Environmental Science Advances

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: C. N. Albers and D. D. Voutchkova, *Environ. Sci.: Adv.*, 2025, DOI: 10.1039/D5VA00181A.

ROYAL SOCIETY OF CHEMISTRY

rsc.li/esadvances

View Article Online
DOI: 10.1039/D5VA00181A

Sea spray aerosols can be a source of PFAS pollution in coastal aquifers

Christian Nyrop Albers*, Denitza Voutchkova

Department of Geochemistry, Geological Survey of Denmark and Greenland (GEUS), Øster Voldgade 10, DK-1350 Copenhagen, Denmark

Environmental significance statement:

In Denmark, like in most other countries, many groundwater wells are polluted with PFAS. Often, known sources can explain this, however sometimes PFAS are detected in groundwater without any likely source. We demonstrate a very high detection frequency for certain PFAS in shallow groundwater wells located in Danish nature areas close to the North Sea coast with concentrations often exceeding local drinking water guideline values. Based on several observations, it is concluded that the only plausible explanation is transport from sea to land via sea spray aerosols. This process therefore needs to be considered as an important source of diffuse PFAS pollution in coastal areas.

View Article Online
DOI: 10.1039/D5VA00181A

Sea spray aerosols can be a source of PFAS pollution in coastal aquifers

Christian Nyrop Albers*, Denitza Voutchkova

Department of Geochemistry, Geological Survey of Denmark and Greenland (GEUS), Øster Voldgade 10, DK-1350 Copenhagen, Denmark

Abstract

Pollution with PFAS is found in several types of environmental matrices across the globe. In groundwater, the occurrence is usually attributed to point sources like firefighting training areas, landfills or direct industrial use. During the last 15 years it has become clear that some PFAS are highly preconcentrated in sea spray aerosols and recently this was proposed to be a significant source of PFAS on land. To see, if such a source is strong enough to affect groundwater, we analysed a nationwide dataset for PFAS in shallow wells. By focusing on wells located in forests or other nature areas, it became clear, that groundwater within 5 km of the 400 km long Danish west facing North Sea coast is clearly affected by a diffuse PFAS source, most likely sea spray aerosols. PFOA dominated, but PFHxS was detected almost as frequently and the concentration ratio between these two PFAS was relatively constant. Four very shallow monitoring wells with 2–21-year-old groundwater were repeatedly sampled over 3–5 years, all showed an almost constant concentration of PFOA, PFHxS, PFOS and PFBS. A screening of 60 PFAS, showed that legacy PFAAs dominated wells affected by sea spray aerosols. The observed diffuse PFAS pollution in groundwater is most likely a world-wide coastal phenomenon, but additional studies are needed to achieve sufficient understanding of the drivers.

Introduction

Per- and polyfluorinated alkyl substances (PFAS) is a diverse group of compounds, that may be divided into some major subgroups with specific chemical characteristics. The compounds most commonly detected in aqueous environmental matrices all belong to the group of perfluorinated alkyl acids (PFAA) which can be further divided into the subgroups of perfluorinated carboxylic acids (PFCA) and perfluorinated sulfonic acids (PFSA), their most “famous” members being PFOA and PFOS, respectively. Many PFCAs and PFSAs have surfactant-like molecular characteristics that make them adsorb to air/water interfaces[1]. While these molecular characteristics are well studied, their environmental implications are only beginning to be recognized.

A potentially critical aspect of the air/water adsorption of PFAA compounds is their tendency to accumulate in aerosols derived from sea spray. In laboratory experiments, it has been shown that compounds within the PFCA and PFSA subgroups may be enriched more than 1000 times during the aerosol emission process[2–5]. Aerosol sampling at coastal sites in Norway have provided further evidence for PFAA enrichment in sea spray aerosols using sodium ions as tracer for the sea-derived aerosols[6]. The same authors underpin that sea spray

View Article Online
DOI: 10.1039/D5VA00181A

aerosols may travel hundreds of kilometres before the PFAA present in the aerosols at some point will be scavenged from the atmosphere by wet and dry deposition providing a transport pathway from sea to land. In a subsequent study, it was estimated that in coastal areas more than 100 ng PFAA per m^2 per year may be emitted from sea water and that 15 to 30% of the PFAA emitted from the global oceans is transported and deposited on land, with more than 80% of this deposition occurring in what is defined in the study as coastal grid cells[7]. Theoretically, the relatively low background pollution of the oceans may hence be an important regional diffuse PFAS source on land. The actual size of such source is largely unknown, but it is well known that those PFAS compounds that are present in the world's oceans and that possess the ability to adsorb to air/water interfaces are found ubiquitously in rain[8–10]. For example, concentrations of PFOA are typically in the range of 0.2-2 ng/L at inland locations, which theoretically would be higher in coastal areas, if sea spray aerosols are major contributors. The toxicologically derived guideline value for PFOA in drinking water is 2 ng/L in Denmark and 4 or 4.4 ng/L in several other EU countries and recently the US-EPA has set an enforceable Maximum Contaminant Level of 4 ng/L for PFOA. Diffuse atmospheric PFOA pollution, which ultimately will make it to groundwater by percolation through the soil, is therefore potentially important with regards to maintaining a safe groundwater-based water supply. Recently, it was concluded that the reason for a groundwater-fed waterworks close to the Danish North Sea coast having PFAS above the drinking water standard most likely is due to PFAS in sea foam and sea spray aerosols[11]. In order to explore the hypothesis that the transport of PFAS with sea spray aerosols is large enough to affect groundwater resources, we analysed publicly available data for PFAS in Danish groundwater. In addition, we studied four selected PFAS-contaminated shallow coastal monitoring wells with regards to time trends of PFAS concentrations, groundwater age, potential sources of PFAS and occurrence of a broad range of PFAS compounds.

Methods

Two types of groundwater wells were included in the study; wells belonging to the national groundwater monitoring program (GRUMO) and waterwork wells used for drinking water abstraction. The GRUMO wells typically have short screens (1-3 m) and are not directly affected by groundwater abstraction. The waterwork wells typically have 3-10 m long screens, but longer screens exist. To focus the data analysis on diffuse PFAS sources, we did not include groundwater wells which were sampled for the purpose of investigating PFAS point sources, but such sources may still influence some of the monitoring and waterworks wells. In Denmark, PFAS are only rarely detected in groundwater wells below 40 m depth, and we therefore exclusively focused on shallow wells with 40 m or less to top of screen. This also secured a relatively homogeneous distribution of wells across the country. Before 2021, where new drinking water standards were introduced, reporting limits for PFAS in groundwater were often relatively high in Denmark. To minimize the risk of including non-detects solely due to high reporting limits, we therefore included only wells that were analysed between 2021 and 2024. A total of 1538 groundwater wells fulfilled these criteria, of which 1136 were drinking water abstraction wells and 402 belonged to the national monitoring program.

