

ENVIRONMENTAL DEGRADATION OF PERFLUOROCARBOXYLIC ACIDS (PFCAs) AND PERFLUOROSULFONIC ACIDS (PFSA)S - ARE THESE REAL PERSISTENT ORGANIC POLLUTANTS?

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Introduction

Initially, research on perfluoro alkyl substances (PFASs) was focused on residue analysis in biota and the investigations expanded to freshwater/coastal water and air with a focus on atmospheric transportation. Although recent investigations have suggested that "direct input" through ocean water current has significant role in global distribution of PFASs, long range transportation of volatile precursors by atmosphere is still a potential pathway of "indirect input" of PFASs through possible breakdown from several precursors. However, investigations supporting atmospheric transportation hypothesis were mostly based on laboratory studies and conceptual models. Although PFASs are thought to be persistent, the number of real field evidences on environmental degradation of PFAS precursors is very few. In this study, we attempted to answer the question, "what happens to PFASs and their precursors in the real environment" using three ideas; one is photolysis experiment at high altitude mountains with strong solar irradiations. The second is an experiment on snow surface which is supposed to be an "environmental chamber of photochemistry" because of strong reflection of solar irradiation on snow surface. Thirdly, a photo degradation experiment in open ocean environment on board a research vessel, "sea surface" irradiation experiment.

Here we present several findings on "environmental degradation of PFCAs and PFSA)S, themselves.

Materials and methods

Photodegradation experiments at high altitude mountains were conducted both under field and laboratory conditions. The field study involved exposure of test PFAS solutions to sunlight in two high altitude mountain locations, in the USA and Japan. One of the locations selected for the field experiments was Mt. Mauna Kea in Hawaii Island, Hawaii, USA. Experiment was carried out in Mt. Mauna Kea at an altitude of 4200 m, for 106 days from September 10, 2010 to December 24, 2011. Strong solar radiation, coupled with better air quality at this high altitude offered favorable environmental conditions for the examination of photodegradation of PFASs. According to the World Health Organization (WHO), solar radiation intensity at the top of Mt. Mauna Kea was approximately 40% stronger than that at the mean sea level. Another location of field photodegradation study was Mt. Tateyama (at an altitude of 2500 m) in Toyama Prefecture in Japan. Top of this mountain is mostly covered with snow from late September to end of June with no human activity until the beginning of April, when it is open for tourists. This is a conserved location for the investigation of snow chemistry in Japan. The sunlight exposure duration for the study in Mt. Tateyama was 20.5 hours on 17-18 April 2011 (total duration the samples left in the field was 31.5 hours). The third experiment, on board a research vessel, for "sea surface" irradiation experiment, was carried out during open ocean surveys using JAMSTEC research vessel "Mirai" (MR11-08, the northeastern Pacific Ocean and MR12-05, the Antarctic Sea).

After the exposure period described above, each test solution of PFASs was kept at -20°C in darkness until analysis. Test solutions from the photodegradation experiments were diluted with methanol and analyzed by following a method reported elsewhere¹. To avoid co-elution problem on HPLCMSMS identification, all of the samples were injected onto both RSpak JJ-50 2D (2.0 mm i.d. × 150 mm length; Shodex, Showa Denko K.K., Kawasaki, Japan) and Keystone Betasil C18 column (2.1 mm i.d. × 50 mm length, 5 µm, 100 Å pore size, end-capped) separately to confirm accuracy of identification. If the results from the two columns did not match, samples were re-analyzed. Seven PFSA)S (PFETs, PFPrS, PFBS, PFHxS, PFHpS, PFOS, PFDS), fifteen PFCAs (TFA, PFPrA, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTTrDA, PFTeDA, PFHxDA, PFOcDA), FOSA, N-EtFOSA, N-EtFOSAA, saturated fluorotelomer carboxylates (8:2FTCA),

unsaturated fluorotelomer carboxylates (6:2, 8:2, 10:2FTUCA) and fluorotelomer alcohols (4:2, 6:2, 8:2FTOH) were analyzed¹⁻³). The analysis of FTOHs, N-EtFOSE was also performed using gas chromatography with tandem mass spectrometry (GC-MS/MS). GC-MS/MS analysis was performed using an Agilent 6890A gas chromatography system, equipped with a Quattromicro™. Separation was achieved on a DB-WAX capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness) from J & W Scientific (Folsom, CA, USA). Helium was used as carrier gas.

