





An Investigation of PFAS Emissions from UK Paper Mills

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An Investigation of PFAS Emissions from UK Paper Mills

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Date:	20th June 2023
Report Reference:	UC16743.3
Project Manager:	Paul Eades
Project No.:	2770466
Client:	Environment Agency
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Document History

Version number	Purpose	Issued by	Quality Checks Approved by	Date
V1.0	Draft Final Report	Graham Mustard	Jane Turrell	08-Mar-23
V2.0	Final Report	Graham Mustard	Jane Turrell	31-Mar-23
V3.0	Final Report edit to client confidential information	Jane Turrell	Jane Turrell	20-Jun-23

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Glossary

CPI	Confederation of Paper Industries
POPs	Persistent Organic Pollutants
EA	Environment Agency
UoB	University of Birmingham
DL	Detection Limit
IDL	Instrument Detection Limit
SDL	Sample Detection Limit
PFAS	Per- and Polyfluorinated Substances
PFBA	Perfluorobutanoic acid
PFPeA	Perfluoropentanoic acid
PFHxA	Perfluorohexanoic acid
PFHpA	Perfluoroheptanoic acid
PFOA	Perfluorooctanoic acid
PFNA	Perfluorononanoic acid
PFDA	Perfluorodecanoic acid
PFUnDA, PFUnA; PFUdA	Perfluoroundecanoic acid
PFDoDA, PFDoA	Perfluorododecanoic acid
PFBS	Perfluorobutanesulfonic acid
PFPeS	Perfluoropentanesulfonic acid
PFHxS	Perfluorohexanesulfonic acid
PFOS	Perfluorooctanesulfonic acid
PFHpS	Perfluoroheptanesulfonic acid
PFDS	Perfluorodecanesulfonic acid
PFNS	Perfluorononanesulfonic acid
PFUnDS	Perfluoroundecane sulfonic acid
6:2 diPAP	6:2 Fluorotelomer phosphate diester
8:2 diPAP	8:2 Fluorotelomer phosphate diester
10:2 diPAP	12:2 Fluorotelomer phosphate diester
6:2 FTSA; 6:2 FTS	6:2 Fluorotelomer sulfonic acid
PFOSA, FOSA	Perfluorooctanesulfonamide
EtFOSAA	2-(N-Ethylperfluorooctanesulfonamido)

Executive Summary

PFAS are a group of chemicals that have been used in a wide range of products, including paper products such as food packaging. A testing programme was undertaken on behalf of the Environment Agency which aimed to:

- Collect samples from five paper mills accepting different recycled paper inputs (news and magazines, packaging products and coated papers) and which produce different paper products including: white and brown roll, cardboard, coloured paper, tissue and speciality products.
- Quantify a broad range of PFAS in samples of paper mill process effluent, input paper, output paper products and the paper sludge (crumb).
- Estimate the PFAS loading to land and water for each of the paper mills included in the testing programme.

Samples of input paper (which included a wide range of recycled paper types), input water, effluent, sludge (referred to as crumb) and output products were collected and analysed to determine concentrations of 23 PFAS, including PFOS, PFOA and PFHxS.

The key findings of the testing programme were:

- 1. All 65 samples had concentrations of PFAS well below 1 mg/kg, including PFOS, PFOA and PFHxS, which are listed as persistent organic pollutants. When identified above the limit of detection PFOS, PFOA and PFHxS were <0.001 mg/kg.
- 2. PFOS, PFOA and PFHxS were not identified above the limit of detection in any of the 15 input paper samples analysed. However, those compounds were found to be present in several input water, effluent and crumb samples (at very low concentrations). The dataset suggests that PFOS, PFOA and PFHxS are not present in a wide range of input paper sources, which included food packaging and coffee cups. The dataset indicates that PFOS and PFOA originate in the input water rather than the recycled waste paper stream and may be concentrated into effluent and crumb during the process.
- 3. Polyfluoroalkyl phosphate esters (PAPs) were identified in several samples. Further analysis, particularly for 10:2 diPAP, is required to quantify the concentrations due to the lack of available standards at the time of analysis and as such reported concentrations should be considered indicative of presence or absence.

1. Introduction

1.1 Background

Perfluoroalkyl and polyfluoroalkyl substances (PFAS) are a large group of several thousand synthetic chemicals that have been widely used in many cross-sector applications to provide water and oil repellence amongst other uses. PFAS chemicals are characterised by a strong C-F bond, which means they are resistant to thermal, chemical and biological degradation and as a result can persist and accumulate in the environment. A number of different PFAS have been confirmed to have negative impacts on human and environmental health, this has resulted in regulation and banning of specific compounds.

Perfluorooctanesulfonic acid (PFOS), including its salts and related compounds, were listed under Annex B of the Stockholm Convention in 2009 as persistent organic pollutants (POPs). PFOS can result in negative health effects including reproductive, developmental liver, kidney, thyroid and immunological impacts in humans. Historically, PFOS has been used as a fabric protector, in firefighting foams and as additives in textiles (particularly for carpet fibres), some types of paper, paints and cleaning products. Since 2006, most uses of PFOS have been restricted under an amendment to the Marketing & Use Directive¹, however some uses including for coating applied to photographic films, papers/printing plates, were exempted from the restriction. Those exemptions were removed in 2019. An Environment Agency study² identified PFOS as a widespread environmental contaminant with sources likely including historic consumer products, particularly textiles such as carpets and upholstery, industrial discharges and sites where historical contamination occurred (such as where firefighting foams containing PFOS were used or stored). In the UK any waste that is found to contain PFOS at a concentration greater than 50 mg/kg is considered a POPs waste and therefore must be destroyed (by means such as thermal treatment), rather than reused or recycled.

Perfluorooctanoic acid (PFOA) its salts and PFOA-related compounds, were listed in 2019 under Annex A, which requires complete elimination, and will be brought into UK regulation under the national implementation plan of the Stockholm Convention. PFOA is a suspected carcinogen and is toxic to reproduction and causes a range of other negative health impacts in humans including to liver health. PFOA and PFOA-related compounds have been widely used in the past in the production of fluoroelastomers and fluoropolymers (particularly PTFE), the production of non-stick surfaces for kitchenware and in the manufacture of surfactants for

¹ Council Directive 76/769/EEC of 27 July 1976 on the approximation of the laws, regulations and administrative provisions of the Member States relating to restrictions on the marketing and use of certain dangerous substances and preparations.

² Environment Agency. 2019. Perfluorooctane sulfonate (PFOS) and related substances: sources, pathways and environmental data.

applications in textiles, papers, paints and firefighting foams. One particularly relevant use of PFOA was as a surfactant for paper and card used as food packaging, such as pizza box cardboard.

Perfluorohexanesulfonic acid (PFHxS) its salts and PFHxS-related compounds were listed under Annex A of the Stockholm Convention in 2022. PFHxS has been used in electrical equipment, firefighting foam, surfactants for paper and water/stain proofing agents.

Other PFAS such as Perfluoroalkyl acids (PFAA), and C9-14 Perfluoroalkyl carboxylic acids (PFCAs) are listed as substances of high concern and are currently on the 'Community Rolling Action Plan' for evaluation. In January 2023, a proposal from Denmark, Germany, the Netherlands, Norway and Sweden was submitted to restrict the use and production of all PFAS under the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH). At the time of writing, the legal and technical aspects of the proposal are currently under review by the EU Chemical Agency (ECHA).

As a result of the widespread usage of PFAS and the potential significant long-term environmental and health implications, the Environment Agency have commissioned this project to evaluate their presence in the environment and identify sources of emissions. PFAS have been identified in soil, ground water and surface water, including in freshwater and estuarine water between 2016 and 2019 (DEFRA, 2021)³. As PFAS have historically seen usage in paper manufacturing, particularly in food paper and card, evaluation of paper mills accepting recycled paper and card is required to confirm whether they are a source of PFAS or not.

The large majority of paper mills in the UK do not add PFAS to newly manufactured products. However, it is possible PFAS from recycled paper could be emitted from the process via process effluent or residual paper sludge (commonly referred to as 'crumb') from the pulping process which is commonly spread to land as a soil improver on agricultural land or used as animal bedding material. A lack of requirements to undertake PFAS monitoring at paper mills means that the effective loading of PFAS to the environment from these two routes is currently uncertain.

In the UK, the majority of paper mill operators are members of the UK Confederation of Paper Industries. The CPI represents 86 member companies operating 47 paper mills. In 2021, the CPI estimated that 7.1 Mt of wastepaper fibre was recycled, generating approximately 3.64 Mt of paper. In the same year, over 70% of paper being processed by CPI members was recycled paper. The high proportion of recycled paper as in-feed could result in PFAS being present in that recycled paper if there is a degree of concentration during processing. However, it is not expected that the majority of paper entering paper mills would contain PFAS as they are not

³ Department for Environment, Food and Rural Affairs. 2021. National Implementation Plan for the Stockholm Convention on Persistent Organic Pollutants

typically adding during the manufacturing process in the UK for standard newsprint, and white and brown paper products. If recycled feedstock contains paper from elsewhere in the world, where PFAS are added during manufacturing, this could be is a possible source of PFAS.

1.2 <u>Aims</u>

The testing programmed aimed to:

- Collect samples from five paper mills accepting different paper types (specialist paper, packaging products and coated papers) and covering different geographic locations in England.
- Quantify the amount of a broad range of PFAS at paper mills in input water, process effluent, input paper products and the paper sludge (crumb).
- Calculate the PFAS loading in process outputs for each of the paper mills included in the testing programme.

This report provides the results of the testing programme. The approach adopted is detailed in Section 2, the results are provided in Section 3, the calculated PFAS loadings are provided in Section 4 and the conclusions of the testing programme are included in Section 5.

1.3 <u>Study Limitations</u>

The findings presented in this report should be considered within the context of the following limitations in the testing programme:

- While every attempt was made to collect representative samples on each sampling visit it should be noted that the samples collected only represent a small percentage of the input and output streams produced in the longer term. Therefore, it is possible that the full range of variability of any of the input and output streams were not fully captured by this sampling programme.
- Input paper samples were taken from the different types of paper that were ready for processing at the time of sampling. However, due to the inherent variability of the paper input at any given time, the results of these samples may not be reflective of a variable and multiple source input feed.
- The paper mills included in the testing programme operated large, complex processes which placed some practical constraints on sample collection. Collection of matched input and output samples by the project team was not possible due to periods of storage of prepared pulp, crumb and effluent as part of normal process operation.
- The sampling programme was completed over a six-week period and therefore the test data represents a snapshot in time. Any long-term trends or temporal variations in PFAS concentrations cannot be evaluated with this set of samples. However, if we assume that any variability in the input feedstock is random and the processes are operated within a defined operational window the samples are likely to be representative of a wider operational period than the six weeks sampled.

- The analysis of PFAS compounds is an emerging field, and development in analytical techniques constantly evolving. A comprehensive suite of PFAS were included in the test suite, but in some cases mass labelled internal standards are not commercially available for all identified compounds which include PFPeS, PFHpS, PFDS, PFNS, PFUnDS and 10:2 diPAP. However, native calibration standards were available for all but 10:2 diPAP. Therefore, we were able to validate the remaining compounds and can distinguish these peaks/retention times by comparison with the native peaks/retention times in the calibration standards. Without native or mass labelled internal standards for 10:2 diPAP this data must be considered to be indicative.
- PFAS loadings have been calculated based on qualitative throughput data provided by the operators taking part in the study. Detailed process mass balance data would be required to refine the loading calculations which was outside of the scope of this project.

2. Testing Programme Approach

2.1 <u>Summary of Approach</u>

The testing programme was split into the following main activities:

- Selection of sites to be included in the testing programme: discussions were held between WRc, the Environment Agency and the UK Confederation of Paper Industries to identify sites that provided a cross section of UK operations. The sites selected accepted the full range of recycled paper inputs (news, magazines, food and general packaging materials and coated papers) and produced different paper products which included: white and brown roll, cardboard, coloured paper, tissue and speciality products.
- Collection of data on selected sites: following selection of the five papers mills to be included in the testing programme, data was collected on each site including input materials, volume of materials processed, process water source and disposal/reuse route for process effluent and crumb.
- 3. Development of a sampling approach and collection of sampling: discussions were held with the sites taking part in order to develop specific sampling plans to collect representative samples of input water, effluent, input paper and crumb, taking into account any practical limitations at the sites.
- 4. **Sample preparation**: for the input paper and crumb samples, sample preparation at WRc's laboratory was undertaken to produce representative test samples for analysis.
- 5. **Analysis of PFAS concentrations**: concentrations of twenty-three PFAS compounds were determined by liquid chromatography mass spectrometry (LC-MS) at the University of Birmingham.
- 6. **Calculation of PFAS loading:** based on determined concentrations of PFAS and the throughput of each site, the relative loading of PFAS were calculated for the waste water and crumb.

The following sub-sections provide details on each of those activities. A summary of the testing programme is provided in Figure 2.1.



Figure 2.1 PFAS testing programme summary

2.2 <u>Site Selection</u>

The CPI produced an initial shortlist of paper mills. At an inception meeting these were discussed with the Environment Agency and a short-list of five were selected for sampling. The site selection rationale included sites that would cover and represent UK paper mills based on:

- Scale of operation: the sites represent different scales of operation (ranging from production of several thousand tonnes per annum to hundreds of thousands of tonnes per annum)
- Infeed composition: the sites selected accept card, office paper waste, off-cuts, recycled paper and more specialised paper waste/off-cuts as input material. The sites selected all included input feed at least partially made up of recycled paper, which was considered as an important potential source of PFAS.

- Paper production: Sampling included sites which produce: specialist papers; packaging products; coated papers; graphical paper; brown paper rolls; cardboard; and specialist paper products.
- Potential PFAS discharge: All five sites selected included a discharge point of solids and/or effluent, such as effluent discharge directly to surface water or solids reuse for agricultural purposes.
- Geographical location: The sites included in the testing programme also represented a range of geographical locations.

2.3 Collection of Site Data

Table 2.2 provides a summary of key operating parameters collected from the five paper mills providing samples for the testing programme. The sites were coded Site 1 to 5 to protect the identity of the operators taking part in the testing programme. The data provided in Table 2.2 was provided by the site operators. The data is an overview of inputs and outputs and in some cases the mass balance is not at face value consistent. The main differences are seen in the balance between input water and output process effluent. This is due to water losses at various stages in the process, which include evaporation during product drying and moisture held within the waste paper crumb and contaminant removal in the pulper which means that water is diverted from the final process effluent.

2.4 Sampling Approach and Sample Collection

Samples were collected from each of the process input water, the process wastewater effluent, the input paper and the crumb as well as the output product(s), for the first round of samples only. Three sets (referred to as sampling rounds) of samples were taken from each of the five sites covering a three-week period between November and December 2022. Table 2.1 provides a summary of the approach adopted for collection of each sample type. This approach allowed for an evaluation of whether PFAS were input into the process via input water or input paper and comparison to the different potential discharge routes. A time series of three samples allowed for variability over time to be considered. WRc personnel attended the five sites in order to collect all samples for analysis.

