“Novel” and Ultrashort PFAS: Two Groups of Growing Concern

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Abbreviations:

ADONA = Ammonium 4,8-dioxa-3H-perfluorononanoate; BCF = Bioconcentration factor; 6:2 Cl-PFESA = 9-chlorohexadecafluoro-3-oxanonane-1-sulfonate; F-53B = see 6:2 Cl-PFESA; FRD-902 = see HFPO-DA; FTAB = Fluorotelomer sulfonamide alkylbetaine; FTCA = Fluorotelomer carboxylic acids; FTSaAm = Fluorotelomer sulfonamide amine; FTUCA = Fluorotelomer unsaturated carboxylic acids; FTS = Fluortelomer sulphonates; FTSAS = Fluorotelomermercapto-dimethylamido sulfonate; GenX = see HFPO-DA; HFPO-DA = 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate; HCFC = Hydrochlorofluorocarbon; HFC = Hydrofluorocarbons; HFO = hydrofluoroolefin; PAP = Poly- and perfluoroalkyl phosphate; PBT = Persistent, bioaccumulative, toxic; PFAS = Poly- and perfluoroalkyl substances; PFBA = Perfluorobutanoate; PFCA = Perflourinated carboxylic acids; PFECA = Perfluoroalkyl ether carboxylic acids; PFECHS = Perfluoro-4-ethylcyclohexane sulfonate; PFEtS = Perfluoroethane sulfonate; PFESA = Perfluoroalkyl ether sulfonic acids; PFHxA = Perfluorohexanoate; PFHxS = Perfluorohexane sulfonate; PFHxSA = Perfluorohexanesulfonamide; PFMeCHS = Perfluoromethylcyclohexane sulfonate; PFPA = Perfluorophosphonic acid; PFPeA = Perfluoropentanoate; PFPrA = Perfluoropropanoate; PFOA = Perfluorooctanoate; PFOS = Perfluorooctane sulfonate; PFOSA = Perfluorooctanesulfonamide; PFPiA = Perfluorophosphinic acid; PFPrS = Perfluoropropane sulfonate; PFSA = Perfluoroalkyl sulfonic acids; PreFOS = PFOS precursors; PTFE = Polytetrafluoroethene; SAmPAP = 2-(N-ethylperfluorooctane-1-sulfonamido)ethyl phosphate; SVHC = Substance of very high concern; TFA = trifluoroacetate; TOF = Total organic fluorine; TOP = Total oxidizable precursors; vPvB = Very persistent, very bioaccumulative; WWTP = Waste water treatment plant

Introduction

PFAS, per- and polyfluorinated substances are a broad group of chemicals that have been used for various purposes since the 1950’s. Examples of application areas and products are polymer manufacturing, surface coating, firefighting foams, cosmetics and paints. The widespread contamination as well as human and environmental exposure of PFAS has been paid much attention to over the last 20 years. This concerns not at least the more long-chained PFAS with >6-7 carbons. As the historically most used PFAS substances, especially the C8 substances PFOS and PFOA, have been banned and/or phased out there has been a shift in production to shorter perfluorinated (e.g. C4 or C6) carboxylic acids (PFCA) and sulphonates (PFSA) as well as telomers (e.g. 6:2 and 8:2).

However, there are also other fluorinated alternatives and replacement products, often referred to as “novel” PFAS, which are gradually brought into focus as well. The “classic” perfluorinated compounds, such as PFOS/PFOA, consist of a fully fluorinated alkyl chain with a functional group (e.g. sulphonate) at the end. The new PFAS can have other structures and, for example, be ether or cyclic molecules. Moreover, other substituted atoms such as chlorine may also be present. Not all replacement compounds are completely new; some have existed alongside PFOS and PFOA for a number of years. E.g. 6:2 Cl-PFESA (F53-B) has been manufactured in China for decades as a PFOS alternative (Joerss et al., 2019).

