

¹²⁹I in sediment cores from the Celtic Sea by AMS through a microwave digestion process

Lérida-Toro, Victoria^{1*}, Abascal, Unai¹, Villa-Alfageme, María^{1,2}, López-Gutiérrez, José María^{1,3};
Klar, Jessica⁴, Hicks, Natalie⁵,

¹Centro Nacional de Aceleradores (Universidad de Sevilla, CSIC, Junta de Andalucía) (Spain),

²Dpto. Física Aplicada II, ETSIE, Universidad de Sevilla (Spain), ³Dpto. Física Aplicada I, EPS,

Universidad de Sevilla (Spain), ⁴Université de Perpignan UPVD - CEFREM (France), ⁵School of

Life Sciences, University of Essex (UK)

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ABSTRACT

Radiochemical methods before measurement are indispensable to determine Iodine-129 by Accelerator Mass Spectrometry (AMS) in environmental samples. In particular, in sediments, iodine is associated with both inorganic and organic matter, and it presents in several chemical forms. Therefore, the radiochemical procedure must be designed to extract all the different iodine species from the matrix, whilst being as robust and time effective as possible. In this work, different microwave digestion methods, together with the processing of the iodine species to be measured by

AMS, were tested and their performances are presented here. Two sediment cores, one with muddy sediment (core A) and one with permeable sandy sediment (core I), collected in the Celtic Sea, were used and the results were evaluated to determine an optimized iodine extraction. The method consisted of a microwave digestion with concentrated nitric acid followed by a double liquid-liquid extraction and the final precipitation of silver iodide (AgI), required to measure iodine by AMS. Back extraction of iodine in a reducing solution during purification was carried out with hydrazine (NH₂-NH₂). Subsequent additional steps were added to optimize all iodine species extraction. First, hydrochloric hydroxylamine (NH₂OH·HCl) and sodium bisulfite (Na₂S₂O₅) were used to homogenize all iodine species before extraction through a redox process. Second, sodium hypochlorite (NaOCl) was added to remove any final organic matter after digestion. The final method incorporated sodium hydroxide (NaOH) combined with NaOCl to facilitate reduction of iodine in solution and enhance the NaOCl effect. The different methods were validated against an internal standard and the last method was chosen, as it showed the most reproducible and accurate results. As practical application, Iodine-129 concentration from both cores were compared, showing concentrations between 0.19 x 10¹² at/kg and 7.16 x 10¹² at/kg for core A and between 0.28 x 10¹² at/kg and 2.40 x 10¹² at/kg for core I. Despite the ¹²⁹I diffusion detected in the deeper layers, depth profiles accurately reproduced Sellafield discharges, which is the nuclear fuel reprocessing plant closest to the cores.

1. INTRODUCTION

¹²⁹I is a long-lived radioisotope (T_{1/2}=15.7×10⁶ years) naturally present in the environment (5.4×10⁻⁶ kg·year⁻¹ [1]). It is also produced anthropogenically. Its main artificial sources are i) fallout from nuclear testing carried out between 1945-1980 (43-150 kg ¹²⁹I [2]), ii) nuclear accidents (for example, less than 2 kg ¹²⁹I were produced by Chernobyl accident [3]) and iii) discharges from Nuclear Fuel

Reprocessing Plants (NFRPs) [4,5]. In Europe, the greatest releases of ^{129}I to the environment come from Sellafield (United Kingdom) and La Hague (France) NFRPs, with well documented discharges. More than 6000 kg of ^{129}I have been discharged to the atmosphere and the marine environment up to 2013 by liquid and gaseous emissions from these facilities [6].

Due to its long half-life, the fact that it is very conservative in water, and its sources are well established temporally and spatially (due to the continuous releases in reported concentrations from NFRPs), ^{129}I has proved to be an excellent ocean tracer, especially in the Atlantic and Arctic Oceans [7–9].

The concentration of ^{129}I in the environmental and geological samples is normally too low to be measured by radiometric techniques ($<5 \times 10^{14}$ at/g for solid samples, or $<5 \times 10^{12}$ at/kg for water samples) [7]. For this reason, ^{129}I in environmental levels is usually measured by Accelerator Mass Spectrometry (AMS) [10], which is an ultrasensitive technique that combines conventional mass spectrometry techniques with a particle accelerator so that particles are accelerated to energies much higher than in other mass spectrometry techniques, obtaining very high sensitivities [11].

