



Minimizing the environmental impact of PFAS by using specialized coagulants for the treatment of PFAS polluted waters and for the decontamination of firefighting equipment



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ABSTRACT

Per- and polyfluoroalkyl substances (PFASs) represent an increasingly global challenge for keeping water and soil “non-toxic”. 100 of millions of people are exposed to PFAS levels of concern, in particular, around PFAS production sites and sites where PFASs are/were used and released or disposed. The Stockholm Convention established recommendations to systematically assess PFOS pollution which can be transposed to all PFASs considering that PFASs are an issue of concern under The Strategic Approach to International Chemical Management (SAICM). One major wide-spread source of environmental pollution is the long-term use of PFAS-containing fire extinguishing agents. Strategies for the reduction of human exposure need to reduce and were feasible eliminate the current uses of PFASs and reduce and eliminate the human exposure from the contamination of the environment from past uses including contaminated drinking water.

The current study shows that well-known methods of water treatment, especially the use of materials for adsorption and ion exchange, can often neither guarantee satisfactory cleaning results nor economically justifiable filter running times at high PFAS concentrations and complex matrix conditions. Their combination with a pre-precipitation stage using specialized precipitants can significantly optimize treatment successes.

PFAS is still being released into the environment in considerable quantities by e.g. the use of so-called aqueous film forming foams (AFFF). Fire departments are increasingly trying to reduce the risks associated with the use of AFFF agents for the health of firefighting personnel and the environment by replacing AFFF foaming agents with fluorine-free foaming agents. If the fluorine-containing foaming agents are simply replaced, considerable residual PFAS loads often remain in the fire extinguishing systems contaminated with PFAS (fire engines, fire boats, stationary fire extinguishing systems, etc.), which are then discharged further into the environment during renewed operations - normally at a reduced concentration. The current study demonstrates that a conscientious decontamination of systems previously in contact with PFAS is therefore urgently required. Here, too, precipitants specialized for PFAS adsorption can make an important contribution to protecting the environment. Sites where firefighting equipment has been cleaned over years can also be considered contaminated and need assessment and possibly remediation.

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1. Introduction

The use of per- and polyfluoroalkyl substances (PFAS) in a wide range of industrial applications and consumer products (Glüge et al., 2020) has resulted in widespread global contamination [1–5,55]. To address this problem, the Stockholm Convention has

listed the first two PFAS groups as persistent organic pollutants (POPs) namely perfluorooctane sulfonic acid (PFOS) and related compounds in 2009 [6] and perfluorooctanoic acid (PFOA) and related compounds added in 2019 [7]. Furthermore, the Strategic Approach to International Chemical Management (SAICM) has listed PFAS as an issue of concern. Recently the European Commission published its Chemicals Strategy including phasing out the use of PFAS in the EU, unless their use is essential [8,9].

PFOS and PFOA and some other PFASs accumulate in biota and humans and resulted in ubiquitous contamination of human blood, human milk and protein rich organs [10–14]. PFOS is normally the most prevalent PFAS in humans followed by PFOA. Other PFASs substances are normally found in lower concentrations but in special instances perfluorononanoic acid (PFNA) or perfluorohexane sulfonic acid (PFHxS) can also be high [15–17]. According to the current state of knowledge, several PFAS substances are classified as carcinogenic, developmentally toxic, endocrine, immunotoxic and genotoxic as well as having an influence on the metabolism [15,18,19,52,53] (Hocevar & Kamendulis, 2018). Recently the European Food Safety Authority reduced the tolerable weekly intake of the sum of PFOS, PFOA, PFNA and PFHxS with the result that a considerable share of the population is above this TWI [15]. Therefore the current exposure of humans to PFASs need to be reduced and further releases minimized and avoided.

Meanwhile, several hundred million people globally are exposed to PFOS, PFOA and other PFASs from drinking water pollution due to contamination of ground and surface water [20,54] as well as contamination of soils and related contamination of plants/vegetables and livestock [11,21–23,56]. A recent study in the US estimates that 200 million Americans could have PFASs in their drinking water at a concentration of 1 ng/L and therefore above levels considered safe [19,20]. In China 100 million inhabitants consume drinking water above regulatory limits set in some states in the US and for most measured Chinese cities levels are also above 1 ng/L [54] similarly to US [20]. In the US, Europe and Japan for many areas firefighting foam - frequently from the military - is responsible for the contamination of ground and drinking water [24,25]; Yukioka et al., 2019). Particular high exposure of communities and cities are also caused by PFAS/organofluorine industries including Teflon and other fluoropolymer production [23,26–28,54,55].

Since PFASs are highly persistent and that for the perfluorinated moiety of the PFAS molecules no degradation in soils or groundwater is apparent, PFASs have become known as “forever chemicals” [29]; Blum et al., 2014). Therefore, contaminated sites and polluted ground water impacting populations need to be investigated and possibly remediated. Industrial landfills with high load of PFASs are at risk of long term release and eventually may need to be excavated to protect human health (Weber et al., 2011; [28]). The Stockholm Convention has given recommendations to systematically track and investigate the historic waste management of producers and users of PFOS and associated pollution should be tracked in systematic manner globally [30,31]. In addition a chapter on inventory development for PFOS contaminated sites has been included in the Stockholm Convention PFOS inventory guidance (UNEP 2010 [32]; which can both similarly be applied for other PFASs. While pollution from producers and major users are located around known production sites and industries using PFASs in production, the pollution from firefighting foams are more widely distributed from the diverse uses by the military, airports, oil production and hydrocarbon processing industry and oil storage sites etc. [24,33]. Due to the high mobility of this group of substances in ground and surface waters, individual contaminated sites will increase their footprints in future if no remediation action is taken and can reach drinking water wells sucking ground water and

therefore triggering a migration towards the wells [24]; Oliaei et al., 2011, [34]. Overall there is a lack of systematic information on practical clean-up measures or some specific sources like the contamination of firefighting equipment which can result in releases from memory effects even if the equipment is refilled with fluorine free foams (F3 foams) similarly to plating industries after substitution of PFOS [35,36].

Therefore in this paper we want to:

- Give some relevant information on the risk of (future) PFAS pollution from firefighting foam use
- Give an insight into specific remediation and adsorption methods of PFAS pollution and their optimization
- Describe the largely unknown pollution from the cleaning of firefighting vehicles and equipment and how this can be avoided

2. Materials and methods

2.1. Assessment of PFAS use in extinguishing agents in Germany

An overview on the PFAS use in firefighting in Germany and current global use, has been compiled from available literature.

2.2. Adsorption experiments

The adsorption of PFAS on granulated activated carbon (GAC) or the use of ion exchange materials (IX) has been the most important methods in large-scale applications due to the lack of alternatives. The use of such materials in fixed beds is simulated in so-called column experiments. For a practical assessment of the possibilities and limitations of the use of GAC and IX, different column systems have been constructed for column experiments. The aim was to transfer the results obtained using these columns to large-scale systems in the best possible way. The important filter parameters are filter speed, residence time and the bulk height of the material can be adapted to industrial-scale conditions and thus practical situations can be simulated. The filter parameters used in the experiments mentioned below are noted in Fig. 1.

For highly contaminated waters, where only small bed volumes are expected before PFAS breaks through, the column system shown in Fig. 1 was used. The water volumes to be used in this system can be synthesized on a semi-industrial scale and then treated in the column systems.

2.3. Monitoring of PFAS release from firefighting trucks

In contrast to experiments on water treatment on a semi-industrial scale, the simulation of cleaning successes of PFAS-contaminated surfaces located within complex plant or pipe systems is hardly possible. Although laboratory-scale tests were carried out to assess the cleaning of PFAS-contaminated surfaces on defined systems, this report documents results from real cleaning processes that can be achieved when treating firefighting vehicles or other equipment with the PerfluorAd method [37].

The evaluation of the results was based on an investigation of the PFAS contents in the first rinse water solution (first flush) after the foam agent concentrate had been emptied and on an investigation of the PFAS contents of the last flush solution.

2.4. Analysis of PFASs

2.4.1. PFAS individual substances

As standard parameters the PFASs shown in Table 1 were



Column diameter	[m]	0.054
Surface	[m ²]	0.002
Height of bed	[m]	1.000
Volume of adsorber material	[m ³]	0.002

Fig. 1. Columns for an adsorbent bed for a total of 6 × 1.0 m with specification of the filter parameters (manufacturer: Cornelsen Umwelttechnologie GmbH).

