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Environmental contamination and human exposure to PFASs near a fluorochemical production plant: Review of historic and current PFOA and GenX contamination in the Netherlands

Wouter A. Gebbink[1], Stefan P.J. van Leeuwen

Wageningen Food Safety Research (WFSR), 6708 WB Wageningen, the Netherlands

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ABSTRACT

Fluorochemical production plants (FPP) are primary emission sources of per- and polyfluoroalkyl substances (PFASs) to the local environment. An FPP located in the Netherlands has historically used perfluorooctanoic acid (PFOA) for fluoropolymer production and is currently using GenX (HFPO-DA; 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propionic acid) as a replacement. This study reviewed existing data from open access reports and peer reviewed publications on the environmental presence of PFOA and GenX in environmental matrices such as surface water, groundwater, soil and vegetation. Published data on human exposure to PFOA and GenX (i.e. via drinking water and food as well as blood monitoring) were reviewed in order to assess the influence of the FPP on contamination of the local population. Concentrations in environmental and human exposure samples were compared to (inter)national quality standards or risk limits. The data showed higher PFOA and GenX concentrations in surface water, groundwater, soil and vegetation samples taken close to point sources, and the highest observed concentrations exceeded these standards and limits (except for PFOA in soil). Drinking water and food also contained higher PFOA and GenX concentrations in samples taken close to point sources compared to samples further away. Tolerable daily intake (TDIs) for both PFASs were exceeded, however, only in a maximum exposure scenario. Blood monitoring of the local population near the FPP, and FPP workers, confirmed high exposure can occur as blood concentrations of several individuals exceeded the safe level. This paper provides a comprehensive overview on PFOA and GenX contamination close to point sources in the Netherlands.

1. Introduction

Per- and polyfluoroalkyl substances (PFASs) are man-made chemicals that are used for industrial processes as well as in consumer products (Buck et al., 2011). Since the production of PFASs since the 1950s, numerous classes of PFASs have been produced including homologues of perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonates (PFSAs), fluorotelomer alcohols (FTOHs) and perfluoroalkyl ether carboxylic acids (PFECAs) (Wang et al., 2017). Chemicals belonging to some of these homologue groups have been shown to possess persistent, bioaccumulative and/or toxic (PBT) characteristics. For example, based on the REACH Regulation (EU No 1907/2006), perfluorooctanoic acid (PFOA) is a PBT substance and in 2013 it was included in the Candidate list of Substances of Very High Concern (SVHC) (https://echa.europa.eu/nl/candidate-list-table, consulted 4 September 2019). Due to these PBT properties, production of several PFASs, such as PFOA or perfluorooctane sulfonate (PFOS), have been phased out in North America and Europe and replaced by other PFASs. An example of a PFOA replacement is GenX (trade name for 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoic acid). This substance has, however, itself been added to the SVHC Candidate List in 2019 because of the concern of having effects on the environment and humans (https://echa.europa.eu/nl/candidate-list-table, consulted 4 September 2019).

Primary emission sources of PFASs into the environment (water and air) are fluorochemical production plants (FPP), and once released into the environment via air or waste water, PFASs distribute to other abiotic media such as soil and sediment and accumulate into biota including in human food chains. Recent studies have shown that based on waste water or downstream surface water analyses, FPPs are emitting dozens of PFASs including PFCAs, PFSAs, but also per- and polyfluoroether carboxylic and sulfonic acids (PFECAs/PFESAs) (Gebbink et al., 2017; Liu et al., 2015; Song et al., 2018). These studies have shown that the local environment is contaminated to a larger extent

E-mail addresses: wouter.gebbink@PFAgroup.eu (W.A. Gebbink), stefan.vanleeuwen@wur.nl (S.P.J. van Leeuwen).
[1] Present address: PFA-Brussels Sprl, 1040 Brussels, Belgium.

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than sites further away from the FPP.

One of the FPP is located near the city of Dordrecht in the Netherlands and has been in production since the 1970s. In this production plant, fluoropolymers PTFE (polytetrafluoroethylene) and FEP (fluorinated ethylene propylene) have been produced using PFOA until 2012, after which it was no longer used. From 2013 onward GenX has been used as a replacement for PFOA for the production of fluoropolymers. An intense debate on the safety of the area around the FPP as a result from GenX and PFOA emissions developed over the last years, involving stakeholders like the fluoropolymer company, local and national authorities, the general public, institutes involved in risk assessment, environmental and food safety research, surface water organisations and drinking water organisations. This resulted in peer-reviewed literature and reports on the presence of PFOA and GenX in the Dutch environment (including surface and groundwater, soil and vegetation), and on human exposure to these two substances. Besides reports on monitoring data of PFOA and GenX in various environmental matrices, national authorities and institutes (National Institute for Public Health and the Environment, RIVM) also published reports setting PFOA and GenX risk limits for water (surface water, groundwater, drinking water) and soil, and tolerable intakes for human exposure (see Table 2 for specific risk limit and tolerable intake values).

The aim of this study was to review the emissions and waste stream from the FPP in the Netherlands, and to assess the contamination of the local environment near the FPP with PFOA and GenX relative to other locations in the Netherlands by using data published in the peer-reviewed literature as well as in the grey-literature. Besides environmental contamination, this review will also report on contamination of human exposure pathways (drinking water, food, blood monitoring) with PFOA and/or GenX on a local and national level. Finally, the results are assessed against national standards and/or guideline values for various matrices set by national regulatory bodies.

2. Methods

A literature search was made in the major databases (namely Web of Science, Scopus, Dioxin database on the Dioxin20XX website and Google search) to find published results on the occurrence of PFOA and GenX (or FRD-902/903 or 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy) propanoic acid (HFPO-DA)) in the Netherlands. Keywords used for the search included ‘perfluorooctanoic acid’ OR ‘PFOA’; ‘GenX’ OR ‘FRD-902/903’ OR ‘HFPO-DA’; Netherlands; ‘water’ OR ‘soil’ OR ‘sediment’: ‘food’ OR ‘drinking water’. Additionally, the official websites of the Dutch Government, institutes and companies were searched for additional reports in English and Dutch on PFOA and GenX occurrence in the Netherlands. This study contains studies published up until August 2019. The searches resulted in 12 peer-reviewed studies, 9 governmental reports and 19 company reports that reported on PFOA and/or GenX in the Netherlands. Many of the publications reported on concentrations of other chain length PFCAs and PFSAs, however, they are not mentioned in this review as they fall outside of the scope of this review.

3. PFOA and GenX emissions and waste streams

From the FPP in Dordrecht, PFOA and GenX are emitted to the air and water (waste and surface water). Information of emissions of PFOA to air is limited, while no information on emissions to (waste) water were found. PFOA emissions via air were reported for the period of 1985 until 2012 (although no data were available for several individual years between 1985 and 1997) (van Poll et al., 2017; Zeilmaker et al., 2016). In 1985, approximately 2500 kg PFOA was emitted to the air, and the emission peaked in 1995 at approximately 6800 kg. Since 1995, PFOA emissions gradually decreased to 134 kg in the last year of its usage. The cumulative emissions to air based on the years for which there was data available was approximately 36 tonnes. Emissions of PFOA to waste or surface water have not been reported. However, a report estimated historic surface water concentrations and found that downstream of the FPP PFOA concentrations peaked around the year 2000 at concentrations in the range of 200 ng/L (Nauta and Roelandse, 2016). Information on GenX emissions and releases are described in more detail in recent publications. A report published in 2018

Table 1
Concentration range in ng/L (number of samples analysed) of PFOA and GenX reported in surface water taken at sampling sites located downstream from the FPP, upstream from the FPP or at other locations in the Netherlands.

