

Concentration profiles of perfluorinated organic compounds in groundwater bodies influenced by rainwater or infiltrated river water in The Netherlands

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Abstract

Perfluorinated compounds were determined, using SPE and LC-MS/MS, in groundwater samples collected in a dune area from aquifers consisting of rainwater and infiltrated river water, respectively. Concentrations of the most dominant PFCs amount to 1-10 ng/L in the rainwater aquifer and 2-26 ng/L in the river water aquifer. Abundance profiles of PFCs were significantly different in the two aquifers. While PFBS was the dominant PFC in the infiltrated water aquifer, PFOA and PFHxS were dominating in the rainwater aquifer. In a transect sampled in the infiltrated water aquifer trends were observed that probably reflect past and recent emissions of PFCs. The results show that depending on the source of the groundwater in the aquifer - atmospheric or riverine - different abundance profiles of PFCs in groundwaters can be observed. Concentrations of total PFCs in rainwater dominated aquifers are significantly lower than those in aquifers that are influenced by river water.

Introduction

The occurrence of PFCs in surface waters that are used for drinking water production and consumption can be an important exposure pathway for humans. In a study in a contaminated area in Germany PFCs were measured in water prepared from river water high levels of PFCs were found in drinking water, e.g., 22 - 519 ng/L (PFOA) and 3 - 22 ng/L (PFOS). In this case PFC concentrations detected in water supplies prepared with riverbank filtration and artificial recharge did not significantly differ from those detected in the surface waters¹. In another study concentrations of different PFCs found in lake Maggiore in Italy were almost identical to the concentrations in the tap water from the same area. Rainwater in the same area contained even higher amounts of PFCs than in the lake and feeding river water did not contain PFCs suggesting that a major route of PFCs is from atmospheric sources². Dutch drinking water resources are known to contain PFCs³, from non detect to 43 ng/L. Little is known about the behavior of these compounds in the drinking water preparation cycle. The dune areas of the Netherlands provide an opportunity to study the behavior of PFCs after the artificial infiltration of river water in the dunes, as well as from atmospheric deposition of PFCs by analyzing rainwater lenses. Both water bodies can be sampled by varying the sampling depth. The present study compares results of the analysis of groundwater present in the dunes originating from both types of sources.

Water analysis.

Sampling. Samples were taken from the infiltration channel, and from wells along a transect (in which the water has a travel time of 18yr) at infiltrated river water depth and rainwater lens depth, and finally from the drain channel. Figure 1 shows a cross sectional view of the groundwater bodies and the location of the wells in the dune area. The groundwater wells are equipped with a series of mini-filters at regular intervals enabling the sampling of water at different depths. Samples were taken in one liter glass bottles and transported to the laboratory for analysis.

Analysis. Briefly, in the laboratory, approximately 100 ml of the water sample was carefully weighed in an Erlenmeyer flask. The internal standards were subsequently added to the water sample: (40 µl of a PFC mixture standard containing approx. 160 µg/l ¹³C of PFacids and PFsulfonates). C18 SPE cartridges were conditioned by eluting with 10 ml of methanol and 10 ml of nanopure water, respectively. The water sample was transferred to the column and the effluent was discarded. The cartridge was subsequently dried under a gentle N₂ flow. The SPE cartridge was desorbed with 10 ml of methanol in a 30 ml PP tube (pre-rinsed with methanol). The solution was placed on a water bath at 45 °C and evaporated to a volume of 1ml under a constant N₂ flow. The residue was diluted in 500 µl of methanol. Finally, the solution was filtered through an Acrodisc LC 13 GHPPall into a 2 ml

vial. The PP tube was washed with 500 μL methanol and this was also added to the vial (after filtration). The samples were stored at 4 $^{\circ}\text{C}$ prior to analysis.

