Atmospheric Dispersal of ^{129}Iodine from Nuclear Fuel Reprocessing Facilities

JEAN E. MORAN,*,[†] SARAH OKTAY,[‡]
PETER H. SANTSCHI,[‡] AND
DAVID R. SCHINK[†]

Department of Oceanography, Texas A&M University, College Station, Texas 77845, and Department of Oceanography, Texas A&M University at Galveston, Galveston, Texas 77551

^{129}I/^{127}I ratios measured in meteoric water and epiphytes from the continental United States are higher than those measured in coastal seawater or surface freshwater and suggest long-range atmospheric transport of ^{129}I from the main source for the earth's surface inventory, viz., nuclear fuel reprocessing facilities. The median ratio for 14 meteoric water samples is 2100×10^{-12}, corresponding to a ^{129}I concentration of 2.5×10^7 atoms/L, whereas 9 epiphyte samples have a median ratio of 1800×10^{-12}. Calculated deposition rates of ^{129}I in the continental United States reveal that a small but significant fraction of the atmospheric releases from the nuclear fuel reprocessing facilities at Sellafield, England, and Cap de La Hague, France, is deposited after distribution by long-range transport. The inferred dominant mode of transport is easterly, within the troposphere, mainly in the form of the organic gas methyl iodide.

Introduction

The long-lived isotope of iodine, ^{129}iodine (half-life = 15.6 m.y.), is produced naturally in the atmosphere by the interaction of high-energy cosmic rays with xenon isotopes. Beginning in about 1945, and peaking in 1963, nuclear bomb tests added tens of kilograms of ^{129}I to the atmosphere, resulting in ^{129}I/^{127}I ratios several orders of magnitude higher than natural ratios (*1, 2*). Unlike most radionuclides produced during atmospheric bomb testing, which have returned to near prenuclear levels, the amount of ^{129}I in the atmosphere and in surface waters has continued to increase due to releases from nuclear fuel reprocessing facilities. ^{129}Iodine releases into the North Sea from two such fuel reprocessing facilities (at Sellafield, England, and Cap de La Hague, France) continue at very high levels (*3*), providing, in effect, a point source for the total surface inventory.

The total natural ^{129}iodine in the surface environment was ~80 kg (5×10^{-4} kg in the atmosphere). For comparison, atmospheric bomb tests produced 50 kg (*3*), and the Chernobyl reactor accident released 1.3 kg (*1*). Boone et al. (*4*) estimate that 2.8 kg/year was released into the atmosphere from the Savannah River Plant during the peak years of 1964−1965; this release rate fell to 0.7 kg/year in the late 1970s. On a larger scale, the facilities at Sellafield and La Hague have cumulatively released 1440 kg since operations began in the late 1960s (*3*). As of 1994, direct ^{129}I releases from the facilities at Sellafield and La Hague into the ocean were ~200 kg/year, with a steep increase from the La Hague facility from about 1990 and continuing to the present. McKay et al. (*5*) give evidence that the method of trapping off-gases at the Sellafield facility allows 3−6% of the ^{129}I produced to be released in gaseous discharges. If conditions were similar at the Cap de La Hague facility, that would indicate total releases of 6−12 kg/year to the atmosphere from both facilities combined. Another estimate based on measurements of iodine activity in the air near the Sellafield plant puts this figure at 9% [or 18 kg/year (*6*)]. A recent study of ^{129}I in mosses near the La Hague facility, conducted by a private nuclear monitoring group (CRIIRAD), also indicates that there are significant atmospheric releases (*7*).

Additional studies of ^{129}I in the atmosphere focused on regional emissions from known point sources, such as the Hanford, WA, site (*8*), the reactor at Chernobyl (*1*), the Bhabha Atomic Research Centre (*9*), the Karlsruhe fuel reprocessing facility (*10*), the Savannah River Plant (*4*), and the now defunct fuel reprocessing facility at West Valley, NY (*11*). In many cases the goal of the study was to assess the dose of ^{129}I to humans, which is acquired from foodstuffs via the rainwater−soil−plant pathway.

In contrast, our goal in the present study is to identify and quantify the source(s) of global atmospheric ^{129}I deposition onto the continents. This is part of a larger study for which we have determined ^{129}I levels in river and coastal waters, soils, and near-shore marine sediments. On the basis of data presented herein for ^{129}I/^{127}I ratios measured in rainwater and epiphytes from the continental United States and Europe, it is our contention that ^{129}I released into the atmosphere from nuclear fuel reprocessing facilities in northwestern Europe comprises the largest fraction of ^{129}I in the modern global atmosphere. This has important implications for mechanisms of atmospheric transport of iodine, sources of ^{129}I in the terrestrial biosphere and hydrosphere, and the global iodine cycle.