Ultrashort PFAS are substances typically characterized as having two or three carbon atoms. Since PFCAs and PFSAs are the two most common types of PFAS this means that there are four ultrashort compounds frequently included; trifluoroacetic acid (TFA), perfluoropropionic acid (PFPrA), perfluoroethanesulphonic acid (PFEtS) and perfluoropropanesulphonic acid (PFPrS). These substances may not always be directly used as PFAS products, but rather occur as impurities, degradation products or manufactured for other purposes (TemaNord, 2019; Janda

et al., 2019a). Ultrashort PFAS have not received much attention in the past, partly because of both regulatory and chromatographic reasons. Though, a growing number of reports demonstrate their presence in the environment, especially in water.

Regardless of the source or for how long the compounds have been produced, “novel” and ultrashort PFAS can be regarded as two groups of emerging contaminants. Increasing interest and growing knowledge will most likely make it more important to consider these PFAS classes in the future.

Characteristics of novel PFAS

As mentioned above novel PFAS may have other structures than the old legacy PFAS. Two examples are per- and polyfluoroalkyl ether carboxylic and sulphonic acids (PFECA and PFESA; Joerss et al., 2019a). Among the PFECAs, GenX can be mentioned and is perhaps the replacement compound that has drawn most attention. In fact GenX is the technology where 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate (FRD-902; HFPO-DA) is used as a process agent in manufacturing of fluoropolymers e.g. PTFE (Teflon) instead of PFOA. Consequently HFPO-DA is commonly referred to as GenX. Another replacement for PFOA is (A)DONA (4,8-dioxa-3H-perfluorononanoate) commonly available as its ammonium salt (A in acronym). Like GenX it is a PFECA ether that is used as processing aid during polymerization. For how long these two chemicals have been produced in somewhat uncertain but 2009/10, or as early as 2005 for GenX, could be suggested from industry documents and environmental studies (Wang et al., 2013; RIVM, 2016).

In the past PFOS has been used as wetting- and mist suppressing agents in various processes of metal plating. Over time PFOS has been replaced by other fluorinated compounds. One substitute that is now being monitored is the ether sulfonic acid 6:2 Cl-PFESA (F-53B) with one chlorine atom. The substance seems to have properties similar to PFOS (Xiao, 2017). In addition, the homologues 4:2 and 8:2 have been identified. F-53B may have been used in China since the late 70’s (Wang et al, 2013; Joerss et al., 2019).

The most frequently mentioned cyclic PFAS is PFECHS (Perfluoro-4 ethylcyclohexane-sulfonate). PFECHS is like PFOS a perflourinated C8 sulphonate, and seems to have similar properties. Its major use has been as an anticorrosive additive (F-98 by 3M; Xiao, 2017) in aircraft hydraulic fluids, though production has most likely stopped. Given the application much focus has been directed to airports and surrounding areas. In addition, there is a possibility that it exists as an impurity in e.g. PFOS based AFFF (Joerss et al., 2019).

Besides the classes of novel PFAS above, several others have been brought to attention. Among these can phosphonic acids (PFPA), phosphinic (disubstituted; PFPiAs), and molecules identified in products such as various, SAmPAP and telomer sulphonamides (especially 6:2 and 8:2) e.g FTAB, FtSaAm and FtTAoS (or FTSAS) (Xiao, 2017) be mentioned. The understanding of many of these compounds has been hampered by factors such as knowledge of their existence and structure, analytical methods for both identification and quantification and the availability of pure standards.