Table 1
Analysed individual PFASs.

No.	Name of Substance	Shortname	CAS-No.
1	Perfluorobutanoic acid	PFBA	375-22-4
2	Perfluoropentanoic acid	PFPeA	2706-90-3
3	Perfluorohexanoic acid	PFHxA	307-24-4
4	Perfluoroheptanoic acid	PFHpA	375-85-9
5	Perfluorooctanoic acid	PFOA	335-67-1
6	Perfluorononanoic acid	PFNA	375-95-1
7	Perfluorodecanoic acid	PFDA	335-76-2
8	Perfluorodecanoic acid	PFUnA	2058-94-8
9	Perfluorododecanoic acid	PFDoA	307-55-1
10	Perfluorobutanesulfonic acid	PFBS	29,420-49-3
11	Perfluoropentane sulfonic acid	PFPeS	2706-91-4
12	Perfluorohexane sulfonic acid	PFHxS	355-46-4
13	Perfluoroheptane sulfonic acid	PFHpS	357-92-8
14	Perfluorooctane sulfonic acid	PFOS	56,773-42-3
15	Perfluorodecanesulfonic acid	PFDS	335-77-3
16	Fluorotelomer sulfonate 4:2 FTS	4:2 FTS/H4PFHxS	757,124-72-4
17	Fluorotelomer sulfonic acid 6:2 FTS	6:2 FTS/H4PFOS	27,619-97-2
18	Fluorotelomer sulfonate 8:2 FTS	8:2 FTS/H4PFDS	39,108-34-4
19	Perfluorooctane sulfonamide	PFOSA	754-91-6
20	DPOSA ^a	Capstone A	80,475-32-7
21	CDPOS ^a	Capstone B	34,455-29-3

^a See supporting information Figure S1 for the structure.

analysed in accredited laboratories (EN17025). The 21 substances contained in this list are subdivided into nine perfluorocarboxylic

¹ A DIN standard is a voluntary standard developed under the direction of the German Institute for Standardization, in which tangible and intangible objects are standardized. DIN 38407–42 is the German standard procedure for the analysis of water, waste water and sludge - Jointly identifiable groups of substances (Group F) - Part 42: Determination of selected polyfluorinated compounds (PFC) in water.

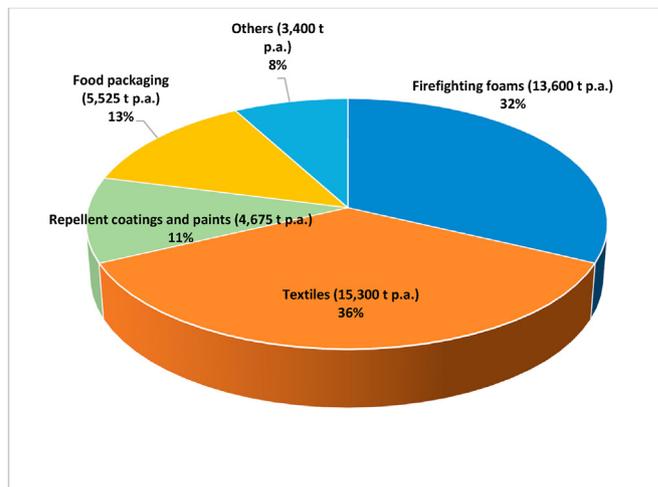


Fig. 2. Estimated production and consumption volumes of fluorine telomers for 2019 (in t p. a. and share of total volume in %) based Klein et al. [42].

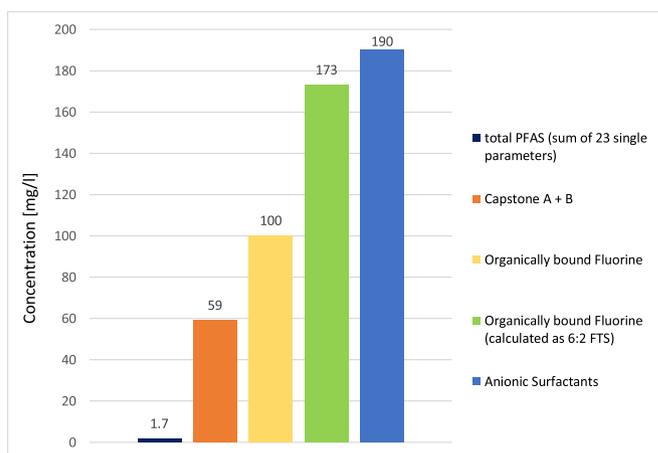


Fig. 3. Example of a composition of fire extinguishing water from 2019 (1% AFFF extinguishing agent concentrate in water, without fire by-products).

acids (PFCAs), six perfluorosulfonic acids (PFSAs), three (poly-fluorinated) fluorotelomer alcohols, one sulfonic acid amide, and two precursor substances, which are found especially in newer fire extinguishing foams.

DIN 38407–42 (status March 2011)¹ served as the basis for the determination of PFASs. Methods using high-performance liquid chromatography and mass spectrometric detection (HPLC-MS/MS) after solid-liquid extraction (F42). With a simple matrix, determination limits of 10 ng/l can be achieved with this method for the individual congeners. However, in the case of complex matrix loads, the determination limits are often increased to several 100 ng/l.

The analysis of PFAS were carried out by an accredited external environmental laboratory for the PFASs listed in Table 1.

2.4.2. Organically bound fluorine

In order to determine the content of all fluorine organic compounds and to be able to evaluate the water treatment process for its effectiveness with regard to the total potential of PFASs, the content of organically bound fluorine was used.

For the determination of the organically bound fluorine, the

water sample is directly combusted without preparation or enrichment. A previous adsorption or elution of the water contents is explicitly not performed with the chosen method. The resulting gases are captured in an absorption solution and the resulting solution is analysed by ion chromatography (IC). The organic fluorine content is determined from the measured concentration of total fluorine minus the inorganic fluoride.

Due to the combustion of the water sample without previous enrichment, the determination limits of 0.0004% (4.0 mg/l) achievable with this method are relatively high, so that this method was only used for more highly contaminated media, such as fire extinguishing water.

The analysis of PFASs were carried out by Fraunhofer UMSICHT, Oberhausen, a German research institute.

3. Results and discussion

3.1. PFAS use in firefighting foam and related risk for pollution of water bodies due to the use of fluorine-containing extinguishing agents

In a research relating to Germany, Held comes to the conclusion that by the production of extinguishing agents (2%), by the handling of extinguishing agents at fire stations (7%), by the use of extinguishing agents at fire training areas (10%) and by the use of extinguishing agents in fire incidents (29%), in total 48%, the PFAS-containing extinguishing agents, must be assumed as the most frequent cause of environmental contamination [38].

In 2008, approx. 800 t of PFAS-containing extinguishing foams with a total PFOS content of approx. 6.3 t were registered in Germany. According to the State Office for Nature, Environment and Consumer Protection of North Rhine-Westphalia (LANUV NRW), PFOS in fire extinguishing agents has since then been increasingly replaced by polyfluorinated surfactants. According to the European Directive 2006/122/EC, fire-fighting foams with a PFOS concentration of more than 0.005% may no longer be used since 2011. However it seems that still some PFOS foams are present in stationary facilities. A similar finding has recently been made by the Japanese Environmental Ministry.

For larger fire incidents, such as fires in tire or plastic warehouses, LANUV NRW has conducted research and found that 10 to 20 t of AFFF foaming agents with a content of PFASs of approx. 1–6% are used. Accordingly, PFAS emissions of between 100 kg to over a tonne per fire event are released. In the case of large fires, such as those that can occur in the chemical and petrochemical industry and tank farms, PFAS emissions of up to 20 t are estimated for the required use of large quantities of PFAS-containing extinguishing foams [39]. This large open use and release of PFASs with associated groundwater contamination [24,40,41] requires alternatives to PFAS foams which have been developed in the last decade and can substitute PFAS foams [42,43].