In AMS the $^{129}\text{I}/^{127}\text{I}$ ratio is measured, then ^{127}I is determined and ^{129}I is obtained indirectly from this. The first measurements step is a radiochemical procedure to separate iodine from the sample matrix, purify it and finally precipitate it as silver iodide (AgI), which is the chemical form needed to measure iodine by AMS. Radiochemical methods must be designed to efficiently extract all iodine species from the matrix, using methods as simple as possible and guaranteeing a low-probability contamination.

Extracting iodine from solid samples, such as marine sediments, can be done using different methods which include alkaline fusion, oxidizing pyrolysis, or microwave acid digestion. In the alkaline fusion method [12], decomposition of samples takes place in open crucibles using an oven set to above

250°C, with slow temperature ramps up to this temperature (to avoid iodine volatilization, temperature has to be increased less than 1°C/min, therefore, samples are obtained next day). Oxidizing combustion [13] is a more commonly used method for separation of iodine from solid sample, using quartz boats to hold the samples through a special combustion system. Using microwave, you get the sample in a solution completely digested in approximately one hour.

In this work, a microwave digestion procedure previously applied to solid materials [14], was adapted and optimized for the extraction of iodine from sediments and the determination of ^{129}I through AMS, in a fast method with low risk of contamination.

The microwave digestion process requires special equipment that use PTFE closed vessels and allows the simultaneous digestion of more than 10 samples. Key advantages of microwave digestion include the shorter processing time if several samples are digested; the small amount of sample need; a low probability of cross-contamination; and the reduced loss of volatile species as is typical with iodine in an acidic environment.

After the digestion of the sample, the next step eliminates the remaining organic matter, avoiding any loss due to volatilization, and the homogenization of all iodine species through a redox process. Next, the iodine is purified through a double liquid-liquid extraction with a solvent and, finally, the extracted iodine is precipitated as AgI.

Different modifications of former methods were evaluated, to streamline the process making it less time consuming, and ensure the extraction of all iodine species was achieved, whilst increasing reproducibility. Aliquots from two sediment cores from the Celtic Sea with contrasting characteristics and a standardized sediment sample were used in the optimization of this new radiochemical method.

The final optimized version of this procedure was used for the measurement of the ^{129}I concentration in the both sediment cores to produce a full sediment profile of ^{129}I in each.

2. MATERIAL AND METHODS

2.1. Samples description

Two sediment cores (A and I) from the Celtic Sea (Figure 1) were collected in March 2015 during the DY030 sampling campaign of the new RRS Discovery. The sampling campaign was included in the Shelf Sea Biogeochemistry (SSB) project supported by Natural Environment Research Council from UK. A Core ($51^{\circ} 13' 59''\text{N}$; $6^{\circ} 7' 59'' \text{W}$) was sampled on May the 11th and I Core ($50^{\circ} 36' 0'' \text{N}$; $7^{\circ} 5' 59'' \text{W}$), five days later, on May the 16th. Core A is 25 cm long and Core I is 21 cm. Both cores (10 cm diameter) were sliced into segments of different thicknesses, 0.5 cm segments in the most superficial part (top 2 cm), 1 cm segments in the middle (2-15 cm) and 2 cm segments in the deepest layers to the bottom of the core.

2.2. Measurement technique

^{129}I was measured by AMS using the 1MV Tandem AMS system (HVEE) in the Centro Nacional de Aceleradores (CNA) in Sevilla, Spain. A detailed description of AMS system has been reported in [15,16] and recent status and updates in [17,18].

Iodine is extracted as I^- through a Cs^+ sputtering process as the source. The ions are selected according to their mass and injected into accelerator using a low energy 90° injector magnet (LEM). Negative ions are accelerated, and charge inversion takes place in the accelerator. Helium gas is used as stripper gas at an optimum pressure of 1.8×10^{-2} mbar. This stripper gas has shown to give high transmission for heavy ions in AMS [19]. To select charge state 2+ after the stripping process, terminal voltage is

set to approximately 700 kV. In these conditions, transmission is approximately 40%. After that, a high-energy 90° analyzing magnet (HEM) selects $^{129}\text{I}^{+2}$ ions and an 120° electrostatic deflector (ESA) performs the final charge, energy and mass analyses of the beam. The detector consists of a gas ionization chamber where the energy of the ions is measured.

