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Iodine-129 and plutonium isotopes in Arctic kelp as historical indicators of transport of nuclear fuel-reprocessing wastes from mid-to-high latitudes in the Atlantic Ocean

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Abstract Iodine-129:iodine-127 ratios were determined using accelerator mass spectrometry in 34 Arctic marine algae collected between 1930 and 1993. A smaller set (5) of marine algae were also analyzed mass spectrometrically to determine plutonium-isotope ratios. The $^{129}\text{I}:$ ^{127}I ratio increased as much as three orders of magnitude from a mean of $< 1 \times 10^{-11}$ (atom/atom) in the pre-nuclear era (before 1945) to nearly 1000×10^{-11} in 1993 for marine algae collected from the Novaya Zemlya archipelago separating the Barents and Kara Seas. The predominant basis for the higher ratios in the Novaya Zemlya kelps appears to be upcurrent sources of ^{129}I from nuclear fuel-reprocessing facilities at Sellafield (UK) and La Hague (France). Relatively high $^{241}\text{Pu}:$ ^{239}Pu ratios (compared to observed bomb fallout at boreal latitudes, decay corrected to the date of collection) also corroborate the influence of non-fallout sources. The small size of the data set precludes determining if there are significant contributions of ^{129}I and other radionuclides from Russian sources. In contrast,

marine algae collected between 1969 and 1993 in the Bering, Beaufort and East Siberian Seas had much lower $^{129}\text{I}:$ ^{127}I ratios (mean = $14.04 \times 10^{-11} \pm 3.15$ SD) than those observed in the European Arctic. The narrow range of ratios in Amerasian Arctic kelps, and the modest change over that time period, indicate that there were no major contributions of non-fallout ^{129}I to North American Arctic surface waters at the time that the algae were collected. The potential for timing the transport of fuel-reprocessed ^{129}I through analysis of additional archived samples is outlined.

Introduction

The capacity for some marine algae, particularly kelps and other members of the Laminariales, to concentrate iodine, is well known (e.g. Grimm 1952; Chapman 1970; Saenko et al. 1978; Bollard 1983). On a dry weight basis, iodine can make up 1% of the weight of the kelp *Laminaria digitata*, and concentrations can reach four to five orders of magnitude over the concentration of iodine in seawater (Shaw 1959; Pais and Jones 1997). This capacity for bioaccumulation has been used to study the mechanisms for iodine uptake in marine algae (e.g. Shaw 1959). The short-term uptake of ^{131}I (half-life 8 d) by marine algae world-wide after the accident at the Chernobyl nuclear reactor in 1986 (Druehl et al. 1988) provided a field example of the use of marine algae to trace the transport and fate of anthropogenically-derived radioiodine. The development of accelerator mass spectrometry (AMS) techniques (Elmore and Phillips 1987; Kilius et al. 1992) for the more routine measurement of another, much longer-lived isotope, ^{129}I (half-life 15.7 million years), has presented the possibility that archived marine algae collected at appropriate times and locations might provide a useful record of the dispersal of anthropogenic ^{129}I since the beginning of the nuclear era. Given the potential for long-distance dispersal of a semi-conservative element such as iodine in seawater, an appropriately constructed record of ^{129}I accumulation in

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archived marine algae could help elucidate the timing and transport of the element in surface ocean waters. Although ^{129}I is a nuclear fission product and was dispersed globally during the atmospheric bomb-testing era, discharges from nuclear fuel-reprocessing plants, including atmospheric releases, are currently the dominant source, and are larger than the bomb-fallout contribution (Wagner et al. 1996). Water-borne disposal of the radionuclide from the Sellafield (UK) and La Hague (France) nuclear fuel-reprocessing plants is providing a temporally varying point source of the radionuclide in the north Atlantic Ocean; contributions from the La Hague plant in particular increased in the late 1980s/early 1990s period (Raisbeck et al. 1995). Raisbeck et al. recently used ^{129}I measurements in archived marine algae and contemporaneous water samples to show the dispersal of ^{129}I as a tracer plume northward from Sellafield and La Hague in the Norwegian Coastal Current into the Barents and Kara Seas of the Arctic Ocean (see Fig. 1).

We have expanded upon this work both geographically (Fig. 1) and temporally (Fig. 2) by measuring the ratios of ^{129}I relative to stable iodine (^{127}I) in Arctic marine algae from archived sources dating back to before the nuclear era, when only a very low background of natural ^{129}I was present from cosmic ray spallation of atmospheric xenon and natural fission sources. The focus on Arctic marine algae is the result of interest in the magnitude of contributions of western European nuclear fuel-reprocessing discharges in the Arctic Ocean relative to discharges from Russian nuclear fuel-cycle plants on the Ob and Yenesei Rivers, and the enclosed, estuarine nature of the Arctic Ocean. The Arctic has no deep (>50 m) connections to any ocean other than the Atlantic, and flow through Bering Strait is predominantly northward from the Pacific (Roach et al. 1995). Dispersal of ^{129}I from point sources in the north Atlantic can therefore be approximated as plume dispersal within a single reservoir. This approximation neglects the permanently stratified nature of the Arctic Ocean (Aagaard and Carmack 1989), but since marine macroalgae are only present in surface waters, temporal and geographical differences in ^{129}I : ^{127}I ratios in Arctic marine algae should reflect the impact of the north Atlantic point source plume on Arctic surface-water dispersal of ^{129}I . Mass balance considerations can be used to separate and constrain the relative sizes of the contributions to Arctic Ocean surface waters of ^{129}I from atmospheric bomb-testing and other sources (e.g. Chernobyl) compared to western European fuel-reprocessing plants (Beasley et al. 1998a).