Target Material	Sampling approach	
Input water 2 litres after running of pipe or tap (Round 1, 2 & 3)		
Input paper	~20 kg of paper from all input sources. Source types kept separate and proportionally milled at WRc's in-house laboratory (Round 1, 2 & 3)	
Process effluent	2 litre sub-sample from ~20 litre incremental sample (Round 1, 2 & 3)	
Crumb	~ 40 litres of crumb taken from different areas of the storage bay (Round 1, 2 & 3)	
Product	~5 kg sampled off the line (Round 1 only)	

Table 2.1 Sampling Approach Summary

	Site 1	Site 2	Site 3	Site 4	Site 5
Product	Brown containerboard reels for production of corrugated board	Moulded fibre medical products	Paper rolls for retail used for toilet paper (40%) and hand towels (60%)	Retail specialist coloured and finished paper	Graphical paper, commercial printer paper (for advertising) and uncoated magazines
Variability	Slight variation in process inputs to meet client specifications	Minimal variability, different products produced on different lines (10 lines in total)	Switch between the two products and recipe is dependent on client (c. 12 process changes a week)	High variability in thickness, finish and colour. Weekly runs colour coded to avoid cross-contamination. Client can specify a percentage of recycled fibre	Separate lines for different products with continuous production (1.06, 1.11 and 2.02) with different proportions of old news, to magazines
Output Product production rate	430,000 tonnes/year	5,250 tonnes/year (Assuming no fibre loss)	47,700 tonnes/year	55,000 tonnes/year	400,000 tonnes/year
Are PFAS added?	No	1 out of 10 lines (wash bowls that need to be detergent proof)	No	No	No
Percentage of recycled paper	100%	100%	97-98%	Wide variation of recycled fibre content dependent on product specification	100%
Paper source	Predominately waste cardboard with some wastepaper (produce five grades of rolled card)	Waste newspapers cardboard cut-offs (KLS), 50/50 mix	Process off-cuts, printer off- cuts, shredded office waste	Mainly virgin fibre, and shredded office. Occasional use of post-industrial cups (off-cuts) and post-consumer waste cups	Pre- and post-consumer (print rooms, national collection of unsold NP and magazines, HH segregated, MRF outputs and small quantity EU
Input paper rate	504,000 tonnes/year (50 to 60 loads per day)	5,250 tonnes/year (40 bales/day)	75,000 tonnes/year	Undisclosed (redacted due to commercial sensitivity)	500,000 tonnes/year
Water source	Canal	Mains (towns) water	River 70-75%, 10% on-site ponds, borehole 5%	River source from reservoir	Flood relief channel
Input water rate	6,800 m ³ /day	108 m ³ /day	3,200 m ³ /day	7,000 m ³ /day	15,000 m ³ /day

	Site 1	Site 2	Site 3	Site 4	Site 5
Effluent discharge point	Canal	Canal Sewer Sewer Sewer		Sewer	River
Effluent output rate	5,500 m³/day	48.5 m³/day	2,054 m³/day	7,000 m³/day	15,000 m³/day
Crumb use	Predominately combustion 75% with some used for animal bedding and land spreading	N/A	Animal bedding	Land spreading Land spreading	
Crumb output rate	34,000 tonnes/year	N/A	37,000 tonnes/year	6,600 tonnes/year	120,000 tonnes/year
Crumb moisture content	54%	N/A	45%	60%	30%
Input water sample approach	Tap before treatment	Mains tap before process	Input mixed after treatment may need to sample from predominant source or collect representative sample from each source	Tap sample at beginning of process	Storage tank before treatment
Input paper sample approach	Core one random bale from every load 24 hr before sampling visit	Grab samples from bales in storage area	Mostly loose paper so grab sample from storage area	Grab sample from bales in storage area	Sample point from conveyor into process over a period of 30 mins
Effluent sample approach	Tap sample point available (normally a 24 hr composite sample)	Effluent discharge drain	Tap sampling ahead of sewer discharge	Tap sampling ahead of sewer dischargeSampling point at discharge (normally a 24 hr composite sample)	
Crumb sample approach	sample achSample point from conveyer ahead of storage bayN/ASample point from ahead of storage		Sample point from conveyer ahead of storage bay	Sample from falling stream after press before removal from site	Sample point from conveyer ahead of storage bay

Table 2.3 provides a summary of the sampling locations for each sample type for each of the five facilities. A summary of the approach adopted for each sample type are provided in the following sub-sections, full details of sampling for each site are provided in Appendix A.

Site	Input Water	Input Paper	Paper Crumb	Effluent	Product
Site 1	Tap on storage tank	Core samples	Storage bay	Tap on discharge pipe	Sample taken for lab
Site 2	Tap on input pipe	Storage bay	No crumb produced	Sample point of drainage system	Sample taken from storage
Site 3	Tap on input pipes	Storage bay	Storage bay	Sample point of drainage system	Sample taken directly from roll
Site 4	Tap on storage tank	Storage bay	Storage bay	Tap on discharge pipe	Sample taken from offcuts
Site 5	Tap on input pipe	Storage bay	Storage bay	Tap on storage tank	Samples taken directly from roll

 Table 2.3
 Site Specific Sampling Approach Summary

Ideally, sampling of inputs and process outputs would have been fully linked or matched to allow for cross-comparison of PFAS concentrations entering and exiting the process. However, all of the mills sampled have multiple pulp storage tanks which leads to a disconnect between sampling of paper inputs to that source paper going into production even where it may go directly into processing. Therefore, samples of effluent/crumb should not be considered to be produced from the exact input water/paper taken during the same sampling round although best attempts were made to match samples.

Details of the sampling carried out at each site are presented in Appendix A.

2.4.1 Input Paper

Recycled paper fibre is commonly transported to each site in bales and is stored in stacks. One site accepts predominantly loose paper and only a small proportion of bales. Typically, the material is compacted whole paper rather than shredded material. The input paper samples were collected trying to represent the infeed to the sampling day of paper production. Where possible, a similar amount of paper was collected in each round (2 large sacks, corresponding

to 20-25 kg of material). Where multiple sources of recycled fibre where input into the system these were separately collected, information over the composition of the infeed collected and they were then recombined in the correct proportions at WRc during the sample preparation process.

At the smaller sites, Sites 2, 3 and 4, where the material was baled, grab samples were collected from a representative cross-section of bales representing the material that would go into the next 24 hours of production. Following site personnel instructions over the composition of the infeed, a grab of input paper was collected from the largest possible number of bales present in the storage bays. Sampling conditions limited the maximum amount of material that was allowed to be collected at each round. This was commonly around 20 bales of each input material on each sampling visit. In all cases the quantity of material collected was fixed at two sackfuls.

At Site 1, where access to the reception storage area was not allowed due to health & safety restrictions a different approach was taken. A random bale is taken from each incoming load and a core sample taken. WRc instructed site personnel to take an additional core from all bales arriving at the facility in the 24-hour period before on-site sampling. Samples were collected from approximately 50 bales ahead of each visit.

At Site 5, input paper was collected from the in-feed process conveyor over a 30 minute period on each sampling occasion. The sample collected from the conveyor was tailored to match the mix of input paper on the conveyor and consisted of 2 large sacks, corresponding to 20-25 kg of material.

2.4.2 Input Water

Each sample of input water was taken from a metal tap located on the infeed pipe (which was free of any PTFE contamination) to the process. As flow through the system was high and constant only a short period (30 seconds) was required to flush the tap ahead of collecting a representative sample as there was no 'standing water' in the pipe. Two 1 litre sample bottles were collected at each site with the tap on low flow to avoid sample agitation for immediate return to the UoB laboratory.

2.4.3 Effluent

The effluent was sampled at a tap or sump ahead of site discharge. Effluent quality may fluctuate depending on paper production. However, with the exception of site 4 production, where production runs tended to be short most batch runs commonly spanned multiple days. This means that sampling effluent within a run would produce a sample that is representative of a reasonable period of time. Although some sites operate full-time auto-samplers to collect composite samples to measure effluent quality, it was agreed with the Environment Agency that a sample would be collected by WRc during the site visit. This ensured that the sample had not been in contact with any plastic materials in the autosampler that may lead to loss of PFAS or

contamination. Site 4 tends to run multiple batch runs across a day, which may impact on effluent quality but without the use of an auto-sampler it would not be possible to capture this variability. At all sites samples were taken across a 30 minute period made up of 20 increments at all sites.

Overall, the sampling of the effluent was carried adapting to each site layout and processes, each sampling round is described in details in Appendix A. a summary of each site effluent sampling conditions are here presented.

- Site 1 has a very large and constant production, with high volumes of wastewater effluent discharged. A 25 litres sample was collected at the tap sump right before discharging over a period of 30 minutes circa. A jug was used to collect at least 20 increments. The sample was mixed in the container which was 2/3 full by rolling and up-ending it and then sub-sampled into two 1 L bottles.
- At Site 2, where production is small, but consistent, sampling took place at the process sump due to a timed process discharge making it difficult to take samples from an interim storage tank. Twenty incremental samples of 1 L were taken over a period of 30 minutes to fill a 25L bucket. The sample was mixed in the container which was 2/3 full by rolling and up-ending it and then sub-sampled into two 1 L bottles.
- Site 3 produces a consistent paper product. The effluent was collected from the site sampling point on the streamline right before discharge into sewer. The flow-rates were low but at least twenty 1 L increments were collected ahead of mixing and sub-sampling the container as identified above.
- Due the site layout and multiple batch runs in a day. Process effluent from Site 4 is also mixed ahead of discharge with a sister plant operating a non-paper based process. Sampling was completed to try and separate the inputs from each process and the combined discharge stream. Twenty increments of 1 L were collected and mixed as described above. Further details are presented in Appendix A4.3.

2.4.4 Crumb

The crumb was collected from active stockpiles being fed by process conveyors. Incremental samples were collected from different locations of recently deposited material. There are some minor differences between the collection methodologies, which are detailed in Appendix A to take into account access and storage differences between the sites. A brief description of the sampling conducted at each site can be found below in Table 2.2.

2.4.5 Sampling Quality Control

To ensure high quality representative samples and test data several steps were taken:

- The basic sampling approach detailed in an overarching sampling plan was adopted at each site to ensure that the basic random statistical approach and scale of sampling was fixed across the five sites.
- Sample collection vessels and equipment were selected to be free of PFAS compounds (such as high-density polyethylene) to reduce contamination risks. Polytetrafluoroethylene containers were not used for sample collection, transportation or analysis.
- Sample containers for collection of liquid samples were rinsed thoroughly with 10% nitric acid and then deionised water in the laboratory, before further rinsing with the liquid sample to be collected.
- Field blanks were generated on site by pouring deionised water into through any equipment used in sample collection to allow quantification of any contamination from the used equipment. The laboratory produced separate quality control samples as part of sub-sampling and extraction. The field blank data is provided in Appendix C4.
- The liquid samples (input water and effluent) were directly delivered to the analytical test facility at the University of Birmingham to reduce sample storage times. Samples were transported and stored under refrigerated conditions (4°C) and were not opened until they were extracted for analysis.
- All solid samples were returned to WRc for sample preparation. All samples were subjected to a range of particle size reduction steps on arrival at the laboratory and then immediately despatched to the test facility to minimise time between sample collection and analysis.

2.5 <u>Sample preparation</u>

Input paper, crumb and output product samples underwent preparation at the WRc laboratory ahead of analysis. The samples underwent the following steps ahead of being sent to the analytical test facility:

- Each sample underwent a coarse shredding step to reduce the particle size of any large (>10 mm) particles. The shredder was cleaned with a stiff brush and vacuum ahead of any shredding and part of the test sample was passed through the equipment which was then discarded ahead of processing the test sample to minimise the risk of contamination. These steps were repeated between samples. Where samples were made up of multiple different types of paper, the different types were shredded separately.
- 2. Each sample was dried at 40°C until a consistent mass was achieved in order to confirm the moisture content. Separate paper types from any samples which included multiple types were dried separately.

- 3. The samples were then milled to a particle size of <1 mm using a Fritsch P-19 cutting mill (the milling chamber is made of stainless steel and contains hardened stainless steel blades). The milled samples were discharged into a glass bottle. Between samples the blade was removed and the blade, chamber and discharge bottle thoroughly cleaned to remove any residual sample material to minimise any cross-sample contamination.</p>
- 4. Samples that included multiple paper types were mixed in the correct input ratio. For instance, where an input paper stream included 25% cardboard off-cuts and 75% coloured paper, the sample prepared included a weighed amount of cardboard equal to 25% and a weighed amount of coloured paper equal to 75%. A summary of the materials taken for each paper input sample, replicated during sample preparation, is provided in Table 2.4. The complete breakdown for each sample at each site is presented in the respective section of Appendix A.

Table 2.4	Ratio of different materials taken in input paper samples, replicated
	during sample preparation

Site	Sampling Round	Material type (proportion of sample, %)						
		Newsprint	Cardboard	Office waste	Mixed paper	Coloured paper	Others	
1	R 1 – 3	-	100	-	-	-	-	
2	R1 - 3	50	50	-	-	-	-	
	R1	-	40	50	5	-	5 ¹	
3	R2	-	-	60	20	20	-	
	R3	-	-	55	25	20	-	
	R1	-	-	50	-	-	50 ²	
4	R2	-	-	-	-	-	15 ¹ / 15 ² / 70 ³	
	R3						20 ² / 80 ⁴	
5	R1 - 3	100	-	-	-	-	-	

¹ Paper process off-cuts; ² Unused coffee/paper cup off-cuts; ³ Bleached virgin pressed fibre sheets; ⁴ Recycled process paper.

Reserve analytical samples were retained by WRc in the event that further corroboratory testing is required.

2.6 Determination of PFAS concentrations

Analysis of 23 PFAS (Table 2.5) was completed at University of Birmingham by LC-MS. Full details on the analytical methods, are provided in Appendix B.

CAS Number	Name	Abbreviation	
375-22-4	Perfluorobutanoic acid	PFBA	
2706-90-3	Perfluoropentanoic acid	PFPeA	
307-24-4	Perfluorohexanoic acid	PFHxA	
375-85-9	Perfluoroheptanoic acid	PFHpA	
335-67-1	Perfluorooctanoic acid	PFOA	
375-95-1	Perfluorononanoic acid	PFNA	
335-76-2	Perfluorodecanoic acid	PFDA	
2058-94-8	Perfluoroundecanoic acid	PFUnDA, PFUnA; PFUdA	
307-55-1	Perfluorododecanoic acid	PFDoDA, PFDoA	
375-73-5	Perfluorobutanesulfonic acid	PFBS	
2706-91-4	Perfluoropentanesulfonic acid	PFPeS*	
355-46-4	Perfluorohexanesulfonic acid	PFHxS	
1763-23-1	Perfluorooctanesulfonic acid	PFOS	
375-92-8	Perfluoroheptanesulfonic acid	PFHpS*	
335-77-3	Perfluorodecanesulfonic acid	PFDS*	
68259-12-1	Perfluorononanesulfonic acid	PFNS*	
749786-16-1	Perfluoroundecane sulfonic acid	PFUnDS*	
57677-95-9	6:2 Fluorotelomer phosphate diester	6:2 diPAP	
678-41-1	8:2 Fluorotelomer phosphate diester	8:2 diPAP	
1895-26-7	10:2 Fluorotelomer phosphate diester	10:2 diPAP**	
27619-97-2	6:2 Fluorotelomer sulfonic acid	6:2 FTSA; 6:2 FTS	
754-91-6	Perfluorooctanesulfonamide	PFOSA, FOSA	
2991-50-6	2-(N-Ethylperfluorooctanesulfonamido) acetic acid	EtFOSAA	

Table 2.5Target Substances

* PFAS compound where a certified mass labelled internal standard was not available and a native calibration standard was used. Quantitation utilised labelled PFAS which are a close match to these compounds in terms of chemical structure and instrumental responses.

** A certified mass labelled internal standard nor a native standard were available for 10:2 diPAP, and any reported concentrations should be taken as indicative.

2.7 Calculation of PFAS loading

PFAS loadings were calculated based on the total PFAS concentration for each stream type (input paper, crumb, output product, input water and effluent). The average concentrations across the three sampling rounds were used to determine the loading to the environment, based on crumb as a discharge point to land and effluent as a discharge point to water.

In order to calculate the PFAS loading to the environment several assumptions were made:

- 1. Where any sample had a PFAS concentration determined to be below the limit of detection, the limit of detection concentration value was used for the purpose of calculating an average concentration (a worst-case scenario assumption).
- 2. The crumb production rates have been adjusted to account for moisture content and loadings are calculated on a dry weight basis (including PFAS concentrations).

