

ACCIDENTAL INPUT OF PERFLUOROALKYL SUBSTANCES FROM LAND TO OCEAN BY THE DISASTER OF TSUNAMI, EQ3.11, JAPAN

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Introduction

PFOS and related perfluoroalkyl substances (PFASs) detected in remote marine locations and indicate a concern for the study of sources and pathways tracing of these compounds into the oceans. Although there are several reports on global transportation of PFASs, which are based on computer and conceptual models, very few actual monitoring data of PFASs are available on a global scale open ocean environment in these ten years, after the finding of PFASs in wild life in the Polar Regions in 2000. In order to determine the mechanism of global transport and distribution of PFASs, global ocean monitoring of PFASs was initiated in 2002 at the National Institute of Advanced Industrial Science and Technology (AIST) in collaboration with the Ocean Research Institute (ORI) of Tokyo University, Japan, and the Leibniz-Institute of Marine Sciences in Kiel, Germany^{1,2}. Monitoring studies in Open Ocean and relatively remote regions from point sources of continents is difficult to carry out because of the need for ultra-trace analysis. However, the concept of long range transportation can be simplified by monitoring PFASs because of the equilibrium reached by the local pollutions in both the atmosphere and the hydrosphere. Several open ocean surveys were carried out recently and providing good consistency with our early study, and now PFASs are known as a novel and useful chemical tracers for global modeling.

PFASs are targeting as chemical tracers not only for general monitoring study, but also a useful tool for reconstruction of disaster event such as 9.11 in USA^{3,4}. The recent disaster of earthquake followed by TSUNAMI and fire has resulted in serious environmental problems in Japan⁵. The disaster started at 14:46, JST, on March 11th, in the northeastern region (Tohoku and Kanto regions) of Japan. From current estimation (May 7th, 2011), more than 15,000 people died and more than 3,000 are missing. The minimum number of completely destroyed buildings was 83,000. The earthquake was a trigger, followed by the tsunami (more than 90% people were drowning) and fires that caused the “catastrophe”. The earthquake on March 11th (EQ 3.11) in Japan had specific combination of three calamities; the strongest (M9.0) earthquake recorded, the highest (almost 10 m) tsunami recorded and followed by serious disaster of nuclear power plants in Fukushima prefecture. The three concomitant catastrophes caused the most serious damage in Japan after the Great Kanto earthquake in 1923.

The first research survey using the sample set collected just after EQ3.11 was reported in the 32nd International Symposium on Halogenated Persistent Organic Pollutants (Dioxin 2011, Brussels⁵) six months after EQ3.11. In the previous report, it's revealed that both PFASs used in land and accumulated in coastal areas were totally disturbed and redistributed over the disaster areas. Here we present the second report of EQ3.11 as a part of open ocean survey of PFASs, the last 10 years project.

Materials and methods

In addition to the global open ocean survey from 2002 until now, several environmental samples including, soil, sediment, ash, river water, seawater and tsunami-discharged pool-water were collected from Miyagi, Iwate, Fukushima, Ibaraki and Chiba prefectures which were areas affected by the EQ 3.11 and consequent tsunami-related damages. Sampling was conducted within one month after the EQ 3.11. Open ocean seawaters were collected by two research cruises using Tansei Maru (KT-11-06) and Hakuho Maru (KH-11-07) from April to August in 2011. In this report, we will focus into seawater samples collected from these cruises. 500 to 1000 ml of seawater samples were analyzed by following the modified International Standard Method (ISO25101:2009, published in March 1st)⁶ and the Japanese Industrial Standard Method (JIS K0450-70-10:2011, published in March 22nd)⁷. Briefly, water samples were extracted using Oasis[®] WAX cartridges following the published methods^{8,9}. Separation and determination of target PFASs was performed using HPLC-MS/MS (EI negative

