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^{129}I from nuclear fuel reprocessing; potential as an oceanographic tracer

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Using the technique of accelerator mass spectrometry (AMS), we have measured ^{129}I in samples of seaweed and seawater taken at various distances along the coasts from the nuclear fuel reprocessing facilities at La Hague, France and Sellafield, Great Britain, as well as in the North Sea and in the North Atlantic. The deduced seawater ^{129}I/^{127}I ratios, which vary by 4 orders of magnitude, demonstrate the modest sized samples required for such measurements; less than 1 ml from the English Channel or Irish Sea, less than 1 litre in the North Atlantic. It thus should be possible to monitor not only surface circulation but also deep water formation in this latter area, which is believed to have considerable climatic influence. Given its high sensitivity for detection, and the well defined temporal and spatial distribution of its source function, ^{129}I is a potentially attractive addition to the available suite of oceanographic tracers.

1. Introduction

Because of its long half-life (16 My), determination of ^{129}I by radioactive decay counting is quite inefficient. Several other techniques, including activation analysis, low energy mass spectrometry and laser spectroscopy, have been used (for a brief review, see ref. [1]) but have not found widespread adoption. This is presumably due to the rather sophisticated instrumentation necessary and, perhaps even more important, the fact that the sensitivity of these alternative techniques is generally limited by the value of the ^{129}I/^{127}I ratio in the sample to be measured. AMS was first applied to the determination of ^{129}I more than 10 years ago, using a very large tandem accelerator [2]. Kilius et al. [3] have recently demonstrated that, by using sufficiently high resolution electrostatic and electromagnetic analysis both before and after the accelerator, a small tandem accelerator can give AMS measurements of comparable quality to the larger systems.

Before the nuclear era, when ^{129}I on the earth was principally due to spontaneous fission of ^{238}U and cosmic ray induced spallation of Xe in the atmosphere, the ratio of ^{129}I/I in the ocean is estimated to have been $\sim 10^{-12}$ [4–7]. In the post-nuclear era, anthropogenically produced ^{129}I, principally from nuclear reactor operation and nuclear bomb testing, overwhelmingly dominates natural production. The total release of ^{129}I in nuclear weapons testing is estimated to have been $\sim 2 \times 10^{26}$ atoms [8]. Assuming this quantity has been homogenized in an ocean mixed surface layer of 100 m depth, and using an ocean ^{127}I concentration of 60 μg/l [9], the resulting ^{129}I/^{127}I ratio would be $\sim 2 \times 10^{-11}$. This is within the range, but somewhat lower than the average ($\sim 10^{-10}$), of the relatively few available measurements on post-bomb marine material [5–7]. This may be due to incorporation into some of those samples before complete homogenization had occurred.

In the thermal neutron induced fission of ^{235}U, ^{129}I is produced with a yield of $\sim 0.6\%$. During the reprocessing of spent nuclear fuel, a significant fraction of the ^{129}I so formed is released to the oceans. The largest nuclear fuel reprocessing facilities presently operating are located at La Hague, France and Sellafield, Great Britain. Based on ^{129}I/I measurements in archived seaweeds, together with available discharge data, we tentatively estimate that the ^{129}I input of these two facilities to the oceans during the past 25 years has been ~ 1.2 ton or 5×10^{27} atoms [10]. This is an order of magnitude larger than the total estimated ^{129}I in the pre-nuclear era ocean, approximately 25 times the input due to nuclear weapons testing, and several hundred times that released by Chernobyl. It is expected therefore that the reprocessing signal will dominate these other sources of ^{129}I in the North Atlantic and Arctic oceans. This can be compared to certain other fission nuclides such as ^{137}Cs or ^{90}Sr for example, where the yearly reprocessing emissions were

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never larger than ~ 1%, and are currently ~ 0.01%, of the cumulative weapons fallout.

