bonded 1.0 μm pore size HYTREX II polypropylene filter cartridges (Osmonics Inc, Minnetonka, MN, USA) were wetted by flushing in a 5 ml/l Decon detergent solution. After thorough rinsing with distilled water the cartridges were directly immersed in a 45 °C saturated KMnO₄ bath for 24 hours to produce the MnO₂ impregnation. Cartridges were rinsed with deionized water, dripped dried and sealed in individual plastic zip lock bags to maintain the moisture.

2.1. Sample collection and pre-concentration methods

In Figure 2 the two different methods for Pu collection in seawater are outlined, i.e. the *in-situ* sorption of Pu on MnO₂ cartridges and the MnO₂ co-precipitation technique. Below follows a brief description of the methods used and we refer to the work of La Rosa *et al.*, 2001, for a more detailed description.

2.1.1. Plutonium pre-concentration by adsorption on MnO₂ impregnated cartridges

The cartridge filtration system used on-board Research Vessel Polarstern was composed of four polypropylene cartridge housing units (CUNO Inc, Meriden, CT, USA) and a flow meter connected in series with tubing as shown in Figure 3. In the first cartridge housing a pre-filter (Micro Wynd II, CUNO Inc, Meriden, CT, USA) was mounted with a pore size of 1.0 µm in order to remove particulate matter from the seawater. In the following three housings half-length (12.5 cm) MnO₂ cartridges were placed. The filtration system was attached to “Klaus”-membrane pump (Klaus Union, Germany) and approximately 1500 l of surface seawater was pumped through the system with an average flow rate of 2.7 l/min. After filtration the cartridges were removed from their housings and sealed in individual plastic bags for transportation for further processing in the laboratory.

The approach to separate Pu from seawater using a MnO₂ cartridge system with two Mn-cartridges connected in series (Figure 3) relies, apart from the precise knowledge of the filtered water volume, on the same Pu adsorption efficiency (eff) of the two MnO₂ cartridges (i.e. effC1=effC2). Under such circumstances it is possible to calculate the Pu collection efficiency of the MnO₂ cartridge and thus the seawater Pu activity concentration. The Pu adsorption efficiency in the system can be calculated from equation 1 (Schell *et al.*, 1978, Baskaran *et al.*, 2009). We used a third MnO₂ cartridge to check if some inconsistency in the efficiency could be observed and to ensure that the system was not malfunctioning, e.g. that some water bypassed one of cartridge C1 and C2 in the system. If bypassing had occurred, it would result in higher activity fraction on the later cartridge in the system.

$$eff = \left(1 - \frac{AC2}{AC1}\right) \cdot 100\% \quad (1),$$

Where:

eff = absorption efficiency [%]

AC1 = Pu activity in the first cartridge [Bq]

AC2 = Pu activity in the second cartridge [Bq]

The initial plutonium activity concentration, A_0 , can then be calculated from equation 2

$$A_0 = \frac{AC1}{eff \cdot V} \quad (2),$$

in which:

A_0 = dissolved seawater Pu activity concentration [Bq/l]

$AC1$ = Pu activity in the first cartridge [Bq]

eff = absorption efficiency [%] from equation 1

V = volume of seawater passed through the system [l]

2.1.2. MnO₂ cartridge treatments

The MnO₂ cartridges were placed into 960 ml quartz beakers and covered with aluminum foil to avoid cross contamination between the samples as several cartridges were incinerated in a muffle furnace to 510°C for about 6 hours concurrently. The chemical yield determinants were added to the incinerated samples. Concentrated HNO₃ and 30% H₂O₂ were added and the solution was refluxed under watch glass for 6 to 8 hours. Sample solutions were transferred in 400 ml beakers and evaporated to near dryness. The precipitated salts were dissolved using approximately 150 ml of MilliQ –water.

2.1.3. Pu pre-concentration from discrete water samples

Approximately 270 l of surface seawater was pre-filtered upon collection through 0.45 µm pore size nitrocellulose membrane filter (Millipore). The filtrated water was poured and collected into carefully cleaned polypropylene barrel. The filtered seawater was immediately acidified with concentrated HCl until pH 1-2 and the chemical yield determinants were added and the sample was left for 15 min. Saturated KMnO₄ was added to the seawater sample that oxidized Pu and destroyed any organic compounds in the sample. After 15 minutes mixing, the pH was raised to 8-9 with 10 M NaOH and MnO₂ was precipitated using 0.5 M MnCl₂. The MnO₂-precipitate was allowed to settle, after which the supernatants were carefully siphoned and was further processed for ¹³⁷Cs and ⁹⁰Sr analysis. The precipitates were later dissolved with concentrated HCl and hydroxylamine (NH₂OH·HCl).

2.2. Chemical separation and purification of plutonium

2.2.1. Separation of Pu from excess MnO₂ with Fe(OH)₃ co-precipitation

In Figure 4 the flow chart of the chemical separation and purification of Pu is given. The sample solutions resulting from the pre-concentration steps described in section 2.1. were first subjected to a controlled reduction-oxidation sequence to ensure that the Pu in the sample was adjusted to tetravalent state. For the cartridge samples, FeCl_3 and 25 % hydrazine ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) were added. The sample was then heated to reduce Fe(III) to Fe(II). Ferrous ions together with some excess hydrazine will rapidly convert all soluble Pu species to trivalent oxidation state. Concentrated HNO_3 was added to destroy excess $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$. The sample was cooled and NaNO_2 was added to oxidize Pu(III) to Pu(IV). Excess nitrous acid was destroyed by gentle boiling.

As $\text{NH}_2\text{OH} \cdot \text{HCl}$ was present in the discrete water samples from the dissolution of the MnO_2 precipitates, hydroxylamine-reduction nitrite-oxidation sequence was used to oxidize Pu instead. After adding FeCl_3 , $\text{NH}_2\text{OH} \cdot \text{HCl}$ was used to reduce Fe(III) to Fe(II) with heating. Dissolved NaNO_2 was added to the sample to oxidize the excess $\text{NH}_2\text{OH} \cdot \text{HCl}$ and convert Pu(III) to Pu(IV).

Finally, $\text{Fe}(\text{OH})_3$ was precipitated by adding concentrated NH_3 until the solution reached pH 6-7. After centrifugation, the precipitate was dissolved with concentrated HNO_3 and prepared for the anion exchange column.

2.2.2. Separation of Pu with anion exchange chromatography

For further purification using anion exchange separation the Pu in the HNO_3 solution was first adjusted to the tetravalent state with hydrazine-reduction nitrite-oxidation method as described above. The solution was allowed to cool and then transferred to 7-8 M HNO_3 . In the next step the solution was poured directly over a preconditioned (8 M HNO_3) anion exchange column (Bio-Rad AG 1X8) (Wong, 1971, La Rosa et al., 2001). The column was then washed with 8 M HNO_3 , eluting interfering elements like e.g. U, Am and rare earths, followed by a 10 M HCl wash to remove Th. Pu was finally eluted from the column with a freshly prepared 0.1 M NH_4I in 9 M HCl solution. The Pu fraction was evaporated to near dryness and iodide was removed by repeated additions of concentrated HNO_3 and 30% H_2O_2 . For the next purification step the final residue was dissolved in 1 M HNO_3 .

Remaining traces of U, Th and Po were removed from the Pu fraction by repeating the anion exchange separation described above. Pu was washed of the columns using a freshly prepared mixture (1/100) of 30% H_2O_2 and 1.2 M HCl. After evaporation, the Pu fraction was converted from hydrochloric residue to nitrate salt residue by repeating addition and evaporation of concentrated HNO_3 .

