

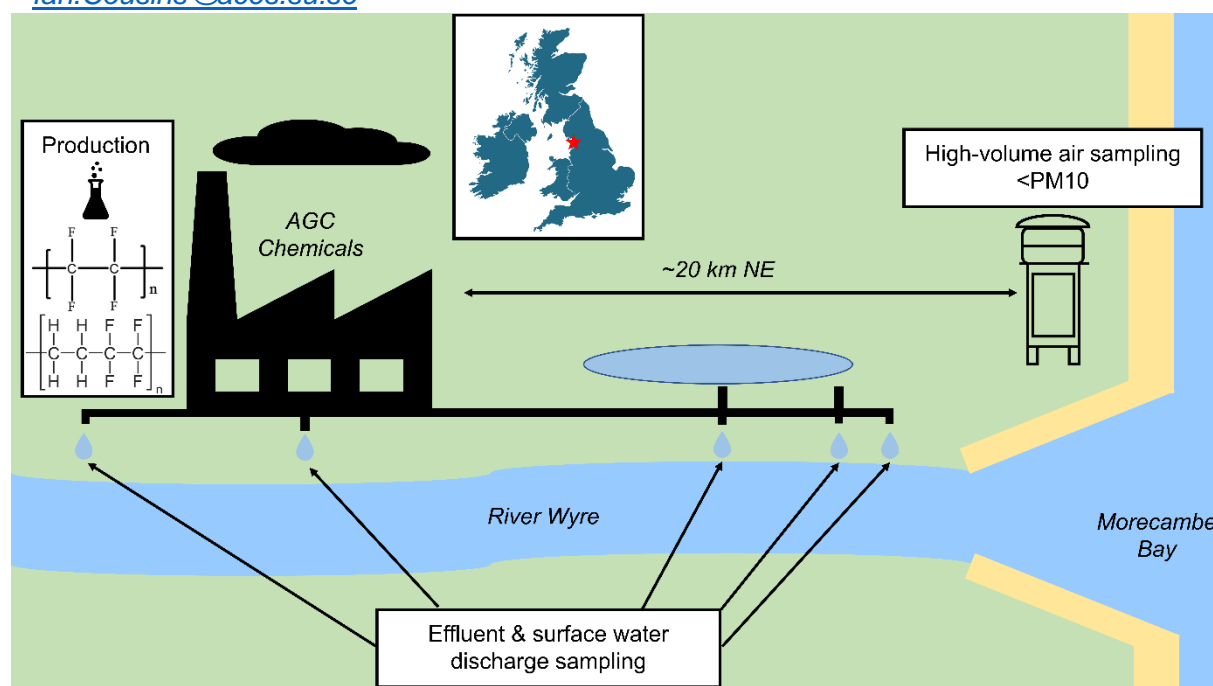
# Perfluoro(2-ethoxy-2-fluoroethoxy)-acetic acid (EEA) and other target and suspect PFAS in the vicinity of a fluoropolymer production plant

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## Abstract

Multiple target and suspect per- and polyfluoroalkyl substances (PFAS), including the replacement fluoropolymer processing aid perfluoro(2-ethoxy-2-fluoroethoxy)-acetic acid ("EEA"), were measured in both air and surface water in the vicinity of a fluoropolymer production plant (FPP) in Thornton-Cleveleys (United Kingdom) during sampling campaigns in 2021 and 2023, respectively. Targeted and suspect screening methods were conducted using ultra-high-performance liquid chromatography (UHPLC) coupled with Q-Exactive HF Orbitrap high-resolution mass spectrometry (HRMS). Summed PFAS levels in water nearby the plant ranged from 30 ng/L to 22.5 µg/L and were dominated by perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl ether carboxylic acids (PFECAs), most notably perfluorooctanoic acid (PFOA; up to 20.6 µg/L), EEA (up to 1.7 µg/L) and perfluorohexanoic acid (PFHxA; up to 650 ng/L). Additionally, various homologous series of PFAS suspects, such as hydrogen-substituted PFCAs (H-PFCAs), chlorine-substituted PFCAs (Cl-PFCAs) and monoether perfluoroether alkyl carboxylic acids (ME-PFECAs) were identified, some for the first time in Europe. In air, PFOA was detected in all but one sample collected 20 km from the plant at concentrations ranging from 0.51 to 2.50 pg/m<sup>3</sup>. The three air samples that showed detectable EEA concentrations also displayed evidence of long-chained targets and suspects and were associated with high wind speeds from a southwesterly direction. Overall, this study shows that this site continues to be a source of a complex mixture of legacy and scarcely monitored

PFAS that occur in multiple environmental media. This highlights the importance of further research that assesses the toxicity of these substances and resulting impacts on humans and wildlife.

**Keywords:** Suspect screening, Air Sampling, Surface Water Sampling, By-products, High-Resolution Mass Spectrometry

**Synopsis:** PFAS were measured in air and water near a UK fluoropolymer production plant. Diverse target and suspect compounds were identified with potential risks to human and environmental health.

## 1. Introduction

Fluoropolymers are a subset of per- and polyfluoroalkyl substances (PFAS) consisting of a carbon-fluorine backbone that are produced through the polymerization of low molecular weight fluorinated organic monomers. Well-known fluoropolymers include polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF) and fluoroelastomers (FKMs).<sup>1,2</sup> Owing to the presence of multiple carbon-fluorine bonds, these specialty materials have various useful and unique properties, such as high thermal and chemical resistance and low surface energy.<sup>3</sup> As a result, fluoropolymers are widely used in many different industrial and consumer applications where these properties are desired.<sup>4</sup> Fluoropolymers are the second-largest subgroup of PFAS globally with several hundreds of thousands of tons produced annually and second only to fluorinated gases.<sup>5</sup>

A wide variety of PFAS and other fluorinated organic substances are used and/or formed during the production of fluoropolymers.<sup>6</sup> Fluorosurfactants, which consist of a hydrophobic per- or polyfluoroalkyl chain and a hydrophilic head group (e.g. carboxylate or sulfonate) are among the most well-known substances associated with FP production.<sup>7</sup> Fluorosurfactant salts (e.g. with ammonium, sodium or potassium counter ions), are used as processing aids that serve to stabilize and disperse aqueous emulsions of monomers in the emulsion polymerization process. Additionally, fluorosurfactants can be formed as by-products during fluoropolymer production.<sup>8,9</sup>

While PFAS fluorosurfactants play an important role in the emulsion polymerization process, other processes that are employed in fluoropolymer production such as suspension polymerization, the synthesis of fluoromonomers through pyrolysis and further processing steps such as polymer crosslinking and molecular weight adjustment also involve the use or formation of PFAS or fluorinated organic substances. Examples of these substances include fluorinated monomers, pyrolysis by-products, fluorinated solvents, oligomers, chain transfer agents and crosslinking agents.<sup>6</sup>

When considering PFAS emissions, unchecked releases of the long-chain perfluoroalkyl carboxylic acid (PFCA) fluorosurfactant processing aids perfluorooctanoic acid (PFOA) and perfluorononanoic acid (PFNA) by the fluoropolymer production industry from the 1950s until the early 2010s has contributed significantly to global levels of these substances.<sup>7</sup> Following concerns about their persistence, bioaccumulation potential and toxicity, these long-chain fluorosurfactants were voluntarily phased out in Europe, Japan and the USA between 2002 and 2012. Various replacement substances have since emerged. Many of these replacement fluorosurfactants are proprietary ammonium salts of perfluoroalkyl ether carboxylic acids (PFECAs) and used in company-specific processes.<sup>10</sup> Examples include Chemours' hexafluoropropylene oxide dimer acid (HFPO-DA, "Gen-X"), 3M Dyneon's ammonium 4,8-dioxa-3H-perfluorononanoate ("ADONA"), the cyclic perfluorinated C6 quad-ether "C6O4"-used by Solvay/Syensqo and perfluoro(2-ethoxy-2-fluoroethoxy)-acetic acid ("EEA") used by Asahi Glass Co. (AGC).<sup>10,11</sup> In addition to the introduction of alternative substances, industry

has also been pressured by authorities to introduce various emission abatement measures to limit emissions of fluorosurfactants and other PFAS.<sup>12</sup> Although most replacement fluorosurfactants have a higher solubility and thus a lower bioaccumulation potential compared to PFOA and PFNA, their continued release, persistence, toxicity and classification as PFAS warrants further research.<sup>13</sup> Additionally, relatively little is known about the emissions by the fluoropolymer production industry of PFAS that are not used as fluorosurfactant processing aids.

