



Contribution of selected perfluoroalkyl and polyfluoroalkyl substances to the adsorbable organically bound fluorine in German rivers and in a highly contaminated groundwater



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HIGHLIGHTS

- A simplified AOF protocol enables higher throughput of environmental samples.
- Less than 5% of AOF in German surface waters can be explained by single PFASs.
- At least 50% of AOF remains unknown in a highly AFFF contaminated groundwater.
- Fluorinated organic chemicals other than target PFASs can contribute to AOF.
- AOF is a powerful tool for the future to follow PFAS removal processes.

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ABSTRACT

Due to the lack of analytical standards the application of surrogate parameters for organofluorine detection in the aquatic environment is a complementary approach to single compound target analysis of perfluoroalkyl and polyfluoroalkyl chemicals (PFASs). The recently developed method adsorbable organically bound fluorine (AOF) is based on adsorption of organofluorine chemicals to activated carbon followed by combustion ion chromatography. This AOF method was further simplified to enable measurement of larger series of environmental samples. The limit of quantification (LOQ) was 0.77 µg/L F. The modified protocol was applied to 22 samples from German rivers, a municipal wastewater treatment plant (WWTP) effluent, and four groundwater samples from a fire-fighting training site.

The WWTP effluent (AOF = 1.98 µg/L F) and only three river water samples (AOF between 0.88 µg/L F and 1.47 µg/L F) exceeded the LOQ. The AOF levels in a PFASs plume at a heavily contaminated site were in the range of 162 ± 3 µg/L F to 782 ± 43 µg/L F.

In addition to AOF 17 PFASs were analyzed by high performance liquid chromatography–tandem mass spectrometry. 32–51% of AOF in the contaminated groundwater samples were explained by individual PFASs whereas in the surface waters more than 95% remained unknown.

Organofluorine of two fluorinated pesticides, one pesticide metabolite and three fluorinated pharmaceuticals was recovered as AOF by >50% from all four tested water matrices. It is suggested that in the diffusely contaminated water bodies such fluorinated chemicals and not monitored PFASs contribute significantly to AOF.

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1. Introduction

Production and use of organofluorine compounds have steadily

increased since the middle of the last century (Key et al., 1997). A well-known field of application of organofluorine compounds is the use of perfluoroalkyl and polyfluoroalkyl substances (PFASs), for example as surfactants in aqueous film forming foams (AFFFs) (Backe et al., 2013; D'Agostino and Mabury, 2014; Houtz et al., 2013; Place and Field, 2012; Weiner et al., 2013) or as impregnating agents for carpets, leather and clothes, paper and packaging (Kissa,

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2001; Lindstrom et al., 2011). These applications led to a large-scale distribution of fluorinated compounds in the environment. PFASs have been produced since 1950 (Kannan, 2011). Since then, the production volume of fluorinated compounds has increased steadily for the following 50 years (Prevedouros et al., 2006).

The drawback of the unique characteristics of PFASs, such as high thermal stability and resistance under oxidizing or reducing conditions, is their persistence in the environment. As a result PFASs are still present in remarkable concentrations for example at sites of present or legacy use of AFFFs or accidental releases into ground- and surface waters, even five or more years after the last incident (Backe et al., 2013; Houtz et al., 2013; Moody and Field, 1999; Moody et al., 2001, 2003; Schultz et al., 2004).

PFAS can be found in rain water (Eschauzier et al., 2010; Kwok et al., 2010), snow (Cai et al., 2012), surface waters (D'eon et al., 2009; McLachlan et al., 2007), groundwater (Backe et al., 2013; Houtz et al., 2013; Moody and Field, 1999; Moody et al., 2003; Schultz et al., 2004), and in the oceans (Benskin et al., 2012; Yamashita et al., 2008), which are regarded as one of the major sinks for fluorinated compounds (Benskin et al., 2012; McLachlan et al., 2007; Yamashita et al., 2008) besides sediment burial (Prevedouros et al., 2006). Furthermore, fluorinated compounds were even detected in waters of remote regions like the Arctic (Benskin et al., 2012) and Antarctic (Cai et al., 2012).

Two of the most frequently investigated fluorochemical classes are the perfluorinated carboxylic acids (PFCAs) and the perfluorinated sulfonic acids (PFASs) of which perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) are well-known representatives (Becker et al., 2010; Loi et al., 2011; McLachlan et al., 2007). Due to the bioaccumulative and toxic properties of some longer chained PFASs several voluntary and regulative restrictions concerning the use of PFOS and its salts were established worldwide, e.g. EU (2006), US EPA (2006). PFOS is also listed in Annex B of the Stockholm convention (UNEP, 2010).

Other important organofluorine compounds are active ingredients in crop protection products (Jeschke, 2004) and pharmaceuticals (Isanbor and O'Hagan, 2006; Müller et al., 2007; O'Hagan, 2010).

Isanbor and O'Hagan (2006) estimated conservatively that globally about 20–25% of drugs in the pharmaceutical pipeline contain at least one fluorine atom, which was further supported by O'Hagan (2010) who stated that such fluorinated drugs make up 30% of the leading 30 blockbuster drugs by sales in the USA in 2008. According to the German report of prescribed pharmaceuticals (Arzneiverordnungs-Report) (Schwabe and Paffrath, 2011) in 2010 twelve of the prescribed drugs ranked in the top 100 contained at least one fluorine atom. Important representatives are pantoprazole (O'Hagan, 2010), a proton pump inhibitor, and fluoroquinolone antibiotics like ciprofloxacin, ofloxacin or levofloxacin (Müller et al., 2007; O'Hagan, 2010).

Crop protection products are applied on large acreages so that these enter the water cycle usually uncontrolled by leaching and surface run-off as diffuse sources. Jeschke (2004) presented a survey on commercial products containing halogenated active ingredients available from 1940 to 2003 which showed that nearly 30% of products on offer accounted for fluorinated substances. Moreover, Jeschke (2004) expected a definite growth of the contribution of fluorinated products for the 21st century by extrapolating the available data. More than half of the fluorinated agrochemicals are used as herbicides or safeners which usually contain three to five fluorine atoms. Typical representatives are flurtamone and diflufenican, which are used in combination for application in crops, or flufenacet, which has a broad application spectrum in weed control (Jeschke, 2004).

