

THE ENVIRONMENTAL ALTERATION OF PERFLUOROALKYL SUBSTANCES BY PHOTOCHEMICAL REACTION

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Introduction

Perfluorooctanesulfonate (PFOS) and related perfluoroalkyl substances (PFASs) have been revealed as an ubiquitous contaminants in the global environment. The most important characteristic of PFOS and perfluorooctanoic acid (PFOA) is their “persistence” in the environment, which is similar to those known legacy pollutants such as dioxins (PCDD/DFs). PCDD levels in sediment cores change from surface to bottom, as shown in Figure 1(a)¹. On the other hand, PFOA concentrations in ice core show a considerable variability in concentrations in each layer of ice core (Figure 1(b)²). The differences observed in the formation and the stability could be explained by the relatively constant sedimentation rate of the sediment core compared to the variable seasonal precipitation rate (Flux) of the ice core. Thus, flux estimation of the contaminants from the snow/ice cores alone is not adequate enough to understand the temporal variability since movement of melted pore water from surface to bottom can contribute alterations to the actual trends. This raises the question; “*Are PFASs truly persistent in snow / ice cores?*”

Laboratory photolysis experiments³ on PFOA indicated significant degradation by UV irradiation. There is no reliable evidence of photodegradation of PFOS and PFOA in the real environmental conditions. To date, photodegradation of PFASs has not been investigated by other researchers.

In this study, photodegradation experiments were carried out under real environmental conditions. This study provides clear evidence that “photodegradation” of PFASs could occur in natural environmental conditions, on the high altitude mountains and the snow surface. The results indicated that decomposition of PFASs is one of the reasons for the variability observed in the vertical profiles of PFAS in snow cores and ice cores. It was a striking finding because even PFOS which is known as the most non-degradable PFASs was found to be degradable under strong solar radiation in the environment.

Materials and methods

Photodegradation experiments were conducted under both field and laboratory conditions. The field study involved exposure of test solutions (i.e., PFAS mixture) in water under sunlight on two high altitude mountain locations, in the USA (Experiment 1) and Japan (Experiment 2). The laboratory experiment was carried out by exposing test solutions under UV radiation in a chamber (Experiment 3). List of tested and measured chemicals is shown in Table 1.

Experiment 1

Experiment was carried out in Mt. Mauna Kea in Hawaii Island, Hawaii, USA, at an altitude of 4,200 m, for 106 days from September 10, 2010 to December 24, 2011. Solar radiation at the top of Mt. Mauna Kea was estimated at 40% stronger than that at of the sea level, according to WHO. Solar radiation (UV-B) at Mt. Mauna Kea was reported as 4.668 W/m², and this strong radiation was due to the high and clean environment located at low latitude. PFASs were individually weighed and dissolved into methanol, and were then diluted into 10 mL of Milli-Q water in polypropylene tubes. The methanol content in the final test solution was <2%. Test solutions were then split into three tubes of 3 mL each. The test tubes were made of pyrex glass (5 mL) with butyl rubber septum cap and were tightly closed during the solar irradiation. Under solar irradiation, test tubes were kept on a clear polyethylene container with no cover. The total solar irradiation time was 1,232 hrs.

Experiment 2

Another field study was also conducted in Mt. Tateyama (at an altitude of 2,500 m) in Toyama Prefecture in Japan. Annual solar radiation reported by the Meteorological Survey of Japan reported 14 kJ/m² (UV-B) in Tsukuba city, Japan. It can be assumed that 25% stronger irradiation energy can be expected in Mt. Tateyama (at

an altitude of 2,500 m) than in Tsukuba city. During the exposure period, the ground was covered with fresh snow at Mt. Tateyama. Stronger radiation was expected, as UV-B was not only coming from the direct sunlight but also reflection by the snow surface (assuming that 80% of sunlight reaching the snow surface can be reflected). The duration of solar irradiation for the study in Mt. Tateyama was 20.5 hrs on 17-18 April 2011 (total duration the samples left in the field was 31.5 hrs).

Experiment 3

Differences in photolysis rates of PFASs between pyrex and quartz glass tubes were evaluated for eight PFASs. Individual PFAS solutions were prepared similar to that described for the field experiments and split into both pyrex and quartz glass tubes. All test tubes were irradiated in an UV chamber for 216 hrs (9 days).

