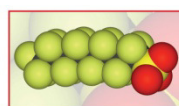


Determining the environmental presence of PFOS and assessing its threats to the environment and human health

Identifying locations of particular concern



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Contents

Summary	5
Chapter 1 Introduction.....	7
1.1 Introduction to PFOS	7
1.2 Current state of research	8
Chapter 2 Methodology	11
Chapter 3 Review of environmental presence of PFOS and its risk assessment	13
3.1 Surface water	13
3.2 Biota	17
3.3 Soil	20
Chapter 4 Case study groundwater Drenthe.....	23
4.1 Introduction.....	23
4.2 Spatial properties	23
4.3 Selected monitoring wells	24
4.4 Results	27
Chapter 5 Discussion	31
5.1 Introduction.....	31
5.2 Tolerable Daily Intake (TDI)	31
5.3 Related fluorinated chemicals.....	35
5.4 Contribution of drinking water.....	37
5.5 Contribution of fish consumption	37
5.6 Actual daily intake	38
5.7 Potential sources	38
Chapter 6 Conclusion	41
Acknowledgements	43
Literature.....	45

Summary

This thesis addresses the research question: to what extent is perfluorooctanesulfonic acid (PFOS) present throughout the environment and what are the threats to the environment and human health? PFOS was labeled as a persistent organic pollutant in the Stockholm Convention on Persistent Organic Pollutants in 2009 because of its persistent, bioaccumulative and toxic properties. It might have negative consequences on the environment and human health when it is present in substantial concentrations. PFOS has frequently been considered to be ubiquitous, although this statement was not always supported by any of the observed concentrations. The research question of this thesis was posed to address this point of concern. It was pursued by a literature review in which studies were reviewed on data concerning PFOS concentrations in the Netherlands.

This study also includes an experimental part: eighteen groundwater samples were taken in the proximity of potential PFOS sources and analysed for their concentrations of PFOS and perfluorooctanoic acid (PFOA), a perfluorinated chemical that is related to PFOS. A spatial analysis was performed in order to make a well-informed decision on what monitoring wells to select. This survey was executed as a case study to confirm or deny the presence of PFOS in the groundwater in Drenthe.

The threats to the environment and human health were then, in case of confirmation of the presence of PFOS in the environment in the Netherlands, identified by comparing the concentrations with environmental quality standards (EQSs). Based on the literature review and the experimental study, it was concluded that PFOS is present in all considered environmental media in the Netherlands, which are ground and surface water, biota and soil. PFOS may be present in ground and surface water with concentrations in the order of 10 ng/l. Concentrations in biota, mainly fish, were reported in the range from the order of magnitude of 1 ng/kg to over 1000 ng/kg. Concentrations in soils are present in a large range from the order of magnitude of 1 ng/kg to concentrations of over 10000 ng/kg. The EQS for surface water for fish consumption, which is 0.65 ng/l, was thereby consequently exceeded. The EQS for freshwater that is intended for the production of drinking water, which is 0.53 µg/l, was on the other hand not reached by any of the observed water concentrations.

However, the comparison between observed concentrations and EQSs is insufficient to convincingly assess threats to the environment and human health. The adequacy of the EQSs is challenged by various assumptions and uncertainties. Adjustments should arguably be made with respect to the considered Tolerable Daily Intake (TDI), the possible impact of related fluorinated chemicals, the contribution of drinking water, the contribution of fish consumption and the actual intake of PFOS. Adjusting the EQSs with respect to the TDI and the impact of related fluorinated chemicals would lead to tighter EQSs that were set to protect human health. This is an order of magnitude in case of both adjustments. The implementation of suggested adjustments would logically lead to the consideration of certain concentrations as threats that are well below current EQSs because they exceed the adjusted EQSs. These include the vast majority of ground and surface water concentrations. A revision of EQSs with respect to the suggested adjustments is therefore essential to give a conclusive answer on whether or not the presence of PFOS in the environment is an actual threat to the environment and human health. Locations in the proximity to PFOS sources are in the first place expected to have increased PFOS concentrations that are likely to exceed EQSs. Soil, lithology and streams are likely to have an influence in the distribution of PFOS.

Chapter 1 Introduction

1.1 Introduction to PFOS

Perfluorooctanesulfonic acid (PFOS) was introduced in 1949 and from the 1960s onwards produced on a large scale with an annual production of 4481 metric tons in 2000 (3M Company, 2000). It has been used since its introduction in a variety of branches and products as a surface active chemical (Moermond et al., 2010: pp. 12-13). Some concrete examples are fire fighting foams, coating additives, cleaning products, textiles and leather products, metal plating, photographic industry and photolithography, paper and packaging, pesticides, semiconductors and glue (eg. Moermond et al., 2010: p. 3; US EPA, 2012: pp. 1,2).

The chemical formula of PFOS is presented in Figure 1. The formula has been simplified by not depicting the carbon atoms that are present on each node. PFOS is most commonly present as the linear isomer that is presented in this Figure (US EPA, 2012: p. 3). Several isomers exist in addition, which means that the chain that is depicted in Figure 1 branches one or several times (eg. Riddell, 2009).

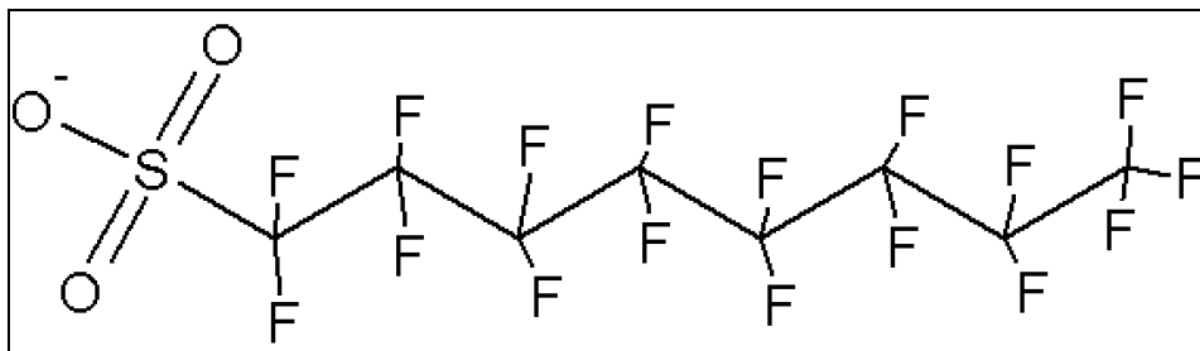


Figure 1: Simplified structural formula of PFOS (EFSA, 2008: p. 14).

There are several reasons why the environmental presence of PFOS might be problematic. A large number of publications has for example been written on the presence of this toxic chemical and negative consequences that might be caused by PFOS (eg. Austin et al., 2003; Moermond et al., 2010; US EPA, 2012). The intake of PFOS could occur after skin contact and inhalation, although ingestion, in particular of contaminated fish, in which PFOS is concentrated after bioaccumulation and biomagnification, has been considered the main pathway (US EPA, 2012: p. 3). After the intake of PFOS by humans PFOS accumulates in the liver, kidneys and serum (3M, 2005: pp. 1-2). Threats to human health that are associated with the intake of PFOS are target organ effects, including central nervous system depression and liver effects, adverse developmental effects, adverse reproductive effects including a decline in sperm quality and delayed pregnancy, adverse effects on the neuroendocrine system, other systematic effects, development of tumors, disrupt metabolism of lipids and lipoproteins and development of bladder cancer (Austin et al., 2003; 3M, 2005: pp. 1-2; Fei et al., 2009; Nordström Joensen et al., 2009; US EPA, 2012: p. 4).

In addition, PFOS might result to negative environmental effects (eg. Moermond et al., 2010). The study Moermond et al. (2010) gives an overview of negative effects on the various species of algae, fishes and invertebrates. PFOS was found to be lethal to each of the considered species if concentrations are high enough. Negative effects that occur at lower concentrations include a

decline in reproduction, larval survival and a disrupt metamorphosis (Moermond et al., 2010: pp. 30-31).

These and other threats to human health and the environment have led to the labeling of PFOS as a persistent organic pollutant in the Stockholm Convention on Persistent Organic Pollutants in 2009 (UNEP, 2009: pp. 45-46). This means that the properties of PFOS are claimed to be persistent, bioaccumulative and toxic. Several preliminary environmental quality standards (EQSs) were set for various environmental media to prevent these negative consequences from occurring (eg. Moermond et al., 2010). These EQSs are very low. They are in the order of 1 ng/l and in the order of µg/kg in other instances. PFOS concentrations need therefore to be that low to prevent negative consequences on the environment and human health from occurring, while considering the current EQSs as adequate.

The labeling of PFOS as a persistent organic pollutant in the Stockholm Convention was followed, and partially preceded, by a phase-out of production. It is still used in small quantities in applications in which it was found difficult to replace. PFOS is both lipid and water repellent, which is an unusual, and therefore useful, combination of properties. The steep decline in production that was initiated around the year 2000 has however not yet led to a proportional decline in the environmental presence of PFOS. PFOS is resistant to naturally occurring thermal, chemical, including oxidation, hydrological, photolytic and biological degradation processes (eg. EFSA, 2008: p. 1; US EPA, 2012: pp. 1, 3). The reported threats to human health would therefore continue to occur without any further interference. The actual impact of PFOS does, however, not solely depend on the properties of the chemical. The extent of its concentration in the environment also plays an important role.

1.2 Current state of research

A large and growing number of peer-reviewed articles was published on PFOS and related fluorinated substances. This number increased from around 300 in 2000 to around 2100 in 2012 (Lau, 2012: p. 405). First of all, this observation indicates that PFOS is considered a chemical of concern. However, considering these studies in general, it could be said that they do not quite manage to determine the essence of the threats PFOS might impose on the environment and human health. The extent of these threats depends on the presence of PFOS in the environment. The claim that PFOS is ubiquitous was however often made without referring to any field data containing actual observed concentrations (eg. RIWA, 2006). This contradiction could be illustrated by the comparison between citations from the document RIWA (2006). The RIWA observes a lack in thorough studies on the presence of PFOS and related fluorinated chemicals, in surface water intended for drinking water production (RIWA, 2006: p. 67). This claim contradicts clearly with the widespread presence of PFOS which was observed in the same document (RIWA, 2006: p. 67).

In addition, studies that include PFOS observations usually consider them with respect to one specific environmental medium, like surface water, biota or soil, whereas knowledge on the presence of PFOS in all compartments is required to assess the full extent to which PFOS is present in the environment. Such studies include RIWA (2006) that solely includes observations of PFOS in surface water and the study Schouten (2008) that includes PFOS observations in several fish species. However, PFOS observations were never performed to systematically keep track of the presence of PFOS in the environments and the threats that are related to it. RIWA (2006) presented monthly

concentrations of a large number of chemicals including PFOS. There was therefore no particular interest in PFOS; the obtained PFOS data were merely presented. The observations that were presented in the study Schouten (2008) were performed to find out what the consequences were of a particular discharge of PFOS near Schiphol. The performance of these observations was therefore a single event. The sample size that was used in this study was too small to support conclusive statements on what PFOS concentrations to expect in fishes (Schouten, 2008: p. 5).

Moreover, studies that actually incorporate reported concentrations do not explicitly consider them with respect to a spatial dimension (eg. Schouten, 2008; Moermond et al., 2010). It remains therefore uncertain what has caused PFOS to occur at the particular location and what concentrations to expect in other locations.

This thesis addresses the research question: to what extent is PFOS present throughout the environment and what are the threats to the environment and human health? This study has academic significance because current studies on PFOS do not present comprehensive information concerning its environmental presence, as was outlined in the previous section. In addition, this study is relevant from a societal perspective. The magnitude by which PFOS is present in the environment has implications for human health, as was indicated by the sizeable number of negative consequences that are associated with the intake of PFOS. Therefore, the results of this study contribute in a broader context in providing sufficient background to formulate a conclusive statement on whether or not the environmental presence of PFOS is an actual problem.

Chapter 2 Methodology

This study was started with a literature review to find data on concentrations of PFOS in the environment. This approach was useful, because PFOS concentrations were reported in various studies. However, PFOS concentrations were frequently merely presented (eg. RIWA, 2006). Various studies that included PFOS concentrations only reported a small number of observations. These were therefore insufficient to make conclusive statements on what concentrations could be considered normal or at what locations PFOS could be particularly expected to occur in increased concentrations.