2.3. Source preparation and alpha particle measurements

Plutonium was electroplated on stainless disks in a sulfate medium (Talvitie, 1972, Hallstadius, 1984). The Pu discs were counted in alpha chambers equipped with PIPS detector with counting efficiency between 0.25 - 0.30 for 30 - 60 days. The ^{238}Pu pulses in the alpha spectra were corrected for possible interfering ^{224}Ra and ^{228}Th pulses. This was done by letting the disks rest for 3 weeks before inserted into the detector chamber, allowing secular equilibrium between ^{228}Th and ^{224}Ra to be achieved. The ^{238}Pu pulses were corrected by subtracting ^{224}Ra pulses calculated from the ^{228}Th peak. In addition, the alpha spectra were corrected from background pulses and the final Pu results for the mean blank sample activities (see 2.4 for blank sample information). The detection limits were calculated on the basis of Currie's formula (Currie, 1968).

2.4. Quality control samples

In this study the water samples have extremely low Pu concentrations. Low decay counting is a challenge in several aspects. Long counting times sets demands on ultralow background detectors with a stable and know background count statistics of the alpha spectrometric system. Moreover, activity contributions of isotopic impurities of the ^{242}Pu tracers used must be known, which is usually stated in the tracer certificate. Relatively easy is to estimate the activity contribution from chemicals used by performing chemical blank sample analysis. More difficult is to estimate the contribution from cross-contaminated equipment, e.g. precipitation tanks, laboratory beakers, electrodepositions system etc. These values are never constant and will change between analysis, but it is crucial that all equipment is controlled and carefully handled. Even though minute precisions of the later is taken in consideration, this might the main contribution to the uncertainty in ultralow level counting. There is no easy or standard way to adequately deal with this issue as it very much depends on the whole analytical procedure, from preparing sampling (e.g. preparation or tracer sets for sea going sampling missions), during sampling (e.g. cleaning of sampling equipment onboard the ship), storing samples (e.g. cubic container cross-contamination), during sample preparation, during radiochemical separation and source preparation. It is for that reason important to run as many as possible process blank samples to get an estimate on the levels and variance of the activity levels. These blank test samples require a lot of work and are usually over seen, probably as in "medium" environmental levels of Pu they will to contribute significantly to the final results.

In this study cartridge samples were analyzed in batches and for every batch a process blank sample was determined. In total 8 process blanks were analyzed. In addition, 3 unused MnO₂ cartridges (blank Pu cartridges) were analyzed with the respect to their Pu content. For the co-precipitation technique, two blanks analysis were conducted, including tracer spiked deionized water precipitated in the tanks used onboard. These quality control samples were analyzed following the same procedure as described for the seawater samples. In addition, 5 reference seawater samples (IAEA-381) were analyzed for Pu content to check our analytical performance. For these samples we used between 0.55-0.66 kg of IAEA-381.

3. Results and discussion

3.1. Method comparison and efficiency calculation

We have determined the dissolved Pu activity concentration of the seawater by two independent methods, the MnO₂ cartridge system and the MnO₂ precipitation technique.

In Table 3 and in Figure 5 the comparison of the activity concentrations determined by the two independent techniques are shown. Apart from one outlier, a good 1:1 correlation between the two sampling techniques can be observed (adjusted $R^2 = 0.96$). The outlier may result from the MnO₂-cartridge system samples water from the moving vessel and the typical sampling time was ~ 10 hours. Thus, the Pu concentrations determined in this way represent an average concentration in seawater over a distance of about 200 km. For the precipitation method, however, a discrete water sample was collected at the stations about 5 hours after the start of the MnO₂-cartridge sampling. Station 4 is located in an area where a large difference in Pu concentrations occurs for the station 3 and station 5. Therefore, we attribute the mismatch between the results of the MnO₂-cartridge and MnO₂ precipitation methods to be caused by that variations in the Pu concentration at the station and the average concentration differ significantly from the water sampled with the discrete sampled. So for this station the methods cannot be compared and the results are not used in the linier regression analysis of the comparison. The oceanographic implication of these data is dealt with elsewhere (Eriksson et al, 2019) It is possible to calculate the Pu adsorption efficiency for each of the MnO₂ cartridge in the system (effC1, effC2, effC3) (see Figure 3 for more detailed explanations). The average efficiencies for each cartridge were effC1 = 0.57 ± 0.09 , effC2 = 0.54 ± 0.18 and effC3 = 0.69 ± 0.42 , i.e. no significant difference between the cartridges in the sampling system. It can be noticed that the uncertainties of the efficiencies increase from the first to the third cartridge. The Pu activity on the later cartridges in the

system (C2 and C3) is much less compare to the first (C1) and consequently the alpha particle counting statistics is lower for these cartridges. The weighted (with respect to the uncertainties) mean efficiency for all cartridges was found to be 0.58 ± 0.07 . Our efficiencies are slightly higher than those reported in the literature (Wong et al., 1978, Crespo et al., 1989). These differences in the efficiencies may be due to the fact that the flow rate of seawater passing through the MnO_2 -cartridge system was different. We would expect higher efficiencies for low flow rates, however we found no statistical difference in the flow rate range used in this study (1.6-5.2 l/min). Furthermore, different types of fibers and different protocols for loading MnO_2 on the fibers may be responsible for the different efficiencies observed (Henderson et al., 2013). It has also been reported that the MnO_2 crystalline structure may be a critical factor for the adsorption efficiency of Pu (Koulouris et al., 2000). In Figure 6 the efficiency of cartridge C1 is shown versus different seawater parameters as temperature (A), conductivity (B), salinity (C). Figure 6 D shows the efficiency along the transect passing through different water masses. None of these parameters show a statistical significant dependency with the efficiency. The other two parameters related to the sampling system, i.e. flow rate (Figure 6 E) and total sample volume (Figure 6 D) showed no significant correlation with the efficiency, giving confidence that the system works for Pu seawater sampling and activity determination.

By comparing the activity concentration derived by summing the activity determined on each of the three cartridges with the activity derived from the MnO_2 precipitation technique (as we refer to reference activity concentration) it is possible to calculate the total efficiency of the MnO_2 cartridge system, i.e. $\text{toteff} = (\text{activity concentration derived by summing the three cartridges} / \text{activity concentration derived the } \text{MnO}_2 \text{ precipitation technique})$. We found that the total efficiency for our system was 0.96 ± 0.17 .

In Figure 7 the activity fractions in each MnO_2 cartridge at all 19 stations sampled are shown (normalized to total summed activity of the three cartridges). It can be seen that no systematic differences in the activity fractions between the sampling stations occur indicating no major failure of the sampling system. This is also supported by our results on the efficiency calculation above, where all efficiencies were almost the same for the three cartridges in the series. If a failure would occur, e.g. a leaking cartridge holder or bypassing of water over a cartridge this would probably be reflected in the activity fractions and the efficiencies of the cartridges.

The cartridge system also seems to perform well in all different water-masses (upwelling areas, Saharan dust rich waters, and oligotrophic waters) sampled on this ocean transect indicating that

different Pu sources and chemical forms can be present in the seawater, e.g. from atmospheric nuclear test fallout, potential re-suspended soil from the France nuclear test in Algerian desert. However, the potential different Pu sources and forms seems to be equally effectively absorbed, if present.