Environmental concentrations of novel PFAS

GenX is so far the substance that has been subject to the biggest number of studies, and the worldwide occurrence of the chemical has been demonstrated. The interest has to some part revolved around two major contamination cases, Cape Fear River (N:th Carolina, US; e.g. Sun et al, 2016) and Dordrecht by the River Rhine, The Netherlands (RIVM, 2016). At both places releases, to air and water, have been associated with fluoropolymer (e.g. PTFE) production plants. In the Cape Fear River watershed concentrations of HFPO-DA ranging between 55-4500 ng/l (mean 630 ng/l; n=37) were detected in drinking water downstream the plant (Sun et al., 2016). A range of other non-quantified suspected PFECAs were also seen. In the Dutch case Gebbelink et al (2017) observed HFPO-DA, up to 810 ng/l in the vicinity of the factory. Groundwater near the plant (<2km) showed a level up to 660 ng/l while rainwater could amount to about 3000 ng/l (<1km; RIVM, 2018). Concentrations in the same range was determined by Heydebreck et al (2015) in Xiaoqing River (CN), up to 3800 ng/l. In a paper by Pan et al (2018) HFPO-DA was found in twelve Chinese, European and American rivers/lakes with averages between 0.7 to 14 ng/l. In some waters e.g. Mälaren in Sweden HFPO-DA (mean ~1.5 ng/l) showed concentrations comparable to PFOA. In the study also the similar HFPO-TA was identified at lower concentrations but with a strong correlation to HFPO-DA. Joerss et al (2019) studied GenX in the North and Baltic Seas along the German coast. In the German bight the mean level was 1.6 ng/l, and HFPO-DA was the individual compound with the greatest contribution (27% on average) to the sum of PFAS. There was a significant correlation between salinity and HFPO-DA which was interpreted as transport of the compound from the Rhine River.

ADONA has also been analysed in investigations the last few years. Near a fluoropolymer plant by the River Alz (Bavaria, DE) concentrations of ADONA between <LOQ - 17000 ng/l, with an average of about 2500ng/l have been measured in the years 2009 to 18 (LfU, 2019). Pan et al. (2018) found ADONA in the River Rhine (DE), up to 1.5 ng/l. In addition, ADONA has been included in other studies of water but found to be below LOQ (Joerss et a., 2019; TemaNord, 2019).

Considering ether sulphonic acids the presence of F-53B (6:2 Cl-PFESA) has been shown in environmental waters. Wang et al (2016) measured F-53B in the mouths of 19 Chinese rivers and found concentrations ranging from <0.6-79 ng/l with the highest levels probably associated with metal plating facilities. Also Pan et al (2018) identified F-53B in Chinese rivers and lakes (1-8 ng/l; n=7), but also in western water bodies (UK, US, DE, SE) albeit at lower concentrations (0.01-4 ng/l). It should be noted that in many CN samples the amount of F-53B could be directly compared to PFOA and PFOS. The cyclic sulphonate, PFECHS, seems to occur worldwide. Da Silva et al. (2011) observed concentrations of 0.2-5.6 ng/l in water from the Great Lakes (CAN). Moreover, the similar PFMeCHS was seen but at lower levels. PFECHS was found in most samples taken in the Baltic Sea along the German coast (up to 0.14 ng/l) by Joerss et al (2019). Measurement of surface water near Beijing airport showed levels up to 195 ng/l (Xiao, 2017 and refs within). In the TemaNord (2019) report, PFECHS was identified in WWTP effluent (mean 0.1; range 0.01-0.4 ng/l) in SE, DK and FI, and in surface water (<LOQ-0.94 ng/l) in SE and FI. The highest level was observed in a lake close to Helsinki Vantaa Airport, while in Lake Vättern (SE) 0.24 ng/l was quantified.

To date most studies regarding novel PFAS has dealt with occurrence in water. Concerning environmental solid matrices the knowledge is more limited but the number of reports is growing. The presence of GenX (HFPO-DA) in soil near the fluoropolymer facility in Dordrecht (NL) was documented in an official report (RIVM, 2018), and concentrations taken from two

studies presented were in the range 0.1-4.7 µg/kg DM. Joerss et al. (2019) could not find GenX above LOQ in sediments from the German coast despite concentrations in water. In the case of ADONA it was determined in topsoil (30 µg/kg) at a monitoring station impacted by emission from the polymer plant by the River Alz (LfU, 2019). In TemaNord (2019) ADONA and GenX could not be detected in biota (bird egg, fish, marine/terrestrial mammals) or WWTP sludge, but it should be mentioned that the LOQ was in many cases higher for these two novel compounds than some of the legacy PFAS. However, near the fluoropolymer factory in DE, ADONA was found in six of fifteen deer liver samples in the range 0.6-1.5 µg/kg FW (LfU, 2019). In lysimeter experiments with added ADONA, included in the LfU report, it was also shown that the substance could be detected in meadow cut in some cases (0.06-0.16 µg/kg FW).