Sampling year	Sampling sites upstream from FPP[a]		Sampling sites downstream from FPP[a]		Other sampling sites[a]		References
	PFOA	GenX	PFOA	GenX	PFOA	GenX	
2006					5.0–32 (26)		(RIWA-Rijn, 2007)
	12 (3)						(McLachlan et al., 2007)
2007					5.0–11 (13)		(RIWA-Rijn, 2008)
2008	2.9–3.4 (3)		1.9–38 (12)		2.6–23 (17)		(Möller et al., 2010)
	3.0–6.0 (9)				5.0–11 (8)		(RIWA-Rijn, 2009)
2009	2.0–9.0 (13)				3.3–6.0 (8)		(RIWA-Rijn, 2010)
2010	3.6 (14)				1.8–10 (108)		(Eschauzier and de Voogt, 2014)
	2.0–10 (13)				5.0–5.9 (8)		(RIWA-Rijn, 2011)
2011	3.2 (14)		22 (13)		2.5–26 (134)		(Eschauzier and de Voogt, 2014)
	< 1–8.0 (13)				< 1–5.3 (21)		(RIWA-Rijn, 2012)
2012	3.9 (14)		22 (13)		3.3–31 (142)		(Eschauzier and de Voogt, 2014)
	< 1–6.0 (13)				1.6–5.5 (13)		(RIWA-Rijn, 2013)
2013	5.4–8.9 (5)	< 0.5–0.75 (5)	5.6–7.5 (3)	< 0.5–91 (3)	5.7–6.3 (2)	< 0.5 (2)	(Heydebreck et al., 2015)
	2.0–4.0 (13)		1.6–2.9 (4)		< 1–7.9 (39)		(RIWA-Rijn, 2014)
2014	< 1–4.0 (13)		1.8–3.6 (12)		1.8–5.1 (39)		(RIWA-Rijn, 2015)
2015	2.0–5.0 (13)		1.9–4.0 (13)		1.5–5.9 (39)		(RIWA-Rijn, 2016)
2016	2.8–3.0 (3)	< 0.2–22 (3)	3.5–12 (13)	1.7–812 (13)	2.9–3.0 (2)	< 0.2 (2)	(Gebbink et al., 2017)
	< 1–6.0 (13)		1.8–2.8 (4)		1.8–5.3 (39)		(RIWA-Rijn, 2017)
	2.7–2.9 (3)	0.59–2.0 (3)			2.8–3.4 (3)	0.66–1.5 (3)	(Pan et al., 2018)
2017		< 1 (1)		1–128 (9)		< 1–47 (34)	(Versteegh and de Voogt, 2017)
	< 1–4.0 (13)		2.0–2.7 (18)	1.6 (8)	1.1–5.2 (39)		(RIWA-Rijn, 2018)
	1.4 (3)	< 6 (3)	1.2–3.7 (9)	< 12–102 (9)	1.1–11 (12)	< 6–35 (12)	(Rijkswaterstaat. 2017)
2018					< 20–4900 (8)	< 20–6800 (8)	(van Bentum et al., 2018b)
	< 1–4.0 (12)	< 10 (8)	1.9–3.4 (24)	0.11–0.67 (24)	1.4–4.9 (39)	< 0.1–1.1 (39)	(RIWA-Rijn, 2019)

Note: where possible, average concentrations were generated for a specific location when multiple measurements were performed at that site within a study.
[a] See Fig. 1 for location of upstream and downstream sampling sites. “Other sampling sites” are sampling sites not located up- or downstream from the FPP.

estimated a mass balance for the use of GenX in the FPP and stated that approximately 55% of the GenX used for fluoropolymer production goes into the waste stream (incineration), 40% is recycled, while the emission to water and air were estimated at approximately 4% and 1%, respectively (ILT, 2018). This means that with a reported usage of 50.000 kg in 2017, approximately 2000 kg and 500 kg were emitted to water and air, respectively. Approximately 0.5% of the used GenX is not removed from the fluoropolymers and end up in endproducts. Although not reported specifically for PFOA, most likely a similar mass balance at the FPP as for GenX would have existed until the end of its usage in 2012.

In order to monitor the emissions of GenX and PFOA at the FPP via water, a monitoring program was run early 2017 with samples being taken every couples of days during a 2 month period (Rijkswaterstaat, 2017). Waste streams that were directly emitted to surface water contained on average 0.15 μg/L PFOA and 2.2 μg/L GenX. Both PFASs were also indirectly emitted to surface water, meaning that waste water was first treated in an on-site waste water treatment plant (WWTP) followed by a municipal WWTP, which also processes waste water from the local community. Concentrations of PFOA and GenX in effluent from the municipal WWTP were 0.27 and 375 μg/L, respectively. Two additional on-site sampling locations were also monitored, i.e. the effluent of the on-site WWTP (which feeds an on-site collection pond) and the effluent of the collection pond (which feeds the municipal WWTP). The effluent of the on-site WWTP contained on average 0.014 and 134 μg/L for PFOA and GenX, respectively, while the effluent of the collection pond contained on average 1.5 and 2600 μg/L for PFOA and GenX, respectively. The higher concentrations in the effluent of the pond compared to the effluent from the on-site WWTP (influent pond) are likely the result of untreated wastewater discharge from other on-site activities, as well as from discharge from cleaning activities into the pond. Based on the monitoring data, concentrations of PFOA are comparable in direct and indirect releases to surface water, however, for GenX, concentrations in indirect releases to surface water were about two orders-of-magnitude higher compared to concentrations in direct releases. This can be explained by the fact that waste water for indirect releases of GenX to surface water can contain up to 1000 times higher concentrations than in waste water directly released to surface water. As there is poor removal of GenX in the municipal WWTP, the GenX concentrations in WWTP effluent remain elevated and subsequently higher compared to direct releases. It should be noted that concentrations reported during the study period were highly variable depending on the sampling site, relative standard deviations for PFOA ranged from 24 to 171% and for GenX from 26 to 303%. This could likely be linked to day-to-day differences in the production process.

4. Environmental presence of PFOA and GenX

4.1. Surface water

The presence of PFOA in surface water in the Netherlands has been reported since 2006, and there are published peer-reviewed articles or national institutional reports that have reported data providing yearly data at multiple location in main rivers and waterbodies, such as the rivers Rhine, Lek, Waal, IJssel, and Meuse, as well as in Lake IJssel and in the Scheldt delta (Table 1). The monitoring of GenX in Dutch surface water started more recently. The first reporting was in 2013, after which it was reported only during the 2016–2018 (Table 1).

In order to determine the influence of the FPP on the concentrations of PFOA and GenX in Dutch surface water, the sampling locations in the literature were grouped in upstream from the FPP, downstream from the FPP and other locations. Upstream sampling sites were located on the rivers Boven Merwede, Waal and Rhine, the downstream sites were located on the rivers Noord, Nieuwe Maas, Het Scheur, Nieuwe Waterweg, Oude Maas, Hollands Diep and Haringvliet (Fig. 1). Sampling sites on any other river or waterbody was grouped as 'Others'. In the earlier years of the 2006–2018 period, no data on PFOA were available for downstream sites with the exception of 2008, while for upstream and other sampling sites data was available for almost all years (Table 1). In upstream sites, the PFOA concentration that was reported between 2006 and 2018 ranged from < 1 to 12 ng/L, at downstream locations the concentration range was greater and varied from < 1 to 38 ng/L, while the concentration range at other sites varied from < 1 to 4900 ng/L (see Table 1 for concentration ranges per year and references).

Up to and including 2012, PFOA concentrations found at downstream locations were generally higher compared to upstream locations. Möller et al. (2010) reported that in samples taken in 2008, upstream samples contained between 2.9 and 3.4 ng/L, while downstream sites contained up to 38 ng/L. In 2011 and 2012, PFOA concentrations were approximately a factor 6 higher in downstream sites compared to upstream (Eschauzier and de Voogt, 2014). Elevated PFOA concentrations that were reported at other locations indicate other sources. For example, in the river Scheldt downstream from Antwerp, Belgium, concentrations up to 31 ng/L were reported (Eschauzier and de Voogt, 2014; Möller et al., 2010). This could be explained by an FPP located in Antwerp (Olsen and Zobel, 2007). In 2018, PFOA concentrations up to 4900 ng/L were found in surface water near the city of Helmond (van Bentum et al., 2018b). In this municipality, a company was located that processed products originating from the FPP in Dordrecht and subsequently emitted PFOA. In local enclosed waterbodies (ponds) PFOA concentrations ranged from 170 to 4900 ng/L, while in local rivers this was from < 20 to 80 ng/L. After the phase-out of PFOA by the FPP in Dordrecht, concentrations between 2013 and 2018 appeared to have decreased compared to prior to the phase-out. During this post phase-out period PFOA concentrations downstream from the FPP ranged from < 1 to 12 ng/L and were in the range of concentrations found in upstream sites (< 1–8.9 ng/L) and at other sites (< 1–12 ng/L) (excluding the results reported near Helmond in 2018).