In addition to the analyses of ^{129}I : ^{127}I ratios, we were also interested in the plutonium-isotope ratios of a subset of the samples. As with radioiodine, plutonium isotopes can be a sensitive indicator of non-fallout sources of anthropogenic radionuclides, and we expected that these analyses might also corroborate indications of the transport of ^{129}I from western European sources. These ratios might also assist in the identification of

Russian sources of anthropogenic radionuclides, given the slower dispersal of particle-reactive plutonium and the presence of several potential local sources in the Novaya Zemlya archipelago. Both ^{240}Pu : ^{239}Pu and ^{241}Pu : ^{239}Pu ratios can be used for identifying non-fallout ratio material, but we expected that decay-corrected ^{241}Pu : ^{239}Pu ratios would be the more sensitive indicator of Sellafield-derived plutonium. This expectation was based on the greater differences between decay-corrected bomb-fallout ^{241}Pu : ^{239}Pu ratios (~ 0.0051 in the 1980s) and decay-corrected, Sellafield-origin ^{241}Pu : ^{239}Pu (~ 0.020) (Kershaw and Baxter 1995; Kershaw et al. 1995a) relative to the difference between bomb-fallout ^{240}Pu : ^{239}Pu (~ 0.18) and Sellafield-derived ^{240}Pu : ^{239}Pu ratios. The Sellafield-derived ^{240}Pu : ^{239}Pu ratio increased from 0.06 to 0.25 between the 1960s and the mid-1980s (Kershaw and Baxter 1995; Kershaw et al. 1995a; Beasley et al. 1998a). Mass-balance considerations also suggest that releases of low ratio ^{240}Pu : ^{239}Pu from Irish Sea sediments of Sellafield origin (Kershaw et al. 1995b) will complicate the use of the ratio of the two most common isotopes of plutonium for tracking Sellafield releases.

Materials and methods

Marine algae analyzed as part of this study were obtained from the Komarov Botanical Institute, St. Petersburg, Russia, as well as collections of V. Vozzhinskaya of the Shirshov Institute of Oceanology, Moscow. Additional samples were collected by two authors of this study (Cooper and Dunton). Locations of collection are provided in Table 1, including latitude and longitude in those cases where coordinates were readily available from the herbarium label, or from other information made available to the authors. In cases where the collection locality was a relatively large island or region of coastline and was not precisely specified, named geographic features are provided in Table 1 and shown on Fig. 1. In all cases, thallus blades were the kelp tissues analyzed.

Iodine was isolated from the samples using the procedure described by Kilius et al. (1994), but with modifications. In this procedure, Na_2O_2 is used in combination with NaOH fusions to destroy organic matter and to oxidize lower valence states of iodine to iodate, thereby preventing its volatilization at elevated fusion temperatures (600 °C). However, preliminary experiments with kelp-sample mineralization showed that it was possible to fuse the organic matter with NaOH alone without appreciable loss of iodine. Because our interest centered on measuring the ^{129}I : ^{127}I atom ratio rather than the absolute abundance of ^{129}I in the kelp, Na_2O_2 was not used in the fusion process, and we therefore do not report absolute concentrations of ^{129}I in these samples.

The dried kelp (1 to 3 g) was placed in a 100 ml nickel crucible and allowed to equilibrate overnight with 4 ml saturated NaOH to ensure thorough sample-wetting. During the equilibration process, the samples were sealed in plastic Ziploc® bags to prevent uptake of ambient iodine from the atmosphere. The crucibles were then covered with watch glasses and heated to dryness under infrared heat lamps. Destruction of the organic matter was then accomplished by heating the covered crucibles in a muffle furnace using stepped temperature increases. Initially, the temperature was raised to 100 °C (30 min) and then to 200 °C (30 min). The samples were then cooled, thoroughly mixed using a pestle, and then fused at 600 °C for 2 h.

Following cooling, the residue was removed from the crucibles by (1) leaching with two consecutive 50 ml aliquots of doubly-distilled water while the samples were heated under infrared heat lamps, and (2) two consecutive 25 ml aliquots of a stock, high-

Table 1 Marine algal samples analyzed for ^{129}I : ^{127}I ratios (*Toronto ID* Toronto Iodine number on record for each analysis at Isotracer accelerator mass spectrometry facility, University of Toronto) Samples were analyzed in order presented in table (oldest first). Locations are shown on Fig. 1