In general, many organofluorine compounds which enter the

aquatic environment and are either not readily degraded or even persist, such as PFSAs and PFCAs, contribute to the total organofluorine load of surface and groundwaters. Recently discussed approaches for a more exhaustive determination of organofluorine compounds in the aqueous environment are measurement of the extractable organic fluorine (EOF) (Loi et al., 2011; Miyake et al., 2007a), the adsorbable organic fluorine AOF (Wagner et al., 2013), and a hydroxyl radical oxidation approach (Houtz and Sedlak, 2012; Houtz et al., 2013).

The surrogate parameter EOF, as defined for aqueous samples by Miyake et al. (2007a), comprises all neutral and anionic organofluorine compounds which are extractable using a polymer-based weak anion exchanger and sequential elution with methanol and 0.1% NH₄OH/methanol. Besides aqueous samples, the surrogate parameter EOF has been applied successfully to human blood (Miyake et al., 2007b), blood of rats (Yeung et al., 2009a), and to livers of Indo-Pacific humpback dolphins and finless porpoises (Yeung et al., 2009b).

The surrogate parameter approach of Houtz and Sedlak (2012) and Houtz et al. (2013) is based on a comparison of PFSA and PFCA concentration between a non-oxidized and oxidized water sample. This method gives an estimate on the amount of unknown PFSA and PFCA precursors. This fluoroalkyl chain specific approach lies between the high selectivity of single compound target analysis by HPLC-ESI-MS/MS and the low selectivity of the element specific approaches EOF and AOF.

In contrast to the EOF and the oxidation method of Houtz et al. the AOF represents all organofluorine compounds, i.e. cationic, anionic, neutral, and zwitterionic, which are present in a water sample and can be adsorbed to an activated carbon.

Earlier measurements of surrogate parameters in the aquatic environment (Houtz and Sedlak, 2012; Houtz et al., 2013; Miyake et al., 2007; Wagner et al., 2013) have shown that PFAS analysis by high performance liquid chromatography-tandem mass spectrometric (HPLC-MS/MS) methods can vastly underestimate the overall organofluorine concentrations. In particular, this should be true for the application of the standard methods, such as ISO 25101 (2009) for analysis of PFOA and PFOS or DIN 38407-42:2011-03 (2011) validated for analysis of ten PFASs, i.e. seven PFCAs and three PFSAs. However, the results of these standard methods are currently the basis for decision making, for example handling legacy PFAS contaminations in groundwater.

The aim of this study was to apply a modified AOF protocol, which allows higher sample throughput than the original protocol developed by Wagner et al. (2013), to different kinds of water samples. A wastewater treatment plant (WWTP) effluent, 22 diffusely contaminated surface waters, and groundwater samples from an airport, heavily contaminated with PFASs from AFFFs, were analyzed to get an overview on typical environmental AOF levels in German freshwaters. The AOF levels were compared with organofluorine calculated from individual PFAS analysis by HPLC-ESI-MS/MS in order to evaluate the contribution of frequently monitored PFASs to AOF. To test, if organofluorine of other fluorinated chemicals than PFASs, such as fluorinated pharmaceuticals and crop protection agents, would also be assessed by AOF measurement, the recoveries of some important representatives of these two compound classes were evaluated.

To the best of our knowledge, except for the AOF results of one WWTP effluent, two river water samples, and three weakly contaminated groundwater samples reported by Wagner et al. (2013) to demonstrate the applicability of the AOF method, this is the first report of a broader application of the AOF analysis for screening of municipal wastewater, river waters, and samples from a heavily contaminated groundwater aquifer.

2. Materials and methods

2.1. Sampling of WWTP effluent, surface water and groundwater

The effluent of the municipal WWTP in Karlsruhe (Fig. 1) was directly taken from a tap on a bypass of the main effluent line. Before sampling the effluent was allowed to run for about five minutes to avoid sampling stagnant effluent. The effluent was filled into a 10 L high-density polyethylene canister which had been flushed with effluent before.

The map in Fig. 1 shows the location of the 22 surface water sampling sites, i.e. five samples along the Rhine, one from Main and Danube each, nine from the Neckar, two from the Steinlach, and one from the Fils, Körsch, Jagst, and Kocher each. The latter five rivers are tributaries of the Neckar. Sampling was conducted between June and September 2012. For further information on the sample matrices, i.e. fluoride and TOC concentrations, see Table S2.

In May 2012, groundwater was sampled at an airport from wells located around a basin which was formerly used for routine fire-fighting trainings and subsequent wastewater discharge (Fig. 2). It is not known to what extent the basin was loaded with fire-fighting foam. Moreover, it is unknown which fire-fighting foams were deployed. Nevertheless, this would only give limited information about their composition since this is widely proprietary.

A MP1 submersible pump (Grundfos GmbH, Erkrath, Germany) and a polyvinylchloride (PVC) hose were used for sampling. The

well depths were approximately 11 m and the diameters were about 125 mm. The samples were taken at a depth of 6 m at a flow rate of 10 L/min after the stagnant water was replaced at least twice by the surrounding groundwater and when constant values of pH, conductivity, oxygen content, and redox potential were achieved (approximately after 25 min of pumping). The samples were filled into narrow neck amber glass bottles (1 L) and transported in cooling boxes to the lab. All samples were stored at 6 °C in the dark until analysis.

2.2. Chemicals and standards

All dilutions and standards were prepared with ultrapure water (18.1 MΩ cm, TOC < 10 ppb) from a Millipore system using a SimPak 2 purification pack (Merck KGaA, Darmstadt, Germany). Sodium nitrate (≥99.5%, p.a.), nitric acid (≥65%, p.a.) and an orthophosphate standard (1000 mg/L) for AOF analysis were purchased from Merck KGaA. For adsorption of organofluorine compounds Ujotit AK-200-1200 (Dr. Felgenträger & Co. Öko.-chem. und Pharma GmbH, Dessau-Roßlau, Germany) was used. Information about all PFASs standards and other organofluorine chemicals used in this study are given in the Supporting Information.