In the white paper “The doubtful future for short-chain PFAS” [42], an expert panel compiled by the International POPs Elimination Network (IPEN), estimates that the annual production of PFASs in the form of fluorotelomers is still considerable, so that there is a risk that a large proportion of contaminated extinguishing water and foam continues to be released onto soil and into ground water and the wider environment with only minor activities on contaminated extinguishing water retention [42]. According to research conducted by IPEN and the expert panel, it is unlikely that the estimated production volumes already take into account the production of many developing countries or reflect the diversity of newly developed PFAS such as fluoropolymers, GenX, F53 and Adona [42]. Also, PFOS and PFOA still has an exemption in the Stockholm Convention for use in firefighting foam and are still

produced and used.

Forecast production of fluorotelomers in 2019 estimated by IPEN based on data from the Global Market Insight in 2016 is assumed to be 42,500 t. Since 2016 an annual increase in production of 12.5% has been estimated (Fig. 2).

Of the estimated total production of fluorotelomer compounds, IPEN estimates that more than 13,000 t or approximately 1/3 of the total annual production in 2019 will be used for fire extinguishing agents (32%) with associated release risk and environmental pollution. This highlights the future risk of PFAS pollution from further AFFF use.

Even if no continuous input of PFASs into the environment results from fire incidents, but rather diffuse pollutant inputs from individual events, the research conducted by Held and IPEN clearly illustrates the environmental relevance of the case-related high PFAS emission volume. Thus, fire extinguishing agents containing PFASs have to be given high attention with regard to precautionary as well as aftercare soil and water protection.

For waters with an undefined PFAS composition, as is to be assumed especially when using current AFFF foaming agents, an evaluation of the water load as well as the achievable cleaning results is not possible if only the quantifiable individual PFASs are evaluated. Held & Reinhard assume that AFFF foaming agents contain hundreds of precursor substances which include approx. 40 PFAS classes [44] and are highly complex and difficult to determine by classical analytical methods [45]. However, the precursors in such complex mixtures can be assessed by the Total Oxidisable Precursor (TOP) Assay [46].

Fig. 3 shows the composition of fluoro-organic substances in water contaminated with 1% of an AFFF extinguishing agent in 2019. In practice, dilutions between 1 and 6% are used, i.e. the content of PFAS is correspondingly higher with higher AFFF foam concentrate additions than in the example shown below.

Individual PFAS substances, as can be determined from parameter lists currently available on the market, have a total content of only 1.7 mg/l PFAS. Precursor substances such as Capstone A and Capstone B (See supporting Information Fig. S1) are not yet included as parameters in the standard lists of environmental laboratories. These “Capstones” are polyfluorinated substances that degrade in the environment to persistent perfluorinated compounds. In the example shown, these PFASs, which are often not yet quantifiable by measurement technology, have a concentration of 59 mg/l alone, i.e. these substances are almost 35 times higher in concentration than the individual PFAS compounds that are quantified by PFAS standard analysis in laboratories.

In order to address the total content of fluorine-organic substance in complex contaminated waters, the organically bound fluorine was therefore used as an additional parameter for PFAS-contaminated waters that were contaminated due to exposure to AFFF foams. In the example in Fig. 3, the concentration of organically bound fluorine is 100 mg/l. Assuming that the average chain length and structure of the PFAS structures contained in current AFFF foams are significantly similar to the structure of the 6:2 FTS (H4PFOS), a hypothetical total PFAS concentration of 173 mg/l can be calculated.

The hypothetical total concentration of PFAS leads, on the basis of the example shown to the conclusion, that the fluoro-organic substances in the water that cannot be detected as PFAS single substances can be a factor of 100 higher (or more) than the actually measured PFAS by single substance analysis. This knowledge leads to the need to evaluate PFAS that are not known or quantifiable as single substances by sum parameters. However, there is currently no normative standard for this.

Table 2
Raw water compositions from different dilutions with AFFF foaming agent.

		1%-AFFF-Premix	0,5%-AFFF-Premix	0,25%-AFFF-Premix
Organic Bound Fluorine	[mg/l]	101.8	52.7	20.8
Sum of 21 PFASs incl. Capstone	[µg/l]	3593.0	2157.6	739.0
Sum of perfluorinated PFASs	[µg/l]	66.3	50.1	23.9
Total Capstone A + B	[µg/l]	1117	703	199
6:2 FTS	[µg/l]	2400	1400	513
DOC	[mg/l]	1900	850	423

Table 3
Filter parameters.

Column diameter	[m]	0.054
Surface	[m ²]	0.002
Height of bed	[m]	1.000
Volume of adsorber material	[m ³]	0.002
Flow rate	[m ³ /h]	0.030
Filter speed	[m/h]	13.30
Retention time	[min.]	5

3.2. Water treatment methods and adsorption studies for PFASs

In 2016, Dickenson & Higgins prepared a comprehensive compilation and evaluation of processes for the treatment of PFAS-contaminated water. Membrane processes (nanofiltration, reverse osmosis) are attested a general elimination efficiency of >90%. Adsorption (activated carbon, ion exchanger) is also said to have a high elimination performance and thus a good suitability - with certain limitation for short-chain PFASs. All other processes discussed by Dickenson & Higgins are only certified as having low elimination performance [47]. The study of the German Federal Environment Agency “Remediation management for local and wide-spread PFAS contaminations” comes to a similar conclusion [48].

Our experiments demonstrate that starting with PFAS substances that have at least 4 carbon atoms in the alkyl chain, these compounds can be separated from water by using suitable adsorber or ion exchange materials. The effectiveness of the application of such materials are discussed below. The results presented in the following were obtained by using columns and are intended to provide a direct link to practical applications. The difference to numerous scientific publications, which describe the adsorption behaviour of PFAS congeners using different materials, is therefore on the one hand the exclusive use of real water, which often has a high organic background, and on the other hand the fact that the adsorption tests were carried out in continuously operated semi-technical column systems.

Table 4
Characterization of the adsorber materials GAC and IX.

GAC	
Material	Hard coal
fresh or reactivated coal	reactivated
Impregnation Y/N	unimpregnated
Total Surface (BET)	[m ² /g]
Iodine number	[mg/g]
Bed Density	[kg/m ³]
IX	
Material	Polystyrene crosslinked with divinylbenzene
Functional Group	Complex Amino
Appearance	Spherical Beads
Bed Density	[kg/m ³]
	650–700

Table 5a
Raw water PFAS concentration [µg/l].

Parameter	Concentration [µg/l]	Percentage [%]
PFBA	9.0	0.53
PFPeA	11.0	0.65
PFHxA	31.0	1.83
PFHpA	25.0	1.48
PFOA	4.8	0.28
PFNA	0.5	0.03
PFDeA	1.9	0.11
PFBS	0.0	0.00
PFPeS	0.0	0.00
PFHxS	0.0	0.00
PFHpS	0.0	0.00
PFOS	0.0	0.00
4:2 FTS	0.0	0.00
6:2 FTS	1500.0	88.59
8:2 FTS	110.0	6.50

Table 5b
Raw water PFAS substances groups and DOC.

Substance group	Concentration [µg/l]	Percentage [%]
short-chain PFAS	51.0	3.01
long-chain PFAS	1642.2	96.99
total PFAS	1693.2	100.00
short-chain PFCA	51.0	3.01
long-chain PFCA	32.2	1.90
short-chain PFSA	0.0	0.00
long-chain PFSA	0.0	0.00
short-chain FTSA	0.0	0.00
long-chain FTSA	1610.0	95.09
total PFAS	1693.2	100.00
DOC	1750.0	[mg/l]

The application of granulated activated carbon (GAC) is the most established process in Germany for the treatment of PFAS ($\geq C4$) contaminated water. As an example we refer to applications in the treatment of drinking water, where at very low PFAS concentrations and inconspicuous water conditions filter runtimes of up to 37,000 BV are known (Kasprzyk & Rodriguez, 2019). Investigations, such as those carried out by Maimaiti, among others, however, illustrate the competition between the individual PFAS compounds, which in individual cases can lead to a significant reduction in the achievable filter running times (Maimaiti et al., 2018).

3.3. Influence on the adsorption by an organic background load

In the presence of two or more adsorbable organic substances in a solution, the resulting influence of competing adsorption with a concomitant decrease in adsorption capacity for each of the competing substances has been known for a long time. As early as 1985, Sontheimer described data-based examples of possible effects of competitive adsorption (Sontheimer et al., 1985). The effects of competing adsorption on PFAS single substances are not described there, since this group of substances was not yet the focus of water purification at that time.