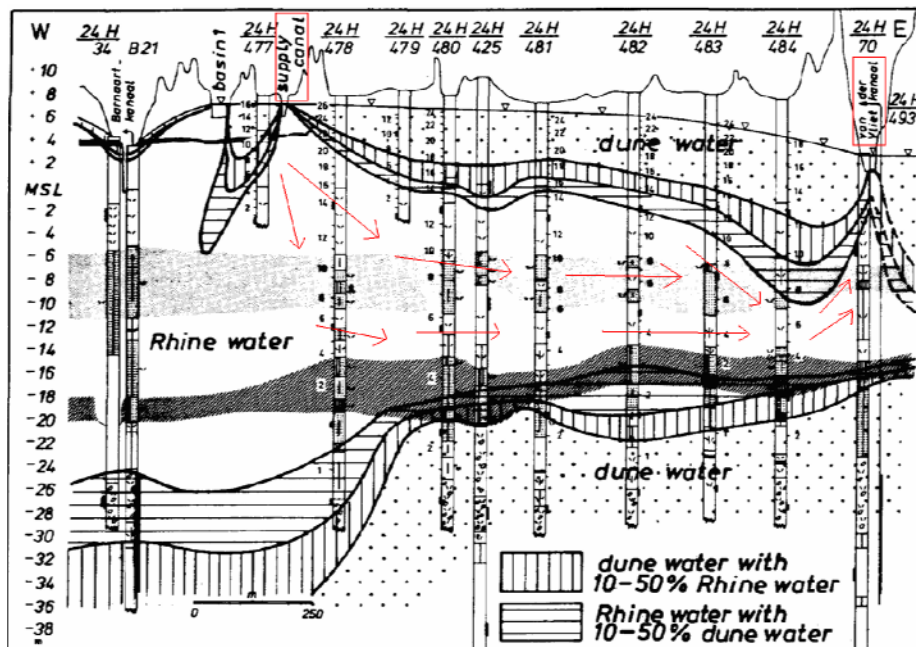


Figure 1. Schematic cross section along the dune transect sampled in this study (note difference in horizontal and vertical scales: full scale = $\sim 1500\text{m} \times \sim 50\text{m}$). A more or less stationary rain water lens floats on top of infiltrated river Rhine water. Deep dune water is being displaced by Rhine water. The red arrows show the water flow direction and the red boxes indicate supply and drainage channels. Groundwater wells used for sampling are indicated by numbered and lettered codes and vertical bore holes (not on scale). From each well samples were collected at different depths so as to obtain water from different groundwater bodies. Adapted from ref 4.

Sample analysis by LC-MS/MS. The PFCs were analysed by injecting a volume of 20 μL into a high performance liquid chromatography (HPLC) system consisting of a Shimadzu pump (LC-20AD), autosampler (SIL-20A), and system controller (SCL-10A VP). An ACE 3 C18 column (ID 2.1 mm; length 150 mm) with a particle diameter of 3 μm was used for the separation and was held at a temperature of 30 $^{\circ}\text{C}$ in a column oven (CTO-20AC). The pre-column used for lowering the background of PFCs from the system was a Pathfinder 300 PS C18 (ID 4.6 mm; length 50 mm) with a particle diameter of 3.5 μm placed before the injection valve. Gradient elution with a flow of 0.2 ml/min. was applied with the following solvent composition: A 95:5 methanol:water and B 40:60 methanol:water (both with 5 mM ammonium acetate). After an equilibration time of 8 min., the solvent composition decreased from 100 % at the start of the analysis to 20% B at 8 min. and further decreased to 0% B at 17 min. After 20 min., the solvent composition increased to 100% B again until 22 min. The mass transitions of the PFCs were measured with a tandem mass spectrometer (4000 Q-Trap MS/MS, Applied Biosystems) operating in the negative ionization mode.

Quality control.