The literature review was continued with the search for standards. Reported concentrations could then be compared with these standards to assess if PFOS is a threat to the environment and human health. Legally valid standards have not been set in the Netherlands. Concentrations needed therefore to be compared with other EQSs. The distinction was then made between PFOS concentrations that were el in surface water, biota and soil. Studies that report PFOS concentrations and EQSs do this also with respect to these environmental media.

The results of the steps that are listed in the two paragraphs above demonstrate in the first place if PFOS is present in the environment at all and, in case of confirmation, in what concentrations and, after comparison to EQSs, to what extent PFOS is a threat to the environment and human health. PFOS concentrations and threats to the environment and human health that are associated with them do however only apply to the locations where these concentrations were observed. However, assumptions were made on what PFOS concentrations can be expected at any location. Eighteen groundwater samples and one tap water sample were analysed to verify if locations that were expected to have high PFOS concentrations actually have high concentrations. These samples were taken in the province of Drenthe because of interest expressed by local officials in cooperating in a study on PFOS. The observed concentrations were also compared with EQSs, in addition to the verification of assumptions.

All samples were taken according to the methodology that is outlined in SIKB BRL 2000, protocol 2002 and NEN 5744 (Nederlandse norm, 2011; Stichting Infrastructuur Kwaliteitsborging Bodembeheer, 2013a; Stichting Infrastructuur Kwaliteitsborging Bodembeheer, 2013b). Precautionary measures to prevent contamination were taken during sampling. The most important one is that the contact with Teflon and glass should be prevented. These materials could cause additional PFOS to enter the sample and draw PFOS from the sample. The outcome of the analysis on the tap water sample would indicate contamination that might have occurred even though precautionary measures were taken, assuming that PFOS is not present in tap water.

The chemical analyses were performed by Alcontrol Laboratories (UK). The samples were analysed with Liquid Chromatography, coupled to Triple Quadruple Mass Spectrometer (LC-QQQ) for the linear isomers of PFOS and Perfluorooctanoic acid (PFOA), a fluorinated chemical that is related to PFOS. The limit of quantification was 10 ng/l. The level of detection was stated to be smaller than 1 ng/l in case of both chemicals.

Chapter 3 Review of environmental presence of PFOS and its risk assessment

3.1 Surface water

The RIWA monitors monthly average PFOS concentrations at different locations in the river Rhine and adjacent waterways. These sampling sites are Rhine at Lobith, in the Lek Canal at Nieuwegein and in the Amsterdam-Rhine Canal at Nieuwersluis. These concentrations were then compared with the EQS that has been established for freshwater by the RIVM because official standards do not exist in the Netherlands. The RIVM set a Maximum Permissible Concentration (MPC) for freshwater to prevent consequences that could occur after direct ecotoxicity, secondary poisoning and consumption of fish by humans (Moermond et al., 2010: p. 5). When the annual average freshwater concentration remains below this value, none of these consequences are expected to occur (Moermond et al., 2010: p. 5).

The overall MPC for freshwater was determined by setting MPCs for the three considered consequences separately (direct ecotoxicity, secondary poisoning and consumption of fish by humans). The lowest concentration that is supposed to cause one of these becomes then the MPC because a concentration that remains below this value is required to prevent all three undesirable consequences. The consequences of the consumption of fish by humans occur at the lowest concentration, which is 0.65 ng/l, and determines thereby the MPC for freshwater (Moermond et al., 2010: p. 14). The MPCs for secondary poisoning and direct ecotoxicity were estimated at 2.6 ng/l and 23 ng/l respectively (Moermond et al., 2010: p. 36).

The overall MPC for marine water is 0.53 ng/l (Moermond et al., 2010: p. 14). The consequences of secondary poisoning are supposed to occur at lower concentrations in the marine environment as the result of an additional biomagnification factor of five that accounts for the accumulation in birds and mammals and determines in this case the overall MPC (Moermond et al., 2010: pp. 16, 22). The MPC for human fish consumption is 0.65 ng/l and thereby the same as the MPC for freshwater. The MPC for direct ecotoxicity is 4.6 ng/l and thereby, like the MPC for secondary poisoning, five times lower than that of freshwater.

The EQSs for fresh and marine water are thereby paradoxically three orders of magnitude lower than that of surface water intended for drinking water production, which is 0.53 µg/l. This contradictory difference occurs because of the bioaccumulating and biomagnifying properties of PFOS (Moermond et al., 2010: p. 36). Drinking water that contains a certain amount of PFOS is therefore as a rule less hazardous than eating organisms that live in this water. A Tolerable Daily Intake (TDI) of 0.15 µg/kg b.w./day was used to calculate both the EQS for freshwater and that of freshwater that is intended for the production of drinking water.

The RIVM also set Maximum Admissible Concentrations (MACs). These should not be exceeded at any time. The MACs of freshwater and marine water were set at 36 µg/l and 7.2 µg/l respectively (Moermond et al., 2010: p. 14). These values were derived from short-term toxicity tests whereas the negative consequences mainly express themselves in the long-term. MACs are therefore inadequate to use in risk assessment (Moermond et al., 2010: p. 13).

Figure 2 depicts monthly average PFOS concentrations (µg/l) in the Rhine at Lobith, in the Lek Canal at Nieuwegein and in the Amsterdam-Rhine Canal at Nieuwersluis. These graphs are based on annual

reports that all together cover the period January 2006 (the first month) until December 2010 (the 60th month). Observations that were performed do not cover the entire interval and were usually performed with lower frequencies than twelve monthly observations a year. Observed concentrations from all three locations are predominantly within the range 0.005 $\mu\text{g/l}$ - 0.030 $\mu\text{g/l}$. These values were compared with the EQS for freshwater which is 0.65 $\mu\text{g/l}$ and is depicted in Figure 2 as a horizontal line. This value does however largely overlap the x-axis and is therefore not clearly visible in this Figure.

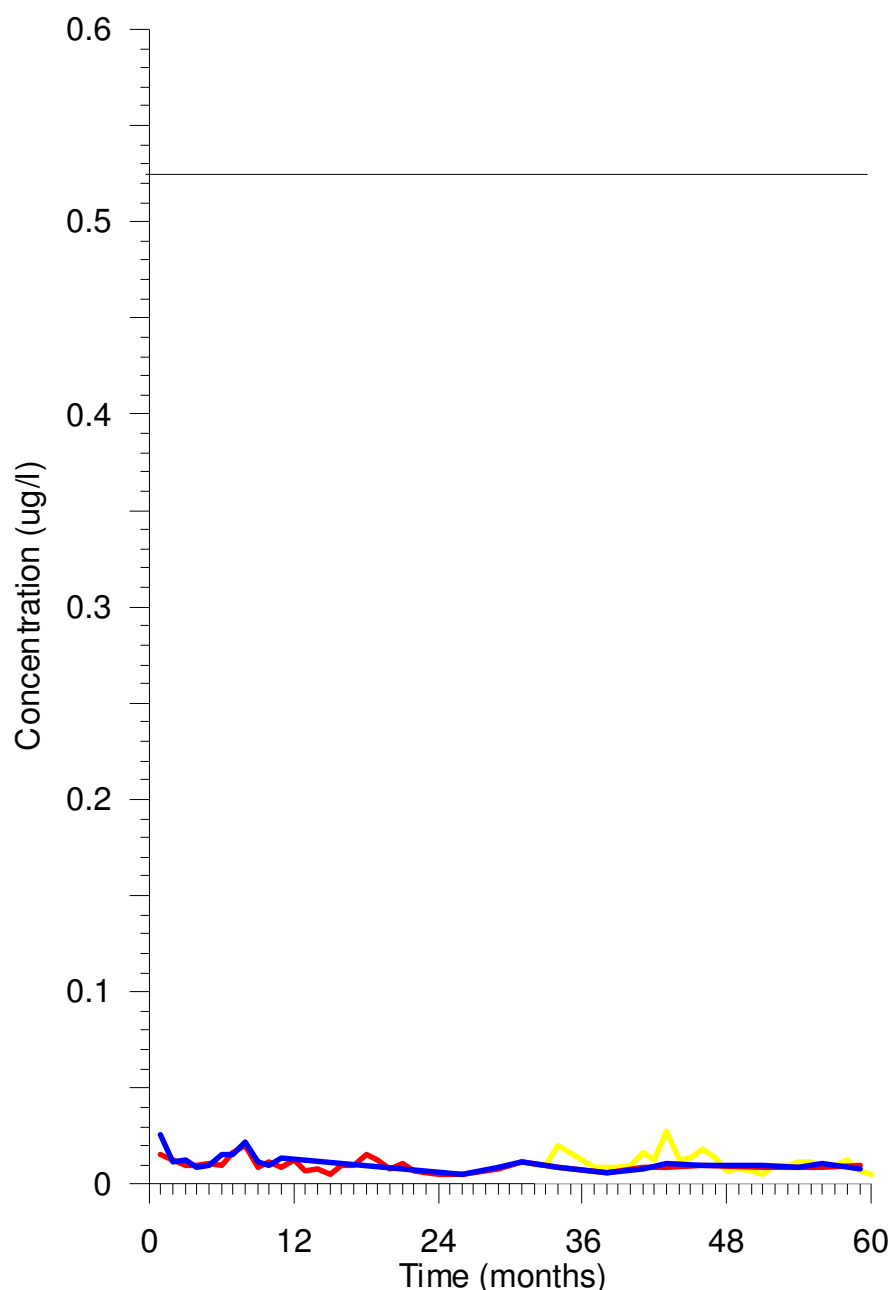


Figure 2: Monthly average PFOS concentrations ($\mu\text{g/l}$) of surface water derived from the Rhine at Lobith (yellow), the Lek Canal at Nieuwegein (red) and the Amsterdam-Rhine Canal at Nieuwersluis (blue), within the interval January 2006, the first month, until December 2010, the 60th month, compared with the EQS for fish consumption which is 0.00065 $\mu\text{g/l}$ and with the EQSs for freshwater that is intended for the production of drinking water which is 0.53 $\mu\text{g/l}$. The data were obtained from RIWA (2006), RIWA (2007), RIWA (2008), RIWA (2009) and RIWA (2010).

It is clearly visible that all observed PFOS concentrations exceed the EQS for freshwater of 0.65 ng/l. These waterways were therefore unsuitable to harvest fishes for human consumption at all times during the entire considered time span.

The PFOS concentrations from the three considered locations were also compared with the EQS for surface water intended for drinking water production which is 0.53 µg/l. It is clearly visible all PFOS concentrations that are presented in this Figure 2 are below this EQS. These waterways were therefore suitable as freshwater that is intended for the production of drinking water at all times during the considered time span.

The developments in PFOS concentrations in all three waterways tend to demonstrate seasonality. The observed concentrations from these waterways were combined in one file and sorted per month to illustrate monthly variations. These are presented in Figure 3, in which each month was represented by four to nine observations. It is visible that peak values of 0.015 µg/l or higher occur in most months. A difference occurs, however, in the base level. The lowest values from December until March are around 0.005 µg/l. This is in contrast to the months April until November, during which the lowest values still remain moderately high around values of 0.01 µg/l.

