Survey on Occurrences of Polyfluoroalkyl Phosphate Esters (PAPs) in Cosmetics and Wastewater Treatment Plants

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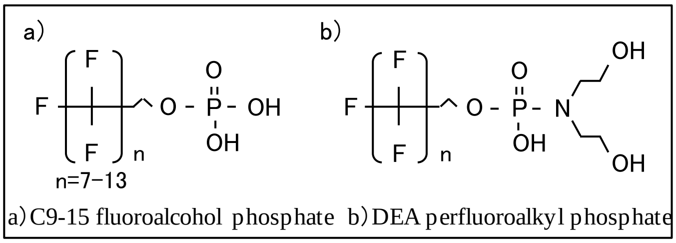
Introduction

Per- and polyfluoroalkyl substances (PFASs) are a group of anthropogenic organic fluorinated compounds which have been widely used in many products. Recently, it has been a growing concern that PFASs pose adverse effects on water environment and human health, and special attentions have been paid to perfluoroalkyl acids (PFAAs), such as perfluorooctanoic acid (PFOA). Fluoropolymer manufactures have tried to phase out the production and use of PFOA under 2010/2015 PFOA Stewardship Program initiated by U.S.EPA [1]. In 2016, twelfth meeting of the Persistent Organic Pollutants Review Committee (POPROC-12) adopted the risk profiles for PFOA and PFOA-related compounds, and they are planning to require a risk management evaluation that includes an analysis of possible control measures [2]. European Chemical Agency (ECHA) reported that cosmetics in European market contained PFOA and PFOA-related compounds [3]. Cosmetics contain the ingredients which are suspected of precursors of perfluoroalkyl carboxylic acids (PFCAs). Our research group reported PFAAs and their total oxidisable precursors (TOP) were detected in cosmetics made in Asian and European countries (Total concentration of 15 kinds of PFAAs was 202-8,170 ng/g-wet and total concentration of their TOP was 6-93,200 ng/g-wet) [4]. Some researchers suggested that polyfluoroalkyl phosphate esters (PAPs) were used as ingredients in cosmetics [5]. However, the occurrence of PAPs in cosmetics is still not investigated globally. Meanwhile, cosmetics are a kind of daily products and may flow into the sewerage system so that the occurrence in wastewater treatment plants (WWTPs) is suspected. In previous studies, five kinds of diPAPs were observed in sewage sludge, and they were transformed into perfluroalkyl carboxylic acids (PFCAs) by experimental degradation test [6] [7]. Main objective of this study was to understand occurrences of PAPs in cosmetics and WWTPs.

Materials and methods

Sample Preparation

Cosmetic samples were purchased in Japan, Thailand, and Italy, from December 2015 to March 2016. In total, 23 samples including foundation and sunscreen have been collected. Three types of cosmetic ingredients were shown in **Figure 1**. They are C9-15 fluoroalcohol phosphate or DEA perfluoroalkyl phosphate. Survey was conducted in five WWTPs in Kinki area on August 2016. Samples of influent, primary sedimentation tank effluent, primary sedimentation tank sludge, biological reaction tank effluent, final sedimentation tank effluent, return sludge and effluent were collected.



a) C9-15 fluoroalcohol phosphate b) DEA perfluoroalkyl phosphate

Fig. 1 Chemical Structure of cosmetics ingredients

Sample pre-treatment

Cosmetics: Firstly, 10 mg of cosmetic sample, 1mL of tetrabutylammonium (0.5M), 1 mL of sodium carbonate buffer solution (0.25M) and 3 mL methyl tert-butyl ether (MTBE) were mixed and centrifuged in PP tube. The MTBE phase was taken out in a new PP tube. The solution was exchanged to methanol without complete dryness under purging with N_2 gas. After that, sample was passed through 0.2 µm syringe filter and ENVI-carb^{TM} cartridge (Supelco) for clean-up.

Wastewater: Firstly, samples were filtrated or centrifuged to separate to dissolved phase and particulate phase. Dissolved phase of samples (50 mL) were extracted by solid phase extraction passing through an Oasis® WAX cartridge (Waters). Target compounds were eluted from the cartridge with methanol and methanol with 0.1% ammonium (2 mL each). Particulate phase of samples (0.5 g/g-dry) were extracted by shaking with methanol after freeze drying. These steps were repeated twice. Clean-up was processed for each sample in the same way of cosmetics pre-treatment and samples were reconstituted into a final volume of 1 mL.