The aim of the current study was to investigate the emissions and occurrence of the replacement fluorosurfactant processing aid EEA and other PFAS in air and water collected in the vicinity of a fluoropolymer production plant (FPP) in Thornton-Cleveleys, UK (Figure 1). To the best of our knowledge, this study is the first to quantify EEA in any matrix.

## 2. Materials & methods

### 2.1 Study site

The AGC Chemicals fluoropolymer production plant (FPP) produces both PTFE and (poly)ethylene- tetrafluoroethylene (ETFE), with production volumes of 4000 and 2000 tonnes per year respectively.<sup>14</sup> For the production of PTFE, the plant uses emulsion polymerization, while ETFE is produced in granular form using suspension polymerization. From 1955 until 2012 ammonium perfluorooctanoate (APFO) was used as a processing aid for PTFE production.<sup>15</sup> The UK Environmental Agency (UK EA) estimated that around 145 tonnes of this substance were released to the local environment (75 tonnes to the River Wyre and 70 tonnes to the atmosphere) during this time. Additionally, <5 tonnes of PFOA were landfilled.<sup>15</sup> From 2012 onwards, APFO was replaced by EEA-NH<sub>4</sub> (CAS 908020-52-0), the ammonium salt of a linear six-carbon PFECA with two ether linkages, one between the second and third carbon and one between the fourth and fifth carbon (Figure 2.). Synonyms for this substance include SAA-1000, PFO2OA and 'Asahi's product'.<sup>10, 13, 14, 16</sup> According to the UK EA, around 800 kilograms of the ammonium salt of EEA (EEA-NH<sub>4</sub>) is discharged into the River Wyre on a yearly basis.<sup>13</sup> Additionally, <100 kg of the substance is emitted to the atmosphere.<sup>13</sup> In addition to the fluoropolymers produced through polymerization, the monomer tetrafluoroethylene (TFE) is also produced on-site through the pyrolysis of chlorodifluoromethane (HCFC-22).<sup>14</sup>

Emissions of HCFC-22, fluoroform (HFC-23), trifluoroethylene (TrFE), TFE, hexafluoropropylene (HFP), perfluoroisobutylene (PFIB) and difluoromethane (HFC-32) are permitted to the air.<sup>6 14</sup> Additionally, emissions of 1H-perfluorohexane (1H-PFHx), perfluorobutyl ethylene (PFBE) and perfluoropropyl vinyl ether (PPVE) are reported for which no permitting requirements are posed.<sup>6, 17, 18, 19</sup>

The plant has three discharge points to surface water that all ultimately lead to the River Wyre estuary (Figure 1). The main discharge point 'W1' is a direct discharge to the River Wyre that, according to the emission permit, receives all process water effluent that has been treated by an on-site effluent treatment plant. The second discharge point 'W2' releases water to the Hillylaid Pool, a small tributary to the River Wyre. According to the emission permit, only uncontaminated surface water and roof water from the installation is discharged here. The third discharge point, 'W3', is a storm runoff discharge that only discharges overflow from the west effluent pit under very high rainfall conditions to a local stream called Royles Brook.<sup>14</sup>

Atmospheric emissions of various PFAS and fluorinated organic substances were reduced through the installation of a thermal oxidizer facility in 2017, which treats both flue gases and liquid waste. In 2007, prior to the installation of this thermal oxidizer, PFOA levels of up to of

828 pg/m<sup>3</sup> were detected at the Hazelrigg Meteorological Station, one of the sampling sites of this study (section 2.2.1).<sup>20</sup>

## 2.2 Standards and reagents

Standards for a total of 50 native PFAS (including EEA) as well as multiple isotope-labeled internal standards (ISs) were obtained Wellington Labs (Guelph, ON, CA) and Apollo Scientific (Bredbury, UK). A full list is provided in Table S1 of the Supporting Information (SI)).

## 2.3 Sampling & extraction

### 2.3.1 Air samples

Air samples were collected between 11 June and 24 September 2021 using a Tisch TE-1000 (Tisch Environmental, Cleves, OH, US) high volume air sampler located at the Hazelrigg Meteorological Station at Lancaster University on 110 mm quartz fiber filters (QFFs). This sampling site is located about 20 kilometers northeast (downwind) of the AGC Chemicals site in Thornton-Cleveleys (Figure 1) and was chosen because a) PFAS measurements could be compared to a previous study<sup>20</sup> from the same site; b) meteorological data (e.g. wind speed and direction) are collected that could be analyzed as meteorological drivers of PFAS air concentrations; c) it is located near-shore (6.5 km) and downwind of the FPP, giving the possibility of assessing the influence of sea-spray aerosol (SSA) on the atmospheric levels of PFAS; and d) practical reasons, including a power supply for active sampling.

QFFs were baked in an oven at 450 °C for 24 hours and subsequently packed in aluminum foil prior to use. A flow rate of 0.19-0.25 m<sup>3</sup>/min was used and about 1500 m<sup>3</sup> of air was collected per sample, corresponding to sampling times between 96 and 165 hours.

### 2.3.2 Surface water samples

Duplicate water samples were taken at the main discharge of the site on the River Wyre ('W1') and a discharge point by the lagoon north of the main discharge. Single water samples were taken at the surface water discharge near the Hillylaid Pool (the tributary receiving discharge 'W2'), at a land drain to the north of the lagoon and a leaking pipe leading to the River Wyre close to this land drain (Figure 1 and Figure S3-S7 in the SI). Unfortunately, the discharge point 'W3' could not be sampled due to access limitations.

Water samples (50 mL each) were extracted in duplicate using Weak Anion Exchange (WAX) solid-phase extraction (SPE) cartridges (Waters, Milford, MA, USA). Briefly, prior to extraction the samples were spiked with 2000 pg <sup>13</sup>C-labelled internal standards (IS, Table S1 in the SI). The 3cc (60 mg) WAX cartridges were conditioned using 4 mL of methanol (MeOH, Supelco Lichrosolv, Merck, Darmstadt, DE) with 0.1% ammonium hydroxide (NH<sub>4</sub>OH, 28-30% v/v, ACS-Reagent, Sigma-Aldrich, Steinheim, DE), subsequently the cartridges were equilibrated using 4 mL of ultrapure water (Milli-Q, Merck, Darmstadt, DE). The samples were then loaded and washed with 2 mL of pH 4 acetate buffer containing 2 mM acetic acid (>99.8% ACS-Reagent, Sigma-Aldrich, Steinheim, DE) and 2mM ammonium acetate (NH<sub>4</sub>CH<sub>3</sub>CO<sub>2</sub>, ACS-Reagent, Merck, Darmstadt, DE) in Milli-Q and, subsequently, with 2 mL of MeOH. Elution was performed using 2 x 750 µL of MeOH with 0.1% NH<sub>4</sub>OH. After elution the samples were evaporated to almost dryness and reconstituted with MeOH and Milli-Q with 4 mM of NH<sub>4</sub>CH<sub>3</sub>CO<sub>2</sub>, transferred to a LC-MS vial and spiked with 2000 pg Recovery Standard (RS).

Additionally, due to the possibility of high PFAS concentrations expected in some samples, 300 µL aliquots were taken from all water samples for direct injection. Prior to analysis, the aliquots were spiked with 2000 pg IS and passed through a nylon centrifuge filter in an Eppendorf tube. These were subsequently diluted 50:50 with MeOH and transferred to a 600 µL LC-MS vial, after which 2000 pg RS was added and the samples were ready for injection and analysis.

