Perfluoroalkyl acids in drinking water: Sources, fate and removal
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Chapter 8  Synthesis and outlook

The work performed and presented in the preceding chapters had as common identifier the behavior of PFAAs in the drinking water production cycle environment.

8.1 Synthesis

Research question 1:  
To what extent are PFAAs present in the raw water sources used for drinking water production and what are the source of these compounds?

The literature review performed in Chapter 2 and the work performed in all the chapters of this thesis showed that PFAAs, and especially PFOA and PFOS, are present at a base level in the low ng per liter range in most water sources used for the production of drinking water. The literature shows that the majority of the work was and is still focussed on PFOA and PFOS only, while short chain PFAAs often are not analyzed. It was observed that in the case of an environmental spill (use of aqueous film forming foams at an airport or contaminated sludge on agricultural land) or a point source (wastewater treatment plant, factory), surface water or groundwater concentrations can increase dramatically. Central and Southern European rivers such as the rivers Po, Rhine and Seine appear to be the major rivers in Europe discharging PFAAs into the oceans. The PFAAs of highest interest are PFOA and PFOS, however, as a result of substitution of C7-C8 chemistry by C3-C4 perfluorinated and polyfluorinated telomer compounds, the concentrations of the substitutes or their metabolites have been shown to increase in the environment. This was observed in the surface water samples analyzed in this thesis (Chapter 4), but also in the surface water monitoring results of the Dutch government and several other scientific publications (e.g. Moeller et al., 2010). Unfortunately, PFBA and PFBS still are monitored only scarcely thus far. The work performed in this thesis shows that these short chain PFAAs are not removed during water treatment and therefore are a problem for drinking water companies that use surface waters as a source of water.

In all groundwater samples analyzed in this thesis, concentrations were usually much lower than those observed in surface waters. However, still little information on groundwater concentrations of PFAAs is available in the literature. While surface water treatment for the production of drinking water in the Netherlands is very thorough and will remove PFAAs to a large extent, groundwater treatment is usually much simpler (e.g. aeration, rapid sand filtration). In the case of an unknown contamination of the groundwater this can lead to high concentrations in drinking water so that occasionally the existing German provisional guideline value (300 ng/L for the sum of PFOA and PFOS) can be exceeded. It was shown that point sources such as a fire fighting practice areas (especially near airports), and former landfills (Chapter 3) can be important sources of PFAAs to groundwater. However, their impact on overall water quality will often be low due to strong dilution in the extracted water and long travel times in the aquifer such as shown in Chapter 3. The results from the present study show that groundwater bodies may become contaminated by PFAAs from different sources. Overall, the allocation of sources of PFAAs in groundwater is complicated due to the simultaneous processes occurring such as sorption, degradation, formation from precursors, changes in emissions
and input over time (Chapter 4). The coupling of PFAA concentrations to different inorganic and organic tracers was shown to be successful in identifying origin and processes affecting concentrations. It was observed several times (Chapters 3 and 4) that infiltrated rainwater can be contaminated with PFAAs and this can be a source of diffuse background contamination observed in drinking water prepared from groundwater. PFAAs observed in infiltrated rainwater are likely to originate from atmospheric transport of precursors. The relative importance of groundwater contamination compared to surface water contamination with respect to overall contamination of drinking water is hard to assess since little monitoring data are available. The fact that little information is available on PFAAs concentrations in groundwater compared to surface water is disproportional since 60% of the Dutch drinking water is produced from groundwater.

In cases where groundwater appeared to be contaminated with PFAAs, the mitigation approach has been either to mix the water with clean water or to shut production wells from contaminated locations. In the Netherlands only, more than 1000 former landfills exist of which 50 in the vicinity of groundwater abstraction areas. Virtually no monitoring data are available on the presence of PFAAs in drinking water produced from these locations. Large scale monitoring would seem appropriate in order to gain more knowledge on the contamination of drinking water produced from groundwater from these abstraction areas.

As for the Dutch drinking water practice, margins to existing guideline values that have been shown to be approached in heavily contaminated areas (such as the Moehne area reported by Skutlarek et al., 2006) (Schriks et al., 2010) are sufficiently large in the case of PFOA and PFOS in the groundwater abstraction areas sampled in this thesis.

Research question 2:
What is the influence of the drinking water production process and beverage production processes on the PFAAs present in the raw drinking water?

