



The PFOA substitute GenX detected in the environment near a fluoropolymer manufacturing plant in the Netherlands

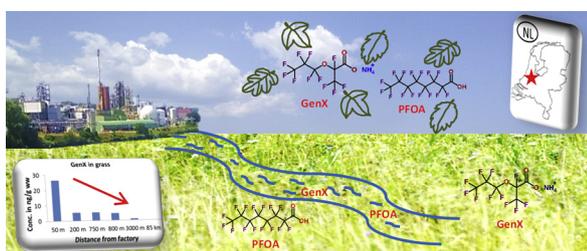
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HIGHLIGHTS

- GenX detected in grass and leaves collected within 3 km from Teflon plant.
- Declining gradient of GenX with increasing distance from plant.
- Strong indications of plant being a point source of GenX.
- GenX and PFOA also detected in drinking water samples.

GRAPHICAL ABSTRACT



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ABSTRACT

The ban on perfluorooctanoic acid (PFOA) has led to the production and use of alternative fluorinated compounds such as GenX. Limited information is available on the occurrence of this PFOA substitute. In this pilot study, we investigated the presence of GenX in/on grass and leaf samples collected near a fluoropolymer manufacturing plant in the Netherlands and in drinking water produced from surface and surface-water influenced groundwater intake points within 25 km from the plant. GenX was detected in/on all grass and leaf samples collected within 3 km north-east from the plant, with levels ranging from 1 to 27 ng/g wet weight (ww) and 4.3–86 ng/g ww, respectively. The PFOA levels in/on grass and leaves were lower, ranging from 0.7 to 11 ng/g ww and 0.9–28 ng/g ww, respectively. A declining concentration gradient of GenX and PFOA with increasing distance from the plant was observed, which suggests that the plant is a point source of GenX and was a point source for PFOA in the past. In all drinking water samples, GenX and PFOA were detected with levels ranging from 1.4 to 8.0 ng/L and 1.9–7.1 ng/L, respectively. The detection of GenX, which is only used since 2012, in/on grass and leaves and in drinking water indicates that GenX is now distributed through the environment. The presence of GenX and PFOA in/on grass and leaves within 3 km north-east of the plant also suggests that these chemicals could also be present on the locally grown food in gardens around the factory.

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Abbreviation list: perfluorooctanoic acid, (PFOA); Per- and polyfluoroalkyl substances, (PFASs); polymerization processing aid, (PPA); persistent organic pollutants, (POPs); Registration, Evaluation, and Authorization of Chemicals, (REACH); 2,3,3,3- tetrafluoro-2-(heptafluoropropoxy)propanoic acid, (HFPO-DA); bioconcentration factor, (BCF); drinking water treatment plant, (DWTP); tetrahydrofuran, (THF); solid phase extraction, (SPE); limit of detection, (LOD); limit of quantification, (LOQ); perfluorobutanoic acid, (PFBA); perfluorodecanoic acid, (PFDA); perfluoroundecanoic acid, (PFUDA); perfluorobutane sulfonic acid, (PFBS); perfluoroheptane sulfonic acid, (PFHpS); 6:2 fluorotelemer sulfonate, (FTSA); perfluorohexane sulfonic acid, (PFHxS); perfluorohexanoic acid, (PFHxA); perfluoroheptanoic acid, (PFHpA); perfluorononanoic acid, (PFNA); perfluoroundecanoic acid, (PFUnA); perfluorododecanoic acid, (PFDoA); perfluoropentanoic acid, (PFPeA).

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1. Introduction

Per- and polyfluoroalkyl substances (PFASs) are man-made chemicals. Due to their unique properties, they are used in various industrial applications such as in firefighting foams, and as a surfactant in consumer products. They are useful because of their stain/water/oil/grease repellency (Giesy and Kannan, 2002). Some of the PFASs are bioaccumulative, highly persistent, and toxic, and ubiquitously present in the environment and humans (Houde et al., 2011; Buck et al., 2011; Itoh et al., 2016). In the Netherlands, perfluorooctanoic acid (PFOA) has been used from 1970 to 2012 as polymerization processing aid (PPA) in a fluoropolymer production plant in Dordrecht, situated in the delta of the rivers Rhine and Meuse (Van Poll et al., 2017). Due to its persistence, bioaccumulation potential, and toxic effects, PFOA is under review for addition to the Stockholm Convention POPs (persistent organic pollutants) list and has been listed by the European Chemical Agency as a substance of very high concern (SVHC) under REACH (Registration, Evaluation, and Authorization of Chemicals) (Stockholm Convention, 2017; ECHA, 2018). In 2017, the European Union restricted the use of PFOA and its salt (EU, 2017). Manufacturers had, therefore, to select alternative fluorinated compounds (Wang et al., 2013; Scheringer et al., 2014). One of them is GenX. GenX is the commercial name for the ammonium salt of 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoic acid (HFPO-DA) (Fig. 1).

Although limited toxicokinetic data are available for GenX, it was selected as a suitable alternative for PFOA because initial studies indicated that GenX is much less bioaccumulative than PFOA (Wang et al., 2013; Gannon et al., 2016; Beekman et al., 2016). Pan et al. (2017) calculated a bioconcentration factors (Log BCF) for GenX of 0.86 in carp (*Cyprinus carpio*) blood, 0.50 in carp liver and 0.61 in carp muscle, which are lower than the Log BCF of 1.93 in carp blood, 1.24 in carp liver, but higher than the 0.46 in carp muscle reported for PFOA. Wang et al. (2015) summarized that under environmentally relevant conditions perfluoroether chains are resistant to abiotic and biotic degradation similar as the perfluoroalkyl chains, which may indicate that GenX is just as persistent as PFOA. Based on a toxicokinetic model study for male rats, GenX was also found to have similar or higher toxic potency than PFOA (Gomis et al., 2015, 2018).