## 2.4 UHPLC-HRMS analysis

Extracts were injected in a Dionex Ultimate 3000 ultra-high-performance liquid chromatograph (UHPLC) linked to a Q-Exactive HF Orbitrap (Thermo Fisher Scientific, Waltham, MA, USA) high-resolution mass spectrometer (HRMS). The mobile phase consisted of A: Milli-Q:Acetonitrile (ACN, HPLC-grade, VWR, Rosny-sous-Bois-Cedex, FR) (95:5) and B: ACN:Milli-Q (99:1), both with 2 mM ammonium acetate ( $\text{NH}_4\text{CH}_3\text{CO}_2$ ) and was led through a Waters PFC Isolator column (Waters, Wilmslow, UK) after mixing. For separation, a 1.7  $\mu\text{m}$ , 50 x 2.1 mm Waters Acquity BEH C18 column was used coupled with Waters Acquity BEH C18 guard column (Waters, Wilmslow, UK), both maintained at 50°C. The analytes were ionized using an electrospray ionization source (ESI) operated in negative mode. The Orbitrap was used in full scan mode (scan range: 150 – 1800 Da, resolution: 120,000 FWHM) and data-dependent  $\text{MS}^2$  mode (resolution: 15,000 FWHM), with an inclusion list created from around 5000 potential PFAS masses derived from homologous series of PF(E)CAs and PF(E)SAs with different moieties.

## 2.6 Data handling

The data analysis was conducted using Thermo Fisher TraceFinder™ version 4.1 software. Quantification of individual PFAS was based on relative response of exact masses (5 ppm mass error tolerance) to matched ISs using an 8-point calibration curve ranging from 0.03 to 135 pg/ $\mu\text{L}$ . Because isotopically labeled standards were not available for all PFAS in this study, surrogate internal standards (i.e. non-exact matches) were used to quantify certain substances as detailed in Table S1. Internal standard recoveries were calculated by comparing their response areas to those of the recovery standards (RS;  $^{13}\text{C}_8$  PFOA or  $^{13}\text{C}_8$  PFOS; Table S1).

For the water samples, the instrumental limits of detection (LODs) and quantification (LOQs) were calculated by taking the standard error of the residuals from the lowest three points on the calibration curve. This value was then divided by the slope of the calibration curve and multiplied by 10 to determine the LOQ and by 3.3 to calculate the LOD. For the air samples, due to matrix effects leading to overall lower and more variable IS responses, method LODs (MDLs) and LOQs (MQLs) were determined by taking the response area of the internal standard in the sample into account.

## 2.7 Quality control

### 2.7.1 Air samples

Multiple field blanks were taken by inserting a QFF into the sampler and following the same storage and transport procedure as the sample filters. Lab blanks were included in every extraction by adding triplicate unused burned QFFs to the extraction procedure. Additionally, a spike-and-recovery test was performed by fortifying a QFF with native analytes (2000 pg each) and following the same extraction procedure.

### 2.7.2 Water samples

Included in the water SPE and direct injection samples were triplicate lab blanks consisting of Milli-Q water and for the SPE-method a spike-and-recovery test was performed consisting of Milli-Q water which was additionally spiked with 1000 pg mix of native ( $^{12}\text{C}$ ) PFAS.

## 2.8 Data processing

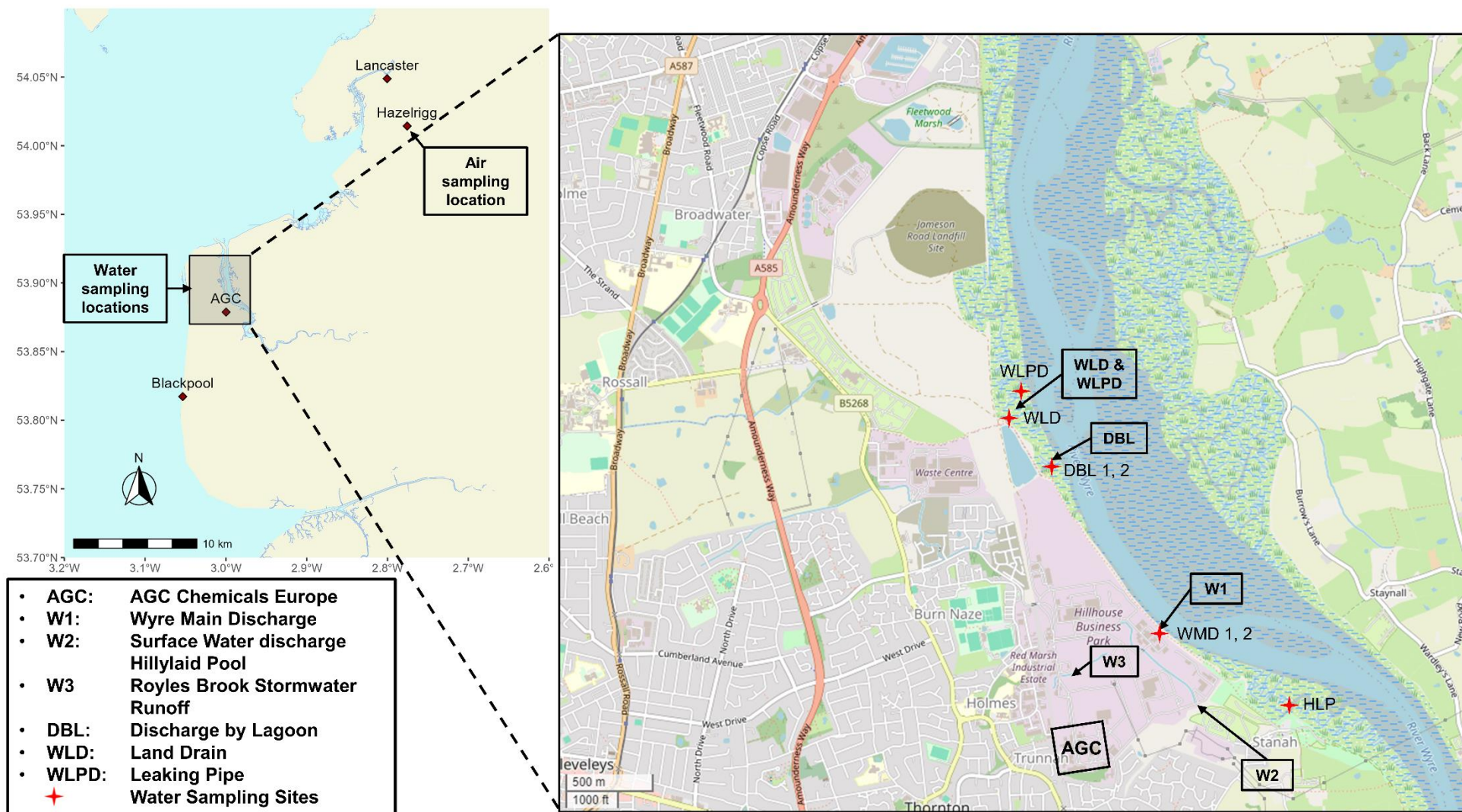
The suspect screening method used Thermo Fisher TraceFinder™ version 4.1 software in conjunction with Thermo Fisher Xcalibur™ Qual Browser. The initial list of suspects was based on matches (within 5 ppm mass error) to an in-house database used for the inclusion list during instrumental analysis. This inclusion list was based on homologous series of perfluoroalkyl acids with various moieties and functional groups and contained about 5000 exact masses. Thereafter, suspect peaks were inspected manually for  $\text{MS}^2$  and in-source fragmentation patterns, isotopic ratios, and retention times, which were compared to available literature.



217 Using the Schymanski scale <sup>21</sup>, suspects were either assigned level 2a) when an MS<sup>2</sup> scan  
218 and a library spectrum match were acquired; 2b) without library match but with acquired MS<sup>2</sup>  
219 and diagnostic evidence supporting the identification, such as retention time relative to PFCAs,  
220 presence of homologous series and fragmentation patterns in MS<sup>1</sup>; or 3) similar diagnostic  
221 evidence as 2b, but without acquired MS<sup>2</sup>. <sup>21</sup>

## 222 2.9 Tracer ion analysis and meteorological parameters

223 Using previously described methodology <sup>22</sup>, analyses of the presence and concentrations of  
224 SSA tracer ions were carried out on punches of all QFFs. Average wind speed and direction  
225 during sampling was calculated using equations S1-S5 in the SI.



