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PFAS IN FIBRE-BASED PACKAGING

APCO AUSTRALIAN PACKAGING COVENANT ORGANISATION

Contents

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Acknowledgments

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Executive Summary

Per- and polyfluoroalkyl substances (PFAS) are a group of more than 4700 synthetic organic compounds. They are very resistant to heat, stains, grease and water, which makes them useful for a range of applications, including some food packaging. They are also resistant to degradation in the environment, which makes them potential environmental pollutants.

The Commonwealth and state and territory governments have developed the National PFAS Position Statement, which establishes that industry participants should inform themselves about the presence of PFAS in their products, and phase them out where possible. This study piloted a scientific methodology to identify the presence and type of PFAS in a range of fibre-based, food contact packaging, and understand potential implications for recycled content in packaging and compostable packaging.

A total of 74 confidential packaging samples were provided by nine APCO Member companies for analysis. Scientific testing of the samples was performed in two phases. First, all 74 samples were screened using a high-throughput method for 'total fluorine', which is an indicator of PFAS. In the second phase, a subset of 35 samples were then tested to see whether they contained 28 specific members of the PFAS family. These 28 PFAS are readily identifiable through established scientific testing.

The Phase 1 results indicated that just over a quarter of the samples contained high levels of PFAS (above 800 ppm). The samples with high total fluorine were concentrated in the 'bagasse' category of packaging products. Other packaging types had variable levels of PFAS. Roughly a quarter of the samples tested had no detectable PFAS.

When the samples with high total fluorine were tested for 28 specific PFAS in Phase 2, these 28 PFAS did not appear in most cases. This indicates that other members of the PFAS family are responsible for the Phase 1 results. A TOPA analysis confirmed the likely presence of unknown PFAS 'precursors' and other 'polymeric' PFAS. While the identity of these unknown PFAS cannot be easily determined, unidentified PFAS should be treated in the same way as known PFAS and steps taken to transition them out of packaging.

This study did not consider the migration of PFAS into food, but instead focused on understanding the relevance of PFAS in packaging in the context of a circular economy. Food Standards Australia New Zealand (FSANZ) has undertaken several surveys of PFAS in the Australian food supply including packaged foods. The most recent of these, the 27th Australian Total Diet Study (2021) looked at PFAS levels in a broad range of Australian foods and beverages. The study found that PFAS levels in the general Australian food supply are very low and there are no food safety concerns. An overview of FSANZ's work on PFAS can be found on the FSANZ **website**.

In the context of a circular economy, PFAS in fibre-based recyclable or compostable packaging have the potential to contaminate recovery systems over time. If composted, most of these chemicals will not break down, and those that do will form other PFAS. If recycled, these chemicals may transfer to recycled products – though this has not yet been confirmed in Australia. To avoid these problems, APCO is working with industry to deliver a phase-out of PFAS in fibre-based, food contact packaging – consistent with the objectives of the National PFAS Position Statement.

The outcomes of the study illustrate the value of testing for PFAS using a screening approach, and combined with the National PFAS Position Statement, provide the impetus to develop an Action Plan to phase out PFAS in packaging.

Introduction

PURPOSE

The purpose of this study was to pilot a scientifically rigorous methodology to identify the presence and types of per- and polyfluoroalkyl substances (PFAS) in a range of fibre-based, food-contact packaging, and potential implications for recycled content in packaging and compostable packaging. The study focused on fibre-based, food-contact packaging. The international literature has identified that PFAS are often added to this type of packaging as a barrier to heat, grease and water.

WHAT ARE PFAS?

PFAS are a group of several thousand synthetic organic compounds. The characteristic feature of all PFAS molecules is the carbon-fluorine bond, which is the strongest chemical bond in nature and makes these chemicals highly resistant to heat, stains, grease and water. These properties make PFAS chemicals useful for a range of applications, including some food packaging.

However, PFAS are also very resistant to degradation in the environment, which makes them potential environmental pollutants. Some types of PFAS are known to be toxic and to bioaccumulate in organisms.

More information on PFAS can be found in Appendix 1.

INTERGOVERNMENTAL AGREEMENT AND NATIONAL PFAS POSITION STATEMENT

In February 2018, the Commonwealth and state and territory governments established the Intergovernmental Agreement on a National Framework for Responding to PFAS Contamination[1] (the Intergovernmental Agreement), revised in February 2020, which supports collaboration and cooperation between jurisdictions to respond consistently and effectively to PFAS contamination. The Intergovernmental Agreement establishes that a precautionary approach should be taken to PFAS exposure, stating that:

> *"While it is clear that PFAS can persist in humans, animals and the environment, understanding of the human health effects of long-term PFAS exposure is still developing. As a precaution, governments in Australia recommend that exposure be reduced wherever possible while research into any potential health effects continues".*

Governments have also agreed, and included as Appendix D to the Intergovernmental Agreement, the National per- and polyfluoroalkyl substances (PFAS) Position Statement. The purpose of the National PFAS Position Statement is set out as:

> *"All Australian governments agree that further release of PFAS into the environment from ongoing use should be prevented where practicable, and that actions to reduce or phase out the use of PFAS should be nationally consistent.*
>
> *The purpose of this Position Statement is to outline a nationally unified vision for reducing future PFAS use in Australia, so that governments and PFAS users (whether industry, businesses, manufacturers, regulators, or policy-makers) can work towards an agreed and clear set of objectives.*
>
> *This Position Statement seeks to encourage discussion with industry and other stakeholders about how PFAS should be managed… It does not, in itself, impose regulatory measures, time-frames or create mechanisms for controlling PFAS use."*

The Position Statement establishes that transitioning away from PFAS should be the ultimate goal in Australia, and states that:

> *"Importers, sellers and users of chemicals should inform themselves about the presence of PFAS in products and articles, due to their potential negative environmental, health and socioeconomic impacts.*
>
> *Entities that currently sell or use long- or short-chain PFAS are encouraged to develop a strategy that outlines their current uses, and how and when they will transition away from these chemicals."*

The Position statement also recognised that:

> *"Until effective and economically feasible non-PFAS alternatives are developed, the ongoing sale and use of products and articles containing short-chain PFAS may be necessary for uses for which no suitable and less hazardous alternatives are available".*

[1] Intergovernmental Agreement on a National Framework for Responding to PFAS Contamination available at https://federation.gov.au/about/agreements/intergovernmental-agreement-national-framework-respondingpfas-contamination

Provision of samples for testing

Packaging samples were provided for this study by nine APCO Member companies, including packaging manufacturers, major retailers, and a quick service restaurant chain. The fibre-based food packaging samples that were provided were categorised into seven categories (Table 1 – below).

These categories of fibre-based, food-contact packaging have been shown to contain PFAS in international studies. PFAS are added as a barrier to heat, grease and water. While some information on the origin and nature of the packaging was provided along with the samples, this did not include complete information on recycled content and compostability.

Table 1 - Categories of packaging provided for testing

	Packaging Category
1	Baked goods packaging (e.g. cake boxes), muffin cups, greaseproof paper, butter wrap
2	Bags, chips (crisps) and microwave popcorn packaging, cake mix bags
3	Paperboard food boxes, e.g. pizza boxes, takeaway boxes, salad boxes, hot chip boxes
4	Fast food wrappers, burgers, chip bags, sandwich wraps
5	Clamshell-style products not listed elsewhere
6	Pails, cups, and buckets for food and hot drinks
7	Bagasse packaging
8	Not easily classified

Scientific testing of the samples was performed in two phases. The first phase of testing involved screening all samples for 'total fluorine' which is an indicator of PFAS. In the second phase, a subset of 35 samples underwent more detailed testing to determine whether certain specific types of PFAS could be identified in the samples. This method is based on an approach published in the scientific literature for testing for PFAS in fast food packaging in the US.[2]

[2] Laurel A. Schaider, Simona A. Balan, Arlene Blum, David Q. Andrews, Mark J. Strynar, Margaret E. Dickinson, David M. Lunderberg, Johnsie R. Lang, and Graham F. Peaslee Environmental Science & Technology Letters **2017** 4 (3), 105-111

Phase 1: Total fluorine concentration using particle-induced gamma-ray emission (PIGE) analysis

METHODOLOGY

In Phase 1, 74 samples were subjected to particle-induced gamma-ray emission (PIGE) analysis at the Australian Nuclear Science and Technology Organisation (ANSTO). This method measures the 'total fluorine' content of each sample, and can be done relatively quickly.

Total fluorine content is an indicator of the presence of PFAS. High total fluorine indicates high concentrations of PFAS, low/no total fluorine indicates low/no PFAS. However, this analysis does not reveal which specific PFAS are present in the samples.

Further detail on the testing methodology is provided in Appendix 1. All samples were tested in duplicate.