Although it is biophillic [11] (and thus may also be useful as a "marker" of organic matter formation, transport and regeneration) the observed residence time of iodine in the ocean (~ 10^5 years) suggests that it behaves almost conservatively in the open sea. Realizing that the technique of AMS can detect as few as 10^6 atoms of ^{129}I, it appeared to us that such emissions could potentially be a very sensitive oceanographic tracer in the European polar seas region, where ocean circulation and deep water formation are believed to have important climatic influences [12]. An advantage of ^{129}I compared to certain other transient tracers (chorofluorocarbons, nuclear bomb derived fallout, ^{85}Kr) is its more specific spatial source function. Thus its use, either alone or in combination with one of the above tracers [13,14], might help better understand the formation of North Atlantic deep water, which is a subject of continuing interest [15,16].

2. Experimental procedure

In order to demonstrate its potential as an oceanographic tracer we have measured ^{129}I in samples of seaweed and seawater taken at various locations as shown in Fig. 1. Seaweed was originally chosen because of its characteristic of strongly concentrating iodine although, as will be shown below, the sensitivity of the AMS technique usually makes such concentration totally unnecessary. However, the characteristic of sea-

Table 1
Sample characteristics and experimental results

Location	Map code	Sample date	Sample type	Water depth [m]	Sample wt [g] or vol. [ml]	^{129}I/^{127}I measured (10^{-11})	^{127}I [ppm] [b] or [μg/l]	^{129}I/^{127}I in sample (10^{-10})
Doélan (I) [a]	1	1/9/91	Seaweed	0	17.53	95 ±20	–	9.5 ± 2.0
Doélan (II)		1/9/91	Seaweed	0	19.27	97 ±20	–	9.7 ± 2.0
Doélan (I)		1/12/91	Water	0	100	0.29 ± 0.04	120 ± 6.0	12.3 ± 1.8
Doélan (I)		1/3/92	Water	0	100	0.13 ± 0.02	52.1 ± 2.6	12.7 ± 2.1
Roscoff	2	26/6/85	Seaweed	0	11.76	50.3 ± 1.1	990 ±50	500 ±30
Cancale	3	9/6/91	Seaweed	0	11.30	343 ±23	300 ±15	3400 ±300
Carteret	4	4/2/91	Seaweed	0	18.42	124 ± 2	650 ±65	7600 ±800
Herquemoulin	5	15/6/84	Seaweed		12.41	108 ± 3	525 ±53	10000 ±1000
		6/2/91	Seaweed	0	11.03	213 ± 6	690 ±70	37000 ±3800
Fermanville	6	5/2/91	Seaweed	0	12.07	185 ± 5	754 ±75	15000 ±1500
Gatteville	7	5/4/91	Seaweed	0	7.40	796 ±63	310 ±15	8000 ±700
Luc sur Mer	8	15/1/91	Seaweed	0	11.18	310 ±19	340 ±17	3100 ±250
Honfleur	9	27/2/91	Seaweed	0	10.75	445 ± 8	450 ±19	4500 ±240
49°52′N, 00°00′E	10	1/12/91	Water	0	100	27 ± 3	55.5 ± 2.8	4900 ±600
Gravelines	11	11/1/91	Seaweed	0	11.45	311 ± 7	790 ±40	3100 ±200
Lowestoft	12	20/3/92	Water	0	100	3.9 ± 0.5	46.5 ± 2.3	430 ±60
Heysham	13	5/4/92	Water	0	100	32 ± 4	36.5 ± 1.8	8900 ±1200
Maryport	14	5/4/92	Water	0	100	18 ± 2	36.2 ±1.8	5100 ±600
56°00′N, 06°00′E	15	27/11/91	Water	0	100	2.4 ± 0.3	52.8 ± 2.6	460 ±60
Lossimouth	16	7/4/92	Water	0	100	1.8 ± 0.2	57.8 ± 2.9	160 ±20
61°20′N, 7°53′W	17	20/8/90	Water	200	900	0.32 ± 0.04	58.0 ± 2.9	3.1 ± 0.4
Thorshavn	18	18/7/89	Seaweed	0	17.31	29 ± 4	–	2.9 ± 0.4
Sørvagur	19	15/7/89	Seaweed	0	10.01	39 ± 5	–	3.9 ± 0.5
63°50′N, 6°05′W	20	19/8/90	Water	50	300	0.29 ± 0.03	52.9 ± 2.7	9.3 ± 1.1
		19/8/90	Water	200	300	0.23 ± 0.04	52.8 ± 2.6	7.4 ± 1.3
		19/8/90	Water	1000	300	0.29 ± 0.03	58.9 ± 3.0	8.4 ± 1.0
Vestmarnaeyjar	21	6/12/91	Seaweed	0	18.01	24 ± 5	–	2.4 ± 0.5
Grimsy	22	15/12/90	Seaweed	0	10.00	29 ± 6	–	2.9 ± 0.6
		6/12/91	Seaweed	0	17.60	39 ± 6	–	3.9 ± 0.6
Raudfjorden	23	8/9/92	Seaweed	0	1.94	26.0 ± 0.5	194 ± 8	37.2 ± 1.2
Adventfjorden	24	8/9/92	Seaweed	0	1.92	0.23 ± 0.004	1.90 ± 0.06	32.2 ± 1.1
70°23′N, 31°31′E	25	9/9/92	Water	0	250	1.76 ± 0.18	48.7 ± 2.5	110 ±12