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Figure 1. Map showing the locations of the fluoropolymer production plant of AGC Chemicals, discharges mentioned in the permit, water sampling locations and the sampling location at the Hazelrigg Meteorological Station and the cities of Lancaster and Blackpool.<sup>23</sup>

### 3. Results & discussion

#### 3.1 QA/QC

Similar to HFPO-DA and various other PFECAs, EEA shows very pronounced in-source fragmentation.<sup>24</sup> As such, the most intense fragment is not the molecular ion ( $[M-H]^-$ ) but rather the  $[M-CF_2-COOH]^-$  fragment, which could have an intensity up to an order of magnitude higher than the molecular ion (Figure 2.). Therefore, this in-source fragment is used in the quantification method along with the molecular ion by summing the response. The retention time of EEA on the C18 column is similar to that of perfluoroheptanoic acid (PFHpA), indicating that the insertion of ether linkages slightly increases the hydrophobicity of the perfluoroalkyl chain as EEA has the same number of perfluorinated carbons and the same head group as PFHxA. Spike- and recovery tests with EEA for both the QFF and water extraction methods yielded a recovery of  $96\% \pm 6\%$  and  $109\% \pm 5\%$  respectively and was similar to other PFAS with comparable perfluoroalkyl chain lengths (Table S3 in the SI).



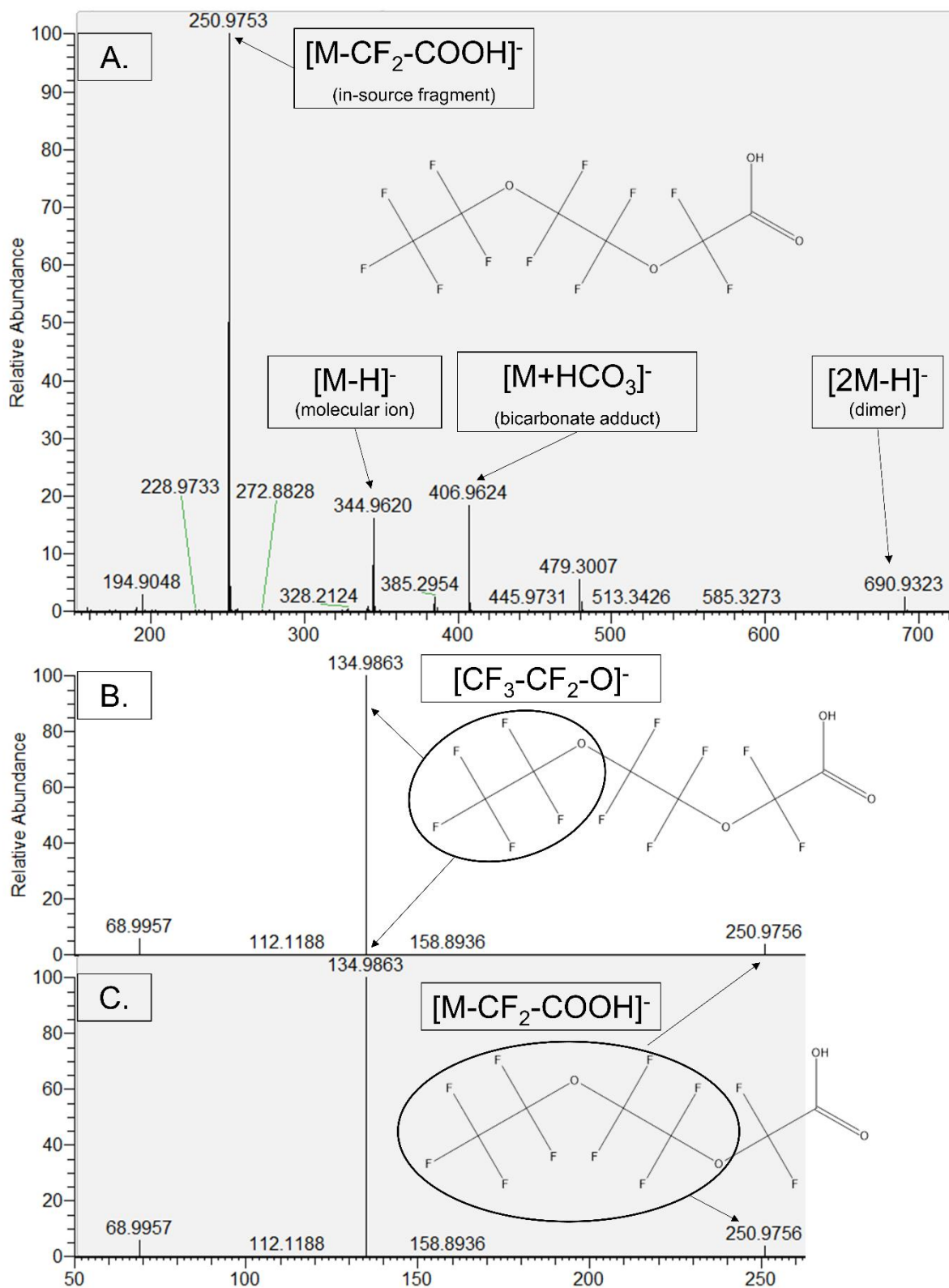


Figure 2. Typical full-scan mass spectrum of EEA (A) along with product ion scans of the major EEA in-source fragment ( $m/z$  250.9753; B) and molecular ion (344.9620; C). Note the relatively low response for the molecular ion in the MS1 spectrum.

## 3.2 Water samples

### 3.2.1 Targeted analysis

$\Sigma$ PFAS concentrations in water samples varied by nearly three orders of magnitude during the sampling campaign (30 ng/L to 22.5  $\mu$ g/L; Table S4). Remarkably, the main discharge (W1) of the process water effluent had the lowest PFAS concentrations compared to all the other sampling points. At the main discharge, the total measured PFAS concentrations ( $\Sigma$ PFAS) were 30 ng/L (Main Discharge in Wyre 1) and 33 ng/L (Main Discharge in Wyre 2), while the other sampling points all had PFAS levels within the  $\mu$ g/L range (Figure 3). Overall three different PFAS profiles were encountered near the plant. The highest PFAS concentrations were found to the north of the plant at a discharge near a lagoon (DBL) and at a land drain north of the lagoon (WLD) and a leaking part of a long discharge pipe (WLPD) leading to the River Wyre. PFOA was very prominent in these samples, with concentrations ranging from  $891 \pm 37$  ng/L to  $20.62 \pm 0.56$   $\mu$ g/L. Furthermore, in these samples other PFCAs, such as perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), PFHxA, PFHpA and PFNA are present in relatively high levels. There was also evidence of additional C<sub>8</sub> PFAS, such as hydrogen-substituted PFOA, chlorine-substituted PFOA, and ether-PFOA (Section 3.2.2 on suspect screening). Concentrations of EEA in these samples ranged from  $120.8 \pm 0.3$  ng/L to  $205.5 \pm 1.0$  ng/L and were in a similar range as the levels of the C<sub>4</sub>-C<sub>7</sub> PFCAs.

The Hillylaid Pool water had the highest levels of the replacement polymerization processing aid EEA out of all of the discharge locations ( $1744.1 \pm 106.8$  ng/L). However, in samples taken from the Hillylaid Pool and the main discharge, EEA had only slightly higher levels than PFOA (Figure 3). For duplicates collected at the main discharge EEA concentrations were  $21.17 \pm 0.04$  ng/L and  $17.12 \pm 0.40$  ng/L respectively, considerably lower than the concentrations at the Hillylaid Pool.

The levels of PFOA in the samples taken at the discharge by the lagoon (DBL) and the leaking pipe (WLPD) were quantified using direct injection, which also yielded similar concentrations and accuracy for PFOA as the SPE samples for the Hillylaid Pool and the Wyre land drain (Figure S1 in the SI). The PFOA concentrations of the SPE samples DLB and WLPD were not reported because the integrated areas of PFOA fell well above the calibration range and significant detector saturation effects occurred associated with these high PFOA concentrations, which led to suppression of the internal standard response and unreliable quantification (Table S4 in the SI).

