

## Emissions of perfluorinated alkylated substances (PFAS) from point sources—identification of relevant branches

M. Clara, C. Scheffknecht, S. Scharf, S. Weiss and O. Gans

### ABSTRACT

Effluents of wastewater treatment plants are relevant point sources for the emission of hazardous xenobiotic substances to the aquatic environment. One group of substances, which recently entered scientific and political discussions, is the group of the perfluorinated alkylated substances (PFAS). The most studied compounds from this group are perfluorooctanoic acid (PFOA) and perfluorooctane sulphonate (PFOS), which are the most important degradation products of PFAS. These two substances are known to be persistent, bioaccumulative and toxic (PBT). In the present study, eleven PFAS were investigated in effluents of municipal wastewater treatment plants (WWTP) and in industrial wastewaters. PFOS and PFOA proved to be the dominant compounds in all sampled wastewaters. Concentrations of up to 340 ng/L of PFOS and up to 220 ng/L of PFOA were observed. Besides these two compounds, perfluorohexanoic acid (PFHxA) was also present in nearly all effluents and maximum concentrations of up to 280 ng/L were measured. Only *N*-ethylperfluorooctane sulphonamide (*N*-EtPFOSA) and its degradation/metabolisation product perfluorooctane sulphonamide (PFOSA) were either detected below the limit of quantification or were not even detected at all. Beside the effluents of the municipal WWTPs, nine industrial wastewaters from six different industrial branches were also investigated. Significantly, the highest emissions of PFOS were observed from metal industry whereas paper industry showed the highest PFOA emission. Several PFAS, especially perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluorododecanoic acid (PFDoA) and PFOS are predominantly emitted from industrial sources, with concentrations being a factor of 10 higher than those observed in the municipal WWTP effluents. Perfluorodecane sulphonate (PFDS), *N*-Et-PFOSA and PFOSA were not detected in any of the sampled industrial point sources.

**Key words** | emerging pollutants, industrial wastewater, municipal wastewater, PFAS, PFOA, PFOS, point sources

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### INTRODUCTION

Perfluorinated alkylated substances (PFAS) make up a large group of chemicals that have been used in different industrial and consumer products since the 1950s. PFAS are a diverse class of chemicals characterised by a hydrophobic alkylated chain saturated with fluorine atoms, usually attached to a hydrophilic head. Because of their structures, PFAS have both lipid and water-repellent properties making them ideal for several commercial uses, mainly those

requiring surface-active properties. They are constituents of a wide range of products including fluoropolymers (for example polytetrafluoroethylene—PTFE, or polyvinylidene fluoride—PVDF), liquid repellents for paper, packaging, textiles, leather, carpet goods, industrial surfactants, additives, protective coatings and firefighting foams. From these uses the substances are likely to end up in waste dumps, sewage water and the general environment.

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Two groups of PFAS are of particular concern for human health and the environment, namely perfluoroalkyl sulphonates and perfluoroalkyl carboxylates (PFACs). The OECD hazard assessment of perfluorooctane sulphonate (PFOS) and its salts (OECD 2002) concluded with regard to human health, that:

- PFOS is persistent, bioaccumulative and toxic in mammals;
- PFOS has been detected in the serum of occupational and general populations;
- there is a statistically significant association between PFOS exposure and bladder cancer; and
- there appears to be an increased risk of episodes for neoplasms of the male reproductive system, the overall category of cancers and benign growths and neoplasms of the gastrointestinal tract.

With regard to the environment, the OECD hazard assessment concluded that:

- PFOS is persistent and bioaccumulative;
- PFOS is highly toxic (acute) to honey bees and bioconcentrates in fish; and
- it has been detected in tissues of wild birds and fish, in surface water and sediment, in wastewater treatment plant effluent, sewage sludge and in landfill leachate.