[a] Doélan (I) and Doélan (II) refer to two nearby locations.

[b] For seaweed this concentration is the amount extracted (expressed as ppm of dry seaweed wt). This is the relevant factor for determining the dilution factor for ^{129}I, even though it may not represent total ^{127}I in seaweed.

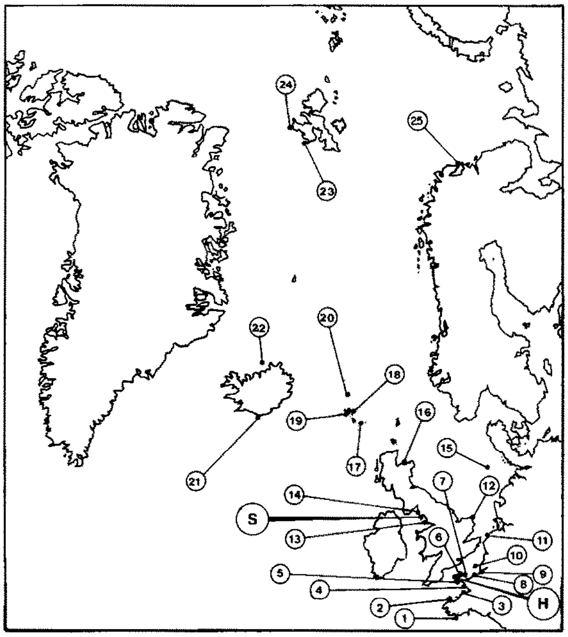

Fig. 1. Map showing sample locations. H and S indicate the reprocessing plants at La Hague and Sellafield, respectively.

weed to "integrate" an ^{129}I signal over several weeks may be advantageous when monitoring close to rapidly varying emission sources. The advantage of using seawater, of course, is that samples may be taken from any ocean location, and even at depth.

Seaweed samples were treated either at Toronto by a simplified version of a procedure described in ref. [6] or at Orsay by a procedure to be described in detail elsewhere [Z.Q. Zhou, thesis, in preparation]. Briefly, ~ 10 g of dried and ground up seaweed were charred to reduce bulk and burned in O_2, (Toronto) or dissolved in NaOH and ashed at 650°C in air (Orsay). The resulting ash was leached with H_2O. For samples where the $^{129}I/^{127}I$ ratio was estimated to be too large to measure directly (in order not to contaminate the ion source of the accelerator), the iodine in the leachant was determined by neutron activation analysis (Toronto) or colorimetry (Orsay). Aliquots of these samples were then diluted with I carrier. After being oxidized to I_2, the iodine was extracted into CCl_4, then reduced and back-extracted into aqueous solution, and finally precipitated as AgI. The dried AgI was mixed with niobium powder and pressed into cathodes for introduction into the ion source of the accelerator. The seawater samples were processed at Orsay by a procedure which will be described in detail elsewhere [Z.Q. Zhou, thesis, in preparation]. Briefly, an aliquot was first taken for determination of stable iodine by a colorimetric procedure [17]. KI carrier was then added and the iodine was transformed to IO_4^- in order to ensure isotopic equilibrium. The IO_4^- was then transformed to I_2 and extracted into CCl_4, after which the treatment was similar to that described for the seaweed. The AMS measurements were carried out at the IsoTrace facility according to the procedure described in ref. [6].