The high PFOA concentrations are likely attributable to the extensive use of APFO for PTFE production at the plant between 1955 and 2012, and unabated emissions of PFOA to the environment during this time. Therefore, it could be that a large reservoir of PFOA and related substances still exists within the perimeter of the industrial site. For instance, the samples with the highest PFAS levels were taken around a discharge by a lagoon to the north of the site. This lagoon was unfortunately not accessible during sampling, but should be the subject of further investigation. Furthermore, documentation of the UK Environment Agency (UK EA), points to the existence and former use of various other discharges, including a 'North' discharge.<sup>25</sup> Additionally, a landfill to the north of the site has been used until 2014 for disposal of material from the plant, which included <5 tonnes of PFOA.<sup>15</sup> This landfill could potentially be leaching large amounts of PFAS to the environment.

AGC Chemicals Europe has admitted that small amounts of PFOA and other PFCAs are formed non-intentionally due to a process in which the molecular weight of PTFE micropowders is altered using irradiation and thermal degradation.<sup>26</sup> These impurities are removed from the polymer on-site and whether subsequent emissions occur remains unclear. However, it does

not seem likely that emissions could account for the levels found in the discharges, as a maximum PFOA concentration in the ppb range is expected in the PTFE polymer itself.<sup>26</sup>

Another interesting aspect of the detected PFCAs is the prominence of branched isomers. These were identified by their shorter retention times and more pronounced in-source fragmentation (e.g. decarboxylation and lower relative [M-H]<sup>+</sup> associated with shorter perfluoroalkyl chains) relative to the linear isomer and IS (Figure S8 in the SI). Both the presence of PFCAs of multiple chain lengths and the formation of branched isomers are associated with PFCA production through electrochemical fluorination (ECF).<sup>27</sup> This process is known to yield various structural isomers of PFOA as impurities.<sup>28</sup> However, as these samples are taken post-polymerization, it could not be excluded that the formation of polymerization by-products also plays a role in the presence of these substances.

Additional future research and sampling is necessary around the AGC Chemicals plant in order to verify the very high PFAS levels (µg/L range) and possible emissions from these 'alternative' discharges. Elevated PFAS concentrations at these locations could potentially be explained by re-emission from existing on-site PFAS reservoirs. However, it is crucial to rule out the possibility that current production processes still involve either the use or formation of significant quantities of PFOA and other PFAS, which could lead to subsequent emissions. Further investigation is also needed to determine whether process water discharge points other than W1 exist.

The high concentration of EEA (1744 ± 107 ng/L) found in the Hillylaid Pool is especially interesting in this regard. Due to this elevated level and the occurrence of the suspects of class 7. (Section 3.2.2), the PFAS profile in this water might more accurately reflect current use and emissions. Additionally, the relatively high level of the monoether-PFBA quantified here could possibly be a byproduct of the liquid-phase fluorination process used to produce EEA<sup>29</sup> or a product of the hydrolysis of PPVE, a co-monomer used on-site.

Lastly, it should be emphasized that PFAS concentrations found in these water samples are potentially problematic regardless of their origins and should be abated in order to prevent further contamination of the River Wyre and the estuarine area.

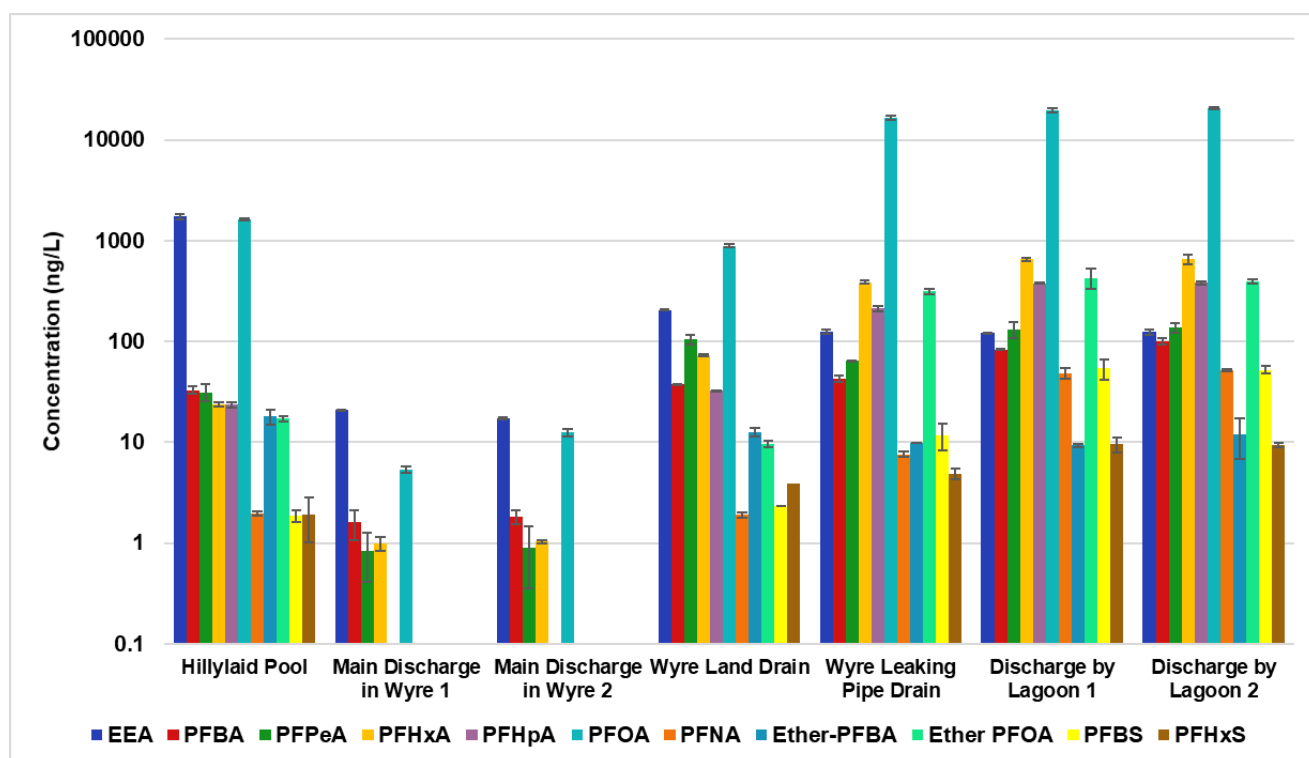


Figure 3. Levels of PFAS that were >LOD in the water samples taken around AGC Chemicals in Thornton-Cleveleys. Note the logarithmic scale.

### 3.2.2 Suspect screening

In addition to the PFAS that were quantified using standards, a total of 55 different PFAS suspects were identified in the water samples through the analysis of homologous series consisting of multiple per- or polyfluoroalkyl chain lengths ( $-\text{CF}_2-$ )<sub>x</sub> (Table S8 in the SI). These suspects were classified into seven groups: 1. hydrogen-substituted PFCAs (H-PFCAs), 2. chlorine-substituted PFCAs (Cl-PFCAs), 3. monoether PFECAs. (ME-PFECAs) 4. cyclical monoether PFECAs (Cyc. ME-PFECAs) 5. dihydrogen-substituted PFOA (6:2 FTA and structural isomers), 6. hydrogen-substituted homologs of class 2. and 3. and 7. polyhydrogenated PFCAs (H=3-5).