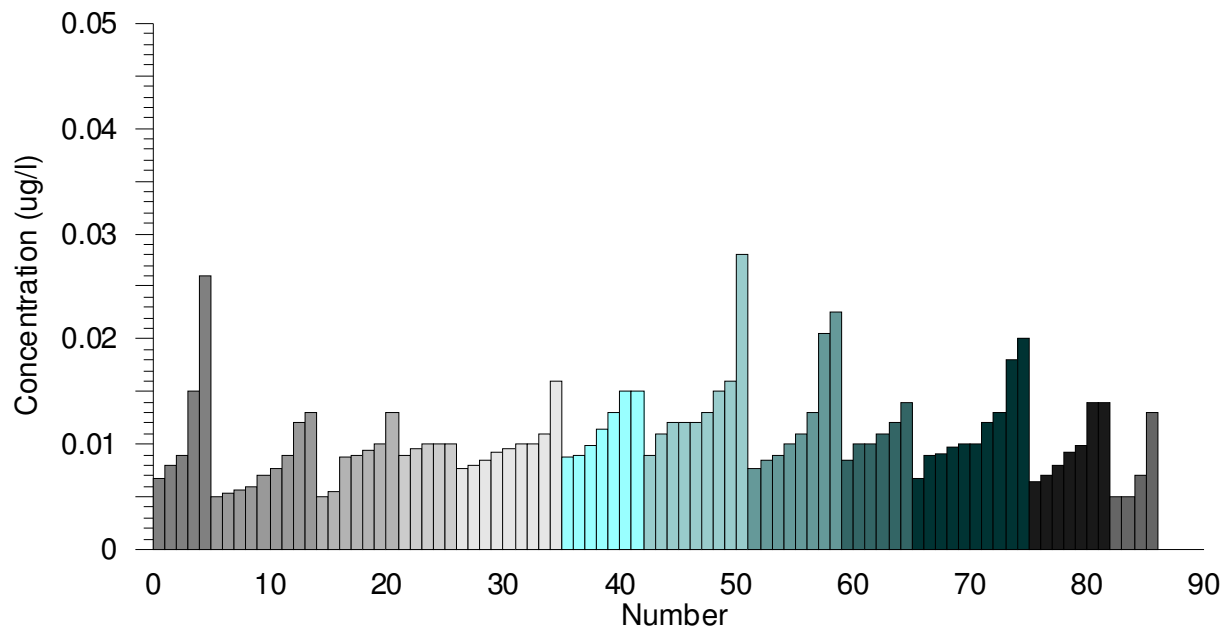


Figure 3: Monthly average PFOS concentrations (µg/l) of water derived from the Rhine at Lobith, the Lek Canal at Nieuwegein and the Amsterdam-Rhine Canal at Nieuwersluis within the interval January 2006 until December 2010 sorted per month. The data were obtained from RIWA (2006), RIWA (2007), RIWA (2008), RIWA (2009) and RIWA (2010).

The concentrations during summer are higher than during winter. The period in which higher PFOS concentrations occur, coincides thereby with the period in which waterways have the lowest discharge as a consequence of an increased evaporation because of higher temperatures. An increase in monthly average concentrations does therefore not necessarily have to be the result of an increase in discharged quantity of PFOS.

Figure 4 depicts the discharge of PFOS (kg/day) by the Rhine at Lobith (yellow) and by the Lek Canal at Nieuwegein (red). This Figure was made to find out if high PFOS concentrations were actually

caused by an increased amount of PFOS that was discharged at that time. The discharge of PFOS was calculated using PFOS concentrations and the discharge of these waterways that was also observed by the RIWA. Only two waterways were considered because these were the only two of which both PFOS concentrations and discharges were known. The depicted period, as before, covers January 2006 until December 2010.

In the publication RIWA (2009: p. 25) it is claimed that the amount of discharged PFOS tends to show a declining trend over the first 48 months. However, these data series appear to cover too short a time span to support conclusive statements on temporal trends. The effectiveness of the Stockholm Convention in reducing the environmental release of PFOS could therefore for example not be analysed.

Moreover, the declining trend that exists according to the study RIWA (2009: p. 25) is not visible in any of the Figures. Figure 4 presents an even more stable pattern than the Figures that present concentrations. The graph that represents the discharge by the Rhine at Lobith appears to have a baseline level around 1.3 kg/day. These do not show an evident declining trend. The discharges by the Lek Canal at Nieuwegein of the years 2008 and 2009 are lower than those of the two previous years. However, the discharges of PFOS do not decline consistently. The discharges in 2010 are higher again than those of 2008 and 2009. A declining trend of PFOS concentrations in these waterways does therefore not have to be supported by an equal decline in amount of PFOS that was discharged.

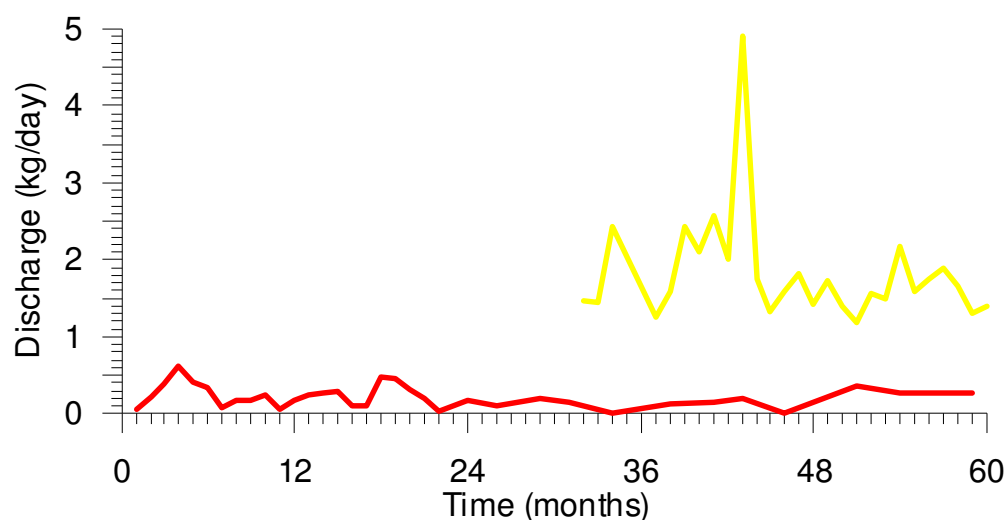


Figure 4: Discharge of PFOS (kg/day) by the Rhine at Lobith (yellow) and by the Lek Canal at Nieuwegein (red), within the interval January 2006, the first month, until December 2010, the 60th month. The used data were obtained from RIWA (2006), RIWA (2007), RIWA (2008), RIWA (2009) and RIWA (2010).

The presence of PFOS in the waterways Rhine at Lobith, in the Lek Canal at Nieuwegein and in the Amsterdam-Rhine Canal at Nieuwersluis was ascribed to a point source in Germany that was close to the Dutch border (RIWA, 2009: p. 25). The policies of these companies to discharge PFOS might therefore have had an even larger influence on the PFOS concentrations than seasonality in water discharge when adopting this claim.

However, a point source in Germany is not the only PFOS source that contributed PFOS to these three waterways. PFOS concentrations of the Lek Canal at Nieuwegein and the Amsterdam-Rhine Canal at Nieuwersluis are occasionally higher than those in the Rhine at Lobith where the river enters the Netherlands. This is visible in Figure 2. It was therefore concluded that PFOS was discharged to these waterways in the Netherlands as well. This conclusion is supported by the data series that are presented in Figure 4. A peak in the amount of PFOS that is discharged by the Lek Canal coincides with a relative low PFOS discharge of the Rhine at Lobith. These data do therefore strongly suggest that the Rhine is not the only contributor of PFOS to the Lek Canal.

The actual discharge of PFOS (kg/day) of the Lek Canal is depicted in Figure 5 with respect to what this would have been if the PFOS concentration of the Lek Canal was the same as that of the Rhine. This Figure indicates that PFOS was added in some interval whereas the water was diluted in other intervals.

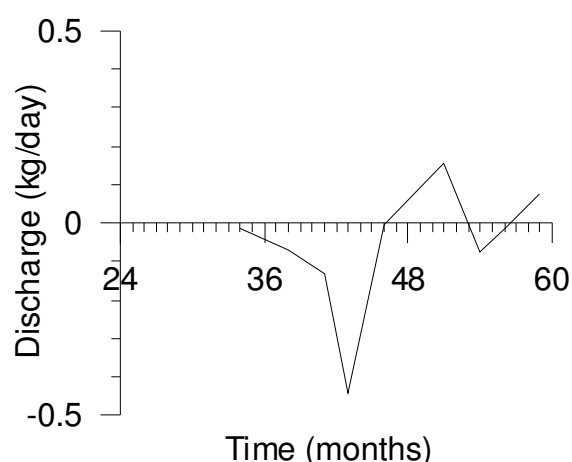


Figure 5: Difference between the actual discharge of PFOS (kg/day) by the Lek Canal at Nieuwegein and what would have been the discharge in case the Lek Canal at Nieuwegein had the same PFOS concentration as the Rhine at Lobith, within the interval January 2008, the 25th month, until December 2010, the 60th month. The used data were obtained from RIWA (2008), RIWA (2009) and RIWA (2010).

3.2 Biota

Analyses of PFOS concentrations in biota took place mainly by observing PFOS concentrations in whole fishes. A large quantity of PFOS containing fire fighting foam was discharged near Schiphol in July 2008 (Schouten, 2008: p. 1). Fishes from different species were sampled and analysed for their PFOS content (Schouten, 2008: p. 1). A concentration of 30 µg/kg was observed in an eel that was sampled upstream of the location where the release of PFOS has taken place and was therefore considered as a reference value (Schouten, 2008: p. 3). The highest concentrations that were observed per sampled species were 400 µg/kg in eel, 760 µg/kg in pike and 1500 µg/kg in perch (Schouten, 2008: p. 3). These results were, however, based on a small number of samples. The organisation that carried out the analyses underlines the need for subsequent studies to substantiate these findings (Schouten, 2008).

The data that were presented in the study Schouten (2008) suggest a vast increase in PFOS concentrations in whole fishes that were influenced by released PFOS compared with the reference value. The data that were presented in the study Van Leeuwen & De Boer (2006) point out that the

background value is not uniform. Concentrations ranging from 2 µg/kg – 720 µg/kg were observed for different fish species (Van Leeuwen & De Boer, 2006). These differences could however also partly occur as a consequence of the locations where the samples were taken, which are likely to differ with respect to PFOS sources. This presented range does therefore not necessarily match the range in background values.

PFOS concentrations of fillet of various fish species were reported in the study Van Leeuwen et al. (2013). Concentrations in fillet of the species herring, mackerel, cod, European plaice, haddock and common dab were all reported to be below 2.6 µg/kg (Van Leeuwen et al., 2013: pp. 11-14). The fillet of common sole was reported to have a substantial higher concentration of < 5 µg/kg. All these observed concentrations are much lower than the reference value of 30 µg/kg that was reported in (Schouten, 2008: p. 3). This could be explained by differences between species although these differences appear to be rather small considering the study Van Leeuwen et al. (2013). It could alternatively have resulted from the locations where the samples were taken. The samples from the study Schouten (2008) were taken from inland waters whereas those from the study Van Leeuwen et al. (2013) were taken in the open North Sea. The difference between species would then be less important.

Several food products were analysed for their PFOS content in the study Noorlander et al. (2010). The PFOS concentration in fatty fish was set at 0.061 µg/kg whereas that of lean fish was set at 0.308 µg/kg (Noorlander et al., 2010: p. 9). These concentrations could not, like the concentrations of fillet from the study Van Leeuwen et al. (2013), be compared with values that represent a whole. PFOS is not uniformly distributed throughout a fish (eg. Van Leeuwen & De Boer, 2006). It is likely that the concentrations of food products and fillet are closer to concentrations that match the human intake after the consumption of fish. The methodology in studies in which PFOS concentrations of whole fishes were obtained is usually not explained in detail. The samples that are supposed to represent a whole fish might therefore as well only represent part of it.

The EQSs that were set by the RIVM were based on experimental data that are presented in Table 1. These include the No observed effect concentration (NOEC) and Concentration lethal (or effective) to 50% of the organisms tested (L(E)C50). These were obtained from 35-day experimental studies and collected by the RIVM for various organisms that were categorized as: algae, invertebrates and fishes (Moermond et al., 2010: pp. 30-31).

Most NOEC and (L(E)C50) values are five to seven orders of magnitude higher than the estimated MAC values for freshwater of 0.0065 µg/l. The lower values that are presented in this Table are still three orders of magnitude higher than the MAC values for freshwater. The values presented in Table 1 can therefore not be used as reliable indicators of water quality. It should be noted that none of the species in which PFOS concentrations were observed were used to set the EQSs.

Table 1: NOEC and L(E)C50 of various algae, invertebrates and fishes reviewed in the study Moermond et al. (2010, pp. 30-31).

