SOURCE APPORTIONMENT, TRANSPORT AND FATE OF POLLUTANTS IN THE PAPER RECYCLING CHAIN - AN ANALYTICAL EXPLORATION OF THE SOUTH AFRICAN CONTEXT



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DECLARATION

I declare that this thesis is my own, unaided work. It is being submitted for the Degree of Doctor of Philosophy at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination at any other University.



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27th day of **August 2024** at **Johannesburg**

ABSTRACT

This thesis presents the analytical exploration of pollutants in the South African paper recycling chain. Recycled paper is a valuable commodity that forms an intrinsic part of actualising a circular economy. In South Africa, the recycled paper value chain includes largely unsorted waste paper recovered from household waste, businesses, retail, schools, industry as well as paper collected from public areas, solid waste disposal sites and landfills by informal waste pickers. Extensive research has been undertaken in Europe, America, and Asia on the implications of using recycled paper; specifically, in packaging intended for food, toys, and electric equipment. In South Africa, however, research on pollutants in recycled paper does not exist. As the global impetus towards sustainability increases, it is imperative to determine the type of pollutants that may arise from the recycled paper value chain as these may negatively affect humans and the surrounding biota. This study extended beyond typical food packaging migration studies and investigated the holistic extraction of both food and non-food paper-based materials. The stages of paper recycling that were investigated were pre-consumer, retail and post-consumer.

In **Paper 1**, liquid and gas chromatography, both in tandem with mass spectrometry, were used for the chemical characterisation of various paper recycling grades prepared by accelerated solvent extraction and ultrasonic assisted extraction, respectively. The findings indicated that polymer-associated chemicals such as plasticizers, antioxidants, flame retardants, and polymer degradants have infiltrated the paper recycling chain. Multi-residue quantification of 11 pollutants in recycling paper grades in South Africa using GC-MS after accelerated solvent extraction was the main focus of **Paper 2**. The target analytes included BBP, DEP, DBP, DEHP, DIBP, DIDP, DIPN, NBBS, BHT, AO168, and AO168O. A plot of the VIP_{scores} showed that DEHP and DBP were the most prominent pollutants, whilst AO168 and BHT were the least significant pollutants in the examined samples. **Paper 3** explored the previously unexplored contamination of paper by pharmaceuticals, emerging contaminants that have been historically detected in South African environmental matrices. The analyses were achieved by ultrasonic-assisted

extraction of paper samples before targeted and suspect screening by UHPLC-Q Orbitrap. This study was able to uncover the presence of dexamethasone, ketoprofen, and 17β-estradiol in paper-based samples. In addition, suspect screening was able to tentatively identify additional pharmaceuticals through spectral database matches. **Papers 4 and 5** studied PFAS prevalence in recycling paper grades used for the manufacture of recycled paperboard. In **Paper 4**, targeted analysis of per- and polyfluoralkyl carboxylic and sulphonic acids was undertaken. The possible propagation and amplification of PFAS was explored by comparing the concentrations detected in pre-consumer samples to those detected in retail and post-consumer samples. Suspect screening in **Paper 5** tentatively identified additional PFAS present in the samples through the development of a study-specific suspect screening protocol reported with its associated confidence level. The samples were prepared using two extraction techniques; accelerated solvent extraction with solid-phase extraction and ultrasonic-assisted extraction. The different functional groups identified indicated the importance of both selective and non-selective extraction in understanding PFAS occurrence. It further demonstrated an urgent global need to understand the different PFAS that can occur in the paper recycling chain.

In these Papers, manufacturing additives and retail activities were identified as possible exposure sources. Post-consumer usage, collection, sorting, and co-mingling of various waste materials were also identified factors that influence the prevalence of pollutants. The presence of certain pollutants in pre-consumer showed that certain compounds may potentially remain within the paper recycling chain, propagate and accumulate along with those from the retail and post-consumer stages. The lower abundance in comparison to retail and post-consumer samples indicated that other pollutants may likely be removed during the reprocessing of recycled fibre. This study thus showed that it is imperative that South Africa develop and implement legislation and guidelines that address the use, risk, and standardised waste management strategies that ensure a safe circular economy in the paper recycling chain.

DEDICATION



ive thanks to the LORD, for He is good.

His love endures forever.

Psalms 136: 1

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OVERVIEW OF THESIS BY PUBLICATION

The following published articles and manuscripts, in which the candidate was the principal author, are presented as the basis of this thesis:

1. Nondumiso Mofokeng, Lawrence Madikizela, Ineke Tiggelman, Luke Chimuka: Chemical profiling of paper recycling grades using GC-MS and LC-MS: An exploration of contaminants and their possible sources. Manuscript published in **Waste Management** (2024) 189, 148–158. https://doi.org/ 10.1016/j.wasman.2024.08.014

Nondumiso Mofokeng: Principal author, conceptualisation, methodology, formal analysis, writing of original draft. Lawrence Madikizela: Supervision, reviewing and editing. Ineke Tiggelman: Advisor, reviewing and editing. Luke Chimuka: Conceptualization, supervision, reviewing and editing.

2. Nondumiso Mofokeng, Lawrence Madikizela, Luke Chimuka: Source apportionment and transport of semi-volatile organic pollutants within the South African paper recycling chain. Manuscript under review in the **South African Journal of Science** submission reference 17228.

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3. Nondumiso Mofokeng, Lawrence Madikizela, Ineke Tiggelman, Luke Chimuka: Emerging Contaminants as Unintentional Substances in Paper and Board: A Case of Unexpected Pharmaceuticals Detection in the Paper Recycling Chain. Manuscript published in **Journal of Hazardous Material** (2024) 472, 134419. https://doi.org/10.1016/j.jhazmat.2024.134419.

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4. Nondumiso Mofokeng, Lawrence Madikizela, Ineke Tiggelman, Edmond Sanganyado, Luke Chimuka: Determination of per- and polyfluoroalkyl compounds in paper recycling grades using ultra-high performance liquid chromatography – high resolution mass spectrometry. Manuscript published in **Environmental Science and Pollution Research** (2024) 31:30126–30136. https://doi.org/10.1007/s11356-024-33250-9.

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5. Nondumiso Mofokeng, Lawrence Madikizela, Ineke Tiggelman, Edmond Sanganyado, Luke Chimuka: Suspect screening of per- and polyfluoroalkyl substances in paper by selective and non-selective extraction with UHPLC-Q Orbitrap MS. Manuscript published in **Chemosphere** (2024) 363, 142904. https://doi.org/10.1016/j.chemosphere.2024.142904

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Peer-reviewed journals of good standing were selected according to their recognition by the South African Department of Higher Education and Training, their cite score and their associated impact score. Where applicable, the articles are presented in as close a representation as possible to the published version, with changes made to suit the format of this thesis.

CONFERENCE OUTPUTS

1. Nondumiso Mofokeng, Lawrence Madikizela, Luke Chimuka. Source apportionment, transport and fate of pollutants in the paper recycling chain: an analytical exploration of the South African recycled paper chain. Conference: 44th SACI National Convention 2023
Location: Stellenbosch
This presentation was based on **Paper 2**.

2. Nondumiso Mofokeng, Lawrence Madikizela, Ineke Tiggelman, Edmond Sanganyado, Luke Chimuka. Determination of per- and polyfluoroalkyl compounds in South African paper recycling grades using Ultra Performance Liquid Chromatography - Orbitrap High Resolution Mass Spectrometry.
Conference: 2023 SACI Chromatography Postgraduate Student Workshop
Location: Pretoria
This presentation was based on **Paper 4**.

3. Nondumiso Mofokeng, Lawrence Madikizela, Ineke Tiggelman, Edmond Sanganyado, Luke Chimuka. Determination of per- and polyfluoroalkyl compounds in South African paper recycling grades using UHPLC – Q Orbitrap.
Conference: 2024 Analitika Conference
Location: Drakensberg
This presentation was based on **Papers 4** and **5**.

4. Nondumiso Mofokeng. The challenges of food contact regulation in the Global South: The South African perspective.
Conference: 2023 Smithers Global Food Contact 2023
Location: Prague, Czech Republic
This presentation outlined the framework of this study in **Chapter 2 2.2–2.3**.

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LIST OF ABBREVIATIONS

ASE	: Accelerated solvent extraction
AO168	: Tris(2,4-ditert-butylphenyl)phosphite (Irgafos 168)
AO168O	: Tris(2,4-ditert-butylphenyl)phosphate
BHT	: butylated hydroxytoluene
BBP	: Butylbenzyl phthalate
BP	: Benzophenone
BPA	: Bisphenol A
BPS	: Bisphenol S
DBP	: Dibutyl phthalate
DEHP	: Diethylhexyl phthalate
DEP	: Diethyl phthalate
DIBP	: Di-isobutyl phthalate
DIDP	: Didecyl phthalate
DIPN	: Diisopropylnaphthalene
DMP	: Dimethyl phthalate
EPA	: Environmental Protection Agency
ESI	: Electron spray ionisation
GC-MS	: Gas chromatography-mass spectrometry
HRMS	: High resolution mass spectrometry
LC-MS	: Liquid chromatography-mass spectrometry
LOD	: Limit of detection
LOQ	: Limit of quantification
NBBS	: N-Butylbenzene sulphonamide
PAA	: Primary aromatic amines
PFAS	: Per- and polyfluoroalkyl substances
POPs	: Persistent organic pollutants
RT	: Retention time
SDGs	: Sustainable development goals
SPE	: Solid phase extraction
sPLS-DA	: sparse partial least square discriminant analysis
UHPLC	: Ultra-high performance liquid chromatography
UAE	: Ultrasonic-assisted extraction
VIP	: Variable importance in projection
WAX	: Weak anionic exchange

CHAPTER ONE

1 INTRODUCTION

Paper recycling is the process of collecting, sorting and reprocessing waste paper into new products (Scott, 2019; Senarathna et al., 2023) and has been practised in South Africa for over 30 years (Godfrey & Oelofse, 2017). Paper collected for the manufacture of recycled paper can be used, unused, or unsold paper-based material, and is commonly referred to as recovered paper, waste paper, collected paper, paper stock, recycled fibre or secondary fibre (Miranda et al., 2013; Pivnenko et al., 2016; Scott, 2019). It reduces the need for landfills, minimises waste, saves energy and ensures ecological conservation, making it an important environmentally sustainable waste management tool (Geueke et al., 2018; Lipkiewicz et al., 2021; Senarathna et al., 2023). In addition, it is a source of income for many informal waste pickers who play an important role in South Africa's paper recycling chain (Omotoso, 2017). Recycling strategies generally aim to promote high-quality recycled goods with as few contaminants as possible (Blanco et al., 2013; Miranda et al., 2013). The quality of recycled paper is often evaluated in terms of fibre morphology properties, optical characteristics, fines content and the presence of contaminants (Keränen & Retulainen, 2016). This, in turn, is often influenced by the availability of high-quality materials, their collection rates and the market demand for recycled paper (Keränen & Retulainen, 2016). Separated-at-source collection systems are considered to be of a higher quality than recycled paper from co-mingled recycling systems (Miranda et al., 2013), where paper destined for recycling can be collected prior to use by consumers (pre-consumer) or after consumer usage (post-consumer). Pre-consumer recycled paper is associated with the highest quality recycled paper in comparison to post-consumer paper that may have been re-used or contaminated during consumer usage (Senarathna et al., 2023).

Contaminants refer to the presence of impurities whilst pollutants are impurities that result in adverse effects on living organisms, plants, or the environment (Guidotti, 2015). The distinction between the two often varies with species,

environmental factors, concentrations and bioavailability (Fadare et al., 2024) In paper recycling, physical or visible objects such as staples, adhesives, plastic fragments, stones, food remnants and other characteristics such as wetness and dirt are considered contaminants (Chaudhary et al., 2023). These reduce the value and quality of the newly manufactured paper, lead to pulping difficulty, affect sheet formation and cause runnability issues (Huber et al., 2013). The actual microchemical constituents are generally not considered as a criteria for the acceptance or rejection of waste paper at recycling facilities, although it has been established that printing inks present in recovered paper influence the whiteness and brightness of the resulting recycled goods (Vukoje et al., 2022).

In South Africa, the paper recycling chain is divided into the formal and informal sectors; both of which operate in co-mingled waste systems. These encompass the recovery of paper material from household waste, schools, retail, industry as well as paper collected on kerbsides, solid waste disposal sites, and landfills. This differs considerably from developed countries such as the Netherlands and Poland where waste is separated at source (Seyring et al., 2016) with legislative regulations and guidelines in these countries based on segregated waste streams (Blanco et al., 2013; Monte et al., 2009). In recent years, there has been a drive towards the regulation of paper recycling and packaging waste with regulations related to Extended Producer Responsibility (EPR) advocating for the recycling of various substrates including paper, glass and plastics (Godfrey & Oelofse, 2017). There is, however, currently no legislation pertaining to the regulation of chemical additives used in the manufacture of paper-based materials or any limitations prescribed on expected chemical contaminants or pollutants after the recovered paper has undergone reprocessing. South African manufacturers of recycled paperboard thus rely on international regulations and protocols designed for separated waste paper streams, which may not be applicable to the South African context. It is thereby important to analytically characterise the South African paper value chain to identify its key chemical features and to encourage the development of customised regulations for improved waste management.

In the present work, a mixed-mode research study was undertaken which comprised quantitative analysis supplemented by qualitative research aimed at filling knowledge gaps in this untapped research area. This study was the exploration of the chemical pollutants that were present in the paper recycling chain as well as an investigation into their possible propagation and accumulation. Chromatography is a versatile analytical tool used to qualitatively separate homogenous and heterogenous organic mixtures into their chemical constituents (Gupta & Biswas, 2023). In this work, it was employed in tandem with mass spectrometry to identify and in certain instances, quantify these chemical constituents. Chromatography with mass spectrometry may be performed using gas or liquid in gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-mass spectrometry (LC-MS), respectively, as the mobile phase. The choice in the selection of chromatographic mode depends on the chemical properties of the organic compounds under study; such as boiling point, polarity, volatility, thermal stability and ionizability (Bengtström et al., 2016). Both targeted and untargeted approaches were employed for the investigation of organic chemical constituents by GC and LC-MS. Targeted analysis employed selective and specific methods to determine an analyte or analytes of interest (Ballin & Laursen, 2019) with sample pre-treatment designed for the isolation and enhancement of the detector response based on the target compounds. The untargeted analysis was more explorative in its nature where a broad range of compounds were identified. Through these two complementary techniques and approaches, this study thus identified pollutants and other chemicals of interest in the paper recycling chain, their possible sources, propagation and fate.

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CHAPTER TWO

2 LITERATURE REVIEW

2.1 Paper recycling as a vehicle for a circular economy

The main principle of the circular economy is one in which 'waste' becomes a resource from which products of the same value or higher can be produced (Banaite & Tamošiuniene, 2016; Kalkanis et al., 2022). This value is measured in terms of the product meeting the desired performance specification, physical and chemical characteristics, as well as its suitability in the desired application (Velenturf & Purnell, 2021). The concept of a circular economy can be seen as a strategic tool for the implementation of sustainable development (Banaite & Tamošiuniene, 2016). It specifically speaks to Goal 12 of the United Nation's 17 Sustainable Development Goals (SDGs) which addresses sustainable consumption and production through recycling and resource management (Dobbelstein & Lochner, 2023; Niero & Rivera, 2018). The circular economy expands beyond the traditional "3Rs" of sustainable development, which are reduce, reuse and recycle, to recycle, repair, reuse, refurbishment, remanufacture, product sharing, eco-design, and waste prevention (Banaite & Tamošiuniene, 2016). Recycling aligns with these principles by promoting efficient resource utilisation, conservation of natural resources, minimisation of adverse environmental effects, and reduction in waste generation (Kalkanis et al., 2022). The increasing use of paper-based materials for modern amenities has led to increased volumes of waste and depletion of natural resources (Iacovidou et al., 2017; Oloyede & Lignou, 2021). It is, therefore, important to effectively manage waste and ensure the availability of such conveniences for future generations. In the paper industry, the circular economy aims to reduce the use of forestry products and promote efficient resource utilisation where inputs and outputs remain in closed loops (Geueke et al., 2018). Paper recycling, in addition, offers a better alternative to waste disposal at landfills or incineration (Dobbelstein & Lochner, 2023). This is especially true in South Africa where many landfills have reached capacity (Schenck et al., 2019).

To successfully achieve sustainable consumption, the waste paper recovered after consumer usage should be in a physical and chemical state that is suitable as a raw material input for high-value products (Geueke et al., 2018). For paper recycling, the value may be measured in relation to its end-use application, strength properties as well as visual characteristics. For instance, a corrugated box used for direct food contact packaging should be recycled into packaging meeting specifications for a similar application. The disadvantage of the circular economy is that it may introduce unwanted, hazardous substances in the subsequent product's life cycle that may recirculate and cause harm to both the biota and the environment (Geueke et al., 2018). Hazardous substances in paper-based products can often be traced back to chemicals through various exposure pathways directly related to manufacturing and converting processes as well as indirectly from chemical adulteration that results from consumer usage and the waste management protocols employed.

2.2 The South African paper recycling chain

In South Africa, paper recycling is based predominantly on co-mingled waste recovery which entails the combined collection of paper, glass, cans and plastics, with separation or sorting usually done downstream at recycling or recovery centres. This mode of collection has been reported to result in higher cross-contamination of materials (Blanco et al., 2013). According to Miranda *et al*. (2013), co-mingled collection systems result in between 5 and 20% unusable materials whilst source-separated collections result in less than 1% unusable materials (Miranda et al., 2013).

The South African paper recycling sector consists of formal and informal waste collectors with sorting facilitated by private companies and municipalities. The paper recycling chain consists of paper collected before exposure to consumers (pre-consumer), in the form of off-cuts i.e broken material at paper manufacturing and converting plants; in the retail space as unsold material as well as after consumer usage (post-consumer) from households, businesses, schools, retail and industry. It can also include paper disposed of at landfills as well as paper from solid waste disposal sites, often retrieved by informal waste pickers. Figure 1

illustrates the material flow loop in the South African paper recycling chain. Paper that has been designated for municipal waste collection by households is also often collected by informal waste pickers. Informal waste pickers collect waste paper discarded in streets, parks and other public areas. In addition, many waste pickers collect waste directly from landfills. In 2017, there were reportedly as many as 215,000 informal waste pickers earning a livelihood from waste in South Africa (Godfrey & Oelofse, 2017). The visible increase in the number of informal waste pickers over the past few years has been partly due to the increase in unemployment in South Africa, which has forced people to seek a livelihood in the informal sector (Godfrey & Oelofse, 2017). In addition to the socio-economic effects of poverty and unemployment; poor administration of waste management by municipalities (Omotoso, 2017) has adversely affected the government's ability to deliver basic services such as waste removal. Waste pickers have thus become an important bridge between the municipal service chain and the formal as well as private sector (Godfrey, 2021).

Recovered or collected paper is usually directed to recycling centres or buy-back centres where informal and formal waste paper collectors are paid according to the grade and usable weight of paper they bring in. The recovered paper is then sorted and baled; at material recovery or recycling facilities. The recycling facilities then send the sorted paper to paper mills for reprocessing or remanufacturing into recycled paperboard. The paper mills may also further sort and check the baled waste paper, depending on their specific needs and requirements. Manual sorting by hand is currently the most common separation technique used in South Africa, which may be highly subjective or susceptible to human error as it is dependent on the sorters' knowledge and interpretation. Automated sorting techniques may either be mechanical or optical (Rahman et al., 2014). Various grades of paper are used in the manufacture of recycled paperboard. These may include office paper, newspaper, corrugated boxes and magazines. Recycled paperboard may be made from a single grade or a combination of different paper grades. It may be a combination of recycled and virgin fibre or may be made from only recycled fibre.

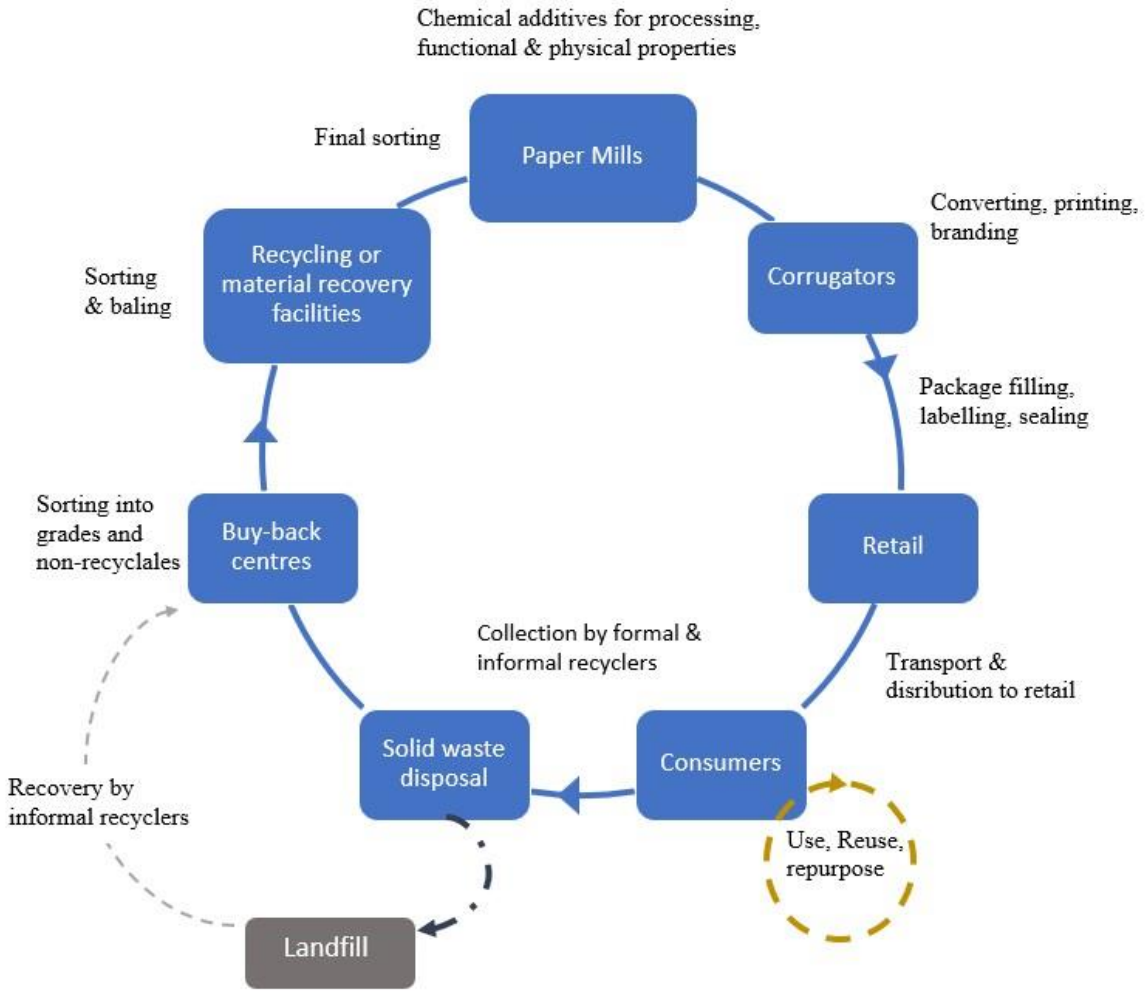


Figure 1 Overview of South African Paper Recycling Chain

Contaminants such as staples, textiles, and tapes are removed by hand during sorting. Water is used to repulp the paper and may also include washing with sodium hydroxide or surfactants (Çiçekler et al., 2023; Wang et al., 2021). Coarse contaminants such as light plastic contaminants and cellulose fibres are usually mechanically separated by perforated plates followed by screening to further remove other contaminants that may remain. This separation is based on the physical size and shape of the contaminants where fibre material is pushed by a rotary and screened through small holes and slots leaving behind non-fibrous contaminants such as small metals, plastics and other adhesives (Licursi et al., 2016). The subsequent pulp can also be cleaned chemically, thermally and/or mechanically as well as bleached or deinked, depending on the desired end product

(Rahman et al., 2014). The re-manufacturing process, however, is not able to completely remove all the various chemicals that are known to be present in paper-based materials. These chemicals may be printing inks, varnishes, coating components, adhesives, photoinitiators, plasticizers, sizing agents, and strength aids, to mention a few (Pivnenko et al., 2014). Certain inks may, to some extent, be removed from recovered paper by washing or flotation in a process referred to as deinking (Fillat et al., 2015). Washing is used when the ink particles are small and flotation is used when the particles are larger and hydrophobic. During flotation, the foam that contains ink can be removed by overflow or by vacuum (Fillat et al., 2015). These methods, however, focus on the removal of pigment or colour and not necessarily the chemical compounds that may remain present in the paper at microscopic levels.

There are currently 16 South African paper recycling grades (FibreCircle, 2020), as shown in Table 1, with their allowable prohibitions and out-throws. Prohibitive materials are any objects that may cause damage to paper manufacturing machinery or lead to interruptions during processing and production. They include metal, plastic, glass, textiles, wood, sand and building materials (synthetic materials and synthetic paper). Out-throws refer to papers that are manufactured or treated or are in such a form as to be unsuitable for consumption to the given grade specified.

Table 1
South African paper recycling grades

Definition	Abbreviation	Description	Prohibitive Materials Allowed	Total Out-Throws Allowed
Common mixed waste paper	[CMW]	A mixture of various grades of paper and board without restriction on fibre content.	1%	10%
Industrial mixed waste paper	[IMW]	Consists of new cuttings of paperboard as are used in the manufacture of folding paper cartons and similar boxboard products.	1%	2%
Mechanical grades				
Special news	[SN]	Consists of newspapers, magazines and sorted graphic paper from kerbside and other post-consumer collections. All kraft paper must be removed.	1%	3%
Over issue news (flat news)	[FN]	Consists of overrun unsold newspapers containing not more than the normal percentage of inserts. No flexographic printed material allowed.	None permitted	1%

Magazine	[SBM]	Consists of unsold magazines and trims from magazine printers including catalogues and brochures with or without latex bindings. May contain up to 10% of uncoated news type paper.	None permitted	2%
Special magazine	[SSBM]	Unsold magazines and trims from magazine printers, including catalogues, and brochures without latex bindings. May contain a small percentage of news type paper.	None permitted	2%
High grades				
White one	[W1]	Consists of unprinted white wood-free paper or board, off cuts or shavings free from water-insoluble matter.	None permitted	None permitted
Heavy letter one	[HL1]	Consists of white printed or unprinted sheets, and shavings originating from printers or office records. This grade must be free of heavily printed or coloured stock and non-water soluble adhesives.	None permitted	2%
Heavy letter two	[HL2]	Consists of pastel-coloured printed or unprinted sheets, shavings and cuttings originating from printers or office records. This grade must be free of heavily printed or coloured stock and non-water soluble adhesives.	1%	2%

Supermix	[SMW]	Consists of mix of HL1 / HL2 in ratio 50% HL1, 50% HL2. This grade must be free of non-water soluble adhesives.	1%	2%
Sorted office paper	[SOP]	Consists of paper typically generated by offices, containing primarily white and coloured ground wood-free paper, free of unbleached fibre. It may include a small percentage of carbonless paper.	1%	5%
Kraft grades				
Corrugated containers	[K4]	Consists of corrugated containers having liners of kraft or test liner.	1%	5%
New corrugated kraft waste	[K3]	Consists of new corrugated cuttings, sheets and unused boxes as generated by corrugating convertors having liners of kraft or test liner.	None permitted	2%
Unused kraft bags	[K1]	Consists of new kraft multi-wall bag cuttings, sheets and misprint bags, free of stitched papers, poly liners and wet strength paper.	None permitted	2%
Special grades				

Liquid board packaging	[LBP]	Used or unused liquid packaging boards including used PE–coated liquid packaging board (with or without aluminium content). Containing a minimum of 50% by weight of fibres and the balance being aluminium or coatings.	None permitted	3%
Telephone directories	[TD]	Consists of clean telephone directories printed for or by telephone directory publishers.	None permitted	2%

In practice, not all grades of paper are collected at recycling facilities, as they are dependent on consumption patterns and availability. It is also important to note that not all waste collectors (formal or informal) collect all grades of paper as there is often a focus on those with increased economic returns or those that can be collected in larger volumes.

2.3 Recycling regulatory landscape in South Africa

In South Africa, waste paper is categorised as general solid waste derived from domestic waste, business waste and waste packaging. It is regulated by the South African Constitution (Act 108 of 1996), the Hazardous Substances Act (Act 15 of 1973), the Health Act (Act 63 of 1977), the Environment Conservation Act (Act 73 of 1989), the Occupational Health and Safety Act (Act 85 of 1993) and the National Environmental Management (NEM) Act (Act 107 of 1998). In 2008, the NEM: Waste Act (Act 59 of 2008) was promulgated and became the principle governing waste regulation. It was later amended to the NEM: Waste Amendment Act (Act 26 of 2014) (Godfrey & Oelofse, 2017). The first National Waste Management Strategy (NWMS), a legislative requirement of NEM, was developed in 2020 for the drive towards zero waste (Dobbelstein & Lochner, 2023). The 2020 NWS, the most recent version, promotes separation at source through a concerted effort to raise public awareness and private sector investment in the delivery of infrastructure and services such as kerbside collection, drop-off centres and buy-back centres, all linked to a national awareness campaign around recycling. It focuses on addressing the UN SDG 12 in recognition of the Basel Convention on the Transboundary Movements of Hazardous Wastes and their Disposal, the Stockholm Convention on Persistent Organic Pollutants (POPs) and the Rotterdam Convention on Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade. The NWS identifies separation at source as an effective means of reducing waste and enhancing recycling through the provision of more homogenous and higher-value waste streams, allowing for better resource recovery. In this strategy, separation at source is seen as a possible means of contamination reduction and as an alternative to landfill disposal. The NWS further identifies the obstacles that must be overcome in South Africa for effective implementation of separation at source. These obstacles have been identified as littering and illegal

dumping, lack of infrastructure for recycling, lack of a recycling culture, backlogs in waste service delivery, inconsistent waste collection and the lack of education and awareness in many districts. At an administrative level, better implementation and monitoring of policies and legislation is still required to better align government and industry. Other hindrances that have been identified in the NWS relate to budgetary constraints, the lack of end-markets for certain recyclables as a consequence of constraints in manufacturing capacity, as well as markets subject to global economic trends and cycles. These particular hindrances often result in landfilling being viewed as the cheaper, short-term option.

The most pertinent regulation to paper recycling in recent years was the promulgation of the Extended Producer Responsibility (EPR) regulations in 2021, under the NEM: Waste Act (Act 59 of 2008). EPR is a policy concept aimed at extending producers' responsibility for their products to the post-consumer stage of their product's lifecycle (Nahman, 2010). Producers are thereby obligated to establish, contribute or participate in the financial and/or operational responsibility associated with the collection, recycling, recovery or disposal of packaging material (UNEP, 2019). Through the EPR, the South African paper and packaging recycling economy is subsidised by brand owners, converters and retailers with the EPR schemes managed by FibreCircle, the paper recycling Producer Responsibility Organisations (PROs) (Godfrey, 2021). The grades of paper listed in the EPR differ in their designations from those used in paper recycling grades shown in Table 1. The recycling rates are defined for seven grades which are newspaper, magazines, office and graphic paper, mixed and other paper, corrugated cases and kraft papers, liquid board packaging, paper and paper packaging labels as well as paper and paper packaging paper sacks. It is not fully known what the effect of this non-cohesion will be in the long run. Following the EPR regulation, the Department of Forestry, Fisheries and Environment released a government notice inviting comments for the NEM Waste Act: Packaging Guideline: Recyclability by Design for Packaging and Paper in South Africa. The main purpose of this proposed Packaging Guideline is to reduce the volume of packaging ending up in landfill sites by improving product design and incorporating environmental implications into design decisions. It can thus be seen that although a regulatory framework exists for the management of

waste, it does not specifically address the chemical constituents that may be in waste paper and the hazardous nature thereof.