Table 1 List of tested* and measured chemicals

abbreviation	compound name	formula	tested chemicals		
			Exp.1 (Mt. Mauna Kea)	Exp.2 (Mt. Tateyama)	Exp.3 (UV irradiation)
PFEtS	perfluoroethyl sulfonate	$F(CF_2)_2SO_3^-$	*	*	
PFPtS	perfluoropropyl sulfonate	$F(CF_2)_3SO_3^-$	*	*	
PFBS	perfluorobutane sulfonate	$F(CF_2)_4SO_3^-$	*	*	
PFHxS	perfluorohexane sulfonate	$F(CF_2)_6SO_3^-$	*	*	
PFHpS	perfluoroheptane sulfonate	$F(CF_2)_7SO_3^-$			
PFOS	perfluorooctane sulfonate	$F(CF_2)_8SO_3^-$	*	*	*
PFDS	perfluorodecane sulfonate	$F(CF_2)_{10}SO_3^-$	*	*	
PFOSA	perfluorooctane sulfonamide	$F(CF_2)_8SO_2NH_2$			
N-EtFOSA	N-ethyl perfluorooctane sulfonamide	$F(CF_2)_8SO_2N(H)C_2H_5$			*
N-EtFOSAA	N-ethyl perfluorooctane sulfonamido acetate	$F(CF_2)_8SO_2N(C_2H_5)CH_2COOH$			*
N-MeFOSE	N-methyl perfluorooctane sulfonamidoethanol	$F(CF_2)_8SO_2N(CH_3)C_2H_4OH$			
N-EtFOSE	N-ethyl perfluorooctane sulfonamidoethanol	$F(CF_2)_8SO_2N(C_2H_5)C_2H_4OH$			*
PFOSi	perfluorooctane sulfinate	$F(CF_2)_8SO_2^-$	*	*	
PFOSF	perfluorooctanesulphonyl fluoride	$F(CF_2)_8SO_2F$	*	*	
TFA	trifluoroacetic acid	CF_3COOH	*	*	
PFPrA	perfluoropropionic acid	$F(CF_2)_3COOH$			
PFBA	perfluorobutyric acid	$F(CF_2)_4COOH$	*	*	
PFPeA	perfluoropentanoic acid	$F(CF_2)_5COOH$			
PFHxA	perfluorohexanoic acid	$F(CF_2)_6COOH$			
PFHpA	perfluoroheptanoic acid	$F(CF_2)_7COOH$			
PFOA	perfluoro-n-octanoic acid	$F(CF_2)_8COOH$	*	*	*
PFNA	perfluoro-n-nonanoic acid	$F(CF_2)_9COOH$	*	*	
PFDA	perfluorodecanoic acid	$F(CF_2)_{10}COOH$	*	*	*
PFUnDA	perfluoroundecanoic acid	$F(CF_2)_{11}COOH$			
PFDoDA	perfluorododecanoic acid	$F(CF_2)_{12}COOH$			
PFTrDA	perfluorotridecanoic acid	$F(CF_2)_{13}COOH$			
PFTeDA	perfluorotetradecanoic acid	$F(CF_2)_{14}COOH$			
PFHxDA	perfluorohexadecanoic acid	$F(CF_2)_{16}COOH$			
PFODA	perfluorooctadecanoic acid	$F(CF_2)_{18}COOH$			
8:2 FTCA	2-perfluorooctyl ethanoic acid	$F(CF_2)_8CH_2COOH$	*	*	
8:2 FTCUA	2H-hexadecafluoro-2-decenoic acid	$F(CF_2)_7CF=CHCOOH$	*	*	*
4:2FTOH	2-(perfluorobutyl)ethanol	$F(CF_2)_4(CH_2)_2OH$	*	*	
6:2FTOH	2-(perfluorohexyl)ethanol	$F(CF_2)_6(CH_2)_2OH$	*	*	
8:2FTOH	2-(perfluorooctyl)ethanol	$F(CF_2)_8(CH_2)_2OH$	*	*	*
PFOE	(perfluorooctyl)ethylene	$F(CF_2)_8CH=CH_2$	*	*	
8:2 FAMAC	2-(perfluorooctyl)ethyl methacrylate	$F(CF_2)_8(CH_2)_2O(CO)C(CH_3)=CH_2$	*	*	
8:2 FAAC	2-(perfluorooctyl)ethyl acrylate	$F(CF_2)_8(CH_2)_2O(CO)CH=CH_2$	*	*	

Analysis

Test solutions from the photodegradation experiments were diluted with methanol and analyzed by following the modified International Standard Method for PFOS and PFOA⁴ published in March 1st as described elsewhere and the Japanese Industrial Standard Method⁵ published in March 22nd. Briefly, PFAS concentrations were determined by the use of Agilent HP1100 liquid chromatograph interfaced with a Micromass Quattro Ultima Pt mass spectrometer that was operated in an electrospray negative ionization mode. 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 the accuracy of the result⁶. If the results from the two columns did not match with each other, samples will be re-analyzed.