3. Results

This section includes a summary of the findings from the testing programme, full results can be found in Appendix C and in the accompanying full dataset report UC16748.1. Values for solid samples were reported in ng/g by the test laboratory and have been converted into μ g/kg for the purpose of reporting. As a result, the detection limit values appear inflated.

The reported detection limit values have been calculated for each sample (referred to as the sample detection limit or SDL) and therefore vary between samples and between different PFAS. Detection limits are discussed further in the following section.

As highlighted in the previous section, results are reported on a dry weight basis to provide a common comparison denominator.

3.1 Data Quality

This sub-section provides details on the detection limits, the recovery rates of tested PFAS, corrections made to the data and limitations of the analysis which should be considered when evaluating the PFAS dataset.

3.2 Detection Limits and Internal Standard Recovery

The instrument detection limit (IDL) is a statistical measurement of analytical sensitivity, the IDL was defined as the amount of a PFAS that gives a signal to noise ratio of 3:1. It was calculated based on the signal to noise ratio in the calibration standards. The IDLs are provided in Appendix C4. Analysis was completed in 'batches' due to the large number of samples included in the testing programme. Each batch, for liquid and solid samples, has a IDL for each PFAS analysed. The samples included in each batch are listed in Appendix C4.

The sample detection limit (SLD) for each PFAS was then calculated on a per-sample basis as:



Where FEV = final extract volume (μ 1), VFEI = volume of final extract injected (μ 1); SS = sample size (m³ or g); and %IS recovery = percentage recovery of internal standard used to quantify the target PFAS in a particular sample.

The percentage recovery of internal standards (%IS) are provided in Appendix C6. It should be noted that mass labelled internal standards were not available for PFPeS, PFHpS, PFDS, PFNS, PFUnDS and 10:2 diPAP, as none are currently commercially available. However, native standards were utilised by the test laboratory for these PFAS with the exception of 10:2 diPAP. The quantitation of the sulfonate compounds (PFHpS, PFDS, PFDS, PFUnDS) used the peak

area for the IS M8PFOS and PFPeS used MPFHxS. These labelled PFAS are the closest to these compounds in terms of chemical structure and instrumental responses. The full list of standards used during analysis is provided in Appendix C6, Table C10.

M4-8:2 diPAP was used for the quantitation of the 10:2 diPAP. Due to the lack of an available native or labelled standard, the exact peak selection on the chromatograms were not able to be validated in the same way as the other PFAS reported, i.e., by comparing with the peak retention times in the calibration standard/internal standard. Additionally, no optimisations or other instrumental parameters could be performed for this compound without the native and labelled standards available. Therefore, the 10:2 diPAP concentrations should be considered to be indicative of its potential presence in a sample.

The internal standard recovery percentages for all samples and blanks analysed are provided in Appendix C6. Overall, recoveries were between around 50 - 150% although there were a few excessive recoveries (of between around 150 - 300%) which mostly affected 10:2 diPAP, 8:2 diPAP, PFBA, 6:2 FTSA; 6:2 FTS and PFPeA. These excessive recoveries are discussed further within the context of concentrations identified within the field and laboratory reagent blanks in the following section.

3.3 Blanks and Blank Correction

Field reagent blanks were included in the sampling campaign which consisted of deionised water taken to site which were then subjected to the same conditions, sample preparation methods and analytical procedures. A total of six field reagent blanks were analysed across the two batches of analysis (the field reagent blanks were analysed at the same as all liquid samples taken during the testing programme). Four laboratory reagent blanks were also analysed for the solid paper samples. The laboratory reagent blanks underwent the same extraction procedure as the solid paper samples. Fortified reagent blanks which included additions 0.5, 10 and 50 ng/l of a PFAS compound were analysed acts as an indicator of method accuracy and were used to support method development to improve precision of PFAS concentration determination. The results of the fortified reagent blanks are provided in Appendix C7. Further details on blanks are provided in Appendix B1.3.

The concentrations of PFAS in the field reagent blanks was very low, with most parameters being below the respective SDL. PFOA was detected in all six field reagent blanks at concentrations between. 0.002 and 0.003 μ g/l. Similarly, PFDoDA/PFDoA was detected in all six field reagent blanks at concentrations around 0.002 μ g/l. The internal standard recovery for both PFOA and PFDoDA/PFDoA was between around 70 and 160 % for those field reagent blanks. It is plausible that as PFAS are ubiquitous they may be present at low concentrations in the blanks. However, false peak selection during quantitation, particularly at very low concentrations where peaks approach the noise baseline and in samples with higher than usual matrix interferences may also account for the detected concentrations.

Concentrations of several PFAS, including PFOS and PFOA were identified in the laboratory reagent blanks, however all concentrations were below 1 μ g/kg. The exception was two field reagent blanks which contained a concentration of around 8 and 11 μ g/kg of 10:2 diPAP. However, due to the previously noted limitations regarding the analysis of 10:2 diPAP the concentrations should be considered indicative, rather than quantitative.

Based on the determined PFAS concentrations of the field reagent blanks and the laboratory reagent blanks, the PFAS concentrations were adjusted were required, according to the following:

- Where the blank concentration of a PFAS was between 5 20 % of the PFAS concentration identified in a sample, the PFAS concentration of the blank was subtracted from the sample concentration.
- Where the blank concentration of a PFAS was between ≥20 % of the PFAS concentration identified in a sample, the sample concentration was reported as below the sample detection limit.

Any adjustments to the data were made on a batch basis. For instance, the first batch of liquid samples contained nine samples and two field reagent blanks and therefore adjustments were based on the average concentrations of PFAS in the two field reagent blanks. The samples included in each batch are provided in Table C9. An internal standard quantification method, using relative response factors (RRFs), was used which meant that no correction of concentrations for recovery was required as such an adjustment is already factored into the quantitation using RRFs. Further discussion of the internal standard quantification method is provided in Appendix B1.2.

3.4 Findings by material type

3.4.1 Input water

The analysis results on the input water samples are presented in Figure 3.1. Only PFAS identified above the level of detection in at least one sample are shown.

All three POPs compounds (PFOS, PFOA, PFHxS) were detected in at least one of the input water samples. The highest PFAS concentration recorded in the input water was PFOS in Site 5 - Round 3 with a value of 0.011 μ g/l. PFOS was detected in all three samples from Sites 1 and 5 and in a single sample from Site 3. PFOA was only detected in the Round 1 sample from Site 1, while PFHxS was detected at very low levels in two of the Site 1 samples and at consistently higher concentration in all three Site 5 samples.

PFBD, PFDA and PFHFxA, were detected at low levels with the highest concentration recorded being PFBS with a value of 0.0058 μ g/kg in the Round 1 sample. None of the 23 target PFAS compounds were detected in any of the Site 4 input water samples. While only a very low

reading (0.0005 μ g/l) of PFDA was detected in the Round 3 input water sample from Site 2. Although low, the other three sites consistently have at least one compound above 0.005 μ g/l.



Figure 3.1 Input Water Concentration Results

3.4.2 Effluent

The results of the analysis conducted on the effluent samples collected are presented in Figure 3.2. All three POPs PFAS compounds were detected in at least one effluent sample. The highest POPs concentration detected was PFOA in the Round 1 Site 2 sample with a value of 0.059 μ g/l but was below the limit of detection for the following two samples.

PFOS was detected in all samples from Site 1, Site 2 & Site 5 at a concentration of less than 0.01 μ g/l. As for Site 1 and Site 5, the PFOS concentration remained at similar levels to the input water with some fluctuations while Site 3 saw a consistent increase in PFOS concentration.

A range of other PFAS were detected in effluent samples that were not identified in the input water. Specifically, 10:2 diPAP was detected in the Site 2 Round 2 effluent sample . However, as neither a mass labelled internal reference or native standard was available for 10:2 diPAP reported concentrations must be considered to be indicative of its presence. Additionally, a single reading of 0.060 μ g/l EtFOSAA (third highest concentration in an effluent sample) was detected in the Site 5 Round 1. This compound was not detected in any other sample in the entire programme. None of the 23 target PFAS compounds were detected in Site 4 samples, in agreement with the results determined for the input water samples.



Figure 3.2 Effluent Concentration Results

3.4.3 Input Paper

PFAS concentrations determined for input paper samples are provided in Figure 3.3 (results are reported in $\mu g/kg$). PFOS, PFOA and PFHxS were not detected in any of the input paper samples. The Site 5 Round 2 sample was identified to have a PPHxA concentration of 17.2 $\mu g/l$ and PFHpA of 2.76 $\mu g/kg$. Many other PFAS were found to be below the detection limit.

10:2 diPAP was identified at high concentrations in some samples, however the elevated concentrations should be considered indicative of the presence of the substance rather than a quantification of the concentration due to analytical limitations caused by a lack of quantitative standards.

3.4.4 Crumb

PFAS concentrations identified above the limit of detection for crumb samples are provided in Figure 3.4.

PFOA and PFHxS were not identified above the limit of detection in any of the crumb samples analysed. PFOS was detected in the crumb samples in two samples from Site 1, two samples from Site 3 and one sample from Site 5. The highest concentration was found in the Round 1 crumb sample from Site 1 with a value of $1.68 \mu g/kg$.

The compounds 6:2 diPAP and PFHpS were identified in several crumb samples, which were the only samples of all samples of any type tested where those compounds were identified above the limit of detection. 10:2 diPAP was identified in two samples.

3.4.5 Paper product

The results of the analysis conducted on the paper product samples collected are provided in Figure 3.5.

PFOS, PFOA and PFHxS were not identified above the limit of detection in any of the paper product samples. Several other PFAS were found at low levels in all six product samples. One sample (Round 3 sample taken at Site 5) was found to contain 10:2 diPAP.

PFAS concentrations were very low in these paper product samples. Even in those paper products where PFAS were directly and authorised to be used (Site 2) almost no PFAS were detected. PFUnDA, PFUnA; PFUdA was detected in at least one product from each site at low levels (<0.15 μ g/kg).

Despite not being detected in any of the input samples (paper and water) and at low levels in the Round 2 crumb sample from Site 1, PFBS was detected in several of the output products samples (Site 3, Site 4 and Site 5-Round 1) with a maximum concentration of 2.19 μ g/kg.



Figure 3.3 Input Paper Concentration Results







Figure 3.5 Paper Product Concentration Results

3.5 Summary of Findings

Overall, concentrations of PFAS, including PFOS, PFOA and PFHxS were low in all samples analysed. The specific findings of the PFAS testing are as follows:

1. PFOS

- Input water: PFOS was found above the DL in 7 out of 15 samples with the recorded concentration ranging from 0.001 µg/l to 0.011 µg/l. PFOS was detected in all Site 1 and Site 5 input water samples as well as a single Site 3 sample. PFOS was not detected in any of the Site 2 & Site 4 samples.
- Input Paper: PFOS was not detected in any of the 15 input paper samples.
- Effluent: PFOS was detected in 9 out of 17 samples with the recorded concentration ranging from 0.0026 µg/l to 0.0097 µg/l. PFOS was detected in all Site 1, Site 3 and Site 5 effluent samples and was not detected in any of the Site 2 & 4 effluent samples.
- Crumb: PFOS was detected in 5 out of 15 crumb samples with a recorded concentration range of 0.79 µg/kg to 1.53 µg/kg. PFOS was not detected in any of the Site 4 samples.
- Product: PFOS was not detected in any of the 6 product samples.

2. PFOA

- Input Water: PFOA was detected in 1 out of 15 input water samples. The Sample was from Site 1 and had a PFOA concentration of 0.0084 µg/kg.
- Input Paper: PFOA was not detected in any of the 15 input paper samples.
- Effluent: PFOA was detected in 4 out of 17 effluent samples with a recorded concentration ranging from 0.022 µg/l to 0.058 µg/l. PFOA was detected in all three Site 1 effluent samples and one Site 2 effluent sample.
- Crumb: PFOA was not detected in any of the 15 crumb samples.
- Product: PFOA was not detected in any of the 6 product samples.

3. PFHxS

- Input Water: PFHxS was detected in 5 out of 15 samples with a recorded concentration range of 0.0010 µg/l to 0.0099 µg/l. PFHxS was detected in all the Site 5 input water samples and two of the Site 1 input water samples.
- Input Paper: PFHxS was not detected in any of the 15 input paper samples.
- Effluent: PFHxS was detected in four out of 17 effluent samples with a recorded concentration ranging from 0.0014 µg/l to 0.0046 µg/l. PFHxS was detected in all three Site 5 effluent samples and one Site 1 effluent sample.
- Crumb: PFHxS was not detected in any of the 15 crumb samples.
- Product: PFHxS was not detected in any of the 6 product samples.
- 4. The majority of other PFAS were detected in at least one sample. In 48 out 65 samples one or more PFAS (excluding PFOS, PFOA and PFHxS) were found above the respective sample detection limit. It should be noted that the concentrations of all PFAS identified were low in all samples. 10:2 diPAP was identified in several samples, but the concentrations provided should be used with caution. Comparing the input water samples to the effluent samples there is a significant increase in the number of PFAs compound above the limit of detection. A list of PFAS compounds that were not found in the input water samples but were detected in the effluent samples can be found below:
 - 10:2 diPAP
 - 6:2 FTSA; 6:2 FTS
 - EtFOSAA
 - PFHpA
 - PFNA
 - PFPeA

4. **PFAS Environmental Loading**

4.1 PFAS Data

The testing programme aimed to collect matched samples, meaning that a crumb sample would be made up of material which was directly sampled from the input paper. These results would then be directly comparable. However, it was not possible to achieve matched samples particularly at the larger sites, due to large lag times within the process. The lag time meant that there was uncertainty that any output samples (crumb or effluent) were directly related to the material input into the process. The inherent heterogenous nature of the paper materials, as well as the input water, meant that some degree of variability is expected between samples taken during the same round. Therefore, making detailed comparisons of single samples carries a degree of uncertainty and as such conclusions should be drawn based on the larger dataset.

Figure 4.1 provides a summary of the PFAS analysed in all samples taken during the testing programme. The PFAS identified above the respective level of detection are shown in the various sample types where they were identified. The different coloured text indicates differences between the inputs / outputs at each site. Black text indicates there is a link between the input and the output, for example, PFOS was identified in both the input water and the effluent in the samples taken from Site 1. In contrast, white text shows compounds that were identified in an input or output without being identified in the corresponding sample. For instance, PFOA was identified in the effluent from Site 2, but was not identified in the input. Grey text relates specifically to the output products and indicates where a substance was identified in the product and also identified in one of the inputs – water or paper.

PFOS, PFOA and PFHxS were not identified in any of the 15 paper input samples which covered a wide range of paper and card types including food packaging and coloured papers which may historically have contained those three compounds, particularly PFOS and PFOA. Those compounds were identified, at low concentrations, in some input water samples at some sites (as shown in Figure 4.1). The data produced during this testing programme therefore suggests that 'background' concentrations of PFOS, PFOA and PFHxS in the input water is the source of those compounds rather than waste paper input to the process.

PFOS was identified in 5 out of 15 crumb samples analysed, which suggests that input water used in the process may transfer PFOS into the crumb which could then subsequently act as a source to environmental discharge when reused for agricultural purposes.

Variation due to the local water courses is likely an explanatory factor for some differences observed in PFAS concentrations between sites.

PFDA,

PFUnDA, PFUnA;

PFUdA, PFBS, 6:2



Figure 4.1 Summary of PFAS detected in all sample types
4.2 Persistent Organic Pollutants

Of the 23 compounds included in this analysis only three are currently listed as persistent organic pollutants under the Stockholm Convention – PFOS, PFOA and PFHxS. PFOS is currently regulated in the UK with a POPs waste concentration threshold of 50 mg/kg.

DEFRA opened a consultation on potential amendments to the Persistent Organic Pollutants Regulation on 3rd March 2023 which in ongoing until 27th April 2023. The 'lead option' suggested by DEFRA is a concentration threshold of 1 mg/kg for both PFOA and PFHxS (and their salts) as well as a concentration threshold of 40 mg/kg for both PFOA and PFHxS and their related compounds.