All samples, standards and blanks were measured for at least four different cycles in each measurement. One standard is measured for every four or five samples and approximately one blank for every twelve samples. The average value of measured blanks is calculated and subtracted to the isotopic ratios obtained for samples and standards. The uncertainty associated with the average blank isotopic ratio was estimated as a maximum between statistical errors and standard deviations of the mean. Then, standard correction was carried out for all sample isotopic ratios. [20]

Table I shows the values of ratio $^{129}\text{I}/^{127}\text{I}$ for instrumental blanks and standards, samples and chemical blanks. Instrumental blanks isotopic ratios are $^{129}\text{I}/^{127}\text{I} = 0.9\text{-}2 \times 10^{-13}$. The standard used, Q2, was prepared in our laboratory by isotopic dilution and has been determined by AMS to have an isotopic ratio of ratio of $^{129}\text{I}/^{127}\text{I} = (1.117 \pm 0.046) \times 10^{-11}$ in the ETH Zurich.

2.3. Radiochemical procedure

All reagents used were commercial products of analytical grade. Solutions were prepared using ultrapure water ($\text{H}_2\text{O-MQ}$).

The carrier solution was prepared by weighing 50 mg of solid iodine (*Woodward Iodine*) and dissolving it in a reducing alkaline solution prepared with 1 g of sodium hydroxide (NaOH) lentils and hydrazine hydrate ($\text{NH}_2\text{-NH}_2$) 80% dissolved in 50 mL ultrapure water. The iodine solution concentration is calculated accurately, it must be 1 mg I per ml.

At least one procedure blank was prepared for all sample series, in order to control and check for contamination during the preparation process. Blanks were prepared following the same method as the samples but without adding any sample material.

The general radiochemistry consisted essentially of extracting the iodine from the sample, previously digested as described, using a double liquid-liquid extraction with a solvent and, finally, precipitating the extracted iodine in the required AgI form. One first microwave oven based method was implemented by Guzman et al. [14] and consisted of a microwave digestion with concentrated nitric acid directly followed by double liquid-liquid extraction, first in an organic solvent and then in a reducing solution. Back extraction of iodine in a reducing solution during purification was carried out with sodium hydrogen sulfite (NaHSO_3). Finally, the iodine was precipitated as AgI using silver nitrate (AgNO_3). In an intermediate step, SO_3^{2-} and SO_4^{2-} ions, added to the solution through the NaHSO_3 , had to be eliminated. They were removed in an additional step by the addition of saturated barium nitrate solution ($\text{Ba}(\text{NO}_3)_2$) followed by centrifugation several times, to avoid precipitation as silver sulfate and silver sulfite (AgSO_4 and AgSO_3 , respectively).

Previous tests showed that, generally, the elimination of SO_3^{2-} and SO_4^{2-} ions was not completely efficient and the purity of the AgI was reduced due to the coprecipitation of AgSO_4 and AgSO_3 , which were responsible for lower measurement currents. In this work, to avoid the precipitation of these sulfates and to make the procedure less time consuming, we have implemented a modification of that former method to avoid the addition of sulfur and the extra step of removing SO_4^{2-} and SO_3^{2-} ions. This way, in all the methods we present and evaluate here, NaHSO_3 was substituted by $\text{NH}_2\text{-NH}_2$ as reducing agent in the iodine back extraction during purification. This first method (denoted as method A), that only included reducing reagent substitution, did not provide robust results, as they were not

reproducible and showed high variability. Sediments are complex matrices that contain organic and inorganic fractions in highly variable proportions, including iodine attached in multiple species. For this reason, several amendments to method A were introduced to maximize the extraction of all the iodine species. Four versions were denoted successively as A (described above), B, C and D, different changes were added from method A through to method D in subsequent additions and/or modifications. Each method developed the improvements already made in the previous version, building on the improved methodology each time. The aim was to ensure organic matter decomposition and chemical equilibrium between iodine species, as well as avoiding the loss of iodine by volatilization after acid digestion. The scheme of the modifications implemented are shown in Figure 2 and can be described as follows:

Method A. As described above, hydrazine ($\text{NH}_2\text{-NH}_2$) is used as extracting solution, in place of NaHSO_3 .

Method B. Includes a redox adjustment after microwave digestion by the addition of $\text{NH}_2\text{OH}\cdot\text{HCl}$ and $\text{Na}_2\text{S}_2\text{O}_5$, in order reduce iodate (IO_3^-) to iodide (I^-), to homogenize iodine chemical forms prior to iodine purification. This way ensures that the iodine extracted from the sample and the iodine from the carrier are in chemical equilibrium.