The groundwater wells were analysed for 22 PFAS compounds; PFCAs with 3-12 fluorinated carbons, PFSAs with 4-13 fluorinated carbons and two PFAA precursors (6:2-FTS and PFOSA). Names and typical reporting limits are shown in Table S1. The 22 PFAS were selected due to a national guideline value of 0.1 µg/L for the sum of these. The analyses were executed at different commercial accredited laboratories in Denmark. We sampled four selected monitoring wells near the Danish North Sea Coast in November 2024 and had them analysed for 60 PFAS at Eurofins Sweden AB. Compound names and details on analytical methods are in Table S2. The age of the water was also determined in these four wells using the tritium-helium-method, with analyses performed at Bremen University as previously described[12,13]. The concentration of the

View Article Online
DOI: 10.1039/D5VA00181A

ultrashort-chain PFAS trifluoroacetate (TFA), which also provides information on water age, was analysed on four monitoring wells using an in-house LC-MS/MS method with a reporting limit of 0.03 µg/L, as described previously[13].

The data on 22 PFAS in 1538 groundwater wells were extracted from the open database Jupiter[14] (https://www.geus.dk/produkter-ydelser-og-faciliteter/data-og-kort/national-boringsdatabase-jupiter) on 30th August 2024 and quality assured. Some data below Reporting Limits (<RL) had relatively high RL and were therefore excluded from the analysis. For the four PFAS with guideline value 2 ng/L (PFOA, PFNA, PFHxS, PFOS), the values <RL with RL > 1 ng/L were excluded. For the rest of the PFAS, values <RL with RL > 50 ng/L were excluded. For all analyses passing these criteria, the values <RL were substituted with 0, and were aggregated (summarized), so that each well-screen is represented by a single value per parameter for the study period. The aggregation was done in two steps: first at a sample level, and then at well-screen level. Median was used at both steps. The sample-level aggregation was done to ensure that each sample would have equal weight in the aggregation at well-screen level over the period. This was important, because in some cases replicates were taken, and it is also possible that the same laboratory analysis is reported twice, using both the current and obsolete database code for the specific parameter. Median was used for aggregation at the well-screen level to avoid bias due to potential outliers.

For the purposes of this study, we calculated percentage of specific land-use within a 200 m buffer zone around each well. The 200 m buffers were calculated in QGIS v. 3.38 (http://qgis.org). The zonal statistics calculation (percent area per land use type within buffer) was done in R v. 4.4.0[15] with the function "exact_extract" from the R package "exactextractr" v. 0.10.0 (https://CRAN.R-project.org/package=exactextractr). This function provides a precise estimation, because it considers raster pixels partially covered by polygons. The land-use/land-cover (LULC) raster used for this calculation was Basemap03[16] with 10m resolution. For the purposes of this work the following LULC categories were aggregated into two types of LULC:

1) "nature and fresh waters": including the categories 411000 lake, 412000 stream, 321000 nature, dry (habitat types on dry ground, which are not categorised as forest), 322000 nature, wet (habitat types on wet ground, which are not categorised as forest); In total this aggregated category has area 3345.4 km2 (7.7% of the terrestrial area in Denmark)[16]
2) "forest" including the categories: 311000 forest, and 312000 forest, wet (forested land on wet ground). In total this aggregated category covers 5634.7km2 (13.1 %)[16]

The distance from the wells with PFAS data to the Danish coastline was calculated in QGIS, as the distance to the "nearest hub", where the hubs are the vertices of the coastline shape-file (line type). This could introduce some minor uncertainty in the distance calculation, especially for long straight stretches of the coastline. The distance to the coast for the well-screens included in this study is from 0.1-44.0 km.

To determine which well-screens are relevant to the North Sea coast, all well-screens within a manually outlined area along the west coast of Denmark were flagged. The flagged wells, which were with < 5 km distance from the coastline, were included in the sub-set "< 5 km from North Sea coast". Additional supporting data for Cl^-, Mg^{2+} and Na^+ concentrations in the wells were also extracted from the Jupiter database on 28 August 2025. The data were quality assured and aggregated in a similar manner to the PFAS data, except there were no values < RL and there was no period restriction. The periods with data were well-screen specific, but overall, the data spanned the period 1966 – 2025.

Kruskal-Wallis chi-squared test[17] and post-hoc Dunn test for multiple comparisons[18] with Bonferoni adjustment of the p-value (as implemented in the R package `FSA` v. 0.10.0, https://CRAN.R-

View Article Online
DOI: 10.1039/D5VA00181A

project.org/package=FSA) were used for testing for significant differences between subsets. Three different tests were performed for testing for significant differences in the two subsets "< 5 km from North Sea coast" and the other well-screens in forest and nature ("Other (F&N)": 1) difference in depth to top of well-screens, 2) difference in common PFAS, and 2) difference in the PFOA/PFHxS ratio. The post-hoc Dunn test was used when the Kruskal-Wallis test was positive (significant difference) when testing for differences in more than two subsets, e.g. "<5km to North Sea coast (F&N)", "<5km to other coast (F&N)", and ">5km to coast (F&N)" or "<5km to North Sea coast (F&N)", "Nationwide dataset", "Nationwide w/o <5km to North Sea coast (F&N)", and "North Sea marine samples". For all statistical tests, the significance level was set to α=0.05, but we also report exact (adjusted) p-values.

Results and discussion

PFAS in Danish groundwater

A total of 1538 shallow groundwater wells fulfilled the criteria to be included in the nationwide dataset. The wells were distributed across the country (Figure S1). At least one PFAS was detected in 300 of the 1538 wells, with PFOA as the most frequently detected (206 out of 1538 wells corresponding to 13%), followed by PFHxS and PFOS, which were detected in 11 and 10% of the wells. None of the wells in the dataset are deliberately placed near point sources of PFAS, but the wells are placed in all landscape types including urban and industrial areas and the PFAS-affected wells in the complete dataset are most likely polluted by a variety of diffuse and point sources. To see any effect of a diffuse sea spray aerosol source, we therefore focused the subsequent analyses on 137 wells in the dataset that are located in forests or nature areas where the chance of having PFAS point sources affecting the groundwater is very low (Figure 1).