In this study, concentrations of parent compounds in the test tubes were determined after the exposure period; the concentrations were then compared with original concentrations and the differences were reported as photodegradation rates (reported as percentage reduction). The test solutions were also analyzed for the degradation products. Concentrations of degradation products were reported on a molar basis to estimate the percentage of yield from the parent compound.

Result and Discussion

Photodegradation in high altitude mountains: Residual amounts of target PFASs present in test solutions following exposure to sunlight for 1232 hours (106 days) at Mt. Mauna Kea are as follows. No significant photolysis was observed for PFETs whereas little photolysis occurred for PFPrS, PFBS, PFHxS, PFBA. Other target PFASs showed some level of photodegradation. The concentrations of the following PFASs were decreased following exposure to sunlight in Mt. Mauna Kea, in comparison with the original concentrations. The relative percentage reduction in concentrations of PFASs was as follows, PFOS; 29%, PFDS; 53%, PFOSi; 100%, TFA; 6%, PFOA; 5%, PFNA; 19%, PFDA; 35%, 8:2FTCA; 62%, 8:2FTCUA; 56%, 4:2FTOH; 18%, 6:2FTOH; 75%, 8:2FTOH; 90%. The reduction in the concentrations of PFASs following exposure to sunlight at high altitudes for 106 days was remarkable. It is worth to note that long chain PFASs degraded at higher proportions than short chain PFCAs, PFSA and FTOHs.

Figure 1 shows the photo-degradation products formed from each of the parent PFAS following sunlight exposure at Mt. Mauna Kea. Y axis represents of percentage of product formed from parent chemicals on a molar basis. Following sunlight exposure in Mt. Mauna Kea, PFOSi was 100% decomposed, and resulted in the formation of 73% PFOA, 6.1% PFHpA, 0.8% PFHxA, 0.3% PFPeA and 7.2% PFOS. Complete degradation of PFOSi by photolysis was not surprising because even the commercial analytical standard solution of this compound is unstable for long term storage. Photodegradation of PFDA yielded PFNA followed by PFOA and PFHpA. In general, PFCAs with n number of carbons (C_n) yielded products containing n-1 carbons (C_{n-1}) as the major degradation product, which is explained by step wise removal of CF₂ moiety. Exposure of 8:2FTCA to sunlight yielded 8:2FTUCA and PFOA as the major photodegradation products. 8:2FTUCA yielded much higher amounts of PFOA than that of 8:2FTCA. 4:2FTOH yielded PFBA as the major degradation product followed by PFPrA and TFA. Similarly, 6:2FTOH produced PFHxA followed by shorter chain PFCAs and 8:2FTOH produced PFOA followed by shorter chain PFCAs.