Heydebreck et al. (2015) were the first to detect GenX in Dutch river water with a concentration of 73 ng/L, close to the village of Rozenburg, near Rotterdam. Their hypothesis was that the possible source of GenX could be the chemical plants located in the Port of Rotterdam and the fluoropolymer manufacturing plant in Dordrecht. Previously, Gebbink et al. (2017) detected GenX in Dutch river water with concentrations ranging from 1.7 to 812 ng/L. An increase of GenX concentrations downstream the fluoropolymer plant was observed, suggesting the fluoropolymer manufacturing plant as the main source. Approximately 40% of the river water in the Netherlands is used as a source of drinking water. GenX is more

water-soluble than PFOA and, therefore, difficult to remove by drinking water production facilities (Sun et al., 2016). The levels in the raw water from the drinking water treatment plant (DWTP) in North Carolina were for example comparable with the GenX levels in the finished drinking water (drinking water ready for distribution) (Sun et al., 2016). During the production process at the fluoropolymer manufacturing plant GenX is not only emitted into the river water but also to the air (Beekman et al., 2016). PFASs are persistent and could, therefore, accumulate after atmospheric deposition in the area around the plant. Besides river and drinking water, only limited data is available on GenX in the Dutch environment. The objective of this pilot study was to investigate the presence of GenX on grass and leaves collected near the fluoropolymer manufacturing plant in Dordrecht (Netherlands). Measuring GenX near suspected sources may give a first impression on its potential risk for people living near the plant and provides information on the distribution of this substance. The GenX levels were compared with levels of a suite of PFASs measured in the same samples for an initial risk estimation. In addition, six drinking water samples were analyzed for GenX and PFASs.

2. Materials and methods

2.1. Samples

2.1.1. Grass and leaves

Grass or leaves were collected in August 2016 at five locations within 3 km north-east from the fluoropolymer manufacturing plant. The north-east direction was based on the prevailing south-westerly winds. Prior to the sampling of the grass and leaves it had not rained for five days. The leaves were taken from different tree species hawthorn (*Crataegus monogyna*), birch (*Betula pendula*), ash (*Fraxinus excelsior*), plane (*Platanus hispanica*), and raspberry (*Rubus fruticosus*). Because the highest GenX and PFOA levels were detected in/on the leaves of the hawthorn (*Crataegus monogyna*) we decided to collect also the leaves from the hawthorn (*Crataegus monogyna*) at the reference location in Amsterdam 85 km north from the manufactory plant. Beside the leaves also grass was collected at this reference location. The sample locations are highlighted in Fig. 2. Approximately 20 g grass or leaves were collected in a pre-cleaned 50 mL Greiner tube. Grass was collected at various spots within 1 m², whereas leaves were randomly collected at 80–150 cm from the ground. After sampling, the grass and leaves were cut in small pieces (<5 mm) with a pre-cleaned stainless steel scissors. After homogenizing approximately 1 g of grass or leaves were weighted for extraction. Prior to analysis, the samples were stored in the fridge. The objective of this pilot study was to investigate the worst case scenario. Therefore, the leaves and grass samples were not pre-washed. No distinction was made between the PFASs levels in grass and leaves or on grass or leaves. Through the whole manuscript, the levels will, therefore, be reported as in/on the grass and leaves.

2.1.2. Drinking water

Drinking water was collected at residential homes from six different municipalities (Dordrecht, Alblasterdam, Gouda, Rotterdam, Spijkenisse, Goedereede) within 50 km from the fluoropolymer manufacturing plant (Fig. 2). The drinking water is coming from two different water companies; one which delivers drinking water to Dordrecht, Rotterdam, Spijkenisse, Goedereede; and one which delivers drinking water to Alblasterdam and Gouda. The source of the drinking water for Dordrecht, Rotterdam, Spijkenisse is river water from the river Meus (S1) and for Goedereede river water from the river Meus (S1) and from the Haringvliet (S2). The source of the drinking water in Alblasterdam is surface-water

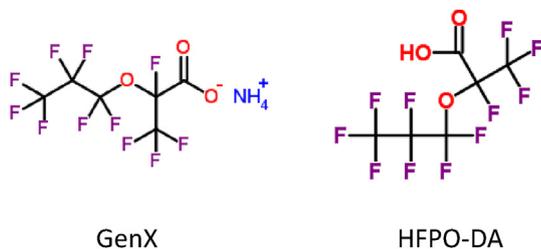


Fig. 1. Structures of GenX and HFPO-DA.