PHASE 1 RESULTS

Figure 1 below shows the total fluorine concentrations (in µg/g or ppm) of the duplicate samples tested in Phase 1. Of the 74 samples, 21 samples had average total fluorine concentrations > 800 µg/g. Six samples had medium concentrations of between 200 – 800 µg/g and seven samples had low total fluorine concentrations between 100 – 200 µg/g. A further 19 samples had very low, but detectable total fluorine concentrations of less than 100 µg/g. The remaining 21 samples had no detectable fluorine. The data collected is displayed in Table 3 in Appendix 2.

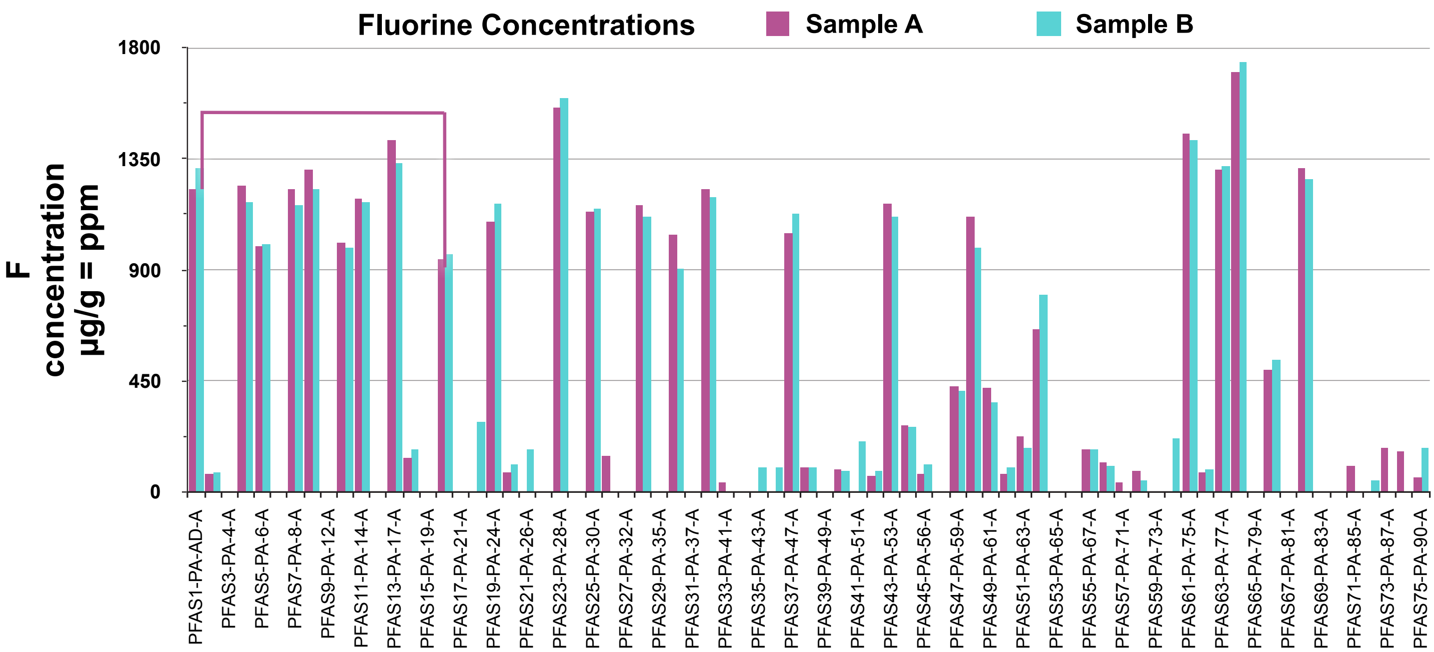

Figure 1 - Total fluorine concentration of each of the 74 samples tested in Phase 1

Table 2 (below) shows the number of packaging samples in each category with high, medium and low total fluorine concentrations, and those with very low or no detectable fluorine levels. The highest average levels of total fluorine were found in samples from Category 7 - Bagasse packaging, of which all 13 samples had average total fluorine concentrations above 800 µg/g. Bagasse is made from sugar cane pulp to create fibre-based packaging that can be moulded into various formats.

In two other categories (Category 2 – Bags, chips (crisps) and microwave popcorn packaging, cake mix bags, and Category 5 – Clamshell style products not listed elsewhere), at least half of the samples had high or medium total fluorine concentrations (50% and 55% respectively). Categories 3, 4 and 6 had relatively few or no samples with high or medium total fluorine concentrations. Just over a quarter of the samples in Category 1 had high or medium total fluorine concentrations.

Table 2 - Total numbers of samples and numbers of samples with high and medium total fluorine concentrations detected in Phase 1 testing

	Packaging Category	Total number of samples	Samples with high total fluorine (>800 µg/g)	Samples with medium total fluorine (200<800 µg/g)	Samples with low total fluorine (100<200 µg/g)	Samples with no detectable or very low total fluorine (<100 µg/g)
1	Baked goods packaging (e.g. cake boxes), muffin cups, greaseproof paper, butter wrap	22	3 (14%)	3 (14%)	2 (9%)	14 (64%)
2	Bags, chips (crisps) and microwave popcorn packaging, cake mix bags	4	1 (25%)	1 (25%)	1 (25%)	1 (25%)
3	Paperboard food boxes, e.g. pizza boxes, takeaway boxes, salad boxes, hot chip boxes	9	0	0	0	9 (100%)
4	Fast food wrappers, burgers, chip bags, sandwich wraps	5	0	1 (20%)	1 (20%)	3 (60%)
5	Clamshell style products not listed elsewhere	9	4 (44%)	1 (11%)	2 (22%)	2 (22%)
6	Pails, cups, and buckets for food and hot drinks	7	0	0	1 (14%)	6 (86%)
7	Bagasse packaging	13	13 (100%)	0	0	0
8	Not easily classified	5	0	0	0	5 (100%)
	TOTAL	74	21 (28%)	6 (8%)	7 (9%)	40 (54%)

Phase 2: Detection and quantification of target PFAS

METHODOLOGY

Of the 74 packaging samples, 35 were selected for further analysis. These samples were tested for 28 common members of the PFAS family. These 28 PFAS are readily identifiable through established experimental techniques.

The samples selected for Phase 2 included all of the 21 samples with high total fluorine concentrations, as well as additional samples selected to ensure testing of a cross-section of packaging categories from different suppliers, a range of samples with high and low total fluorine concentrations, and some samples that had duplicates with inconsistent low total fluorine levels in Phase 1. Ten of the 35 samples were selected at random to be tested in duplicate to check for reproducibility.

Further detail on the testing methodology is provided in Appendix 1.

PHASE 2 RESULTS

Of the 35 samples that were tested in Phase 2, very few contained any of the 28 PFAS that were tested for. This indicates that the total fluorine measured in these samples in Phase 1 is due to other members of the PFAS family that cannot be readily identified.

These may include chemicals sometimes referred to as PFAS 'precursors'. Precursors can break down under the right conditions into simpler, more common PFAS – including the 28 that can be tested for.

The presence of some PFAS precursors was confirmed through a Total Oxidisable Precursor Assay (TOPA) analysis. In the TOPA analysis the packaging samples were exposed to harsh conditions that can break down precursors. After treatment, the samples were tested and some of the 28 identifiable PFAS appeared. However, the TOPA results did not account for all of the fluorine measured in Phase 1 (i.e. more PFAS was detected in Phase 1 than appeared after TOPA and Phase 2 testing). This again indicates that other, still unidentified PFAS are also present. More detail about the TOPA analysis can be found at Appendix 1.

The packaging manufacturers and suppliers were unable to assist by narrowing down the possibilities because they use proprietary PFAS formulations from overseas companies.

Little is known globally about the specific PFAS used in packaging. The OECD has recently published a report on PFAS in packaging that highlights this knowledge gap.[3] One possible explanation for the 'missing' fluorine between Phases 1 and 2 is the use of 'perfluoropolyethers'. Perfluoropolyethers are a class of PFAS that have historically been used in packaging.[4] These long, chain-like chemicals do not break down easily – even under the harshest conditions (e.g. TOPA). Therefore, these PFAS would be detected in Phase 1 but not in Phase 2, and may explain the observed results.

[3] OECD (2020), PFASs and Alternatives in Food Packaging (Paper and Paperboard) Report on the Commercial Availability and Current Uses, OECD Series on Risk Management, No. 58, Environment, Health and Safety, Environment Directorate, OECD.
[4] Moffett, et al., Perfluoroalkylpolyethers. In Synthetics, Mineral Oils, and Bio-Based Lubricants. Chemistry and Technology, Rudnick, L. R., Ed. Taylor & Francis, 2020.