2.3. Fluoride analysis

For water matrix characterization fluoride concentrations in the

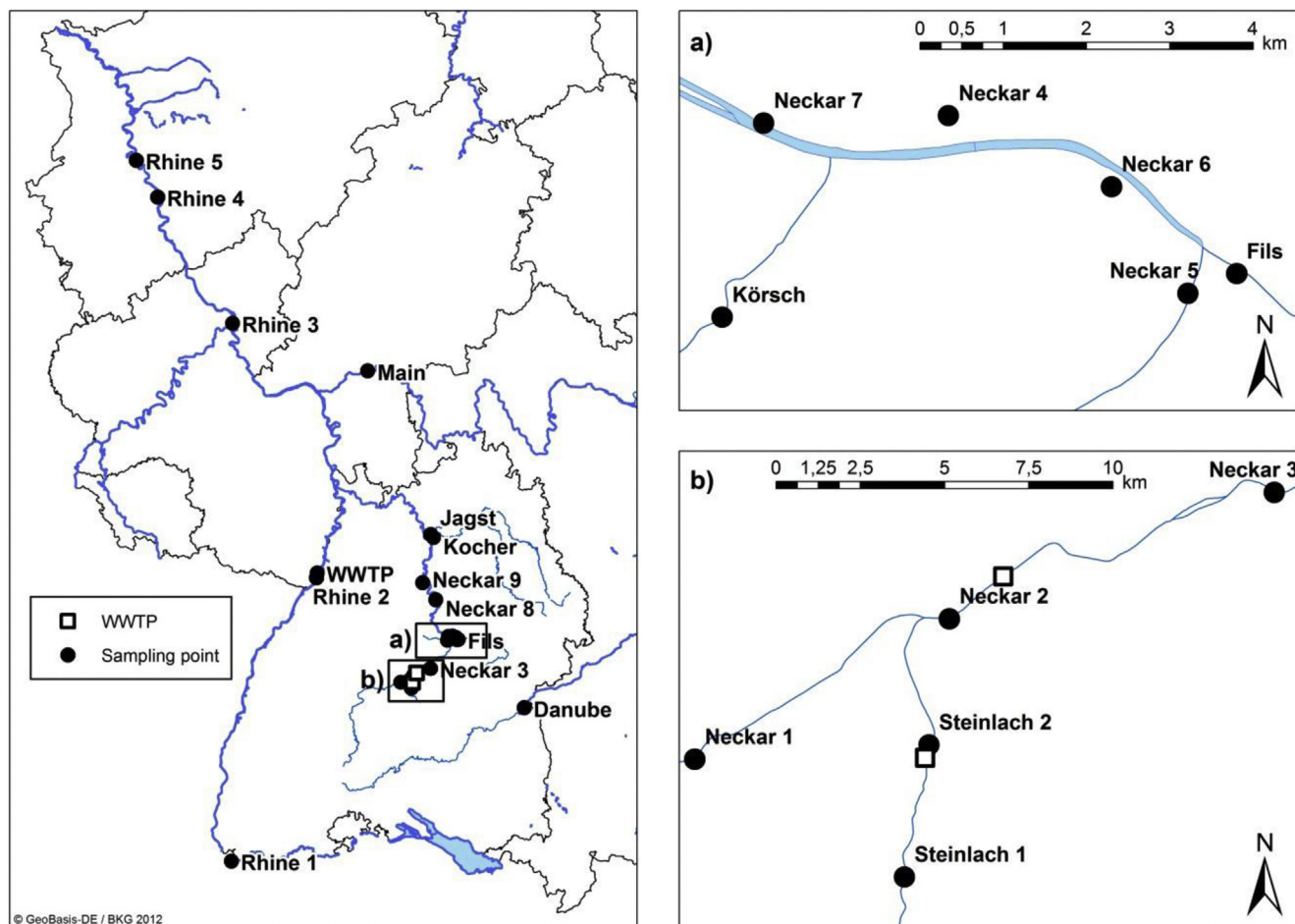


Fig. 1. Map showing the surface water sampling sites and the location of the sampled municipal WWTP; WWTPs marked with an open square indicate the presence of a WWTP where no sample was taken.

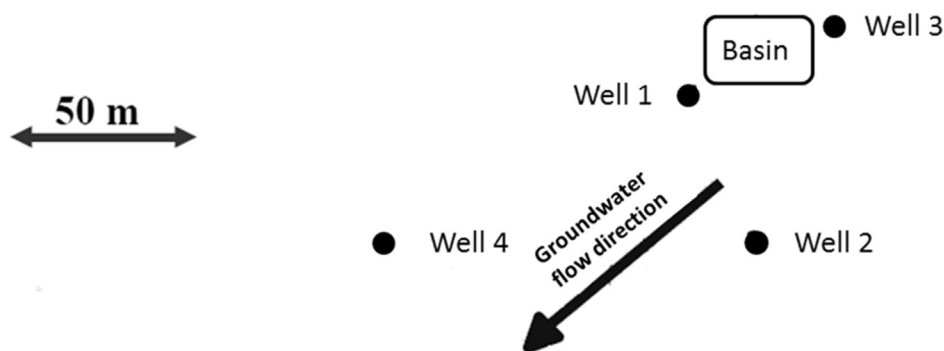


Fig. 2. Schematic representation of distribution of the wells around the basin which was used for the water discharge of routine fire-fighting trainings at the airport sampling site.

water samples were determined by ion chromatography according to EN ISO 10304-1:2009-07 (2009).

2.4. AOF analysis

For AOF analysis the previously described method of Wagner et al. (2013) was applied with some modifications. A scheme of the complete method for AOF determination using the CIC including the ASC-120S autosampler for sample introduction is schematically shown in Figure S1 (see Electronic Supplementary Material). To achieve a higher sample throughput the autosampler ASC-120S (Mitsubishi Chemical Analytech Co., Ltd., purchased from a1-envirosciences GmbH (Düsseldorf, Germany)) was integrated into the CIC-F system. Compared to former manual introduction of the loaded activated carbon this improvement allowed processing a sequence of 20 sample boats, i.e. 10 samples. A simplified combustion program was developed (Figure S2, Table S1). The combustion time was shortened from previously 25 min (Wagner, 2012) to 14 min including the time needed for absorption and rinsing of the absorption tube. To further simplify the analysis, the combustion gases of the loaded activated carbon from the two serial extraction columns used for extraction of one sample were accumulated in one absorption solution. A 1 mL aliquot of this solution was analyzed by ion chromatography.

