Environmental Science & Technology

Article

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Iodine-129 in Seawater Offshore Fukushima: Distribution, Inorganic Speciation, Sources, and Budget

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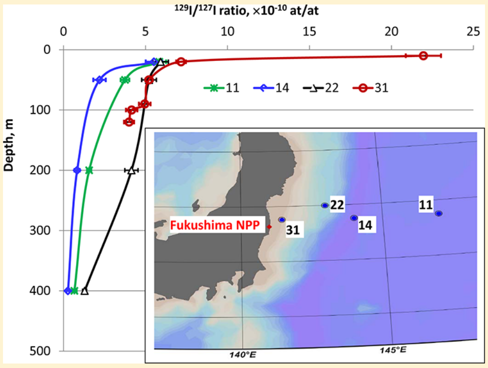
Supporting Information

ABSTRACT: The Fukushima nuclear accident in March 2001 has released a large amount of reactive pollution to the environment. Of the pollutants, iodine-129 is a long-lived radionuclide and will remain in the environment for millions of years. This work first report levels and inorganic speciation of ^{129}I in seawater depth profiles collected offshore Fukushima in June 2011. Significantly elevated ^{129}I concentrations in surface water were observed with the highest ^{129}I/^{127}I atomic ratio of 2.2×10^{-9} in the surface seawater 40 km offshore Fukushima. Iodide was found as the dominant species of ^{129}I, while stable ^{127}I was mainly in iodate form, reflecting the fact that the major source of ^{129}I is the direct liquid discharges from the Fukushima NPP. The amount of ^{129}I directly discharged from the Fukushima Dai-ichi nuclear power plant to the sea was estimated to be 2.35 GBq, and about 1.09 GBq of ^{129}I released to the atmosphere from the accident was deposited in the sea offshore Fukushima. A total release of 1.2 kg of ^{129}I from the Fukushima accident was estimated. These Fukushima-derived ^{129}I data provide necessary information for the investigation of water circulation and geochemical cycle of iodine in the northwestern Pacific Ocean in the future.



■ INTRODUCTION

A nuclear accident at the Fukushima Dai-ichi nuclear power plant (1FNPP), Japan, occurred in March 2011 due to failure of the cooling system after the Tohoku earthquake and the Tsunami on March 11, 2011. Hydrogen explosions occurred in unit 1 on March 12 and unit 3 on March 14, and in the spent fuel storage building in unit 4 on March 15, as well as an internal explosion in reactor 3 on March 15, 2011.[1−3] Significant quantities of radioactive materials were emitted to the atmosphere from March 12 through 24, with estimated atmospheric releases of 150−160 PBq (peta becquerels, or 10^{15} Bq) of ^{131}I and 10−15 PBq of ^{137}Cs.[4−6] These radionuclides were transported and deposited over large areas of the northern hemisphere; radioisotopes of cesium and iodine have been observed in the atmosphere over America, Europe, and Asia. Fortunately, due to the dominant westerly wind, the radionuclides were transported and deposited mainly in the Pacific Ocean, with less than 20% of them deposited over the land of Japan.[1,6,7]

The damage in the containment vessel of the reactor of unit 2 at the 1FNPP due to an internal hydrogen explosion caused a leakage of highly contaminated water to the sea from March 25 to April 5.[3,8,9] Large volumes of contaminated water were produced during cooling of the reactors using fresh water and seawater, and some of this water was intentionally discharged directly to the sea April 4−20, 2011 to leave space for more highly contaminated water. In addition, some contaminated

Received: November 1, 2012
Revised: March 4, 2013
Accepted: March 5, 2013

groundwater was also directly discharged to the sea.[2,8,10] This direct discharge of contaminated water to the sea has significantly elevated ^{137}Cs and ^{131}I concentrations in seawater at the coast as well as offshore, starting from March 21 and rapidly increasing from March 27, with peak values on March 30 (47 kBq/L of ^{137}Cs) and on April 6 (68 kBq/L) at the discharge point of the 1FNPP.[9] Therefore liquid discharge directly to the sea was another major source of radionuclides to the environment, especially to the ocean.

^{137}Cs and ^{131}I, which were two major radionuclides released from the Fukushima accident, have been intensively investigated. However, many other radionuclides have also been released to the environment, especially through the liquid discharge to the sea, because of high leaching efficiency of radionuclides from the damaged fuel rod materials when corrosive brine water was used to cool the reactor. Among these radionuclides, ^{129}I is a fission product with relative high fission yields of 0.6%. However, few data on ^{129}I from the Fukushima accident have been reported, especially in the sea surrounding Fukushima.

^{129}I is a long-lived radioisotope of iodine with a half-life of 15.7 Ma. It is a soft beta-emitter with maximum beta-energy of 154 keV. Therefore, ^{129}I is less radiologically harmful, and less important in view of radiation protection. However, due to its high solubility and the long residence time of iodine in the ocean, ^{129}I is an ideal oceanographic tracer for investigation of water circulation in the ocean,[11] and a useful environmental tracer for the investigation of the interaction of atmosphere and seawater, as well as for the biochemical cycle of stable iodine through chemical speciation analysis of ^{129}I.[12,13] ^{131}I ($t_{1/2}$ = 8 days) is the most harmful radionuclide from the nuclear accident, due to its large release during the accident, and the high uptake and enrichment in human thyroid. Its short half-life prevents it from being well measured in the environment to evaluate the radiation risk to children exposed to the radioactive contamination. The long-lived ^{129}I provides a good analogue to reconstruct levels and distribution of short-lived ^{131}I in the environment.[14] In addition, iodine is highly concentrated in seaweed, and some types of seaweed are popular seafood in Japan and other Asian countries.[15] ^{129}I discharged to the sea will be concentrated in the seaweed and some sea fish,[16] which might cause an increased radiation to humans who consume seafood from a highly contaminated area.