View Article Online
DOI: 10.1039/D5VA00181A

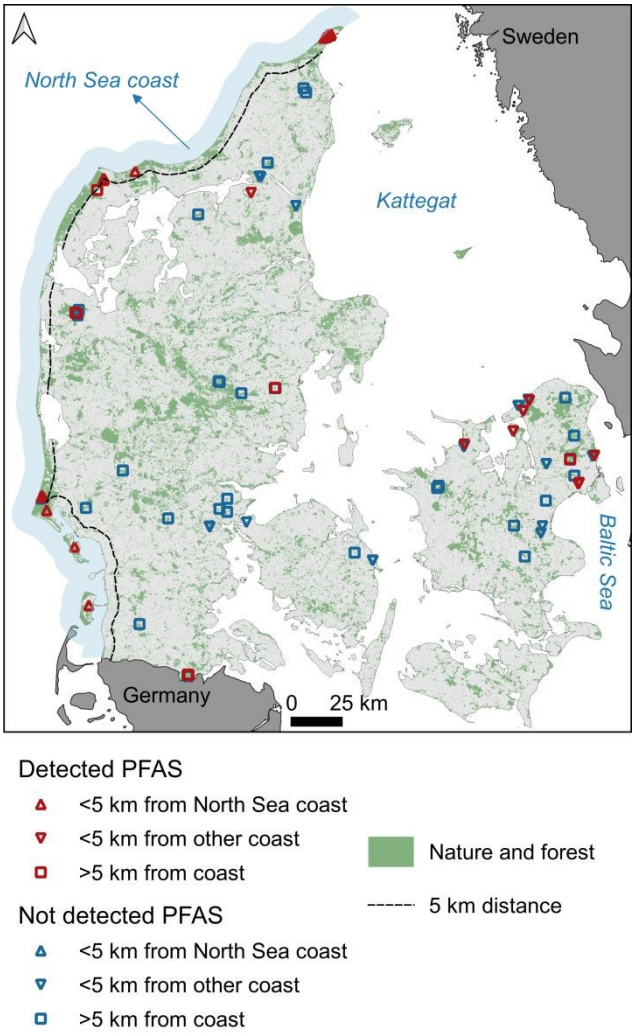


Figure 1 . Map with location of the 137 Danish well-screens located in forest and nature (F&N) areas. Not detected (blue) denotes median value below detection limit for all 22 PFAS; Detected (red) denotes median value above detection limit for at least one of the 22 PFAS. Well screens with detection are shown on top and may therefore cover well screens without detection. For more information about "F&N" see main text. The coast line defined as North Sea in this study is shown with blue shading and with the dotted line depicting the 5 km distance to the North Sea coast.

For these 137 wells a clear pattern appeared when dividing the wells into coastal and inland wells located less or more than 5 km from a sea shoreline, respectively and furthermore dividing the coastal wells into wells located along the North Sea coast or close to other Danish coasts like Kattegat and the Baltic Sea: 52 wells were located in forest/nature more than 5 km from a seacoast, and for these, the detection frequencies were similar or lower as for the whole dataset. 40 wells were located less than five kilometres from seacoasts other than the North Sea and for these, the pattern was similar. However, for the 45 wells located within 5 km from the North Sea coast, almost all wells had detections of at least one PFAA. PFOA, PFHxS and PFOS showed the highest detection frequency (78 to 89%) but also the PFBA, PFPeA, PFHxA, PFHpA and PFBS were detected very frequently (in 36-67%). For all the compounds shown in Figure 2, there is a statistically significant difference between the wells close to the North Sea and all other wells in forest/nature areas (Table S7) and they all have significantly higher detection frequency in the wells close to the North Sea using a Kruskal-Wallis chi-squared test (Table S7). In Denmark, the threshold value in

View Article Online
DOI: 10.1039/D5VA00181A

drinking water is 2 ng/L for the sum of PFOA, PFNA, PFHxS and PFOS. For the individual compounds, PFOA very frequently solely exceeded this limit in wells close the North Sea coast.

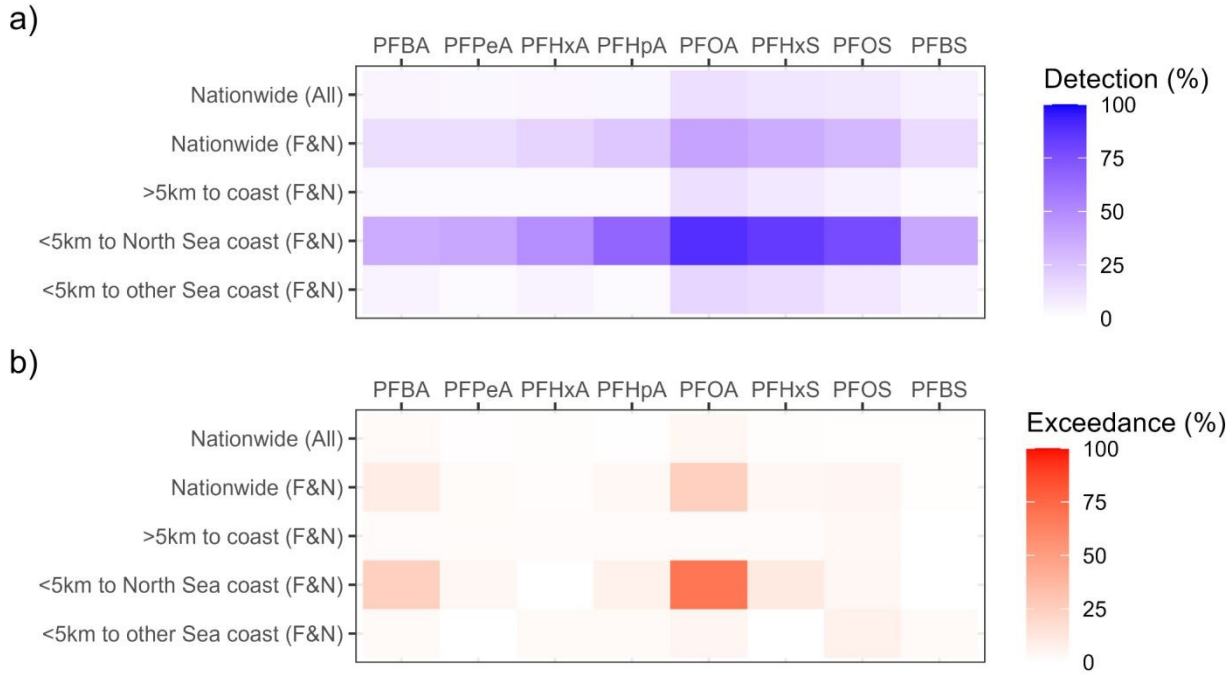


Figure 2. Heatmap with frequency of detections (a) and exceedances of the 2 ng/l national threshold limit (b) of most common PFAS in different subsets, where: row 1 "Nationwide (All)" is the complete nationwide dataset of shallow wells (n=1521 to 1538 depending on compound); row 2 "Nationwide (F&N)" is subset with the shallow wells located in areas dominated by forest or other nature types (n=137); row 3 is subset of "Nationwide (F&N)" containing only the wells located more than 5 km from the coast (n=52); row 4 is the subset of "Nationwide (F&N)" with less than 5 km to the North Sea Coast (n= 45) and row 5 is the subset of "Nationwide (F&N)" with less than 5 km to any other sea coast than the North Sea (n=40). Below is a similar heatmap of wells where concentrations of the individual compounds exceed the threshold limit for the sum of PFOA, PFNA, PFHxS and PFOS in Denmark (>2 ng/L).