Method C. NaOCl is added after the microwave digestion to decompose any remaining organic matter.

Method D. NaOH was added after microwave digestion to facilitate reduction of iodine in solution, enhancing the NaOCl effect.

In summary, the most complex method (D) includes the following steps:

- 1) digestion of approximately 250 mg of sample and 3 mg of carrier with 10 mL of concentrated HNO_3 for 20 min total time at 200°C and 1800 MW potency (5 min at 100 °C, 10 min at 160 °C, 20 min at 200°C) using a microwave system (Milestone ETHOS™ EASY with SK-15 easy TEMP high-pressure rotor featuring 15 TFM vessels with a volume of 100 mL).
- 2) Recovery of the digested solution with H_2O -MQ water to a final volume of 100-150 mL.
- 3) Addition of 0.5 g NaOH lentils and 1 mL NaOCl 14%.
- 4) Redox adjustment using 1 mL of 1M $\text{NH}_2\text{OH}(\text{HCl})$ and 5 ml of 1M $\text{Na}_2\text{S}_2\text{O}_5$.
- 5) Purification of iodine in a double liquid-liquid extraction. First, iodine is oxidized with 2 ml 0.45 g/l NaNO_2 in an acidic environment to extract it in 100 mL of CH_3Cl . Second, a back extraction in a reducing aqueous solution (containing 0.5 mL of $\text{NH}_2\text{-NH}_2$ 80% + 30 mL H_2O -MQ) is used.
- 6) Iodine is precipitated as AgI using 0.5M silver nitrate (AgNO_3) solution in excess.
- 7) Finally, the precipitate is cleaned, dried and pressed, mixed with Niobium, in a copper cathode.

The four methods were tested using different aliquots of cores A, I and a standard sediment sample. Figure 3 shows the results of the measurement of the cores and the standard in the four cases and the averaged results are shown in Table II.

3. RESULTS AND DISCUSSION

3.1. Radiochemical method optimization and validation

In order to evaluate the effect of the proposed variations of method A, triplicates of depth sections 19-21 cm of core I and 15-17 cm of core A were prepared, applying the four methods A, B, C and D.

In addition, an internal standard of soil from Xi'an AMS Center (XASTD), for which the ^{129}I concentration was already known, has been prepared to optimize and validate the radiochemical methods.

It is important to emphasize that both ^{129}I and the carrier ^{127}I have to be correctly extracted from the sample. As AMS measures isotopic ratios $^{129}\text{I}/^{127}\text{I}$, and considering that ^{127}I from the sample is much lower than ^{127}I from the carrier, ^{129}I in the sample is determined as the product of the AMS isotopic ratio times the added carrier ^{127}I . The results are correct if both ^{129}I from the sample and ^{127}I are extracted in the same proportion. When a method is not efficiently and robustly extracting all iodine forms some results would be overestimated and others will be underestimated, presenting high variability. Underestimated ^{129}I values can be obtained if there is an incomplete extraction of ^{129}I from the samples. But in the case that the carrier ^{127}I is not completely recovered overestimated ^{129}I values can be also found. This could be the case of volatilization losses during digestion or other treatments during the process. In our case, recovery tests have not been carried out because the validity of the method has been checked through the preparation of different aliquots and a previously measured sample. This way the selected optimized method should provide the most reproducible values in all cases and within the range of the expected value given by the standard.

In addition to selective extraction of ^{127}I , overestimated ^{129}I values may also be due to contamination with external ^{129}I during sample preparation or cross contamination during measurement. The contamination with ^{129}I can be checked by preparing blank samples in the same way as real samples ("chemical" blanks). High chemical blank values would indicate contamination during sample preparation and high values of instrumental blanks (non processed) indicate that cross contamination is happening at the ion source.

Figure 3 displays ^{129}I concentration results and average of the triplicates for the four methods, prepared for the two layers of core A and I (Figures 3A and 3B), and for the internal standard sediment (Figure 3C). The average values of the triplicates and their associated uncertainties are shown in Table II.

The substitution of hydrogen sulfite for hydrazine in method A comprises a significant simplification in the sample preparation process in relation to the original method but results still have a large variability between aliquots in both cores and the results for core I aliquots are overestimated. The application of the redox process before extraction in method B provides a significant improvement of the results in core I, as results become relatively homogeneous, but not in core A, where results within aliquots are still highly variable. Again, method C provides reproducible results for core I, however, the reproducibility was not significantly improved in core A. Finally, it is the most complex method (D) which shows the most constant values and hence lowest standard deviation uncertainties for both cores.

