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PFAS IN INFLUENT, EFFLUENT AND SEWAGE SLUDGE RESULTS OF A MONITORING CAMPAIGN AT EIGHT WWTPS

REPORT 2021 46E

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REPORT 2021 **46E**

ISBN 978.90.5773.954.5

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STOWA publications can be ordered at www.stowa.nl

COLOPHON

PUBLICATION STOWA
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PRODUCTION Kruyt Grafisch Adviesbureau bv
STOWA STOWA 2021-46E
ISBN 978.90.5773.954.5

FOREWORD

PFAS are present in sewage water and are not removed, or are barely removed, at wastewater treatment plants (WWTPs). Research on the origin of PFAS in sewage water is recommended.

This report presents the findings of a broad-based monitoring campaign to detect PFAS in influent, effluent and sewage sludge at wastewater treatment plants (WWTPs) in the Netherlands. The results show that PFAS were hardly removed, or not removed at all, at WWTPs. Influent contained well-known and highly persistent PFAS, such as PFOS and PFOA, in addition to other PFAS groups, including various degradable PFAS – also called precursors. Precursors are not persistent: known and unknown precursors in influent appear to be transformed at WWTPs, resulting in higher concentrations of persistent PFAS (and other precursors) leaving the WWTPs in the effluent than in the influent.

PFAS in the environment is problematic. PFAS are hazardous, they are poorly biodegradable and they are extremely persistent and found everywhere. Various national studies have been conducted or are underway to better understand PFAS sources. The current study of PFAS in influent, effluent and sewage sludge at WWTPs is one of these. This study answers to the question of what PFAS are found at WWTPs, and in what concentrations. With the results in hand, the Dutch water boards and Ministry of Infrastructure and Water Management will be better able to determine what remedial actions are necessary.

Eight WWTPs were included in this monitoring campaign. These were a mix of WWTPs, including some known to have high PFAS emissions (hotspots), a former hotspot (where PFAS emissions had previously been reduced at the source) and WWTPs processing differing proportions of industrial wastewater. The largest PFAS contributions by far were found at the hotspots. However, PFAS were found in the influents at all WWTPs. Based on the variation in PFAS found in influent, there appears to be a level of background contamination from domestic wastewater, and in addition, a variety of other sources. What these sources are is not always known. In addition, there is strong evidence of an important role played by PFAS precursors. Precursors can degrade into persistent PFAS. At most WWTPs, greater quantities of persistent PFAS left the WWTP than entered it.

A number of persistent PFAS, including PFOS and PFOA, have been designated as priority hazardous substances and/or Substances of Very High Concern (SVHC). That means their release into the environment must be reduced to zero. Intervention at the source is the preferred option, because once PFAS are in the environment they are difficult if not impossible to remove. The Netherlands is collaborating with a number of countries on a proposal for a European restriction on all PFAS. At the national level, the water boards and other government authorities are cooperating with business and industry in the PFAS Action Programme. Via this platform they are pursing interventions to reduce the release of PFAS into the environment and to limit human exposures. Specific attention is being given to the various links in the chain, from the production of PFAS, to its use in industrial processes, to the different emission pathways. The current study offers valuable information in that respect. However, as this study also shows, unless emissions of PFAS precursors can be reduced, it will be very difficult to achieve a reduction in PFOS and PFOA emissions.

Further research on precursors will therefore be proposed to the national working group on emerging substances.

WWTPs with elevated levels of PFAS and PFAS precursors can be identified by carrying out measurements. Once these WWTPs are identified, water boards, provincial and municipal authorities and environmental services can work in collaboration to better understand the sources. If sources can be identified, dialogues can then be initiated to seek ways to reduce emissions at the source.

Joost Buntsma, Director STOWA
Liz van Duin, Director Water Quality, Soil and Marine Directorate, Ministry of Infrastructure and Water Management

SUMMARY

An extensive monitoring campaign was carried out to measure PFAS levels in influent, effluent and sewage sludge at WWTPs in the Netherlands. In total, eight WWTPs were studied, with a mix of characteristics. These included WWTPs known to have high PFAS emissions (hotspots), a former hotspot (where PFAS emissions had previously been reduced at the source) and WWTPs with differing proportions of industrial wastewater. In addition, a number of special wastewater streams were examined, all of which are discharged to Dordrecht WWTP.

Total concentrations of PFAS in influent and effluent were found to be approx. 10–1,000 ng/l, and for sewage sludge approx. 10–100 μg/kg dry matter (DM). Most PFAS found in the influent and effluent were those with short fluorinated chains (C4–C8), while in sludge most PFAS found were those with longer fluorinated chains as well as precursors. Of the total amount of PFAS found, most left the WWTPs via effluent. The proportion removed via sludge ranged from 2.6% to 41% of the total amount of PFAS that left the treatment plants.

PFAS were hardly removed, or not removed at all, at the WWTPs. The PFAS concentrations in effluent were often found to be even higher than those in influent. PFAS precursors appear to play a role in these increasing concentrations. Precursors are PFAS compounds that can degrade into persistent PFAS. Precursors often have a non-fully fluorinated carbon chain, while persistent PFAS have fully fluorinated carbon chains. Known and unknown precursors in influent can be transformed into persistent PFAS, such as PFOS (C8), PFOA (C8) and perfluoroalkyl carboxylic acids with shorter chain lengths (C4–C7). At most WWTPs, our measurements showed increased quantities of precursors and/or of these persistent PFAS in the effluent.

The characteristic occurrence pattern of individual PFAS compounds in influent (the PFAS ‘fingerprint’) differed for each WWTP. This indicates differing sources of the PFAS. These sources are not always known or understood. The share of industrial wastewater was found to be a poor predictor of the PFAS concentrations at the WWTPs. This study therefore grouped the WWTPs into three categories – high, moderate and low PFAS levels – based on the PFAS concentrations measured in their effluent. The release of PFAS into surface waters with effluent discharge was approx. 50 mg/PE 150 per year for the WWTPs with high PFAS loads; 5 mg/PE 150 per year for the moderate PFAS-load WWTPs; and 1 mg/PE 150 per year for the low PFAS-load WWTPs. For the Netherlands as a whole, this translates into an estimated 65–180 kg PFAS per year released into the environment via effluent, with 15–45 kg PFAS estimated as leaving the treatment plants via sewage sludge.

At the hotspot locations, the found concentrations of PFOA, HFPO-DA and/or total PFAS in effluent exceeded the environmental quality criteria for surface water. Furthermore, PFOS concentrations in effluent exceeded the environmental quality criteria for surface water at all of the treatment plants studied. Whether effluent discharge could lead to PFAS environmental quality criteria being exceeded in the receiving surface waters would depend on the local situation. Regarding sewage sludge, only at one WWTP were PFAS concentrations found to exceed the quality criteria set by other countries for sludge application on land (though it must be noted that such application is extremely rare in the Netherlands).

PFAS have a huge number of applications. There are therefore many potential sources. To identify possible means to reduce PFAS emissions into the environment, further measurements are recommended to identify WWTPs with elevated PFAS levels and, for these WWTPs, to initiate follow-up efforts to find the sources of those PFAS. This effort will require collaboration between municipalities, environmental services and other actors. The indicative estimates presented in this report of PFAS emissions via various pathways and products can provide valuable leads to identify sources.

PFAS precursors also warrant more attention, as without reducing emissions of PFAS precursors, it will be very difficult to achieve further reductions in emissions of persistent PFAS into the environment. Further research is therefore also recommended to better understand the nature, magnitude and sources of PFAS precursors.

Although the current study did not make extensive comparisons to other studies conducted in the Netherlands and elsewhere, its findings confirm those of other research. The hotspots included in this study were assumed to be special cases, and the findings from the other WWTPs were considered as providing a reasonable reflection of the most common situations at WWTPs in the Netherlands. Some uncertainty does remain, however, about the extent to which all major sources of PFAS were covered in this study. It is also difficult to gauge what proportion of the WWTPs in the Netherlands has low PFAS loads, and what proportion has moderate PFAS loads.

DE STOWA IN BRIEF

The Foundation for Applied Water Research (in short, STOWA) is a research platform for Dutch water controllers. STOWA participants are all ground and surface water managers in rural and urban areas, managers of domestic wastewater treatment installations and dam inspectors.

The water controllers avail themselves of STOWA's facilities for the realisation of all kinds of applied technological, scientific, administrative legal and social scientific research activities that may be of communal importance. Research programmes are developed based on requirement reports generated by the institute's participants. Research suggestions proposed by third parties such as knowledge institutes and consultants, are more than welcome. After having received such suggestions STOWA then consults its participants in order to verify the need for such proposed research.

STOWA does not conduct any research itself, instead it commissions specialised bodies to do the required research. All the studies are supervised by supervisory boards composed of staff from the various participating organisations and, where necessary, experts are brought in.

The money required for research, development, information and other services is raised by the various participating parties. At the moment, this amounts to an annual budget of some 6,5 million euro.

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PFAS IN INFLUENT, EFFLUENT AND SEWAGE SLUDGE

RESULTS OF A MONITORING CAMPAIGN AT EIGHT WWTPs

CONTENT

1

INTRODUCTION

1.1 BACKGROUND

Some of the bottlenecks surrounding PFAS-containing soil and dredging sludge have been resolved with the Temporary Action Framework on the Re-use of PFAS-Containing Soil and Dredging Sludge. Attention has therefore shifted to PFAS in waste streams (e.g., waste and municipal sewage sludge) and in water (surface water, groundwater and wastewater influent and effluent). With respect to these, a temporary working group of the Netherlands Association of Sewage Treatment Professionals (Dutch acronym: VvZB) presented a set of recommendations to the Association of Water Boards in February 2020. One of those recommendations was to conduct a sound monitoring campaign to obtain a representative picture of PFAS in influent, effluent and sewage sludge at wastewater treatment plants (WWTPs) in the Netherlands. On that basis, a monitoring campaign was carried out commissioned by STOWA and the Ministry of Infrastructure and Water Management. In this monitoring campaign, samples of influent, effluent and sewage sludge were collected from eight WWTPs. At one treatment plant, samples of industrial wastewater streams entering the WWTP along with the influent were also collected. The current report presents the approach and results of that monitoring campaign and discusses the findings in more detail.

1.2 OBJECTIVE AND SCOPE

The monitoring campaign sought to answer the question of what PFAS-type substances can be found in influent, effluent and sewage sludge at WWTPs in the Netherlands, and in what concentrations. The aim was to obtain a nationally representative picture. At the same time, an indication was sought of the extent that PFAS are removed at WWTPs and what remains present in sewage sludge. These results can assist water boards and the Ministry of Infrastructure and Environment in determining what further interventions, if any, are necessary.

The goals of the study were the following:

- Insight into PFAS concentrations in influent and effluent, as well as PFAS loads (magnitudes, differences between treatment plants and weekly patterns if any)
- Insight into the removal of PFAS in the water line (i.e., removal efficiency)
- Insight into the possible contribution of households and other sources, including industry
- Insight into PFAS concentrations and loads removed with sludge

1.3 STRUCTURE OF THE REPORT

Chapter 2 provides general background about PFAS and the behaviour of PFAS in the environment and at WWTPs. Chapter 3 presents the design of the monitoring campaign. The results are elaborated in chapter 4 (on PFAS concentrations), chapter 5 (on PFAS loads) and chapter 6 (on removal efficiencies). Chapter 7 then zooms in on the PFAS loads found in the influent and effluent at individual WWTPs. Chapter 8 discusses the findings in more detail, while chapter 9 presents conclusions and recommendations. Key sources are listed in chapter 10, while chapter 11 defines abbreviations and terms used.

2

WHAT ARE PFAS?

2.1 GENERAL

PFAS stands for per- and polyfluoroalkyl substances. It is a collective term for man-made fluorinated compounds that do not occur naturally in the environment. PFAS have been utilised since about 1940, mainly due to their dirt, oil and water-resistant properties (ITRC, 2020). The number of applications is large. PFAS are used, among other things, in firefighting foams, textiles and carpet, food packaging materials, paper, construction materials, coatings and more (Jans & Berbee, 2020; Pancras et al., 2021; see section 8.3.2 for more applications).

PFAS are persistent, mobile and hardly biodegradable. Due to their poor degradability, they are also called ‘forever chemicals’; as what ends up in the environment doesn’t just disappear with time. Some PFAS have been shown to be toxic and/or bioaccumulative. The substances PFOS, PFOA and GenX have been classified as so-called Substances of Very High Concern (SVHC). A number of other substances in the PFAS family are on the candidate list of substances of very high concern.

A distinctive characteristic of PFAS is that they consist of one or more carbon chains, with fluorine atoms attached. The carbon chain can be fully occupied with fluorine atoms (perfluoroalkyl substances), or partly occupied with fluorine atoms (polyfluoroalkyl substances). The number of different PFAS is extremely large, with estimates ranging from 3,000 to 9,000 substances. No consensus has yet been reached on the exact definition of what substances are and are not included in the PFAS family.

PFAS are categorised into different groups (figure 1). The naming structure for PFAS compounds is complex and not entirely uniform. An extensive discussion of the different groups of PFAS[1] is beyond the scope of the present study. Section 2.2 briefly introduces the groups of PFAS that were investigated in this monitoring campaign. The introduction is based largely on Pancras et al. (2018). Fluoropolymers are not considered in this report. They are not particularly mobile in the environment and they are expected to be of low concern for humans and the environment (unless they degrade into nano- or microplastics).

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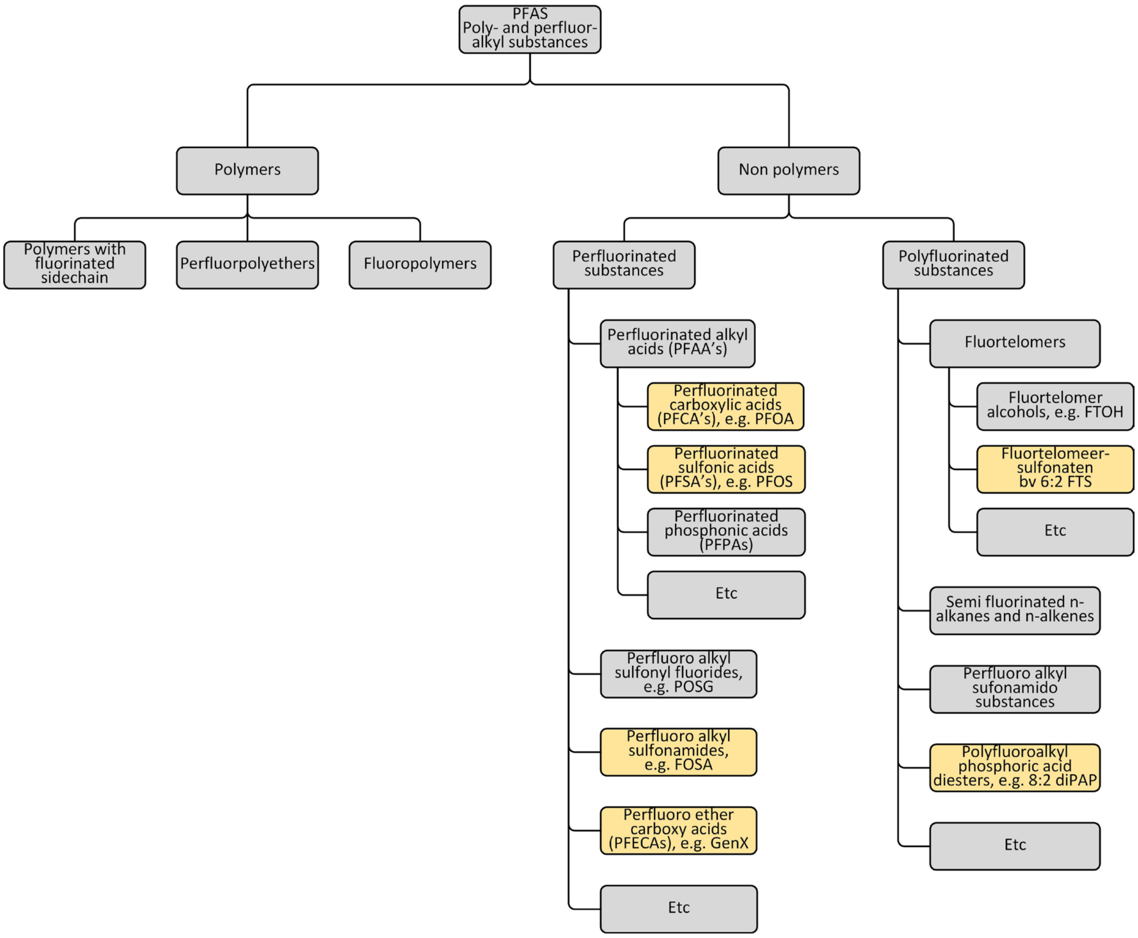
[1] The complete list of analysed PFAS is found in appendix 4. See section 3.4 for details on the selection of this analysis package.

FIGURE 1 PFAS GROUPS: THE SUBSTANCE GROUPS INVESTIGATED IN THE CURRENT MONITORING CAMPAIGN. THESE ARE BRIEFLY INTRODUCED IN SECTION 2.2. ADAPTED FROM PANCRAS ET AL. (2018)

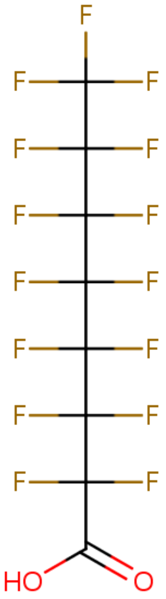


2.2 PFAS GROUPS STUDIED

2.2.1 PFCAS: PFOA-RELATED SUBSTANCES

Perfluorinated carboxylic acids (PFCAs) are substances that consist of a perfluorinated carbon chain between 2 and 16 carbon atoms in length with a carboxylic acid as a functional group at the end. The number of carbon atoms (C) is used to indicate the length of the carbon chain. Perfluorooctanoic acid (PFOA, also called C8) is the PFCA most commonly found. PFOA is often used as an adjuvant in the manufacture of fluoropolymers, especially PTFE, such as in the production of Teflon by DuPont (currently Chemours) in Dordrecht. In 2012, DuPont ceased using PFOA in its production processes, replacing it with GenX technology (Zeilmaker et al., 2016). PFOA has eight carbon atoms: seven perfluorinated carbon atoms and a carboxylic acid group containing the eighth carbon atom (see figure 2 for the structure of PFOA).

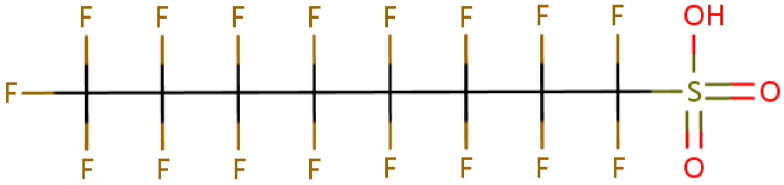
FIGURE 2 CHEMICAL STRUCTURE OF PFOA



2.2.2 PFSAS: PFOS-RELATED SUBSTANCES

Perfluoroalkylsulphonic acids (PFSAs) are substances that contain a chain of fully fluorinated carbon atoms attached to a sulfonate group as functional group on the last carbon atom. Perfluorinated sulfonic acids have carbon chains of varying lengths, typically from C2 to C16. The length of the carbon chains is reflected in the naming structure of the components. PFOS, or perfluorooctanoic acid, is made up of a chain of eight fully fluorinated carbon atoms with a sulfonate group as functional group on the last carbon atom (see figure 3 for the structure of PFOS). PFOS is the best known perfluoroalkylsulfonic acid. Short-chain PFSAs are increasingly being used to replace PFOS, for example, PFBS (perfluorobutanesulfonic acid), a C4 PFSA.

FIGURE 3 **CHEMICAL STRUCTURE OF PFOS**



2.2.3 FLUOROTELOMER SULFONATES, POLYFLUOROALKYL PHOSPHORIC ACID DIESTERS AND PERFLUOROALKANE SULFONAMIDES: PRECURSORS

Precursors are PFAS that can degrade into stable PFCAs or PFSAs. These can be fluorotelomer-derived substances, or fluorinated polymers with one or more poly- or perfluorinated side chains (OECD, 2018). There is a huge number of possible precursors. The OECD (2018) has identified more than 1,000. Only a limited number of precursors can be (and are) measured in conventional PFAS analyses. In the current monitoring campaign, precursors from three groups were studied (figure 4):

1. Fluorotelomer sulfonates
   An example of this substance group is 6:2 fluorotelomer sulfonate (6:2 FTS). 6:2 FTS is made up of six fully fluorinated carbon atoms, two non-fluorinated carbon atoms and one sulfonate group. It is an example of a PFCA precursor. 6:2 FTS is used as a replacement for PFOS for various purposes, among others, in firefighting foam and as a surfactant in industrial applications.

2. Polyfluoroalkyl phosphoric acid diesters
   An example of this substance group is 8:2 fluorotelomer phosphate diester (8:2 diPAP). PAPs are used in the paper industry, among others.

3. Perfluoroalkane sulfonamides
   An example of this substance group is perfluorooctane sulfonic acid (PFOSA). This an example of a precursor that can degrade into PFOS.

2.2.4 OTHER PFAS

Next to the groups of substances mentioned above, a number of other substitutes for, among others, PFOA were studied. Specifically, these were HFPO-DA ('GenX'), ADONA and two components of F53B (major component 9ClPF3ONS and minor component 11ClPF3OUdNS). HFPO-DA is used by Chemours, ADONA is used by 3M in Antwerp, and F53B is used in China (Pancras et al., 2021).

Chemours uses GenX technology as a replacement for PFOA in the production of Teflon. Three components play a role in GenX technology (see figure 5). In the current research, HFPO-DA (or FRD-903) was analysed. FRD-902 dissociates in water into FRD-903 and ammonium. ADONA also dissociates in water into DONA.

FIGURE 4 CHEMICAL STRUCTURE OF 6:2 FTS (ABOVE LEFT), 8:2 DIPAP (BELOW) AND PFOSA (ABOVE RIGHT). SOURCE: WWW.COMPTOX.EPA.GOV

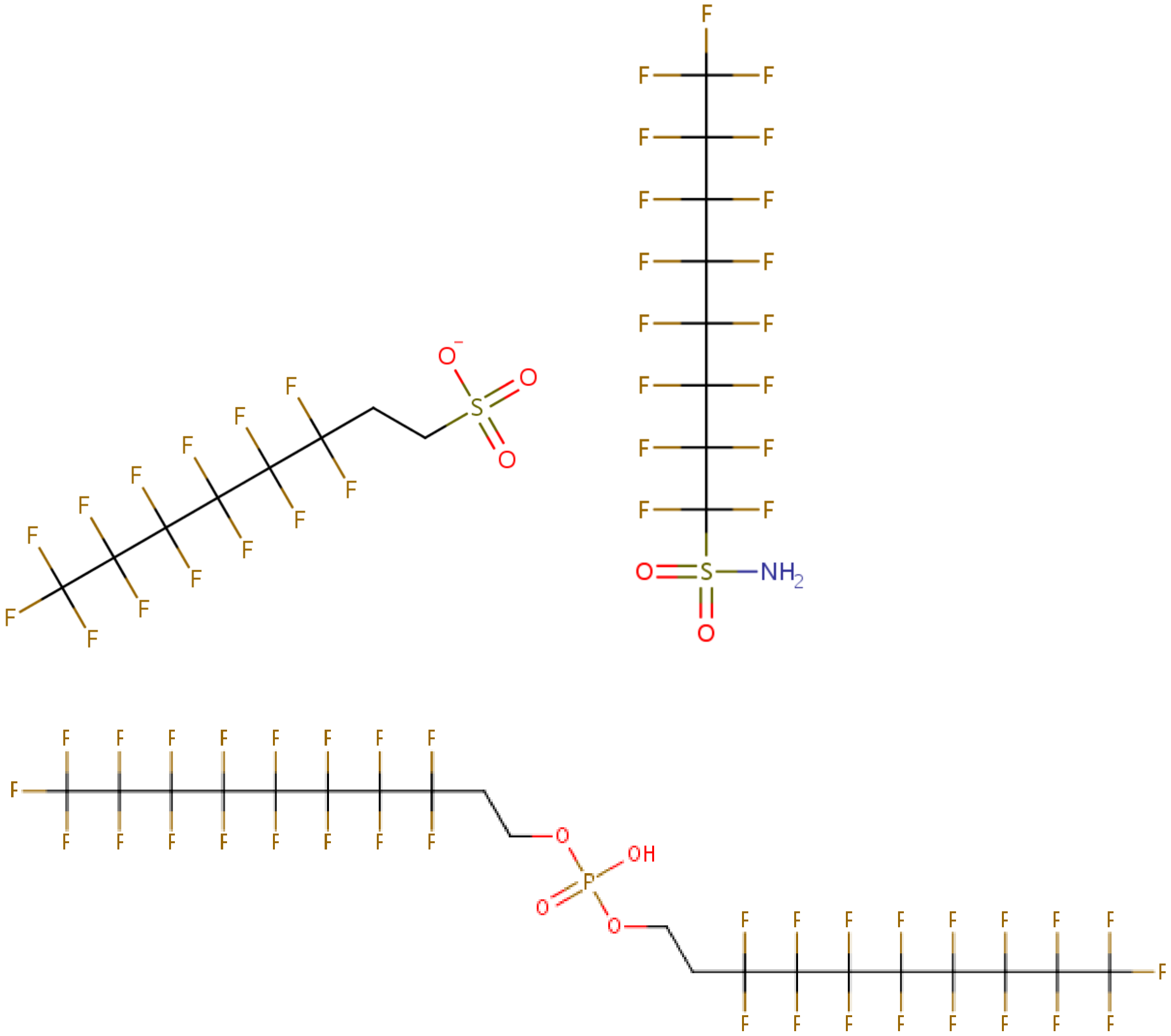
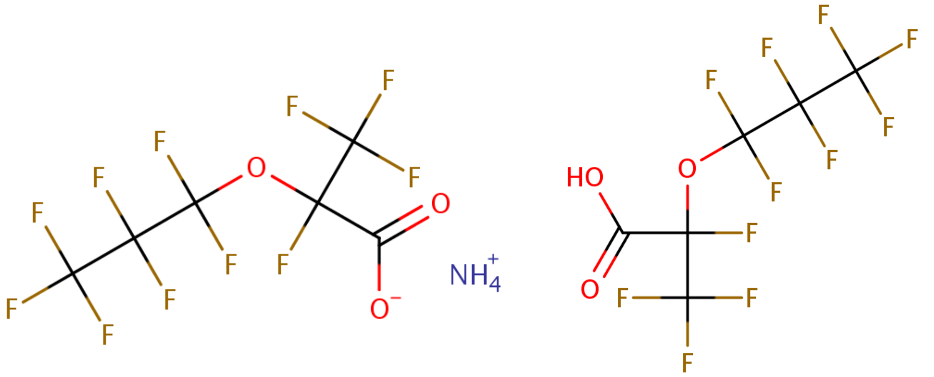


FIGURE 5 COMPONENTS OF GEN-X TECHNOLOGY: FRD902 (LEFT) AND FRD903 (RIGHT). SOURCE: WWW.COMPTOX.EPA.GOV



2.3 BEHAVIOUR OF PFAS IN THE WATER TREATMENT PROCESS

Degradation

Precursors can degrade into more stable PFAS, such as PFOA, PFOS and other PFAS with shorter carbon chains. It is for this reason that precursors are receiving increasing attention. Much is still unknown, however, about applications, behaviour, degradation pathways and terminal products of precursor degradation. Van Gijn et al. (2021) sheds light on a large number of degradation pathways. In many cases, other precursors are formed as intermediates in the degradation process.

Based on findings from the literature and from the current monitoring campaign, Van Gijn et al. (2021) concluded that quantities of most perfluorinated compounds (such as PFOS- and PFOA-related substance groups) increase at WWTPs, due to their formation from precursors. A number of subgoups within the polyfluorinated compounds generally decrease at WWTPs, but these reductions are insufficient to explain the increases in perfluorinated compounds. That means there are still unknown precursors in the water. Other subgroups within the polyfluorinated compounds, especially those with a sulfonate or carboxylic acid group, do not always exhibit a clear decrease. These subgroups are more stable at WWTPs than other subgroups within the polyfluorinated compounds.

Precursors appear to degrade better in the presence of oxygen (i.e., in aerobic conditions) than in anoxic (anaerobic) conditions (Eggen et al., 2019).

Sorption

Partition coefficients are usually used to describe the distribution of a substance between the solid phase and water. The sorption behaviour of PFAS, however, differs from that of ‘traditional’ contaminants, because PFAS tends to bind to cell membranes and proteins instead of oil (Baresel et al., 2015).

In general, it can be stated that PFAS with short chains are mainly found in the water phase and PFAS with long chains bind more to sludge. PFSAs (such as PFOS) bind more strongly to sludge than do PFCAs (e.g., PFOA). Many precursors bind to sludge as well (Xiao, 2017).

Volatilisation

Most PFAS have a negligible volatility. However, many precursors, such as fluorotelomer alcohols and perfluoroalkane sulfonamido ethanols are volatile (Baresel et al., 2015). It is not yet clear whether, and if so to what extent, volatilisation of these substance groups occurs at WWTPs.

3

STUDY DESIGN

3.1 WWTP SELECTION

Eight WWTPs were selected for this study. A mix of WWTPs was sought, including (former) hotspot locations, WWTPs treating a relatively large proportion of industrial wastewater, WWTPs treating mixed domestic and industrial wastewater and WWTPs treating almost exclusively domestic wastewater.

The expectation was that background levels emitted by households could be quantified based on findings from the WWTPs treating almost exclusively domestic wastewater, while the remaining WWTPs would provide insight on the contributions of particular sources, both industrial and non-industrial.

However, the PFAS concentrations and loads[2] found were not always consistent with expectations beforehand (see chapter 5). Therefore, for the presentation and interpretation of results, the choice was made to group the WWTPs into three categories – high, moderate and low – based on the emission factors in their effluent (i.e., the amount of PFAS discharged with the effluent per population equivalent (PE) per day). Table 1 summarises the reasons for selecting the included WWTPs and their categorisations according to the extent of PFAS found. For further details on the selected WWTPs, see appendix 1.

TABLE 1 **SELECTED WWTPS, BASIS FOR SELECTION, AND EXTENT OF PFAS LOAD. THE EXTENT OF PFAS LOAD REPRESENTS MEASURED EMMISSION FACTORS IN EFFLUENT**

WWTP	Description/basis for selection	High PFAS load	Moderate PFAS load	Low PFAS load
Dordrecht	Hotspot	x		
Aarle Rixtel	Former hotspot		x	
Bath	Large proportion industry	x		
Lelystad	Mixed WWTP		x	
Hattem	Mixed WWTP			x
Asten	Almost exclusively domestic wastewater			x
Hapert	Almost exclusively domestic wastewater			x
Piershil	Almost exclusively domestic wastewater		x	

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[2] That is, the load per population equivalent (PE). Population equivalents are used to indicate the capacity of and load on a WWTP. There are different types of PE. In this report PE 150 is used. This expresses an oxygen-binding capacity of 150 grams of oxygen per inhabitant per day. The load (or contaminant concentration) can be from domestic wastewater, industrial wastewater, rainfall runoff and/or other surface runoff and wastewater. Expressing loads in population equivalents enables the PFAS levels at the different WWTPs to be compared to one another.

3.2 SAMPLING

This section outlines some of the main choices made and other aspects of the sampling procedure. Appendix 2 presents the sampling design in more detail.

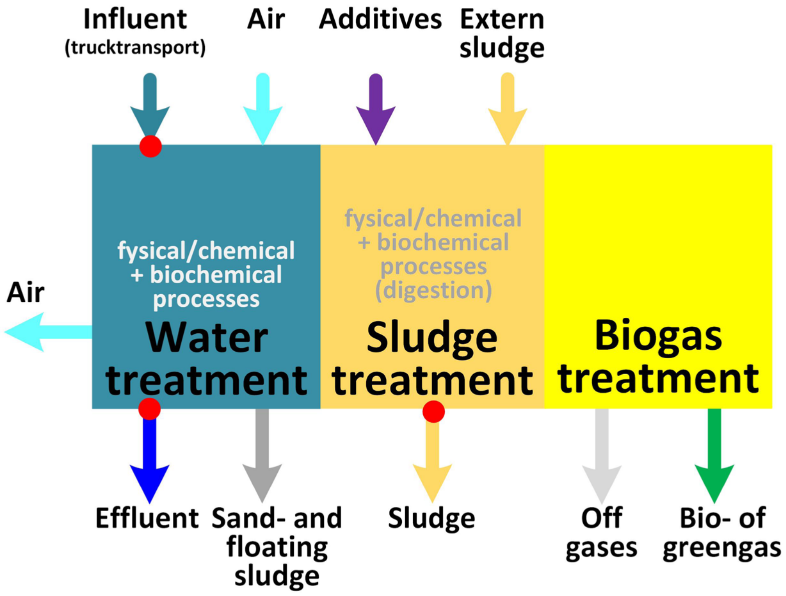
3.2.1 GENERAL

Some WWTPs have complex internal water and sludge streams (see process diagrams in appendix 1). Figure 6 presents a simplified schematic diagram of incoming and outgoing flows at a WWTP. Sample collection was limited to the following incoming and outgoing flows at the WWTPs:

- Influent
- Effluent
- Sludge removed

The choice was made to sample only the sludge removed. Incoming sludge (from own WWTP and delivered per ash) and the way this was processed at the different treatment facilities was so diverse and complex as to make representative and uniform sampling difficult. Moreover, the main question was whether the sewage sludge transported elsewhere contained a large enough quantity of PFAS as to cause problems for its end use.