Recent studies - e.g. by Qiu and Dickenson & Higgins - take up this effect, which is very important for the practical application of adsorption processes, and provide information on the possibly significant influence on the adsorption capacity that can be

recognized under different matrix conditions. (Qiu, 2007) [47].

In the following, the influence of organic background loads on the adsorption of PFAS single compounds is shown by means of column experiments. Table 3 shows the main filter parameters (see Table 3).

The prepared media were prepared as 0.25%, 0.5% and 1.0% dilutions of commercial AFFF concentrate. Based on the assumption that AFFF concentrates are used as 1.0–3.0% dilutions in fire extinguishing operation, the above mentioned test mixtures appear to be practically relevant, since in large-scale industrial applications a dilution of the retained extinguishing water due to the addition of extinguishing water without foam concentrate is to be assumed. No other substances were added to the dilutions. Table 2 shows the relevant water contents (see Table 2).

As this is a “new” extinguishing agent from 2018, the product does not contain any perfluoro sulfonic acids (PFSA) or short-chain perfluoro acids (PFCAs). However, high concentrations of poly-fluorinated compounds, such as FTSA and Capstone products (Table 1; Fig. S1), are detectable. Organically bound fluorine is used as a parameter to assess the total PFAS content. With this parameter the content of PFASs, so-called precursor substances, which cannot be detected by single substance analysis, can be estimated.

The GAC and IX products characterized in Table 4 were used as filter materials (see Table 4). The composition of the water for testing is shown in Tables 5a and 5b.

The breakthrough curves (Figs. 4 a-f) show that the higher

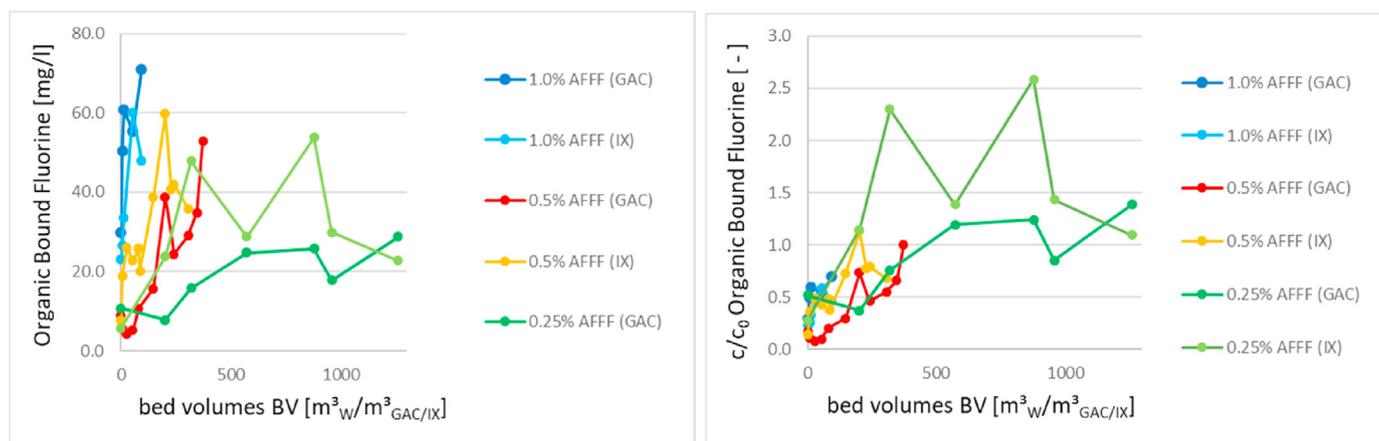


Fig. 4. a+b: Breakthrough behaviour of organically bound fluorine a) Effluent concentration of organically bound fluorine [mg/l] and b) c/c_0 organically bound fluorine [-].

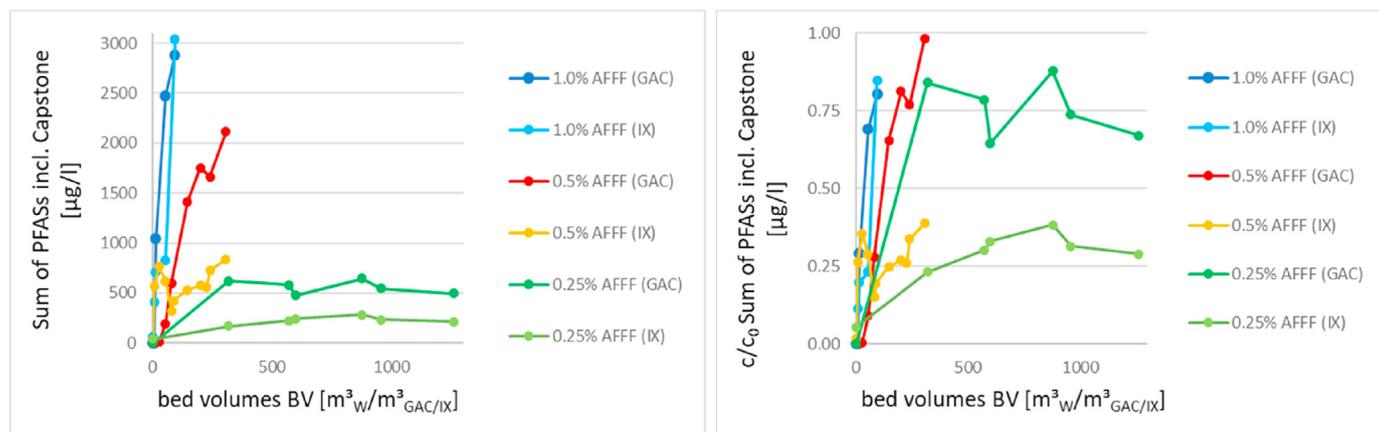


Fig. 4. c+d Breakthrough behaviour of total PFAS incl. “Capstones” a) Effluent concentration of total PFAS incl. “Capstones” [µg/l] and b) c/c_0 total PFAS incl. “Capstones” [-].

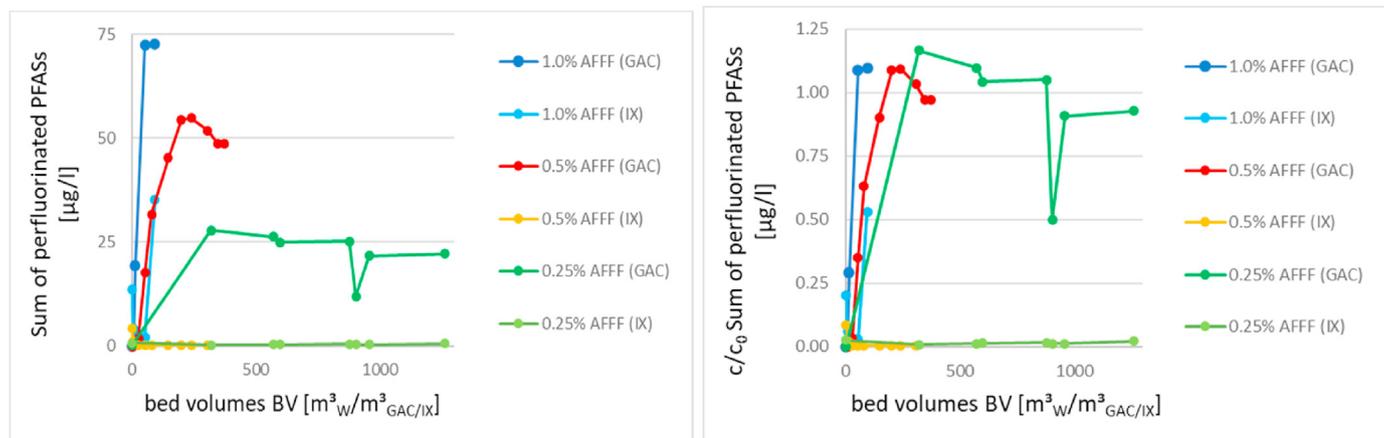


Fig. 4. e+f: Breakthrough behaviour of sum of perfluorinated PFAS a) Effluent concentration of sum of perfluorinated PFAS [$\mu g/l$] and b) c/c_0 sum of perfluorinated PFAS.

concentrated fire extinguishing water leads to a very early breakthrough of the fixed-bed filters. In particular for the fluoro-organic precursor substances shown as “organically bound fluorine”, an increase in the PFAS concentration in the filter effluent can be detected very early during operation. This means that the effluent concentration temporarily exceeds the PFAS content of the raw water.