Toronto ID	Species	Location of collection	^{129}I : ^{127}I ($\times 10^{-11}$) $\pm 1\sigma$	Date collected
TOI-3175	<i>Laminaria digitata</i>	Russkaya gavan, Novaya Zemlya (76°14'48"N; 62°39'06"E)	0.100 \pm 0.013	1930
TOI-3176	<i>Laminaria digitata</i>	Severnaya Sulmeneva guba, (north of Krestovaya guba), Novaya Zemlya	0.369 \pm 0.024	2 August 1931
TOI-3177	<i>Laminaria digitata</i>	Sosnovka Region, White Sea	0.135 \pm 0.017	31 July 1938
TOI-3178	<i>Laminaria digitata</i>	Dvinskaya guba, White Sea	0.137 \pm 0.014	11 July 1930
TOI-3179	<i>Laminaria saccharina</i>	Sosnovetz Island, White Sea	0.192 \pm 0.028	3 August 1938
TOI-3181	<i>Saccorhiza dermatodea</i>	Rugozyorskaya guba, White Sea	1.236 \pm 0.062	June 1954
TOI-3182	<i>Laminaria digitata</i>	Dalnezelenetskaya guba, Murmansk region	15.87 \pm 0.41	June 1966
TOI-3183	<i>Laminaria saccharina</i>	Kanin Nos, Kanin Peninsula	4.57 \pm 0.12	28 July 1966
TOI-3184	<i>Fucus serratus</i>	Kruglaya Levaya Bay, White Sea (66°29'N; 33°38'E)	26.22 \pm 0.61	16 July 1967
TOI-3185	<i>Fucus distichus</i>	Kruglaya Levaya Bay, White Sea (66°29'N; 33°38'E)	15.78 \pm 0.41	21 July 1967
TOI-3186	<i>Fucus vesiculosus</i>	Kruglaya Levaya Bay, White Sea (66°29'N; 33°38'E)	21.72 \pm 1.09	21 July 1967
TOI-3187	<i>Laminaria solidungula</i>	Chaunskaya guba, East Siberian Sea	10.25 \pm 0.30	12 August 1969
TOI-3188	<i>Laminaria digitata</i>	Dalnezelenetskaya guba, Murmansk region	34.12 \pm 0.77	20 July 1967
TOI-3189	<i>Laminaria digitata</i>	Kandalakshskaya guba, White Sea	27.18 \pm 0.68	16 July 1971
TOI-3190	<i>Laminaria digitata</i>	Kashkaranzi, west of Kuzomen, White Sea	26.07 \pm 0.61	19 July 1971
TOI-3191	<i>Laminaria saccharina</i>	Anderma, Kara Sea	41.99 \pm 0.95	26 August 1969
TOI-3192	<i>Fucus serratus</i>	Kola Peninsula, near mouth of Ponoy River	146.2 \pm 3.6	10 July 1972
TOI-3193	<i>Fucus vesiculosus</i>	Sosnovetz, Tersky Coast, White Sea (66°29'N; 40°43'E)	72.9 \pm 2.0	14 July 1972
TOI-3194	<i>Laminaria solidungula</i>	Stolbovoy Island, New Siberian Islands	37.93 \pm 0.89	1 August 1973
TOI-3195	<i>Laminaria solidungula</i>	Kotel'nyy Island, New Siberian Islands	0.747 \pm 0.27	10 August 1979
TOI-3196	<i>Laminaria saccharina</i>	Teriberka, Murmansk Region	856 \pm 19	11 September 1988
TOI-3197	<i>Laminaria digitata</i>	Belush'ya guba, Novaya Zemlya	481 \pm 11	26 August 1989

(continued overleaf)

Table 1 (continued)

Toronto ID	Species	Location of collection	$^{129}\text{I}:^{127}\text{I}$ ($\times 10^{-11}$) $\pm 1\sigma$	Date collected
TOI-3199	<i>Laminaria solidungula</i>	Boulder Patch, Stefansson Sound, Beaufort Sea (70°24'N; 147°50'W)	9.57 \pm 0.23	November 1980
TOI-3200	<i>Laminaria digitata</i>	Pityunia Bay, Svalbard (78°40'N; 16°30'E)	147.5 \pm 3.8	30 August 1990
TOI-3201	<i>Laminaria digitata</i>	Matochkin Shar, Novaya Zemlya	718 \pm 16	15 August 1993
TOI-3202	<i>Laminaria saccharina</i>	near Stolbovoy, Novaya Zemlya	746 \pm 17	1993
TOI-3203	<i>Chorda filum</i>	Obsedya, Novaya Zemlya (72°08'N; 52°15'E)	616 \pm 14	30 August 1993
TOI-3204	<i>Alaria esculenta</i>	Serabyrnka Fjord (guba), Novaya Zemlya (73°25'N; 54°10'E)	826 \pm 19	1993
TOI-3205	<i>Fucus vesiculosus</i>	Gribovaya Fjord (guba), Novaya Zemlya (73°00'N; 53°50'E)	801 \pm 18	8 August 1993
TOI-3206	<i>Alaria fistulosa</i>	Sweepers Cove, Adak Island, Bering Sea (51°51'N; 176°37'W)	17.94 \pm 0.55	9 June 1993
TOI-3207	<i>Laminaria</i> sp. (beach drift)	St. Matthew Island, Bering Sea (60°20'N; 172°22'W)	13.57 \pm 0.37	23 June 1993
TOI-3208	<i>Laminaria solidungula</i>	Boulder Patch, Stefansson Sound, Beaufort Sea (70°24'N; 147°50'W)	14.84 \pm 0.35	1986
TOI-3212	<i>Laminaria solidungula</i>	Boulder Patch, Stefansson Sound, Beaufort Sea (70°24'N; 147°50'W)	15.34 \pm 0.36	1986
TOI-3213	<i>Laminaria solidungula</i>	Boulder Patch, Stefansson Sound, Beaufort Sea (70°24'N; 147°50'W)	16.79 \pm 0.39	1987
None	<i>Laminaria saccharina</i>	Lumborsky Bay (zaliv), White Sea (67°49.5'N; 40°27.5'E)	Plutonium isotope data only (Table 3)	1991

