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PERFLUORINATED ALKYL SUBSTRATES AND THEIR PRODUCTS FROM SOLAR IRRADIATION ON THE OCEAN SURFACE LEVEL

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Introduction

Perfluorinated alkyl substances (PFASs) are anthropogenic contaminants.¹⁻² They are transported via atmosphere and hydrosphere to any place in the world³⁻⁵. The strong carbon-fluoride bonds in the carbon chain make PFASs highly resistant for degradation in nature. In laboratory condition PFAS undergo photochemical degradation – as reviewed recently⁶.

Question is if perfluorinated carboxylic acids (PFCAs), perfluorinated sulfonic acids (PFSAs) and other, which do not absorb solar radiation (actinic light) undergo indirectly photochemical degradation in nature?⁷⁻⁸ PFASs in aqueous solution (methanol at 2%) were sensitive to solar radiation mimicking natural high mountain condition⁹. It has been proposed, that some PFCAs can be excited via interfacial electron transfer from the ground state to the singlet or triplet states and next undergo photolytical degradation¹⁰. This study aimed to gain further insight into photochemical degradation of PFASs.

Materials and methods

Experiment was carried out for 124 days during two consecutive cruises of the r/v 'Mirai' in the North Pacific and Arctic Oceans. Total time of the solar irradiation of PFASs in the experiment was 1488 hours. The compounds tested were three PFSAs, three PFCAs, FOSA, N-EtFOSA, and one unsaturated fluorotelomer carboxylate (8:2FTUCA) dissolved in methanol and diluted with Milli-Q water (methanol 2%). The test solutions were in (A) Quartz glass tubes and (B) Pyrex glass tubes. The control samples were (C) Pyrex glass tube and (D) PP tube and all samples. Directly after preparation all samples were protected from the light until a beginning of the solar irradiation experiment (A, B) or in situ examination in laboratory (C, D). Before the HPLC-MS analysis all liquid samples from the test and (C) control solutions were quantitatively transferred into a polypropylene (PP) tubes. Analysis of PFASs was conducted by high performance liquid chromatography interfaced with tandem mass spectrometer (HPLC-MS). The Agilent HP1100 LC equipped with RSpak JJ-50 2D (2.0 mm i.d. x 150 mm length) and Micromass Quattro Ultima Pt mass spectrometer operated in an electrospray negative ionization mode were used. Analytical control and analytical quality (AC/AQ) protocols were used rigorously during a whole study. A diluted solutions from the photodegradation experiment were analysed using modified, the ISO and the Japanese methods¹¹⁻¹². Residual abundance (%) of PFAS was calculated respectively for irradiated and control samples.

Results and discussion

Data on percentage residual abundance of PFASs in the solar irradiated samples are presented in Figure 1. No significant change has occurred in irradiated solutions of PFBS and PFBA in (A) quartz and (B) Pyrex tubes. Concentrations of other eight compounds tested decreased significantly after irradiation and some products of photochemical degradation could be detected. A major decrease was noted for 8:2FTUCA. A percentage decrease in concentration of the compounds from the (A) quartz and (B) Pyrex irradiated solutions respectively was at 20% and 14% for PFOS, 10% and 28% for PFDS, 17% and 7% for PFOA, 29% and 36% for PFDA, 96% and 98% for 8:2FTUCA, 75% and 79% for FOSA, and 58% and 41% for N-EtFOSA (Fig. 1). Breakdown rate of PFCAs and PFSAs increased with an increase in the carbon chain length of a compound.

Products of PFASs photodegradation from the quartz and Pyrex tubes irradiation experiments were comparable both qualitatively and quantitatively for each compound regardless a kind of tube. No significant products were detected from the irradiation of PFCAs and PFSAs in Pyrex tubes, and the only one identified after degradation of PFDA in quartz tube was PFNA. Photochemical degradation of 8:2FTUCA yielded PFCAs such as PFOA, PFHpA, PFHxA, PFBA and TFA. Photochemical degradation of FOSA and N-EtFOSA resulted in PFOA as the major photodegradation product followed by PFHpA.

Additionally, PFOS at 1% was detected as a product of FOSA from a Pyrex tube. Moreover, PFOS in amount lower than 1% was also found after irradiation of N-ETFOSA (in Pyrex and quartz) and FOSA (in quartz). Exposure of N-EtFOSA to solar irradiation yielded FOSA.

Results from a present study agreed largely with data from an earlier experiment concerning photochemical degradation of PFASs after solar irradiation in the Pyrex tubes at high altitude mountains⁹. In present study 8:2FTOH degraded at 14% lower than in experiment on Mt. Tateyama, and at 60% lower than on Mt. Mauna Kea⁹.

The compounds such as FOSA, 8:2FTCUA and N-EtFOSA can be considered as the precursors respectively of some PFCAs or PFSA in the aquatic environment, while a final product of the photochemical degradation of PFCAs and PFSA in this study is not yet confirmed. Fluoride ion was a final fluorine product from the photodegradation of PFOS in a catalyst-free aqueous solution (initial pH: 7.4, final pH: 3.5, temperature: 90 °C) under UV irradiation of medium pressure mercury lamp (500 W), and suggested mechanism was via a reductive route with hydrated electrons as the major photo-generated reductive species while an oxidative route was ineffective⁶.

Figure 1. Residual abundance (%) of PFASs in test solution after solar irradiation at cruises.

References

1. Yamashita, N., Taniyasu, S., Petrick, G., Wei, S., Gamo, T., Lam, P. K., and Kannan, K. (2008) *Chemosphere*, 70, 1247-1255.
2. Butt, C.M., Berger U., Bossi R., and Tomy G.T. (2010) *Science of the Total Environment*, 408, 2936-2965.
3. Falandysz, J., Taniyasu, S., Gulkowska, A., Yamashita, N., and Schulte-Oehlman, U. (2006) *Environmental Science and Technology*, 40, 748-751.
4. Scheringe, M. (2010) *EPJ Web of Conferences*, 9, 35–42.
5. Zhao, Z., Xie, Z., Möller, A., Sturm, R., Tang, J., Zhang, G., and Ebinghaus, R. (2012) *Environmental Pollution*, 170, 71-77.
6. Lyu, X-J., Li, W-W., Paul, K.S., and Yu, H-Q. (2015) *Scientific Reports*, 5, 9353; doi.10.1038/srep09353.
7. Yamazaki, E., Falandysz, J., Taniyasu, S., Hui, G., Jurkiewicz, G., Yamashita, N., Yang, Y.-L., and Lam P.K.S. (2015) *Journal of Environmental Science and Health, Part A* 51, 63-69.
8. Kwok, K.Y., Yamazaki, E., Yamashita, N., Taniyasu, S., Murphy, M.B., Horii, Y., Petrick, G., Kallerborn, R., Kannan, K., Murano, K., and Lam, P.K.S. (2013) *Science of the Total Environment*, 447, 46–55.
9. Taniyasu, S., Yamashita, N., Petrick, G., and Kannan, K. (2013) *Chemosphere*, 90, 1686-1692
10. Zhang, F., Wu, Ch., Hu, Y., and Wei, Ch. (2014) *Progress in Chemistry*, 26, 1079-1098.
11. ISO (2009) Water quality – determination of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) – method for unfiltered samples using solid phase extraction and liquid chromatography/mass spectrometry. ISO 25101.
12. JIS (2011) Testing methods for perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) in industrial water and wastewater. JIS K 0450-70-10.