Should the concentration thresholds be adopted, waste contained PFOA or PFHxS above ~ 1 mg/kg or PFOS above 50 mg/kg would be considered a POPs waste and requires high temperature incineration to achieve destruction. PFOA in particular is a highly resilient compound and resists thermal degradation up to temperatures of around 1000°C. As such waste containing PFOA requires destruction at hazardous waste incinerators or suitable cement kilns which operate high temperature processes.

In Europe, a joint submission for a universal restriction of PFAS by several countries is under review by the European Chemical Agency. Should the restriction be adopted, and then subsequently also adopted by the UK, similar restrictions as those for PFOS, PFOA and PFHxS could apply to many other PFAS.

The data produced from the testing programme completed has been considered within the context of current and proposed regulations. None of the 65 samples analysed as part of this testing programme were found to have a concentration that exceeded 1 mg/kg (or mg/l for liquid samples). All concentrations of PFAS were significantly below 1 mg/kg.

4.3 **PFAS Environmental Loadings**

The environmental loadings of PFOS, PFOA and PFHxS have been calculated on a dry weight basis. The calculations are based on the average concentrations detected in the three rounds of sampling for every 1,000 m³ of effluent discharged or 1,000 tonnes of crumb used for agricultural purposes.

The calculation method and assumptions adopted are detailed in Section 2.7. As the concentrations below the level of detection have been assumed to be present at the concentration of the limit of detection for the purpose of generating loading data, the results should be considered as a worst-case scenario based on the existing dataset.

Due to the large difference in processing capacity between the sites, the effluent and crumb production numbers have been normalised to provide a comparison between sites. The normalised data provides an opportunity to assess if there are any significant differences in the

different paper manufacturing processes under review. Three target PFAS were included in the loading calculations: PFOS, PFOA and PFHxS (POPs compounds).

The results of the normalised environmental loadings for selected PFAS per 1,000 m³ of effluent discharge (Table 4.1) and 1,000 tonnes of crumb (Table 4.2) are summarised in the corresponding tables. The environmental loading to water has also been calculated on a mg per annum basis, which highlights the substantial difference in discharge between sites due to differences in the scale of site operations.

PFAS	Environmental loading (mg per 1,000 m ³)						
	Site 1	Site 2	Site 3	Site 4	Site 5		
PFOS	3.40	< 0.95	7.76	< 0.86	5.97		
PFOA	23.4	20.2	< 0.83	< 0.89	< 1.13		
PFHxS	1.06	< 1.14	< 0.80	< 0.62	3.32		

 Table 4.1
 Target PFAS environmental loadings to water per 1,000 m³ effluent

Note: Site 4 values for the loading is calculated using the limit of detection data as no PFAS compounds were detected above detection limits in any of the effluent samples.

PFAS	Environmental loading (mg per annum)						
	Site 1	Site 2	Site 3	Site 4	Site 5		
PFOS	6,800	< 17	5,800	< 2,100	33,000		
PFOA	47,000	360	< 620	< 2,200	< 6,200		
PFHxS	2,100	< 20	< 600	< 1,600	18,000		

Table 4.2 Target PFAS Water Environmental Loadings

Table 4.3 Target PFAS environmental loadings to land

PFAS	Environmental loading (mg per 1,000 tonnes)							
	Site 1 *	Site 3	Site 4	Site 5 *				
PFOS	260	913	< 112	304				
PFOA	< 71	< 223	< 217	< 165				
PFHxS	< 21	< 73	< 65	< 62				

Note: Loadings adjusted to account for the proportion of crumb used for agricultural purposes that therefore has a land discharge route. Site 2 does not produce a crumb.

Total PFAS loadings (i.e. for all 23 PFAS) have not been calculated as the majority of the concentration data is below the limit of detection which means the calculated loading is a reflection of analytical sensitivity rather than actual loadings.

The results of the annual environmental loading calculations are provided in Appendix B1.4.

4.3.1 Calculated direct or indirect PFAS loadings to surface water

The PFAS loadings to surface water from effluent discharge from paper mills (as shown in Table 4.1) indicate that PFOA discharge from Site 1 and Site 2 is slightly elevated when compared to the other sites. Concentrations of PFOS and PFHxS were generally below the limit of detection and therefore the loadings to the environment are stated as below respective detection limit concentrations. However, PFOS was discharged from Site 1, Site 3 and Site 5. Similarly, PFHxS was discharged by Site 1 and Site 5. The total discharge to water per annum is significantly affected by the throughput of each facility.

Site 1 was found to contain a concentration of PFOA in the input water of up to 0.0084 μ g/l (two of three samples were found to have a PFOA concentration below the limit of detection), whereas the effluent had a concentration between 0.022 μ g/l and 0.027 μ g/l. PFOA was not identified in any of the input paper samples at Site 1. Similarly, PFOA was not identified in the input paper or the input water for samples taken from Site 2. However, one effluent sample had a PFOA concentration of 0.059 μ g/l (the other two samples were found to have a PFOA concentration below the limit of detection). As such, there is not a particularly clear link between the process inputs and outputs at these sites. Similar trends were observed for PFOS and PFHxS where concentrations were identified above the limit of detection.

PFOS, PFOA and PFHxS were not identified in any of the 15 input paper samples analysed which suggests that any potential input of those compounds is related to input process water rather than the paper mill processes. Several of the paper mills operate low temperature drying steps which results in a lower effluent discharge rate than the rate of water input (specific data provided in Table 2.2) into the process, due to evaporation. This drying step and volume reduction may have the impact of concentrating PFAS in the effluent, when compared to the input water. Should concentration of PFAS in the effluent be a factor, this mechanism would account for some of the observed trends in the data outlined above.

4.3.2 Calculated Environmental Loadings to Land

The environmental loadings to land are provided in Table 4.2. PFOS was identified in crumb samples taken from Site 1, Site 3 and Site 5. However, as discussed in the previous section, corresponding input paper samples were not found to contain PFOS. The PFOS identified in the crumb which may act as a discharge route to land therefore likely originates in the input water to the paper mill processes. PFOA and PFHxS were not identified in any crumb samples above the limit of detection and therefore the loading is reflective of the analytical sensitivity.

5. Conclusions

A total of 65 samples were taken from five paper mills between November and December 2022 representing a variety of operational scales, type of input paper and geographical locations in England. The samples included input paper, crumb, input water, effluent and output product samples in order to provide data on both the inputs and outputs of the processes. The samples underwent analysis to determine the concentration of 23 PFAS. The conclusions of the testing programme are as follows:

- 1. All sixty-five samples had concentrations of PFAS substantially below 1 mg/kg, including PFOS, PFOA and PFHxS. When identified above the limit of detection PFOS, PFOA and PFHxS were three orders of magnitude lower than 1 mg/kg.
- 2. PFOS, PFOA and PFHxS were not identified above the limit of detection in any of the 15 input paper samples analysed. However, those compounds were found to be present in several input water samples (at very low concentrations). The dataset suggests that PFOS, PFOA and PFHxS are not present in a wide range of input paper types, which included food packaging and coffee cups.
- 3. Papers mills are a discharge point of a small amount of PFOS, PFOA and PFHxS. Based on this dataset, the PFOS, PFOA and PFHxS originate in the input water rather than the recycled waste paper stream and may be concentrated into effluent and crumb during the process.
- 4. Polyfluoroalkyl phosphate esters (PAPs) were identified in several samples. Further analysis, particularly for 10:2 diPAP, is required to quantify the concentrations due to the lack of available standards at the time of analysis and as such reported concentrations should be considered indicative of presence or absence.

Appendix A Sample Collection

All sampling equipment was pre-soaked at WRc with 10% nitric acid and rinsed with deionised water ahead of each visit. Separate site-specific containers were used for collection of input water and output effluent to avoid cross contamination.

A1 Site 1

A1.1 Input paper

At Site 1 the samples of input paper were collected by site personnel ahead of WRc attending site. Due to the high volume of traffic the delivery area is not accessible to external staff. The site carries out independent sampling of a randomly selected bale from every incoming load of paper using a core bore sampler, a picture of which is presented in Photograph A.1 (left).

The site were instructed to collect additional cores for this testing programme across the 24 hours prior to each sampling visit. These were placed in individual bags and then a combined sack for WRc collection. The average sample size was ~5-10 kg. A typical picture of the samples is presented in Photograph A.1(right)

Photograph A.1 Site 1 input paper: core bore sampler (left), bored samples (right)





A1.2 Process effluent

During Round 1 a sample of water effluent was collected from an automatic sampling point post the effluent treatment plant (ETP). Each sampling cycle generates 4-5 litres of effluent . In total a 20 litre sample was collected into a plastic container across 4 to 5 sampling cycles. This was then thoroughly mixed and two bottles each of 1 litre were subsampled as shown in Photograph A.2 (left).

During Rounds 2 and 3, samples were taken from a tap located inside the treatment building to make sampling easier, this pipe takes the same effluent as that from the automatic sampling point. The tap was slowly opened to control the flow and the pipe was left to run and used to rinse the PFAS free sample collection bucket Photograph A.2 (centre). Once sufficient time had passed a rinsed empty bucket was placed under pipe and allowed to slowly fill to ~15 litres. Once the bucket was sufficiently full the tap was turned off and the effluent mixed. Bottles and funnel were rinsed using the effluent prior to filling two 1 litre bottles (Photograph A.2 (right)).

Photograph A.2 Site 1 process effluent: Round 1 sampling point (left), Rounds 2-3 sampling point (centre), sample (right)



A1.3 Input water

Three samples of input water were collected in the same way and at the same location point in each round of sampling. Input water was samples from a dedicated tap located on the process infeed system. The tap was left to run for a few minutes ahead of sampling and water used to rinse each sampling bottle ahead of sample collection. As sampling point was low to the ground a pre-rinsed jug was used to facilitate sample collection. The sampling location and samples are shown in Photograph A.3.



Photograph A.3 Site 1 input water: sampling point (left), sample (right)

A1.4 Crumb

Samples of paper crumb were collected from the covered storage bay. A conveyor system brings crumb to the bay and this is then stockpiled at the rear of the bay. A stockpile of fresh crumb was mixed with a mechanical excavator ahead of sampling (Photograph A.4). Two 20 litre buckets were filled with the mixed material.

Photograph A.4 Site 1 crumb storage bay: older stockpiles (left), fresh pile (right)





A1.5 Product

During Round 1 a sample of paper product was collected for testing. At Site 1 this sample was taken from the site's internal laboratory where quality tests are carried out on each roll of produced paper. Multiple sheets of paper were collected.

A2 Site 2

A2.1 Input paper

Input paper was sampled from the storage area immediately before the infeed process conveyor ahead of a shredder. Grab samples of input paper were taken from circa 20 bales. In Round 1 the bales consisted of newsprint (with low levels of magazines) and cardboard including food takeaway and cereal boxes. These samples were mixed in a 50/50 ratio at WRc to reflect the mix of bales entering the process. In sampling Rounds 2 and 3 the input was composed of the same ratio, with 50% of overissued papers and 50% of shredded cardboard. An example of the input paper sampled is shown in Photograph A.5.

Photograph A.5 Site 2 input paper: shredded cardboard (left), News waste (right)





A2.2 Process effluent

The process effluent (all fibre is used within the process) was sampled from a process sump which collects removed water from all production lines. Utilising a jug and plastic container to collect circa 20 litres of liquid. The bulk sample was then mixed and two 1 litre bottles filled.

A picture of the water effluent sampling at site is provided in Photograph A.6.

Photograph A.6 Site 2, process effluent: sampling point (left), sample (right)



A2.3 Input water

Photograph A.7

The process input water sample was taken from the tap ahead of the processing line. The tap was left to run for a few minutes at a high flow. The sample bottles were rinsed, flushed and samples taken. A picture of the sampling point and bottle is presented in Photograph A.7.



Site 2, input water: collection point (left), sample (right)

A2.4 Crumb

All input paper fibres are used in this process and no crumb is produced.

A2.5 Product

Samples of two products were collected during sampling Round 1. The samples were collected from at ransom from the days production. Each sample was shredded and mixed to produce a sample with 10/90 ratio to replicate the contribution from the production lines.

A3 Site 3

A3.1 Input paper

Input paper was sampled according to the mix of material being used in the process on the day of sampling. Grab samples were collected from the available bales in the storage area on each sampling day. An example of the bales is provided in Photograph A.8.

- R1: Bag 1 50% shredded office waste, Bag 2 40% brown card off-cuts/ 5% mixed paper waste and 5% process off-cuts.
- R2: Bag 1 60% shredded office waste, Bag 2 loose 20% multigrade paper (municipal collection), and small plastic bags 10% coloured letters and 10% coloured cards.
- R3: 55% shredded office waste, 25% mixed grade paper, 20% heavy coloured card (paper and card separated at WRc).

Photograph A.8 Site 3, input paper: shredded office waste (left), paper waste mixed (right)





A3.2 Input water

Input water consists of 85% surface water abstraction from the river, the remaining water is sourced from a rainwater collection reservoir upgradient of the site. Picture of the two sampling points are provided in Photograph A.9 (left and centre). A single 1 litre bottle of surface water

was collected from the reservoir and two 1 litre bottles of abstracted river water from the input line tap. The water samples were then combined in the ratio of 85% river to 15% rainwater as shown in Photograph A.9 (right).

Photograph A.9 Site 3, input water: reservoir collection point (left), Tap collection point for abstracted river water (centre), collected sample (right)



A3.3 Process effluent

Process effluent is usually sampled by site personnel at an automatic sampling station where composite samples are produced. However, the incremental volumes were too small to be sufficient for this testing programme. An alternative location was therefore identified where it was possible to sample from the complete stream right before it discharged to sewer. A half-litre bottle hanging on a string was submerged into the stream to collect several incremental effluent samples as shown in Photograph A.10. Overall, approximately 10-15 litres were collected into the 25 L bucket at each round of sampling. The content was well mixed and then used to fill two 1 litre bottles. The process effluent is characterised by a temperature of circa 30 °C and the presence of particulates. During Round 3 one of the discharge pumps was out of action and the steam had a lower flow rate than the previous two rounds.



Photograph A.10 Site 3 process effluent sampling point (left), sample (right)

A3.4 Crumb

The crumb is stored in a bay area right below the outfeed process conveyor belt as showed in Photograph A.11. Once the storage bay area on one side is full the belt is moved across to the second bay. A representative sample of crumb was taken by collecting material from both stockpiles, one 20L bucket from material produced the previous day / night and the second with material coming from the conveyor. During Round 3 sampling switched from producing paper roll to tissue during sample collection.



Photograph A.11

Site 3 crumb storage bay



A3.5 Product

The sample of paper product collected during Round 1 was taken directly at the end of the production line. Due Health and safety restriction, the area is not accessible to external staff, therefore the action was completed by site's staff at the end of a production cycle.

A4 Site 4

A4.1 Input paper

Input paper composition is changed to meet the required paper production quality / grades. Grab samples were collected from the available bales in the paper storage area which matched the daily production input requirements. A batch consists of 4 tonnes of input feed, although production runs may be multiples of this number.

- R1: equal proportions of shredded office waste and coffee cup off-cuts.
- R2: 1 part post-industrial coffee cup off-cuts, 1 part post-industrial white paper waste, and 4 parts bleached virgin pressed fibre sheets.
- R3: 4 parts recycled process paper (rolls), 1 part paper cup off-cuts.

Photograph A.12 shows examples of the virgin pulp (left), paper cup off-cuts (centre) and shredded office waste (right).

Photograph A.12 Site 4, input paper: (left to right) bleached virgin pressed fibre, paper cup off-cuts, shredded office waste, recycled process paper



A4.2 Input water

Input water is abstracted from the adjacent river, the water is stored and filtered before being used in the process. A sample of the input water was taken from the tap on the storage tank after filtration ahead of it being used in the process (Photograph A.13).