Inconsistencies in Pu activity determinations using a MnO₂ cartridge system have been reported (Crespo et al., 1989) which were attributed to possible different adsorption efficiencies of the reduced and the oxidized forms of Pu. It was also proposed that in a MnO₂ cartridge system Pu would be oxidized when passing the first cartridge, resulting in an increased Pu adsorption on second cartridges. Others (Wong et al., 1978) have found equal adsorption of Pu independent on the oxidation states. We did not see any increase of the adsorption efficiency in our system, maybe due to the fact that all our Pu was in the oxidized form or that the adsorption was equal for all Pu oxidation species present in sampled waters. In our study we used two different pore sizes on the pre-filter, 0.45 µm (precipitation method) and 1 µm (cartridge system), however, we could not observe any differences in the results due to this difference. It seems that the Pu was associated with colloids less than 0.45 µm and/or that Pu was not associated to particles between 0.45-1 µm as this would be noticed in the comparison of the results. It should be noted that the MnO₂ cartridge system might not work in anoxic seawaters, as the MnO₂ might be reduced and dissolves from the cartridges (Roos P., Personal communication, 2015). The in-situ pre-concentration technique is very practical to use on sea going missions as no chemicals need to be handled on board. Another advantage is the possibility to sample large water volumes (up to 3000 liters), enabling determination of Pu-isotopic ratios with a low relative standard deviation. Compared to the more commonly used precipitation techniques more radiochemical work is needed in the laboratory after the sampling cruise (more than two times more). However, the major limitation with the precipitation techniques is the sample size (< 300 liters), especially when analyzing low level Pu contaminated waters (< 1 µBq/l ²³⁹Pu), resulting in high uncertainties of the Pu-isotopic ratios and concentration results.

Our studies found a very good agreement between the dissolved Pu concentrations of reference seawater samples and the samples collected with the *in-situ* MnO₂ cartridge system, in addition the adsorption efficiency were constant and independent of the seawater temperature in the range of 18.3-29.2 °C, salinity range 34.2 – 37.1 ‰, conductivity range 46.8 -58.4 mS/cm. in the range, showing that the system can be used to determine dissolved Pu in open surface seawaters.

3.2. Quality control

The Pu chemical recoveries for the MnO₂ cartridge analyses were 82 ± 7 % (n=57, three cartridges per station) and for the bulk water analysis slightly lower, 77 ± 10 % (n=19). Our detection limits for ²³⁹⁺²⁴⁰Pu were found to be 0.03 mBq per cartridge samples and 0.04 mBq per bulk water samples for 30 days counting and mostly dependent on the background pulses in the alpha spectra originated from the PIPS detectors.

In Table 4 the results of IAEA-381 reference seawater are presented. The Pu reference values for IAEA-381 are: ²³⁹⁺²⁴⁰Pu 0.0135 Bq/kg (95% Confidence Interval: 0.0131 to 0.0145 Bq/kg) and the ²³⁸Pu/²³⁹⁺²⁴⁰Pu activity ratio equal to 0.24 ± 0.03 . For all these analyses we were within or slightly over the 95% confidence interval for the activity concentration. This might be due to some evaporation during storage of the reference seawater resulting in slighter higher activity concentration. For the ²³⁸Pu/²³⁹⁺²⁴⁰Pu activity ratio we were within the reference value. For these samples we had a chemical recovery between 67 – 94 %. In Table 5 the results from the process blank are presented. The variation in the process blank level reflects that poor counting statistics due to very low blank activity and low background levels in the alpha measurements. These blank activity levels are very low and the activity calculations are based on few net counts in the alpha spectra for each isotope. The activity levels for the blank MnO₂ cartridges (lower part in Table 5) are also very low and in the same order as the process blank samples.

4. Conclusions

In this study we compared two techniques for Pu determination: an in-situ MnO₂ cartridge system consisting of a particle filter and three Mn-cartridges in series, and discrete water sampling followed by on-board pre-concentrations techniques. The comparisons were conducted on real water samples collected on an ocean transect in the Southeast Atlantic, from Vigo (Spain) to Cape Town (South Africa). This transect covered the upwelling region in the East Atlantic, Saharan dust-rich waters near the Canary Islands as well as oligotrophic waters in the Angola Basin. We found that the efficiency of a single MnO₂ cartridge to adsorb Pu was on average 58 % when using flowrates of about 3 l/min, and that the total efficiency of our three MnO₂ cartridge system was about 96%. The constant Pu adsorption efficiency of the MnO₂ cartridges suggest that it is sufficient to use two instead of three MnO₂ cartridges for pre-concentration of Pu from seawater. Using the constant efficiency assumption to determine the dissolved Pu seawater concentration will result in a relative combined uncertainty of

about 10 %, however dependent of total sample volume and sea water concentrations. We have shown that *in-situ* MnO₂ cartridge technique can be used in a reliable way for the determination of dissolved Pu seawater concentration in open ocean waters.

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Reference:

Aarkrog, A., 2003. Input of anthropogenic radionuclides into the World Ocean. Deep Sea Research Part II: Topical Studies in Oceanography 50, 2597–2606.

Ballestra, S., Holm, E., Fukai, R., 1978. Low-level determination of transuranic elements in marine environmental samples; Proceedings of symposium on the determination of radionuclides in environmental and biological materials., Londres, paper nr 15.

Baskaran, M., Swarzenski, P.W., Biddanda, B.A., 2009. Constraints on the utility of MnO₂ cartridge method for the extraction of radionuclides: A case study using ²³⁴Th, Geochem. Geophys. Geosyst. 10, Q04011, doi:10.1029/2008GC002340

Buesseler, K.O., Cochran, J.K., Bacon, M.P., Livingston, H.D., Casso, S.A., Hirschberg, D., Hartman, M.C., Fleer, A.P., 1992. Determination of thorium isotopes in seawater by non-destructive and radiochemical procedures. Deep-Sea Research 39 (7-8), 1103–1114.

Choppin, G.R., Kobachi, A., 1990. Distribution of Pu(V) and Pu(VI) in seawater. Marine Chemistry 30, 241–247.

Choppin, G.R., 2006. Actinide speciation in aquatic systems. Marine Chemistry 99, 83–92.

Crespo, M.T., Los Arcos, J.M., Granados, C.E., Aceña, M.L., 1989, On the concentration and determination of plutonium in natural waters by adsorption on MnO₂ filters, *Journal of Radioanalytical and Nuclear Chemistry* 130, 99-110

Currie, L.A., 1968. Limits for Qualitative Detection and Quantitative Determination: Application to Radiochemistry, *Anal. Chem.* 40, 586-593.

Eriksson, M., Levy, I., Chamizo, E., Gastaud, J., Ämmälä, K., Scholten, J., 2019, On the Plutonium isotopic composition in east Atlantic surface waters, levels and trends, In preparation

Fukai, R., Yamato, A., Thein, M., Bilinski, H., 1987. Oxidation states of fallout plutonium in Mediterranean rain and seawater, *Geochemical Journal* 21, 51-57.

Gastaud, J., Povinec, P.P., Aoyama, M., Hirose, K., Sanchez-Cabeza, J.A., Levy, I., Roos, P., Eriksson, M., Bosc, E., Rezzoug, S., 2011. Transport and scavenging of Pu in surface waters of the Southern Hemisphere Oceans, *Progress in Oceanography* 89, 92–100

GEOTRACES, Internet site: <http://www.geotraces.org>, 2018.

Hamilton, T.F., 2005, Linking legacies of the Cold War to arrival of anthropogenic radionuclides in the oceans through the 20th century. In: Livingston, H.D. (Ed.), *Marine Radioactivity, Radioactivity in the Environment*. Elsevier, pp. 23–78.

Hallstadius, L.A., 1984. A method for the electrodeposition of actinides. *Nucl. Instrum. Meth. Phys. Res.* 223, 382–385

Hartman, M.C., Buesseler, K.O., 1994. Adsorbers for In-Situ Collection and At-Sea Gamma Analysis of Dissolved Thorium-234 in Seawater. WHOI Technical Report, WHOI-94-15

Henderson, P., Morris, P., Moore, W., Charette, M., 2013. Methodological advances for measuring low-level radium isotopes in seawater. *Journal of Radioanalytical and Nuclear Chemistry* 296, 357-366

Hirose, K., Kim C.S., Yim, S.A., Aoyama, M., Fukasawa, M., Komura, K., Povinec, P.P., Sanchez-Cabeza, J.A., 2011. Vertical profiles of plutonium in the central South Pacific, *Progress in Oceanography* 89, 101–107

Holm, E., Fukai, R., 1976. Determination of americium and curium by using ion-exchange in nitric acid-methanol medium for environmental analysis. *Talanta* 23, 853-855.