FIGURE 6 SCHEMATIC DIAGRAM OF THE MAIN WATER AND SLUDGE STREAMS WITHIN A WWTP. RED DOTS INDICATE THE SAMPLING LOCATIONS. INFLUENT IS PARTLY DELIVERED BY TRUCK TRANSPORT



3.2.2 INFLUENT AND EFFLUENT

At each WWTP, 24-hour flow-proportional samples were collected of influent and effluent on nine consecutive days. The sampling method was chosen to provide insight into the variability PFAS concentrations and removal efficiencies. Sampling was continued during periods of wet weather. This provided information about influent concentrations and removal efficiencies in conditions of both dry weather flow (DWF) and wet weather flow (WWF).[3]

3.2.3 SEWAGE SLUDGE

During the nine-day sampling period, the outgoing sludge line was sampled by means of grab samples. In most cases, three grab samples were analysed per treatment plant. An indication could thus be obtained of the ranges of concentrations occurring in the sludge. Concentration ranges in the sludge were expected to be less pronounced than in the influent and effluent.

3.2.4 OTHER SAMPLES

A number of special samples was also analysed in this monitoring campaign. These were the following:

1. Sieved material (Aarle Rixtel)
   At Aarle Rixtel WWTP, a large amount of fibrous matter made up of mainly toilet paper residue, termed 'sieved material', was removed from the influent. Three grab samples of this sieved material were analysed.

2. Industrial wastewater streams discharged to Dordrecht WWTP which were known or suspected to contain PFAS. These were the following:
   a. Three separate wastewater streams from the HVC Group (energy and waste disposal company), made up of
      - Wastewater from sludge incineration (HVCsvi)
      - Wastewater from domestic and hospital waste incineration (HVCara)

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[3] In mixed sewage systems the influent entering the treatment facility is mixed with stormwater runoff. In the case of a separated sewage system (in this study only Lelystad WWTP), stormwater runoff is removed separately via a stormwater sewer to surface waters and does not end up at the WWTP.

- Drainage water from a landfill mixed with stormwater runoff from the terrain of HVC (HVCdov) (hereinafter: landfill wastewater)

All three of these wastewater streams underwent a separate wastewater treatment, consisting of physical or physical/chemical processes. Appendix 1 presents block diagrams of the wastewater treatment processes at the sampled WWTPs. The 24-hour flow-proportional effluent samples were collected by HVC and made available for analysis.

b. Wastewater originating from Chemours.
This regards manufacturing wastewater from Chemours, which uses PFAS compounds, among others, in its production processes. Chemours wastewater was treated using various physical/chemical processes, such as solid matter filtration, reverse osmosis and absorption with activated carbon filters, before being discharged to the WWTP. Chemours collected samples of the treated wastewater using 24-hour flow-proportional sampling.

3. Sludge from HVC
This is the sewage sludge originating from different water boards and delivered to HVC. HVC had Eurofins analyse four mixed samples of this sludge and made the results available for the present study.

The block diagrams in appendix 2 also include the industrial wastewater streams. The red dots in the diagrams indicate where in the process the sampling was performed.

Appendix 3 summarises the analysed samples and sample data. In addition to these, HVC took four mixed samples of incoming sludge and had these analysed by Eurofins. That analysis package is somewhat different from the one applied in our analyses.

3.3 SAMPLING QUALITY CONTROL

Before sample collection began, all of the WWTPs were visited for an inspection to look for possible sources of PFAS contamination, in accordance with the guidelines published by the PFAS Expertise Centre for sampling and analysis of PFAS compounds in soil and groundwater.[4] A detailed inspection report was produced for each WWTP. To ensure that sample collection was performed in the same manner throughout and to reduce the risk of exposure to PFAS, sampling of the influent and effluent was performed by specially trained staff of the water board laboratories Aquon and Aqualysis.

The sludge samples were collected by staff of the treatment plants themselves. The HVC and Chemours wastewater streams, and the sludge samples from HVC, were sampled by staff from these companies.

The samples were collected in conformance with the NEN 6600-1 standard.[5] Among other things, this sets specific requirements for the sampling equipment, and mandates that sample collection be done in accordance with the NEN 6600 criteria. These findings were recorded separately. When, during the sample collection procedure, there was any indication that one or more of the set criteria were not met, the sampling staff consulted with the project team on whether the sample could be included. In a few cases, this meant that the sampling cycle had to be extended in order to obtain an adequate sample serie.

[4] https://www.bodemplus.nl/onderwerpen/wet-regelgeving/bbk/publicaties/bemonstering-pfas/

[5] NEN (2019). NEN 6600-1. Water – Sampling – Part 1: Waste water.

3.4 ANALYSIS

PFAS analyses

The PFAS analyses were performed by VU Amsterdam. In selecting the laboratory, consideration was given to, among other things, use of a validated analysis methodology, the reporting limits attainable, the analysis package (as broad as possible, including HFPO-DA ('GenX') and PFAS precursors) and experience with PFAS analyses in the relevant matrix. Appendix 4 presents the analysis package, which encompasses a total of 35 substances from different PFAS groups. The analytical method is presented in appendix 5.

Normally a reporting limit is given (i.e., the lowest concentration which can be reliably quantified). In this case, the VU also reported the detection limit (i.e., the lowest concentration detectable, though less reliable for quantification).

General parameters

To obtain representative samples, it was important for the WWTPs to function normally during the sampling period. To assess this, the effluent samples were analysed for undissolved components, ammonium and Kjeldahl nitrogen content. These analyses were performed by Aquon or Aqualysis, depending on the WWTP. All of the WWTPs were found to have functioned normally during the sampling period.

3.5 DATA PROCESSING

The data processing method is set out in more detail in appendix 6.

In elaborating the results, quantities between the detection limit (DL) and the reporting limit (RL) were taken as values for the calculations. In calculations of the total quantity, average and loads, levels below the detection limit were replaced according to the Volkert-Bakker method (i.e., calculations were performed with a substitution value that was dependent on the percentage of observations above the detection limit). The choice was made to do the calculations using the detection limit instead of the reporting limit in order to be able to perform more of the calculations using a numeric rather than a substitution value. While this numeric value is less reliable, it is still considered more reliable than a substitution value.

4

CONCENTRATIONS

4.1 INFLUENT AND EFFLUENT

Of the 35 PFAS studied, 28 were found at least once in influent and/or effluent. PFAS were found in all of the samples analysed, with the number of individual substances ranging from 4 to 21 per sample (average: 14). Table 2 summarises the concentrations in influent and effluent, based on maximum concentrations. Figure 7a, 7c and 7d graphically present the *average* concentrations[6] found at WWTPs with, respectively, high, moderate and low PFAS loads. As the wastewater streams from HVC and Chemours were treated at Dordrecht WWTP, they are presented in figure 7b (directly under the high-load WWTPs). Note: the y-axis scales differ per figure.

Total PFAS concentrations in influent and effluent were found to be markedly different across the WWTPs, ranging from 9.6 to 1,360 ng/l in influent and from 13.6 to 809 ng/l in effluent. The main compounds found were PFCAs and PFSAs with shorter carbon chains (up to and including C10 and C9, respectively). In addition, HFPO-DA ('GenX'), fluorotelomers (especially 6:2 FTS) and sporadic FOSAs were found. PFCAs and PFSAs with longer carbon chains (C10 and higher) were seldom or never found.

As expected, the highest concentrations were measured at Dordrecht and Bath WWTPs, and the lowest concentrations were measured at the WWTPs receiving primarily domestic wastewater. However, there were exceptions. For example, PFAS concentrations at Piershil WWTP were higher than was expected based on the type of wastewater it receives (i.e., almost exclusively domestic flows). At Hattem WWTP, PFAS concentrations were lower than expected considering the type of wastewater it receives (i.e., this WWTP handles a mixture of domestic and industrial wastewater). In view of these results, as outlined in section 3.1, a categorisation was made, with WWTPs grouped as having 'high', 'moderate' or 'low' PFAS loads.

The results clearly show that PFAS were not removed at the WWTPs, or were hardly removed; in many cases, concentrations of precursors and/or stable PFAS even increased (see chapters 5 and 7 for details).

Next to the concentrations, the WWTPs differed in contamination pattern (i.e., the distribution and proportion of the different individual substances found in the samples), as seen in table 2 and in figure 7a, 7c and 7d. A similar pattern was found in influent and effluent at most WWTPs, but at some, in particular at Lelystad and Hattem WWTPs, a shift was observed to other PFAS in the effluent. Chapter 7 zooms in on this finding and discusses possible explanations for it.

No clear weekly pattern was observed in the measurements. Largely similar concentrations were measured on the different sampling days. But there were a number of exceptions. For example, a wide range was found in concentrations of 6:2 FTS (77–410 ng/l) and PFBA (13–930 ng/l) measured in the influent at Bath WWTP, and peaks of 6:2 FTS (up to 45 ng/l) were observed at Hapert WWTP. Whether these were related to wet weather was not examined in detail.

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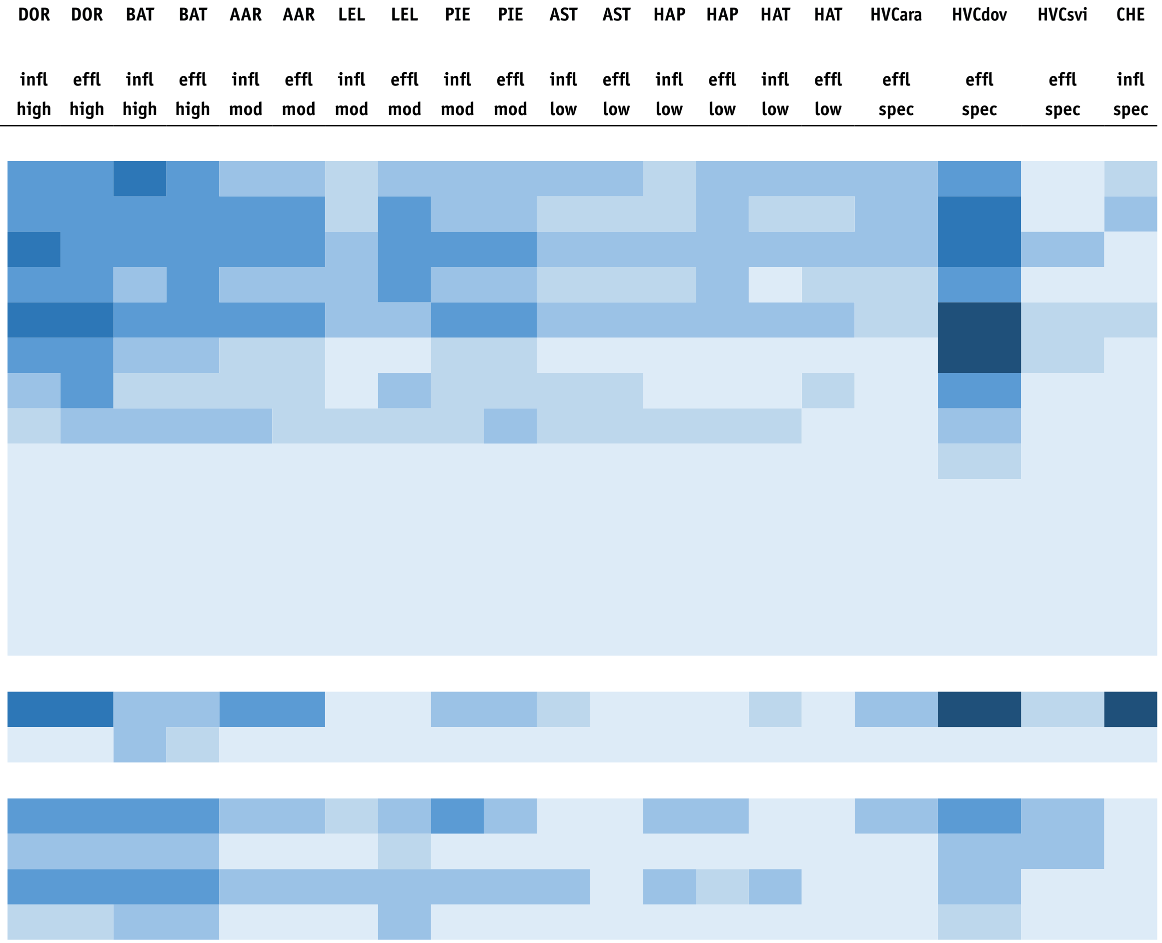
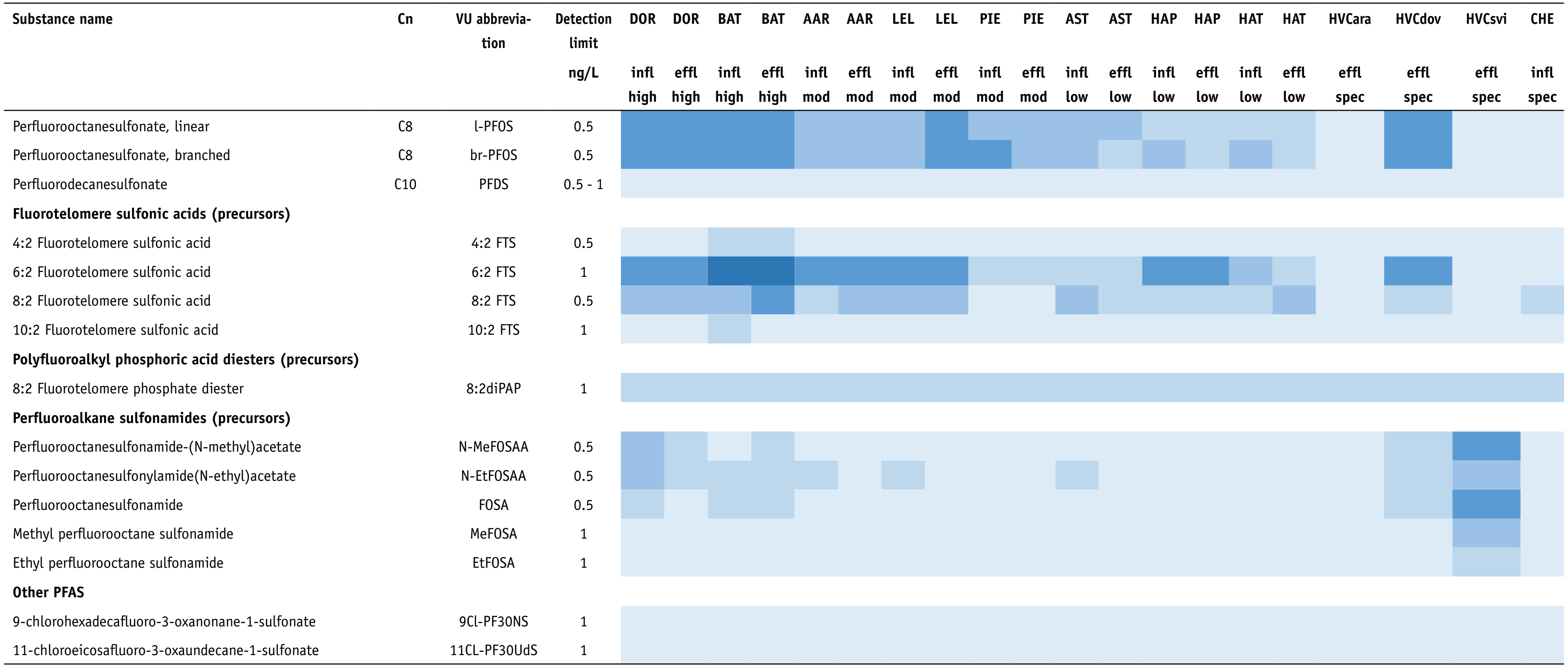
[6] What is termed 'average concentrations' in the text are actually weighted average concentrations. See appendix 6.

TABLE 2 SUMMARY OF *MAXIMUM* CONCENTRATIONS FOUND IN INFLUENT AND EFFLUENT AT EIGHT WWTPS AND SEVERAL SPECIAL WASTEWATER STREAMS.). HVCARA = WASTEWATER FROM DOMESTIC AND HOSPITAL WASTE INCINERATION, HVCDOV = WASTEWATER FROM FORMER LANDFILL, HVCSVI = WASTEWATER FROM SLUDGE INCINERATION AT CHEMOURS AND CHE = WASTEWATER FROM CHEMOURS

Heatmap PFAS in influent and effluent
Substance group name adopted from PFAS guidelines by the PFAS Expertise Centre (Pancras et al., 2018).
Cn = number of carbon atoms in the fluorinated carbon chain
N.A. = could not be determined, all levels were greater than the reporting limit

Substance name	Cn	VU abbreviation	Detection limit ng/L
Perfluoroalkyl carboxylic acids (PFCAs)			
Perfluorobutanoic acid	C4	PFBA	1
Perfluoropentanoic acid	C5	PFPeA	1
Perfluorohexanoic acid	C6	PFHxA	0.5
Perfluoroheptanoic acid	C7	PFHpA	0.5
Perfluorooctanoic acid, linear	C8	l-PFOA	0.5
Perfluorooctanoic acid, branched	C8	br-PFOA	0.5
Perfluorononanoic acid	C9	PFNA	0.5
Perfluorodecanoic acid	C10	PFDA	0.5
Perfluoroundecanoic acid	C11	PFUnDA	0.5
Perfluorododecanoic acid	C12	PFDoA	0.5
Perfluorotridecanoic acid	C13	PFTrDA	0.5
Perfluorotradecanoic acid	C14	PFTeDA	0.5
Perfluorohexadecanoic acid	C16	PFHxDA	0.5 - 1
Perfluorooctadecanoic acid	C18	PFODA	1
Perfluoroalkyl ether carboxylic acids (PFECAs)			
TetraFluoro-2-heptafluoropropoxy) propanoic acid		HFPO-DA	0.1
Dodecafluoro-3H-4,8-dioxanonanoate		DONA	0.1
Perfluoroalkyl sulfonic acids (PFSAs)			
Perfluorobutanesulfonate	C4	PFBS	0.5
Perfluoropentanesulfonate	C5	PFPeS	0.25
Perfluorohexanesulfonate	C6	PFHxS	0.25
Perfluoroheptanesulfonate	C7	PFHpS	0.25





Substance name	Cn	VU abbreviation	Detection limit ng/L	DOR infl high	DOR effl high	BAT infl high	BAT effl high	AAR infl mod	AAR effl mod	LEL infl mod	LEL effl mod	PIE infl mod	PIE effl mod	AST infl low	AST effl low	HAP infl low	HAP effl low	HAT infl low	HAT effl low	HVCara effl spec	HVCdov effl spec	HVCsvi effl spec	CHE infl spec
Perfluorooctanesulfonate, linear	C8	l-PFOS	0.5																				
Perfluorooctanesulfonate, branched	C8	br-PFOS	0.5																				
Perfluorodecanesulfonate	C10	PFDS	0.5 - 1																				
Fluorotelomere sulfonic acids (precursors)																							
4:2 Fluorotelomere sulfonic acid		4:2 FTS	0.5																				
6:2 Fluorotelomere sulfonic acid		6:2 FTS	1																				
8:2 Fluorotelomere sulfonic acid		8:2 FTS	0.5																				
10:2 Fluorotelomere sulfonic acid		10:2 FTS	1																				
Polyfluoroalkyl phosphoric acid diesters (precursors)																							
8:2 Fluorotelomere phosphate diester		8:2diPAP	1																				
Perfluoroalkane sulfonamides (precursors)																							
Perfluorooctanesulfonamide-(N-methyl)acetate		N-MeFOSAA	0.5																				
Perfluorooctanesulfonylamide(N-ethyl)acetate		N-EtFOSAA	0.5																				
Perfluorooctanesulfonamide		FOSA	0.5																				
Methyl perfluorooctane sulfonamide		MeFOSA	1																				
Ethyl perfluorooctane sulfonamide		EtFOSA	1																				
Other PFAS																							
9-chlorohexadecafluoro-3-oxanonane-1-sulfonate		9Cl-PF3ONS	1																				
11-chloroeicosafluoro-3-oxaundecane-1-sulfonate		11CL-PF3OUdS	1																				

Colour coding influent and effluent according to maximum:

Limit of detection (DL)
Limit of Quantification (reporting limit, RL)
<10 ng/l
10-100 ng/l
100 – 1,000 ng/l
> 1,000 ng/l

FIGURE 7A AVERAGE PFAS CONCENTRATIONS (IN NG/L) IN INFLUENT AND EFFLUENT FOR WWTPS WITH HIGH PFAS LOADS: DORDRECHT WWTP (DOR) AND BATH WWTP (BAT)

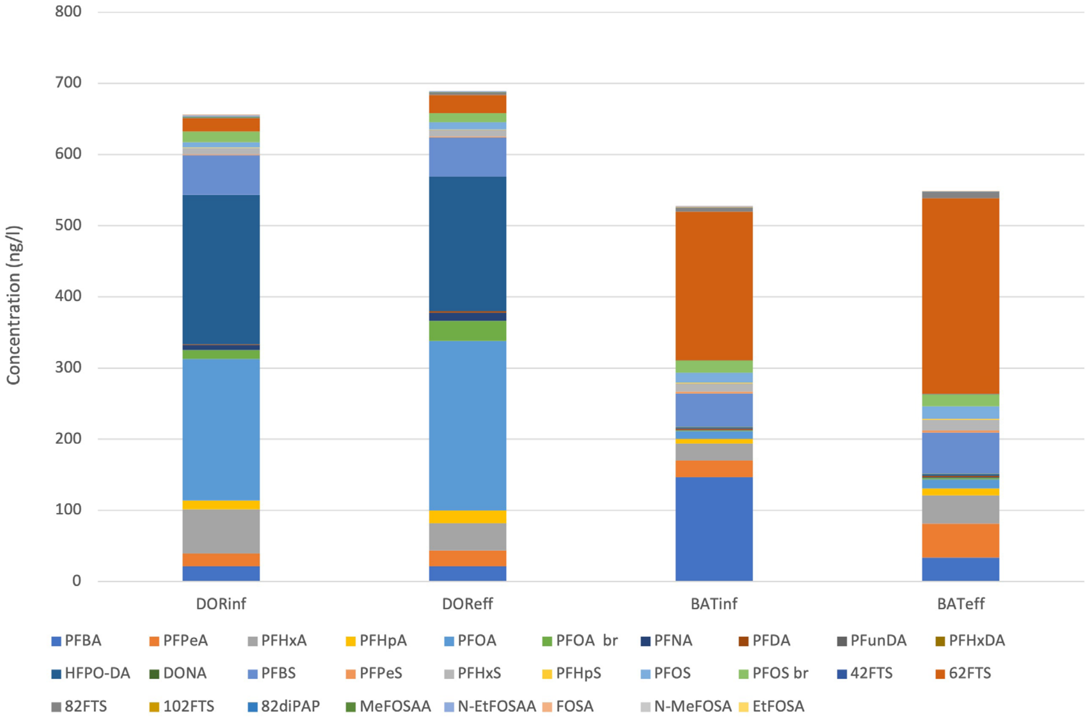


FIGURE 7B AVERAGE PFAS CONCENTRATIONS IN WASTEWATER STREAMS ORIGINATING FROM HVC ENERGY AND WASTE DISPOSAL COMPANY AND CHEMOURS (CHE). HVCARA = WASTEWATER FROM DOMESTIC AND HOSPITAL WASTE INCINERATION, HVCDOV = DRAINAGE WATER FROM FORMER LANDFILL MIXED WITH STORMWATER RUNOFF FROM THE HVC INDUSTRIAL GROUNDS AND HVCSVI = WASTEWATER FROM SLUDGE INCINERATION AT CHEMOURS. A DISTINCTION IS MADE INTO PERIODS WITH LOW (CHEINFLAAG) AND HIGH (CHEINFHOOG) CONCENTRATIONS (SEE TEXT)

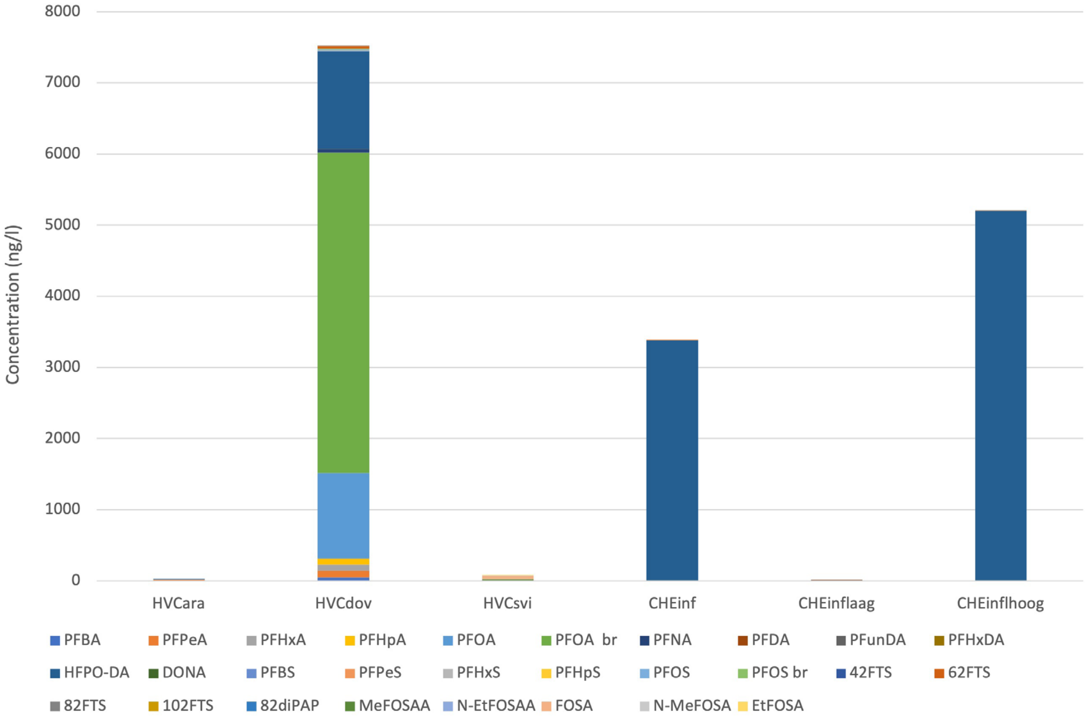


FIGURE 7C AVERAGE PFAS CONCENTRATIONS (IN NG/L) IN INFLUENT AND EFFLUENT FOR WWTPS WITH MODERATE PFAS LOADS: AARLE RIXTEL WWTP (AAR), LELYSTAD WWTP (LEL) AND PIERSHIL WWTP (PIE)

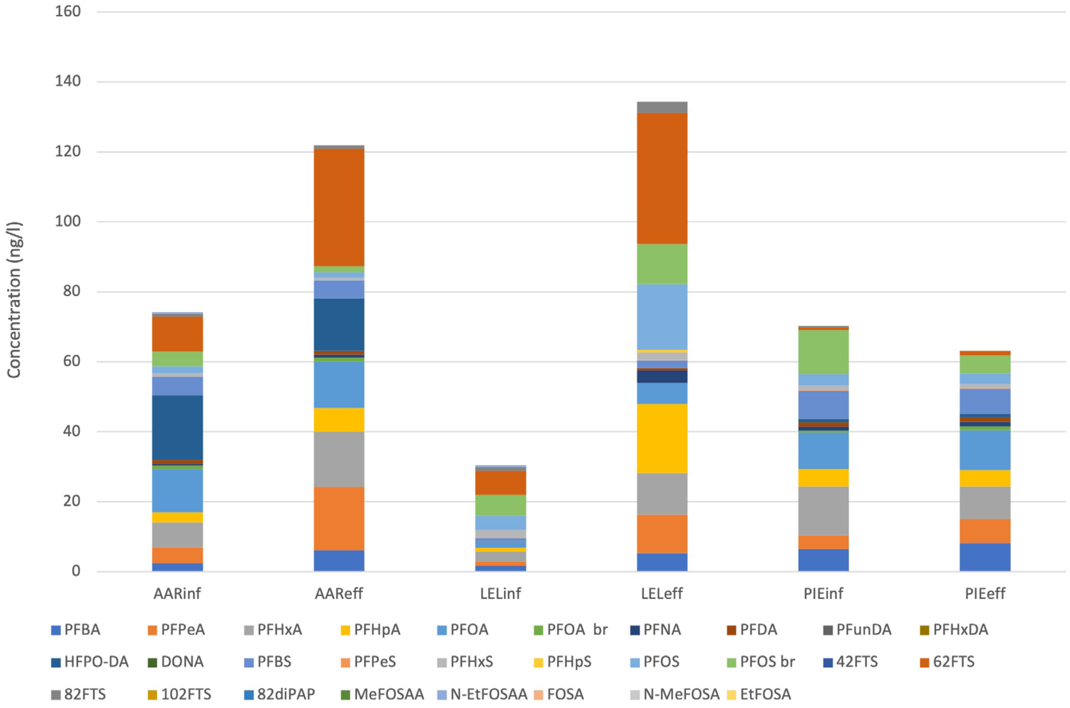
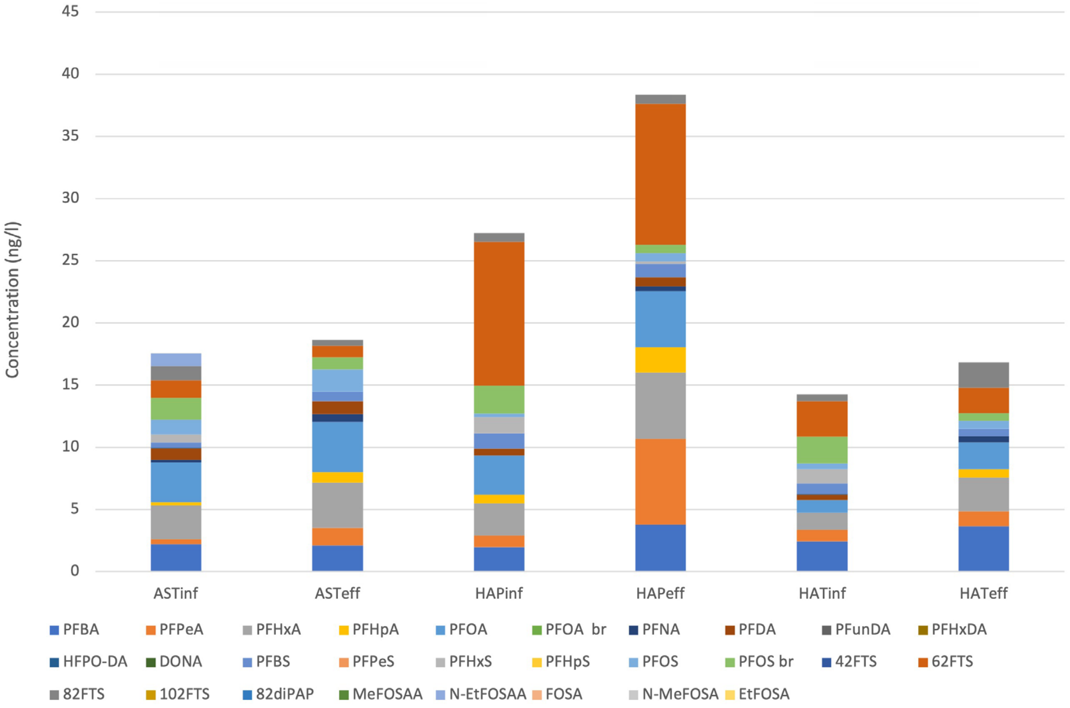


FIGURE 7D AVERAGE PFAS CONCENTRATIONS (IN NG/L) IN INFLUENT AND EFFLUENT FOR WWTPS WITH LOW PFAS LOADS: ASTEN WWTP (AST), HAPERT WWTP (HAP) AND HATTEM WWTP (HAT)



4.2 SPECIAL WASTEWATER STREAMS

Figure 7b presents the average concentrations found in the special wastewater streams. All of these wastewater streams – following treatment by HVC and Chemours – are discharged to Dordrecht WWTP, where alongside domestic wastewater, they form the influent.