For the validation of the modified protocol fluorine blanks and fluorine recoveries from model compounds were checked. For blank determination ten blank samples of 100 mL of ultrapure water were processed. The cover of the autosampler was not removed before the last sample in the chamber was combusted to avoid contaminations from the laboratory air. Recoveries, including extraction of a number of model compounds (single compounds and a PFAS mix) from tap water and wastewater were reported elsewhere (Wagner et al., 2013). High (80–100%) recoveries were found for most of the PFASs also quantified by HPLC-MS/MS, only weakly dependent from the studied water matrix (tap water, wastewater). Following the practice of other authors (Miyake et al., 2007a, Houtz and Sedlak, 2012) organofluorine concentrations of quantified PFASs were not corrected for recoveries in the AOF measurement. Thus, the calculated gap of not yet identified AOF is rather slightly underestimated. To verify that the modified combustion method (Table S1) gives equivalent recoveries to the method of Wagner et al. (2013), fluorine recoveries of 3 µg/L F of the two model compounds PFOA and PFBS from ultrapure water were evaluated. For this purpose, samples spiked with these model compounds were analyzed as described above for the blanks.

2.5. HPLC-ESI-MS/MS analysis of PFAS

17 individual PFASs were analyzed in the water samples by high

performance liquid chromatography tandem mass spectrometry (HPLC-ESI-MS/MS) according to DIN 38407-42:2011-03 (2011) including the QA/QC measurements specified there. A HPLC 1200 system (Agilent Technologies, Waldbronn, Germany), consisting of the vacuum degasser G1379B, the binary pump G1312B, the auto-sampler G1367C with the thermostat G1330B, the temperature controlled column compartment G1316B, set to 40 °C, and the instant pilot G4208A, was used. The analytical column was Gemini™ C18 (250 mm × 2 mm, particle size 5 µm, pore size 110 Å, Phenomenex (Aschaffenburg, Germany)) with a SecurityGuard™ precolumn (4 mm × 2 mm) of the same type. Water and methanol, each containing 10 mM ammonium acetate were used as solvents A and B. The following gradient elution was carried out at 0.2 mL/min: 45% B rising to 100% B in 24 min, holding 100% B for 7 min, decreasing B to 45% within one minute and equilibrating for 8 min at this composition. The target PFAS were detected by tandem-mass spectrometry in negative ionization mode using two mass transitions, where possible. Mass spectrometric settings were: ion spray voltage –4.5 kV, heater temperature 350 °C, collision gas: medium; ion source gas 1/2: 60/80 psi and curtain gas: 40 psi. Further details of the detection settings are given in the Electronic Supplementary Material, Table S4.

3. Results and discussion

3.1. Validation of the modified AOF protocol

3.1.1. Determination of LOD_{α} , $LOD_{\alpha,\beta}$ and LOQ

LOD_{α} , $LOD_{\alpha,\beta}$ and LOQ were calculated according to the German standard DIN 32645:2008-11 (2008). The limit of decision (LOD_{α}) – often also referred to as limit of detection by other authors – takes the alpha error into account, i.e. the limit value at which it is possible to discriminate the analyte signal significantly from the blank value. For calculation of LOD_{α} the blank method was applied which includes, inter alia, the slope of the calibration line and the standard deviation of $n = 10$ blank samples (here: 100 mL of ultrapure water each). The limit of detection ($LOD_{\alpha,\beta}$, sometimes referred to as limit of capture) also takes the beta error into account, so that the resulting value gives the minimum concentration of the analyte in the sample. The limit of quantification (LOQ) gives the concentration above which the quantitative determination of the analyte is possible. The significance level of α and β were chosen at $P = 0.01$, the degrees of freedom were $f = n - 1$. During the AOF procedure 100 mL of each sample was enriched on the activated carbon and absorbed in 3.5 mL absorption solution after the combustion. Thus, for calculation of the AOF in the original sample a factor of 0.035 was accounted for the preconcentration. The resulting values for LOD_{α} , $LOD_{\alpha,\beta}$ and LOQ were 0.23 µg/L F, 0.46 µg/L F and 0.77 µg/L F, respectively. Hence, it is possible to screen

moderately PFAS contaminated waters or to identify hotspot areas with the newly developed AOF method.

3.1.2. Determination of the fluorine recoveries during AOF analysis

Due to the change from manual sample introduction as used by Wagner et al. (2013) to introduction by the autosampler (this work) and due to the simplification of the combustion program compared to Wagner (2012) (see Table S1), the organofluorine recoveries from solutions of the model PFASs PFBS and PFOA were compared to the recoveries reported for the former conditions. The determined recoveries are shown in Figure S4.

The overall fluorine recovery from PFBS and PFOA were in the same range as reported by Wagner et al. (2013). All recoveries were between 88% and 107%. However, as with the blanks, a small but significant (according to *t*-test with $P = 0.05$) increase of the fluorine concentration with the latency of the samples on the auto-sampler was observed (Figure S3). This small increase was neglected for the further measurements. It gives rise to a comparatively low (approximately $\leq 15\%$) additional analytical error at concentrations close to LOQ. It was abandoned to correct the results for this systematic error since the slope was varying slightly between measurement days. The most likely explanation is that at these low trace levels laboratory air borne contaminations caused this drift in the measurements. If a lower LOQ should be necessary, additional measures will have to be taken, e.g. the use of higher purity protective gas or clean room conditions, in order to further reduce this effect.

The mean F recoveries of the pharmaceuticals in the four tested matrices (Fig. 3) were all above 75% except for pantoprazole sodium hydrate ($65\% \pm 12\%$ from surface water). The mean recoveries of ciprofloxacin hydrochloride from ultrapure water, tap water, and WWTP effluent and of fluoxetine from WWTP effluent were above 90%. For the herbicidal agents and the metabolite flufenacet oxalamic acid the mean F recoveries from all four matrices were above 60% except for flurtamone ($51\% \pm 11\%$ and $57\% \pm 5\%$ from ultrapure water and tap water, respectively).