Levels of replacement products for PFOS have been monitored as well. Xiao (2017) reviewed studies where F53-B was included, and the substance was shown to be present in matrices such as sewage sludge (up to 210 µg/kg DM; CN), liver of marine mammals (0.02-0.27 µg/kg FW; Greenland) and blood serum (mean 0.8-2.3 ng/ml; CN). In some cases the concentrations of 6:2 Cl-PFESA (F-53B) was in the same order as PFOS e.g. sludge, and along with 6:2 the 8:2 homologue was frequently observed but at lower levels. Lescord et al (2015) found 0.07 µg/kg of PFECHS in sediment from an Artic lake (CAN) while in sediments from the German coast (n=24), analysed by Joerss et al (2019), F-53B and PFECHS could not be found. Da Silva et al (2011) found PFECHS in fish (and water, see above) from the Great Lakes, up to 3.7 µg/kg FW. PFECHS was identified in fish liver (up to 0.44 µg/kg FW) and marine mammals (up to 0.87 µg/kg FW) in TemaNord (2019). In a short literature compilation in the same report, the presence of PFECHS was seen in fish also in other studies (0.5-70 µg/kg FW), and moreover in Polar bears (0.1-1.5 µg/kg FW).

The ability of adsorption of contaminants onto solids such as soil, sediment and sludge is of great importance for their distribution between different environmental compartments. The adsorptive capacity is often expressed in the Log K_{OC} (organic carbon adsorption coefficient) value. For GenX, a Log K_{OC} of 1.08 was given in RIVM (2019) based on data from Chemour, while a higher value of 1.92 was modelled by Xiao (2017). It is interesting to note that in the study by Sun et al. (2016) the adsorption onto active carbon (GAC) for GenX was limited (<20%), comparable to PFBA. No value could be found for ADONA but given its structure a comparable perhaps slightly higher Log K_{OC} than for GenX can be expected. The adsorption for PFAS sulphonates is typically somewhat stronger than for carboxylates. Modelled values of Log K_{OC} for F-53B of 3.73 and for PFECHS 3.37 were computed by Xiao (2017). These numbers are in the same span as typically seen for PFOS. A rough calculation based on values presented by Lescord et al (2015) for one lake (sediment and water) would indicate a lower Log K_{OC} for PFECHS, around 2.2-2.5, but there are large uncertainties.

Characteristics of Ultrashort PFAS

As stated above the group of ultrashort PFAS are commonly regarded to comprise TFA, PFPrA, PFEtS and PFPrS i.e. PFCA and PFSAs with two and three carbons. Concerning the origin of TFA and PFPrA it may (in part) differ from their longer homologues. In precipitation one source can be contamination in, and phototransformation of the refrigerants HFC-134a, HFO-1234yf (Zhang et al., 2019) and possibly other HFC/HCFC (Janda et al, 2019a). TFA may also be formed from sources for example pharmaceuticals and pesticides (e.g. Flurtamone) having trifluoromethyl moieties (Janda et al, 2019a and refs within). Moreover, TFA is employed as a reagent in different organic syntheses. Concerning PFEtS and PFPrS they have been used for applications such as ion conductive agents, photolithography processing and can be present in AFFF (Yeung

et al, 2017). For the latter matrix Barzen-Hanson and Field (2015) showed an average content of 0.22% and 3.5% for PFEtS and PFPrS, respectively, related to total PFSA content in old 3M foams (n=5) dominated by PFOS and PFHxS. The four ultrashort compounds are all associated with high water solubility and low pKa values (not shown), which besides small molecular size, suggests that long-term the aquatic environment becomes the eventual sink (Ateia et al., 2019).