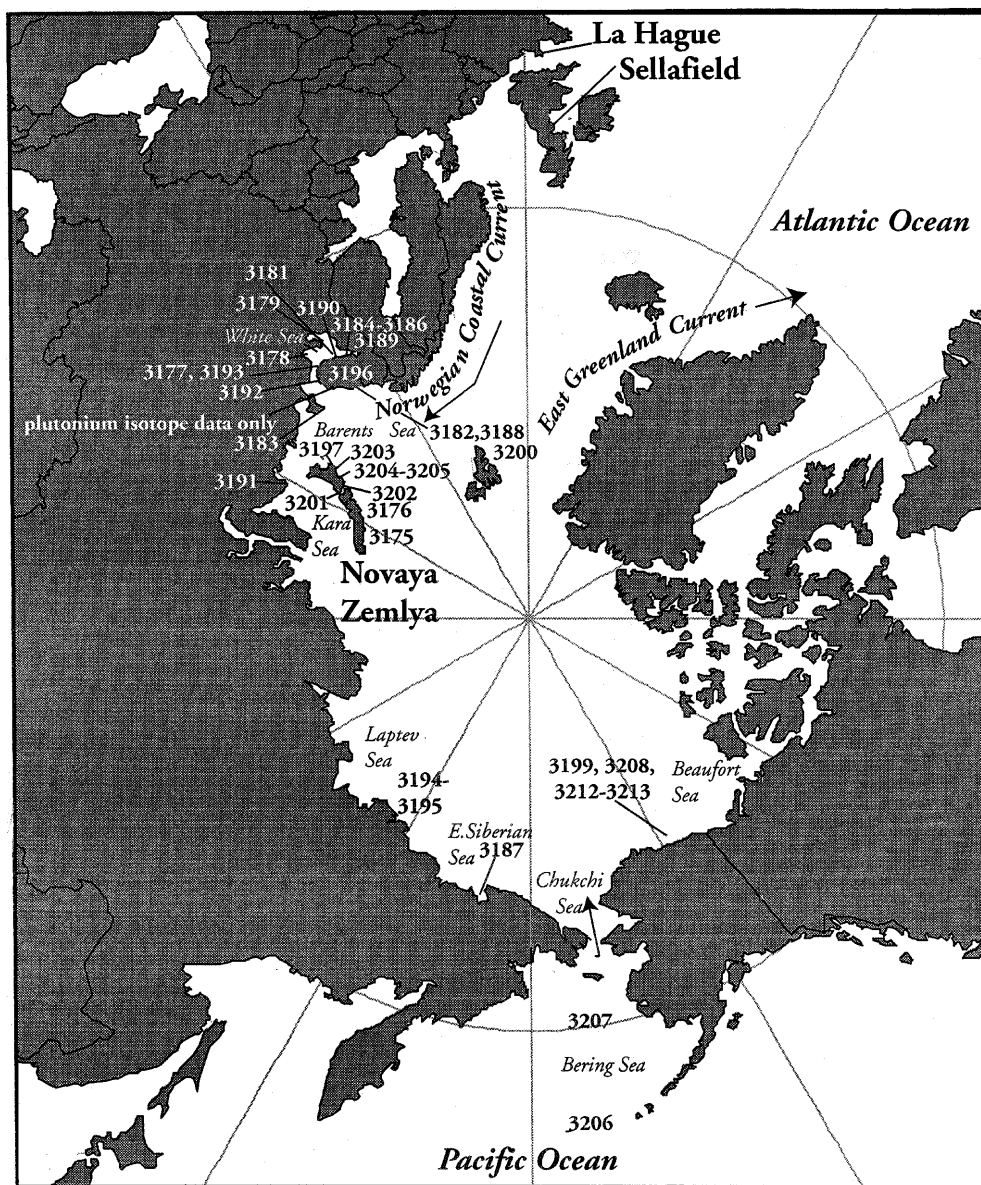
purity 6 N HCl solution. The leachates were placed in acid-washed, 240 ml (8 fluid ounces) round-bottom bottles fitted with Polyseal® caps. Any visible residue in the crucibles was removed by small volume washes with 6N HCl. A teflon-covered stirring bar was then added to the bottles and, while stirring, the pH of the solutions was adjusted to ~ 1 by addition of stock 6N HCl. Iodine species were reduced to iodide by the addition of 1 ml 1 N NaHSO₃, with a mixing period of 3 min. Thereafter, the isolation and purification of iodine and the subsequent preparation of the AgI AMS target followed the protocol described by Mann and Beasley (1994).

To test reproducibility and possible sample cross-contamination during fusion, we analyzed aliquots of a large kelp sample prepared by the Iso Trace Laboratory, University of Toronto, as a quality assurance/quality control (QA/QC) sample. Six separate aliquots of this sample were processed according to the procedure described above. Two samples and a reagent blank were processed on consecutive weeks to determine if "memory" effects could be detected in the reagent blanks. Table 2 lists the results of the experiments (April 1996) and shows the excellent reproducibility of the $^{129}\text{I}:^{127}\text{I}$ ratios measured in the QA/QC sample and the uniformly low ratios recorded in the reagent blanks. Samples of the QA/QC kelp were also processed as blind samples concurrently with Arctic Basin kelp (Table 2: January 1997) to monitor cross-

contamination and as a check on the reproducibility of the AMS measurements. In both cases, the mean $^{129}\text{I}:^{127}\text{I}$ ratios in reagent blanks processed in April 1996 are indistinguishable from those accompanying the Arctic Basin Kelp analyses, indicating the absence of ^{129}I cross-contamination during the fusion process. Moreover, the concordance of the $^{129}\text{I}:^{127}\text{I}$ ratios in the QA/QC kelp sample at different analysis times is indicative of the overall reproducibility of the AMS measurements.