Large differences were observed in the wastewater streams from HVC. In the wastewater from the sludge incineration facility (HVCsvi) and in the wastewater from incineration of domestic and hospital waste (HVCara), PFAS were hardly found (respectively, a maximum of 99 ng/l and 28 ng/l total PFAS). It is notable that in the wastewater from the sludge incineration facility, mainly precursors in the perfluoroalkane sulfonamides group were found, especially FOSA and MeFOSAA. This group of substances was not, or hardly, found in the wastewater at the other facilities, though it was found in the sewage sludge at all the facilities.

Very high concentrations were found in the wastewater from the landfill (HVCdov), that is, 6,225 to 9,171 ng/l total PFAS. These high concentrations were made up mainly of PFOA, branched PFOA and HFPO-DA (‘GenX’), though a large number of other PFAS were found as well. These were the same substances that were also found in the influents and effluents. Earlier research found high PFAS concentrations in wastewater from landfill sites (Jans et al., 2020). The results from HVCdov are therefore in line with expectations.

In the wastewater from Chemours, primarily HFPO-DA was found, alongside relatively low concentrations of a few other PFAS. The most notable finding from the Chemours wastewater was a large increase in HFPO-DA concentrations starting on day 4 (from approx. 10 ng/l to 5,000–6,000 ng/l). Chemours stated in a response that this result reflects a normal variation in effluent quality at their wastewater treatment facility. No operational anomalies were reported at the Chemours wastewater treatment plant during the sampling period from late November to early December 2020. The sudden increase in HFPO-DA concentrations in the effluent could be a function of variations corresponding to batch-wise production of PTFE and FEP, thus causing fluctuating PFAS concentrations in process wastewater. According to Chemours’ own measurements (a total of 317 samples over a 2.5 year period), HFPO-DA concentrations averaged 754 ng/l, and had decreased over time (see appendix 7). This is much less than the average concentration measured in the current study, which was approx. 3,500 ng/l. After the sampling period the activated carbon filter was replaced as part of regularly scheduled maintenance.

4.3 SEWAGE SLUDGE

Of the 35 PFAS studied, 32 were found at least once in sewage sludge. PFAS were found in all of the sludge samples analysed. The number of individual substances ranged from 24 to 31 per sample (average: 28). Table 3 summarises the concentrations found in sewage sludge, based on the *maximum* concentrations measured. Figure 8a and 8b present the average concentrations found at WWTPs with, respectively, high, moderate and low PFAS loads. Note: the *y*-axis scales differ per figure.

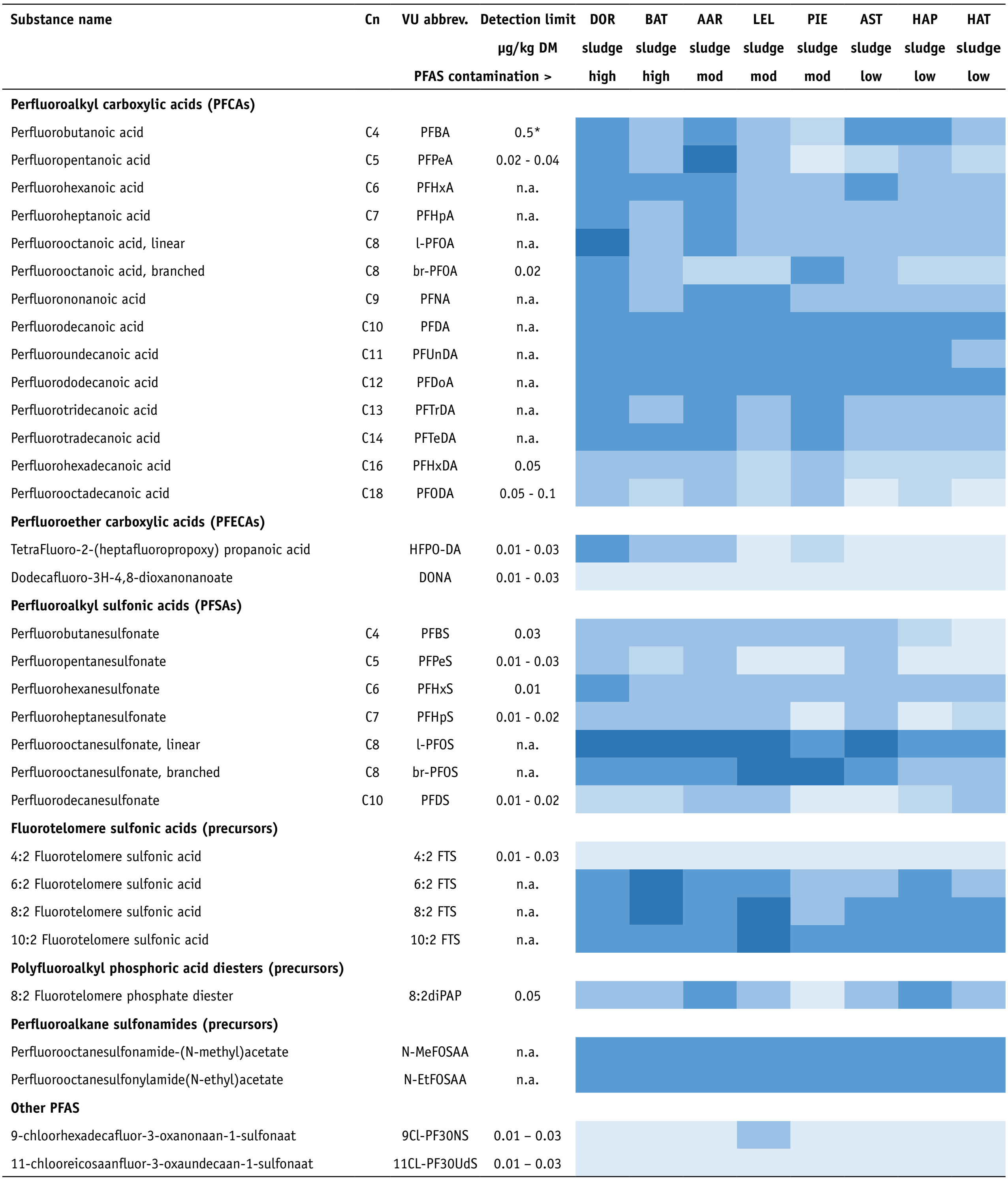
In figure 8b we see that the contamination patterns at the low-load WWTPs were fairly similar, while many differences were observed among the high- and moderate-load WWTPs (figure 8a). Particularly notable are the high concentrations of PFOS and 10:2FTS at Lelystad WWTP and of PFPeA at Aarle Rixtel.

The concentrations measured were similar across the sampling days for the most part. Only at Aarle Rixtel WWTP was the range in concentrations somewhat larger, mainly stemming from differences in concentrations of PFOS and C5-C8 PFCAs.

In the sieved material at Aarle Rixtel, 3.1–11 µg PFAS(35)/kg DM was found. The contamination pattern was similar to that of the sewage sludge at Aarle Rixtel.

TABLE 3 **SUMMARY OF *MAXIMUM* CONCENTRATIONS FOUND (IN µG/KG DM) IN SEWAGE SLUDGE AT EIGHT WWTPS**

Heatmap PFAS in sludge
Substance group name adopted from PFAS guidelines by the PFAS Expertise Centre (Pancras et al., 2018).
Cn = number of carbon atoms in the fluorinated carbon chain
N.A. = could not be determined, all levels were greater than the reporting limit



Substance name	**Cn**	**VU abbrev.**	**Detection limit**	**DOR**	**BAT**	**AAR**	**LEL**	**PIE**	**AST**	**HAP**	**HAT**
			µg/kg DM	**sludge**	**sludge**	**sludge**	**sludge**	**sludge**	**sludge**	**sludge**	**sludge**
			PFAS contamination >	**high**	**high**	**mod**	**mod**	**mod**	**low**	**low**	**low**
Perfluoroalkyl carboxylic acids (PFCAs)											
Perfluorobutanoic acid	C4	PFBA	0.5*	▓	▒	▓	▒	░	▓	▓	▒
Perfluoropentanoic acid	C5	PFPeA	0.02 - 0.04	▓	▒	█	▒	·	░	▒	░
Perfluorohexanoic acid	C6	PFHxA	n.a.	▓	▓	▓	▒	▒	▓	▒	▒
Perfluoroheptanoic acid	C7	PFHpA	n.a.	▓	▒	▓	▒	▒	▒	▒	▒
Perfluorooctanoic acid, linear	C8	l-PFOA	n.a.	█	▒	▓	▒	▒	▒	▒	▒
Perfluorooctanoic acid, branched	C8	br-PFOA	0.02	▓	▒	░	░	▓	▒	░	░
Perfluorononanoic acid	C9	PFNA	n.a.	▓	▒	▓	▓	▒	▒	▒	▒
Perfluorodecanoic acid	C10	PFDA	n.a.	▓	▓	▓	▓	▓	▓	▓	▓
Perfluoroundecanoic acid	C11	PFUnDA	n.a.	▓	▓	▓	▓	▓	▓	▓	▒
Perfluorododecanoic acid	C12	PFDoA	n.a.	▓	▓	▓	▓	▓	▓	▓	▓
Perfluorotridecanoic acid	C13	PFTrDA	n.a.	▓	▒	▓	▒	▓	▒	▒	▒
Perfluorotradecanoic acid	C14	PFTeDA	n.a.	▓	▓	▓	▒	▓	▒	▒	▒
Perfluorohexadecanoic acid	C16	PFHxDA	0.05	▒	▒	▒	░	▒	░	░	░
Perfluorooctadecanoic acid	C18	PFODA	0.05 - 0.1	▒	░	▒	░	▒	·	░	·
Perfluoroether carboxylic acids (PFECAs)											
TetraFluoro-2-(heptafluoropropoxy) propanoic acid		HFPO-DA	0.01 - 0.03	▓	▒	▒	·	░	·	·	·
Dodecafluoro-3H-4,8-dioxanonanoate		DONA	0.01 - 0.03	·	·	·	·	·	·	·	·
Perfluoroalkyl sulfonic acids (PFSAs)											
Perfluorobutanesulfonate	C4	PFBS	0.03	▒	▒	▒	▒	▒	▒	░	·
Perfluoropentanesulfonate	C5	PFPeS	0.01 - 0.03	▒	░	▒	·	·	▒	·	·
Perfluorohexanesulfonate	C6	PFHxS	0.01	▓	▒	▒	▒	▒	▒	▒	▒
Perfluoroheptanesulfonate	C7	PFHpS	0.01 - 0.02	▒	▒	▒	▒	·	▒	·	░
Perfluorooctanesulfonate, linear	C8	l-PFOS	n.a.	█	█	█	█	▓	█	▓	▓
Perfluorooctanesulfonate, branched	C8	br-PFOS	n.a.	▓	▓	▓	█	█	▓	▒	▒
Perfluorodecanesulfonate	C10	PFDS	0.01 - 0.02	░	░	▒	▒	·	·	░	▒
Fluorotelomere sulfonic acids (precursors)											
4:2 Fluorotelomere sulfonic acid		4:2 FTS	0.01 - 0.03	·	·	·	·	·	·	·	·
6:2 Fluorotelomere sulfonic acid		6:2 FTS	n.a.	▓	█	▓	▓	▒	▒	▓	▒
8:2 Fluorotelomere sulfonic acid		8:2 FTS	n.a.	▓	█	▓	█	▒	▓	▓	▓
10:2 Fluorotelomere sulfonic acid		10:2 FTS	n.a.	▓	▓	▓	█	▓	▓	▓	▓
Polyfluoroalkyl phosphoric acid diesters (precursors)											
8:2 Fluorotelomere phosphate diester		8:2diPAP	0.05	▒	▒	▓	▒	·	▒	▓	▒
Perfluoroalkane sulfonamides (precursors)											
Perfluorooctanesulfonamide-(N-methyl)acetate		N-MeFOSAA	n.a.	▓	▓	▓	▓	▓	▓	▓	▓
Perfluorooctanesulfonylamide(N-ethyl)acetate		N-EtFOSAA	n.a.	▓	▓	▓	▓	▓	▓	▓	▓
Other PFAS											
9-chloorhexadecafluor-3-oxanonaan-1-sulfonaat		9Cl-PF30NS	0.01 – 0.03	·	·	·	▒	·	·	·	·
11-chlooreicosaanfluor-3-oxaundecaan-1-sulfonaat		11CL-PF30UdS	0.01 – 0.03	·	·	·	·	·	·	·	·

Color codes sludge based on maximum:

· < Limit of detection (DL)
░ < Limit of Quantification (reporting limit, RL)
▒ <1 µg/kg DM
▓ 1-10 µg/kg DM
█ 10-100 µg/kg DM
■ >100 µg/kg DM

** Exception, lowest measurement = 0.17 µg/kg DM*

FIGURE 8A AVERAGE PFAS CONCENTRATIONS (IN µG/KG DM) IN SEWAGE SLUDGE FOR HIGH AND MODERATE PFAS-LOAD WWTPS: DORDRECHT WWTP (DOR), BATH WWTP (BAT), AARLE RIXTEL WWTP (AAR), LELYSTAD WWTP (LEL) AND PIERSHIL RWZI (PIE)

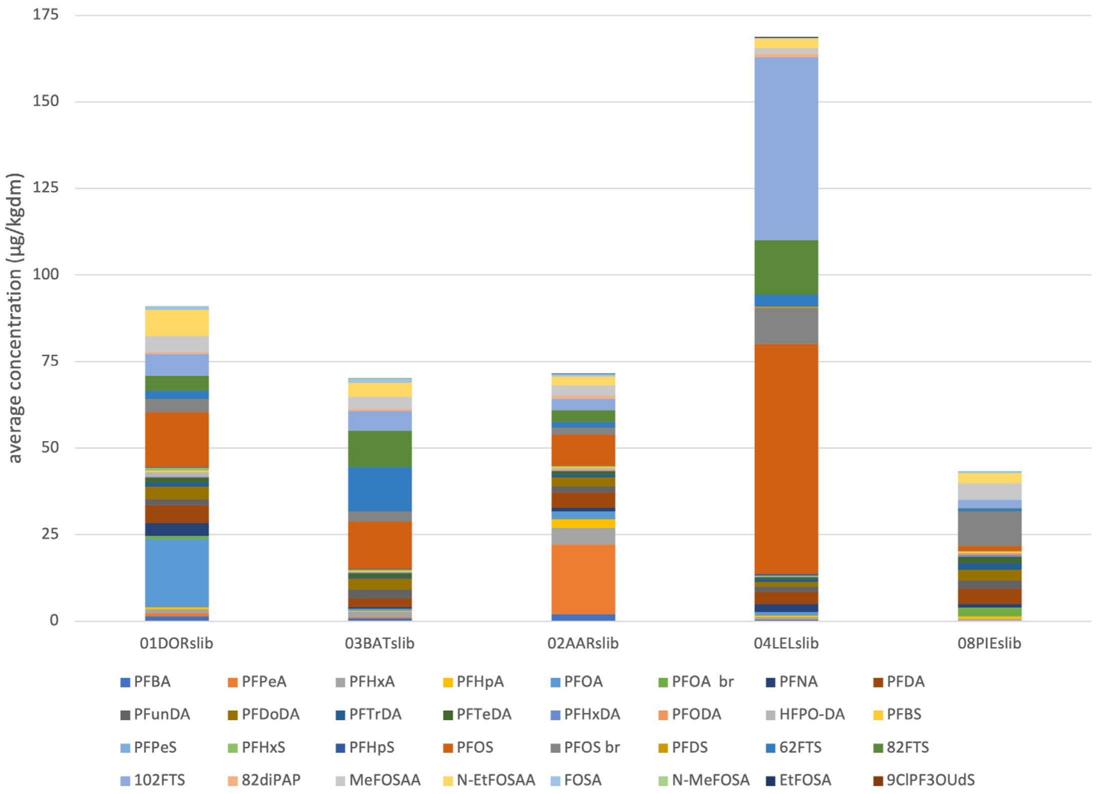
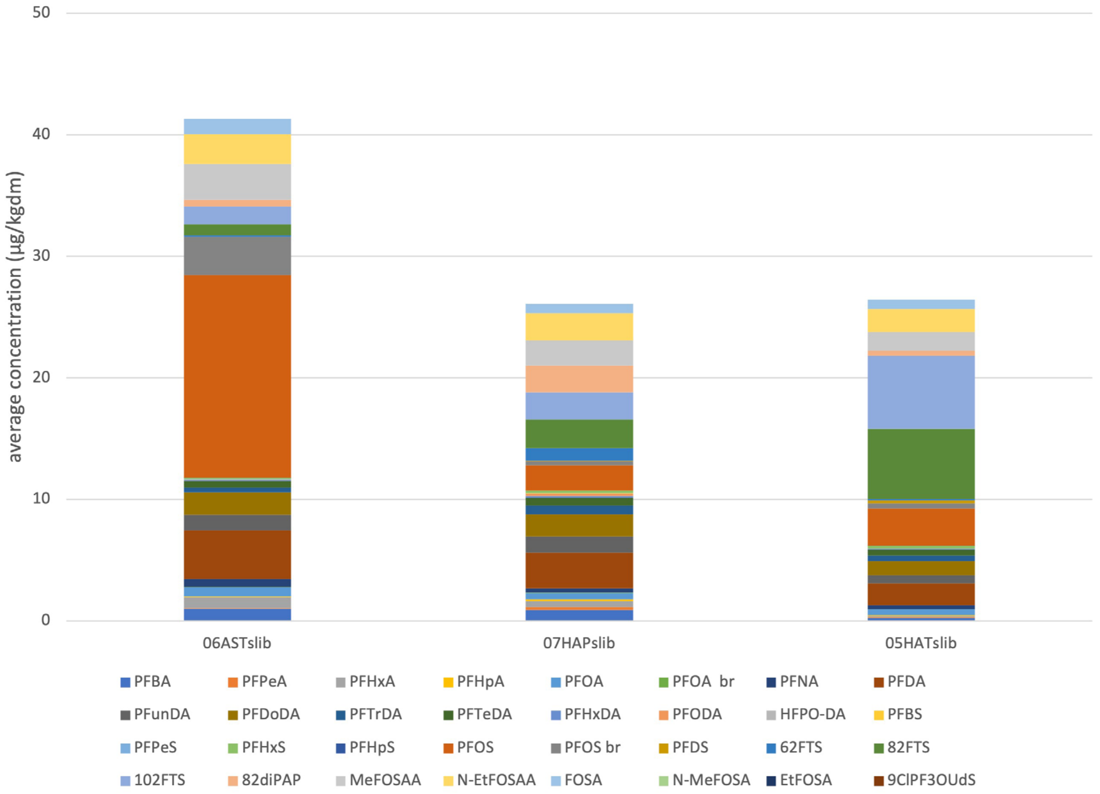


FIGURE 8B AVERAGE PFAS CONCENTRATIONS (IN µG/KG DM) IN SEWAGE SLUDGE FOR LOW PFAS-LOAD WWTPS: ASTEN WWTP (AST), HAPERT WWTP (HAP) AND HATTEM WWTP (HAT)



5

LOADS

The PFAS loads in influent, effluent and sewage sludge are summarised in table 4 (for the loads in the special wastewater streams, see section 7.1). For each WWTP, the loads are expressed both in grams per year and in population equivalents (PE 150). Population equivalents are used to quantify the amount of wastewater treated at the WWTPs in a standardised way. Large WWTPs process a large number of PEs, while small WWTPs process smaller numbers of PEs. The load (or contaminant concentration) can come from domestic wastewater, industrial wastewater, stormwater runoff and/or other surface runoff, and from wastewater. The load per population equivalent is also termed the immission factor (in influent) and the emission factor (in effluent or sewage sludge). Expressing PFAS loads in population equivalents enables the facilities to be compared, regardless of differences in their size. The calculated emission factor in the effluent served as the basis for our categorisation of the WWTPs into high, moderate and low PFAS-load groups.[7]

TABLE 4 **SUMMARY OF TOTAL PFAS LOADS CALCULATED PER WWTP, AND THE IMMISSION AND EMMISSION FACTORS (LOADS PER POPULATION EQUIVALENT PER YEAR). THE COLOURS INDICATE ONLY DIFFERENCES BETWEEN THE LOCATIONS AND HAVE NO OTHER SPECIAL SIGNIFICANCE**

Relative PFAS(35) load		**Dordrecht high**	**Bath high**	**Aarle Rixtel moderate**	**Lelystad moderate**	**Piershil moderate**	**Asten low**	**Hapert low**	**Hattem low**
WWTP capacity reference year 2020	PE 150	230,750	509,246	317,886	116,193	7,003	73,553	56,179	60,334
Annual load PFAS(35)									
influent	g/y	11,945	20,035	1,452	148	44	40	68	47
effluent	g/y	12,542	20,840	2,379	647	38	65	95	56
sludge	g/y	463	585	474	312	3.3	46	30	20
sieved material	g/y			3.5					
Emission factors PFAS(35)									
influent	mg/PE150 per year	51.8	39.3	4.6	1.3	6.3	0.54	1.2	0.78
effluent	mg/PE150 per year	54.4	40.9	7.5	5.6	5.4	0.88	1.7	0.92
sludge	mg/PE150 per year	2.0	1.1	1.5	2.7	0.47	0.62	0.54	0.33
Share via sludge		3.5%	2.6%	17%	33%	8.0%	41%	24%	26%

Large variation was found in total PFAS loads per WWTP: 40–20,035 g/year via influent, 38–20,840 g/year via effluent and 3.3–585 g/year via sewage sludge. This variation corresponds largely to the different sizes of the WWTPs.

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[7] This categorisation is based on the emission factor in the effluent and not the immission by influent. This is because it is the effluent that ultimately determines what enters the environment. Furthermore, in many cases higher PFAS concentrations were measured in the effluent than in the influent.

Nonetheless, the extent of contamination with PFAS also differed per WWTP, as evidenced by the loads per PE in influent (immission factor) and effluent (emission factor). In table 4 we see that the loads, measured by emission factor in the effluent, were by far the highest at Dordrecht and Bath WWTPs (40.9–54.4 mg/PE 150 per year), in line with expectations. Aarle Rixtel, Lelystad and Piershil WWTPs had moderate loads (5.4–7.5 mg/PE 150 per year), while Hattem, Asten and Hapert had low loads (0.88–1.7 mg/PE 150 per year).

For sludge the picture was less consistent, particularly among WWTPs with moderate PFAS loads. At these, large differences in emissions were observed, expressed in mg/PE 150 per year. Emissions via sludge at Lelystad were especially high. Sections 7.2 and 8.4 examine possible explanations for this finding. Of the total amount of PFAS that left the WWTPs, 2.6% to 41% was removed with sludge. No explanation could be found for why this share differed so markedly between the WWTPs.

Loads per population equivalent were also calculated separately for PFOA, PFOS and PFCAs with a chain length of four to seven carbon atoms (C4–C7). Appendix 8 presents these results. In the appendix we see that in all cases, PFOA (C8) emissions increased at the treatment plant.

At most of the facilities, the same applied to other PFCAs with a chain length of four to seven fluorinated carbon atoms (C4–C7); only at Dordrecht and Bath WWTPs were emissions of this group reduced. PFOS emissions remained more or less the same, or were reduced, at most of the WWTPs, except at Lelystad, where a three-fold increase was observed. Section 8.4 explores possible explanations for this increase.

6

REMOVAL EFFICIENCIES

Removal efficiencies were not calculated for the individual sampling days (see appendix 9 for the reasons). The removal efficiencies were calculated based on the average of the weighted concentrations for all measurement days (i.e., 7 to 9 days, see appendix 6 for details on the calculation method).

Appendix 9 presents the calculated removal efficiencies. What immediately stands out is the negative removal efficiencies for many substances. Negative efficiencies indicate an increase in PFAS at the WWTP. At Lelystad WWTP in particular many, often very high, negative efficiencies were calculated. The high efficiencies correspond in part with low concentrations, in which small differences in concentrations yielded large changes in percentage terms. In section 4.1, however, we also found evidence of a marked increase in a number of substances. Chapter 7 and section 8.4.2 discuss this finding in more detail. For the 35 PFAS compounds in our analysis, PFAS removal was observed only at Piershil WWTP, where a 15% removal rate was found. At all of the other WWTPs, the removal efficiency was negative (i.e., more PFAS were found in the effluent than in the influent).

7

A CLOSER LOOK AT INDIVIDUAL WWTPs

This chapter takes a closer look at the PFAS loads in the incoming and outgoing streams using Sankey diagrams. Sankey diagrams present the origin and destination of PFAS loads as incoming (left) and outgoing (right) flows. The difference between the total incoming and outgoing flows is expressed as a residual.

By way of example, this chapter examines three WWTPs in greater detail:

1. Dordrecht WWTP, to illustrate the contribution of the studied industrial wastewater streams from HVC and Chemours to the total PFAS load
2. Lelystad WWTP, as an extreme example of a residual on the influent side, which is indicative of the presence of unknown PFAS in the influent
3. Piershil WWTP, because this is the only WWTP where PFAS was removed (based on total PFAS)

The other five WWTPs are all variations of the Sankey diagram for Lelystad WWTP, but with different magnitudes of residual. The Sankey diagrams for those treatment plants are found in appendix 10.

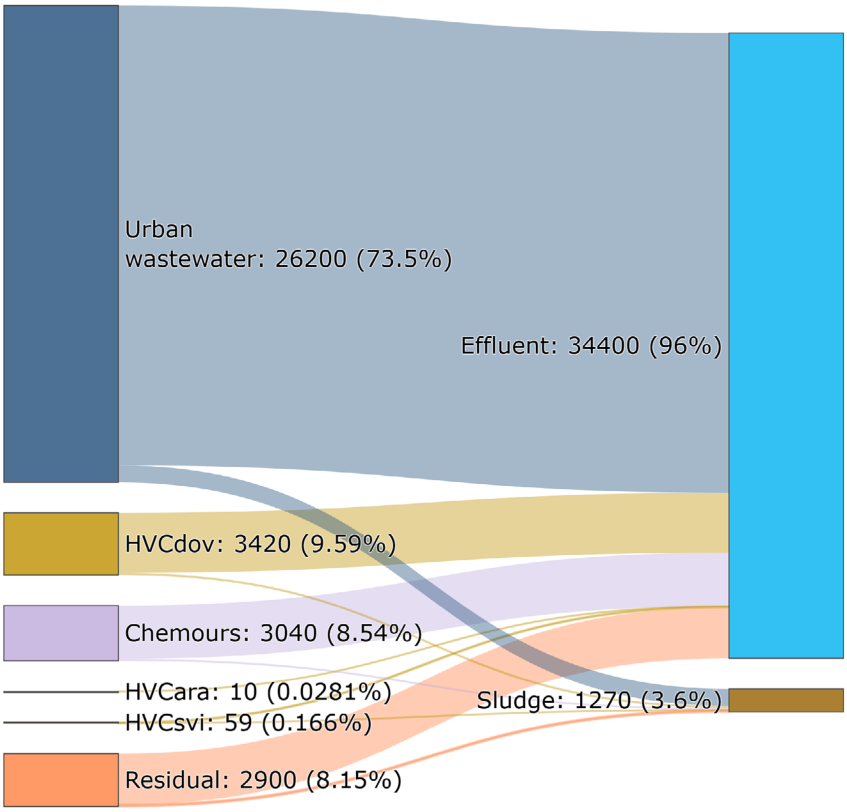
7.1 DORDRECHT WWTP

Figure 9 presents the Sankey diagram for Dordrecht WWTP. Dordrecht WWTP is a special case as it processes four separate wastewater streams that are known or suspected to contain PFAS. In figure 9 we see that the loads from two of these streams were very small; that is, in the wastewater stream from the sludge incineration facility (HVCsvi) and in the wastewater stream from domestic and hospital waste incineration (HVCara). The loads in the other two streams – i.e., the wastewater from the landfill (HVCdov) and the wastewater from Chemours – contributed a larger share, but still less than 10%. In this regard it should be noted that the load at Chemours is based on the average concentration that was measured in this research. During the sampling period, however, two distinct periods were observed: a period with low PFAS concentrations (approx. 10 ng/l) and a period with high PFAS concentrations (more than 5,000 ng/l). In the period with low concentrations, the contribution from Chemours was very small (<1%), whereas in the period with high concentrations it was higher (some 13%).

By far, most of the PFAS load came into Dordrecht WWTP with the urban wastewater. A contributing factor in this regard is that the area surrounding Dordrecht has elevated PFAS concentrations due to historical emissions. Urban wastewater contains stormwater runoff as well as inflowing groundwater (where there are leaks in sewage pipes). PFAS in the surroundings can thus enter urban wastewater via these pathways as well. Because of historical loads in the area, there are higher PFAS concentrations in the urban wastewater at Dordrecht WWTP compared to the other WWTPs.

Furthermore, in figure 9 the residual is shown to the left in the diagram, meaning that more PFAS leaves the WWTP than enters it. Both known and unknown precursors in the influent likely play a role here (see section 8.4).

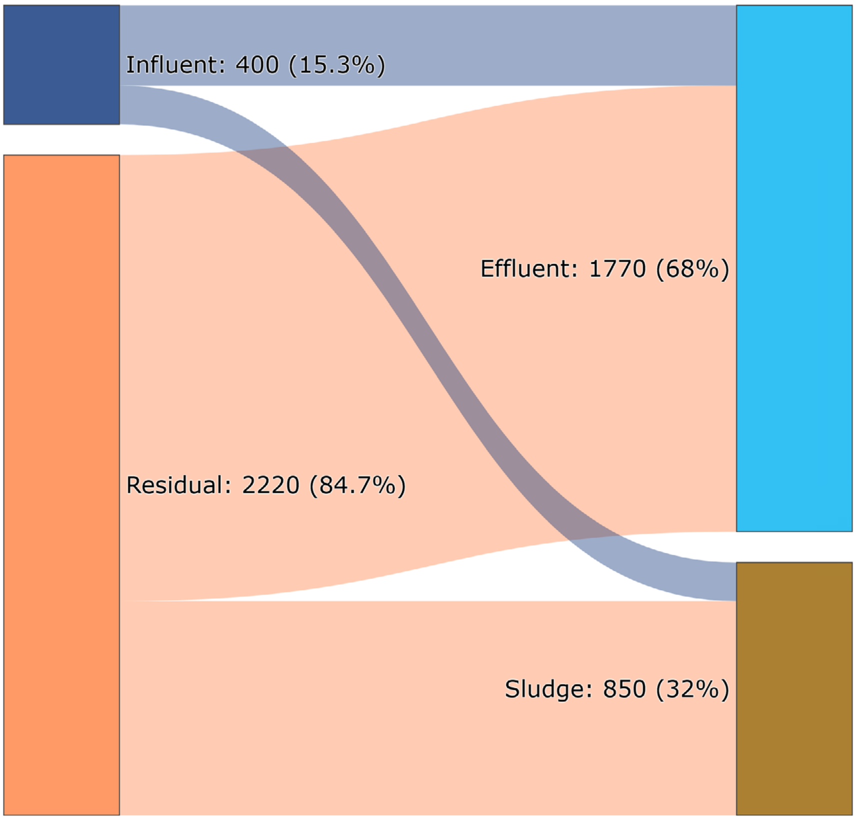
FIGURE 9 SANKEY DIAGRAM FOR DORDRECHT WWTP, BASED ON THE TOTAL CONTENT OF THE 35 PFAS, ANALYSED, I.E., PFAS (35). THE NUMBERS INDICATE THE AVERAGE LOAD IN MG/DAY. THE CONTRIBUTION OF CHEMOURS IS BASED ON THE AVERAGE CONCENTRATION (I.E., NO DISTINCTION IS MADE HERE BETWEEN THE PERIODS WITH LOW AND HIGH CONCENTRATIONS)



7.2 LELYSTAD WWTP

Figure 10 presents the Sankey diagram for Lelystad WWTP. Lelystad is a special case among the studied WWTPs due to the large increase in PFOS and 6:2 FTS found in the effluent. In addition, high concentrations of PFOS and 10:2 FTS were found in the sludge. This results in a very large residual, seen on the left in the Sankey diagram. In other words, much more PFAS left the treatment plant than entered it. This strongly suggests the presence of unknown precursors in the influent which degrade into other precursors, both known (such as 10:2 FTS) and unknown, and into PFOS. Identifying possible sources of these precursors is a topic of further study by the local water board.