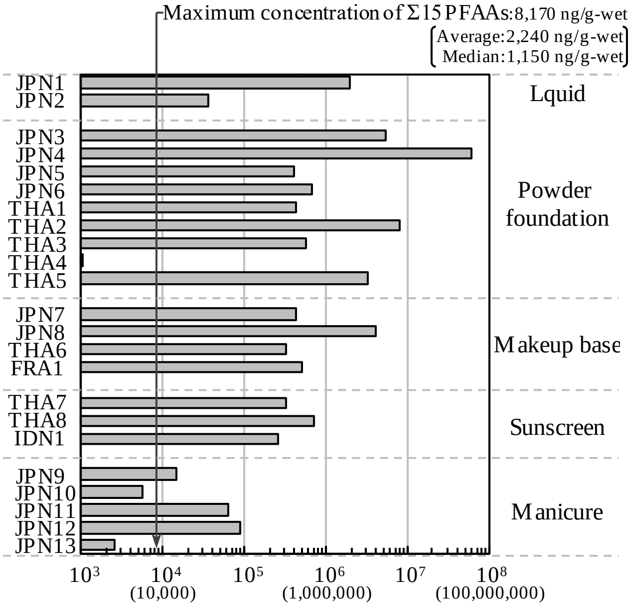
Instrumental Analysis and Quantification

Three kinds of diPAPs (6:2diPAP, 6:2/8:2diPAP, 8:2diPAP), 12 PFCAs (C4-14, 16) and 3 perfluoroalkyl sulfonic acids (PFSAs) (C4, 6, 8) were analyzed by LC-MS/MS (Agilent). Instrumental detection limit of target compounds was 0.01-0.03 ng/mL. Details of separation and quantification about the instrument were explained in a previous publication [8]. Recovery rates of three diPAPs were 23-26% for cosmetics and 9-37% for wastewater, having relative standard deviation (*RSD*) (*n*=3) basically less than 30%. Those of four Mass-labelled PFAAs ($_{13}$C-labeled, MPFAAs) were 79-82% for cosmetics and 63-113% for wastewater, having *RSD* (*n*=3) basically less than 20%.

Results and discussion

Occurrences of PAPs in cosmetics

Concentration of diPAPs in cosmetics was shown in **Figure 2**. The total concentration of three diPAPs ranged 1,030-58,500,000 ng/g-wet. Their concentrations of 6:2diPAP, 6:2/8:2diPAP, 8:2diPAP in foundation, makeup base or sunscreen were 780-12,000,000 ng/g-wet, 226-39,900,000 ng/g-wet, 19-6,590,000 ng/g-wet, respectively, and they were higher than those in manicure. In case of PFAAs, total concentration of 15 PFAAs ranged 417-8,170 ng/g-wet in cosmetics, which contained 39-2,170 ng/g-wet PFHxA, 6-1,960 ng/g-wet PFOA, 4-28 ng/g-wet PFOS [4]. It was similar to the results obtained by other researchers (total concentration of PFCAs in foundation: *N.D.*-5,900 ng/g-wet and sunscreen: *N.D.*-19,000 ng/g-wet) [5]. Concentrations of diPAPs were higher than those of PFAAs, assuming due to the fact that diPAPs were contained in cosmetic as their ingredients. It was expected that other diPAPs were contained in



※diPAPs:6:2diPAP, 6:2/8:2diPAP, 8:2diPAP
Cosmetics were made in Japan(JPN), Thailand(THA), Indonesia(IDN), France(FRA)

Fig.2 Concentration of diPAPs in cosmetics

cosmetics, because Gebbink *et. al.* found 16 kinds of diPAPs in water- and grease-proof food packaging materials [9] and Eriksson *et. al.* found 14 kinds of diPAPs in household dust [10]. Unknown diPAPs in cosmetics whose packages labellings indicated "C9-15 fluoroalchohol phosphate" were analyzed by LC-MS/MS. A part of detected chromatograms of diPAPs was shown in **Figure 3**. 14 kinds of diPAPs (4:2/6:2diPAP, 4:2/8:2diPAP, 4:2/10:2diPAP, 4:2/12:2diPAP, 6:2/10:2diPAP, 4:2/14:2diPAP, 6:2/12:2diPAP, 8:2/10:2diPAP, 6:2/14:2diPAP, 8:2/12:2diPAP, 10:2diPAP, 6:2/16:2diPAP, 8:2/14:2diPAP, 10:2/12:2diPAP) were detected. It was indicated that various type of diPAPs were contained in cosmetics.

<u>Occurrences of PAPs in WWTP</u>

In five WWTPs, 6:2diPAP, 6:2/8:2diPAP 8:2diPAP were detected from influent, primary sedimentation tank sludge, biological reaction tank effluent, return sludge samples at all WWTPs. They were rarely detected from final sedimentation tank effluent and effluent. Concentrations of diPAPs in wastewater were shown in **Figure 4**. Total concentrations of three diPAPs were 32±8 ng/L in influent, 479±361 ng/L in primary sedimentation tank effluent, 37±24 ng/L in primary sedimentation tank sludge, 123±31 ng/L in biological reaction tank effluent, 5±1 ng/L in final sedimentation tank effluent, 269±12 ng/L in return sludge and 5±0 ng/L in effluent. Most of them found from solid phase similarly to long-chain PFAAs. Other researchers reported that total concentration of three diPAPs in WWTPs in Hong Kong were 7-12 ng/L in influent and 1-7 ng/L in effluent [11], and it was similar with this result. Total concentrations of three diPAPs were 62±20 ng/g-dry in primary sedimentation tank sludge, 41±12 ng/g-dry in biological reaction tank effluent and 44±8 ng/L in return sludge. In case of other studies, those of diPAPs in sewage sludge were 122±42 ng/g-dry in Hong Kong [11], 30 ng/g-dry in Ontario [7]. Other six kinds of diPAPs (6:2/10:2diPAP, 6:2/12:2diPAP, 8:2/10:2diPAP, 6:2/14:2diPAP, 8:2/12:2diPAP, 10:2diPAP) were found in sludge.