Holm, E., Aarkrog, A., Ballestra, S., 1987. Determination of ^{237}Np in large volume samples of sea water by a radiochemical procedure, *Journal of Radioanalytical and Nuclear Chemistry* 115 (1), 5-11.

Koulouris, G., Slowikowski, B., Pilviö, R., Bostrom, T., Bickel, M., 2000. Pre-concentration of actinoids from waters: a comparison of various sorbents, *Applied Radiation and Isotopes* 53 (1), 279 – 287.

La Rosa, J.J., Burnett, W., Lee, S.H., Levy, I., Gastaud, J., Povinec, P.P., 2001. Separation of actinides, cesium and strontium from marine samples using extraction chromatography and sorbents, *Journal of Radioanalytical and Nuclear Chemistry* 248 (3), 765-770.

León Vintrol, L., Mitchell, P.I., Smith, K.J., Kershaw, P.J., Livingston, H.D., 2005. Transuranium nuclides in the world's oceans. In: Livingston, H.D. (Ed.), *Marine Radioactivity, Radioactivity in the Environment*. Elsevier, pp. 79–108.

Lindahl, P., Lee, S.H., Worsfold, P., Keith-Roach, M., 2010. Plutonium isotopes as tracers for ocean processes: a review. *Mar Environ Res*. Mar 69 (2), 73-84

Livingston, H.D., Cochran, J.K., 1987. Determination of transuranic and thorium isotopes in ocean water: in solution and in filterable particles, *Journal of Radioanalytical and Nuclear Chemistry* 115 (2), 299-308.

Mann, D.R., Surprenant, L.D., Casso, S.A., 1984, In situ chemisorption of transuranics from seawater, *Nuclear Instruments and Methods in Physics Research*, 223, 235-238

Martin, J.M., Thomas, A.J., 1990. Origins, concentrations and distributions of artificial radionuclides discharged by the Rhône River to the Mediterranean Sea, *Journal of Environmental Radioactivity* 11, 105-139.

Mitchell, P.I., Vives Batlle, J., Downes, A.B., Condren, O.M., León-Vintró, L., Sánchez-Cabeza, J.A., 1995. Recent observations on the physico-chemical speciation of plutonium in the Irish Sea and West Mediterranean, *Applied Radiation and Isotopes* 46 (11), 1175-1190.

Pillai, K.C., 1975. Determination of plutonium in the marine environment. Technical Report Series nr 169, IAEA, Vienna, 97-105.

Qingjiang, C., Dahlgaard, H., Nielsen, S.P., Aarkrog, A., Christensen, L., Jensen, A., 2001. Determination of ^{237}Np in marine sediment and seawater, *Journal of Radioanalytical and Nuclear Chemistry* 249 (3), 527-533.

Ristic, M., Degetto, S., Ast, T., Cantallupi, C., 2002. Sample preparation for the determination of ^{241}Am in sediments utilizing γ -spectroscopy, *Journal of Environmental Radioactivity* 59, 179-189.

Rutgers van der Loeff, M.M., 2007. The Expeditions ANT-XXIII/1 of the Research Vessel Polarstern in 2005. *Berichte zur Polar- und Meeresforschung (Reports on Polar and Marine Research)*, Bremerhaven, Alfred Wegener Institute for Polar and Marine Research 556, 140p.

Schell, W.R., Nevissi, A., Huntamer, D., 1978. Sampling and analysis for Pu and Am in natural waters, *Marine Chemistry* 6, 143-153.

Strand, P., Balonov, M., Aarkrog, A., Bowers, M.J., Howard, B., Salo, A., Tsaturov, Y.S., 1998. AMAP Assessment Report: Arctic Pollution Issues Radioactivity, Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway, 542–578

Talvitie, N.A., 1972. Electrodeposition of actinides for alpha spectrometric determination, *Analytical Chemistry* 44 (2), 280-283.

Wong, K.M., 1971. Radiochemical determination of plutonium in sea water, sediments and marine organisms, *Analytica Chimica Acta* 56, 355-364.

Wong, K.M., Brown, G.S., Noshkin, V.E., 1978. A rapid procedure for plutonium separation in large volumes of fresh and saline water by manganese dioxide coprecipitation, *Journal of Radioanalytical and Nuclear Chemistry* 42, 7-15

Table 1. Information for the MnO₂ cartridge Pu sampling.

Station	start latitude	start longitude	stop latitude	stop longitude	distance [km]	Flow rate [l min ⁻¹]	Volume [l]
St 1	37°14,411' N	12°11,654' W	35°59,265' N	12°59,276' W	156.2	2.1	1024
St 2	34°7,923' N	14°8,990' W	32°43,232' N	15°0,998' W	176.4	1.8	956
St 3	30°20,482' N	16°26,727' W	29°1,560' N	15°55,146' W	154.8	2.8	989
St 4	26°8,052' N	17°11,312' W	24°50,329' N	18°37,805' W	204.2	5.2	2700
St 5	22°30,02' N	20°29,86' W	22°30,04' N	20°29,81' W	0.0	2.8	1081
St 6	19°13,518' N	20°54,456' W	17°23,414' N	20°56,746' W	204.1	2.2	1230
St 7	14°33,844' N	20°57,610' W	13°1,847' N	20°38,138' W	174.1	2.8	1425
St 8	10°37,540' N	20°7,827' W	10°34,686' N	20°7,258' W	0.0	3.9	1571
St 9	7°37,280' N	17°59,915' W	6°13,294' N	16°49,562' W	202.4	2.2	1241
St 10	4°24,247' N	15°18,528' W	2°56,146' N	14°5,347' W	212.1	2.9	1653
St 11	0°48,515' N	12°26,053' W	0°35,184' S	11°20,962' W	196.5	2.5	1477
St 12	1°7,896' S	10°55,519' W	2°48,017' S	9°37,626' W	235.0	2.2	1605
St 13	4°50,161' S	8°2,446' W	6°6,072' S	7°3,148' W	178.2	2.3	1258
St 14	8°22,387' S	5°16,293' W	9°34,966' S	4°19,156' W	170.4	2.7	1675
St 15	11°52.33' S	2°31.00' W	14°16.14' S	0°35.68' W	338.2	2.5	1489
St 16	13°51,679' S	0°55,283' W	16°0,027' S	0°48,037' E	301.3	1.6	1452
St 17	17°30,997' S	2°1,918' E	18°44,029' S	3°1,626' E	171.4	2.8	1652
St 18	20°35,654' S	4°33,852' E	21°49,383' S	5°35,352' E	173.1	2.5	1414
St 19	25°0,085' S	8°16,909' E	25°0,212' S	8°17,138' E	0.0	2.7	1620

Table 2. Information for the MnO₂ precipitation sampling for Pu determination.