The data above demonstrate that with the reported method non-PFAS compounds are recovered in the same range as it had been found for PFASs with carbon chain lengths ≥ 4 by Wagner et al.

(2013). Therefore, the AOF method is not only applicable in the field of PFAS contaminations but also for assessment of the organofluorine load in the environment, which is caused by a mixture of fluorinated compounds like PFASs, pharmaceuticals, crop protection products, and others.

3.2. Analysis of environmental samples

The total fluorine content of the samples was not determined since it is obvious and has already been found by previous studies (Loi et al., 2011; Miyake et al., 2007a; Wagner et al., 2013) that the total fluorine content in natural waters mainly consists of inorganic fluoride or non-extractable or non-adsorbable fluorine containing species so that no valuable information would be gained by this parameter. This assumption is further supported by the fluoride concentrations which are in the upper $\mu\text{g/L}$ F-range (Tables S2 and S3) in contrast to expected AOF concentrations in the high ng/L to low $\mu\text{g/L}$ -range. Either the native fluoride concentrations of the samples analyzed in this study were $<200 \mu\text{g/L}$ (WWTP effluent, surface water samples) or the fluoride concentration was lowered by dilution with ultrapure water (contaminated groundwater samples). At fluoride concentrations $<200 \mu\text{g/L}$ no interfering inorganic fluoride background occurs (Wagner et al., 2013).

3.2.1. Municipal WWTP effluent and diffusely polluted surface waters

In four of the 23 analyzed samples, i.e. the WWTP effluent, Rhine 2, Rhine 3, and Körsch, AOF concentrations were above the LOQ of $0.77 \mu\text{g/L}$ F (Fig. 4a). Nine samples, i.e. Neckar 1, 3, 4, and 9, Steinslach 1, Fils, Rhine 5, Main, and Kocher, showed AOF concentrations which were below the LOQ but above the $\text{LOD}_{\alpha,\beta}$, i.e. $\geq 0.46 \mu\text{g/L}$ F. In nine further samples the AOF concentration was between LOD_{α} and $\text{LOD}_{\alpha,\beta}$. Only at one site, Rhine 4, AOF was below LOD_{α} . The corresponding organofluorine contributions of individual PFASs are shown in Fig. 4b.

With $1.98 \mu\text{g/L}$ F the AOF concentration of the WWTP effluent was the highest of this set of 23 samples analyzed. The AOF concentrations of the surface waters with AOF $>$ LOQ (Fig. 4a) ranged from $0.88 \mu\text{g/L}$ F in the sample Rhine 3 to $1.47 \mu\text{g/L}$ F for the Rhine 2

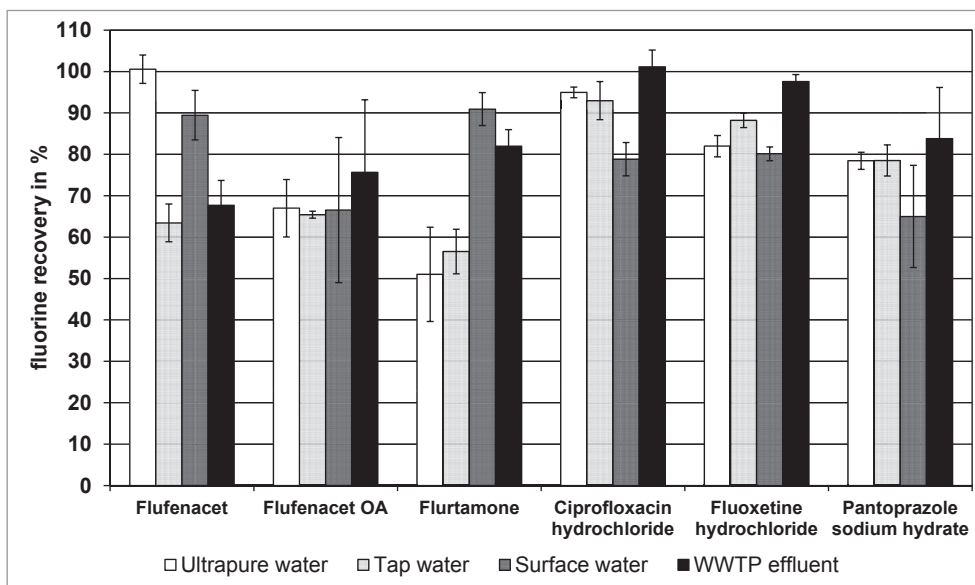


Fig. 3. Recovery of organofluorine ($3 \mu\text{g/L}$ F) from different fluorinated target compounds during AOF analysis from ultrapure water, tap water, surface water, and a municipal WWTP effluent; error bars represent the standard deviation of three replicates.

