

## ENVIRONMENTAL CONTAMINATION BY PERFLUORINATED CARBOXYLATES AND SULFONATES FOLLOWING THE USE OF FIRE-FIGHTING FOAM IN TOMAKOMAI, JAPAN

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### *Introduction*

On September 26, 2003, a magnitude (*M*) 8.3 offshore earthquake struck Hokkaido, Japan. The earthquake and ensuing tsunami injured hundreds of people and resulted in significant damage to port and coastal communities. Immediately following the earthquake, a major fire occurred at an oil storage facility of a refinery (Idemitsu Kosan Company Ltd) located in the west part of Tomakomai, a Pacific coast city in southern Hokkaido. Idemitsu Kosan Company is the second largest oil refinery in Japan, with a capacity of 140,000 barrels per day (bpd) in Tomakomai. Forty-five of the 105 oil storage tanks were damaged following the earthquake and resulted in release of petroleum naphtha, which ignited accidentally. The first fire was reported immediately after the earthquake on 26 September 2003 and was extinguished after 7 hours. The second fire occurred on 28 September and lasted for 44 h. More than three hundred fireman and about one hundred fire engines were brought from several prefectures by air carriers to extinguish the fire. More than 130,000 L of fire fighting foams (FFF) was delivered to extinguish these fires and at least 40,000 L was used. Detailed information regarding the type of FFF used was not available, but aqueous film forming foams (AFFF) have been used in the control of fuel-related fires. Perfluorooctane sulfonate (PFOS) and related perfluorinated acids are a component of AFFF (1). The issue of environmental pollution by perfluorinated compounds (PFCs) including perfluorinated carboxylates and sulfonates has received much attention in the last four years (2,3). PFCs possess unique physicochemical properties and exhibit a wide range of volatility/ water solubility depending on the functional group. Environmental dynamics of PFCs is complex due to their unique characteristics and to their release from multitude of sources with various compositions. Previous studies have reported on environmental contamination by PFCs due to accidental release of AFFF (4,5). Large amount of release of AFFF in Tomakomai oil refinery fire provided an opportunity to study environmental dynamics of PFCs in the environment. A monthly monitoring survey of the environmental levels of PFCs in the Tomakomai region was conducted since October 2003. This study presents the results of initial survey conducted between October and December 2003.

### **Materials and Methods**

Surface water samples were collected from the Pacific coast of Tomakomai and lake Utonai; snow, soil, and run off water samples were also collected from twenty four locations in the those areas affected by the fire. Surface and run-off water and melted snow samples were analyzed by ultra-trace, solid phase extraction (SPE), method. Soil samples were extracted into methanol with ultrasonication and then applied to SPE method. Instrumental determination of perfluorinated sulfonates (PFOS, perfluorohexane sulfonate or PFHS, perfluorobutane sulfonate or PFBS), perfluorooctane sulfonamide (PFOSA) and perfluorinated carboxylates (perfluorododecanoic acid - PFDoA, perfluoroundecanoic acid -PFUnA, perfluorodecanoic acid -PFDA, perfluorononanoic acid -PFNA, perfluorooctanoic acid -PFOA, perfluoroheptanoic acid -PFHpA, perfluorohexanoic acid -PFHxA,) were performed using a high performance liquid chromatograph-tandem mass spectrometer (HPLC-MS/MS), comprising an Agilent HP1100 liquid chromatograph interfaced with a Micromass® (Beverly, MA, USA) Quattro Ultima Pt mass spectrometer operated in the electro spray negative ionization mode. A 5 or 10- $\mu$ L aliquot of the sample extract was injected into a guard column (XDB-C8, 2.1 mm i.d. x 12.5 mm, 5 $\mu$ m; Agilent Technologies, Palo Alto, CA) connected sequentially to a Betasil C18 column (2.1 mm i.d. x 50 mm length, 5 $\mu$ m; Thermo Hypersil-Keystone, Bellefonte, PA) with 2 mM ammonium acetate/methanol as mobile phase, starting at 10% methanol. At a flow rate of 300  $\mu$ L/min, the gradient was increased to 30% methanol at 0.1 min, 75% methanol at 7 min, and 100% methanol at 10 min, and was kept there until 12 min before reversion to original conditions at 20-min. The capillary was held at 1.2 kV. Cone-gas and desolvation-gas flows were kept at 60 and 650 L/h, respectively. Source and desolvation temperatures were kept at 120 and 420°C, respectively. MS/MS parameters were optimized so as to transmit the [M-K]<sup>-</sup> or [M-H]<sup>-</sup> ions. Eight calibration curve points bracketing the concentrations in samples were prepared routinely, to check for linearity. Detailed analytical procedure has been reported elsewhere (6).