GenX was only detected at upstream locations in three studies. Heydebreck et al. (2015a,b) found GenX in the river Rhine by the Netherlands-Germany border at a low concentration (i.e. 0.75 ng/L) in 2013. The detection of GenX at sampling sites further upstream in Germany could explain the presence of GenX at this location in the Rhine in the Netherlands. This was corroborated by Pan et al. (2018) who found GenX at low concentrations (0.59–2.0 ng/L in surface water from upstream locations) and in the Rhine in Germany. Gebbink et al. (2017) detected GenX in surface water < 1 km upstream from the FPP at 22 ng/L in 2016. The tidal changes in the North Sea reverse the current in the rivers twice each day which could have resulted in the presence of GenX just upstream of the FPP. Two other reports that included upstream sites reported concentrations below the detection limit (Rijkswaterstaat, 2017; Versteegh and de Voogt, 2017). At downstream locations, higher concentrations were found relative to the upstream sites and ranged from < 0.5 to 812 ng/L. Heydebreck et al. (2015a,b) first detected GenX in 2013 downstream in the river Nieuwe Waterweg at 91 ng/L although at two other downstream sites GenX was not detected. In 2016, the spatial distribution of GenX downstream of the FPP was investigated at 13 locations (Gebbink et al., 2017). At all sites GenX was detected with concentrations between 1.7 and 812 ng/L and the highest concentration was found at the first sampling site downstream from the FPP. A generally declining trend was seen from this first site after the FPP to further sites downstream. In 2017 and 2018, no GenX was detected in upstream sampling sites, while at several downstream locations GenX was detected. One of these studies monitored GenX in several sampling sites in the region of the FPP and reported average concentrations for downstream sites up to 102 ng/L, concentrations were below the LOQ in an upstream site, and average concentrations ranged between < LOQ and 35 ng/L at other sites (Rijkswaterstaat, 2017). A second report also investigated the presence of GenX near the FPP but also performed a detailed survey on the river Meuse (Versteegh and de Voogt, 2017). GenX was detected in all downstream sites with

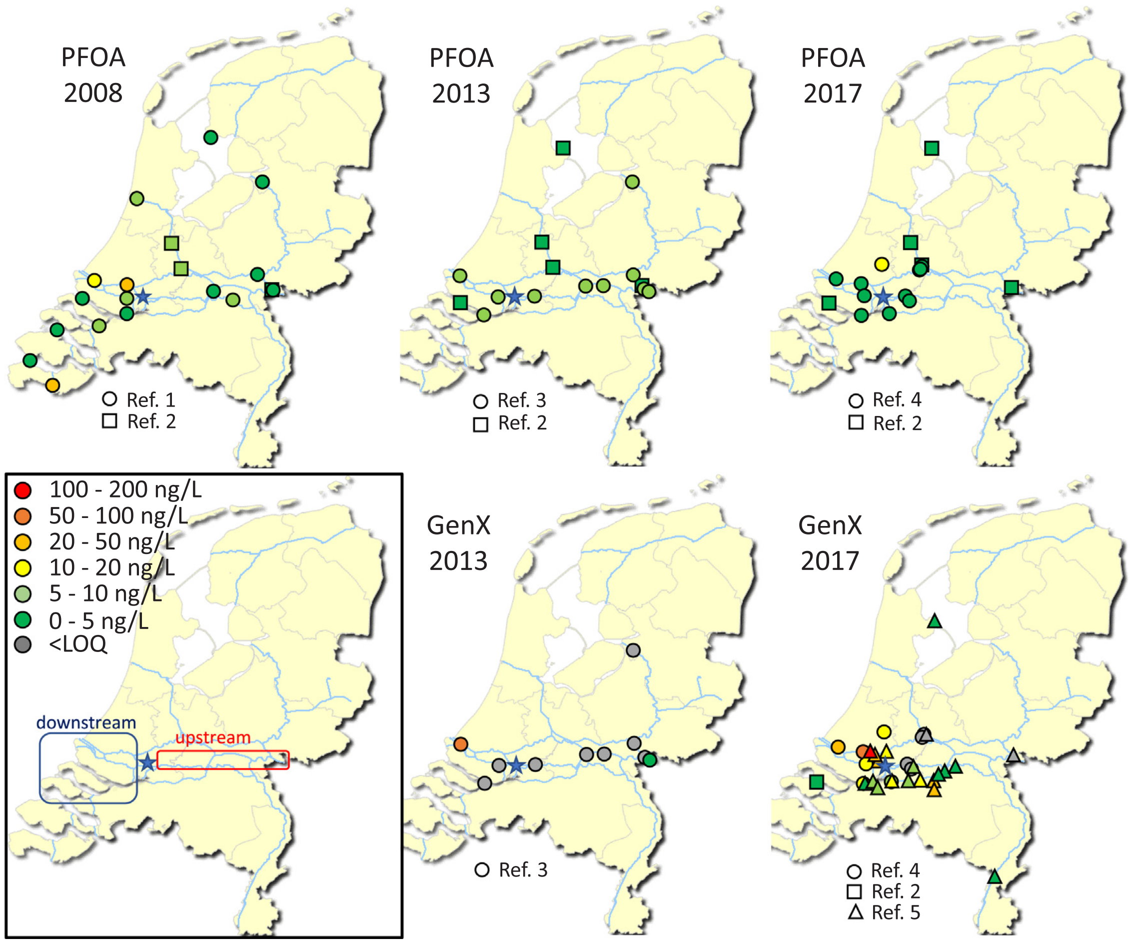

Fig. 1. Reported PFOA (top plots) and GenX (bottom plots) concentrations (ng/L) in surface water at different locations in main rivers and waterbodies in the Netherlands in 2008, 2013 and 2017. For 2008, no data on GenX in surface water is available. Major rivers are highlighted in blue, and the location of the FPP is indicated by the blue star. Data from references 1, 3 and 5 are represented by individual measurements, data from references 2 and 4 are represented by mean concentrations. References: 1. (Möller et al., 2010) 2. (RIWA-Rijn, 2009; 2014; 2018); 3. (Heydebreck et al., 2015a) 4. (Rijkswaterstaat, 2017); 5. (Versteegh and de Voogt, 2017). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the highest concentrations (61–128 ng/L) in samples collected at municipalities near the FPP (i.e. Papendrecht, Ridderkerk and Kinderdijk). At several of the sampling sites along the river Meuse concentrations of GenX ranged from < 1 to 9 ng/L, however, at specific sites concentrations up to 47 ng/L were found. The finding of elevated concentrations found at non-downstream locations indicate that there are other point sources of GenX. An example of this was shown in 2018, where GenX concentrations up to 6800 ng/L were found in surface water in Helmond. The same company that historically processed PFOA-containing products had also processed GenX-containing products and thereby contaminated the local environment, resulting in local pond contamination (40–6800 ng/L) and river (i.e. river Aa) contamination (< 20–50 ng/L) (van Bentum et al., 2018b).

When looking on a national level, PFOA concentrations in surface water declined over time as exemplified in Fig. 1. In 2008, when PFOA was still in use, concentrations up to 38 ng/L were found in surface water in the Netherlands, while in 2013 when PFOA was phased-out, the highest concentration reported in surface water was 8.9 ng/L. In 2017, the highest reporting of PFOA in surface water was 12 ng/L. Temporal changes of PFOA concentrations in surface water were further investigated for 3 specific sampling locations where sufficient data was available. It should be noted that not all reports from which data was used to estimate temporal changes (see Fig. 2) reported on the quality control of the analytical method. At the upstream site near Lobith on the river Rhine, PFOA concentrations overall declined between 2006 and 2017 (Fig. 2). Declining emissions from the FPP since the year 2000 (Zeilmaker et al., 2016) and likely other sources could explain this decline in surface water concentrations. PFOA concentrations also declined in samples collected near Nieuwegein on the river Lek between 2006 and 2017. Highest average concentrations were reported in 2006 (i.e. 7 ng/L) and there was a gradual decline until 2017 when an average of 2.3 ng/L was reported. At the downstream location in the Haringvliet data were available for 2008 and 2011–2017, and at this site no clear trend in the PFOA concentration was observed. Overall the PFOA concentrations in Dutch surface water declined over time. Although the phase-out of the PFOA use by the FPP played a role in this decline as concentrations declined at downstream sites, the phase-out of PFOA (and its precursors) by industry in general in 2012 also likely contributed to the general decline in Dutch surface water, including upstream and other sampling sites. Since the use of GenX and the first monitoring in Dutch surface water in 2013, concentrations throughout the Netherlands have increased in surface water from 2013 to 2016/2017 (Table 1, Fig. 1), although it should be mentioned that in recent years the extent of monitoring has increased considerably.

