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Emission, Dynamics and Transport of Perfluoroalkyl Substances from Land to Ocean by the Great East Japan Earthquake in 2011

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Ⓦ Web-Enhanced Feature Ⓢ Supporting Information

ABSTRACT: Water samples collected along the Japanese coast and in the open Pacific Ocean in 2010, 2011, and 2012 were analyzed for perfluoroalkyl substances (PFASs) to evaluate the effect of Great East Japan Earthquake (EQ 3.11), which occurred on March 11, 2011, on the dispersion of chemical pollutants. Ultratrace analysis of PFASs in water, a super computer simulation, and an inventory analysis from industrial records revealed the sources and dynamics of PFASs during the EQ 3.11 disaster. In this respect, EQ 3.11 destroyed solid infrastructure on land, and within minutes, PFASs stocked therein were released into the open environment. The historically significant tsunami backwash swept them away from their origin to the coastal water within several hours. It was estimated that from 0.8 to 1.0 tons of perfluorooctanesulfonate (PFOS) and 4.8 to 5.1 tons of PFOA were discharged into the coastal waters after EQ 3.11 and the tsunami that followed. The reconstruction of EQ 3.11 also traced the influence of this pollution in open ocean water until March 2012, and a statistical and finger printing analysis revealed that there were different distribution mechanisms in coastal regions than in the open ocean for PFOS, other shorter chain perfluorinated sulfonic acids and perfluorinated carboxylic acids.
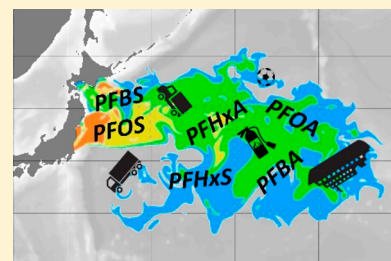
INTRODUCTION

Perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) were first detected in open ocean water collected in 2002 from the Eastern Pacific Ocean.[1] At that time, it was found that deep seawater (at depths of 4400 m) from the Central to Western Pacific Ocean contained significant amounts of PFOS and PFOA. That study suggested the need for research on pathways for tracing sources of PFOS and associated perfluoroalkyl substances (PFASs) on a global scale. Although there were several reports on the global transportation of PFASs,[2−4] the estimation of inventories was based on computer simulations and conceptual models because only few actual monitoring data have been available[5−9] on a global-scale open ocean environment during these 15 years, even after the discovery of PFASs in wildlife in the polar regions in 2001.[10] In order to determine the mechanism of global transport and distribution of PFASs, ocean monitoring of PFASs was initiated in 2002 at the National Institute of Advanced Industrial Science and Technology (AIST) in collaboration with the Atmosphere and Ocean Research Institute (AORI) of Tokyo University, Japan, and the Leibniz-Institute of Marine Sciences in Kiel, Germany. During the last 14 years of open ocean survey, PFASs were considered

as chemical tracers of global ocean cycling, and as a chemical markers of exposures in people in disasters such as world trade center (WTC) collapse in the U.S.[11,12]

A similar disaster to WTC occurred in Japan on March 11th, 2011, namely The Great East Japan Earthquake (EQ 3.11). The earthquake was quickly followed by one of the biggest tsunamis ever recorded, which began at 14:46 (Japan Standard Time) on March 11, in the northeastern region (Tohoku and Kanto regions) of Japan, which consequently resulted in serious environmental damage.[13−15] Furthermore, the tsunami resulted in mass human causalities with 90% of the people living in that area were deceased, and also created localized fires and explosion of a nuclear power plant. EQ 3.11, thus, caused a specific combination of three major environmental calamities; the strongest (M9.0) earthquake ever recorded, the highest (almost 10 m) tsunami wave ever recorded, and a nuclear power plant disaster in the Fukushima Prefecture. These concomitant catastrophes caused the most serious damage in

Table 1. Concentrations (ng/L) of PFASs in Water Samples Collected from the Disaster Hit Area in Japan in April 2011[a]