Besides the fact that PFAS produce adverse effects to human health and the environment (Giesy & Kannan 2001; RPA 2004), they are ubiquitous in the environment. PFAS have been detected in different environmental matrices as surface water (Moody *et al.* 2002; Simcik & Dorweiler 2005; Skutlarek *et al.* 2006), rainwater (Loewen *et al.* 2005), drinking water (Harada *et al.* 2003; Skutlarek *et al.* 2006) and wastewater (Boulanger *et al.* 2005; Gonzales-Barreiro *et al.* 2006; Schultz *et al.* 2006a). Skutlarek *et al.* (2006) observed up to 598 ng/L of PFAS in drinking water from the Rhine–Ruhr area in Germany with PFAS as the major component (519 ng/L). The authors found a direct correlation between concentrations in drinking waters and the respective concentrations in surface waters. Drinking water concentrations decreased with decreasing raw water concentrations, leading to the conclusion that treatment technologies actually applied in drinking water treatment are not suitable for the removal of PFAS (Skutlarek *et al.* 2006). Given the problematic properties of PFAS

(persistence, mobility, toxicity, bioaccumulation), measures have to be taken in order to protect human health and the environment.

As a consequence of the hazardous potential, PFOS should be phased out. With the 30th amendment (2006/122/EC), PFAS have been included in Directive 76/769/EEC defining restrictions on the marketing and use of certain dangerous substances and preparations).

PFOS and its related compounds are relevant pollutants in the aquatic environment and potential priority hazardous substances in terms of the Water Framework Directive WFD (EC 2000). Currently, a proposal defining environmental quality standards for water relevant hazardous substances undergoes the co-decision procedure (COM(2006)397 final). During the first reading, the European Parliament amended this proposal with a list of additional substances to be added to the Annex X (priority substances) of the WFD. This list also included perfluorinated compounds, PFOS and its salts, as well as perfluorooctanoic acid (PFOA). This proposed amendment was rejected by the Council and is not included in the Common position (CEU 2007) but might be retabled during the second reading.

Wastewater treatment plant effluents are relevant emission pathways for PFAS to surface waters. Schultz *et al.* (2006a) investigated fluorochemicals in influents and final effluents of 10 wastewater treatment plants (WWTPs). The authors did not detect any systematic increases or decreases for the studied compounds despite the investigated WWTPs operated with similar treatment processes. Sinclair & Kannan (2006) measured concentrations of PFOA in WWTP effluents ranging from 58 up to 1,050 ng/L and much lower PFOS concentrations ranging 3 to 68 ng/L. The authors concluded that primary treatment had no effect on the mass flows of PFAS, whereas during activated sludge treatment an increase of the mass flows is observed (dissolved phase only). The observations were explained to result from degradation of precursor compounds such as fluorotelomer alcohols (Sinclair & Kannan 2006). These findings were confirmed by Schultz *et al.* (2006b). The authors concluded that conventional wastewater treatment is not effective in removing these compounds. Furthermore, a net increase in the mass flows of the investigated substances in activated sludge treatment plants was observed, which is attributed to degradation of precursor molecules.

Due to the reported persistency of PFAS during wastewater treatment (Sinclair & Kannan 2006; Schultz *et al.* 2006a,b; Loganathan *et al.* 2007) and the only marginal seasonal variations in the observed concentrations (Loganathan *et al.* 2007), the present study focuses on emissions from point sources to the aqueous environment. Effluents of 21 municipal WWTPs and effluents from nine industrial point sources were investigated. Eleven compounds were examined in this study including perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA) and perfluorododecanoic acid (PFDoA), perfluorooctane sulphonate (PFOS), perfluorodecane sulphonate (PFDS), perfluorooctane sulphonamide (PFOSA) and *N*-ethylperfluorooctane sulphonamide (*N*-Et-PFOSA).