Photograph A.13 Site 4 input water sampling point



A4.3 Process effluent

A treatment plant is used to treat paper fibre effluent and technical fibre effluent from an adjoining facility. The paper mill produces 7,000 m³ of effluent and the technical fibre facility 40 m³. During Round 1 the process effluent was collected from the combined source at the treatment plant. A sampling tap was used to collect 25 litres of that was consequentially mixed and subsampled into two 1 litre bottles, as shown in Photograph A.14. The effluent appeared contained particulates and was characterised by the coloured dye being used in paper production.

Photograph A.14 Site 4, Round 1, process effluent sampling point (Tap)



In Round 2 the water was sampled from the effluent line at the end of the paper production line. The effluent was collected from the open channel (Photograph A.15) ahead of entering the treatment plant and before mixing with the Site 2 effluent. The effluent stream was flowing at speed and easy to access. A spare bottle was immersed in the stream to take increments into a 25 litre plastic drum which was mixed and then this was subsampled into the two 1 litre bottles. The only treatment done on the effluent ahead of sampling is a pH neutralisation step. Production during the Round 2 sampling event was white paper and the effluent was white in colour.

Photograph A.15 Site 4, Round 2, process effluent sampling point (channel)



In Round 3 a sample of effluent was collected from both sampling points used in Round 1 (tap – combined) and Round 2 (flowing channel – single stream). The Tap-sample was characterised by a weak grey/blue colour and the channel-sample a strong dark blue colour (blue paper was in production). In Photograph A.16 are shown the tap sample (left) and the channel sample (right).

Photograph A.16 Site 4 Round 2, process effluent tap-sample (left), channel-sample (right)



In Round 3 separate samples were collected from the paper production and technical fibre production lines. Due to site maintainance operations, the combined effluent outflow line of the

technical fiber process was not accessible and the sample was taken off directly from an open channel at the end of the processing line by submergining the sampling bottles. The effluent as shown in Photograph A.17 had a white cloudy colour.



Photograph A.17 Site 4: Round 3 technical fibre process effluent

A4.4 Crumb

Crumb is discharged directly from the process into a storage skip which is not accessible due to safety restrictions. Sampling of the crumb was therefore only possible from the outside tipped stockpiles (see Photograph A.18). During Round 1 crumb was not being produced and the stored residues therefore corresponded to the previous weeks paper production. The crumb was characterised by a dark blue and purple colour (linked to the coloured paper production run). This crumb sample was particularly high in moisture. During the week, the paper production tends to start with light colours and it goes gradually darker. On each sampling round two 20L buckets were filled with crumb that was representative of the stockpiles in the storage area.

In Round 2 the skip was emptied outside crumb pile was discharged at 6.00 hrs, from crumb produced between 22.00 hrs the previous evening and 6.00 hrs. Unlike the colour of the paper being produced at the time (white) the crumb was dark representing effluent and fibre held in process storage tanks (which contain 2.5 million litres of liquid / fibre).

In Round 3 the crumb stockpiles were characterised by 3 to 4 colours (greens and purple / black). The sample was created by taking equal portions of each pile. The latest pile was discharged at 4.30 hrs on the morning of sampling.



Photograph A.18 Site 4 Crumb storage area

A4.5 Product

A sample of the paper being produced during Round 1 was collected for testing. This was taken from the production off-cuts at the end of the production line.

A5 Site 5

A5.1 Input paper

There are 8 bays holding circa 1,000 tonnes, each of mainly loose paper. The paper is fed by a shovel loader into a levelling drum ahead of the conveyor which also de-wires any bales (20% of total). The input is composed of mixed off-cuts from newspaper and magazine production and mixed news and magazine returns. During the sampling days the process was running smoothly. Grab samples were collected from the conveyor belt over a period of 15 minutes using a sturdy litter picker as shown in photograph A.19. Two sacks of mixed paper input were collected.

Photograph A.19 Site 5 input paper conveyor



A5.2 Process effluent

The process effluent was sampled from a tap in the effluent treatment facility (ETF) using a jug which was repeatedly emptied into a 25 litre bucket. This was then mixed and subsampled to fill two 1 litre sample bottles. The tap was initially turned on and left to run (drainage from concrete floor into drain) as shown in Photograph A.20. The effluent was clear of significant particulates and characterised by a light amber colour.



Photograph A.20 Site 5 water effluent sampling point

A5.3 Input water

The input water is abstracted from the river. The tap is located directly on the river inlet pipe in the ETF. For sampling the tap was opened to high flow and left to run for 5 minutes. A 'clean' jug was used to fill the two sample bottles as shown in Photograph A.21.



Photograph A.21 Site 5 input water sampling point

A5.4 Crumb

The conveyor discharges the crumb to an external storage bay. The crumb was sampled from the storage heaps (older) and adjacent to conveyor that is adding fresh material (Photograph A.22).

Photograph A.22 Site 5 Crumb storage bay



A5.5 Product

During Round 1 a sample of paper product was collected. This was taken directly from the roll at end of production line.

Appendix B Methodology/Analysis

The complete list of samples collected in the three rounds of sampling in Table B.1.

Table B.1	List of samples collected with respective codes
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Site	Round	Paper input	Water input	Water effluent	Crumb	Paper product
	R1	EA-PFAS-Site1- R1-PaperInput- 081122	EA-PFAS-Site1- R1-WaterInput- 081122	EA-PFAS-Site1-R1- Effluent-081122 X2539	EA-PFAS- Site1-R1- Crumb-081122	EA-PFAS- SITE1-R1- PaperProduct- 081122
Site 1	R2	EA-PFAS-Site1- R2-PaperInput- 221122	EA-PFAS-Site1- R2-WaterInput- 221122	EA-PFAS-Site1-R2- Effluent-221122	EA-PFAS- Site1-R2- Crumb-221122	
	R3	EA-PFAS-Site1- R3-PaperInput- 061222	EA-PFAS-Site1- R3-WaterInput- 061222	EA-PFAS-Site1-R3- Effluent-061222	EA-PFAS- Site1-R3- Crumb-061222	
	R1	EA-PFAS-Site2- R1-PapaerInput- 081122	EA-PFAS-Site2- R1-WaterInput- 081122	EA-PFAS-Site2-R1- Effluent-081122		EA-PFAS- SITE2-R1- PaperProduct- 081122
Site 2	R2	EA-PFAS-Site2- R2-PaperInput- 221122	EA-PFAS-Site2- R2-WaterInput- 221122	EA-PFAS-Site2-R2- Effluent-221122		
	R3	EA-PFAS-Site2- R3-PaperInput- 061222	EA-PFAS-Site2- R3-WaterInput- 061222	EA-PFAS-Site2-R3- Effluent-061222		
	R1	EA-PFAS-Site3- R1-PaperInput- 091122	EA-PFAS-Site3- R1-WaterInput- 091122	EA-PFAS-Site3-R1- Effluent-091122	EA-PFAS- Site3-R1- CRUMB- 091122	EA-PFAS- SITE3-R1- PaperProduct- 091122
Site 3	R2	EA-PFAS-Site3- R2-PaperInput- 211122	EA-PFAS-Site3- R2-WaterInput- 211122	EA-PFAS-Site3-R2- Effluent-211122	EA-PFAS- Site3-R2- Crumb-211122	
	R3	EA-PFAS-Site3- R3-PaperInput- 051222	EA-PFAS-Site3- R3-WaterInput- 051222	EA-PFAS-Site3-R3- Effluent-051222	EA-PFAS- Site3-R3- Crumb-051222	
Site 4	R1	EA-PFAS-Site4- R1-PaperInput- 091122	EA-PFAS-Site4- R1-WaterInput- 091122	EA-PFAS-Site4-R1- Effluent-091122	EA-PFAS- Site4-R1- Crumb-091122	EA-PFAS- SITE4-R1- PaperProduct- 091122
	R2	EA-PFAS-Site4- R2-PaperInput- 231122	EA-PFAS-Site4- R2-WaterInput- 231122	EA-PFAS-Site4-R2- Effluent-231122	EA-PFAS- Site4-R2- Crumb-231122	

Site	Round	Paper input	Water input	Water effluent	Crumb	Paper product
	R3	EA-PFAS-Site4- R3-PaperInput- 071222	EA-PFAS-Site4- R3-WaterInput- 071222	EA-PFAS-Site4-R3- combined Effluent- 071222 EA-PFAS-Site4-R3- Paper Effluent- 071222 EA-PFAS-Site4-R3- Tech fibre Effluent- 071222	EA-PFAS- Site4-R3- Crumb-071222	
	R1	EA-PFAS-Site5- R1-PaperInput- 091122	EA-PFAS-Site5- R1-WaterInput- 091122	EA-PFAS-Site5-R1- Effluent-091122	EA-PFAS- Site5-R1- Crumb-091122	EA-PFAS- SITE5-R1- PaperProduct- 091122
Site 5	R2	EA-PFASr- Site5-R2- PaperInput- 231122	EA-PFAS-Site5- R2-WaterInput- 231122	EA-PFAS-Site5-R2- Effluent-231122	EA-PFAS- Site5-R2- Crumb-231122	
	R3	EA-PFAS-Site5- R3-PaperInput- 071222	EA-PFAS-Site5- R3-WaterInput- 071222	EA-PFAS-Site5-R3- Effluent-071222	EA-PFAS- Site5-R3- Crumb-071222	EA-PFAS- SITE5-R3- PaperProduct- 071222

B1.1 Test methods

All chemical analyses conducted within the POPs research group at Birmingham were undertaken using in-house quality procedures developed by Harrad *et al.* The complexities of PFAS analysis in the matrices required for this project meant that some modifications to current testing approaches, for example extraction methods and testing suites were required to generate robust data for this project.

The PFAS laboratory extraction and clean up method applied to liquid samples was as follows:

- 1. Take a 50 mL aliquot of water sample into a precleaned glass measuring cylinder.
- 2. Using a syringe / micropipette, spike each 50 mL water sample with 50 ng of mass labelled internal standards (e.g. 50 μL of a 1 ng/μL mixture).
- 3. Set up the SPE vacuum manifold and pump, and sonicate valves with methanol to clean.
- 4. Place Chromabond SPE cartridges on the manifold
- 5. Pre-condition the cartridges with 2 x 6 mL of 0.1% NH4OH in Methanol and allow to run through at 1-2 drops/second.

- 6. Pre-condition the cartridge with 2 x 6 mL of distilled water at 1-2 drops/second.
- 7. Rinse reservoir adaptors with methanol and attach to top of SPE cartridge.
- 8. Decant spiked water into the reservoir and allow to run through the cartridge at around 1 drop/second (use the vacuum pump if necessary to increase flow).
- 9. Once the entire sample has passed through the cartridge, use the vacuum pump to dry the cartridge for 30 minutes.
- 10. When the sample is dry, turn off pump and add labelled collection tubes to the manifold below each corresponding sample.
- 11. Elute PFAS compounds with 14 mL of 0.1% NH4¬OH in methanol at 1 drop per second, collecting all eluate in tubes.
- 12. Transfer tubes to nitrogen blow-down unit and concentrate samples at 40 °C under a very gentle stream of nitrogen to exactly 1 mL.
- 13. Filter the extracted solution with 0.2 μ m membrane (Fisher brand, 33mm syringe filter) and transfer to 2 mL GC vials.
- 14. Add 50 μL of recovery standard (1 ng/μL M4-PFOS and M4-PFOA in methanol) to each sample.
- 15. Vortex each sample for 15-20 seconds.
- 16. Transfer a 50 μL aliquot of final clean extracts to labelled glass insert vials and store in freezer until analysis on LC-MS/MS.

The PFAS laboratory extraction and clean up method applied to solid samples was as follows:

- 1. Take an aliquot of approximately 100mg of paper sample into a clean 15mL centrifuge tube and record exact weight of each sample.
- Using a syringe / micropipette, spike each sample with 50 ng of internal standards (e.g. 50 μL of a 1 ng/μL mixture)
- 3. Allow at least 30 mins to reach equilibrium (preferably overnight).
- 4. Add 5mL of Methanol (HPLC grade) to paper sample and vortex for 30 secs and sonicate for 10 mins.
- 5. Add a further 5 mL and repeat vortex 30 secs and sonicate for 10 mins.
- 6. Centrifuge 10 mL extracts at 3500 RPM for 5 mins (2-4 at a time).
- 7. Transfer 10mL extract to clean tube and concentrate extract to 1mL.
- 8. Set up the SPE vacuum manifold and pump, and sonicate valves with methanol to clean.
- 9. Place CHROMABOND SPE cartridges on the manifold.

- 10. Pre-condition the cartridges with 2 x 6 mL of 0.1% NH₄OH in Methanol and allow to run through at 1-2 drops/second.
- 11. Pre-condition the cartridge with 2 x 6 mL of distilled water at 1-2 drops/second
- 12. Transfer the concentrated 1 mL sample extract to the SPE cartridge slowly and allow to run through the cartridge at around 1 drop per second (use the pump if necessary to increase flow being careful with the valves).
- 13. Once the entire sample has passed through the cartridge, use the vacuum pump to dry the cartridge for 5 minutes.
- 14. When the sample is dry, turn off pump and add labelled collection tubes to the manifold below each corresponding sample.
- 15. Elute PFAS compounds with 14 mL of 0.1% NH₄OH in methanol at 1 drop per second, collecting all eluate in tubes.
- 16. Transfer cleaned extract tubes to nitrogen blow-down unit and concentrate samples at 40 °C under a gentle stream of nitrogen to exactly 200 μ L.
- 17. Add 30 μL of recovery standard (1 ng/μL M4-PFOS and M4-PFOA in methanol) to each sample and briefly vortex mixture.
- 18. Transfer a 50 μL aliquot of the final clean extracts to labelled glass insert vials and store in freezer until analysis on LC-MS/MS.

Extraction efficiencies were checked for the study matrices and an optimum extraction regime identified. This method required some adaptation to measure PFAS additional to the C4-C13 PFCAs and PFSAs and for application to solid or semi-solid matrices.

Stringent precautions were required to avoid contact of the sample with any material containing PTFE. For example, PTFE-lined caps for sampling receptacles or LC/MS were not used as they have potential to introduce contamination with one or more of the target PFAS.

B1.2 LC-MS analysis conditions

A 10 µL aliquot of the sample extract was injected onto a Sciex Exion HPLC coupled to a Sciex 5600+ triple TOF MS. This was fitted with a ZORBAX Eclipse Plus C18 RRHD column (internal diameter: 2.1; length: 100 mm; particle size: 1.8 um, Agilent) equipped with a ZORBAX Eclipse Plus C18 Fast Guard column (internal diameter: 2.1; length: 5 mm; particle size: 1.8 um, Agilent). The mass spectrometric conditions have been developed for a Sciex 5600+ time of flight mass spectrometer (TOF-MS). The TOF-MS was equipped with a Turbo V source which was operated in negative mode using electrospray ionisation at a voltage of -4,500 V. The curtain gas was set at 25 psi, whilst the nebuliser gas (source gas 1) was set at 25 psi and the drying gas (source gas 2) at 30 psi. The CAD gas was set to medium and temperature was 450 °C. The MS data was acquired using automatic information dependent acquisition (IDA) with two experiment types: (i) survey scan, which provided TOF-MS data; and (ii) dependent product

ion scan using a collision energy of -10 V and a collision a spread of 30 V. Quantification of individual PFAS were performed using MRM transitions and retention times for identification. Quantification of PFAS concentrations was undertaken based on the internal standard principle. In most instances, for those PFAS for which the internal standard was the corresponding isotopically labelled standard (e.g. PFBA quantified relative to 13C4-PFBA), quantification follows the isotope dilution principle. Recovery standards were used to quantify extraction efficiencies (13C4-PFOA and 13C4-PFOS).