sample	PFSAs		PFCAs										
ID	PFHxS	PFOS	PFPrA	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	sample type
RT1	–	7.7	69.2	19.1	–	5.3	9.8	21.7	9.1	1.4	1.5	1.1	tsunami water pool, 3 km from coast
RT2	–	5.1	17.2	–	–	–	–	2.4	1.0	–	–	–	tsunami water pool, 1 km from coast
RT3	–	4.8	–	–	–	–	–	2.6	–	–	–	1.1	harbor water
OF1	8.2	9.4	11.9	–	–	–	–	11.6	3.3	1.5	1.6	1.3	harbor water
KN1	–	7.9	46.7	7.3	–	–	–	8.7	3.2	1.5	1.4	1.0	tsunami water pool, serious fire damage
KN2	–	6.1	35.4	8.5	–	–	–	10.1	4.4	1.9	1.0	1.1	tsunami water pool, serious fire damage
SG1	–	7.8	5.7	–	–	–	–	4.5	4.7	1.2	1.9	–	pond water, oil refinery fire
KS1	–	6.1	25.9	10.3	–-	–	–	8.1	2.3	1.0	1.5	–	tsunami water pool
KS2	–	5.6	25.6	19.2	–	–	6.0	6.5	2.8	1.4	1.2	–	tsunami water pool
KS3	–	5.2	16.8	8.6	–	–	–	20.8	10.7	1.7	1.5	–	harbor water
KS4	–	6.8	14.6	7.7	–	–	6.7	26.2	14.2	1.8	2.0	–	coastal seawater
KS5	–	6.7	11.5	3.7	–	–	–	4.4	2.9	1.1	1.0	1.2	coastal seawater
KS6	–	4.7	7.9	1.9	–	–	–	2.2	1.0	–	1.2	–	coastal seawater

[a]"–" Indicates a concentration below the LOQ.

Japan that had occurred since the Great Kanto earthquake in 1923. In 2015, four years after the event, 228 800 people remain evacuated from their homes.

Following this disaster, several research groups have studied environmental catastrophes including nuclear fallout from the region. Our research group collected water samples a month after EQ 3.11 disaster on April 6 and 7, 2011 and monitored the levels of PFASs in water from inland and coastal regions of Japan.[16] In this study, we present results pertaining to environmental emissions of PFASs and their transportation from land to open ocean following EQ 3.11. To accomplish our aims, we used field samples stored in a specimen bank, from April 6, 2011 to 2015, in combination with a super computer simulation and an inventory analysis of industrial records.

■ MATERIALS AND METHODS

Water samples just after EQ 3.11 were collected from tsunami water pools in inland areas, and coastal waters using polypropylene bottles on April 6 and 7, 2011 (Table S1). Offshore and open ocean water samples were collected during the research cruises of KH10-02 (June and July 2010), KH11-07 (July and August 2011), and KH12-03, KH12-04 (July and August 2012) by Hakuho Maru (JAMSTEC). During the research cruise, surface water was collected using a stainless steel bucket (0 m) and underwater inlet (5 and 10 m). To avoid contamination by the ship, the bucket was carefully washed with methanol prior to use and used to collect surface water only in front of the ship when it was moving slowly. Deep water was collected using the CTD Rosetta system equipped with X-Niskin samplers. A list of seawater samples collected is shown in Table S2. All samples were frozen until analysis. Approximately one liter of water samples was analyzed using the modified International Standard Method (ISO25101:2009) and the Japanese Industrial Standard Method (JIS K0450-70-10:2011); detailed information regarding the analysis is available in the literature.[17−21] To enable high accuracy and precision in analysis, all samples were quantified using two HPLC columns simultaneously (RSpak JJ-50 2D column and Keystone Betasil C18). Samples were analyzed for six perfluorinated sulfonic acids (PFSAs), ten perfluorinated carboxylic acids (PFCAs), FOSA, N-EtFOSA, N-EtFOSAA, saturated fluorotelomer carboxylate (8:2 FTCA) and unsatu-

rated fluorotelomer carboxylate (8:2 FTUCA). In most cases, only PFSAs and PFCAs were detected at significant levels and remaining analytes were below the detection limit shown in SI. PFPrA was only measured in water samples from land and coast.

Detailed information regarding the instrumental parameters used and QA/QC from the interlaboratory trial are shown in the Supporting Information and reported elsewhere.[22] Overall recovery of the above chemicals using the specified analytical procedure ranged from 81% to 125%.

■ RESULTS AND DISCUSSION

Destruction of Land and Environmental Disturbance in Relation to EQ 3.11 and the Subsequent Tsunami. Concentrations of PFASs determined in water samples collected from the disaster area in April 2011, are shown in Table 1. Although the disaster region was not highly populated in comparison with other regions in Japan, relatively high concentrations of PFASs were found in water samples collected one month after EQ 3.11. A schematic illustration of environmental disturbance following EQ 3.11 was conceptualized in Figure S1. Prior to EQ 3.11 (I), the steady state of concentration of pollutants was expected on land, coastal seawater, and sediments as represented by chemicals A, B, and C, respectively. Infrastructure on land was destroyed during EQ 3.11, and chemical A was released into the open environment in the disaster region. The tsunami then dredged up the coastal sediment, which mixed with coastal water to surge onto land, producing most of the disaster region to be covered (II) by a mixture of chemicals A, B, and C. Then obliterating land and releasing further pollutants, the backwash of the tsunami swept mixture of pollutants away from inland to coastal waters (III).