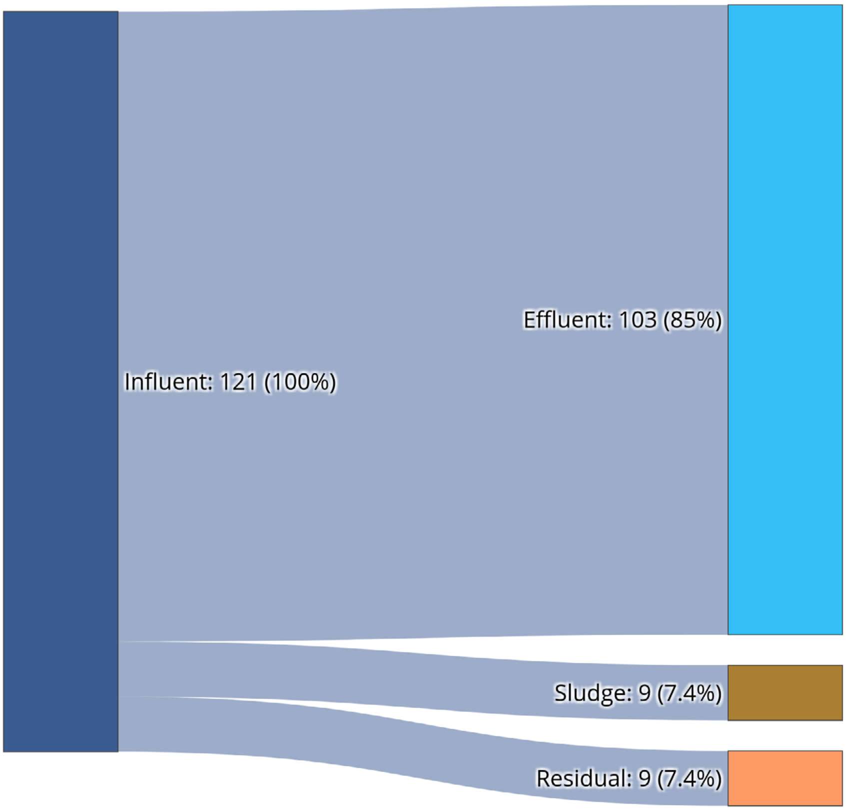
FIGURE 10 SANKEY DIAGRAM FOR LELYSTAD WWTP, BASED ON THE TOTAL CONTENT OF THE 35 PFAS ANALYSED, I.E., PFAS (35). THE NUMBERS REPRESENT THE AVERAGE LOAD IN MG/DAY



7.3 PIERSHIL WWTP

Figure 11 presents the Sankey diagram for Piershil WWTP. Piershil WWTP is a special case among the studied WWTPs because it is the only WWTP where PFAS were removed. This is reflected in a residual shown on the right side of the Sankey diagram.

FIGURE 11 **SANKEY DIAGRAM FOR PIERSHIL WWTP, BASED ON THE TOTAL CONTENT OF THE 35 PFAS ANALYSED, I.E., PFAS (35). THE NUMBERS REPRESENT THE AVERAGE LOAD IN MG/DAY**



7.4 OTHER WWTPS

The Sankey diagrams for the other WWTPs are found in appendix 10. These are all variations on the Sankey diagram for Lelystad. In other words, there is a residual on the left side of the diagram, indicating the presence of unknown PFAS in the influent. This suggests that at these WWTPs too, known and unknown precursors in the influent play a role. The magnitude of the residual (6.5%–63%), and thus, the potential contribution, differed per WWTP. As the pattern of PFAS found differed per WWTP (see figure 7 and 8), which precursors were involved also differed from one WWTP to the next.

8

DISCUSSION

8.1 REPRESENTATIVENESS OF THE RESULTS

This monitoring campaign focused on PFAS loads in influent, effluent and sewage sludge at WWTPs, answering the question of what substances are found at WWTPs and in what concentrations. The aim was to obtain a nationally representative picture. The WWTPs selected for study included both current and former hotspots (Dordrecht and Aarle Rixtel), a WWTP with a large proportion of industrial wastewater (Bath), WWTPs handling mixed types of wastewater (Lelystad and Hattem) and WWTPs with primarily domestic wastewater (Asten, Hapert and Piershil). Dordrecht and Bath WWTPs are considered unique cases: Dordrecht WWTP due to its high levels of PFOA and HFPO-DA and special wastewater streams, and Bath WWTP due to the large proportion of industrial wastewater originating from the Moerdijk industrial complex. The results from the other WWTPs indicate that the proportion of industrial wastewater is not, in itself, the primary factor determining PFAS loads. Of greater importance is what present sources (i.e., companies or activities) discharge their wastewater to the WWTP in question. These present sources are not always known or identifiable. Moreover, considering the large number of potential sources (see section 8.3.2), it is no easy task to get a clear picture of them.

The studied WWTPs can be considered as providing a reasonable reflection of the types of situations most commonly found in the Netherlands. Uncertainty does remain regarding the extent to which all major PFAS sources (including firefighting foam, paper recycling and landfills; see also section 8.3.2) were covered within this study. It is also difficult to gauge what proportion of WWTPs in the Netherlands has low PFAS loads, and what proportion has moderate PFAS loads. Nonetheless, the current study does provide substantially more measurements than earlier research. Taking the given assumptions and limits into account, the current measurements provide a basis for a more reliable estimate of the PFAS loads leaving WWTPs via effluent and sewage sludge, compared to previously published indicative load calculations (Jans & Berbee, 2020; Pancras et al., 2021).

We know that only a very small percentage of all PFAS are, and can be, analysed (<1%). In the current study, 35 PFAS were analysed. While other laboratories offer slightly more extensive analytical packages (up to 45 PFAS), these often come with higher reporting limits. Differences between analytical packages are mainly in the precursors and replacements for PFOA and PFOS which are or are not analysed. All laboratories analyse PFCAs and PFSAs. These subgroups contain known PFAS, such as PFOS and PFOA. Indeed, PFOS and PFOA are the PFAS most frequently found in the environment (though they are also the ones most frequently studied). These are fully fluorinated compounds, which are extremely persistent. When PFAS precursors degrade, PFCAs with short chains (C4–C8) are formed as persistent terminal products. Due to their high stability, PFCAs and PFSAs are very relevant subgroups for study. Research into known and unknown precursors warrants greater attention. Measurement methodologies that screen for adsorbable organic fluorine (AOF), extractable organic fluorine

(EOF) and total oxidisable precursors (TOP) and/or which broadly screen for individual PFAS[8] could also be beneficial (see also section 8.4).

8.2 DISCUSSION OF CONCENTRATIONS

8.2.1 COMPARISONS WITH STANDARDS

Lack of national quality standards for PFAS in wastewater and sewage sludge

Comparing the found concentrations of PFAS with set environmental quality standards is one way to understand the PFAS levels measured in the current study. However, the Netherlands has no environmental quality standard for PFAS in wastewater and sewage sludge. There are standards for PFAS in surface and drinking water (as well as in drinking water resources).[9] However, these standards are not intended to apply to wastewater. For lack of better, these standards are nonetheless referred to here, to provide some perspective on the found concentrations and to give an indication of their significance. The Netherlands does have interim guidelines providing environmental quality standards for PFAS in dredged material and soil.[10] However, comparing the concentrations found in sewage sludge to standards for dredged material and soil is not considered useful, as the matrices are too different. A comparison can made with existing or proposed quality standards in other countries for sewage sludge applied on land. It must be noted, however, that application of sewage sludge on land in the Netherlands is very rare. In the Netherlands, virtually all sewage sludge is incinerated, often after (biological) dewatering.

Comparison of concentrations in wastewater with quality standard for surface and drinking water (as well as drinking water resources)

Table 5 presents quality standard for PFOS, PFOA and HFPO-DA in surface water. In addition, in early 2020 the EU Drinking Water Directive established safety threshold standards for both the sum of 20 different PFAS and for total PFAS (that is, the total of all per- and polyfluoroalkyl substances). These establish minimum safety thresholds for evaluation of the quality of water intended for human consumption. The EU Drinking Water Directive must be implemented in national legislation by 12 January 2023. Once technical guidelines have been developed for monitoring the parameters, EU member states can decide for themselves whether to use one or both parameters. The ‘total PFAS’ standard represents the sum of all per- and polyfluoroalkyl substances, and is 500 ng/l. The standard for the subset of 20 PFAS is 100 ng/l, and represents the sum of 20 substances, namely, C4–C13 PFCAs (including PFOA) and C4–C13 PFSAs (including PFOS).

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[8] An analytical method is currently under development.

[9] On 17 September 2020, the European Food Safety Authority (EFSA) released a new scientific opinion regarding health risks due to the presence of PFAS in food. In it, EFSA derived a health-based limit for exposure to the sum of four PFAS compounds (PFOS, PFOA, PFNA and PFHxS) via food. This health-based limit for PFAS exposure is lower than the earlier derived limits for PFOS and PFOA. The Netherlands’ National Institute for Public Health and Environment (RIVM) is currently studying whether the EFSA opinion provides reason for amending the environmental quality standards in existing Dutch law. The RIVM was set to provide recommendations to the ministries in this regard.

[10] Dutch Temporary Framework for Action Regarding the Reuse of PFAS-Containing Soil and Dredged Material (updated version, 2 July 2020). For the original text in Dutch see https://www.rijksoverheid.nl/documenten/rapporten/2020/07/03/bijlage-geactualiseerd-tijdelijk-handelingskader

TABLE 5 DUTCH QUALITY STANDARDS FOR PFOS, PFOA AND HFPO-DA IN FRESH SURFACE WATERS: AA-EQS = ANNUAL AVERAGE ENVIRONMENTAL QUALITY STANDARD, MAX-EQS = MAXIMUM ALLOWABLE CONCENTRATION ENVIRONMENTAL QUALITY STANDARD. SOURCE: RVS.RIVM.NL

Standard	Form	Status	PFOS	PFOA	HFPO-DA
AA-EQS freshwater	Total	Statutory	0.65 ng/l		
	Total	Non-statutory		48 ng/l	
	Dissolved	Non-statutory		48 ng/l	
	Dissolved	Indicative			118 ng/l
MAX-EQS freshwater	Total	Statutory	36 µg/l		
	Total	Non-statutory		2,800 µg/l	
	Dissolved	Non-statutory		2,800 µg/l	

The table in appendix 11 compares the concentrations found in wastewater with the Dutch standards and with the European standard for the sum of 20 PFAS in surface water and drinking water (and drinking water resources). The comparison shows that various standards were exceeded at Dordrecht WWTP in the drainage water from the former landfill (HVCdov) and in the wastewater from Chemours.[11] These are the locations with the highest PFAS levels, and particularly, the highest PFOA concentrations. The concentrations at Bath WWTP exceeded the limit set for the sum of 20 PFAS. The standard for PFOS is extremely low. In all influent and effluent analysed and at HVCdov, the levels of PFOS found exceeded the PFOS standard for surface water.

When WWTPs discharge effluent into surface waters, dilution occurs. The degree of dilution differs per WWTP, from practically none to a high extent of dilution (with the proportion of effluent being less than 1%). Therefore, whether effluent discharge leads to the PFOS limit being exceeded in the receiving waters will depend on the local situation.

Comparison of sludge concentrations with quality standards for sewage sludge in other countries
According to Blyt et al. (2018), in Norway a standard of 100 µg/kg DM for total PFAS has been proposed for sewage sludge applied on land. This value was exceeded only at Lelystad WWTP, where concentrations of 154–173 µg PFAS/kg DM were found in the sludge. This was due mainly to high concentrations of PFOS, 10:2 FTS and 8:2 FTS. Germany's fertilisers regulation (*Düngemittelverordnung* 2012)[12] also includes threshold limits for sewage sludge applied on land: 100 µg/kg DM for the sum of PFOA and PFOS. These threshold limits were not exceeded at any of the WWTPs.

8.2.2 CONCENTRATIONS IN PFOA EQUIVALENTS

Zeilmakers et al. (2018) and Bil et al. (2021) derived relative potency factors (RPF) for different PFAS based on liver toxicity in male rats after semi-chronic exposure. Using these relative potency factors, the toxicity of exposure to a mixture of PFAS can be expressed in equivalents of the toxicity of PFOA. This is similar to the toxicity equivalency (TEQ) approach used for dioxins.

Table 6 presents RPF values for the substances found in the current research. Appendix 12 presents the full list of available RPF values. Depending on the substance, these range from 1,000 times less toxic to 10 times more toxic than PFOA. For several substances, insufficient experimental toxicity data are available. For these, RPF values have been derived by read across; i.e., based on comparisons with substances for which the RPF is known. For these, upper and lower confidence boundaries are therefore provided.

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[11] Only in the period with high concentrations.

[12] https://www.gesetze-im-internet.de/d_mv_2012/

TABLE 6 **RELATIVE POTENCY FACTORS (RPF) FOR PFAS; I.E., THE POTENCY EXPRESSED IN RELATION TO THAT OF PFOA. THE RPF IS PROVIDED ONLY FOR THE SUBSTANCES FOUND IN THE CURRENT STUDY. CN = NUMBER OF CARBON ATOMS IN THE FLUORINATED CARBON CHAIN. VALUES IN BOLD TYPE WERE DERIVED BASED ON LIVER TOXICITY IN MALE RATS AFTER SEMI-CHRONIC EXPOSURE. VALUES IN ITALICS WERE DERIVED BY MEANS OF READ ACROSS (I.E., ON THE BASIS OF COMPARISONS WITH SUBSTANCES FOR WHICH THE RPF IS KNOWN); THEREFORE UPPER AND LOWER CONFIDENCE BOUNDARIES ARE PROVIDED**

Substance name	Cn	VU abbreviation	CAS nr	Relative potency factor
Perfluoroalkyl carboxylic acids (PFCAs)				
Perfluorobutanoic acid	C4	PFBA	375-22-4	0.05
Perfluoropentanoic acid	C5	PFPeA	2706-90-3	0.05
Perfluorohexanoic acid	C6	PFHxA	307-24-4	0.01
Perfluoroheptanoic acid	C7	PFHpA	375-85-9	1
Perfluorooctanoic acid, linear	C8	l-PFOA	335-67-1	1
Perfluorooctanoic acid, branched	C8	br-PFOA	n.a.	1
Perfluorononanoic acid	C9	PFNA	375-95-1	10
Perfluorodecanoic acid	C10	PFDA	335-76-2	10
Perfluoroundecanoic acid	C11	PFUnDA	2058-94-8	4
Perfluorohexadecanoic acid	C16	PFHxDA	67905-19-5	0.02
Perfluoroalkyl sulfonic acids (PFSAs)				
Perfluorobutanesulfonate	C4	PFBS	375-73-5	0.001
Perfluoropentanesulfonate	C5	PFPeS	2706-91-4	0.6
Perfluorohexanesulfonate	C6	PFHxS	355-46-4	0.6
Perfluoroheptanesulfonate	C7	PFHpS	375-92-8	2
Perfluorooctanesulfonate, linear	C8	l-PFOS	1763-23-1	2
Perfluorooctanesulfonate, branched	C8	br-PFOS	n.a.	2
Perfluoroalkyl ether carboxylic acids (PFECAs)				
2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propionic acid		HFPO-DA		0.06
Ammonium dodecafluoro-3H-4,8-dioxanonanoate		ADONA		0.03

Using the RPF values, the concentrations in influent and effluent were expressed in concentrations of PFOA equivalents. As a precaution, the upper confidence boundary (i.e., the worst case) was used in the calculations for substances for which the RPF value was derived by read across.[13] Appendix 13 presents the results of these calculations.

High PFOA concentrations are a main determinant of the concentration in PFOA equivalents. As expected, this was then found to be very high at HVCdoc (in the wastewater from the former landfill), followed by Dordrecht WWTP. This also applies, though to a lesser extent, to Bath and Piershil WWTPs, as at these facilities, PFOA concentrations were also found to be relatively high.

Appendix 13 also presents the relative contributions of the different individual PFAS. In the influents and effluents at the WWTPs, more than 80% of the concentration in PFOA equivalents was determined by PFOA (C8), PFOS (C8), PFNA (C9) and PFDA (C10). However, with respect to PFNA and PFDA, it should be noted that these substances, in most cases, were found only in concentrations at or near the reporting limit (i.e., twice the reporting limit at most). But because these substances are up to 10 times more toxic than PFOA, their contribution is nevertheless relatively high. Higher concentrations of PFNA and PFDA were found in influent and effluent at Dordrecht WWTP, in the effluent at Lelystad WWTP and in the drainage water from the former landfill (HVCdov).

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[13] That is, the RPF value was derived based on a comparison with substances for which the RPF is known.

It is worth emphasising here that concentrations expressed in PFOA equivalents do not provide a complete picture of the relative toxicity of the different water samples, because other PFAS were also found which are not included in the calculation. This applies, for example, to the precursor 6:2 FTS, which was found in influent and/or effluent at Dordrecht, Aarle Rixtel, Bath, Lelystad and Hattem WWTPs, and in the drainage water from the landfill (HVCdov).

8.3 DISCUSSION OF LOADS

8.3.1 TRANSLATION INTO NATIONAL LOADS

The calculated emission factors can be used to estimate annual PFAS emissions into the environment via WWTPs in the Netherlands as a whole. In doing so, the WWTPs where PFAS loads were found to be high are assumed to be special cases for the Netherlands. The emission from these two WWTPs combined was 33 kg PFAS (35) per year. Together, these facilities process more than 700,000 population equivalents. All WWTPs in the Netherlands combined process 30 million population equivalents per year (design capacity). As a lower confidence boundary, the other WWTPs can be assumed to have an emission equivalent to that of the WWTPs found to have low PFAS loads. The emission for this group of WWTPs was approx. 30 kg per year (29.3 million PE 150 with an emission factor of 1 mg PFAS (35)/PE 150 per year). For an upper boundary, the group with a capacity of 29.3 million PE 150 was assumed to have an emission equivalent to the WWTPs with moderate PFAS loads. This group’s emission was 29.3 million PE 150 x 5 mg/PE 150 = 147 kg PFAS (35) per year. With these assumptions, the annual emission of PFAS (35) via effluent from the WWTPs in the Netherlands would amount to approx. 65–180 kg/year.

For sludge, the emission factors for the hotspot WWTPs and moderate PFAS-load WWTPs were found to be of a similar order of magnitude (see table 4). Thus, for the lower boundary, all WWTPs were assumed to have an emission equivalent to the low PFAS-load WWTPs, and for the upper boundary, all WWTPs were assumed to have an emission equivalent to the high and moderate PFAS-load WWTPs. Applying these assumptions, the annual emission of PFAS (35) via sewage sludge from WWTPs in the Netherlands would be approx. 15–45 kg per year.

Sludge processors GMB, SNB and HVC estimated the total amount of PFAS they received via sludge delivered to them at 2.4–7.4 kg per year (see appendix 14 for calculation). This translates to a national load of 17–54 kg per year.

All of these load calculations should be interpreted with caution, as they are based only on the group of PFAS analysed, while thousands of PFAS exist. Actual PFAS loads will therefore be higher.

8.3.2 CONTRIBUTIONS FROM DIFFERENT SOURCES

Specific sources

In this monitoring campaign, as part of the study at Dordrecht WWTP, four specific industrial wastewater streams were examined: wastewater from Chemours (CHE), wastewater from a domestic and hospital waste incinerator (HVCara), drainage water from a landfill where PFAS-containing waste is known to have been dumped, and wastewater from a sewage sludge incinerator (HVCsvi). No other specific sources were identified or studied, as this was considered beyond the scope of the current monitoring campaign.

Nonetheless, for all moderate PFAS-load WWTPs, specific sources should be identifiable, as the measured load size exceeds the background level. PFAS are applied for many purposes. Glüge et al. (2020) identified in excess of 200 applications in 64 categories for more than 1,400 individual PFAS. Known PFAS uses include electronic products (printed circuit boards, LCD screens, mobile telephones), paints and coatings, cosmetics, personal care products, pharmaceuticals, printer inks, adhesives and sealants, air conditioning systems, ammunition, medical equipment and supplies, pesticides, wind turbines, solar collectors, batteries, drilling fluids for the oil and gas industry and the automotive industry. Though the number of applications currently known is huge and diverse, the actual number is likely much higher. There are therefore also many potential sources of PFAS in the environment. Furthermore, major PFAS sources were prioritised by Pancras et al. (2021), Jans & Berbee (2020) and Pancras et al. (2018).

In the Netherlands, a variety of source studies have been conducted to obtain a more detailed picture of the various pathways of PFAS emissions into the environment (see figure in appendix 15). The current study of PFAS at WWTPs is one of those source studies. The findings of research on PFAS sources in surface waters in the Netherlands were published in Jans & Berbee (2020), and results of a study on PFAS in products and wastewater streams are found in Pancras et al. (2021). Research on PFAS in food contact materials is complete (BuRO, 2020), but follow-up work is still underway. A study of PFAS in the soil and groundwater, a broad screening of PFAS in drinking water and drinking water resources, and a study of PFAS in building materials have not yet been completed.

Table 7 presents indicative estimates of PFAS emissions in the Netherlands via various pathways and products. These estimates are based, among other things, on the abovementioned source studies. It should be noted that the estimates, in most cases, are based on only a very limited number of samples, and therefore should be interpreted as initial indications. In addition, studies differ in the analysis packages used for load calculations. They therefore vary in what substances are included in the load calculations. Moreover, as noted earlier, only a limited number of PFAS are measured. Actual PFAS loads will therefore be higher.

Table 7 provides indicative estimates of several of the most relevant pathways of PFAS emissions to the environment: sewage and wastewater treatment plants, wastewater from specific companies, wastewater from landfills where PFAS-containing waste was dumped and the paper industry (probably mainly paper recycling). This includes both direct discharges (to surface waters) and indirect discharges via WWTPs. For all of these pathways, the contribution per plant can amount to a several kilograms per year. The contribution of the studied hotspot WWTPs was several dozen kilograms per year. The total amount discharged from the WWTPs via effluent was estimated as 65–180 kg per year, while the amount of PFAS removed with sewage sludge was estimated at 15–45 kg per year. Moreover, substantial quantities of PFAS enter the Netherlands via the major rivers, especially the Rhine.

For a number of pathways, the magnitudes are as yet poorly understood, such as firefighting foam (including subsequent to their use at airports), PFAS transport via the air followed by deposition with rainfall, and use of PFAS in food contact materials. Via all these pathways, known and unknown precursors appear to play an important role (Held & Reinhard, 2020; Pancras et al., 2021; Straková et al., 2021).

Historical contamination is another pathway for which magnitudes remain poorly understood. Depending on the local situation, urban wastewater can contain stormwater runoff and inflowing groundwater (due to leaks in sewage pipes). In places where there is a historic source, PFAS in the environment can enter urban wastewater via these pathways as well. This is a factor at least at Dordecht and Aarle Rixtel WWTPs.

Research on products (Pancras et al., 2021) has identified a number of product groups and industries with relevant levels of emissions into the environment. These include water- and soil-resistant products (such as coated textiles, carpet and leather), paper recycling, cleaning products, fluoroelastomer products (fluororubbers), pesticides, fluoropolymer products and fireworks. In addition, Pancras et al. (2021) noted a variety of other products and industries for which emissions into the environment can be considered relevant, though magnitudes could not be determined. These include, among others, the electroplating industry, various products for automobiles, semiconductors, and medical and health care products.

Background levels

The current study included three WWTPs which were expected, beforehand, to receive almost exclusively domestic wastewater; namely Asten, Hapert and Piershil WWTPs. However, the PFAS concentrations measured in influent and effluent (figure 7) show Piershil WWTP to have substantially higher concentrations than the two other WWTPs. In contrast, the concentrations at Hattem WWTP, which received an average share of industrial wastewater, were found to be lowest of all the facilities studied. It appears that while there does seem to be a background level of contamination from domestic wastewater, there are also other sources that have not yet been identified.

The background levels presented in table 7 were estimated based on findings from the three WWTPs with the lowest emissions (Hattem, Asten and Hapert). Emissions from these WWTPs ranged from 0.88 to 1.7 mg/PE 150 per year. Assuming a total combined design capacity of WWTPs in the Netherlands of 30 million PE 150, this would suggest a national background level of approx. 25–50 kg PFAS (35) per year.

TABLE 7 **INDICATIVE ESTIMATES OF PFAS EMISSIONS INTO THE ENVIRONMENT IN THE NETHERLANDS VIA DIFFERENT PATHWAYS AND PRODUCTS. NOTE: THE ANALYSIS PACKAGES ON WHICH THE LOAD CALCULATIONS WERE BASED DIFFER PER STUDY**

Pathway	Load	Explanatory notes	Reference
WWTPs			
WWTP effluent	65–180 kg/year for NL as a whole, of which: Hotspots (Dordrecht and Bath): 33 kg/year; Background contamination: 25–50 kg/year	Based on measurements at eight water treatment facilities	This study
WWTP effluent	Hotspots: 13–21 kg/year per WWTP; Other WWTPs: 0.04–2.4 kg/year per WWTP	Based on measurements at eight water treatment facilities	This study
WWTPs	0.11–7.0 kg/year per WWTP	Indicative calculations based on measurements at four WWTPs	Jans & Berbee (2020)
WWTP effluent	Difficult to calculate	Difficult to calculate because the emission factors include only observations above the reporting limit. This leads to substantial overestimations.	Watsondatabase (2021)
Sewage sludge	15–45 kg/year for NL as a whole	Based on measurements at eight water treatment facilities	This study
Sewage sludge	17–54 kg/year for NL as a whole	Estimate based on data from sludge processors	Calculations in appendix 14
Sewage sludge	10–100 kg/year for NL as a whole	Rough estimate based on analyses for four WWTPs	Arcadis (2021)
Industrial wastewater / non-domestic wastewater			
Wastewater treatment plants	0.14 kg/year (per plant, based on 2 plants); 5.5 kg/year (per plant, based on 1 plant)	Indicative calculations based on measurements at three wastewater treatment plants; high loads correspond to central facility processing wastewater from various companies, including chemical producers and food producers	Jans & Berbee (2020)
Paper industry	0.03–3.5 kg/year per company	Indicative calculation based on measurements at four companies; high loads appear to be correlated with paper recycling	Jans & Berbee (2020)
Landfills	1.6–1.8 kg/year per landfill	Indicative calculations based on measurements at two landfills	Jans & Berbee (2020)
Landfill (with PFAS-containing waste)	1.25 kg/year	Based on measurements: Relates to treated drainage water from the former Crayenstein dump in Dordrecht	This study
Wastewater from Chemours	0.005 kg/year (low); 1.7 kg/year (high) (average 1.1 kg/year)	Based on measurements; for PFAS (35); Two periods were distinguished: one with low concentrations and one with high concentrations (see section 4.2)	This study
Wastewater from Chemours	0.33 kg HPFO-DA/year (2019) 0.12 kg HPFO-DA/year (2020)	Own estimates from Chemours	Calculations in appendix 7
Wastewater from Chemours	Max 2 kg/year (indirect via wastewater in sewer)	Based on permit. Relates to HFPO-DA.	DCMR (2021)
Production of synthetic fibres, detergent and surfactants, water-repellent textiles, tank cleaning and reverse osmosis concentrate	Reverse osmosis concentrate 1.0 kg/year, remainder due to unknown flows	Possibly relevant, more research needed; reverse osmosis concentrate: indicative calculation based on one measurement	Jans & Berbee (2020)
Processors of building, demolition and industrial waste	Unknown	Relevant pathway based on measurements at two companies, no load calculations could be performed	Jans & Berbee (2020)
Sludge incineration facility	0.02 kg/year	Based on measurements	This study
Domestic and hospital waste incineration facility	0.004 kg/year	Based on measurements	This study

Pathway	Load	Explanatory notes	Reference
Waste incineration facility, concrete industry, metal industry, a cable producer, a tire producer, a car wash, runoff from highways, a dry cleaner, extraction water from non-stick pans and rainwater	Metal <0.001–0.013 kg/year per company; other companies <0.001 kg/year or could not be calculated due to unknown flows	Appear less relevant; research suggests that other industries warrant higher priority	Jans & Berbee (2020)
Other pathways PFAS-containing firefighting foams (Aqueous Film Forming Foam of AFFFs)	Unknown	Known to be a significant source of PFAS in the environment; very high concentrations measured in the non-diluted product; in exercises, firefighters no longer use PFAS-containing foams, and development research is underway for non-PFAS-containing foams effective in combating fire; after use, residual firefighting foam is another source of PFAS emissions into the environment	Jans & Berbee (2020)
Airports	Unknown	Relevant pathway of PFAS to the environment due to past usage of PFAS-containing firefighting foam	Pancras et al. (2018)
Air	Unknown	Relevant pathway considering the spread of PFAS around the word, increased background levels and increased levels around production sites; pathway assumed to be via transport of volatile fluorotelomer alcohols, which are converted to stable PFCAs in the air	Held & Reinhard (2020); Pancras et al. (2021)
Rainwater	Unknown	Relevant pathway for point source plumes; otherwise probably less relevant; in Germany deposition of total PFAS (*n*=34) via precipitation was estimated at 2–91 ng per m2 per day	De Kort et al. (2019); Wintersen et al. (2020); Jans & Berbee (2020); LUBW (2016)
From abroad via major rivers	1,591 kg/year (Rhine); 177 kg/year (Meuse); 614 kg/year (Scheldt)	Based on measurements in 2019 by Lobith (Rhine), Eijsden (Meuse) and Schaar van Ouden Doel (Scheldt)	Jonker (2021)
Products Water- and dirt-repellent products, e.g., coated textiles, carpet and leather	>100 kg/year	Very relevant source of PFAS emissions to the environment	Pancras et al. (2021)
Paper recycling	>100 kg/year	Very relevant source of PFAS emissions to the environment	Pancras et al. (2021)
Cleaning products	10–100 kg/year	Moderate relevance as source of PFAS emissions to the environment	Pancras et al. (2021)
Fluoroelastomer products (fluororubbers)	10–100 kg/year	Moderate relevance as source of PFAS emissions to the environment	Pancras et al. (2021)
Pesticides	10–100 kg/year	Moderate relevance as source of PFAS emissions to the environment	Pancras et al. (2021)
Fluoropolymer products	<10 kg/year	Low relevance as source of PFAS emissions to the environment	Pancras et al. (2021)
Fireworks	<10 kg/year	Low relevance as source of PFAS emissions to the environment	Pancras et al. (2021)
Food contact materials	Unknown	Screening study found only a few PFAS in significant quantities in papers and cardboards that come into contact with food; further research is underway; a European study found multiple PFAS in fast food packaging materials	BuRO (2020); Straková et al. (2021)

8.4 THE ROLE OF PRECURSORS

8.4.1 USE OF PRECURSORS

Much uncertainty continues to surround what precursors are used in what applications. The amounts used are similarly unknown. However, there are indications that both the number of substances and the amounts used are potentially large. The OECD has identified 4,730 PFAS-related CAS numbers. Of those, 4,186 (88%) can degrade to perfluoroalkyl acids (PFAAs, such as PFCAs and PFSAs), and thus into more persistent substances (OECD, 2018). Liu et al. (2013) found precursors to be a significant source of PFAS in the environment: the worldwide production of polyfluorochemicals (most of which are precursors) is many times larger than that of PFOS and PFOA combined. According to Van Gijn et al. (2021), the literature and various monitoring campaigns clearly show precursors to be very relevant in the total PFAS loads at WWTPs. In extreme cases, transformation of precursors into persistent terminal products can result in more than ten-fold increases in concentrations (though such extreme cases were not found in the current monitoring campaign). The precursors that can now be analysed are often insufficient to explain the total observed increases in PFAS. This means that relevant concentrations of unknown PFAS precursors are likely to be present in influent.

Research on PFAS in products and waste streams (Pancras et al., 2021) indicates that a number of these contain precursors in substantial quantities. That research applied a three-step measurement strategy: (1) screening samples for extractable organic fluorine (EOF analysis), (2) target substance analysis for individual PFAS and (3) total oxidisable precursors (TOP) assay on a selection of samples to better understand of the extent of precursors within the sample. For 90% of the products, less than 10% of the PFAS quantities measured by EOF could be explained by the PFAS target substance analysis. This points to the presence of other, unknown fluorine-containing organic compounds, possibly PFAS precursors. For several samples, this was confirmed by TOP assays. Precursors are often found in large quantities in products used to impart water and dirt resistance in textiles, carpet, leather, tile and glass. High concentrations of PFAS, especially PFPrA (C3 PFCA), have been found in fireworks paper and in pulp in paper recycling. These could be a degradation product of PFAS precursors with short carbon chains.