Methods

Sampling. Meteoric water samples were collected in rain samplers at W. Lafayette, IN, Galveston, TX, and College Station, TX, and by scooping fresh snow into a container at Mansfield, OH, and Sauverny, France (Figure 1). The rain samples are wet-only deposition. With the exceptions of a series of 1 L samples collected in College Station (which did not give a strong enough ^{129}I signal to calculate a ^{129}I/^{127}I ratio) and a 1 L snow sample from Sauverny, France (near Geneva, Switzerland), sample sizes were 4−8 L. These were not collected during a single precipitation event, and in some cases were combined from events several weeks apart. The epiphyte samples were pulled off of living trees with a gloved hand and stored refrigerated, in plastic bags. Sample locations for Spanish moss (Figure 1), *Tillandsia usneoides* L. (Bromeliaceae), nearly covered the range (the southeastern coastal plain from Virginia west to central Texas) for this vascular epiphyte. The sample of desert mistletoe, *Phoradendron californicum* (Loranthaceae) from Tucson, AZ, was collected from a Saguaro cactus.

Sample Preparation. Meteoric water samples were decanted into large flasks and combined with 10 mL of 10 mM $NaHSO_3$ for each liter processed. One to eight liters of meteoric water was then concentrated to a volume of ~200 mL by rotary vacuum distillation. Two milligrams of iodine

* Address correspondence to this author at L-231, P.O. Box 808, Lawrence Livermore National Laboratory, Livermore, CA 94550; phone: (925) 423-1478; fax: (925) 422-3160; e-mail: moran10@llnl.gov.
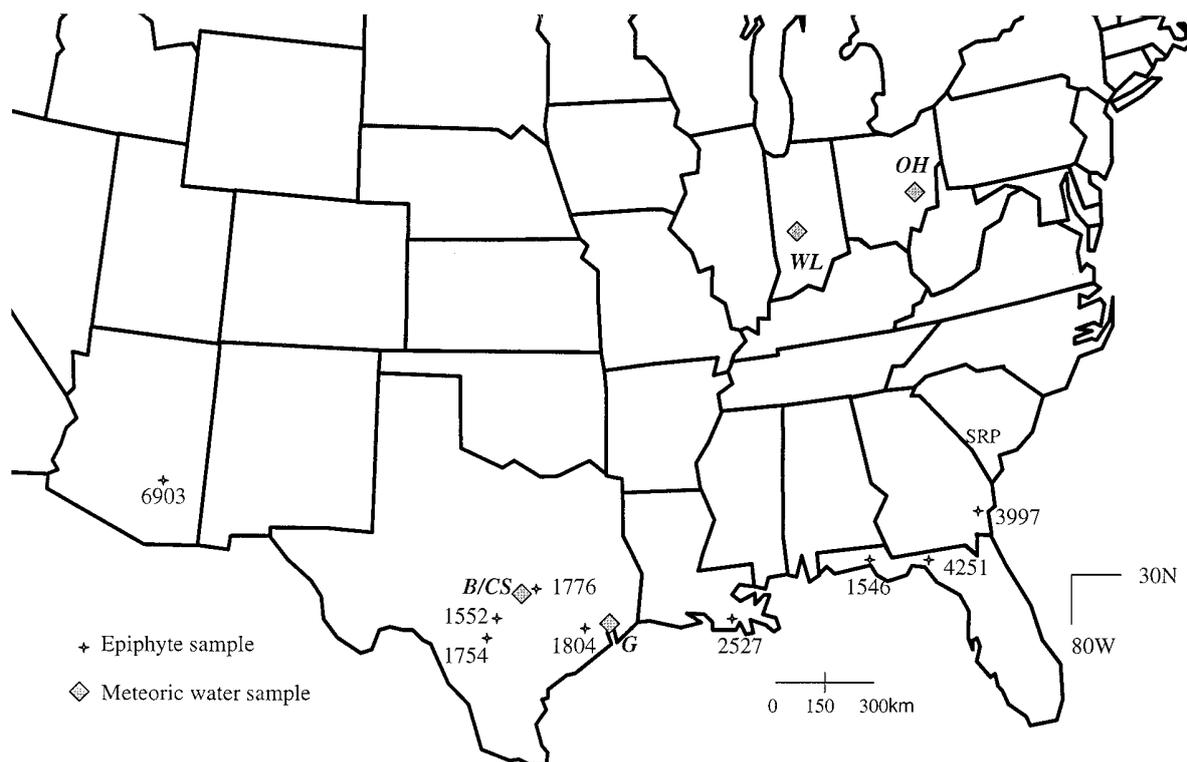[†] Texas A&M University, College Station.
[‡] Texas A&M University, Galveston.