The 45 wells located within 5 km from the North Sea coast in general have very little industry or build areas nearby (on average 0.16% of the 200 m buffer, while for the remaining 92 wells located in forest/nature in the rest of the country it is 1.5%). The source of PFAS for the North Sea wells is therefore very unlikely to be local point sources, leaving a diffuse atmospheric source as the most plausible explanation. The question is then if the much higher detection frequency in wells close to the North Sea is simply caused by a faster transport of PFAS? Well depth is often used as a proxy for the transport time from surface to well screen, but the depth of the screens in the subsets are not different to a degree that would be likely to cause such a big difference in PFAS occurrence (average 17 m for wells < 5 km from the North Sea Coast and 24 m for the remaining wells), moreover, there is no statistically significant difference (p=0.08) (Supplementary Table S5). The estimated yearly recharge rate of the wells (Figure S2a) is also very similar at 324 mm on average for the wells close to the North Sea and 286 mm for the remaining wells.

In addition, for many of the PFAS-polluted wells close to the North Sea, the PFAS concentrations are much higher than one would expect from the general atmospheric deposition. For example, the median concentration of PFOA is 4 ng/L and 25% of the wells have 5 ng/L or higher (maximum 19 ng/L). For comparison, the concentration of PFOA in precipitation in Denmark has recently been measured to an average of 0.25 ng/L[19], while slightly higher concentrations, typically between 1 and 2 ng/L, have been

View Article Online
DOI: 10.1039/D5VA00181A

measured in the neighbouring country Sweden[10]. The most plausible explanation for the observed geographical pattern of PFAS in groundwater is therefore transport from sea water to land with sea spray aerosols, as no other known PFAS source could cause such a pattern. PFAS in sea spray aerosols has not been measured at sea or coastal areas around Denmark, but it is well known that PFAS are present in sea water all over the world, although the measured concentrations vary geographically, in time and from study to study[20]. For example, within the sea areas most relevant for aerosol deposition in Denmark, the median seawater concentrations of PFOA between 2010 and 2014 were around 0.1, 0.5, and 1.1 ng/L for samples from the North Atlantic Ocean, the Baltic Sea, and the North Sea, respectively. A study of sea spray aerosols 20 km from the coast at a site in Southern Norway located only a few hundred kilometres from the Danish North Sea coast, showed some influence of sea spray aerosols on PFAS deposition[6]. For a parallel study site in Northern Norway, located just 1 km from the coast, the relationship between PFAS and aerosol tracers (magnesium and sodium) was much stronger indicating that distance to the coast is important for the strength of sea spray aerosols as a PFAS source on land[6]. While aerosol tracers such as Cl^-, Mg^{2+} and Na^+ could be less useful for groundwater, since some fractionation may occur during infiltration, the concentration of all three ions are much higher in the 45 wells close to the North Sea coast compared to the rest of the dataset (Figure S3). Also, the ratio between Mg^{2+} and Na^+ is on average 0.14 in wells close to the North Sea with little variation (std. dev. 0.03), which is equal to the ratio of 0.12-0.14 found in sea spray aerosols in Norway and the Netherlands[6,21]. The ratio between Mg^{2+} and Na^+ in the remaining 92 wells was much more varying and having a very different average of 0.47. While the direct relationship between aerosol tracer and PFAS concentration was not very strong (Figure S4), this is a clear indication that the wells close to the North Sea Coast, of which almost all had detectable PFAS, are affected by sea spray aerosols.

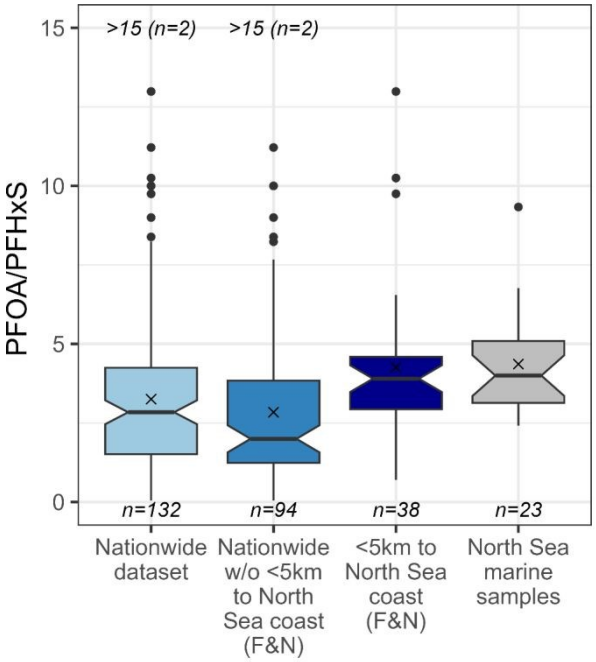
In addition to the small number of analyses of sea spray aerosols, there are several measurements of PFAS in sea foam, which can be seen as a closely related environmental medium. In the North Sea, high concentrations of a range of PFAS have been found in collapsed/condensed sea foam with PFOA and PFOS as the dominating compounds (1800-73000 ng/L) and with also PFHxS occurring in high concentration (60-16600 ng/L)[22–24]. PFNA and PFDA were found in sea foam at also relatively high concentrations (300-17400 ng/L) and are probably also deposited inland by sea spray aerosols as was also concluded by Sha et al[6]. The reason we do not (yet?) detect PFNA and PFDA in the groundwater could be due to higher retention in the soil caused by sorption to organic matter and air/water interfaces. Such retention is probably also causing the relatively lower concentration and detection frequency of PFOS in the groundwater despite an expected historical input with sea spray aerosols of at least the same magnitude as PFOA. On the other hand, PFPeA, PFHxA and PFBS are retained only to a very minor degree in soil, which could explain their frequent detection in wells near the North Sea coast, despite smaller preconcentration factors in sea spray aerosols[3,5].

PFOA and PFHxS as indicators of a sea spray aerosol source?

PFOA and PFHxS are both ubiquitously present in sea water across the world, with PFOA typically at about 10 times higher concentration, though this varies with location[20]. These two compounds have quite similar enrichment factors in sea spray aerosols[3–5] and will be retained in soil to also quite similar degree both with regards to sorption to organic matter[25] and air/water interfaces in soil[26,27]. One could therefore hypothesize, that presence of both compounds at concentration ratios not too different from that of the sea water source would be found in groundwater polluted by a diffuse sea spray source. To test this hypothesis, we calculated the ratio between PFOA and PFHxS in all groundwater samples. Both compounds