8.4.2 ROLE OF PRECURSORS AT WWTPS

Van Gijn et al. (2021) studied the role of precursors at WWTPs. They found degradation pathways of PFAS precursors to be extremely complex, with other precursors often formed as intermediate products. Ultimately, stable PFAS are formed, specifically, PFOA, other PFCAs with a C4–C7 chain length and PFOS. In many cases, the conditions that influence these conversions are not yet understood. Indications from the literature suggest that higher temperatures might lead to faster conversion speeds.

Findings from the literature also confirm that known and unknown precursors in influent at WWTPs can be expected to be converted into other precursors and/or stable PFAS. To test this expectation, table 8 presents the increase or reduction of precursors and stable PFAS at the eight WWTPs examined in the present study.

TABLE 8 INCREASE OR REDUCTION OF PRECURSORS AND STABLE PFAS, WITH THE AVERAGE LOAD IN INFLUENT (INGOING) COMPARED TO THAT IN EFFLUENT AND SLUDGE (OUTGOING). EXPRESSED IN MG/DAY

WWTP		Precursors (12)		Stable PFAS (PFCAs and PFSAs)	
		increase	reduction	increase	reduction
Dordrecht	mg/d	734	-	3,225	-
Bath	mg/d	8,011	-	-	4,267
Aarle Rixtel	mg/d	1,522	-	2,500	-
Lelystad	mg/d	819	-	1,405	-
Piershil	mg/d	3	-	-	11
Asten	mg/d	15	-	180	-
Hapert	mg/d	40	-	119	-
Hattem	mg/d	40	-	38	-

As shown by the data in table 8, there was an increase in precursors at all of the studied WWTPs, and an increase in stable PFAS (PFCAs and PFSAs) was found at most WWTPs. At Bath WWTP, there was an increase in precursors, but a decrease in stable PFAS. No good explanation for this was found. At Piershil, precursor concentrations remained the same, while stable PFAS decreased. From the table we can conclude that precursors likely play a role in the increase of stable PFAS in effluent, though this relationship was not found at all the WWTPs. Further research on precursors is recommended.

Far from all precursors were (or can be) measured. However, there is an analytic screening method for determining the total quantity of precursors present: the TOP (total oxidisable precursor) assay. The TOP assay procedure begins with an analysis of the standard suite of PFAS compounds. The sample is then oxidised with hydroxyl radicals and analysed again for the standard suite of PFAS. The oxidation step converts the precursors present in the sample into stable PFAS compounds (primarily perfluorocarboxylic acids). With this process, a total amount of PFAS is determined, and thus the perfluorinated compounds originally present, as well as the precursors that can be transformed, e.g., by biodegradation, into stable PFAS, such as PFOS and PFOA. Use of this type of analysis technique could shed more light on the presence of as yet unknown precursors.

8.5 COMPARISON WITH OTHER RESEARCH

This study did not make extensive comparisons to other research in the Netherlands or elsewhere. Comparisons with other research are difficult for a number of reasons:

- Analysis packages differ per study. This leads to differences in total concentrations and in the substances found.
- Reporting limits differ per study. This also produces differences in the substances found.
- The high concentrations measured in the past are not always realistic in the present day, due to remedial measures already taken. This certainly applies to point sources.
- Substances that are used as replacements for regulated PFAS are often not included in the analysis packages.
- There seems to be many more PFAS sources and pathways than initially thought. The influence of specific point sources on research locations is by no means always clear.
- Various studies indicate an important role of precursors (e.g., Van Gijn et al., 2021; Pancras et al., 2021). Yet, the inclusion of precursors in analysis packages is only rather recent. Even where precursors have been included, only a limited number are analysed.

Nonetheless, we can conclude that the results of the current study align with those from other research. A general comparison reveals the following:

- The quantities this study found in effluent are in the same range as those measured by Jans & Berbee (2020) and similar to measurements from various projects brought together in the Watson database[14] (except for special cases, see final point below).
- The levels found in sewage sludge are similar to those measured by HVC (see appendix 16). They are also in the same range as those measured by other sludge processors and by Pancras et al. (2021).
- The loads calculated in effluent, sewage sludge and the special wastewater streams are in the same range as those found in other studies (table 7).
- The removal efficiencies reported in the Watson database vary for different PFAS from 100% removal to very high (more than 1,000%) negative removal efficiencies. These are efficiencies calculated based on simultaneously collected 24-hour samples. The data from the Watson database therefore confirm the finding of the current monitoring campaign that removal efficiencies are extremely variable and often negative.
- The current study found lower GenX levels than previous measurements at Dordrecht WWTP and Chemours (De Kort et al., 2019). This suggests that their emissions have been reduced.

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[14] The Watson database brings together measurement data on microcontaminants in WWTP influent and effluent. The database is used for the Netherlands' emissions inventory and other purposes.

9

CONCLUSIONS AND RECOMMENDATIONS

9.1 CONCLUSIONS

High, moderate and low PFAS-load WWTPs

This study measured PFAS levels in influent, effluent and sewage sludge in a broad-based monitoring campaign. In total, eight WWTPs were studied, including WWTPs known to have high PFAS emissions (hotspots), a former hotspot (where PFAS emissions had previously been reduced at the source) and WWTPs with differing shares of industrial wastewater as well as domestic wastewater. In addition, a number of special wastewater streams were examined, all of which discharged to Dordrecht WWTP.

From the results it became clear that the extent of PFAS loads was not always as expected. In particular, the share of industrial wastewater processed by a WWTP turned out to be a poor predictor of the PFAS levels found. The WWTPs were therefore categorised into three groups – high, moderate and low – depending on the PFAS loads measured in their effluent.

By simultaneously sampling influent, effluent and sludge streams over a period of nine consecutive days, a picture was obtained of the PFAS loads coming into the WWTPs with influent and the loads discharged with effluent, as well as the share of PFAS retained in the sludge.

The results for the studied WWTPs can be assumed to provide a reasonable representation of situations commonly found at other WWTPs in the Netherlands. The number of measurements performed in this study was considerably greater than in other earlier research, therefore providing a more reliable picture of the PFAS loads and quantities leaving WWTPs with effluent and sludge. Some uncertainty does remain, however, about the extent to which all major sources of PFAS were covered in this study. It is also difficult to gauge what share of the WWTPs in the Netherlands has low PFAS loads, and what share has moderate PFAS loads. The hotspot locations can be viewed as special cases.

Concentrations

PFAS were found in all of the analysed samples, in concentrations of 8.6–1,360 ng PFAS (35)/l in influent, 13.6–809 ng PFAS (35)/l in effluent and 20–179 μg PFAS (35)/kg DM in sewage sludge (digested and undigested). Particularly high concentrations were found in the sewage sludge from Lelystad WWTP, especially of PFOS and fluorotelomer sulfonic acids. In Lelystad, total PFAS (35) was measured as 154–179 μg/kg DM, compared to 26–91 μg/kg DM at the other WWTPs. At Aarle Rixtel WWTP, sieved material was collected from the influent. That sieved material, which was made up mainly of cellulose, contained 3.1–11 μg PFAS (35)/kg DM. These are low values compared to the sewage sludge.

In the water, mainly PFAS with short fluorinated chains (C4–C8) were found, while in sludge PFAS with longer fluorinated chains and precursors were identified.[15] The contamination

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[15] Precursors are PFAS compounds that can degrade into stable PFAS. They often have a non-fully fluorinated carbon chain, while stable PFAS have fully fluorinated carbon chains.

pattern (i.e., the distribution of different PFAS in the samples) differed per WWTP. No clear weekly pattern was observed in inflows. The range of concentrations was in most cases small across the different monitoring days, though peaks of certain PFAS were sometimes found. Whether these were related to wet weather was not examined in detail.

Regarding the special wastewater streams, high PFAS concentrations were measured in the wastewater from the landfill, where PFAS-containing waste was known to have been dumped (6,000–9,000 ng PFAS (35)/l; mainly PFOA and HFPO-DA). This wastewater was made up of drainage water from the landfill and stormwater runoff from the HVC grounds. High concentrations were also measured in the wastewater from Chemours (mainly HFPO-DA). At Chemours, two periods were distinguished: a period with low PFAS loads (approx. 10 ng/l) and a period of high loads (approx. 5,000 ng/l). This difference could be related to batch production processes, which could produce large fluctuations in the wastewater quality. According to Chemours' own measurements, HFPO-DA concentrations in its water treatment facility effluent averaged 378 ng/l in 2020 (see appendix 7). The concentration of PFAS (35) in the wastewater from the domestic waste incinerator was similar to that of the low PFAS-load WWTPs. The concentration of PFAS (35) in the wastewater from the sewage sludge incinerator was on par with that of the moderate PFAS-load WWTPs. The wastewater from sludge incineration was found to contain mainly PFAS from the perfluoroalkane sulfonamides group (a group of precursors). The concentrations found in the sludge processed at HVC were in the range of the low PFAS-load WWTPs.

Removal efficiencies

PFAS were not, or were hardly, removed in the normal treatment processes of WWTPs. In most cases, an increase in precursors and/or stable PFAS was found, particularly of PFOS (C8), PFOA (C8) and shorter-chain perfluoroalkyl carboxylic acids[16] (C4–C7).

The role of PFAS precursors

The increase found in precursors and/or stable PFAS in the effluent can probably be explained by precursor degradation. Only a small proportion of the precursors present was (or could be) analysed. Comparisons of ingoing and outgoing PFAS loads showed larger PFAS loads leaving the WWTPs than entering at most WWTPs. This applied to the WWTPs with high, moderate and low PFAS loads.

Precursors are a largely unknown element. Very few precursor applications are currently known, and potential sources are not yet well understood. The current study demonstrates that there are probably many more potential sources than oftentimes assumed.

Loads and emission factors

Substantial variation was found in PFAS loads at the studied WWTPs. Loads were in the range of 40–20,035 g/year via influent, 38–20,840 g/year via effluent and 3.3–585 g/year via sewage sludge. This variation corresponded largely to WWTP size. However, the extent of PFAS contamination also differed per WWTP, as demonstrated by the emission factors (i.e., the loads in the effluent per population equivalent (PE 150) per unit of time). PFAS emissions via effluent to surface waters amounted to approx. 50 mg/PE 150 per year for the high PFAS-load WWTPs, 5 mg/PE 150 per year for the moderate PFAS-load WWTPs and 1 mg/PE 150 per year for the low PFAS-load WWTPs. Approx. 1.2 mg/PE 150 per year was removed with the sludge.

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[16] These belong to the same group as PFOA.

The emission via effluent from all WWTPs in the Netherlands combined was broadly estimated as 65–180 kg per year; with the combined emission via sewage sludge estimated as 15–45 kg per year.

Contributions from different sources
Results from the monitoring campaign indicate a background level of PFAS at all WWTPs, with in addition, loads from various different sources. The contamination pattern (i.e., the distribution and proportions of individual PFAS in the samples) differed per WWTP, suggesting a variety of present sources, which by no means are all currently known or understood. There appears to be more sources than previously envisaged. Furthermore, the extent of the PFAS loads could not always be accurately predicted: minimal loads were found at facilities where higher loads were expected based on the known activities of contributing companies and industrial loads in the collection area. At locations where households were expected to be the only source, higher than expected PFAS loads were found.

Although high PFAS levels were found in the special wastewater streams processed at Dordrecht WWTP, urban wastewater from the city of Dordrecht and its surroundings turned out to be the largest contributor by far to the total PFAS load entering the WWTP.

Comparisons with quality standards
To provide some perspective on the PFAS loads found, we compared these to the Dutch quality standards for surface waters and the European quality standards for drinking water (and drinking water resources). These standards were found to be exceeded at Dordrecht WWTP, in the drainage water from the landfill and in the Chemours wastewater. These were also the locations where the highest PFAS levels were measured, particularly, the highest PFOA concentrations. At Bath WWTP, the concentrations found exceeded the European quality standard for the sum of 20 PFAS compounds. The quality standard for PFOS is extremely low. PFOS levels exceeded the standard for surface waters in all influents, effluents and at HVCdov. Whether effluent discharge leads to PFAS standards being exceeded in the receiving surface waters would depend on the local situation.

PFAS concentrations in sewage sludge remained, with the exception of the sludge from Lelystad WWTP, within the margins set by other countries for application of sewage sludge on land. Such application, however, does not take place in practice in the Netherlands.

Comparison with other studies
The results of the current study were not extensively compared to other studies conducted in the Netherlands and elsewhere. However, the findings from the current monitoring campaign do confirm those of other research.

9.2 RECOMMENDATIONS

Cooperation in European and nationwide initiatives
A number of persistent PFAS, including PFOS and PFOA, have been designated as priority hazardous substances and Substances of Very High Concern (SVHC). That means their release into the environment should be reduced to zero. Intervention at the source is the preferred option, because once PFAS are in the environment they are difficult or impossible to remove. The Netherlands is working together with a number of other countries on a proposal for a European restriction on all PFAS. Furthermore, the Netherlands is working towards agree-

ments with neighbouring counties to address PFAS in the context of the International River Commissions.

At the national level, the water boards and other government authorities are cooperating with business and industry in the PFAS Action Programme. Via this platform they are pursing interventions to reduce the release of PFAS into the environment and to limit human exposures. That cooperation looks specifically at the various links in the chain, from the production of PFAS, to its use in industrial processes, to the different emission pathways. Furthermore, a nationwide campaign is currently underway to update the permits of industrial and other parties using SVHCs. It offers potential for better mapping and regulation of PFAS emissions. The current study provides valuable information to that end.

Better understanding of sources

This study provides starting points for regional identification of PFAS sources in wastewater. Water boards can work together with provincial and municipal authorities and with environmental services to map potential PFAS sources. The indicative estimates presented in this report of PFAS emissions via various pathways and products can provide valuable leads in such identification and mapping exercises. In addition, by conducting monitoring measurements at WWTPs, and perhaps also higher up in the water chain, locations can be identified where PFAS contamination is relatively high, and thus where as yet unknown sources may be found. If sources can be identified, dialogues can then be initiated to determine ways to reduce emissions at the source.

Research on the nature, magnitude and sources of precursors

Measures have been taken to reduce emissions of a number of persistent PFAS (such as PFOS and PFOA). Yet, after initial decreases, concentrations in the environment now appear to be stabilising (Jonker, 2021). A variety of studies show that PFAS precursors can be transformed to persistent PFAS. This means that any further reductions in persistent PFAS in the environment will be very difficult to achieve without reducing emissions of PFAS precursor. More research is needed to better understand the nature, magnitude and sources of PFAS precursors. For that reason, further research on precursors will be proposed to the national working group on emerging substances (Dutch acronym: WGAOS).

For future monitoring campaigns, use of TOP assay is additionally desirable, to obtain more insight into precursors. This analysis method provides a measure of the total quantity of precursors present, without it being exactly known what these precursors are.

More attention for shorter-chain PFAS

PFAS with shorter chains (C2–C7) are increasingly used as alternatives for longer-chain PFAS (such as PFOS and PFOA). Few studies include PFAS with C2 and C3 chains in their analysis. These short-chain PFAS dissolve easily in water and are not expected to be removed at WWTPs. Pancras et al. (2021) found high concentrations of PFPrA (C3 PFCA) in paper recycling. It is therefore recommended that future research include these short chains as well. New analytical techniques may need to be developed for this purpose.

Removal efficiency by advanced treatment techniques

With the current state of knowledge, it is unclear whether removal of PFAS at WWTPs using advanced treatment techniques (such as activated carbon binding) is technically possible and cost effective. Further research in this regard is recommended.

10

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11

ABBREVIATIONS AND TERMS

4:2 FTS	2-(perfluorobutyl)ethane-1-sulfonic acid (4:2 fluorotelomer sulfonic acid)
6:2 FTS	2-(perfluorohexyl)ethane-1-sulfonic acid (6:2 fluorotelomer sulfonic acid)
8:2 diPAP	8:2 polyfluoroalkyl phosphate diester
8:2 FTS	2-(perfluorooctyl)ethane-1-sulfonic acid (8:2 fluorotelomer sulfonic acid)
9Cl-PF3ONS	2-[(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyl)oxyl]-1,1,2,2- tetrafluoroethanesulfonic acid (main component in F53B)
10:2 FTS	2-(perfluorodecyl)ethane-1-sulfonic acid (10:2 fluorotelomer sulfonic acid)
11Cl_PF3OUdS	11-chloroeicosafluoro-3-oxa-undecane-1-sulfonic acid (minor component in F35B)
ADONA	Ammonium 4,8-dioxa-3H-perfluorononanoic acid
AFFF for	Aqueous Film-Forming Foam; a type of firefighting foam used for liquid fires
WWTP	Wastewater treatment plant
Br_PFHxS	Perfluorohexane sulfonic acid (branched)
Br_PFOS	Perfluorooctane sulfonic acid (branched)
Cx	Expression of the number of carbon atoms in the fluorinated chain
DONA	4,8-dioxa-3H-perfluorononanoic acid
EOF	Extractable organic fluorine (analytical method)
EtFOSA	N-ethyl perfluorooctane sulfonic acid
EtFOSAA	N-ethyl-perfluorooctane sulfonamidoacetic acid
FEP	Fluorinated ethylene propylene
Fingerprint	Distribution and relative proportions of different individual PFAS compounds in sample
FRD-902	Ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate
FRD-903	2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoic acid
GenX	Technology used in the manufacture of coatings (e.g., Teflon), in which two very similar fluorine-containing substances are utilised: FRD-902 ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate (an ammonium salt) and FRD-903 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoic acid (an acid)
HFPO-DA	2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoic acid (FRD-903)
L_PFBS	Perfluorobutanesulfonic acid (linear)
L_PFDS	perfluorodecane sulfonic acid (linear)
L_PFHpS	Perfluoroheptane sulfonic acid (linear)
L_PFHxS	Perfluorohexane sulfonic acid (linear)
L_PFOS	Perfluorooctane sulfonic acid (linear)
L_PFPeS	Perfluoropentane sulfonic acid (linear)
MinIenW	Ministry of Infrastructure and Water Management
ng/l	Nanogram per litre
N-MeFOSAA	N-methylperfluorooctanesulfonamidoacetic acid
FPSA	Dutch Food and Consumer Product Safety Authority (Dutch acronym: NVWA)
PE	Population equivalent. Population equivalents are used to express the capacity and load of a WWTP. There are different types of PE. The load (or contaminant amount) can be from domestic wastewater, industrial wastewater, stormwater runoff and/or other surface runoff and waste water.
PE 150	Population equivalent based on an oxygen binding capacity of 150 g oxygen per day.
PFAS	Per- and polyfluoroalkyl substances

PFAS(x)	Used when PFAS concentrations are summed; x denotes the number of PFAS compounds included in the summation
PFBA	Perfluorobutanoic acid
PFBS	Perfluorobutanesulfonic acid
PFCA	Perfluoroalkyl carboxylic acid
PFDA	Perfluorodecanoic acid
PFDoA	Perfluorododecanoic acid
PFHxA	Perfluorohexanoic acid
PFHxS	Perfluorohexane sulfonic acid
PFHpA	Perfluoroheptanoic acid
PFNA	Perfluorononanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonic acid
PFPeA	Perfluoropentanoic acid
PFPeS	Perfluoropentane sulfonic acid
PFSA	Perfluoroalkyl sulfonic acid
PFTDA	Perfluorotridecanoic acid
PFUdA	Perfluoroundecanoic acid
PTFE	Polytetrafluoroethylene; also known under the brand name Teflon
Read across	Technique by which an unknown value for a substance property (for example, toxicity) is derived on the basis of comparison with substances for which the substance property is known.
WWTP	Wastewater treatment plant
STOWA	Foundation for Applied Water Research
TOP	Method for analysing total oxidisable precursors

APPENDIXES

APPENDIX 1

SELECTED WWTPs AND OTHER STUDY LOCATIONS

OVERVIEW OF WWTPS AND COMPANIES STUDIED

A mix of WWTPs was sought, including a (former) hotspot location, WWTPs treating a relatively large proportion of industrial wastewater, WWTPs treating mixed domestic and industrial wastewater and WWTPs treating almost exclusively domestic wastewater. The table below presents the selected WWTPs and the reason for their selection.

WWTP	Description/basis for selection
Dordrecht	Hotspot
Aarle Rixtel	Former hotspot (discharge stopped, but residual flows remained)
Bath	Large proportion industry
Lelystad	Mixed WWTP
Hattem	Mixed WWTP
Asten	Almost exclusively domestic wastewater
Hapert	Almost exclusively domestic wastewater
Piershil	Almost exclusively domestic wastewater

In addition to the eight WWTPs, this study included two companies that discharged their wastewater after treatment into the sewer. The wastewater was then treated a second time, together with domestic wastewater, at Dordrecht WWTP. These companies were Chemours and HVC. Chemours is a chemical company that utilises PFAS and other chemicals in its production processes. HVC is a waste collection and processing company. It processes domestic waste, hospital waste and sewage sludge in incinerators. HVC also manages the former Crayenstein landfill where industrial waste used to be dumped, including waste containing PFAS. The landfill has since been remediated and covered. The leachate generated from the landfill is extracted via a management system and then treated by activated charcoal filter.

The table below presents the main characteristics of the WWTPs.

Reference year 2019	WWTP	Dordrecht	Bath	Aarle Rixtel	Lelystad	Piershil	Asten	Hapert	Hattem
Design capacity	PE 150	281,100	472,000	272,000	160,500	6,600	72,500	64,400	64,000
Connected residents		115,000	285,000	188,000	76,300	5,450	43,500	37,100	37,400
Contaminant load of connected companies	PE 150	78,000	188,000	87,000	40,000	530	7,300	14,200	13,000
Annual flow	Million m^3/y	18.2	36.4	24.6	4.7	0.7	5.0	4.5	3.7
Share external sludge also processed	% of sludge production	20	10	7	0	0	0	0	0
Sludge digestion share of sludge processing		no	yes	no	no	no	yes	no	no
Liquid waste received per ash	Tons/y	0	0	0	4,000	0	0	0	0

PROCESS DIAGRAMS WWTPS

The following pages present process diagrams for the studied WWTPs.

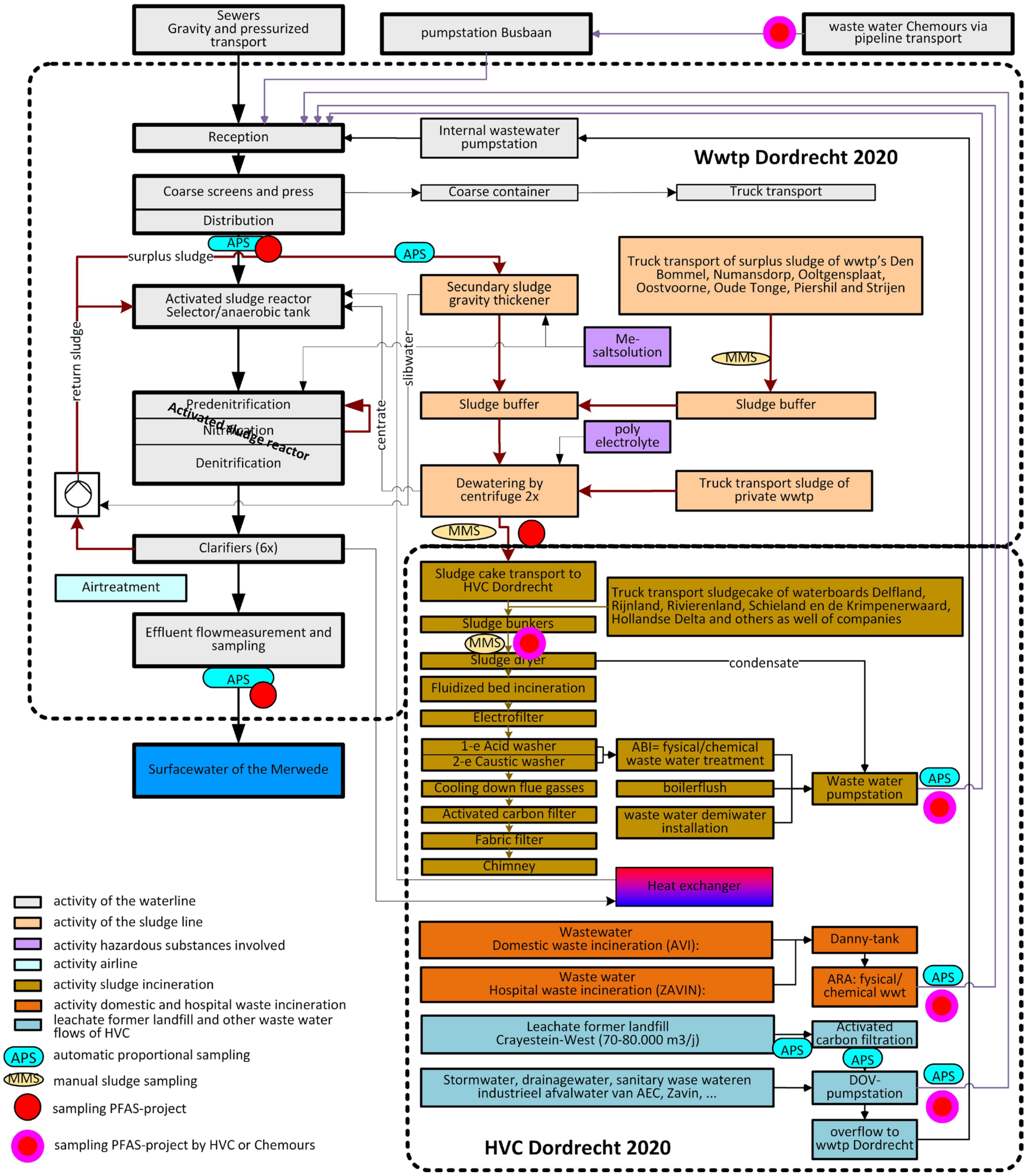
Because the HVC process is so intertwined with that of Dordrecht WWTP, these two facilities' wastewater streams are presented together in the Dordrecht WWTP diagram. The wastewater from HVC can be divided into three types. These are treated in separate physical/chemical processes. The treated wastewater is discharged via a separate pressure pipe network to the inflow installation of Dordrecht WWTP. On the influent side of Dordrecht WWTP, the process diagram includes the company Chemours. Wastewater from Chemours is treated on-site via a physical/chemical process consisting of activated charcoal filtering. After this treatment, the wastewater is transported via the municipality of Dordrecht to the WWTP.

Each process diagram presents the key data on the facility, with 2019 as the reference year. These characteristics are the following:

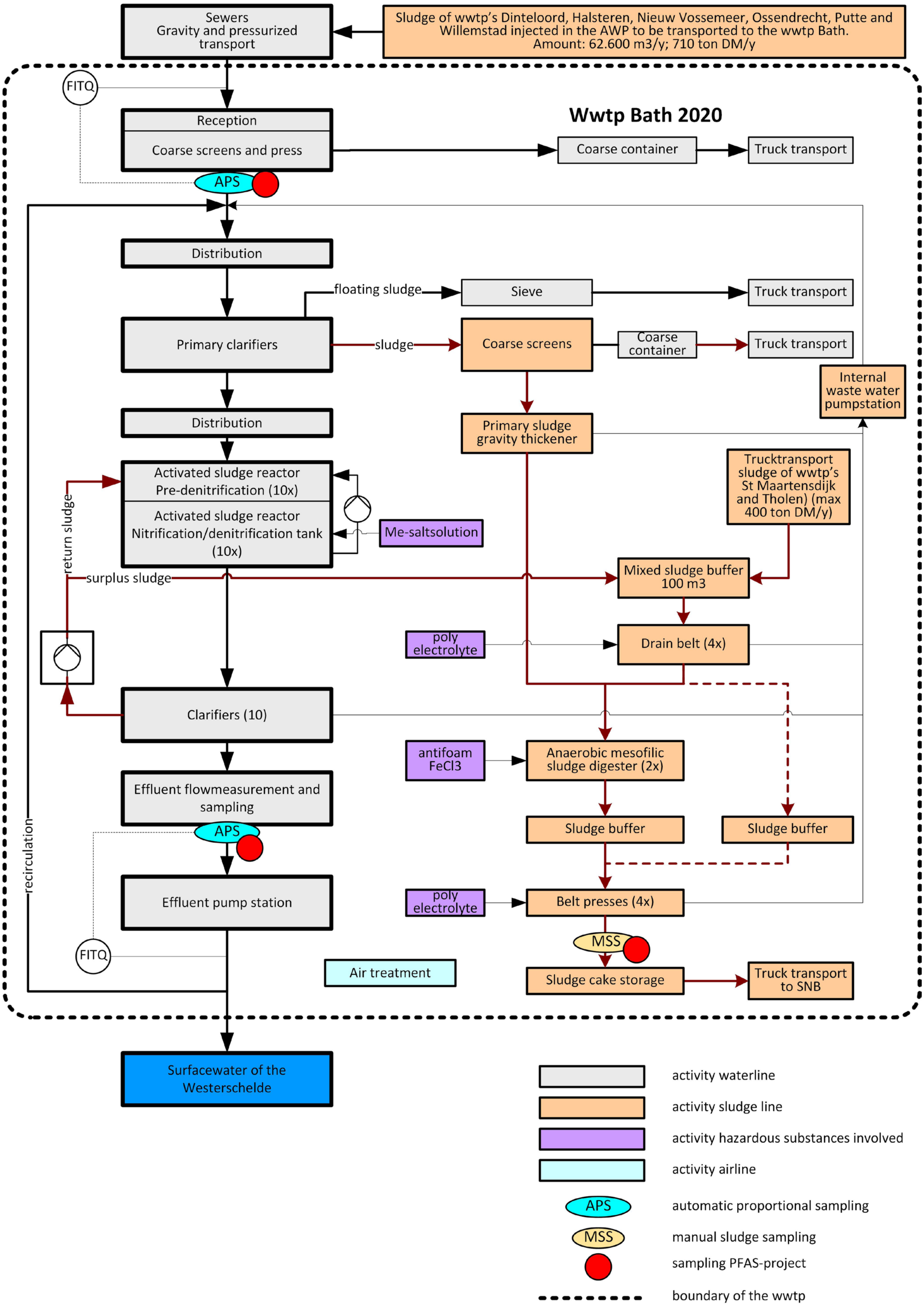
- Load on WWTP, expressed in PE 150
- Amount of urban wastewater treated annually and discharged as effluent
- Amount of internal sludge produced
- Amount of sludge from external sources that is also processed

In each process diagram red dots indicate where the samples were collected for the current study (influent, effluent and sludge).

