

Treatment and recovery of PFAS-contaminated water by means of atmospheric water-plasma processes

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Outline

Treatment and recovery of PFAS-contaminated water by means of atmospheric water-plasma processes

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 - Potential problems and solution strategies
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Project description & background

Project description

AtWaPlas – Treatment and recovery of PFAS contaminated water by means of atmospheric water plasma

Project partner:

- Fraunhofer Institute for Interfacial Engineering and Biotechnology IGB
 - Field of research: Functional surfaces and materials
 - 30 years of experience in plasma technology
- HYDR.O. GEOLOGEN UND INGENIEURE
 - Specialized in remediation and monitoring of contaminated groundwater and soil.

Aim:

- Development of an innovative treatment method for an efficient degradation / mineralization of PFAS compounds in realistic matrices of PFAS-contaminated groundwater and seepage.

Scope:

- Sponsored project duration: 01.07.2021 – 30.06.2023 (Federal Ministry of Education and Research Germany (BMBF))
- "KMU-innovativ: Resource efficiency and Climate Protection", promotional reference 02WQ1601A/B, FONA federal research program on water

Background

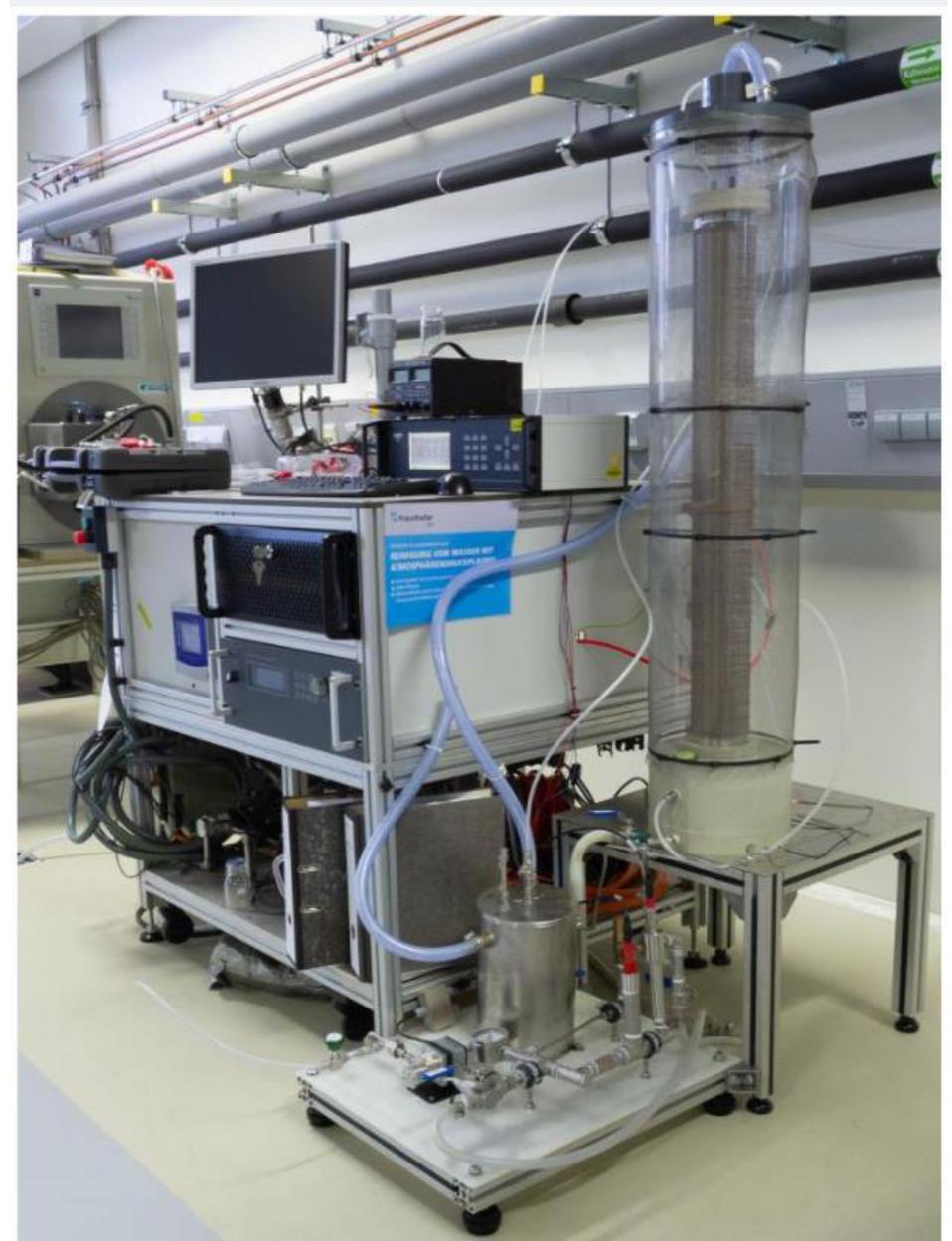
Why atmospheric water plasma?