Biodegradation of precursors to form ultrashort

The ability of telomer precursors to biodegrade in environmental systems has been shown in a number of publications as reviewed by (Liu and Avendaño, 2013). Estimated half-lives ($t_{1/2}$) in soil, sediment and sludge were found in the range <2 up to >210 d for telomers studied, mainly 6:2 and 8:2-based. Though it should be stressed that $t_{1/2}$ expresses the disappearance of the original substance not the final perflourinated products. In the case of telomer precursors these most commonly degrade to PFCA, and shorter chained end products can be observed. E.g. for 6:2 FTOH formation of PFHxA, PFPeA and PFBA is possible and for 6:2 FTS, PFHxA and PFPeA (Liu and Avendaño, 2013). With regard to ultrashort PFCA there is a potential that these are formed at e.g. 4:2 precursor degradation with 4:2 FTS being one example. However, this process is still to be elucidated in experimental studies, but is supported by results from chemical oxidation (see below). 4:2 FTS is sometimes observed, especially along 6:2 FTS e.g. in marine fish (TemaNord, 2019) and in landfill leachate (Avfall Sverige, 2018).

Total oxidizable precursor (TOP) assay is a method to chemically oxidize both telomer and sulphonamide precursors into perfluorinated PFCAs while maintaining the original PFCA and PFSA in the sample (Houtz et al., 2012). Telomers (n:2) form a series of PFCA with the highest concentration typically seen for the homologue with n-1 carbons e.g. in the case of 6:2 FTS it would be PFPeA . Sulphonamides are oxidized, more or less, only to the corresponding PFCA with the same number of C:s e.g. in the case of PFOSA, PFOA is yielded. Until recently analysis after TOP has not included ultrashort PFCAs. Martin et al (2019) studied TOP of 23 precursors which comprised among others 4:2 FTS, 6:2 FTS, 5:3 FTCA and 6:2 FTUCA. For all of these PFPrA was the second largest and for 4:2 FTS largest PFCA formed (TFA was not measured). Significant increases in overall molar yields were observed compared to earlier investigations e.g. for 6:2 FTS. In the work by Janda et al (2019b) also TFA was determined besides PFTrA. The oxidation of PFEtSA was found to produce 88 mol% TFA demonstrating the formation of ultrashort PFCAs also for small sulphonamides.

Environmental Concentrations of Ultrashort PFAS

As for novel PFAS the largest number of studies has focused upon water. Ateia et al (2019) compiled the occurrence of short and ultrashort in different waters presented in papers from 1995 to 2017. For precipitation (rain/snow) concentrations of TFA varied between 45-700 ng/l with a single value for PFTrA of 25 ng/l. Two additional values of 10-20 ng/l were given by Yeung et al (2017). In studies where ultrashort PFCA/PFSA was measured together with other PFAS (up to C8-C11) they corresponded to 40-90% of the total.

Levels of TFA in sea water were reported to range between 0.5-230 ng/l in Ateia et al. (2019). In the case of river water Yeung et al (2017) reported 11 ng/l TFA, 110 ng/l PFPrA and 13 ng/l , PFPrS making up 34% of total PFAS in one sample while for a second site no ultrashort was found above LOQ. In the study by Janda et al (2019a) TFA was found to be the dominant PFAS in surface water samples (n=43) not affected by any known PFAS contamination with a median

value of ~500 ng/l. A similar median value was found for tap water (n=21). Some extreme observations, up to 17000 ng/l later on revealed an unknown industrial release. In a report by Ericson Jogsten and Yeung (2017) about 20 surface waters in the vicinity of industrial and military sites as well as airports were analysed for PFTrS and PFEtS. The compounds could with few exceptions be detected in all samples ranging from <0.1-190 ng/l. The levels corresponded to 0.1-20% of total PFAS.

In the TemaNord (2019) study PFPrA was identified in some surface waters with concentrations between 0.3-0.4 ng/l, though it should be mentioned that LOQ was raised to <15 ng/l in others. TFA was not included in the work. PFPrS and more frequently PFEtS were detected too, ranging between <0.02 to 0.9 ng/l (n=13). However, in WWTP effluent PFPrA was present in all but one waters measured (<1.4-47 ng/l; n=14). PFEtS and/or PFPrS were seen in most samples in a range slightly larger than for surface waters, <0.14 to 6.0 ng/l (n=14). Ultrashort PFAS in effluent made up on average 6% of the total in all samples but four from Iceland and Greenland with a mean of 39%, while contributions between approximately 2-10% in surface waters were estimated.