Discussion and implications of results

This study found that a significant proportion of fibre-based, food contact packaging samples contained PFAS, while 54% of samples either contained no detectable levels of PFAS or very low detectable levels. Of the 74 samples tested, 21 samples (28%) had high total fluorine concentrations, 6 samples (8%) had medium concentrations and 7 samples (9%) had low total fluorine concentrations.

High total fluorine concentrations (>800 µg/g) are an indicator of intentionally added PFAS. At low and very low levels (below 200 µg/g total fluorine) it is more difficult to conclude that the concentrations are due primarily to intentionally added PFAS. A possible source of low concentrations of non-intentionally added PFAS could be from recovered fibre (i.e. recycled paper and cardboard used in manufacturing the packaging). Recycled content is a very important source of raw material in Australia, with over 60% of fibre used in Australia sourced from recycled products. However, it is not possible to draw any conclusions about the presence or effect of recycled content in this study, due to the absence of information on recycled content in the samples tested.

With the exception of **Category 7 – Bagasse packaging**, all categories of packaging had at least some samples with low or no detectable PFAS. This suggests that alternatives to PFAS are available for most types of fibre-based packaging, particularly paper and paperboard in various applications. **Category 3 – Paperboard food boxes**, e.g. pizza boxes, takeaway boxes, salad boxes, hot chip boxes, has many applications that require heat, grease and moisture barriers, but none of the samples were identified with high or medium total fluorine concentrations.

The finding that all samples in Category 7 contained high total fluorine concentrations suggests a heavy dependence on PFAS for this category of packaging products. It also suggests that non-PFAS alternatives are less likely to be currently available than or as effective as PFAS, or at least are not as widely used for bagasse packaging in Australia.

Bagasse packaging is often associated with claims of composability and recyclability. Composting of packaging that contains PFAS contaminates compost. Therefore, it is important that compostability standards account for PFAS, and that packaging materials marketed as 'compostable' do not contain significant levels of PFAS. The Phase 1 screening approach employed in this study can be used to verify this.

Category 5 – Clamshell style products not listed elsewhere also contained a high proportion of samples with high and medium total fluorine concentrations. This category contained products where sufficient information was not available to enable them to be placed in other categories.

Microwave popcorn packaging is the 'poster child' for international studies of PFAS in packaging. The one popcorn packaging sample tested here contained high levels of PFAS, consistent with international observations.

Category 1 - Baked goods packaging (e.g. cake boxes), muffin cups, greaseproof paper, butter wrap included samples with high, medium and low/no total fluorine. This indicates that different products/brands within this category have different reliance on PFAS. For example, amongst the greaseproof paper samples tested, one had a high total F concentration, one had medium and three had low total fluorine concentrations.

COMPARISON WITH TOTAL FLUORINE LIMIT IN THE UNITED STATES

Total fluorine limit for compostable packaging certification in the United States

As of March 2019, the Biodegradable Products Institute (BPI)[5], the largest US certifier of compostable products, requires manufacturers who seek compostability certification to meet standard EN 13432, which sets a 100-µg/g limit for total fluorine. As of January 2020, BPI also requires that manufacturers provide a statement of no intentionally added fluorine.

Implications of this study for industry's response to the National PFAS Position Statement

The results of the analysis were considered in the context of the National PFAS Position Statement, particularly the position that industry should inform itself about the presence of PFAS in its products and develop a strategy to transition away from PFAS.

Approach to testing for PFAS in packaging

The PIGE analysis used in Phase 1 of the study was an efficient and effective methodology to screen for PFAS in fibre-based packaging. The method can be adopted by industry to indicate what levels of PFAS are present in fibre-based packaging samples, and could potentially be used to verify claims about compostability.

The Phase 2 testing did not readily identify any of the 28 PFAS members were tested for – indicating that other members of the PFAS family were present in the packaging samples. The identity of these unknown PFAS cannot be easily determined without further expensive investigation by specialist analytical laboratories that can do untargeted analyses. Unidentified PFAS should be treated in the same way as known PFAS and steps taken to transition these chemicals out of packaging. More detail about the TOPA analysis can be found in Appendix 1.

The value of the Phase 2 results was in demonstrating that some PFAS precursors were likely present, along with other unidentifiable PFAS. While this provided useful insights in the context of the current study, Phase 2-type testing is likely to be of more limited value for businesses that want to screen for PFAS in packaging because it can only identify a very limited number of PFAS (a few dozen out of several thousand). Where these are not detected, the identity of the PFAS remains unknown.

Consideration could be given to further refining the methodology used in this study, including with regard to:

- Sample preparation: The sampling technique used in this study was manual and time consuming. Some form of automation of the task by the testing facility may prove worthwhile providing that cross contamination can be avoided.
- Location of sampling points: Some packaging types involve combinations of surfaces in three dimensions and therefore different surfaces that may need to be sampled and replicated.

Phasing out PFAS in fibre-based, food-contact packaging in Australia

Fibre-based food contact packaging placed on the market includes both certified compostable packaging and other packaging. The amount of certified compostable fibre-based packaging placed on the market in Australia is currently very small – around 10,000 tonnes in 2019-20. A similar amount of fibre packaging (mostly cardboard) was disposed into organics collections in 2019–20 (this estimate is based on a small survey of composters nationally and is indicative only)[6]. However, the identified potential of compostable packaging to support increased recovery of food waste and the current policy focus on compostable packaging as an alternative to single-use plastics in some jurisdictions suggests that the amount of compostable, fibre-based food contact packaging placed on the market and collected for composting will increase in the coming years.

Given the presence of high concentrations of PFAS in 28% of the samples and medium concentrations of PFAS in 8% of the samples in this study, it is appropriate that industry develop an action plan to transition away from PFAS in this type of packaging.

In the context of a circular economy, PFAS in recyclable or compostable packaging have the potential to contaminate recovery systems over time. If composted, most of these chemicals will not break down, and those that do will form other fluorochemicals. Composting packaging containing PFAS will therefore result in contaminated compost. The unknown identity of the PFAS used in packaging, their potential toxicity and bioaccumulation properties, and their definite persistence in the environment mean ongoing use in compostable packaging should be avoided where practicable – in line with the objectives of the National PFAS Position Statement. If recycled, these chemicals may accumulate in packaging and more work is needed to understand both the potential for accumulation in recycled content as well the bioaccumulation rate.

In response to the findings of this study the Australian Government and APCO are working with industry to deliver a phase-out of PFAS in packaging in Australia. This may include thresholds for PFAS in packaging, and a methodology for screening packaging products against these thresholds.

[6] APCO report: Australian Packaging Consumption and Recycling Data 2019-20

Conclusion

The National PFAS Position Statement sets out a precautionary approach to identifying and the presence of PFAS in products and phasing out the use of PFAS where it is possible to do so.

This study has successfully piloted a methodology that can be used by industry to test fibre-based packaging for the presence PFAS. APCO encourages companies in the packaging supply chain to use this methodology to inform themselves about the presence of PFAS in the products they are putting on the market.

This report will be followed by further guidance to support and assist industry to identify alternatives to PFAS and phase out PFAS in packaging.

Phasing out PFAS will meet the expectations set in the National PFAS Position Statement. It will also ensure that the presence of PFAS does not become a barrier to realising the potential of compostable food packaging to support the greater recovery of food waste and contribute to the phase-out of problematic and unnecessary single-use plastic packaging. APCO looks forward to working with its Members and stakeholders on the development and implementation of the Action Plan.

Appendix 1: Additional information about this study

WHAT ARE PFAS?

PFAS are per- and polyfluoroalkyl substances, a group of several thousand synthetic organic compounds.[7] The characteristic feature of PFAS molecules is the carbon-fluorine bond (see Figure 2), which is the strongest chemical bond in nature. This makes these chemicals very resistant to heat, stains, grease and water, which makes them useful chemicals for a range of applications. They are used in products as diverse as non-stick cookware, stain-resistant furniture and carpet, electrical wire insulation, waterproof clothing, cosmetics, medical devices, some types of firefighting foam, and certain types of food packaging materials.

PFAS are also very resistant to degradation in the environment, which makes them potential environmental pollutants. Some members of the PFAS family have other properties of concern. For example, some are well-known to be toxic to organisms, and to bioaccumulate (build-up) in organisms. 'Long-chain' PFAS are of greatest concern, as they can be highly mobile in water (which means they travel long distances from their source-point); they do not fully break down naturally in the environment; they can build up in the bodies of animals and humans and can be toxic to animals. Two long-chain PFAS – PFOS and PFOA[8] – are listed under an international agreement known as the 'Stockholm Convention on Persistent Organic Pollutants' because of these concerns. 'Short-chain' PFAS are also known to be highly mobile in water and not fully break down naturally in the environment.