For plutonium-isotope measurements, the marine algal samples were fused with NaOH in nickel crucibles as with the $^{129}\text{I}:^{127}\text{I}$ sample preparations. Thereafter, sample preparation followed that described by Cooper et al. (1998): dry-ashing at 600 °C for 16 h, the residue dissolved in a mixture of HCl and HF, with co-precipitation of oxalate salts, using a rare earth carrier, from a strongly reducing hydroxylamine hydrochloride, Fe⁺² solution ($\sim 1N$ HCl). Additional purification was accomplished using ion-exchange chromatography. Final purification was accomplished using a 100 μl anion-exchange column-separation. The purified Pu was incorporated into the mass spectrometer source on individual 150 μm diam anion-exchange resin beads from 1 μl of 7.2 N nitric acid. Individual beads were then transferred into the trough of a rhenium filament formed in a V-shape (Stoffels and Lagergren 1984). Measurement of plutonium-isotope abundances was made with a

Fig. 1 Locations of marine algal collections used in study [Numbers “Toronto Iodine” (TOI-) numbers on record for each analysis at IsoTrace accelerator mass spectrometry facility, University of Toronto (see Table 2)]. Also shown are sites of nuclear fuel-reprocessing facilities at Sellafield (UK) and La Hague (France), and surface currents to and from Atlantic and Pacific Oceans into the Arctic



thermal ionization mass-spectrometer at Pacific Northwest National Laboratory, Richland, Washington (Lagergren and Stoffels 1970). Additional descriptions of the instrumentation used, its sensitivity, process blank results, isotope dilution, and sources of tracers used, as well as protocols undertaken for data assurance are provided elsewhere (Beasley et al. 1998b).

Results

Iodine-129:iodine-127 ratios in the marine algae analyzed (Table 1) increased by as much as three orders of magnitude from a mean of $<1 \times 10^{-11}$ (atom/atom) in the pre-nuclear era (before 1945) to nearly 1000×10^{-11} in 1993 (Fig. 2). The collection location played a secondary role to temporal trends in determining the isotope ratios observed. For samples collected during the

same time period, locations in the North American Arctic (Beaufort and Bering Seas) had lower $^{129}\text{I}:^{127}\text{I}$ ratios than those in the European Arctic (Barents Sea). The differences are most striking for recent samples collected after 1985. Marine algae collected from the Beaufort and Bering Seas during the 8 yr period between 1986 and 1994 had $^{129}\text{I}:^{127}\text{I}$ ratios similar to that observed on the Barents Sea coast of the Kola Peninsula in the mid-1960s, immediately following the cessation of most atmospheric nuclear testing. Following the mid-1960s, however, $^{129}\text{I}:^{127}\text{I}$ ratios in marine algae in the Eurasian Arctic generally continued to increase by an order of magnitude or more, approaching 1000×10^{-11} . However, ratios observed in Russian Barents Sea marine algae remained slightly lower than $^{129}\text{I}:^{127}\text{I}$ ratios reported for seawater within Norwegian coastal waters (1110 to 4890×10^{-11} ; Raisbeck et al. 1995).

Table 2 $^{129}\text{I}:$ ^{127}I ratios in quality assurance/quality control (QA/QC) kelp samples and reagent blanks

Sample	$^{129}\text{I}:$ ^{127}I atom ratio ($\times 10^{-11}$) ^a	Process date
QA/QC-1	14.22 ± 0.26	April 1996
QA/QC-1	13.79 ± 0.34	
(Reagent Blank 1)	0.022 ± 0.003	
QA/QC-2	14.23 ± 0.23	
QA/QC-2	14.24 ± 0.23	
(Reagent Blank 2)	0.010 ± 0.001	
QA/QC-3	14.14 ± 0.21	January 1997
QA/QC-3	14.15 ± 0.20	
(Reagent Blank 3)	0.013 ± 0.001	
QA/QC-4	13.97 ± 0.31	
QA/QC-4	13.86 ± 0.31	
[Reagent blanks (3)] ^b	0.013 ± 0.005^b	

^a Uncertainty (1σ) applies to uncertainties associated with accelerator mass-spectrometry measurements only

^b Uncertainty represents standard deviation about mean for the three measurements (1σ)

Plutonium-isotope determinations for five of the marine algae indicate that, once decay of ^{241}Pu (half-life 14.33 yr) is taken into account for each collection date for the marine algae analyzed, $^{241}\text{Pu}:$ ^{239}Pu ratios are typically higher than would be expected from global fallout alone (Table 3).

Discussion

The dispersal of anthropogenic radionuclides of western European-reprocessing origin, particularly soluble radionuclides with conservative and semi-conservative behavior, into Arctic waters has been widely recognized (e.g. Aarkrog et al. 1983; Livingston et al. 1985). The data presented here indicate that given adequate geographical and temporal coverage, the transport and

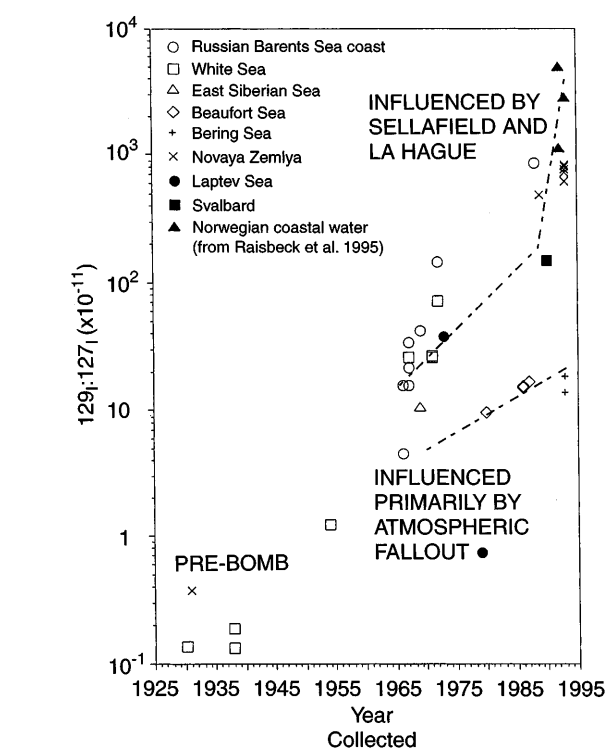


Fig. 2 $^{129}\text{I}:$ ^{127}I ratios in archived marine samples relative to date of collection (Dashed lines indicate samples affected by contributions from water-borne discharge from nuclear fuel-reprocessing plants and those affected by atmospheric fallout only)