An investigation of five contaminated groundwater samples by Janda et al (2019a) showed that TFA was the PFCA present at the highest concentration (800-2200 ng/l) in three of them even as compared to PFOA (450-1700 ng/l). PFPrA was also found but at much lower levels, <150 ng/l. PFSAs were not presented. TFA plus PFPrA comprised about 35% of the sum of PFCA on a concentration basis. The authors concluded that degradation of 4:2 telomers was one possible source of TFA and PFPrA, but for TFA other sources were probably more important. The median value for groundwater (n=42) without known PFAS pollution was 600 ng/l, to some extent underpinning the reasoning. In two heavily polluted groundwaters near a Swedish military airfield PFPrS (11000-39000 ng/l) almost equaled PFBS in concentration while the observed level of PFEtS was much less (1600-5700 ng/l). The two sulphonates made up 6-11% of total PFAS. On the contrary, three groundwater samples former hard chromium plating facility PFPrS and PFEtS were of more limited quantitative importance corresponding to 1-15 ng/l vs 110-2400 ng/l for PFBS (Ericson Jogsten and Yeung, 2017).

Studies of environmental solids with respect to ultrashort PFAS are still scarce. Li et al (2011) determined TFA and PFPrA in sediment, soil and WWTP sludge (all n=3) from the Shanghai area. In sediments average figures of TFA = 63 µg/kg and PFPrA = 2.8 µg/kg were observed, for soils 126 and 0.6 µg/kg and for sludge 560 and 4.4 µg/kg. The share of ultrashort compounds in the three matrices was relatively large, 54% (sediment), 89% (soil) and 86% (sludge). On the contrary Janda et al (2019a) did not detect any ultrashort PFAs in a contaminated soil profile with sample taken at four depths. Similarly, in TemaNord (2019) no ultrashort PFAS were identified above LOQ in Nordic WWTP sludge, but it should be stressed that TFA was not measured. Clearly more research is needed to elucidate the importance of ultrashort PFAS and their sources, and also analytical methods need to be further developed.

Uptake mechanisms of C2-C8 PFCA plus PFOS into wheat were addressed by Zhang et al (2019). In hydroponics experiments the largest shoot and root concentration factors were calculated for TFA (1100-1600 times). From inhibition experiments it was concluded that an energy dependent active process was the main mechanism but for the ultrashort PFCAs uptake also through aquaporins and anion channels contributed. In TemaNord (2019) no ultrashort PFAS could be identified above LOQ in biota (fish, mammals) possibly reflecting low bioaccumulation.

As discussed above ultrashort PFCAs can be of importance in the TOP assay when accounting for shorter precursors. In the investigation of a soil profile by Janda et al (2019a) TFA and PFPrA were formed after TOP (<LOQ – 20 µg/kg DM). The greatest contribution of TFA to the PFCA

produced was found for the deepest layer (60-70 cm) corresponding to 12% of the additional PFCA. This observation was set in relation to overall TOP pattern indicating presence of 6:2-10:2 precursors and PreFOS in the uppermost horizons, and possibly migration of smaller precursors through the soil. Martin et al (2019) observed formation of PFPrA (TFA was not measured) in eight of nine AFFF impacted groundwater samples. PFPrA made up 10-16% of the PFCA appearing after oxidation. Computations for the most polluted water suggested that the major part (65-70%) of the PFPrA formed originated from unidentified precursors, while 20-25% could be explained by 6:2FTS degradation.