Technology:

- Non-thermal plasma (NTP) = Incomplete ionized gas ($T > 333 \text{ K}$) produced through voltage application.

Potential

- Excellent results for the degradation of other pollutants in water.
- Effectiveness of PFAS degradation with NTP has been proven in many previous academic studies [1, 2, 3, 4, 5].
- Mineralization of PFAS – e.g., instead of sorption as in currently used activated carbon solutions.
- Solution for the problematic deposition of PFAS-containing waste by providing a solution for seepage water treatment.
- Degradation of long-chain and short-chain PFAS compounds.
- Prospected mobile applicability (when implemented as pump & treat technology).



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Methodology

Methodology

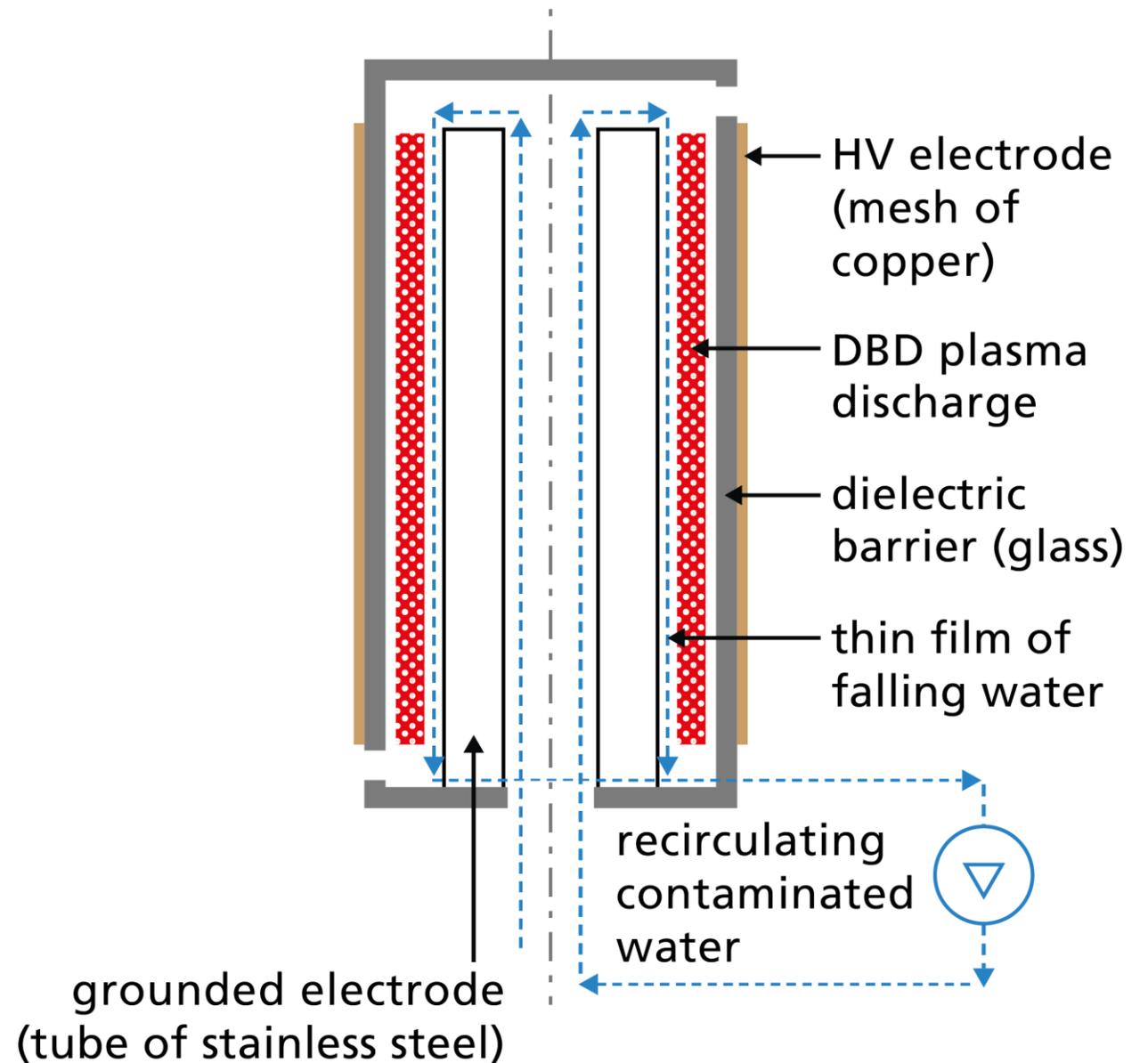
Technical set-up

Key-features:

- Dielectric Barrier Discharge (DBD): Glass column (90 cm)
- Inner electrode: Hollow steel cylinder
- High voltage electrode: Copper foil
- Plasma generation: Redline G2000
- Process gas: He, O₂
- Monitoring: pH, ozone, water temperature

Operating principle:

- The contaminated sample is pumped through the inner steel cylinder and runs down at its outside - resulting in contact with the discharged plasma.
- Interactions with reactive species of the plasma cause the degradation of PFAS in the aqueous sample.



