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Reassessment of ^{90}Sr, ^{137}Cs, and ^{134}Cs in the Coast off Japan Derived from the Fukushima Dai-ichi Nuclear Accident

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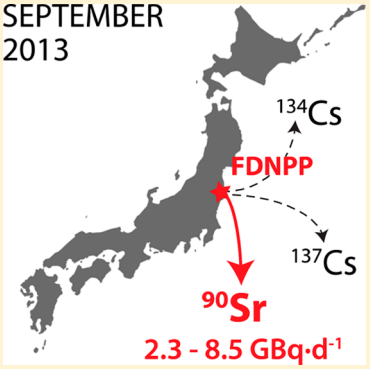
Supporting Information

ABSTRACT: The years following the Fukushima Dai-ichi nuclear power plant (FDNPP) accident, the distribution of ^{90}Sr in seawater in the coast off Japan has received limited attention. However, ^{90}Sr is a major contaminant in waters accumulated within the nuclear facility and in the storage tanks. Seawater samples collected off the FDNPP in September 2013 showed radioactive levels significantly higher than pre-Fukushima levels within 6 km off the FDNPP. These samples, with up to 8.9 ± 0.4 Bq·m^{-3} for ^{90}Sr, 124 ± 3 Bq·m^{-3} for ^{137}Cs, and 54 ± 1 Bq·m^{-3} for ^{134}Cs, appear to be influenced by ongoing releases from the FDNPP, with a characteristic ^{137}Cs/^{90}Sr activity ratio of 3.5 ± 0.2. Beach surface water and groundwater collected in Sendai Bay had ^{137}Cs concentrations of up to 43 ± 1 Bq·m^{-3}, while ^{90}Sr was close to pre-Fukushima levels (1−2 Bq·m^{-3}). These samples appear to be influenced by freshwater inputs carrying a ^{137}Cs/^{90}Sr activity ratio closer to that of the FDNPP fallout deposited on land in the spring of 2011. Ongoing inputs of ^{90}Sr from FDNPP releases would be on the order of 2.3−8.5 GBq·d^{-1} in September 2013, likely exceeding river inputs by 2−3 orders of magnitude. These results strongly suggest that a continuous surveillance of artificial radionuclides in the Pacific Ocean is still required.



INTRODUCTION

On March 11, 2011, the Tohoku earthquake and the subsequent series of tsunamis severely damaged the Fukushima Dai-ichi nuclear power plant (FDNPP). Failure of cooling systems caused a temperature increase resulting in the production of hydrogen and other gases within the reactors. This led to explosions releasing radioactive gas and debris to the atmosphere. Additionally, cooling water was directly discharged to the sea after being in contact with the nuclear fuel. The resulting release of ^{90}Sr ($T_{1/2}$ = 28.9 years), ^{137}Cs ($T_{1/2}$ = 30.17 years), and ^{134}Cs ($T_{1/2}$ = 2.07 years), among other radionuclides (e.g., ^{85}Kr, ^{129,131}I, ^{132}Te, and ^{133,135}Xe), was the largest ever uncontrolled input of artificial radionuclides into the ocean.[1,2]

Before the FDNPP accident, the dominant source of ^{90}Sr and ^{137}Cs in the coast off Japan was global fallout from nuclear weapon tests. Pre-Fukushima concentrations in surface waters in the ocean were on average 1 Bq·m^{-3} for ^{90}Sr[3,4] and 1−2 Bq·m^{-3} for ^{137}Cs (HAM database).[5] Due to the short half-life of ^{134}Cs, prior sources of this isotope were no longer detectable in the coast off Japan.

Studies following the accident in 2011 focused on ^{137}Cs and ^{134}Cs because they showed some of the highest activities and are relatively easy to determine by gamma spectrometry, thus providing rapid information about the radioactive releases from FDNPP. Cesium is a volatile element that was released to the atmosphere and through liquid discharges in comparable amounts, with a ^{134}Cs/^{137}Cs activity ratio ∼1, e.g., ref 1. The total atmospheric releases of ^{137}Cs have been estimated to range from 13 to 36 PBq,[6−8] from which the majority was deposited in the Pacific Ocean while about 20% were deposited on land.[6,7] Most of the atmospheric releases occurred during the first week after the accident, leading to radiocesium concentrations up to 10 Bq·m^{-3} in surface seawater as far as 1700 km off FDNPP (160°E and 40°N) in April 2011.[9,10] Estimates of total liquid discharges of ^{137}Cs varied from 3.5 to 27 PBq by May−July 2011.[11−15] The amount of ^{137}Cs directly discharged into the ocean was comparable to authorized releases from nuclear reprocessing plants (i.e., ∼ 39 PBq from 1970 to 1998 from Sellafield, U.K.)[16] but larger than ^{137}Cs releases from Chernobyl (∼16 PBq).[17]

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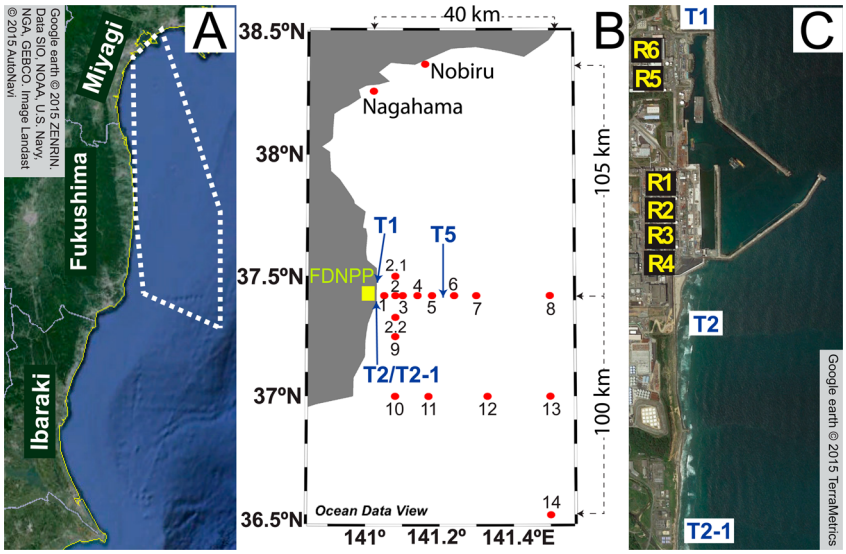