Results and discussion

Experiment 1

No significant photodegradation was observed for C₂ to C₆ PFASs, PFBA and PFOA; however, the rest of the PFASs were shown to be degraded. This is a striking result because even PFOS, which was assumed to be non-degradable, was significantly degraded by strong solar radiation at high altitude mountains. Another remarkable finding is that longer chains PFASs were relatively much more degradable than shorter chain PFASs (C₂ to C₁₀), PFCAs (C₂ to C₁₀) and FTOHs (4:2 to 8:2 FTOH). The major photo-degradation products were PFOA from PFOSi, PFHxA from 6:2 FTOH and PFOA from 8:2 FTOH. 8:2 FTOH produced C₂ to C₉ PFCAs and 8:2 FTCA. 8:2 FTUCA produced C₃ to C₈ PFCAs.

Experiment 2

Results for the photolysis of PFASs at Mt. Tateyama were similar to Mt. Mauna Kea although the exposure duration was shorter in the former location. No significant photodegradation was observed for C₂ to C₆ PFASs, TFA, PFBA and PFOA; however, rests of PFAS were shown to be degraded. Longer chains PFASs were relatively much degradable than shorter chains in PFASs (C₂ to C₁₀), PFCAs (C₂ to C₁₀) and FTOHs (4:2 to 8:2FTOH). Photo-degradation products were not remarkably observed for the test compounds except for PFOSi. The major photo-degradation product of PFOSi was PFOA.

Experiment 3

There was no significant degradation of PFOS, PFOA, PFDA and 8:2 FTUCA in Pyrex tubes.

Negligible degradation of PFOA in Pyrex (borosilicate glass) tube was also confirmed in a previous report⁷. Only *N*-EtFOSA, *N*-EtFOSAA, *N*-EtFOSE and 8:2FTOH showed significant degradation. The differences observed in the degradation rates of PFOS, PFDA and 8:2 FTUCA between the laboratory and field study may be due to the spectrum of radiation energy produced by sunlight, because UV light radiation has only limited wavelength compared to the full spectrum of sunlight. Hence, less energy is produced for degradation of PFASs.

All eight chemicals exposed to UV light in quartz glass tube showed remarkable degradation. This suggests that UV-B wavelength can be cut by Pyrex (borosilicate glass) and has much greater potency to degrade PFASs. This means that the photo-degradation of PFASs observed in Mt. Mauna Kea and Mt. Tateyama (using pyrex) is an underestimate of the actual degradation potentials of solar radiation. Actual photo-degradation potentials of PFASs was estimated to vary from 1.4 (PFOS and PFOA) to 6.3 times (*N*-EtFOSAA) higher than the results observed using Pyrex (borosilicate glass) tube.

Photo-degradation products were not remarkably observed for the test compounds in the laboratory. It suggests that long exposure under real sunlight at Mt. Mauna Kea has much greater potency for photo-degradation than simple laboratory experiment using UV lamp. Photo-degradation products in quartz glass tube showed remarkable results. The major photo-degradation products were 8:2 FTCA from 8:2 FTOH (19% of original chemical) and PFOA from 8:2 FTUCA (16% of original chemical). 8:2FTOH produced C₂ to C₉ PFCAs, 8:2 FTCA and 8:2 FTUCA. 8:2 FTUCA produced C₄ to C₈ PFCAs. PFDA (C₁₀) produced C₄ to C₉ PFCAs with greater proportion of PFNA (C₉) were measured. PFOA (C₈) produced C₄ to C₇ PFCAs, PFHpA(C₇) was detected at highest proportion. In general, the major photo-degradation products of PFCAs (C_{*n*}) were smaller PFCAs with a loss of CF₂ (C_{*n-1*}). *N*-EtFOSA, *N*-EtFOSAA, *N*-EtFOSE produced PFCAs (smaller than C₈) and group of sulfonic amides (PFOSA and *N*-EtFOSA).