Algae		Invertebrates (such as Daphnia)	
NOEC (µg/l)	L(E)C50 (µg/l)	NOEC (µg/l)	L(E)C50 (µg/l)
8200 (<i>Chlorella vulgaris</i>)	82000 (<i>Chlorella vulgaris</i>)	7000 (<i>Daphnia magna</i> (Crustacean))	48000 (<i>Daphnia magna</i> (Crustacean))
191000 (<i>Navicula pelliculosa</i>)	28300 (<i>Navicula pelliculosa</i>)	400 (<i>Moina macrocopa</i> (Crustacean))	124000 (<i>Daphnia pulicaria</i> (Crustacean))
53000 (<i>Pseudokirchneriella subcapitata</i>)	120000 (<i>Pseudokirchneriella subcapitata</i>)	< 2.3 (<i>Chironomus tentans</i> (Insect))	18000 (<i>Moina macrocopa</i> (Crustacean))
		< 10 (<i>Enallagma cyathigerum</i> (Insect))	9300 (<i>Neocaridina denticulate</i> (Crustacean))
Fish		250 (<i>Americamysis bahia</i> (Marine Crustacean))	18000 (<i>Dugesia japonica</i> (Platyhelminth))
NOEC (µg/l)	L(E)C50 (µg/l)		165000 (<i>Physa acuta</i> (Mollusc))
< 10 (<i>Oryzias latipes</i>)	6400 (<i>Lepomis macrochirus</i>)		59000 (<i>Unio complamatus</i> (Mollusc))
27 (<i>Pimephales promelas</i>)	6600 (<i>Pimephales promelas</i>)		3600 (<i>Americamysis bahia</i> (Marine Crustacean))
	13000 (<i>Oncorhynchus mykiss</i>)		8300 (<i>Artemia</i> sp. (Marine Crustacean))
	13000 (<i>Oncorhynchus mykiss</i> , in the marine environment))		

Figure 6 depicts all reported PFOS concentrations of whole fishes and fish fillet. The observed concentrations were sorted according to magnitude. These are compared with the preliminary rejection limit of 200 µg/kg that was set in the study Schouten (2008). Around 10 % of the concentrations exceed the preliminary rejection limit. This also means that around 90 % of fishes that were present in water that was considered unsuitable for fish consumption by humans are still consumable.

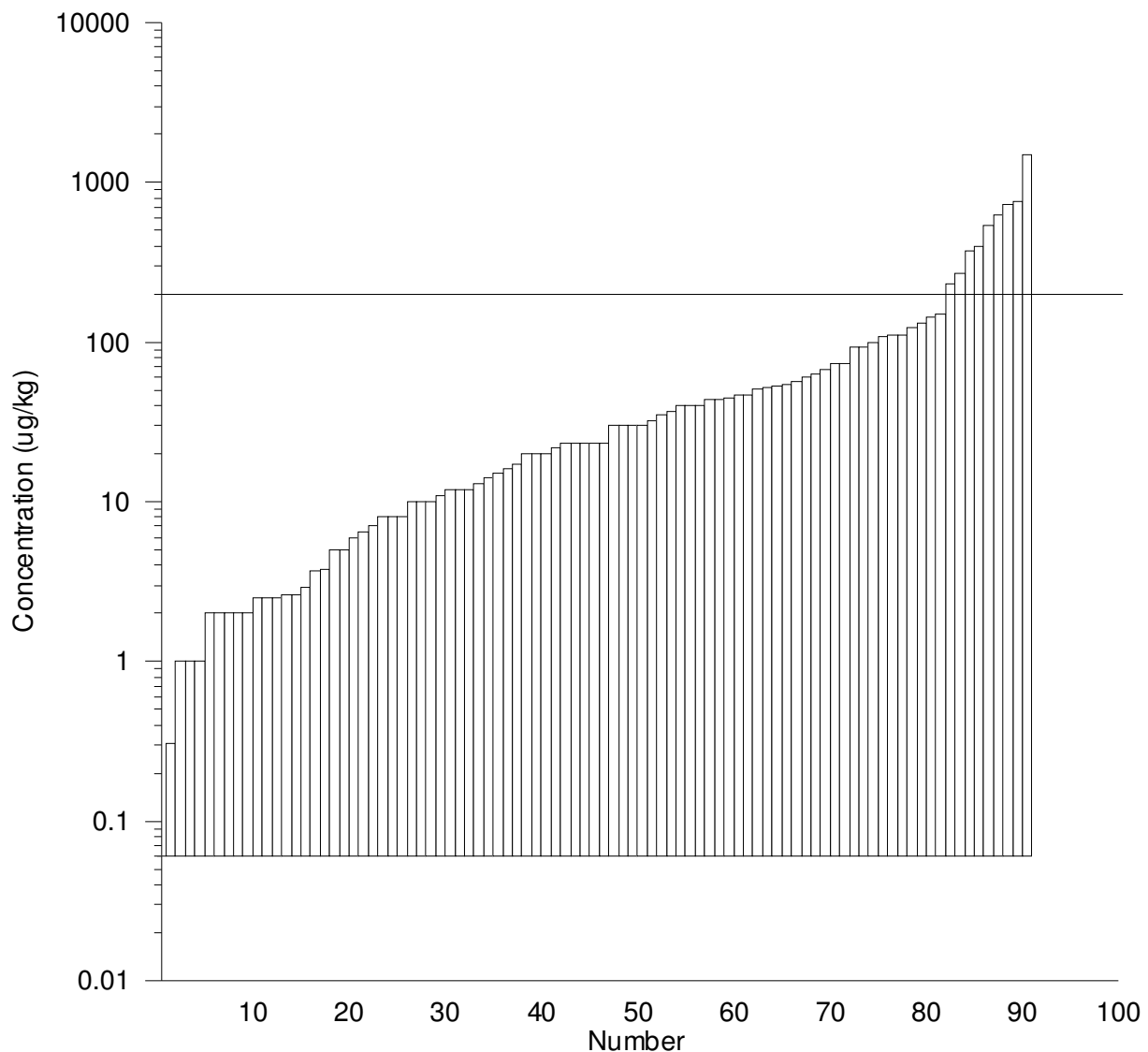


Figure 6: PFOS concentrations of whole fishes and fish fillet from various species presented on a logarithmic scale and compared with the preliminary rejection limit which is 200 $\mu\text{g/kg}$ (Schouten, 2008). The used data were obtained from the studies Schrap et al. (2004), Van Leeuwen & De Boer (2006), Schouten et al. (2008), Kotterman & Kwadijk (2009), Noorlander et al. (2010), Hoek- van Nieuwehuis et al. (2012) and Van Leeuwen et al. (2013).

3.3 Soil

Soil samples have not been observed frequently in studies on PFOS. However, the study Kotterman & Kwadijk (2009: p. 9) presents an average concentration of sludge of 3.7 $\mu\text{g/kg}$. This value was determined after the analysis of nineteen samples that were all taken in the Netherlands. The PFOS concentrations of these ranged between 1.1 $\mu\text{g/kg}$ and 8.7 $\mu\text{g/kg}$ (Kotterman & Kwadijk, 2009: p. 9). The study Kotterman & Kwadijk (2009: p. 8) also identified a reference value of sludge which was set on 6.5 $\mu\text{g/kg}$. The average PFOS concentration of sludge is 3.7 $\mu\text{g/kg}$ and thereby exceeds the maximum tolerable risk level of soil which is 3.2 $\mu\text{g/kg}$ (Bodar et al., 2011). However, there might be a difference between the definitions of soil and sludge as they are used in these studies.

Three sediment samples were analysed for their PFOS content in the study RPS Advies B.V. (2010: p. 34). The concentrations were all lower than the limit of quantification. The samples were taken near Wastewater treatment plant *De Cocksdorp*, located on the island of Texel that was identified as a potential PFOS source.

A maximum tolerable risk level of 3.2 µg/kg of soil was set in Bodar et al. (2011). A value of 2.3 µg/kg was mentioned in the same document. The latter is probably a typing error. This value is much higher than the guideline value that is in use in Norway. This value is 0.1 µg/kg soil. Figure 7 presents reported PFOS concentrations in soil, including some that were observed in Norway, compared with the guideline value that is in use in Norway. The observed concentrations were sorted according to magnitude. In this Figure it is clearly visible that the vast majority of the considered concentrations exceed the guideline value that, on the scale of this graph, overlaps the x-axis.

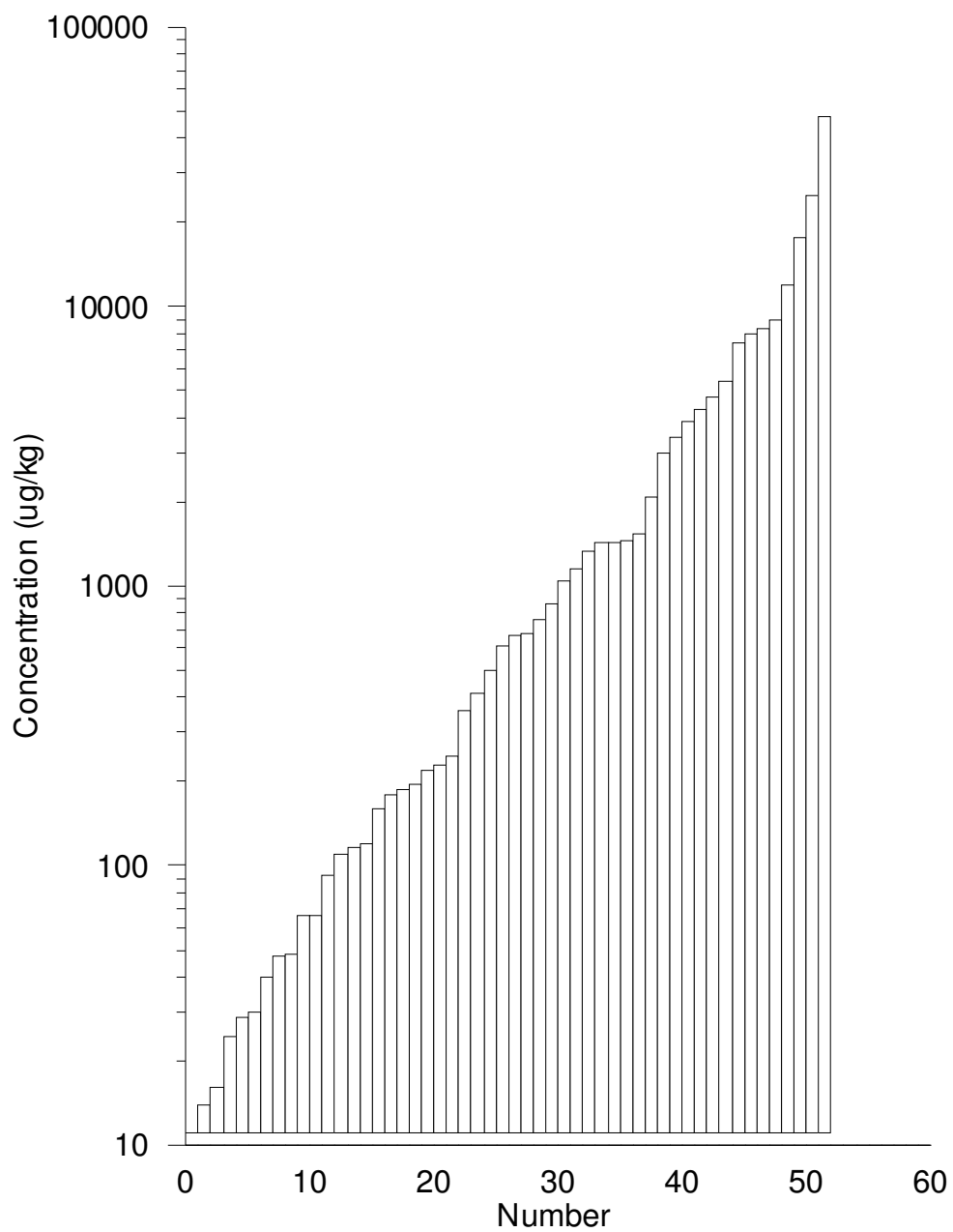


Figure 7: PFOS concentrations ($\mu\text{g/kg}$) in sediment presented on a logarithmic scale. All concentrations exceed the EQS of sediment of $3.2 \mu\text{g/kg}$ (Bodar et al., 2011).

Chapter 4 Case study groundwater Drenthe

4.1 Introduction

Data on PFOS concentrations in groundwater are scarcely available. The study Noorlander et al. (2010: p. 5) pointed out that there were no data available on ground water that specifically apply to the Netherlands. A European average concentration of 7 ng/l was therefore adopted from its context to a Dutch setting. This value was derived from EFSA (2008). An average PFOS groundwater concentration of 15 ng/l was used in the study Kwadijk et al. (2008) which is about two times higher than the value mentioned earlier.