Figure 1. (A) Prefectures of Miyagi, Fukushima, and Ibaraki. Dashed line shows study area of the *Daisan Kaiyo Maru* cruise in September 2013. (B) Magnified view of the study area showing the location of sampling sites, TEPCO's monitoring sites (T1, T2/T2−1, and T5), and FDNPP. (C) FDNPP, reactor units 1−6, and TEPCO's monitoring sites (T1, T2, and T2−1).

Liquid discharges to the North Pacific Ocean peaked on April 6, 2011, when concentrations of ^{137}Cs of up to 68 ·10^{6} Bq·m^{-3} were recorded near the discharge channels of the FDNPP.[1] In the same month, ^{137}Cs concentrations were 10−1000 times lower 30 km offshore along a transect at 141° 24′ N conducted by the Japanese Ministry of Education, Culture, Sports, Science, and Technology (MEXT).[1] In June 2011, maximum radiocaesium concentrations were ∼3.9 ·10^{3} Bq·m^{-3} in waters between 30 and 600 km off FDNPP,[18] while levels near the discharge channels at that time were still of ∼33·10^{3} Bq·m^{-3}.[1]

At the time of the accident, the total inventory of ^{90}Sr in reactor core units 1−3 was ∼500 PBq, which is about 70% of the ^{137}Cs inventory.[19,20] Due to the lower volatility of ^{90}Sr compared to ^{137}Cs, the majority of ^{90}Sr remained within the reactors while only a small fraction reached the atmosphere. Levels of ^{90}Sr in FDNPP fallout recorded on land were in fact up to 4 orders of magnitude lower than for ^{137}Cs.[21−23] Most of ^{90}Sr was discharged as cooling water to the Pacific Ocean. ^{90}Sr input estimates range from 0.09−0.9 PBq[24] to ∼1−6.5 PBq.[21] These amounts are comparable to the total authorized liquid discharges into the ocean from the nuclear reprocessing plants in Sellafield and La Hague between 1970 and 1998 (∼4 PBq, decay-corrected to year 2000).[17] Between April 2011 and February 2012, ^{90}Sr concentrations near the discharge channels and as far as 15 km off the FDNPP were up to 5 orders of magnitude higher (max of 4·10^{5} Bq·m^{-3}) than pre-Fukushima levels, according to data made public by the Tokyo Electric Power Company (TEPCO).[21,25] Beyond 15 km off the coast of Fukushima, the concentrations of ^{90}Sr ranged from 0.8 to 85 Bq·m^{-3} between 30 and 600 km off FDNPP and from 1 to 31 Bq·m^{-3} further east (145−150°E and 34−40°N) in June 2011.[24,26] In surface waters off Miyagi, Fukushima and Ibaraki prefectures (see Figure 1 for location), ^{90}Sr was below 5 Bq·m^{-3} and close to pre-Fukushima levels by the end of August and mid-December 2011, respectively.[27] More recent data for May−June 2012 shows ^{90}Sr (0.5−3.6 Bq·m^{-3}) close to or slightly higher than pre-Fukushima concentrations around Taiwan and off Japan between 145−155°E and 25−35°N.[26]

After the accident, efforts at the FDNPP attempted to reduce the amount of groundwater flowing into reactor buildings (frozen soil wall and groundwater bypass), isolating highly radioactive stagnant water located in trenches (ice wall) and preventing further leakages from tanks or the nuclear facility reaching the ocean (seaside wall).[25] Despite the measures listed above, as of June 2015, ∼300 m^{3}·d^{-1} of groundwater infiltrated the reactor buildings, becoming highly enriched in radioactivity once in contact with melted nuclear fuel or previously contaminated water. This has resulted in ∼90·10^{3} m^{3} of contaminated water accumulating under the FDNPP facility in 2014−2015.[25] To compensate for this, water is pumped out at a rate of ∼600 m^{3}·d^{-1} and treated in situ with primary Cs sorbents (e.g., zeolite) to reduce radioactivity levels. Approximately half of this water is reused for cooling the reactors down, while ∼300 m^{3}·d^{-1} are stored in tanks. Stored water (a total of 665·10^{3} m^{3} by June 11, 2015)[28] is treated using additional Cs removal systems since May 2011. Additional decontamination systems such as the Multiple Nuclide Removal System (ALPS) have been used for the partial removal of ^{90}Sr (reduction factor of 100−1000),[29] among other radionuclides, routinely since late 2014.[25] Despite this treatment, significant amounts of ^{90}Sr and tritium (which cannot be readily removed with current technology) remain in the stored water today.

The monitoring of ^{90}Sr is desirable for two main reasons. First, ^{90}Sr is a long-lived fission product of high radiological concern, particularly over long time periods. Chemically similar to calcium, ^{90}Sr is incorporated in bone tissue, emitting highly energetic β particles mainly during decay of its short-lived daughter ^{90}Y that can increase the chance of leukemia or bone cancer. Second, due to its conservative behavior in seawater, ^{90}Sr is also a suitable tracer of ocean circulation and can be used to identify sources with a characteristic ^{137}Cs/^{90}Sr activity ratio (e.g., ref 24). Nevertheless, ^{90}Sr has been much less studied than radiocesium, either because of its laborious chemical separation or because its initial releases were not expected to be as high as for other radionuclides during the Fukushima accident in March−April 2011. Today, ^{90}Sr is a major radioactive contaminant in reactors and storage tanks and leaks of this isotope from the FDNPP to the ocean should be monitored.