The carbon backbone chain length covered with bonded fluorine atoms is an important feature of PFAS. In the case of perfluorocarboxylic acids, like PFOA, a long-chain type is defined as one with seven or more carbon atoms in the backbone, but in the case of perfluoroalkyl sulphonates, like PFOS, a long-chain type is defined as one with six or more carbon atoms in the backbone. Short-chain analogues have four or five carbon atoms, and those with two or three carbon atoms are called ultra-short chain analogues.

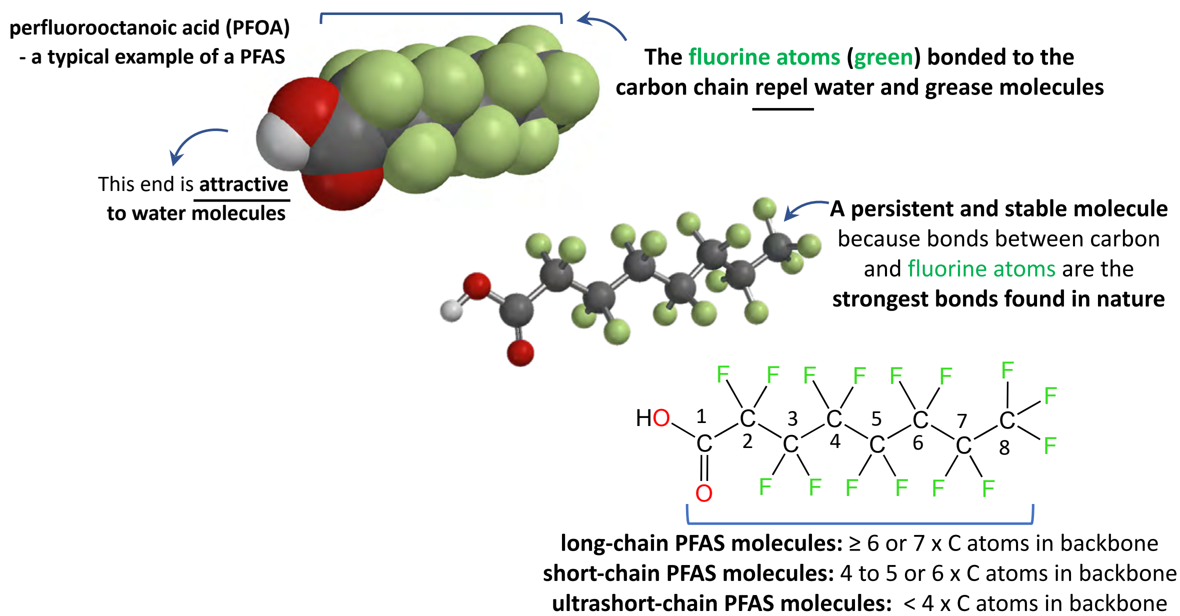

Figure 2 - Characteristic features of molecules in PFAS responsible for their chemical stability and behaviour. The carbon chain length determines their mobility in the environment, accumulation in living tissues, and toxicity. The PFOA molecule has an acidic end group on the carbon backbone, and PFAS with this feature are called perfluoroalkyl acids (PFAA) or perfluorocarboxylic acids (PFCA).

[7] Buck, R.C., Franklin, J., Berger, U., Conder, J.M., Cousins, I.T., de Voogt, P., Jensen, A.A., Kannan, K., Mabury, S.A. and van Leeuwen, S.P. (2011), Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins. Integr Environ Assess Manag, 7: 513-541.
[8] PFOS = perfluorooctane sulfonate, also known as perfluorooctane sulfonic acid; PFOA = perfluorooctanoic acid

Polyfluoroalkyl substances are distinguished from perfluoroalkyl substances by not having fluorine atoms bonded to all carbon atoms in the backbone (see Figure 3). Instead, they have a non-fluorine atom (typically hydrogen or oxygen) attached to at least one, but not all, carbon atoms, while at least two or more of the remaining carbon atoms in the carbon chain tail are bonded to fluorine atoms. Both these types of PFAS exist in two main structural forms – as separate molecules or chains of repeating molecular units (polymers, see Figure 3). Their structural form and composition determine not only their desired function and behaviour, but their ease of degradation to other PFAS, mobility in water or air or soil, and potential toxicity when released to the environment.

Most PFAS currently used in consumer products are precursors, such as complex molecules with fluorinated side chains, or polymers in which the fluorinated side chains are attached to a polymeric backbone (see Figure 3 below). These side chains can cleave off, leading to PFAS degradation products, mainly perfluoroalkyl acids, PFAA.

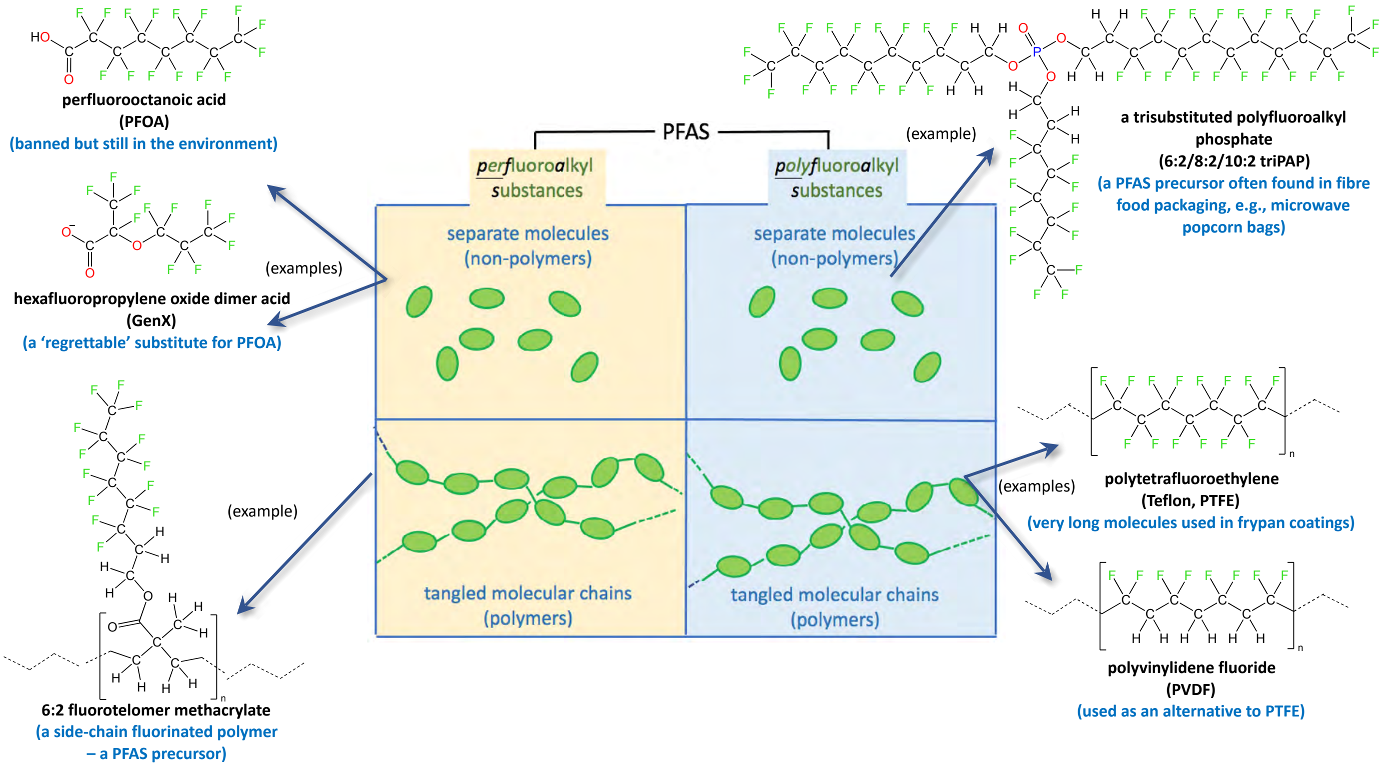

Figure 3 - PFAS are classified as perfluoroalkyl substances or polyfluoroalkyl substances, depending on the extent of fluorination on the carbon backbone in their molecules. They are further distinguished by their molecular structure depending on whether they exist as separate molecules, or as polymers, tangled molecular chains with a repeating pattern. The examples shown are commonly found in food packaging or cookware.

COLLECTION AND HANDLING OF SAMPLES

Samples of a range of fibre-based food packaging were provided for analysis in this study by nine APCO Member companies, including packaging manufacturers, major retailers, and a quick service restaurant chain. The study focused on fibre-based, food-contact packaging because international studies have shown that PFAS is often added to this type of packaging as a barrier to heat, grease and water. While some information on the origin and nature of the packaging was provided along with the samples, this did not include complete information on recycled content and compostability.