Station	Latitude	Longitude	Volume [l]	Temp [°C]	Conductivity [mS cm ⁻¹]	Salinity [‰]
St 1	36°43.53N	12°31.19W	259.3	21.02	51.06	36.64
St 2	33°33.27N	14°30.42W	286.1	21.91	52.18	36.76
St 3	29°41.56N	16°23.34W	282	23.76	54.52	37.03
St 4	25°32.34N	17°51.16W	268	24.64	55.66	37.14
St 5	22°29.99N	20°29.97W	278	25.14	55.37	36.52
St 6	18°22.37N	20°55.37W	284	25.72	55.71	36.31
St 7	13°54.38N	20°48.86W	281.4	28.70	57.92	35.59
St 8	10°37.51N	20°7.76W	272	29.15	58.39	35.57
St 9	7°1.42N	17°29.61W	281	29.16	57.08	34.66
St 10	4°0.96N	14°59.11W	276	28.41	55.63	34.22
St 11	0°29.20N	12°12.20W	277	26.67	56.42	36.07
St 12	1°57.99S	10°18.65W	260.6	25.98	55.76	36.14
St 13	4°58.60S	7°55.86W	271.5	24.51	54.06	36.05
St 14	8°33.95S	5°7.20W	277.5	23.33	52.88	36.11
St 15	11°52.22S	2°30.99W	270.6	22.14	52.01	36.41
St 16	14°5.74S	0°44.02W	271.9	20.91	50.83	36.52
St 17	17°32.43S	2°1.96E	270.6	19.26	48.43	35.97
St 18	20°46.16S	4°42.55E	271.7	18.40	47.73	35.75
St 19	24°2.23S	7°27.50E	272.1	18.26	46.80	35.64

Table 3. Dissolved $^{239+240}\text{Pu}$ activity concentration in surface water on the ANT XXX-1 transect from Vigo Spain to Cap Town, South Africa. Calculated by two different approaches for the MnO_2 cartridge system and compared with a reference MnO_2 precipitation method.

Station	$^{239+240}\text{Pu}$ by MnO_2 precipitation (reference value) (A)		$^{239+240}\text{Pu}$ by assuming constant MnO_2 cartridge efficiency (B)		Activity concentration ratio (B)/(A)		$^{239+240}\text{Pu}$ by summing all MnO_2 cartridge Pu activity (C)		Activity concentration ratio (C)/(A)	
	$\mu\text{Bq/l}$	$\Delta\mu\text{Bq/l}$	$\mu\text{Bq/l}$	$\Delta\mu\text{Bq/l}$	Ratio	Δratio	$\mu\text{Bq/l}$	$\Delta\mu\text{Bq/l}$	Ratio	Δratio
St 1	1.88	0.19	1.92	0.19	1.02	0.14	1.87	0.09	0.99	0.11
St 2	2.68	0.18	2.76	0.19	1.03	0.10	2.77	0.11	1.03	0.08
St 3	3.69	0.20	3.30	0.25	0.89	0.08	3.20	0.12	0.87	0.06
St 4	3.33	0.38	2.10	0.14	0.63	0.08	1.92	0.05	0.58	0.07
St 5	1.78	0.16	1.50	0.18	0.84	0.13	1.51	0.07	0.85	0.09
St 6	1.11	0.16	1.38	0.15	1.24	0.22	1.41	0.07	1.27	0.19
St 7	1.06	0.16	0.94	0.11	0.89	0.17	0.90	0.05	0.85	0.14
St 8	1.18	0.16	0.92	0.11	0.78	0.14	0.89	0.05	0.76	0.11
St 9	0.90	0.15	0.78	0.10	0.86	0.18	0.75	0.05	0.84	0.15
St 10	0.96	0.16	0.69	0.08	0.72	0.14	0.72	0.05	0.75	0.13
St 11	0.71	0.14	0.99	0.22	1.39	0.41	0.76	0.05	1.07	0.22
St 12	0.73	0.15	0.68	0.10	0.93	0.24	0.60	0.04	0.83	0.18
St 13	0.34	0.14	0.36	0.07	1.06	0.49	0.37	0.04	1.08	0.46
St 14	0.27	0.13	0.39	0.07	1.43	0.73	0.37	0.04	1.37	0.67
St 15	0.37	0.14	0.31	0.11	0.85	0.43	0.27	0.04	0.73	0.29
St 16	0.13	0.13	0.25	0.06	1.89	1.95	0.22	0.04	1.69	1.71
St 17	0.21	0.13	0.24	0.07	1.15	0.79	0.25	0.03	1.17	0.74
St 18	0.35	0.13	0.35	0.10	0.99	0.47	0.32	0.04	0.91	0.35
St 19	0.74	0.16	0.65	0.07	0.87	0.21	0.68	0.04	0.92	0.21

Table 4. Pu determination of the IAEA-381 reference material. The Pu reference values are: $^{239+240}\text{Pu}$ 0.0135 Bq/kg (95% Confidence Interval: 0.0131 to 0.0145 Bq/kg) and the $^{238}\text{Pu}/^{239+240}\text{Pu}$ activity ratio equal to 0.24 ± 0.03

$^{239+240}\text{Pu}$		$^{238}\text{Pu}/^{239+240}\text{Pu}$		Chemical recovery
Bq/kg	$\Delta\text{Bq/kg}$	act. ratio	Δ ratio	%
0.0138	0.0006	0.24	0.02	67
0.0141	0.0006	0.25	0.02	71
0.0149	0.0006	0.24	0.02	71
0.0148	0.0004	0.23	0.01	83
0.0146	0.0004	0.24	0.01	94

Table 5. Pu activity determination in blank samples.

Blank type: sample number	$^{239+240}\text{Pu}$		Chemical recovery
	μBq	$\Delta\mu\text{Bq}$	%
Process blank:1	38	10	75
Process blank:2	24	7	90
Process blank:3	4	8	83
Process blank:4	13	6	95
Process blank:5	6	6	85
Process blank:6	0	16	84
Process blank:7	0	17	88
Process blank:8	20	13	89
Cartridge blank:1	2	8	76
Cartridge blank:2	17	8	88
Cartridge blank:3	30	8	92
Blank	17	5	
precipitation:1			65
Blank	37	7	
precipitation:2			68