3.4. Precipitation using specialized coagulants (PerfluorAd process)

3.4.1. Principle of the method

The technology known as PerfluorAd® process uses specialized coagulants. The application of the PerfluorAd® process does not require sophisticated plant engineering equipment, but is based on standard processes and standard components. Conventional stirred and tubular reactors can be used in this process.

The process is a precipitation process which separates significant amounts of the dissolved PFASs present in the raw water in the form of precipitates. The basic approach of this technology is to use a precipitation process in an easy-to-operate pre-treatment stage to significantly reduce the load on the subsequent treatment stage(s) (usually GAC or ion exchangers (IX)), thereby contributing to an optimization of the cleaning result as well as achieving a noticeable cost advantage and a resource-saving process (see Fig. 5).

Resource-saving means a minimized use of active ingredients as the sum of specialized coagulants and GAC or IX and a resulting minimized formation of residual substances (sum of precipitates and GAC/IX). Instead of an optional after-treatment with powdered activated carbon, GAC and/or IX, alternative processes can also be applied. After precipitation using PerfluorAd® an aftertreatment is not mandatory. The arrangement of an aftertreatment stage depends on the project-related conditions as well as on the desired cleaning objectives or possible official requirements.

PerfluorAd consists in its basic structure of a fatty acid of plant origin and is thus very biodegradable under the simplest conditions. This basic structure has been specially applied by adding cationic groups.

Details are subject to IP. The intellectual property rights are protected by the patent and can be read there.” According to the safety data sheet, PerfluorAd does not contain any hazardous ingredients. Therefore, possible risks of PerfluorAd related to health are classified as minimal.

In contrast to many commercially available coagulants, PerfluorAd is naturally biodegradable, which means that any residues of the active ingredient that remain will degrade on their own.

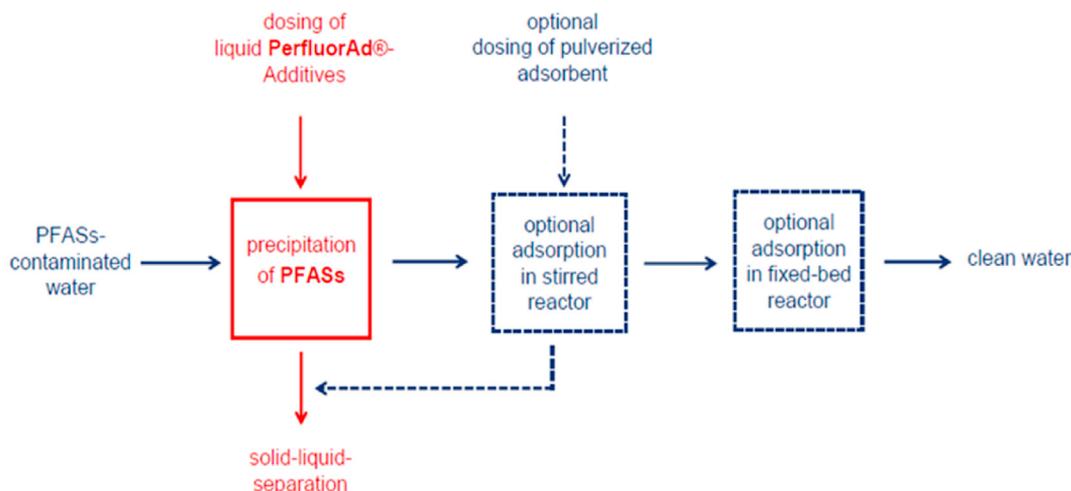


Fig. 5. Application principle of the PerfluorAd pretreatment process [49].

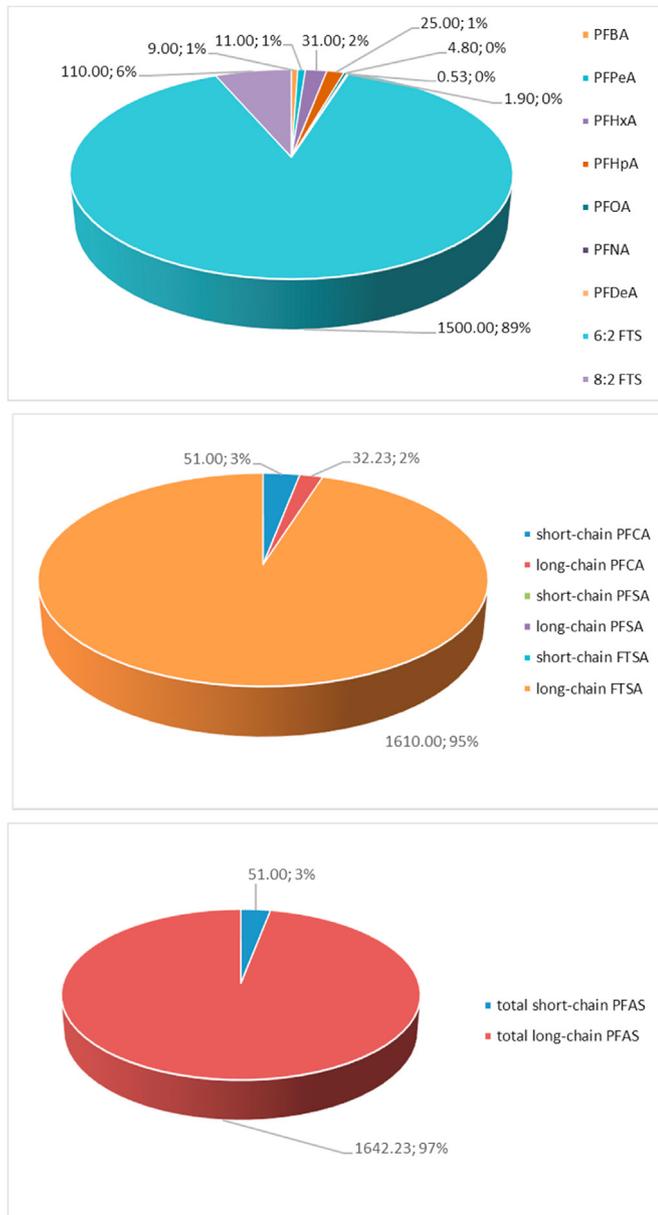


Fig. 6. a–c: PFAS load in raw water with composition [µg/l] and percentage of total load [%].

3.4.2. Advantages from the use of specialized coagulants (PerfluorAd)

In contrast to the treatment of drinking water or regular waste water, the treatment of contaminated fire extinguishing water, contaminated ground water and some industrial waste water often causes significant fluctuations in the concentration of pollutants and also in accompanying parameters in the raw water. Furthermore, it cannot be assumed that the volume flows to be treated are constant over the entire remediation period. Since it is the declared aim of a groundwater remediation measures that in the course of the remediation not only the concentrations of pollutants on the raw water side but also the water volumes to be treated are reduced, the changing boundary conditions must be taken into account when selecting the treatment methods.

When using fixed-bed filters, regardless of whether they are equipped with GAC or IX, not only their dimensioning but also the material selection - at least for the initial filling - must be carried

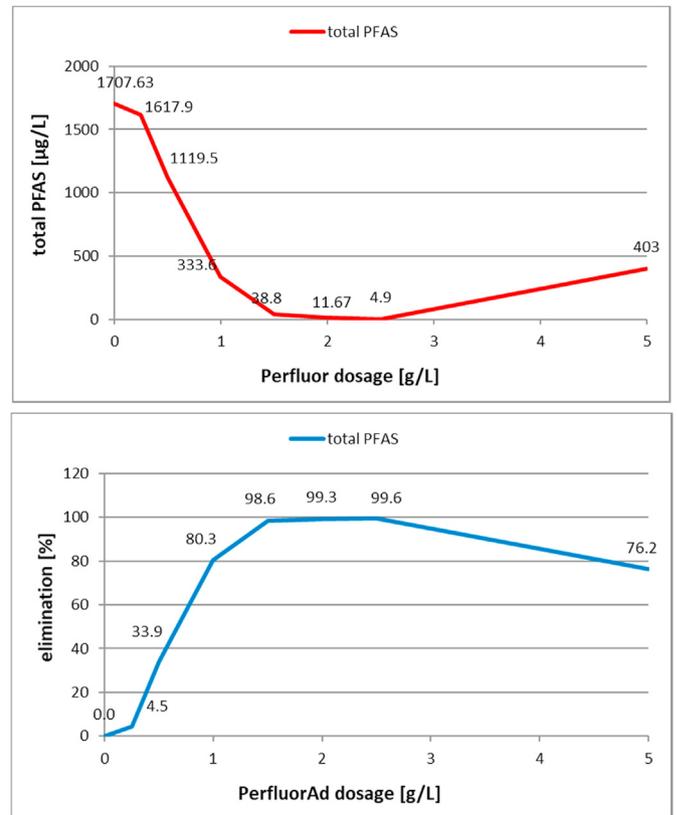


Fig. 7. a+b: a) Residual concentration total PFASs [µg/l] and b) elimination rate total PFASs [%] for 1% AFFF premix after addition of PerfluorAd®.