The results of water analysis suggested that, in general, the concentrations of PFOS, PFDA, PFUnDA, and PFDoA found in the disaster area did not vary significantly. Water samples collected from the city of Rikuzentakada, which is not very industrialized, provided a considerable insight into the sources and pathways of PFASs. A tsunami water pool located inland (RT1, 3 km from coast) showed higher concentrations of PFASs compared to another water pool (RT2), which was located one kilometer from the coast in the same city. Concentrations of PFOS and PFOA were comparable between
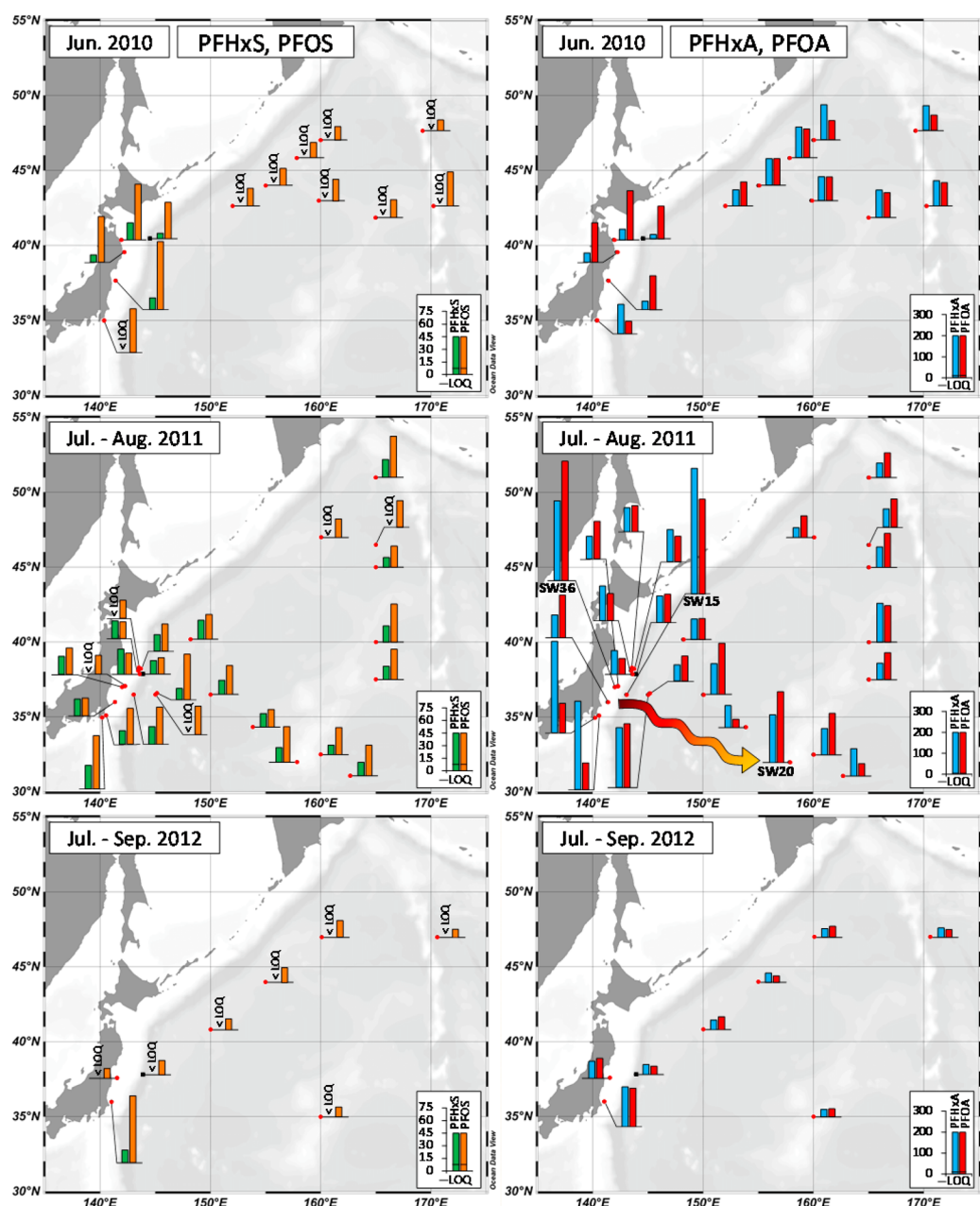
Figure 1. Temporal trends of PFHxS, PFOS, PFHxA, and PFOA (pg/L) in surface water from 2010 to 2012. Note: Red circles are general sampling points. Black squares are for vertical water collections in the Japan Trench.