The different performance of the methods in both cores is due to the very different composition of the two cores: core I is sandy mud (66% sand and 35% clay) and core A is mud (35% sand and 65% clay) [21]. Important differences in the matrices are found in their different content of organic matter, usually being higher in the muddiest samples (core A) than in sandy matrices (core I). Iodine is strongly bound to the organic matter and hence its extraction from core A, with a higher concentration of organic material due to the finer cohesive particles, is more difficult. For this reason, the reproducibility of ^{129}I concentration in core A increases when extra steps are included to fully decompose all organic matter and release all iodine species, obtaining a total recovery of both ^{127}I and ^{129}I isotopes.

The best performance of method D was corroborated by the analysis of the Internal Standard of Xi'an AMS Center (XASTD) [22]. In Figure 3C, XASTD ^{129}I concentration results showed that the simplest modified method (A) does not perform well, as ^{129}I results were not within the uncertainties of the reference value given for the standard, and results differ in 64.1% over the reported value. When extra steps were added in the successive modifications (B, C, D), results were more reproducible and showed lower relative deviations. However, method B still presents variability within aliquots and the result is overestimated. ^{129}I measured values obtained using method C and D were the closest to the reported reference value (Table II). Note that one of the samples prepared using method D corresponded to an outlier and this value was discarded in the calculation of the average value shown in Figure 3C, because a low current value was detected during the measurement of this sample, and inconsistent results are usually found in these cases.

Average values for the XASTD standard for method C and D are, respectively, $(0.391 \pm 0.017) \times 10^{11}$ at/kg and $(0.390 \pm 0.046) \times 10^{11}$ at/kg (when the result obtained from low current value is discarded). Both results are in good agreement within 2-sigma with the reported reference value $(0.328 \pm 0.030) \times 10^{11}$ at/kg. Both methods performed well in the evaluation of the value of the standard sample, however the variability of the results in the sediment cores when method C was applied suggests that method D is the best choice for our method for ^{129}I sediment measurement.

Finally, to analyze the potential contamination introduced during sample preparation process, compiled $^{129}\text{I}/^{127}\text{I}$ ratios of instrumental blanks and standards, samples and chemical blanks are shown in Table I. Note that chemical blanks showed instrumental blanks typical of isotopic ratios levels, concluding that contamination is negligible in our samples. In any case, the detection limit is strongly

determined by the limits of the measurement technique, for example the need of stable Γ currents extracted from the source and background level.

3.2. ^{129}I determination in Celtic Sea sediment cores

In Figure 1, the general circulation of water masses in the Celtic Sea shows how the ^{129}I , released from the two NFRP operating in this zone, La Hague and Sellafield, is transported into and out of the Irish Sea. Liquid discharges are released directly to the Irish Sea, in the case of Sellafield, and to the English Channel, in the case of La Hague. Most of the ^{129}I from Sellafield is transported out of the Irish Sea, into the North Sea and finally, through the Norwegian Coastal Current, to the Arctic Ocean [7].

Concentrations ranged from $(0.19-7.16) \times 10^{12}$ at/kg in core A to $(0.28-2.40) \times 10^{12}$ at/kg in core I. The ^{129}I concentration results of core A have greater variability than those of core I. In addition, the core ^{129}I concentration corresponding to more superficial sections (less than 10 cm deep) are significantly higher in core A than in core I. These differences in ^{129}I concentration levels might be accounted for to the different content of organic matter in both cores. As a biophilic element, ^{129}I is preferably bounded to the smaller particles of the muddy A core, with a higher organic content within the matrix. Whereas there is lower organic content and larger sand particles in the more loosely bound core I. This is confirmed by the amount of organic carbon content measured in both cores for every depth [21]. Values ranged between 0.211 mg and 0.579 mg for core A and between 0.084 mg and 0.233 mg for core I [23].

The main currents in the Nordic Seas transport ^{129}I from NFRPs to different areas of North Atlantic and the Arctic Oceans [24–29], nevertheless, part of those discharges are transported south-west having a direct impact in the Atlantic Ocean [30–33]. Therefore, the results from the sediment cores

A and I from the Celtic Sea, South-West of Sellafield (Figure 4) show how, apart from the visible ^{129}I diffusion in the deep layers, depth profiles accurately reproduced Sellafield discharges shape.