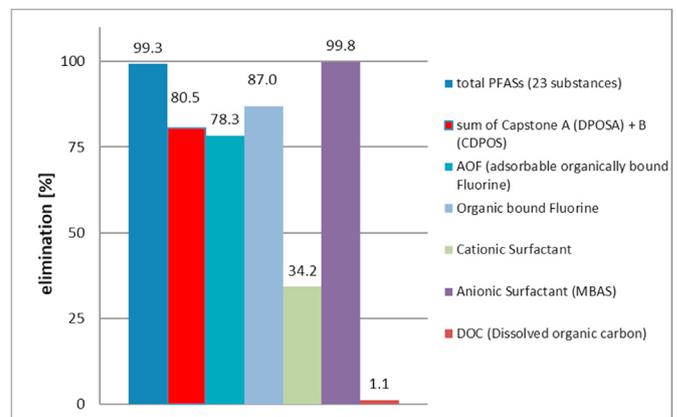


Fig. 7. c: Elimination rates for different parameters [%] at an optimal dosing rate of 2.0 g/l PerfluorAd for this application.

Table 6
Filter parameters.

Column diameter	[m]	0.054
Surface	[m ²]	0.002
Height of bed	[m]	1.000
Volume of adsorber material	[m ³]	0.002
Flow rate	[m ³ /h]	0.030
Filter speed	[m/h]	13.30
Retention time	[min.]	5

out before the corresponding plant is commissioned. After commissioning of the treatment process, there is no or only a minor possibility to influence the process. By monitoring the development of pollutants during the course of the treatment stages, the suitability of the installed adsorber material can be assessed in order to switch to an alternative product in case of an upcoming material change.

In addition to the possibility to actively influence the process at any time, the stability of the PerfluorAd® precipitation process even under strongly fluctuating raw water conditions is a further positive aspect. This property, which can also be described as technical resilience, means, in the context of the use of specialized precipitants, the maintenance of pollutant elimination even under extreme conditions. This can mean, for example, extreme pollutant peaks, which could lead directly to pollutant breakthroughs if a GAC filter is largely preloaded. With precipitation reactions it can be assumed that the process does not necessarily come to a complete shut-down under extreme conditions, but that the elimination of pollutants is only temporarily reduced.

3.4.3. No negative influence from the organic background on the treatment process when using specialized coagulants (PerfluorAd)

In order to evaluate the elimination performance and, if applicable, influences of water highly contaminated with PFAS and at the same time with a complex DOC background, the following Jar test was performed with a synthetically produced fire extinguishing water (Fig. 6).

An AFFF concentrate was prepared in a 1% dilution in tap water. Such a dilution (sometimes up to 3%) is often used by fire fighters to fight burning liquids. The water is characterized by a high content of FTSA's (95%).

In the dosing range between 1.5 and 2.5 g/l PerfluorAd, elimination rates of approx. 99% for total PFAS (without "Capstones") are achieved (see Fig. 7 a+b). With this dosage, an elimination rate of approx. 80% is achieved for "Capstones" and 87% for organically bound fluorine (Fig. 7 c). The elimination of DOC is only 1.1%, which can be seen as a clear indication of the specialization of the PerfluorAd active ingredient in the anionic surfactants (Fig. 7 c).

3.4.4. High elimination efficiency, especially at high PFAS concentrations, with use of specialized coagulants (PerfluorAd)

In the experiments documented below, different dilutions of the AFFF concentrate were used (0.25%/0.50%/1.00%) (Table S1 Supporting information). These waters were initially applied to adsorber materials without pretreatment. Filter parameters including adsorbents description are compiled in Table 6. The GAC and IX products characterized in Table 7 were used as filter materials (see Table 7).

Following these test campaigns, the identical waters were

pretreated by a PerfluorAd dosing (see Fig. 8). It should be mentioned that the "supposedly suitable PerfluorAd dosing quantity" was determined exclusively on the basis of orienting preliminary tests, which were not based on a measurement, but only on a visual assessment of flocculation. No great effort was explicitly made to determine the best possible PerfluorAd dosage in order to represent an approach that was as close as possible to practice.

It should be pointed out that fluctuations or outliers in the following curves may be explained by different raw water qualities. Each experiment was carried out with several m³ of synthetically produced water. Due to the time and effort involved, the tests lasted several months, so that different batches of AFFF foam concentrate were used. Furthermore, inaccuracies in the chemical analysis have to be considered. Thus, not the single measured value but the trend of the curve and the overall level should be evaluated.

At this point, we would like to point out a study by Xiao et al. which assumes that short-chain precursor substances originating from AFFF foams may pass through GAC filters, since the criteria for changeover have so far been based on the known and analytically determinable perfluorinated PFAS [50]. Particularly in connection with "new foaming agents", which contain hardly any perfluorinated PFASs at all, but rather precursor substances that cannot be determined analytically to a large extent, it is therefore important to use procedures or combinations of procedures that also remove unknown molecular structures in the best possible way.

The parameter "organically bound fluorine" is used to address the potential of precursor substances that have so far been indeterminable by single substance analysis. The breakthrough curves shown in Fig. 8 a-b suggest that the potential of these unknown PFAS can be significantly reduced, especially in highly contaminated waters, by means of PerfluorAd preprecipitation. At the 1% AFFF dilution, the PerfluorAd application achieves a reduction of the initial level by approx. 90%, whereas the GAC and IX used show a strongly increasing breakthrough curve after less than 50 BV already. After PerfluorAd pretreatment, the breakthrough curves are almost parallel to the X-axis, which indicates a significant improvement in material utilization.

Figs. 9 and 10 show the breakthrough behaviour for the sum of 21 PFAS substances as currently determined by many environmental laboratories, or for the so-called Capstone compounds (see Supporting Information Fig. S1). These polyfluorinated substances are often used as substitutes for the perfluorinated PFASs, which are increasingly under criticism, as no regulations currently exist for this group of substances yet. However there are policies suggested or on the way to regulate PFASs as a group (Blum et al., 2014; [8,9,51]).

Both diagrams show that very good purification levels are achieved for both the analyzable PFAS and the capstone compounds when PerfluorAd technology is applied, resulting in a significant

Table 7
a+b: Characterization of the adsorber materials a) GAC and b) IX.