mode). For high accuracy, all extracted samples were injected into both RSpak JJ-50 2D column (2.0 mm i.d. × 150 mm length, 5 μm; Shodex, Showa Denko K.K., Kawasaki, Japan), with 50 mM ammonium acetate and methanol as the mobile phase and Keystone Betasil C18 column (2.1 mm i.d. × 50 mm length, 5 μm, 100 Å pore size, end-capped), with 2 mM ammonium acetate and methanol as the mobile phase. Seven perfluorinated sulfonic acids (PFSA), fourteen perfluorinated carboxylic acids (PFCA), FOSA, N-EtFOSA, N-EtFOSAA, unsaturated fluorotelomer carboxylates (8:2, 10:2 FTUCA) and fluorotelomer alcohols (8:2, 10:2 FTOH) were analyzed.

Results and discussion

Global Ocean monitoring of PFASs was initiated in 2002 and continued up to now. Concentrations of PFOS and PFOA in surface seawaters collected all over the world were presented in Figure 1. Concentrations of PFOA and PFOS in western and eastern Pacific Ocean waters ranged from 15 to 62 and from 1.1 to 20 pg/L, in respectively. These concentrations were an order of magnitude lower than the concentrations found in offshore waters, and four orders of magnitude lower than the concentrations measured in Tokyo Bay waters. These values appear to be the background values for remote marine waters far from local sources. The remarkable difference between residue level of PFCs in the Pacific and the Atlantic Ocean seems to be influenced by several local sources in the latter region.

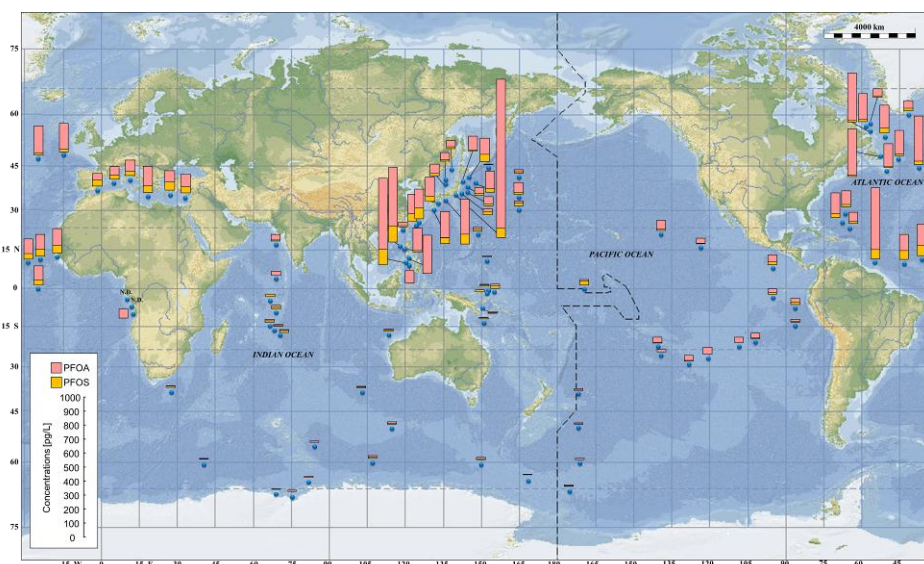


Figure 1. Concentrations of PFOS and PFOA in surface seawaters collected from open oceans from 2002 to 2012. – The last 10 years study -

Figure 2 shown concentrations of PFOA and PFOS in surface seawaters collected in KT11-06 and KH11-07. Generally, offshore seawaters of Japan shown higher concentrations of PFOS and PFOA than open ocean seawaters. However, seawater samples collected along the TSUNAMI line estimated shown remarkably difference. From X to Z, offshore to open ocean, continuous increase of PFOA concentration (202 to 301 pg/L) were observed and then decreased to 176 pg/L. In other word, Surface water collected in 1780 km far (Z) from the Japan coast shown the maximum concentration in July 2011. We assumed that this was caused by the historical disaster TSUNAMI happen in March 11. Estimated speed of dragged out PFOA into surface water was 445 km/month. This estimation was similar to the report by Japanese coastal guard, which they estimated the speed of the drifting debris by TSUNAMI is 507 km/month. Interestingly, this estimation was applicable to PFOA but not for PFOS, its concentration decreased from coast to open ocean even along the TSUNAMI line. These results suggested the difference in mechanism of transportation/partitioning between PFSA and PFCA in ocean waters.