Eighteen groundwater samples were taken in the province of Drenthe because of interest local officials expressed in cooperating in a study on PFOS. The case study in Drenthe was mainly performed to find out whether or not PFOS is actually present in groundwater. Measuring wells were therefore purposefully selected on their likelihood to have a substantial PFOS concentration. The differences in spatial properties of the measuring wells were then considered to be decisive for the differences in PFOS concentration in the measuring wells. This Chapter considers spatial properties with respect to PFOS concentrations in groundwater. The same properties would, however, determine to a certain extent PFOS concentrations in other environmental media. PFOA was analysed simultaneously with PFOS. However, PFOA was not taken into account while deciding what monitoring wells to sample.

4.2 Spatial properties

The proximity to potential PFOS sources was used as the initial criterion in the selection procedure. Potential sources are facilities that have been frequently considered with respect to increased PFOS concentrations and include:

- Locations where PFOS has been discharged;
- Locations where fire fighting foams might have entered the environment (fire fighting departments, storage facilities of fire fighting foams, training facilities of the fire department and locations of former fires);
- Metal working industry;
- Carpet industry and textile industry;
- Textile laundries;
- Wastewater treatment plant;
- Landfills;
- Paper mills and materials recovery facilities (eg. Schouten, 2008; RPS Advies B.V., 2010).

An internet search was conducted to find potential sources in Drenthe. It is, however, likely that a number of potential sources was not identified.

Groundwater that is close to a potential source is likely to have a higher PFOS concentration than groundwater at a larger distance. Monitoring wells were therefore favoured in the case study that are located within 500 meters of potential sources. The distance of 500 meters was chosen while considering an average groundwater flow of 20 meters annually and a time span of at least 25 years that could have effectively contributed to the release of PFOS. The duration of the considered time span and the groundwater flow thereby influence the locations where PFOS could be expected.

Groundwater flow occurs in a predominant direction. PFOS does therefore occur at a particular side of the potential source. Monitoring wells that are located upstream of the potential sources were therefore removed. These could not have been reached by released PFOS from a potential source by groundwater flow.

The lithology of the surrounding area of the potential sources and monitoring wells also influences the distribution of PFOS. Impermeable clays layers could for example prevent PFOS from reaching certain locations whereas a sandy soil would allow this. None of the monitoring wells was conclusively obstructed by its surrounding lithology. However, a clay layer could also be favourable when the monitoring well is located just above it. The impermeable properties of the clay layer would then prevent PFOS-enriched water from avoiding the location of the monitoring well.

The soil of the surrounding area of the potential sources and monitoring wells does also play a role. The presence of peat would for example lead to a smaller distribution, because PFOS attaches to peat. This is in contrast to sand, through which PFOS could pass. Peat is favourable when a monitoring well is on very close approximation of its associated potential source. Released PFOS remains then near the potential source after which it would be observed in the monitoring well. Peat might on the other hand prevent PFOS from reaching the monitoring well when it is located at a greater distance. The distribution of both sand and peat are quite fragmented. Only a very few pathways between potential sources and monitoring wells are connected with one of them as a consequence. It is therefore unknown if the lithology favoured any of the monitoring wells over others.

4.3 Selected monitoring wells

The monitoring wells that were sampled are listed in Table 2. The sampled wells are presented along with the identification codes LOC_ID + PB_ID or TNO_NR, the potential sources they supposedly address, their geographic coordinates according to the *Rijksdriehoekstelsel* (RD), soil type, depth (m) and distance (m) to the potential source. These were taken from seventeen individual monitoring wells. These were selected while keeping the spatial properties of each of them in mind. The monitoring well 'Landfill site Wijster' was sampled at two different depths. There are two more potential sources that are addressed by two monitoring wells. These are 'Groningen Airport Eelde' and 'Landfill site near Groningen Airport Eelde'. These were covered by two monitoring wells that occupy a relatively large area. The nineteenth sample contained tap water and was taken as a blank sample. The locations of the measuring wells are presented in Figure 8 to show their spatial distribution. Seventeen of the nineteen suggested monitoring wells were actually sampled and analysed. Two of them could not be sampled. Monitoring well 81 B02.1 was dry and monitoring well 18CA3063 did not have a filter at the right depth. One of these was replaced by the monitoring well 22EA31.40.1.

Table 2: Eighteen selected monitoring wells presented with the identification codes LOC_ID + PB_ID or TNO_NR, the potential sources they supposedly address, their geographic coordinates according to the *Rijksdriehoekstelsel* (RD), soil type, depth (m) and distance (m) to the potential source.

LOC_ID + PB_ID / TNO_NR	Potential source	X (RD)	Y (RD)	Soil type source	Depth (m)	Distance (m)
152A01.1	Fire fighting department Emmer-Compasuum	264912	537007	Peat	4	600
17DA3087	Landfill site Wijster	232620	533600	Sand	25	1200
18C3063.1	Landfill site easterly of Emmen	262222	535369	Peat	10	1400
22EA31.40.1	Fire fighting department Coevorden	246514	521560	Sand	5	500
292B01.1	Groningen Airport Eelde	235744	571995	Sand	5	300
292B04.1	Groningen Airport Eelde	235907	571944	Sand	2	400
300B09.1	Landfill site near Groningen Airport Eelde	235725	571081	Sand	5	0
70B06.1	Industrial park Coevorden	245463	517923	Peat	4	400
17A01.1	Wastewater treatment plant – Gieten	248378	559776	Peat	5	400
Tap water						
12BA3136	Wastewater treatment plant – Eelde	237144	571975	Peat	5	700
17DA3087	Landfill site Wijster	232620	533600	Sand	10	1200
210B02.1	Industrial park Hoogeveen	229167	527864	Sand	3	500
214B01.1	Horse blanket laundry 'De Washoek'	232838	521025	Peat	3	200
222B01.2	Company fire fighting department Fokker Aerostructures B.V.	230221	527666	Sand	4	500
239B04.1	Fire fighting department Meppel	208405	524336	Sand	4	600
282B02.1	Fire fighting department Dwingeloo	221515	539535	Sand	3	200
300B04.1	Landfill site near Groningen Airport Eelde	235682	570931	Sand	5	0
71B05.1	Civic amenity site	246005	519838	Peat	4	200

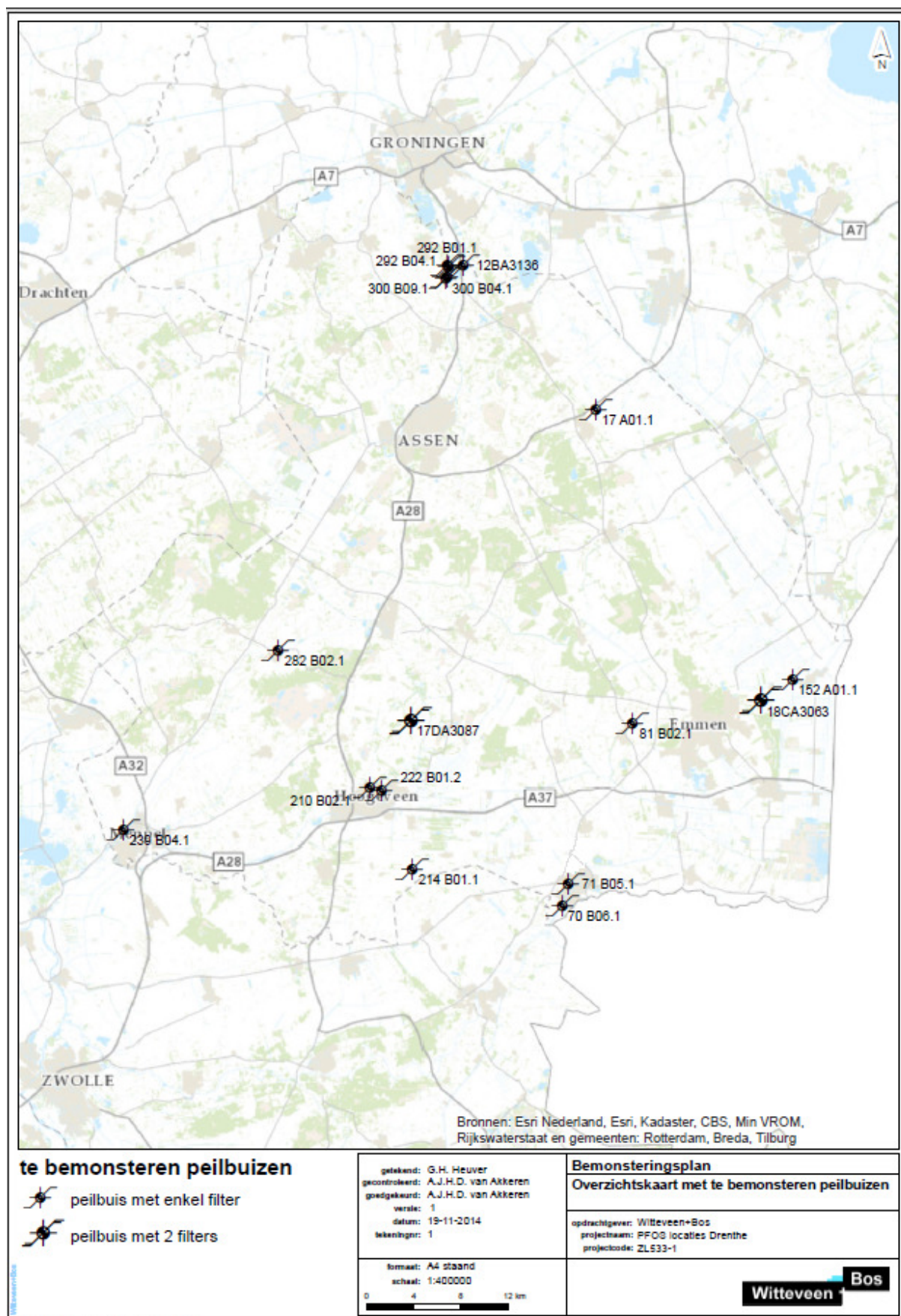


Figure 8: Map of the province of Drenthe depicting the selected monitoring wells. The two wells that were intended to sample twice are depicted as larger symbols.

4.4 Results

Table 3 presents the results of the analysis of the water samples that were taken in the province of Drenthe. The PFOS and PFOA concentrations of ten out of nineteen water samples were below the limit of quantification of the laboratory involved of 10 ng/l. The tap water sample is one of these. The PFOS concentration remains below the limit of quantification whereas the PFOA concentration exceeds it in seven cases. Two samples have both PFOS and PFOA concentrations exceeding their limits of quantification.

The observed PFOS concentrations of the two samples that exceed the limit of quantification were 19 ng/l and 25 ng/l. These are higher than the average concentrations that were mentioned in the studies EFSA (2008) and Kwadijk et al. (2008). All other concentrations remain below the average concentration of 15 ng/l. It is, however, unclear how they relate to the average concentration of 7 ng/l, because this average value is below the limit of quantification of the laboratory involved. The data of Table 3 could therefore not be used to support or invalidate the adaptation of any of the average concentrations in a Dutch context.

No official standards are set in the Netherlands for groundwater. However, the RIVM set a preliminary EQS for freshwater that is intended for the production of drinking water. This value was set at 0.53 µg/l (Moermond et al., 2010: p. 36). The reported average groundwater concentrations and groundwater concentrations are compared with this EQS in Figure 9. The EQS exceeds all four concentrations with more than an order of magnitude. However, it could not be ruled out that negative environmental effects occur because they have not been taken into account.

Table 3: Overview of the analysed water samples with location specific information.