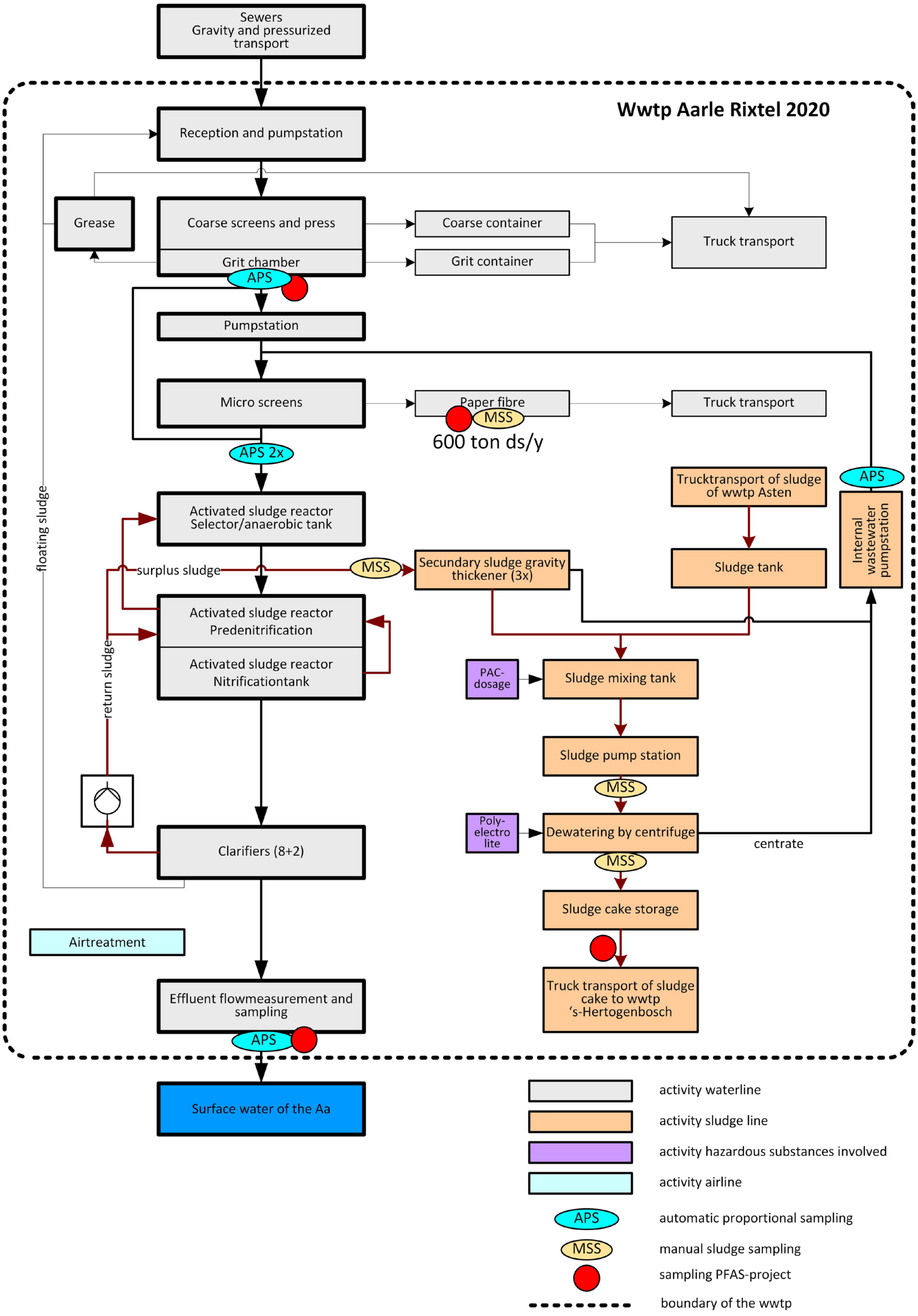
PROCESSCHEMA RWZI DORDRECHT



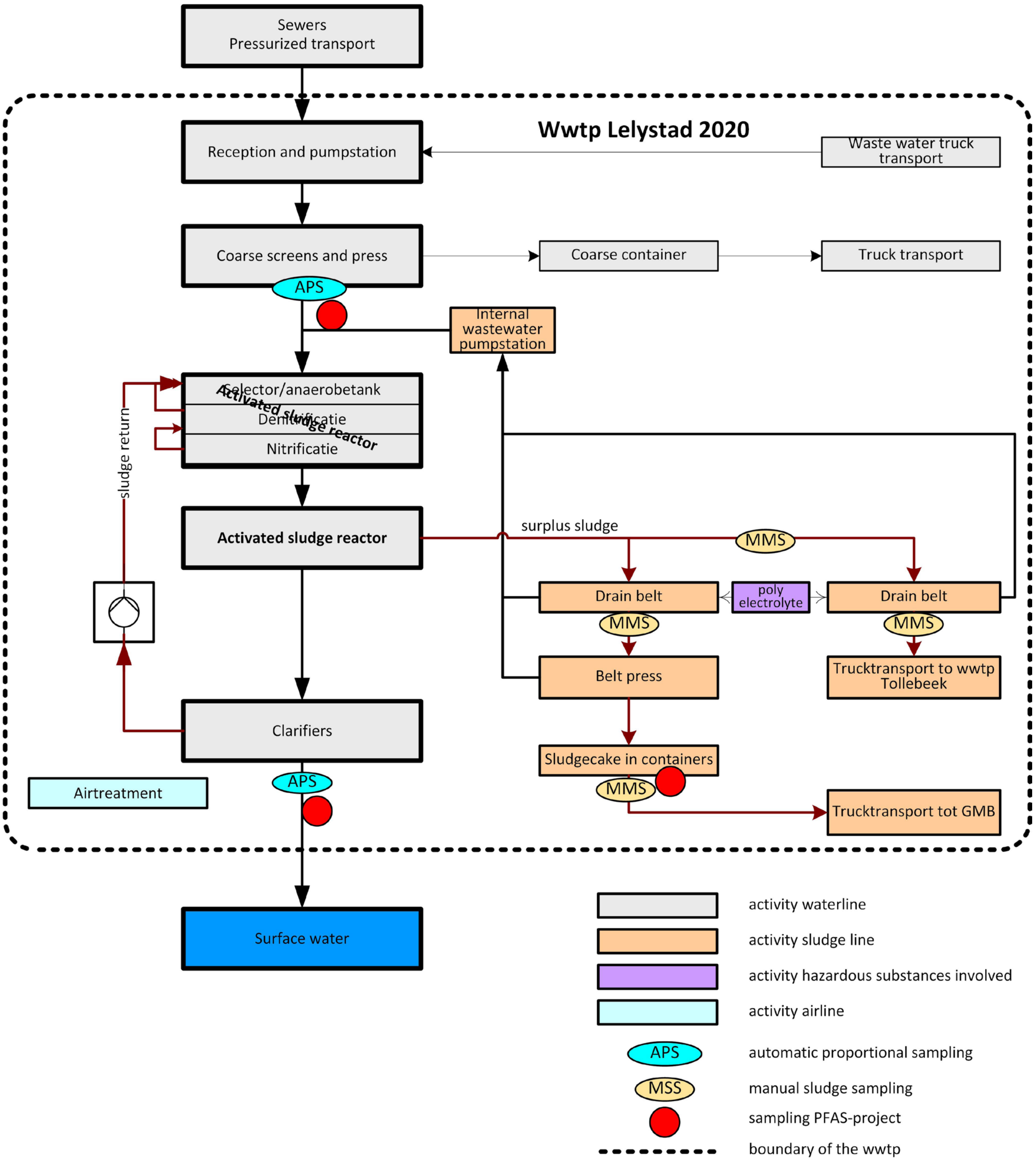
PROCESSCHEMA RWZI BATH



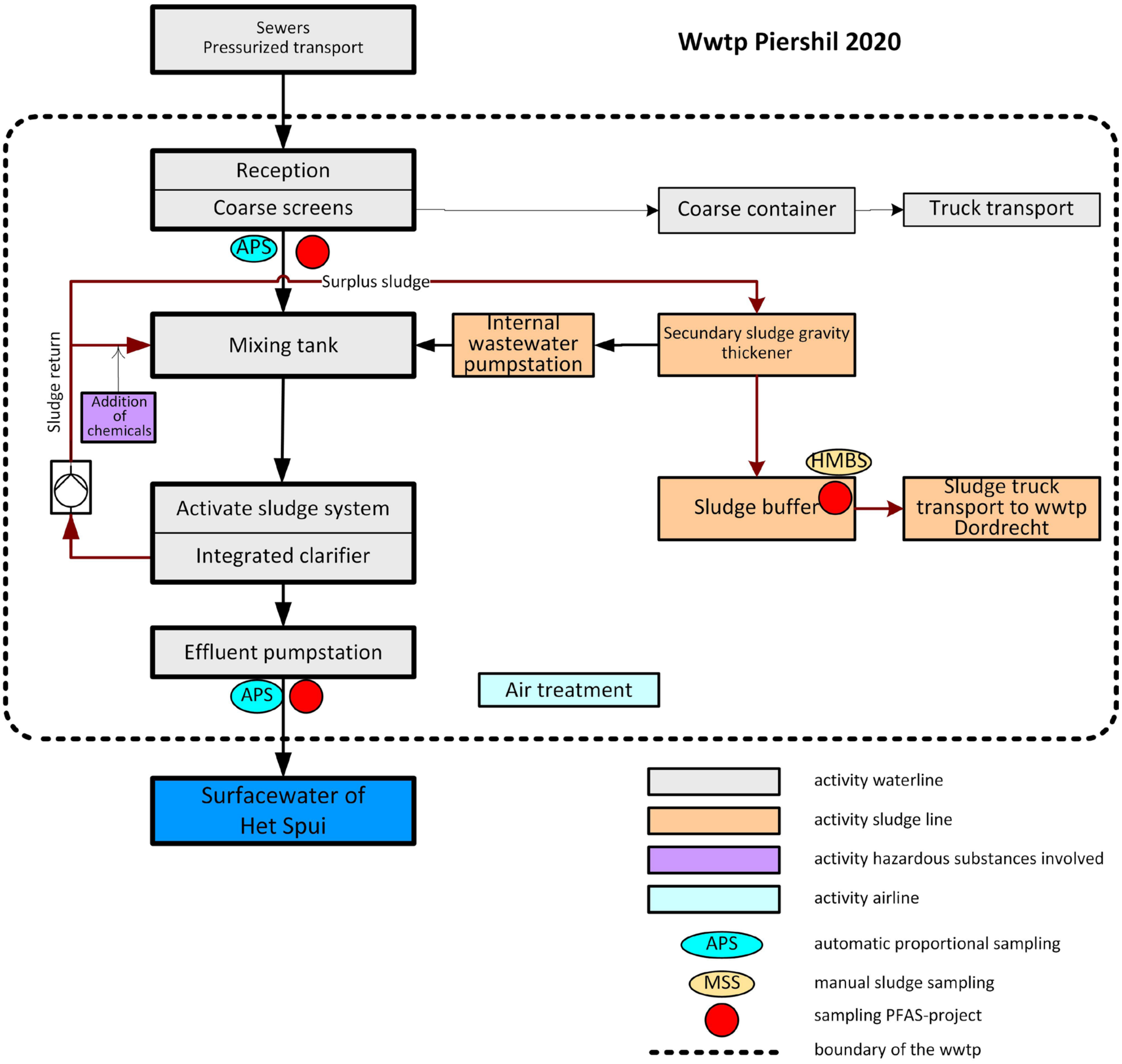
PROCESSCHEMA RWZI AARLE RIXTEL



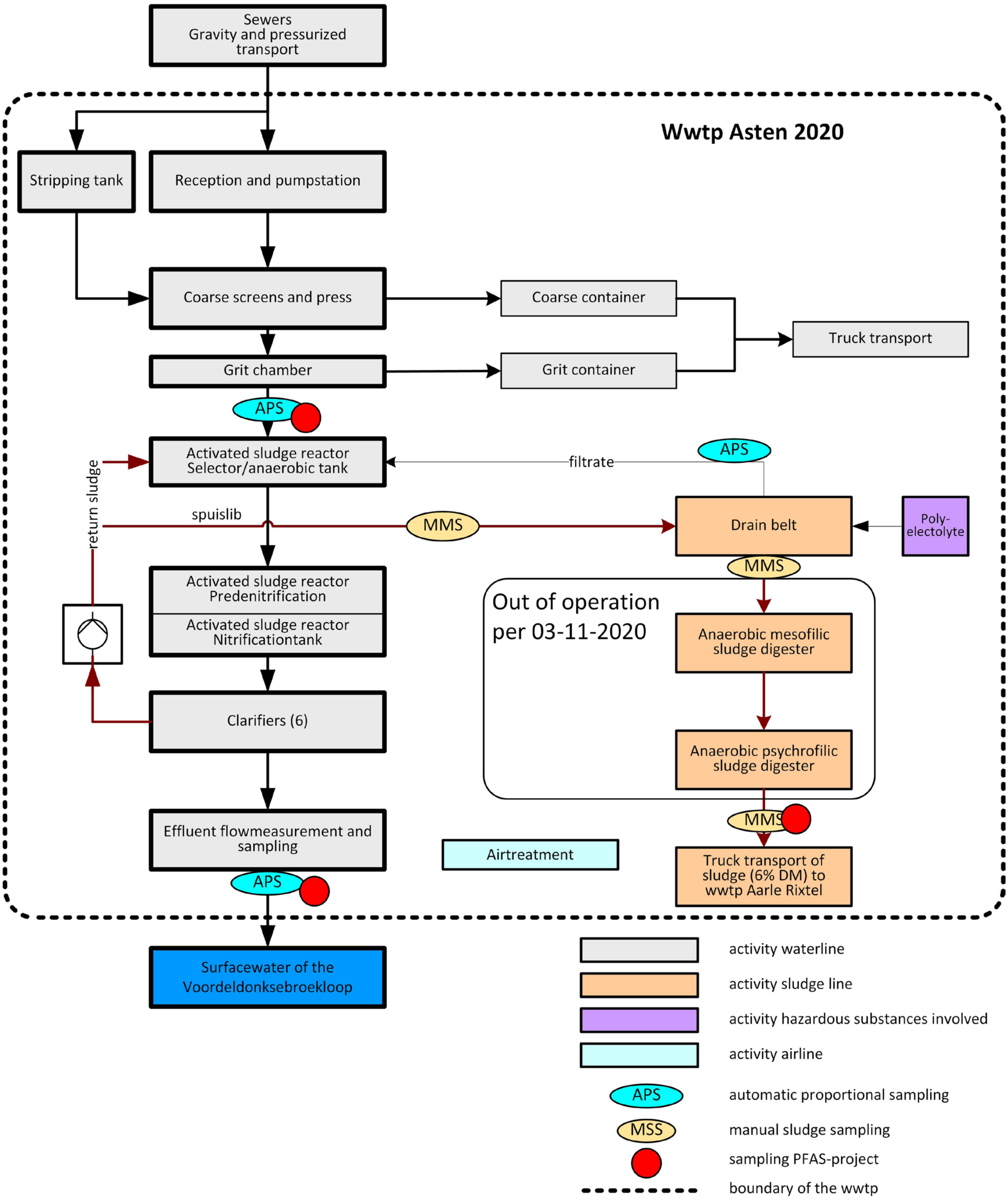
PROCESSCHEMA RWZI LELYSTAD



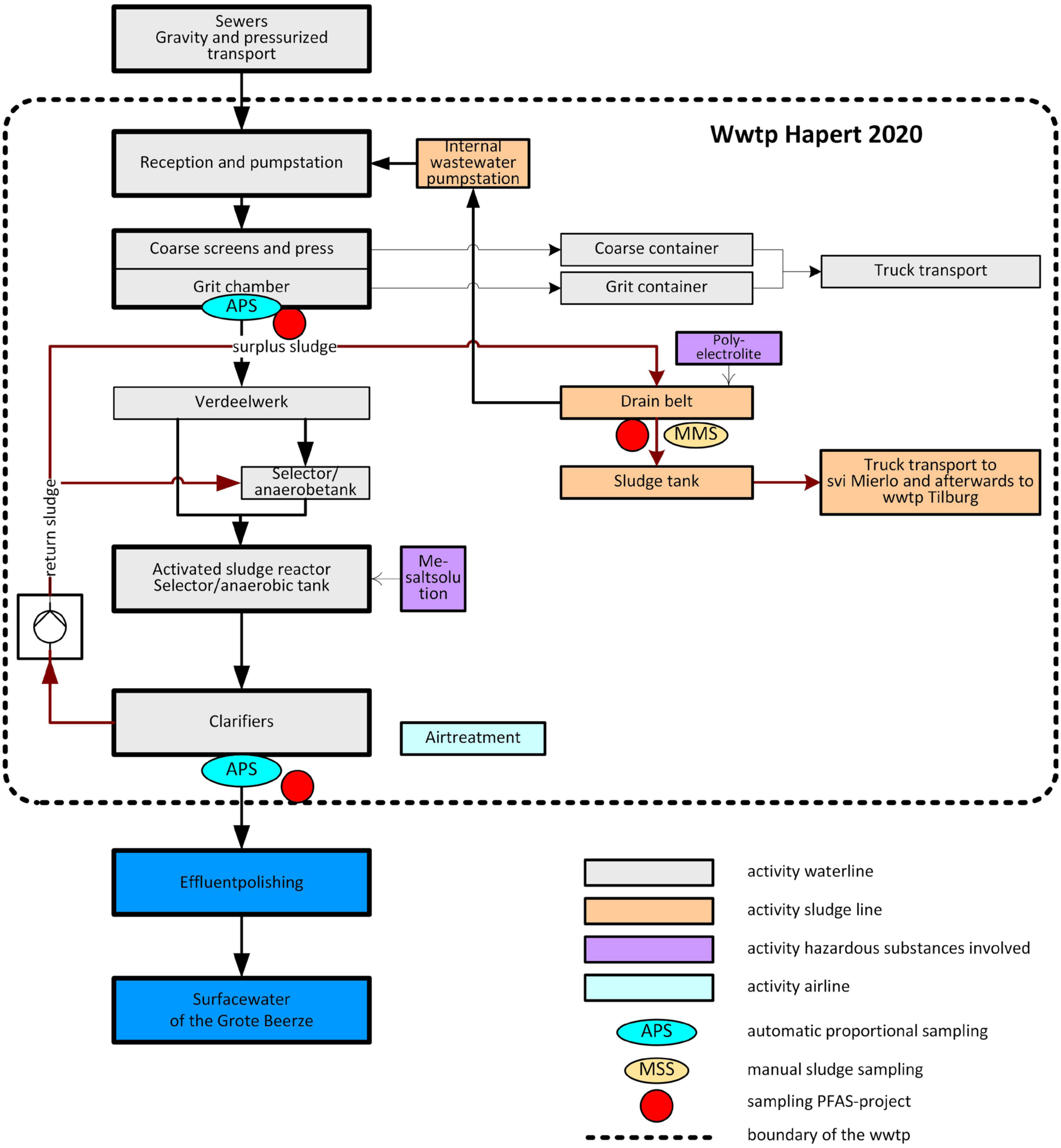
PROCESSCHEMA RWZI PIERSHIL



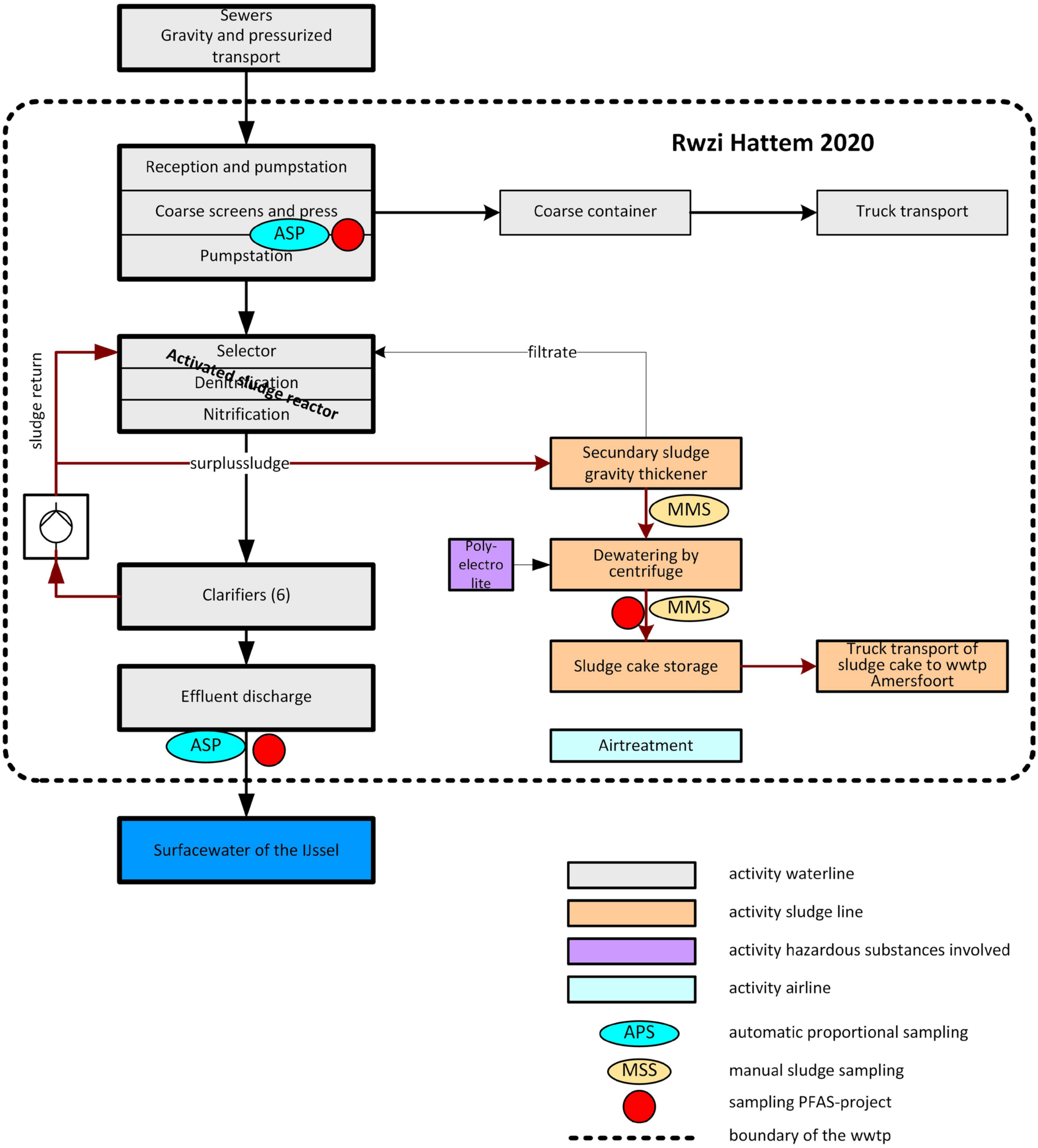
PROCESSCHEMA RWZI ASTEN



PROCESSCHEMA RWZI HAPERT



PROCESSCHEMA RWZI HATTEM



APPENDIX 2

SAMPLING PROCEDURE

WATER LINE AT THE WWTPS

The samples were collected in November 2019. Influents and effluents were simultaneously sampled on nine consecutive days. No consideration was made for wet weather days. Sampling was performed under conditions of both dry weather inflow (DWI) and wet weather inflow (WWI).

SLUDGE LINE AT THE WWTPS

For sludge, a maximum of three samples were collected at most WWTPs. A higher sampling frequency was not considered useful, considering the sludge age, which was approx. 15 days. The retention time of sludge at WWTPs with sludge digestion (Asten and Bath in the current study) was even longer, up to 40 days. Higher sludge ages and retention times have an equalising effect on substance concentrations in the sludge. In addition, sludge could not be sampled on all days, because sludge processing is not a continual operation.

At Dordrecht WWTP, the sludge – i.e., the dewatered sludge from the centrifuges – was sampled seven times. This WWTP was sampled more frequently because it processed a lot of sludge from other WWTPs.

At Piershil WWTP, only one sludge sample was collected. At that WWTP, the sludge buffer tank was emptied beforehand. Virtually all of the sludge produced during the sampling period was retained in the sludge buffer tank. Then, at the end of the nine-day sampling period, a composite grab sample was obtained.

At Asten WWTP, the sludge digester was taken out of operation at the start of the sampling period. Therefore, digested sludge samples were collected on three consecutive days prior to the sampling period.

At Aarle Rixtel WWTP, sieved material was sampled in addition to influent, effluent and sludge. This is cellulosic matter filtered out of the influent using fine sieves and separately disposed of. This cellulosic matter is derived from toilet paper among other things.

In addition, the HVC Group (energy and waste disposal company) took four mixed samples of their incoming sludge and had these samples analysed by Eurofins. Its analytical package is somewhat different from the one applied by this monitoring campaign.

SPECIAL WASTEWATER STREAMS

Next to the abovementioned samples, several special wastewater streams were also sampled. These originated from companies known or suspected to contain PFAS, and were treated together with the influent of Dordrecht WWTP. This regards three wastewater streams from the HVC Group (energy and waste disposal company) and the wastewater from Chemours:

- Wastewater from sludge incineration (HVCsvi)
- Wastewater from domestic and hospital waste incineration (HVCara)

- Drainage water from the landfill mixed with stormwater runoff from the HVC terrain (HVCdov) (hereinafter: landfill wastewater)
- Wastewater from Chemours (CHE)

All four of these wastewater streams underwent their own treatment processes at the companies of origin (for details, see section 3.2.4 and the block diagram for Dordrecht WWTP in appendix 1). Samples of these wastewater streams were collected by staff at HVC and Chemours.

SUMMARY OF NUMBERS OF SAMPLES

The table below presents the numbers of samples analysed. For details (sample codes, sample data and explanations of deviations in numbers) see appendix 3.

WWTP / wastewater stream	Number of influent samples	Number of effluent samples	Number of sludge samples
Dordrecht (DOR)	9	9	7
Bath (BAT)	7	9	3
Aarle Rixtel (AAR)	9	9	3 (+3 sieved material)
Lelystad (LEL)	9	9	3
Piershil (PIE)	9	8	1
Asten (AST)	9	9	3
Hapert (HAP)	9	9	3
Hattem (HAT)	8	8	3
HVC – wastewater sludge incineration facility (HVCsvi)		3	
HVC – domestic and hospital wastewater incineration facility (HVCara)		3	
HVC – landfill wastewater (HVCdov)		9	
Chemours – wastewater (CHE)		9	

SAMPLING PROCEDURE

The influent, effluent and special wastewater stream samples were all collected by means of 24-hour flow-proportional sampling. The sludge/sieved material samples were composite grab samples. That is, staff took grab samples of the sludge at regular intervals during the day. These grab samples were then mixed by hand, after which a representative composite sample was obtained. This procedure was applied for the sludge samples from Dordrecht, Bath, Aarle Rixtel (including sieved material), Lelystad, Hapert and Hattem.

The sludge sample from Piershil was just a single grab sample from the sludge buffer tank, and the grab samples collected at Asten WWTP were from the circulation lines of the sludge digester. This is by definition a well-mixed sludge.

INSPECTION PRIOR TO SAMPLING

An inspection team including representatives of the water analysis laboratories visited all the WWTPs prior to the start of the sampling programme. These inspections had several aims:

- Documenting current WWTP operational procedures, as well as any distinctive features of their processes
- Assessment of the sampling infrastructure and discussing any potential adjustments (e.g., extra refrigerators, sampling equipment, multi-vessel systems, plastic or glass collection vessels)
- Logistics: determining who would implement the different tasks, time intervals for sample collection, WWTP accessibility, etc.

- Conducting a detailed check of the sampling equipment for the presence of any PFAS in parts and for parts that could adsorb/absorb PFAS and, if found, to replace these
- Elimination of any PFAS-containing materials in operational processes to prevent, insofar as possible, contamination due to PFAS in such materials
- Determination of the exact location of sample collection for sludge and sieved material and finalising the sampling procedure in consultation with facility managers
- Gathering necessary data for processing (determining sludge production), etc.

A detailed report was made up for each of these visits. For each sampling point, both the sampling method and the sampling situation were reviewed on-site with the sample collector, the facility manager and the project leaders. In addition, photos were taken of each sampling location.

The following protocols and documents were employed during the inspections:

- NEN 6600
- Guidelines for sampling and analysis of PFAS compounds in soil and groundwater[17]

Based on the inspection reports, tailored work instructions were drawn up for each WWTP. The inspection reports, as well as the work instructions, are available upon request.

VALIDATION OF SAMPLING PROCEDURE

Influent and effluent samples were collected in conformance with NEN 6600 by staff of two water board laboratories, Aquon and Aqualysis.

These staff also carried out continual controls throughout the sampling period. These controls focused on the following NEN 6600 criteria:

- Number of grab samples during a daily cycle
- Volumes per grab sample
- Daily comparisons of the achieved number of grab samples and grab volumes with pre-set values
- Total sample volumes compared to expected volumes
- Temperature of the sampling equipment
- Correct set-up of the sampling equipment

At a number of WWTPs, these controls led to the sampling period being prolonged or being started over to achieve nine consecutive measurement days (see appendix 3 for details).

No validation was performed for the sludge sampling, as this would have been virtually impossible, due to the nature of the processes and the sampling.

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[17] https://www.bodemplus.nl/onderwerpen/wet-regelgeving/bbk/publicaties/bemonstering-pfas/

APPENDIX 3

NUMBER OF ANALYSED SAMPLES AND DATES

NUMBER OF SAMPLES ANALYSED AND SAMPLE DATES (IN 2020). 09HVCSVI = WASTEWATER FROM SLUDGE INCINERATION FACILITY, 09HVCARA = WASTEWATER FROM DOMESTIC AND HOSPITAL WASTE INCINERATION FACILITY, 09HVCDOV = DRAINAGE WATER FROM LANDFILL, 10CHEINFL = WASTEWATER FROM CHEMOURS

Location	Matrix	Code	day 1	day 2	day 3	day 4	day 5	day 6	day 7	day 8	day 9	Number
Dordrecht	influent	01DORinfl	24/11	25/11	26/11	27/11	28/11	29/11	30/11	1/12	2/12	9
Dordrecht	effluent	01DOReffl	24/11	25/11	26/11	27/11	28/11	29/11	30/11	1/12	2/12	9
Dordrecht	sludge	01DORslib	24/11	25/11	26/11	27/11			30/11	1/12	2/12	7
Aarle Rixtel	influent	02AARinfl	3/11	4/11	5/11	6/11	7/11	8/11	9/11	10/11	11/11	9
Aarle Rixtel	effluent	02AAReffl	3/11	4/11	5/11	6/11	7/11	8/11	9/11	10/11	11/11	9
Aarle Rixtel	sludge	02AARslib	3/11			6/11			9/11			3
Aarle Rixtel	sieved material	02AARsiev	3/11			6/11			9/11			3
Bath	influent	03BATinlf	10/11	11/11	12/11	13/11	sample lost	15/11	sample lost	17/11	18/11	7
Bath	effluent	03BATeff	10/11	11/11	12/11	13/11	14/11	15/11	16/11	17/11	18/11	9
Bath	sludge	03BATsludg		11/11			14/11		16/11			3
Lelystad	influent	04LELinlf	3/11	4/11	5/11	6/11	7/11	8/11	9/11	10/11	11/11	9
Lelystad	effluent	04LELeffl	3/11	4/11	5/11	6/11	7/11	8/11	9/11	10/11	11/11	9
Lelystad	sludge	04LELsludg	3/11			6/11					11/11	3
Hattem	influent	05HATinfl	7/11	8/11	9/11	10/11	not taken	12/11	13/11	14/11	15/11	
Hattem	effluent	05HATeffl	7/11	8/11	9/11	10/11	not taken	12/11	13/11	14/11	15/11	
Hattem	sludge	05HATsludg				9/11	11/11		13/11			3
Asten	influent	06ASTinfl	3/11	4/11	5/11	6/11	7/11	8/11	9/11	10/11	11/11	9
Asten	effluent	06ASTeffl	3/11	4/11	5/11	6/11	7/11	8/11	9/11	10/11	11/11	9
Asten	sludge	06ASTsludg	28/10	30/10	3/11							3
Hapert	influent	07HAPinfl	5/11	6/11	7/11	8/11	9/11	10/11	11/11	12/11	13/11	9
Hapert	effluent	07HAPeffl	5/11	6/11	7/11	8/11	9/11	10/11	11/11	12/11	13/11	9
Hapert	sludge	07HAPsludg	5/11				9/11		11/11			3
Piershil	influent	08PIEinfl	24/11	25/11	26/11	27/11	28/11	29/11	30/11	1/12	2/12	9
Piershil	effluent	08PIEeffl	24/11	25/11	26/11	27/11	28/11	29/11	30/11	1/12	sample lost	8
Piershil	sludge	08PIEsludg									2/12	1
HVC	special wastewater	09HVCsvi	24/11		26/11						2/12	3
HVC	special wastewater	09HVCara	24/11		26/11						2/12	3
HVC	special wastewater	09HVCdov	24/11	25/11	26/11	27/11	28/11	29/11	30/11	1/12	2/12	9
Chemours	special wastewater	10CHEinfl	24/11	25/11	26/11	27/11	28/11	29/11	30/11	1/12	2/12	9

APPENDIX 4

ANALYSIS PACKAGE AND REPORTING LIMITS

PFAS MEASURED AND ATTAINED REPORTING LIMITS

Substance group name adopted from PFAS guidelines by the PFAS Expertise Centre (Pancras et al., 2018).
Cn = number of carbon atoms in the fluorinated carbon chain.
N.A. = cannot be determined, all measurements were above the limit of detection