To establish calibration plots and derive relative response factors (RRFs), five separate calibration standard mixtures were prepared containing each individual native, internal, and recovery determinations. When using this method for the first time, all five calibration standard mixtures were analysed and RRF values derived for each native PFAS in each calibration standard mixture. The relative standard deviation (i.e. (σ_{n-1} /average) x 100%) of RRFs for a given target compound should not exceed 10%. Where they did, an corrective action was taken before proceeding with sample analysis. The full 5-point calibration (see below) was suspected to have evaporated; when the LC-MS had been shut down for a long period, undergone a general maintenance; or when an on-going check on method accuracy such as a proficiency test or analysis of a laboratory fortified blank (see below) proved unsatisfactory.

RRF values should be calculated via the equation:
$$RRF = \frac{A_{NAT}}{A_{IS}} \times \frac{C_{IS}}{C_{NAT}}$$

where A_{NAT} is the peak area for the "native" PFAS in the calibration standard; A_{IS} is the peak area of the internal standard in the calibration standard; C_{NAT} is the concentration of the "native" PFAS in the calibration standard; and C_{IS} is the concentration of the internal standard in the calibration standard.

Before each batch of samples were analysed on the LC/MS, one of the 5 calibration standards was run as a continuing calibration. The RRFs obtained from this analysis must be within \pm 25 % of the RRFs obtained for that standard in the initial full calibration. If they were not, corrective action was be taken, i.e. the standard was re-run and acceptable RRFs (i.e. within 25% of those obtained in the full calibration) obtained before sample analysis commenced. At the end of each batch of samples, the same calibration standard was run. The RRFs obtained from this analysis must be within \pm 25 % of the RRFs obtained for that standard in the initial 5-point calibration. The RRFs that must be used for calculating concentrations in samples in that batch will be an average of those obtained for the 2 standards run for that batch. A minimum of two continuing calibrations were conducted every 24 hours that samples were run.

Concentrations in samples may be calculated:

$$Concentration = \frac{A_{NAT}}{A_{IS}} \times \frac{1}{RRF} \times \frac{M_{IS}}{SS} \quad (equation \ 2)$$

Where AIS = peak area of internal standard in sample; A_{NAT} = peak area of target PFAS in sample; RRF = relative response factor for the target PFAS (see equation 1); M_{IS} = mass of internal standard added to sample (ng) and SS = sample size (L).

B1.3 Quality assurance and quality control measures

To ensure satisfactory method performance before introducing the method to a laboratory, the following quality assurance/quality control samples were undertaken:

Laboratory Reagent Blank for solid samples (LRB) – An aliquot of reagent water previously determined to contain acceptably low concentrations of all target PFAS, that is treated as a sample in all respects, including exposure to all analytical procedures. This can be used to evaluate the extent of any contamination or possible interferences introduced by laboratory analysis procedures.

Field Reagent Blank for liquid samples (FRB) – An aliquot of reagent water that is placed in a sample container in the laboratory and treated as a sample in all respects, including exposure to shipping, sampling location conditions, storage, preservation, and all analytical procedures. This can be used to evaluate the extent of any contamination with target analytes or possible interferences introduced by sampling, storage, and laboratory analysis procedures.

Laboratory Fortified Blank (LFB) – An aliquot of reagent water that is treated with known quantities of all target PFAS native standards (treatment with quantities equivalent to a concentration of each individual target PFAS in the LFB of 5.0 ng/l) and is then treated as a sample in all respects, including exposure to all analytical procedures. The LFB acts as an indicator of method accuracy and were used to support method development to improve precision of PFAS concentration determination.

With each batch of up to 20 samples analysed in 1 working day, at least one LRB, FRB, and LFB will be run. If the criterion for LFB data to be deemed acceptable are not met for any of the target PFAS, then all data for the PFAS(s) concerned must be considered invalid for all samples in that batch. Likewise, a record of concentrations of target PFAS detected in LRBs and FRBs should be maintained. Over time, this record will be used as a check on background laboratory as well as sampling and storage contamination. Should concentrations of any target PFAS in the LRB or FRB for a given batch exceed 1/3rd of the mean LRB or FRB concentrations + 3σ , or 3 times the mean LRB or FRB concentration (whichever is greater), then all data for the PFAS concerned would be considered invalid for all samples in that extraction batch. In such events, further sample analysis would be suspended until the source of the contamination is brought under control.

B1.4 PFAS Environmental Loading

Three POPs classified PFAS and 10:2 diPAP concentrations have been used to produce an environmental loading to land and water from the paper mill sites included in the testing programme. A loading for the complete list of PFAS analysed has not been completed as most of the data was below analytical detection limits which would mean the calculated loading reflects analytical sensitivity rather than real life.

At a first step the average concentration of each of the four compounds was calculated between each round of testing for each stream type. The results of this analysis can be found below in Tables B.6 to B.10. Data below the detection limit has been included at face value.

PFAS	Site 1	Site 2	Site 3	Site 4	Site 5		
	Average Concentration (µg/l)						
PFOS	0.005	<0.001	0.001	<0.001	0.008		
PFOA	0.003	<0.001	<0.001	<0.001	<0.001		
PFHxS	0.001	<0.001	<0.001	<0.001	0.007		

Table B.2 Average Concentration for target PFAS in Input Water

Table B.3 Average Concentration for target PFAS in Effluent

PFAS	Site 1	Site 2	Site 3	Site 4	Site 5	
	Average Concentration (µg/I)					
PFOS	0.003	<0.001	0.008	<0.001	0.006	
PFOA	0.023	0.020	<0.001	<0.001	<0.001	
PFHxS	0.001	<0.001	<0.001	<0.001	0.003	

Table B.4 Average Concentration for target PFAS in Input Paper

PFAS	Site 1	Site 2	Site 3	Site 4	Site 5		
	Average Concentration (µg/kg)						
PFOS	<0.14	<0.14	<0.10	<0.11	<0.12		
PFOA	<0.32	<0.25	<0.16	<0.23	<0.22		
PFHxS	<0.09	<0.10	<0.07	<0.07	<0.09		

PFAS	Site 1	Site 2	Site 3	Site 4	Site 5		
	Average Concentration (µg/kg)						
PFOS	1.0	N/A	0.91	<0.11	0.34		
PFOA	<0.28	N/A	<0.22	<0.22	<0.18		
PFHxS	<0.084	N/A	<0.073	<0.065	<0.069		

Table B.5 Average Concentration for target PFAS in Crumb

Table B.6 Average Concentration for target PFAS in Paper Product

PFAS	Site 1	Site 2	Site 3	Site 4	Site 5		
	Average Concentration (µg/kg)						
PFOS	<0.13	<0.13	<0.16	<0.12	<0.18		
PFOA	<0.19	<0.19	<0.21	<0.17	<0.33		
PFHxS	<0.087	<0.088	<0.11	<0.082	<0.12		

Using this data and the annual mass balances of residues and discharged process effluent supplied by the paper mills the total annual loafing of the targeted PFAS compounds can then be calculated. The results of this analysis can be found in Tables B11 to B15.

Table B.7 Annual Loading of target PFAS in Input Water

	Site 1	Site 2	Site 3	Site 4	Site 5	
	Annual loading (mg/year)					
PFOS	11,864	<27	<901	<1,763	46,242	
PFOA	8,416	<28	<802	<1,763	<4,143	
PFHxS	2,605	<27	<825	<1,763	38,261	

Table B.8	Annual Loading of target PFAS in Effluent
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	Site 1	Site 2	Site 3	Site 4	Site 5						
	Annual loading (mg/year)										
PFOS	6,830	<17	5,818	<2,197	32,694						
PFOA	47,041	358	<625	<2,274	<6,205						
PFHxS	2,125	<20	<600	<1,576	18,193						

	Site 1	Site 2	Site 3	Site 4	Site 5						
	Annual loading (mg/year)										
PFOS	<60,297	<638	<7,137	<5,537	<53,532						
PFOA	<143,003	<1,152	<11,107	<11,399	<102,476						
PFHxS	lxS <41,132 <451		<4,963	<3,583	<42,367						

Table B.9 Annual Loading of target PFAS in Input Paper

Table B.10 Annual Loading of target PFAS in Crumb

	Site 1 *	Site 2	Site 3	Site 4	Site 5 *					
	Annual loading (mg/year)									
PFOS	5,107	N/A	19,257	<204	22,439					
PFOA	<1,391	N/A	<4,711	<397	<12,185					
PFHxS	PFHxS <414		<1,547	<120	<4,586					

Note: Loadings adjusted to account for the proportion of crumb used for agricultural purposes that therefore has a land discharge route. Site 2 does not produce a crumb.

The final annual water and land environmental loadings are calculated directly from the effluent and crumb values.

Table B.11	Annual Loading of target PFAS in Paper Product
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	Site 1	Site 2	Site 3	Site 4	Site 5						
	Annual loading (mg/year)										
PFOS	<55,900	<683	<7,632	<6,600	<70,000						
PFOA	<81,700	<998	<10,017	<9,350	<132,000						
PFHxS	<37,410	<462	<5,247	<4,510	<48,000						

	Site 1	Site 2	Site 3	Site 4	Site 5					
	Environmental loading (mg/1,000 m ³)									
PFOS	3.40	< 0.95	7.76	< 0.86	5.97					
PFOA	23.4	20.2	< 0.83	< 0.89	< 1.13					
PFHxS	1.06	< 1.14	< 0.80	< 0.62	3.32					

Table B.12 Loading of target PFAS in Effluent

Table B.13 Environmental Loading of target PFAS in Crumb

	Site 1*	Site 2	Site 3	Site 4	Site 5*					
	Environmental loading (mg/1,000 tonnes)									
PFOS	260	N/A 913		<112	304					
PFOA	<71	N/A	<223	<217	<165					
PFHxS	<21	N/A	<73	<65	<62					

Note: Loadings adjusted to account for the proportion of crumb used for agricultural purposes that therefore has a land discharge route. Site 2 does not produce a crumb.

Appendix C Results

C1 Moisture Content

After initial pre-shredding of any oversized input paper, the collected solid samples were dried at 40°C in trays before being milled down to <1 mm for analysis at the UoB. The moisture content results of the drying stage can be found below in Table C.1.

Stream	Round	Site 1	Site 2	Site 3	Site 4	Site 5
Input paper (%)	1	13%	20%	7%	6%	6%
	2	14%	5%	5%	10%	14%
	3	10%	8%	5%	17%	5%
	1	42%		45%	71%	39%
Crumb (%)	2	39%	N/A	42%	74%	39%
	3	46%		43%	71%	38%

tent

The results show that all moisture content readings for the crumb are higher than the input paper. This was expected given the way paper mills processing is designed with some of the input water being lost to the crumb stream. There is some variation in moisture content for the input paper especially in Site 4 and 5 this is due to exposure to precipitation during storage/transportation. For Sites 1, 3 & 5 the moisture content of the crumb is approximately 40% of the sample. Site 4 crumb has a significantly higher moisture content averaging 72%, this is due to the fact that the crumb is stored outside and was exposed to precipitation before collection. Regardless of the storing condition the use of a screw press over a filter press may have different effects in reducing the moisture content of the crumb.

C2 Reported Results

This section contains the raw data reported by the University of Birmingham divided by sample type. Only compounds recorded above the limit of detection have been included for a complete list of results see WRc Report UC16748.1. Values for solid samples were reported in ng/g by the test laboratory and have been converted into ng/kg for the purpose of reporting. As a result, the detection limit values appear inflated. As discussed in Appendix B the detection limit varies between batches and samples depending on the quality control results and exact weights taken for testing.

C2.1 Input Water

Site	1			2	3			5				
WRc Code	X2538	X2542	X2546	X2559	X2563	X2567	X2571	X2587	X2591	X2595		
Anonymised Code	Site1-R1	Site1-R2	Site1-R3	Site2-R3	Site3-R1	Site3-R2	Site3-R3	Site5-R1	Site5-R2	Site5-R3		
Unit		μg/l										
PFOS	0.0062	0.0039	0.0043	<0.00071	<0.00067	<0.00067	0.0010	0.0078	0.0069	0.011		
PFOA	0.0084	<0.0009	<0.00092	<0.00071	<0.00068	<0.00069	<0.00069	<0.0008	<0.00074	<0.00073		
PFHxS	0.0010	<0.00099	0.0012	<0.00068	<0.00068	<0.00068	<0.00076	0.0048	0.0063	0.0099		
PFBS	0.0058	0.0055	0.0053	<0.0014	0.0062	0.0048	0.0044	<0.0015	0.0016	0.0023		
PFDA	0.0005	0.0004	<0.0004	0.0005	<0.00041	<0.00041	<0.00041	<0.00052	<0.00048	<0.00051		
PFHxA	0.0030	<0.0027	0.0034	<0.0019	0.0018	<0.0017	<0.0018	0.0042	0.0042	0.0059		

 Table C.2
 Input Water - PFAS concentrations (identified above detection limit in at least one sample)

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C2.2 Effluent

Site		1		2	2		;	3		5		
WRc Code	X2539	X2543	X2547	X2552	X2556	X2560	X2564	X2568	X2572	X2588	X2592	X2596
Anonymised Code	Site1-R1	Site1-R2	Site1-R3	Site2-R1	Site2-R2	Site2-R3	Site3-R1	Site3-R2	Site3-R3	Site5-R1	Site5-R2	Site5-R3
Unit						μ	g/I					
PFOS	0.0033	0.0044	0.0026	<0.00088	<0.001	<0.00098	0.0073	0.0097	0.0063	0.0086	0.0049	0.0044
PFOA	0.022	0.022	0.027	0.059	<0.00098	<0.0011	<0.00081	<0.00093	<0.00076	<0.0012	<0.0011	<0.0011
PFHxS	0.0014	<0.00085	<0.00093	<0.001	<0.0015	<0.00093	<0.00074	<0.00091	<0.00075	0.0022	0.0032	0.0046
10:2 diPAP	<0.0034	<0.004	<0.0043	0.042	0.20	0.061	<0.0066	<0.011	<0.0052	<0.0077	<0.0095	<0.011
6:2 FTSA; 6:2 FTS	0.012	0.014	0.018	<0.0081	<0.0088	<0.0092	0.014	<0.013	<0.01	<0.014	<0.012	<0.012
EtFOSAA	<0.0019	<0.002	<0.0017	<0.0019	<0.0022	<0.0023	<0.0016	<0.0017	<0.0013	0.060	<0.0022	<0.002
PFBS	0.012	0.013	0.016	<0.0026	<0.0029	<0.0026	0.0082	0.0057	0.0060	0.0073	0.0086	0.0097
PFDA	<0.00045	<0.00045	<0.00037	0.035	<0.00055	<0.00056	<0.0004	<0.0004	<0.00033	<0.00058	<0.00054	<0.00048
PFHpA	0.0039	0.0075	0.0091	0.0061	<0.0041	<0.0046	<0.003	<0.0034	<0.0027	<0.005	<0.0043	0.0046
PFHxA	0.016	0.023	0.023	0.025	0.020	0.015	0.015	0.0069	0.0072	0.0095	0.0099	0.012
PFNA	0.0009	0.0012	<0.0008	0.014	<0.00096	<0.00098	0.0030	<0.00084	0.0021	0.0016	<0.00096	0.0009
PFPeA	<0.013	0.020	<0.017	<0.015	<0.014	<0.017	0.021	<0.017	<0.014	<0.02	0.023	0.023

Table C.3 Effluent - PFAS concentrations (identified above detection limit in at least one sample)