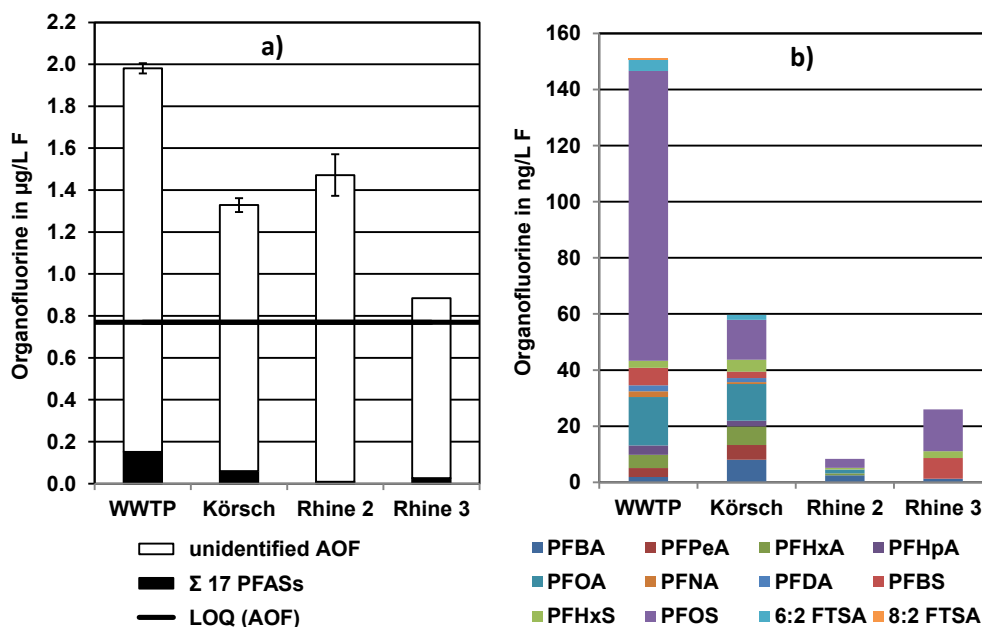


Fig. 4. a) AOF concentrations in the studied WWTP and three surface waters in comparison to $\Sigma 17$ PFASs; error bars for AOF values represent the standard deviation of three replicates for the WWTP, Rhine 2, and Kör sch; Rhine 3 represents a single measurement. b) Contribution of individual PFASs to $\Sigma 17$ PFASs in the municipal WWTP effluent and three surface water samples with AOF > LOQ; PFAS concentrations were determined as single values.

sample. The sum of organofluorine concentrations of the 17 PFASs ($\Sigma 17$ PFASs, in $\mu\text{g/L F}$) accounts only for 8% in the WWTP effluent and less than 5% of the AOF in these three surface water samples. This observation is consistent with the results of Wagner et al. (2013) who detected AOF concentrations in two exemplarily investigated surface waters in the same range (1.01 $\mu\text{g/L F}$ and 0.93 $\mu\text{g/L F}$, respectively) as in the present study and could also explain less than 5% by organofluorine of identified PFASs. This result is in line with the findings of Miyake et al. (2007a). In their study at two seawater reference sites without known PFAS pollution, quantified PFASs ($\Sigma 20$ PFASs) accounted for only 1% and 2% of the surrogate parameter EOF. In contrast 34% and 36% of EOF could be explained by the $\Sigma 20$ PFASs of two samples at a sea water site contaminated by AFFFs.

In the surface water sample from Rhine 2 PFBA, PFHxA, PFOA, PFHxS, and PFOS were detected above the LOQ (1 ng/L each) whereas in the Rhine 3 sample only PFBA, PFBS, PFHxS, and PFOS could be quantified (Fig. 4b). The detected PFASs above the LOQ in the WWTP effluent and in the Kör sch were PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, PFHxS, PFOS, and 6:2 FTSA. Additionally, 8:2 FTSA could be quantified in the WWTP effluent sample. PFOS was the dominating compound in all four samples contributing 68%, 39%, 57%, and 24% to $\Sigma 17$ PFASs in the WWTP effluent and at Rhine 2, Rhine 3, and Kör sch sampling sites, respectively.

This finding shows that PFOS was still emitted into the German environment probably due to the exemptions made in the Directive 2006/122/EC (EU, 2006) or the Stockholm Convention (UNEP, 2010). Furthermore, it confirms previous conclusions of Becker et al. (2010) and Sinclair and Kannan (2006) that WWTPs are important emitters of PFOS into the environment. The second highest percentage of the $\Sigma 17$ PFASs was found for PFOA at 23% and 11% for Kör sch and the WWTP effluent, respectively. In the samples from the Rhine short-chained PFASs ranked at the second highest position which was 30% for PFBA in the Rhine 2 and 29% for PFBS in the Rhine 3 sample.

For the nine samples where AOF was $\geq \text{LOD}_{\alpha,\beta}$ (0.46 $\mu\text{g/L F}$) $\Sigma 17$

PFASs ranged between 4 ng/L F at Steinlach 1 and 30 ng/L F at Rhine 5 (Fig. 5a). Thus organofluorine of $\Sigma 17$ PFASs in the samples in Fig. 5a) explains at maximum between 1% of AOF at Steinlach 1 and 7% at Rhine 5. All these surface water samples contained PFBA which was the dominating compound at Steinlach 1, Neckar 3, 4, and 9, and Fils with 66%, 34%, 28%, 34%, and 22%, respectively. Moreover, all these samples contained PFOS. In summary, the AOF of the samples shown in Fig. 5a) and b) was significantly higher than the fraction which could be explained by the quantified PFASs so that 93% up to 99% of the AOF remained unknown.

Comparing sites Rhine 3, 4, and 5, a significant increase of the PFBS concentration from Rhine 3 and 4 with 13 ng/L F and 11 ng/L F, respectively, to a PFBS concentration of 28 ng/L F at Rhine 5 can be denoted. This finding indicates a point source of PFBS between sampling sites Rhine 4 and 5. In 2006, Lange et al. (2007) have made a similar observation for samples taken at Leverkusen and at Düsseldorf-Flehe as well as Möller et al. (2010) four years later.

It was expected to find increased concentrations of AOF and individual PFASs after a WWTP effluent discharge. This assumption could be confirmed for the sample from the Kör sch. Several WWTPs which use the Kör sch as a receiving water body can be found along the river. On average the river consists of 36% WWTP effluents which may increase to more than 80% during dry periods (Metzger et al., 2003). The sampling sites Steinlach 2 and Neckar 3 were located downstream of a WWTP (Fig. 1). The previous expectations could only partly be confirmed. The AOF at Steinlach 2 was $< \text{LOD}_{\alpha,\beta}$ (0.46 $\mu\text{g/L F}$) whereas the AOF at Steinlach 1 had been above this limit. Contrary to this observation the $\Sigma 17$ PFASs at Steinlach 1 gave 4 ng/L F whereas the $\Sigma 17$ PFASs accounted for 15 ng/L F at the Steinlach 2 site. This might be explained by introduction of PFAS enriched water with an overall low organofluorine content which has caused a dilution of AOF but an increase of individual PFASs. For the samples at sites Neckar 2 and 3 the results were opposite. The AOF at Neckar 3 was $> \text{LOD}_{\alpha,\beta}$ whereas the AOF of the Neckar 2 sample was $< \text{LOD}_{\alpha,\beta}$. The $\Sigma 17$ PFASs at Neckar 2 was 12 ng/L F and similar to the $\Sigma 17$ PFASs at Neckar 3 with 13 ng/L F. Since the PFAS profiles of these two samples have not changed