## MATERIALS AND METHODS

### Analytical methods

Chemical analysis was performed according to the method described by Gonzales-Barreiro *et al.* (2006). Briefly, wastewater samples were extracted by liquid–liquid extraction (LLE) and analysed and quantified with liquid chromatography coupled with tandem mass spectrometry after electrospray ionisation (LC-ESI-MS-MS). For LLE, NaCl was added to the water samples (400 and 900 mL) to give a final concentration of 50 g/L, and the pH was adjusted to 4 with sulphuric acid. After this step the target analytes were extracted thrice with MTBE. The solvent was removed by rotary vacuum concentration (75 mbar, 35°C) to a final volume of 1 mL with previous exchange of the solvent for methanol. Separation was performed with an Agilent 1100 high performance liquid chromatograph (HPLC) with a 100 × 2 mm (5 µm particle) Luna C18 analytical column from Phenomenex HPLC Service and a 4 × 2 mm (5 µm particle) pre-column. The temperature of the HPLC column was kept constant at 25°C. The mobile phase was a gradient from water/ammonium acetate (component A) and methanol (component B). Mass spectrometry was performed with a Quattro Ultima triple-quadrupole mass

spectrometer (Micromass, Manchester, UK) equipped with a Z-spray electrospray interface operating in negative-ion mode. The instrument was operated in multiple reaction-monitoring (MRM) mode for quantification of each compound.

As surrogate standards perfluoro-*N*-[1,2,3,4-<sup>13</sup>C<sub>4</sub>]octanoic acid ([<sup>13</sup>C<sub>4</sub>]-PFOA, >98%), perfluoro-*N*-[1,2-<sup>13</sup>C<sub>2</sub>]decanoic acid ([<sup>13</sup>C<sub>2</sub>]-PFDA, >98%), and *N*-ethyl-d<sub>5</sub>-perfluoro-1-octanesulphonamide (*N*-d<sub>5</sub>-EtPFOSA, >98%), purchased from Wellington Laboratories (Ontario, Canada), were used. The internal standard perfluoro-*N*-[1,2-<sup>13</sup>C<sub>2</sub>]octanoic acid ([<sup>13</sup>C<sub>2</sub>]-PFOA, 98.1%) was supplied by Perkin–Elmer Life and Analytical Sciences (Wellesley, MA, USA).

Mean recoveries rates, limits of determination (LOD) and limits of quantification (LOQ) are summarised in Table 1.

### Sampling and sampling sites

Daily composite samples were taken from the effluents of the 21 investigated municipal WWTPs, whereas grab samples were analysed from the industrial facilities.

Apart from WWTP 2, all municipal WWTPs are activated sludge plants, whereas WWTP 2 operates an imhoff tank with a trickling filter. The design capacities in terms of BOD (biological oxygen demand) ranges from 2,000 population equivalents (p.e.) up to approximately 1,000,000 p.e., with one p.e. corresponding to 60 g BOD per day. The wastewater characteristics of approximately half of the investigated plants is purely domestic with nearly no industrial or commercial impact (proportion of chemical oxygen demand COD in influent originating from industries is less than 25%). The other WWTPs have a drainage area with mixed uses and proportional impacts (in terms of influent COD) from industrial or commercial facilities ranging between 25 and 60%.

The wastewater from the nine industrial point sources (IPS) derives from different industrial sectors. The branches addressed are textile industry, laundry and cleaning industry, paper industry, electrical industry, metal industry and printing industry. The main wastewater relevant activities of the different industrial point sources are summarised in Table 2.

**Table 1** | Mean recoveries [%], limit of determination LOD [ng/L] and limit of quantification LOQ (ng/L) for the eleven investigated PFAS (values in brackets are valid for the industrial wastewater samples)