From the two NFRP's that operate in NW Europe, Sellafield is the one that mostly influences Celtic Sea radionuclide concentrations, although dispersion models [33] and previous studies [32,34] have determined that only 20% of Sellafield releases are transported southbound to the Celtic Sea.

To study the release and dispersion of aqueous ^{129}I from Sellafield to reach South West of the Irish Sea, where the cores are located, sediment rates and delay times were estimated in a qualitative way, through the comparison of the ^{129}I concentration profiles and the history of liquid emissions from Sellafield (also included in Figure 4).

Two marked maximums in both cores are located in the most superficial layers (above 10 cm depth), and then, a considerable downward trend in the levels of ^{129}I in the deepest layers of the core.

For Core A, the maximum level of 7.16×10^{12} at/kg is found at 8.5 cm depth. We correlate it to the Sellafield liquid discharges maximum value of 1998. In addition, there is secondary maximum value of 6.71×10^{12} at/kg in 3.5 cm depth that we have associated to the Sellafield liquid discharges maximum values between 2002 and 2004.

For Core I, there is a maximum level of 2.40×10^{12} at/kg in 3.5 cm depth associated to the Sellafield liquid discharges maximum values between 2002 and 2004. The secondary maximum of 1.77×10^{12} at/kg around 6.5 cm depth might correspond to a maximum value in the Sellafield discharges in 1998. Then, the delay time between the discharge and the arrival to the sampling points as well as the sedimentation rates are calculated using simple approach, that chose the values of both parameters that best optimize the fitting between the ^{129}I profile and the historical liquid discharges.

Through this optimization, the time and depth elapsed between peaks, the transit time from Sellafield to the sampling points is calculated as approximately 6 years in both cases. This time is supported by the fact that it is found to be the same in both cores, that were sampled at closed locations. Furthermore, transit time of 6 years from Sellafield to the cores site is supported by Villa-Alfageme et al. [33], which used a dispersion lagrangian model to estimate that the age of ^{129}I in that area is between 5 and 7 years.

Finally, from the optimized fitting of ^{129}I concentrations and ^{129}I releases from Sellafield, we estimated a sedimentation rate of $7.1 \text{ mm}\cdot\text{year}^{-1}$ for Core A and $5.9 \text{ mm}\cdot\text{year}^{-1}$ for Core I, assuming that the concentration in the shallowest layer correspond to the year where the cores were sampled, in 2015. From a carbon or sediment fluxes perspective, this is the first evaluation of the sedimentation rates in the area of study [21]. Our estimations are in agreement with the rates estimated offshore of the Irish Sea measuring Pu isotopes, $5.20 \text{ mm}\cdot\text{year}^{-1}$ [35]. The good agreement between techniques shows the potential of this technique to estimate sedimentation rates. Nevertheless, the results should be further improved in future works analyzing in detail iodine properties and diffusivity and comparing to independent techniques not relying on radioactive measurements.

When we compared with the La Hague discharges, it can be seen that apparently there is a maximum in Core A and Core I that seems to coincide with a maximum in the emissions. However, that would imply that the transport of ^{129}I from La Hague to south West of the Irish Sea occurs in less than a year, whilst according to Villa-Alfageme et al. [33] dispersion model, transit time from La Hague to that area is at least 5 years. Therefore, based on sea currents in the North Sea and the results of this model, releases from La Hague do not enter back into the Celtic Sea, so would not be expected in these profiles from these Celtic Sea sites.

4. CONCLUSIONS

Microwave digestion is a novel method, which is fast, presents the lowest possibility for cross contamination, uses very little sample amount and reduces loss of iodine by volatilization. This method (method D) is the most reproducible and accurate method, which adds several additional steps to the digestion for complete organic matter decomposition and for redox adjustment to improve iodine recovery in relation to previous methods. Comparison between aliquots and with a sediment standard show results are robust and show small variability. Depth ^{129}I profiles of core sediments analyzed accurately reproduce Sellafield discharges, with a six years' delay and similar deposition rates, of approximately $6 \text{ mm}\cdot\text{year}^{-1}$, in two different cores. This approach could be used to estimate sedimentation rates in shelf seas sediments of areas affected by ^{129}I releases.

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7. TABLES

Table I. Summary of measured isotopic ratios $^{129}\text{I}/^{127}\text{I}$ of instrumental blanks and standards, samples, internal standard and chemical blanks.