Report Reference: UC16743.3/2770466

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C2.3 Input paper

Site	1	2	2	3			4			5		
WRc Code	X2540	X2557	X2561	X2565	X2569	X2573	X2577	X2581	X2585	X2589	X2593	X2597
Anonymised Code	Site1- R1	Site2- R2	Site2- R3	Site3- R1	Site3- R2	Site3- R3	Site4- R1	Site4- R2	Site4- R3	Site5- R1	Site5- R2	Site5- R3
Units		μg/kg										
10:2 diPAP	<0.18	14.6	8.07	<0.21	<0.20	2.96	<0.20	62.1	5.11	<0.14	4.57	7.95
6:2 FTSA; 6:2 FTS	<0.092	<1.8	<1.0	<0.076	0.82	1.74	<0.12	<1.5	<1.8	<0.090	<1.7	<1.0
8:2 diPAP	<0.18	<1.5	<0.42	<0.21	<0.20	0.45	<0.20	<0.81	<0.78	<0.14	<0.90	<0.29
PFDA	<0.033	<0.11	<0.071	0.13	0.097	<0.056	<0.050	<0.083	<0.093	<0.034	<0.11	<0.069
PFHpA	<0.15	<0.82	<0.50	<0.16	<0.16	<0.39	<0.20	<0.60	<0.68	<0.20	2.76	1.06
PFHxA	<0.19	<0.45	<0.42	<0.20	<0.20	<0.27	<0.24	<0.31	<0.43	<0.32	17.2	<0.38
PFPeA	1.33	<0.73	<1.5	<1.1	<1.0	<0.98	<1.2	<1.5	<1.7	<1.5	<1.6	<1.7
PFUnDS	<0.055	<0.097	<0.060	<0.053	<0.062	<0.052	0.48	<0.064	<0.064	<0.063	<0.087	<0.055
PFUnDA, PFUnA; PFUdA	0.049	<0.13	<0.077	0.14	0.10	<0.064	0.076	<0.11	<0.13	0.098	<0.14	<0.091

Table C.4	Input Paper - PFAS concentrations ((identified above detection	limit in at least one sample)

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C2.4 Crumb

Site	1				3		4		5	
WRc Code	X2541	X2545	X2549	X2566	X2570	X2574	X2586	X2590	X2594	
Anonymised Code	Site1-R1	Site1-R2	Site1-R3	Site3-R1	Site3-R2	Site3-R3	Site4-R3	Site5-R1	Site5-R2	
Unit					µg/kg					
PFOS	1.68	1.31	<0.14	1.12	1.53	<0.094	<0.095	<0.099	0.79	
10:2 diPAP	<0.19	13.2	<0.48	<0.21	<1.1	<0.40	5.35	<0.16	<0.69	
6:2 diPAP	<0.26	<0.60	<0.77	<0.25	<0.67	0.87	<0.43	<0.25	<0.54	
6:2 FTSA; 6:2 FTS	<0.11	<1.7	<1.3	0.72	<1.9	<0.83	<1.2	<0.075	<1.1	
PFBS	0.24	<0.26	<0.22	<0.19	<0.22	<0.15	<0.12	<0.19	<0.18	
PFHpS	<0.061	<0.082	<0.068	0.055	<0.068	<0.047	<0.048	<0.047	<0.061	
PFHpA	<0.19	<0.74	0.91	<0.14	<0.77	<0.31	<0.45	<0.15	<0.57	
PFUnDA, PFUnA; PFUdA	0.10	<0.13	<0.11	0.073	<0.14	<0.064	<0.083	0.071	<0.11	

 Table C.5
 Crumb - PFAS concentrations (identified above detection limit in at least one sample)

C2.5 Paper Product

Table C.6 Output Product - PFAS concentrations (identified above detection limit in at least one sample)

Site	1 2		3	3 4		5					
WRc Code	X2605	X2606	X2607	X2608	X2609	X2625					
Anonymised Code	Site1-R1	Site2-R1	Site3-R1	Site4-R1	Site5-R1	Site5-R3					
Units	µg/kg										
10:2 diPAP	<0.24	<0.17	<0.31	<0.23	<0.24	42.5					
6:2 FTSA; 6:2 FTS	<0.13	<0.11	1.14	0.37	<0.17	<2.7					
PFBS	<0.27	<0.35	2.19	0.25	0.56	<0.36					
PFDA	0.11	0.82	0.085	<0.049	<0.057	<0.13					
PFUnDA, PFUnA; PFUdA	0.069	0.13	<0.072	0.12	0.11	<0.17					

C3 Compound Detection Table

Figure C.6 Below is a table recording what compounds were detected for each site by sample type.

Site	Site 1					Site 2				Site 3				
Sample Type	Input Water	Effluent	Input Paper	Crumb	Paper Product	Input Water	Effluent	Input Paper	Paper Product	Input Water	Effluent	Input Paper	Crumb	Paper Product
PFOS	✓	✓		✓						✓	✓		✓	
PFOA	✓	✓					✓							
PFHxS	✓	✓												
10:2 diPAP				✓			✓	✓				✓		
6:2 diPAP													~	
6:2 FTSA; 6:2 FTS		✓									~	~	~	✓
8:2 diPAP												\checkmark		
EtFOSAA														
PFBS	✓	✓		~						✓	✓			✓
PFBA														
PFDS														
PFDA	✓				✓	✓	~		✓			✓		✓
PFDoDA, PFDoA														
PFHpS													\checkmark	
PFHpA		✓		\checkmark			✓							
PFHxA	✓	✓					✓			✓	✓			
PFNS														
PFNA		✓					✓				✓			
PFOSA, FOSA														
PFPeS														
PFPeA		✓	✓								✓			
PFUnDS														
PFUnDA, PFUnA; PFUdA			~	\checkmark	✓							~	~	

Table C.7	PFAS identified above limit of detection (Site 1 – 3)											
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Site		Site 4		Site 5								
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Sample Type	Input Paper	Crumb	Paper Product	Input Water	Effluent	Input Paper	Crumb	Paper Product				
PFOS				✓	✓		✓					
PFOA												
PFHxS				\checkmark	✓							
10:2 diPAP	✓	✓				✓		✓				
6:2 diPAP												
6:2 FTSA; 6:2 FTS			~									
8:2 diPAP												
EtFOSAA					\checkmark							
PFBS			✓	✓	✓			✓				
PFBA												
PFDS												
PFDA												
PFDoDA, PFDoA												
PFHpS												
PFHpA					✓	\checkmark						
PFHxA				\checkmark	✓	\checkmark						
PFNS												
PFNA					✓							
PFOSA, FOSA												
PFPeS												
PFPeA					✓							
PFUnDS	✓											
PFUnDA, PFUnA; PFUdA	~		✓			✓	~	✓				

Table C.8	PFAS identified above limit of detection (Site 4 – 5
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C4 Instrument Detection Limits

Batch Number	1	2	3	4	5
Sample Material Type		Solid		Liq	uid
Unit			ng		
PFOS	0.00053	0.00040	0.00052	0.00043	0.00045
PFOA	0.0011	0.00075	0.00099	0.00041	0.00044
PFHxS	0.00040	0.00031	0.00041	0.00040	0.00050
10:2 diPAP	0.0049	0.0027	0.0036	0.0035	0.0023
6:2 diPAP	0.0025	0.0017	0.0023	0.0017	0.0012
6:2 FTSA; 6:2 FTS	0.0086	0.0011	0.0088	0.0095	0.011
8:2 diPAP	0.0049	0.0027	0.0036	0.0035	0.0023
EtFOSAA	0.0019	0.0012	0.0017	0.0011	0.00094
PFBS	0.00098	0.00083	0.00095	0.00088	0.00097
PFBA	0.039	0.031	0.021	0.041	0.029
PFDS	0.00014	0.00010	0.00013	0.00011	0.00009
PFDA	0.00041	0.00029	0.00038	0.00033	0.00029
PFDoDA, PFDoA	0.00048	0.00036	0.00038	0.00018	0.00016
PFHpS	0.00029	0.00019	0.00026	0.00021	0.00023
PFHpA	0.0032	0.0012	0.0026	0.0017	0.0020
PFHxA	0.0017	0.0015	0.0017	0.00099	0.0012
PFNS	0.00027	0.00019	0.00026	0.00021	0.00020
PFNA	0.00060	0.00045	0.00057	0.00046	0.00045
PFOSA, FOSA	0.00058	0.00041	0.00045	0.00042	0.00040
PFPeS	0.00076	0.00062	0.00075	0.00062	0.00082
PFPeA	0.0063	0.0068	0.0060	0.0058	0.0081
PFUnDS	0.00032	0.00022	0.00028	0.00020	0.00016
PFUnDA, PFUnA; PFUdA	0.00055	0.00040	0.00047	0.00041	0.00037

Table C.9 Instrumental Detection Limit for Each Run of Analysis

Samples included in each batch number (for a full list of sample code see Report UC16748.1):

1. X2581, X2625, X2593, X2557, X2594, X2582, X2545, X2570

2. X2569, X2565, X2577, X2589, X2553, X2540, X2541, X2590, X2578, X2566, X2608, X2605

- 3. X2598, X2574, X2549, X2586, X2548, X2597, X2585, X2573, X2561, X2544
- 4. X2539, X2543, X2552, X2556, X2560, X2576, X2588, X2592, X2596
- 5. X2538, X2542, X2546, X2547, X2551, X2555, X2559, X2563, X2564, X2567, X2568, X2571, X2572, X2575, X2579, X2580, X2583, X2584, X2587, X2591, X2595, X2614, X2615

C5 Blank Results

Sample Type	Solid									
Batch Number	1	3								
Blank Number	1	2	3	4						
Units		μg	/kg							
PFOS	<0.16	<0.11	0.13	0.26						
PFOA	0.52	0.43	0.51	0.54						
PFHxS	<0.10	0.088	<0.073	0.081						
10:2 diPAP	<0.93	7.83	10.82	<0.36						
6:2 diPAP	<0.46	<0.17	<0.16	<0.28						
6:2 FTSA; 6:2 FTS	<2.5	<0.14	<0.14	<1.5						
8:2 diPAP	<0.93	<0.26	<0.23	<0.36						
EtFOSAA	<0.44	<0.17	<0.16	1.60						
PFBS	<0.26	<0.21	<0.20	<0.17						
PFBA	<13.6	<2.8	<2.6	<2.5						
PFDS	<0.040	0.068	0.037	<0.027						
PFDA	0.13	<0.046	<0.041	0.18						
PFDoDA, PFDoA	0.93	0.81	0.86	1.01						
PFHpS	<0.086	<0.054	<0.053	<0.054						
PFHpA	<0.96	0.30	0.25	<0.54						
PFHxA	<0.49	0.32	0.26	<0.34						
PFNS	<0.078	<0.054	<0.052	<0.054						
PFNA	<0.19	0.15	0.089	<0.13						
PFOSA, FOSA	<0.20	<0.074	<0.067	<0.097						
PFPeS	<0.20	<0.16	<0.14	<0.13						
PFPeA	<2.1	<1.2	<1.2	<1.2						
PFUnDS	<0.093	<0.063	0.065	<0.058						
PFUnDA, PFUnA; PFUdA	<0.16	<0.068	<0.060	0.10						

Table C.10 Solid Blank Results for Each Testing Batch

Sample Type	Liquid												
Batch Number	2	1		Ę	5								
Blank Number	5	6	7	8	9	10							
Units			μg/l										
PFOS	<0.0008	<0.0009	<0.00062	<0.00067	<0.00068	<0.0007							
PFOA	0.0031	0.0020	0.0019	0.0020	0.0017	0.0021							
PFHxS	<0.00083	<0.00089	<0.00067	<0.00072	<0.00076	<0.00073							
10:2 diPAP	<0.0058	<0.0074	<0.0033	<0.0059	<0.0043	<0.0033							
6:2 diPAP	<0.0027	<0.0032	<0.0018	<0.0029	<0.0024	<0.0021							
6:2 FTSA; 6:2 FTS	<0.017	<0.019	<0.015	<0.015	<0.016	<0.017							
8:2 diPAP	<0.0058	<0.0074	<0.0033	<0.0059	<0.0043	<0.0033							
EtFOSAA	<0.002	<0.0021	<0.0013	<0.0015	<0.0014	<0.0015							
PFBS	<0.0028	<0.0038	<0.0013	<0.0014	<0.0015	<0.0013							
PFBA	<0.048	<0.055	<0.022	<0.025	<0.022	<0.026							
PFDS	<0.0002	<0.00022	<0.00012	0.0002	<0.00014	<0.00014							
PFDA	<0.00048	<0.00054	<0.00038	<0.00041	<0.00043	<0.00044							
PFDoDA, PFDoA	0.0022	0.0019	0.0018	0.0021	0.0022	0.0021							
PFHpS	<0.0004	<0.00045	<0.00032	<0.00034	<0.00035	<0.00036							
PFHpA	<0.0035	<0.0037	<0.0028	<0.003	<0.0031	<0.0031							
PFHxA	<0.0025	<0.0028	<0.0017	<0.0018	<0.0018	<0.0018							
PFNS	<0.00039	<0.00044	<0.00027	<0.00029	<0.0003	<0.00031							
PFNA	<0.00081	<0.00094	<0.00063	<0.00068	<0.00069	<0.00074							
PFOSA, FOSA	<0.0011	<0.0012	<0.00079	<0.00096	<0.0009	<0.00093							
PFPeS	<0.002	<0.0027	<0.0011	<0.0012	<0.0013	<0.0012							
PFPeA	<0.015	<0.016	<0.011	<0.013	<0.013	<0.012							
PFUnDS	<0.00037	<0.00042	<0.00022	<0.00023	<0.00024	<0.00025							
PFUnDA, PFUnA; PFUdA	<0.00074	<0.00084	<0.0005	<0.00059	<0.00056	<0.0006							

Table C.11 Liquid Blank Results for Each Testing Batch

C6 Internal Standard recovery

PFAS Compound	PFAS Internal Standard Used
PFOS	M8PFOS
PFOA	MPFOA
PFHxS	MPFHxS
10:2 diPAP	M4-8:2diPAP*
6:2 diPAP	M4-6:2diPAP
6:2 FTSA; 6:2 FTS	M2-6:2FTS
8:2 diPAP	M4-8:2diPAP
EtFOSAA	d5-N-EtFOSSA
PFBS	MPFBS
PFBA	MPFBA
PFDS	M8PFOS*
PFDA	M2PFDA
PFDoDA, PFDoA	MPFDoA
PFHpS	M8PFOS*
PFHpA	MPFHpA
PFHxA	MPFHxA
PFNS	M8PFOS*
PFNA	MPFNA
PFOSA, FOSA	MFOSA
PFPeS	MPFHxS*
PFPeA	M3PFPeA
PFUnDS	M8PFOS*
PFUnDA, PFUnA; PFUdA	M7PFUdA

Table C.12 Internal Standard Reference Table

*Samples where the true internal standard was not used.