2.4 Bibliometric analysis

Bibliometric analysis was conducted using Bibliometrix in order to fully examine and understand the published information related to pollutants in the paper recycling chain. Bibliometrics, the statistical analysis of published data and its related metadata, is used to explore publishing trends and to illustrate relationships between published works (Ninkov et al., 2022). Scopus, a curated bibliometric and citations database that includes metadata from peer-reviewed journals, conference proceedings and books, was used to generate a bibliometric data set (Baas et al., 2020). The Scopus keyword search made use of both Boolean operators and wildcards to refine the search using "paper* AND contamin* OR pollut* OR recyc*". The search generated 2212 documents, with the majority of the studies being from the USA (64) and China (34). It further highlighted that the research in this field on a regional level was limited with only two papers meeting the search criteria, both of which emanated from this present study (Mofokeng et al., 2024a; Mofokeng et al., 2024b).

A co-occurrence network map was generated using Bibliometrix, shown in Figure 2, using the authors' keywords with normalisation by association. It can be seen that on a global level, research has centred mostly around food packaging and migration studies on phthalates, mineral oil and bisphenol A (Bengtström et al., 2016; Biedermann & Grob, 2012, 2019; Carlos et al., 2021; Parigoridi et al., 2023; Rosenmai et al., 2017), where the size of each node and the width of links were reflective of the studies centred on the same themes and links between these, based on keyword co-occurrence in the 2212 documents. The research on food packaging was shown to draw links to research related to paperboard and recycling, which further expanded to composites (Bhardwaj, 2023; Cheng et al., 2024; Goll et al., 2018; Zhang et al., 2022), barrier coatings (Chi et al., 2023; Maes et al., 2019; Shorey & Mekonnen, 2022; Zhang et al., 2016) and circular economy (Moqbel et al., 2024; Pavelski et al., 2024; Zhu et al., 2022). This indicated that this study on pollutants in the South African paper recycling chain uniquely lay within these two

key research clusters where emerging contaminants and pollutants would be explored against the circularity of paper recycling.

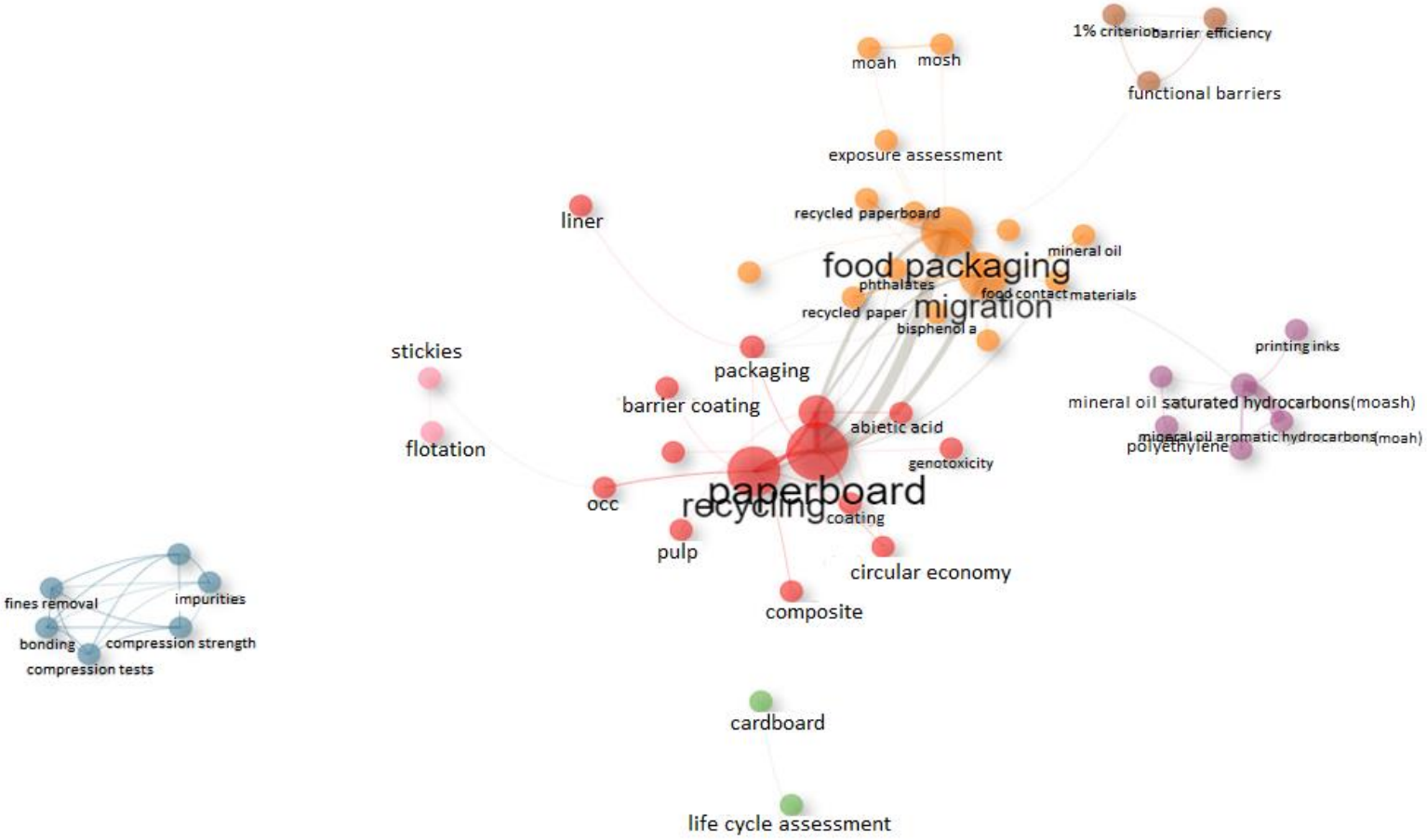


Figure 2 Bibliometric co-occurrence network map

A trends analysis in the topics of interest related to the search results, in Figure 3, shows the trend topics in this research area have evolved over time from “waste disposal” in the early 2000s to chemical contamination and food safety from 2011 onwards. Most recently, studies related to grease resistance from 2017 onwards and the circular economy, from 2019, have been of high interest. Studies on grease resistance are related to barrier properties (Basak et al., 2024; Keresztes & Csóka, 2023) and to per- and polyfluoroalkyl substances (PFAS), which have gained considerable attention due to their persistent and bioaccumulative properties (Dueñas-Mas et al., 2023; Manojkumar et al., 2023; Sapozhnikova et al., 2023; Schwartz-Narbonne et al., 2023; Zabaleta et al., 2020). It was thereby important to ensure that this study was aligned with current trends to ensure relevant, novel and pioneering research from South Africa.

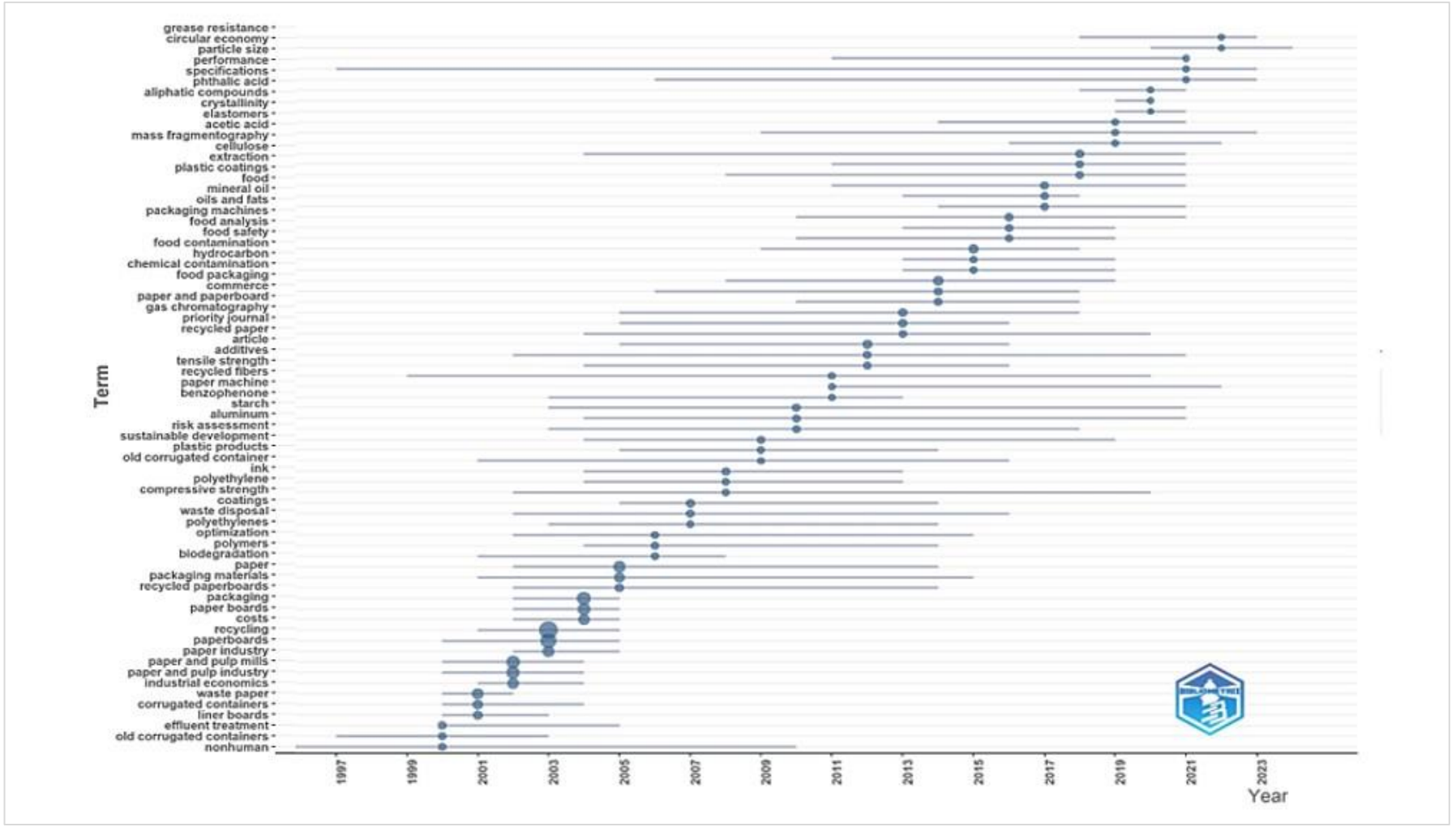


Figure 3 Trend topics progression on a yearly basis

2.5 Techniques for analytical exploration

The process of identification and quantification of organic compounds is strongly influenced by the sample pre-treatment or extraction process used prior to the chromatographic analysis (Bengtström et al., 2016). This in turn is influenced by the solubility of the compounds in the extraction medium and was a driving factor in ensuring compatibility with the chromatographic analytical instrumentation used. Chromatography in tandem with mass spectrometry allows for the separation, identification and quantification of detected organic compounds of varying physical and chemical properties, based on their solubility, volatility, ionizability and stability (Bengtström et al., 2016).

Since this study aimed to utilise both gas chromatography (GC) and liquid chromatography (LC), it was important to understand the different sample pre-treatment techniques that have previously been studied for extraction of paper-based materials in relation to the chromatographic state, the analytes targeted and the choice of a solvent. For GC-MS-based analysis, as shown in Table 2, Soxhlet extraction, accelerated solvent extraction (ASE), solid-phase extraction (SPE) and ultrasonic-assisted extraction (UAE) (Boccacci Mariani et al., 2015; Carlos et al., 2021; Parigoridi et al., 2023; Pivnenko et al., 2016) have been used for extraction and pre-concentration of phthalates, phenols and benzophenone using dichloromethane (DCM), acetone, methanol and hexane. Table 3 provides an overview of LC-MS-based analysis where UAE and liquid extraction (LE) were the prominent extraction methods used for the isolation of bisphenols, PFAS and primary aromatic amines with ethanol, methanol and acetonitrile being shown to be the solvents of choice (Vavrouš et al., 2016; Sapozhnikova et al, 2023; Sanchis et al., 2019). The significance of the detection level lies in whether the analytical exploration aims to achieve trace or ultra-trace analysis. Trace analysis refers to analyses performed at less than 100 parts per million (ppm) whilst ultra-trace refers to those performed below 1 ppm (Brown & Milton, 2005). Both trace and ultra-trace analyses are important in understanding latent contamination and pollution, possible exposure pathways and likely sources (Lowe et al., 2021; Peters et al., 2019; Vápenka et al., 2016). It can be seen in Tables 3 and 4 that generally lower detection limits were achieved in LC-based detection when compared to GC-based

analysis; although this was strongly influenced by the detector sensitivity as shown in Vavrouš et al. (2016) where the use of a triple quadrupole GC-MS/MS enhanced sensitivity.

Table 2

GC-MS-based paper analysis

Sample extraction technique	Target compounds	Types of paper extracted	Solvent used	LOD	Reference
ASE-SPE	Benzophenone (BP), diisopropyl naphthalene (DIPN), 2-hydroxybenzophenone, 4-methylbenzophenone, diisobutyl phthalate (DIBP), dibutyl phthalate (DBP), benzylbutyl phthalate (BBP), diethylhexyl phthalate (DEHP), 4,4 bis(diethylamino)benzophenone (DEAB)	Mill paperboard	Acetone: hexane (4:1)	0.05 - 0.1*	Boccacci Mariani et al., 2015
LE	DBP, BBP, DEHP, dioctyl phthalate (DOP), dimethyl phthalate (DMP), diethyl phthalate (DEP), diethylhexyl adipate (DEHA)	Dry food packaging	DCM	-	Parigoridi et al., 2023
UAE	DBP, BBP, DEHP, DOP, DMP, DEP, DEHA	Dry food packaging	DCM	-	Parigoridi et al. 2023
UAE	DBP	Recycled paperboard	DCM	0.04*	Anggarkasih et al., 2018
UAE	DBP, BBP, DEHP, di-n-octyl phthalate (DNOP), diisononyl phthalate (DINP), didecyl phthalate (DIDP)	Fast food packaging	DCM: hexane (2:1)	0.12*	Carlos et al. 2021
Head space-solid phase microextraction (HS-SPME)	DBP, BBP, DEHP, DOP, DMP, DEP, DEHA	Dry food packaging	-	-	Parigoridi et al. 2023

LE-SPE	BBP, DBP, dicyclohexyl phthalate (DCHP), DEHP, DEP, DIBP, DIDP, DNOP, Di (2-methoxyethyl) phthalate, DMP, dipropyl phthalate (DPP).	Municipal wastepaper, magazines, books, tissues, newspapers, paper plates and cups	Ethyl acetate	0.014-2.5 **	Pivnenko et al. 2016
Microwave-assisted extraction with SPE	Nonylphenol, phenylphenol, chloro methylphenol, octylphenol, tert-octylphenol.	Municipal wastepaper, magazines, books, tissue, newspapers, paper plates and cups etc.	Methanol: water: triethylamine (78:20:2)	0.0079-0.79**	Pivnenko et al. 2016
Soxhlet extraction	BPA, DEHP	Paperboard Food packaging	BPA extraction in ethanol, DEHP in acetone: hexane (4:1)	0.015–0.017*	Sanchis et al. 2017
Soxhlet extraction	Pentachlorobiphenyls, dioxins	Pizza box	Ethanol	-	Bengtström et al. 2016
#UAE and LE with quechers clean-up	Phthalates, polycyclic aromatic hydrocarbons, naphthalenes, benzophenones	Bakery paper, food cardboard, paper coffee filters	1:1 Acetonitrile and water: 1:1 propanol and water (1:1)	0.0007-0.069*	Vavrouš et al., 2016

UAE	BP, pentachlorophenol, DEHP, DBP, DIPN	Pastry packaging	DCM and anhydrous sodium sulphate, reconstituted in methanol: DCM (1:1)	0.001-0.005***	Ahmadkhaniha and Rastkari, 2017
UAE with SPE	PFAS	fast food packaging	Hexane: isopropanol (4:1) followed by methanol: acetonitrile (1:1)	0.001-0.37****	Schwartz-Narbonne et al., 2023

* LOD values in mg/L, mg/kg or µg/g (ppm) **mg/kg dm, *** mg/dm2, **** ng

Table 3

LC-MS-based paper analysis

Sample extraction technique	Target compounds	Types of paper extracted	Solvent used	LOD	Detector	Reference
UAE and LE with quechers clean-up	Per- and polyfluoroalkyl substances (PFAS) and bisphenols	Bakery paper, food cardboard, paper coffee filters	1:1 Acetonitrile and water: 1:1 propanol and water (1:1)	0.4- 4*	MS/MS	Vavrouš et al., 2016
Focused ultrasonic solid-liquid extraction (FUSLE)	Bisphenol A (BPA), bisphenol F (BPF), bisphenol A diglycidyl-ether (BADGE), bisphenol F diglycidyl-ether (BFDGE)	Retail kitchen paper, food boxes	Methanol	16-47*	Q-TOF	Pérez-Palacios et al., 2012
FUSLE	PFAS	microwave popcorn bags, moulded fibre bowl, wrappers	Ethanol	-	Q-Orbitrap	Silva et al., 2021
UAE	PFAS	cardboard paper food packaging	1. Methanol 1% acetic acid,	0.002-0.027*	MS/MS and Q-Orbitrap	Sapozhnikova et al, 2023

				2.1% Formic acid in methanol 3. 95% Ethanol in water		
LE	BP, DEAB, 4,4′-bis(dimethylamino), benzophenone (Michler's ketone, MK), 2,2′-dimethoxy-2-phenylacetophenone, 2,4-diethyl-9H-thioxanthen-9-one (DTX), 4-methylbenzophenone, isopropylthioxanthone (ITX) ,2-ethylhexyl-4-dimethylaminobenzoate, 4-phenylbenzophenone, monobutyl phthalate (MBP), BBP, DCHP, DEHP, acetyl tributyl citrate, caprolactam and BPA	cardboard, cupcake paper mould, baking paper	Acetonitrile reconstituted in methanol	0.002-7**	Q-Orbitrap	Blanco-Zubiaguirre et al 2020
UAE with SPE	PFAS	fast food packaging	Hexane: isopropanol (4:1) followed by methanol: acetonitrile (1:1)	0.001-0.62 **	MS/MS	Schwartz-Narbonne et al., 2023
UAE	PFAS	paper-based food packaging	Methanol with 1% acetic acid	0.001-0.7*	MS/MS	Zabaleta et al., 2016
UAE with SPE	PFAS	recycled fibre pulp and paper	Ethyl acetate			Langberg et al., 2021
Soxhlet	BPA, methylparaben, BADGE, PFAS and abietic acid	paper food packaging	Ethanol	1-8*	MS/MS	Bengtström, 2014

UAE	BPA and its analogues	thermal paper	Methanol	50*	MS/MS	Banaderakhshan et al., 2022
UAE	BP, butylated hydroxytoluene, MK, triphenylphosphine, tris(2,4-ditert-butylphenyl) phosphite, tris(2,4-ditert-butylphenyl) phosphate, tetrakis [methylene-3- (3,5-di-tert-butyl-4-hydroxyphenyl-propionate)] methane	magazines	Acetonitrile	0.15-9***	MS/MS	Liu and Mabury, 2021
LE	hydroxycyclohexyl phenyl ketone, MK, DTX, 2-ethylhexyl dimethylamino benzoate, hydroxy methyl propiophenone, ITX, 4-benzoylbiphenyl, BP, toluendiamine, aniline, naphthalene diamine, phenylenediamine, diamino diphenyl ether, dimethyl benzidine, ethylhexyl diphenyl phosphate, tris(2-choloroisopropyl) phosphate and triphenyl phosphate	liquid packaging carton (tetra brick)	3% Acetic acid in water & DCM reconstituted methanol: water (1:1)			

* LOD values in ng/mL, ng/g or µg/kg (ppb), ** ng, *** ng/dm^2

2.6 Analytical approach

2.6.1 Understanding the targeted and untargeted approaches

Two main approaches are applied in analytical chemistry, targeted quantification of pre-selected analytes and untargeted identification of unknown compounds. Targeted analysis of paper-based material has covered the various classes of compounds shown in Tables 3 and 4 using GC and LC-based analysis, respectively. These allow for the detection of unreported organic chemical compounds by reducing sample pre-treatment and analytical method selectivity and specificity. Selectivity refers to the capacity of a method to determine an analyte of interest without interferences from other components whilst specificity is optimum selectivity to a specific analyte or group of analytes with the removal of all other components (Raposo & Ibelli-Bianco, 2020). Selectivity is applied in the targeted analysis in order to enhance signal response and remove interfering compounds. The enhanced selectivity is generally validated using reference standards for identity confirmation, calibration curve plotting for quantification as well as by the determination of coefficients of determination, limit of detection and quantification, accuracy and precision (Blanco-Zubiaguirre et al., 2020; Graíño et al., 2018; Raposo & Ibelli-Bianco, 2020). In recent years, targeted analysis has employed the use of isotopically-labelled internal standards in conjunction with external standards to enhance accuracy, reduce extraction variability and correct matrix interference (Harris et al., 2022; Rawn et al., 2022).

Untargeted analysis, on the other hand, aims for the identification of a broader class of compounds by optimising parameters to suit compounds with a wider range of polarity, pH and boiling temperatures (Peters et al., 2019) in order to reduce selectivity whilst making considerations for possible matrix interferences and losses in sensitivity (Hajeb et al., 2022). Untargeted analysis can further be categorised as suspect screening or as non-targeted analysis (Badea et al., 2020; Blanco-Zubiaguirre et al., 2020; Charbonnet et al., 2022; Joseph et al., 2023; Manz et al., 2023). In suspect screening, tentative identification is confirmed by preliminary information such as molecular mass, isotope pattern and/or expected adducted matched against a known spectral library or database (Hajeb, 2022). Non-targeted analysis, on the other hand, is not dependent on a spectral library and instead

theoretically elucidates the possible identity of the unknown compound from the acquired chromatograms and mass spectra using information such as the isotope pattern, probable adducts, fragmentation patterns, retention times and mass defects (Hajeb et al., 2022). For both suspect screening and non-targeted analysis, the establishment of confidence levels against which identification is reported has become common practice (El-Deen & Shimizu, 2022; Joseph et al., 2023; Wang et al., 2018). These confidence levels are used as a measure of probable identification where the highest confidence, usually referred to as Level 1, is associated with matching against certified reference material (Charbonnet et al., 2022). The lower confidence levels from 2 onwards are usually associated with a slight decrease in likelihood or probability, based on thresholds established (Charbonnet et al., 2022). These thresholds may include spectral databases, retention indexes, accurate mass, fragmentation pattern, etc., and are generally study or chemical class-specific. From the aforementioned studies and Tables 3 and 4, a general overview of the approach to analytical exploration is shown in Figure 4.

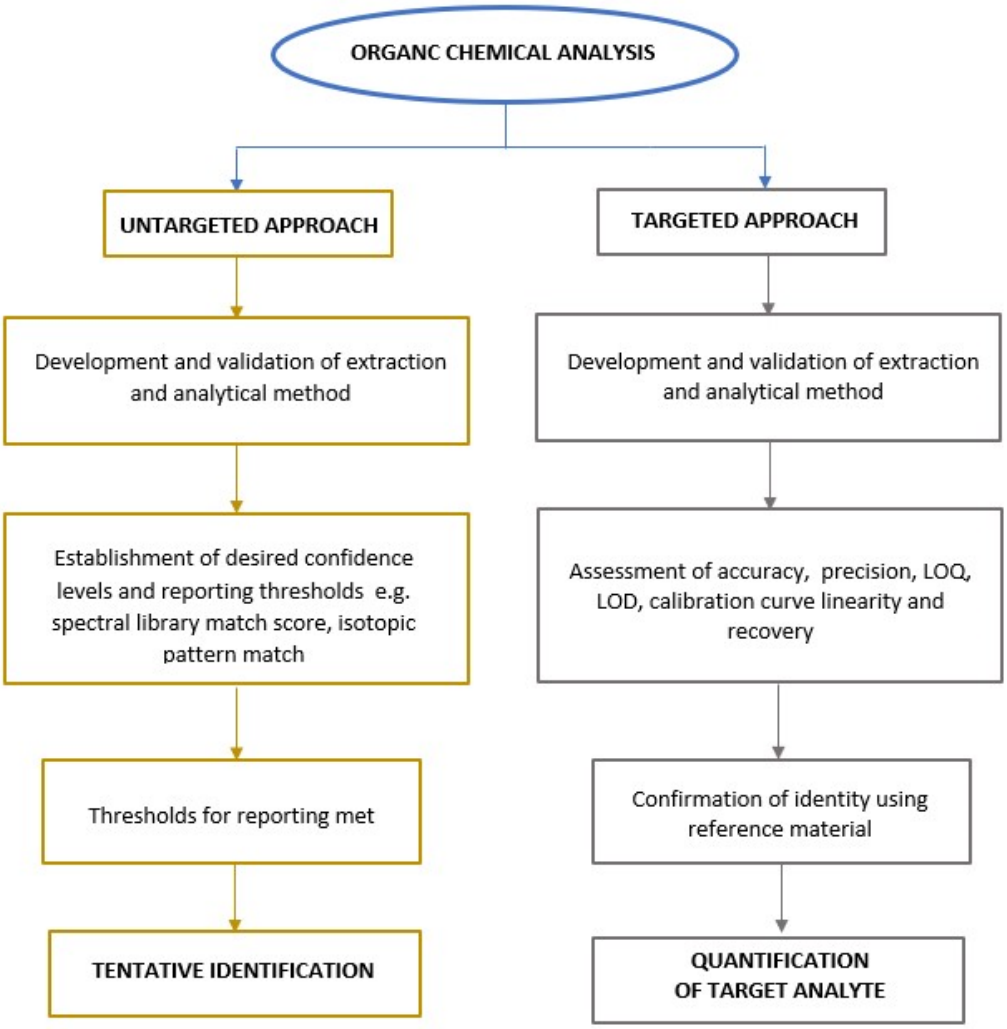


Figure 4. Overview of analytical approach

The targeted and untargeted approaches can be combined in order to achieve a broader understanding of chemical constituents (Blanco-Zubiaguirre et al., 2020; Harris et al., 2022; Joseph et al., 2023; Munoz et al., 2019; Sanchis et al., 2017; Schwartz-Narbonne et al., 2023). In such studies, it is vital to strike a balance between selectivity, sensitivity and robustness (the ability of an analytical method to remain unbiased regardless of small changes in the experimental conditions (Ferreira et al., 2017).

2.6.2 Application of chemometrics to strengthen analytical exploration

In addition to the targeted quantification and untargeted identification of chemical compounds, chemometrics can be used to further analyse the data obtained from the chromatographic instrument. Chemometrics is the statistical analysis of chemical data (Héberger, 2008). It has been used extensively in analytical chemistry (Joseph et al., 2023; Joshi, 2023; Kumar et al., 2014) from food (Castañeda et al., 2024), plastics (Wu et al., 2023) and paper (Guazzotti et al., 2015; Li et al., 2023), to metabolomics (Karabagias, 2022), materials science (Schmitz et al., 2022) and environmental media research (El-Deen & Shimizu, 2022). The premise of chemometrics is to take the data obtained, usually in the form of occurrences, or detected concentrations and determine if there are distinct patterns in the data, to spatially show similarities and differences and to predict future trends or model the data. The most commonly used modelling techniques include principal component analysis (PCA) (Adjei et al., 2019; Guazzotti et al., 2015), partial least squares (PLS) analysis (Jiménez-Carvelo et al., 2021), heat maps (Castañeda et al., 2024), and hierarchical clustering analysis (HCA) (Li et al., 2023). The choice in the statistical tool used is usually dependent on the type of data to be assessed (continuous versus categorial), if there is a relationship between any of the components (linear or non-linear regressions and correlations), the presence of set or predefined descriptors (supervised versus unsupervised), whether the data is normally distributed (parametric versus non-parametric) as well as the presence of outliers (Castañeda et al., 2024; Galindo-Prieto et al., 2014; Joshi, 2023; Kumar et al., 2014).

2.6.3 Analytical approach in the present study

The combination of chemical analysis using extraction techniques, chromatographic instrumentation, chemometrics and interviews was used to facilitate the analytical exploration of the organic chemical constituents of paper recycling, the identification and quantification of emerging contaminants and persistent organic pollutants as well as apportionment of their possible sources, transport and fate in the South African paper recycling chain. For chemical profiling of organic chemicals using LC and GC-MS in **Paper 1**, ASE as well as UAE were utilised in conjunction in order to expand the range of differing compounds

identified in the untargeted analysis. ASE was then used for polar and non-polar semi-volatile pollutant quantification using GC-MS in single ion monitoring for improved signal selectivity and sensitivity in **Paper 2**. The targeted and suspect screening of pharmaceuticals was enhanced by polar extraction using ultrasonic-assisted extraction using LC-MS in **Paper 3**. This was followed by ASE with weak anionic exchange SPE clean-up in **Paper 4** for PFAS analysis promoting enhanced selectivity by employing pH control and data-dependent mass spectrometry acquisition with pre-selected precursor and product ions. Both selective and non-selective workflows using ASE with SPE and UAE without SPE were then compared in the suspect screening of PFAS in **Paper 5**. The chemometric tools employed included sparse partial least squares-discriminant analysis (sPLS-DA) (**Paper 1**), PLS variable importance in projection (VIP) scores (**Paper 2**) as well as Spearman rank correlation and HCA with a dendrogram (**Paper 4**). To further enhance the analytical exploration, qualitative interviews were conducted to better understand the data generated in the various analyses. The objective of the interview process was to bridge the gap between industry practices and the limited research available on chemical compounds in South African research on paper recycling.

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CHAPTER THREE

3 AIMS AND OBJECTIVES

3.1 General aims

The purpose of this study was to analytically explore the organic pollutants present in the South African recycled paperboard value chain. Further, to investigate the possible sources, transport and fate of identified pollutants. Various analytical chemistry techniques and methods were employed to extract, analyse and interpret the results. Data analysis from chemical analysis, chemometrics and interviews were used to determine if chemical pollutants could be linked to a specific process, chemical additives, waste management protocols and recycling practices employed in South Africa. The objective of the interview process was to bridge the gap between industry practices and the limited research available on chemical compounds in South African research on paper recycling.

This study aimed to chemically profile the various paper recycling grades used in the manufacture of recycled paperboard. The key stages explored were pre-consumer, retail and post-consumer which included, amongst others, paper mills, retail stores, recycling facilities and waste pickers.

3.2 Specific objectives

The specific objectives of the research were:

3.2.1 To develop and perform untargeted chemical analysis to identify semi-volatile and non-volatile organic pollutants that may be present in different paper recycling grades, in paper collected key stages of the recycled paper chain using gas and liquid chromatography in tandem with mass spectrometry.

3.2.2 To develop, validate and perform targeted chemical analysis of compounds of interest using gas and liquid chromatography in tandem with mass spectrometry.

3.2.3 To apportion the source of chemical constituents detected in samples under investigation, prevalence, as well as their possible propagation and fate in the South African recycling value chain.

3.2.4 To employ chemometrics to analyse the results for trends, correlations and predictive modelling.

3.2.5 Where applicable, to fill information gaps by conducting interviews with identified key stakeholders in the South African recycling sector.

3.3 Study limitations

The variable nature of recycled paper, waste management strategies, and the environment in which waste paper is disposed and collected as well as consumer usage patterns meant that findings are related to the samples under investigation or those of similar properties. Differentiating between paper made from virgin fibre and that made of recycled fibre could only be confirmed for pre-consumer samples but was not established for retail and post-consumer (unless specified on the packaging).