The highest responses for suspect classes 1-6 were found in the samples with the highest targeted PFAS levels taken at the discharge close by the lagoon (Table S9 in the SI). Furthermore, most of the detected homologous series had the highest response at the C<sub>8</sub> homolog (Table S9 and Figure S9-S12 in the SI). Response areas in the quantification injections of these samples for C<sub>8</sub> homologs were comparable to those of EEA: H-PFOA (8.8e7), Cl-PFOA (2.8e7), cyclic-ether PFOA (2.8e7), EEA (4.9e7). Thus, when assuming similar response factors for these suspects as PFOA, the concentrations of these suspects in this sample could be similar to those of EEA and C<sub>4</sub>-C<sub>7</sub> PFCAs and in the hundreds of ng/L. Although the response areas were lower, these suspects were identified in other samples too (Table S8 in the SI) and have been identified in other studies close to fluoropolymer production plants in Asia.<sup>30,31</sup>

For all suspect classes it is probable that multiple branched isomers are present in the samples, due to multiple peaks for the same exact masses at earlier retention times in the chromatograms, similar to the PFCAs. Due to the very high concentrations of PFOA with a probable ECF signature in these samples (μg/L range), it is likely that most of these suspects are by-products of ECF such as H-PFCAs, along with the cyclical monoether PFECAs which have also been reported as impurities or by-products of ECF.<sup>28, 32</sup> Cl-PFCAs have also been

reported in Asia, where ECF PFOA is still used<sup>30</sup> and some fluorination processes used by AGC reportedly use chlorinated molecules as starting materials.<sup>29</sup> Unfortunately, and similar to earlier reported data from Asia<sup>30,33</sup>, it remains difficult to acquire accurate MS<sup>2</sup> spectra for Cl-PFCAs using Orbitrap HRMS. Although MS<sup>2</sup> scans are triggered by the molecular ions, these scans contain only noise and no clear fragment peaks. We suspect that only a chlorine fragment ( $m/z = 35$  or  $37$ ) is ionized, which is below the lower mass threshold ( $m/z = 50$ ) of the Orbitrap scan range and that the rest of the molecule could form a neutral loss. Still, and similar to PFCAs, decarboxylated fragments were detected for Cl-PFCAs in MS<sup>1</sup> (Figure S9 in the SI). These fragments also triggered MS<sup>2</sup> scans with similar issues as those of the molecular ion.

AGC currently uses liquid-phase fluorination instead of telomerization for producing EEA and other fluorochemical building blocks.<sup>29</sup> It should be investigated whether this method still leads to significant formation of impurities and by-products and if these products could be present in the fluoropolymer processing aid that is subsequently used on-site.

Other possible formation processes may also contribute to the presence of the reported suspects. H-PFCAs, for instance, are known polymerization by-products in the production of PTFE.<sup>8</sup> Additionally, H-PFCAs have been reported to form as a result of reductive dechlorination of Cl-PFCAs.<sup>34</sup> Lastly, the substance chlorotrifluoroethylene (CTFE) is registered by AGC Chemicals Europe and so it cannot be excluded that the chlorinated PFAS encountered in this study are a result of by-product formation after the use of CTFE as co-monomer.

In addition to the highest EEA concentrations, samples from the Hillylaid Pool also had the highest responses of class 7 suspects. Due to the multiple hydrogen substitutions, it could be that these suspects are more susceptible to biotransformation than PFAS with perfluoroalkyl chains and therefore over time have gradually disappeared from the other PFAS reservoirs. This observation, along with the relatively high levels of EEA and the overall different PFAS profile in the Hillylaid Pool compared to the samples taken north of the main discharge could support the hypothesis that the PFAS measured in the Hillylaid Pool reflects recent emissions. The PFAS profile of the samples taken north of the discharge could reflect leaching of PFAS that have accumulated over multiple years.

### 3.3 Air samples

PFAS were detected in all air samples taken at the Hazelrigg Meteorological Station with concentrations ranging from 0.29 to 5.43 pg/m<sup>3</sup> (Figure 4 and Table S5). PFOA was prominent in these samples, with detection in 20 out of 21 of these samples and concentrations ranging from 0.51 to 2.50 pg/m<sup>3</sup> (Figure 4). Branched PFOA isomers were also detected in all of these samples. For the one sample where PFOA was not detected, the response of the IS was very poor, resulting in high MDLs/MQLs for all analytes (Table S6-S7 in the SI). High air concentrations of PFOA and  $\Sigma$ PFAS were associated with high wind speeds from the southwest direction (Figure 5 & Table S5). PFOS and PFHxS were detected in all air samples, albeit with lower peak concentrations (PFOS; 0.49 pg/m<sup>3</sup>) or at levels between MDL and MQL (PFHxS).

Notably, EEA was only detected in three out of the four samples with the highest PFOA concentrations. The concentrations of EEA in these samples were 0.28 (between MDL and MQL), 0.66 and 2.02 pg/m<sup>3</sup> and PFHxA and PFBA were also above MDL in these samples, but below MQL, while PFHpA and the long-chain PFNA, PFDA, PFUnDA were above MQL and PFDoDA was above MQL in the two of these samples (Figure 4 and 5 and Table S5 in the SI).



The presence of PFOA, EEA and the PFCAs in the samples not only coincided with high wind speeds from the direction of the AGC Chemicals plant, but also with high sodium ( $\text{Na}^+$ ) tracer ion concentrations that are a proxy for the levels of sea-spray aerosols (SSA). The two air samples (HAZ-14 and HAZ-15) with the highest PFOA concentrations, EEA responses and only samples with  $\text{C}_9\text{-C}_{12}$  PFCA levels all above MQL and with responses of the suspects previously described were also samples with highest  $\text{Na}^+$  levels (Table S5 in the SI). For PFOA and PFHxS the Spearman's rank correlation coefficients ( $\rho$ ) with  $\text{Na}^+$  were 0.41 and 0.50 respectively. However, for PFOA, this correlation was not statistically significant by a slight margin ( $p=0.07$ ), while for PFHxS it was ( $p=0.02$ ). As such, the concentrations of atmospheric PFOA could also be influenced to a minor extent by other sources, such as direct emissions by AGC Chemicals, the re-suspension of previously deposited PFOA from other areas and transformation of volatile precursors or urban emissions. PFOS did not show a statistically significant correlation with  $\text{Na}^+$  ( $\rho = 0.17$ ,  $p=0.45$ ) and for the other analytes the concentrations and detection frequencies were too low to draw conclusions on correlations with the  $\text{Na}^+$  tracer ion.

In the samples with the highest PFOA and EEA concentrations, trace responses of some of the suspects described in section 3.2.2 were also detected (Figure S12 and S13 in the SI). Compared to the water samples, these responses and those of the other PFCAs were more pronounced for the longer-chained homologs ( $>\text{C}_8$ ). SSA enrichment factors of perfluoroalkyl acids with a perfluoroalkyl chain length of seven or more are significantly higher than those with shorter perfluoroalkyl chain lengths.<sup>35, 36</sup> As such, with similar water concentrations, air concentrations of these homologs would be relatively higher compared to their shorter-chained counterparts. On the other hand, the long-range atmospheric transport potential of shorter-chained PFAS is similar or higher compared to long-chained PFAS, due to PFAS preferably binding to particle size ranges in the accumulation mode.<sup>37, 38</sup> If direct emissions were the dominant source for the measured air PFAS concentrations, the relative concentrations of short-chained homologs and PFCAs would be expected to be similar at Hazelrigg. However, these are measured at lower concentrations or not measured at all compared to concentrations in the water in the direct vicinity of the plant. More sampling data needs to be collected to statistically strengthen the correlations between air concentrations of PFOA, EEA, long-chain PFAS and the  $\text{Na}^+$  tracer ion at Hazelrigg. Although the current evidence remains largely circumstantial and based on a limited sample size ( $n=21$ ), it is suspected that enrichment of PFAS in SSA is currently the dominant driver of the atmospheric concentrations of PFAS related to AGC emissions measured in Hazelrigg. Additionally, the measured concentrations of PFOA (peak  $2.50 \text{ pg/m}^3$ ) and EEA (peak  $2.02 \text{ pg/m}^3$ ) are much lower than the PFOA peak level of  $828 \text{ pg/m}^3$  found in 2007<sup>20</sup>, before the installation of the emission abatement system that could have significantly reduced the impact of air emissions directly from the stacks of the plant. However, documents from the UK EA indicate that this system was not operational during the first quarter of 2023 and part of the first quarter of 2024.<sup>39,40</sup> Further investigation is necessary in order to understand how periods of non-operational emission abatement system affect environmental PFAS levels.