FIGURE 1. Sample location map. Epiphyte sample locations are shown by "+", with $^{129}I/^{127}I$ ratios ($\times 10^{-12}$). Meteoric water sample locations are shown by diamonds, with location letters matching the sample identifications in Table 1. "SRP" gives the approximate location of the Savannah River Plant.

carrier in the iodide form was added. Iodine was extracted into CCl_4, back extracted into a sodium bisulfite/sulfuric acid solution, and precipitated as AgI.

Plant samples weighing 1−2 g were crushed and dried in an oven at 90 °C overnight. The alkali leach and fusion method described by Nishiizumi (12) was followed, and the resulting leachate was processed as described above for the preconcentrated meteoric water samples. Recovery rates by this method were not determined for plant samples, but Nishiizumi (12) reports 85% recovery for rock samples. An aliquot of the leachate was preserved for stable iodine determination. A carefully determined amount of carrier iodine (~2 mg), as iodide, was added before extraction into CCl_4.

For ratio measurement by accelerator mass spectrometry (AMS), carrier iodine of low $^{129}I/^{127}I$ ratio is added to increase the bulk sample size and to reduce the probability of contaminating the ion source with high-ratio material. To calculate $^{129}I/^{127}I$ ratios, the amount of ^{127}I contributed from the sample must be determined. Then a weighted average between the sample and the carrier, for which the amount and ratio are known, is used to determine the ratio in the sample. The calculated ratio is very sensitive to the stable iodine concentration in the rainwater, and much of the propagated error in our reported data derives from uncertainty in very low stable iodine concentrations. We assume that carrier iodine and iodine from the sample (which are in the same −1 oxidation state) are recovered in equal proportion.

^{127}I and $^{129}I/^{127}I$ Measurements. Iodine concentrations in the samples and extracts were measured on a Hewlett-Packard model 4500 inductively coupled plasma mass spectrometer equipped with HPChem Station software. Memory effects in the sample introduction system (Cetac autosampler and Meinhard-type cocentric nebulizer) were circumvented by running samples and standards in the range from 100 ppt to 20 ppb. A blank was measured after every

2 samples, and a check standard was measured after every 10. The method detection limit was 0.1 ppb, and relative standard deviations (RSD) were 1−15%. Suppression of the internal standard (rhodium) occurred for samples with high (>1%) total dissolved solids (plant extracts). For those samples, several different dilutions were measured, and an average was taken. Chloride concentrations in meteoric water samples were determined by ion chromatography, with RSDs of ~10%.

$^{129}I/^{127}I$ ratios were measured by AMS at Purdue University's PRIME Lab. A thorough description of the conditions for running ^{129}I has been reported (13). Because the ratios measured for atmospheric samples were all >5.0 × 10^{-12} (well above the detection limit of 5 × 10^{-15}), errors due to counting statistics in the detector are relatively small, and 1σ errors are <10%. Procedural blanks were 0.07−0.5 × 10^{-12}, which were in the range expected for the carrier iodine, and therefore no corrections to the measured ratios were made for blanks.

Results and Discussion

Total iodine concentrations and the $^{129}I/^{127}I$ ratios measured and calculated for meteoric water and plants are shown in Table 1. The atmospheric chemistry of iodine is quite complex. Iodine can take many chemical forms in the atmosphere, each with a relatively long residence time; iodine in its uncharged forms is volatile; moreover, iodine is preferentially injected into the atmosphere from seawater. Because we have not made direct measurements from air samples, nor determined the chemical forms of ^{129}I or ^{127}I, we are restricted to suggesting plausible mechanisms for the mixing, transport, and deposition of anthropogenic ^{129}I and naturally occurring ^{127}I, based on our meteoric water and epiphyte data.

Stable Iodine in Rain and Epiphytes. Our total iodine concentrations in rainwater, measured by ICP-MS, agree well

TABLE 1. Analytical Data

	I (ppb)	measd ^{129}I/^{127}I ratio (10^{-12})	sample[a] ^{129}I/^{127}I ratio(10^{-12})	1σ propagated error (10^{-12})	^{129}I atoms/L (10^7)	Cl$^-$ (ppm)	I/Cl
			Rain/Snow[b]				
WL 12/95-2	1.4	12.03	5756	202	3.7		
WL 12/95-3	0.9	12.45	8327	250	3.7	0.2	0.0045
WL 12/95-4	0.6	13.85	12390	1222	3.7		
B 11/95	1.2	7.38	2027	201	1.1	1.6	0.0008
CS 8/22/96	6.6	10.39	755	86	2.3		
CS 9/1/96−9/15/96	1.9	4.17	913	403	2.4	0.3	0.0061
CS 9/15/96−10/15/96	2.5						
CS 10/20/96−10/26/96	2.0					1.2	0.0017
CS 10/26/96−11/24/96	1.7	2.03	893	112	0.7	1.1	0.0015
CS 11/24/96−/30/96	3.3					1.6	0.0021
CS 12/21/96−1/16/97	2.9	26.80	3408	319	4.5		
CS 1/20/97−1/30/97	2.5	7.60	2121	174	2.5		
CS 2/20/97−2/26/97	1.8	5.30	975	158	0.9		
CS 3/18/97-1	1.4						
CS 3/18/97-2	1.3						
CS 3/18/97-3	0.6						
CS 3/19/97-4	0.8						
CS 3/19/97-5	0.7						
G 1/96−10/96	1.9	9.44	1735	170	1.6		
G 11/96	12.1	27.90	1064	52	6.0	46.5	0.0003
G 12/6/96−1/6/97	1.7					4.9	0.0003
G 1/7/97−1/16/97	1.2	14.87	3946	399	2.3		
Ohio snow 1/14/97	0.7	11.10	9150	1565	3.0		
Sauverny snow	0.2	14.83	48059	6823	6.7	0.2	0.0010