The work in this thesis showed that concentrations of different PFAAs in surface waters correlate well to the corresponding drinking water concentrations, indicating that the removal of certain PFAAs was unsatisfactory. This was also observed in other parts of the world such as Japan, America and Australia as shown in scientific publications (e.g. Takagi et al., 2008; Quinones and Snyder, 2009; Thompson et al., 2011). The experimental studies performed in the literature focus in general on the removal of PFOA and/or PFOS only, not investigating the short chain PFAAs such as PFBA or PFPA. The work in this thesis shows that short chain PFAAs need to be included in future studies. Sampling campaigns and experiments performed in this thesis showed that behavior of PFAA throughout drinking water treatment is varying for the different homologues investigated. The results in Chapter 5 show that most treatment steps in the purification process (coagulation, pellet softening, sand filtration, ozonation, slow sand filtration) do not remove PFAAs. Longer chain PFAAs such as PFOS and PFNA will be readily removed with GAC while the shorter chain PFAAs such as PFHxA, PFBA and PFBS will not or only partly be removed. A decreasing removal capacity of the GAC was observed with increasing carbon loading and with decreasing carbon chain length of the PFAAs creating an enrichment of short chain PFAA in drinking water. It is expected that PFBS and PFHxA will be-
come more abundant in Europe in the future as they are slowly replacing C7-C8 chemistry as a result of reductions in emissions and production volumes of PFOA and PFOS due to voluntary phase out, legal restrictions and emission reduction programs. PFAA removal efficiencies of the individual GAC filters were shown to depend on the age of the applied carbon filters. Branched isomers of PFOA and PFOS were removed to a lesser extent than non-branched isomers, creating an enrichment of the branched PFOS and PFOA in the drinking water.

In a broader context it is generally observed that little removal of the PFAAs present in raw water occurs. Exceptions being treatment plants where the GAC was refreshed shortly before sampling or treatment plants where a Membrane system was used. However, membrane filtration is not often used due to the high operational costs in general (fouling of the membranes, disposal of the brine and electricity). In contaminated areas remediation of the water quality often consists of the placement of activated carbon filters, which are regenerated more often than in non-contaminated areas.

The results from Chapter 6 demonstrate that the level of contamination by PFAAs of water based beverages depends on the contamination level of the ingredients used. The most important contribution is the source water itself. This means that for areas where surface water is used for drinking water production the chances of a higher beverage contamination will be larger than in an area where groundwater is used for the drinking water production. Leaching experiments with different fluorine containing polymeric tubing materialsshowed that the absolute contribution from leaching out of the three polymers tested to the total amount of PFAAs in the drink will be very low. Consequently, in the assessment of human exposure of PFAAs via the diet it is important to take into account the contribution from tap-water based beverages.

**Research question 3:**

*How can the removal of PFAAs from drinking water be optimized based on the basis of the physical-chemical characteristics of PFAAs?*

In Chapter 5 it was shown that short chain PFAAs, e.g. PFBA, PFPeA and PFHxA are often not removed from drinking water. Adsorbent materials where selected on the basis of the physicochemical properties of the PFAAs (hydrophobic tail and the hydrophilic charged head). It was shown that materials consisting of a large number of anion exchange sites (e.g. positively charged N-atoms) and an apolar matrix are well suited for the removal of short chain PFAAs and are thermodynamically favourable. Hydrophobic adsorbents have a less favourable free energy of adsorption for PFBA and PFPeA than WAX and MAX indicating that for the removal of the short chain PFAAs anion exchangers will be much better suited than hydrophobic materials such as activated carbon, however due to the high price its use in the short term future is still unlikely. It was shown that the sorption process was predominantly governed by the interaction between head group and sorbent, and the tail and sorbent. The adsorbentia investigated possibly can be used for other negatively charged polar compounds such as ibuprofen which are increasingly present in surface waters used for drinking water production.
8.2 Outlook