3.4 Novelty

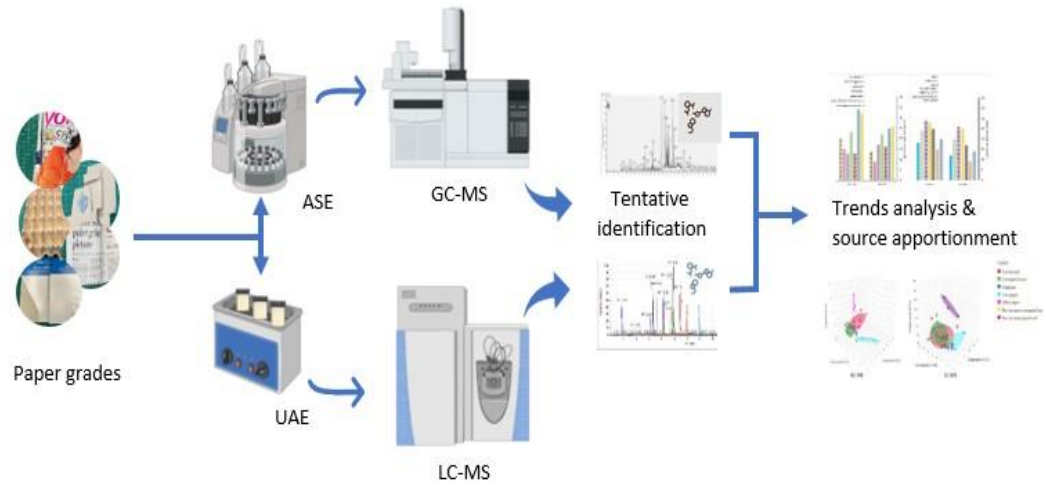
To the best of my knowledge, this becomes the first scientific-based research performed in South Africa on the identification of chemical constituents of different paper recycling grades paper considering the uniquely South African paper recycling chain. On a global level, there are limited published studies that focus on an optimised extraction method for a variety of paper-based matrices such as newsprint, magazine, office paper, corrugated board and paperboard, as shown in this study. The pollutants identified in the collected paper indicated that the South African paper recycling chain has common pollutants to those reported in Global North studies as well as previously unreported pollutants. This study is the first study to investigate the presence of pharmaceuticals in paper-based material, highlighting the migratory interface between consumer goods, pharmaceuticals and the environment. Further, it highlights the presence of many compounds such as plasticisers, flame retardants and antioxidants, which were previously linked only to plastic materials. It can thus be said that this study is novel in both its analytical and investigative approach.

CHAPTER FOUR

4 PAPER 1

This paper titled “Chemical profiling of paper recycling grades using GC-MS and LC-MS: An exploration of contaminants and their possible sources” published in **Waste Management** (2024) 189, 148–158. This paper looks at the organic chemical characteristics of paper recycling grades using GC-MS and LC-MS. It further identifies sources of the various compounds and explores possible trends in the chemical constituents by paper grade and by site of sample collection.

GRAPHICAL ABSTRACT



Chemical profiling of paper recycling grades using GC-MS and LC-MS: An exploration of contaminants and their possible sources

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Abstract

Paper packaging made with recycled paperboard is used to pack various consumer goods that can include amongst others, electronics, toys, food, cosmetics, and stationery. Chemical profiling of the various paper recycling grades used in the manufacture of recycled paperboard was undertaken to investigate possible sources of contaminants and their propagation in the paper recycling chain. Pre-consumer, retail and post-consumer paper-based materials were collected at papermills, corrugators, grocery stores, household waste, solid waste disposal sites and recycling facilities. In the GC-MS analysis, phthalates, long-chain aliphatic compounds, and fatty acids were the most commonly detected compounds whilst phthalates and bisphenols featured most prevalently in the LC-MS analysis. The factors that were identified as likely contributors to the detection of the different chemical compounds included the presence of wood derivatives, the use of certain chemical additives during manufacturing, and exposure of paper to contaminants from consumers, other goods and the environment. Waste mingling, recovery, sorting and reprocessing into recycled paper were shown to also influence the chemical profile of paper materials. Sparse partial least squares-discriminate analysis indicated that newspaper and office paper had unique chemical constituents, whilst cartons were shown to have higher variability. By looking at key stages of paper recycling, this study showed that the possible persistence and transformation of chemical compounds in additives must be evaluated when considering the recyclability of paper-based materials. Further, it highlighted that different separation approaches may be required to reduce contaminant exposure opportunities in post-consumer paper materials.

Keywords: Recycled paper; Contaminants; Chemical compounds; Untargeted analysis; Mass spectrometry

4.1 Introduction

Paper packaging is designed to serve multiple purposes that include storage, protection of goods from damage and contamination, providing information to consumers, brand ownership, and ease of transportation (Sanchis et al., 2017). Paper recycling is a critical component of sustainable waste management as it reduces the need for landfills, minimises waste, saves energy and ensures ecological conservation (Lipkiewicz et al., 2021; Senarathna et al., 2023). Recycling strategies generally aim to promote high-quality recycled goods with as few contaminants as possible (Blanco et al., 2013; Miranda et al., 2013). Separated-at-source collection systems tend to be considered as being of a higher quality than co-mingled recycling systems (Miranda et al., 2013). Paper destined for recycling can be collected prior to use by consumers (pre-consumer) or after consumer usage (post-consumer). Pre-consumer recycled paper is considered higher quality than post-consumer paper which may be contaminated during or after usage (Senarathna et al., 2023). Recycled paperboard may be made from a single paper recycling grade or a combination of different paper recycling grades that may include corrugated boxes, magazines, office paper and newspaper. It is thus important to understand how the differing chemical characteristics of paper recycling grades and post-consumer sites, where waste paper is recovered, may influence the quality of recycled paperboard, in terms of the chemical contaminants.

In paper manufacturing, chemicals are often added to impart specific physical properties and for aesthetic purposes (Bajpai, 2018), some of which may degrade and transform during application and usage. The increasing trends toward paper-based material for traditionally plastic applications means that different chemical additives may now be commonly used to impart properties such as moisture resistance, flexibility and strength; than in previous years (Oloyede & Lignou, 2021). In addition to intentionally used chemicals, waste paper may be exposed to a variety of foreign chemical compounds during and after consumer usage, mingling with other waste streams, recovery, environmental exposure and re-manufacturing into new products (Lowe et al., 2021). Since the circular nature of paper recycling increases the possible propagation and accumulation of some of

these chemicals, it is important to evaluate the chemical profile of various grades used in the paper recycling chain.

Previous studies in recycled paper have not examined paper in the key stages of paper recycling with only limited studies on the various grades such as magazines, newspapers and office paper used to manufacture recycled paperboard (Pivnenko et al., 2016; Tripathi et al., 2022). For paper packaging, untargeted analysis, which aims to screen for the presence of a range of compounds identified through spectral libraries (Hajeb et al., 2022), has mainly been performed under the auspices of food contact safety focused on the migration of intentional (IAS) or non-intentionally added substances (NIAS) (Sanchis et al., 2017). The compounds identified in such studies include primary aromatic amines, photoinitiators, bisphenol A, mineral oil, and phthalates, amongst others (Bengtström et al., 2016; Blanco-Zubiaguirre et al., 2021; Peters et al., 2019; Sanchis et al., 2019, 2017; Suciu et al., 2013). Currently, no single analytical method is able to comprehensively detect every chemical in a sample. Mass spectrometry (MS) serves as a powerful, useful tool for untargeted analysis where gas chromatography (GC) and liquid chromatography (LC) can be employed together for constituent separation and identification. The combination of LC and GC allows for the detection of organic compounds with varying functional groups, molecular masses, solubility, vapour pressures, and boiling points (Lowe et al., 2021; Bengtström, 2014).

The focus of this present study was to expand beyond food packaging to the holistic extraction of both food and non-food paper products at different stages of the paper recycling chain, with the aim of performing an in-depth, untargeted investigation of the organic chemical profiles and their likely sources. Non-selective extraction techniques aimed to identify a wide range of organic chemical constituents present in the different paper samples. Pre-consumer paperboard with a recycled fibre component, retail paperboard-based packaging and the various recycling grades used in the manufacture of recycled paperboard collected at post-consumer sites were investigated. These post-consumer paper grades comprised newspapers, magazines, corrugated boxes, cartons, and office paper collected in household waste, at recycling facilities, solid waste disposal sites, and from waste pickers

(informal waste collectors who reclaim recyclable material) (Godfrey, 2021). The advantage of this untargeted analysis approach was that it could be used to identify previously unreported chemicals, uncover chemical usage trends, and reveal possible exposure pathways (Lowe et al., 2021) previously not linked to paper products that may need further investigation.

4.2 Materials and methods

4.2.1 Chemicals

Acetone (HPLC grade) and hexane (HPLC grade), sourced from Merck, Johannesburg, South Africa, were used in the GC-MS sample preparation. The chemicals and solvents used in sample preparation for LC-MS, were LC-MS grade methanol (Anatech, Cape Town, South Africa), water (Merck, Johannesburg, South Africa), and ethanol (Merck, Johannesburg, South Africa). Diisobutyl phthalate was sourced from Merck (Johannesburg, South Africa).

4.2.2 Sample collection

Samples were collected from the pre-consumer, retail, and post-consumer stages of the paper recycling chain at various sites in Cape Town, South Africa. Fig.1. gives an overview of these three stages and sampling chosen to reflect the manufacture of recycled paperboard.

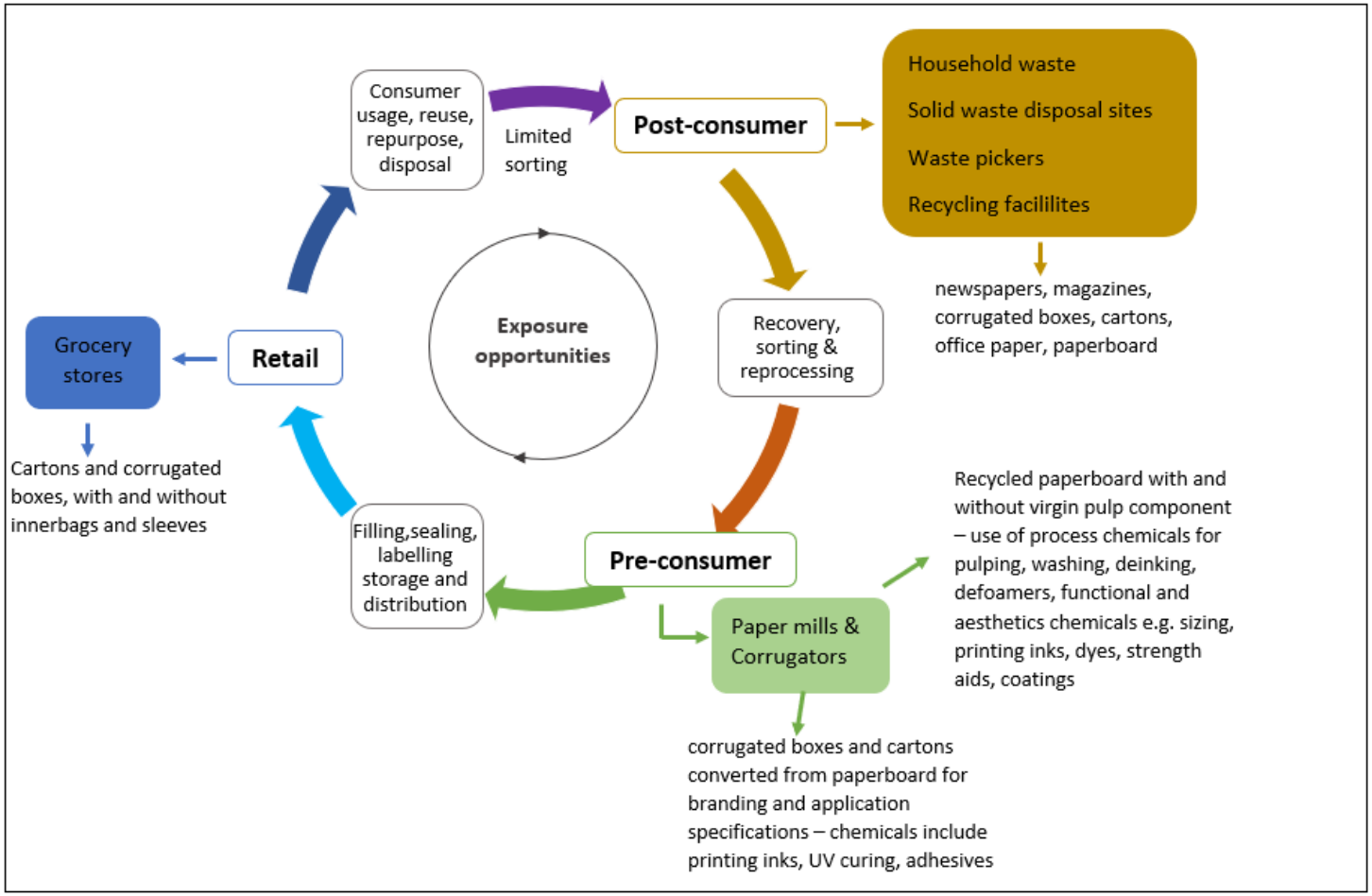


Fig. 1. Overview of paper recycling chain and stages of sample collection

The 39 samples collected included paperboard, cartons, corrugated boxes, newspaper, magazines, and office paper. In this study, paperboard was generally considered to be high grammage (greater than 125 gram per square metre (Adamopoulos et al., 2014)) or thick paper whilst cartons included converted paperboard such as fast-food containers, cereal cartons, and chocolate packaging. Corrugated boxes consisted of corrugated, converted paperboards with at least one liner and a fluting medium. The individual samples are depicted in Fig. S1.

4.2.3 Sample pre-treatment

Each sample was cut into small pieces and then shredded to a dry pulp using a kitchen blender. Samples were prepared in triplicate. For GC-MS, samples were extracted using accelerated solvent extraction (ASE) employing a Dionex 350 ASE system (Anatech, Cape Town, South Africa) which entailed the extraction of 3.5 g of a shredded paper sample using a 5:2 acetone: hexane mixture at 70 ℃. The combination of a polar, aprotic (acetone), and non-polar solvent (hexane) meant that a wider range of compounds could be extracted. Preliminary findings attained when performing the extraction indicated that an increase in the non-polar component led to what was likely a hydrocarbon "hump" and reduced chromatographic resolution (Fig. S2). This correlated with the observation already reported in literature where such humps were evident and attributed to unresolved alkane C11-C35 aliphatic chains (Biedermann et al., 2013; Biedermann & Grob, 2012). The overall aim of the present study was thus to add sufficient non-polar solvent to obtain sufficient peak resolution and increase the number of components detected, whilst also improving the detector response without the need for sample clean-up and thereby introducing undesirable selectivity to the untargeted analysis. The final 40 mL volume of extract was reduced to 1 mL by evaporation under nitrogen at 45 ℃ using a Biotage TurboVap (Anatech, Cape Town, South Africa) followed by filtration with 0.45 µm syringe filter prior to GC-MS injection. For LC-MS, 1.0 g of shredded paper was extracted using a 2:1:1 water: ethanol: methanol combination placed in a 60 mL glass vial prior to sonic-assisted extraction at 60 ℃ for 2 hours in a sonic bath (Power Sonic 405, United Scientific, Cape Town) for ultrasonic-assisted extraction (UAE). Bengtström et al. (2016) reported that polar

compounds present in paperboard are expected to strongly interact with polar hydroxyl groups in an aqueous medium (Bengtström et al., 2016) and are better separated by LC than by GC. Extraction in a polar medium was important when considering that repulping of recycled fibre occurs in water and would thereby give insight into the leachability of chemical compounds (Lowe et al., 2021). The resulting extract was filtered using a 0.22 µm syringe filter before LC-MS injection. The LC-MS analysis was thus performed to expand the identification of more polar, more non-volatile compounds in paper-based samples.

4.2.4 Chromatographic acquisition

GC-MS analysis was achieved using Thermo Scientific Trace GC Ultra ISQ MS with a TriPlus RSH Autosampler (Anatech, Cape Town, South Africa) fitted with a Phenomenex ZB-5MS capillary column with a guard column (30 m+10 m Guardian x 0.25 mm ID x 0.25 µm thickness) (Separations, Cape Town, South Africa). The chromatographic separation included temperature programming with the inlet temperature set at 260 °C, initial oven temperature at 40 °C initially held for 5 min followed by a ramp to 315 °C at 8 °C/min, then held for 15 min, before being cooled down to 220 °C at 15 °C/min. High-purity helium gas purchased from Air Products (Cape Town, South Africa) was used as the carrier gas. For MS measurements, the scan mode was set from 40 to 1100 m/z.

The separation and detection of chemical compounds by LC-MS was achieved using a Thermo Scientific Vanquish UHPLC+ Q Exactive Focus Orbitrap (Anatech, Cape Town, South Africa) equipped with a Hypersil Gold aQ (100 mm x 2.1 mm x 1.9 µm) column (Anatech, Cape Town, South Africa) set at 30 ^{o}C. The binary mobile phase comprised 0.1% formic acid in water (Merck, Johannesburg, South Africa) with 5 mM ammonium formate (Merck, Johannesburg, South Africa) and 0.1% formic acid in methanol, also with 5 mM ammonium formate. The gradient method was initiated at 30% solvent B at 0.3 mL/min (held for 1 min) before increasing to 100% solvent B. The flow rate was increased to 0.35 mL/min for 4 min before returning to 30% solvent B and 0.3 mL/min. A 10 µL injection volume was used. Tandem mass spectrometry was coupled to a heated electron spray ionisation spray in positive and negative modes. The full scan acquisition range was

83.4 to 1250 m/z at a resolution of 70 000 in MS1 full scan and data-dependent acquisition (dd-MS2) in discovery at a resolution of 35 000. Stepped collision energy was selected at 15 and 30 eV with the Automatic Gain Control target set at 2E+04.

4.2.5 Quality assurance

When not in use, each sample was wrapped in aluminium foil for storage at room temperature. The blender was washed after each sample pre-treatment with warm water and detergent, then rinsed with purified, deionised water followed by an ethanol rinse before air drying. To minimise cross-contamination after each extraction, the ASE stainless steel cells were washed in warm water, rinsed with the extraction solvent, and then baked out in an oven for 4 hours at 160 °C. For UAE, borosilicate glass vials were heat-treated in a furnace for 2 hours at 400 °C then allowed to cool to room temperature before use. A chemical standard of diisobutyl phthalate (DIBP) was prepared in triplicate to estimate instrument sensitivities. For GC-MS, 0.2 mg/L DIBP in 5:2 acetone: hexane was prepared and for LC-MS, 0.1 mg/L DIBP was made up in methanol. The limit of detection (LOD) was measured at a signal-to-noise ratio of 3.

4.2.6 Data analysis

Thermo Scientific FreeStyle 1.8 SP2 software was used for GC-MS data in conjunction with Automated Mass Spectral Deconvolution and Identification System (AMDIS) for tentative identification using the 2020 National Institute of Standards and Technology (NIST) GC-MS spectral library. The AMDIS parameters included a minimum match of 80%, deconvolution of 32 component width, 2 adjacent subtractions, and medium resolution using 2 scans. The inclusion of deconvolution software was to aid in the identification of compounds in complex matrices. For LC-MS, data analysis was performed using Thermo Scientific FreeStyle 1.8 SP2 and TraceFinder 5.0. TraceFinder 5.0 includes a built-in deconvolution plug-in, matrix interference removal and retention time alignment, strengthening the qualitative analysis. The threshold for positive tentative identification was based on match factors where the acceptable similarity index (SI)

was above 750 and the reverse similarity index (RSI) above 800 and above for both GC-MS and LC-MS. The mass tolerance for LC-MS was set at 10 ppm and below. The mass tolerance was defined by equation (1).

$$Mass\ tolerance\ (ppm) = \left|\frac{Theoretical\ mass\ expected - Mass\ Observed\ (m/z)}{Theoretical\ mass\ expected\ (m/z)}\right| \times 10^6 \quad (1)$$

In high resolution mass spectrometry (HRMS), the mass tolerance is often used as an indication of an instruments' mass accuracy for the tentatively identified compound, where the smaller the mass tolerance, the more accurate the measurement is, in comparison to the theoretically expected value (Yu et al., 2016; Zubarev & Makarov, 2013). In recent years, it has become important to measure the tentative identification of compounds against a confidence level. In such instances, the highest confidence is associated with verification of compound identity against certified reference standards, with a lack of structural evidence and molecular formula generation considered the lowest confidence level (El-Deen & Shimizu, 2022). In this study, tentative identification was performed against NIST libraries for both GC-MS and LC-MS to give an overall level 3 confidence level (Schymanski et al., 2014). Although matching against spectral libraries gave a lower level of confidence than the use of a reference standard, it was considered to provide a relatively high probability of correct identification, given the verification and validation processes followed by NIST.

To further interrogate the data, each incident of positive identification was equally weighted to convert the categorial, qualitative data into a continuous data set. MetaboAnalyst 6.0 was used to perform sparse partial least square–discriminate analysis (sPLS-DA), a variant of partial least square-discriminate analysis. In sPLS-DA, the assumption is made that only a few features are responsible for characterisation (Ruiz-Perez et al., 2020). Since all papers can be considered a sheet of plant-based fibre (Jixing, 2008), many common chemical constituents were expected to be present and it was thereby important to apply a supervised model that could discriminate effectively and discard non-informative features (Jiménez-Carvelo et al., 2021). In this study, the categorised chemical groups were evaluated for each sample according to recycling paper grade and collection site.

4.3 Results and discussion

4.3.1 Chemical compounds identified

A total of 340 chemical compounds were tentatively identified in the samples using the tentative identification criteria set out in section 2.6 (Table S1- S3). Of these, 165 compounds were identified using GC-MS, 144 with LC-MS in positive ionisation mode, and 31 with LC-MS in negative ionisation mode. The compounds were then classified into broad categories based on their chemical similarities, functions, and related compounds. The compounds identified using GC-MS were grouped into 29 categories which included phenols, phthalates, long-chain aliphatic chains, and acrylates (Table S1). For GC-MS, the long-chain aliphatics had the highest number of unique compounds (44) detected in all the samples, followed by fatty acids (20) and wood derivatives (14) (Table S1). The compounds identified by LC-MS consisted of 39 chemical classes including sulphonated benzenes, phenols, long-chain sulphates, and bisphenols (Table S2 and S3). The amides class was found to have the highest number of compounds (15) followed by cyclic acids (10) and glycerols (8). Several common classes were identified by LC and GC, with differences also observed. Phenols, phthalates, butyrates, benzophenones, glycol ethers, and fatty acids were detected by both LC-MS and GC-MS, which indicated that there was a degree of similarity in their application range for certain compounds. Other compounds were outside this common region; those that were more volatile, such as methyl styrene, were detected solely by GC-MS, and others that were more non-volatile, such as organophosphonates, were detected only by LC-MS.

The application range of GC and LC is influenced by volatility, polarity, ionizability, and thermal stability of organic compounds (Sapozhnikova, 2021). In general, mass spectrometry coupled to gas chromatography (GC-MS) is more suited for volatile and semi-volatile compounds with lower polarity whilst liquid chromatography in tandem with mass spectrometry (LC-MS) is amenable to semi-volatile and non-volatile, generally more polar compounds (Gallart-Ayala et al., 2013; Martínez-Bueno et al., 2019). Each separation technique is influenced by the chemical properties of chemical compounds, the solvents selected, the chromatographic column employed, and in the case of LC, the pH and mobile phase

composition (Lowe et al., 2021; Martínez-Bueno et al., 2019). Using boiling point as a measure of volatility, the boiling points of the identified compounds ranged from 80 ℃ for 2-butanone to 610 ℃ for tris(2,4-ditert-butylphenyl)phosphate for GC-MS, and from 122 ℃ for 3-methyl-3-pentanol to 1689 ℃ for potassium sulphate in the LC-MS analysis (Tables S1-S3). The choice of extraction solvent also played a key role in the classes of compounds detected. GC-MS was able to identify several long-chain aliphatics from the use of a portion of non-polar extraction in the 5:2 acetone: hexane solvent as well as from GC-MS' general suitability to non-polar analysis. The 5% phenyl-arylene fused silica GC column promoted the elution of certain polar and non-polar compounds, but was not as amenable to amides and organic acids, as the LC-MS. Using LogP as a measure of a compound's affinity to an aqueous or non-polar medium, more compounds with LogP < 0, an indication of hydrophilicity, were observed for LC-MS identified compounds (Tables S1-S3). The use of the polar endcapped C18 LC column also contributed to enhanced retention and resolution of polar compounds. The LC-MS, was also able to readily ionise compounds such as bisphenols and primary aromatic amines (Banaderakhshan et al., 2022; Sanchis et al., 2019). For suitable GC-MS elution of such compounds, chemical derivatization or a more targeted approach with optimised operating conditions would have had to be employed. It is important to highlight that the LC-MS was an ultra-high-performance liquid chromatography - Q Orbitrap that made use of high-resolution mass spectrometry (UHPLC-HRMS). The high resolving power of this instrument is designed for high sensitivity and more accurate mass analysis (García Ibarra et al., 2019; Hecht et al., 2019). For comparison, using a compound amenable to both GC-MS and LC-MS (in positive ionisation mode), the sensitivity was measured by determining the limit of detection (LOD) for diisobutyl phthalate. The LOD of DIBP was 1.987 ng/g for the GC-MS and 0.017 ng/g for the LC-MS. Although this sensitivity likely differed for different compounds and classes detected, based on ionisation efficiencies, matrix interaction, and behaviour in the mobile phase and column, it provided a comparative indicator of sensitivity. This sensitivity difference showed that better comparisons of the differences in compounds detected by the two techniques would likely have been made with instruments of equivalent sensitivity. The lower

sensitivity of GC-MS was consequently compensated for in the sample preparation, amplified seven times to 3.5 g. The was followed by the concentration of the resulting supernatant to 1 mL, to further enhance the detector response. The number of tentatively identified compounds as well as different chemical classes showed that the choice of extraction solvent, the chromatographic column used, and mobile phase composition influenced the qualitative assessment of chromatographic techniques.

4.3.2 Exploration of sources of chemicals identified

The possible sources of the identified chemical compounds were investigated using a unique approach based on reported uses and occurrences in paper manufacturing as well as from interactions between paper and other elements in the paper recycling chain. The limitation of this study was the absence of concentrations of the detected compounds. The possible sources were thereby studied for a broader understanding of the chemical compounds that occur in the paper recycling chain. The occurrence of the detected compounds is shown in the supplementary Tables S4 to S24.

4.3.2.1. Wood derivatives

Since the main building block of paper materials is cellulose found in wood, it was important to identify likely wood derivatives and pulping-related organic compounds. Traces of these wood extractives, hemicellulose and lignin may remain in paper products depending on removal efficiencies and pulping, with chemical pulping considered more efficient at wood extractives removal than mechanical pulping (Lehr et al., 2021). Several compounds comprising alkanes, terpenes and terpenoids, fatty acids, and phenols were identified in this study related to wood derivatives. The terpenes and terpenoids detected included limonene, carene, isopimarol, abietic acids, and sitosterol. Phenols that were likely residual lignin compounds included compounds such as methyl phenol and vanillin (detected by GC-MS) as well as cresol, coniferyl aldehyde, and syringaldehyde (detected by LC-MS). The main components of wood alkanes are C_{22}-C_{30} alkanes (Stenius et al., 2000) such as eicosane (C_{20}) and pentacosane (C_{25}), which were detected by GC-MS in all investigated samples. Fatty acids, also wood derivatives (Stenius et al., 2000), included dodecanoic acid, myristic (tetradecanoic acid), palmitic

(hexadecanoic acid), and octadecanoic acid, also detected through the GC-MS analysis. Many of these compounds were detected across the sample population which strongly advocated that certain wood derivatives remain in paper. The wood alkanes, however, extended beyond C30, showing that other sources of long-chain aliphatics were present. Quinones were found to be a chemical group whose occurrence was intertwined in both wood extractives (Stenius et al., 2000) and pulping chemicals (AbdElsalam & Abubshait, 2009). In addition to pulping, 9,10-anthraquinone (detected by GC-MS) is also reportedly used as a dye solvent for plastics, and as a colourant for printing inks, resins, and paint (Valduga et al., 2024). Overall, the compounds linked to wood derivatives were generally neither site-specific nor paper-grade specific and were a common feature in the samples investigated in this study.

4.3.2.2 Chemical additives identified in the paper recycling chain

Chemical additives are added to enhance the production of a continuous webbed sheet of paper and to impart the desired physical and chemical characteristics. These chemical additives can include strength aids, optical brighteners, surfactants, waxes, photoinitiators, and flame retardants (Geueke et al., 2018; Ren et al., 2023; Wen et al., 2023). A number of chemical additive components used in paper manufacturing are similar to wood extractives, making the apportionment of the identified compounds complex. Alkyl ketene dimers, common sizing agents, contain a mixture of palmitic and stearic acids which when hydrolysed may form ketones (Stenius et al., 2000). Alkenyl succinic acid anhydride or ASA, also a sizing agent, is produced from C_{16}-C_{18} alkanes reacted with maleic acid anhydride forming ester acids which form dicarboxylic acid. Rosin sizing agents primarily comprise abietic acid and dehydroabietic acids (Stenius et al., 2000), tricyclic compounds with phenanthrene skeletons (Li et al., 2023). This thereby meant that the detection of palmitic acid, stearic acid, ketones, ester acids, dicarboxylic acids, abietic and dehydroabietic acids, as well as certain C_{16}-C_{18} alkanes, which were detected in most of the investigated papers, may have been contributions from different types of sizing chemicals that are used in paper manufacturing, in addition to the possible wood derivative link. In this study, abietic derivatives were predominantly detected

in newspaper samples in the GC-MS analysis (Table S2), this may have been possibly from wood extractives from mechanical pulping as well as adhesives, pigments, or dyes; as dehydroabietic acids are also used in printing inks and adhesives (Lowe et al., 2021; Sanchis et al., 2019).

Different printing techniques are used for different types of paper products. Magazines and newspapers often make use of non-polar offset printing (Fillat et al., 2015; Yang et al., 2023) whilst corrugated boxes and cartons generally employ water-based flexographic printing. Offset printing may include mineral oil hydrocarbons as carriers whilst flexographic printing is known to employ binders such as polyamides, acrylic resins, and maleic resins with water or alcohols as carriers. Recycling of paper grades that employ mineral oil-based printing inks may lead to the presence of saturated and unsaturated hydrocarbons ranging from C_{11}-C_{50} (Biedermann et al., 2013). This meant that the presence of certain long-chain aliphatics and polycyclic compounds could be linked to the possible use of mineral oil in newspaper, magazine or office paper printing inks, in paraffin wax or palm oil coatings used in paper and corrugated boxes (Graíño et al., 2018), or from mineral-oil containing consumer goods such as foods and cosmetics packaged in paper-based material. To further confound the apportionment, plastic material such as polypropylene, polyethylene, and polyethylene terephthalate, which can be in contact with paper during goods packaging and waste mingling, also contain hydrocarbons (García Ibarra et al., 2019; Rani et al., 2015), that can transfer into paper. It is important to add that GC-MS, as an analytical technique, could not differentiate alkanes from petrochemical sources and those of wood origin that were detected in the same carbon-chain region. Since wood alkanes are expected to be in the C_{22}-C_{30} region (Stenius et al., 2000), it could thereby be postulated that lower carbon alkanes such as dodecane (C_{12}), tetradecane (C_{14}), tridecane (C_{13}), octadecane (C_{18}), or those with longer carbon chains such as pentriacontane (C35) or tetratriacontane (C_{34}) had a larger possibility of arising from petrochemical alkanes than those expected in the wood alkane region. Further, if ASA is known to be the sizing agent used, the C_{16}-C_{18} alkanes, to some extent, could also be attributed to ASA. The presence of other petrochemical-linked compounds, such as methyl phenanthrene, benzopyrene, and benzenes such as ethyl and butyl benzene,

detected in the waste picker, pre-consumer, and recycling facility samples, indicated that a portion of the alkanes detected in this study likely arose from petrochemical sources (Sanchis et al., 2017; Smith et al., 1999). This observation was found to be critical in understanding issues such as mineral oil contamination of recycled paperboard as it showed that the detection of compounds must not be investigated in isolation or reduced to a single feature.

The identification of glycol ethers, triethanolamine, 2-nitropropane, and glycols were apportioned to printing inks, coatings, dyes, inks, adhesives, detergents and cleaners (Fernandes et al., 2020; Guazzotti et al., 2015; Rameshrad et al., 2017; Höke and Schabel, 2000; BfR XXXVI, 2023). Primary aromatic anilines in particular, can form from the degradation of azo dyes; and can also be formed by hydrolysis of aromatic isocyanates in polyurethane adhesives (Sanchis et al., 2019). One such aniline, 4-(4-aminophenoxy) aniline, was detected by LC-MS in a corrugated box sample.