	I (ppm)	measd ^{129}I/^{127}I ratio (10^{-12})	sample[a] ^{129}I/^{127}I ratio(10^{-12})	1σ propagated error (10^{-12})	^{129}I atoms/kg (10^7)
			Epiphytes		
Spanish moss					
CS, Texas	0.6	3.42	1776	320	487
New Braunfels, TX	4.4	5.00	1552	145	3157
Houston, TX	3.2	12.84	1804	81	2678
Altamaha, GA	2.9	1.90	3997	957	5370
New Orleans, LA	4.9	11.50	2527	221	5821
Suwanee, FL	0.9	1.18	1546	362	634
Apalachiola, FL	3.9	1.51	4251	387	776
San Marcos, TX	0.4	0.75	1754	612	295
other					
Desert Mistletoe, Tucson, AZ	0.9	11.31	6903	1243	2782

[a] Ratio calculated from measured ratio, known carrier ratio, and relative proportions of sample and carrier. [b] WL, West Lafayette, IN; B, Bryan, TX; CS, College Station, TX; G, Galveston, TX.

with the range measured by previous workers (14−16). Concentrations decrease during the course of a single rain event and are lower during the rainy season (Figure 2). For example, a 6 month drought in Texas (during which very stable air masses are set up) preceded sample CS 8/22/96, which had a high iodine concentration of 6.6 ppb. In contrast, samples taken during the rainy season of January, February, and March had lower iodine concentrations (∼2 ppb). A long precipitation event in West Lafayette, IN, showed decreasing iodine concentrations (samples WL-2, WL-3, and WL-4). A similar pattern was observed over the course of a precipitation event in College Station, TX (samples CS 3/5/97-1−5). Although the measured concentrations are near the method detection limit, this pattern suggests that iodine is stored in the atmosphere during dry periods and is washed out during precipitation events.

Epiphytes are plants that have no root system, acquire nutrients from the air, and have been used as atmospheric samplers for other constituents. High iodine concentrations have been reported for lichens and other mosses (17, 18), suggesting that these plants actively take up atmospheric iodine. The high iodine concentrations we measured in Spanish moss (Table 1) corroborate that conclusion. The lifetime of Spanish moss is on the order of months to years (19), offering a longer term average of atmospheric iodine behavior.