4.2. Groundwater

Both PFOA and GenX were reported in groundwater in the Netherlands, whereby atmospheric deposition of PFOA and GenX as well as surface water are potential sources of groundwater contamination. The presence of PFOA and GenX in groundwater was mainly monitored in samples collected in the region of the Netherlands

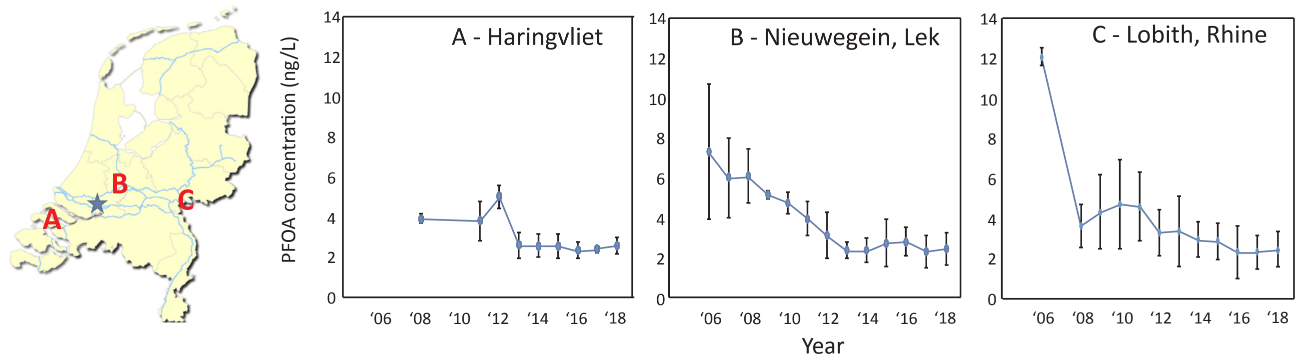

Fig. 2. Temporal changes of PFOA concentrations (mean ± SD) between 2006 and 2017 in surface water collected at three different sampling location in the Netherlands. Data sources Lobith: Heydebreck et al., 2015; McLachlan et al., 2007; Möller et al., 2010; Eschauzier and de Voogt, 2014; RIWA-Rijn, 2007; data sources Nieuwegein: Eschauzier and de Voogt, 2014, Rijkswaterstaat, 2017, RIWA-Rijn, 2007-2019; data sources Haringvliet: Eschauzier and de Voogt, 2014, Möller et al., 2010, RIWA-Rijn, 2007-2019.

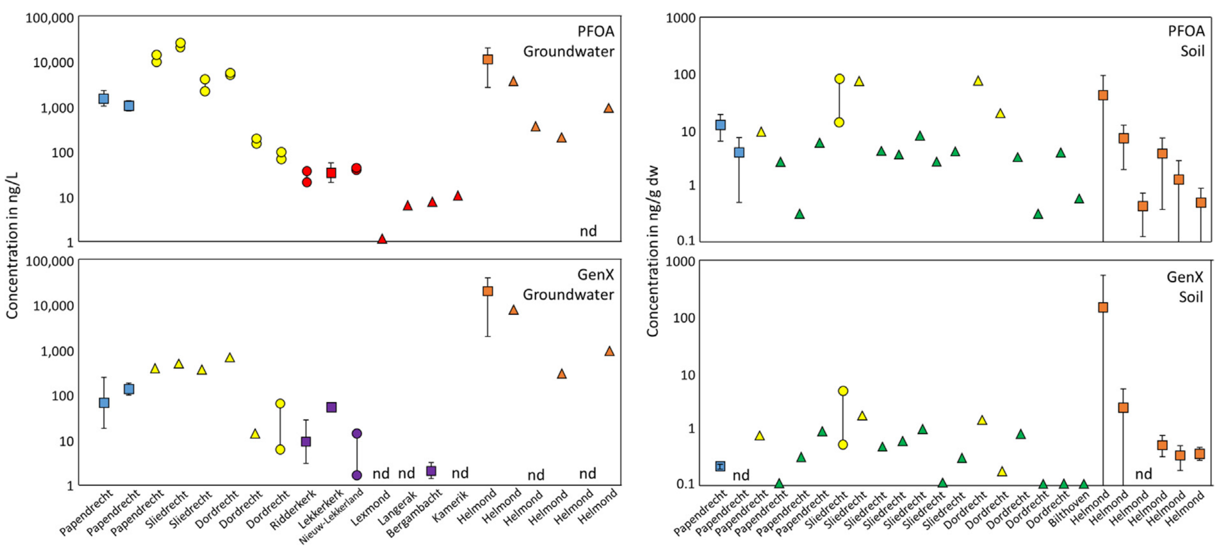

Fig. 3. Reported concentrations of PFOA and GenX in groundwater and soil at different locations in the Netherlands. Concentrations displayed as squares represent mean ± SD, connected circles represent the range of 2 measurements and triangles represent a single measurement. The colours indicate the source of the data: Blue – (Francken, 2018); Yellow – (van Bentum et al., 2017); Red – (Nauta and Roelandse, 2016); Purple – (Roelandse and Timmer, 2017); Orange – (van Bentum et al., 2018b); Green – (RIVM, 2018). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

where the FPP is located. In three studies, groundwater was collected in 2017 and 2018 in bordering municipalities to the FPP, i.e. Papendrecht, Sliedrecht and Dordrecht (van Bentum et al., 2018a; van Bentum et al., 2017; Francken, 2018). At sampling locations within 2 km distance from the FPP, PFOA was found in the µg/L concentration range with concentrations reaching 25 µg/L (Fig. 3). Locations further away from the FPP contained lower PFOA concentrations, which were between 66 and 190 ng/L. GenX concentrations reported in these studies were lower compared to PFOA. At the sampling locations < 2 km from the FPP, GenX concentrations ranged from 100 to 660 ng/L in the groundwater, whereas at sampling sites further away (4–5 km distance) the concentrations were between 6 and 66 ng/L. Van Bentum et al. (2018a) investigated PFOA and GenX concentrations in samples taken in six different directions from the FPP (N, NE, E, S, SW and W) up to 10 km distance. PFOA concentrations ranged between < 5 and 3400 ng/L, while GenX was only detected in 20% of the samples with concentrations ranging between < 10 and 200 ng/L. Highest concentrations were generally found in the North wind direction, although closest sampling location to the FPP in other directions contained elevated concentrations. Other studies reported on both chemicals in groundwater collected in 2016/2017 from municipalities further away (10–50 km) from the FPP (Nauta and Roelandse, 2016; Roelandse and Timmer, 2017). Both PFOA and GenX concentrations reported in these studies were lower compared to the previous mentioned studies with sampling sites closer to the FPP (Fig. 3). PFOA concentrations were between 1 and 59 ng/L, while GenX concentrations ranged from 1 to 73 ng/L. Generally higher concentrations of PFOA and GenX were seen in samples collected from municipalities downstream from the FPP (i.e. Ridderkerk, Lekkerkerk and Nieuw-lekkerland) and decreased with further distance from the FPP. Groundwater samples analysed for these reports are used for drinking water production. A report published in 2018 by van Bentum et al. reported on PFOA and GenX concentration in groundwater collected in the municipality of Helmond (van Bentum et al., 2018b). As mentioned earlier, the local environment was contaminated due to emissions from a company that processed PFOA and GenX-containing products. At six sampling locations, PFOA concentrations were between < 0.02 and 9.8 µg/L (Fig. 3) with the highest concentrations found at the sampling closest to the company and concentrations declining at greater distance from the company in a downwind direction. GenX concentrations at these sampling sites ranged between 0.02 and 18 µg/L (Fig. 3) and a comparable distribution was seen as for PFOA, i.e. highest concentrations closest to the company and declining concentrations with greater distance. The groundwater contamination with PFOA in Helmond is in the same range as municipalities close by the FPP, whereas the groundwater contamination with GenX in Helmond is at some sampling sites higher than the groundwater contamination in municipalities nearby the FPP.