RT2 and the harbor water (RT3), even though the fisherman's wharf and the port area were more populated than the highland areas in the region. It is considered that these findings relate to the physical mechanism of the tsunami. After tsunami, the area covered by the wave diminished gradually over a period of few hours, which suggests that the strength of tsunami backwash was minimal at the edge of the tidal wave, as it reached inland areas, and thus, the chemical dispersal would be expected to be higher in coastal areas than inland areas (Figure S1, III). This finding suggests that the residue level and type of chemicals disturbed by the tsunami dependent on the water solubility of chemicals, altitude above the sea level, and location and distance from the coast. Miyazaki[23] reported significantly lower concentrations of water-soluble metals, Bi, Tl, and In were discovered in the coastal waters collected just after EQ 3.11 than in the samples collected in the same region in 2008.

However, higher concentrations of less water-soluble substances such as PbS were obtained in coastal waters and on land. A similar mechanism of removal of water-soluble PFASs by tsunami was expected.

Another interesting finding was the possible secondary fire in Kesennuma (Figure S1, IV). Samples KN1 and KN2 showed the highest concentrations of PFPrA, PFOA, and PFNA of all tsunami water pools located near the coast (except RT1 located on high land). Although the background concentrations before EQ 3.11 were not available, a number of less fluorinated chemicals are known to be formed by fire-related activities. Higher levels of PFHxS and PFOA were found in the blood of firsthand responders at the World Trade Center after September 11 disaster[12] than in workers exposed to dust only. The aqueous firefighting form (AFFF), used in fire fighting activities, was reported to be a significant source of
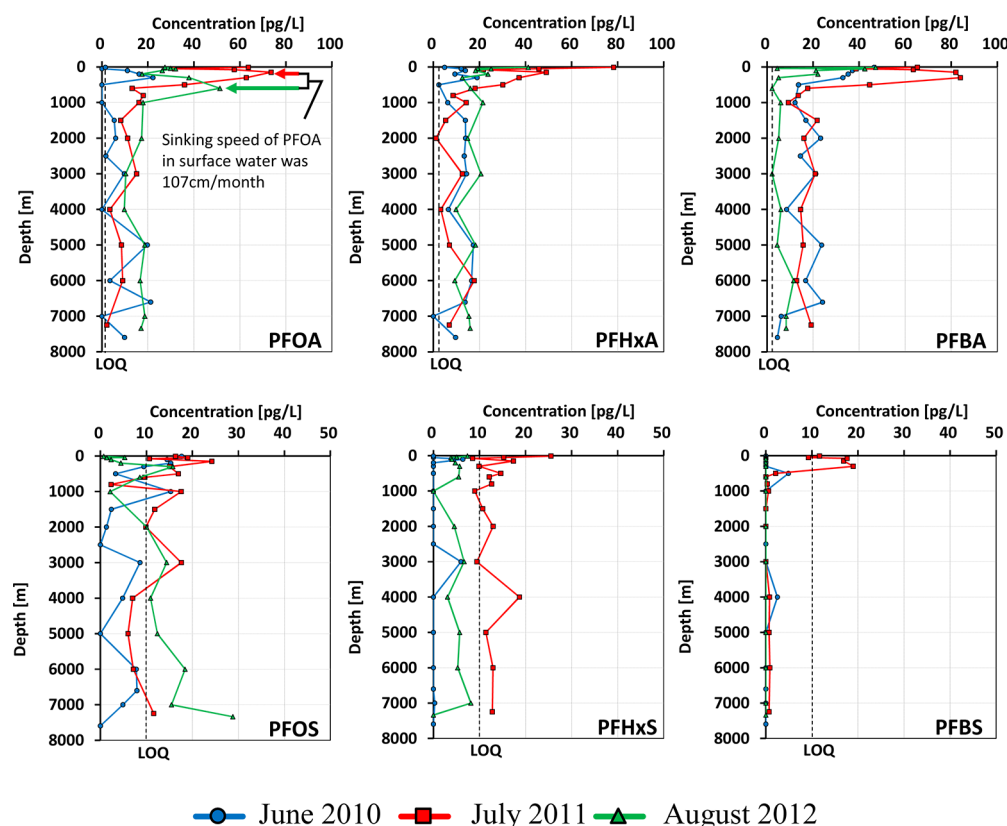
Figure 2. Vertical profiles of PFBA, PFHxA, PFOA, PFBS, PFHxS, and PFOS in water columns collected from the Japan Trench before and after the earthquake EQ 3.11 (2010, 2011, and 2012).