To minimise any chemical contamination of packaging samples with other sources of PFAS, the participating companies were asked to follow a protocol for the collection and submission of samples. The protocol included minimising handling of the samples, and a checklist of actions as set out below:

- Wash your hands with soap and water, and dry them thoroughly
- Select ONE container and handle it on the sides that would not come into contact with food
- Place it into a plastic zip-lock bag, and seal the bag to prevent any further contamination
- Complete the Food Packaging Sample Information sheet for the sample
- Staple the completed Food Packaging Sample Information sheet to the top of the zip-lock bag.

Upon receipt, each sample was allocated a sample code and the bags were stored in cardboard boxes.

Of the samples provided, 74 were selected for testing, covering a wide range of packaging applications, types and origins.

Scientific testing of the samples was performed in two phases. In the first phase, all 74 samples were tested for 'total fluorine'. Measuring total fluorine provides a strong indicator of whether or not a sample contains PFAS. The first phase of testing was therefore essentially a screening phase to determine whether each sample contained PFAS. In the second phase, a subset of 35 samples underwent more detailed testing to determine whether certain specific types of PFAS could be identified in the samples.

PHASE 1: TOTAL FLUORINE CONCENTRATION USING PIGE

Methodology

Sample Preparation

For each packaging sample, one container was selected, and a 25-mm diameter disc punched out of a part of the container that would be exposed to food or beverage. The side not facing the food was marked with pencil. The hole punch and all surfaces were cleaned with methanol, and the samples and discs handled with tweezers (see Figure 4).

Figure 4 - Discs were removed in duplicate, near to one another on the packaging surface, and both stored in the same labelled, sealed plastic bag.

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Instrumentation

The 74 bags containing duplicates of each sample were posted to the Australian Nuclear Science and Technology Organisation (ANSTO).

Each disc was weighed and loaded into the carousel shown below for automated loading into a target chamber to be bombarded by high-energy particles.

Figure 5 - The sample discs were loaded into a metal carousel that was automatically programmed to move into a target chamber to be bombarded by high-energy particles.

Each disc was exposed to protons produced within the STAR accelerator (see Figure 6). The beam of these positively-charged particles had an energy of 2.54 MeV, with a current of 10 nA and charge of 5 µC, with a beam diameter of 10 mm aimed in the centre of each 25-mm diameter disc, with a penetration of <0.1 mm.

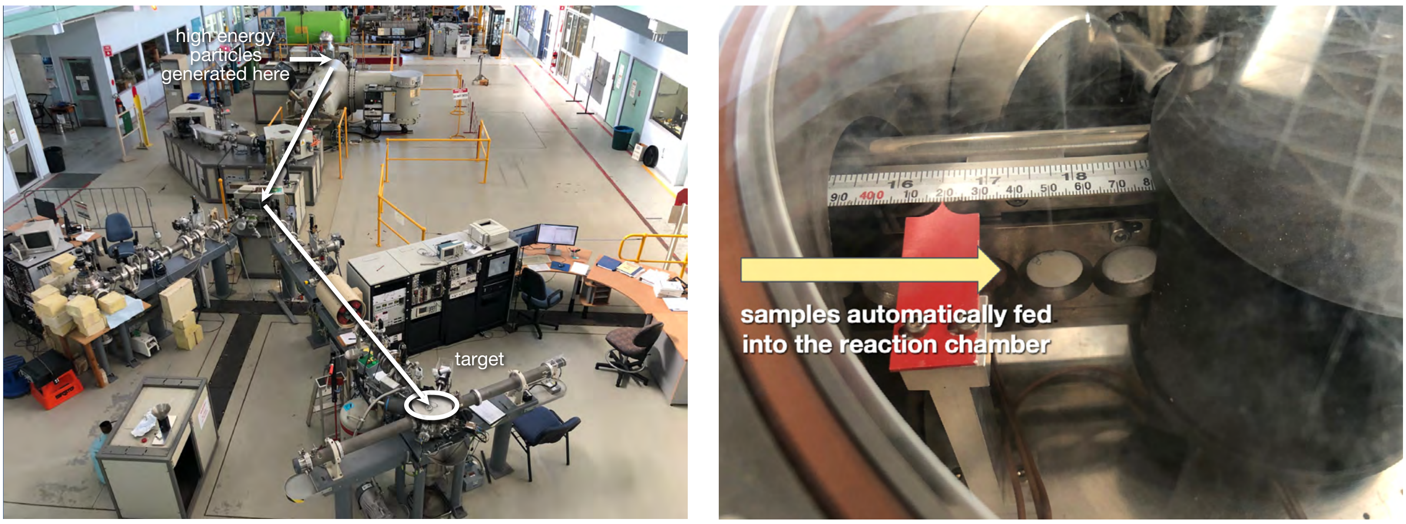

Figure 6 - The STAR accelerator generates a beam of fast particles aimed at samples in the target chamber (shown on the right). The automation of handling many packaging samples makes this an efficient system for measuring the total fluorine concentrations in large numbers of food packaging samples.

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The high-energy particles bombard and penetrate the top 100 μm layer of the packaging. Some of these particles hit the nuclei in the atoms, losing some energy in the form of gamma radiation, which can be detected. The energy of the gamma radiation is different for each type of atom, and observed as a peak in a spectrum with a peak area (above background) dependent on the total number of atoms of that type in the packaging. In the case of fluorine atoms in the sample, gamma-ray emission occurs with an energy of 197 keV. The phenomenon is called Particle Induced Gamma-ray Emission (PIGE).

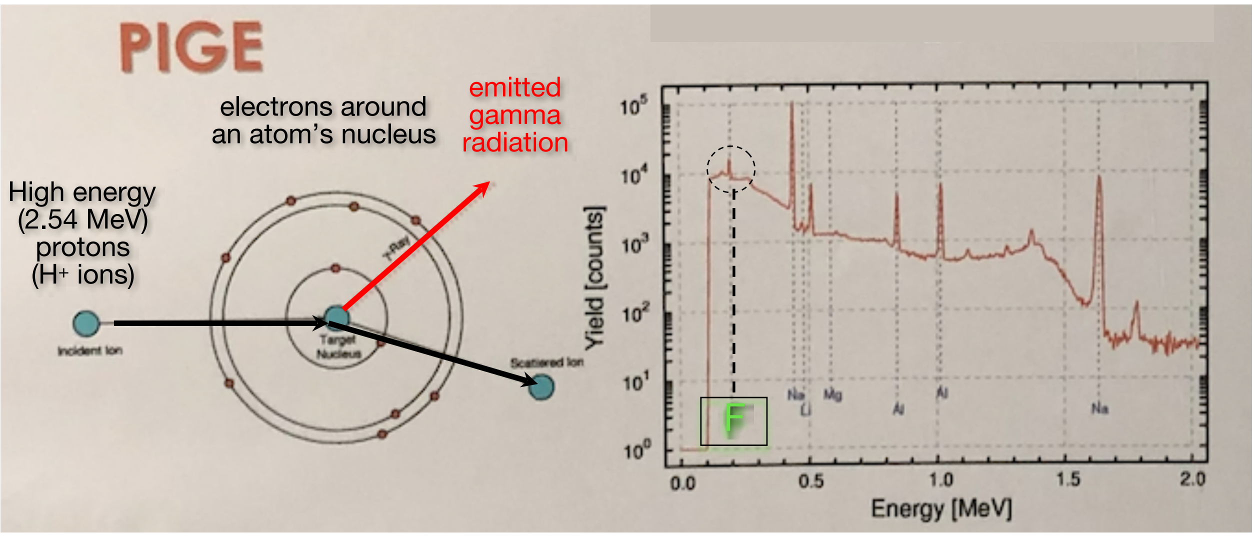

Figure 7 - If a high-energy particle collides with the nucleus of a fluorine atom, gamma radiation with a characteristic energy is emitted. The sum total of all this energy emitted by the fluorine atoms in the sample is recorded as a peak, the area of which is related to the total number of fluorine atoms in the sample.

The PIGE spectral fluorine peaks for all 74 packaging samples are superimposed on each other below to show the range of total fluorine concentrations in the samples. The background-subtracted integrated area of each peak is compared with that of a NaF standard (412 ppm F) and converted to a total fluorine concentration in ppm.