### **Results and Discussion**

Concentrations of PFCs in selected environmental samples collected after the Tomakomai fire are shown in Table 1. Concentrations of PFCs in open ocean waters (Atlantic Ocean and Pacific Ocean) and Tokyo Bay water are also presented for comparison. Water samples collected in October, approximately a month after the Tomakomai fire, showed two to six times higher concentrations of PFOS, PFHS and PFOSA than those from Tokyo Bay, a most contaminated waterbody in Japan. However, concentrations of perfluorinated carboxylates and PFBS were low in water samples collected in and around the oil refinery in Tomakomai than in Tokyo Bay. Fig 2 and 3 show the concentrations of PFOS and PFOA in water samples collected from Tomakomai and several other locations in Japan. Typical ratio of PFOS to PFOA concentrations in water samples around Japan was less than 0.7 (7,8). Water samples collected in December, approximately two months after the fire, showed a PFOS/PFOA ratio of 10 suggesting greater composition of PFOS in AFFF. After two months of AFFF usage, concentrations of all PFCs decreased dramatically, from 2- to 13- fold, compared to the samples collected in October except for PFHpA. Only at station 8 concentrations of PFOS and PFOA were similar. Relatively high concentrations of PFCs were found in in snow. This suggests that significant amount of PFCs in AFFF were released into the air and deposited to land through wet deposition process. Concentrations of PFCs in soil (pg/g dry weight basis) were also high for most PFCs; however, concentrations of PFBS were low. It may be due to that PFBS concentrations are low in AFFF. The highest concentration of any PFCs detected

in Tomakomai samples was 3,680ng/L of PFOS in run-off water collected in October. Run-off water contained all PFCs at the highest concentrations except PFDoA.

Figures 4 and 5 show the composition of perfluorinated sulfonate and carboxylates, respectively, in several water, snow and soil samples from Japan and open ocean. Composition of PFCs in central to eastern Pacific Ocean water represent background profiles of PFCs. North Atlantic Ocean profile reflects relatively contaminated open ocean water. Tokyo Bay water shows typical contaminated coastal water profiles in Japan. Compound specific composition of perfluorinated sulfonates and PFOSA provides several insights. High percentage of PFBS may be suggestive of non-contaminated water samples. Differences in the composition of PFCs between October and December may have been caused by dramatic decrease in PFOS concentrations.

From the above results, following hypothesis regarding environmental dynamics of PFCs can be made. PFCs released from AFFF into coastal water were at highest concentrations in October but removed readily by dilution and exchange of coastal and offshore waters. PFCs released into the atmosphere (gas phase and particulated matters) during AFFF usage was trapped by snow and deposited onto soil and water. PFCs deposited on soils can continue to be a source of exposure in the environment because of the high concentrations observed in soils in December. Soil contamination was also caused by the highly contaminated run-off water.

Further investigations and continuous monitoring are necessary clarify environmental dynamics and sources of PFCs. Accidents such as this involving large-scale releases of PFCs would provide more insights on the fate of PFCs.

### **References**

- (1) Moody, C., Field, J. *Environ. Sci. Technol.*, 33, 2800-2806, 1999
- (2) Giesy J. P., Kannan K. : *Environ. Sci. Technol.*, 35, 1339-1342, 2001
- (3) Kannan, K. Kannan, K.; Koistinen, J.; Beckmen, K.; Evans, T.; Garzelany, J.; Hansen, K.J.; Jones, P.D.; Giesy, J.P. : *Environ. Sci. Technol.*, 35, 1593-1598, 2001
- (4) Moody, C., Field, J. *Environ. Sci. Technol.*, 34, 3864-3870, 2000
- (5) Moody, C., Martin, J., Kwan, W., Muir, D., Mabury, S. *Environ. Sci. Technol.*, 36, 545-551, 2002
- (6) Yamashita N., Kannan K., Taniyasu S., Horii Y., Okazawa T., Petrick G., Gamo T., *Environ. Sci. Technol.*, (submitted)
- (7) Yamashita, N.; Taniyasu, S.; Horii, Y.; Kannan, K.; Gamo T. : *Organohalogen Compounds*, 62, 339-342, 2003
- (8) Taniyasu, S., Kannan, K., Horii, Y., Hanari, N. and Yamashita, N. *Environ. Sci. Technol.*, 37, 2634-2639, 2003