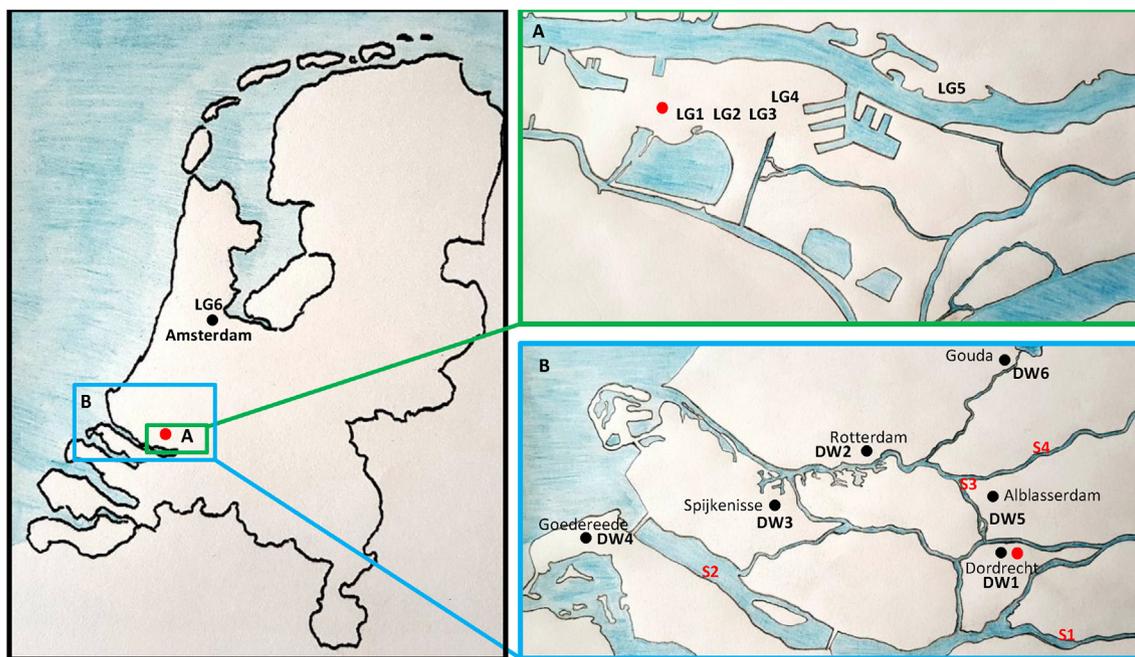


Fig. 2. Sample locations of the leaves and grass (Map A; LG1-LG6) and drinking water (Map B; DW1-DW6) collected near the fluoropolymer manufacturing plant in Dordrecht, The Netherlands. The fluoropolymer manufacturing plant is marked with a red dot. The location of the intake points (S1–S4) for the drinking water samples are also shown in map B. Intake point for DW1–3 is S1, intake point for DW4 is S1 and S2, intake point for DW5 is S3, intake point for DW6 is S4. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

influenced groundwater of the river Lek, a branch of the river Rhine (Nieuw-Lekkerland, S3) and for Gouda, surface-water influenced groundwater and deep groundwater of the river Lek (Bergambacht, S4). The samples were collected in pre-rinsed 250 mL high-density polyethylene bottles and stored in the fridge prior to analysis.

2.2. Extraction and cleanup

2.2.1. Grass and leaves

The extraction method was based on the method of Zafeiraki et al. (2016). Samples were not prewashed before analyzed. Briefly, 1 g of grass or leaves was fortified with 50 μL of $^{13}\text{C}_4$ -PFOA and $^{13}\text{C}_3$ -GenX labeled internal standard (100 ng/mL) and 2 mL of 200 mM sodium hydroxide (added for alkaline digestion). After adding 10 mL of methanol as the extraction solvent the solution was vortexed for 1 min and shaken for 30 min at 250 rpm. After centrifugation for 10 min at 10,000 rpm, for precipitation and removal of insoluble particles, the supernatant was transferred to a new tube. The extraction was repeated with another 8 mL of methanol. The combined supernatant was diluted with 20 mL of Milli-Q and neutralized by adding a 150 μL of 4 M hydrochloric acid.

The cleanup was performed by solid phase extraction (SPE) using weak anion exchange Oasis WAX cartridges (6 mL 150 mg, 30 μm). SPE was conditioned with 4 mL of methanol and 4 mL of HPLC water. After the sample was added the SPE was washed with 4 mL of 25 mM sodium acetate buffer (pH 4) and 6 mL tetrahydrofuran (THF): methanol (75:25, v/v). The PFASs were eluted from the SPE with 4 mL of 0.1% NH_4OH in methanol. The extract was evaporated to dryness under a gentle stream of nitrogen. The dried residue was dissolved in 100 μL Milli-Q and 100 μL of $^{13}\text{C}_8$ -PFOA injection standard (100 ng/mL) in methanol.

2.2.2. Drinking water

The sample volume for the analysis of PFOA and GenX in drinking water was 100 mL. The cleanup was performed with the

similar SPE method as described for the grass and leaves, with the exception that for the wash step 8 mL of tetrahydrofuran (THF): methanol (75:25, v/v) was used instead of 6 mL.

2.3. Measurement

GenX was analyzed on a Bruker (Bremen, Germany) Elute OLE UHPLC system coupled to a Bruker EVOQ triple quadrupole mass spectrometer. The measurement was performed in negative electron spray ionization (ESI) mode with a capillary voltage of 4000 V and a source temperature of 350 $^\circ\text{C}$. The mobile phase consisted of 5 mM ammonium formate (eluent A) and methanol (eluent B) using the following gradient conditions: 0–1 min 10% eluent B; 1–15 min 95% eluent B; 15–16 min 10% eluent B; 15–20 min 10% eluent B. Labeled internal standard ($^{13}\text{C}_3$ -GenX) was used for the quantification of GenX. The MS was run in the MS-MS mode using multiple-reaction monitoring of the ions, m/z 285; $[\text{M}-\text{COOH}]^- \rightarrow 169$; $[\text{C}_3\text{F}_7]^-$ (Quantifier) and 285; $[\text{M}-\text{COOH}]^- \rightarrow 185$; $[\text{C}_3\text{F}_7\text{O}]^-$ & 119; $[\text{C}_2\text{F}_5]^-$ (Qualifiers) for GenX, m/z 287 \rightarrow 169 (Quantifier) and 287 \rightarrow 185 (Qualifier) for $^{13}\text{C}_3$ -GenX.