Benzophenone, 4-methyl benzophenone, 4-dodecyloxy-2-hydroxybenzophenone, 2-hydroxy-4-methoxybenzophenone, and 2,2-dimethoxy-1,2-diphenyl ethanone were identified by LC-MS and GC-MS as possible photoinitiators (Lowe et al., 2021; Mucci & Vallo, 2012; Sanchis et al., 2019). Photoinitiators are important in the UV curing of inks and lacquers for paperboard and corrugated boxes (Altuntaş et al., 2016) as well as in initiating polymerisation in polymers (Mucci & Vallo, 2012). Benzaldehyde, a known photolytic decomposition product of benzophenone photoinitiators (Scarsella et al., 2019) was detected in office paper and a carton sample. However, the presence of benzaldehyde and 4-hydroxy-3,5-dimethoxybenzaldehyde (also present in several samples) may have also been due to lignin residues (Rodrigues et al., 2012) contributing to their occurrence.

Along with photoinitiators, bisphenol A and phthalates are well-reported paper contaminants (Banaderakhshan et al., 2022; Jurek & Leitner, 2018; Rosenmai et al., 2017). Bisphenol A, and its analogues, bisphenol S, bisphenol F and bisphenol P were identified by LC-MS in numerous samples in the paper recycling chain. Bisphenol A, S and F have been historically detected in paper material (Sanchis et al., 2017) but not bisphenol P, a common bisphenol A-substitute in plastic

packaging (Ma et al., 2023). In this study, phthalates and terephthalates, common plasticizers (X. Li et al., 2018), were detected by both GC and LC-MS, with diethylhexyl phthalate, dibutyl phthalate, and dimethyl phthalate being the most frequently detected phthalates. Remarkably, phthalic anhydride, a starting raw material in phthalate synthesis (Bajracharya et al., 2021) was detected in an office paper sample collected at a recycling facility. The ubiquitous, endocrine-disrupting nature of phthalates has led manufacturers of consumer goods to switch to phthalate alternatives with fewer adverse effects (Graíño et al., 2018; Horie et al., 2023). Acetyl tributyl citrate, bis(2-ethylhexyl) adipate, bis(2-ethylhexyl) maleate, bis(2-ethylhexyl) fumarate, and bis(2-ethylhexyl) sebacate are such alternatives that were detected in the samples under investigation. Diethyl maleate, used to functionalize polymers such as polyolefins (Graíño et al., 2018), may have also been present as a breakdown product of diethylhexyl phthalate (Erythropel et al., 2015). Thus, the detection of diethyl maleate in pe-consumer paperboard samples could thereby be hypothesized to partly be a result of diethylhexyl phthalate degradation during the reprocessing of diethylhexyl phthalate-containing recycled fibre. Many samples (shown in Tables S4-S10) were found to contain both traditional phthalates and phthalate alternatives. It was postulated that since paperboard can contain a multitude of chemicals, it was possible that, as an example, the adhesive used in the paper packaging could have contained a phthalate whilst the printing ink or coating made use of a phthalate alternative component. Secondly, the use of recycled fibre containing phthalates could have led to unintentionally introduced contaminants into the final product. Lastly, a paperboard using only a phthalate alternative could have come into contact with ubiquitous phthalates during consumer usage, disposal, collection, and sorting. The widespread use of phthalate alternatives such as tributyl citrate (Graíño et al., 2018) makes it possible that these phthalate alternatives could also become ubiquitous, regardless of their non-toxicity.

A large number of plastics-associated chemical compounds were identified in this study. Many paper manufacturing additives contain polymer resins for polymer-based coatings, barriers, adhesives, UV cures, wet and dry strength aids, fixing agents, sizing agents, retention aids, defoamers, and as barriers in paper (BfR XXXVI, 2023; Höke & Schabel, 2000). The detection of various acrylates, amides,

and styrene such as trimethylolpropane triacrylate, stearamide, and methyl styrene, was linked to the possible use of such polymer-based chemical additives. In addition, in the paper recycling chain, the occurrence of styrene, triphenyl cyclohexane, and benzaldehyde in cartons and corrugated boxes, could be associated with possible stickies, the small fragments of adhesives, films and plastics that remain in recycled pulp (Guazzotti et al., 2015; Höke & Schabel, 2000; Huber et al., 2013). The occurrence of triacetin in corrugated boxes was indicative of plastic-laminated corrugated boxes (Guazzotti et al., 2015). Erucamide, oleamide, and stearamide, detected in samples by LC-MS, are often used as slip agents in polymers (Narayana et al., 2022; Tolinski, 2009), although erucamide does have historical use in paper coatings and waterproofing purposes (Molnar, 1974). This further highlighted the complexity of determining sources of specific compounds in the paper recycling chain where compounds such as benzaldehyde can be linked to wood extractives, photoinitiators, and polymers.

In addition to the use of polymer-containing additives and resins, paper packaging is often sealed in plastic sleeves or contains a polymer-based inner bag where exposure to such compounds could occur. This further demonstrated the inherent presence of plastics-associated compounds in the paper recycling chain. Several antioxidants were detected in this study in the form of butylated hydroxytoluene, a phenol-associated antioxidant degradant and organophosphates. Butylated hydroxytoluene, used in polyolefins, paper, polyurethane adhesives, cosmetic products, and food (Tortosa et al., 2020) was detected in a carton, corrugated boxes, newspaper, and magazine samples. Another prevalent antioxidant detected mostly in recycling facility collected samples by GC-MS, was the organophosphate, tris(2,4-ditert-butylphenyl)phosphite or Irgafos 168. It is considered a ubiquitous plastic additive found in food packaging, dust, printing paper, and aquatic systems (Liu & Mabury, 2021; Shi et al., 2020; Zhang et al., 2021). Other organic phosphorus compounds detected, used as flame retardants, antioxidants, or plasticizers (Ho Sohn et al., 2011; Lowe et al., 2021; Sanchis et al., 2019) included triphenylphosphine oxide in cartons and corrugated boxes by LC-MS, tributyl phosphate in corrugated and magazines, and tris(2-chloroethyl) phosphate in a magazine by GC-MS. The degradation products linked to organophosphates

included the detection of tris(2,4-ditert-butylphenyl)phosphate and 2,4-ditert-butylphenol (Hermabessiere et al., 2020); although 2,4-ditert-butylphenol may have also been as a result of residual lignin (Zhao et al., 2020). The breakdown product of antioxidant Irganox 1010 (tetrakis [methylene-3- (3,5-di-tert-butyl-4-hydroxyphenyl-propionate)] methane) in the form of 7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6-9-diene-2,8-dione was detected in carton and corrugated boxes from recycling facilities and office paper from a recycling facility and a solid waste site. This compound has been detected in both plastic and paper packaging (Graíño et al., 2018). This study thereby showed that the choice of chemical additives used and subsequent degradation products have an influence on the next lifecycle of recycled paperboard. Moreover, many chemical compounds used in paper manufacturing have multiple functions in different applications and can be detected as a result of direct use, contact during storage and transport in paper-based packaging as well as mingling with other waste during disposal, collection and sorting processes. Consideration of the recyclability of chemical additives used in both food and non-food paper manufacturing and converting processes may likely reduce the propagation or occurrence of certain compounds in the paper recycling chain.

4.3.2.3 Papermaking, recycling, and auxiliary processes

Since paper can be recycled numerous times, the detection of compounds in recycled paper may be from the current or previous product life. Surfactants are present in a wide number of paper-making additives for wetting, dispersing, and emulsifying (Ren et al., 2023) and may also be used in the washing of recovered paper before remanufacturing origin (Höke & Schabel, 2000). Several compounds identified in this study were linked to possible surfactants, these included fatty acids such as octadecanoic and hexadecanoic acids (García Ibarra et al., 2019) and sulphonated benzenes, such as sodium dodecyl benzene sulphonate, are common anionic surfactants used in papermaking (Ren et al., 2023). Long-chain sulphates such as ethylene glycol dodecyl ether sulfate, detected by LC-MS, could also be linked to surfactants as they are used in soaps and detergents (Ranji et al., 2019). A possible surfactant intermediate, 2,2,4-trimethyl-1,3-pentanediol diisobutyrate, was

detected in newspapers, and office paper, however its presence may have also been due to its other uses in plasticizers, pesticides, and resins (Kazama et al., 2022).

Certain compounds detected in the study were linked to a broad range of industrial processes that could have introduced the compounds during manufacturing or contamination during disposal, collection, and sorting. Phosphonates, used for scale inhibition, dispersion, and deflocculation of process waters in various industries including paper, detergents, textiles, household cleaners, and cosmetics as well as wastewater treatment plants (Rott et al., 2018) were detected by LC-MS in waste picker and solid waste disposal site corrugated boxes, recycling facility newspaper and unconverted mill paperboard. The LC-MS analysis also identified several chemicals that could be linked to agricultural applications. The herbicides, pesticides, and fungicides identified included potassium chlorate, dichlorprop, mefenpyr-diethyl, flutriafol, and potassium nitrate in the various paper samples analysed (Karwowska & Kononiuk, 2020; Qiu et al., 2022). The presence of such compounds could have been due to exposure of paper to contaminated soil or water, as wood chip contamination prior to pulping as well as exposure during disposal, collection, mingling, and/or recycling.

4.3.3 Distribution of chemical classes

The chemical classes detected in the samples were evaluated by count in order to transform the data into quantitative variables. The prevalence of chemical classes by occurrence was plotted as a percentage occurrence in Fig. 2. For GC-MS, phthalates, long-chain aliphatic compounds, and fatty acids occurred in the highest percentage with phthalates detected in 90% of the samples analysed. Phthalates were also the most detected in compounds in LC-MS (97%), followed by bisphenol A and its analogues at 90%.

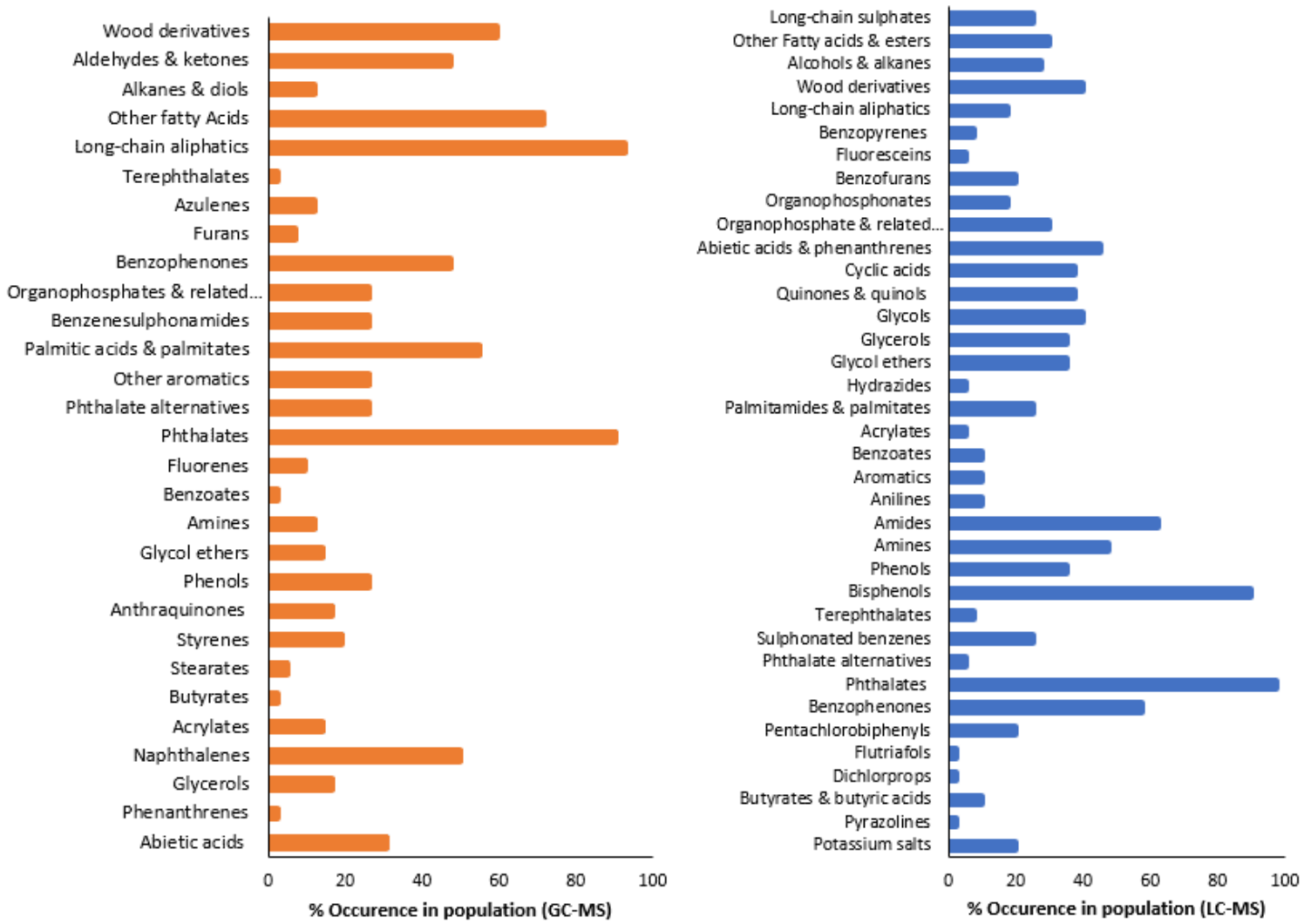


Fig.2 Occurrence of chemical classes by GC-MS and LC-MS

The number of classes identified per site was plotted against their collection site and paper grade, as shown in Fig 3. This was done as a measure of prevalence, in the absence of known concentrations.

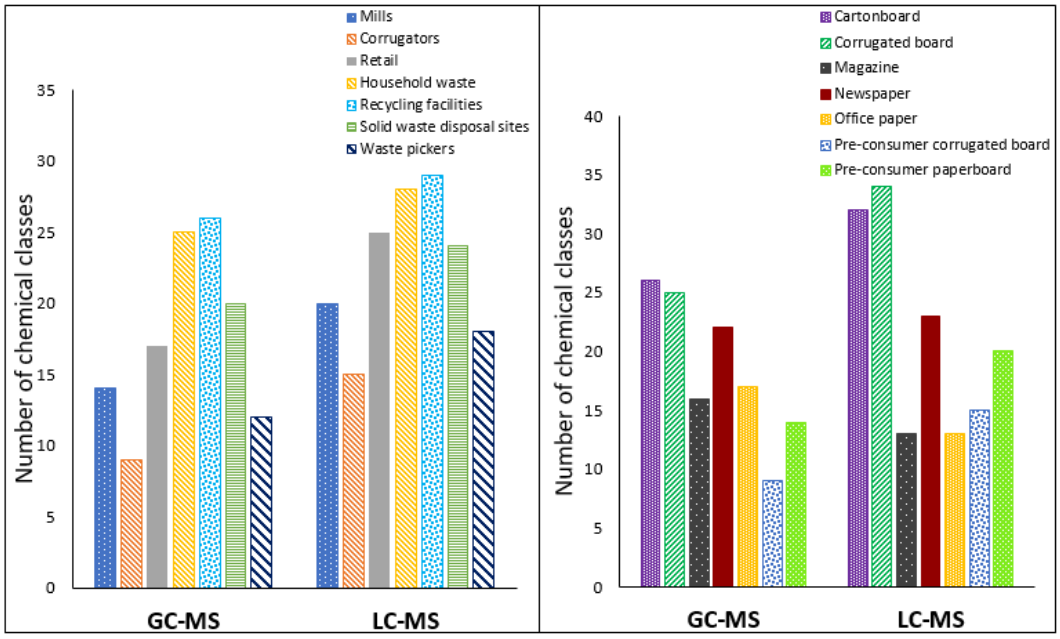


Fig. 3 Chemical classes identified by a) sample collection site b) paper recycling grade

The highest number of different chemical classes per site was found in samples collected from recycling facilities and household waste for both GC-MS and LC-MS. The samples collected from corrugator sites were found to have the lowest number of different chemical classes followed by the waste picker and mill collected samples, for both GC-MS and LC-MS. This thereby indicated that possible exposure to various chemicals occurred at retail, household, recycling facilities, and solid waste disposal sites. In terms of paper grades, corrugated boxes and carton board were both found to have the highest number of chemical classes present followed by newspapers for both GC-MS and LC-MS. This could have been due to the various types of additives used in these paper materials as well as their ability to absorb chemical compounds during packing, consumer usage, transport, storage, disposal, and recycling. Pre-consumer corrugated boxes were found to have significantly fewer chemical classes than corrugated boxes collected at other sites further suggesting possible circulation and propagation of chemical compounds

through the paper recycling chain. Quantification of such compounds would be required to confirm this trend.

4.3.4 Predictive modelling using sPLS-DA

Predictive modelling was used to investigate discriminate features in the samples by paper recycling grade and by collection site, where chemical classes were taken as the features or variables of interest. Recycled paperboard is often made using a combination of different paper grades, it is thus important to understand what such combinations would have on the overall chemical profile of the resulting recycled paper products. It could be seen that in the scores plot by paper grade (Fig. 4), unique features were present in newspaper samples in both LC-MS and GC-MS as well as office paper in GC-MS. The sPLS-DA loadings plot assigns a colour to each feature, in this case, chemical classes, that occurs in each paper grade according to whether the detection of that feature is higher (in red) or lower (in blue) in comparison to the median of the population for that particular feature, in loading 1. The significance of the distinguishing chemical classes is shown in descending order in the vertical axis related to the loadings value on the horizontal axis. The higher detection of abietic acids, benzenesulphonamides, benzoates, and butyrates in newspapers in comparison to the other paper recycling grades, as shown in Fig 5 for GC-MS were the source of unique features. In the LC-MS analysis, pre-consumer paperboard had unique chemical features that were distinct from other paper grades. From the loadings plot in Fig. 5 for LC-MS analysis, pre-consumer paperboard was found to have generally lower detection of the majority of chemical classes which may have been due to less exposure opportunities or possible removal of contaminants after repulping, except for wood derivatives, organophosphonates, and benzopyrenes. Corrugated boxes and cartons were shown to have common chemical features for both GC-MS and LC-MS, with more frequent detection of more chemical classes observed for cartons in the loadings plot. Both carton and corrugated board were found to have higher detection of bisphenols, phthalates, glycols, fatty acids and esters, pentachlorobiphenyls, and sulphonated benzenes than other paper grades, as seen in the LC-MS loadings plot. The remaining paper grades were found to cluster closely together, with similar variability in their features. This thereby indicated that the use of certain paper grades with differing

chemical characteristics would likely influence the overall chemical profile of recycled products. More research on a broader set of paper collected from a different geographical area with their detected concentrations would be required to further examine this trend.

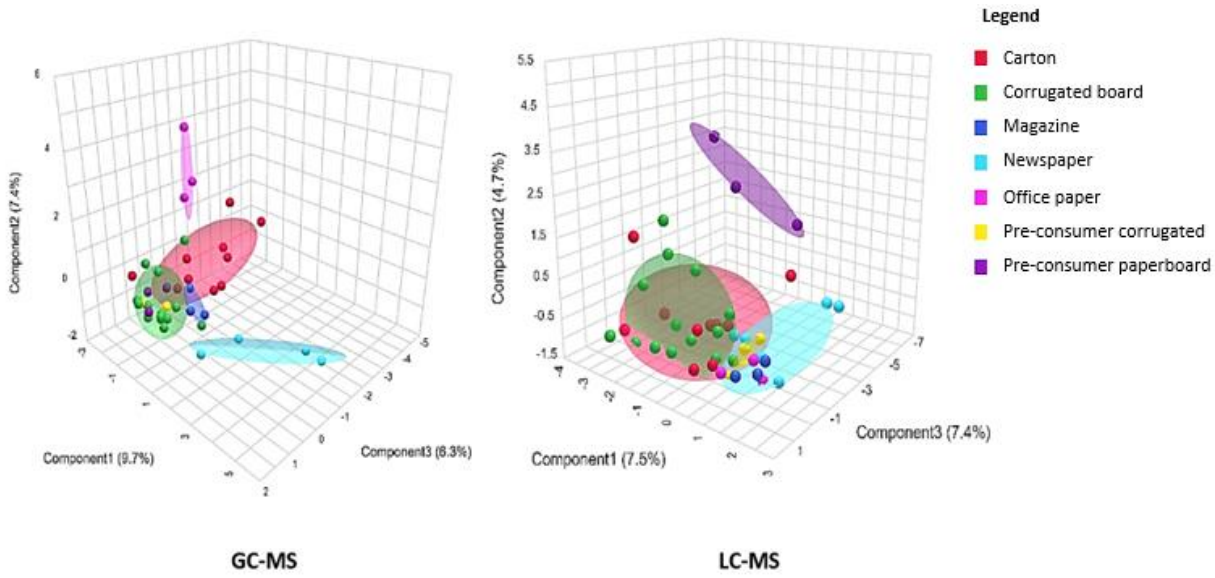


Fig. 4 sPLS-DA scores plot for GC-MS and LC-MS by paper grade

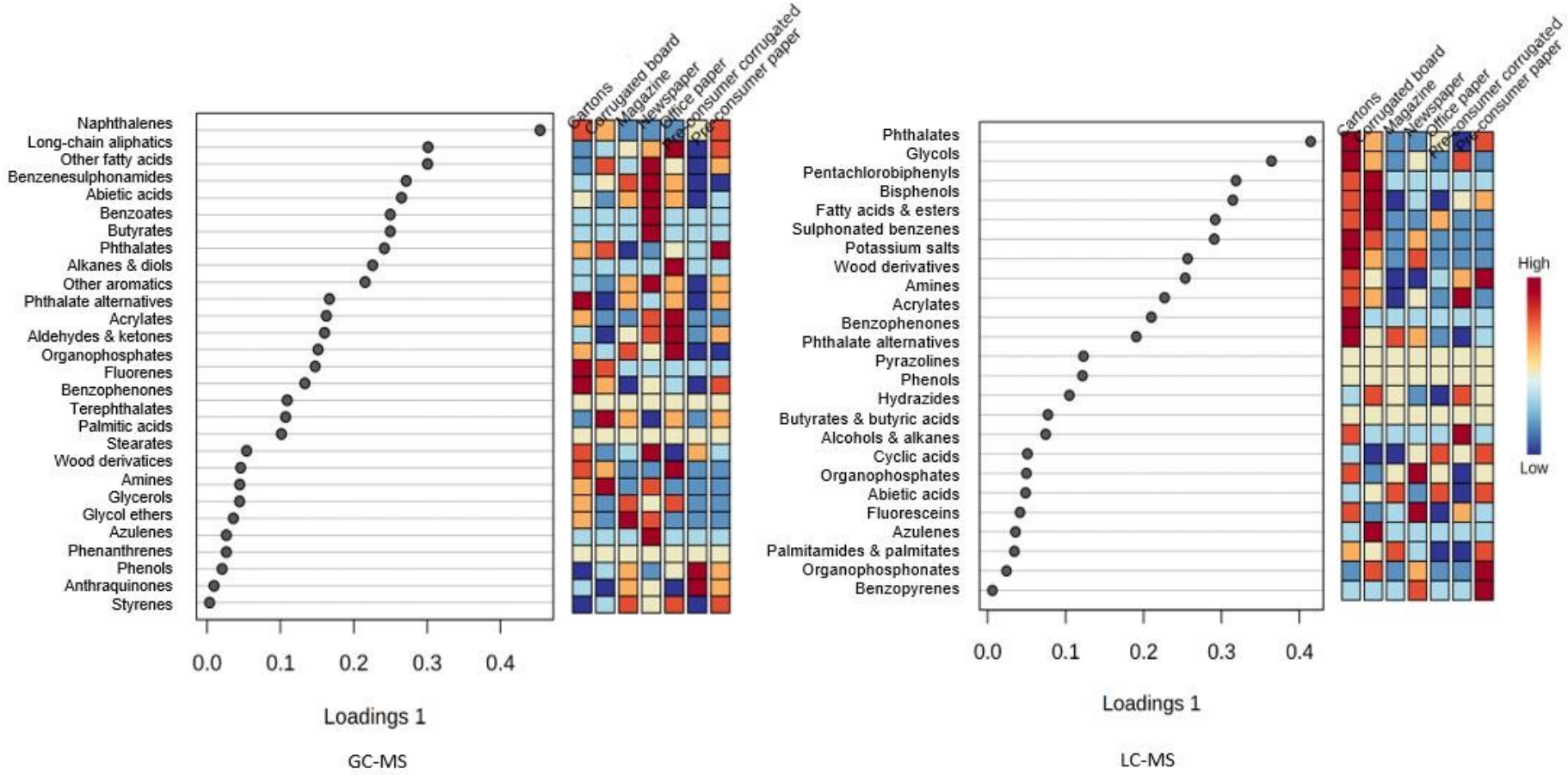


Fig. 5 sPLS-DA Loadings plot for GC-MS and Analysis by paper grades

The sites where the samples were collected were also shown to influence the chemical features as shown in the scores plot for GC-MS and LC-MS in Fig. 6.

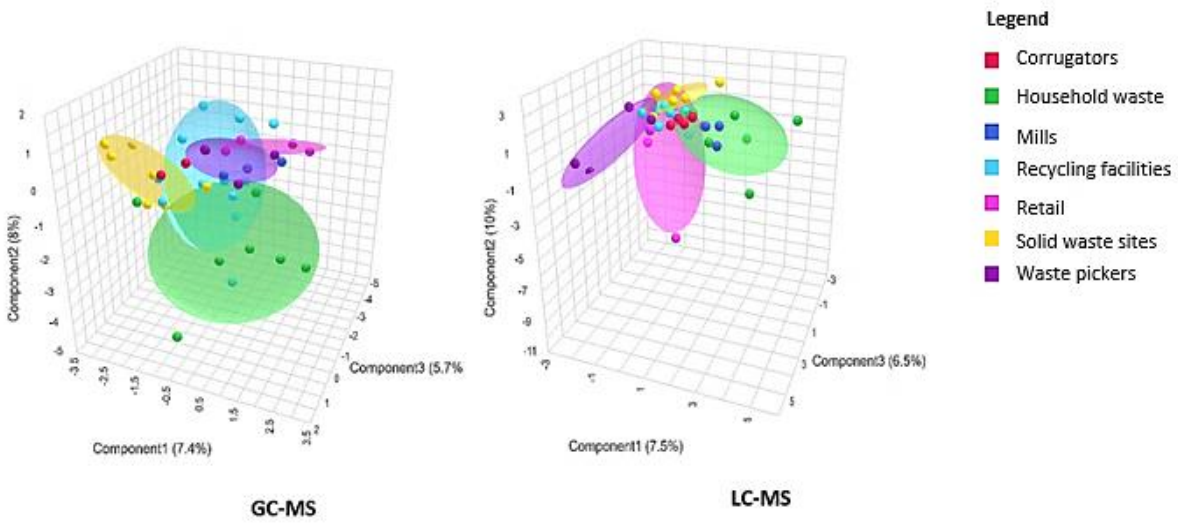


Fig. 6 sPLS-DA scores plot for GC-MS and LC-MS by collection site

The collection sites were all found to cluster close together whilst showing distinct features. Samples collected in household waste had wider variability than samples from other sites. In the loadings plot for GC-MS in Fig. 7, household waste papers had higher detection count over the greatest number of distinguishable classes with higher detection of phthalate alternatives, acrylates, benzoates, terephthalates, and aromatic compounds. Paper collected at recycling facilities was shown to detect more classes of chemical compounds in the GC-MS giving them distinct features. In the LC-MS analysis, household waste samples were found to have higher detection in more distinct chemical classes that included wood derivatives, glycol ethers, amines, aromatics, benzopyrenes, quinones, and quinols. The higher detection of organophosphates and phthalates in retail samples further showed that certain chemical compounds are present prior to any contact with consumers. This may be from the use of certain additives during conversion, contaminants present in recycled fibre, contact with packed goods as well as distribution and storage. Notably, samples collected at mills had higher detection of certain classes than corrugators. The study showed that certain newly produced paper products with a recycled fibre component may be prone to retain glycol ethers, phthalates, phthalate

alternatives, amines, benzopyrenes, and naphthalenes after manufacture. More research is therefore needed to understand how different washing or repulping, in conjunction with the types of paper grades selected for recycling, affect the type and amounts of retained chemical contaminants. It further suggested that to minimise contamination in the paper waste stream, separation of paper grades at source may be an effective means of reducing cross-contamination between paper grades. Whilst current practices attempt to separate paper from other substrates such as plastics, metals, and glass; the sorting into their respective grades mostly occurs downstream at recycling facilities where further cross-contamination may occur.

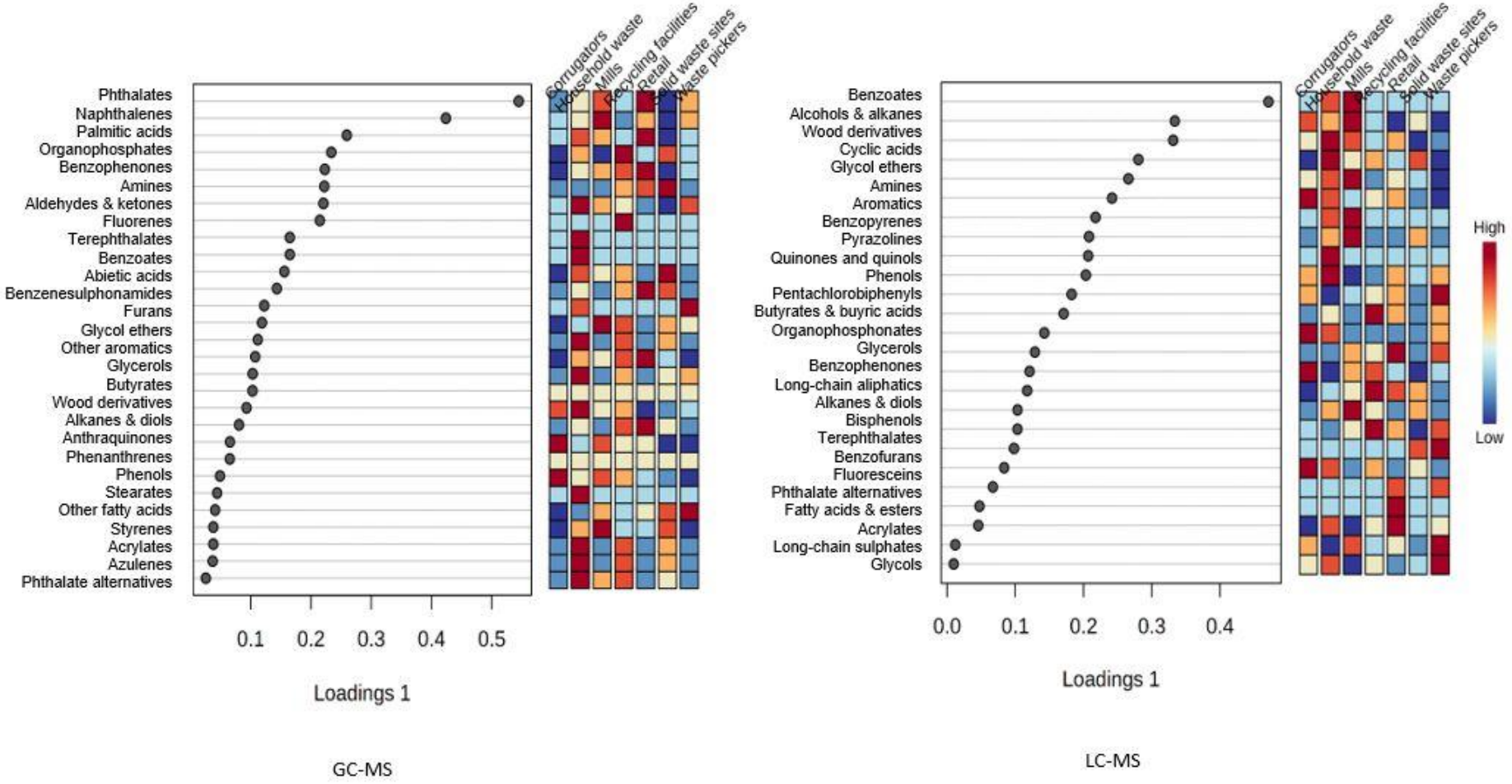


Fig. 7. sPLS-DA Loadings plot for GC-MS and LC-MS analysis by collection sites

4.4 Conclusions

A unique approach was employed to understanding the various exposure pathways of the compounds identified by looking beyond known paper manufacturing uses to include chemical interactions that may occur in the paper recycling chain. The results indicated that the paper grade may influence the chemical profile and contaminants present in paper-based material as well as the site at which paper is collected. The present study highlighted that plastic-associated additives may have infiltrated the paper recycling chain. This suggested that there may be shortcomings in current regulations and guidelines which currently do not include the monitoring of contaminants beyond those expected chemicals from paper manufacturing, unregulated use of chemicals or the possible cumulative effects of contaminant propagation in the paper recycling chain. The identification of various transformation and degradation products showed that certain compounds initially considered non-critical, may evolve into chemicals of concern. The feasibility of further separation of paper recycling grades based at source stage may need to be further investigated to reduce contamination opportunities and ensure a sustainable paper recycling chain. The quantification of the various chemical constituents detected was identified as an important follow-up step in this study to evaluate possible risks and the extent of chemical constituents. This study revealed that the prominence of emerging contaminants not previously studied in paper matrices, such as phthalate alternatives, organophosphate and sulphonated benzenes, as well as degradation products that result from commonly used additives. Further studies are required to evaluate such compounds and to understand how they influence the recyclability of both food and non-food paper materials.