Iodine concentrations in seawater are 50−60 ppb, substantially higher than concentrations in surface freshwater and meteoric water. Since cessation of the practice of burning seaweed, anthropogenic sources for stable iodine in the atmosphere are not known. Iodine in the atmosphere has an almost exclusively marine source owing to its intense injection from surface seawater and lack of terrestrial sources. The I/Cl ratio in atmospheric samples is dramatically greater than in bulk seawater, which has led to the suggestion that iodine is photochemically oxidized and volatilized (20) or that organic films on the ocean surface, enriched in I, are released during bubble breaking (21 and references cited therein). The relative proportions of iodine in aerosol, inorganic gaseous, and organic gaseous forms vary by location and season, with aerosol on average one-fourth or less of the total (14, 16) and the organic gas CH_3I making up 40−80% of the total (15). Estimates for the atmospheric residence times of these various forms are as follows: particulate, 14 days; inorganic gass, 10 days; organic gas, 18 days (16). Given that the residence time for water vapor in the atmosphere
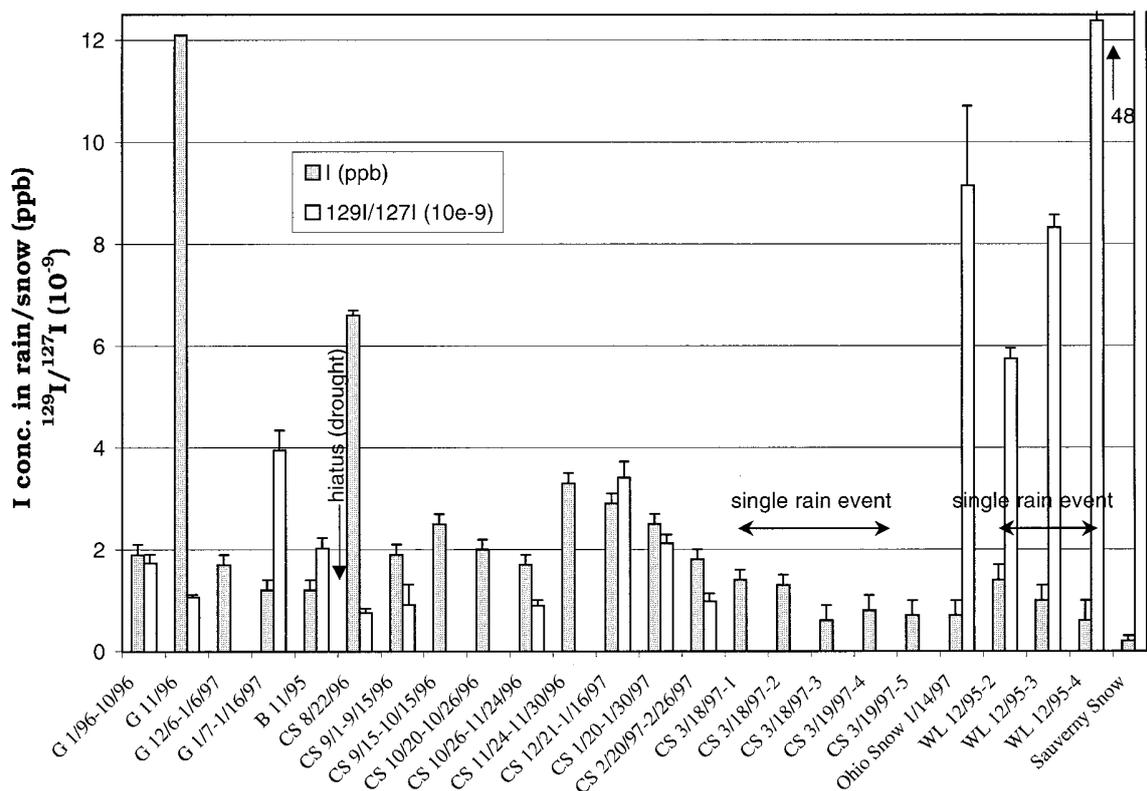
FIGURE 2. Stable iodine concentrations and $^{129}I/^{127}I$ ratios for meteoric water samples, listed from closest to the coast to furthest inland and from least to most recent within a given sample location. Error bars are RSDs from ICP-MS measurement of iodine and propagated 1σ errors for ratios.

is 9 days, the relatively long residence times of atmospheric iodine allow for extended global transport and substantial mixing.

Many workers contend that iodine concentrations in rain and in soil decrease with increasing distance from the coast (*22, 23*). However, the pattern is not as distinct for iodine as it is for chlorine. Chlorine concentrations in Spanish moss have a strong, inverse correlation with distance from the Texas Gulf coast (*24*). However, although the concentrations of iodine we measured in Spanish moss are relatively high for plant material (*17*), there is no apparent pattern with distance from the coast (or, more pertinently, with sea salt deposition patterns). Furthermore, our meteoric water data suggest that higher levels of iodine in rain may be found in coastal locations, but the effect is apparently restricted to a narrow band near the shoreline during strong marine winds. One sample from Galveston, TX (November 1996) has by far the highest iodine concentration measured in rain for our sample set. However, for the same time periods, iodine concentrations in rain from Galveston were often the same as or lower than those in rain from College Station, which is >200 km inland. Locations in continental interiors (W. Lafayette, IN, Mansfield, OH, and Sauverny, France), which have high annual precipitation rates, show somewhat lower (≤1.4 ppb) iodine concentrations in meteoric water.

The chloride concentrations and I/Cl ratios we measured for a few meteoric water samples (Table 1) agree well with those reported by Duce et al. (*14*). I/Cl ratios are lower for coastal locations compared to inland locations. It therefore appears that iodine entrained in the marine atmosphere, which is not immediately deposited on the near-shore continent, is mixed into the atmosphere and can be distributed globally. Furthermore, recycling of iodine that has been deposited onto the continent can occur via the atmosphere when iodine is volatilized from soils or plants (*22*).