This work aims to investigate the levels and distribution of ^{129}I in the sea offshore Fukushima by determination of ^{129}I in depth profiles of seawater, and to evaluate the source term and budget of ^{129}I by chemical speciation of ^{129}I and ^{127}I for iodide and iodate in seawater profiles.

■ MATERIALS AND METHODS

Samples and Reagents. Seawater samples were collected from offshore Fukushima during the research cruise organized by American scientists June 3−17, 2011 using the research vessel Kaimikai-O-Kanaloa of the University of Hawaii.[3] The samples were stored in dark at ambient temperature before analysis. Of these samples, depth profiles from 4 sampling stations with distances of 40−530 km from Fukushima Dai-ichi nuclear power plant (Figure S-1 and Table S-1 in the Supporting Information) were used for ^{129}I.

All chemical reagents used were of analytical grade and all solutions were prepared using deionized water (18.2 MΩ cm). ^{129}I standard (NIST-SRM-4949c), carrier free ^{125}I (Amersham Pharmacia Biotech, Little Chalfout, Buckinghamshire, UK), ^{127}I carrier (Woodward iodine, MICAL Specialty Chemicals, New Jersey, USA), TEVA extraction chromatographic resin (100−150 μm) (TRISKEM International, Bruz, France), and Bio-Rad AG1-×4 anion exchange resin (50−100 mesh, Cl form, Bio-Rad laboratories, Richmond, CA, USA) were used in the experiments.

Analytical Methods for Determination of ^{129}I Species. Anion exchange chromatography was used for separation of iodide, iodate, and total inorganic iodine from seawater. A schematic diagram of the separation procedure is shown in Figure S-2, and the separation methods are presented in the Supporting Information. The detailed methods for speciation analysis of ^{129}I in seawater have been reported elsewhere.[13]

Filtered seawater (0.5−1 L) was transferred to a beaker, and ^{125}I$^-$ was added. After loading the prepared solution to an anion exchange column (AG1-×4 resin, NO_3^- form), and washing with 0.2 mol/L $NaNO_3$, iodide on the column was eluted with 5% NaClO; effluent and wash were combined for iodate separation. A 1.0 mL solution of the iodide fraction, the iodate fraction, and the original seawater were taken to a vial for ^{127}I measurement using ICP-MS. Iodine in the remaining solutions of the iodide and iodate fractions, as well as in the original seawater, was separated using $CHCl_3$ extraction based on adjusting the oxidation state of iodine. The separated iodine from each fraction in iodide form was used to prepare AgI sputter target by adding $AgNO_3$ solution for AMS measurement of ^{129}I.

Before extraction, the eluate of iodide from the anion exchange column was also measured for ^{125}I by gamma-spectrometer to monitor chemical recovery of iodide during column separation. This measurement is used to correct the ^{127}I$^-$ and ^{129}I$^-$ concentrations in seawater.[12,13]

An ICP-MS system (X Series II, Thermo, Waltham, MA) equipped with an Xs- skimmer cone and standard concentric nebulizer was used for the measurement ^{127}I. A 1.0 mL portion of the separated fractions or the original seawater was diluted to 20 mL using 1% ammonium solution, and spiked with Cs$^+$ (to 2.0 ppb) as internal standard. The detection limit of the method for ^{127}I was calculated as 3 SD of the procedure blank to be 0.03 ng/mL.

The ^{129}I/^{127}I ratios in total iodine samples were determined by AMS at the Vienna Environmental Research Accelerator (VERA)[17] and the University of Arizona AMS Laboratory, both using a 3MV National Electrostatics Corporation AMS.[18] The ^{129}I/^{127}I ratios in iodide and iodate samples were measured using the 3 MV AMS facility at the Xi'an AMS center.[19] The machine backgrounds of the ^{129}I/^{127}I ratio are around (2−4) × 10^{-14}. Procedure blanks using the same procedure as the samples were also prepared; the highest measured ^{129}I/^{127}I ratio is 2.8×10^{-13}, which is significantly lower than measured ^{129}I/^{127}I ratios in the samples. No seawater from uncontaminated deep ocean with ^{129}I/^{127}I close to preanthropogenic level of 2×10^{-12} in marine environment has yet been analyzed.[20] However, a ^{129}I/^{127}I ratio as low as 3×10^{-13} (or 5×10^{5} atoms for a target with 0.5 mg ^{127}I) has been measured in a procedure background sample, which was produced by addition of ^{127}I carrier to deionized water and separation of iodine and measuring it using the same procedure and method as for the samples analyzed in this work.[21] The ^{129}I levels for any species presented in this work (>7.7×10^{6} at/L for ^{129}I concentration in >0.5 L water or 2.6×10^{-11} for ^{129}I/^{127}I atomic ratio) are 1−