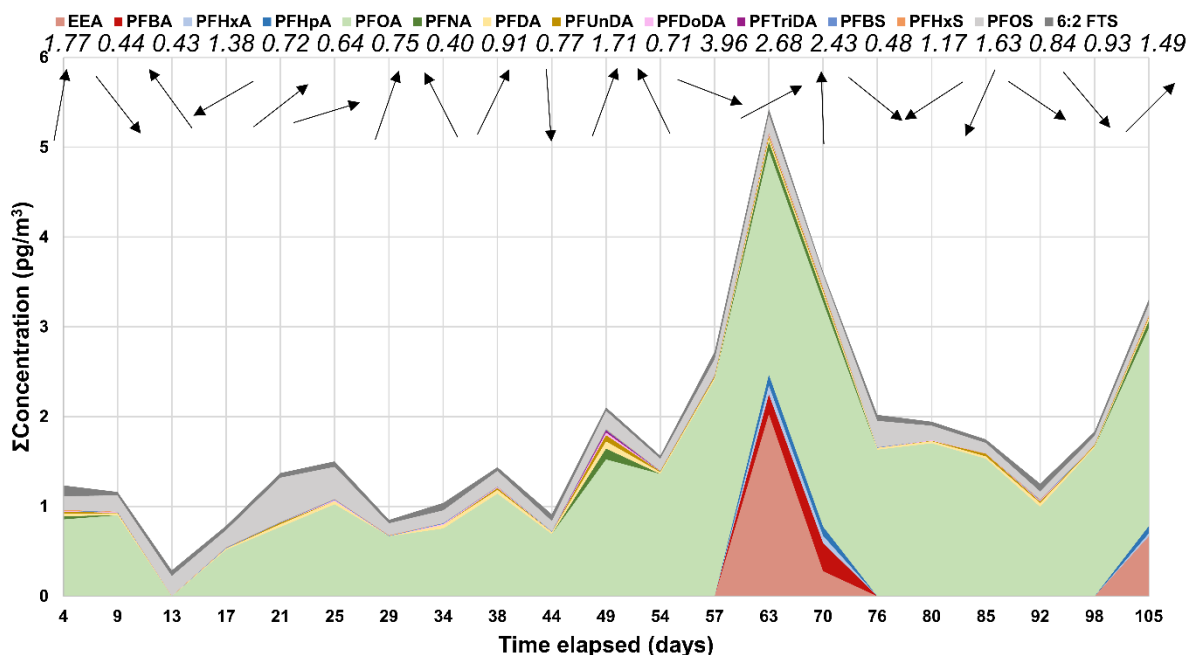


Figure 4. Air concentrations of PFAS that were >MDL at the Hazelrigg Meteorological Station during the sampling period. The arrows note average wind direction during the sampling time, while the values above are the average wind speed ( $\text{ms}^{-1}$ ).

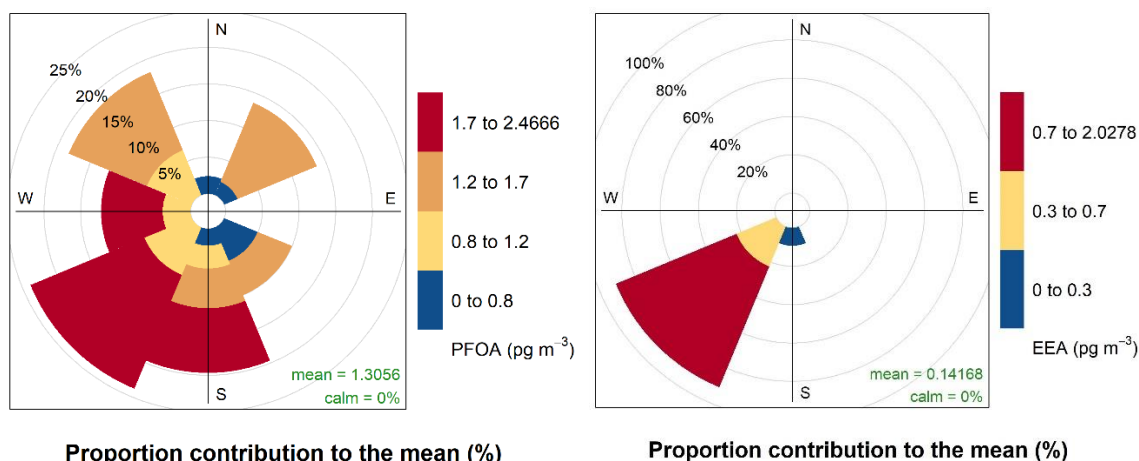


Figure 5. Pollution roses<sup>41</sup> of PFOA (left) and EEA (right) at the Hazelrigg Meteorological Station, showing which wind directions contributed the most to mean PFOA and EEA air concentrations

### 3.4 Implications

This study shows that the AGC Chemicals site continues to be a source of legacy and scarcely monitored PFAS to the local environment through direct emissions and/or leaching of PFAS reservoirs such as old discharges, the local landfill or lagoon. A large fraction of these emissions flow into the River Wyre estuary, which drains into the strongly tidal Morecambe Bay. This area is important as a wildlife habitat and for shellfish harvesting. Recently, elevated levels of PFOA were reported in otters with their habitats close to the AGC Chemicals plant.<sup>42</sup> Further monitoring data are required to establish the extent of PFAS contamination in the River Wyre and Morecambe Bay food web in order to assess the effects of the continued emissions of legacy and alternative PFAS from the AGC Chemicals site. Very little is known about the properties of the scarcely monitored PFAS identified in this study, but one might assume given their similar structures to PFCAs that they might have similar persistence, bioaccumulation potential and toxicities. Further research on the properties, including toxicities, of the identified

PFAS is required before human and environmental risk assessments can be performed. Secondary emissions of PFAS from the ocean due to their enrichment on sea spray aerosol could lead to additional deposition of long-chain homologs in coastal areas in the Morecambe Bay and our study shows that sea spray aerosol transport of PFAS could also be an additional secondary source to air for several legacy PFAS (notably PFHxS, PFOA and some long-chain PFCAs) as well as the replacement substance EEA and the scarcely monitored suspects (H-PFCAs, Cl-PFCAs and ME-PFECAs). These identified suspects are most likely to be by-products of electrochemical or liquid-phase fluorination or polymerization.

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## Supporting information

The supporting information (SI) includes the target analyte list, parameters of the instrumental method, calculations, sample concentrations, mass spectra, chromatograms and photos of the sampling site.

## References

1. Buck RC, Murphy PM, Pabon M. Chemistry, Properties, and Uses of Commercial Fluorinated Surfactants. In *Polyfluorinated Chemicals and Transformation Products*.: Springer Berlin Heidelberg; 2011. p. 1–24.
2. Wang Z, Buser AM, Cousins IT, Demattio S, Drost W, Johansson O, et al. A New OECD Definition for Per- and Polyfluoroalkyl Substances. *Environmental Science & Technology*. 2021 November;55: p. 15575–15578.
3. Thomas RR. Material properties of fluoropolymers and perfluoroalkyl-based polymers. In *Fluoropolymers 2: Properties*.: Springer; 1999. p. 47–67.
4. Glüge J, Scheringer M, Cousins IT, DeWitt JC, Goldenman G, Herzke D, et al. An overview of the uses of per- and polyfluoroalkyl substances (PFAS). *Environmental Science: Processes & Impacts*. 2020;22: p. 2345–2373.
5. Evich MG, Davis MJB, McCord JP, Acrey B, Awkerman JA, Knappe DRU, et al. Per- and polyfluoroalkyl substances in the environment. *Science*. 2022 February;375.
6. Dalmijn J, Glüge J, Scheringer M, Cousins IT. Emission inventory of PFASs and other fluorinated organic substances for the fluoropolymer production industry in Europe. *Environmental Science: Processes & Impacts*. 2024;26: p. 269–287.
7. Prevedouros K, Cousins IT, Buck RC, Korzeniowski SH. Sources, Fate and Transport of Perfluorocarboxylates. *Environmental Science & Technology*. 2005 December;40: p. 32–44.
8. Sworen JC, Morken PA, Smith AP, Boyle JE, Cervantes Garcia MD, Kramer J, et al. Interrogation of a fluoropolymer dispersion manufactured with a non-fluorinated polymerization aid for targeted and non-targeted fluorinated residuals by liquid