Quantification of all measurements was performed with a linear nine point calibration line (with $r^2 > 0.98$ for all analytes) with the intercept forced through zero. Measured analyte concentrations were corrected for recovery of the mass labeled internal standards. Data were not reported when theoretical and measured levels differed by more than 30%. The limit of quantification (LOQ) was defined as the amount equal to a signal to noise (S/N) ratio of 10,

determined for each sample and analyte. The S/N was given by the software program (Analyst® v1.5). Recoveries of the analytes amounted to: 105±34% for PFHxA; 119±22% for PFOA; 152±45% for PFNA; 116±37 for PFDA; 100±28% for PFUnA; 96±23% for PFDoA; 101±31% for PFBS; 123±38% for PFOS and 116±31% for PFOSA. A blank sample of the glass field sampling bottles was prepared by filling a bottle of 1 liter with nanopure water to test for possible contamination occurring during the sampling campaign. The analysis of this control follows the same procedure as the samples mentioned above. During the extraction procedure, three blank samples were prepared to test for possible contamination from the laboratory. The average concentration in the blanks were subtracted from the measured values. Injection of methanol in between the sample injections did not show any contamination, suggesting that analytes measured in the blanks are coming from the extraction procedure and are not leached from the LC-MS/MS system.

Results and discussion

Concentrations of PFCs found in infiltrated rain water were generally lower than those in infiltrated river water, except for PFOA and PFHxS. Figure 2 presents the mean concentrations of 7 PFCs in two water bodies sampled, viz. the upper groundwater (corresponding to the rainwater lens) and the deeper groundwater. Figure 2 shows that clear differences can be observed between the abundance patterns of the several PFCs in the upper water lens and in the lower water body. The differences between the upper water body and the lower groundwater flows can be attributed to several factors. It is highly probable that the PFCs found in the rain water lens in the dunes originate from PFCs circulating in the atmosphere. On the other hand, concentrations and patterns found in deep infiltrated water in the dunes are most probably originating from river water mostly. This is clearly illustrated with PFOA and PFBS. In the rain water body PFOA is the dominating PFC and PFBS is only a minor compound, whereas in the deeper groundwater PFBS predominates. For PFHxA, PFHpA and PFOS, river water seems to be the major source of their occurrence in dune water. PFHxA is clearly present in lower quantities in rain water. In infiltrated river water, PFBS accounts on average for more than 50% of the total PFCs present, whereas this is less than 10% in rain water. Skutlarek et al. also reported PFBS to be the major component in the river Rhine and selected tributaries¹, at levels in close agreement with those observed in the present study. The compound PFHxS accounts for 40% of the total PFC concentration in rain water, whereas this is less than 10% in infiltrated river water. Concentrations of other PFCs ranged between 0.5 and 1.3 ng/L (PFNA) and 0.2-0.4 (PFUnA, PFDoA). PFTrA, PFTeA, PFHpS and PFDS were present in very low concentrations or below detection limits (0.01 ng/L).

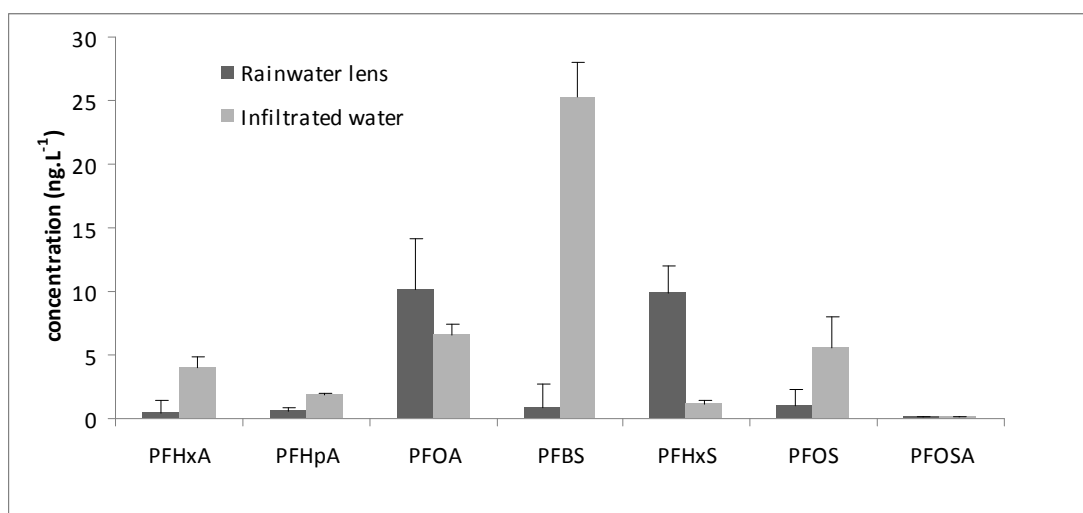


Figure 2. Mean concentrations of 7 PFCs in 2 groundwater bodies sampled in an infiltration area of the dunes in The Netherlands