Table 1. Distribution of ^{129}I, ^{127}I, ^{129}I/^{127}I Ratios, and Speciation of ^{129}I and ^{127}I in Four Seawater Profiles Offshore Fukushima Collected in June 2011[a]

sampling station	depth (m)	total ^{129}I concn ($\times 10^7$ atoms/L)	^{127}I concn (μg/L)	^{129}I/^{127}I ($\times 10^{-10}$ at/at)	iodide/iodate (mol/mol) ^{129}I	iodide/iodate (mol/mol) ^{127}I
11	400	1.89 ± 0.40	60.44 ± 1.29	0.66 ± 0.14	NM	NM
11	200	4.46 ± 0.36	60.32 ± 1.30	1.56 ± 0.13	2.89 ± 0.47	0.074 ± 0.001
11	50	9.87 ± 0.65	55.53 ± 1.24	3.75 ± 0.26	6.01 ± 0.52	0.162 ± 0.004
11	20	15.63 ± 1.07	56.40 ± 1.08	5.84 ± 0.42	8.54 ± 2.11	0.173 ± 0.005
14	400	0.77 ± 0.09	61.64 ± 1.22	0.26 ± 0.03	NM	NM
14	200	2.30 ± 0.16	58.68 ± 1.00	0.83 ± 0.06	NM	NM
14	50	5.68 ± 0.38	54.60 ± 1.15	2.19 ± 0.15	3.61 ± 0.28	0.185 ± 0.004
14	20	14.75 ± 0.50	56.42 ± 1.21	5.51 ± 0.22	6.08 ± 0.78	0.181 ± 0.004
22	400	3.74 ± 0.34	61.38 ± 1.36	1.28 ± 0.12	NM	NM
22	200	11.80 ± 1.12	60.05 ± 1.42	4.14 ± 0.40	NM	NM
22	50	14.31 ± 1.20	57.88 ± 1.18	5.21 ± 0.45	3.74 ± 0.46	0.067 ± 0.002
22	20	16.14 ± 1.25	57.46 ± 1.08	5.92 ± 0.47	3.81 ± 0.71	0.115 ± 0.003
31	120	10.47 ± 0.76	55.23 ± 1.32	4.00 ± 0.30	NM	NM
31	100	10.68 ± 0.87	54.20 ± 1.10	4.15 ± 0.35	2.28 ± 0.51	0.262 ± 0.007
31	90	13.61 ± 0.93	57.95 ± 1.18	4.95 ± 0.35	3.35 ± 0.34	0.235 ± 0.006
31	50	13.31 ± 0.49	53.83 ± 1.14	5.21 ± 0.22	3.77 ± 0.40	0.270 ± 0.007
31	20	20.70 ± 0.75	60.87 ± 1.21	7.17 ± 0.30	7.40 ± 1.33	0.194 ± 0.005
31	10	62.90 ± 2.72	60.40 ± 1.39	21.95 ± 1.08	8.74 ± 0.33	0.255 ± 0.008

[a] NM: not measured; the uncertainties shown in the table are 2σ analytical uncertainty. The distances from the sampling stations 31 (37.52° N, 141.44° E), 22 (38.00° N, 143.0° E), 14 (37.50° N, 144.00°E), and 11(37.50° N, 147.00° E) to the Fukushima NPP are about 40, 180, 260, and 530 km, respectively.

2 orders of magnitude lower than the procedure plank, confirming that the applied method is well suitable for the analysis of these samples.

■ RESULTS AND DISCUSSION

Distribution of ^{129}I in Seawater Offshore Fukushima. In 4 seawater profiles offshore Fukushima, the highest concentration of ^{129}I up to 62 × 10^7 atoms/L was measured in the surface water from the station 31 about 40 km from the 1FNPP (Table 1). In the other 3 stations (11, 14, and 22), similar ^{129}I concentrations of (14−16) × 10^7 atoms/L at depth 20 m were observed, which is slightly lower than that at station No. 31 with the value of 20 × 10^7 atoms/L at the same depth (Table 1). At station 31, the ^{129}I concentrations decrease with increasing depth to about (10−13) × 10^7 atoms/L in the depth 50−120 m (Figure 1). The decreasing ^{129}I concentrations with depth were observed at all stations. The lowest ^{129}I concentration of 0.77 × 10^7 atoms/L was observed at a depth of 400 m at station 14, which is about 260 km offshore Fukushima. A similar low ^{129}I concentration of 1.9 × 10^7 atoms/L was measured at depth of 400 m at station 11 (the most distant location 530 km from Fukushima). These values are 30−80 times lower than that of the surface water at station 31. Relative lower concentrations of ^{129}I in subsurface water (50−400 m depth) from station 14 compared to those at station 11 were measured, although station 11 is relatively far from Fukushima (530 km) compared to station 11 (260 km), these might be attributed to the pathway of water current as well as the contaminated water plume in this area.