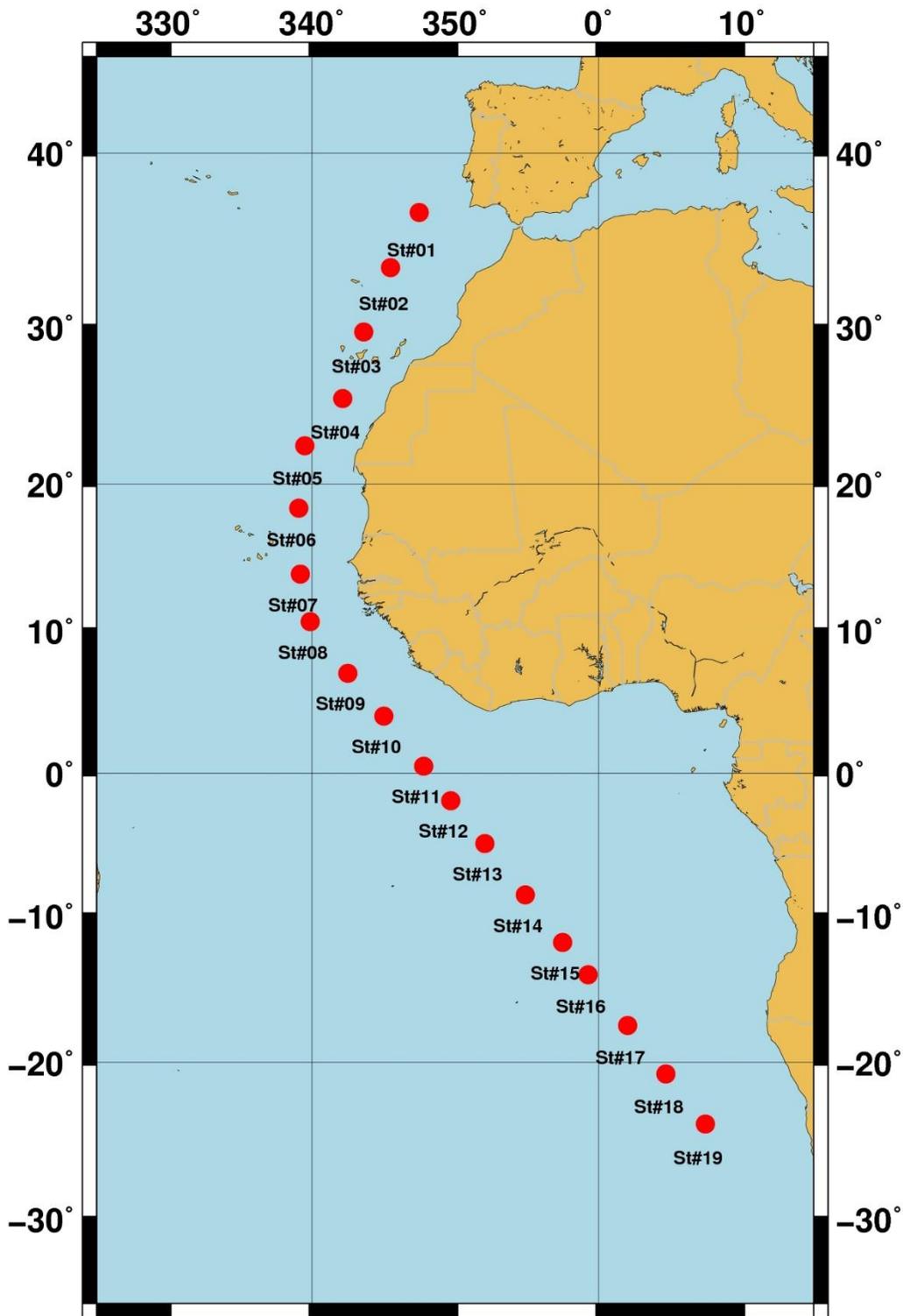


Figure 1: The Pu sampling stations at R/V Polarstern ANT XXX-1 cruise.

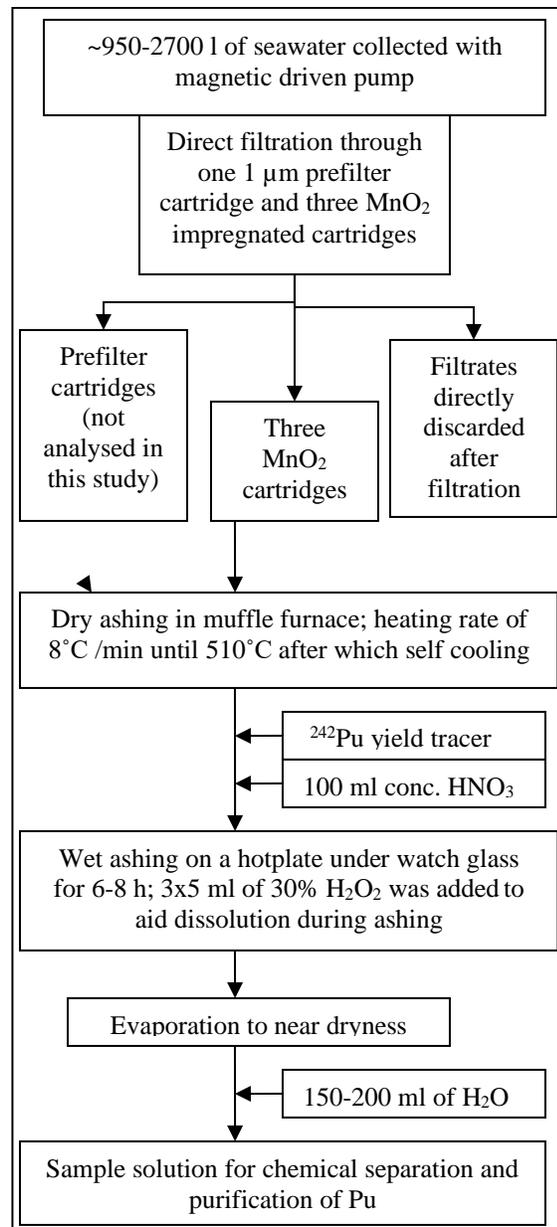
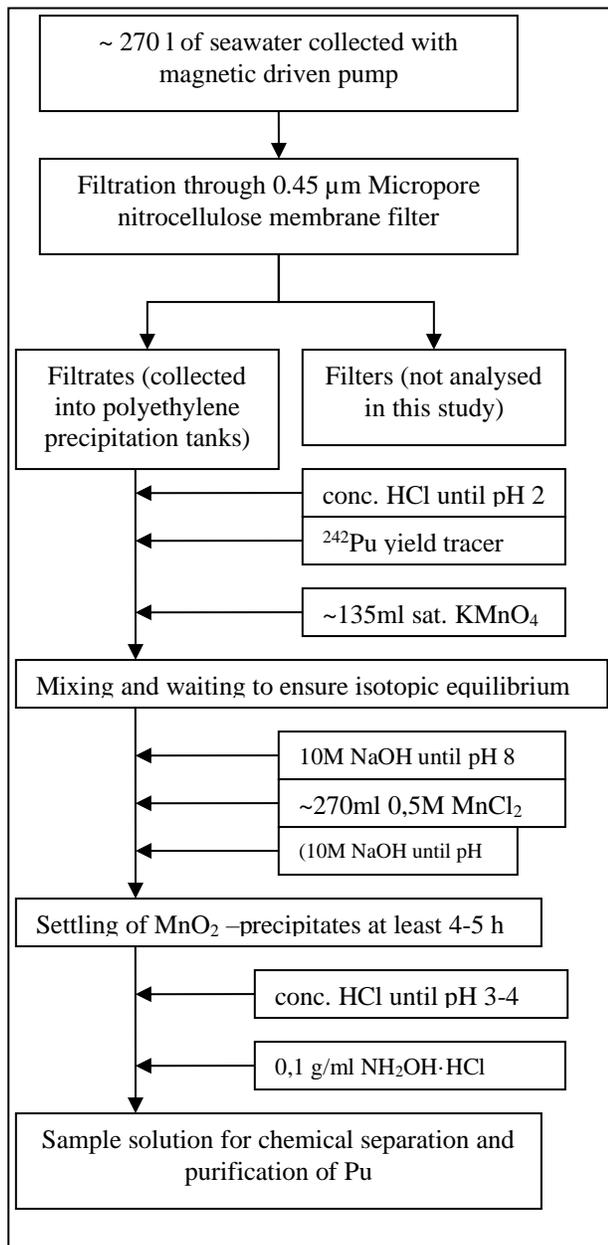


Figure 2. Seawater sampling and pre-concentration methods.

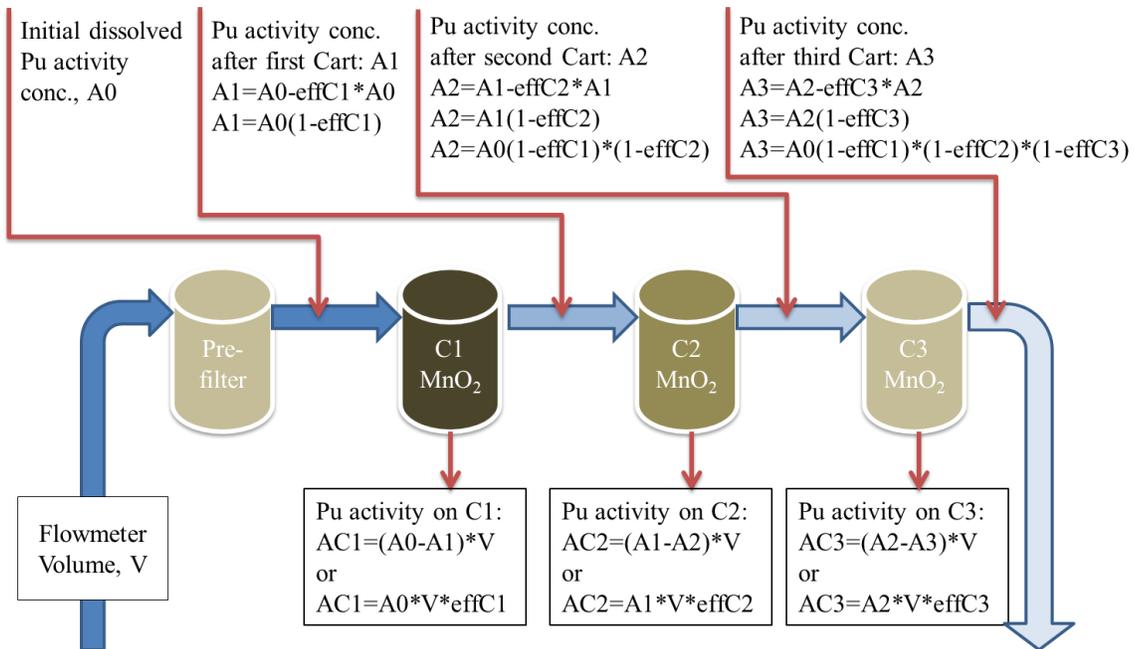


Figure 3. An illustration of the MnO_2 cartridge system used on board. Also show is the principle of the involved system components with the equation used for the calculation of the results.