Compound	Formula	Molecular weight [g/mol]	Recovery [%]	LOD [ng/L]	LOQ [ng/L]
PFHxA	C <sub>6</sub> HF <sub>11</sub> O <sub>2</sub>	314.06	64	4.40 (0.54)	16.00 (1.90)
PFHpA	C <sub>7</sub> HF <sub>13</sub> O <sub>2</sub>	364.06	73	0.48 (0.23)	1.70 (0.84)
PFOA	C <sub>8</sub> HF <sub>15</sub> O <sub>2</sub>	414.07	80 (96)	0.33 (0.22)	1.20 (0.79)
PFNA	C <sub>9</sub> HF <sub>17</sub> O <sub>2</sub>	464.08	90	0.26 (0.19)	0.95 (0.70)
PFDA	C <sub>10</sub> HF <sub>19</sub> O <sub>2</sub>	514.09	88 (81)	0.30 (0.23)	1.10 (0.83)
PFUnA	C <sub>11</sub> HF <sub>21</sub> O <sub>2</sub>	564.09	98	0.27 (0.21)	1.00 (0.78)
PFDoA	C <sub>12</sub> HF <sub>23</sub> O <sub>2</sub>	614.10	99	0.26 (0.21)	0.95 (0.77)
PFOS	C <sub>8</sub> HF <sub>17</sub> O <sub>3</sub> S	500.13	97 (113)	0.26 (2.20)	0.94 (4.40)
PFDS	C <sub>10</sub> HF <sub>21</sub> O <sub>3</sub> S	600.15	97	0.39 (2.20)	1.50 (4.40)
N-Et-PFOA	C <sub>8</sub> F <sub>17</sub> SO <sub>2</sub> NH <sub>2</sub>	499.15	76	0.62 (2.20)	2.30 (4.40)
PFOSA	C <sub>8</sub> F <sub>17</sub> SO <sub>2</sub> NHCH <sub>2</sub> CH <sub>3</sub>	527.20	89	0.35 (2.20)	1.30 (4.40)

(x) mean recovery rates, LOD and LOQ for the industrial water samples.

## RESULTS AND DISCUSSION

Measured concentrations of the 11 investigated compounds in the 21 sampled WWTP are summarised in Table 3.

PFOS was the dominant compound and was measured in all investigated WWTPs in concentrations above the LOQ. The measured concentrations averaged 60 ng/L, achieving a maximum concentration of 340 ng/L analysed in the effluent of WWTP 9. With the exception of WWTP 9 and 21, the PFOS concentrations in the effluents are comparable. This fact suggests that there is an industrial influence to these two plants. Whilst no relevant industrial emittent could be identified for WWTP 9, WWTP 21 is influenced by wastewater originating from the paper industry as well as from the metal industry.

Notably lower concentrations are reported in the literature. Sinclair & Kannan (2006) report PFOS concentrations in the effluents of six activated sludge WWTPs in New York State ranging from 3 to 68 ng/L. As the study reports dissolved concentrations (water samples after decanting), this might be an explanation for the lower concentrations observed. However, Schultz *et al.* (2006b) also report PFOS values ranging from 15 to 34 ng/L, thus being clearly below the results obtained in the presented study. Loganathan *et al.* (2007) observed PFOS concentrations in two wastewater treatment facilities in Kentucky and Georgia between 1.8 and 28 ng/L. These values also refer to decanted samples.

Besides PFOS, PFOA was also found in all investigated effluents. The measured values averaged 60 ng/L with

**Table 2** | Description of the investigated industrial point sources

	Branch	Relevant activities
IPS 1	Printing industry	Printing of newspapers
IPS 2	Textile industry	Yarn manufacturing, bleaching and dyeing
IPS 3	Textile industry	Cloth production, dyeing, décor
IPS 4	Laundry and cleaning	Laundry and dry cleaning
IPS 5	Laundry and cleaning	Laundry and dry cleaning
IPS 6	Paper industry	Paper and corrugated board production
IPS 7	Electrical industry	Lamp production, varnishing, pickling, phosphating
IPS 8	Metal industry	Pickling, galvanising, nickel/chromium-plating, anodising
IPS 9	Metal industry	Pickling, phosphating

**Table 3** | Measured concentrations [ng/L] of investigated perfluorochemicals in effluent samples of 21 municipal WWTPs