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Supplementary material

Chemical profiling of paper recycling grades using GC-MS and LC-MS: A source apportionment study

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Fig. S1 Samples Collected

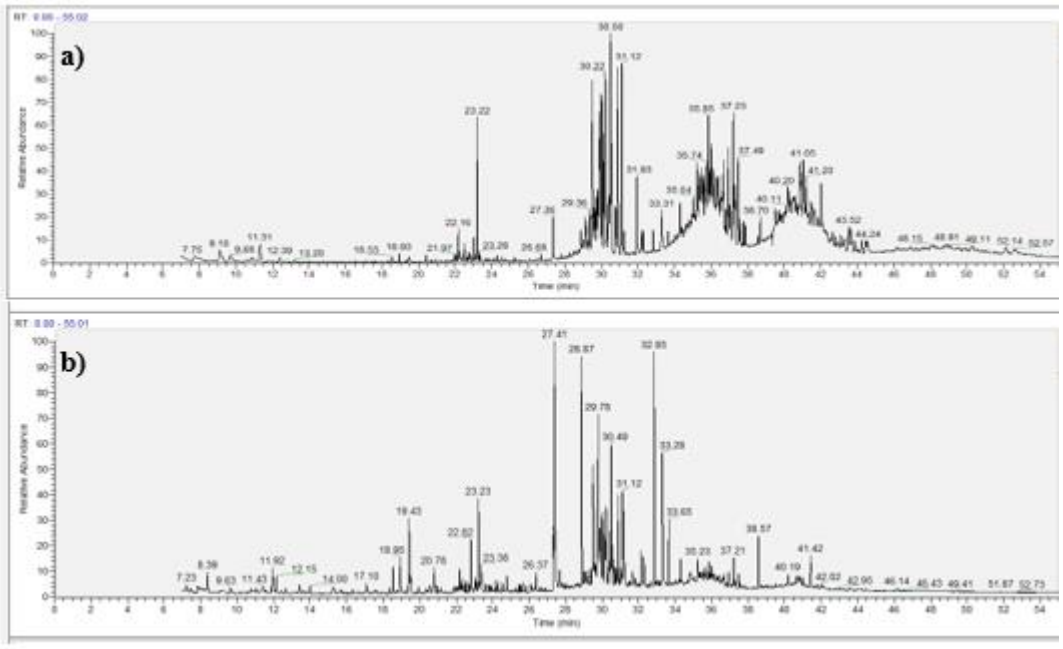


Fig. S2 a) 1:1 Hexane: acetone extraction b) 5:2 Hexane: acetone extraction

Table S1
Chemical compounds identified by GC-MS

	Chemical Groups	RT ± 0.5 min	Chemical Formula	Mol Weight	LogP	Boiling Point
1	**ACRYLATES**					
1	trimethylolpropane triacrylate	25.42	$C_{15}H_{20}O_6$	296.3	2.70	381
2	hexamethylene diacrylate	22.24	$C_{12}H_{18}O_4$	226.27	2.81	295
3	dodecyl acrylate	24.19	$C_{15}H_{28}O_2$	240.38	6.51	260
2	**ALDEHYDES AND KETONES**					
1	2,2-dimethoxy-1,2-diphenyl ethanone	26.34	$C_{16}H_{16}O_3$	256.3	2.90	169
2	2-butanone	10.10	C_4H_8O	72.1	0.31	80
3	2-chloro acetophenone	10.96	C_8H_7ClO	154.6	2.33	247
4	2-hexanone	6.76	$C_6H_{12}O$	100	1.42	127
5	2-heptanone	8.86	$C_7H_{14}O$	114.19	1.97	149
6	4-Hydroxy-3,5-dimethoxybenzaldehyde	23.86	$C_9H_{10}O_4$	182.173	0.86	192
7	4-hydroxy-4-methyl-2-pentanone	7.72	$C_6H_{12}O_2$	116.16	-0.1	168
8	acetophenone	9.95	C_8H_8O	120.14	1.58	202
9	benzaldehyde	17.94	C_7H_6O	106.12	1.48	178
10	2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione	22.59	$C_{14}H_{20}O_2$	220.31	3.90	285
3	**ALKANES & DIOLS**					
1	2-nitropropane	12.82	$C_3H_7NO_2$	89.09	0.68	120
2	1,3,5-triphenyl cyclohexane	17.97	$C_{24}H_{24}$	312.4	6.9	422

3	2,4,7,9-tetramethyl-5-decyn-4,7-diol	19.52	$C_{14}H_{26}O_2$	226.35	3.11	255
4	**GLYCOL ETHERS**					
1	2-(2-butoxyethoxy)-ethanol (diethylene glycol monobutyl ether)	15.74	$C_8H_{18}O_3$	162.22	0.44	231
2	2-(2-ethoxy)-ethanol (diethylene glycol monoethyl ether)	15.84	$C_6H_{14}O_3$	134.17	-0.62	202
3	2-methoxy ethanol (ethylene glycol monomethyl ether)	7.95	$C_3H_8O_2$	76.09	-0.80	125
4	2-phenoxy ethanol (Ethylene glycol monophenyl ether)	23.57	$C_8H_{10}O_2$	138.16	1.16	247
5	2-[2-(2-methoxyethoxy)ethoxy]-ethanol (triethylene glycol monomethyl ether)	20.54	$C_7H_{16}O_4$	164.20	-1.51	122
5	**LONG-CHAIN ALIPHATICS**					
1	(Z)-2-nonenal	24.28	$C_9H_{16}O$	140.22	3.17	89
2	10-methyleicosane	34.19	$C_{21}H_{44}$	296.57	11.73	368
3	1-docosene	33.22	$C_{22}H_{44}$	308.58	11.94	365
4	1-eicosene	31.98	$C_{20}H_{40}$	280.53	10.87	151
5	2,6,10,14-tetramethylpentadecane	24.83	$C_{19}H_{40}$	268.52	10.11	296
6	2,6,10-trimethyltetradecane	34.20	$C_{17}H_{36}$	240.47	9.24	282
7	2-ethyl-1-hexanol	26.34	$C_8H_{18}O$	130.23	2.82	185
8	2-methyl-1-hexadecanol	24.75	$C_{17}H_{36}O$	256.47	7.60	318
9	2-methyltricosane	32.11	$C_{24}H_{50}$	338.65	13.32	371
10	2-undecenal	18.69	$C_{11}H_{20}O$	168.28	4.23	244
11	4-methyldecane	29.01	$C_{11}H_{24}$	156.31	6.42	187
12	6-methyloctadecane	25.02	$C_{19}H_{40}$	268.52	10.67	324
13	9-hexylheptadecane	31.05	$C_{23}H_{48}$	324.63	12.79	397
14	dodecanol	33.01	$C_{12}H_{26}O$	186.33	5.13	260
15	eicosane	33.98	$C_{20}H_{42}$	282.55	11.38	366
16	heneicosane	34.08	$C_{21}H_{44}$	296.57	11.91	356
17	hentriacontanone	29.23	$C_{31}H_{62}O$	450.82	14.72	450
18	heptacosane	34.97	$C_{27}H_{56}$	380.73	15.10	422
19	heptadecane	23.71	$C_{17}H_{36}$	240.47	9.79	302
20	heptatriacotanol	30.76	$C_{37}H_{76}O$	536.99	18.41	490
21	hexacosane	34.18	$C_{26}H_{54}$	366.71	14.57	412
22	hexadecane	22.4	$C_{16}H_{34}$	226.44	9.26	287
23	hexadecanol	27.82	$C_{16}H_{34}O$	242.44	7.25	311
24	hexadecene	28.84	$C_{16}H_{32}$	224.43	8.75	274
25	nonadecane	26.32	$C_{19}H_{40}$	268.52	10.85	330
26	nonanal	14.21	$C_9H_{18}O$	142.24	3.56	191
27	octacosane	35.89	$C_{28}H_{58}$	394.76	15.63	474
28	octadecanal	24.28	$C_{18}H_{36}O$	268.48	8.35	321
29	octadecane	25.04	$C_{18}H_{38}$	254.49	10.32	317
30	octadecanol	32.08	$C_{18}H_{38}O$	270.49	8.31	334

31	pentacosane	33.12	$C_{25}H_{52}$	352.68	14.04	449
32	pentadecane	20.66	$C_{15}H_{32}$	212.41	8.73	270
33	pentatriacontanone	30.81	$C_{35}H_{70}O$	506.93	16.85	543
34	pentatriacontene	35.36	$C_{35}H_{70}$	490.93	18.83	554
35	tetracosane	31.97	$C_{24}H_{50}$	338.65	13.51	391
36	tetradecane	19.22	$C_{14}H_{30}$	198.39	8.19	254
37	tetradecanol	28.72	$C_{14}H_{30}O$	214.39	6.19	263
38	triacontane	37.65	$C_{30}H_{62}$	422.81	16.70	450
39	tricosane	30.91	$C_{23}H_{48}$	324.63	12.98	380
40	tridecane	23.72	$C_{13}H_{28}$	184.36	7.66	235
41	tritriacontan-16-one	39.39	$C_{33}H_{66}O$	478.88	15.78	521
42	undecane	20.69	$C_{11}H_{24}$	156.31	6.60	196
43	undecanol	31.21	$C_{11}H_{24}O$	172.31	4.59	243
44	undecyl cyclopentane	31.14	C16H32	224.42	8.40	296
6	**AMINES**					
1	hexa(methoxymethy)melamine	32.80	C15H30N6O6	390.44	3.07	487
2	O-decylhydroxylamine	24.19	C10H23NO	173.30	4.55	120
3	O-(3-methylbutyl)-hydroxylamine	10.29	$C_5H_{13}NO$	103.16	1.71	143
7	**ANTHRAQUINONES**					
1	9,10-anthraquinone	21.18	$C_{14}H_8O_2$	208.21	3.38	377
8	**AZULENES**					
1	decahydro-4,8,8-trimethyl-9-methylene-1,4-methanoazulene	20.32	C15H24	204.35	6.39	252
9	**BENZENESULPHONAMIDES**					
1	N-butylbenzenesulphonamide	25.97	$C_{10}H_{15}NO_2S$	213.30	2.57	314
10	**BENZOATE**					
1	diethylene glycol dibenzoate	33.24	$C_{18}H_{18}O_5$	314.33	3.64	408
11	**BENZOPHENONES**					
1	(1-hydroxycyclohexyl)phenyl-methanone	23.97	$C_{13}H_{16}O_2$	204.27	2.34	337
2	benzophenone	22.98	$C_{13}H_{10}O$	182.22	3.18	305
3	[1,1'-biphenyl]-4-ylphenyl-methanone	33.15	$C_{19}H_{14}O$	258.31	4.83	420
12	**BUTYRATES**					
1	2,2,4-trimethyl-1,3-pentanediol diisobutyrate	18.55	C16H30O4	286.41	4.70	280
13	**FLUORENES**					

1	9-(2',2'-dimethylpropanoilhydrazono)-3,6-dichloro-2,7-bis-[2-(diethylamino)-ethoxy]fluorene	33.58	C30H42Cl2N4O3	577.59	7.0	
14	**FURANS**					
1	2-pentyl furan	21.07	$C_9H_{14}O$	138.21	3.77	176
15	**GLYCEROL**					
1	glycerin	15.80	$C_3H_8O_3$	92.09	-2.32	335
2	glycerol tricapyrylate	38.46	$C_{27}H_{50}O_6$	470.68	9.33	508
3	1,2-diacetate glycerol	18.43	$C_7H_{12}O_5$	176.17	-0.54	240
4	triacetin	20.77	$C_{21}H_{42}O_4$	358.56	7.23	466
16	**NAPHTHALENES**					
1	diisopropylnaphthalene	23.90; 24.02; 24.59; 24.69; 24.78	$C_{16}H_{20}$	212.33	6.13	280
17	**ORGANOPHOSPHATES & RELATED COMPOUNDS**					
2	7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione	26.56	$C_{17}H_{24}O_3$	276.37	3.08	426
3	tris(2,4-ditert-butylphenyl)phosphate	43.67	$C_{42}H_{63}O_4P$	662.92	14.23	610
4	tris(2,4-ditert-butylphenyl)phosphite	41.10	$C_{42}H_{63}O_3P$	646.92	17.56	594
5	tris(2-chloropropyl) phosphate	40.12	$C_9H_{18}Cl_3O_4P$	327.57	1.53	359
18	**OTHER FATTY ACIDS & ESTERS**					
1	2-(2-hydroxyethoxy)ethyl ester octanoic acid (diglycol stearate)	29.66	$C_{22}H_{44}O_4$	372.58	7.70	473
2	2-ethyl hexanoic acid	22.17	$C_8H_{16}O_2$	144.21	2.72	229
3	butanoic acid (butyric acid)	13.19	$C_4H_8O_2$	88.11	0.78	164
4	butyl 4,7,10,13,16,19-docosahexaenoate	30.18	$C_{26}H_{40}O_2$	384.60	8.83	470
5	butyl 9,12-octadecadienoate	29.79	$C_{22}H_{40}O_2$	336.55	9.24	417
6	dodecanoic acid (lauric acid)	21.94	$C_{12}H_{24}O_2$	200.32	5.03	330
7	hexanoic acid (caproic acid)	12.86	$C_6H_{12}O_2$	116.16	1.84	203
8	methyl ester octadecanoic acid (methyl stearate)	28.18	$C_{19}H_{38}O_2$	298.50	8.68	182
9	methyl ester octadecenoic acid (methyl oleate)	29.42	$C_{19}H_{34}O_2$	296.49	8.16	351
10	nonanoic acid	17.45	$C_9H_{18}O_2$	158.24	2.59	255
11	octadecanoic acid (stearic acid)	29.39	$C_{18}H_{36}O_2$	284.48	8.22	413
12	octanoic acid (caprylic acid)	16.36	$C_8H_{16}O_2$	144.21	2.90	237

13	oleic acid	29.52	$C_{18}H_{34}O_2$	282.46	7.70	467
14	pentadecanoic acid	32.07	$C_{15}H_{30}O_2$	242.40	6.62	356
15	pentanoic acid (valeric acid)	14.15	$C_5H_{10}O_2$	102.13	1.31	186
16	tetradecanoic acid (myristic acid)	24.71	$C_{14}H_{28}O_2$	228.37	6.09	326
17	tridecanoic acid	22.33	$C_{13}H_{26}O_2$	214.34	5.56	331
18	octadecenoic acid (vaccenic acid)	28.95	$C_{18}H_{34}O_2$	282.46	7.70	398
19	**OTHER AROMATICS**					
1	2-propenyl benzene	8.02	C9H12	120.19	3.74	160
2	butylated hydroxytoluene	20.98	$C_{15}H_{24}O$	220.35	5.32	265
3	butyl benzene	8.88	$C_{10}H_{14}$	134.22	4.27	183
4	ethyl benzene	7.98	C_8H_{10}	106.16	3.21	136
5	indene	15.87	C_9H_8	116.16	2.91	182
6	α,α-diphenyl benzenemethanol	14.26	$C_{19}H_{16}O$	260.33	4.59	360
7	hydroxy toluene (a-cresol)	13.01	C_7H_8O	108.14	1.94	191
20	**PALMITIC ACIDS & PALMITATES**					
1	glycerol 1-palmitate	33.46	$C_{19}H_{38}O_4$	330.50	6.17	451
2	glycidyl palmitate	34.36	$C_{19}H_{36}O_3$	312.49	7.66	396
3	palmitic acid vinyl ester	29.64	$C_{18}H_{34}O_2$	282.46	8.17	354
4	palmitic anhydride	34.68	$C_{32}H_{62}O_3$	494.83	17.40	489
5	hexadecanoic acid	27.46	$C_{16}H_{32}O_2$	256.42	7.15	352
6	6-methylheptyl palmitate	33.10	$C_{24}H_{48}O_2$	368.64	11.15	407
21	**ABIETIC ACIDS & RELATED COMPOUNDS**					
1	abietic acid	33.51	$C_{20}H_{30}O_2$	302.45	6.51	440
2	methyl dehydroabietate ((1-phenanthrenecarboxylic acid, 1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-, methyl ester)	32.66	$C_{21}H_{30}O_2$	314.46	6.75	390
3	1-phenanthrenecarboxylic acid, 1,2,3,4,4a,9,10,10a-octahydro-6-methoxy-1,4a-dimethyl-9-oxo-, methyl ester, (1s,4as,10ar)-	32.96	C19H24O4	316.39	4.42	439
4	dehydroabietal (1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-[1-R-(1α,4β,10aα)]-1-phenanthrene carboxaldehyde)	30.86	$C_{20}H_{28}O$	284.44	6.48	379
5	dehydroabietinol (1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-[1-R-(1α,4β,10aα)]-1-phenanthrenemethanol)	32.08	$C_{20}H_{34}O$	290.48	6.90	387
6	4a-methyl-1-methylene-1,2,3,4,4a,9,10,10a-octahydrophenanthrene	34.51	$C_{16}H_{20}$	212.33	5.96	291

7	18-Norabieta-8,11,13-triene	29.39	$C_{19}H_{28}$	256.43	7.76	340
8	podocarpan-14-ol	30.11	$C_{17}H_{30}O$	250.42	5.95	336
9	tetradecahydro-4,5-dimethyl-phenanthrene	28.44	$C_{16}H_{28}$	220.39	7.46	296
22	**PHENANTHRENES**					
1	1-methyl-phenanthrene	26.51	$C_{15}H_{12}$	192.26	5.14	354
23	**PHENOLS**					
1	2,4-ditertbutyl phenol	19.41	$C_{14}H_{22}O$	206.32	4.86	265
2	2,6-dimethoxy-4-(2-propenyl) phenol	22.75	$C_{11}H_{14}O_3$	194.23	1.79	340
3	3,5-ditert-butylphenol	21.09	$C_{14}H_{22}O$	206.32	4.86	265
4	3-methylphenol (m-cresol)	16.22	C_7H_8O	108.14	1.94	204
5	4-tert-butyl phenol	17.61	C10H14O	150.22	3.17	267
24	**PHTHALATES**					
1	dibutyl phthalate	27.16	$C_{16}H_{20}O_4$	276.33	4.92	340
2	diisobutyl phthalate	25.98	$C_{16}H_{22}O_4$	278.34	4.46	327
3	diethyl phthalate	22.41	$C_{12}H_{14}O_4$	222.24	2.70	295
4	diethylhexyl phthalate	33.58	$C_{24}H_{38}O_4$	390.56	8.71	386
5	benzylbutyl phthalate	30.22	$C_{30}H_{34}O_4$	458.59	8.50	573
6	didecyl phthalate	39.21	$C_{28}H_{46}O_4$	446.66	11.20	454
7	nonyl phthalate	36.60	$C_{26}H_{42}O_4$	418.61	10.14	436
25	**PHTHALATES ALTERNATIVES**					
1	bis(2-ethylhexyl) maleate	29.69	$C_{20}H_{36}O_4$	340.50	7.69	410
2	tributyl acetylcitrate	30.56	$C_{20}H_{34}O_8$	402.48	6.92	418
3	tributyl citrate	31.16	$C_{18}H_{32}O_7$	360.44	4.68	325
4	diethylhexyl adipate	31.95	$C_{22}H_{42}O_4$	370.57	8.10	375
5	diethylhexyl fumarate	30.28	$C_{20}H_{36}O_4$	340.50	7.69	410
6	dibutyl adipate	24.67	$C_{14}H_{26}O_4$	258.35	4.22	305
26	**WOOD DERIVATIVES**					
1	2-norbornene	16.59	C_7H_{10}	94.15	2.75	96
2	3-carene	17.24	$C_{10}H_{16}$	136.23	4.37	172
3	borneol	18.84	$C_{10}H_{18}O$	154.25	2.71	212
4	cis-Vaccenic acid	28.95	$C_{18}H_{34}O_2$	282.46	7.70	398
5	ethyl iso-allocholate	36.86	$C_{26}H_{44}O_5$	436.63	3.61	553
6	homopterocarpin	31.01	$C_{17}H_{16}O_4$	284.31	2.96	401
7	isopimarol	41.54	$C_{20}H_{32}O$	288.47	6.60	382
8	sitosterol	40.76	$C_{29}H_{50}O$	414.71	10.73	502
9	stigmasta-3,5-dien-7-one	41.17	$C_{29}H_{46}O$	410.67	9.75	514
10	vanillin	19.73	$C_8H_8O_3$	152.15	1.19	285

11	xylopic acid	40.83	$C_{22}H_{32}O_4$	360.49	5.37	475
12	α-pinene	10.91	$C_{10}H_{16}$	136.23	4.37	156
13	β-acorenol	40.81	$C_{15}H_{26}O$	222.37	4.67	312
14	limonene	19.81	$C_{10}H_{16}$	136.23	4.45	178
27	**STEARATES**					
1	methyl stearate	28.96	$C_{19}H_{38}O_2$	298.50	8.68	400
28	**STYRENES**					
1	styrene	8.88	C_8H_8	104.15	2.70	146
2	α-methyl styrene	11.14	C_9H_{10}	118.18	3.25	166
29	**TEREPHTHALATES**					
1	bis(2-isopropylphenyl) terephthalate	38.49	$C_{26}H_{26}O_4$	402.48	8.07	558
165	**TOTAL COMPOUNDS**					

Note: No retention alignment performed for GC-MS, tolerance of 0.5 min

Table S2

Chemical compounds identified by LC-MS Positive ionisation

	Chemical groups	**RT ± 0.1 min**	**Chemical Formula**	**Mol weight**	**Log P**	**Boiling Point**
1	**ACRYLATES**					
1	2-{2-[2-(acryloyloxy)-1-methylethoxy]-1-methylethoxy}-1-methylethyl acrylate (tripropylene glycol diacrylate)	4.78	$C_{15}H_{24}O_6$	300.35	1.75	369
2	3-[4-hydroxy-3-(1,1,4,4,7-pentamethyltetralin-6-yl)phenyl]acrylic acid	7.94	$C_{24}H_{28}O_3$	364.48	7.55	508
2	**ALCOHOLS & ALKANES**					
1	1,4,7,10,13,16-hexaoxacyclooctadecane	3.88	$C_{12}H_{24}O_6$	264.32	-0.81	410
2	2-ethyl-1-hexanol	7.70	$C_8H_{18}O$	130.23	2.82	186
3	2-ethylcyclohexanol	6.23	$C_8H_{16}O$	128.21	2.36	175
4	3-aminopentan-2-ol	8.52	$C_5H_{13}NO$	103.16	-0.08	187
5	3-methyl-3-pentanol	6.53	$C_6H_{14}O$	102.17	1.57	122
6	6-methyl-2-heptanol	4.60	$C_8H_{18}O$	130.23	2.63	172
7	1,7-bis(4-hydroxyphenyl)heptane-3,5-diol	6.11	$C_{19}H_{24}O_4$	316.39	2.32	570
3	**LONG-CHAIN ALIPHATICS**					
1	trans-2-dodecenal	7.93	$C_{12}H_{22}O$	182.30	4.76	263

2	2-tridecenal	7.67	$C_{13}H_{24}O$	196.33	5.30	272
3	1-phenylicosane-1,3-dione	5.77	$C_{26}H_{42}O_2$	386.61	11.0	493
4	pentadecylamine	8.68	$C_{15}H_{33}N$	227.43	6.78	301
4	**GLYCOL ETHERS**					
1	2-(2-butoxyethoxy)ethanol (diethylene glycol n-butyl ether)	4.42	$C_8H_{18}O_3$	162.23	0.44	230
2	1,2-di(1h-benzimidazol-2-yl)ethanol	12.48	$C_{16}H_{14}N_4O$	278.31	0.04	667
3	diethylene glycol monohexyl ether	10.78	$C_{10}H_{22}O_3$	190.28	1.50	260
4	tetraethylene glycol monomethyl ether	2.58	$C_9H_{20}O_5$	208.25	-1.87	358
5	triethylene glycol monobutyl ether (butoxytriglycol)	4.43	$C_{10}H_{22}O_4$	206.28	0.08	278
6	triethylene glycol monoethyl ether (2-[2-(2-Ethoxyethoxy)ethoxy]ethane)	3.02	$C_8H_{18}O_4$	178.23	-0.98	256
7	di(propylene glycol) tert-butyl ether	3.52	$C_{10}H_{22}O_3$	190.28	0.85	264
5	**AMINES**					
1	(3-methylbutyl)(6-methylheptan-2-yl)amine (octamylamine)	7.45	$C_{13}H_{29}N$	199.38	4.86	229
2	1-methyl-3-phenylpropylamine	1.75	$C_{10}H_{15}N$	149.23	2.18	222
3	auramine O	4.86	$C_{17}H_{22}ClN_3$	303.83		406
4	bis-(4,6-diazido-1,3,5-triazin-2-yl)-amine	7.52	C_6HN_{19}	339.20	4.15	
5	cyclooctylamine	6.26	$C_8H_{17}N$	127.23	2.52	190
6	methoxyphenamine	7.19	$C_{11}H_{17}NO$	179.26	1.86	252
7	N-methyl-1-phenylethylamine	5.74	$C_9H_{13}N$	135.21	1.87	179
8	N-tosylethylenediamine	5.76	$C_9H_{14}N_2O_2S$	214.28	0.86	363
9	triethanolamine	1.79	$C_6H_{15}NO_3$	149.19	-1.11	335
10	tribenzylamine N-oxide	7.05	$C_{21}H_{21}NO$	303.40	2.61	602
6	**HYDRAZIDES**					
1	2-(1-azepanyl)acetohydrazide	1.86	$C_8H_{17}N_3O$	171.24	0.17	341
7	**AMIDES**					
1	2,2'-azobis-2-methylpropanimidamide	8.25	$C_8H_{18}N_6$	198.27	-0.41	267
2	2-chloro-N-(1,3,4-thiadiazol-2-yl)acetamide	1.77	$C_4H_4ClN_3OS$	177.6	-0.23	379
3	3-chloro-N-cyclopentylpropanamide	1.74	$C_8H_{14}ClNO$	175.66	1.04	335
4	3-hydroxy-N-(2-oxo-2,3-dihydro-1H-benzimidazol-5-yl)-2-naphthamide	6.67	$C_{18}H_{13}N_3O_3$	319.31	3.95	401
5	4-(benzyloxy)-N-butylbenzamide	8.37	$C_{18}H_{21}NO_2$	283.36	4.28	464
6	4-chloro-N-(2-(hydroxyamino)-2-oxoethyl)benzamide	3.76	$C_9H_9ClN_2O_3$	228.63	-0.04	484

7	4-tert-butyl-N-(6-imidazol-1-ylimidazo[1,2-a]pyridin-2-yl)benzamide	11.92	$C_{21}H_{21}N_5O$	359.42	3.34	
8	erucamide	12.01	$C_{22}H_{43}NO$	337.58	8.87	474
9	N-(2,4-Dihydroxy-6-methyl-5-pyrimidinyl)benzamide	4.43	$C_{12}H_{11}N_3O_3$	245.23	0.18	569
10	N-(3-Hydroxyphenyl)-2-(4-isobutylphenyl)propanamide	6.43	$C_{19}H_{23}NO_2$	297.39	4.48	506
11	N-(4-Ethoxyphenyl)-3-hydroxy-2-naphthamide	3.02	$C_{19}H_{17}NO_3$	307.34	4.98	439
12	N,N-bis(2-hydroxyethyl)dodecanamide	6.78	$C_{16}H_{33}NO_3$	287.44	3.94	443
13	N-[2-(1H-Benzimidazol-2-yl)ethyl]-2-phenylacetamide	9.57	$C_{17}H_{17}N_3O$	279.34	2.13	613
14	oleamide	9.75	$C_{18}H_{35}NO$	281.48	7.07	395
15	stearamide	10.23	$C_{18}H_{37}NO$	283.49	7.59	448
8	**ANILINES**					
1	4-(4-aminophenoxy)aniline (4,4'-Oxydianiline)	3.02	$C_{12}H_{12}N_2O$	200.23	0.51	562
2	4-(4-chloroanilino)tetrahydro-3-thiophenol 1,1-dioxide	8.23	$C_{10}H_{12}ClNO_3S$	261.72	0.15	559
3	4-(4-methoxyanilino)-2H-chromen-2-one	6.23	$C_{16}H_{13}NO_3$	267.28	2.88	460
4	4-[5-(benzylsulphanyl)-4-methyl-4H-1,2,4-triazol-3-yl]aniline	2.94	$C_{16}H_{16}N_4S$	296.39	3.88	540
5	4-Chloro-2-ethylaniline	3.84	$C_8H_{10}ClN$	155.62	2.75	250
9	**BENZOATES**					
1	ethyl 2,4-dihydroxy-6-methylbenzoate	6.27	$C_{10}H_{12}O_4$	196.20	2.91	350
2	methyl 2-benzoylbenzoate	5.46	$C_{15}H_{12}O_3$	240.25	2.61	352
3	(5-benzoyloxy-1,2,6-trihydroxycyclohex-3-en-1-yl)methyl benzoate	7.85	C21H20O7	384.4	1.5	545
10	**BENZOFURANS**					
1	(4aR,5S)-9,9a-dihydroxy-3,4a,5-trimethyl-5,6,7,8,8a,9-hexahydro-4H-benzo[f][1]benzofuran-2-one	6.39	C15H22O4	266.33	1.7	439
2	benzo[1,2-b:4,5-b']difuran-4-ethanamine, 8-bromo-2,3,6,7-tetrahydro-α-methyl-	2.74	$C_{13}H_{16}BrNO_2$	298.18	2.39	421
11	**BENZOPYRENES**					