PFOS in a oil refinery fire occurred in Tomakomai on September 26, 2003.[24] The importance of AFFF containing PFOS needs to be investigated to gain a better understanding of release of PFASs into the land following EQ 3.11.

PFASs Discharge from Land to Ocean. The concentrations of PFASs in surface waters from offshore Japan and the northwestern Pacific Ocean collected in June and July 2010 (pretsunami samples), July and August 2011 (four months after tsunami), and July and August 2012 (16 months post tsunami), are shown in Table S3. Figure 1 describes the temporal trends of PFHxS, PFOS, PFHxA, and PFOA levels those were found at significant level in surface water collected during the sampling campaign and supposed to be accurate value because of lower LOQ compared to others.

In general, seawater collected off the coasts of Japan had 2–3 times higher concentrations of PFOS than the open ocean water collected in 2010. There was a similar trend for PFOA, but the results for PFHxA were unclear. Many water samples contained concentrations of PFCAs that were more than four times higher than those of PFSAs. Concentrations of PFASs in the open ocean waters in 2010 were considered to be general level, and were comparable to other open ocean waters previously investigated.[5-7,25] However, seawater samples collected in 2011, just four months after EQ 3.11 showed remarkably higher concentrations of PFASs than those collected in 2010. Although there was a huge disturbance in coastal waters because of the accidental input of PFASs due to the tsunami, surface water collected at a location 1780 km away from the Japanese coast (SW20 in Figure 1) contained significantly higher concentrations than other open ocean water samples.

Furthermore, water samples collected in 2012 revealed relatively low, or comparable, levels of PFASs in surface waters to those analyzed in 2010. This indicates that the higher level of PFASs found in 2011 were related to a particular phenomenon, and were most likely due to the tsunami related to EQ 3.11.

Although it was expected that the highest concentrations of PFOA would be found in offshore water (506 pg/L in SW36, and 401 pg/L in SW15), the third highest concentration was found in the open ocean water at SW20, which was collected 1780 km away from the coast. This is inconsistent with the expectation that concentrations of PFOA would gradually decrease from offshore to the open ocean. We, therefore, assumed that PFOA detected in SW20 was due to accidental emissions from land obliterated by EQ 3.11, which had been carried out in the backwash of the tsunami wave and then transported via the Kuroshio Extension Current (KEC) (Figure S2). This hypothesis was consistent with the lower concentrations observed in other water samples from the open ocean. Based on this hypothesis, we estimated the rate of PFOA transport through the KEC was 445 km/month, which was similar to the estimation made by the Japanese coast guard, who estimated the speed of drifting debris from tsunami to be 507 km/month.[26] Interestingly, this estimation was applicable to both PFOA and PFHxA levels measured in water, but not for PFOS and PFHxS, because concentrations of the latter decreased gradually from the coast to the open ocean, even along the KEC. These results suggest that there is a difference in the transportation/partitioning mechanisms between PFSAs and PFCAs in ocean waters.

Figure S3 describes the correlation between the concentrations of PFOS, PFHxS, PFBA, PFHxA, PFNA, PFOA, and

PFDA in surface seawater collected in 2011; only these chemicals showed a significant correlations ($p < 0.01$) in Pearson product moment correlation analysis (Table S4). The surface water samples were categorized into two groups: samples collected along the KEC (in red) and the "other" samples (in blue). Both groups showed independent results for the correlation analysis. In the KEC samples only, significant positive correlations were found between PFOA and PFHxA ($r = 0.802$), PFHxA and PFDA ($r = 0.823$), PFOA and PFDA ($r = 0.914$), but both groups showed positive correlations between PFBA and PFNA ($r = 0.699$ in KEC and $r = 0.851$ in other). This provided further evidence for the transportation of PFCAs though the KEC. Interestingly, a negative correlation ($p < 0.01$) was found in the "other" group between PFBA and PFDA, but not in the KEC samples. The "other" samples were mostly representative of coastal seawater and might be related to the different mechanisms involved in the input of shorter and longer chain PFCAs to the coastal waters.

