

Branched and linear forms of PFAS – A means of a more comprehensive assessment of environmental impacts

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Abbreviations:

ECF = Electrochemical fluorination; FTOH = Fluorotelomer alcohols; N-EtFOSA = N-ethylperfluorooctanesulfonamide; N-EtFOSE = N-ethylperfluorooctanesulfonamidoethanol; N-MeFOSA = N-methylperfluorooctanesulfonamide; N-MeFOSE = N-methylperfluorooctanesulfonamidoethanol; PFAS = Poly- and perfluoroalkyl substances; PFCA = Perfluorinated carboxylic acids; PFHxS = Perfluorohexane sulfonate; PFOA = Perfluorooctanoate; PFOS = Perfluorooctane sulfonate; PFOSA = Perfluorooctanesulfonamide; PFSA = Perfluorinated sulphonic acids; PreFOS = Perfluorooctane sulfonate precursors; TOP = Total oxidizable precursors

Introduction

Over the last 20-25 years the research on both environmental and health related effects of PFAS has been intense. During the last 5-10 years the difference between isomeric forms of the substances has emerged as an additional factor. The physicochemical properties of the linear and branched forms vary slightly which leads to significant differences in biochemical reactions/transformations, bioaccumulation and thus potential toxic exposure. Adsorption onto solid phases is another property affected. All these factors also influence the relative distribution in environmental compartments such as water, soil and sediment. The research has also created an opportunity to develop environmental forensic applications.

Manufacturing processes

Electrochemical fluorination (ECF) and telomerisation are the two major methods employed to produce PFAS. The branched isomers of PFAS are mainly manufactured in the ECF method, which has historically been used to produce the major part of the two dominant PFAS, PFOS and PFOA. ECF gives rise to complex mixtures of linear and branched compounds. PFOA produced by this method has typically had an isomer composition of 78% linear (n-PFOA) and 22% branched isomers (br-PFOA). ECF-PFOS shows a distribution of around 70% linear (n-PFOS) and 30% branched (br-PFOS). Precursors and similar substances e.g. N-methyl and N-ethyl perfluorooctane sulfonamido ethanols (Me- and EtFOSEs) and sulfonamides (Me- and EtFOSAs) have ratios in the same range. On the other hand the telomerisation process keeps the structure of the starting telogen and a pure linear or isopropyl form is produced (Benskin et al., 2010; Jiang et al, 2015).

Distribution in environmental matrices

The differing properties of linear and branched PFAS isomers can affect the partitioning and migration of the substances in the aquatic environment. A number of studies have reported

enrichment of br-PFOS in natural waters as compared to technical products (Benskin et al., 2010; Chen et al., 2015 and references within).

In a nationwide study in France it was found that n-PFOS was the dominant isomer in sediments (88% of total; n=129), while in water n-PFOS comprised 48% (n=333) (Munoz et al., 2015). A similar distribution was observed by Houde et al. (2008). In an investigation of composition and seasonal variation in 10 Swedish rivers (NV, 2018) br-PFOS comprised around 50% in the samples (n=40) with the highest concentrations (up to 6 ng/l) and was completely dominant in samples with less than 2 ng/l. Chen et al. (2015) studied PFOS, PFOA and PFOSA in water, water particulate phase and sediment. For PFOS and PFOSA there was more of the linear form adsorbed to the solid phases than found in water (PFOS 70-85% vs 40-43%; PFOSA: 93-95% vs 64-75%). For PFOA the difference was not as large in absolute numbers but calculations still indicated a higher log K_{oc} for n-PFOA.

However, enrichment of branched isomers is not always observed in water. In the paper by Gobelius et al (2018) a programme with surface and groundwater samples (n=450) showed more limited fractions of branched PFOS (8-20%), PFOSA (0-2%) and PFHxS (5-7%) with the highest numbers seen for surface waters. Still an overall conclusion was that branched forms should be included in monitoring. Pellizzaro et al (2018) found that five contaminated groundwaters had on average less br-PFOS (19%) than in typical ECF products and PFOA about the same (18%).

In a study by Kärrman et al. (2011) soil from a fire-fighting training platform contained 63% n-PFOS but this fraction had increased to 80-85% 200m away from the site. In the receiving lake the sediment was also enriched in the linear form (75-85%). However, in the seepage water from the site the opposite was observed where n-PFOS accounted for a little less than 60%. PFOA showed a similar pattern. At the source 80% was in the form of n-PFOA in the soil, which rose to 100% within 75m distance. In seepage the corresponding figure was 75%. PFOA was not found in the sediment.

In an investigation of three Swedish sites drinking water, untreated and treated waste water and sewage sludge, branched and linear forms of PFOS, PFOSA, PFHxS and PFOA were determined (Filipovic and Berger, 2015). The contribution of n-PFOS was on average 62% in the untreated waste water while in the sludge was 86%. Also for PFOSA a tendency for a higher percentage of the linear form in the sludge as compared to influent water was observed (83% vs 68%). For PFOA >91% was linear in the untreated water and in the sludge no branched forms could be detected. Results for PFHxS were not conclusive since all sludge samples had concentrations below limit of detection.