4.3. Soil

Four studies investigated soil contamination of PFOA and GenX in municipalities near the FPP. The local contamination of the soil is primarily caused by deposition of PFOA and GenX from the air. In a study by van Bentum et al. (2017) core samples were taken at 5 locations in Dordrecht, Sliedrecht and Papendrecht. At most locations the top 10 cm of soil was analysed, while at sites 2 and 3 deeper soil samples were also analysed. PFOA concentrations ranged between 9 and 84 ng/g dry weight (dw) and GenX concentrations ranged between 0.18 and 4.7 ng/g dw (Fig. 3). PFOA concentrations were consistently higher in the soil samples compared to GenX ranging by a factor of 3 to 165. In a follow up study, soil samples were collected in different wind directions from the FPP (N, NE, E, S, SW and W) and PFOA concentrations in the top soil ranged between 0.23 and 64 ng/g dw (van Bentum et al., 2018a). GenX was only detected at one location within 1 km distance from the FPP at 1.9 ng/g dw. As was seen for groundwater concentrations reported in the same study, the highest PFOA concentrations in soil were seen in a North and Northeast wind direction from the FPP. A third report investigated the presence of PFOA and GenX in soil from the city of Papendrecht where at 2 locations several samples were taken in 2018 (Francken, 2018). PFOA concentrations at the first location were between 4.9 and 21 ng/g dw (mean is 12 ng/g dw), while GenX was only detected in half the samples between 0.12 and 0.16 ng/g dw. At the second location PFOA concentrations ranged from 1.0 to 10 ng/g dw (mean is 4 ng/g dw), and GenX was below the LOQ in all the samples. At both locations higher concentrations were found in top soil samples (0–0.5 m); samples taken at a greater depth (up to 1.7 m depth) generally contained less PFOA. A fourth study performed in 2018 also investigated soil contamination in local vegetable gardens in the vicinity of the FPP (Fig. 3) (RIVM, 2018). The soil samples originated from 11 local gardens less than 4 km away from the FPP and 1 control location in central Netherlands. At all locations homogenate samples were analysed of the top 30 cm soil. The PFOA concentrations in soil collected nearby the FPP ranged from 0.3 to 7.7 ng/g dw, whereas the control location contained 0.6 ng/g dw. The highest reported GenX concentration was 1.0 ng/g dw and the lowest was 0.1 ng/g dw. With the exception of one location where concentrations of both PFASs were the same, PFOA concentrations were higher than GenX at all the other locations by a factor of 3 to 37. In the study performed in Helmond (van Bentum et al., 2018b), PFOA concentrations at the sampling locations were on average between 0.5 and 41 ng/g dw (Fig. 3). A similar pattern compared to the distribution among the groundwater sampling location was seen for the soil samples, with the highest concentration closest to the company. The GenX concentrations in the soil samples ranged from < 0.1 to 132 ng/g dw (Fig. 3). The distribution of GenX in soil followed a similar distribution compared to GenX in groundwater and PFOA in soil and groundwater.

PFOA concentrations in Helmond soil were comparable to soil samples collected in municipalities bordering the FPP. For GenX, the closest sampling location near the company in Helmond contained by far the highest concentrations compared to all other sampling sites. These remaining sites contained comparable GenX concentrations regardless of location, i.e. nearby the FPP or in Helmond. In all studies, the highest concentration of both chemicals was measured in samples collected < 1 km or 1–2 km distance away from the source (FPP or company in Helmond). Van Bentum et al. (2017) reported the lowest concentrations in the soil samples taken the furthest away from the FPP (4–5 km), however, this clear trend was not observed among all the locations (RIVM, 2018). For example, locations with 1–2 km distance from the FPP contained lower concentrations relative to sites 2–4 km distance from the FPP, although all concentrations were low (i.e. < 1 ng/g dw). Potential deposition further down wind could have resulted in these (slightly) higher concentrations at farther sampling sites. Air deposition was identified as a major source of the soil contamination near the FPP and in Helmond, and van Bentum et al. (2017) reported on a similarity in soil concentrations relative to modelled air concentrations around the FPP (Zeilmaker et al., 2016), although irrigation could have been an additional source for some soil samples (RIVM, 2018).

4.4. Vegetation (leaves and grass)

In 2018, a study was published that determined the presence of PFOA and GenX in leaves and grass collected near the FPP in order to investigate the ongoing and historic emission of GenX and PFOA (Brandsma et al., 2019). Leaves and grass were collected at different distances nearby the FPP, ranging from 50 until 3000 m downwind from the FPP. Control samples were also collected from a control site at 85 km distance from the FPP. Within the 3 km distance, GenX and PFOA were detected in all the leaves and grass samples, and for both chemicals the highest concentrations were found in samples collected at 50 m from the FPP. At a distance of 50 m GenX concentrations in the grass and leaves were 26.6 and 86.5 ng/g, respectively, while PFOA concentrations were lower, i.e. 10.9 and 27.9 ng/g, respectively. Declining concentrations were observed with increasing distance from the FPP, and at 3 km GenX and PFOA concentrations were generally 15–25 times lower compared to 50 m. At the control site, reported concentrations were either below or just above the LOQs. With the exception of one sample, GenX concentrations were higher compared to PFOA concentrations in the same samples by a factor of 2–17. This could be the result of ongoing emissions of GenX. Only in leaves collected at 3 km distance was the concentration of PFOA greater than GenX. A strong correlation was observed between the GenX concentrations in leaves and grass collected at the same location ($r = 0.986$), whereas this correlation was less profound for PFOA ($r = 0.591$). This could be due to differences in uptake for the two PFASs (i.e. air deposition or uptake from the soil). In the grass samples, a strong correlation between the two PFASs was seen ($r = 0.975$), while this was less profound in leaves ($r = 0.724$). Besides direct emission from the FPP for GenX, accumulation from contaminated soil and/or groundwater could be a source of the PFOA and GenX contamination. The study mentioned the presence of a waste incinerator near by the FPP which could also be a potential source of these chemicals. The different sources could have resulted in the lack of correlation between the PFASs in the investigated samples.

5. Human exposure to PFOA and GenX

5.1. Drinking water

The presence of PFOA in drinking water was first reported in samples collected in Amsterdam in 2010 and 2011, with average concentrations of 7.1 and 3.7 ng/L, respectively (Eschauzier et al., 2013a; Ullah et al., 2011). Subsequently, a nationwide survey on PFOA in drinking water was performed in 2013/2014 by Zafeiraki et al. (2015) which included 37 sampling locations. In 24 of the samples PFOA concentrations were < LOQ, in the remaining 13 samples the concentration ranged from 1.4 to 11 ng/L. Two other studies investigated the presence of PFOA in drinking water collected in 2016 in the vicinity of the FPP (Gebbink et al., 2017; Nauta and Roelandse, 2016). Drinking water collected at drinking water treatment plant (DWTP) or from city halls in several municipalities (Dordrecht, Papendrecht, Zwijndrecht, Ridderkerk, Lekkerkerk) contained concentrations up to 23 ng/L PFOA. Brandsma et al. (2019) also investigated the presence of PFOA in drinking water obtained in 2016 from municipalities close to the FPP and from downstream areas of the FPP, and concentrations ranged between 1.9 and 7.1 ng/L.

Recently, several reports and peer-reviewed publications reported on the presence of GenX in drinking water in samples collected from 2016. Gebbink et al. (2017) investigated the presence in GenX in drinking water from four municipalities near the FPP and at 2 control municipalities > 50 km from the FPP. Of the four municipalities, drinking water from three of them contained GenX > LOQ and the concentrations ranged from 0.25 ng/L in Zwijndrecht until 11 ng/L in Papendrecht. In Sliedrecht and the 2 control locations no GenX was detected in the drinking water. In 2016 and 2017, ten drinking water companies performed a survey on the presence of GenX in drinking water from across the Netherlands (Roelandse and Timmer, 2017; Versteegh and de Voogt, 2017). At total of 47 locations were analysed and at 15 of them GenX was > LOQ with the highest concentration at 29 ng/L at Ridderkerk. At the 32 remaining locations the GenX concentrations were < LOQ, which was reported to vary between 0.1 ng/L and 5 ng/L. In 2019, Brandsma et al. (2019) reported on the presence of GenX in drinking water collected in 2016 from sampling sites that included municipalities nearby and downstream from the FPP. Concentrations in drinking water from downstream areas (3.1–8.0 ng/L) were higher compared to drinking water samples collected further away (1.4–1.8 ng/L).

Fig. 4 shows the distribution of PFOA and GenX in drinking water across the Netherlands based on all the samples. For both PFASs, drinking water in the western part of the Netherlands (provinces of North and South Holland and Zeeland) contained concentrations > LOQ, while in central and eastern Netherlands concentrations were in most cases < LOQ. The highest concentrations of PFOA (up to 23 ng/L) and GenX (up to 29 ng/L) were found in drinking water collected from municipalities nearby the FPP. In the western part of the Netherlands surface water together with groundwater are used for drinking water production while in central and eastern parts of the Netherlands only groundwater is used for drinking water production. The presence of PFOA and GenX in surface water and groundwater together with the poor removal during drinking water treatment (Sun et al., 2016) could explain elevated concentrations in drinking water collected from the western part of the Netherlands.