timing of the dispersal of water-borne ^{129}I from such well-characterized sources as bomb-fallout and the Sellafield/La Hague reprocessing discharges (recently reviewed by Beasley et al. 1998a) to surface waters of the Arctic Ocean could be potentially analyzed in a quantitatively rigorous way. These data may also be relevant for evaluating the magnitude of other potentially de-

Table 3 Plutonium concentrations and atom ratios in Arctic Ocean kelp (Toronto ID numbers as in Table 1; locations shown in Fig. 1; nd not determined) All atom concentrations are in g dry wt

Toronto ID	Location	^{239}Pu (10^7 atoms g^{-1})	^{240}Pu (10^6 atoms g^{-1})	^{241}Pu (10^4 atoms g^{-1})	$^{240}\text{Pu}:$ $^{239}\text{Pu}^a$	$^{241}\text{Pu}:$ $^{239}\text{Pu}^b$	$^{241}\text{Pu}:$ $^{239}\text{Pu}^c$
TOI-3200	Pituynia Bay, Svalbard	1.53 ± 0.02	2.79 ± 0.05	7.41 ± 0.49	0.182 ± 0.002	0.00484 ± 0.00032	0.00306 ± 0.00021
TOI-3201	Matochkin Shar, Novaya Zemlya	1.51 ± 0.04	2.43 ± 0.09	nd	0.161 ± 0.004	nd	nd
TOI-3203	Obsedya, Novaya Zemlya	8.90 ± 0.13	14.8 ± 0.23	25.8 ± 1.0	0.166 ± 0.001	0.00291 ± 0.0010	0.00264 ± 0.00018
TOI-3205	Gribovay Fjord, Novaya Zemlya	6.75 ± 0.09	11.5 ± 0.02	24.8 ± 0.7	0.170 ± 0.001	0.00367 ± 0.00009	0.00265 ± 0.00018
None	Lumborsky guba, White Sea	1.01 ± 0.02	1.87 ± 0.05	4.12 ± 1.22	0.185 ± 0.004	0.00409 ± 0.00122	0.00295 ± 0.00020

^a Relative uncertainties in atom ratios are less than those of atom concentrations, as they are independent of uncertainties with yield-determinant recoveries

^b Decay corrected to collection date using ^{241}Pu half-life = 14.33 yr

^c Decay-corrected global fallout at time of collection. Global fallout value determined by measuring Pu isotopes in 30 cm soil cores collected north of 50°N (Beasley et al. 1998b)

tectable anthropogenic sources, including dumped waste in the Kara Sea, river runoff from Russian continental nuclear fuel-cycle facilities, close-in fallout from nuclear weapons-testing on Novaya Zemlya, and anthropogenic radionuclides transported from the site of the Chernobyl accident. The data we present here are too sparse in geographical and temporal variation to address most of these transport problems in more than a preliminary manner, but the patterns observed could serve as a useful starting point for future work.

It is apparent from the data, that contributions of relatively recent (~ 1980 s) ^{129}I from western European reprocessing-sources are a dominant feature of $^{129}\text{I}:$ ^{127}I ratios in Arctic marine algae in the Barents Sea. Ratios reported in Norwegian coastal water by Raisbeck et al. (1995) are higher than observed in any of the marine algae that we analyzed (Fig. 2). A pattern of dilution is observable in the European Arctic samples, with the time of collection and distance from the Sellafield and La Hague sources being most important in determining the relative $^{129}\text{I}:$ ^{127}I in marine algae. For example, *Laminaria saccharina* collected in 1988 at Teriberka, east of Murmansk, on the Kola Peninsula coast, where plants grow exposed to northward-flowing Norwegian coastal-current water, had a higher $^{129}\text{I}:$ ^{127}I ratio ($856 \pm 19 \times 10^{-11}$) than *L. digitata* collected on the southwest coast of Novaya Zemlya, 700 km northeast, 1 yr later ($481 \pm 11 \times 10^{-11}$). Iodine-129:iodine-127 ratios in marine algae on Novaya Zemlya apparently increased from 1989 to 1993, when the mean ratio reached $741 \times 10^{-11} \pm 82$ SD; $n = 5$ (Fig. 2). It is notable that Novaya Zemlya was heavily impacted by Soviet atmospheric and underground weapons-tests, and its waters have also been subject to dumping of liquid and solid nuclear waste. Although there are insufficient data to rule out local contributions of ^{129}I , the geographical and temporal dilution pattern that is apparent on Fig. 2 is consistent with the predominant importance of transport of ^{129}I from western European sources.