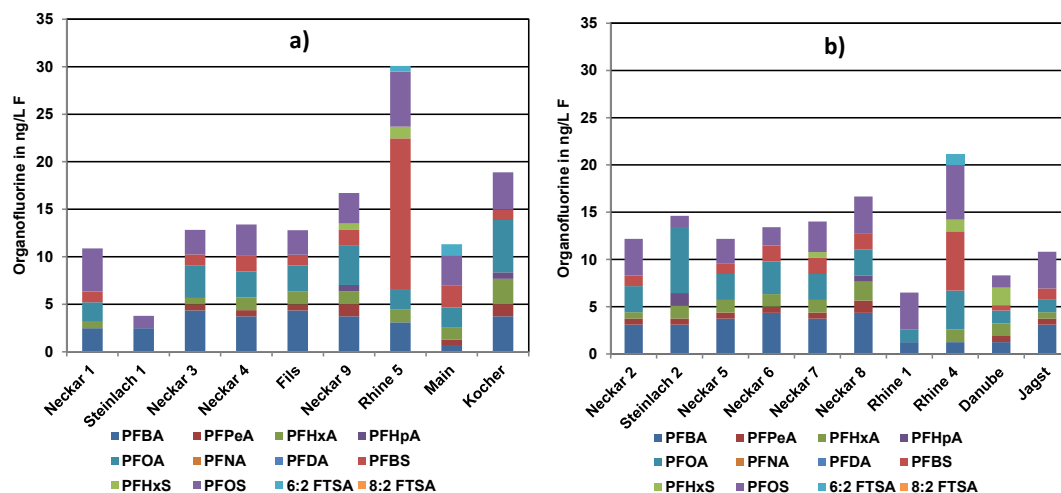


Fig. 5. Contribution of individual PFASs to the $\Sigma 17$ PFASs in a) nine surface water samples with $\text{LOD}_{\alpha,\beta} < \text{AOF}$ and b) ten surface water samples with $\text{LOD}_{\alpha} < \text{AOF} < \text{LOD}_{\alpha,\beta}$ except for Rhine 4 ($\text{AOF} < \text{LOD}_{\alpha}$).

significantly this finding could indicate an elevated introduction of organofluorine compounds not covered by individual analysis of PFASs.

3.2.2. Groundwater samples highly polluted with PFAS from application of AFFFs

The AOF concentrations in the samples from a contaminated site at a German airport (Fig. 2), where fire-fighting trainings with AFFFs were practiced in the past, ranged from $162 \pm 3 \mu\text{g/L F}$ at Well 4 up to $782 \pm 43 \mu\text{g/L F}$ at Well 1 (Fig. 6a). Wagner (2012) found an AOF concentration of $0.55 \pm 0.07 \mu\text{g/L F}$ for a non-polluted groundwater, i.e. the concentrations shown in Fig. 6a are about 300 to 1.400 times higher compared to a pristine groundwater. Of the 17 individual PFASs analyzed PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, PFHxS, PFOS, FOSA, 4:2 FTS, 6:2 FTSA, and

8:2 FTSA were detected in all samples with few exceptions: 6:2 FTSA was not detected at Well 2 and PFDA and FOSA were not detected at Well 4 (Fig. 6b).

The $\Sigma 17$ PFASs measured accounts for 51% at Well 1, 47% at Well 2, 42% at Well 3, and 32% at Well 4. Wagner et al. (2013) analyzed three different samples located at the border area of a groundwater plume contaminated with PFAS containing AFFFs. 42% up to 50% of the detected AOF could be identified by the quantified PFASs. These results are complementary to the findings of Moody et al. (2001) who analyzed surface water from Etobicoke Creek after an accidental AFFF spill from the Toronto airport, Canada. Analysis for PFASs was conducted by HPLC-MS/MS. The three PFASs PFHxS, PFOS, and PFOA were quantified and their total concentration was compared to the total surfactant concentration determination by ^{19}F NMR (quantified as PFOS through the signals of the terminal

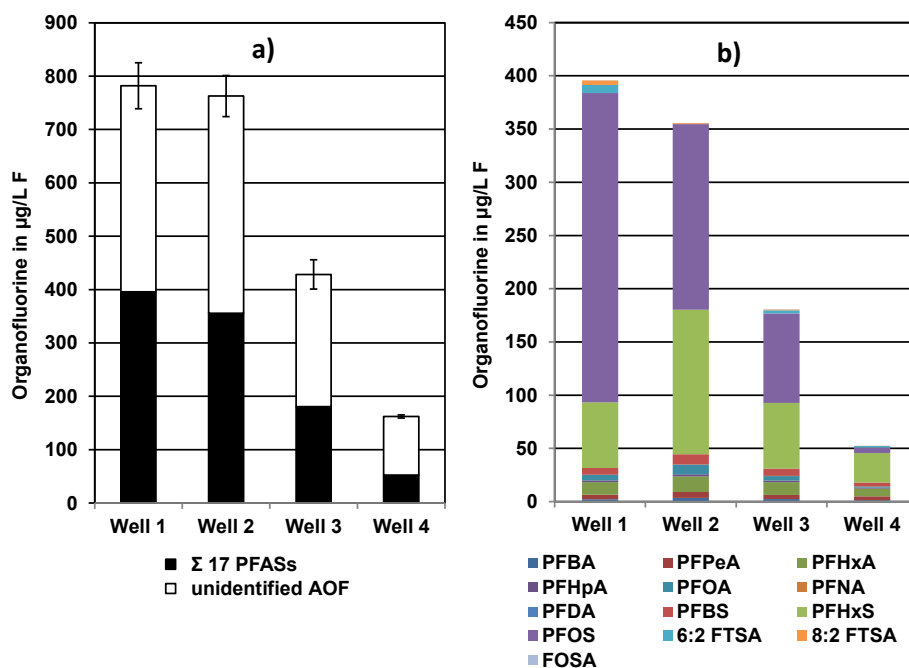


Fig. 6. a) Analysis of AOF in the contaminated groundwater samples Well 1–4 in comparison to $\Sigma 17$ PFASs. Error bars represent the standard deviation of three replicates of AOF measurements. b) Contribution of individual PFASs to $\Sigma 17$ PFASs in the four groundwater samples highly contaminated with AFFFs from fire-fighting trainings.