1	2H-1-benzopyran-2-one, 7-[[6-(acetyloxy)decahydro-5,5,8a-trimethyl-2-methylene-1-naphthalenyl]methoxy]-	7.66	C26H32O5	424.51	5.5	538
12	**BENZOPHENONES**					
1	4-dodecyloxy-2-hydroxybenzophenone	7.74	$C_{25}H_{34}O_3$	382.54	9.48	506
2	4-methyl benzophenone	6.12	$C_{14}H_{12}O$	196.24	3.64	328
3	benzophenone	5.94	$C_{13}H_{10}O$	182.22	3.18	305
13	**BISPHENOLS**					
1	bisphenol P	2.69	$C_{24}H_{26}O_2$	346.46	6.12	515
2	3,3',5,5'-Tetramethylbisphenol A	3.80	$C_{15}H_{12}Br_4O_2$	543.87	7.29	418
14	**BUTYRATES & BUTYRIC ACIDS**					
1	2,2,4-trimethyl-1,3-pentanediol diisobutyrate	7.53	$C_{16}H_{30}O_4$	286.41	4.04	280
2	3-amino-4-(4-hydroxyphenyl) butyric acid	2.37	$C_{10}H_{13}NO_3$	195.21	0.59	402
15	**CHLORENDATES**					
1	dibutyl chlorendate	2.6	$C_{17}H_{20}Cl_6O_4$	501.06	8.86	501
16	**AROMATICS**					
1	benzyl alcohol (a-Cresol)	2.04	C_7H_8O	108.14	1.03	205
17	**CYCLIC ACIDS**					
1	1,1'-binaphthyl-8,8'-dicarboxylic acid	6.32	$C_{22}H_{14}O_4$	342.34	5.79	616
2	2-(1,1'-biphenyl-4-ylcarbonyl)benzoic acid	7.52				
3	2,2'-bipyridine-3,3'-dicarboxylic acid	1.83	$C_{12}H_8N_2O_4$	244.20	-1.18	454
4	2-benzoylbenzoic acid	5.44	$C_{14}H_{10}O_3$	226.23	2.31	265
5	2-hydroxy-3-methoxybenzoic acid	1.96	$C_8H_8O_4$	168.15	1.98	316
6	2-hydroxybenzene-1,3-dicarboxylic acid	2.59	$C_8H_6O_5$	182.13	2.73	403
7	3-furancarboxylic acid, tetrahydro-4-methylene-2-octyl-5-oxo-, (2R,3S)-rel-	7.65	C14H22O4	254.32	4	337
8	4-methylphenylacetic acid	6.18	$C_9H_{10}O_2$	150.17	1.97	266
9	5-phenyl-2-thiophenecarboxylic acid	2.74	$C_{11}H_8O_2S$	204.24	3.64	394
10	phenylacetic acid	1.75	$C_8H_8O_2$	136.15	1.50	266
18	**DICHLOROPROPS**					
1	dichlorprop	7.60	$C_9H_8Cl_2O_3$	235.06	2.93	348

19	**OTHER FATTY ACIDS & ESTERS**					
1	diethyl 2-benzylmalonate	1.72	$C_{14}H_{18}O_4$	250.29	2.76	300
2	methyl linoleate	7.42	$C_{19}H_{34}O_2$	294.47	7.64	208
3	methyl tetradecanoate	4.43	$C_{15}H_{30}O_2$	242.40	6.55	323
4	11-hydroxyundecanoic acid	7.19	$C_{11}H_{22}O_3$	202.29	2.49	345
5	1-naphthalenepentanoic acid, 3,4,4a,5,6,7,8,8a-octahydro-β,2,5,5,8a-pentamethyl-3-oxo-, (8aS)-	7.64	$C_{20}H_{34}O_2$	306.48	7.41	409
6	3-hydroxydodecanoic acid	3.52	$C_{12}H_{24}O_3$	216.32	3.11	348
7	8-(3-octyl-2-oxiranyl)octanoic acid	7.20	$C_{18}H_{34}O_3$	298.46	6.14	423
8	8,9-dihydroxy-5Z,11Z,14Z-eicosatrienoic acid	7.85	$C_{20}H_{34}O_4$	338.48	4.34	515
9	cis-15-tetracosenoic acid (nervonic acid)	11.18	$C_{24}H_{46}O_2$	366.62	10.89	479
10	propanoic acid, 3-[(1,4-dihydro-5,8-dimethoxy-1,4-dioxo-2-naphthalenyl)thio]-	3.41	$C_{15}H_{14}O_6S$	322.33	2.19	608
20	**FLUORESCEINS**					
1	dichlorofluorescein	4.07	$C_{20}H_{10}Cl_2O_5$	401.20	4.10	635
21	**FLUTRIAFOLS**					
1	Flutriafol	6.81	$C_{16}H_{13}F_2N_3O$	301.29	2.31	507
22	**GLYCEROLS**					
1	1,2-dioleoyl-sn-glycerol	11.89	$C_{39}H_{72}O_5$	620.99	15.43	671
2	1-oleoyl-2-palmitoyl-rac-glycerol	11.75	$C_{37}H_{70}O_5$	594.95	14.89	648
3	1-palmitoylglycerol	10.72	$C_{19}H_{38}O_4$	330.50	6.17	451
4	2-arachidonoylglycerol	11.97	$C_{23}H_{38}O_4$	378.54	6.24	509
5	2-linoleoylglycerol	8.97	$C_{21}H_{38}O_4$	354.52	6.42	485
6	glycerol 1-myristate	7.63	$C_{17}H_{34}O_4$	302.45	5.10	425
7	glycerol monostearate	9.85	$C_{21}H_{42}O_4$	358.56	7.23	477
8	triacetin	3.92	$C_{21}H_{42}O_4$	358.56	7.23	466
23	**GLYCOLS**					
1	hexaethylene glycol	3.55	$C_{12}H_{26}O_7$	282.33	-2.95	378
2	neopentyl glycol	1.72	$C_5H_{12}O_2$	104.15	-0.34	212
3	tetraethylene glycol	2.43	$C_8H_{18}O_5$	194.22	-2.23	328
4	triethylene glycol	4.59	$C_6H_{14}O_4$	150.17	-1.87	288
5	tripropylene glycol	3.51	$C_9H_{20}O_4$	192.25	-0.83	293
6	undecaethylene glycol	3.88	$C_{22}H_{46}O_{12}$	502.59	-4.74	571

24	**ORGANOPHOSPHATES AND RELATED COMPOUNDS**					
1	1-(1,2-dioctanoylphosphatidyl)inositol-3,5-bisphosphate	6.26	$C_{25}H_{49}O_{19}P_3$	746.57	3.81	906
2	3-hydroxy-2-((9Z,12Z)-octadeca-9,12-dienoyloxy)propyl 2-(trimethylazaniumyl)ethyl phosphate	8.37	$C_{26}H_{50}NO_7P$	519.65	2.87	
3	tributyl phosphate	8.72	$C_{12}H_{27}O_4P$	266.31	4.26	288
4	triisobutyl phosphate	8.93	$C_{12}H_{27}O_4P$	266.31	3.71	261
5	triphenyl phosphate	2.95	$C_{18}H_{15}O_4P$	326.28	4.10	448
6	triphenylphosphine oxide	5.69	$C_{18}H_{15}OP$	278.28	2.87	360
25	**ORGANOPHOSPHONATE COMPOUNDS**					
1	dibutyl hydroxy(phenyl)methylphosphonate	1.18	$C_{15}H_{25}O_4P$	300.33	2.96	416
2	diethyl 2-hydroxyphenylphosphonate	2.19	$C_{10}H_{15}O_4P$	230.20	1.28	322
3	diethyl 4-bromobenzylphosphonate	7.94	$C_{11}H_{16}BrO_3P$	307.12	2.83	376
26	**PALMITATES & PALMITAMIDES**					
1	isopropyl palmitate	4.07	$C_{19}H_{38}O_2$	298.50	8.49	390
2	methyl palmitoleate	11.96	$C_{17}H_{32}O_2$	268.43	7.10	394
3	palmitamide	9.26	$C_{16}H_{33}NO$	255.44	6.20	392
27	**PENTACHLORINATED BIPHENYLS**					
1	4-hydroxy-2,2',3',5',6'-pentachlorobiphenyl	6.21	$C_{12}H_5Cl_5O$	342.43	5.72	394
28	**ABIETIC ACIDS & RELATED COMPOUNDS**					
1	abietic acid	9.08	$C_{20}H_{30}O_2$	302.45	6.51	440
2	15-hydroxydehydroabietic acid	6.60	$C_{20}H_{28}O_3$	316.43	4.52	463
3	15-hydroxy-7-oxoabieta-8,11,13-trien-18-oic acid	5.79	$C_{20}H_{26}O_4$	330.42	3.45	522
4	7-oxoabieta-8,11,13-trien-18-oic acid	5.67	$C_{20}H_{26}O_3$	314.42	5.27	475
29	**PHENOLS**					
1	2,6-di-tert-butyl-4-(4-morpholinylmethyl)phenol	10.67	$C_{19}H_{31}NO_2$	305.45	3.82	363
2	phenol, 5-(1,1-dimethylheptyl)-2-[(1S,3R)-3-hydroxycyclohexyl]-	1.70	$C_{21}H_{34}O_2$	318.49	6.42	421

3	3-(5,5-dimethyl-5,6-dihydro[1,2,4]triazolo[3,4-a]isoquinolin-3-yl)phenol	5.75	$C_{18}H_{17}N_3O$	291.35	4.95	533
30	**PHTHALATES**					
1	dimethyl phthalate	2.49	$C_{10}H_{10}O_4$	194.18	2.64	284
2	di(2-nonyl) phthalate	11.34	$C_{26}H_{42}O_4$	418.61	10.15	435
3	di(3-methyl-4-octyl) phthalate	15.69	$C_{28}H_{46}O_4$	446.66	10.47	496
4	monoethyl phthalate	7.07	$C_{10}H_{10}O_4$	194.18	1.66	339
5	dipropyl phthalate	6.27	$C_{14}H_{18}O_4$	250.29	3.76	392
6	diethylhexyl phthalate	11.45	$C_{24}H_{38}O_4$	390.56	8.71	386
7	dibutyl phthalate	6.51	$C_{16}H_{20}O_4$	276.33	4.92	340
8	diisobutyl phthalate	6.65	$C_{16}H_{22}O_4$	278.34	4.46	327
31	**PHTHALATE ALTERNATIVES**					
1	dibutyl maleate	6.28	$C_{12}H_{20}O_4$	228.28	3.81	281
2	2-ethylhexyl sebacate	4.43	$C_{26}H_{50}O_4$	426.67	9.86	435
3	dihexyl adipate	10.43	$C_{18}H_{34}O_4$	314.46	6.34	351
32	**WOOD DERIVATIVES**					
1	acetylsyringic acid	3.88	$C_{11}H_{12}O_6$	240.21	1.43	339
2	coniferyl aldehyde	4.22	$C_{10}H_{10}O_3$	178.18	1.35	382
3	stigmastadienone	10.54	$C_{29}H_{46}O$	410.67	9.72	503
4	syringaldehyde	3.80	$C_9H_{10}O_4$	182.17	0.86	193
5	β-eudesmol	9.02	$C_{15}H_{26}O$	222.37	4.68	302
33	**POTASSIUM SALTS**					
1	potassium chlorate	7.14	$ClKO_3$	122.55	-0.97	400
2	potassium nitrate	4.25	KNO_3	101.10	-2.6	400
3	potassium sulphate	4.11	K_2O_4S	174.26	-0.84	1689
34	**PYROZOLINES**					
1	mefenpyr-diethyl	7.14	$C_{16}H_{18}Cl_2N_2O_4$	373.23	3.20	451
35	**QUINONE & QUINOLINES**					
1	2-(1H-benzimidazol-2-yl)quinoline	5.63	$C_{16}H_{11}N_3$	245.28	3.52	505
2	2,2',6,6'-tetra-tert-butyldiphenylquinone	6.38	$C_{28}H_{40}O_2$	408.62	7.32	493
3	2-tert-pentylanthra-9,10-quinone	5.42	$C_{19}H_{18}O_2$	278.34	5.60	433
4	4-chloro-5,6,7,8-tetrahydroquinazoline	2.95	$C_8H_9ClN_2$	168.62	2.16	292
5	4-phenyl-3,4-dihydrobenzo[h]quinolin-2(1H)-one	6.64	$C_{15}H_{13}N$	207.27	3.26	329

6	8-(2-chlorophenyl)-7,8-dihydro[1,3]dioxolo[4,5-g]quinolin-6(5H)-one	2.38	$C_{16}H_{12}ClNO_3$	301.72	3.52	443
36	**SULPHONATED BENZENES**					
1	1-benzothiophene-2-sulphonamide	8.24	$C_8H_7NO_2S_2$	213.28	2.41	433
2	3,3'-disulphanediyldibenzoic acid	2,78	$C_{14}H_{10}O_4S_2$	306.36	3.92	538
3	benzenesulphonohydrazide	4.09	$C_6H_8N_2O_2S$	172.20	-0.14	333
4	N-(2,4-dimethylphenyl)-4-methylbenzenesulphonamide	6.42	$C_{15}H_{17}NO_2S$	275.37	3.96	410
5	N-(2-methylphenyl)-3-nitrobenzenesulphonamide	4.95	$C_{13}H_{12}N_2O_4S$	292.31	3.26	457
6	N-(5-chloro-2-phenoxyphenyl)thiophene-2-sulphonamide	5.00	$C_{16}H_{12}ClNO_3S_2$	365.85	5.18	488
37	**TEREPHTHALATES**					
1	3,4-dichlorophenyl undecyl terephthalate	9.06	$C_{25}H_{30}Cl_2O_4$	465.41	10.74	562
144	**TOTAL COMPOUNDS**					

Retention Time alignment performed, RT tolerance of 0.1 min

Table S3

Chemical compounds identified by LC-MS Negative ionisation

	COMPOUNDS	**RT ± 0.1 min**	**Chemical Formula**	**Mol weight**	**LogP**	**Boiling Point**
1	**CYCLIC ACIDS**					
1	1-(diphenylphosphoryl) cyclobutanecarboxylic acid	5.93	$C_{17}H_{17}O_3P$	300.29	1.79	461
2	3-(hydroxymethyl)-7-methoxy-6-oxooxepino[2,3-b]chromene-5-carboxylic acid	4.89	$C_{16}H_{12}O_7$	316.26	0.5	541
3	phenylacetic acid	2.93	$C_8H_8O_2$	136.15	1.41	265
4	1-hydroxy-2-naphthoic acid	5.30	$C_{11}H_8O_3$	188.18	3.29	368
2	**SULPHONATED BENZENES**					
1	tridecylbenzenesulphonic acid	8.28	$C_{19}H_{32}O_3S$	340.52	7.31	471
2	benzenesulphonic acid, 4-undecyl-	7.52	$C_{17}H_{28}O_3S$	312.47	6.24	448
3	**FATTY ACIDS**					
1	3-isobutylpentanedioic acid	5.29	$C_9H_{16}O_4$	188.22	0.72	326
2	9-(2,3-dihydroxypropoxy)-9-oxononanoic acid	4.64	$C_{12}H_{22}O_6$	262.30	0.34	456

3	3-chlorobenzoic acid	4.64	$C_7H_5ClO_2$	156.57	2.90	274
4	**AMINES**					
1	Ethanolamine	9.68	C_2H_7NO	61.08	-1.31	171
5	**AMIDES**					
1	2,4-dichloro-N-(3-methylphenyl)benzamide	9.48	$C_{14}H_{11}Cl_2NO$	280.15	3.71	341
2	N-(sec-butyl)-3,4-dichlorobenzamide	1.70	$C_{11}H_{13}Cl_2NO$	246.13	3.76	339
6	**GLYCOL ETHERS**					
1	2-(2-butoxyethoxy)ethanol (diethylene glycol n-butyl ether)	1.90	$C_8H_{18}O_3$	162.23	0.44	230
7	**QUINONE & QUINOLINES**					
1	9,10-1nthracenedione, 3-(1,2-dihydroxypropyl)-1,6,8-trihydroxy-	6.15	$C_{17}H_{14}O_7$	330.29	2.73	710
8	**BISPHENOLS**					
1	bisphenol A	4.87	$C_{15}H_{16}O_2$	228.29	3.43	430
2	bisphenol F	1.98	$C_{13}H_{12}O_2$	200.23	2.73	390
3	bisphenol S	4.16	$C_{12}H_{10}O_4S$	250.27	1.83	505
9	**LONG-CHAIN SULPHATES**					
1	myristyl sulphate	8.06	$C_{14}H_{30}O_4S$	294.45	6.46	411
2	ethylene glycol dodecyl ether sulphate	7.49	$C_{14}H_{26}O_7S$	338.42	4.61	489
3	diethylene glycol dodecyl ether sulphate	7.54	$C_{16}H_{34}O_6S$	354.50	3.77	550
10	**PHENOLS**					
1	2,2'-methylene-bis(6-tert-butyl-4 methylphenol)	8.96	$C_{23}H_{32}O_2$	340.50	7.03	429
2	2,6-di-tert-butyl-4-methoxyphenol	6.00	$C_{15}H_{24}O_2$	236.35	4.69	299
11	**PHTHALATES**					
1	isophthalic acid, 3-chlorophenyl hexyl ester	10.03	$C_{20}H_{21}ClO_4$	360.83	7.45	487
12	**WOOD DERIVATIVES**					
1	methyl vanillate	3.80	$C_9H_{10}O_4$	182.17	1.54	287
2	syringaresinol diglucoside	5.54	$C_{34}H_{46}O_{18}$	742.72	-3.91	936
3	tricin methyl ether	5.64	C16H12O7	316.26	1.40	562
13	**AROMATICS**					
1	2-methoxyacridin-9-ol	2.71	$C_{14}H_{11}NO_2$	225.24	3.1	403
2	2-benzimidazolinone, 1-benzyl-	1.92	$C_7H_6N_2O$	134.13	1.12	124

14	**BENZOPYRENES**					
1	benzo(a)pyrene	5.99	$C_{20}H_{12}$	252.31	6.40	495
15	**TEREPHTHALATES**					
1	terephthalic acid, hexyl phenyl ester	12.44	$C_{20}H_{22}O_4$	326.39	6.65	461
2	terephthalic acid, 3-chlorophenyl hexyl ester	9.79	$C_{20}H_{21}ClO_4$	360.83	7.60	485
31	**TOTAL COMPOUNDS**					

Table S4

Cartonboard GC-MS Suspect Screening Results

HW- household waste; RF- Recycling facilities; R- Retail; SW- Solid waste disposal sites; WP-Waste pickers; M-Mills, C-corrugators

SAMPLE ID	A2	A4	A7	B1	B7	E1	E5	E6	E8	H1	W3
SITE	**HW**	**HW**	**HW**	**HW**	**HW**	**RF**	**RF**	**RF**	**RF**	**R**	**RF**
ABIETIC ACIDS & RELATED COMPOUNDS											
1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-[1-R-(1α,4β,10aα)]-1-phenanthrene carboxaldehyde		✓									
1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-[1-R-(1α,4β,10aα)]-1-phenanthrenemethanol		✓							✓		
18-Norabieta-8,11,13-triene						✓					
Podocarpan-14-ol		✓									
methyl dehydroabietate (1-Phenanthrenecarboxylic acid, 1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-, methyl ester)		✓				✓			✓		
GLYCEROLS											
Glycerin											✓
glycerol tricapyrylate			✓								
NAPHTHALENES											
diisopropylnaphthalene	✓	✓	✓	✓	✓	✓	✓	✓	✓		✓
ACRYLATES											
trimethylolpropane triacrylate	✓						✓				
hexamethylene diacrylate				✓							
STEARATES											

methyl stearate		✓									
ANTHRAQUINONES											
9,10-anthraquinone		✓							✓		
PHENOLS											
2,4-bis(1,1-dimethylethyl) phenol				✓							
2,4-ditertbutyl phenol							✓				
3,5-bis(1,1-dimethylethyl)-phenol				✓			✓				
GLYCOL ETHERS											
2-(2-butoxyethoxy)-ethanol					✓	✓		✓			
2-(2-ethoxy)-ethanol								✓			
2-methoxy ethanol								✓			
2-phenoxy ethanol								✓			
AMINES											
Hexa(methoxymethy)melamine							✓				
O-decyl hydroxylamine									✓		
BENZOATE											
diethylene glycol dibenzoate					✓						
FLUORENES											
9-(2',2'-dimethylpropanoilhydrazono)-3,6-dichloro-2,7-bis-[2-(diethylamino)-ethoxy]fluorene										✓	
BENZENESULPHONAMIDES											
N-butylbenzenesulphonamide					✓			✓			
PHTHALATES											
octyl 2-phenoxyethyl phthalate	✓										
dibutyl phthalate	✓	✓	✓	✓		✓	✓	✓	✓	✓	

diisobutyl phthalate	✓	✓	✓	✓		✓	✓		✓	✓	✓
diethyl phthalate	✓	✓	✓	✓	✓						✓
diethylhexyl phthalate	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓
benzylbutyl phthalate	✓	✓			✓			✓			
didecyl phthalate		✓		✓		✓					
PHTHALATES ALTERNATIVES											
bis(2-ethylhexyl) maleate						✓					
tributyl acetyl citrate	✓				✓			✓			
tributyl citrate										✓	
dioctyl adipate			✓								
bis(2-ethylhexyl) fumarate			✓		✓	✓				✓	
OTHER AROMATICS											
butyl benzene							✓				
butylated hydroxy toluene	✓									✓	
PALMITIC ACIDS & PALMITATES											
glycerol 1-palmitate	✓										
glycidyl palmitate	✓										
palmitic acid vinyl ester									✓		
hexadecanoic acid		✓			✓				✓		
ORGANO PHOSPHATE AND RELATED COMPOUNDS											
7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione						✓					
tris(2,4-ditert-butylphenyl)phosphite											✓

tris(2,4-ditert-butylphenyl)phosphate					✓	✓		✓				
BENZOPHENONES												
(1-hydroxycyclohexyl)phenyl-methanone				✓								
benzophenone	✓	✓	✓		✓	✓	✓	✓	✓			
TEREPHTHALATES												
di(2-isopropylphenyl) ester terephthalate			✓									
LONG-CHAIN ALIPHATICS												
10-methyl-eicosane						✓						
1-docosene		✓										
1-eicosane		✓										
2,6,10,14-tetramethyl pentadecane						✓						
2-methyl-1-hexadecanol				✓				✓	✓			
2-methyltricosane		✓										
4-methyl decane					✓							
6-methyl-octadecane	✓	✓		✓					✓	✓		
9-hexyl-heptadecane		✓		✓					✓			
9-hexyl-heptadecane						✓						
eicosane					✓				✓			
hentriacontanone		✓		✓								
heptacosane		✓		✓								
heptadecane									✓			
hexadecane				✓	✓						✓	
hexadecanol			✓			✓						
hexadecane												

octacosane		✓									✓
octadecane				✓							
pentacosane				✓							
pentadecane					✓						
pentatriacontanone				✓							
tetracosane				✓			✓				
tridecane			✓		✓			✓			
tritriacontan-16-one		✓									
undecanol								✓			
WOOD DERIVATIVES											
2-norbornene							✓				
ethyl iso-allocholate									✓		
homopterocarpin						✓					
isopimarol		✓									
sitosterol		✓									
stigmasta-3,5-dien-7-one	✓	✓				✓	✓		✓		
vanillin	✓	✓		✓	✓	✓	✓	✓	✓		✓
xylopic acid						✓					
β-acorenol						✓					
β-sitosterol	✓			✓		✓					
ϒ-sitosterol		✓							✓		
Limonene		✓									
ALDEHYDES AND KETONES											
2,2-dimethoxy-1,2-diphenyl ethanone										✓	

4-hydroxy-4-methyl-2-pentanone		✓	✓		✓						
benzaldehyde			✓		✓						
2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene					✓						
OTHER FATTY ACID & ESTERS											
methyl ester octadecanoic acid					✓		✓				
nonanoic acid	✓			✓	✓						✓
oleic acid								✓			
octadecanoic acid		✓						✓			
octanoic acid							✓	✓			
tetradecanoic acid									✓		
pentanoic acid								✓			

Table S5

Corrugated Board GC-MS Suspect Screening Results

SAMPLE ID SITE	B3 HW	D1 RF	D2 RF	J2 R	J3 R	K1 SW	K3 SW	O1 WP	O4 WP	S2 R	T2 WP	U1 WP	EE3 SW
ABIETIC ACIDS & RELATED COMPOUNDS													
1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-[1-R-(1α,4β,10aα)]-1-phenanthrene carboxaldehyde	✓												
4a-methyl-1-methylene-1,2,3,4,4a,9,10,10a-octahydrophenanthrene										✓			
GLYCEROLS													
triacetin	✓												
1,3-diacetin diacetate glycerol		✓	✓					✓					
glycerin								✓					
PHENANTHRENES													
1-methyl phenanthrene											✓		
OTHER AROMATICS													
1,3,5-triphenyl cyclohexane		✓											
butylated hydroxy toluene					✓					✓			
NAPHTHALENES													
diisopropylnaphthalene		✓			✓	✓		✓	✓	✓	✓		
STEARATES													
methyl stearate		✓											
ANTHRAQUINONES													

9,10-anthraquinone				✓								
PHENOLS												
2,4-bis(1,1-dimethylethyl) phenol			✓						✓			
AMINES												
ethylenimine				✓								
FURANS												
2-pentyl furan											✓	
5-dodecyldihydro-2(3H)-furanone											✓	
FLUORENES												
9-(2',2'-dimethylpropanoilhydrazono)-3,6-dichloro-2,7-bis-[2-(diethylamino)-ethoxy]fluorene			✓									✓
PHTHALATES												
nonyl phthalate	✓											
benzylbutyl phthalate				✓	✓			✓	✓	✓		✓
dibutyl phthalate		✓		✓	✓	✓		✓	✓	✓	✓	
diethylhexyl phthalate		✓	✓	✓	✓	✓		✓	✓	✓	✓	✓
diethyl phthalate				✓	✓				✓	✓		✓
diisobutyl phthalate		✓			✓	✓		✓	✓	✓	✓	✓
didecyl phthalate					✓			✓	✓			✓
PHTHALATE ALTERNATIVES												
dioctyl ester hexanedioic acid (adipate)							✓					
STYRENES												
Styrene					✓		✓					
α-methyl styrene			✓									✓

ORGANOPHOSPHATES AND BREAKDOWN PRODUCTS													
7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione	✓												
tributyl phosphate			✓										
tris(2,4-ditert-butylphenyl)phosphite	✓												
AZULENES													
1-acetyl-4,6,8-trimethylazulene									✓				
BENZOPHENONES													
benzophenone	✓	✓	✓	✓	✓	✓		✓	✓		✓	✓	
BENZENESULPHONAMIDES													
N-Butylbenzenesulphonamide			✓	✓	✓								
LONG-CHAIN ALIPHATIC COMPOUNDS													
2,6,10-trimethyl tetradecane							✓				✓		
2-ethyl-1-hexanol			✓										
2-heptanone											✓		
2-hexanone							✓	✓					
2-methyl-1-hexadecanol												✓	
4-methyl decane			✓			✓							
butyl 4,7,10,13,16,19-docosahexaenoate	✓												
dodecanol	✓		✓										
eicosane	✓		✓				✓		✓	✓	✓	✓	
heptacosane	✓							✓					
heptatriacotanol											✓		

hexacosane		✓													
hexadecane		✓								✓		✓			
hexadecanol		✓								✓					
nonadecane			✓		✓	✓	✓								
octacosane			✓												
octadecane		✓			✓		✓			✓	✓				
pentacosane		✓	✓						✓	✓			✓		
pentadecane				✓						✓					
pentatriacontene										✓					
tetracosane		✓	✓						✓			✓	✓		
tetradecane										✓			✓		
tetradecanol					✓								✓		
tricosane									✓	✓					
tridecane		✓		✓			✓		✓			✓			
undecanol				✓											
undecyl cyclopentane															
WOOD DERIVATIVES															
ethyl iso-allocholate		✓								✓		✓			
sitosterol	✓														
stigmasta-3,5-dien-7-one	✓														
vanillin	✓	✓	✓	✓					✓			✓	✓	✓	
GLYCOL ETHERS															
2-[2-(2-methoxyethoxy)ethoxy]-ethanol												✓			
ALDEHYDES & KETONES															
4-hydroxy-3,5-dimethoxybenzaldehyde													✓		
4-hydroxy-4-methyl-2-pentanone									✓				✓	✓	

acetophenone				✓							✓			
ALKANES & DIOLS														
2-nitropropane				✓										
PALMITIC ACIDS & PALMITATES														
palmitic anhydride										✓				
hexadecanoic acid	✓	✓		✓	✓	✓	✓	✓	✓	✓	✓			✓
OTHER FATTY ACIDS & ESTERS														
dodecanoic acid		✓						✓						
hexanoic acid	✓										✓	✓		
nonanoic acid	✓				✓			✓			✓	✓		
octadecanoic acid			✓					✓	✓	✓	✓			
octadecenoic acid		✓		✓	✓									
octanoic acid		✓									✓	✓		
oleic acid	✓													
pentadecanoic acid										✓				
pentanoic acid				✓	✓						✓	✓		
tetradecanoic acid						✓		✓	✓					
methyl ester octadecanoic acid								✓						

Table S6
Newspaper GC-MS Suspect Screening Results

SAMPLE ID	C1	C3	N2	N3
SITE	**RF**	**RF**	**SW**	**SW**
ABIETIC ACIDS & RELATED COMPOUNDS				
1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-9-oxo-methyl ester-1-phenanthrene carboxylic acid		✓		
1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-[1-R-(1α,4β,10aα)]-1-phenanthrene carboxaldehyde	✓			✓
1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-[1-R-(1α,4β,10aα)]-1-phenanthrenemethanol			✓	
(1R,4aR,4bS,7S, 10aR)-1,4A,7-Trimethyl-7-vinyl-1,2,3,4,4a,4b,5,6,7,8,10,10a-dodecahydrophenanthrene-1-carbaldehyde			✓	
podocarpan-14-ol			✓	
tetradecahydro-4,5-dimethyl-phenanthrene		✓		
abietic acid			✓	
methyl dehydroabietate		✓	✓	
GLYCEROLS				
1,2-diacetate glycerol		✓		
ACRYLATES				
trimethylolpropane triacrylate	✓			
BUTYRATES				
2,2,4-trimethy-1,3-pentaediol diisobutyrate		✓		
PHENOLS				
2,4-bis(1,1-dimethylethyl) phenol	✓			

BENZOATES				
diethylene glycol dibenzoate	✓			
FURANS				
2-pentyl furan		✓		
OTHER AROMATICS				
2-propenyl benzene	✓			
butylated hydroxy toluene	✓			✓
indene	✓	✓		
BENZOPHENONES				
(1-hydroxycyclohexyl)phenyl-methanone		✓		
[1,1'-biphenyl]-4-ylphenyl-methanone	✓			
Benzophenone	✓	✓		
BENZENESULPHONAMIDES				
N-butylbenzenesulphonamide	✓	✓		✓
PHTHALATES				
diisobutyl phthalate	✓	✓	✓	✓
diethylhexyl phthalate	✓	✓		✓
benzylbutyl phthalate				✓
didecyl phthalate	✓			
PHTHALATES ALTERNATIVES				
dioctyl ester adipate		✓		
GLYCOL ETHERS				
2-(2-butoxyethoxy)-ethanol	✓			
AZULENES				
decahydro-4,8,8-trimethyl-9-methylene-1,4-methanoazulene	✓			

STYRENES				
α-methystyrene				✓
PALMITATES				
hexadecanoic acid	✓			
ORGANOPHOSPHATES & RELATED COMPOUNDS				
tris(2,4-ditert-butylphenyl)phosphate	✓			
ALIPHATIC LONG CHAINS				
(Z)-2-nonenal		✓		
2,6,10,14-tetramethyl pentadecane	✓			
2-methyl-1-hexadecanol	✓			
2-undecenal		✓		
6-methyl-octadecane		✓		
eicosane				✓
heptacosane				✓
heptadecane			✓	
heptatriacotanol		✓		
hexadecane			✓	
nonadecane		✓		
nonanal		✓		
octadecane	✓		✓	✓
octacosane				✓
pentacosane		✓		
pentadecane	✓	✓	✓	
tetracosane			✓	✓
tricosane		✓		

tridecane		✓	✓	✓
undecane				✓
dodecanol		✓		
WOOD DERIVATIVES				
3-carene	✓			
cis-Vaccenic acid		✓		
ethyl iso-allocholate		✓		✓
stigmasta-3,5-dien-7-one	✓	✓		
vanillin	✓		✓	
xylopic acid		✓		
α-pinene				✓
ALDEHYDES & KETONES				
4-hydroxy-4-methyl-2-pentanone	✓	✓		
acetophenone	✓	✓		
OTHER FATTY ACIDS				
butanoic acid				✓
hexanoic acid	✓	✓		
nonanoic acid	✓	✓	✓	✓
octadecenoic acid	✓			
octanoic acid	✓	✓	✓	✓
oleic acid				
pentadecanoic acid	✓			
pentanoic acid	✓		✓	✓
tridecanoic acid				✓
methyl ester octadecenoic acid		✓		✓