Measuring well	Depth (m)	Potential source	Soil type	Distance (m)	Concentration PFOA (ng/l)	Concentration PFOS (ng/l)
152A01.1	4	Fire fighting department Emmer-Compascuum	Peat	600	14	25
17DA3087	25	Landfill site Wijster	Sand	1200	<10	<10
18C3063.1	10	Landfill site east of Emmen	Peat	1400	<10	<10
22EA31.40.1	5	Fire fighting department Coevorden	Sand	500	<10	<10
292B01.1	5	Groningen Airport Eelde	Sand	300	<10	<10
292B04.1	2	Groningen Airport Eelde	Sand	400	14	<10
300B09.1	5	Landfill site near Groningen Airport Eelde	Sand	0	<10	<10
70B06.1	4	Wastewater treatment plant - Industrial park Coevorden	Peat	400	12	19
17A01.1	5	Wastewater treatment plant – Gieten	Peat	400	<10	<10
Tap water		-	-	-	<10	<10
12BA3136	5	Wastewater treatment plant – Eelde	Peat	700	<10	<10
17DA3087	10	Landfill site Wijster	Sand	1200	13	<10
210B02.1	3	Industrial park Hoogeveen	Sand	500	<10	<10
214B01.1	3	Horse blanket laundry 'De Washoek'	Peat	200	<10	<10
222B01.2	4	Company fire fighting department Fokker Aerostructures B.V.	Sand	500	21	<10
239B04.1	4	Fire fighting department Meppel	Sand	600	10	<10
282B02.1	3	Fire fighting department Dwingeloo	Sand	200	35	<10
300B04.1	5	Landfill site near Groningen Airport Eelde	Sand	0	12	<10
71B05.1	4	Civic amenity site	Peat	200	12	<10

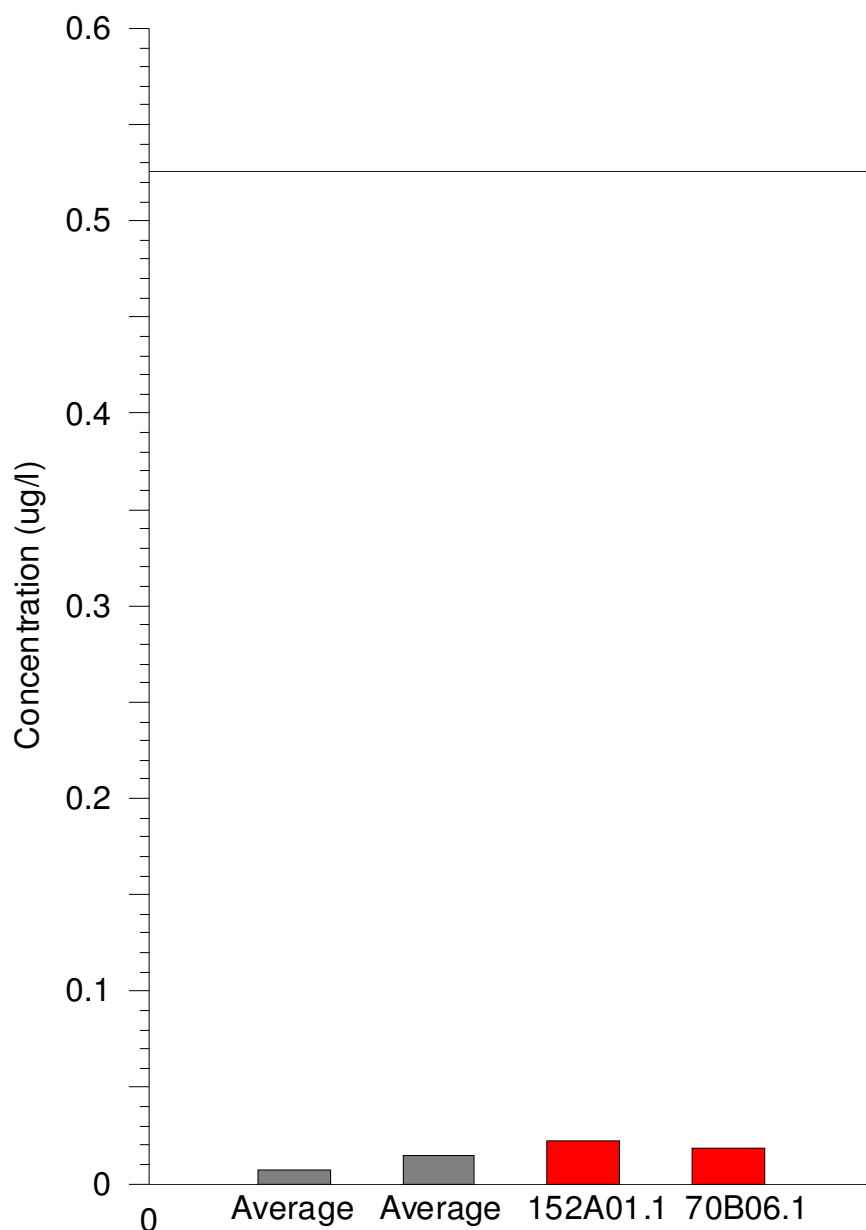


Figure 9: Comparison between average groundwater concentrations of 0.007 $\mu\text{g/l}$ and 0.011 $\mu\text{g/l}$ as reported in the studies Noorlander et al. (2010: p. 5) and Kwadijk et al. (2008) (grey bars) and observed groundwater concentrations of 0.025 $\mu\text{g/l}$ and 0.019 $\mu\text{g/l}$ (red bars) with EQSs for freshwater that is intended for the production of drinking water of 0.53 $\mu\text{g/l}$ (horizontal line).

Chapter 5 Discussion

5.1 Introduction

The results show that some concentrations clearly exceed EQSs whereas other concentrations do not. However, various uncertainties occur while setting these EQSs which make their adequacy debatable. These uncertainties are discussed in this Chapter and include the TDI, the influence of related fluorinated chemicals, contribution of drinking water, contribution of fish consumption and actual daily intake. Other points of concern occur with respect to the manner data were collected and are also discussed in this Chapter.

5.2 Tolerable Daily Intake (TDI)

A TDI of 0.15 µg/kg b.w./day was set by the Panel on Contaminants in the Food Chain (CONTAM) of the EFSA (EFSA, 2008). This value equals an intake of 10.5 µg/day of a person with a body weight of 70 kg. The TDI of 0.15 µg/kg b.w./day was adopted by several parties including the *Voedsel en waren autoriteit bureau risicobeoordeling*, Federal Institute for Risk Assessment (BfR) and the National Institute for Public Health and the Environment (RIVM) (Schouten, 2008). Various EQSs were set using a TDI of 0.15 µg/kg b.w./day as input, including the EQS for freshwater that is intended for the production of drinking water and the EQS for fresh surface water (Moermond et al., 2010). It is, however, not self-evident that this value should be used. Uncertainties and inaccuracies which occur in the process of determining the TDI have therefore led to uncertainties and inaccuracies in EQSs that were based on them.

The TDI of 0.15 µg/kg b.w./day was derived from a subchronic study of 90 days on cynomolgus monkeys where a lowest no-observed adverse-effect level (NOAEL) for thyroid hormones disruption was set at 0.03 mg/kg b.w./day (Seacat et al., 2002; EFSA, 2008: p. 3). However, this value applies specifically to cynomolgus monkeys and may therefore not be representative for humans. An uncertainty factor of 100 was adopted to compensate for inter-species and intra-species differences (EFSA, 2008: p. 3).

Other uncertainties occurred 'in connection to the relatively short duration of the key study and the internal dose kinetics' (EFSA, 2008: p. 3). These were addressed by an uncertainty factor of two resulting in a combined uncertainty factor of 200 (EFSA, 2008: p. 3). The value of 0.15 µg/kg b.w./day was then adopted as TDI.

The Committee on toxicity of chemicals in food, consumer products and the environment (COT) in the UK adopted an alternative TDI which was set on 0.300 µg/kg b.w./day (COT, 2014). The COT based their value on the same experimental study as the EFSA, which is Seacat et al. (2002). They considered the adjustment with the second uncertainty factor redundant leading to a TDI that is two times higher than the one set by the Panel on Contaminants in the Food Chain (CONTAM) of the EFSA. The TDI of 0.300 µg/kg b.w./day has for example been adopted by the Health Protection Agency (Health Protection Agency, 2012: p. 15).

Additional concerns with respect to the accuracy of the TDI are expressed in the study Brambilla (In press: p. 7) in which is claimed that the TDI of 0.15 µg/kg b.w./day might be an order of magnitude too high. This claim was substantiated by undermining the argument to base the TDI on the end

points that were used (Brambilla, In press). The NOAEL of 0.03 mg/kg b.w./day was derived using thyroid hormones disruption and reduced levels of High Density Lipoproteins in plasma as end points (Seacat et al., 2002). There are, however, other negative consequences that occur at lower daily intakes that should arguably be used as endpoints according to the study Brambilla (In press: p. 7). Examples of such effects are a deterioration in sperm quality and delayed pregnancy (Fei et al., 2009; Nordström Joensen et al., 2009). A TDI that is based on these alternative end points would then be an order of magnitude lower (Brambilla, In press). The two empirical studies that address these end points were conducted in 2009, which is one year after the TDI of 0.15 µg/kg b.w./day was set. However, the EQSs that were based on the TDI of 0.15 µg/kg b.w./day and the TDI itself have not been revised afterwards.

Table 4 presents current EQSs for surface water that were set in the study Moermond (2012) using a TDI of 0.15 µg/kg b.w./day. Table 4 presents in addition EQSs that were calculated in this study using TDIs of 0.30 µg/kg b.w./day and 0.015 µg/kg b.w./day as input. The use of a TDI of 0.30 µg/kg b.w./day results in an estimated EQS for the annual average of freshwater of 0.0013 (µg/l). The MPCs for direct ecotoxicity and secondary poisoning remain the same, because TDI is not used as input in these EQSs. Although the MPC for fish consumption by humans is increased by a factor two, it remains the lowest value and determines thereby the annual average of freshwater. The use of a TDI of 0.30 µg/kg b.w./day does not lead to a different annual average marine. The MPC for secondary poisoning using a TDI of 0.15 µg/kg b.w./day was already lower than that of fish consumption in the marine environment and remains thereby decisive for the setting of the annual average marine. TDIs have not been used to set the maximum admissible concentration for freshwater and the maximum admissible concentration marine. These are therefore not sensitive to inaccuracies or uncertainties of the used TDI.

A TDI of 0.015 µg/kg b.w./day was used to get an idea what would happen with the EQSs if a TDI was used that is one order of magnitude lower. There is, however, no scientific support that the adjusted value should be exactly ten times lower than the value than 0.15 µg/kg b.w./day which is currently in use. A TDI of 0.015 µg/kg b.w./day results in an EQS for annual average freshwater of 0.000065 (µg/l). The MPC for the consumption of fish by humans, that was already lowest, decreases ten times and remains thereby decisive for the MPC for annual average freshwater. The MPC for annual average marine would then also be set at 0.000065 (µg/l). The MPC for secondary poisoning in the marine environment remains the same and thereby exceeds the newly derived MPC for consumption of fish by humans.

Table 4: The Surface Water EQSs annual average freshwater (AA FW), annual average marine (AA M), maximum admissible concentration for freshwater (MAC FW) and maximum admissible concentration marine (MAC M) matching different TDIs.

Surface Water EQSs				
Reference	AA FW	AA M	MAC FW	MAC M
EQSs based on a TDI of 0.15 µg/kg b.w./day (Moermond et al., 2002)	0.00065 µg/l	0.00053 µg/l	36 µg/l	7.2 µg/l
EQSs adjusted for a TDI of 0.30 µg/kg b.w./day (This study)	0.0013 µg/l	0.00053 µg/l	36 µg/l	7.2 µg/l

EQSs adjusted for a TDI of 0.015 $\mu\text{g}/\text{kg b.w./day}$ (This study)	0.000065 $\mu\text{g}/\text{l}$	0.000065 $\mu\text{g}/\text{l}$	36 $\mu\text{g}/\text{l}$	7.2 $\mu\text{g}/\text{l}$
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A TDI of 0.15 $\mu\text{g}/\text{kg b.w./day}$ was also used as input for the MPC for freshwater that is intended for the production of drinking water. The use of a different TDI would therefore also influence this value. Table 5 presents the MPCs for freshwater that is intended for the production of drinking water using different TDIs. The change in the MPC for drinking water is proportional to the change in TDI.

Table 5: MPC for freshwater that is intended for the production of drinking water matching different TDIs and different contributions of drinking water to the overall daily intake.

TDI	MPC drinking water
0.15 $\mu\text{g}/\text{kg b.w./day}$	0.525 $\mu\text{g}/\text{l}$
0.30 $\mu\text{g}/\text{kg b.w./day}$	1.05 $\mu\text{g}/\text{l}$
0.015 $\mu\text{g}/\text{kg b.w./day}$	0.0525 $\mu\text{g}/\text{l}$

Figure 10, Figure 11 and Figure 12 are elaborations on Figure 2 and Figure 9. EQSs that are adjusted for different TDIs are presented in addition. Figure 10 demonstrates that all PFOS concentrations that were observed in the Rhine at Lobith, the Lek Canal at Nieuwegein and the Amsterdam-Rhine Canal at Nieuwersluis still clearly exceed EQSs for fish consumption that are adjusted for different TDIs and are all close to the x-axis. All these concentrations are still below the EQS for freshwater that is intended for the production of drinking water that is adjusted for a TDI of 0.015 $\mu\text{g}/\text{kg b.w./day}$, as is visible in Figure 11. The difference between the observed concentrations and the adjusted EQS is however much smaller. The observed groundwater concentrations remain below the EQS for freshwater that is intended for the production of drinking water that is adjusted for a TDI of 0.015 $\mu\text{g}/\text{kg b.w./day}$ as well, as Figure 12 shows. The difference is again much smaller.