Anthropogenic ^{129}I in the Atmosphere. Our measured ^{129}I concentrations in rainwater are lower than those reported by other workers (Table 2). The $^{129}I/^{127}I$ ratio for snow from Sauverny, France, agrees reasonably well with ratios measured in contemporary human thyroids from Germany (*25*), but $^{129}I/^{127}I$ ratios reported on aerosols from outside Tokyo (*26*) were $(3-9) \times 10^{-7}$, or ~100 times higher than our median ratio for rainwater in the continental United States. These large discrepancies reflect increasing distance from the main source and/or from local sources and the method of analysis. In particular, some of the reported data were collected using neutron activation techniques, which have detection limits of ≥20 μBq (equivalent to a ratio of 5×10^{-7} for a typical rainwater sample). For areas distant from fuel reprocessing facilities, the ratio of ^{129}I to ^{127}I and the concentration of ^{129}I in typical meteoric or surface water dictate large sample sizes and the use of the superior method of accelerator mass spectrometry for $^{129}I/^{127}I$ ratio measurements. Our results agree reasonably well with a 1982 rain sample from Israel, measured by AMS [8×10^7 atoms/L (1)]. They are somewhat lower than AMS-measured ^{129}I concentrations in rain samples from western New York (11). This area is presumably affected by ongoing releases to surface waters from the now inactive West Valley Reprocessing Facility.

A small fraction of bomb test fallout ^{129}I that reached the stratosphere may still be cycling in the atmosphere, due to volatilization from plants. Bentley et al. (27) showed that ^{36}Cl, another bomb test product, decreased to near pre-bomb levels in ice cores, but more recent studies (28, 29) suggest that due to biospheric "hold-up" and release of Cl, a small amount of test fallout ^{36}Cl is still cycling in the atmosphere. However, the geographic distribution of ^{129}I in precipitation and ^{129}I mass balance considerations suggest that most of the ^{129}I now in the atmosphere is from European nuclear fuel reprocessing emissions. For instance, a study of ^{129}I in an ice core from the Fiescherhorn glacier in Switzerland showed

TABLE 2. Reported ^{129}I Measurements from Atmospheric Samples

publication	location	estimated release to atmosphere from nearby FRPs	method of measurement	sample type	^{129}I/^{127}I (10^{-9})	^{129}I concn (10^7 atoms/kg)
Brauer and Rieck, 1973	Hanford, WA		INAA	meteoric water		181−70000
Brauer and Strebin, 1982	Spokane, WA		INAA	meteoric water		84−55000
Doshi et al., 1994	Trombay, India		INAA	meteoric water, air		11000−23000
Handl et al., 1993	Germany		INAA	thyroids, epiphytes	*25^a*	
Muramatsu and Ohmono, 1986	Tokaimura, Japan		INAA	meteoric water	*5000*	8000
Paul et al., 1987	Israel, 1987	1.3 kg (from Chernobyl)	AMS	meteoric water		120
	Munich, 1987					2600
	Israel, 1982					8.2
Rao et al., 1997	western New York	1966−1975, 17 kg	AMS	meteoric water		20
Rucklidge et al., 1994	England	several kg/year	AMS	epiphytes	*150−66930*	
Tsukada et al., 1991	Tokaimura, Japan		INAA	aerosols	*300−860*	
Wershofen and Aumann, 1989	WAK, Karlsruhe	1986 and 1987, 0.02 kg/year	INAA	aerosols, inorganic and organic gases	*300−1000*	
this study	France		AMS	meteoric water	*48*	6.7
this study	continental U.S.		AMS	meteoric water, epiphytes	*0.8−12.4* *1.6−6.9*	0.7−6.0 300−5800

^{a} Weighted mean.

that bomb fallout peaked in about 1961 and decreased to 1965, and then the ^{129}I deposition steadily increased from 1965 to 1987 (30). The 1983 ^{129}I deposition rate is almost an order of magnitude greater than the peak bomb fallout value. A slight but steady increase in ^{129}I/^{127}I ratios measured in thyroids from Europe from 1978 to 1994 is also reported (31). The pattern of increase observed in the ice core and dated thyroid samples parallel the increase in emissions over the same time period from the facilities at Sellafield and La Hague.

The ^{129}I that is released into the atmosphere from the fuel reprocessing facilities clearly is not distributed evenly over the globe. ^{129}I/^{127}I ratios measured in epiphytes within 60 km of the Sellafield site were $(15−6693) \times 10^{-8}$ (18), 2−4 orders of magnitude higher than ratios measured in Germany and other parts of Europe (25, 31). Our ratio for meteoric water from Sauverny, France (near Geneva, Switzerland), is the highest in Table 1 and is >1 order of magnitude greater than all but two samples measured in the United States. Even within U.S. locations, the effect of increasing distance from the reprocessing source can be observed, with locations closer to the latitude of the reprocessing facilities having somewhat higher ^{129}I/^{127}I ratios.