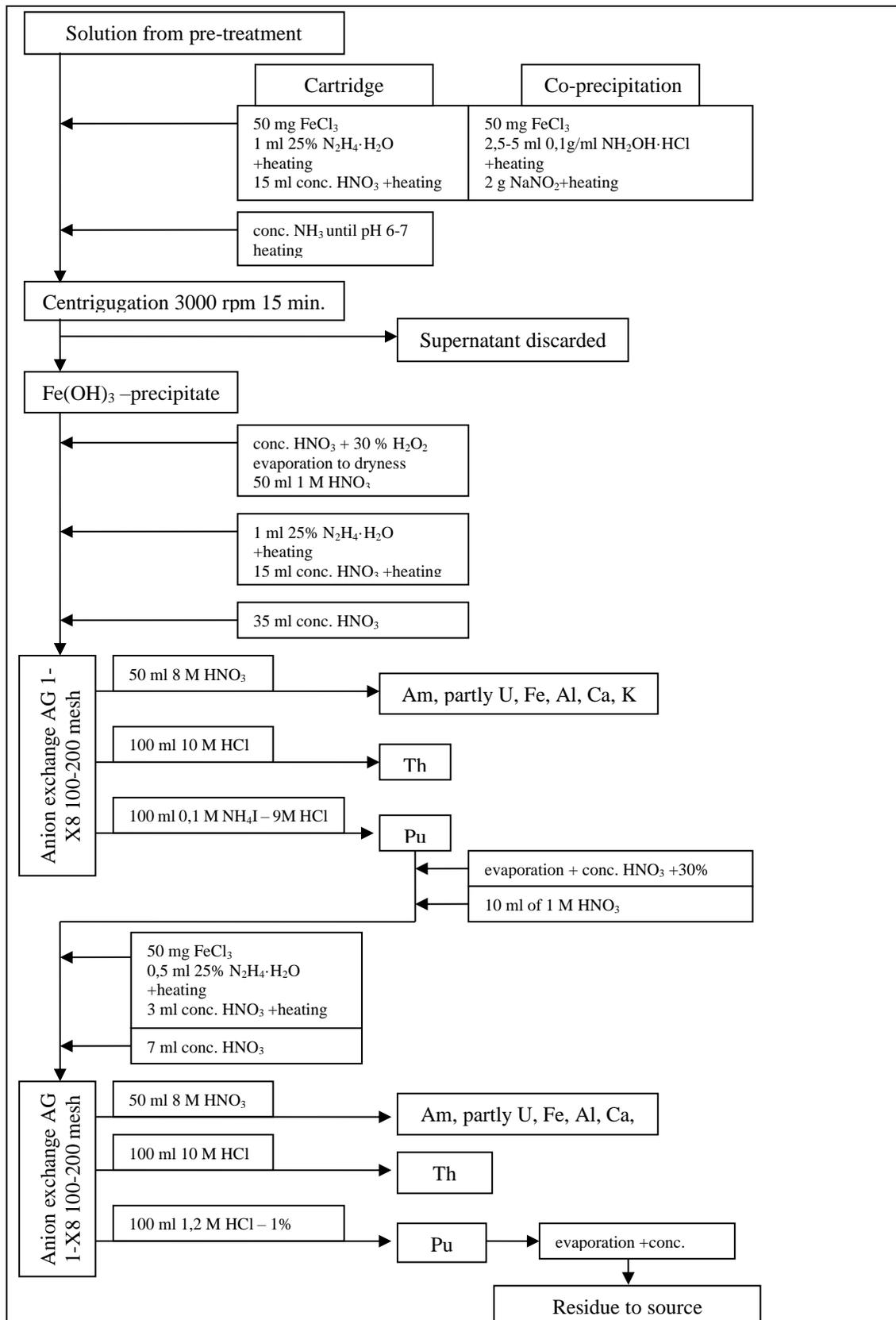


Figure 4. Flow chart of the chemical separation and purification of Pu

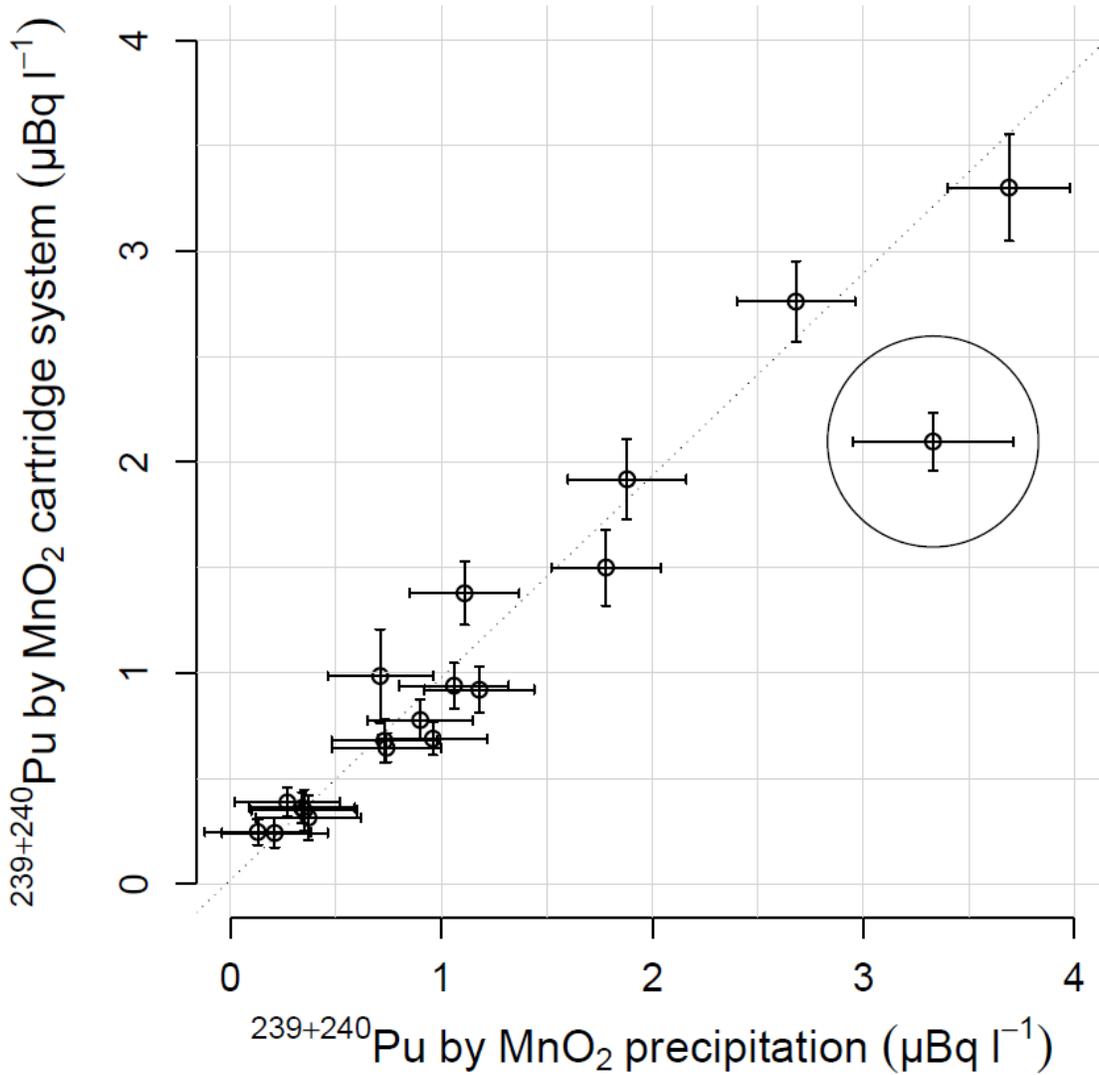


Figure 5. Comparison of $^{239+240}\text{Pu}$ activity seawater concentration determination obtained by MnO_2 precipitation and in-situ absorption on MnO_2 impregnated filters assuming constant absorption efficiency. The slope of the fitted line (excluding the outlier indicated with a large circle) has a value of 0.96 ± 0.06 , an intercept value of 0.02 ± 0.07 and an adjusted R square value of 0.94.

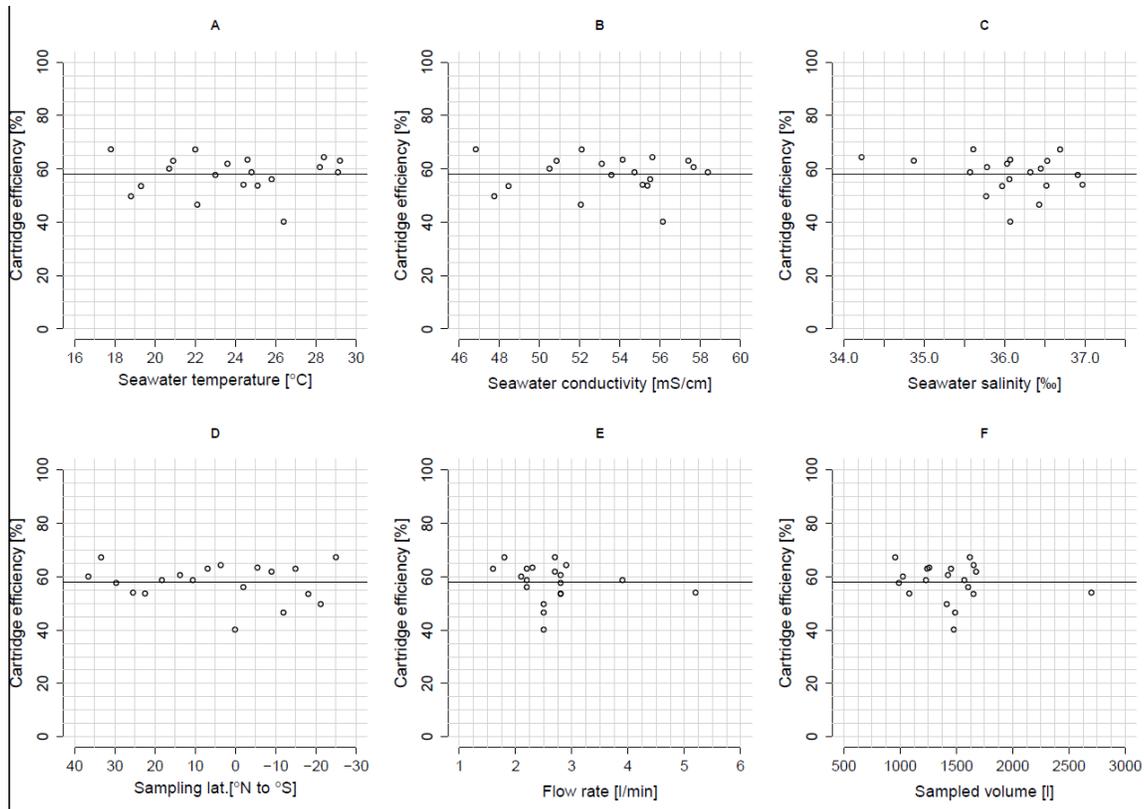