Relatively constant ^{127}I concentrations of 55−61 μg/L were observed in these seawater samples (Table 1). The distribution of the ^{129}I/^{127}I ratios (Figure 2, Table 1) is the same as for the ^{129}I concentrations; the highest ^{129}I/^{127}I ratio of 22 × 10^{-10} was observed at the 10 m depth in station 31, while the lowest ^{129}I/^{127}I ratio is only 0.26 × 10^{-10} in the water from station 14 at a depth of 400 m (Figure 2).

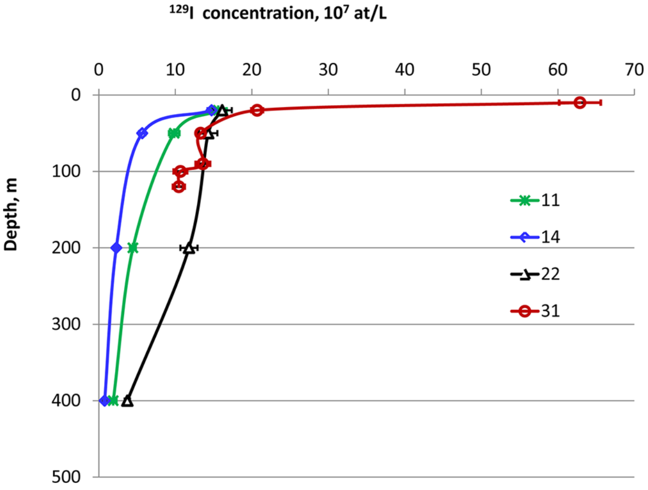


Figure 1. Depth distribution of ^{129}I concentration in 4 seawater profiles (at stations 11, 14, 22, and 31; refer to Table S-1 and Figure S-1 for precise locations) offshore Fukushima, error bars showing analytical uncertainty.

Inorganic Speciation of ^{129}I and ^{127}I in Seawater Profiles. In seawater, especially offshore and in the open sea, iodine mainly exists as iodide and iodate and to a minor extent as organic iodine,[22,23] although a high fraction of iodine in coastal and estuarine seawater and river and lake water was observed in organic form,[24] and increased level of organic iodine was reported in some open sea waters.[25] Two seawater samples collected in the North Sea (open seawater) and offshore Fukushima (surface water at station 31), respectively, were analyzed for both total inorganic ^{129}I and total ^{129}I using a method recently developed in our lab.[26] In this method, organic matter was first decomposed using $K_2S_2O_8$ at pH 1−2 to convert any organic associated iodine to inorganic form, followed by solvent extraction after addition of ^{127}I carrier. The

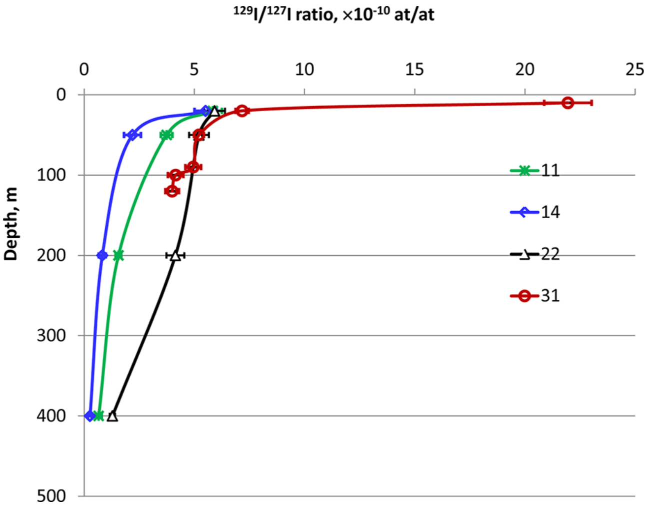


Figure 2. Depth distribution of ^{129}I/^{127}I atomic ratios in 4 seawater profiles (at stations 11, 14, 22 and 31; refer to Table S-1 and Figure S-1 for precise locations) offshore Fukushima, error bars showing analytical uncertainty.

results showed no significant difference between total inorganic ^{129}I and total ^{129}I, confirming that negligible amount of ^{129}I was present in organic form in these open sea and offshore seawater samples. It is therefore shown that the measured total inorganic ^{129}I concentrations represent the total ^{129}I in the seawater measured in this work.

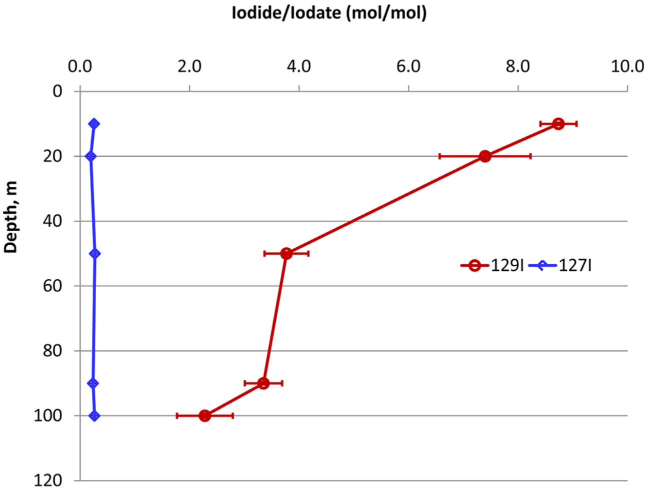


Figure 3. Distribution of ^{129}I and ^{127}I species (iodide/iodate, mol/mol) in seawater profile of station 31 (refer to Table S-1 and Figure S-1 for precise location) offshore Fukushima, error bars showing analytical uncertainty.