The analysis of the fourteen additional PFASs (see Table 1) was performed on a 1260 HPLC (Agilent Technologies, Amstelveen, the Netherlands) with a 150 \times 2.1 mm 5 μm ProteCol-Fluofix-II 120E column (SGE Analytical Science, Breda, the Netherlands). An extra column (Hypercarb guard columns, 10 mm \times 4 mm, 5 μm , Thermo Scientific, Landsmeer, the Netherlands) was used between the pump and injection to retain PFASs background out of the system. The injection volume was 10 μL and the flow 250 $\mu\text{L}/\text{min}$ with a total run time of 27.2 min. The mobile phase consists of 5 mM ammonium formate (eluent A) and methanol (eluent B). Detailed information on the gradient is given in the [supplementary information](#). The HPLC was coupled to a 6410 triple quadrupole MS (Agilent Technologies) with ESI in the negative mode. Capillary voltage was set to 4000 V with a source temperature of 325 $^\circ\text{C}$, nebulizer gas of 25 psi with a flow of 6 L/min. The MS was run in the

MS-MS mode using multiple-reaction monitoring of the parent and two daughter ions (see Table S1 for detailed information on the ions monitored and the labeled standard used for quantification).

2.4. Quality control

The limit of detection (LOD) and limit of quantification (LOQ) was calculated from the signal to noise of $S/N = 3$ and $S/N = 10$, respectively. If blank levels were observed, the LOQ was calculated as three times the blank level. The LOD and LOQ are given in the supporting information (Tables S2 and S3). Two process blanks, following full extraction, cleanup and reconstruction, were included. Measured blank levels were only observed for perfluorobutanoic acid (PFBA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUDA), PFOA, and GenX with an average level of 0.82, 0.03, 0.04, 0.03 and 0.03 ng absolute, respectively. Quantification was performed with isotopic dilution method (Table S1). For two PFASs (perfluorobutane sulfonic acid (PFBS), perfluoroheptane sulfonic acid (PFHpS)) no labeled standards were available. For those two the internal standard with the closest retention time was used. The recovery for the labeled standards in the leaves and grass samples ranged from 38% to 129%, and in the drinking water from 72% to 135% (Tables S4 and S5). The values were corrected for the recovery of the labeled standards. One duplicate analysis was included (sample L3). Comparable values were observed for PFOA: 19.8 and 18.8 ng/g ww and GenX: 28.2 and 28.4 ng/g. For the other PFASs see Table S6.

3. Results and discussion

3.1. GenX in/on grass and leaves

GenX was detected in/on all grass and leaf samples collected within 3 km from the fluoropolymer manufacturing plant, with levels ranging from 1.0 to 27 ng/g ww in/on the grass and from 4.3 to 87 ng/g ww in/on leaves (Table 1). The GenX levels in/on the grass and leaves collected in Amsterdam, 85 km north from the plant were below the LOD (<0.1 ng/g ww). Despite the small sampling size of the study, a declining concentration gradient of GenX with increasing distance from the plant was clearly observed, which may suggest that the plant is the point source for the emission of GenX (Fig. 3). The results of our study confirms the findings of Gebbink et al. (2017) who also observed a declining gradient of GenX in downstream river water with increasing distance from the same plant. Limited data are available on GenX in the environment. To our knowledge, this is the first time GenX was detected in/on grass and leaves. GenX has previously been detected in Dutch river water (up to 800 ng/L) and drinking water (up to 11 ng/L), collected in the same area, and in river water (73 ng/L) approximately 50 km downstream from the plant (Gebbink et al., 2017; Heydebreck et al., 2015). GenX was also detected in river water from the US and China, near fluoropolymer manufacturing plants, with levels in river water up to 4500 ng/L and 3100 ng/L, respectively (Strynar et al., 2015; Sun et al., 2016; Pan et al., 2017; Heydebreck et al., 2015). Pan et al. (2017) observed GenX in blood, liver, and muscle of common carp (*Cyprinus carpio*) ($n = 15$) with median concentrations of 2.09 ng/mL, 1.37 ng/g wet weight (ww) and 1.53 ng/g ww, respectively.

3.2. PFASs in/on grass and leaves

Fourteen PFASs were also measured in grass and leaves (Table 1). PFOA and PFBA were the dominating PFASs with concentrations ranging from 0.7 to 28 ng/g ww and <2.9 –42 ng/g ww, respectively. The concentrations of the other legacy PFASs were an

order of magnitude lower. As observed for GenX, PFOA also exhibited declining concentrations with increasing distance from the plant (Fig. 3). However, the PFOA levels in grass (significant; $r = 0.98$, $p < 0.01$) and leaves (not significant; $r = 0.71$, $p < 0.17$) were in general lower than the GenX levels, most likely because the factory has stopped using PFOA as PPA in their fluoropolymer manufacturing process since 2012. Thus, the presence of PFOA in these environmental samples is another indication of the persistence of this compound. The leaf and grass samples were collected during summer, which means that the leaves of the trees and bushes had already been exposed for at least 5 month. During summer the grass is mowed at least every 4 weeks. The leaves could, therefore, accumulate GenX and legacy PFOA for a longer time compared to the grass which may explain the higher levels observed in/on the leaves compared to the grass.