View Article Online
DOI: 10.1039/D5VA00181A

were present in almost all the 45 shallow wells close to the North Sea coast and within these, PFHxS was never present without PFOA, while the opposite was the case for two wells where the PFOA concentration was close to the reporting limit. For the whole dataset (nationwide), PFHxS was not detected in 35% of the 206 wells where PFOA was detected and PFOA was not detected in 20% of the 164 wells where PFHxS was detected. While even in the whole dataset there is a high overlap between the two compounds, this clearly shows that the overlap is exceptionally high in wells near the North Sea coast where the sea is the most likely source of PFAS. In addition, the ratio between the two compounds is also within a much narrower interval in wells near the North Sea coast compared to the whole dataset (Figure 3). The vast majority of these wells have a ratio between 2 and 6 while the complete range goes from 0.7 to 13. For the nationwide dataset, most wells are within a ratio from 0.4 to 7 but the complete range goes from 0.05 to 109. The ratios for the well-screens within 5 km from the North Sea (n=38 with both compounds detected) are statistically different from the ratios for the rest of the well-screens (n=94 with both compounds detected) (p=0.003, Table S8). For comparison, the two compounds have recently been detected in 23 seawater samples taken from surface waters of the North Sea near the Danish Coast. In these samples the ratio was typically between 2 and 6 with a whole range of 2 to 9 (Figure 3). There is no statistical difference (p=1.00, Table S8) between the ratios in the surface water marine samples and the coastal (North Sea) groundwater wells. This supports the hypothesis that the presence of PFOA and PFHxS at concentration ratios not too different from that of the sea water would be found in groundwater polluted by a diffuse sea spray source. In sea foam sampled close to Denmark, the PFOA/PFHxS ratio has been found to be between 3 and 11[22–24], which also fits with the ratios we observe in Danish groundwater between these two compounds. In conclusion, PFOA seems to always be detected in wells polluted by sea spray aerosols and unless the concentration of PFOA is very low, PFHxS will also be detected, typically at 2-6 times lower concentration. It should be emphasized, though, that although much more common near the North Sea coast, this ratio is also seen in wells further inland with other expected sources of PFAS, and a PFOA/PFHxS ratio in this interval therefore should not in itself be used as a strong indication of the source.



View Article Online
DOI: 10.1039/D5VA00181A

*Figure 3. Ratio between PFOA and PFHxS (ng/L) in groundwater wells where both compounds were detected. The ratio in 23 marine surface samples from the coastal North Sea taken in 2022 and 2023 is shown for comparison (https://miljoedata.miljoeportal.dk/, data extracted on January 13. 2025, Table S4). F&N – forest and nature; boxplot elements: 25th and 75th percentiles for the hinges (box); whiskers extend from the hinges up/down to the largest value ≤/≥ 1.5 * IQR (where IQR is the inter-quartile range, or distance between the first and third quartiles); Data beyond the whiskers is outlier (black dot); median - horizontal thick line; mean – x symbol; the notches extend 1.58 * IQR / sqrt(n), which is approximately 95% confidence interval for the medians.*

Shallow coastal monitoring wells

33 of the 40 PFAS polluted wells near the Danish North Sea coast are groundwater abstraction wells used to provide drinking water. Due to long well screens combined with pumping of large volumes that may vary over time, abstraction wells often represent a mixture of water with different origin and age, which complicates interpretation of origin and age of pollution with organic micropollutants[28]. In the Danish groundwater monitoring system, we have four PFAS-polluted wells near the North Sea coast that are in nature areas with no other suspected source of PFAS nearby, except for atmospheric sources including sea spray aerosols. For all four wells there are more than 1 km to the nearest area with registered activity that could potentially lead to any kind of soil pollution, including PFAS and there are more than 500 m to the nearest house (more than 1 km for three of the wells). In all four wells, the well screens are short (1 to 3 m) and shallow (9-17 m below surface) and there is no pumping of water, except when the wells are sampled. All four wells are situated in quite similar geological and geographical settings, in very sandy sediments, with shallow unconfined groundwater tables and with coniferous trees (spruce and pine) as the dominant vegetation (Table 1 and Figure S5). These wells are therefore expected to represent a constant and relatively small recharge area over time and the groundwater age (recharge time) would be expected to have a small interval and to be constant. Using the tritium-helium tracer method we estimated the groundwater recharge time, to be from a few years in the well with the youngest water to around 20 years in the well with the oldest water. Concentrations between 0.22 and 0.47 µg/L of the ultra-short chain PFCA trifluoroacetate (TFA) that functions as a tracer for young groundwater[13], confirms that the groundwater has recharged recently (Table 1).

Table 1. Selected characteristics and PFAS detections for four monitoring wells located in remote nature areas close to the Danish North Sea coast.

Well no.	Distance to North Sea (km)	Depth to top of screen (m)	Screen length (m)	Depth to GW table last 5 y (m)	Lithology above screen	Surrounding vegetation (in order of dominance)	Tritium-helium GW age (y)	TFA (µg/L)	PFAS detected in latest analysis*
23.487-2	1.8	9.0	1	0.5-1.3	7 m aeolian sand then old seabed sand.	Coniferous forest	2	0.25	PFBA, PFOA, PFBS, PFHxS, PFOS, PFPrA, HFPO-DA
120.236-2	2.7	13.0	3	1.2-2.5	7 m aeolian sand then old seabed sand.	Coniferous forest	16	0.29	PFBA, PFPeA, PFHpA, PFOA, PFBS, PFPeS, PFHxS, PFOS, PFPrA, PFECHS
120.237-2	4.8	15.8	2	1.4-2.4	8 m aeolian sand then old seabed sand.	Coniferous forest, Heathland	21	0.22	PFBA, PFPeA, PFHpA, PFOA, PFPeS, PFHxS, PFHpS, PFOS, PFECHS

View Article Online
DOI: 10.1039/D5VA00181A

148.62-1	3.4	16.5	1	1.3 to 2.5	5 m aeolian sand then old seabed sand.	Coniferous forest, Heathland	6	0.47	PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFBS, PFPeS, PFHxS, PFOS, PFPrA, PFECHS

	Concentration of most dominating PFAS in latest analysis (ng/L), sum of branched and linear							
	PFBA	PFPeA	PFHpA	PFOA	PFBS	PFPeS	PFHxS	PFOS
23.487-2	4.3	<0.3	<0.3	3.5	0.61	<0.3	0.96	2.3
120.236-2	2.2	0.43	1.1	8.7	0.49	0.64	2.6	0.53
120.237-2	0.94	0.43	0.45	7.1	<0.3	2.5	2.5	3.6
148.62-1	4.6	0.78	1.9	11.0	1.2	0.81	5.8	4.2

* The full name of the compounds and analytical reporting limits can be found in Supplementary Table S2.