The analytical results of iodide, iodate, and total iodine for both ^{129}I and ^{127}I (Table S-2) show a completely different distribution of ^{129}I compared to ^{127}I in all seawater analyzed (Figure 3). ^{129}I is mainly in iodide form, with an iodide/iodate molecular ratio up to 8.7 in surface water (< 20 m) and about 2−3 in subsurface water (> 50 m). However, iodate is the dominant species of ^{127}I, with a relative constant molecular ratio of iodide/iodate of about 0.2 (range of 0.07−0.27) (Table 1). In the water profile at station 31, a trend of gradually decreasing iodide/iodate ratios from 8.7 in the surface water (at depth of 10 m) to 2.2 in subsurface water (at depth of 120 m) is observed (Figure 3). ^{129}I/^{127}I ratios show a significantly different distribution for iodide and iodate, with much higher isotopic ratio for iodide compared to iodate (Table S-2). The ^{129}I/^{127}I ratios for iodide increase from 14 × 10^{-10} in the subsurface water to 104 × 10^{-10} in the surface water at station 31, while ^{129}I/^{127}I ratios for iodate are more than 45 times lower compared to those for iodide, only (0.04−0.31) × 10^{-10} (Table S-2).

The different distribution of ^{129}I species compared to ^{127}I can be attributed to two reasons: (1) the different sources of ^{127}I and ^{129}I; (2) relatively long time to reach equilibrium among iodine oxidation states in the open sea. The ocean is the main source of iodine (^{127}I), which accounts for more than 80% of iodine in the earth's crust. Distribution of ^{127}I species in seawater depends on many parameters. In the open sea (oxygenated seawater), iodine mainly occurs as iodate; iodide concentrations might increase in the coastal water and surface water by reduction of iodate through biological, inorganic, and photochemical approaches.[22] Seawaters analyzed in this work were collected from an open sea, and the measured iodide/iodate ratios in these samples are typical values for the open sea.[22,27]

Although the oxidation of iodide to iodate is a favored process in view of chemical dynamics of redox reactions of iodine in oxygenated seawater, investigation in the North Sea, Nordic seas, and the Arctic has shown, however, that oxidation of iodide to iodate in the open sea is a slow process,[13] and chemical species of ^{129}I in offshore water and in the open sea have not significantly changed during their transport from the North Sea to the Norwegian Sea, and further to the Arctic, which takes 1−4 years. The seawater investigated in this work was collected June 9−15, about 2.5 months after direct liquid discharges of contaminated water from 1FNPP. Therefore, the dominant iodide species of ^{129}I should result from its source, i.e. that ^{129}I was discharged to the seawater from the 1FNPP mainly in iodide form. Chemical species of radioiodine in neither the liquid discharges from the 1FNPP nor irradiated fuel in the reactor have been reported. However, it has been observed that radioiodine (^{131}I, ^{123}I, or ^{124}I) in trap solution thermally released from the irradiated uranium or tellurium is mainly in iodide form (Syed M. Qaim, 2012, communication in NRC-9, 2012). This might imply that radioiodine in the contaminated water from the damaged reactor in 1FNPP might be mainly in iodide form. The chemical species of radioiodine in the precipitation of Fukushima are not yet available.

Source Terms of ^{129}I in Seawater Offshore Fukushima. There are 4 possible sources of ^{129}I in the seawater offshore Fukushima: (1) direct liquid discharges from 1FNPP to the sea; (2) atmospheric fallout of ^{129}I from Fukushima accident; (3) runoff of ^{129}I deposited on the land to the sea; (4) global fallout of ^{129}I.

In a seawater profile collected offshore Kushiro (42° N, 146° E) before Fukushima accident in 2007, it has been observed that the ^{129}I/^{127}I ratios decreased with increasing depth from 0.7 × 10^{-10} in surface water, 0.18 × 10^{-10} in depth of 500 m, and <0.07 × 10^{-10} in the deeper water (> 1000 m), corresponding to ^{129}I concentration of 2 × 10^7 atoms/L in the surface water to 0.5 × 10^7 atoms/L at depth about 500 m, and then <0.2 × 10^7 atoms/L in deeper water (> 1000 m).[28] Similar levels of ^{129}I concentrations of (0.8−2) × 10^7 atoms/L in surface and subsurface (> 1000 m) have also been reported in two water profiles collected from the Northwestern Pacific Ocean (35° N, 152° E and 31° N, 170° E) in 1997.[29] Because there is no other source of ^{129}I in the Pacific Ocean except global fallout (and possibly local fallout from the nuclear weapons testing at Bikini and Enewetak atolls[29]) before the Fukushima accident, the ^{129}I level in these waters should be a representative level of ^{129}I in the Pacific Ocean. The ^{129}I level (for both ^{129}I concentrations and ^{129}I/^{127}I ratios) in the surface seawater (< 20 m) offshore Fukushima analyzed in this work is 5−30 times higher than the global fallout value, and 1.5−7 times higher in the subsurface water (> 400 m). A significantly decreased ^{129}I level with the increased depth in the water columns, especially in the top 100 m, was observed (Figures 1 and 2). At station 31, more than 3 times higher ^{129}I level at 10 m compared to at 20 m depth water was measured, this might imply that ^{129}I at surface (<10 m) is even higher, and difference of the ^{129}I concentration at surface water comparing to the preaccident level is even bigger that just comparing with 20 m and 10 m depth water. Investigation of ^{129}I in seawater nearby the discharge point of nuclear power plants in China (the Pacific Ocean) has shown no significant influence of the operation of NPP on the ^{129}I levels in the seawater,[30] and the ^{129}I concentrations of $(0.7−2.5) \times 10^7$ atoms/L in surface water collected in 2−10 km distance from the discharge point of the NPP, corresponding to ^{129}I/^{127}I ratios of $(0.8−2.6) \times 10^{-10}$. It can be assumed that there was no significant influence of the operation of the Fukushima NPP on ^{129}I levels in seawater before the accident. The elevated ^{129}I levels in the surface seawater offshore Fukushima can therefore not be attributed to global fallout and the discharges from the ordinary operation of the Fukushima NPP. However, the global fallout contribution to the ^{129}I levels in the subsurface waters could not be ignored.