A phenomenon similar to that above was found for PFASs in water columns collected in the Japan Trench (Figure 2). Vertical profiles of PFOS, PFHxS, PFBS, PFOA, PFHxA, and PFBA from surface water to a depth of 7500 m were described in three water columns collected in August 2010, July 2011, and August 2012 (the exact locations are shown in Table S2 (SW5, SW30, and SW42) and black squares in Figure 1). There were nearly 4 times higher concentrations of PFOA, PFHxA, and PFBA in the subsurface water collected in 2011 than in 2010. Although these locations were not exactly the same, similar depths and hydrodynamics were observed along the Japan Trench. After a significant increase in PFCAs in subsurface waters occurred in 2011, a relatively lower but comparable level to that of 2010 was observed in 2012. The sharp peak in PFOA concentrations in subsurface water observed in 2011 became a broad peak in the lower depths in 2012. If hydrodynamics is stable in these locations, this result may suggest that PFOA contamination from EQ 3.11 resulted in an estimated sinking rate of PFOA in the subsurface water mass to be 107 cm/month between 2011 and 2012. However, the sinking rate of PFHxA and PFBA was not clear. A similar vertical trend was anticipated to be observed for PFSAs, but the levels of PFSAs were near the detection limit. However, it is of note that an unexpected increase in PFOS in deep water at 7500 m was only observed in 2012, and the value was three times higher than that detected at the same depth in 2011, just four months after EQ 3.11. Although careful interpretation is necessary because only a single survey was conducted, this could be attributed to the slow resuspension of sediment in the bottom water because of an accidental landslide related to EQ 3.11. However, no such phenomenon was found in relation to PFCAs, and this therefore provides further evidence of the different mechanisms of transport of PFSAs and PFCAs in relation to scavenging, transportation, and partitioning in ocean waters and particles.

Figure S4 shows a similar correlation analysis of PFASs in the water columns to that presented in Figure S3. The data from Figure 2 were investigated using Pearson product moment correlation analysis, and the results are shown in Table 2. Significant correlations ($p < 0.01$) were found among eight pairs of chemicals in 10 independent samples: PFOS/PFBA ($r = 0.713$) and PFHxA/PFOA ($r = 0.623$) in 2010, PFBS/PFBA ($r = 0.945$), PFBS/PFHxA ($r = 0.685$), PFBS/PFOA ($r = 0.927$), PFHxS/PFHxA ($r = 0.641$), PFBA/PFHxA ($r = 0.756$), PFBA/PFOA ($r = 0.963$), and PFHxA/PFOA ($r = 0.814$) in 2011, PFBA/PFOA ($r = 0.761$) in 2012, respectively. The high

Table 2. Pearson Product Moment Correlation Coefficients of PFASs in Water Columns from the Japan Trench Collected in 2010, 2011, and 2012[a]

June 2010	PFBS	PFHxS	PFOS	PFBA	PFHxA	PFOA
PFBS						
PFHxS	-0.129^b					
PFOS	-0.217^b	0.222^b				
PFBA	-0.293^b	0.199^b	0.713^c			
PFHxA	-0.476^b	0.199^b	-0.125^b	0.287^b		
PFOA	-0.335^b	0.127^b	-0.0609^b	0.289^b	0.623^c	
July 2011	**PFBS**	**PFHxS**	**PFOS**	**PFBA**	**PFHxA**	**PFOA**
PFBS						
PFHxS	0.165^b					
PFOS	0.482^b	0.185^b				
PFBA	0.945^c	0.275^b	0.583^b			
PFHxA	0.685^c	0.641^c	0.620^b	0.756^c		
PFOA	0.927^c	0.310^b	0.589^b	0.963^c	0.814^c	
August 2012	**PFBS**	**PFHxS**	**PFOS**	**PFBA**	**PFHxA**	**PFOA**
PFBS						
PFHxS	—					
PFOS	—	-0.109^b				
PFBA	—	0.135^b	-0.528^b			
PFHxA	—	0.198^b	-0.589^b	0.761^c		
PFOA	—	0.191^b	-0.271^b	0.143^b	0.134^b	

[a]$n = 48$. "—": PFBS was below LOQ in 2012. [b]: $p < 0.05$. [c]: $p < 0.01$.

frequency of significant correlations between PFASs found in 2011 suggests that most of the PFASs in this water column had the same source of release. In other words, the tsunami backwash carried most of the PFASs from obliterated land and discharged them into coastal water immediately after EQ 3.11. It is of interest that PFBS and PFHxS had positive correlations with other water-soluble PFCAs, and only PFOS did not exhibit any relationship with other PFCAs in 2010 and 2012. The above findings in relation to the different distribution of PFOS (C8) and shorter chain PFSAs (C4 and C6) and PFCAs (C4 to C8), can be explained by their water solubility. Although the water solubility of PFBS and PFCAs (C4 to C8) were similar, there was a remarkable difference between that of PFBS and PFOS; PFOS has a water solubility that is one hundred times less than that of PFBS.[27,28]