	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFOS	PFDS	N-Et-PFOA	PFOSA
LOD	4.4	0.48	0.33	0.26	0.3	0.27	0.26	0.26	0.39	0.62	0.35
LOQ	16	1.7	1.2	0.95	1.1	1.0	0.95	0.94	1.5	2.3	1.3
WWTP 1	128	<1.7	61	5	1	n.d.	n.d.	29	n.d.	n.d.	n.a.
WWTP 2	13	6	35	4	2	<1.0	n.d.	40	3	n.d.	4
WWTP 3	13	5	15	2	<1.1	n.d.	<0.95	12	n.d.	n.d.	<1.3
WWTP 4	6	2	10	<0.95	<1.1	n.d.	n.d.	4	n.d.	n.d.	n.d.
WWTP 5	9	3	15	2	1	n.d.	n.d.	9	n.d.	n.d.	<1.3
WWTP 6	180	31	75	8	3	n.d.	n.d.	36	n.d.	n.d.	n.a.
WWTP 7	20	15	52	7	5	22	85	82	22	n.d.	n.a.
WWTP 8	17	4	14	2	1	n.d.	n.d.	9	<1.5	n.d.	<1.3
WWTP 9	43	12	160	3	<2.4	n.d.	n.d.	340	n.d.	n.d.	3
WWTP 10	280	64	100	7	7	1	n.d.	68	4	n.d.	n.d.
WWTP 11	130	26	68	11	9	7	3	50	41	n.d.	n.a.
WWTP 12	74	15	100	13	16	n.d.	<0.95	41	n.d.	n.d.	n.a.
WWTP 13	16	4	16	2	<1.1	1	<0.95	20	<1.5	<2.3	<1.3
WWTP 14	16	5	21	2	2	n.d.	n.d.	8	n.d.	n.d.	<1.3
WWTP 15	n.d.	n.d.	32	2	2	16	74	62	19	n.d.	n.a.
WWTP 16	<10	<4.1	14	<2.6	<2.4	n.d.	n.d.	100	n.d.	n.d.	n.d.
WWTP 17	8	4	11	1	<1.1	<1.0	1	6	<1.5	<2.3	1
WWTP 18	33	n.d.	77	8	11	n.d.	n.d.	34	n.d.	n.d.	n.a.
WWTP 19	76	26	63	12	8	<1.0	<0.95	44	<1.5	n.d.	4
WWTP 20	280	49	91	6	6	<1.0	n.d.	64	5	n.d.	n.a.
WWTP 21	120	38	220	24	16	n.d.	0	199	n.d.	n.d.	n.a.
Minimum	n.d.	n.d.	10	<0.95	1	n.d.	n.d.	4	n.d.	n.d.	n.d.
Maximum	280	64	220	24	16	22	85	340	41	<2.3	4

n.d. not detected, n.a. not analysed.

maximum values of 220 ng/L. As for PFOS, the highest concentrations for PFOA were also measured in WWTP 9 and WWTP 21. For this parameter, strongly diverging effluent values are reported in the literature. Whereas in the investigations of Sinclair & Kannan (2006) PFOA was the dominant PFAS with concentrations achieving several 100 ng/L (maximum value reported 697 ng/L), Schultz *et al.* (2006b) observed notably lower concentrations varying between 4 and 24 ng/L. Loganathan *et al.* (2007) measured the Kentucky WWTP values between 122 and 183 ng/L and values in the Georgia WWTP were between 6.7 and 102 ng/L. These values vary within the same range as the results of the present study.

Perfluorononanoic acid (PFNA) as well as perfluorodecanoic acid (PFDA) were detected in all investigated effluents, even in lower concentrations than PFOS and PFOA. Concentrations of PFNA ranged from <0.95 and 24 ng/L and concentrations of PFDA from 1 to 16 ng/L. These results are comparable to literature values, which are reported to vary within the same range (Sinclair & Kannan 2006; Schultz *et al.* 2006b; Loganathan *et al.* 2007). Only in plant A were significantly higher concentrations with maximum values of 107 for PFNA and 34 ng/L for PFDA observed (Sinclair & Kannan 2006).

Perfluorohexanoic acid (PFHxA) is found in all investigated WWTPs, apart from WWTP 15. The concentrations

varied between 6 and 280 ng/L, with the highest concentrations observed in WWTP 10 and WWTP 20. *Schultz et al. (2006b)* once again observed clearly lower concentrations with values from not detectable up to a maximum concentration of 15 ng/L.