Figure 6. The Pu cartridge absorption efficiency versus seawater parameters (A-D) and sampling system parameters (E-F). The horizontal line indicates the calculated mean adsorption efficiency for all cartridges. No statistical correlation can be observed, showing that the adsorption efficiency is independent of these parameters in the range presented in the plots.

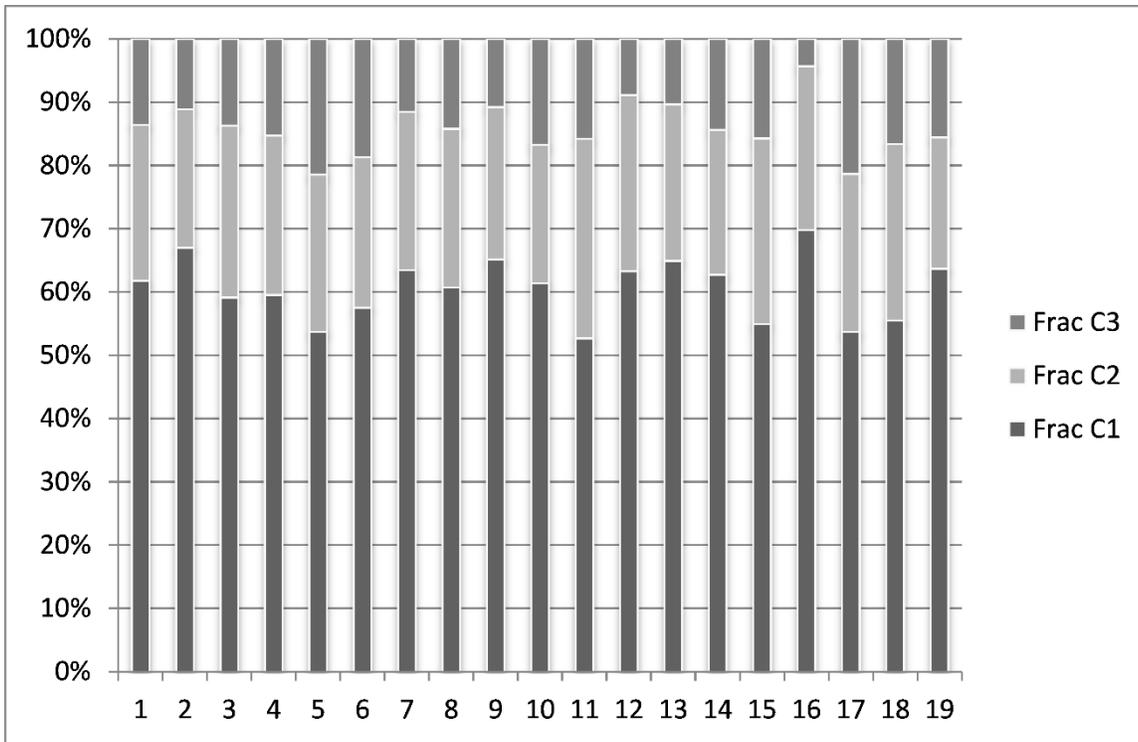


Figure 7. The bar graph shows the Pu activity fractions (normalized to total summed Pu activity of the three cartridges) in each MnO₂ cartridge at all 19 stations sampled on the R/V Polarstern ANT XXX-1 cruise. It can be seen that no systematic difference in the distribution of activity fractions in the cartridges occurs over all the sampling stations.