Methodology

Sampling sites

Types of sampled contaminated sites
(groundwater or seepage samples):

- Airports
- Landfills
- Electroplating plants

Sample characteristics:

- Different background contaminations (PAH, BTEX, CHCs, heavy metals, ...)
- Varying PFAS origin, spectrum and detected initial concentrations (0.1 – 100 µg/L) – LOD = 0.01 µg/L
- Varying degree of turbidity



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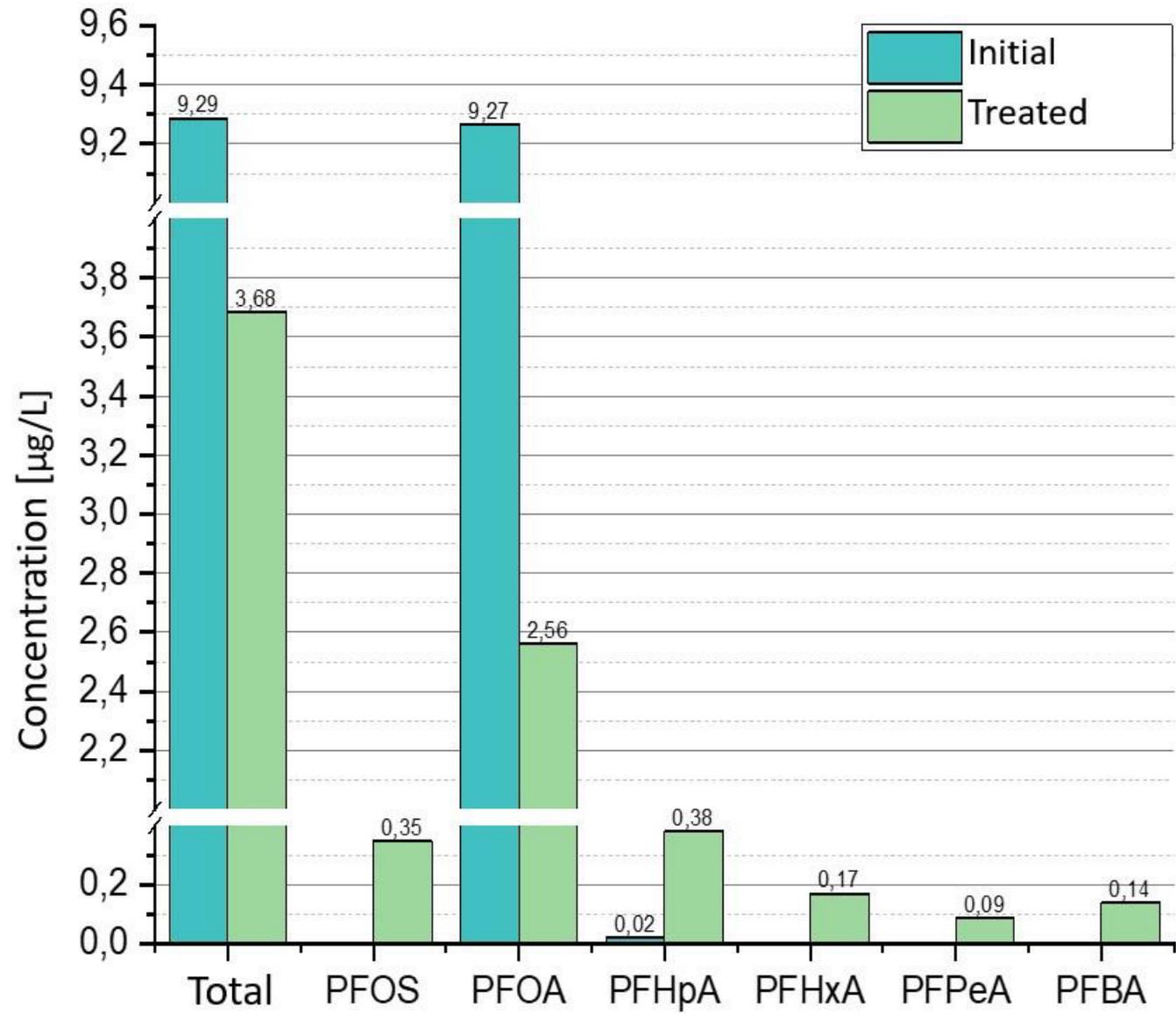
Results & Discussion

Results & discussion

Standardized samples

Treatment of a standardized PFOA solution [10 µg/L]:

- Treatment details:
 - Duration: 120 min
 - Process gas: He
 - Voltage: 250 V (intermediate circuit voltage)
- Results:
 - PFOA degradation: 72 %
 - Total PFAS degradation: 60 %
 - Expected detection of degradation products of PFOA
 - Faster and higher degradation with He as process gas
 - Observed degradation in line with proposed degradation pathways in previous research [4]:
PFHpA (C₇) > PFHxA (C₆) > PFPeA (C₅) > PFBA (C₄)
 - Increasing concentration of degradation products with increasing treatment duration
 - Unexpected detection of PFOS



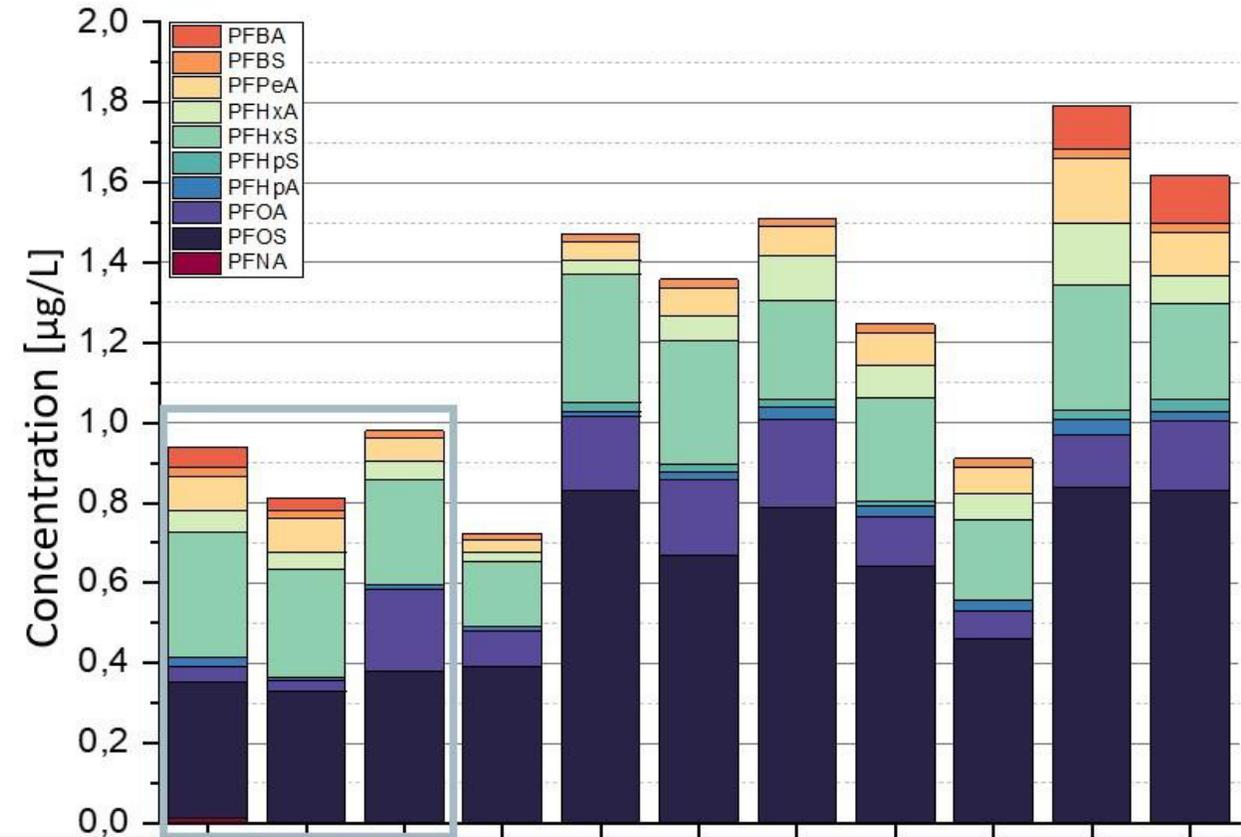
Results & discussion

Samples from existing PFAS contaminated sites

Treatment of a sample from an AFFF-contaminated site [0.29 µg/L]:

- Treatment details:
 - Duration: 60 – 120 min
 - Process gas: He / O₂
 - Voltage: 250 – 300 V

- Results:
 - Degradation of PFAS during treatment
 - Variations in PFAS concentration of the initial sample (SD = 0,09 µg/L).
 - Variations in treated results, depending on parameter combination.
 - Higher detected PFAS concentrations after the treatment in all treatment runs, with only one exception (T1).