Table S7
Office Paper GC-MS Suspect Screening Results

SAMPLE ID	**F1**	**F3**	**M1**
SITE	**RF**	**RF**	**SW**
ACRYLATES			
dodecyl acrylate			✓
PHENOLS			
2,4-bis(1,1-dimethylethyl) phenol		✓	
GLYCOL ETHERS			
2-phenoxy ethanol		✓	
STYRENES			
Styrene	✓		
α-methystyrene			
AMINES			
O-(3-methylbutyl)-hydroxylamine			✓
BENZENESULPHONAMIDES			
N-butylbenzenesulphonamide	✓		
OTHER AROMATICS			
hydroxytoluene	✓		
ORGANOPHOSPHATES & RELATED COMPOUNDS			
7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione			✓
Tris (2,4-diterbutyl tris(2,4-ditert-butylphenyl)phosphate	✓		✓

tris (2,4-diterbutyl..tris(2,4-ditert-butylphenyl)phosphite	✓		
tris(2-chloropropyl) phosphate			✓
BUTYRATES			
2,2,4-trimethy-1,3-pentanediol diisobutyrate	✓		
PHTHALATES			✓
dibutyl phthalate	✓		✓
diethylhexyl phthalate	✓	✓	
diisobutyl phthalate	✓	✓	
Phthalic anhydride		✓	
PHTHALATE ALTERNATIVES			
tributyl acetyl citrate			✓
dibutyl adipate			
BENZOPHENONES			
benzophenone	✓		
PALMITIC ACID & PALMITATES			
hexadecanoic acid			✓
LONG-CHAIN ALIPHATICS			
2-ethyl-1-hexanol		✓	
2-hexanone	✓	✓	
2-undecenal	✓		
3-ethyl-5-(2-ethylbutyl)-octadecane		✓	
2,6,10,14-tetramethyl pentadecane			
4-methyl decane			
6-methyl-octadecane			
dodecanol	✓	✓	✓
heptacosane		✓	✓

heptadecane	✓		
hexacosane			✓
hexadecane	✓	✓	✓
octacosane		✓	✓
pentacosane			
pentadecane			
tetracosane		✓	
tetradecane		✓	✓
tetradecanol	✓		✓
triacontane	✓	✓	
tricosane			
tridecane		✓	
octadecanal			✓
heneicosane			✓
ALDEHYDES & KETONES			
2-butanone	✓		
4-hydroxy-4-methyl-2-pentanone			✓
benzaldehyde	✓	✓	
ALKANES & DIOLS			
1,3,5-triphenyl cyclohexane			✓
2,4,7,9-tetramethyl-5-decyn-4,7-diol		✓	
2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene		✓	
2-nitropropane	✓		

OTHER FATTY ACIDS		
dodecanoic acid	✓	
hexanoic acid	✓	
nonanoic acid	✓	
octadecanoic acid		✓
tetradecanoic acid		✓
tridecanoic acid		✓
WOOD DERIVATIVES		
vanillin		
ethyl iso-allocholate		✓

Table S8
Magazines GC-MS Suspect Screening Results

SAMPLE ID	**L2**	**L3**	**G1**
SITE	**SW**	**SW**	**RF**
ABIETIC ACIDS & RELATED COMPOUNDS			
1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-[1-S-(1α,4β,10aα)]-1-phenanthrene carboxylic acid	✓		✓
abietic acid	✓		
methyl dehydroabietate			
PHENOLS			
2,4-bis(1,1-dimethylethyl) phenol			✓
p-tert-butyl phenol		✓	
PALMITIC ACID & PALMITATES			
6-methylheptyl palmitate		✓	
ORGANOPHOSPHATES & RELATED COMPOUNDS			
triphenylphosphine oxide	✓		
OTHER AROMATICS			
1,3,5-triphenyl cyclohexane		✓	
butylated hydroxy toluene		✓	
propyl benzene		✓	
BENZOPHENONES			
benzophenone	✓	✓	
GLYCOL ETHERS			
2-(2-butoxyethoxy)-ethanol		✓	
AZULENES			

decahydro-4,8,8-trimethyl-9-methylene-1,4-methanoazulene			✓
PHTHALATES			
benzylbutyl phthalate	✓		
diethylhexyl phthalate	✓	✓	
diisobutyl phthalate		✓	
BENZENESULPHONAMIDE			
N-butylbenzenesulphonamide	✓	✓	
PALMITIC ACID & PALMITATES			✓
hexadecanoic acid			
WOOD DERIVATIVES		✓	
borneol		✓	
vanillin			
LONG-CHAIN ALIPHATICS		✓	
2,6,10,14-tetramethyl pentadecane		✓	
butyl 9,12-octadecadienoate			✓
eicosane	✓	✓	✓
hexadecane	✓	✓	✓
tetracosane	✓	✓	✓
tetradecane		✓	
2,6,10-trimethyl tetradecane			
OTHER FATTY ACIDS & ESTERS		✓	
methyl ester octadecanoic acid		✓	
nonanoic acid		✓	
octanoic acid		✓	
2-ethyl hexanoic acid			

ALDEHYDES & KETONES			
2-hexanone			✓
benzaldehyde		✓	

Table S9

Unconverted Paperboard GC-MS Suspect Screening Results

SAMPLE ID	**P1**	**P2**	**P5**
SITE	**M**	**M**	**M**
ABIETIC ACIDS & RELATED COMPOUNDS			
1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-[1-R-(1α,4β,10aα)]-1-phenanthrene carboxaldehyde		✓	
PHENOLS			
3-methylphenol	✓		
2,4-bis(1,1-dimethylethyl) phenol			✓
2,6-dimethoXy-4-(2-propenyl) phenol			
ANTHRAQUINONES			
9,10-anthraquinone		✓	
PHTHALATE ALTERNATIVES			
bis(2-ethylhexyl) adipate		✓	
PHTHALATES			
dibutyl phthalate	✓	✓	✓
diisobutyl phthalate	✓	✓	✓
diethyl phthalate	✓	✓	✓
diethylhexyl phthalate	✓	✓	✓
benzylbutyl phthalate			✓
BENZOPHENONES			

benzophenone	✓		✓
NAPHTHALENES			
diisopropylnaphthalene	✓	✓	✓
WOOD DERIVATIVES			
β-sitosterol			
cis-vaccenic acid	✓		
ethyl iso-allocholate			
vanillin	✓		✓
OTHER AROMATICS			
ethyl benzene			✓
STYENES			
methyl styrene			✓
ALDEHYES & KETONES			
2-hexanone			
4-hydroxy-4-methyl-2-pentanone	✓	✓	✓
LONG-CHAIN ALIPHATICS			
1-dodecanol		✓	
1-dodecanol		✓	
1-octadecanol		✓	✓
2,6,10-trimethyl tetradecane	✓	✓	✓
9-hexyl-heptadecane			
eicosane	✓	✓	✓
heptacosane		✓	
hexacosane		✓	✓
hexadecanol	✓	✓	✓
octacosane			

octadecane	✓		
pentacosane	✓		
pentatriacontanone			
pentatriacontene			✓
tetracosane	✓	✓	✓
tetradecane		✓	✓
triacontane			✓
tricosane			✓
undecyl cyclopentane		✓	
PALMITIC ACID & PALMITATES			
hexadecanoic acid		✓	✓
OTHER FATTY ACIDS & ESTERS			
2-(2-hydroxyethoxy)ethyl ester octanoic acid	✓	✓	
dodecanoic acid			✓
methyl ester octadecanoic acid			✓
octadecanoic acid		✓	
octadecenoic acid			✓
tetradecanoic acid			✓

Table S10
Pre-consumer Corrugated board GC-MS Suspect Screening Results

SAMPLE ID	**Q1**	**Q4**
SITE	**C**	**C**
2,6-dimethoXy-4-(2-propenyl) phenol	✓	
ANTHRAQUINONES		
9,10-anthraquinone	✓	
PHTHALATES		
dibutyl phthalate	✓	✓
diisobutyl phthalate	✓	
diethylhexyl phthalate	✓	✓
NAPHTHALENES		
diisopropylnaphthalene		✓
WOOD DERIVATIVES		
β-sitosterol	✓	
ethyl iso-allocholate		✓
vanillin	✓	
ALDEHYES & KETONES		
2-hexanone	✓	
4-hydroxy-4-methyl-2-pentanone	✓	
LONG-CHAIN ALIPHATICS		
9-hexyl-heptadecane	✓	
heptacosane	✓	
hexacosane	✓	
octacosane		✓

pentatriacontanone	✓
PALMITIC ACID & PALMITATES	
hexadecanoic acid	✓
OTHER FATTY ACIDS & ESTERS	
octadecanoic acid	✓

Table S11
LC-MS results for cartonboard (positive mode)

HW- Household waste, RF- Recycling facilities, R- Retail

SAMPLE ID	**A2**	**A4**	**A7**	**B1**	**B7**	**E1**	**E5**	**E6**	**E8**	**W3**
SITE COLLECTED	**HW**	**HW**	**HW**	**HW**	**HW**	**RF**	**RF**	**RF**	**RF**	**R**
POTASSIUM SALTS										
potassium chlorate		✓	✓				✓			✓
PYROZOLINES										
mefenpyr-diethyl		✓								
BUTYRATES & BUTYRIC ACIDS										
2,2,4-trimethyl-1,3-pentanediol diisobutyrate	✓		✓							
PENTACHLORINATED BIPHENYLS										
4-hydroxy-2,2',3',5',6'-pentachlorobiphenyl					✓		✓		✓	
BENZOPHENONES										
4-methyl benzophenone		✓				✓	✓	✓		
benzophenone		✓	✓	✓		✓	✓	✓	✓	
PHTHALATES & THEIR SUBSTITUTES										
dimethyl phthalate		✓	✓		✓		✓	✓	✓	✓
di(3,7-dimethyl-1-octyl) phthalate									✓	

di(2-nonyl) phthalate			✓					✓			
di-n-octyl phthalate					✓						
monoethyl phthalate		✓	✓								
dipropyl phthalate			✓			✓					
diethylhexyl phthalate	✓	✓	✓	✓	✓	✓		✓	✓	✓	
dibutyl phthalate	✓	✓	✓	✓		✓	✓	✓	✓	✓	
diisobutyl phthalate	✓		✓	✓		✓		✓	✓		
SULPHONATED BENZENES											
N-(2,4-dimethylphenyl)-4-methylbenzenesulphonamide							✓	✓			
N-(2-methylphenyl)-3-nitrobenzenesulphonamide	✓										
N-(5-chloro-2-phenoxyphenyl)thiophene-2-sulphonamide				✓							
1-benzothiophene-2-sulphonamide									✓		
benzenesulphonohydrazide							✓				
BISPHENOLS											
bisphenol P					✓			✓			
3,3',5,5'-tetramethylbisphenol A		✓									
PHENOLS											
phenol, 5-(1,1-dimethylheptyl)-2-[(1s,3r)-3-hydroxycyclohexyl]-								✓			
3-(5,5-dimethyl-5,6-dihydro[1,2,4]triazolo[3,4-a]isoquinolin-3-yl)phenol									✓		
AMINES											
bis-(4,6-di-azido-1,3,5-triazin-2-yl)-amine					✓						
methoxyphenamine			✓								
ethylamine, n,n-diundecyl-2-(2-thiophenyl)-			✓								
N-methyl-1-phenylethylamine	✓				✓						
(3-methylbutyl)(6-methylheptan-2-yl)amine				✓							
triethanolamine	✓	✓		✓			✓			✓	

N-tosylethylenediamine								✓	
tribenzylamine n-oxide					✓				
AMIDES									
3-hydroxy-N-(2-oxo-2,3-dihydro-1H-benzimidazol-5-yl)-2-naphthamide			✓						
erucamide				✓					
N-(2,4-dihydroxy-6-methyl-5-pyrimidinyl)benzamide		✓							
4-chloro-n-(2-(hydroxyamino)-2-oxoethyl)benzamide						✓			
N-(4-ethoxyphenyl)-3-hydroxy-2-naphthamide								✓	
N-(3-hydroxyphenyl)-2-(4-isobutylphenyl)propanamide	✓	✓						✓	
N,N-bis(2-hydroxyethyl)dodecanamide		✓							
oleamide			✓						
ANILINES									
N-(2-phenyl-4(3H)-quinazolinylidene)aniline									✓
ESTERS									
diethyl 2-benzylmalonate			✓						
dioctyl sodium sulphosuccinate								✓	
BENZOATES									
methyl 2-benzoylbenzoate			✓						
(5-benzoyloxy-1,2,6-trihydroxycyclohex-3-en-1-yl)methyl benzoate				✓					
ACRYLATES									
2-{2-[2-(acryloyloxy)-1-methylethoxy]-1-methylethoxy}-1-methylethyl acrylate						✓			
3-[4-hydroxy-3-(1,1,4,4,7-pentamethyltetralin-6-yl)phenyl]acrylic acid			✓						
PALMITATES & PALMITAMIDES									
Palmitamide			✓		✓				✓
GLYCOL ETHERS									

2-(2-butoxyethoxy)ethanol	✓								
triethylene glycol monobutyl ether					✓	✓			
GLYCEROLS									
glycerol 1-myristate									✓
glycerol monooleate	✓								
GLYCOLS									
undecaethylene glycol			✓		✓			✓	✓
tetraethylene glycol		✓					✓	✓	
triethylene glycol									
di(propylene glycol) tert-butyl ether								✓	
neopentyl glycol					✓				
QUINONE, QUINOLINES & QUINOLS									
2,2',6,6'-tetra-tert-butyldiphenylquinone	✓				✓				
2-(1H-benzimidazol-2-yl)quinoline				✓					
2-(1H-benzimidazol-2-yl)quinoline			✓						
4-chloro-5,6,7,8-tetrahydroquinazoline				✓					
8-(2-chlorophenyl)-7,8-dihydro[1,3]dioxolo[4,5-g]quinolin-6(5H)-one	✓		✓		✓			✓	
3-(5,5-dimethyl-5,6-dihydro[1,2,4]triazolo[3,4-a]isoquinolin-3-yl)phenol	✓								
OTHER POLYCYCLIC COMPOUNDS									
2H-1-benzopyran-2-one, 7-[[6-(acetyloxy)decahydro-5,5,8a-trimethyl-2-methylene-1-naphthalenyl]methoxy]-	✓								
OTHER POLYCYCLIC COMPOUNDS									
benzo[1,2-b:4,5-b']difuran-4-ethanamine, 8-bromo-2,3,6,7-tetrahydro-α-methyl-	✓					✓	✓		
CYCLIC ACIDS									
3,3'-disulphanediyldibenzoic acid		✓							

4-methylphenylacetic acid	✓								
2-hydroxy-3-methoxybenzoic acid		✓							
5-(2-chlorophenyl)-2-furoic acid		✓							
1-naphthalenepentanoic acid, 3,4,4a,5,6,7,8,8a-octahydro-β,2,5,5,8a-pentamethyl-3-oxo-, (8as)-	✓					✓			
ABIETIC ACIDS & PHENANTHRENES									
abietic acid	✓	✓	✓		✓		✓		
15-hydroxydehydroabietic acid						✓			
7-oxoabieta-8,11,13-trien-18-oic acid								✓	
ORGANOPHOSPHATE COMPOUNDS & THEIR BREAKDOWN PRODUCTS									
tributyl phosphate			✓						
triphenyl phosphate						✓	✓		
3-hydroxy-2-((9Z,12Z)-octadeca-9,12-dienoyloxy)propyl 2-(trimethylazaniumyl)ethyl phosphate			✓						
FATTY ACIDS									
8-(3-octyl-2-oxiranyl)octanoic acid	✓								
11-hydroxyundecanoic acid								✓	
8,9-dihydroxy-5Z,11Z,14Z-eicosatrienoic acid									
cis-15-tetracosenoic acid									
PLANT DERIVATIVES									
syringaldehyde			✓	✓	✓				
acetylsyringic acid	✓								✓
coniferyl aldehyde		✓	✓						
stigmastadienone					✓				
β-eudesmol				✓					

ALCOHOLS & ALKANES				
6-methyl-2-heptanol		✓		
3-methyl-3-pentanol	✓			
2-ethyl-1-hexanol	✓			
1,4,7,10,13,16-hexaoxacyclooctadecane			✓	✓
3-aminopentan-2-ol	✓			

Table S12
LC-MS results for cartonboard (negative mode)

SAMPLE ID	A2	A4	A7	B1	B7	E1	E5	E6	E8	H1	W3
SITE COLLECTED	HW	HW	HW	HW	HW	RF	RF	RF	RF	RF	R
FATTY ACIDS											
3-isobutylpentanedioic acid										✓	
9-(2,3-dihydroxypropoxy)-9-oxononanoic acid								✓			
AMIDES											
N-(sec-butyl)-3,4-dichlorobenzamide							✓				
LONG-CHAIN SULPHATES											
myristyl sulphate							✓				
PHTHALATES											
isophthalic acid, 3-chlorophenyl hexyl ester		✓									
GLYCOL ETHERS											
2-(2-butoxyethoxy)ethanol			✓								
BISPHENOLS											
bisphenol A				✓		✓		✓	✓	✓	
bisphenol F	✓	✓	✓	✓		✓		✓	✓		✓
bisphenol S			✓	✓		✓		✓	✓	✓	

Table S13

LC-MS results for corrugated board (positive mode)

HW- Household waste, R- Retail,

SAMPLE ID	B3	D1	D2	J2	J3	K1	K3	O1	O4	S2	T2	U1	EE3
SITE COLLECTED	**HW**	**RF**	**RF**	**R**	**R**	**SW**	**SW**	**WP**	**WP**	**R**	**WP**	**WP**	**SW**
POTASSIUM SALTS													
potassium chlorate	✓												
potassium nitrate											✓		
potassium sulphate												✓	
CRESOLS													
benzyl alcohol (Cresol)	✓												
BUTYRATES & BUTYRIC ACIDS													
2,2,4-trimethyl-1,3-pentanediol diisobutyrate												✓	
DICHLOROPROPS													
dichlorprop					✓								
FLUTRIAFOLS													
flutriafol					✓								
PENTACHLORINATED BIPHENYLS													
4-hydroxy-2,2',3',5',6'-pentachlorobiphenyl		✓	✓	✓					✓				✓
BENZOPHENONES													
4-dodecyloxy-2-hydroxybenzophenone			✓										
4-methyl benzophenone			✓										
benzophenone		✓	✓	✓	✓	✓		✓	✓	✓			
PHTHALATES													
dimethyl phthalate	✓	✓		✓	✓		✓	✓	✓	✓		✓	✓
di(2-nonyl) phthalate		✓	✓		✓			✓			✓		
di(3-methyl-4-octyl) phthalate			✓										

di-n-octyl phthalate	✓			✓		✓		✓	✓			
monoethyl phthalate		✓				✓		✓				✓
dipropyl phthalate		✓										
diethylhexyl phthalate	✓	✓	✓		✓		✓	✓				
dibutyl phthalate		✓			✓			✓				
diisobutyl phthalate		✓			✓			✓				
PHTHALATE ALTERNATIVES												
Dibutyl maleate				✓								
SULPHONATED BENZENES												
N-(2,4-dimethylphenyl)-4-methylbenzenesulphonamide	✓						✓					✓
1-benzothiophene-2-sulphonamide					✓							
TEREPHTHALATES												
terephthalic acid, 3,4-dichlorophenyl undecyl ester								✓				
BISPHENOLS												
bisphenol P	✓				✓		✓	✓	✓	✓		✓
PHENOLS												
2,6-di-tert-butyl-4-(4-morpholinylmethyl)phenol					✓							
AMINES												
pentadecylamine						✓						
1-methyl-3-phenylpropylamine							✓					
N-methyl-1-phenylethylamine						✓						
triethanolamine						✓						
benzeneethanamine, 4-chloro-α-ethyl-					✓							
tribenzylamine N-oxide							✓					✓

HYDRAZIDES											
2-(1-azepanyl)acetohydrazide					✓						
AMIDES											
3-hydroxy-N-(2-oxo-2,3-dihydro-1H-benzimidazol-5-yl)-2-naphthamide									✓	✓	
erucamide	✓										
2,2'-azobis-2-methylpropanimidamide		✓									
N-(4-ethoxyphenyl)-3-hydroxy-2-naphthamide				✓							
3-chloro-N-cyclopentylpropanamide			✓								
stearamide							✓		✓		✓
ANILINES											
4-(4-aminophenoxy)aniline						✓					
4-[5-(benzylsulphanyl)-4-methyl-4h-1,2,4-triazol-3-yl]aniline						✓					
4-chloro-5,6,7,8-tetrahydroquinazoline				✓							
ESTERS											
diethyl 2-benzylmalonate	✓							✓			
methyl linolenate			✓								
methyl tetradecanoate						✓					
PALMITATES & PALMITAMIDES											
isopropyl palmitate						✓				✓	
methyl palmitoleate											
palmitamide							✓	✓			
SULPHONATED BENZENES											

benzenesulphonic acid, 2-methyl-5-nitro-, 2-[(6-bromoimidazo[1,2-a]pyridin-3-yl)methylene]-1-methylhydrazide					✓						
GLYCEROLS											
glycerol 1-myristate		✓									
1-oleoyl-2-palmitoyl-rac-glycerol							✓				
1-palmitoylglycerol	✓		✓	✓							
1,2-dioleoyl-sn-glycerol	✓										
2-arachidonoylglycerol		✓									
triacetin									✓		
GLYCOL ETHERS											
di(propylene glycol) tert-butyl ether											
diethylene glycol monohexyl ether											✓
triethylene glycol monobutyl ether			✓	✓							
triethylene glycol monoethyl ether						✓			✓		
tetraethylene glycol monomethyl ether									✓		
GLYCOLS											
tetraethylene glycol			✓				✓		✓		
triethylene glycol									✓		
tripropylene glycol		✓									
hexaethylene glycol						✓					
QUINONES & QUINOLINES											
2,2',6,6'-tetra-tert-butyldiphenylquinone	✓				✓		✓				
2-(1H-benzimidazol-2-yl)quinoline								✓			
2-tert-pentylanthra-9,10-quinone									✓		
CYCLIC ACIDS											
2-hydroxybenzene-1,3-dicarboxylic acid			✓								

2,2'-bipyridine-3,3'-dicarboxylic acid						✓						
3-hydroxydodecanoic acid							✓					
1-naphthalenepentanoic acid, 3,4,4a,5,6,7,8,8a-octahydro-β,2,5,5,8a-pentamethyl-3-oxo-, (8as)-							✓					
2-benzoylbenzoic acid		✓										
ABIETIC ACIDS												
abietic acid		✓			✓	✓			✓	✓		
15-hydroxy-7-oxoabieta-8,11,13-trien-18-oic acid										✓		
ORGANOPHOSPHATE COMPOUNDS & RELATED COMPOUNDS												
tri-Isobutyl Phosphate			✓									
tributyl phosphate				✓						✓		✓
triphenylphosphine oxide		✓		✓								
ORGANOPHOSPHONATE COMPOUNDS												
diethyl 2-hydroxyphenylphosphonate											✓	
diethyl 4-bromobenzylphosphonate											✓	✓
BENZOFURANS												
benzo[1,2-b:4,5-b']difuran-4-ethanamine, 8-bromo-2,3,6,7-tetrahydro-α-methyl-	✓		✓	✓								✓
3-benzofurancarboxylic acid, 4-[3-[1-carboxy-2-(3,4-dihydroxyphenyl)ethoxy]-3-oxo-1-propen-1-yl]-2-(3,4-dihydroxyphenyl)-2,3-dihydro-7-hydroxy-, 3-methyl ester				✓								
FLUORESCEINS												
dichlorofluorescein				✓						✓		

FATTY ACIDS					
8,9-dihydroxy-5Z,11Z,14Z-eicosatrienoic acid		✓			
cis-15-tetracosenoic acid			✓		
PLANT DERIVATIVES					
syringaldehyde	✓		✓		✓
acetylsyringic acid				✓	
stigmastadienone					
β-eudesmol			✓		

Table S14
LC-MS results for corrugated board (negative mode)

SAMPLE ID	B3	D1	D2	J2	J3	K1	K3	O1	O4	S2	T2	U1	EE3
SITE COLLECTED	**HW**	**RF**	**RF**	**R**	**R**	**SW**	**SW**	**WP**	**WP**	**R**	**WP**	**WP**	**SW**
ALKYL ACIDS													
phenylacetic acid												✓	✓
3-chlorobenzoic acid												✓	
SULPHONATED BENZENES													
tridecylbenzenesulphonic acid		✓											
benzenesulphonic acid, 4-undecyl-												✓	
AMINES													
ethanolamine		✓								✓			
AMIDES													
2,4-dichloro-N-(3-methylphenyl)benzamide												✓	
LONG-CHAIN SULPHATES													
myristyl sulphate		✓									✓	✓	
ethylene glycol dodecyl ether sulphate										✓		✓	
diethylene glycol dodecyl ether sulphate											✓		
TEREPHTHALATES													
terephthalic acid, 3-chlorophenyl hexyl ester								✓					
AROMATICS													
2-methoxyacridin-9-ol		✓											
PHENOLS													
2,2'-methylene-bis(6-tert-butyl-4 methylphenol)		✓								✓			
2,6-di-tert-butyl-4-methoxyphenol											✓	✓	✓
BISPHENOLS													

bisphenol A		✓		✓		✓	✓				✓	✓
bisphenol F			✓	✓				✓	✓	✓	✓	✓
bisphenol S	✓		✓	✓		✓	✓	✓	✓			✓
PLANT DERIVATIVES												
syringaresinol diglucoside											✓	
tricin methyl ether												✓

Table S15
LC-MS results for newspaper (positive mode)

SAMPLE ID	**C1**	**C3**	**N1**	**N3**
SITE COLLECTED	RF	RF	SW	SW
POTASSIUM SALTS				
potassium chlorate			✓	
BENZOPHENONES				
4-methyl benzophenone			✓	
benzophenone			✓	
PHTHALATES				
dimethyl phthalate			✓	✓
monoethyl phthalate			✓	✓
diethylhexyl phthalate	✓	✓		✓
SULPHONATED BENZENES				
N-(2,4-dimethylphenyl)-4-methylbenzenesulphonamide			✓	
TEREPHTHALATES				
terephthalic acid, 3,4-dichlorophenyl undecyl ester		✓		
BISPHENOLS				
bisphenol P			✓	✓
PHENOLS				
3-(5,5-dimethyl-5,6-dihydro[1,2,4]triazolo[3,4-a]isoquinolin-3-yl)phenol			✓	
AMINES				
cyclooctylamine		✓		
1-methyl-3-phenylpropylamine			✓	

AMIDES				
4-(benzyloxy)-N-butylbenzamide			✓	
N-[2-(1H-benzimidazol-2-yl)ethyl]-2-phenylacetamide				✓
N-(4-ethoxyphenyl)-3-hydroxy-2-naphthamide			✓	
N-(3-hydroxyphenyl)-2-(4-isobutylphenyl)propanamide			✓	
stearamide		✓		
ANILINES				
4-(4-methoxyanilino)-2H-chromen-2-one				✓
PALMITATES & PALMITAMIDES				
methyl palmitoleate		✓		
GLYCEROLS				
glycerol monostearate		✓		
1-palmitoylglycerol		✓		
GLYCOLS				
neopentyl glycol			✓	
GLYCOL ETHERS				
triethylene glycol monobutyl ether	✓			
QUINONE & QUINOLINES				
2,2',6,6'-tetra-tert-butyldiphenylquinone				
2-(1H-benzimidazol-2-yl)quinoline		✓		
4-phenyl-3,4-dihydrobenzo[h]quinolin-2(1H)-one				✓
CYCLIC ACIDS				
1,1'-binaphthyl-8,8'-dicarboxylic acid				✓
5-phenyl-2-thiophenecarboxylic acid	✓			
1-naphthalenepentanoic acid, 3,4,4a,5,6,7,8,8a-octahydro-β,2,5,5,8a-pentamethyl-3-oxo-, (8aS)-			✓	

2-benzoylbenzoic acid				✓
ABIETIC ACIDS				
abietic acid				
15-hydroxy-7-oxoabieta-8,11,13-trien-18-oic acid	✓		✓	✓
7-oxoabieta-8,11,13-trien-18-oic acid			✓	
ORGANOPHOSPHATE COMPOUNDS & RELATED COMPOUNDS				
3-hydroxy-2-((9Z,12Z)-octadeca-9,12-dienoyloxy)propyl 2-(trimethylazaniumyl)ethyl phosphate	✓			
ORGANOPHOSPHONATE COMPOUNDS				
diethyl 4-bromobenzylphosphonate		✓		
BENZOFURANS				
(4aR,5S)-9,9a-dihydroxy-3,4a,5-trimethyl-5,6,7,8,8a,9-hexahydro-4H-benzo[f][1]benzofuran-2-one	✓			
PLANT DERIVATIVES				
acetylsyringic acid			✓	
LONG-CHAIN ALIPHATICS				
trans-2-dodecenal				
2-tridecenal		✓		
1-phenylicosane-1,3-dione				✓
ALCOHOLS & ALKANES				
1,7-bis(4-hydroxyphenyl)heptane-3,5-diol	✓			
3-methyl-3-pentanol			✓	✓

Table S16
LC-MS results for newspaper (negative mode)

SAMPLE ID	C1	C3	N1	N3
SITE COLLECTED	**RF**	**RF**	**SW**	**SW**
FATTY ACIDS				
3-isobutylpentanedioic acid				✓
BENZOPYRENES				
benzo(a)pyrene				✓
BISPHENOLS				
bisphenol A	✓	✓		
bisphenol F		✓		

Table S17
LC-MS results for office paper (positive mode)

SAMPLE ID	F1	F3	M1
SITE COLLECTED	**RF**	**RF**	**SW**
PHTHALATES			
dimethyl phthalate	✓	✓	✓
monoethyl phthalate	✓	✓	
dipropyl phthalate			✓
BISPHENOLS			
bisphenol P		✓	
AMINES			
auramine O		✓	
AMIDES			
4-(benzyloxy)-N-butylbenzamide			✓
N-(4-ethoxyphenyl)-3-hydroxy-2-naphthamide	✓		
stearamide	✓		
ANILINES			
4-(4-chloroanilino)tetrahydro-3-thiophenol 1,1-dioxide			✓
ESTERS			
(2-acetyloxy-3,6-diphenylcyclohexyl) acetate	✓		
QUINONES & QUINOLINES			
sulphaquinoxaline	✓		
CYCLIC ACIDS			
phenylacetic acid		✓	
ORGANOPHOSPHATE COMPOUNDS & RELATED COMPOUNDS			
1-(1,2-dioctanoylphosphatidyl)inositol-3,5-bisphosphate		✓	

BENZOFURANS			
benzo[1,2-b:4,5-b']difuran-4-ethanamine, 8-bromo-2,3,6,7-tetrahydro-α-methyl-		✓	
PLANT DERIVATIVES			
syringaldehyde	✓		

Table S18
LC-MS results for office paper (negative mode)

SAMPLE ID	**F1**	**F3**	**M1**
SITE COLLECTED	**RF**	**RF**	**SW**
BISPHENOLS			
bisphenol A		✓	✓

Table S19
LC-MS results for magazine (positive mode)