Supercomputer Simulation of the Transportation of PFASs by the Tsunami and the Kuroshio Extension Current. To confirm above findings, a numerical model was used to simulate the possible transportation mechanism of PFOS and PFOA from the coast to the open ocean after EQ 3.11. In this respect, a supercomputer simulation of eddy-resolving ocean reanalysis product (JCOPE2) was developed at JAMSEC. Detailed information on the model, and the type of formula used for the numerical simulation are reported in the literature.[29] Here we briefly describe the results from the numerical model together with an independent correlation analysis. One hundred and 60 four data points of chemical analyses were used for the JCOPE2 simulation. Figure S5 shows an example of a simulation of the PFOA distribution in surface water averaged between July 1 and August 1, 2011. The concentration of PFOA in surface water observed from a field survey (squares in left figure) was significantly consistent with the results of the numerical simulation, except for four data sets

in the Northern Pacific Ocean. The simulation result suggests that PFOA, which was accidentally discharged into coastal water by the tsunami on March 11, 2011, was transported in the KEC, and that it reached 175 E, 35 N on September 1, 2011. The area of polluted surface water then expanded until mid-October, 2011, after which it gradually decreased. By March 2012, a background pollution level of PFOA remained, in relation to its dilution into open ocean water. The simulated kinetics of PFOA in surface water is well explained by the mechanism of advection and diffusion in the Kuroshio Extension and the mesoscale eddies.[29,30] Nevertheless, the concentrations of PFOS in surface water observed from field surveys were "not" well explained using the result of a similar numerical simulation to that used for PFOA. In some locations, the model was unable to completely explain the actual monitoring data. The relatively high concentrations of PFOS and PFOA observed along the line 165E, 38N to 45N did not match the results of the model, and this is explained by the location did not lie in the KEC. In addition, these samples may have been influenced by the direct discharge of PFASs from drifting debris, which was observed by Japanese coast guards (circles in left figure). Although the major part of the transportation and dilution of PFCAs in ocean water after EQ 3.11 appears to have been controlled by the surface water current, the sea surface wind, which also has a strong influence on floating debris, appears to be an additional source of pollution to the open ocean.

The numerical simulation also estimated the total amount of PFOS and PFOA discharged by EQ 3.11 into the open ocean. The area and volume of polluted surface water could be used to "recall" the total amount of chemicals polluting the land and the coasts before EQ 3.11. This amount was estimated from an optimization of the initial condition of the numerical model (the initial amount discharged into coastal water just a few days after EQ 3.11). Miyazawa et al.[29] made two estimations of the initial condition: the highest concentration of PFASs would be assumed (i) at the surface (0 m) and (ii) in subsurface water. The former estimation provided an amount of 4.8 to 5.1 tons of PFOA and 0.8 to 1.0 tons of PFOS, and the latter estimation provided as 6.7 tons for PFOA and 1.8 tons for PFOS for the amounts of PFOS and PFOA stored in the disaster regions and on the coast immediately prior to EQ 3.11.

Inventory Analysis of PFAS Discharge Using the Record of Industrial/Commercial Products. As they have been used in a large number of commercial products over the past 50 years, there is no existing reliable information related to the exact sources of PFASs. Therefore, shipping records related to industrial and commercial products containing PFOS and PFOA were used to estimate the amount of these chemicals stored in the disaster region.[31] Eight major industries were chosen in relation to their PFOS use: textile, pulp/paper and paper products, chemical, plastic products, rubber products, manufacture of iron/steel and fabricated metals, electronic parts, devices, and electronic circuits. The percentage of their total shipping value in the area flooded by the tsunami (531 billion yen) to that of the whole country (93 598 billion yen) was calculated to be 0.57%. In Japan, 92% of PFOS and its salts were used in photoresistant and antireflective coatings for semiconductors (88%), and in etching agents for compound semiconductors and other uses (4%), as categorized by the Stockholm convention for essential use.[32] It was also assumed that the inventory of PFOS used in these industries in 2011 was 92% of that used in 2008, as reported by Ministry of the

Environment.[32] The use of ammonium PFOA, and the amount exported in 2010 ranged from one ton to a thousand tons in Japan, and it was, thus, estimated that the same amount of PFOA was used in 2011, but that 0.57% of PFOA was used in this region in 2011. As a result, the total amount of PFASs used in the industries located in this area was calculated as being 1.17 tons for PFOS, and 5.7 tons (maximum amount) for PFOA.