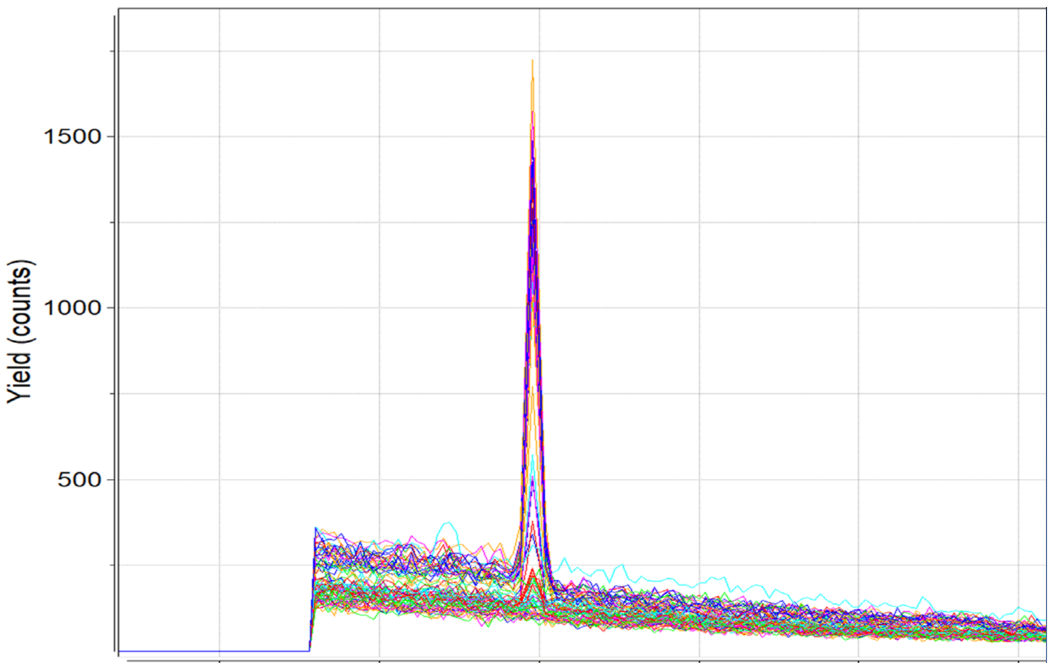

Figure 8 - The emission peaks at 197 keV for all 75 packaging samples are superimposed on each other.

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Phase 1 results and discussion

The bar graph below shows the total fluorine concentrations (in µg/g or ppm) of the duplicate discs for each sample. The average concentrations are shown in Table 3 in Appendix 2.

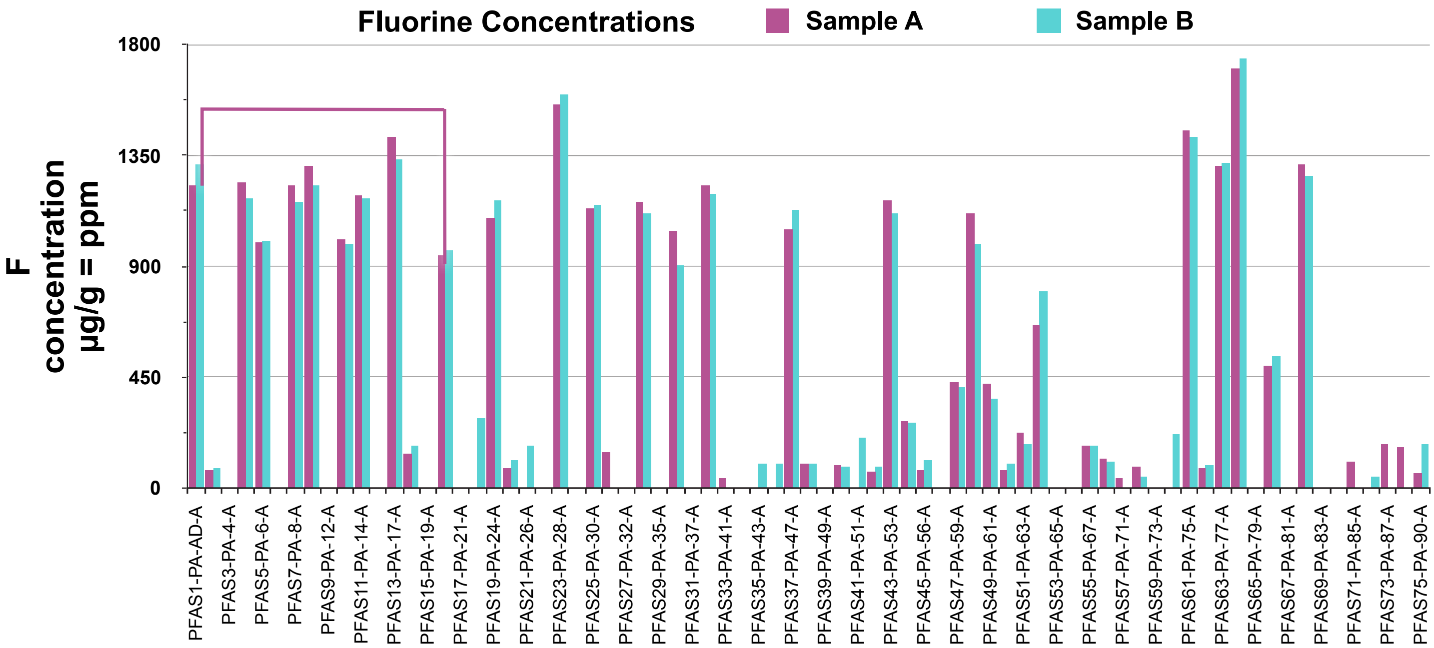


Figure 9 - Total fluorine concentration of each of the 74 samples tested in Phase 1

The reproducibility between duplicates is shown in the graph below. Some of the duplicates were taken from slightly different parts of the packaging.

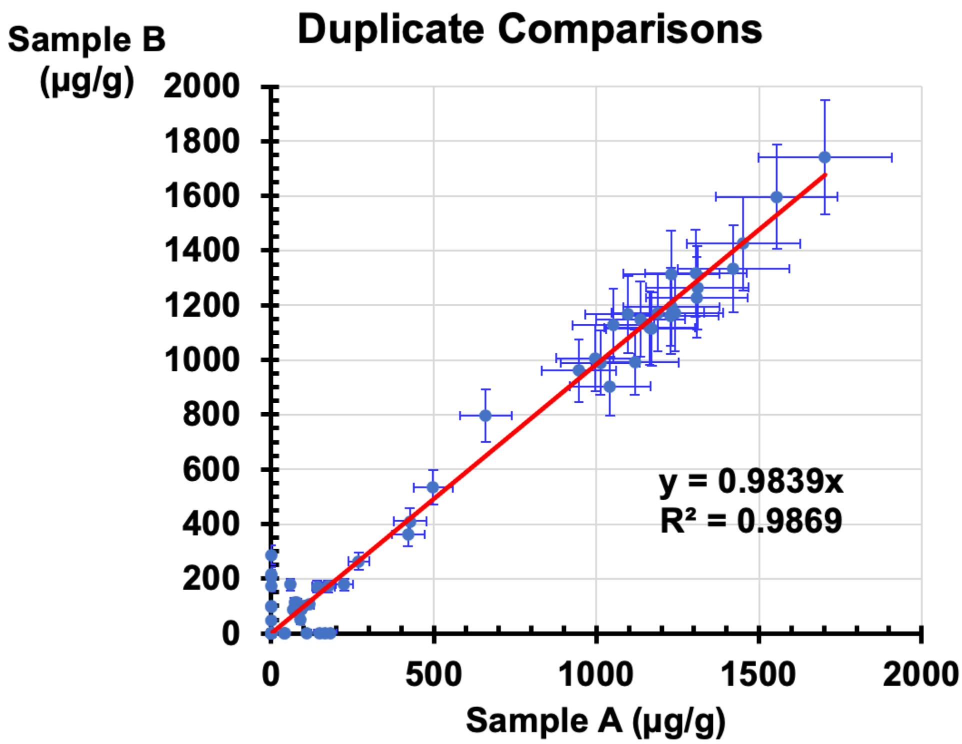


Figure 10 - The correlation between total fluorine concentrations in duplicate samples. There appears to be a distinction between samples containing intentionally added fluorochemicals and those with adventitious or background levels.

Of the 74 samples, 21 samples had average total fluorine concentrations > 800 µg/g. A further 6 samples had medium total fluorine concentrations between 200 – 800 µg/g, while 7 had low concentrations between 100 – 200 µg/g. A further 19 samples had very low, but detectable total fluorine concentrations of less than 100 µg/g. The remaining 21 samples had no detectable fluorine. The data are shown in Table 3 in Appendix 2.

A point of caution

At low fluorine concentrations 12 samples had one duplicate measuring under the detection limit (< 60 µg/g) and the other above it, but all were ≤ 208 µg/g. This anomalous lack of correlation was only seen with samples with these low fluorine concentrations, and could be due to uneven variations in the distribution of low concentrations of fluorochemicals applied to the packaging surface, or in the pulp mixture (virgin or recycled) during manufacture. This problem could be addressed through more rigorous sampling. A possible source of adventitious PFAS could be from recovered fibre (i.e. paper and cardboard recyclate), a very important source of raw material in Australia, with over 60% of fibre used in Australia sourced from recycled products.