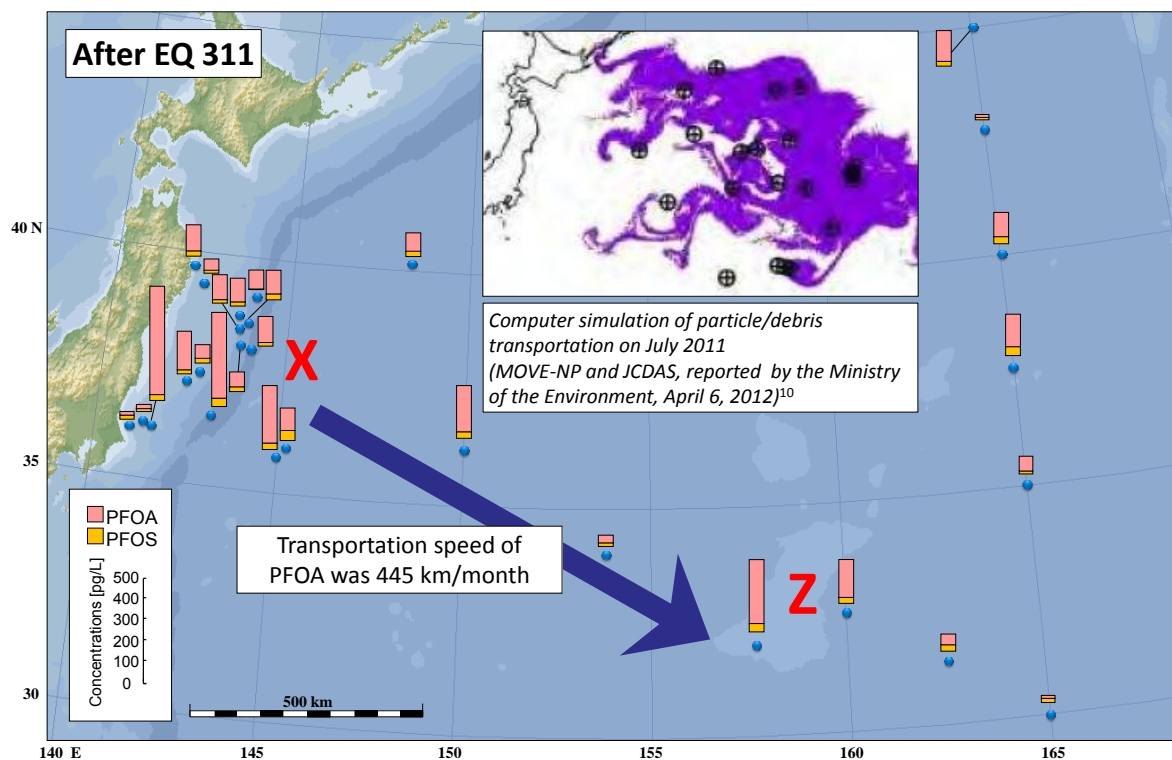


Figure 2. Concentration of PFOS and PFOA in surface waters collected just after EQ3.11 (April to July 2011). - Possible input of PFOA into the Pacific Ocean by the disaster of TSUNAMI -