Novel and ultrashort PFAS – risk assessment and regulation

As novel PFAS also are to a great extent emerging pollutants complete risk assessments and regulation are largely lacking, but the picture is slowly changing. There are numerous aspects to consider, but central properties are PBT/vPvB criteria, exemplified by biodegradation, half-life for elimination and various toxicity studies. Wang et al (2013; 2015) summarized results from investigations available for GenX and ADONA. A more extensive assessment for GenX was made by RIVM (2016). Broadly speaking the data suggest that the two chemicals are not readily biodegraded (i.e persistant), their serum half-lives (<12 to <168h for mice/rats) are generally shorter than for PFOA and that the toxicity is less too. However, similar (toxic) effects as for other PFAS seemed to be observed. For ADONA an elimination value in humans has been reported (half-life 23±11 d), derived from people who were occupationally exposed (i.e. high levels). However, main conclusions were that further studies are warranted and more information needs to be made accessible (Wang et al, 2015). A concern raised was that extrapolation of results from animal testing to humans can be difficult for PFAS, as exemplified by PFOA. This was echoed for GenX by RIVM (2016) and thus that the potential human bioaccumulation could not be fully evaluated. It should also be noted that GenX has a H373 (STOT RE 2) classification due to liver and red blood cell effects, and moreover, liver tumours and increases in pancreas and Leydig cell tumours in rats have been seen (RIVM, 2016). Another observation concerning GenX is that the uptake into plants (BCF; 0.58 µg/kg FW : µg/kg DM soil) is estimated to be 20 times larger than for PFOA (RIVM, 2019).

GenX is the only novel substance that, to the best of the author's knowledge, has been subject to guideline/limit values. Following the Cape Fear contamination case authorities in North Carolina published in 2017 (NCDHHS, 2017) a drinking water guideline value of 140 ng/l. Recently, in Michigan (MPART, 2019), a figure of 370 ng/l was presented. The first draft toxicity assessment (draft oral reference doses; RfD) from US-EPA (2018) suggested a tolerable exposure of 80 ng/kg BW – day for GenX, a value that can be compared to the current for PFOS (20 ng/kg BW – day). The most comprehensive set of guideline values so far was published by RIVM (2019), and included soil, groundwater and groundwater as drinking water. Soil guideline limits ranged between 3-25000 µg/kg DM for different risk scenarios with the lowest calculated for "nature" (3 µg/kg DM) and vegetable gardens (8 µg/kg DM). A concentration of 100 µg/kg DM was given as an indicative level for serious pollution (INEV). The guideline value for groundwater as drinking water, allowing 20% of the total exposure, was 150 ng/l. Due to incomplete input it was stressed that the limits were of a preliminary nature. Furthermore a guideline value for surface water of 118 ng/l was given by RIVM (2018).

In the revision work the EU drinking water directive, PFAS is expected to become included (EU, 2019). In the draft from Feb 19 a parametric (~compliance) value of 100 ng/l for sum of PFAS is stated. The concept of "sum of PFAS" is explained as the sum of a subset of relevant per- and

polyfluoroalkyl substances that contain a perfluoroalkyl moiety with three or more carbons (i.e. –CnF2n–, n ≥ 3) or a perfluoroalkylether moiety with two or more carbons (i.e. CnF2nOCmF2m–, n and m ≥ 1). The compounds selected must be considered a concern for water intended for human consumption. Although the final writing is still to be decided, the current one would comprise PFECA and PFESAs discussed above. Regarding ultrashort the only compound to be covered by the definition of the directive would be PFPrS.

Concerning regulation of products and chemicals GenX was listed as a Substance of Very High Concern (SVHC) by the European Chemicals Agency in July 2019 (ECHA, 2019). Substances are typically included given carcinogenic, mutagenic, reproductive toxic (CMR) properties, persistence and bioaccumulation. The listing of GenX was motivated by its "equivalent level of concern" with regard to probable serious effects to human health and to the environment (ECHA, 2019). In part this was a new approach driven by factors such as persistence, mobility, potential for long-range transport and observed/probable adverse health and environmental effects (e.g. effects on liver, kidney, haematological, immune systems, birds/mammal populations; low adsorption, high water solubility, high bioavailability). As a SVHC substance any product containing >0.1% GenX needs to be registered.

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