Sample Type		So	lid		Water							
Unit					Recov	/ery %						
Blank Number	1	2	3	4	5	6	7	8	9	10		
PFOS	78	82	84	112	113	101	152	141	138	134		
PFOA	71	108	116	94	98	87	141	132	130	124		
PFHxS	89	91	99	133	100	94	155	146	138	143		
10:2 diPAP	121	235	266	230	125	98	144	81	111	143		
6:2 diPAP	126	222	238	192	134	113	136	86	102	116		
6:2 FTSA; 6:2 FTS	79	172	171	132	118	106	153	147	136	133		
8:2 diPAP	121	235	266	230	125	98	144	81	111	143		
EtFOSAA	101	164	185	132	118	110	149	130	138	130		
PFBS	85	92	94	129	66	49	151	149	137	151		
PFBA	66	252	276	194	182	157	277	247	284	238		
PFDS	78	82	84	112	113	101	152	141	138	134		
PFDA	87	146	165	126	145	129	155	165	154	166		
PFDoDA, PFDoA	81	133	157	121	115	106	147	125	133	122		
PFHpS	78	82	84	112	113	101	152	141	138	134		
PFHpA	76	122	132	110	106	98	153	142	136	135		
PFHxA	80	125	139	115	82	75	151	140	136	138		
PFNS	78	82	84	112	113	101	152	141	138	134		
PFNA	72	120	132	103	119	103	150	139	136	127		
PFOSA, FOSA	68	128	141	106	82	75	105	87	93	89		
PFPeS	89	91	99	133	66	49	155	146	138	143		
PFPeA	69	125	135	113	82	75	150	133	130	143		
PFUnDS	78	82	84	112	113	101	152	141	138	134		
PFUnDA, PFUnA; PFUdA	79	136	153	118	116	102	154	131	137	127		

Table C.13 Blank – Percentage Internal Standard (%IS) Recovery

Round	R1						R	2		R3			
Unit						Re	covery	' %					
Sample Type	IW	Е	IP	С	Р	IW	Е	IP	С	IW	Е	IP	С
PFOS	104	105	74	65	54	105	113	51	72	102	98	89	82
PFOA	105	102	115	89	72	102	92	44	63	99	100	47	66
PFHxS	112	106	81	83	64	105	98	63	90	103	113	96	101
10:2 diPAP	87	216	265	286	199	128	181	72	156	108	110	99	160
6:2 diPAP	104	178	112	133	92	133	187	48	84	103	150	45	64
6:2 FTSA; 6:2 FTS	135	205	213	200	152	134	173	87	105	138	193	96	143
8:2 diPAP	87	216	265	286	199	128	181	72	156	108	110	99	160
EtFOSAA	95	124	121	128	99	107	114	61	87	79	118	48	88
PFBS	68	74	67	74	55	60	69	67	75	54	83	86	90
PFBA	227	153	224	162	212	213	119	134	82	170	171	95	178
PFDS	104	105	74	65	54	105	113	51	72	102	98	89	82
PFDA	157	155	160	131	105	162	157	73	84	155	144	57	93
PFDoDA, PFDoA	90	101	134	104	93	97	109	56	75	69	121	46	78
PFHpS	104	105	74	65	54	105	113	51	72	102	98	89	82
PFHpA	123	116	146	128	103	117	93	63	87	115	119	57	95
PFHxA	100	91	140	116	93	95	78	69	79	92	101	49	90
PFNS	104	105	74	65	54	105	113	51	72	102	98	89	82
PFNA	119	121	146	114	99	120	114	56	76	122	117	53	86
PFOSA, FOSA	94	126	71	38	43	100	128	30	30	76	125	24	35
PFPeS	112	74	81	83	64	105	69	63	90	103	113	96	101
PFPeA	87	91	118	104	91	84	78	75	97	70	99	51	93
PFUnDS	104	105	74	65	54	105	113	51	72	102	98	89	82
PFUnDA, PFUnA; PFUdA	93	101	188	128	111	102	116	61	82	76	138	55	90

 Table C.14
 Site 1 – Percentage Internal Standard (%IS) Recovery

*IW=Input Water, E=Effluent, IP=Input Paper, C=Crumb and P=Product.

Round		R	1			R2		R3			
Unit					Recov	very %		•			
Sample Type	IW	Е	IP	Р	IW	Е	IP	IW	Е	IP	
PFOS	135	103	59	60	146	88	74	134	93	106	
PFOA	127	91	87	76	135	88	75	128	82	94	
PFHxS	151	83	59	69	153	56	86	155	90	116	
10:2 diPAP	101	240	228	304	129	249	72	124	248	195	
6:2 diPAP	83	157	138	167	138	121	79	109	136	131	
6:2 FTSA; 6:2 FTS	160	248	194	184	162	228	108	147	218	193	
8:2 diPAP	101	240	228	304	129	249	72	124	248	195	
EtFOSAA	125	120	130	119	132	106	79	133	102	112	
PFBS	150	71	36	46	152	64	69	147	71	91	
PFBA	223	160	168	157	279	142	77	262	151	189	
PFDS	135	103	59	60	146	88	74	134	93	106	
PFDA	149	112	141	104	155	128	87	151	125	120	
PFDoDA, PFDoA	100	115	139	130	126	112	80	116	111	116	
PFHpS	135	103	59	60	146	88	74	134	93	106	
PFHpA	142	87	105	99	141	89	87	140	79	117	
PFHxA	136	82	78	78	137	88	86	135	73	91	
PFNS	135	103	59	60	146	88	74	134	93	106	
PFNA	139	105	119	103	143	100	82	134	98	110	
PFOSA, FOSA	123	77	59	57	129	77	47	120	73	65	
PFPeS	151	71	59	69	153	64	86	155	71	116	
PFPeA	132	82	68	66	134	88	194	130	73	90	
PFUnDS	135	103	59	60	146	88	74	134	93	106	
PFUnDA, PFUnA; PFUdA	106	133	185	160	134	137	94	119	125	139	

 Table C.15
 Site 2 – Percentage Internal Standard (%IS) Recovery

*IW=Input Water, E=Effluent, IP=Input Paper and P=Product.

Round	R1						R	2		R3			
Unit						Re	covery	/ %					
Sample Type	IW	Е	IP	С	Р	IW	Е	IP	С	IW	Е	IP	С
PFOS	142	106	75	68	53	141	100	75	95	142	120	108	115
PFOA	134	113	110	91	74	133	99	111	74	132	121	94	106
PFHxS	155	142	77	77	60	153	114	87	98	138	139	131	140
10:2 diPAP	118	73	231	216	179	98	44	277	104	92	91	217	187
6:2 diPAP	124	85	135	114	153	87	76	146	84	118	183	159	120
6:2 FTSA; 6:2 FTS	152	230	250	193	125	159	175	243	103	153	219	186	220
8:2 diPAP	118	73	231	216	179	98	44	277	104	92	91	217	187
EtFOSAA	133	127	133	149	129	133	117	149	93	133	153	163	140
PFBS	152	106	69	79	55	149	82	81	98	151	92	119	133
PFBA	252	205	248	275	172	252	207	271	88	276	264	199	301
PFDS	142	106	75	68	53	141	100	75	95	142	120	108	115
PFDA	151	156	161	133	110	150	189	155	76	150	140	136	131
PFDoDA, PFDoA	122	73	142	121	109	112	79	157	81	124	133	136	134
PFHpS	142	106	75	68	53	141	100	75	95	142	120	108	115
PFHpA	142	139	134	146	103	152	124	152	92	139	158	133	169
PFHxA	148	121	132	147	104	149	109	159	95	139	130	127	169
PFNS	142	106	75	68	53	141	100	75	95	142	120	108	115
PFNA	142	116	138	141	99	146	112	142	88	140	159	125	152
PFOSA, FOSA	139	121	87	55	91	135	94	90	41	132	127	81	58
PFPeS	155	142	77	77	60	153	114	87	98	138	139	131	140
PFPeA	133	120	115	154	88	137	101	139	141	140	122	123	171
PFUnDS	142	106	75	68	53	141	100	75	95	142	120	108	115
PFUnDA, PFUnA; PFUdA	126	83	165	129	114	116	91	173	87	127	158	147	154

 Table C.16
 Site 3 – Percentage Internal Standard (%IS) Recovery

*IW=Input Water, E=Effluent, IP=Input Paper, C=Crumb and P=Product.

Round			R1			R2					R3				
Unit							Re	covery	' %						
Sample Type	IW	Е	IP	С	Р	IW	Е	IP	С	IW	E1	E2	FE	IP	С
PFOS	142	94	71	75	75	134	128	102	92	134	116	142	107	89	102
PFOA	137	87	100	109	103	130	122	93	86	131	108	134	99	66	89
PFHxS	148	153	85	106	87	155	163	117	108	148	159	175	159	106	148
10:2 diPAP	126	160	264	148	270	123	125	124	129	124	157	15	112	94	85
6:2 diPAP	113	88	162	138	228	109	95	154	97	99	106	25	98	116	101
6:2 FTSA; 6:2 FTS	158	169	174	183	159	146	194	119	119	140	160	179	149	102	133
8:2 diPAP	126	160	264	148	270	123	125	124	129	124	157	15	112	94	85
EtFOSAA	136	113	114	130	151	117	133	103	96	124	63	141	79	88	98
PFBS	152	99	83	102	85	153	146	116	122	149	117	200	71	102	145
PFBA	290	198	227	178	147	287	270	107	98	303	191	307	244	131	148
PFDS	142	94	71	75	75	134	128	102	92	134	116	142	107	89	102
PFDA	145	63	115	128	138	141	95	100	107	145	142	149	118	82	111
PFDoDA, PFDoA	120	68	107	126	135	100	104	103	96	102	85	84	86	70	94
PFHpS	142	94	71	75	75	134	128	102	92	134	116	142	107	89	102
PFHpA	144	94	115	130	114	140	153	109	89	138	119	167	119	76	105
PFHxA	142	90	121	138	126	141	146	113	110	140	105	174	109	79	105
PFNS	142	94	71	75	75	134	128	102	92	134	116	142	107	89	102
PFNA	143	53	100	123	115	133	133	95	89	134	77	141	79	74	87
PFOSA, FOSA	135	60	61	90	116	115	112	66	51	130	75	117	66	71	61
PFPeS	148	99	85	106	87	155	163	117	108	148	159	175	159	106	148
PFPeA	143	90	111	121	117	135	142	87	90	138	109	185	77	74	102
PFUnDS	142	94	71	75	75	134	128	102	92	134	116	142	107	89	102
PFUnDA, PFUnA; PFUdA	119	77	122	137	137	101	116	106	102	105	101	91	99	75	105

 Table C.17
 Site 4 – Percentage Internal Standard (%IS) Recovery

*IW=Input Water, E=Effluent, IP=Input Paper, C=Crumb, P=Product, FE-Final Effluent, E1= Process 1 Effluent and E2=Process 2 Effluent.

Round	R1						R	2		R3				
Unit						•	Recov	very %						
Sample Type	IW	Е	IP	С	Р	IW	Е	IP	С	IW	Е	IP	С	Р
PFOS	110	90	74	77	50	125	88	74	99	123	85	100	92	60
PFOA	115	70	107	116	69	123	79	68	101	126	82	101	102	55
PFHxS	129	73	71	94	52	138	71	75	112	147	74	105	115	71
10:2 diPAP	105	95	395	309	231	108	77	111	146	98	65	240	143	37
6:2 diPAP	73	124	220	123	142	103	120	78	96	89	111	108	58	83
6:2 FTSA; 6:2 FTS	147	142	249	270	126	150	160	102	160	157	167	164	169	69
8:2 diPAP	105	95	395	309	231	108	77	111	146	98	65	240	143	37
EtFOSAA	100	100	185	146	109	107	103	76	108	91	116	90	86	67
PFBS	132	56	60	82	42	144	49	59	110	151	56	73	103	57
PFBA	216	95	197	238	171	213	109	69	122	213	113	154	188	64
PFDS	110	90	74	77	50	125	88	74	99	123	85	100	92	60
PFDA	130	120	182	166	104	120	129	75	120	115	145	106	108	65
PFDoDA, PFDoA	77	95	186	127	105	95	106	72	92	75	108	87	77	66
PFHpS	110	90	74	77	50	125	88	74	99	123	85	100	92	60
PFHpA	125	73	125	148	86	132	84	75	115	134	89	99	95	67
PFHxA	122	62	98	126	88	128	69	64	112	138	77	87	99	63
PFNS	110	90	74	77	50	125	88	74	99	123	85	100	92	60
PFNA	119	88	134	130	91	125	101	73	103	126	106	98	85	60
PFOSA, FOSA	113	107	109	41	78	122	122	40	41	114	122	56	35	49
PFPeS	129	56	71	94	52	138	49	75	112	147	56	105	115	71
PFPeA	121	62	96	136	69	124	69	79	218	131	77	69	98	66
PFUnDS	110	90	74	77	50	125	88	74	99	123	85	100	92	60
PFUnDA, PFUnA; PFUdA	77	97	240	167	113	96	112	77	105	78	107	100	102	70

 Table C.18
 Site 5 – Percentage Internal Standard (%IS) Recovery

*IW=Input Water, E=Effluent, IP=Input Paper, C=Crumb and P=Product.

C7 Fortified Reagent Blanks

Sample Type	Blank	Deionised Water			Wastewater Sample				
Spike Concentration (ng/l)	0	0.5	10	50	0.5	10	50		
Unit	ng/l								
PFBA	8.08	0.56	5.01	46.44	2.42	9.90	33.34		
PFPeA	1.17	2.13	10.29	40.19	0.56	15.53	67.11		
PFHxA	2.51	2.12	11.40	52.64	1.07	8.92	48.25		
PFHpA	0.67	1.41	9.73	49.54	6.07	5.69	82.92		
PFOA	42.45	8.15	17.90	54.27	4.72	13.16	45.46		
PFNA	0.86	2.57	8.96	44.69	1.76	4.22	43.81		
PFDA	4.90	1.60	10.92	27.07	2.79	9.35	61.09		
PFUdA	1.07	0.85	10.54	55.55	1.46	15.95	47.01		
PFDoA	6.32	12.41	13.74	47.03	7.18	4.39	57.81		
PFBS	0.24	1.60	9.54	47.58	0.67	10.61	49.52		
PFPeS	0.03	0.78	14.86	76.57	0.27	24.03	88.93		
PFHxS	0.24	0.69	11.65	38.66	0.20	5.28	36.20		
PFHpS	0.08	0.73	15.27	84.23	0.94	11.87	90.27		
PFOS	1.97	2.46	11.80	53.73	2.49	21.25	60.95		
PFNS	0.21	0.45	16.81	50.76	0.32	2.67	32.86		
PFDS	0.51	0.48	7.82	42.46	0.55	2.18	11.77		
PFUdS	<lod< td=""><td>0.99</td><td>14.65</td><td>55.66</td><td>0.35</td><td>4.04</td><td>16.69</td></lod<>	0.99	14.65	55.66	0.35	4.04	16.69		
6:2 diPAP	<lod< td=""><td>1.97</td><td>15.84</td><td>59.13</td><td><lod< td=""><td>1.50</td><td>38.18</td></lod<></td></lod<>	1.97	15.84	59.13	<lod< td=""><td>1.50</td><td>38.18</td></lod<>	1.50	38.18		
8:2 diPAP	49.25	1.60	11.09	30.70	4.52	17.85	14.26		
6:2 FTS	1.62	1.47	7.18	44.68	0.74	9.15	24.26		
FOSA	0.01	0.01	0.16	0.83	0.05	0.12	0.66		
NEtFOSAA	8.35	3.98	12.54	48.08	46.22	79.34	103.71		

Table C.19 Fortified Reagent Blank Detection Results (ng/l)

*Due to the low concentration of the spikes this data is reported in ng/l. To covert to µg/l these results would need to be divided by 1,000.

Sample Type		DI Water		Wastewater Sample							
Spike Concentration (ng/l)	0.5	10	50	0.5	10	50					
Unit	Recovery %										
PFBA	112	50	93	484	99	67					
PFPeA	427	103	80	112	155	134					
PFHxA	424	114	105	214	89	97					
PFHpA	283	97	99	1214	57	166					
PFOA	1630	179	109	944	132	91					
PFNA	513	90	89	351	42	88					
PFDA	321	109	54	558	93	122					
PFUdA	171	105	111	292	160	94					
PFDoA	2483	137	94	1436	44	116					
PFBS	321	95	95	134	106	99					
PFPeS	157	149	153	54	240	178					
PFHxS	138	116	77	39	53	72					
PFHpS	146	153	168	188	119	181					
PFOS	491	118	107	497	212	122					
PFNS	89	168	102	63	27	66					
PFDS	96	78	85	109	22	24					
PFUdS	199	147	111	71	40	33					
6:2 diPAP	393	158	118	-	15	76					
8:2 diPAP	321	111	61	904	178	29					
6:2 FTS	294	72	89	149	92	49					
FOSA	2.0	1.6	1.7	9.1	1.2	1.3					
NEtFOSAA	797	125	96	9244	793	207					

Table C.20 Fortified Reagent Blank Percentage Recovery