- chromatography high resolution mass spectrometry. *Journal of Chromatography A*. 2024 November;1736: p. 465369.
9. Hintzer K, Schwertfeger W. Fluoropolymers-Environmental Aspects. In Handbook of Fluoropolymer Science and Technology.: John Wiley & Sons, Inc.; 2014. p. 495–520.
  10. Wang Z, Cousins IT, Scheringer M, Hungerbühler K. Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSA) and their potential precursors. *Environment international*. 2013;60: p. 242–248.
  11. Solvay. Phasing out Fluorosurfactants at Solvay. [Online].; 2023 [cited 2023 September 28. Available from: <https://www.solvay.com/sites/g/files/srpend221/files/2023-03/Phasing%20out%20Fluorosurfactants%20V2.pdf>.
  12. DCMR. Ontwerpbeschikking Chemours Netherlands B.V. 2022 April..
  13. UK EA. Environmental risk evaluation report: Perfluoro(2-ethoxy-2-fluoroethoxy)- acetic acid, ammonium salt [EEA-NH<sub>4</sub>] (CAS no. 908020-52-0). 2023..
  14. UK EA. Permitting decisions (variation number EPR/BU5453IY/V004). 2017..
  15. UK EA. Enquiry regarding emissions of fluorinated organic substances by the fluoropolymer manufacturing industry. 2023..
  16. UK EA. Notice of variation and consolidation with introductory note (Permit number EPR/BU5453IY). 2017..
  17. UK EA. Environmental risk evaluation report: 3,3,4,4,5,5,6,6-Nonafluorohexene [Perfluorobutylethylene; PFBE] (CAS no. 19430-93-4). 2023..
  18. UK EA. Environmental risk evaluation report: Trideca-1,1,1,2,2,3,3,4,4,5,5,6,6fluorohexane [1H-PFHx] (CAS no. 355-37-3). 2023..
  19. UK EA. Environmental risk evaluation report: 1,1,1,2,2,3,3-Heptafluoro-3-[(trifluorovinyl)oxy]propane [PPVE] (CAS no. 1623-05-8). 2023..
  20. Barber JL, Berger U, Chaemfa C, Huber S, Jahnke A, Temme C, et al. Analysis of per- and polyfluorinated alkyl substances in air samples from Northwest Europe. *Journal of environmental monitoring*. 2007;9: p. 530–541.
  21. Schymanski EL, Jeon J, Gulde R, Fenner K, Ruff M, Singer HP, et al. Identifying Small Molecules via High Resolution Mass Spectrometry: Communicating Confidence. *Environmental Science & Technology*. 2014 February;48: p. 2097–2098.
  22. Sha B, Johansson JH, Tunved P, Bohlin-Nizzetto P, Cousins IT, Salter ME. Sea Spray Aerosol (SSA) as a Source of Perfluoroalkyl Acids (PFAAs) to the Atmosphere: Field Evidence from Long-Term Air Monitoring. *Environmental Science & Technology*. 2021 December;56: p. 228–238.
  23. Open Street Map. Open Street Map. [Online].; 2024 [cited 2024 August 8. Available from: <https://www.openstreetmap.org/#map=15/53.88418/-2.99446>.
  24. McCord J, Newton S, Strynar M. Validation of quantitative measurements and semi-quantitative estimates of emerging perfluoroethercarboxylic acids (PFECAs) and

- hexfluoropropylene oxide acids (HFPOAs). *Journal of Chromatography A*. 2018 May;1551: p. 52–58.
25. United Kingdom Environment Agency. Determination of an Application for a PPC Permit under the Pollution Prevention and Control (England and Wales) Regulations 2000 (SI 2000). Environmental Permit. Thornton Cleveleys: Permit number BU5453IY, Asahi Glass Fluoropolymers UK; 2006. Report No.: 1973.
  26. AGC Chemicals Europe. Call for comments for the Stockholm Convention on the revised draft Risk Profile for chlorpyrifos and the draft Risk Management Evaluations for MCCPs and long-chain PFCAs - AGC Chemicals Europe Ltd response. [Online].; 2023 [cited 2024 September 13. Available from: <https://www.gov.uk/government/consultations/draft-evaluations-of-3-chemical-substances-proposed-as-persistent-organic-pollutants-pops-call-for-comments/outcome/summary-of-responses-and-government-response>.
  27. Benskin JP, Ahrens L, Muir DCG, Scott BF, Spencer C, Rosenberg B, et al. Manufacturing Origin of Perfluorooctanoate (PFOA) in Atlantic and Canadian Arctic Seawater. *Environmental Science & Technology*. 2011 December;46: p. 677–685.
  28. Ignat'ev NV, Welz-Biermann U, Heider U, Kucheryna A, von Ahsen S, Habel W, et al. Carbon-chain isomerization during the electrochemical fluorination in anhydrous hydrogen fluoride—a mechanistic study. *Journal of Fluorine Chemistry*. 2003 November;124: p. 21–37.
  29. Okazoe T. Development of the “PERFECT” direct fluorination method and its industrial applications. *Journal of Fluorine Chemistry*. 2015 June;174: p. 120–131.
  30. Song X, Vestergren R, Shi Y, Huang J, Cai Y. Emissions, Transport, and Fate of Emerging Per- and Polyfluoroalkyl Substances from One of the Major Fluoropolymer Manufacturing Facilities in China. *Environmental Science & Technology*. 2018 August;52: p. 9694–9703.
  31. Liu Y, Pereira ADS, Martin JW. Discovery of C5–C17Poly- and Perfluoroalkyl Substances in Water by In-Line SPE-HPLC-Orbitrap with In-Source Fragmentation Flagging. *Analytical Chemistry*. 2015 April;87: p. 4260–4268.
  32. Napoli M, Scipioni A, Gambaretto GP, Carlini FM, Bertola M. Yield improvement in the electrochemical production of perfluoro-octanoic acid. *Journal of Fluorine Chemistry*. 1994 June;67: p. 261–264.
  33. Li L, Yu N, Wang X, Shi W, Liu H, Zhang X, et al. Comprehensive Exposure Studies of Per- and Polyfluoroalkyl Substances in the General Population: Target, Nontarget Screening, and Toxicity Prediction. *Environmental Science & Technology*. 2022 September;56: p. 14617–14626.
  34. Jin B, Che S, Gao J, Yu Y, Liu J, Men Y. Anaerobic defluorination of chlorine-substituted per- and polyfluorinated carboxylic acids triggered by microbial dechlorination. 2022 March.
  35. Reth M, Berger U, Broman D, Cousins IT, Nilsson ED, McLachlan MS. Water-to-air transfer of perfluorinated carboxylates and sulfonates in a sea spray simulator. *Environmental Chemistry*. 2011;8: p. 381.



36. Sha B, Johansson JH, Benskin JP, Cousins IT, Salter ME. Influence of Water Concentrations of Perfluoroalkyl Acids (PFAAs) on Their Size-Resolved Enrichment in Nascent Sea Spray Aerosols. *Environmental Science & Technology*. 2020 August;55: p. 9489–9497.
37. Faust JA. PFAS on atmospheric aerosol particles: a review. *Environmental Science: Processes & Impacts*. 2023;25: p. 133–150.
38. Li X, Wang Y, Cui J, Shi Y, Cai Y. Occurrence and Fate of Per- and Polyfluoroalkyl Substances (PFAS) in Atmosphere: Size-Dependent Gas-Particle Partitioning, Precipitation Scavenging, and Amplification. *Environmental Science & Technology*. 2024 May;58: p. 9283–9291.
39. UK EA. Monitoring Returns Q1 2023. Hillhouse:, AGC Chemicals Europe Limited; 2023. Report No.: EPR/BU5453IY.
40. UK EA. Monitoring Returns Q1 2024. Hillhouse:, AGC Chemicals Europe Limited; 2024. Report No.: EPR/BU5453IY.
41. Carslaw DC, Ropkins K. Openair—an R package for air quality data analysis. *Environmental Modelling & Software*. 2012;27: p. 52–61.
42. O'Rourke E, Losada S, Barber JL, Scholey G, Bain I, Pereira MG, et al. Persistence of PFOA Pollution at a PTFE Production Site and Occurrence of Replacement PFASs in English Freshwaters Revealed by Sentinel Species, the Eurasian Otter (*Lutra lutra*). *Environmental Science & Technology*. 2024 May;58: p. 10195–10206.