Treatment run	I1	I2	I3	T1	T2	T3	T4	T5	T6	T7	T8
Process gas	-	-	-	He	O ₂	O ₂	O ₂	He	He	O ₂	He
Voltage [V]	-	-	-	250	250	250	300	250	300	300	300
Treatment duration	-	-	-	120	60	120	120	60	120	60	60

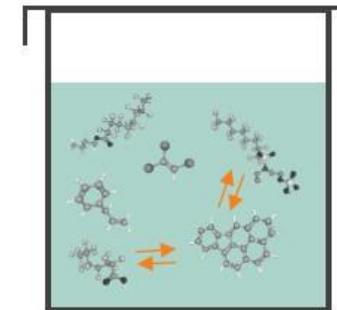
I = Initially detected PFAS concentration; T = PFAS Concentration after treatment

Results & discussion

Potential problem sources

Potential reasons for the increase in PFAS concentration after treatment

- Analytical limitations
 - Detection of non-detectable (polymeric) PFAS or precursors, degraded to detectable substances during the plasma process → Only apparent increase in PFAS concentrations.
 - Limit of detection: Low analytical certainty when analyzing PFAS at concentrations $< 1 \mu\text{g/L}$.
- Sorption
 - Sorption on organic particulate matter, destroyed by the plasma process during treatment, disturbing the quantification of the initial PFAS load.
 - Sorption at test vessels or in the treatment reactor.
- Sample matrix
 - Interactions with additional organic pollutants of the sample matrix.
 - Opportunity of additional matrix remediation in the same treatment process.