Also for water cleaning the isomeric profile can be important. Östlund (2015) investigated PFAS removal in pilot scale column experiments using anion exchange resin and granular activated carbon. The adsorption efficiency of branched and linear PFOS, PFOSA and PFHxS was assessed. For the anion exchanger no difference due to isomeric form was found, while for active carbon a lower removal of the branched form was seen. At the end of the study (33000 bed volumes) the difference in adsorption was 86% vs 78% for PFOS. The same numbers were 69% vs 57% for PFOSA and 57% vs 40% for PFHxS.

Source tracking

Comparison of the isomeric forms of PFAS in environmental samples with commercial products may yield insights to the manufacturing origins (Benskin et al., 2010). Chen et al. (2015) used an isomer profiling technique to calculate the relative contributions of various industrial origins for PFOA in a Chinese river. The outcome indicated that the major source was electrochemical fluorination (ECF) (55%), followed by linear telomerisation (41%) and isopropyl telomerisation (4%). In a similar way Wang et al (2016) could conclude significant contributions from ECF PFOA in 8 of 19 Chinese rivers measured, with the highest br-PFOA fraction close to technical products (26%).

Precursors are compounds, both known and unknown, which have the potential to form PFCA and PFSA at degradation. Thus these substances are of interest both for present and future exposure of humans and biota. A new field of research is to what extent the isomeric composition in e.g. water reflects the transformation of precursors, and the possibility that branched forms are more prone in this regard (Benskin et al, 2010).

Leaching tests of sediments showed that the fraction of n-PFOS in the leachate was much higher than in the water in the field (Chen et al., 2015). The difference between the leaching and field results suggested that PFOS precursors (PreFOS) could make a contribution to the linear/branched ratio of PFOS in the natural system. A similar observation was made by Kärrman et al (2011) where PFOS in soil in the source area contained less linear PFOS (63%) than could be expected from ECF products.

Benskin et al (2011) used the absence of branched perfluorinated carboxylic acids (PFCA) as one line of evidence that the compounds observed (PFOA and longer homologues) originated from oxidation of above all FTOH rather than direct transport (vapour phase and particles) of PFCAs.

It is known that precursors can be chemically oxidized to corresponding perfluorinated substances. TOP (total oxidizable precursors) is a method based on oxidation using hot persulphate in an alkaline solution (Houtz et al., 2012). In comparison to naturally occurring biodegradation sulfonamide precursors form a corresponding C_n PFCA e.g. in the case of PreFOS, PFOA is the resulting product. As in the environment telomer (n:2) oxidation is more complex and a series of PFCAs are produced, which includes the C_{n+1} , C_n , C_{n-1} etc down to the C_4 acid. The possibility to use branched and linear PFCA formed at TOP as an additional means of shedding light on the origin has been put forward (Houtz et al., 2013). This was demonstrated in the work by van Hees et al (2018) where the formation of br-PFOA in soil, seemingly from both PFOSA and unknown C8 precursors, was observed. At the same time a pattern of new C_4 to C_9 PFCAs were seen indicating 6:2 and 8:2 telomers precursors.

Isomer distribution in humans and biota

For PFAS four major pathways for direct and indirect exposure can be outlined: ingestion of dust, dietary and drinking water intake, and inhalation of air (Gebbink et al., 2015). Concerning food, n-PFOS comprised 92% of total PFOS in a general Swedish diet and

estimates for PFOSA indicated about 98% of the linear form. PFOS and PFOSA isomer ratios in drinking water were 60% n-PFOS and 58% n-PFOSA. Considering total PFOS exposure, taking all pathways into account, the proportion was estimated as 84% linear and 16% branched. The number could be dependent upon the diet, especially at high fish consumption (Gebbink et al., 2015). Enrichment of the linear form of PFOS in animal tissue is frequently seen (often >90% n-PFOS) e.g. for fish and pelagic organisms as well as mammals such as rats and polar bears (Kärrman et al., 2011; Greaves and Letcher, 2013; Miralles-Marco and Harrad, 2015). Ocean plankton may be an interesting exception. In the study by Casal et al (2017) the contribution of br-PFOA was up to 45%, and increased with distance to North America both in the North Atlantic and in the North Pacific Ocean. Though the same trend could not be found for PFOS (mean 87% n-PFOS).

In humans the isomeric PFOS profile may be more complicated recent studies suggest (Miralles-Marco and Harrad, 2015). In particular human serum samples can sometimes show a br-PFOS content even higher than in the technical ECF products. It has frequently been put forward that these observations can be explained by either an inaccurate estimation of exposure (e.g., unknown precursors, missing or poorly quantified pathways and/or isomer profiles of PFOS and precursors) or an incomplete understanding of the human pharmacokinetic processes (e.g. biotransformation and elimination kinetics) (Gebbink et al., 2015). More recently, also differences between isomers in terms of medical and toxic effects have been discussed. For example, in the study by Li et al (2017) br-PFOS was associated with a larger decrease in birth weight than n-PFOS.

Also exposure to PFAS contamination can alter the isomeric profile in humans. In a study of young women in Uppsala (SE) higher total levels of PFHxS as well as an increased fraction of br-PFHxS in serum were observed for those who had been exposed to contaminated drinking water. Still the percentage of br-PFHxS in serum was lower than that found in water (6 vs 20%) (Gyllenhammar et al., 2015).

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