Mass flow of diPAPs was calculated from concentration and flow rate at each sampling site. Mass flows of (a): 8:2diPAP and (b): PFOA in during wastewater treatment processes were shown in **Figure 5**. The loading of influent ranged 375-8,840 mg/day. Mass of diPAPs was balanced before and after primary sedimentation tank, and it accounted for 43-98% of diPAPs in effluent of primary sedimentation tank. At four WWTPs among

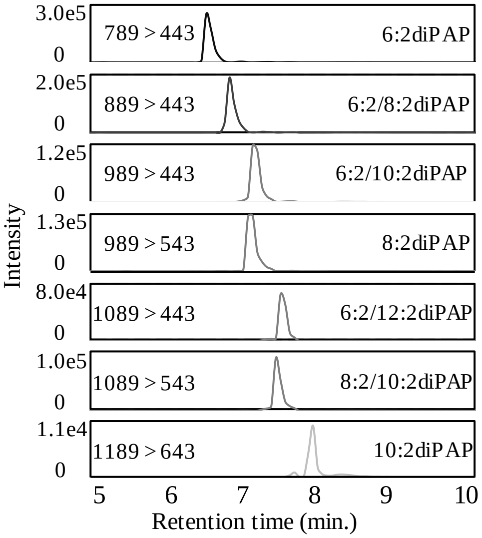
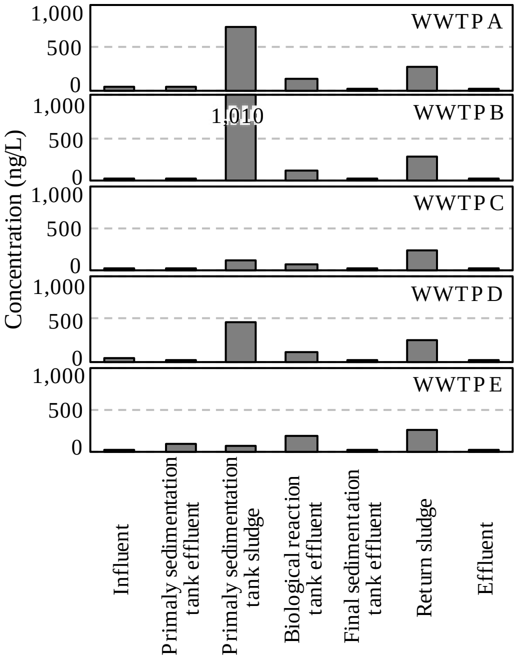


Fig.3 Chromatograms of diPAPs in cosmetics



※diPAPs:6:2diPAP, 6:2/8:2diPAP, 8:2diPAP

Fig.4 Concentrationof diPAPs in wastewater

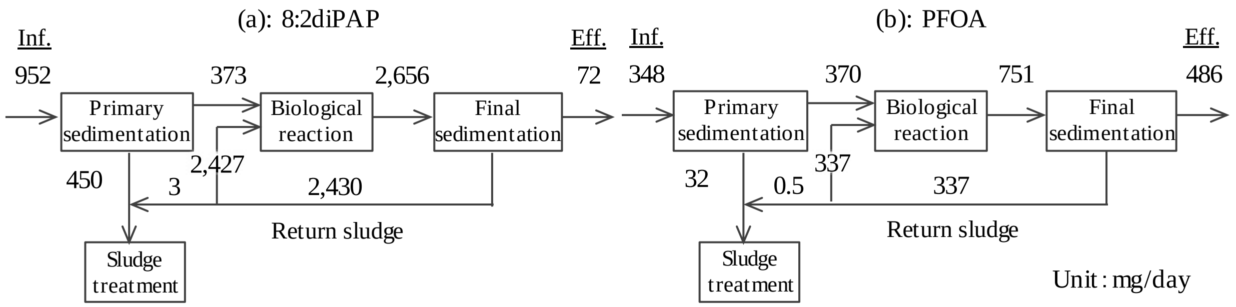


Fig.5 Mass flows of (a): 8:2diPAP and (b): PFOA in during wastewater treatment processes (a case of WWTP D)

five, the removal rate of diPAPs ranged 43-63%. Degradation products were formed as a result of biological reaction. D'eon *et. al.* observed that PFCAs formed from diPAPs in biodegradation test by sewage sludge [6]. It indicated that almost all of diPAPs sorbed to sludge and returned to biological reaction tank via return sludge. DiPAPs were suspected to be remained in biological treatment process for considerably long time period and resulted in converting to PFCAs.

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