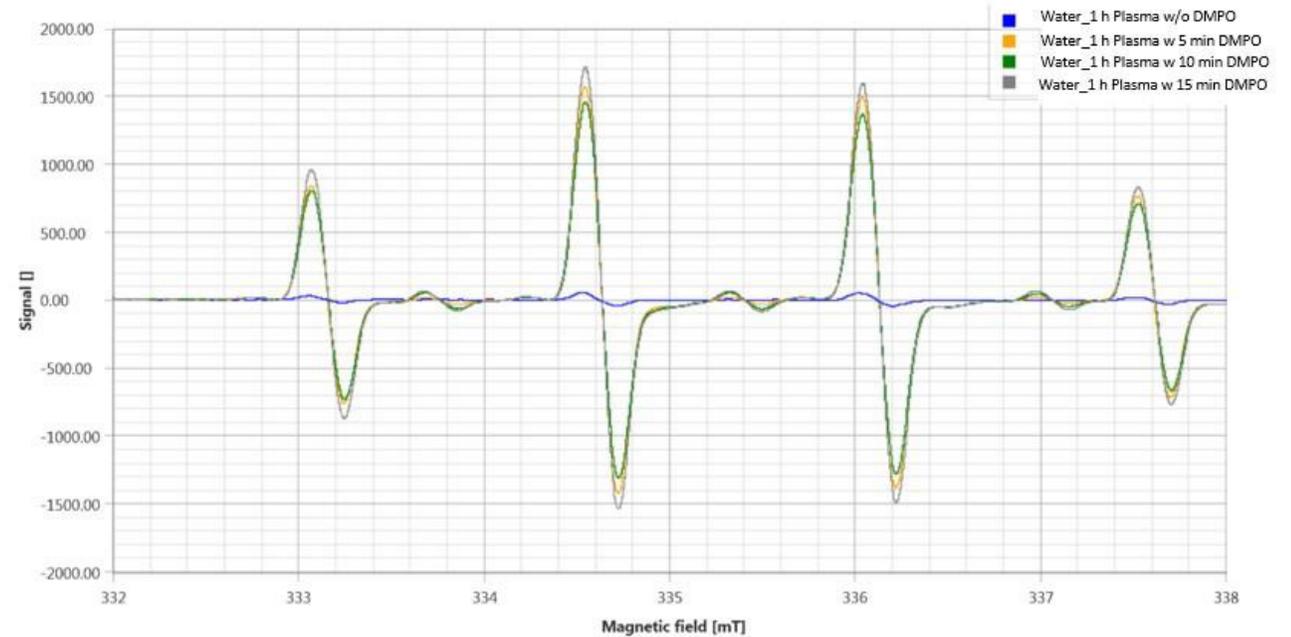


Results & discussion

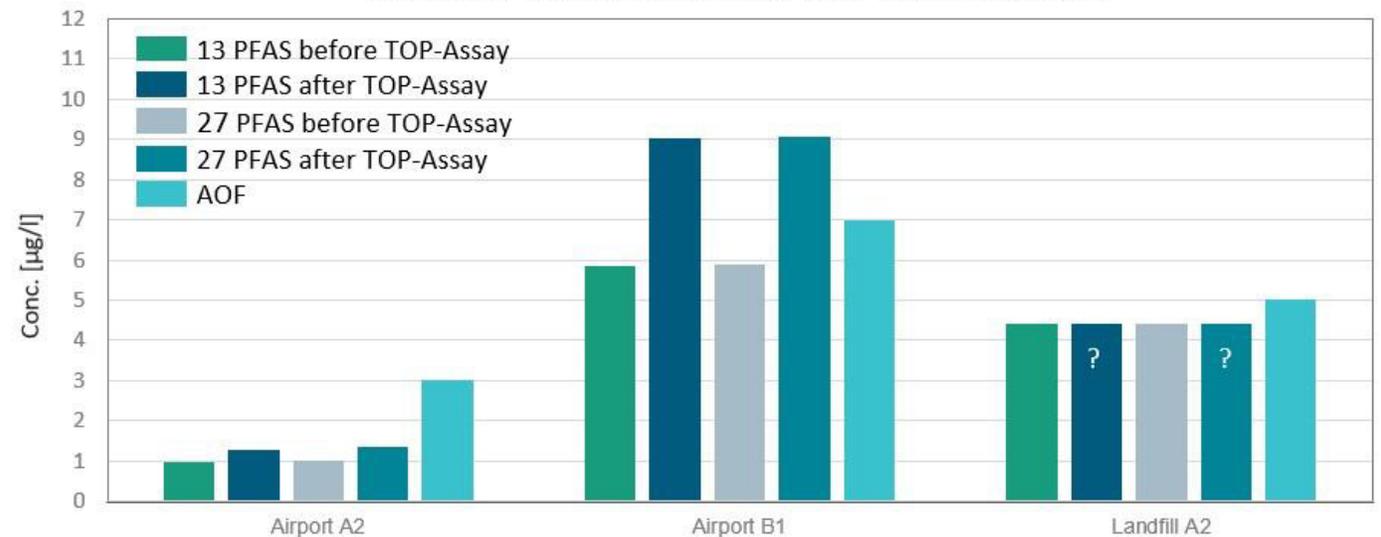
Solution strategies

Adaption of analysis to include a broader spectrum of PFAS

- ESR-Spectroscopy
 - Proof of OH-radical production
 - Result: OH-radicals exist and are produced in the plasma process (proof of functionality of the plasma process).
- AOF, TOP-Assay and ¹⁹F-NMR-analysis
 - Proof of precursor existence.
 - Result: Increase of total PFAS concentration after each TOP-Assay but unexpected partially lower AOF than sum of PFAS concentration.
 - Proof of chain reduction and mineralization.
 - Result: The high LOD suggests that ¹⁹F-NMR-analysis is unsuitable for the quantification of PFAS-containing groundwater contamination.