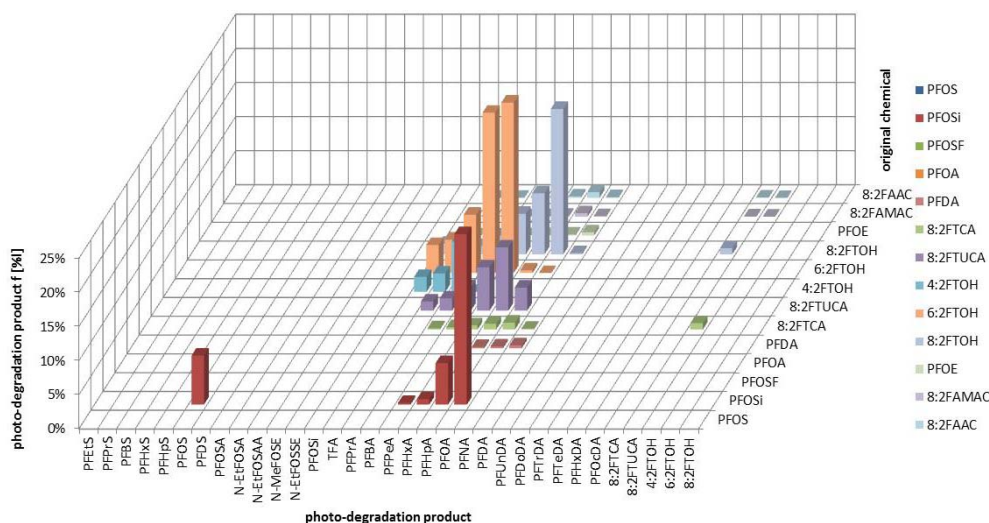


Figure 1. Photo-degradation product [%] of PFASs after sunlight exposure for 106 days at Mt. Mauna Kea (from Taniyasu et. al. ⁴⁾)

Thus, photodegradation of FTOHs yielded PFCAs with carbon numbers same as those in FTOHs themselves. The photodegradation products PFASs suggested stepwise removal of CF₂ moiety from the parent compound as the dominant pathway. In contrast to PFCAs and FTOHs, no photodegradation products were found for PFSAs including PFOS and PFDS. Although the concentrations of PFOS and PFDS in test solutions were 29 and 53%, respectively, lower than in the original solution, following exposures, no degradation products could be found. This suggested that the mechanism of photolysis of PFSAs was different from that of PFCAs. In the case of PFSAs, sulfonate moiety may be attacked first, resulting in some intermediary photoproducts that were not analyzed in this study.

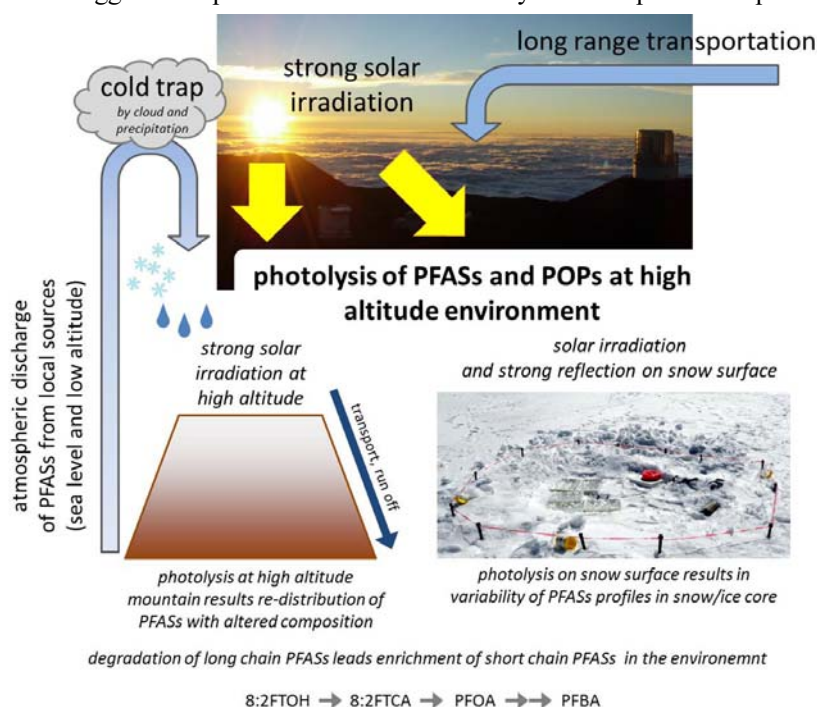


Figure 2. Conceptual model of photolysis of PFASs at high altitude environment .
- Photochemistry at high altitude mountains and snow surface can alter PFASs composition in global scale -

Figure 2 shows conceptual model of photolysis of PFASs in the environment. Although PFASs and PFCAs are known as less degradable by irradiation, they can still undergo photodegradation to some extent based on the photodegradation rate as explained by the following formula.