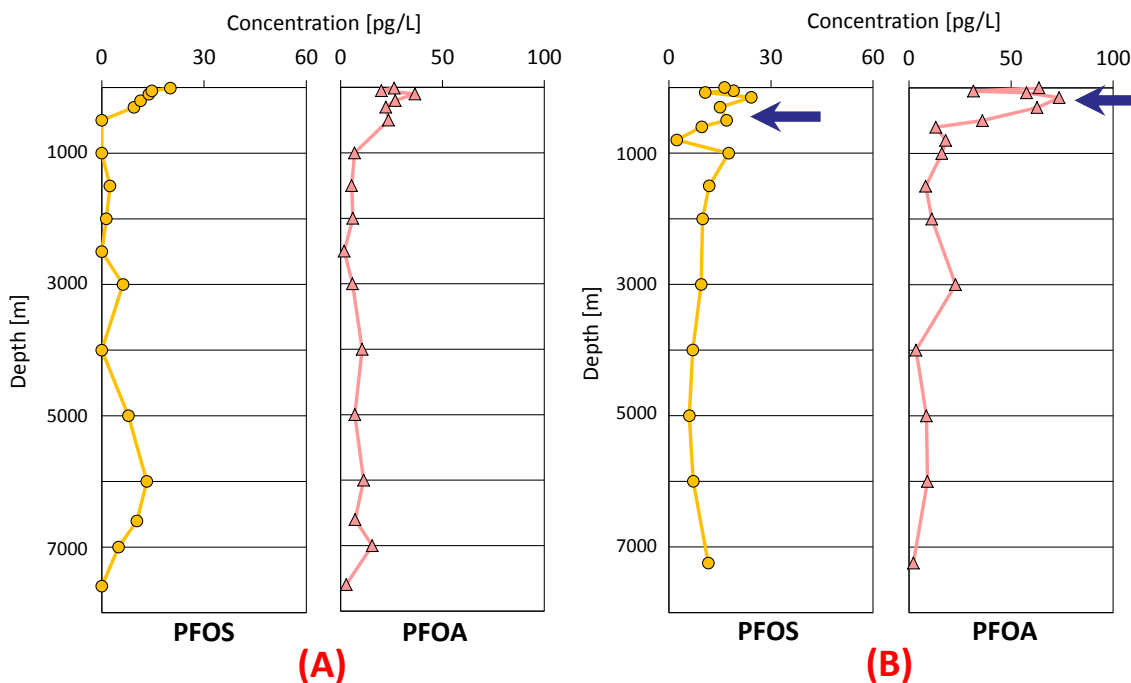


Figure 3. Vertical profiles of PFOS and PFOA in seawaters collected in the Japan Trench. (A) : June 2010, (B) : July 2011

Figure 3 described vertical profiles of PFOS and PFOA in seawaters collected in the Japan Trench, 7000m deep, before (June 2010) and after (July 2011) EQ3.11. In June 2010, it was typical vertical profile of PFASs, continuous decrease of PFASs concentration from surface to middle waters and possible re-distribution by density bottom water from slope of the trench. It is also similar to the trend observed in Japan Sea reported in 2008. However, remarkably change was found in water column collected from similar location in July 2011, four months after EQ3.11.

Sub-surface water (10 to 50 m depth) collected in 2011 contained much higher amount of PFOA than 2010. Vertical profile of sub-surface water showed that PFOA concentration were unusual and seems to be disturbed completely after TUNAMI. Vertical profile of middle to deep water mass (<1500m) were relatively constant even after TSUNAMI but ratio of PFOS to PFOA become higher. This may suggest that higher scavenging rate of PFOS than PFOA because the water solubility of PFOA is higher than PFOS. It seems that PFASs in seawater in the Japan Trench was completely disturbed by EQ311. From these results, it suggests that time course monitoring of PFASs provides useful information of eventual disturbance and re-equilibrium of water column, not only in surface water but also in middle to bottom waters.

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The disaster in Japan has not ended yet, more than 344,000 people are still evacuated. All of your support and concerted action about damaged regions and people are key to recovery and regeneration.

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