3.3. GenX and legacy PFASs uptake route

The uptake routes of GenX and PFASs by the grass and leaves are not entirely understood. The GenX levels observed in/on the grass and leaves collected around the plant could be a result of atmospheric deposition or/and uptake from the contaminated soil or soil pore water. The fluoropolymer plant in Dordrecht has a permit to emit GenX both to the air and to the water (Van Bentum et al., 2017; PZH, 2017). No data is available on GenX in air around the fluoropolymer plant in Dordrecht however, in a non-peer reviewed report, GenX was detected in the soil (sampling depth 0.5–2.8 m) and groundwater (sampling depth 0.5–3.8 m) collected within 1.5 km from the plant with levels ranging from 0.5 to 4.7 ng/g dw and 13–660 ng/L, respectively (Van Bentum et al., 2017). This same report showed that the groundwater and soil around the Dordrecht plant is also contaminated with PFOA with levels ranging from 3900 to 25,000 ng/L in the groundwater (sampling depth 0.5–3.8 m) and 9–84 ng/g dw in the soil (sampling depth 0.5–2.8 m) (Van Bentum et al., 2017). This shows that it is likely that PFOA is transferred from the soil and the groundwater to the grass and leaves of the trees, also because PFOA is not used anymore by the fluoropolymer manufacturing plant since 2012 and therefore atmospheric deposition may be ruled out for PFOA. Although, a waste incinerator near the fluoropolymer manufacturing plant could also be a source of PFOA and PFBA. More research is needed to check the emission of that incinerator.

Previous studies have reported the uptake of PFASs from contaminated soil, groundwater and drinking water by various plant species (Stahl et al., 2009; Yoo et al., 2011; Felizeter et al., 2012/2014; Blaine et al., 2013; Krippner et al., 2014; Wen et al., 2014; Shan et al., 2014; Gobelius et al., 2017; Liu et al., 2017; Tian et al., 2018; Scher et al., 2018). These studies revealed that PFAS uptake is influenced by many parameters such as the chain length of the compound, functional group, type of plant species, lipid and protein content, soil and water characteristics, transpiration streams, etc. In general, these studies show that the short-chain PFASs accumulate in the above-ground plant parts (leaves, seeds, fruit, and floret) and the long-chain PFASs in the roots. This is influenced by the higher water solubility and smaller molecule size of the short-chain PFASs. Therefore, the short-chain PFASs are more easily transported from the soil pore water through the roots to the leaves (Felizeter et al., 2012; Krippner et al., 2014). So, it cannot be excluded that the declining pattern in the leaves observed for GenX, PFOA, and PFBA is somewhat influenced by the difference in uptake ability of the different tree species (Stahl et al., 2009; Krippner et al., 2014; Gobelius et al., 2017). It may also explain why the PFOA levels at 200 and 800 m from the plant are lower than at 700 and 3000 m from the plant. This inconsistent pattern was also observed for PFBA (Table 1). However, in the grass, collected at the same

Table 1
PFAS concentrations (ng/g wet weight) in/on grass and leaves collected around a fluoropolymer manufacturing plant, The Netherlands and in drinking water produced from surface and surface-water influenced groundwater intake points within 25 km from the plant.