PHASE 2: DETECTION AND QUANTIFICATION OF TARGET PFAS

Methodology

Sample Preparation

Of the 74 packaging samples, 35 were selected to determine if they contained 28 of the most common PFAS. The samples selected for Phase 2 included all of the 21 samples with high total fluorine concentrations, as well as additional samples selected to ensure testing of a cross-section of packaging categories from different suppliers, a range of samples with high and low total fluorine concentrations, and some samples that had duplicates with inconsistent low total fluorine levels in Phase 1. Ten of the 35 samples were selected at random to be tested in duplicate to check for reproducibility.

To prepare each sample, 10 – 20 g of the core functional area of the packaging (i.e. the area that would be exposed to food) were cut out and placed in plastic bag, labelled with a code, and sealed. Different packaging had different densities, so the volume of each sample varied greatly. The sample bags were posted to Envirolab[9] in Sydney for testing.

Sample PFAS extraction, separation, identification and quantification

In the Envirolab facility each packaging sample was cut into strips, and mobile, monomeric PFAS (see Figure 11 below) were extracted with an alkaline methanol/ammonia solution, followed by sonication. To identify any complex PFAS precursors in this first extract a Total Precursor Oxidisable Assay (TOPA) was conducted on a fraction of the extract. This fraction was evaporated and reconstituted in a solution containing the strong oxidising agent persulphate and hydroxide ions. The solution was then digested at ~85˚C for at least 6 hours, typically overnight. The pH of this solution was then adjusted, and methanol was added for stabilisation.

For each sample of packaging there were two solutions analysed – one from the extract before the TOPA treatment (referred to as the 'pre-TOPA' analysis), and one after the treatment (referred to as the post-TOPA analysis).

A sample of each pre- and post-TOPA extract was injected onto a liquid chromatography column for separation of the PFAS. They interact differently with the solid stationary phase in the column as they are carried along in the mobile phase (methanol/water/ammonium acetate). The extent and rate of interaction and separation of the PFAS in the column determined when they exited the column. The individual PFAS were detected, and generated peaks in a chromatogram, as shown in the two chromatograms (see Figure 11) for a solution containing standards and for sample 4, the microwave popcorn bag (see Table 3 in Appendix 2).

[9] https://www.envirolab.com.au/Capabilities/PFAS

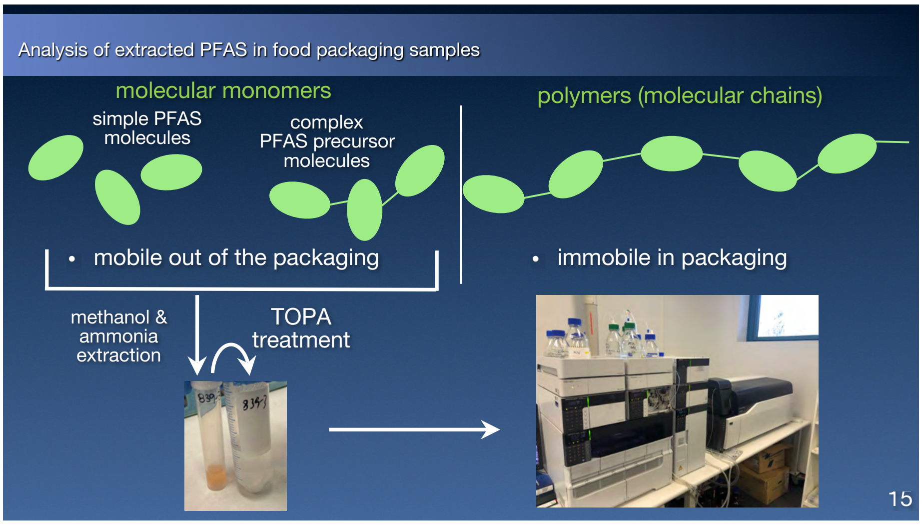
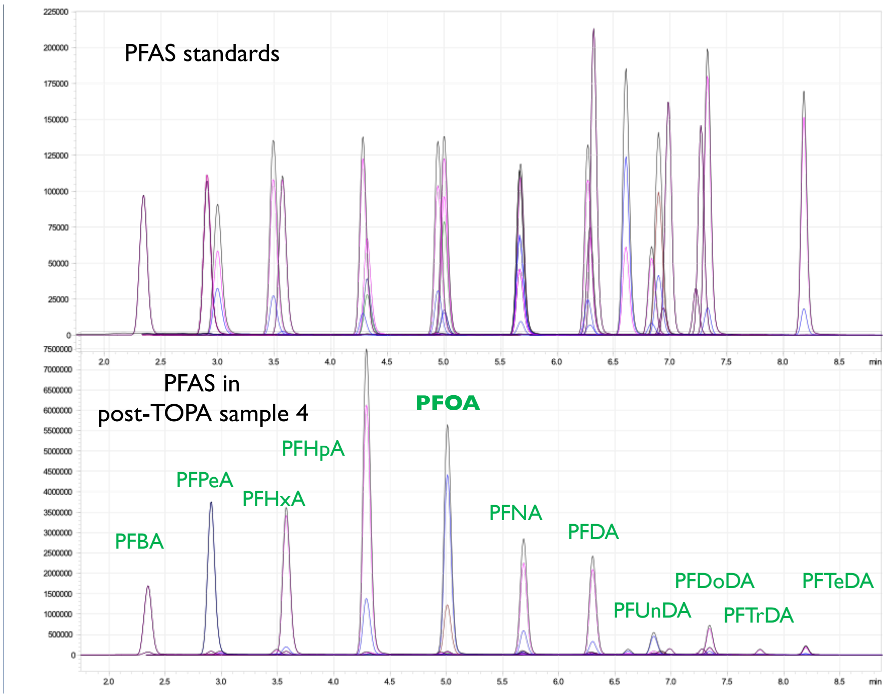


Figure 11 -Three structural types of PFAS are shown graphically – simple molecules, complex precursor molecules, and polymeric chains. The first extraction removes a mixture of simple PFAS, complex PFAS precursors, and possibly some polymer degradation products, leaving any in-tact polymeric molecules in the packaging. The subsequent TOPA treatment of another fraction of the extract degrades some PFAS precursors into simpler PFAS that can then be identified if they are members of the common 28 PFAS identifiable in the experimental protocol..

Internal checks of recovery and TOPA oxidation efficiency

To ensure no PFAS were retained on the column or in the instrumentation, surrogate ^{13}C-labelled PFOA was added to each sample extract and recoveries ranged from 93 – 112% (within acceptable experimental variability). The oxidation efficiency of the TOPA treatment was measured for each sample by adding ^{13}C-labelled PFOSA (perfluorooctane sulfonamide) and testing recovery of the oxidation product. Successful oxidation ranged from 93 – 100% (within acceptable experimental variability).

Upon exiting the analytical column, the separated PFAS are ionised using Electrospray Ionisation (ESI) before entering the tandem mass spectrometer (MS/MS) which consists of two scanning mass analysers separated by a collision cell. Fragments selected in the first analyser are reacted with an inert gas (typically argon) in the collision cell, resulting in further fragmentation. These daughter product ions are then identified and quantified from 28 known standard PFAS (see Figure 12).



Compounds	Acronym
Perfluorobutane sulfonic acid	PFBS
Perfluoropentane sulfonic acid	PFPeS
Perfluorohexane sulfonic acid (short suite)	PFHxS
Perfluoroheptane sulfonic acid	PFHpS
Perfluorooctane sulfonic acid (short suite)	PFOS
Perfluorodecane sulfonic acid	PFDS
Perfluorobutanoic acid	PFBA
Perfluoropentanoic acid	PFPeA
Perfluorohexanoic acid	PFHxA
Perfluoroheptanoic acid	PFHpA
Perfluorooctanoic acid (short suite)	PFOA
Perfluorononanoic acid	PFNA
Perfluorodecanoic acid	PFDA
Perfluoroundecanoic acid	PFUnDA
Perfluorododecanoic acid	PFDoDA
Perfluorotridecanoic acid	PFTrDA
Perfluorotetradecanoic acid	PFTeDA

Figure 12 -The PFAS exit the column approximately in order of carbon chain length and show up as peaks in a chromatogram. The top one was generated from a mixture of known PFAS, and these peaks help to identify the PFAS after the TOPA treatment, in this case with the microwave popcorn bag.

Phase 2 results and discussion

The total fluorine concentrations (in various units) and total PFAS concentrations (pre- and post-TOPA) of all the tested fibre food packaging samples are collected in Table 3 in Appendix 2.

The main finding from Phase 2 testing was that few packaging samples contained any of the 28 PFAS that were tested for. Therefore, the total fluorine measured in Phase 1 is likely due to the presence of other, different types of PFAS.