3. Results

The results are summarized in Table 1. Uncertainties in the measured $^{129}I/^{127}I$ ratios were estimated on the basis of counting statistics, variations of the standard during the measurements, and the reproducibility of duplicate determinations when these were carried out. For seawater, or seaweeds where carrier was added, an additional uncertainty due to the measured ^{127}I (and thus dilution factor) was included.

4. Discussion

The main purpose of the present work was to demonstrate the feasibility of our proposed application. Using the results given in Table 1, one can estimate the minimum sample requirements for ^{129}I analyses in the region studied. Thus in the English Channel or Irish Sea, such determinations could be made on water samples of less than 1 ml (although there is no apparent advantage in working with such small quantities), while 1 litre samples appear sufficient for anywhere in the North Atlantic. This can be compared to other reprocessing derived nuclides (^{137}Cs, ^{90}Sr, ^{99}Tc) that often require in this region tens or even hundreds of litres for analysis.

Knowing their stable iodine content, one can also estimate the minimum sample size for various other potential marine samples (plankton, shellfish, etc). One finds, for example, that over the whole area studied, one could measure ^{129}I in a single oyster!

Because most of the emissions from La Hague and Sellafield end up in the North Atlantic we believe one of the potentially most exciting applications of ^{129}I is as a tracer of deep water formation in this region. While an estimated post-bomb ratio of $\leq 10^{-10}$ for $^{129}I/^{127}I$ in ocean surface water has been cited earlier, the ratio for deep water is expected to be still $\sim 10^{-12}$ (even if the previously cited weapons emissions of $\sim 2 \times 10^{26}$ atoms were homogenized over the entire deep ocean, which will in fact take several thousand years, it would increase the $^{129}I/^{127}I$ ratio there by only $\sim 7 \times 10^{-13}$). In support of this we can note that the four subsurface water samples in Table 1 have been previously analyzed for ^{137}Cs [18]. The atom ratio $^{129}I/^{127}Cs$ for these samples ranges from 20 to 70; i.e. two orders of magnitude larger than the estimated fallout ratio from weapons testing or the Chernobyl accident [8]. This indicates that less than 1% of the ^{129}I in these samples came from those sources. It also suggests that the reprocessing ^{129}I signal in these waters should be traceable in the deep ocean over dilution factors of another two orders of magnitude.

As indicated above, the fraction of ^{129}I discharged to the oceans by the reprocessing facilities at Sellafield and La Hague is much larger than for most other fission products. Therefore, ^{129}I can be used as a very sensitive and specific tracer of the reprocessing signal, even very far from its origin. For example, the atom ratio ^{129}I/^{127}Cs from the above cited reprocessing facilities is currently $\geqslant 10^3$, while the same ratio from unprocessed fission products is ~ 0.1. Thus by measuring ^{129}I/X (where X is another soluble nuclide such as ^{137}Cs, ^{90}Sr, ^{99}Tc, etc.) in an ocean sample, one can estimate what fraction of X originated from reprocessing and, by implication, what fraction came from other sources. Such a possibility should be very useful for trying to identify a signal from accidental or deliberate discharges of unprocessed waste. Using this procedure, we have recently shown that, despite extensive dumping of nuclear waste by the former Soviet Union, most of the ^{129}I in the Kara Sea comes, in fact, from the reprocessing facilities at La Hague and Sellafield [19].

While we have considered here nuclear reprocessing derived ^{129}I in the marine environment, it is likely that use of the AMS technique could facilitate and extend applications for the fraction emitted to the atmosphere, as a tracer of dispersion patterns of iodine in the surrounding environment: water, vegetation, animals (see, for example, Wershofen et al. [20] and references therein). This latter aspect has both fundamental and practical importance because, while ^{129}I is itself not considered a serious radioecological hazard (because of its long half-life) the shorter lived isotope ^{131}I (half-life eight days) is potentially one of the most dangerous nuclides in the case of a nuclear accident. By studying ^{129}I dispersion patterns under controlled situations, one can obtain extremely useful information regarding the expected dispersion of ^{131}I in the event of a hypothetical nuclear accident (or even retrospective information on past accidents such as Chernobyl).

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