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Almost no ^{90}Sr data from seawater collected after 2011 and near FDNPP have been published in peer-reviewed journals, nor has the magnitude of recent releases of this isotope to the ocean been well studied.

The aim of this work is to re-evaluate the concentrations and the distribution of ^{90}Sr, as well as ^{137}Cs and ^{134}Cs, in the coast off Japan in September 2013. We also attempt to identify the current potential sources of these isotopes and estimate the magnitude of recent uncontrolled releases of ^{90}Sr from the FDNPP to the ocean. For this purpose, we present data on ^{90}Sr, ^{137}Cs, and ^{134}Cs in offshore seawater, surface beach water, and groundwater collected in September 2013 and compare it with peer-reviewed literature and TEPCO's data available until June 2015.

MATERIALS AND METHODS

Study Area and Sampling. Water samples for the analysis of ^{90}Sr (n = 30) and ^{134,137}Cs (n = 45) were collected in the area between 0.8 and 110 km off the FDNPP on board the *R/V Daisan Kaiyo Maru* in September 2013 (Figure 1). The main transect was located in front of the FDNPP along 37.42°N and included surface stations and 4 shallow profiles (St.: 1, 3, 5, 7; maximum sampled depths of 10, 25, 55, and 115 m, respectively). A fifth vertical profile (St. 14, max. sampled depth of 500 m) was sampled 110 km southeast of the FDNPP. The area composed of that between stations 1 to 14 is found in the confluence zone of two major western boundary currents. The warm and saline Kuroshio current penetrates from the south along the continental slope and flows off northeastward at ∼35°N south of FDNPP. The Oyashio penetrates from the north flowing southward and separates off Japan at ∼45°N, north of FDNPP. Off-shelf, the confluence of the two currents results on the eastward transport of waters to the open Pacific Ocean characterized by strong and instable jet currents leading to mesoscale eddies and meanders.[11] In addition, along-shore currents govern the coastal region near FDNPP with a predominant north-to-south component, although their direction and strength may change with the wind field every 3−4 days.[30]

Collection of seawater throughout the water column was done using a conductivity−temperature-depth rosette equipped with Niskin bottles. Surface samples were collected during the occupation of each station and between stations for higher temporal and spatial resolution using the ship underway system. Additionally, beach surface water and groundwater were collected at Nagahama and Nobiru beaches, Sendai Bay, about 100 km north of FDNPP. These samples are named the northern beach samples and groundwater, hereinafter.

Extraction and Quantification of Radionuclides. Samples of 20 L were filtered on board using a cartridge filter (GE Hytrex. 1.0 μm nominal retention) and subsequently weighed and acidified with nitric acid to pH ∼1 in the shore-based laboratory.

^{90}Sr, ^{137}Cs, and ^{134}Cs were extracted from each sample. Briefly, acidified seawater was spiked with 0.7 and 200 mg of stable Cs and Sr, respectively. The sample was then passed through columns filled with 5 mL of KNiFC−PAN ion-exchange resin (Czech Technical University, Prague) for the extraction of radiocaesium.[31] The resin was dried and placed in polyethylene vials for γ counting of ^{134,137}Cs using high-purity germanium well detectors. The minimum detectable activity (MDA) was 0.1 Bq·m^{-3} for ^{137}Cs and 0.2 Bq·m^{-3} for ^{134}Cs for typical counting times of 50 h. Concentration uncertainties were calculated by the propagation of uncertainties in the count rate and detector calibration. Stable Cs and Sr were measured by ICP mass spectrometry in aliquots taken before and after the columns to determine the extraction recovery for Cs (87−99%) and to check for any losses of Sr, which averaged <2%.

The determination of ^{90}Sr was carried out in Cs-free samples, following a protocol[32] based on the determination of its daughter ^{90}Y ($T_{1/2}$ = 64 h), adapted for seawater.[24] After the addition of 10 ug of stable Y, ^{90}Y was co-precipitated with iron hydroxides and purified using anion (Bio-Rad AG1-X8, 100−200 mesh) and cation (Bio-Rad AG50W-X8, 100−200 mesh) ion-exchange columns. ^{90}Y decay was measured using a RISØ β counter (RISO National Lab; Roskilde, Denmark). ^{90}Sr activities were corrected for recovery by determining the concentrations of stable Sr and Y from aliquots taken along the entire radiochemical process. Y recoveries ranged from 67% to 93%. The MDA ranged from 0.02 to 0.05 Bq·m^{-3} for typical counting times of 150 h.

Analytical methods used in this study are more sensitive and allow the detection of ^{90}Sr and ^{134,137}Cs at levels 1−3 orders of magnitude lower than MDA's reported by TEPCO: ^{90}Sr (sites T1−T5: average MDA for years 2011−2015 was >10 Bq·m^{-3}) and ^{137}Cs (sites T1 and T2/T2−1: average MDA for years 2012−2015 was ∼1.4 ·10^{3} Bq·m^{-3}). MDA's variability may be partly explained by the smaller sample volumes and shorter counting times often employed by TEPCO. For example, ^{134,137}Cs was initially measured in Marinelli beakers (<5 L) and counted by gamma spectrometry for 1 h, resulting in MDAs > 5·10^{3} Bq·m^{-3} in 2011. Later, they started using larger volumes (30−50 L), chemical separation techniques, and longer counting times (∼1 d) achieving MDAs > 5·10^{2} Bq·m^{-3} at sites T1 and T2/T2−1 by 2015. ^{90}Sr has been determined using a variety of extraction procedures (fuming nitric acid−ion-exchange resin) and measurement techniques ("low background gas flow counters" allowing gross β counting, so-called "pico-β" method, or inductively coupled plasma mass spectrometry techniques) providing ^{90}Sr concentrations in the ∼10 Bq·m^{-3} range level by 2015.[25]

RESULTS

The ranges of concentrations in samples collected in September 2013 were 0.6−8.9 Bq·m^{-3} for ^{90}Sr, 0.9−124 Bq·m^{-3} for ^{137}Cs, and <0.2−54 Bq·m^{-3} for ^{134}Cs. Detailed information on the concentrations of ^{90}Sr, ^{137}Cs, and ^{134}Cs (decay corrected to September 2013), ^{137}Cs/^{90}Sr activity ratio, sampling location and date, temperature, and salinity are provided in Table S.1.