5.2. Food (Fruit and Vegetables)

In 2017–2018, 2 studies were published investigating the presence of PFOA and GenX in fruit and vegetables from local vegetable gardens near Dordrecht and Helmond in order to determine the exposure of the local population that is consuming these fruits and vegetables. The presence of PFOA and GenX in fruit and vegetables could originate from atmospheric deposition and/or through uptake from the soil. Near the FPP in Dordrecht, root vegetables (beets, carrots, potatoes), leafy vegetables (celery, endive, lettuce), fruit vegetables (tomatoes, zucchini, cucumber, bell pepper, pumpkin) and fruit (apple, pear) were collected in 2017 from one or more vegetable gardens in the municipalities of Dordrecht, Papendrecht and Sliedrecht, and from 1 control site (Mengelers et al., 2018). Two of the vegetable gardens were located within 1 km from the FPP, six gardens within 1–2 km, one garden within 2–3 km and 3–4 km and the control garden was > 50 km distance from the FPP. In total 81 samples were analysed for GenX and PFOA. GenX was detected above the LOQ in five vegetables (beets, celery, endive, lettuce and tomatoes) from 3 gardens and concentrations were between 1.1 and 5.4 ng/g. PFOA was only detected in beets from one garden at concentrations ranging from 1.7 to 2.5 ng/g. Only in the beet samples, GenX and PFOA were both detected at comparable concentrations. The three gardens where GenX and/or PFOA was detected were located in the municipalities of Dordrecht and Sliedrecht, and were located either < 1 km (Sliedrecht) or 1–2 km (Dordrecht) distance from the FPP. In fruit and vegetables collected from other vegetable garden further away, including the control site, no PFOA and GenX were detected above the LOQs.

In the second study, a total of 87 vegetables were collected in 2018 from vegetable gardens near (< 500 m) the company in Helmond that processed products from the FPP (Boon et al., 2019). As in the above mentioned study, root vegetables (beets, carrots, potatoes), leafy vegetables (celery, lettuce), fruit vegetables (tomatoes, zucchini, cucumber, bell pepper) and bulb vegetables (onion) were collected and analysed for PFOA and GenX. Out of the 21 pooled samples analysed, PFOA was detected in 12 pooled samples with concentrations ranging between 0.10 (cucumber) and 2.5 ng/g (kale). GenX was detected in 18 pooled samples with concentrations ranging between 0.15 ng/g (onion) and 8.0 ng/g (green beans). In almost all samples, GenX concentrations were higher compared to PFOA concentrations with the exception of carrot. Concentrations of both PFASs in the vegetables from this study were generally lower in the same vegetables as in the samples collected near the FPP (Mengelers et al., 2018).

Using the PFOA and GenX concentrations found in the vegetables, risk assessments were performed in both studies on GenX and PFOA exposure for the local population consuming these fruits and vegetables. Results from fruits and vegetables were grouped as root vegetables, leafy vegetables, fruit vegetables and fruit, and exposure

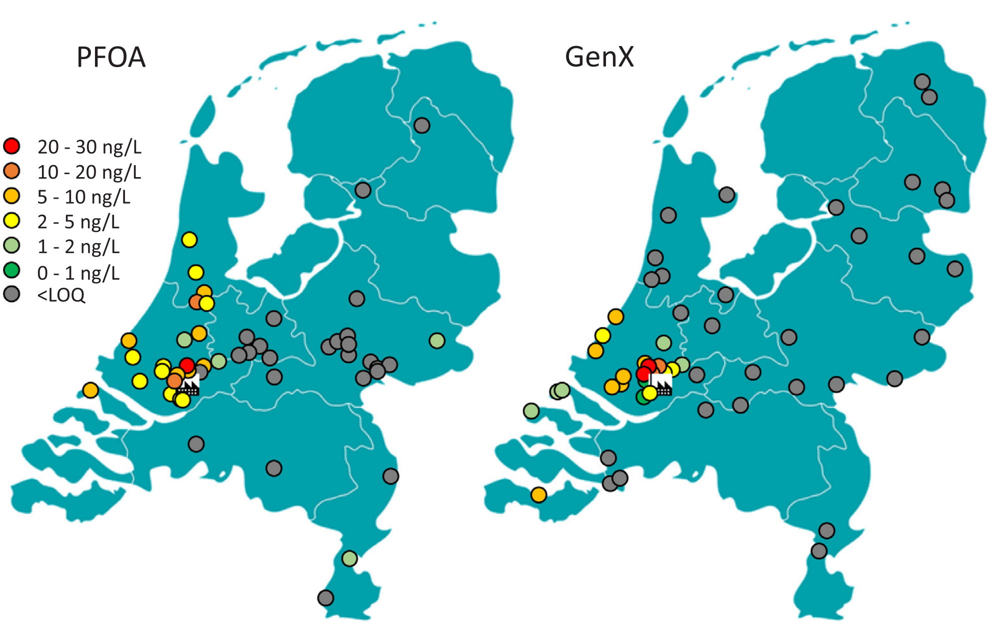

Fig. 4. Average reported PFOA (left plot) and GenX (right plot) concentrations (ng/L) in drinking water from different locations in the Netherlands. PFOA concentrations are based on samples collected between 2010 and 2016, GenX concentrations are based on samples collected during 2016 and 2017. The reported LOQs for PFOA varied from 0.05 to 1 ng/L; the reported LOQs for GenX varied from 0.1 to 5 ng/L. (Brandsma et al., 2019; Eschauzier et al., 2013b; Gebbink et al., 2017; Nauta and Roelandse, 2016; Roelandse and Timmer, 2017; Ullah et al., 2011; Versteegh and de Voogt, 2017; Zafeiraki et al., 2015).

estimates were estimated in a minimum and maximum exposure scenario using the lowest and highest concentrations found per food group. The assumption was made that the local population was consuming fruit and vegetables from their gardens year round. Using the highest concentrations (maximum exposure scenario), the exposure estimates for GenX near the FPP was 7.6 ng/kg bw/day based on average intake values, while using the P95 value for the intake the exposure estimate was determined at 21 ng/kg bw/day. In the same maximum scenario the exposure estimates for PFOA based on average and P95 intake values were 4.3 and 12 ng/kg bw/day, respectively. Based on the vegetables from Helmond, exposure estimates were lower compared to Dordrecht data, based on a worst-case scenario (using the highest concentrations and P95 values for intake) the exposure estimates were 15 and 4.6 ng/kg bw/day for GenX and PFOA, respectively.

A report published by the Dutch Food and Consumer Product Safety Authority (NVWA, 2019) investigated the presence of PFOA and GenX in dairy food chain in the Dordrecht and Helmond areas. Through deposition and subsequent contamination of soil, grass and water, PFOA and GenX could have entered the food chain. The following samples were collected in 2018: ditch water and silage, cow and goat milk, cheese, yoghurt and chicken eggs from the Dordrecht and Helmond area. A carp was also collected from a fishing pond in Helmond. Average concentrations in ditch water were 1.2 and 0.24 µg/L for PFOA and GenX, respectively with the highest concentrations in samples closest to the FPP. Only PFOA was detected in the silage with a highest concentration of 0.6 ng/g. PFOA was detected at 0.14 ng/g in eggs, while in the carp both PFOA and GenX were detected at 1.3 and 4.7 ng/g. In all other samples (milk, cheese, yoghurt) both PFASs were below the detection limit. Based on these concentrations, the highest exposure intakes were estimated based on fish consumption and were 1.5 and 5.4 ng/kg bw/day for PFOA and GenX, respectively.

5.3. Human blood monitoring

Several studies reported on human blood monitoring of PFOA in the Netherlands, while data on human blood monitoring of GenX was not found. Human exposure to PFOA could occur through multiple exposure pathways and include the above-mentioned drinking water and food (fruit and vegetables), however, inhalation of air and ingestion of dust have also been identified as exposure pathways (Gebbink et al., 2015a). A report published in 2017 investigated the presence of PFOA in human blood (sampled in 2016) of people living in the vicinity of the FPP (van Poll et al., 2017). A total of 382 people were divided in four groups: 1) people living prior to 2003 in the near vicinity of the FPP (approx. 1 km diameter from the FPP); 2) people living prior to 2003 in the vicinity of the FPP (approx. 2 km diameter from the FPP); 3) people living within the 2 km diameter from the FPP since 2003; and 4) people living at a distance of 6.5 km from the FPP, this group served as a control group. People who worked at the FPP were not included in this study. Highest PFOA concentrations were found in blood from people belonging to Group 1, median PFOA concentration was 10.2 ng/ml, however, concentrations as high as 147 ng/ml were reported (Fig. 5). Median PFOA concentrations declined in the individuals living further away from the FPP (Group 2) or were only living in the study area since 2003 (Group 3), i.e. 3.4 and 2.8 ng/ml respectively. In the control group, a median concentration of 3.4 ng/ml was found. Median concentrations in Group 1 were reported to be significantly higher compared to Groups 2, 3 and 4 ($p < 0.001$), while the concentration in Group 2 was only significantly higher compared to Group 3 ($p = 0.02$). Exposure via air was indicated as a primary exposure pathway for people belonging to Groups 1 and 2 as the measured concentrations were comparable to modelled concentration based on emission to air for the local population near the FPP.