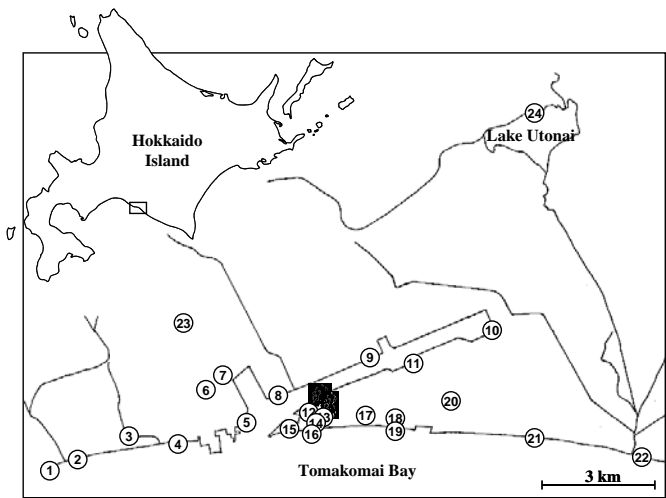


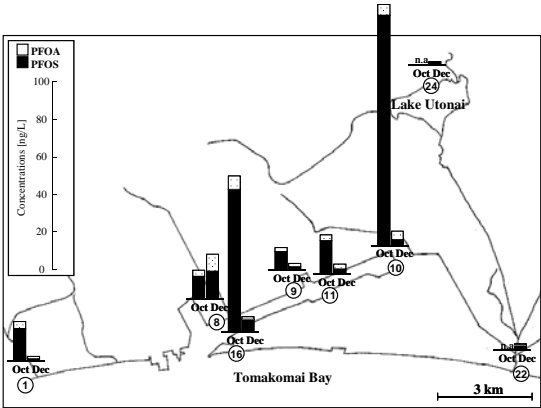
Fig. 1 sampling locations in Tomakomai city.

Table. 1 Mean concentrations (pg/L) of PFCs in environmental samples after the release of AFFF in Tomakomai in December and October, 2003

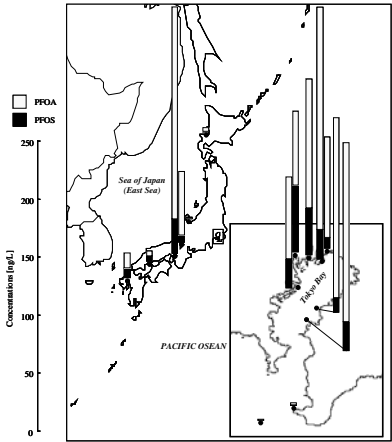
	N	PFOS	PFHS	PFBS	PFOSA
North Atlantic Ocean	9	16	5.6	4.7	1.8
Central to eastern Pacific Ocean	7	10	0.7	2.2	<1.0
Tokyo Bay	5	26,700	3,250	653	381
Tomakomai					
Water - October	6	42,300	6,880	218	2,490
Water - December	8	3,890	1,080	74	889
Run off - October	2	3,690,000	149,000	810	200,000
Snow - December	4	160,000	2,090	236	16,600
Soil - December	2	80,600	1,280	10	5,890