During the Fukushima accident in March 2011, huge amounts of radionuclides including 150−160 PBq of ^{131}I and 10−15 PBq of ^{137}Cs were released to the atmosphere.[4−6] The half-lives of these radionuclides are very much different from a few hours (e.g., ^{132}I) to millions of years (e.g., ^{129}I). For easy discussion, all concentrations and ratios of the radionculides discussed in this work (i.e., ^{137}Cs, ^{131}I, and ^{129}I) are decay-corrected to March 13, 2011, the beginning of the radioactive releases from the nuclear accident at the Fukushima Dai-ichi nuclear power plant, if not otherwise specified. It has been estimated that a total of 5.6 PBq of ^{137}Cs released to the atmosphere has been deposited over Japan and the surrounding ocean (130−150° E and 30−46° N),[6] and a similar value of 5 PBq of ^{137}Cs deposited in the Ocean surrounding Japan has also been estimated by another group.[5] This means that 30−50% of ^{137}Cs released to the atmosphere during the accident was deposited in the ocean surrounding Japan, indicating the deposition of radionuclides from the atmosphere to the ocean is one of important sources of radionuclides in seawater offshore Fukushima. Up to 77 Bq/L of ^{131}I and 24 Bq/L of ^{137}Cs were measured in seawater 30 km offshore Fukushima on March 23, 2011; this is more than 10^4 times higher than the background level of 1 mBq/L of ^{137}Cs in the Pacific Ocean,[8,9] indicating a notable contribution of atmospheric deposition into the sea offshore Fukushima.

It is difficult to estimate the amount of radionuclide runoff from the land to the Sea *via* rivers, because no sufficient data on radionuclide concentrations in rivers are available. It has been reported that iodine can be easily absorbed in soil components, especially in the soil with high organic matter.[31] It can be estimated that only very small fraction of iodine deposited on the lands can be quickly removed to the sea through rain and river runoff. Considering that only 13% of radioiodine released to the atmosphere was deposited on the land of Japan,[7] the runoff of ^{129}I from the land to the sea would not be a significant source of ^{129}I in the seawater offshore Fukushima.

Direct liquid discharges of 3.5−4 PBq of ^{137}Cs from 1FNPP to the sea from 21 March to 30th April 2011 have been estimated.[5,9] Much higher releases of ^{137}Cs of 27 PBq (12−41 PBq) have been estimated using a simple interpolation model of sparsely observed data and relatively coarse horizontal resolution,[32,33] But a small release of ^{137}Cs of only 0.94 PBq in 1−6 April 2011 was estimated by Japanese government.[33] Therefore the direct discharge from 1FNPP to the sea is another important source of ^{129}I in the seawater offshore Fukushima.