The four compounds PFOA, PFBS, PFHxS and PFOS were the most frequently detected short- and long-chained PFAS and were repeatedly detected in all four wells (Figure 4). Over time, there is no clear trend in concentration in the four wells, though PFOS was in all cases highest at the last sampling point. PFOS will expectedly have the highest retardation through the soil layers above the groundwater wells, since it has the highest soil:water and air:water partitioning coefficients among the four compounds[29]. If an increase in PFOS is currently occurring, this does not necessarily imply an increase in the source compared to the other PFAS but could be caused by a delayed arrival in the groundwater. The fact that PFAS concentrations are not yet decreasing even in the very young groundwater of the four monitoring wells, suggest that PFAS from sea spray aerosols may be found in years to come in coastal groundwaters with longer travel times than in these four wells. This seems to be the case even if the PFAS are banned or phased out like PFOA and PFOS, a ban that has resulted in a significant decrease of these compounds from 2007 to 2017 in sea water of the southern part of the North Sea[30]. More likely, the concentrations in coastal groundwater in general, can be expected to increase in the years to come. At the same time, longer-chained PFAA´S with higher retardation factors in soil such as PFNA and PFDA, which have recently been found at relatively high concentration in water and foam from the North Sea[22–24,30] and in sea spray aerosols in Norway[6], may appear.

View Article Online
DOI: 10.1039/D5VA00181A

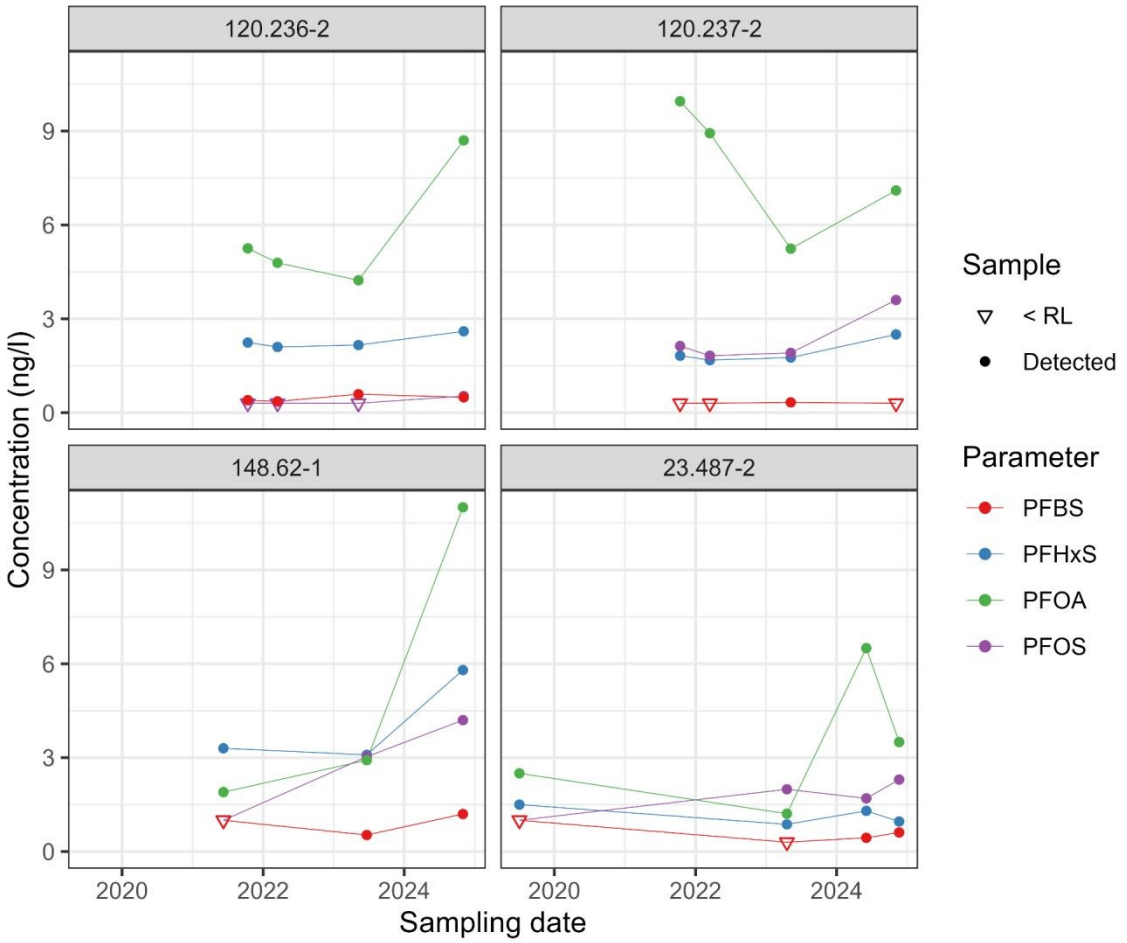


Figure 4. Time series for repeatedly detected PFAS compounds in four wells with the sea spray aerosols from the North Sea as suspected source. Further details of the individual wells are shown in Table 1. Open triangles denote that the compound was not detected at that sampling date with the concentration depicting the Reporting Limit (RL) of that analysis.

To see if other PFAS than the usual legacy PFAAs can be found in groundwater wells with sea spray aerosols as the most likely source of PFAS, the four wells were sampled and analysed for 60 PFAS compounds (Table S2). Three additional compounds were found: The ultrashort-chain PFCA PFPrA (perfluoropropanoic acid) was found in three of the wells in concentrations from 7-14 ng/L, PFECHS (Perfluoro-4-ethylcyclohexane-sulfonic acid) was found in the same three wells at lower concentration (0.4-0.9 ng/L) and HFPO-DA (GenX) was found in one well at a concentration of 0.2 ng/L. The concentration of these three compounds in sea water is little investigated but HFPO-DA and PFECHS have been detected in the seas around Denmark[30]. HFPO-DA was found at higher concentration than PFECHS in sea water, but at air/water interfaces, a relatively larger enrichment factor can be expected for the long-chained PFECHS, compared to HFPO-DA and PFPrA. Indeed, PFECHS has been detected in sea foam at much higher concentration than in corresponding bulk water[22], supporting that the PFECHS detected in the three groundwater wells could be derived from sea spray aerosols. HFPO-DA has also been found in sea foam, with a highly varying enrichment factor of 1 to 410 compared to bulk sea water[31]. It is unknown if PFPrA will be preconcentrated to a level that sea spray aerosols may be the main cause of the detected PFPrA, but there is evidence that PFPrA can be present in precipitation at relatively high concentration, possibly as a degradation product of HFC-and HCFC-gases and other volatile PFCA precursors[10,32].