In order to answer the “so what” question and understand the relative importance of the presence of PFAAs in drinking water, overall human exposure combined with a human risk assessment has to be taken into account. As shown in the literature (e.g. Domingo, 2012; Vestergren and Cousins, 2009; Haug et al., 2010), human exposure to PFAAs is dominated by dietary intake. Fish and meat are two important diet constituents for the longer chain PFAAs: PFOS and longer for the sulfonates and PFNA and longer for the carboxylates (e.g. Vestergren et al., 2012 and Haug et al., 2010). However, to complicate matters, it was shown that exposure can vary significantly from region to region and between the different PFAAs (Haug et al., 2010; Vestergren et al., 2012; Perfood, 2013). Concerning the human exposure via drinking water, overall PFOA and PFOS exposure in areas with background contaminated drinking water will be low (Vestergren et al, 2012), and only become a problem with elevated concentrations (e.g. hotspots) (Perfood, 2013). However, in the case of short chain PFAAs a different scenario can be expected. The increased polarity of the short chain PFAAs will cause these to be present to a lesser extent in dietary items (than meat and fish) and to a larger extent in water. Indeed it was shown that human exposure to PFHxA, PFHpA and PFHxS is originating from drinking water to a much larger extent than PFOA and PFOS (Vestergren et al., 2012). Concerning the human risk assessment, margins to Tolerable Daily Intake (TDI) values, which are only available for PFOA and PFOS (EFSA, 2008), remain large. On this basis one could conclude that further monitoring of the presence of PFAAs in drinking water in areas not suspected of PFAAs contamination is not necessary.

However, these conclusions are based on the TDI values derived from extensive laboratory studies on the toxicology of PFOA and PFOS to rats and monkeys (EFSA, 2008). Observed end-points are amongst others enlargement of the liver, thyroid adenomas, and immunotoxic effects. It is not the scope of this work to discuss the modes of action of PFOA and PFOS; for details see the review by Lau et al. (2007). Extrapolation of toxicological data obtained from animal laboratory experiments to risks posed to humans in the form of a TDI is complicated by the large variation (Melzer and co-workers, 2010) of the toxicokinetic profile between species (see also section 1.5: half-lives). The large discrepancy between species is also illustrated by the large difference between environmental quality standards for PFOS (0.65 ng/L) and current drinking water guideline values (300 ng/L for sum PFOS and PFOA in Germany for example). Epidemiological studies, which seek relations between concentrations of PFOA and/or PFOS and observed/reported pathologies, provide a direct relationship between PFAAs exposure and human pathologies. Several studies are described in the literature where PFOA or PFOS exposure in cohorts (occupationally or geographically due to a hotspot area) is related to pathologies such as thyroid diseases (Melzer et al., 2010), reduced semen quality (Vested et al., 2013), immunotoxicity (Grandjean and Budtz-Jørgensen, 2013) or liver function biomarkers (Gallo et al., 2012). Interestingly, the study performed by Grandjean and Budtz-Jørgensen (2013), with a cohort of children exposed to background levels, shows that a benchmark dose response of 5% corresponded to benchmark dose levels in serum of 1.3 ng/mL for PFOS and 0.3 ng/mL for PFOA. This level for PFOA is low compared to average PFOA serum concentrations of 2-8 ng/mL (Post et al., 2012). Drinking

20 “The concentration of a substance that is associated with an incidence of risk/effect of 5%” taken from http://www.epa.gov/ncea/bmds/bmds_training/appendices/glossary.htm#bmd
water exposure limits derived from these data by Grandjean and Budtz-Jørgensen (2013) show that current drinking water guideline values can be several hundred fold too high and therefore need to be revised. Indeed, when one takes into account an approximate 100:1 ratio between serum and water concentrations (see Introduction 1.5) and one uses these to derive drinking water levels (assuming a 20% exposure contribution from drinking water instead of 100% as was used by Grandjean and Budtz-Jørgensen (2013)), from the benchmark dose level of 0.3 ng/mL in serum a drinking water value of 15 ng/L can be calculated for PFOA.

As for the short chain PFAAs only one provisional drinking water guideline value has been derived for PFBA so far (Wilhelm et al., 2010). This value of 7-8.5 μg/L was derived on the basis of the toxicokinetics of PFBA in the human body and in Cynomolgus monkeys. These values are 20-25 times higher than the proposed drinking water guideline of PFOA. Grandjean and Budtz-Jørgensen (2013) proposed a safe level in drinking water of PFOA of 15 ng/L. If we use the same factor of 20-25, a provisional guideline value of 300 to 375 ng/L would result for PFBA, which is considerably lower than the value proposed by Wilhelm et al. (2010). Although it is generally believed that the toxicity of PFAAs is chain-length dependent (e.g. Olsen et al., 2009; Bijland et al., 2011), recent publications do show that for short and long chain PFAAs different modes of action may be relevant (Naile et al., 2012).

Regarding i) The uncertainties associated with PFAAs toxicology and the corresponding drinking water guideline values derived; ii) PFAAs being recalcitrant in drinking water treatment; and iii) monitoring results of PFAAs in drinking water sometimes approaching these provisional guideline values, it is recommended to include the regular determination of PFAAs, in particular short chain PFAAs, in national monitoring programs.