The seawater samples investigated in this work have also been analyzed for ^{137}Cs [34] using AMP (ammonium molybdophosphate) preconcentration and gamma spectrometry measurement,[35] and 0.01−1.1 Bq/L of ^{137}Cs were measured in these waters, i.e. 60−1100 times higher ^{137}Cs concentrations compared to the global fallout level, indicating its dominant Fukushima source. The ^{129}I/^{137}Cs atomic ratios in the analyzed seawater samples are calculated to be 0.41−0.62 in the top 50 m water column and 0.8−1.7 in subsurface seawaters (> 50 m) at 4 stations. Cesium is considered to be a relatively conservative element in oceans and ^{137}Cs has been widely applied as an oceanographic tracer for water circulation,[36,37] although the residence time of ^{137}Cs is much shorter than ^{129}I due to the shorter physical half-life of ^{137}Cs and relatively higher adsorption of ^{137}Cs to the particulates (especially clay minerals) suspending in the water column. The high ^{129}I/^{137}Cs ratios in the subsurface water might be attributed to the fact that a relatively high fraction of ^{129}I in the subsurface seawater originates from global fallout. Based on the fact that the ^{129}I concentrations in subsurface water measured in this work are 1.5−7 times higher than preaccident values, it can be estimated that 12−75% ^{129}I in subsurface water of >400 m depth originates from the global fallout. In addition, the higher analytical uncertainty of ^{137}Cs in subsurface water samples with low ^{137}Cs concentration also influences this value. By measurement of soil samples collected around the 1FNPP, a ^{129}I/^{131}I atomic ratio of (26.6 ± 7.5) has been reported.[38] Therefore ^{131}I/^{137}Cs atomic ratios in the surface water (<50 m depth) offshore Fukushima can be derived to be 0.015−0.023, or an activity ratio of 21−32. This values are close to the measured ^{131}I/^{137}Cs activity ratio of about 17.8 in coastal waters near the discharge point in the 1FNPP after March 25, 2011.[8,9] Based on the estimated atmospheric releases of ^{131}I (150 PBq) and ^{137}Cs (13 PBq), ^{131}I/^{137}Cs activity ratio in the atmosphere released from the Fukushima accident can be calculated to be 11.5. Measurement of ^{131}I and ^{137}Cs in precipitation (rain and dust) over Japan from March 18 to April 29 has resulted in ^{131}I/^{137}Cs activity ratios ranging from 3.2 to 500 with a median of 15; the higher ratios occurred at downstream inland sites of radioactive plume.[39] The large variation of ^{131}I/^{137}Cs ratio might also result from the different ratios of ^{131}I/^{137}Cs in different reactors. The measured ^{131}I/^{137}Cs ratios in air samples collected over Europe during March 22 to April 11, 2011 also highly varied, with an average of 40−100 for aerosol samples. Considering that only about 20% of ^{131}I occurred in particle-associated forms, the ^{131}I/^{137}Cs ratio in the atmosphere is likely higher than 200.[39] In addition, increased ^{131}I/^{137}Cs ratios with sampling date from March 19, 2011 onward have been observed in aerosols from the Fukushima area,[40] indicating that the radioactive cloud contained more radioiodine at the beginning of the accident. This could be attributed to the properties of higher volatility and longer residence time of iodine in the atmosphere compared to ^{137}Cs. In atmosphere, iodine exists in both gaseous and particle-associated forms, while ^{137}Cs is mainly in particle-associated form. Removal rate of particles from the atmosphere by dry and wet deposition is much higher than gaseous form of iodine due to less efficiency of gaseous iodine capture to droplets. Consequently, residence time of radioiodine in atmosphere is longer than ^{137}Cs (particle), and therefore decreased ^{137}Cs concentrations compared to ^{131}I in the atmosphere or increased ^{131}I/^{137}Cs ratios with the increased time after accident were observed in the atmosphere or precipitation. The relatively high ^{129}I/^{137}Cs ratios measured in surface seawater can therefore be attributed to the contribution of the atmospheric deposition in the seawater offshore Fukushima.

In summary, ^{129}I in the surface water likely mainly originated from the liquid discharges from the Fukushima 1FNPP to the sea; however, the atmospheric deposition has also a visible contribution, and in subsurface waters the contribution from global fallout is not negligible.

Amount of ^{129}I Discharged to the Sea from the Fukushima Daiichi NPP. As described above, ^{129}I in the seawater offshore Fukushima has two major sources, i.e. direct liquid discharge from 1FNPP, and the atmospheric deposition subsequent to the accident. From March 21, 2011, ^{131}I and ^{137}Cs concentrations in coastal seawater samples collected at 3 sites at the discharge channel of 1FNPP and 10 km and 16 km south of the 1FNPP, as well as at 8 sites 30 km off the Fukushima coastline, have been monitored by the operator of 1FNPP, the Tokyo Electric Power Company (TEPCO), and the Ministry of Education, Culture, Sports, Science and Technology (MEXT). A quite constant activity ratio of ^{131}I/^{137}Cs of 17.6 has been observed in the seawater from all coastal sites near to the 1FNPP from March 26, 2011, while scattered and higher ^{131}I/^{137}Cs ratios of >28 have been observed in the seawater from the sites 10 and 16 km south of 1FNPP March 21−25, 2011. A large scatter of ^{131}I/^{137}Cs ratios of 6−20 have been observed in seawater collected at 30 km offshore Fukushima before April 2.[8,9] Similarly lower ^{131}I/^{137}Cs ratios of 3−18 have also been observed at sites >5 km from the coast of Fukushima before April 2.[23] The large scatter before March 25 in coastal sites and before April 2 at sites offshore Fukushima can be attributed to the atmospheric deposition from the Fukushima accident.[8,9] Large variations in the ^{131}I/^{137}Cs activity ratios in atmospheric and precipitation samples have been observed in Japan as well as at far locations in Europe after the Fukushima accident.[39,40] This is attributed to different ratios of ^{131}I/^{137}Cs from different reactors in the 1FNPP, as well as to different behaviors of ^{131}I and ^{137}Cs in the atmosphere. ^{137}Cs is mainly associated with particles, while radioiodine can be in both gaseous and particle-associated form,[40] which cause different dispersion and deposition patterns of ^{131}I and ^{137}Cs. Therefore the ^{131}I/^{137}Cs ratios vary in seawater, to which the atmospheric deposition has a significant contribution (together with liquid discharges). The constant ^{131}I/^{137}Cs ratio (17.6) in the seawater collected from the coastal sites within 16 km of the 1FNPP confirms that the ^{131}I and ^{137}Cs in seawater offshore Fukushima is dominated by the direct liquid discharges from the damaged nuclear reactor 2 in the 1FNPP after March 25, 2011.[8,9,33] Because of the same chemical properties and environmental behaviors of ^{131}I and ^{129}I, the amount of ^{129}I directly discharged to the sea from the 1FNPP can be estimated from the measured ^{131}I/^{137}Cs ratio, and estimated amount of ^{137}Cs directly discharged to the sea from the 1FNPP. Here, we applied the estimated value of 3.5 PBq for direct liquid discharge of ^{137}Cs to the sea,[9] the amount of ^{131}I directly discharged the sea can be estimated to be 61.6 PBq. Based on these data and the measured ^{129}I/^{131}I atomic ratio of (26.6 ± 7.5) for released radioiodine from the 1FNPP,[38] the amount of ^{129}I directly discharged to the sea from the 1FNPP can be estimated to be 2.35 GBq (or 0.35 kg).