This pattern is reinforced by the much smaller data set of plutonium-isotope ratios obtained as part of this study (Table 3). In principle, the atom isotope ratios $^{240}\text{Pu}:$ ^{239}Pu and $^{241}\text{Pu}:$ ^{239}Pu can be used to identify Sellafield-derived Pu as it is advected from the Irish Sea northward to the Arctic Ocean (Kershaw et al. 1995a). The difference between the $^{241}\text{Pu}:$ ^{239}Pu atom ratios in Sellafield-derived and global fallout Pu is greater than that for their respective $^{240}\text{Pu}:$ ^{239}Pu atom ratios, meaning that the $^{241}\text{Pu}:$ ^{239}Pu atom ratio is likely to be a more sensitive Sellafield tracer, despite the short half-life of ^{241}Pu : (14.33 yr). Comparison between the expected, decay-corrected bomb-fallout $^{241}\text{Pu}:$ ^{239}Pu atom ratio at the time of collection, and the actual decay-corrected $^{241}\text{Pu}:$ ^{239}Pu atom ratio in each of the algae (Table 3) shows that all five samples appear to have at least some "excess" ^{241}Pu over and above expectations solely from bomb-fallout. This observation particularly holds true for the kelp sample from Pityunia Bay (Svalbard), which was collected at a latitude where excess $^{238}\text{Pu}:$ $^{239+240}\text{Pu}$

activity ratios have been attributed to Sellafield contributions (Kershaw and Baxter 1995). The observation of "excess" ^{241}Pu is less clear-cut at Lumborsky Bay (White Sea), because of measurement uncertainties. On the other hand, the $^{241}\text{Pu}:$ ^{239}Pu atom ratios observed in Gribovay Fjord and Obsedya (both on the southwestern coast of Novaya Zemlya) are significantly above decay-corrected bomb-fallout $^{241}\text{Pu}:$ ^{239}Pu atom ratios. In addition to having "excess" ^{241}Pu , the Gribovay Fjord sample has a $^{240}\text{Pu}:$ ^{239}Pu atom ratio that is consistent with Sellafield discharges in 1986 (0.170), 7 yr before collection. Even though such timing for transport from the Irish Sea to Novaya Zemlya (7 yr) is within the expected range for water-borne transport from the Irish Sea (Aarkrog et al. 1983; Livingston et al. 1985), ascribing the entire 1993 Pu burden in the kelp to Sellafield discharges would neglect mixing and diffusion during transport, and the particle-reactive chemistry of plutonium. It seems more probable that the lower $^{240}\text{Pu}:$ ^{239}Pu atom ratios observed in the Novaya Zemlya kelps collected at Matochkin Shar, Obsedya, and Gribovay reflect some proportion of local contributions, the possibilities for which include overland runoff from vented underground nuclear tests (Bjurman et al. 1990), or releases from waste-disposal sites. For example, for the three samples collected from Novaya Zemlya, only trace amounts of weapons-grade Pu ($^{240}\text{Pu}:$ ^{239}Pu atom ratio = 0.03 to 0.05) would be required to lower the $^{240}\text{Pu}:$ ^{239}Pu atom ratio from the 0.182 to 0.185 (observed in the Svalbard and White Sea samples) to the 0.161 to 0.170 observed in the Novaya Zemlya samples.

In contrast to the European Arctic samples, $^{129}\text{I}:$ ^{127}I ratios in Amerasian Arctic marine algae did not change greatly between 1969 and 1993. The mean ratio in seven samples collected in the East Siberian, Beaufort, and Bering Seas during this period was $14.04 \times 10^{-11} \pm 3.15$ SD, although a modest increase observable over the period will be discussed below. Beasley et al. (1998a) recently estimated that the probable ^{129}I concentrations in Bering Sea waters (<300 m depth) in the early-to-mid-1980s were on the order of 1×10^6 atoms kg^{-1} . Direct measurements in the 1990s indicate that typical ^{129}I concentrations in shallow waters around Bering Strait were 10^7 to 10^8 atoms kg^{-1} , although a few higher concentrations were also observed (Cooper et al. unpublished data). Given average ^{127}I concentrations in seawater of $50 \mu\text{g kg}^{-1}$ (0.39 μM), the mean $^{129}\text{I}:$ ^{127}I ratio of 14.04×10^{-11} in these marine algae falls within the expected range of $\sim 0.4 \times 10^{-11}$ to $\sim 40 \times 10^{-11}$ if marine algal $^{129}\text{I}:$ ^{127}I ratios faithfully reproduce contemporaneous water $^{129}\text{I}:$ ^{127}I ratios. If the relatively narrow range of ratios observed in the Beaufort, Bering, and East Siberian Sea marine algae are consistent with contributions from atmospheric bomb-fallout only, and there are no oceanically-derived contributions from any nuclear fuel-reprocessing sources in Russia or western Europe, this ratio of $\sim 10 \times 10^{-11}$ approximates the atmospheric bomb-testing era contributions of surface water ^{129}I flowing northward in Pacific waters that has

reached the latitude of Bering Strait. The slow increase in ratios over the past 20 yr could imply transport of non-fallout sources of ^{129}I from lower latitudes. Although some of this fractional increase may be the result of atmospheric emissions from nuclear fuel-reprocessing facilities, at least some portion of this increase is likely to be due to the spreading of bomb-fallout northward from lower latitudes where deposition was greater.

One of two samples collected in the Laptev Sea in 1973 had a higher ratio, $37.93 \times 10^{-11} \pm 0.89$, which was similar to ratios observed in the Barents Sea in the same time period (Fig. 2). The observation of either non-local fallout ^{129}I or nuclear fuel-reprocessed ^{129}I in the 1973 *Laminaria solidungula* sample collected at Stolbovoy Island is consistent with reprocessed contributions of ^{129}I that were apparent in the Nansen Basin of the Laptev Sea in 1993 in surface waters, as well as at ≈ 500 m depth (Beasley et al. unpublished data). Continental-slope waters in the Nansen Basin are ultimately derived from waters of Barents Sea origin (Schauer et al. 1997), so it is not surprising that $^{129}\text{I}:^{127}\text{I}$ ratios in marine algae of the Laptev Sea should resemble the ratios for contemporaneous samples collected in the Barents and Kara Seas.