GAC	
Material	Hard coal
fresh or reactivated coal	reactivated
Impregnation Y/N	unimpregnated
Total Surface (BET)	900
Iodine number	900
Bed Density	450
IX	
Material	Polystyrene crosslinked with divinylbenzene
Functional Group	Complex Amino
Appearance	Spherical Beads
Bed Density	650–700

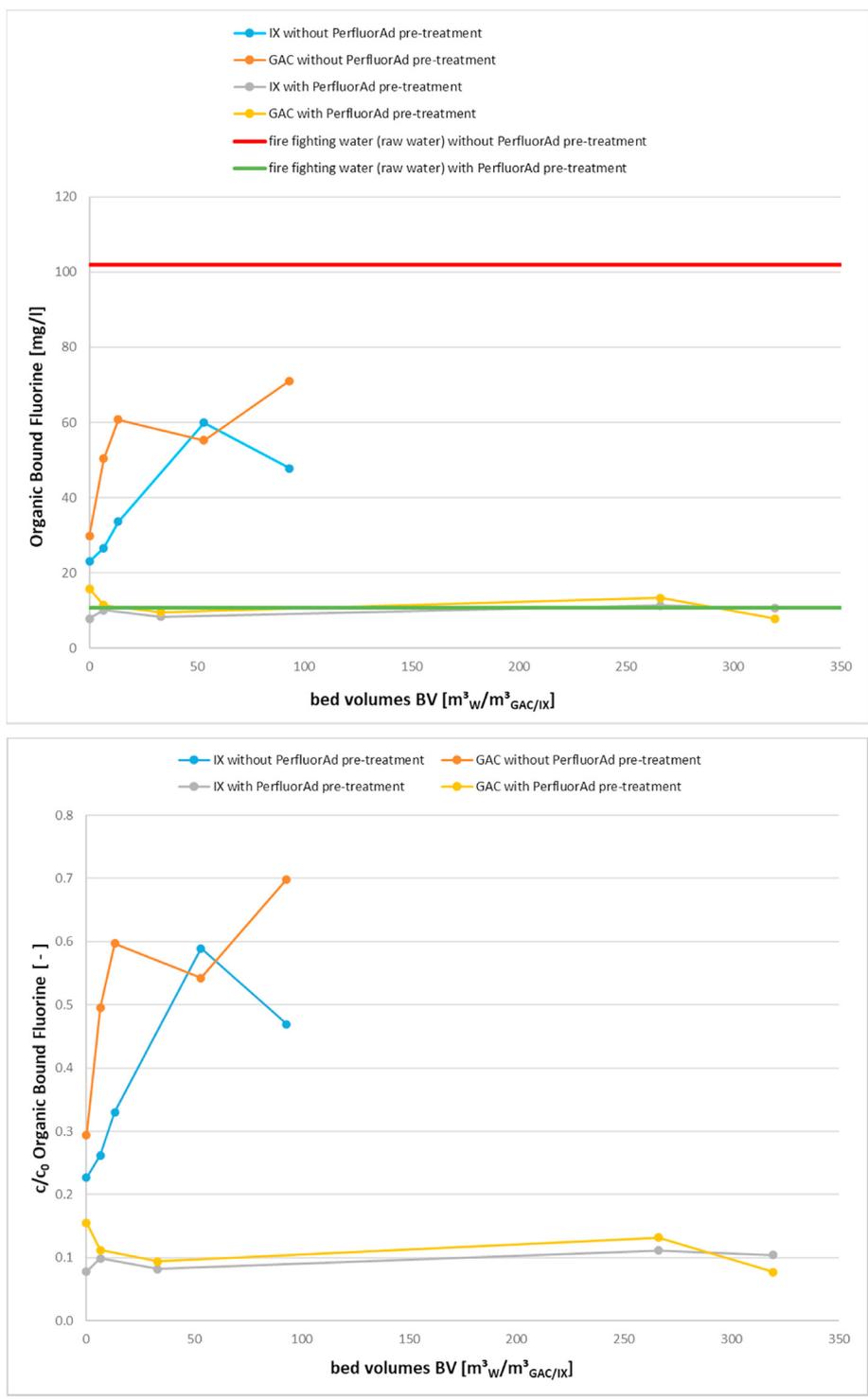


Fig. 8. a+b: Breakthrough behaviour by treating firefighting water as 1% AFFF premix a) Effluent concentration organically bound fluorine [mg/l] and b) c/c₀ organically bound fluorine.

extension of the lifetime of activated carbon and ion exchange filters.

3.5. Cleaning of surfaces contaminated with PFAS in fire extinguishing systems by the use of specialized coagulants (PerfluorAd)

With the increasing recognition that PFAS have a negative

impact on the environment and especially on human health, fire extinguishing agents containing PFAS (so-called AFFF extinguishing foams) are being replaced by fluorine-free foams.

However, replacing the extinguishing agents alone cannot ensure that no more PFAS is emitted into the environment from extinguishing systems that previously contained PFAS-containing products. It can be observed throughout that the PFAS contained in the fire extinguishing agent concentrate remain in considerable

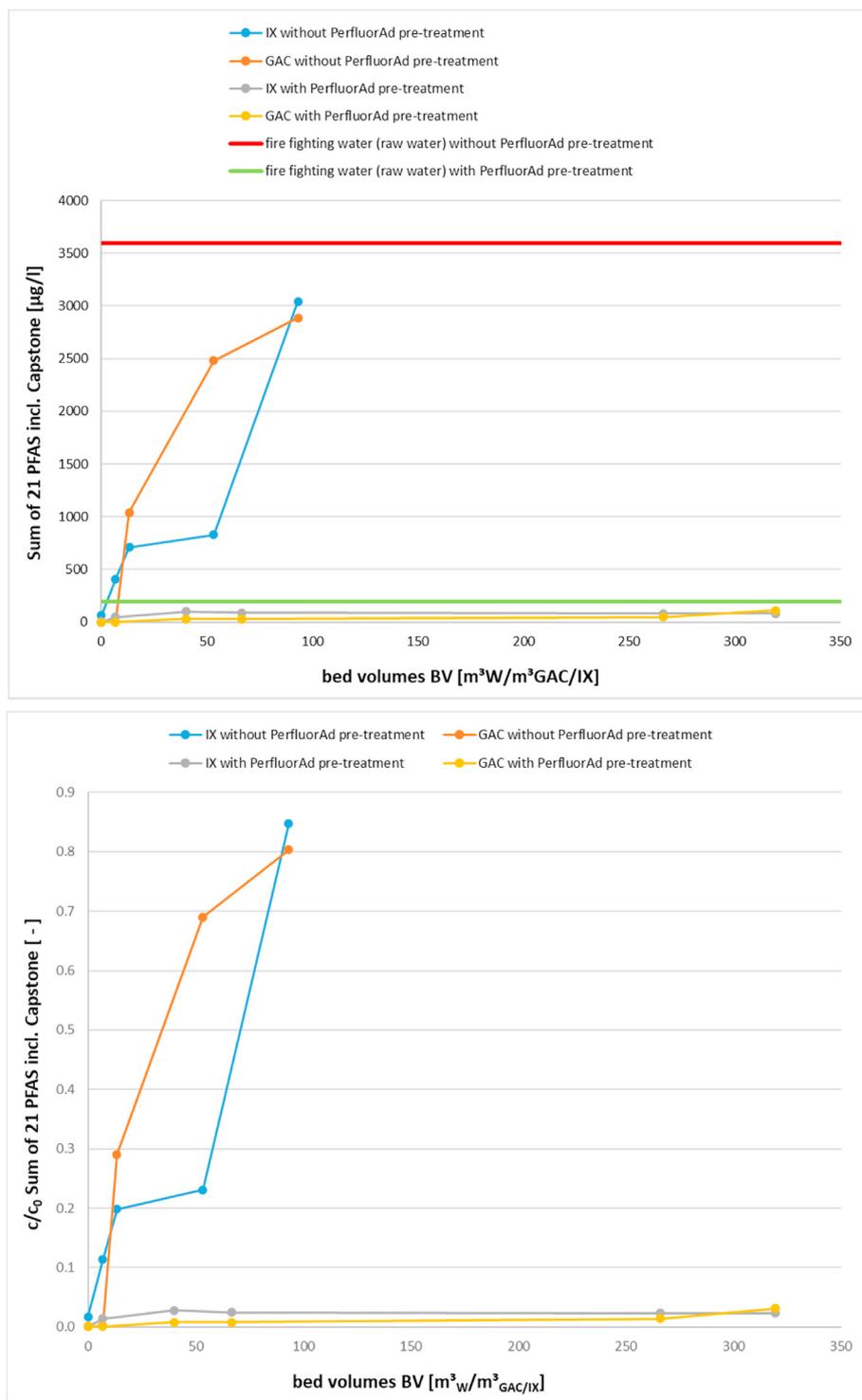


Fig. 9. a+b: Breakthrough behaviour by treating fire fighting water as 1% AFFF premix a) Effluent concentration sum of 21 single PFAS substances incl. Capstone [µg/l] and b) c/c_0 sum of 21 single PFAS substances incl. Capstone [-].

proportions in the systems and bleed out in small concentrations when used with fluorine-free extinguishing agents and thus finally reach the environment if the remaining PFAS in the system is not cleaned and removed.