Code	Sample matrix	Distance from factory (m)	PFBA (ng/g)	PFPeA (ng/g)	PFHxA (ng/g)	PFHpA (ng/g)	PFOA (ng/g)	PFNA (ng/g)	PFDA (ng/g)	PFUnDA (ng/g)	PFDoDA (ng/g)	PFBS (ng/g)	PFHxS (ng/g)	PFHpS (ng/g)	PFOS (ng/g)	6:2 FTS (ng/g)	GenX (ng/g)
G1	Grass	50	<5	0.7	<0.3	<0.3	11	<0.3	<0.3	<0.5	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	27
G2	Grass	200	3.5	0.3	<0.2	<0.2	2.7	<0.2	<0.2	<0.3	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	5.4
G3	Grass	750	<2.9	<0.2	<0.2	<0.2	0.4	<0.2	<0.2	<0.3	<0.2	<0.1	<0.2	<0.2	<0.2	<0.2	5.4
G4	Grass	800	<3.6	<0.2	<0.2	<0.2	0.7	<0.2	<0.2	<0.3	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	4.7
G5	Grass	3000	<3.4	<0.2	<0.2	<0.2	0.7	<0.2	<0.2	<0.3	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	1.0
G6	Grass	85000	<2.7	<0.2	<0.2	<0.2	<0.3	<0.2	<0.2	<0.2	<0.2	<0.1	<0.2	<0.2	<0.2	<0.2	<0.1
L1	Leaves (<i>Crataegus monogyna</i>)	50	42	<0.3	<0.3	<0.3	28	<0.3	<0.3	<0.4	<0.3	0.5	<0.3	<0.3	<0.3	<0.3	86
L2	Leaves (<i>Rubus fruticosus</i>)	200	<3.9	<0.3	<0.2	<0.2	1.0	<0.2	<0.2	<0.3	<0.3	<0.2	<0.2	<0.2	<0.2	<0.2	13
L3**	Leaves (<i>Betula pendula</i>)	750	<4.6	<0.3	<0.2	0.5	20	<0.2	<0.2	<0.4	<0.3	<0.2	<0.3	<0.3	<0.3	<0.3	28
L4	Leaves (<i>Fraxinus excelsior</i>)	800	22	<0.3	<0.3	<0.3	0.9	<0.3	<0.3	<0.4	<0.3	<0.2	<0.3	<0.3	<0.3	<0.3	16
L5	Leaves (<i>Platanus hispanica</i>)	3000	3.5	<0.3	<0.2	0.5	16	<0.2	<0.2	<0.4	<0.3	0.5	<0.2	<0.2	<0.2	<0.2	4.3
L6	Leaves (<i>Crataegus monogyna</i>)	85000	<6.4	<0.5	<0.4	<0.4	<0.7	<0.4	<0.4	<0.6	<0.4	1.1	<0.4	<0.4	<0.4	<0.4	<0.3
Code	Sample matrix (location)	Water intake point	PFBA (ng/L)	PFPeA (ng/L)	PFHxA (ng/L)	PFHpA (ng/L)	PFOA (ng/L)	PFNA (ng/L)	PFDA (ng/L)	PFUnDA (ng/L)	PFDoDA (ng/L)	PFBS (ng/L)	PFHxS (ng/L)	PFHpS (ng/L)	PFOS (ng/L)	6:2 FTS (ng/L)	GenX (ng/L)
DW1	Drinking water (Dordrecht)	Meuse(S1)	<5.0	<4.0	3.0*	2.1*	2.4	<0.5	<0.5	<0.5	<0.5	2.5*	<0.5	<0.5	<1.0	<2.0	3.1
DW2	Drinking water (Rotterdam)	Meuse (S1)	<5.0	5.1*	5.6	3.1*	3.9	<0.5	<0.5	<0.5	<0.5	4.8	0.6*	<0.5	1.3*	<2.0	5.9
DW3	Drinking water (Spijkenisse)	Meuse (S1)	<5.0	4.9*	5.9	3.0*	4.0	<0.5	<0.5	<0.5	<0.5	4.9	0.7*	<0.5	1.3*	<2.0	5.9
DW4	Drinking water (Goedereede)	Meuse (S1)/Haringvliet (S2)	<5.0	<4.0	4.4	3.2*	5.2	<0.5	<0.5	<0.5	<0.5	9.6	1.3*	<0.5	2.6*	<2.0	1.8
DW5	Drinking water (Alblasserdam)	Lek (Nieuw-lekkerland, S3)	8.6*	<4.0	1.6*	<1	7.1	<0.5	<0.5	<0.5	<0.5	10	<0.5	<0.5	1.1*	<2.0	8.0
DW6	Drinking water (Gouda)	Lek (Bergambacht, S4)	10*	<4.0	2.1*	<1	1.9	<0.5	<0.5	<0.5	<0.5	11	<0.5	<0.5	1.2*	<2.0	1.4

**Mean values of the duplicate sample; bold are values higher than LOQ; * level between LOD and LOQ.

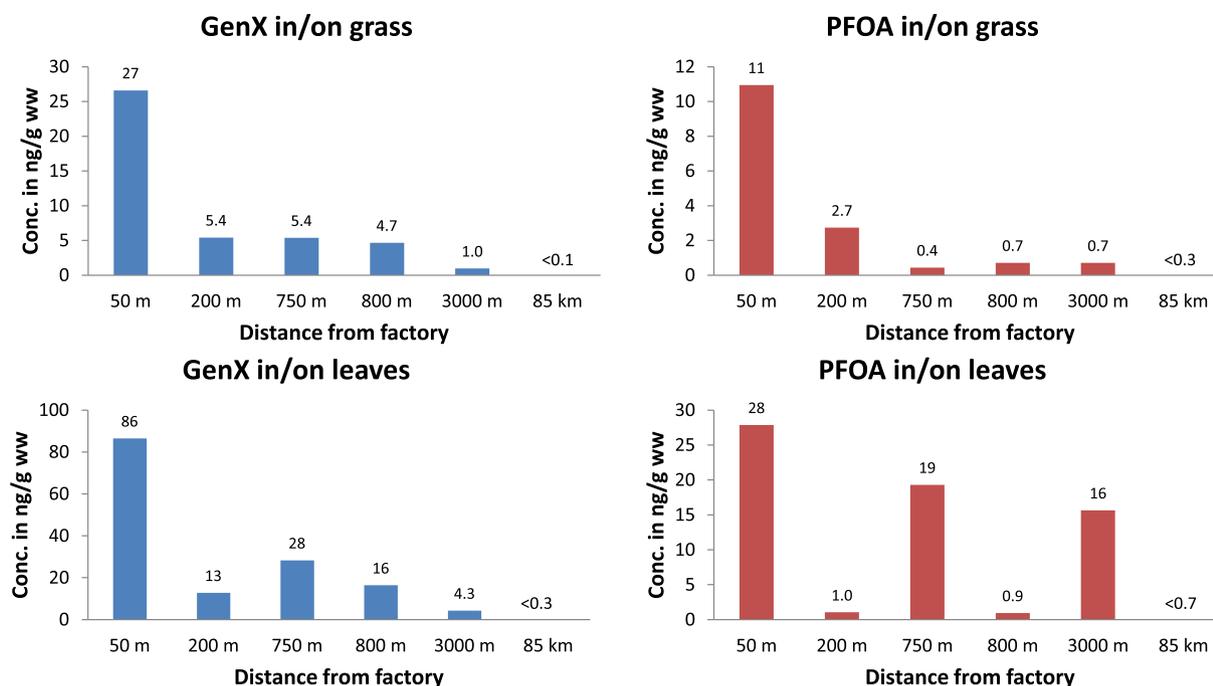


Fig. 3. GenX and PFOA in ng/g ww detected in/on the grass and leaves collected around the fluoropolymer manufacturing plant.