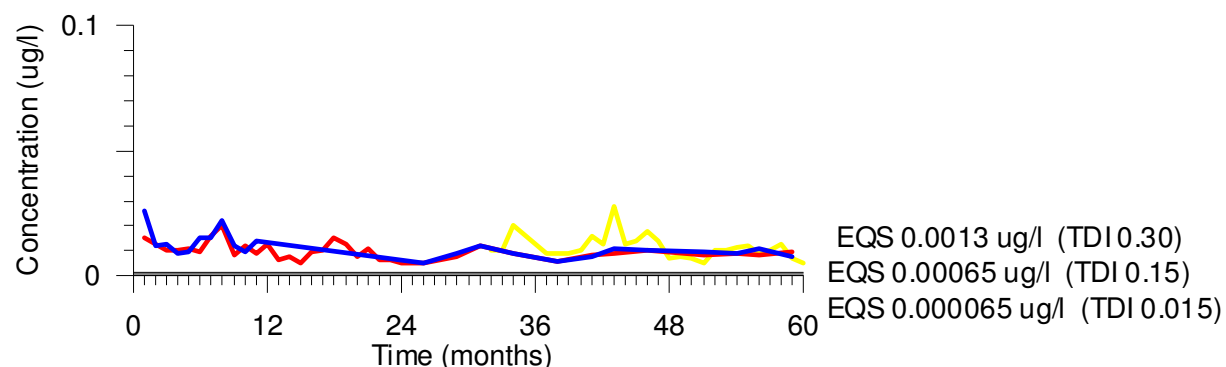


Figure 10: Monthly average PFOS concentrations ($\mu\text{g}/\text{l}$) of surface water derived from the Rhine at Lobith (yellow), the Lek Canal at Nieuwegein (red) and the Amsterdam-Rhine Canal at Nieuwersluis (blue), within the interval January 2006, the first month, until December 2010, the 60th month, compared with the EQS for fish consumption, which is 0.00065, and adjusted EQSs using TDIs of 0.30 and 0.015, which are 0.0013 and 0.000065. The data were obtained from RIWA (2006), RIWA (2007), RIWA (2008), RIWA (2009) and RIWA (2010).

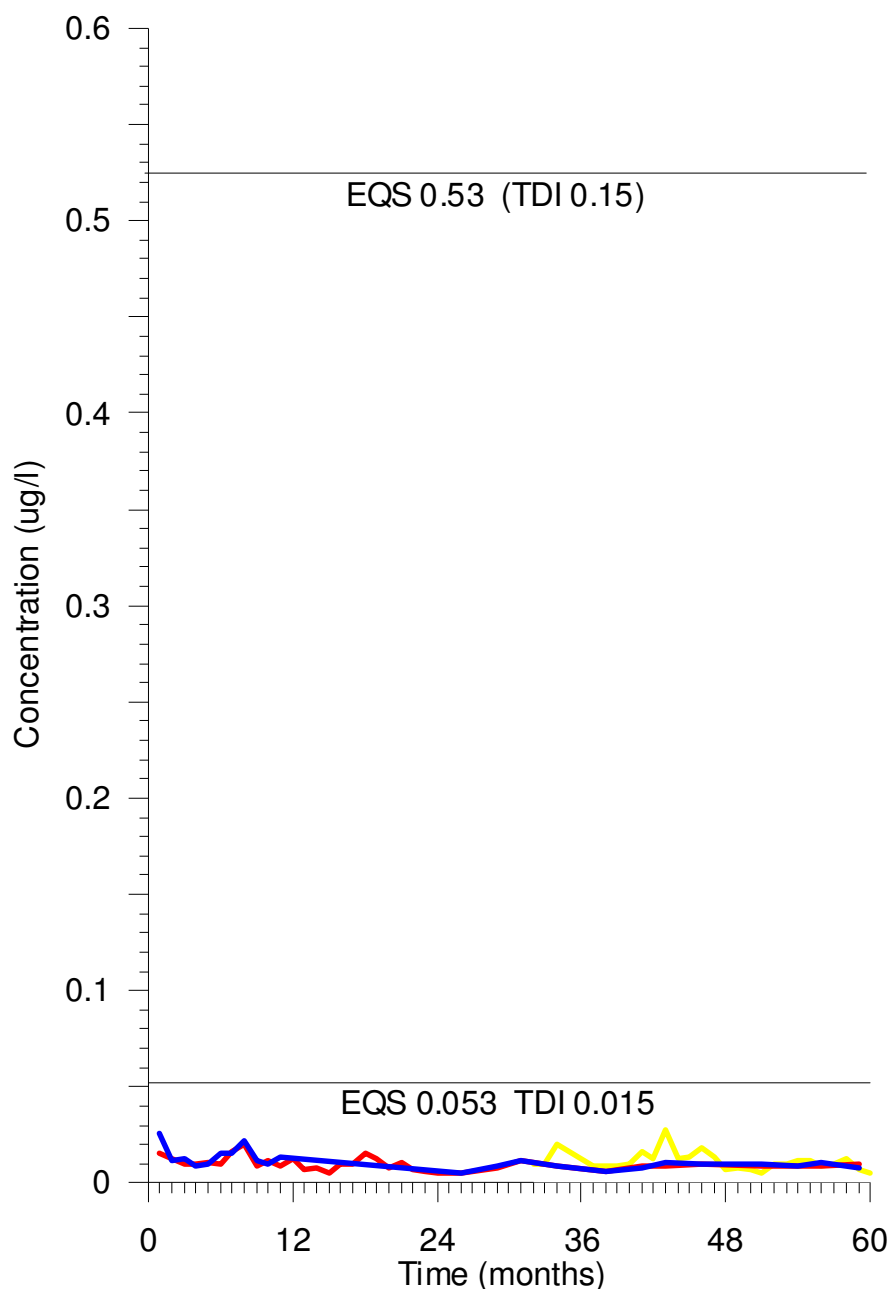


Figure 11: Monthly average PFOS concentrations ($\mu\text{g/l}$) of water derived from the Rhine at Lobith (yellow), the Lek Canal at Nieuwegein (red) and the Amsterdam-Rhine Canal at Nieuwersluis (blue), within the interval January 2006, the first month, until December 2010, the 60th month, compared with EQSs for surface water intended for drinking water production considering for a TDI of 0.015, which is $0.53 \mu\text{g/l}$, and adjusted for a TDI of 0.015, which is $0.053 \mu\text{g/l}$. The data were obtained from RIWA (2006), RIWA (2007), RIWA (2008), RIWA (2009) and RIWA (2010).

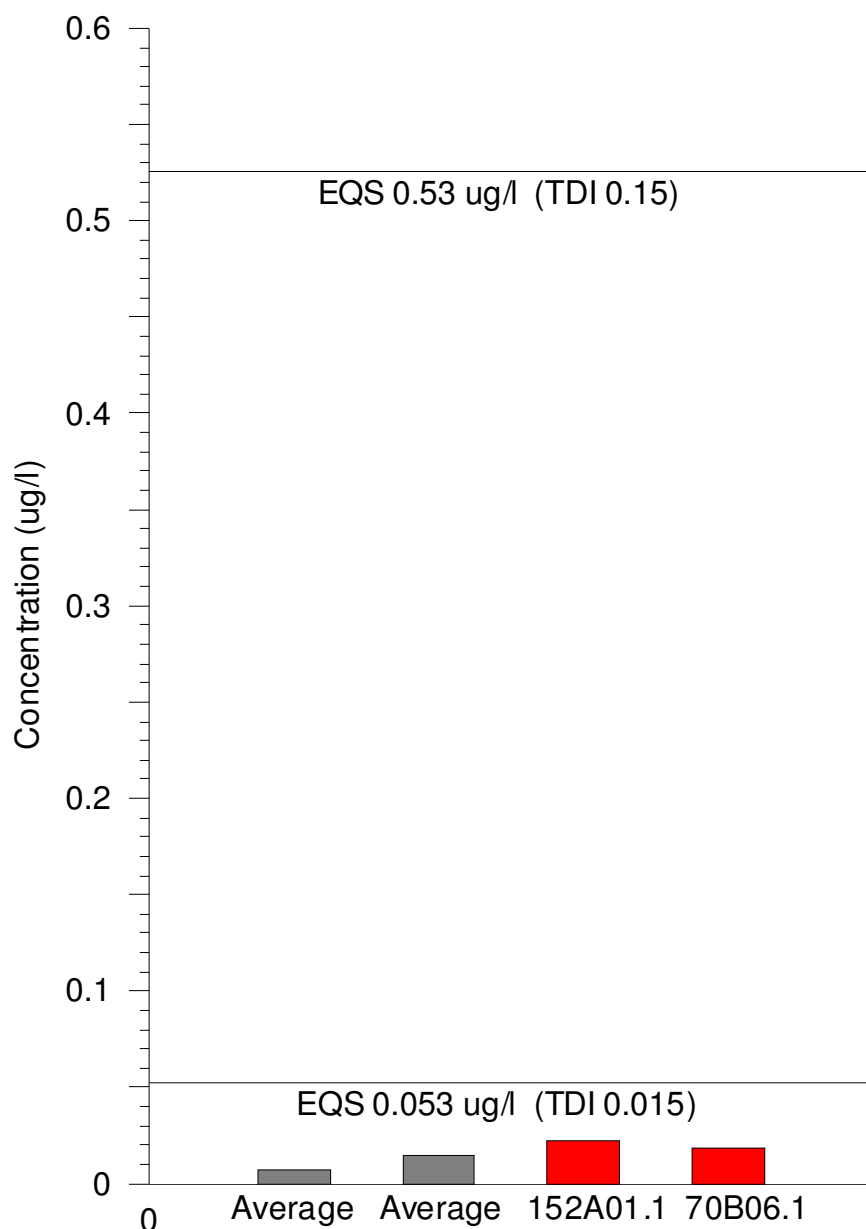


Figure 12: Comparison between average groundwater concentrations reported in the studies Noorlander et al. (2010: p. 5) and Kwadijk et al. (2008) (grey bars) and observed groundwater concentrations (red bars) with EQSs for surface water intended for drinking water production considering different TDIs (horizontal line).

5.3 Related fluorinated chemicals

Negative consequences on the environment and human health do not occur as the sole consequence of the intake of PFOS. They are caused by the combined influence of a number of related fluorinated chemicals. PFOS has however frequently been considered separately from other chemicals in scientific studies and policy making.

Related fluorinated chemicals are likely to have a similar impact on the environment and human health which has not been taken into account while setting EQSs. The linear isomer of PFOS accounts for about 70 % of the total amount of PFOS as it has been produced by 3M (Benshkin et al., 2010: p. 121). The branched isomers may have a different mobility and persistency in the environment and

might have different characteristics with respect to bioaccumulation and biomagnification. The ratio between isomers in the environment does therefore not necessarily have to be same as the ratio in which the isomers were produced. Moreover, the ratio by which the isomers are being made might also be different for different producers.

PFOS is only one of fourteen perfluoroalkylated and polyfluoroalkylated substances (PFAS) which concentrations were presented in the study Noorlander et al. (2010). The others are PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTrA, PFTeA, PFBS and PFHxS (Noorlander et al., 2010: p. 9; Buck et al., 2011). PFOS has for example been replaced by Pentafluorobenzoic acid (PFBA) and Perfluorobutanesulfonic acid (PFBS) (RIWA, 2010: 27). The concentrations of the other PFAS are as a rule of the same order of magnitude or one or occasional two orders of magnitude lower than that of PFOS (Noorlander, 2010: p. 9).

Fluorinated chemicals related to PFOS also include transformation products in which one or more of the fluor atoms are substituted by hydrogen atoms. 1h,1h;2h,2h-PFOS differs from PFOS because two hydrogen atoms are attached to each of the two carbon atoms that are closest to the sulfur atom. The monthly concentrations of 1h,1h;2h,2h-PFOS of water at different locations in the river Rhine were analysed by the RIWA (eg. 2010). Figure 13 depicts monthly average concentrations in the Rhine at Lobith, in the Lek Canal at Nieuwegein, in the Amsterdam-Rhine Canal at Nieuwersluis and in the Lake IJssel at Andijk. The observed concentrations of 1h,1h;2h,2h-PFOS tend to be lower than those of PFOS.