By using the precipitant PerfluorAd, which specializes in PFAS, in rinsing solutions for cleaning fire extinguishing systems (fire trucks, fire boats, stationary extinguishing systems/sprinkler

systems, etc.), the residual contents in the systems can be significantly minimized (Fig. 11 a+b).

The residual PFAS concentrations observed in the systems after the fluorine-containing fire extinguishing agents have been emptied can vary considerably. As Fig. 11 a shows, PFAS concentrations between 10 and 800 µg/l total PFAS are often found. These concentrations can be reduced by using the specialized precipitants

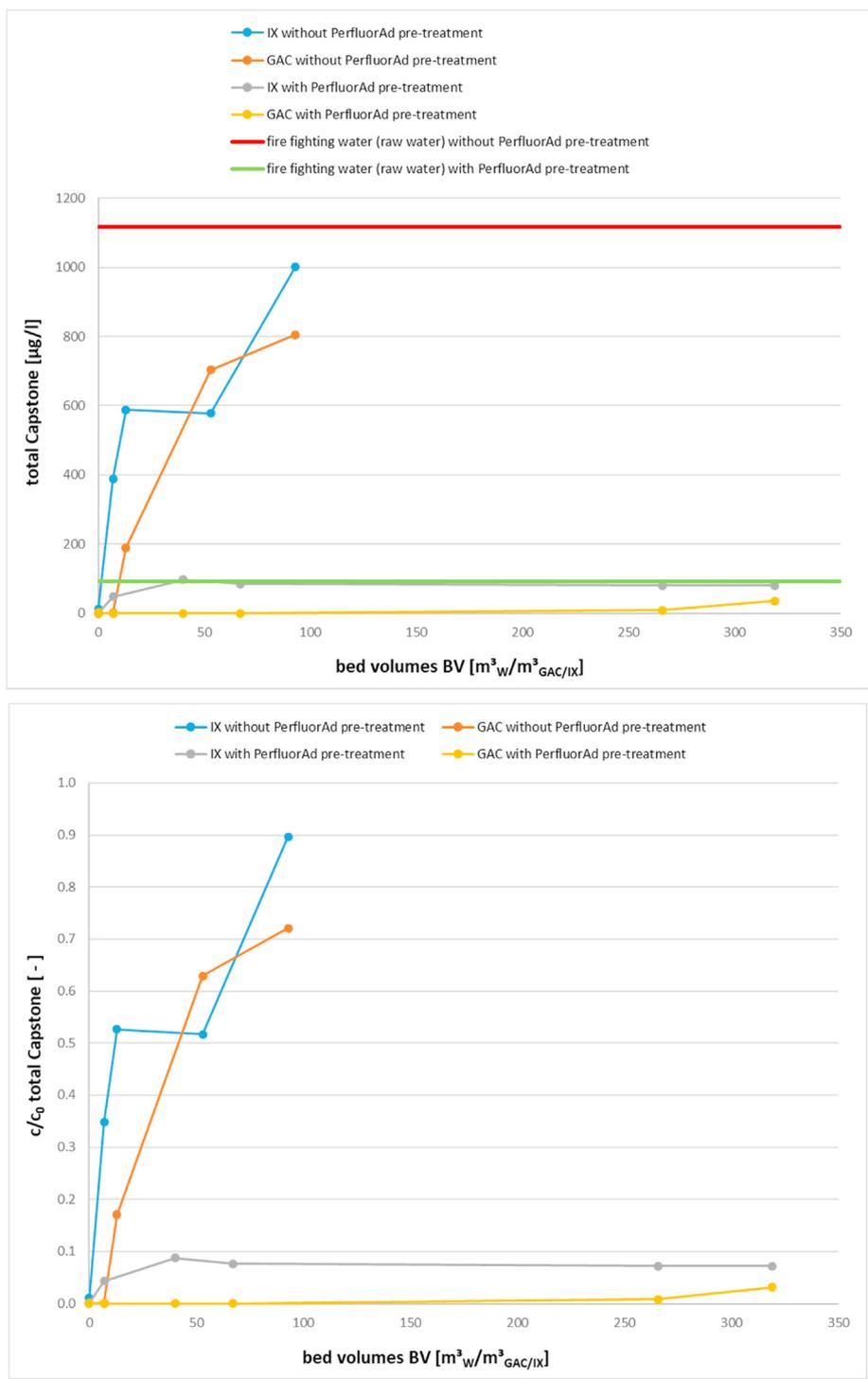


Fig. 10. a+b:: Breakthrough behaviour by treating fire-fighting water as 1% AFFF premix a) Effluent concentration Capstone A + B [µg/l] und b) c/c₀ Capstone A + B [-].

PerfluorAd to significantly less than 1.0 µg/l - in many cases also less than 0.3 µg/l and not detected total PFAS.

These cleaning successes consistently correspond to elimination levels of more than 99%, which can also be as high as 100% if compounds are below detection limit (Fig. S1 in supporting information).

The “strongly organic water” resulting from the rinsing process is cleaned on site by further application of the PerfluorAd precipitant without the need for off-site disposal of this water in high

temperature incinerators.

It has been discovered that sites where firefighting equipment have been cleaned over years can also be contaminated by PFASs and need assessment and possibly remediation.

4. Conclusion

Large amounts of contaminated sites from the former use of PFOS/PFOA and other PFASs in firefighting foam and from

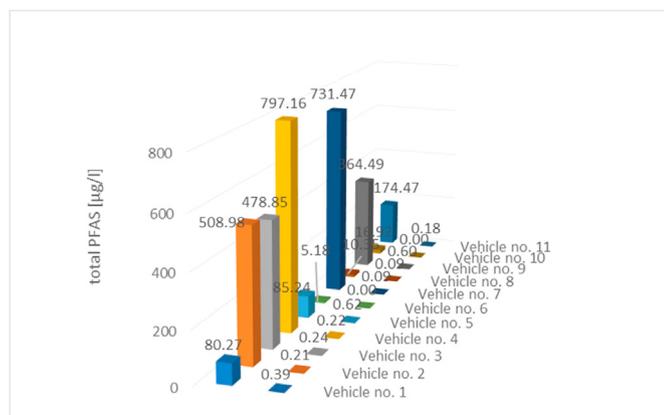


Fig. 11. Concentration of total PFAS [µg/l] before and after using PerfluorAd for the decontamination of PFAS-polluted fire suppression systems.

production and use of PFAS in fluoropolymer production and other industries have been generated in the past with associated exposure and future exposure risk for humans and biota. Furthermore PFASs are still used in firefighting foam with further contamination risk. Fluorine free firefighting foam (F3 foams) are viable alternatives and can substitute PFAS containing foams [42,43]. However if firefighting equipment is not thoroughly cleaned the PFAS pollution can continue even after substitution with F3 foams due to remaining PFASs in the equipment (memory effect) with further associated contamination. The Stockholm Convention recommends to systematically assess producers and users of PFOS and related waste management and contamination. This can be extended to all PFAS considering that SAICM stresses PFAS as an issue of concern.

The current study show that for contaminated ground water and other contaminated water, a separation of currently known perfluorinated PFAS structures ($\geq C4$) using suitable adsorber materials is basically possible. The technical effectiveness, the economic efficiency as well as the ecological sense of an exclusive application of adsorption processes depends however on various boundary conditions. It has been shown that especially with high PFAS loads and a complex organic background load of the medium to be treated, the application of adsorption or ion exchange processes lead to early or immediate filter breakthroughs. An optimized treatment of such demanding contaminated waters can be achieved by a combination of a pre-precipitation with the application of specialized precipitants and a subsequent adsorption or ion exchange.

The precipitants specialized in PFASs can also be used for the decontamination of fire extinguishing systems when PFAS containing foam is substituted by fluorine free foams. Areas where firefighting trucks and other firefighting equipment have been cleaned in the past can also result in contaminated sites and need assessment and possibly clean-up.

Declaration of competing interest

Two authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

One author declare the following financial interests/personal relationships which may be considered as potential competing interests:

Mr. Martin Cornelsen is operating a company doing remediation of PFAS contaminants in water and is the inventor of the PerfluorAd method. This is made transparent by referencing to the patent. The measurements were all done by independent accredited

laboratories and measurements were reported as received."

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.emcon.2021.02.001>.

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