The highest concentrations in surface seawater were found close to FDNPP (0.8−6 km: stations 1−3), with ranges of 0.8−8.9, 2.3−124 and 0.3−54 Bq·m^{-3} for ^{90}Sr, ^{137}Cs, and ^{134}Cs, respectively (Figure 2). Surface concentrations at stations located >6 km off FDNPP were 0.6−1.8, 1.6−4.7 and <0.2−2.6 Bq·m^{-3} for ^{90}Sr, ^{137}Cs, and ^{134}Cs, respectively.

Station 1, the closest sampling site from FDNPP, showed the largest surface to bottom gradient in concentration (Figure S.1). At stations 3, 5, 7, and 14 (6−110 km off FDNPP), concentrations varied only in about 1.0 Bq·m^{-3} with depth and were usually significantly lower than at station 1. Concentrations below 2 m were lower than ∼2.6 Bq·m^{-3} for ^{90}Sr and ∼2.9 Bq·m^{-3} for ^{137}Cs. ^{134}C was below 0.6 Bq·m^{-3} and often undetectable (<0.2 Bq·m^{-3}) in waters between 15 and 500 m.

Concentrations in northern beach samples and groundwater in Sendai Bay were 1.0−1.8, 9−43, and 4−17 Bq·m^{-3} for ^{90}Sr, ^{137}Cs, and ^{134}Cs, respectively (Figure 2). These samples had

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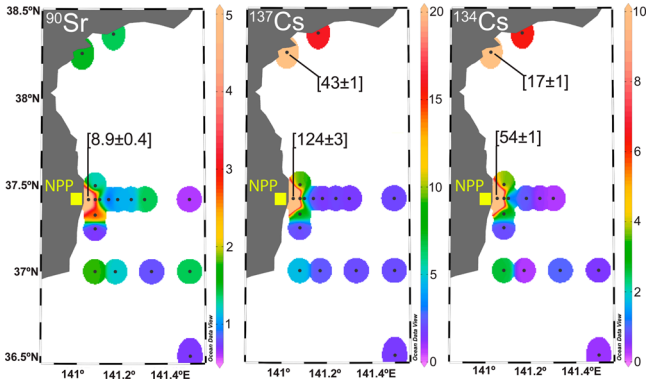

Figure 2. Surface concentrations of ^{90}Sr, ^{137}Cs, and ^{134}Cs in September 2013 (in Bq·m^{-3}). Pre-Fukushima concentrations from literature (decay corrected to sampling) are 0.9−1.1 Bq·m^{-3} for ^{90}Sr[21,17] and 1−2 Bq·m^{-3} for ^{137}Cs.[5]

salinities between 4 and 29, lower than that of seawater samples (salinity >32).

DISCUSSION

Determination of Pre-Fukushima ^{90}Sr and ^{137}Cs. The pre-Fukushima levels of ^{90}Sr and ^{137}Cs in the coast off Fukushima can be calculated from our results using different approaches. One approach assumes that samples free of ^{134}Cs have not been influenced by FDNPP releases. Then, pre-Fukushima levels are calculated taking the average concentrations of ^{90}Sr and ^{137}Cs in these samples, resulting into 1.2 ± 0.7 and 1.8 ± 0.3 Bq·m^{-3}, respectively. This could be inaccurate because decontaminated waters released from the FDNPP could be free of ^{134}Cs but still contain ^{90}Sr. However, only two samples free of ^{134}Cs had somewhat elevated ^{90}Sr concentrations (sample 13 (2.6 ± 0.2 Bq·m^{-3}) and sample 26 (1.8 ± 0.1 Bq·m^{-3})). If these samples are not considered, pre-Fukushima activities are ^{90}Sr = 0.9 ± 0.2 Bq·m^{-3} and ^{137}Cs = 1.8 ± 0.3 Bq·m^{-3} in the coast off Japan. In both cases, calculated levels are in good agreement with the literature prior to the accident (values decay corrected to September 2013): 0.9−1.1 Bq·m^{-3} for ^{90}Sr[21,17] and 1−2 Bq·m^{-3} for ^{137}Cs.[5] Pre-Fukushima levels of ^{137}Cs and ^{90}Sr will not be subtracted in this study unless stated otherwise.

Time Evolution of Concentrations of ^{90}Sr and ^{134,137}Cs in the Coast off Japan. The variation in time of ^{90}Sr (Figure 3A) and ^{137}Cs (Figure 3B) concentrations is presented for TEPCO's sea monitoring sites (T1, T2/T2−1, and T5) near FDNPP,[25,33,34] published data on ^{90}Sr and ^{137}Cs between 2011 and 2015, and this study.