Conclusions

Significant photodegradation and secondary formation of several PFASs on snow surface occurs under normal environmental conditions. Photodegradation under strong solar irradiation on Mt. M Mauna Kea was significant even for PFOS, which has been considered to be a non-degradable compound in the environment. This requires reconsideration of “the persistence” of PFASs in the environment. Three key aspects, namely,

- the traditional flux concept of precipitation
- dynamic movement of melted water in snow/ice cores
- photodegradation/secondary formation of PFASs on snow surface

appear to be the reason for variable profiles of PFASs in snow cores and ice cores reported in the literature (Figure 1 and 2). Careful interpretation of results from snow/ice core studies is necessary to obtain reliable trends and patterns of PFASs in such samples. PFASs residues reported in literatures should be re-evaluated because of photodegradation revealed in this study and possible secondary formations from precursors should be given due to consideration in assigning sources of PFASs.

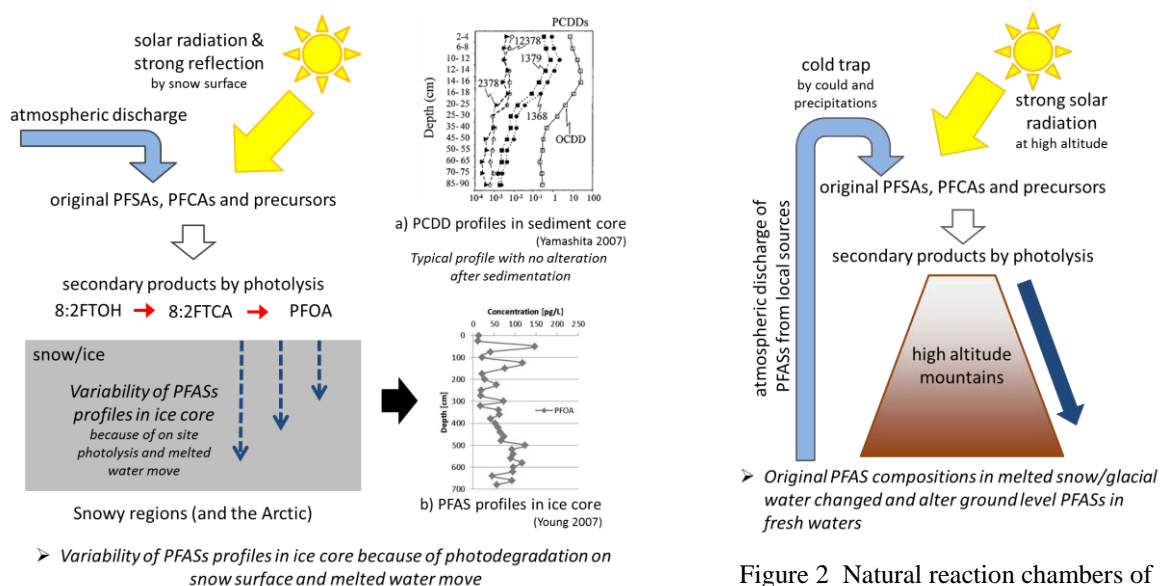


Figure 1 Natural reaction chambers of PFASs on snow and ice surface

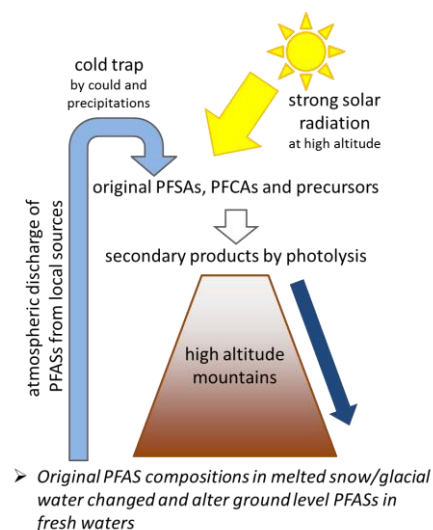


Figure 2 Natural reaction chambers of PFASs at high altitude mountains

Acknowledgements

We thank the support from local team of the International Telescopes at Mt. Mauna Kea. We thank Prof. Jerzy Falandysz (Gdansk University, Poland), Dr. Yuichi Horii (CESS, Saitama, Japan) and Dr. Nobuyasu Hanari (NMIJ, Tsukuba, Japan) for their support. Part of this study was funded by the Environment Research and Technology Development Fund (project no. B-1106) of the Ministry of the Environment, Japan, "Chemical Oceanography to Elucidate Global Kinetics of Persistent Perfluorinated Chemicals (PFCs)" and KAKENHI (project no. 23710032 and 24310020) of the Japan Society for the Promotion of Science (JSPS).

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