Substance name	Cn	VU abbreviation	Aquo code	Substance name in Aquo	CAS nr	Limit of detection water		Limit of detection sludge	
						Given ng/l	Attained ng/l	Given µg/kg DM	Attained µg/kg DM
Perfluoroalkyl carboxylic acids (PFCAs)									
Perfluorobutanoic acid	C4	PFBA	PFBA	perfluorobutanoic acid	375-22-4	1 - 5	1	0.05	0.5*
Perfluoropentanoic acid	C5	PFPeA	PFPA	perfluoropentanoic acid	2706-90-3	0.5 - 2.5	1	0.02	0.02 - 0.04
Perfluorohexanoic acid	C6	PFHxA	PFHxA	perfluorohexanoic acid	307-24-4	0.25 - 1	0.5	0.01	n.a.
Perfluoroheptanoic acid	C7	PFHpA	PFHpA	perfluoroheptanoic acid	375-85-9	0.25 - 1	0.5	0.01	n.a.
Perfluorooctanoic acid, linear	C8	l-PFOA	PFOA	perfluorooctanoic acid	335-67-1	0.5 - 2.5	0.5	0.02	n.a.
Perfluorooctanoic acid, branched	C8	br-PFOA	sverttPFOA	Sum branched PFOA isomers	n.a.	0.5 - 2.5	0.5	0.02	0.02
Perfluorononanoic acid	C9	PFNA	PFNA	perfluorononanoic acid	375-95-1	0.25 - 1	0.5	0.01	n.a.
Perfluorodecanoic acid	C10	PFDA	PFDA	perfluorodecanoic acid	335-76-2	0.25 - 1	0.5	0.01	n.a.
Perfluoroundecanoic acid	C11	PFUnDA	PFUdA	perfluoroundecanoic acid	2058-94-8	0.25 - 1	0.5	0.01	n.a.
Perfluorododecanoic acid	C12	PFDoA	PFDoA	perfluorododecanoic acid	307-55-1	0.25 - 1	0.5	0.01	n.a.
Perfluorotridecanoic acid	C13	PFTrDA	PFTDA	perfluorotridecanoic acid	72629-94-8	0.25 - 1	0.5	0.01	n.a.
Perfluorotradecanoic acid	C14	PFTeDA	PFTeDA	perfluorotradecanoic acid	376-06-7	0.25 - 1	0.5	0.01	n.a.
Perfluorohexadecanoic acid	C16	PFHxDA	PFC16azr	perfluorohexadecanoic acid	67905-19-5	0.25 - 1	0.5 - 1	0.01	0.05
Perfluorooctadecanoic acid	C18	PFODA	PFC18azr	perfluorooctadecanoic acid	16517-11-6	0.5 - 2.5	1	0.05	0.05 - 0.1
Perfluoroalkyl ether carboxylic acids (PFECAs)									
TetraFluoro-2-heptafluoropropoxy) propanoic acid		HFPO-DA	FRD-903	2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propionic acid	13252-13-6	0.1 - 0.5	0.1	0.01	0.01 - 0.03
Dodecafluoro-3H-4,8-dioxanonanoate		DONA	DONA	trifluoro-3-(hexafluoro-3-(trifluoromethoxy)propoxy)propanoic acid	919005-14-4	0.1 - 0.5	0.1	0.01	0.01 - 0.03

Substance name	Cn	VU abbreviation	Aquo code	Substance name in Aquo		Limit of detection water		Limit of detection sludge	
					CAS nr	Given ng/l	Attained ng/l	Given µg/kg DM	Attained µg/kg DM
Perfluoroalkyl sulfonic acids (PFSAs)									
Perfluorobutanesulfonate	C4	PFBS	L_PFBS	perfluorobutanesulfonic acid	375-73-5	0.1 - 0.5	0.5	0.01	0.03
Perfluoropentanesulfonate	C5	PFPeS	PFC5asfzr	perfluoro-1-pentanesulfonic acid	2706-91-4	0.1 - 0.5	0.25	0.01	0.01 - 0.03
Perfluorohexanesulfonate	C6	PFHxS	L_PFHxS	perfluorohexane sulfonic acid	355-46-4	0.1 - 0.5	0.25	0.01	0.01
Perfluoroheptanesulfonate	C7	PFHpS	L_PFHpS	perfluoro-1-heptanesulfonic acid	375-92-8	0.1 - 0.5	0.25	0.01	0.01 - 0.02
Perfluorooctanesulfonate, linear	C8	l-PFOS	PFOS	perfluorooctane sulfonic acid	1763-23-1	0.25 - 1	0.5	0.01	n.a.
Perfluorooctanesulfonate, branched	C8	br-PFOS	sverttPFOS	sum branched PFOS isomers	n.a.	0.25 - 1	0.5	0.01	n.a.
Perfluorodecanesulfonate	C10	PFDS	L_PFDS	perfluoro-1-decanesulfonic acid	335-77-3	0.1 - 0.5	0.5 - 1	0.01	0.01 - 0.02
Fluorotelomere sulfonic acids *(precursors)*									
4:2 Fluorotelomere sulfonic acid		4:2 FTS	H-PFC6asfzr	2-(perfluorobutyl)ethane-1-sulfonic acid (4:2 FTS)	757124-72-4	0.25 - 1	0.5	0.01	0.01 - 0.03
6:2 Fluorotelomere sulfonic acid		6:2 FTS	2PFC6yC2a1sf	2-(perfluorohexyl)ethane-1-sulfonic acid (6:2 FTS)	27619-97-2	0.25 - 1	1	0.01	n.a.
8:2 Fluorotelomere sulfonic acid		8:2 FTS	H-PFC10asfzr	2-(perfluorooctyl)ethane-1-sulfonic acid (8:2 FTS)	39108-34-4	0.25 - 1	0.5	0.01	n.a.
10:2 Fluorotelomere sulfonic acid		10:2 FTS	H-PFC12asfzr	1H,1H,2H,2H-perfluorododecanesulfonic acid (10:2 FTS)	120226-60-0	0.25 - 1	1	0.01	n.a.
Polyfluoroalkyl phosphoric acid diesters *(precursors)*									
8:2 Fluorotelomere phosphate diester		8:2diPAP	bisPFC10yPO4	bisperfluorodecyl hydrogen phosphate (8:2 diPAP)	678-41-1	0.5 - 2.5	1	0.05	0.05
Perfluoroalkane sulfonamides *(precursors)*									
Perfluorooctanesulfonamide-(N-methyl)acetate		N-MeFOSAA	N-MeFOSAA	N-methylperfluorooctane sulfonamidoacetic acid	2355-31-9	0.25 - 1	0.5	0.01	n.a.
Perfluorooctanesulfonylamide(N-ethyl)acetate		N-EtFOSAA	EtFOSAA	perfluorooctanesulfonylamide(N-ethyl)acetic acid	2991-50-6	0.25 - 1	0.5	0.01	n.a.
Perfluorooctanesulfonamide		FOSA	PFOSA	perfluorooctanesulfonamide	754-91-6	0.25 - 1	0.5	0.01	n.a.
Methyl perfluorooctane sulfonamide		MeFOSA	MeFOSA	N-methyl perfluorooctanesulfonamide	31506-32-8	0.25 - 1	1	0.01	0.02 - 0.05
Ethyl perfluorooctane sulfonamide		EtFOSA	EtFOSA	N-ethyl perfluorooctanesulfonamide	4151-50-2	0.25 - 1	1	0.01	0.02 - 0.05
Other PFAS									
9-chlorohexadecafluoro-3-oxanonane-1-sulfonate		9Cl-PF3ONS	9-Cl-PF3ONS	9-chlorohexadecanefluoro-3-oxanone-1-sulfonic acid	756426-58-1	0.25 - 1	1	0.01	0.01 - 0.03
11-chloroeicosafluoro-3-oxaundecane-1-sulfonate		11CL-PF3OUdS	11ClPF3OUdS	11-chloroeicosafluor-3-oxaundecane-1-sulfonic acid	763051-92-9	0.25 - 1	1	0.01	0.01 - 0.03

* *Exception, lowest measurement 0.17 µg/kg DM*

APPENDIX 5

ANALYTICAL METHOD

The water samples were analysed using a method comparable to ISO 21675 (2019), ‘Water Quality: Determination of Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) in Water’.

A solution of 25 isotopically labelled PFAS compounds (internal standard) was added to the sample, after which the pH was brought to approximately 3 using a 10% phosphoric acid solution in water. The non-dissolved components were removed from the sample material by centrifugation.

PFAS compounds were isolated from the sample material by solid-phase extraction (SPE, Oasis Wax type), in which the anions of the ionic compounds interact with the cations in the solid phase. After drying the cartridge under vacuum, the PFAS compounds were eluted from the SPE cartridges using an ammonium hydroxide solution in methanol.

The eluate was then evaporated dry, after which the residue was dissolved in water and methanol.

The sludge samples were analysed using a method equivalent to that of the preliminary Dutch Technical Agreement on PFAS in Soil and Subsoil (390020030002N0015).

After homogenisation of the sample material, the internal standard was added to part of the sample material, after which the sample was lyophilized (freeze dried). PFAS compounds were isolated from the sample material in two steps, using a mixture of acetonitrile, methanol and ammonium hydroxide. After a concentration step of the obtained extract, purification by activated carbon was performed. The eluate was then evaporated dry, and the residue dissolved in water and methanol.

The extracts of both the water samples and the sludge samples were separated by reversed-phase liquid chromatography, after which the target substances were detected and quantified using a mass-selective detector (MSD). In the detector, the compounds were ionised with an electrospray interface operating in negative-ion mode.

APPENDIX 6

DATA PROCESSING

DATASET STATISTICS

	Water samples	Sludge samples
Number of samples provided for analysis	163	29
Number of individual PFAS observations	5,705 (100%)	1,015 (100%)
Number of observations equal to or lower than detection limit (DL)	3,554 (62%)	233 (23%)
Number of observations higher than detection limit (DL) and equal to or lower than the reporting limit (RL)	770 (13%)	64 (6%)
Number of observations higher than the reporting limit (RL)	1,381 (24%)	718 (71%)
Number of observations non-dissolved components	70	
Number of observations N-org	70	
Number of observations N-NH4	70	

The analyses of the industrial wastewater samples from Chemours and HVC are included in the water samples.

EVALUATION FOR IMPROBABLE OUTCOMES

The observations were evaluated for improbable outcomes. These were found for the dry weight content of the sludge from Piershil, Hattem and Asten WWTPs. This led the laboratory to reanalyse the dry weight content of all the sludge samples. The results from Lelystad WWTP were verified by random re-analysis.

OBSERVATIONS UNDER THE DETECTION AND REPORTING LIMITS

Normally a reporting limit (RL) is given (i.e., the lowest concentration that can be reliably quantified). In this study, instead of the reporting limit, the detection limit (DL) is provided (i.e., the lowest concentration detectable, though less reliable for quantification). Amounts between the detection limit and reporting limit are reported as marked values. These were converted into numeric values in the data processing.

To calculate summed parameters and loads, observations smaller than the DL were replaced by a substitution value determined using the Volkert-Bakker method. Thus, the substitution value was calculated by multiplying the percentage of observations higher than the detection limit by the detection limit. In this manner, the substitution value approaches zero if nearly all observations are below the detection limit, and the substitution value approaches the detection limit if nearly all of the observations are above the detection limit. For further details regarding the Volkert-Baker method, see STOWA reports 2015-38 and 2013-W01 (in Dutch).

CALCULATION OF WEIGHTED AVERAGE PFAS CONCENTRATIONS

For each WWTP, weighted average PFAS concentrations were calculated rather than the arithmetic average concentrations. This was done as follows: loads were determined per day and per substance. The average of these was calculated over the nine-day sampling period. The average daily loads were then divided by the average flow volumes on the sampling days.

Using the arithmetic instead of the weighted average would skew the results because lower levels are found on wet weather days, due to dilution with stormwater runoff.

INCOMPLETE INFLUENT AND EFFLUENT MEASUREMENT SERIES

Continuous nine-day measurement series were not obtained for all facilities. In most cases, the missing values were substituted by the arithmetic average of the observations from samples collected on the other days.

In the series for Bath influent, two samples were missing. The first missing sample was substituted with the arithmetic average of the observations from the previous day. The second missing sample concerned wet weather conditions. On that day and the days following, the influent was diluted. Therefore, the arithmetic average concentrations from these days were used to substitute for the missing observation.

The average concentrations were then multiplied by the 24-hour flow volumes to calculate substance loads.

SLUDGE CONTENT

The laboratory reported the results for the sludge samples in both μg/kg and in μg/kg dry matter (DM). The latter reflects the dry matter content (evaporation residue) and is thus in practice the calculation result of two types of analysis. In the calculations, the μg/kg levels were retained for as long as possible, with the contents being converted into μg/kg DM at the end. In the calculations, the dry weight of the sludge samples actually measured during the sampling period was used.

SLUDGE PRODUCTION

For sludge production at Dordrecht, Bath and Aarle Rixtel WWTPs, the actual sludge production figures were used. For Lelystad, Piershil, Asten, Hapert and Hattem WWTPs, the annual production in 2020 was assumed, obtained from the Z-info database. This was done because sludge production exhibited large fluctuations during the sampling period, sometimes deviating substantially from the annual production figures. Highly fluctuating sludge production is common at smaller WWTPs because sludge processing is not a continual operation. Moreover, sludge is not removed every day. Obviously, however, actual sludge growth is a continual process in the water line.

LOAD CALCULATIONS

Average daily loads in influent and effluent were calculated based on weighted average concentrations and average flow volumes on the sampling days.

For the sludge (and sieved material), average PFAS loads were calculated as follows: The arithmetic average was taken of the limited number of PFAS observations, usually three and expressed in μg/kg. These values were applied for all days in the sampling period on which no sample was taken. For sludge production, the actual daily production was taken for Dordrecht, Bath and Aarle Rixtel; and for the other WWTPs, the daily production figures from Z-info were assumed. Daily loads for each PFAS compound were then calculated. These daily loads were averaged over the nine-day period.

SUM PARAMETERS

The water and sludge samples were analysed for 35 PFAS compounds. For further analysis, these 35 individual compounds were categorised into the following five groups:

1. PFAS 35: the sum total of all 35 PFAS compounds
2. PFOA: PFOA and PFOA br
3. PFOS: PFOS and PFOS br
4. PFCA (C4-C7): the sum total of PFBA, PFPeA, PFHxA and PFHpA, all of which are stable PFCAs compounds
5. Stable PFAS: the sum total of PFCAs and PFSAs
6. Precursors: the sum total of 42FTS, 62FTS, 82FTS, 102FTS, 82diPAP, MeFOSAA, N-EtFOSAA, FOSA, N-MeFOSA, EtFOSA, 9ClPF3OUdS, 11ClPF30UdS

OVERVIEWS

Because the daily loads (influent, effluent and sludge) were determined by the procedure described above, overviews could be produced presenting the results per WWTP. In these overviews, ingoing quantities (influent) are compared with outgoing quantities (effluent, sludge and where applicable sieved material). These overviews were graphically depicted in so-called Sankey diagrams.

APPENDIX 7

INFORMATION PROVIDED BY CHEMOURS

TABLE 1 **AVERAGE CONCENTRATION OF HPFO-DA (IN NG/L) IN WASTEWATER FROM CHEMOURS**

Period	Number of analyses	Average concentration HPFO-DA	Average concentration HPFO-DA, calculated according to the Baltussen method
18 Nov. 2018 – 5 July 2021	317	757	754
2018 - 2019	238	912	910
2020	51	395	378
2021 (through 5 July)	28	97	109

Annual flow volumes were 366,957 m3 (2019) and 313,746 m3 (2020). This equates to a load of 334 and 119 g HPFO-DA per year.

APPENDIX 8

LOADS PER POPULATION EQUIVALENT FOR DIFFERENT SUBSTANCES AND SUBSTANCE GROUPS

The table below presents immission and emission factors in influent, effluent and sewage sludge in μg per population equivalent (PE) per day.

The colours indicate differences between the facilities and have no other special significance.

PFAS EMMISSION FACTORS IN MG/PE 150 PER YEAR

		Dordrecht	**Bath**	**Aarle Rixtel**	**Lelystad**	**Piershil**	**Asten**	**Hapert**	**Hattem**
Relative PFAS (35) load		**high**	**high**	**mod**	**mod**	**mod**	**low**	**low**	**low**
PFAS (35)									
immission factor	mg/PE 150/y	52	39	4.6	1.3	6.3	0.54	1.2	0.78
effluent emission factor	mg/PE 150/y	54	41	7.5	5.6	5.4	0.88	1.7	0.92
sludge emission factor	mg/PE 150/y	2.0	1.1	1.5	2.7	0.47	0.62	0.54	0.33
sieved material emission factor	mg/PE 150/y			0.01					
PFOA									
immission factor	mg/PE 150/y	17	0.9	0.8	0.1	1.0	0.08	0.14	0.06
effluent emission factor	mg/PE 150/y	21	1.1	0.9	0.2	1.1	0.16	0.20	0.12
sludge emission factor	mg/PE 150/y	0.5	0.01	0.1	0.02	0.03	0.01	0.01	0.01
sieved material emission factor	mg/PE 150/y			0.0005					
PFOS									
immission factor	mg/PE 150/y	1.8	2.4	0.4	0.4	1.4	0.13	0.11	0.14
effluent emission factor	mg/PE 150/y	1.8	2.6	0.2	1.3	0.70	0.16	0.06	0.07
sludge emission factor	mg/PE 150/y	0.4	0.3	0.2	1.2	0.13	0.30	0.05	0.04
sieved material emission factor	mg/PE 150/y			0.0010					
PFCA (C4-C7)									
immission factor	mg/PE 150/y	9.0	15	1.0	0.3	2.6	0.12	0.27	0.26
effluent emission factor	mg/PE 150/y	7.9	10	2.9	2.0	2.5	0.4	0.80	0.45
sludge emission factor	mg/PE 150/y	0.1	0.0	0.6	0.03	0.02	0.03	0.04	0.01
sieved material emission factor	mg/PE 150/y			0.0029					
precursors (12)									
immission factor	mg/PE 150/y	1.9	16	0.70	0.35	0.11	0.14	0.54	0.19
effluent emission factor	mg/PE 150/y	2.4	21	2.1	1.7	0.11	0.06	0.54	0.22
sludge emission factor	mg/PE 150/y	0.6	0.63	0.32	1.2	0.13	0.15	0.27	0.21
sieved material emission factor	mg/PE 150/y			0.0049					

APPENDIX 9

REMOVAL EFFICIENCIES

The table below presents removal efficiencies calculated based on weighted average concentrations over the entire sampling period (see box for justification). Only substances that were detected are included. Green shading indicates removal of the substance, red indicates negative efficiencies and thus an increase in concentration of the substance in the effluent. The darker the colour, the higher (green) or lower (red) the efficiency.

			Dordrecht	**Bath**	**Aarle Rixtel**	**Lelystad**	**Piershil**	**Asten**	**Hapert**	**Hattem**
		Relative PFAS load>	**high**	**high**	**moderate**	**moderate**	**moderate**	**low**	**low**	**low**
Perfluoroalkyl carboxylic acids (PFCAs)	C4	PFBA	-0.2%	78%	-151%	-215%	-20%	4%	-93%	-69%
	C5	PFPeA	-20%	-117%	-304%	-793%	-68%	-253%	-649%	-45%
	C6	PFHxA	38%	-70%	-121%	-319%	37%	-34%	-104%	-121%
	C7	PFHpA	-39%	-40%	-131%	-1,696%	11%	-207%	-190%	
	C8	PFOA	-20%	-22%	-7%	-259%	-6%	-25%	-43%	-134%
	C8	PFOA br	-118%	-76%	-34%		-61%			
	C9	PFNA	-57%	-41%	-57%		-18%	-251%		
	C10	PFDA	-162%	-40%	8%	-602%	4%	-11%	-32%	100%
Perfluoroalkyl ether carboxylic acids (PFECAs)		HFPO-DA	10%	-14%	18%		6%	100%		100%
Perfluoroalkyl sulfonic acids (PFSAs)	C4	PFBS	1%	-26%	4%	-114%	15%	-92%	12%	19%
	C5	PFPeS	-15%	-32%			-3%			
	C6	PFHxS	-5%	-32%	37%	11%	24%	100%	84%	100%
	C7	PFHpS	-60%	-35%						
	C8	PFOS	-24%	-21%	21%	-357%	8%	-46%	-138%	-47%
	C8	PFOS br	14%	5%	56%	-92%	62%	44%	70%	67%
Fluorotelomer sulfonic acids (FTS) (precursors)		62FTS	-42%	-37%	-233%	-451%	-64%	31%	2%	21%
		82FTS	-148%	-35%	-28%	-178%	100%	60%	-1%	-335%
Perfluoroalkane sulfonamides s (precursors)		MeFOSAA	31%							
		N-EtFOSAA	52%	33%	100%	100%		100%		
		FOSA	100%	-74%						
PFAS (n=35)			-5%	-4%	-64%	-342%	15%	-6%	-41%	-33%

CALCULATION OF REMOVAL EFFICIENCIES OF TARGET SUBSTANCES, AND SIGNIFICANCE FOR STUDY OF PFAS AT WWTPS

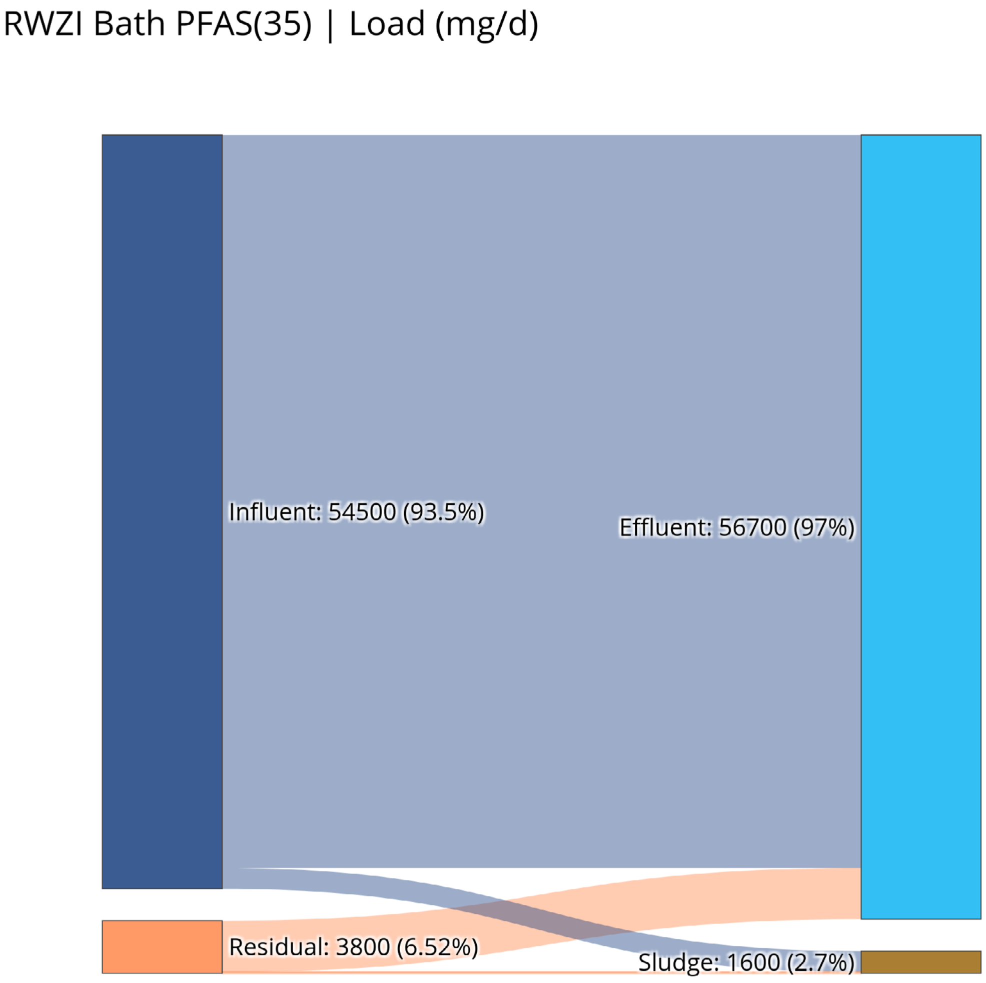
Advanced treatment facilities are being installed at various WWTPs as part of a strategy to address the problem of medicine residues in water. All actors and agencies working on human medicines, from production to disposal – referred to as 'the chain' – play a role in this approach. Via a government programme to incentivise better removal of medicine residues, the Dutch Ministry of Infrastructure and Water Management is providing financial support for demo installations for advanced wastewater treatment. Accompanying such financial support is an obligation to monitor defined target substances (mainly medicines) and effects. A discussion has arisen regarding what methodology is most suitable for reliably calculating removal efficiencies for both the defined target substances and for micropollutants in general (STOWA, 2020). With the usual procedure of simultaneously collected 24-hour samples, extremely variable and often negative efficiencies have been found. Such outcomes can be somewhat reduced – though not entirely eliminated – using the prescribed procedure of 48-hour composite samples and taking into consideration retention time in the treatment plant (Nieuwenhuis & Van den Berg, 2021). Extensive research (Schuman et al., 2021) has demonstrated that variations in removal efficiencies can be explained, at least in part, by the degree of mixing in the active sludge tank, wet weather periods and fluctuations in influent concentrations. The effect of fluctuations in influent concentrations continues to be observed for several days in the effluent, which modulates extremes. This effect can be largely accounted for by calculating removal efficiencies based on average weighted concentrations over a longer measurement period, such as a week.

APPENDIX 10

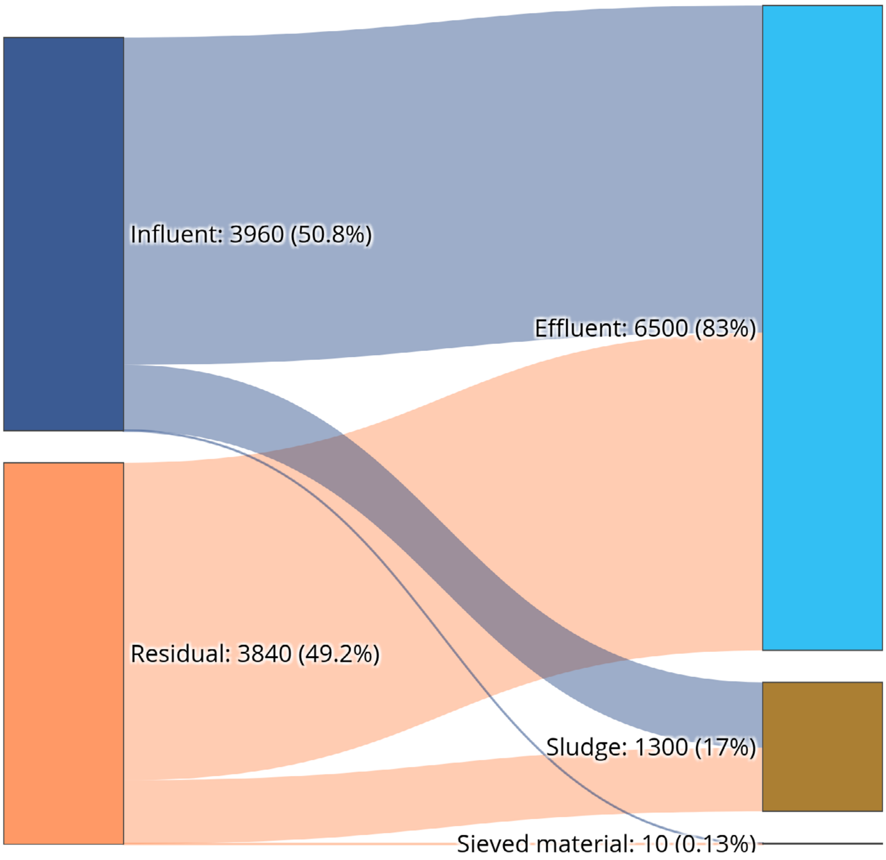
GRAPHICAL PRESENTATION OF LOADS IN INFLUENT, EFFLUENT AND SLUDGE (SANKEY DIAGRAMS)

This appendix provides a more detailed look at loads in incoming and outgoing streams using Sankey diagrams. Sankey diagrams present the origin and destination of PFAS loads as incoming (left) and outgoing (right) flows. A difference between the total incoming and outgoing flow is presented as a residual.

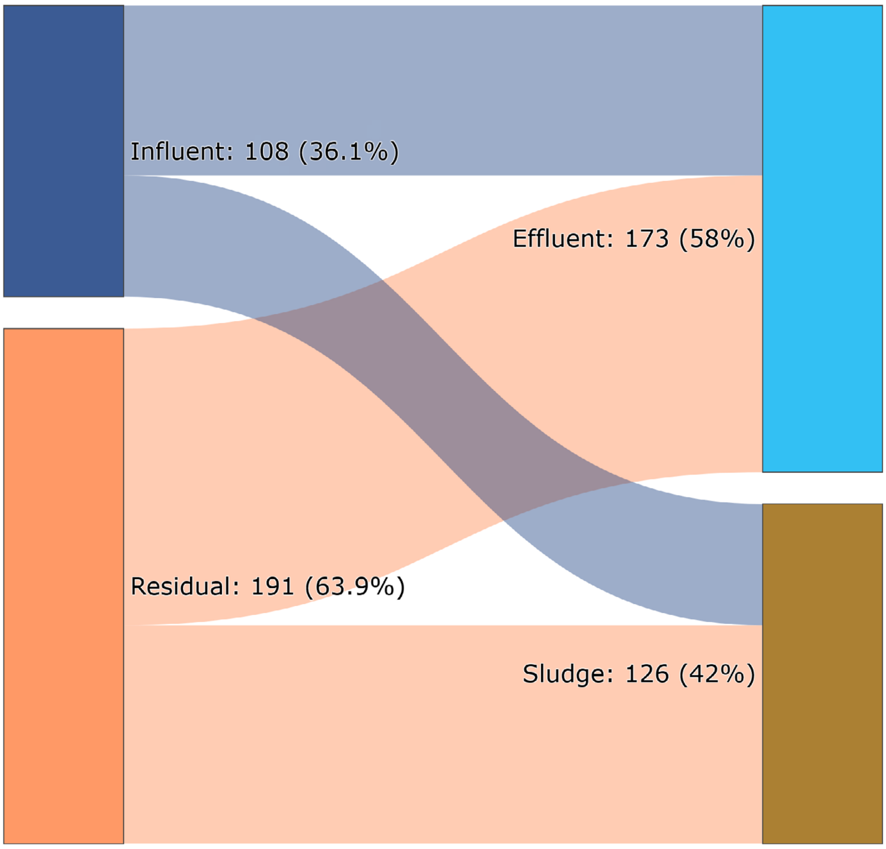
The Sankey diagrams for Bath, Aarle Rixtel, Asten, Hapert and Hattem WWTPs are found in this appendix. The Sankey diagrams for Dordrecht, Lelystad and Piershil WWTPs are found in chapter 7.