	$^{129}\text{I}/^{127}\text{I}$
Instrumental blanks	$1-2 \times 10^{-13}$
Instrumental standard nominal value (Q2)	$(1.117 \pm 0.046) \times 10^{-11}$
Core sediment samples	$2-20 \times 10^{-12}$
Internal standard (XASTD)	$0.6-2 \times 10^{-12}$
Chemical blanks for sediment samples (after blank subtraction)	$1-2 \times 10^{-13}$
Chemical blanks for internal standard (after blank subtraction)	$0.2-0.4 \times 10^{-13}$

Table II. Average values and calculated uncertainty of triplicates prepared by each method of depth section 19-21 cm for core I (sandy), depth section 15-17 cm for core A (muddy) and Xi'an Center Internal Standard (XAST).

Method	Average ^{129}I concentration ($\times 10^{11}$ at/kg)		
	Core I	Core A	XAST
A	2.770 ± 1.139	12.100 ± 1.393	0.969 ± 0.612
B	1.590 ± 0.071	13.000 ± 1.490	0.592 ± 0.348
C	1.727 ± 0.543	13.433 ± 2.255	0.391 ± 0.017
D	1.520 ± 0.121	11.367 ± 0.216	0.432 ± 0.108
			$(0.390 \pm 0.046)^1$
Reported value [21]			0.328 ± 0.030

¹corrected value discarding outlier

8. FIGURES

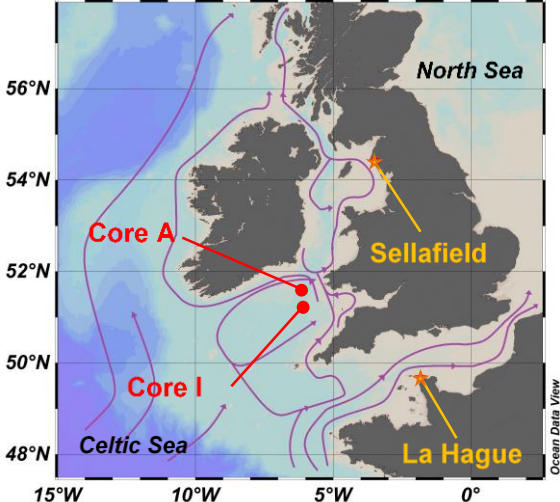


Figure 1. Sampling location and detail of the general circulation of water masses in the Celtic Sea

(based on [33])

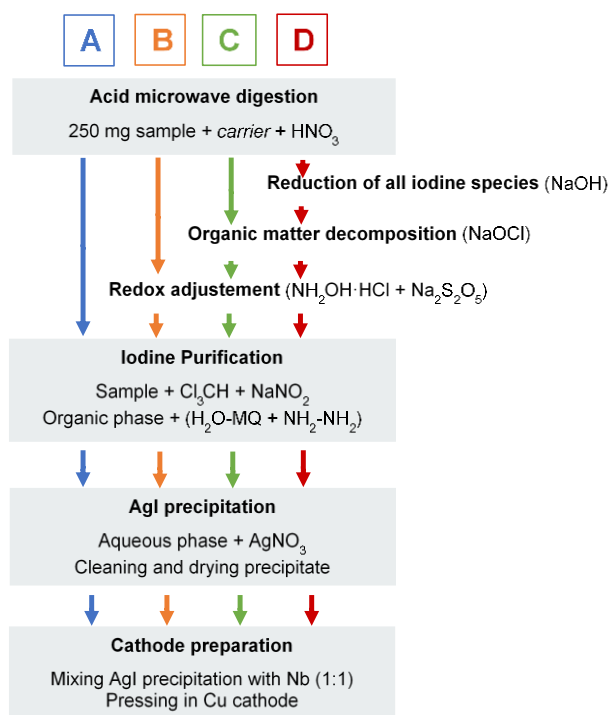


Figure 2. Scheme of the original method [13] with proposed modifications. A: Substitution of NaHSO₃ by NH₂-NH₂ as a reducing agent in back extraction process. B: Addition of NH₂OH·HCl and Na₂S₂O₅ to homogenize iodine chemical forms through a redox adjustment. C: Addition of NaOCl to decompose remaining organic matter. D: Addition of NaOH to facilitate iodine reduction in solution after digestion and enhance NaOCl effect.