Other, unreported, sources of fuel reprocessing ^{129}I to the atmosphere may exist. Although Sellafield and La Hague are by far the largest commercial fuel reprocessing facilities, small commercial facilities in Europe probably have atmospheric ^{129}I emissions, and noncommercial reprocessing facilities exist in many countries with nuclear power plants and research reactors. However, the volume of nuclear fuel reprocessed at these plants, which can be taken as a measure of the amount of ^{129}I released, is very much lower than that for La Hague and Sellafield. Although discharges from the former Soviet Union to the Arctic Ocean are overwhelmed by discharges from Sellafield and La Hague (3, 32), little is known about discharges of ^{129}I to the atmosphere from the former Soviet Union. Likewise, atmospheric emissions of ^{129}I from the Hanford Facility are poorly known. However, atmospheric emissions are likely to be in some proportion to discharges into surface water, which are better known. Annual ^{129}I fluxes from the Columbia River and from rivers draining the former Soviet Union are only slightly elevated compared to those of rivers that have no known ^{129}I sources in their watersheds (32−34). Furthermore, modeled ^{131}I and ^{129}I releases from Hanford show that while as much as tens of kilograms of ^{129}I were emitted to the air in the 1950s, releases since 1986 have been near zero (35). Given that reliably

measured levels of ^{129}I in environmental samples decrease with increasing distance from the main source in northwest Europe, we conclude that the ^{129}I measured in rain and epiphytes from the continental United States has been transported from that area. Further studies are needed on environmental ^{129}I/^{127}I levels in Asia, on biologically mediated transformations during transport, and on volatilization from surface water, soil, and plants.

To estimate the amount of fuel-reprocessed ^{129}I potentially distributed globally from the fuel reprocessing facilities in Europe, we calculate the "standing crop" of ^{129}I in the atmosphere over the continental United States and extrapolate to the northern hemisphere. A conservative estimate of the residence time of total iodine in the atmosphere is 14 days (16). Using a global precipitation rate of 4.96×10^{17} kg/year (36) and our median stable iodine concentration in rain of 1.7 ppb, one calculates a flux of iodine from the atmosphere of 8.4×10^8 kg/year. This agrees well with the estimated global sea to air flux of CH_3I (based on a two-phase model and measurements of CH_3I concentrations in the atmosphere) of 8×10^8 kg/year (37). The median ^{129}I/^{127}I ratio measured in rainwater for U.S. locations is $\sim$2100 $\times$ 10^{-12}. Here it is important to note that 80% of atmospheric radioiodine deposition (at midlatitudes with $\sim$1 m/year of rainfall) occurs during precipitation events, 20% by dry deposition (38). Assuming no inter-hemispheric mixing, and using the median ^{129}I/^{127}I ratio, the mass of ^{127}I in the northern atmosphere, and a 14 day residence time, the mass of ^{129}I in the northern atmosphere at any given time is 0.04 kg. The roughly calculated 0.04 kg can be compared with 0.7 kg (again using the 14 day−0.04 year−mean residence time) of the estimated 18 kg/year released from Sellafield and La Hague in the atmosphere at any given time. Given the great distance between the source and the continental United States, the fact that $\sim$6% of the estimated atmospheric releases reaches the sampling area seems reasonable. The total meteoric flux of ^{129}I over just the continental United States is, however, considerably lower, that is, on the order of 15 g/year, which is only 1 per mil of the estimated athmospheric emission rates from Western Europe. This calculation assumes a surface area of 8×10^{12} m^2, an average rainfall of 0.5 m/year, and median values of 1.7 ppb of ^{127}I and ^{129}I/^{127}I of 2100 $\times$ 10^{-12} in rain.

One can also make a crude calculation of the possible contribution to atmospheric ^{129}I from sea-spray injected from the area affected by direct releases of ^{129}I from Sellafield and

La Hague to surface ocean water. Ratios of $\sim$5000 $\times$ 10^{-10} are reported for the North Sea (3). For a sea to air flux of stable iodine of 8 $\times$ 10^8 kg/year (37 and references cited therein) and an affected area of 22000 km^2 (conservatively large given normal subduction rates of surface ocean water and fast dilution by stable ^{127}I in the ocean), the yearly contribution is only 0.02 kg. This is much less than the estimated 18 kg/year directly released to the atmosphere and has therefore not been taken into account. As further evidence for direct atmospheric emissions affecting rainwater in the United States, maximum ^{129}I/^{127}I ratios in seawater from the Gulf of Mexico (39) and the Mid Atlantic Bight (40) do not exceed 100×10^{-12}, much lower than those observed for the meteoric water.

As fine aerosols or in gaseous forms, ^{129}I can be mixed from top to bottom of the troposphere very quickly ($<$1 day). Global tropospheric circulation patterns show that in winter months, the air mass over northern Europe is transported by strong winds in an easterly northeasterly direction (41). However, during summer months, there is a significant wind component that drives the air mass to the south, along the western edge of Africa, and across the Atlantic via the trade winds. Both of these circulation patterns could result in transport of ^{129}I from European fuel reprocessing facilities to the continental United States. In analogy to the suggested mode of easterly, circumglobal transport, the radioactive air mass generated by the Chernobyl accident was traced (42) across Europe and Asia, across the Pacific, to the continental United States within a period of $\sim$10 days. This air mass was confined almost exclusively to the troposphere and was detectable in the atmosphere for several weeks.