–CF₃ groups). In that study only 13–30% of the total surfactant concentration in the analyzed water samples could be explained. This might be in part due to the small number of quantified target PFASs. However, the composition of AFFFs can vary over a longer time period as it was indicated by the groundwater screenings for fluorotelomer sulfonates by Schultz et al. (2004) at different military bases at which regular fire-trainings had been conducted. The composition also depends on the manufacturer and the employed fluorination process as it was shown by Place and Field (2012). Place and Field (2012) were able to identify ten different fluorochemical classes in seven different AFFF formulations. This implies that in the present study even the HPLC-MS/MS analysis of 17 PFASs, which mainly consisted of PFCAs and PFSAs, is by far not sufficient to identify all fluorinated constituents of a groundwater contaminated with AFFF.

Another feature of Fig. 6a is the relationship of PFAS concentration with the distance from the discharge basin to the sampling wells and the flow direction of the groundwater, respectively. The concentrations found at Well 1 and Well 2 are similar although Well 2 is more than 40 m remote from the basin whereas the distance of Well 1 to the basin is less than 10 m. However, both wells lie approximately within the prevailing flow direction of the groundwater. Although Well 3 has a similar distance to the basin as Well 1 the detected AOF concentration is about half. In contrast to Well 1, Well 3 is located upstream of the basin with regard to the main groundwater flow direction. The lowest concentration of AOF was found approximately 100 m downstream of the basin at Well 4. In past studies on groundwater contaminated with PFASs, such as PFOS or PFOA, elevated concentrations were detected even 500 m downgradient of the fire-training site, which proves a high mobility for these compounds (Moody et al., 2003). Consistently, Gellrich et al. (2012) found in batch experiments that the percolation velocity of PFASs was strongly dependent on the carbon chain length but also on the properties of the soil. Considering these facts the significantly lower AOF concentration at Well 4 could either be attributed to the elapsed time frame which could have been too short to allow migration of longer chained PFASs or to the variability of the flow direction of the groundwater which does not directly flow towards Well 4.

One striking point is the decreasing fraction of quantified individual PFASs contributing to the AOF with decreasing AOF concentrations. Whereas the quantified PFASs accounted for $\approx 50\%$ of the AOF in samples from Well 1 and Well 2, this fraction decreased to $\approx 40\%$ and $\approx 30\%$ at Wells 3 and 4, respectively. This might be explained by unknown organofluorine ingredients (or their transformation products) in the fire-fighting foams discharged to the basin and exhibiting a higher mobility compared to the quantified PFCAs and PFSAs.

The individual PFAS composition for samples at Well 1, 2, and 3 was dominated by PFOS (Fig. 6b) while PFHxS had the second highest percentage. In contrast, the groundwater at Well 4 was dominated by PFHxS and PFHxA. Here, the percentage of PFOS was significantly lower compared to the three other samples. The proportion of PFHxS in these samples increased with the distance of the wells downgradient from the basin in the order of Well 1 < Well 2 < Well 4. This could be understood in terms of the higher mobility of PFHxS compared to PFOS. A less pronounced increase was found for the proportion of PFBS to the identified organofluorine. It increased from 3% in Well 1–4% in Well 2 up to 7% in Well 4. For the group of PFCAs a similar picture was observed. PFOA proportions were 1% for Well 1, 3% for Well 2, and 2% for Well 4. Proportions of PFHxA increased significantly from 3% to 4% for samples of Well 1 and 2 up to 14% for Well 4. These observations for PFSAs and PFCAs strongly confirm that mobility increases with decreasing perfluoroalkyl chain lengths. Similar findings have been made inter-

alia in a study by Moody and Field (1999) for PFASs with perfluoroalkyl chain lengths of six to eight and by Gellrich et al. (2012) for perfluoroalkyl chain lengths from four to thirteen.

If the PFAS profile of the groundwater samples was compared to the PFAS profile of the municipal WWTP effluent and diffusely polluted surface water samples it can be assessed at least for the quantified PFASs that PFOS is the dominating PFAS in all these samples except for Well 4. In contrast to the contaminated groundwater samples PFHxS is only a minor PFAS in the WWTP effluent sample and the surface water samples. This implies that for different contamination sources — local vs. diffuse — different PFAS profiles could exist.

4. Conclusions

Through further automation and reduction of the combustion time with the presented AOF protocol it is now possible to analyze twice as many samples per day as before. Also non-PFASs are assessed with similar recoveries as it was found for PFASs of different carbon chain lengths. Thus, the presented analytical method is not only applicable for detection of PFAS contaminations but also for assessment of the general organofluorine load in the aquatic environment, which, beside PFASs, might be caused by fluorinated compounds like certain pharmaceuticals, crop protection products and their transformation products.

The present study showed that it is possible to explain up to approximately 50% of the surrogate parameter AOF by the sum of organofluorine contributions of the quantified individual PFASs in groundwater heavily contaminated by AFFFs. By contrast, for waters which are contaminated by diffuse sources only less than 5% of the organofluorine fraction could be explained by the investigated $\Sigma 17$ PFASs. These variations of explainable fractions of the developed surrogate parameter show that the information which is usually generated by the analysis of individual PFASs by standard methods such as ISO 25101 (2009) or DIN 38407-42 (2011) is strongly limited. That way it is possible to give information whether a contamination with PFASs exists at all, but no conclusions can be drawn about the extent of the further organofluorine load.

A possible future field of application for the developed surrogate parameter AOF could be the monitoring of WWTP influents and effluents in order to assess the part of AOF which can be removed by a certain treatment technology.

Moreover, programs for the monitoring of tremendous contaminations such as discharge of waters at fire-fighting training sites at airports, refineries, etc. or accidental spills of AFFFs could make use of the AOF method. The developed AOF method is appropriate to monitor the expansion of a groundwater plume and detect possible hazards for drinking water resources. Another option is to use AOF in combination with fluoride measurements to assess the degree of mineralization and formation of unknown transformation products in processes which aim at destroying PFASs in concentrated solution, e.g. by electrochemical defluorination (Trautmann et al., 2015) or similar processes.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.chemosphere.2015.11.113>.

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