PFAS content - before and after the TOP Assay + AOF measurements

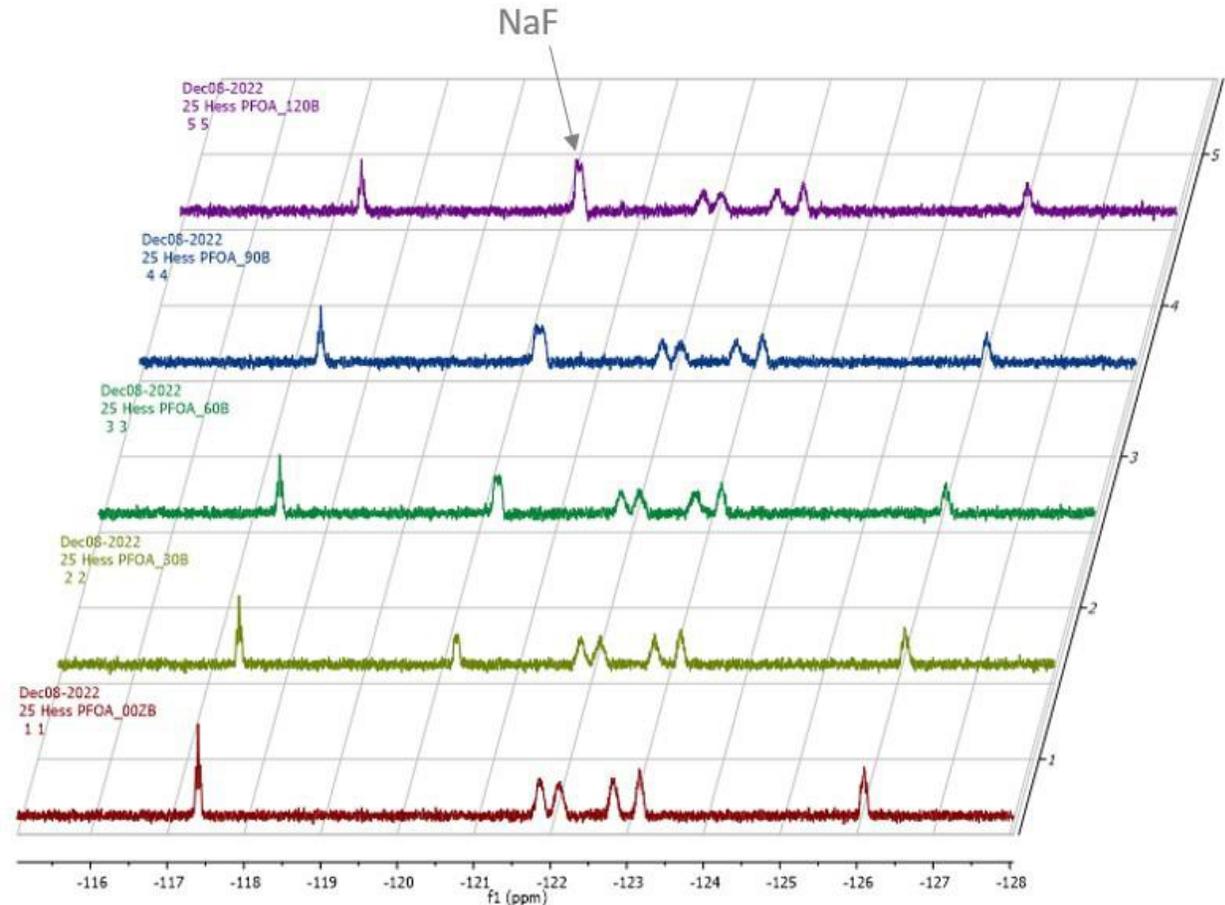


Results & discussion

Solution strategies

Adaption of sample treatment: Test-circulation and filtration

- Test-circulation without plasma treatment paired with ^{19}F -NMR-analysis
 - Assessment of PFAS-Sorption on reactor and sample vessels
 - Result: Reduction of CF_2 by 18.6 % and CF_3 by 16.3 % due to sorption.
- ^{19}F -NMR-analysis of treated standardized PFOA samples
 - Improved knowledge on the degradation pathway and mineralization potential
 - Result: Increase of peaks associated with sodium fluoride (NaF) with increasing duration of the plasma process → Indication of mineralization.
- Long-term treatment test (6 h circulation)
 - Assessment of the time-dependence of degradation
 - Result: Noticeable development towards shorter carbon chain length and smaller concentrations of the 13 analyzed PFAS



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Conclusion

Conclusion

Key messages

Degradation until mineralization of PFAS is possible

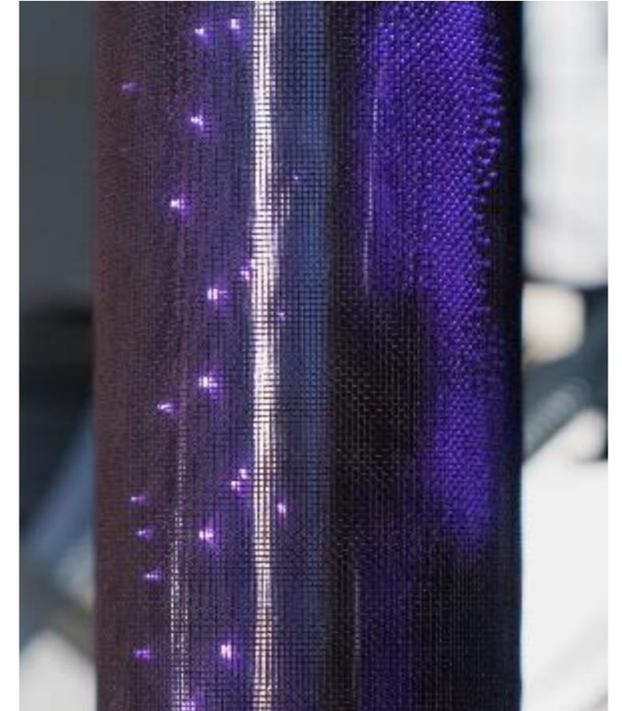
- Most important parameter: Treatment duration and sample matrix.

Limitations of analytical detection challenge process knowledge and reproducible results

- Mineralization is hard to prove and not yet quantifiable.
- Not all PFAS substances and precursors can be detected.

Matrix effects may lead to substantially different results in treatment efficiency

- Treatment of PFAS samples of realistic contaminated sites are challenging and require an extensive time period in methodology development.



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Appendix

Appendix II

Analyzed PFAS according to DIN 38407-42:2011-03

Tabelle 1: Liste der nach DIN 38407-42:2011-03 untersuchten PFAS-Verbindungen.

Substanz	Kurzbezeichnung	Summenformel	Molare Masse [g mol ⁻¹]	CAS-RN ¹
Perfluorbutansäure	PFBA	C ₄ HO ₂ F ₇	214,04	375-22-4
Perfluorpentansäure	PFPeA	C ₅ HO ₂ F ₉	264,05	2706-90-3
Perfluorhexansäure	PFHxA	C ₆ HO ₂ F ₁₁	314,05	307-24-4
Perfluorheptansäure	PFHpA	C ₇ HO ₂ F ₁₃	364,06	375-85-9
Perfluoroctansäure	PFOA	C ₈ HO ₂ F ₁₅	414,07	335-67-1
Perfluomonansäure	PFNA	C ₉ HO ₂ F ₁₇	464,08	375-95-1
Perfluordecansäure	PFDA	C ₁₀ HO ₂ F ₁₉	514,08	335-76-2
Perfluorbutansulfonsäure	PFBS	C ₄ HO ₃ F ₉ S	300,10	375-73-5
Perfluorhexansulfonsäure	PFHxS	C ₆ HO ₃ F ₁₃ S	400,11	355-46-4
Perfluoroctansulfonsäure	PFOS	C ₈ HO ₃ F ₁₇ S	500,13	1763-23-1
Perfluorheptansulfonsäure ²	PFHpS	C ₇ HF ₁₅ O ₃ S	450,12	375-92-8
6:2-Fluortelomersulfonsäure ²	6:2-FTS	C ₈ H ₅ F ₁₃ O ₃ S	428,17	27619-97-2
Perfluoroctansulfonamid ²	FOSA	C ₈ H ₂ F ₁₇ NO ₂ S	499,14	754-91-6