Compared to the measurements from June 2011, concentrations had decreased by 1 order of magnitude for ^{90}Sr and 2−3 orders of magnitude for ^{134,137}Cs by September 2013, although the sampling domain in 2013 was smaller and closer to the FDNPP (*K.O.K* cruise, 2011: 30−600 km; 2013: 0.8−110 km). In September 2013, seawater concentrations clearly above pre-Fukushima levels were recorded only near the FDNPP. Concentrations of ^{90}Sr and ^{134,137}Cs slightly higher than pre-Fukushima levels were also found at site 10, south of FDNPP. These waters were probably advected southward by along-shore coastal currents. Such a pathway was observed for ^{134,137}Cs[35] as well by using surface drifters in year 2011.[11,18] For example, in June 2011, the radioactive plume was advected first south and then east toward the Kuroshio Current, which acted as a barrier to the southern transport of Fukushima waters. Elevated

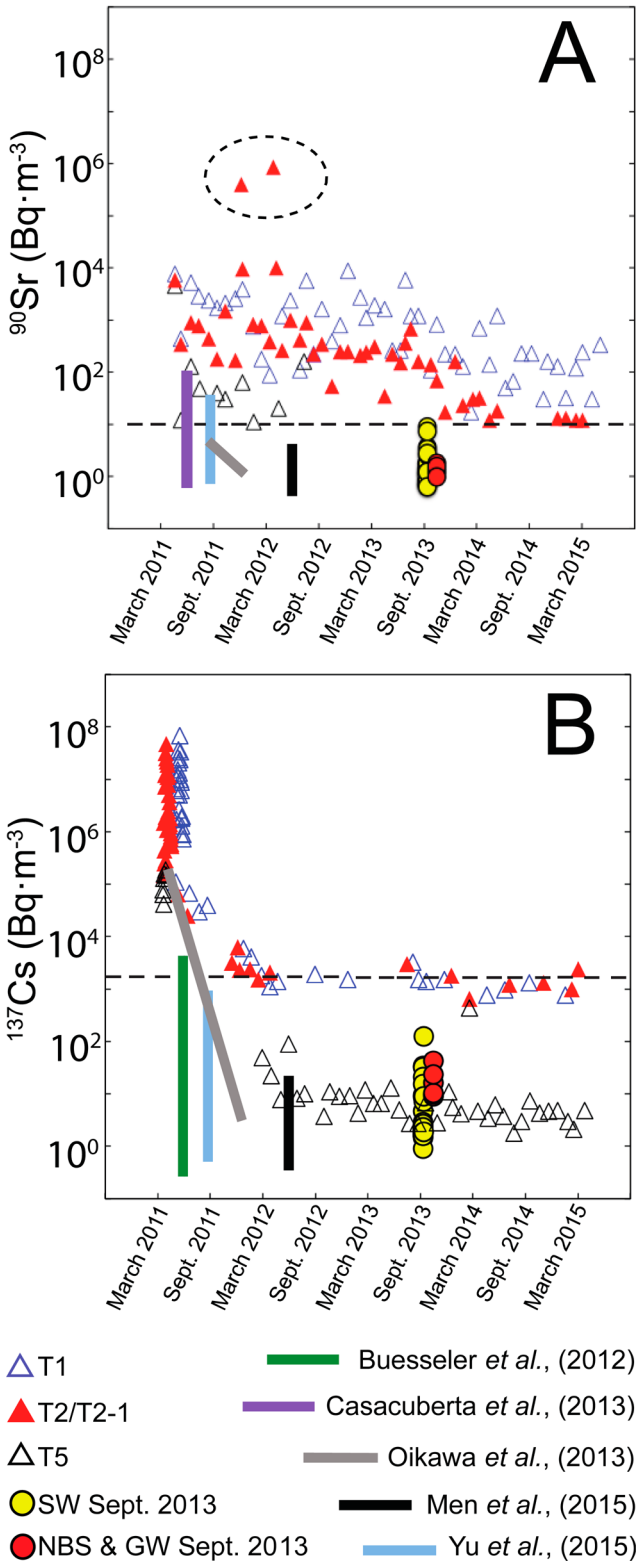

Figure 3. Concentrations in seawater (SW), northern beach samples (NBS), and groundwater (GW) collected in September 2013, TEPCO's sites near FDNPP (T1, T2/T2−1, and T5 surface) and in the coast off Japan (all depth) from March 2011 to July 2015 for: (A) ^{90}Sr and (B) ^{137}Cs. Major reported accidental releases (dashed black circle) and TEPCO's average MDAs for T1 and T2/T2−1 (dashed black line) are indicated.

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concentrations (^{90}Sr up to 30 and ^{134,137}Cs up to ~800 Bq·m^{-3}) were found ~600 km east off FDNPP,[36] and even higher concentrations were detected associated with an eddy located 130 km southeast off FDNPP (^{90}Sr up to 85 and ^{134,137}Cs up to ~3800 Bq·m^{-3}).[18,24]

Concentrations of ^{137}Cs in the coast off Japan in September 2013 were comparable to those measured in August−December 2011, while the ^{90}Sr maximum was about 7 Bq·m^{-3} higher in 2013.[27] Strontium and cesium are highly soluble in seawater, and they were transported within weeks to months to the open Pacific Ocean in 2011,[11,18] being diluted by advection, diffusion, and mesoscale mixing.[37,38] These processes may explain the lower concentrations (^{90}Sr < 3.57 and ^{137}Cs < 18 Bq·m^{-3}) found off Japan in May−June 2012.[26] However, concentrations in samples collected in September 2013 were higher than initially expected because model simulations[39,40] and drifter trajectories[11,18] show that very little ^{90}Sr or ^{134,137}Cs released shortly after the accident in spring 2011 should have remained in our study domain. Furthermore, the decay-corrected (and pre-Fukushima-levels-subtracted) ^{134}Cs/^{137}Cs activity ratio recorded in September 2013 was 0.98 ± 0.01 in samples with ^{137}Cs concentrations above pre-Fukushima levels. This indicates continuing releases from the FDNPP.