It is somewhat more problematic to explain the much lower ratio ($0.747 \times 10^{-11} \pm 0.270$) observed in a *Laminaria solidungula* sample collected at Kotel'nyy Island, also in the Laptev Sea, 6 yr later in 1979. The ratio is nearly as low as that observed in the pre-bomb (<1945) samples (Fig. 2; mean = $0.187 \times 10^{-11} \pm 0.107$). Given the outlying single data-point (Fig. 2), any suggestions are speculative, but the low ratio may correspond to a quick removal of bomb-fallout-contaminated waters containing radioiodine from portions of the Laptev Sea, where sea-ice formation is particularly important. Although the pre-bomb-era samples show good between-sample reproducibility, the mean $^{129}\text{I}:^{127}\text{I}$ ratio observed (0.187×10^{-11}) should only be considered an upper limit for the pre-bomb-era ratio. There is no certainty that the $^{129}\text{I}:^{127}\text{I}$ ratio in these samples was not affected to some degree by handling or atmospheric exposure to post-bomb-era ^{129}I while in curation at the Komarov Botanical Institute in St. Petersburg. Nevertheless, our upper-limit estimate of the pre-bomb $^{129}\text{I}:^{127}\text{I}$ ratio agrees well with independent estimates of 0.15×10^{-11} obtained from pre-bomb sediment analyses (Fehn et al. 1986; Moran et al. 1998).

If the outlying Laptev Sea data point is not considered, two separate clusters can be observed on Fig. 2. For marine algae collected in the Beaufort, Bering, and East Siberian Seas, the $^{129}\text{I}:^{127}\text{I}$ ratios for samples collected in 1986 and 1987 (Beaufort Sea) and 1993 (Bering Sea) are slightly higher than in 1969 (East Siberian Sea) and 1980 (Beaufort Sea). As discussed earlier in this section, the slight increase over 20 yr may be due to transport of ^{129}I from temperate latitudes where ^{129}I bomb fallout was higher, or possibly atmospherically-transported nuclear fuel-reprocessing contributions. The latitudinal difference between two samples collected in

the Bering Sea in 1993, with an $^{129}\text{I}:^{127}\text{I}$ ratio of $17.94 \times 10^{-11} \pm 0.55$ observed at the more southern location (Adak Island, Aleutians) vs $13.57 \times 10^{-11} \pm 0.37$ observed at St. Matthew Island, is consistent with the hypothesis of transport from mid-latitudes. The $^{129}\text{I}:^{127}\text{I}$ ratios of Beaufort Sea *Laminaria solidungula*, all collected from the same kelp bed in 1980, 1986, and 1987, show a slow increase over time, from $9.57 \times 10^{-11} \pm 0.23$ in 1980 to a mean of 15.09×10^{-11} in 1986, and $16.79 \times 10^{-11} \pm 0.39$ in 1987. The small increase in $^{129}\text{I}:^{127}\text{I}$ ratios between 1986 and 1987 support the contention (Beasley et al. 1998a) that contributions of ^{129}I from the Chernobyl nuclear-reactor accident (1986) directly to Arctic Ocean surface waters were relatively insignificant. The increase in $^{129}\text{I}:^{127}\text{I}$ ratios with time in *L. solidungula* from the same Beaufort Sea kelp bed, which is consistent with a slow increase in Amerasian Arctic surface-water $^{129}\text{I}:^{127}\text{I}$ ratios, suggests that this kelp may faithfully reproduce water-column ratios. This species is known to produce new frond growth during the dark, ice-covered period when nutrient levels are higher, using photosynthate produced during the short open-water summer period (Dunton and Schell 1986; Dunton 1990).

Because of the small sample size of this study, we were not able to address some other potentially significant uncertainties, including the possibility of significant isotopic fractionation during uptake, the residence time of iodine within marine algae, and seasonal translocation of iodine to and from different portions of the plant, including the stipe and holdfasts, which were not analyzed during our work. The possibility of significant variations in within-plant $^{129}\text{I}:^{127}\text{I}$ ratios may be important, particularly in species where translocation is significant and in locations where there are seasonal water-mass differences.

Clearly, additional work will be required in order to meet the larger goal of using archived marine algae to time the transport of anthropogenic ^{129}I within the surface waters of the various Arctic marginal seas. We have no information for instance on whether transport of higher $^{129}\text{I}:^{127}\text{I}$ ratio iodine from the Laptev Sea to the East Siberian Sea in coastal currents might have impacted the relatively low ratio observed in the East Siberian sea sample in 1969. Coverage of the changes in $^{129}\text{I}:^{127}\text{I}$ ratios during the 12 yr period between 1973 and 1985 in the European Arctic would help to time the transport of the well-documented releases of ^{129}I from Sellafield and La Hague (tabulated by Beasley et al. 1998a) via Norwegian coastal waters into the Barents Sea. Collections from additional locations within Russia could help ascertain whether specific Russian point-sources of ^{129}I contribute to the $^{129}\text{I}:^{127}\text{I}$ ratios observed in these data. Coverage in the early nuclear era after 1945 is also very sparse.

There is little doubt that many of the samples needed to advance this work exist in Russia and in other countries, in the collections of individual investigators or in herbaria of institutions such as the Komarov Botan-

ical Institute, which has one of the largest plant collections in the world. We anticipate that presentation of these results may facilitate expansion of this work with other marine algal samples, collected at appropriate locations and periods, so that a more detailed historical perspective on the contributions of reprocessed nuclear-fuel constituents to oceanic ecosystems can be obtained.

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