^{129}I and ^{127}I are not thoroughly mixed during transport, as evidenced by the geographic variation in ^{129}I/^{127}I ratios (and variation with time during a precipitation event). Nor should we expect them to be, given their disparate sources. Isotope ratios are somewhat higher for inland locations, although no clear pattern with sea salt deposition is discernible in stable I concentrations. Over the course of a rain event, stable iodine concentrations decrease while ^{129}I/^{127}I ratios increase (W. Lafayette samples), suggesting that the chemical form of the ^{129}I has a slower rate of deposition.

The most likely form of ^{129}I released by fuel reprocessing plants is the organic gas methyl iodide (CH$_3$I). Weshofen and Aumann (10) determined that 34$-$89% of the ^{129}I measured within 23 km of the Karlsruhe reprocessing plant was in an organic gaseous form. UNSCEAR (6) measurements from the Sellafield facility indicated that 60% of the iodine in the off-gases was in organic form, 40% in inorganic, and $\sim$1% in particulate. Within the troposphere, long-ranging transport of the organic gaseous form is likely, given the estimated residence time of 18 days (16). Although the relative proportion in particulate form is small, Tsukada et al. (26) found that ^{129}I aerosols were rich in the fine ($<$1 μm) mode, making both particle to gas conversions and long-range transport more likely. Because mixing into the stratosphere is unlikely, the dispersion is expected to be somewhat confined latitudinally. However, given that the source location is $\sim$50 N and the Texas sampling location is $\sim$30 N, some longitudinal transport takes place. Two possible mechanisms are longitudinal dispersion during circumglobal easterly transport and jet-stream meandering or the more direct route$-$southerly transport from Europe to the region influenced by westerly trade winds.

The fact that ^{129}I/^{127}I ratios in rain and Spanish moss from approximately the same locations (in Texas) agree to within 40% suggests that the pattern of redistribution of ^{129}I in the atmosphere has been about the same for the past several years. Ratios in epiphytes show less variability than those in rain, because seasonal and small scale spatial variations are smoothed out. Accumulation of atmospheric iodine, enriched

in ^{129}I, results in the very high concentrations of ^{129}I observed in epiphytes. Two Spanish moss samples, from locations on the Altamaha River in Georgia and on the Apalachiola River in Florida, may have somewhat elevated ratios due to regional dispersal of ^{129}I from the Savannah River Plant near Aiken, SC. Moss samples (of various genera) from Oregon and Washington also had elevated ratios (averaging 30000 $\times$ 10^{-12}, J. Moran, unpublished data), probably reflecting accumulation of ^{129}I historically dispersed from the Hanford Facility in Washington.

Comparisons with River Water and Soil. All of the anthropogenic ^{129}I measured in rivers and soils not draining a nuclear facility must have been delivered atmospherically. High ^{129}I levels measured in rivers near, but not draining, the Savannah River Plant (34) clearly show that ^{129}I has been transported via the atmosphere. ^{129}I/^{127}I ratios measured in meteoric water samples from the continental United States are $\sim$1order of magnitude higher than those measured in rivers, which are $\sim$1 order of magnitude higher than those measured in near-surface soils (34). The effect of dilution by iodine with much lower (likely pre-anthropogenic) ratios is evident. ^{129}I/^{127}I ratios measured in a few European rivers are as high or higher than ratios in atmospheric samples (43), because of the temporal variability in meteoric samples and because the contribution from a soil iodine component is very small for watersheds draining the Alps. The iodine deposited as rain is likely to be more mobile (as iodide or iodate) than organically bound iodine in soils, and as such gets into the biosphere and into rivers in greater proportion than the older, "dead" iodine. Thus, there is a chemical fractionation, which results in biota and rivers exhibiting higher ^{129}I levels than soils. For example, soil from the Sabine River watershed has a ^{129}I/^{127}I ratio of 80 $\times$ 10^{-12} (34), while Sabine River water has a ratio of 450 $\times$ 10^{-12}, and rain from nearby Galveston, TX, has a median ratio of 1700 $\times$ 10^{-12}. Redistribution of ^{129}I that has been deposited onto the continent from the atmosphere is by leaching from soil inorganic and organic matter and by volatilization from soils, surface water, and plants (22).

Atmospheric deposition of fuel reprocessing-derived ^{129}I affects ^{129}I levels in soils and rivers but has a negligible effect on levels in the ocean. ^{129}I/^{127}I ratios are highest in the atmosphere because they are diluted least there (low ambient ^{127}I concentration) and are lowest in the marine environment (seawater and marine biota) where fast and substantial dilution takes place (high ^{127}I concentration).

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