TEPCO has been routinely monitoring the waters around FDNPP since the accident. Unfortunately, their detection limits were high (see the Methods section), and thus much of their data is reported as below their detection limit. Also, they generally do not report the uncertainties associated with their measurements. This does not allow for a detailed reconstruction of ^{90}Sr releases and distribution in the coast off Fukushima. Nevertheless, TEPCO's data is useful to identify the relevant trends of ^{90}Sr and ^{137}Cs and concentrations near the FDNPP over time (Figure 3). Site T1 is located ~30 m north of the discharge channel of reactor units 5 and 6 (see Figure 1 for site locations). T2 was initially located ~330 m south of the discharge channel of reactor units 1−4 and was moved 1 km further south after December 2012 (renamed T2−1). T5 is 15 km offshore, in front of FDNPP. From the peak of liquid releases on April 6, 2011, to June 2015, ^{137}Cs concentrations (Figure 3B) have decreased by 4−5 and 5−6 orders of magnitude near the discharge channels (T1 and T2/T2−1), and 15 km offshore FDNPP (T5), respectively. By late April 2011, ^{137}Cs was about ~10^{5} Bq·m^{-3} at T1 and T2/T2−1 and decreased gradually to ~10^{3} Bq·m^{-3} by April 2012, remaining detectable above TEPCO's MDA (>1 ·10^{3} Bq·m^{-3}) until June 2015. At T5, ^{137}Cs concentrations were lower and generally have remained within 10^{1}−10^{2} Bq·m^{-3} since the fall of 2012. Concentrations of ^{90}Sr (Figure 3A) ranged between 10 and 10^{4} Bq·m^{-3} between April 2011 and February 2015, but anomalously higher concentrations had been measured at specific times, linked to accidental releases reported by TEPCO (e.g., December 5, 2011: 4 ·10^{5} Bq·m^{-3}; March 26, 2012: 8.5 ·10^{5} Bq·m^{-3}). The high concentrations recorded at these sites are strong evidence of the continuous release of contaminated water to the ocean through the spring of 2015.

Time Evolution of the Sources of ^{90}Sr and ^{134,137}Cs in the Coast off Japan. The sources of artificial radionuclides in the marine environment can be distinguished using the ^{134}Cs/^{137}Cs and ^{137}Cs/^{90}Sr activity ratios. The main sources of ^{90}Sr and ^{137}Cs in the coast off Japan since the accident in 2011 are two: (i) global fallout from nuclear weapon tests, with a characteristic ratio of ^{137}Cs/^{90}Sr ≈1.5 in the world oceans[41] and considered as pre-Fukushima in this study; and (ii) atmospheric fallout and liquid releases from the FDNPP with a ^{134}Cs/^{137}Cs activity ratio of ~1, e.g., ref 1. FDNPP fallout mainly occurred in the first 2 weeks after the accident, with a ^{137}Cs/^{90}Sr ratio of ~1000.[21] Massive liquid releases of cooling water in spring 2011 resulted in seawater ^{137}Cs/^{90}Sr ratios of about 39 ± 1 in waters beyond the coast,[24] but the ratio of liquid releases has changed over time (Figure 4).

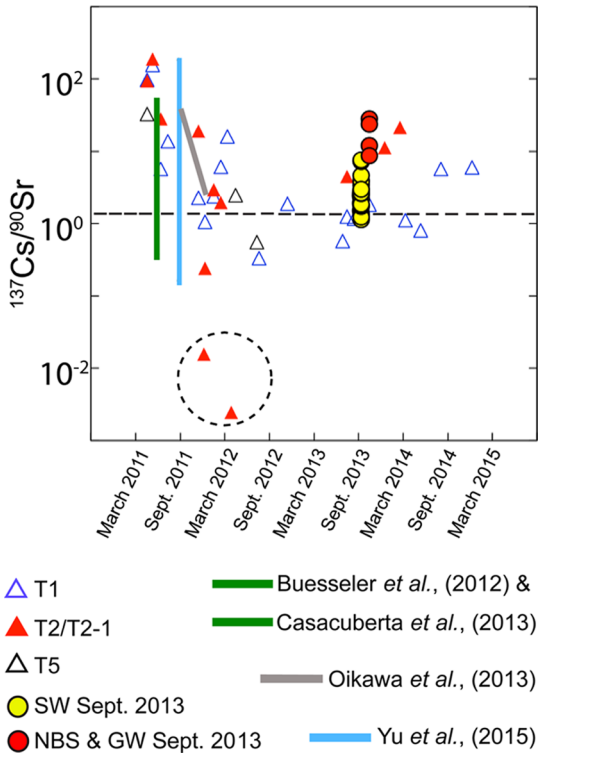

Figure 4. ^{137}Cs/^{90}Sr activity ratio in seawater (SW), northern beach samples (NBS), and groundwater (GW) collected in September 2013, in TEPCO's monitoring sites near FDNPP (T1, T2/T2−1, and T5) and other studies in the coast off Japan from March 2011 to July 2015. Accidental releases (dashed black circle) and pre-Fukushima activity ratio (dashed black line) are indicated.