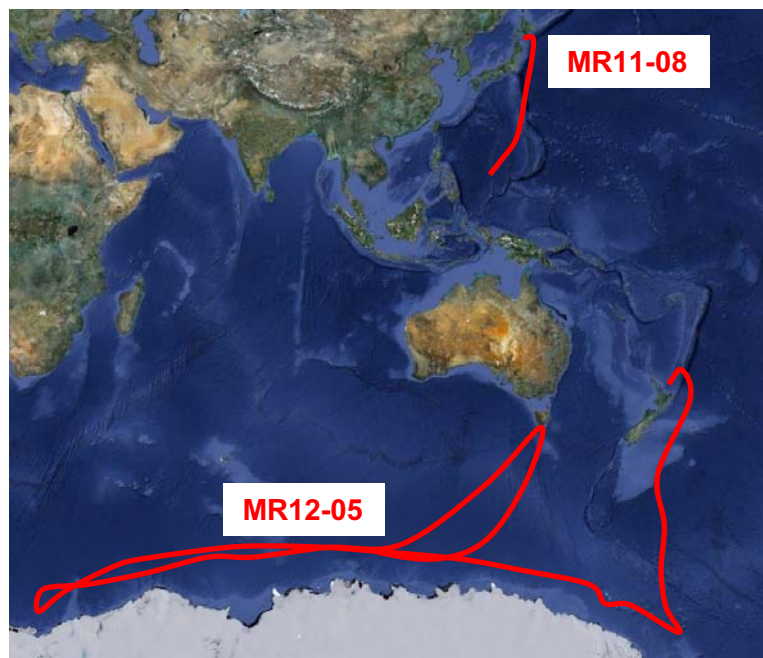


Figure 3. "On board" photodegradation experiment during open ocean cruises, MR11-08 (January to February 2012) and MR12-05 (November 2012 to January 2013).

$$J_i(x, y, z, t) = \int \Phi_i \sigma_i I_0 d\lambda$$

J_i : photolysis rate constant; Φ_i : quantum yield; σ_i : photon absorption cross section; I_0 : solar irradiation intensity

J_i can be small because Φ_i of PFSA is negligible under laboratory conditions, in general. However, photolysis experiments in laboratory do not consider much strong irradiation found at high altitude mountains and significant photolysis may occur under enough strong I_0 value. Indirect photodegradation reaction may also happen because of hydrated electrons in water. McKenzie et al.⁵⁾ reported that short wavelength irradiation energy, UV-B, at Mt. Mauna Loa (alt. 3400 m) was 1.5 times higher than that in Mt. Lauder (alt. 370m).

during the same field experiment at Mt. Mauna Kea (Hanari et. al. 2013⁶⁾) was noted. PCNs were well known persistent organic pollutants (POPs) because they are POPs. PCN was supposed to be difficult to degrade under normal environmental condition. However, such "persistent POPs" may degrade under strong solar irradiation at high altitude mountains and in the environmental reaction chamber "snow surface".

Interestingly, a similar finding of photolysis of polychlorinated naphthalens (PCNs)

The results of the third experiment, photodegradation of PFASs in the open ocean environment, on board "sea surface" irradiation experiment was carried out during open ocean surveys using JAMSTEC research vessel "Mirai" (MR11-08, the northeastern Pacific Ocean and MR12-05, the Antarctic Sea) described in Figure 3. Preliminary result of photolysis on board revealed significant degradation of several PFASs even in the Antarctic Ocean.

Our study shows that photodegradation can occur under strong solar radiation even for PFOS, which was supposed to be non-degradable chemical in the environment. Interestingly, longer chain PFCAs, PFASs, FTOHs, FTUCAs and FTCAs can be degraded to short chain PFASs such as PFBA and PFBS, but the short chain compounds were stable even after 106 days (1232 hours of sunlight) of environmental exposure. This suggests that environmental levels of short chain PFASs such as PFBS and PFBA can increase both due to their formation from photodegradation of long chain PFASs and from direct releases. This can be the reason why significant amounts of shorter chains PFASs were found in the remote environment, although longer chain PFASs are rarely detected in those areas. Most of the earlier photolysis studies were focused on the formation of PFCAs and PFASs from precursor compounds under controlled laboratory conditions. Our study revealed evidences of environmental photodegradation of PFASs and PFCAs themselves. Even though the photolysis rates can be slower, long exposure period to sun light in the environment may lead significant change of PFASs composition from the original source of release.

Acknowledgements

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