View Article Online
DOI: 10.1039/D5VA00181A

Concluding discussions

All in all, the most plausible explanation for the high concentrations of certain PFAA compounds (PFOA, PFHxS, PFOS etc.) in shallow groundwater near the Danish North Sea coastline is transport from sea to land via sea spray aerosols. While this transport process has been previously demonstrated, the fact that it may pollute groundwater to a level above drinking water guideline values has not been demonstrated previously in the scientific literature. On the other hand, there is no clear sign of sea-derived PFAS pollution in groundwater wells in other parts of the country, despite many groundwater wells close to other coastlines. Likely reasons for this observation could be a) less PFAS in other sea bodies, b) less wave energy along other coastlines leading to less preconcentration in sea spray aerosols, c) different geological settings leading to less or slower transport of PFAS to groundwater and d) different land use in the groundwater recharge areas such as agricultural land or deciduous forests instead of coniferous plantations that dominated most affected wells along the North Sea coast. We find explanation a) less likely, as the PFAS concentration in the Baltic Sea is known to be of the same magnitude as in the North Sea[20,30] and recently similar levels of PFAS were found in sea foam from the Baltic Sea just Southeast of Denmark[24] as from the North Sea. The other three explanations seem more likely and may work in combination as the reason that we do not (yet) see PFAS contamination in groundwater caused by sea spray aerosols in other parts of Denmark than along the North Sea coast. Concerning explanation b), the prevailing wind direction in Denmark is between Southwest and Northwest and most strong wind fields come from those directions. Strong wind fields also arrive from easterly directions, but these are less frequent and on a yearly basis, the wave energy is much higher on the North Sea coast[33]. The North sea coast may hence experience both more long-range transport of PFAS in sea spray aerosols, as well as a larger contribution from the surf zone, which can be a major contributor of sea spray aerosols tens of km inland[34,35].

The combination of soil type (c) and land use (d) could also influence, as the North Sea coast is dominated by aeolian sand combined with shallow unsaturated zones and coniferous plantations. Although sandy soils are common in many other areas of Denmark (Figure S2b) and coniferous plantations and shallow unsaturated zones are also common, a combination of these features is not common along other coasts in Denmark. This combination may promote transport of PFAA´s like PFOA to the groundwater compared to other areas due to three reasons: 1) water saturated coarse sand shows little retention of PFOA[36,37], 2) sorption to air/water interfaces in the unsaturated zone will be of less importance compared to areas with deeper unsaturated zones and 3) conifers may effectively filter out the aerosols carrying the PFAS[38,39]. Future research should address these possible explanations for the clear PFAS signal along the Danish North Sea coast and the lack of signal along other coastlines. The observed diffuse PFAA pollution in coastal groundwater is most likely a world-wide phenomenon, as PFAA´S are present in sea water across the world[20]. However, additional studies are needed to achieve a sufficient understanding of the drivers, so that current and future concentration levels of different PFAS compounds in coastal groundwater wells may be predicted.

Author contributions

C.N.A.: Conceptualization, Investigation, Methodology, Formal Analysis, Visualization, Writing – original draft. D.V.: Data curation, Formal Analysis, Visualization, Writing – review & editing.

View Article Online
DOI: 10.1039/D5VA00181A

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

We wish to thank Trine Henriksen, GEUS, for skilful assistance in analysis of TFA and Jürgen Sültenfuss, Bremen University, for skilful assistance in analysis of noble gases and interpretation of groundwater age. The study was financially supported by the Danish Agency for Green Transition and Aquatic Environment that were also responsible for sampling the four monitoring wells during the years 2019-2024.

References

1 E. Psillakis, J. Cheng, M. R. Hoffmann and A. J. Colussi, Enrichment factors of perfluoroalkyl oxoanions at the air/water interface, *J. Phys. Chem. A*, 2009, **113**, 8826–8829.

2 G. Casas, A. Martínez-Varela, J. L. Roscales, M. Vila-Costa, J. Dachs and B. Jiménez, Enrichment of perfluoroalkyl substances in the sea-surface microlayer and sea-spray aerosols in the Southern Ocean, *Environ. Pollut.*, 2020, **267**, 115512.

3 J. H. Johansson, M. E. Salter, J. C. Acosta Navarro, C. Leck, E. D. Nilsson and I. T. Cousins, Global transport of perfluoroalkyl acids via sea spray aerosol, *Environ. Sci. Process. Impacts*, 2019, **21**, 635–649.

4 M. Reth, U. Berger, D. Broman, I. T. Cousins, E. D. Nilsson and M. S. McLachlan, Water-to-air transfer of perfluorinated carboxylates and sulfonates in a sea spray simulator, *Environ. Chem.*, 2011, **8**, 381–388.

5 B. Sha, J. H. Johansson, J. P. Benskin, I. T. Cousins and M. E. Salter, Influence of Water Concentrations of Perfluoroalkyl Acids (PFAAs) on Their Size-Resolved Enrichment in Nascent Sea Spray Aerosols, *Environ. Sci. Technol.*, 2021, **55**, 9489–9497.

6 B. Sha, J. H. Johansson, P. Tunved, P. Bohlin-Nizzetto, I. T. Cousins and M. E. Salter, Sea Spray Aerosol (SSA) as a Source of Perfluoroalkyl Acids (PFAAs) to the Atmosphere: Field Evidence from Long-Term Air Monitoring, *Environ. Sci. Technol.*, 2022, **56**, 228–238.

7 B. Sha, J. H. Johansson, M. E. Salter, S. M. Blichner and I. T. Cousins, Constraining global transport of perfluoroalkyl acids on sea spray aerosol using field measurements, *Sci. Adv.*, 2024, **10**, 1–10.

8 G. Sammut, E. Sinagra, R. Helmus and P. de Voogt, Perfluoroalkyl substances in the Maltese environment – (I) surface water and rain water, *Sci. Total Environ.*, 2017, **589**, 182–190.

9 K. A. Pike, P. L. Edmiston, J. J. Morrison and J. A. Faust, Correlation Analysis of Perfluoroalkyl Substances in Regional U.S. Precipitation Events, *Water Res.*, DOI:10.1016/j.watres.2020.116685.

10 M. K. Björnsdotter, L. W. Y. Yeung, A. Kärrman and I. E. Jogsten, Mass Balance of Perfluoroalkyl Acids, Including Trifluoroacetic Acid, in a Freshwater Lake, *Environ. Sci. Technol.*, 2022, **56**, 251–259.

11 Niras, *Undersøgelser af kystnær PFAS-forurening af jord- og grundvand (In Danish)*, 2023.

12 J. Sültenfuß, W. Roether and M. Rhein, The Bremen mass spectrometric facility for the measurement of helium isotopes, neon, and tritium in water, *Isotopes Environ. Health Stud.*, 2009,

View Article Online
DOI: 10.1039/D5VA00181A

45, 83–95.

13 C. N. Albers and J. Sültenfuss, A 60-Year Increase in the Ultrashort-Chain PFAS Trifluoroacetate and Its Suitability as a Tracer for Groundwater Age, *Environ. Sci. Technol. Lett.*, 2024, **11**, 1090–1095.

14 M. Hansen and B. Pjetursson, Free, online Danish shallow geological data, *GEUS Bull.*, 2011, **23**, 53–56.

15 R, Core Team, 2024. R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria. https://www.R-project.org/.

16 G. Levin, *Basemap03. Technical documentation of the method for elaboration of a land-use and land-cover map for Denmark. DCE Technical Report No. 159. Data downloaded on 11.10.2023.*, 2019.

17 M. Hollander and Wolfe D A, *Nonparametric Statistical Methods. Wiley Series in Probability and Mathematical Statistics.*, Wiley, New York, 1973.