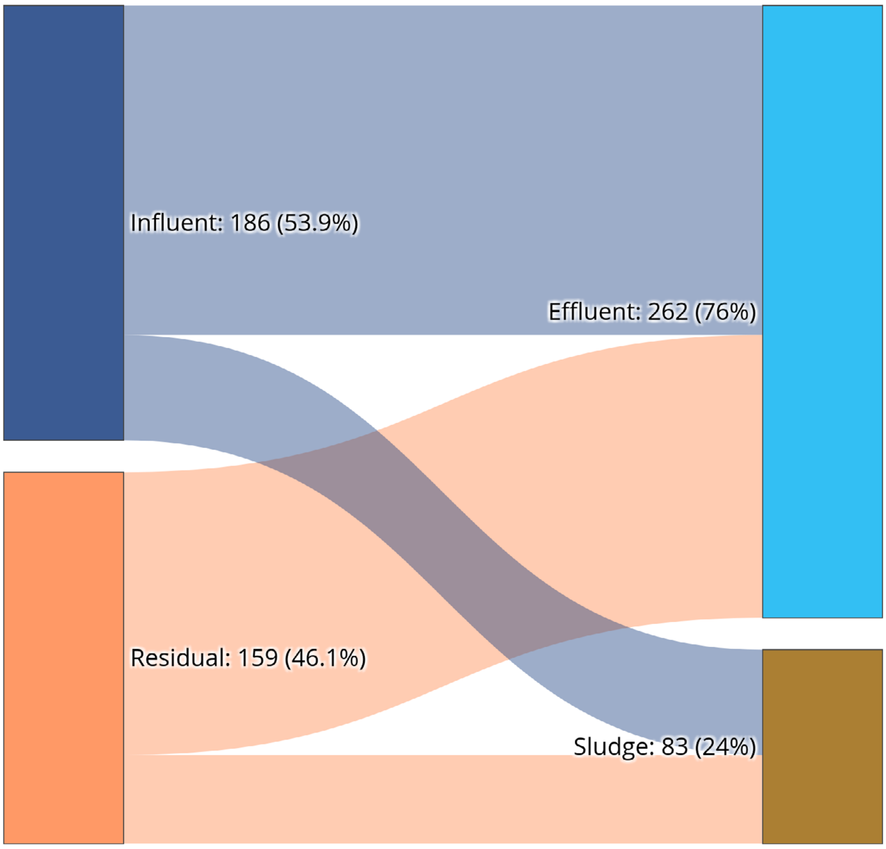
RWZI Aarle-Rixtel PFAS(35) | Load (mg/d)



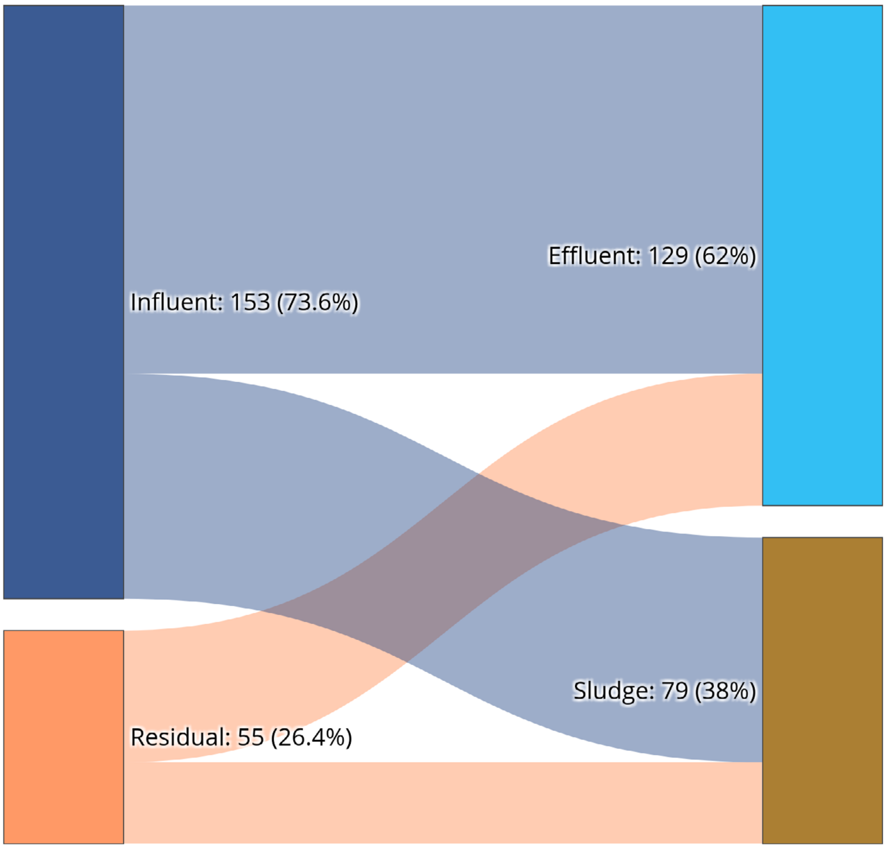
RWZI Asten PFAS(35) | Load (mg/d)



RWZI Hapert PFAS(35) | Load (mg/d)



RWZI Hattem PFAS(35) | Load (mg/d)



APPENDIX 11

COMPARISON OF MEASURED CONCENTRATIONS WITH QUALITY STANDARDS

One way to better understand the concentrations measured in the current study is by comparing the PFAS concentrations found with existing quality standards. However, the Netherlands has no quality standard for PFAS in wastewater and sewage sludge. Standards do exist for PFAS in surface and drinking water (and drinking water resources). However, these limits are not intended to apply to wastewater. For lack of better, these standards are nonetheless referred to here, to provide some perspective on the found concentrations and offer an indication of their significance.

TABLE 1 COMPARISON OF CONCENTRATIONS IN INFLUENT, EFFLUENT AND SPECIAL WASTEWATER STREAMS (NG/L) WITH QUALITY STANDARDS APPLYING TO SURFACE WATER (PFOA, HFPO-DA AND PFOS) OR WATER INTENDED FOR HUMAN CONSUMPTION (SUM PFAS AND TOTAL PFAS). CONCENTRATIONS THAT EXCEED THE STANDARD ARE SHADED. THE 'SUM PFAS' STANDARD PERTAINS TO THE SUM OF 20 SUBSTANCES, NAMELY, C4–C13 PFCAS (INCLUDING PFOA) AND C4–C13 PFSAS (INCLUDING PFOS). THE 'TOTAL PFAS' STANDARD PERTAINS TO THE SUM OF ALL PER- AND POLYFLUOROALKYL SUBSTANCES. SW = SURFACE WATER; DW = DRINKING WATER. PFOA AND PFOS CONCERN THE SUM OF THE LINEAR AND BRANCHED FORM. AT CHEMOURS DIFFERENT PERIODS WERE DISTINGUISHED: THE ENTIRE MEASUREMENT PERIOD (CHEAVG), A PERIOD WITH LOW CONCENTRATIONS (CHELOW) AND A PERIOD WITH HIGH CONCENTRATIONS (CHEHIGH)

Substance(s)	Standard (ng/l)	Matrix	DOR	DOR	BAT	BAT	AAR	AAR	LEL	LEL	PIE	PIE	AST	AST	HAP	HAP	HAT	HAT	HVCara		HVCsvi	CHEavg	CHElow	CHEhigh
			inf	eff	inf	eff	inf	eff	inf	eff	inf	eff	inf	eff	inf	eff	inf	eff						
		Relative PFAS (35) load	high	high	high	high	mod	mod	mod	mod	mod	mod	low	low	low	low	low	low						
PFOA	48	SW	228	273	12	15	13	14	1.6	5.9	12.6	11.9	3.1	3.9	3.2	4.5	0.9	2.3	0.8	5,761	1.4	0.8	0.7	0.9
HFPO-DA	118	SW	194	179	2.4	2.9	16	15	0.0	0.0	0.9	0.9	0.1	0.0	0.0	0.0	0.1	0.0	2.1	1,400	0.2	3,448	10	5,167
PFOS	0.65	SW	24	23	33	34	6.0	3.2	10	30	7.9	16	3.0	2.7	2.6	1.3	2.6	1.3	0.0	21	0.0	0.0	0.0	0.0
Sum PFAS	100	SW/DW	457	477	368	263	43	73	22	94	61	72	13	17	15	26	10	13	25	6,163	8.2	6.1	2.0	8.2
Total PFAS	500	SW/DW	676	687	617	555	70	120	31	134	64	75	16	18	27	38	13	17	27	7,599	80	3,456	13	5,177

APPENDIX 12

RELATIVE POTENCY FACTORS

RELATIVE POTENCY FACTORS (RPF)

The table below presents relative potency factors (RPF) for PFAS, i.e., the harmfulness expressed in relation to the harmfulness of PFOA.

Cn = number of carbon atoms in the fluorinated carbon chain

Values in bold were derived based on liver toxicity in male rats after semi-chronic exposure.

Values in italic were derived by read across (i.e., on the basis of comparisons with substances for which the RPF is known); therefore upper and lower confidence boundaries are provided. As a precaution, for these substances the upper boundary (worst case) was taken for the calculations. Note: Telomere alcohols were not analysed in the current study, but they are listed in the table for the sake of completeness. Source: Bil et al. (2021).

Substance name	Cn	VU abbreviation	CAS nr	Relative potency factor (RPF)	
				low	high
Perfluoroalkyl carboxylic acids (PFCAs)					
Perfluorobutanoic acid	C4	PFBA	375-22-4	0.05	0.05
Perfluoropentanoic acid	C5	PFPeA	2706-90-3	0.01	0.05
Perfluorohexanoic acid	C6	PFHxA	307-24-4	0.01	0.01
Perfluoroheptanoic acid	C7	PFHpA	375-85-9	0.01	1
Perfluorooctanoic acid, linear	C8	l-PFOA	335-67-1	1	1
Perfluorooctanoic acid, branched	C8	br-PFOA	n.a.	1	1
Perfluorononanoic acid	C9	PFNA	375-95-1	10	10
Perfluorodecanoic acid	C10	PFDA	335-76-2	4	10
Perfluoroundecanoic acid	C11	PFUnDA	2058-94-8	4	4
Perfluorododecanoic acid	C12	PFDoA	307-55-1	3	3
Perfluorotridecanoic acid	C13	PFTrDA	72629-94-8	0.3	3
Perfluorotradecanoic acid	C14	PFTeDA	376-06-7	0.3	0.3
Perfluorohexadecanoic acid	C16	PFHxDA	67905-19-5	0.02	0.02
Perfluorooctadecanoic acid	C18	PFODA	16517-11-6	0.02	0.02
Perfluoroalkyl sulfonic acids (PFSAs)					
Perfluorobutanesulfonate	C4	PFBS	375-73-5	0.001	0.001
Perfluoropentanesulfonate	C5	PFPeS	2706-91-4	0.001	0.6
Perfluorohexanesulfonate	C6	PFHxS	355-46-4	0.6	0.6
Perfluoroheptanesulfonate	C7	PFHpS	375-92-8	0.6	2
Perfluorooctanesulfonate, linear	C8	l-PFOS	1763-23-1	2	2
Perfluorooctanesulfonate, branched	C8	br-PFOS	n.a.	2	2
Perfluorodecanesulfonate	C10	PFDS	335-77-3	2	2
Perfluoroalkyl ether carboxylic acids (PFECAs)					
2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propionic acid		HFPO-DA	13252-13-6	0.06	0.06
Ammonium dodecafluoro-3H-4,8-dioxanonanoate		ADONA	958445-44-8	0.03	0.03
Telomere alcohols					
1H,1H,2H,2H-perfluorooctanol		6:2FTOH	647-42-7	0.02	0.02
1H,1H,2H,2H-perfluorodecanol		8:2FTOH	678-39-7	0.04	0.04

APPENDIX 13

CONCENTRATIONS IN PFOA EQUIVALENTS

FIGURE 1 **CONCENTRATIONS IN WASTEWATER, EXPRESSED IN NG PFOA EQUIVALENTS PER LITER FOR THE DIFFERENT SAMPLING DAYS (D1 – D9). FOR SUBSTANCES FOR WHICH THE RPF WAS DERIVED BASED ON READ ACROSS, CALCULATIONS WERE DONE USING UPPER CONFIDENCE BOUNDARIES (I.E., WORST CASE)**

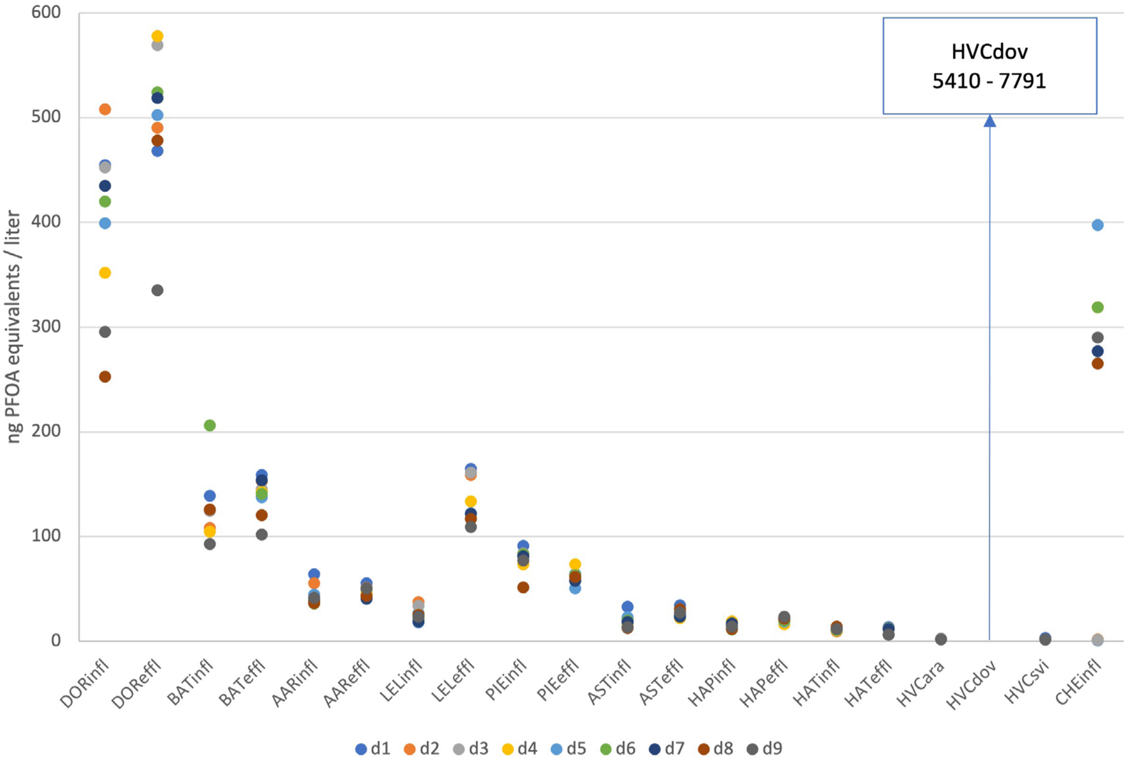


FIGURE 2 RELATIVE CONTRIBUTION TO CONCENTRATION IN INFLUENT AND EFFLUENT, EXPRESSED IN PFOA EQUIVALENTS (ALL SUBSTANCES)

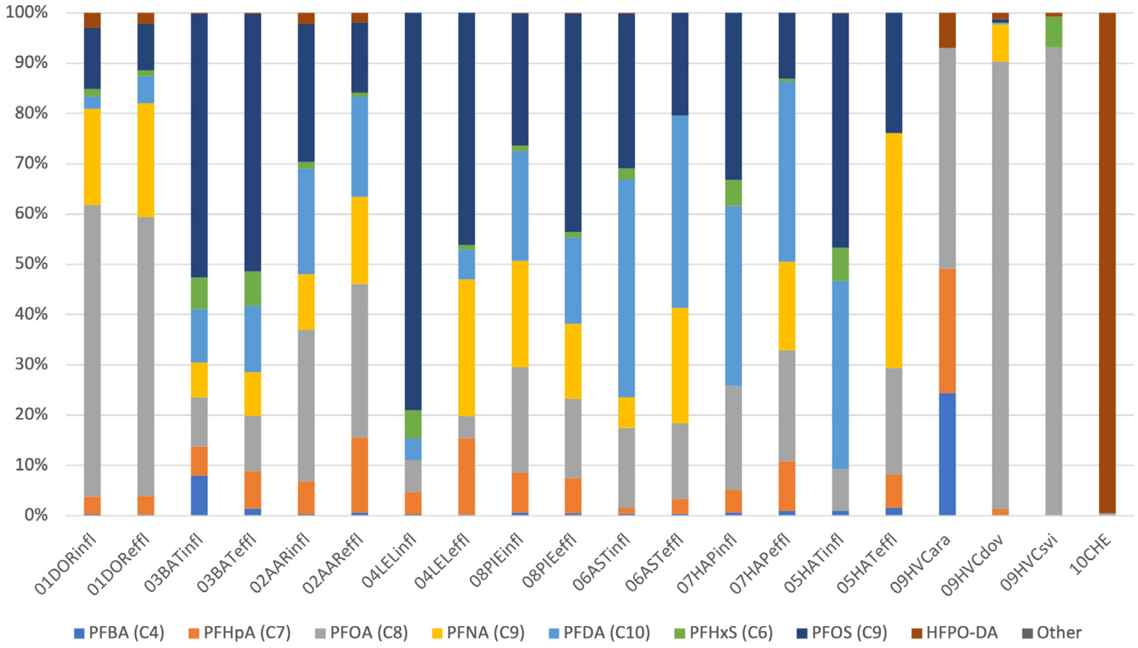
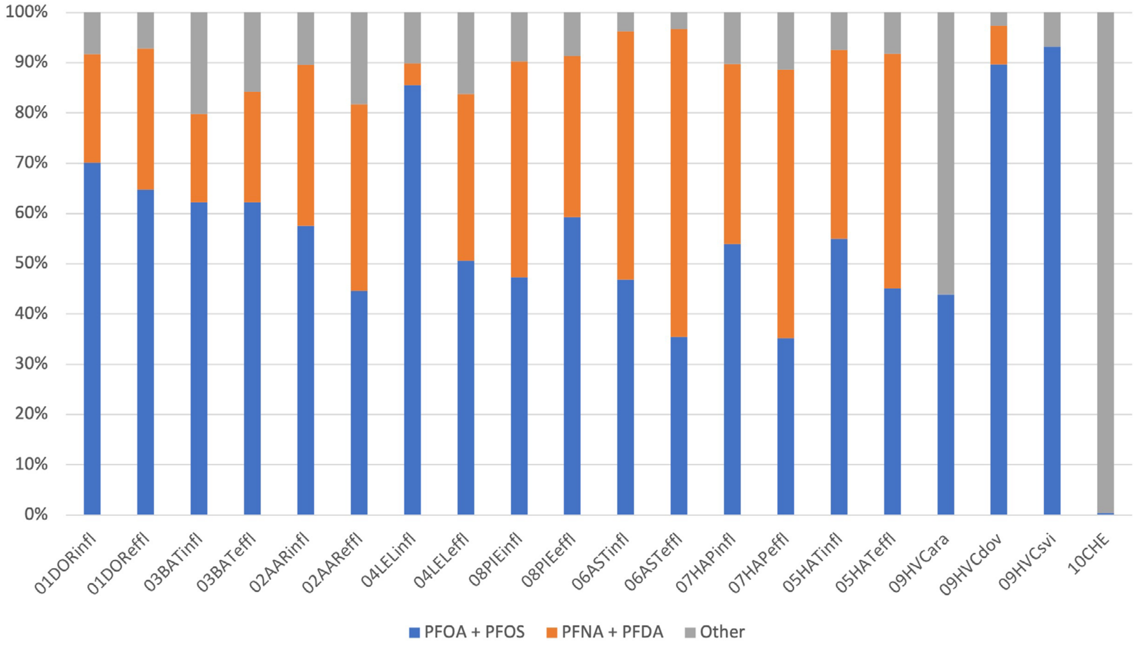


FIGURE 3 RELATIVE CONTRIBUTION TO CONCENTRATION IN INFLUENT AND EFFLUENT, EXPRESSED IN PFOA EQUIVALENTS (FOUR SUBSTANCES WITH THE LARGEST SHARE)



APPENDIX 14

INDICATIVE PFAS LOADS IN SLUDGE AS CALCULATED BY SLUDGE PROCESSORS

Three sludge processing companies – SNB, GMB and HVC – provided data on PFAS concentrations and loads in the sludge they process. The data all related to mixed sludge from multiple WWTPs. The origin of the sludge varied from relatively rural WWTPs (GMB) to the high PFAS-load WWTP in Dordrecht (HVC). These loads cannot be compared one-to-one, as they were derived based on different analytical packages. Therefore, they can be interpreted only as indicative. Calculations were done using a national sludge production of

1,418,000 ton DM per year (reference year 2017). Quantities below the reporting limit were set to zero.

SNB

The sludge processed by SNB contained an average of 7.4 kg PFAS per year (for the lowest value, the reporting limit was set to zero; for the highest value, calculations were done using the reporting limit). Yearly some 435,000 tons of sludge cake were processed. Translating these amounts to the Netherlands as a whole, the yearly PFAS load would be 24 kg.

GMB

GMB processes sewage sludge into biogranulate. In 2020, it processed 203,000 tons of sludge from WWTPs. Of that, approx. 65,000 tons of biogranulate was produced. In the biogranulate, an average amount of 37 µg PFAS/kg DM was measured. This equates to a load of 2.4 kg PFAS per year. Translating these amounts to the Netherlands as a whole, the yearly PFAS load would be 17 kg.

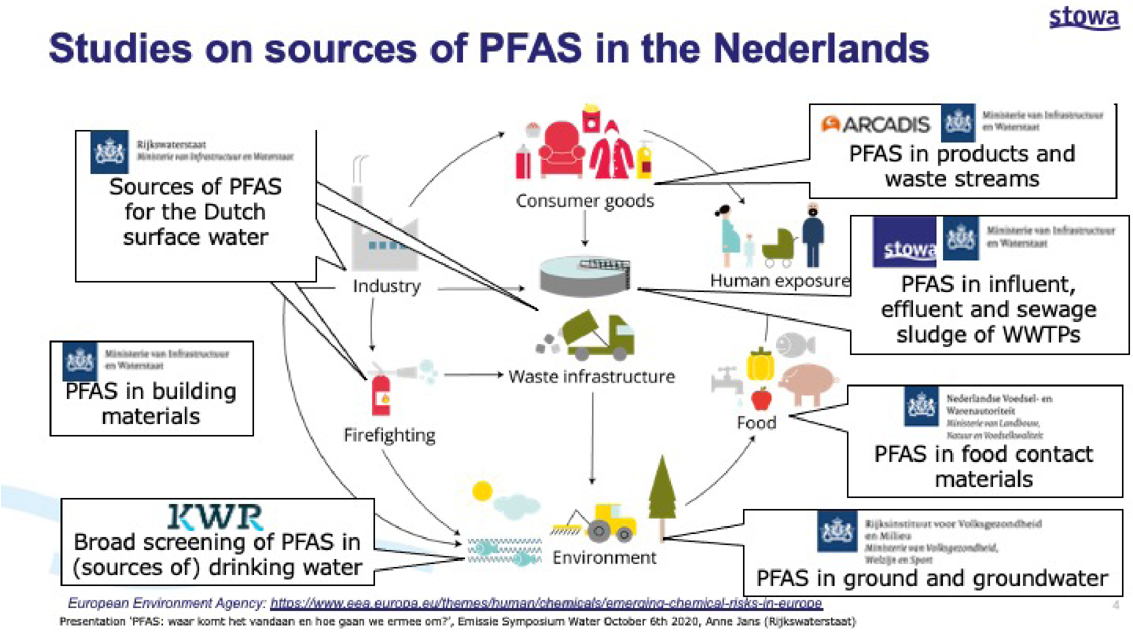
HVC

HVC processes some 80,000 tons of sludge on a yearly basis: 40,000 tons in sludge lines 1, 2 and 3 and about 40,000 tons in sludge line 4. Appendix 15 presents measurement data on HVC-processed sewage sludge. The package of measured substances is broader than in the current study. The calculations below include only the PFAS that were also measured in the current study. Sludge lines 3 and 4 were sampled twice, sludge lines 1 and 2 were sampled once. For line 4, the average amount (over two measurements) was 36 µg PFAS/kg DM, equivalent to a load of 1.44 kg per year. For lines 1, 2 and 3, the quantities found in sludge stream 3 were first averaged, after which an average for sludge streams 1, 2 and 3 was calculated. This average was 41 µg PFAS/kg DM, which equates to 1.64 kg per year. The total load in the sludge processed by HVC was 3.08 kg PFAS per year. Translating these amounts to the Netherlands as a whole, the yearly PFAS load would be 54 kg.

APPENDIX 15

STUDIES ON SOURCES OF PFAS IN THE NETHERLANDS

Various studies of sources of PFAS in the Netherlands have been carried out or are currently being conducted, of which the current study on PFAS at WWTPs is one. The figure below presents an overview of these studies.



Studies on sources of PFAS in the Nederlands

Sources of PFAS for the Dutch surface water

PFAS in products and waste streams

PFAS in influent, effluent and sewage sludge of WWTPs

PFAS in building materials

PFAS in food contact materials

Broad screening of PFAS in (sources of) drinking water

PFAS in ground and groundwater

European Environment Agency: https://www.eea.europa.eu/themes/human/chemicals/emerging-chemical-risks-in-europe

Presentation 'PFAS: waar komt het vandaan en hoe gaan we ermee om?', Emissie Symposium Water October 6th 2020, Anne Jans (Rijkswaterstaat)

The results of the study on sources of PFAS in surface waters in the Netherlands were published in Jans & Berbee (2020), and findings on PFAS in products and waste streams are available in Pancras et al. (2021). The study on PFAS in food contact materials is largely complete (BuRO, 2020), but follow-up work is still underway. The study on PFAS in soil and groundwater, the broad screening for PFAS in drinking water (and drinking water resources), and the study on PFAS in building materials have not yet been completed.

APPENDIX 16

FINDINGS FROM ANALYSES OF HVC SEWAGE SLUDGE

The table below presents results of the sludge analyses performed by HVC in 2020 and during the monitoring campaign 'PFAS in Influent, Effluent and Sewage Sludge at WWTPs' (2020 measurements). Concentrations are given in μg/kg DM.

The analyses concern a mixture of sludge from all WWTPs in the Dutch province of South Holland. Line 4 is primarily incinerated sludge from very large WWTPs with sludge digestion, such as Dokhaven, Harnaschpolder and Houtrust. Sludge in lines 1, 2 and 3, which are fed from the same bunker, derive mainly from oxidation ditches (from smaller WWTPs) and Dordrecht WWTP.

TABLE 3 **SUMMARY OF FOUND CONCENTRATIONS IN THE DIFFERENT INCOMING LINES OF SEWAGE SLUDGE AT HVC**

Substance group name adopted from PFAS guidelines by the PFAS Expertise Centre (Pancras et al., 2018).
Cn = number of carbon atoms in the fluorinated carbon chain. The analysis package is more extensive than in the “PFAS at WWTPs” monitoring campaign. The extra measured substances are listed separately at the bottom of the table.

Colour coding for sludge

Limit of detection (DL)
Limit of quantification (reporting limit, RL)
<1 µg/kg DM
1-10 µg/kg DM
10-100 µg/kg DM

Substance name	Cn	Abbreviation	Sampled line	line 4	line 3	line 3	line 2	line 1	line 4
			start date	23 Sep. ’19 10 hrs	23 Sep. ’19 10 hrs	3 Nov. ’20 10 hrs	4 Nov. ’20 hrs	5 Nov. ’20 10 hrs	9 Nov. ’20 10 hrs
			end date	24 Sep. ’19 08 hrs	24 Sept. ’19 08 hrs	4 Nov. ’20 08 hrs	5 Nov. ’20 08 hrs	6 Nov. ’20 08 hrs	10 Nov. ’20 08 hrs
Perfluoroalkyl carboxylic acids *(PFCAs)*									
Perfluorobutanoic acid	C4	PFBA	µg/kg DM	<0.1	<0.2	<0.3	<0.3	<0.3	<0.3
Perfluoropentanoic acid	C5	PFPeA	µg/kg DM	<0.1	<2	<0.3	<0.3	<0.3	<0.3
Perfluorohexanoic acid	C6	PFHxA	µg/kg DM	0.2	0.6	0.4	0.3	0.4	0.7
Perfluoroheptanoic acid	C7	PFHpA	µg/kg DM	<0.1	<0.4	<0.3	<0.3	<0.3	<0.3
Perfluorooctanoic acid, linear	C8	PFOA	µg/kg DM	0.4	2.9	2.4	2.2	2.8	2.5
Perfluorooctanoic acid, branched	C8	PFOA br	µg/kg DM	<0.1	<0.2	<0.3	<0.3	<0.3	<0.3
Perfluorononanoic acid	C9	PFNA	µg/kg DM	0.1	1.0	0.7	0.6	0.8	0.9
Perfluorodecanoic acid	C10	PFDA	µg/kg DM	0.9	4.5	2.7	2.0	2.7	2.8
Perfluoroundecanoic acid	C11	PFUnDA	µg/kg DM	0.3	1.8	1.1	1.1	1.3	1.7
Perfluorododecanoic acid	C12	PFDoDA	µg/kg DM	0.6	2.9	2.4	2.1	3	3.7
Perfluorotridecanoic acid	C13	PFTrDA	µg/kg DM	<0.1	<0.4	<0.3	<0.3	0.4	<0.3
Perfluorotradecanoic acid	C14	PFTeDA	µg/kg DM	0.2	<0.9	0.7	0.6	0.7	0.9
Perfluorohexadecanoic acid	C16	PFHxDA	µg/kg DM	<0.1	<0.5	<0.3	<0.3	<0.3	<0.3
Perfluorooctadecanoic acid	C18	PFODA	µg/kg DM	<0.1	<0.2	<0.3	<0.3	<0.3	<0.3
Perfluoroether carboxylic acids *(PFECAs)*									
TetraFluoro-2-heptafluoropropoxy) propanoic acid		HFPO-DA	µg/kg DM	<0.1	0.2	<0.3	<0.3	<0.3	<0.3
Dodecafluoro-3H-4,8-dioxanonanoate		DONA	µg/kg DM	<0.1	<0.2	<0.3	<0.3	<0.3	<0.3
Perfluoroalkyl sulfonic acids *(PFSAs)*									
Perfluorobutanesulfonate	C4	PFBS	µg/kg DM	<0.1	<0.2	<0.3	<0.3	<0.3	<0.3
Perfluoropentanesulfonate	C5	PFPeS	µg/kg DM	<0.1	<0.2	<0.3	<0.3	<0.3	<0.3

Substance name	**Cn**	**Abbreviation**	**Sampled line**	**line 4**	**line 3**	**line 3**	**line 2**	**line 1**	**line 4**
			start date	**23 Sep. '19 10 hrs**	**23 Sep. '19 10 hrs**	**3 Nov. '20 10 hrs**	**4 Nov. '20 hrs**	**5 Nov. '20 10 hrs**	**9 Nov. '20 10 hrs**
			end date	**24 Sep. '19 08 hrs**	**24 Sept. '19 08 hrs**	**4 Nov. '20 08 hrs**	**5 Nov. '20 08 hrs**	**6 Nov. '20 08 hrs**	**10 Nov. '20 08 hrs**
Perfluorohexanesulfonate	C6	PFHxS	µg/kg DM	<0.1	0.3	<0.3	<0.3	<0.3	<0.3
Perfluoroheptanesulfonate	C7	PFHpS	µg/kg DM	<0.1	<0.2	<0.3	<0.3	<0.3	<0.3
Perfluorooctanesulfonate, linear	C8	PFOS	µg/kg DM	2.7	13	14	12	15	25
Perfluorooctanesulfonate, branched	C8	PFOS br	µg/kg DM	0.3	1.5	1.7	1.2	2.2	3.6
Perfluorodecanesulfonate	C10	PFDS	µg/kg DM	<0.1	<0.2	<0.3	<0.3	<0.3	<0.3
Fluorotelomere sulfonic acids *(precursors)*									
4:2 Fluorotelomere sulfonic acid		42FTS	µg/kg DM	<0.1	<0.2	<0.3	<0.3	<0.3	<0.3
6:2 Fluorotelomere sulfonic acid		62FTS	µg/kg DM	1.2	4.3	0.7	0.4	0.7	2.0
8:2 Fluorotelomere sulfonic acid		82FTS	µg/kg DM	1.6	9.4	2.3	1.3	1.9	2.4
10:2 Fluorotelomere sulfonic acid		102FTS	µg/kg DM	1.6	3.1	3.5	2.4	3.7	3.8
Polyfluoroalkyl phosphoric acid diesters *(precursors)*									
8:2 Fluorotelomere phosphate diester		82diPAP	µg/kg DM	0.5	<2.5	0.5	0.4	0.6	0.6
Perfluoroalkane sulfonamides *(precursors)*									
Perfluorooctanesulfonamide-(N-methyl)acetate		MeFOSAA	µg/kg DM	<0.1	<0.2	2.5	2.1	2.7	2.6
Perfluorooctanesulfonylamide(N-ethyl)acetate		N-EtFOSAA	µg/kg DM	2.0	5.5	3.8	2.8	3.9	3.8
Perfluorooctanesulfonamide		FOSA	µg/kg DM	<0.1	<0.6	0.8	0.6	0.9	0.7
Methyl perfluorooctane sulfonamide		N-MeFOSA	µg/kg DM	1.8	5.3	<0.3	<0.3	<0.3	<0.3
Ethyl perfluorooctane sulfonamide		EtFOSA	µg/kg DM	<0.1	<0.2	<0.3	<0.3	<0.3	<0.3
Other PFAS									
9-chlorohexadecafluoro-3-oxanonane-1-sulfonate		9ClPF3OUdS	µg/kg DM	<0.1	<0.2	<0.3	<0.3	<0.3	<0.3
11-chloroeicosafluoro-3-oxaundecane-1-sulfonate		11ClPF3OUdS		-	-	-	-	-	-
Substance name		Analytico abbrev.							
8:2 fluorotelomer unsaturated carboxylic acid		-	µg/kg DM	<0.4	<0.8	<0.3	<0.3	<0.3	<0.3
Perfluorobutanesulfonamide		PFBSA	µg/kg DM	<0.1	1.0	0.5	0.4	0.4	0.3
N- methyl perfluorobutane sulfonamide		MeFBSA	µg/kg DM	<0.4	<0.8	<1.2	<1.2	<1.2	<1.2
Perfluorobutanesulfonylamide(N-methyl) acetic acid		MeFBSAA	µg/kg DM	0.7	0.8	2.3	1.3	1.6	2.3
7H-perfluoroheptanoic acid		HPFHpA	µg/kg DM	<0.4	<0.8	<1.2	<1.2	<1.2	<1.2
2H,2H,3H,3H-perfluoroundecanoic acid		H4PFUnA	µg/kg DM	0.4	1.3	<1.2	1.4	<1.2	<1.2
perfluoro-3,7-dimethyloctanoic acid		PF-3,7-DMOA	µg/kg DM	<1.0	<2.0	<3.0	<3.0	<3.0	<3.0
sum linear and branched perfluorooctanoic acid		-	µg/kg DM	0.5	<3.0	2.4	2.2	2.8	2.5