PFHpA is found in nearly all effluents. Only in WWTP 15 and WWTP 18 were these compounds not detected. In the other WWTPs the measured concentrations vary between <1.7 and 64 ng/L. No comparison with literature data could be performed as no values were found.

PFUnA, PFDoA and PFDS were detected only in a few of the investigated WWTPs. It is observed that the maximum values for PFUnA and PFDoA were measured in WWTP 7, achieving concentrations of 22 ng/L for PFUnA and 85 ng/L for PFDoA. Also, relatively high values were observed in WWTP 15 (16 ng/L of PFUnA and 74 ng/L of PFDoA), whereas in all other plants the measured values were below the limit of detection or the limit of quantification. The same observation applies to PFDS. A possible reason for this might be a potential source in the catchment area, but it was not possible to identify such a source.

N-Et-PFOA and PFOA are regarded as minor important PFAS as they were either not found in the analysed effluents or the measured concentrations were below the limit of quantification. PFOA was only found in

four WWTPs with concentrations from 1 up to 4 ng/L. Comparable results are reported also by *Sinclair & Kannan (2006)*, *Schultz et al. (2006a,b)*.

In order to assess and to identify main industrial activities relevant for the emission of PFAS into wastewater or surface waters, nine industrial point sources as described in *Table 2* were sampled and analysed. The results are summarised in *Table 4*.

The evaluation of the data from the industrial point sources shows a more diverging picture than those obtained for the municipal WWTP effluents. PFOS is the compound found in the highest concentration achieving >8 µg/L but it was found only in a few effluents. PFOS was present in the effluents of paper and metal industry. Furthermore, it was found in the effluents of one laundry and cleaning facility and a newspaper printing facility, but only in low concentrations. An interesting difference is observed in the effluents of the sampled metal industries. Whereas in one facility comparable concentrations to those measured in the municipal WWTP effluent were obtained, the second facility shows very high effluent concentrations. As this second plant is also galvanising, nickel and chromium plating and anodising, these processes may be potential sources for the observed high emissions of PFOS.

As in the municipal WWTP, effluents in the industrial effluents PFOA were also found in all samples. Even if

**Table 4** | Measured concentrations [ng/L] of investigated perfluorochemicals in the effluents of nine industrial point sources

	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFOS	PFDS	N-Et-PFOA	PFOA
LOD	0.54	0.23	0.22	0.19	0.23	0.21	0.21	2.2	2.2	2.2	2.2
LOQ	1.9	0.84	0.79	0.70	0.83	0.78	0.77	4.4	4.4	4.4	4.4
IPS 1	n.d.	1.7	7.4	1.0	n.d.	n.d.	n.d.	<4.4	n.d.	n.d.	n.d.
IPS 2	43	55	76	320	96	70	4.2	n.d.	n.d.	n.d.	n.d.
IPS 3	n.d.	n.d.	1.4	1.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
IPS 4	32	22	59	99	66	11	n.d.	7.2	n.d.	n.d.	n.d.
IPS 5	21	4.4	6.5	n.d.	<0.83	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
IPS 6	180	41	64	53	16	3.3	<0.77	91	n.d.	n.d.	n.d.
IPS 7	32	<0.84	3.5	8.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
IPS 8	32	10	20	n.d.	n.d.	n.d.	n.d.	8410	n.d.	n.d.	n.d.
IPS 9	71	6.4	6.7	3.7	1.6	n.d.	<0.77	44	n.d.	n.d.	n.d.
Minimum	n.d.	n.d.	1.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Maximum	180	55	76	320	96	70	4.2	8410	n.d.	n.d.	n.d.

slightly lower, the concentrations are regarded as comparable. The same conclusion is also valid for PFHpA and PFHxA. For PFHxA the highest measured concentrations were obtained for the paper industry effluent achieving a value of 180 ng/L. This substance seems not to be as relevant for the other investigated industries.