locations as the leaves, an almost constant declining pattern was observed with increasing distance from the plant. Also, the highest GenX and PFOA levels in/on the leaves and grass closest to the plant may suggest that the plant is a point source for the emission of GenX and was a point source for PFOA in the past. Although short-chain PFASs are more easily transported from the soil pore water through the roots to the leaves, (Felizeter et al., 2012; Krippner et al., 2014) no clear explanation could be given for the relatively high PFBA levels (42 ng/g ww) observed in/on the leaves taken close to the plant (50 m). PFBA is used as a substitute for perfluorooctane-based compounds (Renner, 2006). However, to our knowledge PFBA was never used during the fluoropolymer manufacturing process in this plant. PFBA is one of the commonly detected PFASs in river water, groundwater and drinking water (Rahman et al., 2014; Eschauzier et al., 2012). In river water collected within 50 km from the plant PFBA was also one of the predominant PFASs with concentrations ranging from 4.6 to 14 ng/L, comparable to PFOA concentrations (2.8–11 ng/L). However, no increasing trend in PFBA and PFOA concentrations towards the plant was observed in the river water (Gebbinck et al., 2017).

3.4. Comparison of PFASs levels in tree leaves and grass from other studies

Most PFAS uptake studies focus on crops and plants (Stahl et al., 2009; Yoo et al., 2011; Felizeter et al., 2012/2014; Blaine et al., 2013; Krippner et al., 2014; Wen et al., 2014; Shan et al., 2014; Liu et al., 2017; Tian et al., 2018; Scher et al., 2018). Only a few studies have reported PFASs on tree leaves. Recently, Gobelius et al. (2017) studied the uptake of PFASs in various plants and trees from a contaminated firefighting training facility at Stockholm Arlanda airport, Sweden. The \sum_{26} PFAS concentrations in soil (sampling depth 0–10 cm) and groundwater (sampling depth 1.1–1.8 m) ranged from 16 to 160 ng/g dw and 1200 to 34,000 ng/L, respectively. The PFAS profile in soil and groundwater was dominated by PFOS (48%) followed by perfluorohexane sulfonic acid (PFHxS) (11%), perfluorohexanoic acid (PFHxA) (4%), and PFOA (2%),

respectively. The highest \sum_{26} PFAS levels in the plant and tree samples were observed in the vegetative compartments with levels up to 97 ng/g ww in the leaves of silver birch (*Betula pendula*) dominated by 6:2 fluorotelomer sulfonate (FTSA) (50% of \sum_{26} PFASs) followed by the more water soluble short chained perfluoropentanoic acid (PFPeA) (24% of \sum_{26} PFAS) and PFBA (7.5% of \sum_{26} PFAS). Comparing these PFASs patterns and levels in the leaves with those observed in our study is somewhat complicated because the PFOA contamination in the groundwater and soil at the firefighting training facility at Stockholm Arlanda airport, Sweden, is almost two orders of magnitude lower than the PFOA levels recently reported by Van Bentum et al. (2017) around the Dutch fluoropolymer manufactory plant. For example; Gobelius et al. (2017) reported PFOA concentrations from 11 to 1780 ng/L in groundwater (sampling depth 1.1–1.8 m) and 0.21–0.87 ng/g dw in soil (sampling depth 0–10 cm), while Van Bentum et al. (2017) reported 3900 to 25,000 ng/L in the groundwater (sampling depth 0.5–3.8 m) and 9–84 ng/g dw in the soil (sampling depth 0.5–2.8 m) around the Dutch plant. This may, therefore, explain why the PFOA levels in the silver birch (*Betula pendula*) leaves reported by Gobelius et al. (2017) (<0.001–0.5 ng/g ww) are also an order of magnitude lower than the mean PFOA level (20 ng/g ww) observed in the silver birch (*Betula pendula*) leaves in our study.

Zafeiraki et al. (2016) analyzed grass (n = 16) harvested from a floodplain of the river IJssel in the Netherlands. PFOS was the only PFAS detected above the LOQ with levels ranging from 0.4 to 0.8 ng/g ww. Which were higher than the PFOS levels (<0.2–<0.3 ng/g) detected in our study. The levels of the other PFASs (PFHxA, perfluoroheptanoic acid (PFHpA), PFOA, perfluorononanoic acid (PFNA), PFDA, perfluoroundecanoic acid (PFUnA), perfluorododecanoic acid (PFDoA), PFBS, PFHxS, PFHpS) in the grass from the floodplain of the river IJssel were all <0.15 ng/g ww. Bräunig et al. (2017) detected PFASs in the grass (n = 7) collected 1–2 km downstream a groundwater flow from a PFOS-contaminated firefighting training area, in Queensland, Australia. In this Australian study PFOS (max. 68 ng/g ww) was the dominant PFAS detected in grass, probably due the initially high