¹ Chemical Abstracts Services Registrier-Nummer, ² Nicht in der Norm enthalten.

Appendix III

Analyzed PFAS included in the TOP-Assay

Teilfluorierte Polyfluoralkansäuren

Perfluorcarbonsäuren (PFCA)

Perfluorsulfonsäuren (PFSA)

Sonstige PFAS (Precursor)

Perfluorbutansäure (PFBA)	µg/l	0,010	EFW-MA-SP 56 (LCMS): 2018-05
Perfluorpentansäure (PFPeA)	µg/l	0,010	EFW-MA-SP 56 (LCMS): 2018-05
Perfluorhexansäure (PFHxA)	µg/l	0,010	EFW-MA-SP 56 (LCMS): 2018-05
Perfluorheptansäure (PFHpA)	µg/l	0,010	EFW-MA-SP 56 (LCMS): 2018-05
Perfluoroctansäure (PFOA)	µg/l	0,010	EFW-MA-SP 56 (LCMS): 2018-05
Perfluornonansäure (PFNA)	µg/l	0,010	EFW-MA-SP 56 (LCMS): 2018-05
Perfluordecansäure (PFDeA)	µg/l	0,010	EFW-MA-SP 56 (LCMS): 2018-05
Perfluorundekansäure (PFUnA)	µg/l	0,010	EFW-MA-SP 56 (LCMS): 2018-05
Perfluordodekansäure (PFDoA)	µg/l	0,010	EFW-MA-SP 56 (LCMS): 2018-05
Perfluortridekansäure (PFTrA)	µg/l	0,010	EFW-MA-SP 56 (LCMS): 2018-05
Perfluortetradekansäure (PFTA)	µg/l	0,010	EFW-MA-SP 56 (LCMS): 2018-05
Summe 11 PFT (Carbonsäuren)	µg/l		EFW-MA-SP 56 (LCMS): 2018-05
Perfluorbutansulfonsäure (PFBS)	µg/l	0,010	EFW-MA-SP 56 (LCMS): 2018-05
Perfluorpentansulfonsäure (PFPeS)	µg/l	0,010	EFW-MA-SP 56 (LCMS): 2018-05
Perfluorhexansulfonsäure (PFHxS)	µg/l	0,010	EFW-MA-SP 56 (LCMS): 2018-05
Perfluorheptansulfonsäure (PFHpS)	µg/l	0,010	EFW-MA-SP 56 (LCMS): 2018-05
Perfluoroctansulfonsäure (PFOS)	µg/l	0,010	EFW-MA-SP 56 (LCMS): 2018-05
Perfluoroctansulfonamid (PFOSA)	µg/l	0,010	EFW-MA-SP 56 (LCMS): 2018-05
Perfluordecansulfonsäure (PFDS)	µg/l	0,010	EFW-MA-SP 56 (LCMS): 2018-05
1H,1H,2H,2H-Perfluorhexansulfonsäure (4:2 FTS)	µg/l	0,010	EFW-MA-SP 56 (LCMS): 2018-05
1H,1H,2H,2H-Perfluordecansulfonsäure (8:2FTS)	µg/l	0,010	EFW-MA-SP 56 (LCMS): 2018-05
1H,1H,2H,2H-Perfluoroctansulfonsäure (H4PFOS)	µg/l	0,010	EFW-MA-SP 56 (LCMS): 2018-05
2H,2H,3H,3H-Perfluorundekansäure (H4PFUnA)	µg/l	0,010	EFW-MA-SP 56 (LCMS): 2018-05
2H,2H-Perfluordodekansäure (H2PFDA)	µg/l	0,010	EFW-MA-SP 56 (LCMS): 2018-05
7H-Dodekanfluorheptansäure (HPFHpA)	µg/l	0,010	EFW-MA-SP 56 (LCMS): 2018-05
Perfluor-3,7-dimethyloktansäure (PF-3,7-DMOA)	µg/l	0,010	EFW-MA-SP 56 (LCMS): 2018-05
Capstone Produkt A	µg/l	0,015	EFW-MA-SP 56 (LCMS): 2018-05
Capstone Produkt B	µg/l	0,015	EFW-MA-SP 56 (LCMS): 2018-05