There is a significant gap in mass balance between the total fluorine concentration from PIGE and the post-TOPA total PFAS concentration in most samples. The total fluorine concentration could be due to any of the three types of PFAS shown in Figure 11, other non-PFAS organic fluorochemicals, or inorganic fluorochemicals such as adventitious fluoride from water contamination (unlikely in significant amounts). The most reasonable interpretation of the gap is that the PFAS, PFAS precursors, and any polymeric degradation products released from the packaging in the first extraction were not on the list of the 28 common PFAS that could be identified using the standard experimental protocol. The subsequent TOPA treatment on this extraction confirmed that there were unknown PFAS precursors that had degraded to form four perfluoroalkyl acids (PFAA) — perfluorobutanoic acid, perfluoropentanoic acid, perfluorohexanoic acid, and perfluoroheptanoic acid — and other unknown products. From the research literature, two possible PFAS precursor types that could be in the packaging are shown in Figure 13 below.

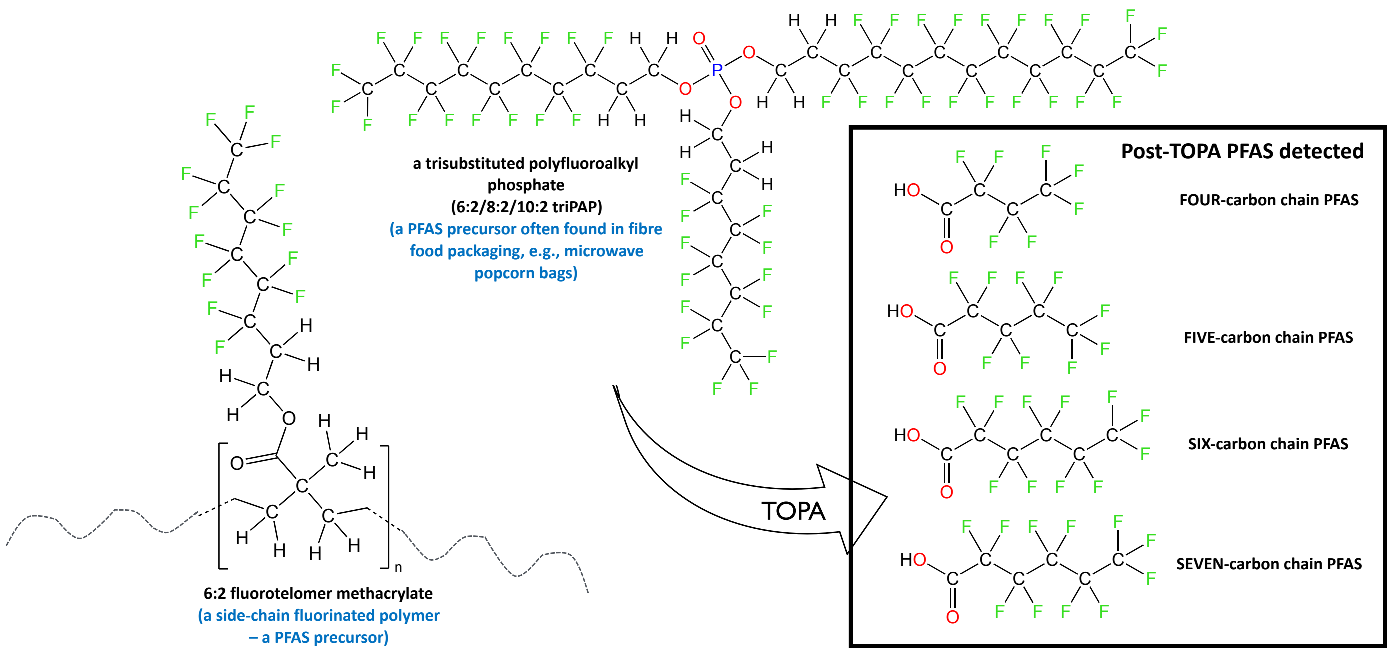


Figure 13 - The packaging samples could contain PFAS precursors like the two compounds shown on the left. The vigorous TOPA treatment degrades such molecules to form PFAA like the four (shown in the box) that were found in this study.

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Appendix 2: Detailed results of Phase 1 and Phase 2 testing

Table 3 - Total fluorine concentrations and total PFAS concentrations (pre- and post-TOPA) of samples with high, medium, low and very low detectable total fluorine concentrations (samples with no detectable fluorine concentrations are excluded from this table). The list is sorted in decreasing total fluorine concentration. Purple indicates samples with high total fluorine concentrations.

NOTE: Total fluorine concentrations are expressed in ppm, and total PFAS concentrations in ppb.
For example, 39,800 ppb is equivalent to 39.80 ppm for comparison purposes.

Simple Sample code	Simplified Sample Description (some samples were duplicated or triplicated for total PFAS)	Average Total fluorine (ppm)	Packaging Category (see table on p6)	Total PFAS PRE-TOPA (µg/kg or ppb)	Total PFAS POST-TOPA (µg/kg or ppb)
59	Large snack carton	1722	5	2	39800
		1722	5	8	54800
		1722	5	9	53500
8	Butter wrap	1576	1	0	0
58	Oval plate	1438	7	24	29400
22	Darker bagasse bowl	1378	7	11	12739
56	Large dinner clam	1311	5	2	25180
83	Salted butter wrap	1287	1	0	0
3	Bagasse bakery tray	1268	7	16	13023
26	Light-coloured rectangular take-out container	1212	7	8	11932
23	Square clamshell bagasse, light-coloured	1207	7	12	26100
34	Small trays	1195	7	4	23800
20	Light-coloured bagasse plate	1180	7	5	8343
		1180	7	5	9433
15	Bagasse trays	1142	7	3	31730
63	Clam shell	1142	5	16	8781
35	Larger cardboard tray	1141	7	28	13720

Simple Sample code	Simplified Sample Description (some samples were duplicated or triplicated for total PFAS)	Average Total fluorine (ppm)	Packaging Category (see table on p x)	Total PFAS PRE-TOPA (µg/kg or ppb)	Total PFAS POST-TOPA (µg/kg or ppb)
24	Square clamshell bagasse, darker-coloured	**1132**	7	8	13331
57	Three-component plate	**1090**	7	10	25490
60	Regular snack carton	**1054**	5	5	29000
		1054	5	5	29000
25	Darker square tray	**1002**	7	7	7972
13	Bagasse plates	**1001**	7	14	10922
45	Overseas-sourced greaseproof paper	**972**	1	2	19090
		972	1	2	17680
		972	1	1	24800
4	Popcorn bag	**953**	2	69	18877
		953	2	65	36465
61	Clam burger box	728	5	< detection limit	31100
73	Kraft box	516	1	Not tested	Not tested
49	Fried coated chicken pieces box	418	2	4	5630
50	Paper wrap	391	4	4	6140
71	Greaseproof paper	266	1	Not tested	Not tested
72	Gloss newsprint	202	1	Not tested	Not tested
64	Uncoated paper plate	173	1	Not tested	Not tested
12	Cake mix bag	157	2	Not tested	Not tested
16	Clamshell box	143	5	< detection limit	17
90	Clamshell box - dark	119	5	< detection limit	8
77	Hot dog tray	112	6	< detection limit	5
75	Burger box	108	4	< detection limit	3
82	Large cake box	104	1	< detection limit	< detection limit

Simple Sample code	Simplified Sample Description (some samples were duplicated or triplicated for total PFAS)	Average Total fluorine (ppm)	Packaging Category (see table on p x)	Total PFAS **PRE-TOPA** (µg/kg or ppb)	Total PFAS **POST-TOPA** (µg/kg or ppb)
51	Pizza box	99	3	< detection limit	28
28	Darker dense clamshell	96	5	Not tested	Not tested
54	Pizza insert card	93	1	Not tested	Not tested
84	Schnitzel tray sleeve	90	2	< detection limit	< detection limit
		90	2	< detection limit	< detection limit
74	Family box kraft carton	90	3	Not tested	Not tested
53	Large pizza box	90	3	Not tested	Not tested
76	Kraft chip box	89	4	Not tested	Not tested
38	Greaseproof paper	87	1	< detection limit	< detection limit
89	Greaseproof paper	83	1	Not tested	Not tested
52	Small pizza box	77	3	Not tested	Not tested
10	Deli wrapping paper	77	1	< detection limit	< detection limit
18	Hot beverage cup	75	6	< detection limit	< detection limit
70	Greaseproof paper	69	1	Not tested	Not tested
87	Clamshell box - white	54	1	Not tested	Not tested
14	Baking paper	50	1	Not tested	Not tested
31	Hot cup	48	6	Not tested	Not tested
88	Cake fold box	23	1	< detection limit	< detection limit
29	Salad box with see-through lid	21	3	Not tested	Not tested
79	Large kraft box	19	3	Not tested	Not tested

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