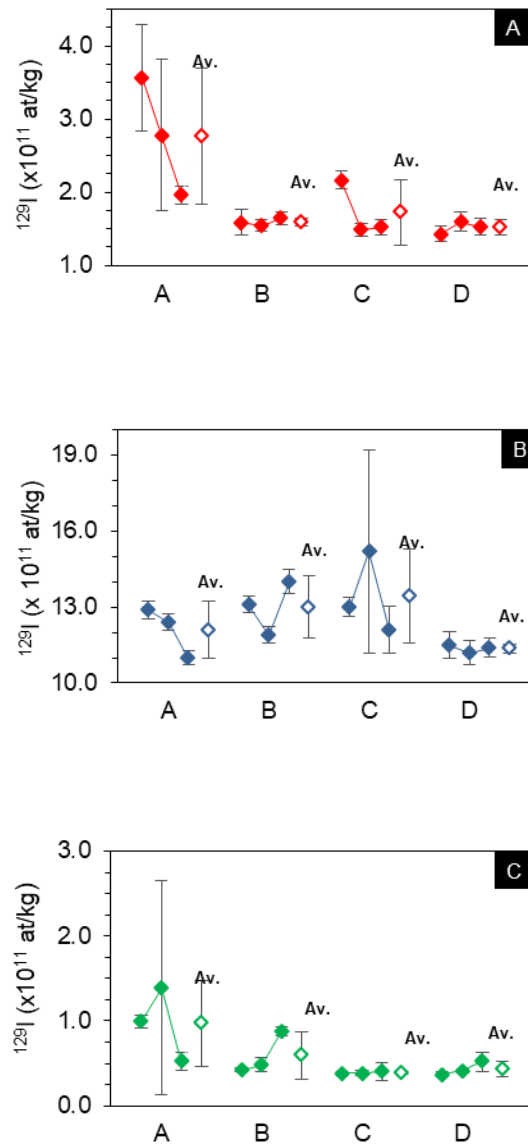


Figure 3. ^{129}I concentration results with error ($\sigma=2$) and average of the triplicates (Av.) with calculated uncertainty prepared by four performed methods for two core samples (I and A) from the Celtic Sea (51°N ; $6^\circ 30' \text{W}$) and an internal standard sediment. A) Depth section 19-21 cm for core I (sandy). B) Depth section 15-17 cm for core A (muddy). C) Xi'an Center Internal Standard (XAST).

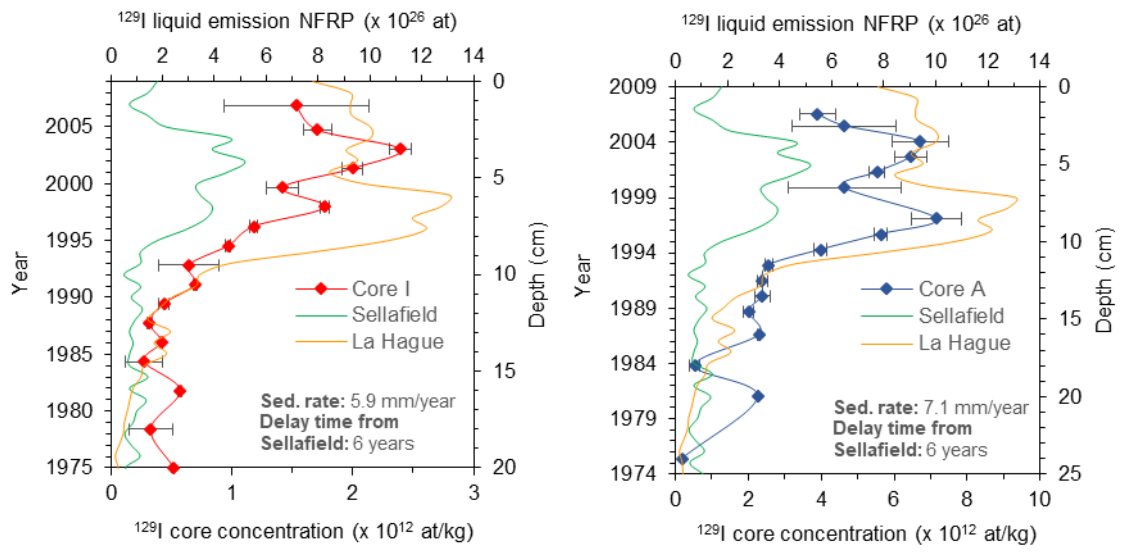


Figure 4. Results of ^{129}I concentration depth profiles for Core-A and Core-I obtained using method D (in 10^{12} at/kg) compared to known Sellafield and La Hague liquid discharges to the ocean (in kg).