For the PFSs investigated in this study, the most obvious difference between the compartments is the high mean concentration of PFBS in infiltrated river water compared to the low mean concentration observed in rain water. Statistical analysis shows that the difference is significant ($P=0.0025$; $\alpha=0.05$). This is opposite to what is seen with PFHxS which appears to be present in higher quantities in rain water than in infiltrated river water. This difference shows to be significantly different ($P=0.0328$; $\alpha=0.05$).

The fact that PFBS is found in highest concentrations in infiltrated river water with a relatively long residence time is not in agreement with its production increase after 2002. Apparently PFBS sources were already discharging into river waters before that time.

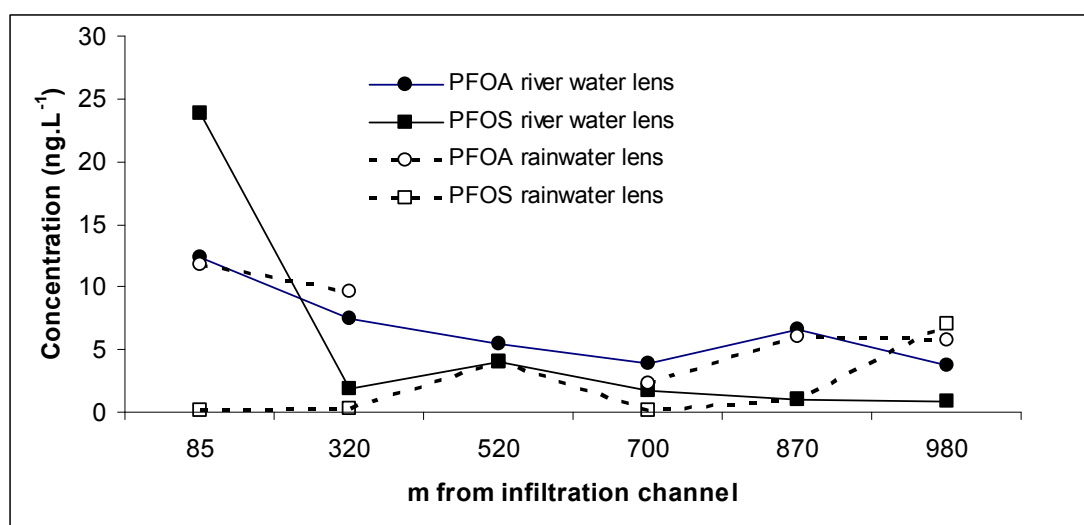


Figure 3. Trends of dissolved concentrations of PFOA and PFOS in different groundwater bodies with increasing distance from infiltration channel

In the transect sampled the PFOS and PFOA concentrations appear to decrease (see Fig. 3) with increasing distance from the infiltration channel, i.e. with the age of the infiltrated water. The estimated age of the infiltrated water varies from 4y (at 85m from the infiltration channel) to almost 20y (at 980m from the infiltration channel). PFHxA, PFBS, and PFHxS concentrations also decrease in time. Apart from reflecting general time trends in past PFC emissions, possible explanations for the trends observed are: sorption to soil particles, degradation, and dilution after infiltration from the channel. PFOS and PFOA were also analyzed in the infiltration channel itself and their mean concentrations amounted to 17.3 and 4.4 ng/L, respectively. Compared to the concentrations at the 85m point (first sampling well of the transect) where PFOS and PFOA levels amount to 23.8 and 12.3 ng/L, respectively, the levels in the infiltration channel are lower, possibly indicating a decrease in river water levels due to decreased emissions of PFOS and PFOA in the most recent past 4 years.

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