Two other studies reported on PFOA concentrations in blood. Quaak et al. (2016) reported on PFOA in cord blood samples from a rural area from the Dutch mother-child cohort LINC (Linking Maternal Nutrition

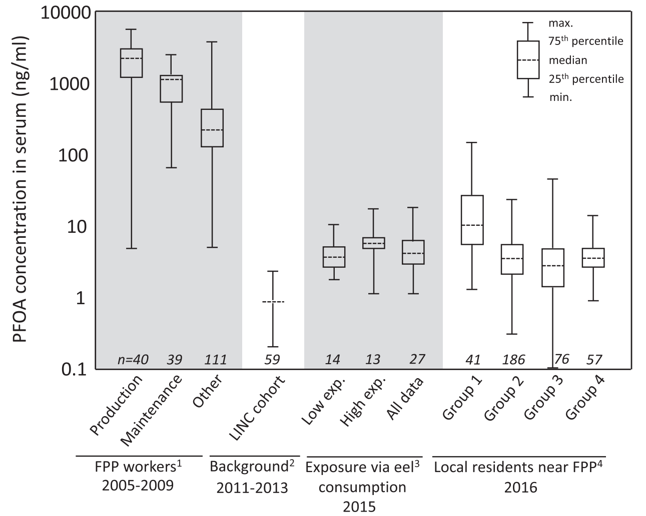

Fig. 5. Reported measured concentrations of PFOA in human serum (ng/ml) collected in the Netherlands: 1) production, maintenance or other type of workers at the FPP (Dupont, 2009); 2) women living in a rural area (LINC cohort) (Quaak et al., 2016); 3) men exposed via eel consumption from high and low contaminated areas (van den Dungen et al., 2016); 4) local residents living near the FPP (van Poll et al., 2017). Years in which the samples were collected are provided. Quaak et al. did not report the 25th and 75th percentile PFOA concentrations in the LINC cohort. The number of samples analysed (n) per study are provided in italics.

to Child Health). In cord blood samples, taken between 2011 and 2013, the median PFOA concentration was 0.87 ng/ml, with a range of 0.20–2.3 ng/ml. Since the women lived in a rural area, these concentrations can be considered as a background exposure group. It should be noted that levels in cord blood serum can be 15–20% higher than in maternal serum (Chen et al., 2017), and levels in males can be 20–25% higher than in females (Siebenaler et al., 2017). Median concentrations in this background exposure group were lower compared to median concentrations found in all local resident groups living nearby the FPP (Fig. 5). van den Dungen et al. (2016) reported on PFOA concentrations in Dutch men with potentially higher exposure due to eel consumption. This study compared PFOA blood concentrations in men consuming eel from high-polluted areas or were consuming eel from aquaculture and relatively low-polluted areas in the Netherlands. Median concentrations in the blood (sampled in 2015) from the low- and high-exposure groups were 3.6 and 5.5 ng/ml, respectively, while maximum concentrations in both exposure groups were 10 and 18 ng/ml, respectively. Although the median concentration in the high-exposure group was higher compared to the low-exposure group, this difference was not significant ($p = 0.06$). Median PFOA concentration using data from both exposure groups (i.e. 4.2 ng/ml) was higher compared to the concentrations reported in the cord blood by Quaak et al. (2016) but were in the same range as was found in Group 2 reported by van Poll et al. (2017) (Fig. 5).

A fourth report reported on the presence of PFOA in serum from FPP workers in Dordrecht between 2005 and 2009 (Dupont, 2009). Workers were grouped in ‘production’, ‘maintenance’ and ‘other’ (administration, technology personnel or outside exposure groups) categories. Median PFOA concentration in production workers were higher compared to maintenance and other workers, i.e. 2.2 µg/ml and with a maximum of 5.6 µg/ml. Median concentrations of PFOA in maintenance and other workers were higher compared to the results from the three previously mentioned studies (Fig. 5). Although it should be noted that the worker exposure was assessed during the 2005–2009 period when PFOA was still in use in the Netherlands, while in the remaining three studies, samples were collected shortly before or after the phase-out in 2012. Temporal trend studies have shown declining

PFOA concentrations in various populations in Europe over time (Gebbink et al., 2015b; Yeung et al., 2013), which could (partly) explain the different in the worker's exposure compared to the more recent studies.

6. PFOA and GenX reported in other countries

GenX and PFOA data from other countries was collected in order to put this study's findings in perspective. There were only a limited number of studies identified where both PFOA and GenX monitoring data were presented. Pan et al. (2018) performed an extensive study in various surface waters in China (various rivers), the UK (Thames), Netherlands (Rhine) and USA (Delaware river). Median PFOA and GenX levels ranged from 1.8 to 12.2 and 0.21–2.02 ng/L, respectively. This compares well to the background levels in the Dutch rivers, but particularly GenX levels were lower than those downstream the Dutch FPP (2017 observations). Heydebreck et al. (2015a,b) investigated GenX in the German rivers Rhine (German part), Elbe, Ems and the North Sea. They found a high GenX level close to Leverkusen-Wiesdorf and levels of 0.6–3.7 ng/L in North Sea water. Li et al. (2020) investigated residential soils throughout China, and found median PFOA levels of 182 pg/g dw, which are lower than those observed in the Netherlands. GenX in that study ranged from non-detected to 967 pg/g dw , which is in the same range as in the Dutch situation (Fig. 3), but lower than the highest observations close to the FPP (Helmond). Sun et al. (2016) investigated drinking water in North Carolina (NC, USA) in 3 communities upstream and downstream an FPP. The reported median levels were < 10–34 and < 10–304 ng/L for PFOA and GenX, respectively. Particularly the GenX levels in drinking water downstream of the local FPP were approx. 10-fold higher than those in the Dutch situation. The North Carolina (NC) Department of Health and Human Services (2018) investigated contaminant levels in blood of local NC residents (n = 30) that switched to bottled water after discovery that their water wells were highly contaminated. Their median blood serum levels were 1.75 μg/L for PFOA and GenX was not detected in any of the samples (< 0.1 μg/L). The PFOA level is slightly lower than observed in serum of local residents in the vicinity of the Dutch FPP (Fig. 5). No Dutch GenX serum data was available for comparison with the NC data. The North Carolina Department of Health and Human Services (2018) suggested that the GenX levels in the serum may have dropped rapidly after switching to bottled water, although no data is available to confirm that.

7. Implications

In recent years, national governmental institutions have determined standards or limits for PFOA and GenX in drinking, surface- and groundwater, soil but also with respect to human exposure Tolerable Daily Intakes (TDIs) and safe blood concentrations were determined (Table 2). The results from the various monitoring reports/studies are evaluated against these national standards/limits.

An environmental quality standard (EQS) for PFOA in surface water was determined based on the accumulation of PFOA in fish and subsequent human consumption (Verbruggen et al., 2017). The EQS for PFOA in surface water was set at 48 ng/L. Based on all the published data, concentrations of PFOA in surface water in the Netherlands only surpass the EQS in surface water from enclosed water bodies (i.e. in Helmond) collected in 2018. In all other studies that included samples between 2006 and 2018 no exceedance of the EQS was observed even at downstream sites when PFOA was used. Recently a water quality standard (QS) was set for GenX at 118 ng/L in surface water, although certain assumptions were made with respect to GenX properties due to lack of data (Smit, 2017). Several studies have reported on GenX concentrations exceeding this QS for surface water. In 2016, Gebbink et al. (2017) reported GenX concentrations higher than the QS at six downstream sampling locations with concentrations peaking at more than 800 ng/L. In 2017, at a downstream sampling location a concentration of 128 ng/L was reported (Versteegh and de Voogt, 2017), and in 2018 a concentration of 6800 ng/L was reported in an enclosed waterbody. These elevated concentrations could pose a risk for human consumption of fish caught in these waters, although more data are needed on accumulation of GenX in fish for a better determination of QS. For PFOA, 4 of the 1097 analyzed surface water samples exceeded the QS, while this was the case for 8 of the 261 samples for GenX.