It is of interest that the result of the computer simulation (a range estimation as 0.8 to 1.0 tons for PFOS and 4.8 to 5.1 tons for PFOA) was consistent with the estimation made using shipping records. In other words, the result using the super computer simulation "model", using the "real concentration" from a trace level analysis, provided the "source function" of PFASs. Both the estimated stock and usage on land and on the coast, before and after transportation by the KEC in relation to EQ 3.11, were consistent with the inventory record from industry production in Japan. This statement is also in line with the remarkably lower concentrations of PFASs found in 2012 compared to the amount in 2010 (Figure 1), and it may be related to the decline of industrial activity on the northeastern coast of Japan, which was supposed to be one of major sources of PFASs before EQ 3.11. Furthermore, the estimated storage of PFOS in AFFF (1.14 tons: calculated as 0.57% of 200 tons of the AFFF storage in Japan[33]) occupied 97% of the amount of PFOS stored on land in this region. Other industrial uses of PFOS were estimated as 0.033 tons (calculated as 0.57% and 92% of the 6.2 tons use and imports of PFOS in Japan, respectively[33]), which were lower than the 3% of total stock used in this region. To avoid environmental release of PFOS from AFFF use, the nationwide reclamation of PFOS contained in AFFF began in 2010. From above estimation, it is expected that there will be an efficient cleanup of direct use of PFOS in Japan. However, indirect discharge of PFOS through its precursors and the photo degradation of related chemicals was recently found,[34] is still unclear.

Figure 3 summarizes the environmental disturbance and open ocean discharge of PFASs caused by EQ 3.11. EQ 3.11 destroyed a considerable amount of infrastructure on land, thereby releasing PFASs into the open environment within minutes. The backwash of the large tsunami then played a major role in sweeping them away from the area of disaster to
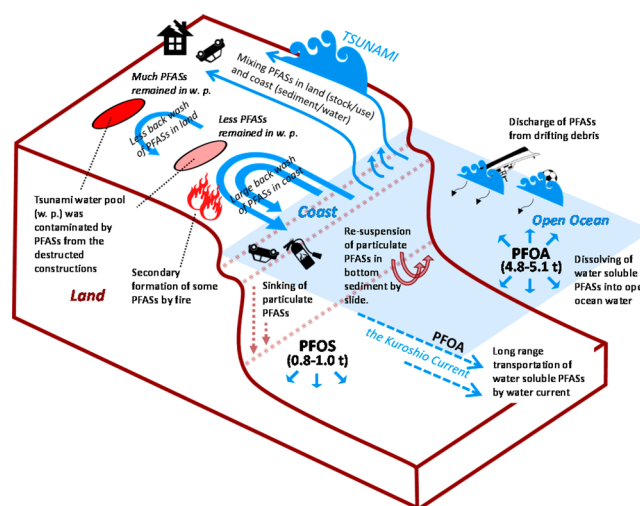
Figure 3. Schematic illustration of perfluoroalkyl substance emissions from land to ocean following the earthquake EQ 3.11.

coastal water, within a time span of several hours. After the coastal water was polluted by tsunami driven water, water-soluble chemicals such as PFOA were transported with the KEC, ultimately reaching a location at 175E, 35 N by September 2011, six months after EQ 3.11. Significantly higher levels of PFOA in the surface water were diluted into open ocean water during transportation in relation to advection and diffusion by the Kuroshio Extension and the mesoscale eddies. Finally, the concentrations of PFOA pollution in surface water had decreased to those of a background level by March 2012.

There have been numerous reports of destruction and possible human exposure to radionuclides and hazardous chemicals such as Pb following EQ 3.11 disaster on a massive scale. However, to our knowledge there has been no report on transport of persistent organic pollutants in relation to tsunami backwash from land just after EQ 3.11. Ironically, the accidental emission of PFASs caused by EQ 3.11 and the tsunami have revealed the first clear evidence of long-range transportation by water currents from land to ocean, and the quantitative dilution mechanism of these water-soluble persistent pollutants on a global scale. The supercomputer simulation using the monitoring results revealed not only the environmental dynamics of PFASs "after" EQ 3.11, but it also successfully estimated the total amount of PFASs stored and used on land "before" EQ 3.11.

■ ASSOCIATED CONTENT

ⓢ Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b01687.

> Detailed information regarding the instrumental parameters used and QA/QC from the interlaboratory trial (PDF)

Ⓦ Web-Enhanced Feature
A movie that shows the the simulation result of PFOA transport.

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Notes
The authors declare no competing financial interest.

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