concentration in the soil (max. 1692 ng/g dw) and groundwater (max. 13 µg/L), followed by the short-chain PFASs with mean levels of 11 ± 8 , 4 ± 5 , 3 ± 2 and 0.6 ± 0.3 ng/g ww for PFBA, PFPeA, PFHxA and PFOA, respectively (Bräunig et al., 2017). In addition to PFOA and GenX, the short-chain PFBA and perfluoropentanoic acid (PFPeA) were also detected in grass in our study. However, the levels were lower, around the LOQ (see Table 1). The PFOA levels in the grass in our study were an order of magnitude higher (0.7 – 11 ng/g ww) compared to the Australian study (<0.2 – 0.8 ng/g ww). That may be related to the higher PFOA concentrations in groundwater and soil around the plant in the Netherlands which were an order of magnitude higher than those found in the Australian study (Van Bentum et al., 2017; Bräunig et al., 2017).

3.5. GenX and legacy PFASs in drinking water

Additionally, drinking water samples from six municipalities within 50 km of the Dutch plant were analyzed for GenX and fourteen legacy PFASs (Table 1 and Fig. 2). The GenX levels ranged from 1.4 to 8.1 ng/L and were comparable with the PFOA levels which ranged from 1.9 to 7.1 ng/L. The GenX and PFOA levels are in the same range as recently detected by Gebbink et al. (2017) in drinking water from the same area. The highest GenX concentration (8.1 ng/L) was observed in drinking water from Alblasserdam (DW5, Table 1). The drinking water inlet point for Alblasserdam is located in the river Lek (S3), downstream from the fluoropolymer plant, and located closest to the fluoropolymer manufacturing plant compared to the other inlet points (Fig. 2). However, GenX was also detected in drinking water from Dordrecht (3.1 ng/L), of which the water inlet point is upstream from the fluoropolymer plant. Detecting GenX in drinking water collected upstream from the plant may be influenced by the tidal changes in this area (open to the North Sea) (Gebbink et al., 2017) or sources upstream. We have found that GenX containing products have been used by a factory in their production processes in the South of the Netherlands, (unpublished data) and also Heydebreck et al. (2015) detected GenX (86.1 ng/L) in river water of the lower Rhine near Leverkusen, Germany, which may eventually end up in the river Meuse. GenX has only been used in the Netherlands since 2012 and the finding in the drinking water reveals that the highly water soluble and persistent GenX is relatively rapid distributed to the river water and groundwater used as a source for drinking water. It also shows that during drinking water treatment the GenX is not entirely removed. Sun et al. (2016) already showed that removing GenX during a water treatment process is rather challenging. The PFOA and GenX levels found in the drinking water are below the safety limits of 87 and 150 ng/L, respectively, as stated by the Dutch government (Bokkers et al., 2016; Janssen, 2017). Nevertheless, the detection of GenX in drinking water in the Netherlands has meanwhile urged the authorities to lower the emission permit for GenX from 6400 kg/yr to 2035 kg/yr to the surface water and from 640 kg/yr to 450 kg/yr to air (PZH, 2017). Since June 2018 the emission permit to the surface water was further lowered from 2035 kg/yr to 148 kg/yr (DCMR, 2018). In addition, GenX was added to the Dutch list of substances of very high concern (SVHC) in January 2018 (RIVM, 2018).

4. Conclusions

The PFOA substitute GenX was detected in/on leaves and grass near a fluoropolymer manufacturing plant in Dordrecht, the Netherlands, and in drinking water produced from surface water and surface-water influenced groundwater that was taken within 25 km from the same plant. A declining concentration gradient of GenX in/on leaves and grass with increasing distance from the

plant was observed. The presence of GenX and PFOA in/on grass and leaves within 3 km north-east of the plant may imply that these chemicals might be present on the locally grown food in gardens around the factory. These findings have recently been confirmed (Mengelers et al., 2018): in/on 40% of the 74 vegetables samples collected within 4 km of the fluoropolymer manufactory plant in Dordrecht detectible levels of GenX (<0.5 – 5.9 ng/g ww) and PFOA (<0.1 – 2.8 ng/g ww) were found. This led to the advice “that vegetable garden crops grown within a radius of 1 km from the company should be consumed in moderation (not too often or too much)”. Previously, Gebbink et al. (2017) detected eleven “new” polyfluoroalkyl acids emitted by the same plant to the river water. These new PFASs may also accumulate in plants, grass and trees and locally grown food from this area. Therefore, further studies on the contamination of locally grown food by emerging PFASs are recommended. As Wang et al. (2017) highlighted, from the more than 3000 PFASs on the global market, only a limited selection is studied by researchers. Therefore, policymakers, “continuing to overlook the vast majority of other PFASs which is a major concern for society”. The present data suggest that this change in production to a less bioaccumulating but, therefore, more water-soluble fluorinated alternative for PFOA only causes a shift to a different environmental compartment and may not be a solution for the pressure on the environment. To limit the exposure to these persistent compounds, the fluoropolymer manufacturers should reduce their emissions during production. Alternatives for PFOA and GenX as PPA in the production of Teflon, containing no fluorine at all, seem to be possible. P1010, a fluorine-free compound based on iron(II) sulfate, polypropylene glycol (surfactant) and lauryl sulfate are options currently under investigation (Janssen and Vermeulen, 2017). Such alternatives are needed to prevent the ongoing pollution of the environment by PFASs. Further research and calculations are also needed to estimate their related risk to the environment and human health.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2018.12.135>.

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