Risk limits for human exposure to PFOA via soil were determined with different scenarios, and a generic risk limit of 900 ng/g dw was proposed based on some soil ingestion and the consumption of homegrown vegetables (Lijzen et al., 2018). The available data showed that PFOA concentrations in soil during 2017–2018 collected in the vicinity of the FPP and in Helmond did not exceed the risk limit. The highest concentrations reported in an individual sample were 84 and 120 ng/g dw in Sliedrecht and Helmond, respectively (van Bentum et al., 2017; van Bentum et al., 2018b). A risk limit for human exposure to PFOA via soil in vegetable garden was set at 86 ng/g dw (Lijzen et al., 2018), however, concentrations in soil from vegetable gardens were all below this limit. For GenX, a generic risk limit was determined (as described for PFOA) and was set at 100 ng/g dw (Rutgers et al., 2019). The average GenX concentration at one sampling site near Helmond exceeded this risk limit, however, this was driven by one high concentration (i.e. 1300 ng/g dw) (van Bentum et al., 2018b). Concentrations in all other samples also did not exceed a lower risk limit for human exposure via soil in vegetable garden (8 ng/g dw) (Rutgers et al., 2019).

A risk limit for PFOA and GenX in groundwater was set at 390 and 660 ng/L, respectively based on the assumption that groundwater will be used as drinking water (Lijzen et al., 2017; Rutgers et al., 2019). Based on samples collected in 2017 and 2018, exceedance of the risk limit of PFOA in groundwater was seen in the municipalities of Papendrecht, Sliedrecht, Dordrecht and Helmond with concentrations as high as 25 μg/L (Francken, 2018; van Bentum et al., 2018a; van Bentum et al., 2017; van Bentum et al., 2018b). For GenX, exceedance of the risk limit was seen in samples collected in Dordrecht and Helmond (van Bentum et al., 2017; van Bentum et al., 2018b). Direct consumption of groundwater in these areas could pose a risk for humans, although it should be mentioned concentrations below the risk limit were also found in these municipalities indicating potential hotspots. For PFOA, 25 of the 69 analyzed groundwater samples exceeded the risk limit, while this was the case for 6 of the 75 groundwater samples for GenX.

For drinking water the QS for PFOA was determined at 87.5 ng/L, while a provisional guideline value for GenX was set at 150 ng/L (Janssen, 2017; Verbruggen et al., 2017). For both PFOA and GenX, concentrations reported in drinking water did not exceed the QS or provisional guideline values. The highest concentrations for PFOA and GenX were 23 and 29 ng/L, respectively, and were found in drinking water from municipalities downstream from the FPP. Based on the existing monitoring data, there is no risk for human exposure to PFOA and GenX via drinking water that exceeds the QS. The highest PFOA concentration found in the Netherlands is also below standards set by other (inter)national authorities (although some standards are for the sum of multiple PFASs), for example the US EPA has set the guidance value for the sum of PFOA and PFOS at 70 ng/L (Cordner et al., 2019), while the sum of eleven PFASs (including PFOA) cannot exceed 90 ng/L in Sweden (NFA, 2018).

The available toxicity data on GenX was evaluated by Beekman et al. (2016), and recently updated by Rutgers et al. (2019) including also recently published toxicity studies (up to 2018). Various effects were observed and described including immune effects in mice, increased bodyweight in maternal rats and hepatotoxicity in rats. One can refer to Rutgers et al. (2019, appendix 2 of the report) for more details as well as the studies cited there. Beekman et al. (2016) found that a NOAEL of 0.1 mg/kg bw/day in an oral chronic study in rats is based on an increase in albumin and the albumin/globulin ratio in male rats

Table 2
Evaluation of reported data in various matrices against National Standards or Limits for PFOA and GenX in the Netherlands.

Matrix	PFOA			GenX		
	Standard/Limit	Value	Number of samples exceeding Standard/Limit	Standard/Limit	Value	Number of samples exceeding Standard/Limit
Surface water	EQS[a]	48 ng/L	4/1097[b]	Water quality standard[i]	118 ng/L	8/261[j]
Soil	Generic risk limit[c]	900 ng/g dw	0/85	Risk limit[k]	100 ng/g dw	1/85[l]
	Risk limit vegetable garden[c]	86 ng/g dw	0/12	Risk limit vegetable garden[k]	8 ng/g dw	0/12
Groundwater	Risk limit[d]	390 ng/L	25/69[e]	Risk limit[k]	660 ng/L	6/75[m]
Drinking water	Quality Standard[a]	87.5 ng/L	0/70	Provisional guideline value[n]	150 ng/L	0/78
	TDI[f]	12.5 ng/kg bw/day	1/2[g]	Provisional TDI[n]	21 ng/kg bw/day	1/2[g]
Blood	HBGV[f]	89 ng/ml	182/673[h]			

[a] EQS: Environmental Quality Standard (Verbruggen et al., 2017).
[b] Samples exceeding the EQS are reported by van Bentum et al., 2018b.
[c] (Lijzen et al., 2018).
[d] (Lijzen et al., 2017).
[e] Samples exceeding the risk limit are reported by Francken, 2018; van Bentum et al., 2017, 2018a,b.
[f] HBGV: Health Based Guidance Value (Zeilmaker et al., 2016).
[g] Samples exceeding the TDI are reported by Mengelers et al., 2018.
[h] Samples exceeding the HBGV are reported by Dupont. 2009; van Poll et al., 2017.
[i] (Smit, 2018).
[j] Samples exceeding the EQS are reported by Gebbink et al., 2017; van Bentum et al., 2018a,b; van Bentum et al., 2017.
[k] (Rutgers et al., 2019).
[l] Samples exceeding the risk limit are reported by van Bentum et al., 2018b.
[m] Samples exceeding the risk limit are reported by van Bentum et al., 2017, 2018b.
[n] TDI: Tolerable Daily Intake (Janssen, 2017).

which may indicate possible immunotoxic effects. None of the more recent studies summarized in Rutgers et al. (2019) showed adverse effects at dose levels below the NOAEL of 0.1 mg/kg bw/day. This NOAEL was used as the best available point of departure (POD) for derivation of the risk limits for soil and the guideline value for drinking water (Table 2) This POD was also used for derivation of a provisional (oral) Tolerable Daily Intake (TDI), and was set at 21 ng/kg bw/day (Janssen, 2017). A TDI for PFOA was derived at 12.5 ng/kg bw/day (Zeilmaker et al., 2016). The European Food Safety Authority (EFSA) has proposed a Tolerable Weekly Intake (TWI) of 6 ng/kg bw for PFOA, however, this is still under review. Therefore, the TDIs set by the National Authorities are used to evaluate potential risk. When assuming year-round consumption of the local vegetables and using a maximum exposure scenario, estimated intakes for PFOA and GenX approached the TDIs in Dordrecht but the intakes were lower than the TDIs based on the vegetables from Helmond. Calculations performed on the dairy products and fish showed no exceedance of the TDIs. It should be noted that when including exposure via drinking water and air in the exposure assessment in Dordrecht, TDIs were exceeded for both PFOA and GenX in a maximum exposure scenario.

A health-based guidance value (HBGV) for PFOA in human serum was determined at 89 ng/mL (Zeilmaker et al., 2016). The existing monitoring data for the local population near the FPP shows that on average there is no exceedance of the HBGV, however, three individual belonging to the investigated group living closest to the FPP had blood serum concentrations that exceeded the HBGV. No exceedance of the HBGV was observed in population living in other regions in the Netherlands, even with greater exposure due to contaminated food consumption. During 2005–2009, FPP workers in Dordrecht were exposed to higher amounts of PFOA resulting in elevated serum contraptions compared to the other studies. In fact, the majority of the samples exceeded the HBGV of 89 ng/mL, i.e. 96% of the production workers, 97% of the maintenance workers and 85% of others. Although several individual workers were monitored several times during the 2005–2009 period, no consistent trend in serum concentrations were seen. For GenX, no data on human serum is available. A total of 182 of the 673 analyzed serum samples exceeded the HBGV for PFOA.

Based on the available data, the FPP is a source of contamination of PFOA and GenX to the local environment. The data also showed the other companies processing PFOA/GenX-containing products can also be point sources for local contamination. In various environmental matrices and human exposure pathways, high concentrations were found close to these point sources and in several cases exceeding national safety standards/limits. It is therefore essential that monitoring of PFOA and GenX continues close to point sources, ensuring low risk for the local environment and population.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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