PFNA, PFDA, PFUnA and PFDoA were found only in the effluents of IPS 2, IPS 4 and IPS 6. As for PFOS in the metal industry it is quite interesting that these four compounds are found only in one of the two sampled textile industries as well as in one of the two laundry and cleaning facilities. In the facility for yarn production, which also implements a bleaching procedure, the highest emission levels were observed for all four PFAS (PFNA 320 ng/L, PFDA 96 ng/L, PFUnA 70 ng/L, PFDoA 4.2 ng/L). It was not possible to identify an influence factor explaining the differences observed in the effluents of the two sampled textile industries. Furthermore, the paper industry seems to be a relevant emission source even if to a lower extent.

In none of the sampled industrial point sources were PFDS, *N*-Et-PFOSA and PFOSA found. The selected industries seem not to be relevant point emission sources for these compounds.

Figure 1 compares the observed effluent concentrations in terms of mean, minimum and maximum values, in order to assess the influence of specific industrial emissions on municipal wastewater.

Due to the measured concentrations in the investigated urban wastewater treatment plants and the industrial facilities, PFNA, PFDA, PFDoA and PFOS are predominantly

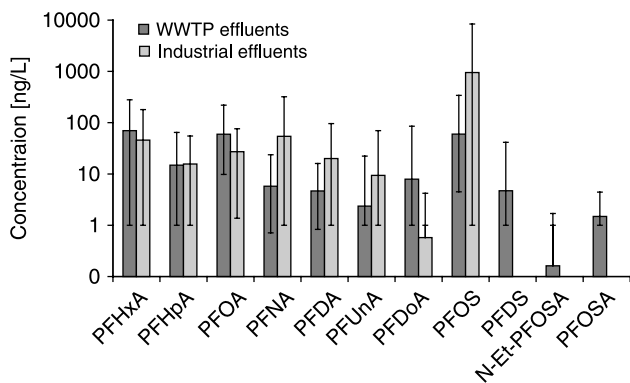


Figure 1 | Comparing measured mean, minimum and maximum concentrations [ng/L] of the investigated 11 PFAS in municipal WWTPs and in industrial effluents.

emitted from industrial sources. As the concentrations in the relevant industrial effluents are approximately a factor of 10 higher than those in the municipal wastewater effluents, and due to the persistency of PFAS during wastewater treatment, emissions from industries may significantly influence the loading situation of a specific WWTP. As an example, WWTP 21 may be mentioned as this WWTP is influenced by the paper industry as well as the metal industry. It can be seen that for the four named compounds the maximum effluent concentrations in the municipal WWTPs are found in this plant (except PFOS, for which the second highest value is measured in WWTP 21 whereas the highest concentration is obtained in WWTP 7).

PFHxA, PFHpA, as well as PFOA, were found in comparable concentrations in the effluents of the municipal WWTPs and the industrial facilities. Whereas PFDoA is found to a minor extent in the industrial effluents and only in a few industrial sectors, it is observed in notably higher concentrations in some of the investigated WWTP effluents.

PFDS, *N*-Et-PFOSA and PFOSA were not detected in the industrial effluents, whereas they were present in a few municipal effluents. Only *N*-Et-PFOSA is not found in any of the investigated samples above the limit of quantification. This can be explained by the degradation of *N*-Et-PFOSA to PFOSA (Fricke & Lahl 2005).

## CONCLUSIONS

The most important PFAS in the effluent of municipal wastewater treatment plants, as well as in industrial effluents, are PFOS and PFOA. This can be explained by their persistency and the fact that PFOS and PFOA are degradation, transformation and metabolisation products which are produced from other PFAS.

PFOS and PFAS are regarded as P(persistent)B(bio-accumulative)T(toxic) substances and regulatory provisions are discussed or even already entered into force. The present study confirmed results from other investigations and showed the evidence of PFAS emission via wastewater treatment plant effluents.

The presented results also highlight the importance of specific industrial emission sources. The highest PFOS emissions were observed from the galvanising industry.

Beside PFOS, PFNA, PFDA, PFDoA are also found to be predominantly emitted from industrial sources. The identification of specific branches which may be main emitters of PFAS into the environment also provides important information for pollution prevention measures.

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