Of the total 150 PBq of ^{131}I and 13 PBq of ^{137}Cs released to the atmosphere from the Fukushima accident,[1,4] it has been estimated that more than 80% of ^{137}Cs has been deposited in the ocean, 18% in Japanese land area, and only 1.9% was deposited over land areas outside Japan.[41] A similar percentage of radionuclide deposition has been estimated by Morino et al.[7] using a 3-dimensional chemical transport model; they reported that 13% of ^{131}I and 22% of ^{137}Cs fell over the land of Japan, 19% ^{131}I and 10% of ^{137}Cs were deposited over the Ocean in the area of 34−41° N and 137−145° E (700 km × 700 km), and the rest was transported and deposited in other areas, mainly in the Pacific Ocean. It can be estimated that about 120 PBq of ^{131}I was deposited in the Ocean, mostly in the Pacific Ocean; of this, 28.5 PBq of ^{131}I was deposited in the sea area of 34−41° N and 137−145° E, mainly offshore Fukushima. Based on the reported ^{129}I/^{127}I atomic ratio of 26.6,[38] about 4.57 GBq (0.68 kg) of ^{129}I released to the atmosphere was deposited in the Ocean, and about 1.09 GBq of ^{129}I (0.16 kg) was deposited in the sea area of 34−41° N and 137−145° E, most in the sea offshore Fukushima. This estimation indicates that liquid discharges from 1FNPP are the major source of ^{129}I in the sea offshore Fukushima, and the atmospheric deposition is the minor source, accounting for about 32% of the total ^{129}I.

If we assume the liquid discharges still remained in the 700 × 700 km area offshore Fukushima and mainly in the top 50 m water column, and it was homogeneously distributed in this area, ^{129}I concentration in the top 50 m seawater can be calculated to be about 1×10^8 atom/L, or a ^{129}I/^{127}I isotopic ratio of about 3.5×10^{-10}. This value agrees relatively well with the measured ^{129}I concentration ($(0.5{-}2) \times 10^8$ atoms/L) and ^{129}I/^{127}I ratios $(2{-}7) \times 10^{-10}$ in the surface water (10−50 m depth) offshore Fukushima.

It has been estimated that Chernobyl accident released about 1.3−6 kg of ^{129}I to the atmosphere.[23,42] A total release of 1.2 kg of ^{129}I from the Fukushima accident estimated in this work is comparable to that released from the Chernobyl accident. However, the ^{129}I released from Chernobyl accident was deposited in a terrestrial area, mainly in European countries, whereas ^{129}I released from Fukushima accident was mainly deposited to the ocean.

Reprocessing plants have released large amounts of ^{129}I to the environment, especially from the two European reprocessing plants at La Hague (France) and Sellafield (UK), which have discharged about 5200 kg of ^{129}I to the sea and 440 kg to the atmosphere (up to 2007).[23] The ^{129}I released from the Fukushima accident accounts therefore to less than 0.3% of the total ^{129}I released from reprocessing plants. However, the ^{129}I from the European reprocessing plants has been mainly discharged and transported to the European seas, and further to the Arctic.[11,13,42] The contribution of ^{129}I from the Fukushima accident to the Pacific Ocean is remarkable, as it has influenced the total inventory of ^{129}I in the Pacific Ocean.

The Fukushima-derived ^{129}I will be therefore a useful tracer for oceanographic research in this area.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed chemical procedure for separation of iodine species in seawater samples; detailed sampling information and analytical results of ^{129}I and ^{127}I in 4 seawater profiles (Table S-1); analytical results of inorganic speciation of ^{129}I and ^{127}I in 4 seawater profiles (Table S-2); a map showing sampling stations and water depth (Figure S-1); and a schematic diagram of chemical procedure for speciation analysis of ^{129}I and ^{127}I (Figure S-2). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We acknowledge Dr. Ken Buesseler (WHOI) and Dr. Harmut Nies (IAEA-EL) for provision of seawater samples. X.L.H. acknowledges financial support provided by Innovation Method Fund China (2012IM030200). P.P.P. acknowledges support provided by the EU Research and Development Operational Program funded by the ERDF (26240220004). Equipment support at the University of Arizona was provided in part by a grant from the National Science Foundation (EAR0929458).

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