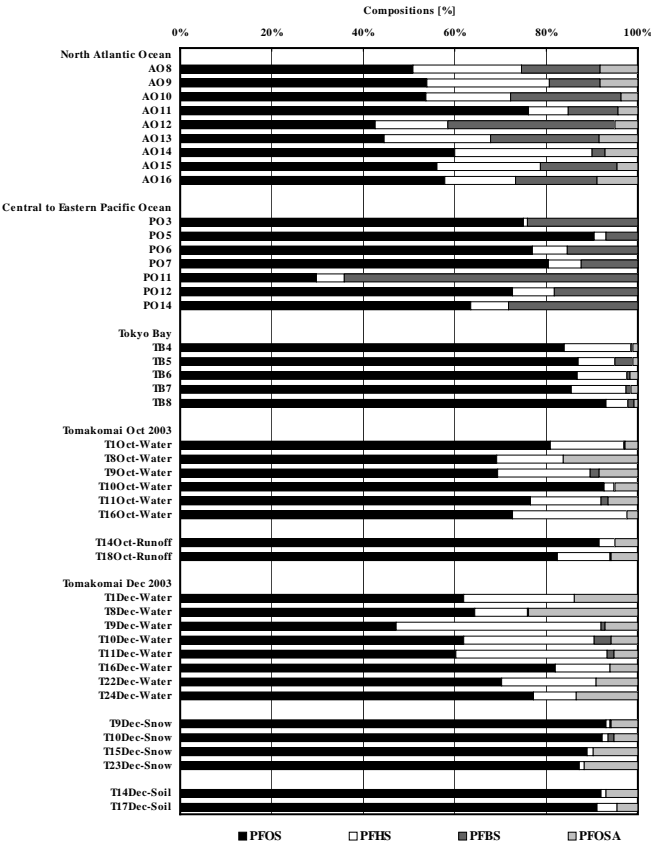
	N	PFD <sub>o</sub> A	PFU <sub>n</sub> A	PFDA	PFNA	PFOA	PFHpA	PFHxA
North Atlantic Ocean	9	<1.0	2.8	4.0	21	227	23	18
Central to eastern Pacific Ocean	7	<1.0	1.5	2.7	4.8	41	3.3	6.4
Tokyo Bay	5	37	1,630	1,170	23,900	66,600	2,050	476
Tomakomai								
Water - October	6	<100	656	434	7,920	4,150	184	263
Water - December	8	<100	184	96	2,150	2,670	304	109
Run off - October	2	<100	35,500	3,640	300,000	162,000	5,250	12,700
Snow - December	4	175	4,430	1,940	27,500	18,100	616	360
Soil - December	2	148	2,440	312	6,520	2,870	188	88



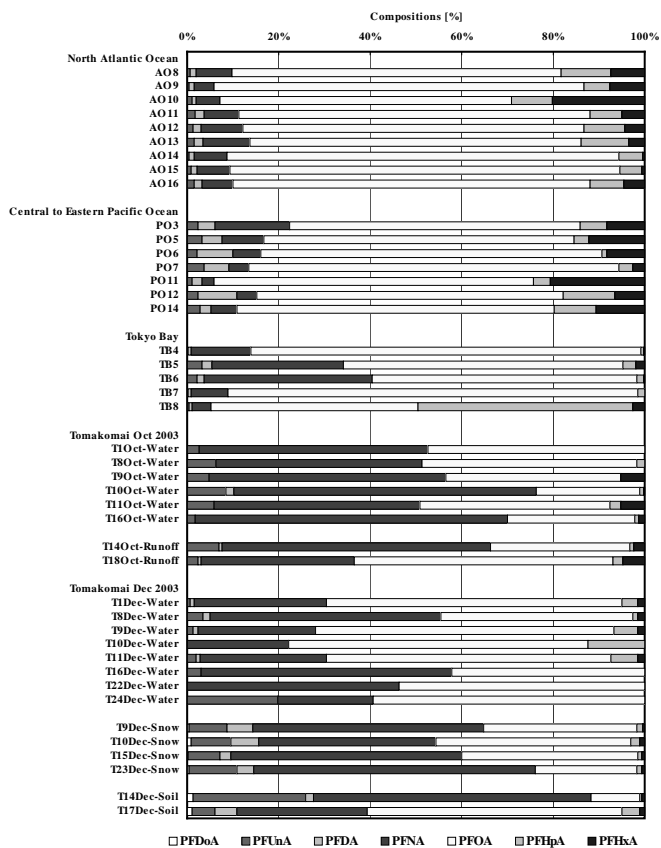
**Fig. 2** Concentration of PFOS and PFOA in water samples collected after the release of AFFF in October and December, 2003, in Tomakomai.



**Fig. 3** Concentration of PFOS and PFOA in coastal and lake water samples collected from several locations in Japan.



**Fig. 4** Composition of perfluorinated sulfonates including PFOSA in several environmental samples from Japan and open ocean.



**Fig. 5** Composition of perfluorinated carboxylates in several environmental samples collected from Japan and open ocean.