18 O. J. Dunn, Multiple Comparisons Using Rank Sums, *Technometrics*, 1964, **6**, 241–252.

19 R. Bossi, *Monitoring of PFAS in air and precipitation (In Danish)*, Roskilde, 2024.

20 D. Muir and L. T. Miaz, Spatial and Temporal Trends of Perfluoroalkyl Substances in Global Ocean and Coastal Waters, *Environ. Sci. Technol.*, 2021, **55**, 9527–9537.

21 E. Amato, F. Béen and D. Vughs, *PFAS in sea-spray aerosols*, Nieuwegein, 2023.

22 K. De Brouwere, J. Gemoets, G. Jacobs and S. Voorspoels, *PFAS in zeewater en zeeschuim. Eindrapport. 2022/SCT/R/2837.*, 2023.

23 Niras, *Screening af forekomsten af PFAS på Naturstyrelsens kystnaere og vestvendte arealer i Jylland og på Sjaelland (In Danish)*, 2023.

24 J. Kontchou, *Untersuchung von per- und polyfluorierten Alkylsubstanzen (PFAS) im Meeresschaum an Nord- und Ostsee-Stränden in Deutschland (In German)*, 2025.

25 M. S. McLachlan, S. Felizeter, M. Klein, M. Kotthoff and P. De Voogt, Fate of a perfluoroalkyl acid mixture in an agricultural soil studied in lysimeters, *Chemosphere*, 2019, **223**, 180–187.

26 T. Buckley, T. Vuong, K. Karanam, P. H. N. Vo, P. Shukla, M. Firouzi and V. Rudolph, Using foam fractionation to estimate PFAS air-water interface adsorption behaviour at ng/L and µg/L concentrations, *Water Res.*, 2023, **239**, 120028.

27 J. F. Stults, Y. J. Choi, C. Rockwell, C. E. Schaefer, D. D. Nguyen, D. R. U. Knappe, T. H. Illangasekare and C. P. Higgins, Predicting Concentration- and Ionic-Strength-Dependent Air-Water Interfacial Partitioning Parameters of PFASs Using Quantitative Structure-Property Relationships (QSPRs), *Environ. Sci. Technol.*, 2023, **57**, 5203–5215.

28 R. Jakobsen, K. Hinsby, J. Aamand, P. van der Keur, J. Kidmose, R. Purtschert, B. Jurgens, J. Sültenfuss and C. N. Albers, History and Sources of Co-Occurring Pesticides in an Abstraction Well Unraveled by Age Distributions of Depth-Specific Groundwater Samples, *Environ. Sci. Technol.*, 2020, **54**, 158–165.

29 M. L. Brusseau, Influence of chain length on field-measured distributions of PFAS in soil and soil porewater, *J. Hazard. Mater. Lett.*, 2023, **4**, 100080.

30 H. Joerss, C. Apel and R. Ebinghaus, Emerging per- and polyfluoroalkyl substances (PFASs) in surface water and sediment of the North and Baltic Seas, *Sci. Total Environ.*, 2019, **686**, 360–369.

View Article Online
DOI: 10.1039/D5VA00181A

31 J. Enders, R. Weed, E. Donovan, D. Phelps, G. Campbell, K. May and E. Baker, Detection and Quantitation of Per- and Polyfluoroalkyl Substances in Sea Foam and the Corresponding Sea Water, DOI:10.1021/acs.est.5c03600.

32 H. M. Pickard, A. S. Criscitiello, D. Persaud, C. Spencer, D. C. G. Muir, I. Lehnherr, M. J. Sharp, A. O. De Silva and C. J. Young, Ice Core Record of Persistent Short-Chain Fluorinated Alkyl Acids: Evidence of the Impact From Global Environmental Regulations, *Geophys. Res. Lett.*, 2020, **47**, e2020GL087535.

33 F. Schlütter, O. S. Petersen and L. Nyborg, Resource Mapping of Wave Energy Production in Europe, *Proc. 11th Eur. Wave Tidal Energy Conf. 6-11th Sept 2015, Nantes, Fr.*, 2015, 1–9.

34 G. De Leeuw, F. P. Neele, M. Hill, M. H. Smith and E. Vignati, Production of sea spray aerosol in the surf zone, *J. Geophys. Res. Atmos.*, 2000, **105**, 29397–29409.

35 A. M. J. Van Eijk, J. T. Kusmierczyk-Michulec, M. J. Francius, G. Tedeschi, J. Piazzola, D. L. Merritt and J. D. Fontana, Sea-spray aerosol particles generated in the surf zone, *J. Geophys. Res. Atmos.*, 2011, **116**, D19210.

36 T. Wanzek, J. F. Stults, M. G. Johnson, J. A. Field and M. Kleber, Role of Mineral-Organic Interactions in PFAS Retention by AFFF-Impacted Soil, *Environ. Sci. Technol.*, 2023, **57**, 5231–5242.

37 Y. Lyu, B. Wang, X. Du, B. Guo and M. L. Brusseau, Air-water interfacial adsorption of C4-C10 perfluorocarboxylic acids during transport in unsaturated porous media, *Sci. Total Environ.*, 2022, **831**, 154905.

38 K. I. Kirkwood, J. Fleming, H. Nguyen, D. M. Reif, E. S. Baker and S. M. Belcher, Utilizing Pine Needles to Temporally and Spatially Profile Per- and Polyfluoroalkyl Substances (PFAS), *Environ. Sci. Technol.*, 2022, **56**, 3441–3451.

39 Q. Wang, Y. Ruan, Z. Zhao, L. Zhang, X. Hua, L. Jin, H. Chen, Y. Wang, Y. Yao, P. K. S. Lam, L. Zhu and H. Sun, Per- and polyfluoroalkyl substances (PFAS) in the Three-North Shelter Forest in northern China: First survey on the effects of forests on the behavior of PFAS, *J. Hazard. Mater.*, 2022, **427**, 128157.

View Article Online
DOI: 10.1039/D5VA00181A

Data availability statement for

Sea spray aerosols can be a source of PFAS pollution in coastal aquifers

Christian Nyrop Albers*, Denitza Voutchkova

Department of Geochemistry, Geological Survey of Denmark and Greenland (GEUS), Øster Voldgade 10, DK-1350 Copenhagen, Denmark

This study was carried out using publicly available data from the Danish National well database (Jupiter) at https://www.geus.dk/produkter-ydelser-og-faciliteter/data-og-kort/national-boringsdatabase-jupiter (accessed on 30th August 2024).

Additional data for 60 PFAS in 4 monitoring wells have been included as part of the Supplementary Information.

Results for noble gas analyses for estimation of groundwater age have been included as part of the Supplementary Information.

Results of in-house-analysis of trifluoroacetic acid (TFA) are in Table 1.

Publicly available data for PFOA and PFHxS in Sea water have been included as part of the Supplementary Information.