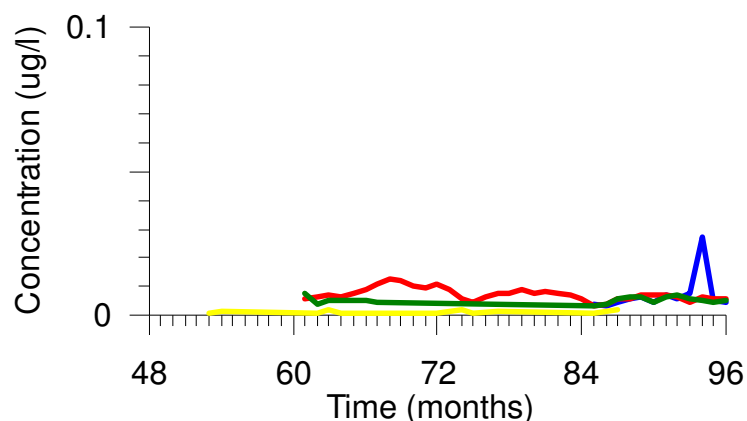


Figure 13: Monthly average concentrations of 1h,1h;2h,2h-PFOS, a transformation product of PFOS, in water derived from the Rhine at Lobith (yellow), Lek Canal at Nieuwegein (red), Amsterdam-Rhine Canal at Nieuwersluis (blue) and the Lake IJssel at Andijk (green), within the interval January 2010, the 49th month, until December 2013, the 96th month. The data were obtained from RIWA (2010), RIWA (2011), RIWA (2012), RIWA (2013).

Notable are the concentrations that were observed at Lobith. These are an order of magnitude lower than those that were observed at the other locations. Because of this, it could be conclusively stated that point sources in Germany are not the only or main source of 1h,1h;2h,2h-PFOS for Dutch rivers. The graph that represents concentrations of 1h,1h;2h,2h-PFOS that were observed in Lek Canal at Nieuwegein shows seasonality, similar to the PFOS concentrations that were observed at the same location. The low and relatively stable concentrations of Lake IJssel at Andijk rise to a level that is similar to that of Lek Canal at Nieuwegein and Amsterdam-Rhine Canal at Nieuwersluis in March

2013. This increase is remarkable when considering this value to represent the Lake IJssel in its entirety. This would mean an increase in 1h,1h;2h,2h-PFOS content of about 18 ton from January 2013 until April 2013. The observed concentrations in Lake IJssel at Andijk do therefore likely not represent the entire lake IJssel since this amount is excessively high.

Another notable feature is the peak concentration that occurred in Amsterdam-Rhine Canal at Nieuwersluis in October 2013. A similar signal is not visible in graphs that represent concentrations at any of the other locations. It is therefore likely that a sizeable quantity of 1h,1h;2h,2h-PFOS was discharged at a location from which Amsterdam-Rhine Canal at Nieuwersluis could be reached without affecting the other signals significantly. This location lies then between the Amsterdam-Rhine Canal between Nieuwegein and Nieuwersluis. The discharge could be considered an incident because only one observation displays an increased value.

It is not clear what the combined effect of all these chemicals is and how TDIs and EQSs should be adjusted for it.

5.4 Contribution of drinking water

There is an additional element of uncertainty in the derivation of the MPC for freshwater that is intended for the production of drinking water. This value was based while considering a contribution of drinking water of 10 % to the total daily intake (Moermond, 2010: p. 34). This value could however be considered an underestimation. The actual contribution of water to the total daily intake of PFOS was set at 33 % based on the data that were presented in the study Noorlander et al. (2010: p. 12). Using a contribution of 33 % instead of 10 % makes the EQS for freshwater that is intended for the production of drinking water 3.3 times less tight than the value that is currently set.

The value of 33 % from the study Noorlander et al. (2010) was calculated by multiplying the amount of product from various food categories with the PFOS concentration per food category. The outcome was then equated with the daily intake. The MPC for freshwater that is intended for the production of drinking water was set while considering a daily intake of 2 l of water. However, a number of people might clearly exceed this amount. Their actual intake might therefore exceed the TDI even though this should not be the case considering the PFOS concentration in drinking water. Setting the aim to prevent people that drink 4 l of water daily to exceed the TDI leads to a tighter EQS for freshwater that is intended for the production of drinking water of two times.

The two adjustments that are mentioned in this section level each other more or less out while applying them both. However, the adjustments with respect to TDI and related fluorinated chemicals that could be justified for considering the two previous sections are both an order of magnitude and therefore far more decisive than all other adjustments. In case it is decided to adjust EQSs, these two adjustments should be considered in the first place. Otherwise it does not make any sense to consider other adjustments.

5.5 Contribution of fish consumption

The EQS for surface water was calculated while considering an average daily freshwater fish consumption of 115 gram per person which is much higher than what most people usually eat

(Moermond, 2010: p. 3). However, some people eat actually this much. Therefore, an average daily freshwater fish consumption of 115 gram per person was taken into account to prevent these people from exceeding the TDI. These people are likely to consume less of other sources of food. The intake of PFOS by fish consumption would then replace PFOS consumption that would otherwise have taken place by the consumption of other food sources.

The study Noorlander et al. (2010: p. 9) demonstrates that the PFOS concentration of Crustaceans, which is 0.582 µg/kg, is approximately two times higher than the reported concentration of lean fish, which is 0.308 µg/kg, and approximately ten times higher than that of fatty fish, which is 0.061 µg/kg. The PFOS concentrations of the twelve other considered food categories were all comparable or one order of magnitude lower than that of fatty fish (Noorlander et al., 2010). The replacement of fish by other food sources leads therefore not necessarily to a decline in intake of PFOS.

While setting EQSs, the contribution of fish consumption to the overall intake of PFOS is supposed to be limited to 10 %, like the contribution of drinking water which was also assumed to be 10 % (Moermond, 2010: p. 23). The study Noorlander et al. (2010: p. 12) confirms that this turned out to be a very accurate approximation. The contribution was actually estimated at 10 % in this study (Noorlander et al., 2010: p. 12).

5.6 Actual daily intake

The total intake of PFOS takes place through ingestion, inhalation and skin contact (US EPA, 2012: p. 3). The first pathway is however usually the only pathway that is considered in studies concerning the TDI, EQSs and in calculations concerning the actual intake of PFOS. The consideration of these other pathways would lead to a decrease in EQSs that are concerned with human health.

5.7 Potential sources

The case study confirms that PFOS is present in groundwater. The number of analysed groundwater samples appears to be too small to give decisive statements on the nature of locations that are particularly susceptible to have high PFOS concentrations. The proximity to potential sources was in this study considered, like in previous studies on PFOS, a major influence on the PFOS concentrations at a location. It could not be confirmed that the PFOS concentrations in groundwater from the monitoring wells that were considered are higher than at locations that are more remote from PFOS sources.

It is also uncertain why PFOS concentrations that exceed the limit of quantification were observed near the potential sources fire fighting department Emmer-Compascuum and Industrial park Coevorden and not in groundwater near other fire fighting departments or other industrial parks. Unfortunately, the limit of quantification of the method used was relatively high and did not allow further conclusions. In case of Industrial park Coevorden it does remain unclear what type of factories may have contributed to the presence of PFOS.

It was noted that both potential sources that were allocated to the groundwater samples with PFOS concentrations that exceed the limit of quantification are located on peat. This might very well be just a coincidence because only two soil types were considered. The pathways between most

potential sources and monitoring wells are through both sand and peat. The actual influence of soil type is therefore not as black and white as is suggested by Table 3.

It remains also unclear what the influence is of depth and distance between potential sources and measuring wells. Both PFOS concentrations were observed at a depth of 4 m. However, other samples were taken at similar depths and did not have PFOS concentrations above the limit of quantification. The distance between the monitoring wells and the potential sources they were allocated to, are 400 m and 600 m. These distances also occur between other potential sources and measuring wells.

It should be noted that both samples with PFOS concentrations that exceed the limit of quantification were taken near streams. These streams might have had a role in the increased PFOS concentrations at these locations and therefore in the distribution of PFOS in general. In case of the sample taken from measuring well 70B06.1 a stream actually flows between the potential source and the measuring well. The groundwater flow from the potential source to the measuring well was thereby likely to be interrupted. In this case, the stream might have brought PFOS to the location of the measuring well. However, the measuring well might also be influenced by PFOS from sources from the industrial park on which it is located that have not been identified. The role of streams in the distribution of PFOS is therefore not confirmed.

The causality between the potential sources and the observed concentrations in the monitoring wells could be further analysed in future studies by placing additional monitoring wells to sample groundwater. These could then for instance be placed between the potential source and the monitoring well, behind the monitoring well and upstream from the potential source.

Chapter 6 Conclusion

This thesis addressed the research question: to what extent is PFOS present throughout the environment and what are the threats to the environment and human health? It was concluded from both a review of current literature and from a survey of PFOS in groundwater monitoring wells that PFOS is present in many environmental media and compartments in the Netherlands, including ground and surface water, biota and soil. PFOS is present in ground and surface water with concentrations in the order of 10 ng/l. Concentrations in biota, mainly fish, were reported in the range from the order of magnitude of 1 ng/l to over 1000 ng/l. Concentrations in soils are present in a large range from the order of magnitude of 1 ng/l to concentrations of over 10000 ng/l. The observed PFOS concentrations of two out of nineteen groundwater samples, that were taken in the province of Drenthe and were analysed as a case study, exceeded the limit of quantification of 10 ng/l and were 19 ng/l and 25 ng/l.

The EQS for surface water for fish consumption of 0.65 ng/l that was set in 2010 was thereby consequently exceeded. The EQS for freshwater that is intended for the production of drinking water, which is 0.53 µg/l and also set in 2010, was on the other hand not approached by any of the observed water concentrations.

However, the comparison between observed concentrations and EQSs is insufficient to convincingly assess threats to the environment and human health. The adequacy of the EQSs is challenged by various assumptions and uncertainties. Adjustments should arguably be made with respect to the considered TDI, the possible impact of related fluorinated chemicals, the contribution of drinking water, the contribution of fish consumption and the actual intake of PFOS. Adjusting the EQSs with respect to the TDI and the impact of related fluorinated chemicals would lead to tighter EQSs that were set to protect human health of an order of magnitude in case of both adjustments.

A revision of EQSs with respect to the suggested adjustments is essential to give a conclusive answer on whether or not the presence of PFOS in the environment is an actual threat to the environment and human health. The implementation of these adjustments would logically lead to the consideration of certain concentrations as threats that are well below current EQSs because they exceed the adjusted EQSs. These include the vast majority of ground and surface water concentrations in the Netherlands.

The proximity to sources appears to determine the PFOS concentrations in the first place. PFOS concentrations that are threats to the environment and human health can therefore be expected in the proximity of PFOS sources as well. Other criteria include the properties of soil and lithology to obstruct PFOS from reaching a given location. The proximity to streams might be an important factor in the distribution of PFOS. This contradicts with the consideration of groundwater flow as the primary distributor of PFOS in groundwater.

Acknowledgements

I would like to thank Witteveen+Bos for offering me the opportunity to do my internship at their company within the framework of Expertisecentrum PFOS, which is a collaboration between Witteveen+Bos and TTE Consultants. In particular, I would like to thank Martijn van Houten of Witteveen+Bos who was my daily supervisor during my internship at Witteveen+Bos and Arne Alphenaar of TTE Consultants. We discussed the progress of my thesis in weekly meetings together with Ingrid Rijk of Witteveen+Bos, initially, and Corrine Koot of Witteveen+Bos, later on. They provided me with adequate literature suggestions on PFOS to support this study, guidance on how to conduct this study adequately and helpful advice on how to improve draft versions of this thesis. I would like to thank them and Martin Heuver of Witteveen+Bos who helped with the execution of the spatial analysis. The case study in Drenthe was also executed on the initiative of Expertisecentrum PFOS that found Alex Scheper of the province of Drenthe interested to collaborate in a study on PFOS. I would like to thank Dick Vethaak of the IVM of the VU Amsterdam and Bert van Hattum of the IVM of the VU Amsterdam. They were VU-Supervisor and second assessor during my internship and gave me feedback on the draft versions of my thesis to improve and finish the document.

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