^{137}Cs/^{90}Sr activity ratios from March 2011 to July 2015 are compiled in Figure 4. The ^{137}Cs/^{90}Sr activity ratio shifted abruptly from the pre-Fukushima ratio (~1.5, dashed black line in Figure 4) due to FDNPP liquid releases and, to a minor extent, FDNPP fallout. This results in a broad range of the activity ratio, from 0.2 to 180 along the *K.O.K* study area and further east at 34−40°N in June 2011.[24,36] In surface waters off the prefectures of Fukushima and neighboring Miyagi to the north and Ibaraki to the south, the ratio was (2.6−50) in August−December 2011,[27] still higher than pre-Fukushima conditions. The ^{137}Cs/^{90}Sr activity ratio in all samples collected in September 2013 ranged from 0.6 to 28. Near FDNPP, the variability of the ^{137}Cs/^{90}Sr activity ratio has been even larger:[21] at T2/T2−1, the ratio has been fluctuating between 10^{-3} and 10^{2} from April 2011 to February 2014 (last recorded data). At T1, ratios were reported until December 2014 and showed a slightly smaller range (~10^{-1}−10^{2}). Since 2013, the ratio at T1 and T2−1 appears to be more stable, yet variations larger than 1 order of magnitude were still observable. After the massive releases of cooling water in spring 2011, other accidental liquid discharges have undoubtedly caused the largest variations in the ratio near FDNPP (dashed black circle, Figure 4). For example, ~150 L of

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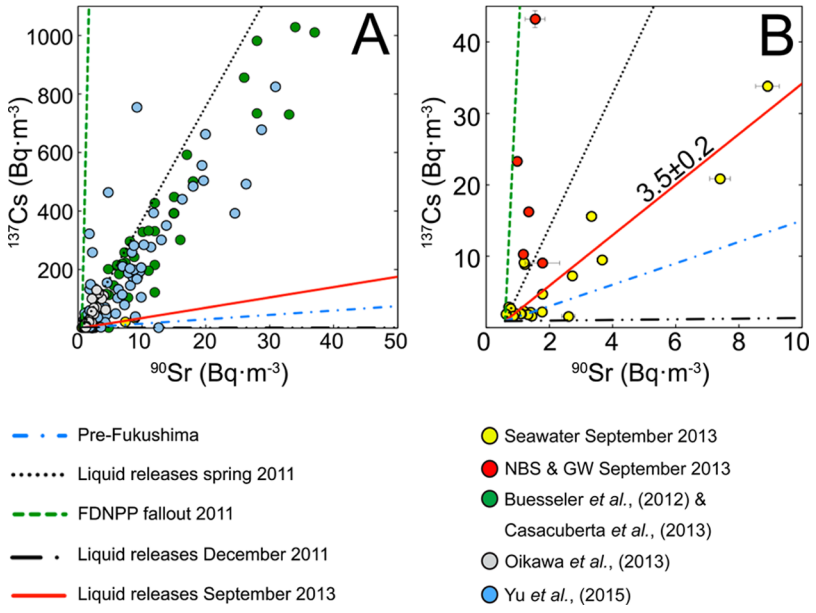

Figure 5. (A) ^{137}Cs/^{90}Sr activity ratios in seawater (SW), northern beach samples (NBS), and groundwater (GW) collected in September 2013 together with data published elsewhere.[18,24,27,36] (B) magnified image of SW, NBS, and GW samples collected in September 2013 (B). ^{137}Cs/^{90}Sr activity ratios of each end-member are included: pre-Fukushima levels from global fallout due to nuclear weapon tests (~1.5),[41] FDNPP liquid releases in the spring of 2011 (i.e., ratio = 39 ± 1),[24] FDPP fallout in 2011 (i.e., ratio ~1000),[21] and FDNPP liquid releases in December 2011 (ratio = 0.016).[21,25] Also indicated are the continuing liquid releases from the FDNPP causing the highest seawater concentrations measured in samples collected within 6 km off FDNPP in September 2013 (ratio = 3.5 ± 0.2).

Cs-treated water containing ~15 GBq of ^{90}Sr was discharged to the ocean in December 5, 2011, leading to a low ^{137}Cs/^{90}Sr activity ratio of 0.016 at T2.[21,25] Another ~120 tons leaked from piping connecting a desalination unit with a concentrated water tank in March 2012.[25] From this volume, at least 80 L reached the discharge channel T2, where the lowest ^{137}Cs/^{90}Sr ratio was recorded (0.002).[25] Many other leaks have been reported likely reaching the Pacific Ocean, although not all of them have been recorded in TEPCO's monitoring areas (e.g., March 11, 2015: 750 tons of contaminated rainwater with maximum concentrations for total β emitters of about $8{\cdot}10^6$ Bq·m^{-3}; ~ 50% of which is commonly considered ^{90}Sr).[25] There might have been other accidental releases of which we are unaware of and whose impact in the ocean could not be identified because of low sampling frequency of the monitoring for ^{90}Sr.

To constrain the contributions of the distinct sources to the cesium and strontium concentrations collected in September 2013, we plotted data from this study together with the characteristic ^{137}Cs/^{90}Sr activity ratios of the known sources (Figure 5A,B). Seawater samples collected in 2013, particularly those with the highest concentrations and located near surface and within 6 km from the FDNPP, were characterized by a ^{137}Cs/^{90}Sr activity ratio of 3.5 ± 0.2 (Figure 5B). The ratio does not differ significantly (3.4 ± 0.6) if we subtract pre-Fukushima levels of ^{90}Sr (1.2 ± 0.7 Bq·m^{-3}) and ^{137}Cs (1.8 ± 0.3 Bq·m^{-3}; Figure S.2). This ^{137}Cs/^{90}Sr activity ratio is about 1 order of magnitude lower than the resulting from the liquid discharges in spring 2011[24] and consistent with the fact that any spills from the tanks or groundwater entering the ocean would be enriched in ^{90}Sr relative to releases in spring 2011, either because cesium has a higher sorption coefficient than strontium on soils[42] or because of the active decontamination of cesium.

In some seawater samples (e.g., sample 13), the measured ^{137}Cs/^{90}Sr activity ratio was even lower than pre−Fukushima values. This can only be explained by FDNPP releases similar to those that occurred in December 2011[21] or February 2012,[25] which were extremely high in ^{90}Sr. Samples collected >6 km away from the FDNPP had relatively low concentrations of ^{90}Sr and ^{137}Cs (and usually undetectable ^{134}Cs) and a ^{137}Cs/^{90}Sr activity ratio closer to pre−Fukushima (i.e., ~ 2). These would be waters mainly originating from the open ocean with little impact from FDNPP, as found around Taiwan and off Japan (145−155°E and 25−35°N) in May−June 2012.[26]

The northern beach samples and groundwater collected in Sendai Bay had a ^{137}Cs/^{90}Sr activity ratio (5−28) much higher than in seawater at that time (0.6−7.5). All of these samples had salinities (Table S.1) much lower than seawater as a result of the mixing of seawater with river runoff or groundwater. Considering the high ^{137}Cs/^{90}Sr activity ratio of the FDNPP fallout, the mixing with fresh water inputs tagged with the ratio from FDNPP fallout on land would result in higher ^{137}Cs/^{90}Sr activity ratios as observed in northern beach samples and groundwater.

Impact of the New Releases in 2013. The magnitude of the continuing releases from the FDNPP, leading to the contamination observed in September 2013, can be estimated using the ^{137}Cs/^{90}Sr activity ratio of 3.5 ± 0.2 defined above together with the estimates of ongoing ^{137}Cs releases available from the literature. A continuous discharge of ^{137}Cs of 8.1 GBq·d^{-1} was estimated for summer 2012 based upon the exchange of waters between the FDNPP harbor and nearby ocean and the concentrations of ^{137}Cs in these waters.[43] Maderich et al.[39,40] modeled the long-term dispersion and fate of radioactive contamination originating from the FDNPP. To match measured seawater concentrations with their model predictions, they estimated an ongoing source of 3.6 TBq·year^{-1} (or 9.9 GBq·day^{-1}) of ^{137}Cs during 2011−2014.[39] A higher release estimate of ^{137}Cs was reported for September 2013 (~30 GBq·day^{-1}),[44] although ^{137}Cs concentrations at T1 and T2/T2−1 remained at ~$1{\cdot}10^3$ Bq·m^{-3} since 2012 suggesting no change in inputs during this time (Figure 3B). Considering a ^{137}Cs release range of 8.1 to

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30 GBq·day^{-1} and the ^{137}Cs/^{90}Sr activity ratio of 3.5 ± 0.2, we estimate a ^{90}Sr release of 2.3−8.5 GBq·day^{-1} (or 71 ± 4 to 261 ± 15 GBq·month^{-1}) in September 2013. Because the ^{137}Cs/^{90}Sr activity ratio changed temporarily due to accidental releases (Figure 4), the calculated release rate would only be valid for that month. As a rough approximation, however, one may assume an average ^{90}Sr release rate of ∼166 GBq·month^{-1}. At this rate, it would take ∼45 years for the ongoing releases to equal the most conservative estimate of ^{90}Sr discharged by June 2011 (90 TBq).[24] In comparison, it would take ∼500 years for the ongoing releases of ^{137}Cs to match some of the lowest estimates of ^{137}Cs released by the end of May 2011 (e.g., 3.5 PBq).[14]

Freshwater inputs from land constitute another source of radionuclides to the ocean. For example, rivers transport significant amounts of particulate radiocaesium, mainly during heavy rain events, to the coast of Japan.[45,46] The Abukama River basin is the largest river system affected by FDNPP-derived fallout in 2011, and its inputs of ^{137}Cs to the ocean were estimated to be of ∼19 GBq·day^{-1} in 2011−2012.[46] Unfortunately, to our knowledge, there is no information on ^{90}Sr concentrations in river water or groundwater. As a rough approximation (and assuming no modification of the FDNPP-derived fallout ^{137}Cs/^{90}Sr activity ratio deposited on land during river transport (i.e., ∼ 1000)),[21] river inputs of ^{90}Sr would be of ∼19 MBq·day^{-1}. The bottom line is that continuing releases of ^{90}Sr from the FDNPP probably exceed by 2−3 orders of magnitude those inputs from rivers.

In addition to ongoing direct releases and river runoff, about 1500 tanks are being used by TEPCO to store more than 665·10^3 m^3 of water as of June 2015.[28] TEPCO has reported several leaks from these storage tanks, as well as from pipes, decontamination units, etc. Major leaks include 300 tons of water with 0.28 TBq·m^{-3} of total β emitters in August 2013 and 100 tons with 0.23 TBq·m^{-3} of total β in February 2014.[25] If these waters reach the ocean, they would add ∼54 TBq of ^{90}Sr (assuming ∼50% of all β is ^{90}Sr). This is equivalent to ∼6−60% of the ^{90}Sr released by June 2011 (e.g., 90 to 900 TBq),[24] suggesting that the storage tanks are a potential large source of ^{90}Sr that needs to be carefully managed.

The decrease in the ^{137}Cs/^{90}Sr activity ratio from ∼39[24] in the spring of 2011 to a ratio higher than the global fallout suggests the ongoing release from the FDNPP to the Pacific Ocean through September 2013. This study shows the potential of using the ^{137}Cs/^{90}Sr activity ratio to constrain sources of artificial radionuclides in the coast off Japan, which varies widely from ∼1000 on land[21] to <1/1000 in waters stored in tanks.[25] The net result of these sources is the shift of the ^{137}Cs/^{90}Sr to ∼3.5 in waters impacted by FDNPP in September 2013.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b03903.

Table S.1: Concentrations of ^{90}Sr, ^{137}Cs, ^{134}Cs; ^{137}Cs−^{90}Sr activity ratios; sampling dates and location; salinity; and temperature in seawater samples collected off Japan and in northern beach samples and groundwater collected in Sendai Bay in September 2013. Figure S.1: Vertical concentration profiles of ^{90}Sr, ^{137}Cs, and ^{134}Cs in samples collected off Japan in September 2013. Figure S.2: Calculation of the ^{137}Cs−^{90}Sr activity ratio in seawater samples collected off Japan in September 2013. (PDF)

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Notes

The authors declare no competing financial interest.

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