SAMPLE ID	**L2**	**L3**	**G1**
SITE COLLECTED	**SW**	**SW**	**RF**
BENZOPHENONES			
4-methyl benzophenone		✓	✓
benzophenone		✓	
PHTHALATES			
dimethyl phthalate	✓	✓	
dipropyl phthalate		✓	
diethylhexyl phthalate	✓	✓	
AMIDES			
2-chloro-N-(1,3,4-thiadiazol-2-yl)acetamide	✓		
oleamide	✓		✓
ESTERS			
diethyl 2-benzylmalonate			
PALMITATES & PALMITAMIDES			
palmitamide	✓		
GLYCEROLS			
1-palmitoylglycerol	✓		
GLYCOLS			
tetraethylene glycol			
ABIETIC ACIDS			
abietic acid			✓
GLYCOL ETHERS			
triethylene glycol monobutyl ether		✓	✓
triethylene glycol monoethyl ether			
ORGANOPHOSPHATE COMPOUNDS & RELATED COMPOUNDS			

tributyl phosphate				✓
QUINONE & QUINOLINES				
2-(1H-benzimidazol-2-yl)quinoline		✓		
2-tert-pentylanthra-9,10-quinone			✓	
CYCLIC ACIDS				
3,3'-disulphanediyldibenzoic acid		✓		
LONG CHAIN ALIPHATICS				
trans-2-dodecenal		✓		
ALCOHOLS & ALKANES				
1,4,7,10,13,16-hexaoxacyclooctadecane				✓

Table S20
LC-MS results for magazines (negative mode)

SAMPLE ID	**L2**	**L3**	**G1**
SITE COLLECTED	**SW**	**SW**	**RF**
LONG-CHAIN SULPHATES			
myristyl sulphate	✓		
CYCLIC ACIDS			
1-hydroxy-2-naphthoic acid	✓		
PHENOLS			
2,2'-methylene-bis(6-tert-butyl-4 methylphenol)	✓		
BISPHENOLS			
bisphenol F		✓	✓
bisphenol S			✓
QUINONES & QUINOLINES			
9,10-anthracenedione, 3-(1,2-dihydroxypropyl)-1,6,8-trihydroxy-	✓		

Table S21

LC-MS results for pre-cons paperboard (positive mode) M- Mills

SAMPLE ID	**P1**	**P2**	**P5**
SITE COLLECTED	**M**	**M**	**M**
BENZOPHENONES			
benzophenone	✓		✓
PHTHALATES			
di(3-methyl-4-octyl) phthalate			✓
diethylhexyl phthalate	✓	✓	✓
BISPHENOLS			
bisphenol P		✓	
AMINES			
triethanolamine			✓
BENZOATES			
ethyl 2,4-dihydroxy-6-methylbenzoate	✓		
methyl 2-benzoylbenzoate	✓		
PALMITATES & PALMITAMIDES			
palmitamide			✓
AROMATICS			
1,2-di(1H-benzimidazol-2-yl)ethanol			✓
GLYCEROLS			
glycerol 1-myristate			✓
1-palmitoylglycerol			✓
GLYCOL ETHERS			
diethylene glycol monohexyl ether		✓	✓
CYCLIC ACIDS			
3-furancarboxylic acid, tetrahydro-4-methylene-2-octyl-5-oxo-, (2R,3S)-rel-		✓	

ORGANOPHOSPHATE & RELATED COMPOUNDS			
tributyl phosphate			✓
ORGANOPHOSPHONATE COMPOUNDS			
diethyl 4-bromobenzylphosphonate		✓	
PLANT DERIVATIVES			
syringaldehyde	✓		✓
coniferyl aldehyde			✓
LONG-CHAIN ALIPHATICS			
trans-2-dodecenal		✓	
ALCOHOLS & ALKANES			
3-methyl-3-pentanol		✓	
2-ethylcyclohexanol			✓

Table S22

LC-MS results for pre-cons paperboard (negative mode)

SAMPLE ID	**P1**	**P2**	**P5**
SITE COLLECTED	M	M	M
CYCLIC ACIDS			
3-(hydroxymethyl)-7-methoxy-6-oxooxepino[2,3-b]chromene-5-carboxylic acid	✓		
1-(diphenylphosphoryl)cyclobutanecarboxylic acid	✓		
AMINES & AMIDES			
ethanolamine	✓		✓
LONG-CHAIN SULPHATES			
ethylene glycol dodecyl ether sulphate	✓		✓
GLYCOL ETHERS			
2-(2-butoxyethoxy)ethanol			✓
AROMATICS			
2-benzimidazolinone, 1-benzyl-	✓		
BENZOPYRENES			
benzo(a)pyrene			✓
BISPHENOLS			
bisphenol A	✓		✓
bisphenol F	✓		✓

Table S23

LC-MS results for pre-cons corrugated (positive mode) C- corrugator

SAMPLE ID	**Q1**	**Q4**
SITE COLLECTED	**C**	**C**
BUTYRATES & BUTYRIC ACIDS		
2,2,4-trimethyl-1,3-pentanediol diisobutyrate		✓
PHTHALATES		
monoethyl phthalate		✓
diethylhexyl phthalate	✓	
dibutyl phthalate		✓
diisobutyl phthalate	✓	
AMINES		
triethanolamine	✓	✓
cyclooctylamine	✓	
AMIDES		
4-tert-butyl-N-(6-imidazol-1-ylimidazo[1,2-a]pyridin-2-yl)benzamide		✓
N-(4-ethoxyphenyl)-3-hydroxy-2-naphthamide	✓	
GLYCEROLS		
1-oleoyl-2-palmitoyl-rac-glycerol		✓

GLYCOLS			
neopentyl glycol			✓
glycol ethers			
Triethylene glycol monobutyl ether			✓
QUINONES & QUINOLINES			
2-(p-tolyl)-1H-quinazolin-4-one			✓
ABIETIC ACIDS			
7-oxoabieta-8,11,13-trien-18-oic acid			✓
BENZOFURANS			
benzo[1,2-b:4,5-b']difuran-4-ethanamine, 8-bromo-2,3,6,7-tetrahydro-α-methyl-			✓
PLANT DERIVATIVES			
syringaldehyde		✓	
LONG-CHAIN ALIPHATICS			
trans-2-dodecenal			✓
ALCOHOLS & ALKANES			
1,4,7,10,13,16-hexaoxacyclooctadecane			✓
3-aminopentan-2-ol			

Table S24

LC-MS results for pre-cons corrugated (negative mode)

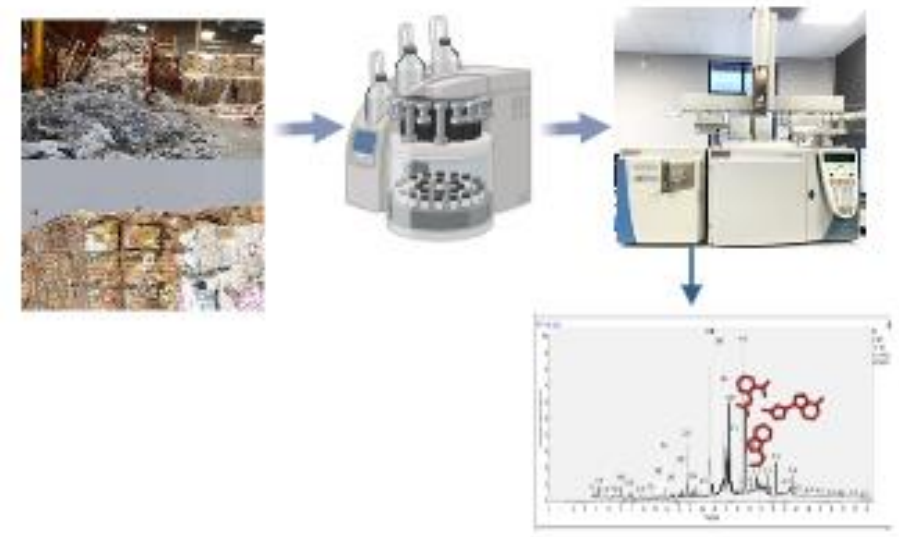
SAMPLE ID	**Q1**	**Q4**
SITE COLLECTED	**C**	**C**
CYCLIC ACIDS		
phenylacetic acid	✓	
LONG-CHAIN SULPHATES		
myristyl sulphate	✓	
BISPHENOLS		
bisphenol A		✓
PLANT DERIVATIVES		
methyl vanillate	✓	

CHAPTER FIVE

5 PAPER 2

This paper titled “Source apportionment and transport of semi-volatile organic pollutants within the South African paper recycling chain” is under review in the **South African Journal of Science** submission reference 17228. This paper looks at the targeted analysis of 11 semi-volatile pollutants by GC-MS followed by their source apportion and transport with the paper recycling chain.

GRAPHICAL ABSTRACT



Source apportionment and transport of pollutants within the South African paper recycling chain

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Abstract

Recycled paper is a valuable commodity that forms an intrinsic part of promoting sustainable resource utilisation. This study aimed to investigate the possible sources and transport of semi-volatile organic pollutants within the South African paper recycling chain. The results showed that diethylhexyl phthalate and dibutyl phthalate were the most prominent pollutants, whilst tris (2,4-di-tert-butylphenyl) phosphite and butylated hydroxytoluene were the least significant pollutants. tris (2,4-di-tert-butylphenyl) phosphate was predominantly detected at the recycling sites, with a maximum concentration of 3.054 mg/kg, whereas *N*-butylbenzene sulphonamide was found in retail and post-consumer samples, but not at pre-consumer sites. Manufacturing additives and retail activities were identified as possible exposure sources. Post-consumer usage, collection, sorting and mingling of various waste materials were also identified as factors that influence the prevalence of pollutants. The presence of pollutants in pre-consumer indicated that certain compounds may potentially accumulate or circulate within the paper recycling chain and that other pollutants may be removed during the reprocessing of recycled fibre.

Significance:

There is limited scientific-based research performed in South Africa on the identification of chemical constituents in different recycling paper grades. The pollutants identified in the collected paper indicated that the South African paper recycling chain has common pollutants to those reported in Global North studies as well as unique pollutants. These included butylated hydroxytoluene, *N*-butylbenzene sulphonamide, tris(2,4-di-tert-butylphenyl) phosphite and its degradation product tris (2,4-di-tert-butylphenyl) phosphate.

Keywords: paper recycling; accelerated solvent extraction; gas chromatography; pollutants; emerging contaminant

5.1 Introduction

The pursuit of a more sustainable approach to resource utilisation and waste management has driven the need for waste management protocols that promote the diversion of waste away from landfill (Godfrey & Oelofse, 2017). The United Nations Sustainable Development Goal 12.5 target is aimed at the substantial reduction of waste generation through prevention, reduction, recycling and reuse (Ghafari, 2022). The promulgation of the Extended Producer Responsibility in South Africa and globally has further pushed the drive towards recycling materials. Paper is recycled more than any other packaging material in Europe and is the second most recycled material in South Africa, after beverage cans (Bezuidenhout, 2017; CEPI, 2020; Paper Manufacturers Association of South Africa (PAMSA), 2024). In 2023, the South African recovery rate of recyclable paper was 65 % which was equivalent to 1 825 944 metric tonnes (PAMSA, 2024). This allowed for a reduction in land used for end-of-life disposal and provided resources as starting material for the manufacture of new goods (Cudjoe et al., 2021).

In this study, semi-volatile organic pollutants were quantified in pre-consumer, retail and post-consumer samples using the internal standard calibration method for eleven of the pollutants and semi-quantification of one pollutant. The study focused on the various paper grades used in the manufacture of recycled paperboard and corrugated board. For this reason, the pre-consumer and retail samples were board, whilst the post-consumer samples included newsprint, magazines, office paper, cartonboard and corrugated board. Accelerated solvent extraction was used for effective isolation and pre-concentration of semi-volatile pollutants in different types of recycling paper grades before gas chromatography-mass spectrometry (GC-MS) analysis. To gain further insight into this untapped research area, interviews were conducted to understand the actual practices used by formal and informal paper recycling role players.

5.2 Literature Review

The main stages of recycling are collecting, sorting and reprocessing of fibre into new products (Yavini et al., 2014). Apart from being sustainable, the collection and

sorting of paper waste is a major source of job creation in South Africa (Viljoen et al., 2012). In most developing countries, many of the poor and underprivileged rely on recycling for income generation and sustenance (Omotoso, 2017). Poorly administered waste management systems in these countries often result in the inconsistent collection of waste, unrestricted waste collection points and inappropriate disposal of waste in open dumps making recyclable waste easily accessible to informal waste pickers (Omotoso, 2017). The manner in which recovered or collected paper is sorted greatly influences the quality of the resulting recycled paper product. Sorted paper has been shown to have fewer undesirable chemical substances (Pivnenko et al., 2015). The majority of paper destined for recycling in South Africa makes use of co-mingled collection systems where paper and board, glass bottles, cans, and plastics are collected together and then sorted at recycling or material recovery facilities. Such sites have been found to have a considerable portion of highly contaminated unusable material (Miranda et al., 2013). Once collected, the paper is then sorted according to its specific grade. The South African standard grades of recovered paper and board consist of 16 grades for mixed grades, mechanical grades (newspaper, magazines), high grades (office-type paper), kraft grades (corrugated and kraft paper) and special grades (liquid packaging and directories) (FibreCircle, 2020). In comparison, the Confederation of European Paper Industries, lists almost 100 grades of paper and the United States Institute of Scrap Recycling Industries defines over 40 paper recycling grades, including specific grades for flyers, grocery bags and wet-strength bags. It is thereby evident that South Africa has considerably less segregation between different grades based on the few types of recovered paper grades.

To estimate contaminant transfer to recycling products, the assessment of recycling must incorporate the risk posed by the accumulation and dispersion of contaminants present in paper (Knapp et al., 2017). Recycled paper is made by repulping collected wastepaper followed by the removal of impurities (Rahman et al., 2014). In addition to the fibre component, chemical additives are fused into paper and paperboard packaging for branding purposes, consumer convenience, to resist various conditions and to protect the packaged goods. These include functional additives such as wet-strength aids, fillers and sizing agents; aesthetic additives comprising of amongst others, varnishes, waxes, coatings and printing inks; along with control

additives in the form of biocides, defoamers, drainage aids and control agents (Bajpai, 2018). Layers of paperboard are often held together by different types of adhesives to make corrugated boards or to form folding cartonboards (Blanco et al., 2013). The manufactured recycled paper may also contain reaction products, degradation products or by-products of chemical additives (Muncke et al., 2020). Extensive research in the Global North has identified several typical pollutants in recycled paper which include, amongst others, phthalates, phenols, benzophenone and naphthalenes (Ahmadkhaniha & Rastkari, 2017; Bengtström et al., 2016; Biedermann et al., 2013; Farzanehfar & Kobarfard, 2017; Geueke et al., 2022; Pivnenko et al., 2015). For virgin, unconverted paper, the most prominent pollutants reported in literature are anthraquinone (Vápenka et al., 2016) used as a pulping aid in paper manufacturing, as well as phenols such as 2,4-di-tert-butylphenol, by-products of semi-chemical pulping (Peters et al., 2019).

In addition to compounds originating from the manufacturing and converting processes, pollutants may arise from recycling collection and mingling of waste as well as post-consumer usage (Geueke et al., 2018). Research on the identification of potential pollutants in recycled paper has been limited in South Africa. Historically, local research on paper recycling has focused on waste management processes (Dlamini, 2016; Godfrey, 2021; Godfrey & Oelofse, 2017; Muzenda, 2013; Nell et al., 2022) and not on the intrinsic chemical constituents of the recycling paper grades. The scientific data gathered in the Global North cannot simply be transposed to the South African paper recycling chain without scientific investigation. Many European countries collect paper destined for recycling as a single fraction (Seyring et al., 2016) as opposed to co-mingled systems; such segregation is currently not extensively practised in South Africa. Differences in the waste collection processes, incorporation of waste pickers, sorting protocols and consequential mingling could potentially influence pollutant prevalence. The use of informal waste pickers is not unique to South Africa. According to the International Alliance of Waste Pickers (IAWP), waste pickers are part of recycling chains in 32 countries in the Global South in Latin America, Asia and Africa, including Brazil, India, Niger, the Democratic Republic of Congo and Mali (IAWP, 2022). This study may thereby be important in understanding other developing countries.

5.3 Materials and methods

5.3.1 Reagents and preparation of standard solutions

Acetone (HPLC grade), dichloromethane (HPLC grade), pentane (GC grade), ethanol (LC grade) and hexane (HPLC grade) were purchased from Merck, Johannesburg, South Africa. The internal standard, deuterated dibutyl phthalate (d-DBP) was obtained from Sigma Aldrich, Johannesburg, South Africa. Analytical grade standards for quantification (Supplementary Table S1) were used to prepare calibration solutions with 1 μg/mL of d-DBP. Butylated hydroxytoluene (BHT), benzylbutyl phthalate (BBP), dibutyl phthalate (DBP), diethylhexyl phthalate (DEHP), diethyl phthalate (DEP), diisobutyl phthalate (DIBP), didecyl phthalate (DIDP), tris(2,4-di-tert-butylphenyl)phosphite (AO168), N-butylbenzene sulphonamide (NBBS) and tris(2,4-di-tert-butylphenyl)phosphate (AO168O) were sourced from Sigma Aldrich, Johannesburg, South Africa. Benzophenone (BP) was acquired from Merck, Johannesburg, South Africa. The standard solutions were prepared in a 5:2 acetone: hexane solvent mixture for trace analysis covering the concentration range of 0.2 to 12 μg/mL. Another set of calibration standards was prepared in the concentration range of 5 to 200 μg/mL.

5.3.2 Sample collection

Samples were collected from various points of the paper recycling chain in Cape Town, South Africa as shown in Fig. 1, making up a population of 108 samples (Fig. S1 and Supplementary Table S2). The five pre-consumer samples consisted of unconverted and unprinted paperboards from five paper mills which were made from recycled fibre and from a combination of virgin and recycled fibre. Four pre-consumer converted corrugated boards were sourced from two corrugators. Retail samples were collected at five retail stores and consisted of 10 cartonboards and 9 corrugated boards. The post-consumer samples were sourced from two household waste sites, two solid waste disposal sites, two recycling facilities and three informal waste pickers. For the post-consumer sites, 25 carton boards, 22 corrugated boards, 7 magazines, 10 office papers, 13 newsprint and 3 coloured papers were collected.



Fig. 1 Sample collection sites in the paper recycling chain

5.3.3 Sample pre-treatment

Each sample was cut into small pieces and shredded using a kitchen blender purchased from a local store. Samples were prepared in triplicate. Target compounds in paper materials were extracted by accelerated solvent extraction using a Dionex 350 ASE system (Anatech, Cape Town, South Africa). The selection of a suitable solvent for extraction was based on recommendations of the U.S. Environmental Protection Agency (EPA) with its Method 3545A (EPA, 2007); which recommended the use of acetone: dichloromethane (DCM) (1:1), acetone: hexane (1:1) or acetone: pentane (2:1) for the extraction of soils, clays, sediments, sludges, and waste solids; as well as studies where hexane: acetone (4:1) was used in the analysis of recycled paperboard for food packaging (Mariani et al., 2015). These solvent combinations and different temperatures of extraction were evaluated to ensure the sufficient extraction of target compounds from paper. The final extraction conditions entailed the extraction of 3.5 g of a shredded paper sample using a 5:2 acetone: hexane mixture at 70 ℃. The resulting final 40 mL volume of extract was then reduced to 1 mL through evaporation using a Biotage TurboVap (Anatech, Cape Town, South Africa) under nitrogen at 45 ℃ (Anggarkasih et al., 2018; Wang et al., 2022), followed by filtration with 0.45 µm syringe filter prior to GC-MS injection.

5.3.4 Gas chromatography-mass spectrometry (GC-MS) analysis

Analysis was performed using Thermo Scientific Trace GC Ultra ISQ MS with a TriPlus RSH Autosampler (Anatech, Cape Town, South Africa) fitted with a Phenomenex ZB-5ms capillary column with a guard column (30 m+10 m Guardian x 0.25 mm ID x 0.25 µm thickness) (Separations, Cape Town, South Africa). A constant flow of high-purity helium (Air Products, Cape Town, South Africa) at 1.2 mL/min was employed. The inlet temperature was set at 260 °C with the 1 ul injection volume performed in splitless injection mode. High-purity helium gas purchased from Air Products (Cape Town, South Africa) was used as the carrier gas with an initial pressure of ~ 7 psi. The oven temperature was initiated at 40 °C and held for 5 min before ramping to 315 °C at 8 °C/min (held for 15 min) before being cooled down to 220 °C at 15 °C/min. For MS measurements, the scan mode was set from 40 to 1100 m/z. The scan mode was used for preliminary screening to identify target compounds aligned to the South African paper recycling chain. The 2020 National Institute of Standards and Technology (NIST) electron ionization GC-MS spectral library was used to identify compounds with spectral matches with reverse similarity indexes above 800 and with commercially attainable chemical reference standards for the target analytes. Once identified, their respective prominent ions (as shown in supplementary table S3) were then used in single ion monitoring (SIM) mode for quantification.

5.3.5 Quality assurance

Calibration curves were plotted factoring in the peak area of the 1 µg/mL of d-DBP internal standard to the peak area of the target compound against the concentration of each investigated target compound. This allowed for the determination of linearity for each compound as the coefficient of determination (R2). Diisopropylnaphthalene (DIPN) was found to elute as a mixture of 5 isomers on the GC-MS. It has already been established that this compound exists as 10 isomers. (Brzozowski et al., 2002) In this study, 5 of the 10 isomers were identified in paper-based samples using the 2020 National Institute of Standards and Technology spectral library and Brzozowski et al. (2002) (Brzozowski et al., 2002). These five isomers were tentatively identified as 1,3-diisopropylnaphthalene (1,3-DIPN), 1,7-

diisopropylnaphthalene (1,7-DIPN), 2,6-diisopropylnaphthalene (2,6-DIPN), 2,7-diisopropylnaphthalene (2,7-DIPN) and 1,6-diisopropylnaphthalene (1,6-DIPN) (Supplementary Fig. S1). For the purposes of this study, semi-quantification was performed using equation (1) assuming a response factor of one and applying it to the sum of the DIPN isomers peak areas:

$$C_{sample} = \frac{C_{is}}{A_{is}} \times A_{sample} \qquad (1) \qquad \text{(Karabagias,2022)}$$

where C_{sample} represents the concentration in the sample, C_{is} the concentration of the internal standard d-DBP, A_{is} is the area of the internal standard and A_{sample}, the sum of the individually integrated DIPN isomer peaks.

To measure the sensitivity of the applied analytical method, the limit of detection (LOD) was measured at a signal-to-noise ratio of 3, whilst the limit of quantification (LOQ) was determined by a signal-to-noise ratio of 10. The accuracy and precision of the analytical method were evaluated by spiking samples in triplicate at three different concentration levels of 0.12, 0.2 and 3 mg/kg. Two sample substrates were used for evaluating the recovery as a measure of accuracy for, paper and paperboard, to reflect the sample population. In each case, such samples were virgin, unprinted and unconverted paper material. These paper samples were expected to contain minimal pollutants.

5.3.6 Data analysis

Data analysis was performed using Thermo Scientific Xcalibur™, MetaboAnalyst 5.0 and Microsoft® Excel. Partial Least Squares (PLS) discriminant analysis was performed using MetaboAnalyst 5.0 to establish the variable importance in projection (VIP) scores. VIP scores were used for calculating the cumulative measure of the influence of individual variables; in this case, target analytes in the system, (Galindo-Prieto et al., 2014) using Equation (2),

$$VIP_{score} = \sqrt{K \times \left(\frac{[\sum_{a=1}^{A}(W_a^2 \times SSY_{comp,a})]}{SSY_{cum}}\right)} \qquad (2)$$

where the VIP_{score} is a weighted combination over all components of the squared PLS weights (W_a), where $SSY_{comp,a}$ is the sum of squares of Y explained by component a, A is the total number of components, K is the total number of

variables and SSY_{cum} is the cumulative sum of squares of Y (Galindo-Prieto et al., 2014).

5.3.7 Interviews

Interviews were conducted with role players involved in paper recycling in South Africa. The objective of the interviews was to gain further insight into the factors that influence the collection and sorting of recycling paper grades. The 16 participants consisted of both informal and formal waste collectors, sorters as well as managers, research analysts and plant supervisors.

5.4 Results and Discussion

5.4.1 Selection of method parameters

The present study was designed for the identification and quantification of semi-volatile organic pollutants present in the South African paper recycling chain. It was crucial to establish a suitable sample extraction method that was efficient in isolating the target analytes prior to their chromatographic analysis. The extraction of target compounds from paper materials was based on accelerated solvent extraction where a randomly selected cardboard sample collected at a recycling site was used for the optimisation of the extraction method. Initially, different solvent combinations were evaluated in the form of acetone: dichloromethane (1:1), acetone: hexane (1:1), acetone: pentane (2:1), hexane: acetone (4:1) were evaluated for the extraction of target compounds at 60 °C by comparing the chromatographic peak shapes, baseline, resolution and overall abundance. The solvent choice had to be able to attain the desirable extraction results for the analytes whilst still being compatible with the ASE equipment solvent specifications as well as the Phenomenex ZB-5ms capillary column non-polar 5% phenyl-arylene, 95% dimethylpolysiloxane stationary phase.

Preliminary findings attained when performing the extraction indicated that an increase in the non-polar component, namely hexane, of the solvent mixture led to what was likely a hydrocarbon “hump” and reduced chromatographic resolution. This was in agreement with the observation already reported in literature where the same hump was evident and could be attributed to unresolved C_{11}-C_{25} aliphatic chains (Biedermann et al., 2013; Biedermann & Grob, 2012). The benefit of the combination of a polar, aprotic (acetone) and non-polar solvent (hexane) was that

it was found to extract a wider range of compounds; in comparison as to the dichloromethane and acetone combination where both solvents were polar, aprotic. The ratio of acetone and hexane was thus varied and acetone: hexane (5:2) was found to be the best solvent mixture for the extraction of target compounds in paper samples.

The extraction temperature was optimised to ensure efficient extraction without the loss of thermally sensitive compounds (Bengtström et al., 2016). The extraction temperature was evaluated at 60°C, 70°C and 85°C by comparing the peak area ratios attained for the target analyte to the internal standard. An increase in extraction temperature from 60°C to 70°C improved the extraction process. This could be due to the improved solubility of the target compounds in the extraction solvent mixture. Furthermore, the extraction temperature likely weakened the cellulose-based fibre bonds allowing for the dissociation of the smaller, target compounds; thus, resulting in their extraction into the solvent mixture. The higher temperature of 85 °C indicated that the extraction efficiency was possibly lost due to the thermal effects on the matrix and/or over-saturation (Mariani et al., 2015). Consequently, all other extractions were performed using a temperature of 70 °C. Thus, the final extraction conditions were a sample mass of 3.5 g loaded into the ASE cell where the extraction process was done at 70 °C using a mixture of acetone: hexane mixture (5:2) for a static time of 12 minutes performed for three cycles. To minimise cross-contamination after each extraction, the ASE stainless cells were washed in warm water, rinsed with the extraction solvent and then baked out in the oven for 4 hours at 160 °C.

5.4.2 Method validation

For the sensitivity of the analytical method, LODs and LOQs were investigated by analysing the extracted paper-based material spiked with the target compounds and internal standard at a concentration level of 1 µg/mL (Supplementary Table S3). The LODs and LOQs ranged from 0.944-3.147 ng/g and 4.488-14.962 ng/g, respectively, as shown in Supplementary Table S3. The LOQs attained in the present study were comparable to those found in literature (Altuntaş et al., 2016; Anggarkasih et al., 2018; Carlos et al., 2021) for the analysis of the same compounds in plastic and paper-based materials using GC-MS. Linearity was confirmed with a coefficient of determinations (R^2) greater than 0.99 for the target

compounds over a wide concentration range. The recoveries obtained for the target compounds extracted from both the paperboard and paper spiked at different concentrations ranged from 73% to 104% (Supplementary Table S3), which was indicative of an efficient analyte extraction method from the investigated samples. It was noted that recoveries for the paper sample were slightly higher than those of the paperboard sample for most of the target compounds, except for NBBS and AO168O. This indicated that, in general, the higher grammage fibre in paperboard may adsorb compounds strongly than smaller grammage paper samples.

5.4.2 Overview of pollutant prevalence

The concentrations of the target compounds detected in pre-consumer, retail and post-consumer (Supplementary Table S4) were quantified using calibration curves whilst semi-quantification of DIPN was performed using equation (1). DBP, DEHP and BP were found to have the highest detected concentrations (Supplementary Fig. S3). A corrugated board collected at a recycling plant was found to have the highest concentration of BP (24.71±0.57 mg/kg) and a cartonboard from household waste was found to have the maximum concentration of DEHP (37.12±6.72 mg/kg). AO168O was found to have the lowest maximum concentration of 3.054 mg/kg for cartonboard found at a recycling site. The target compound found in the highest concentration was DBP detected in a corrugated board sample from household waste with a concentration of 55.64±5.68 mg/kg paper (Supplementary Fig. S3). When comparing this to previous research, this was within the ranges found in literature (Carlos et al., 2021; Li et al., 2018). The three highest combined concentrations were a corrugated box from household waste was found to have the highest combined concentration of pollutants at 85.68 mg/kg, a magazine collected at a recycling site (54.66 mg/kg) and a toilet paper core from household waste (37.98 mg/kg) (Supplementary Table S4). This indicated that consumer usage and exposure to different elements may influence the concentration. An overview of the average pollutants under investigation (Fig. 2.) showed considerably fewer pollutants in pre-consumer samples than those from retail and post-consumer sites.

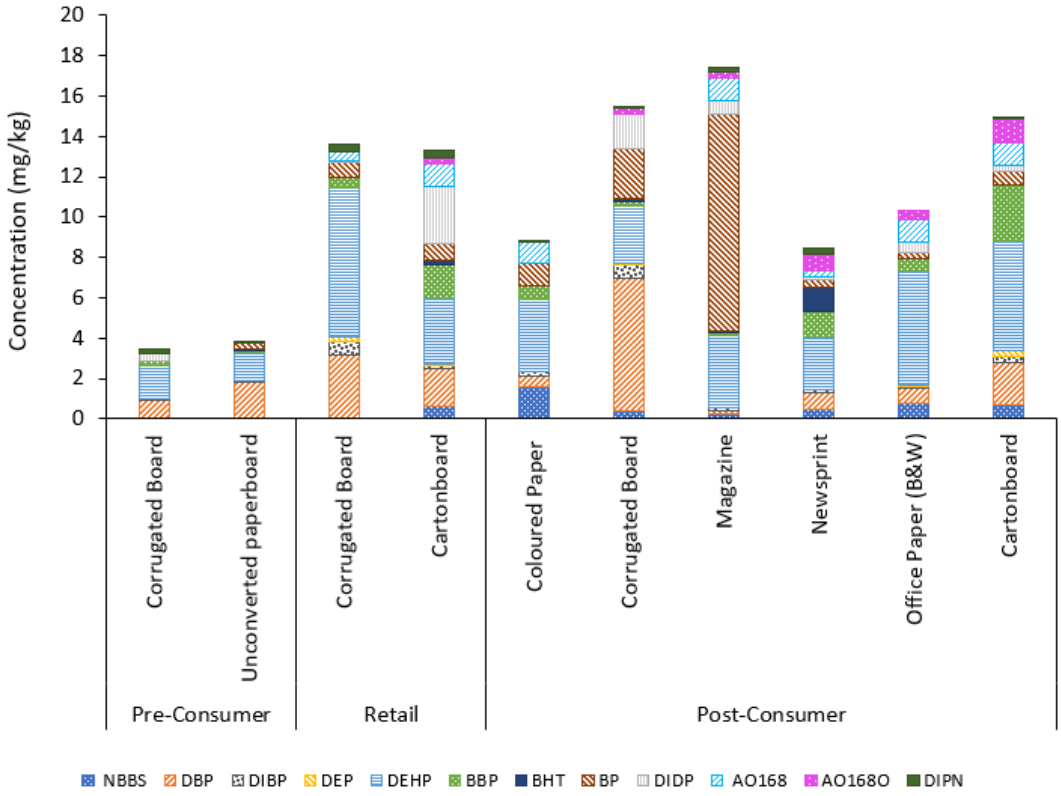


Fig. 2 Overview of Target Compounds

The combined average concentrations detected were 4.06 mg/kg for pre-consumer samples, 12.88 mg/kg for retail samples and 14.98 mg/kg for post-consumer samples. DBP and DEHP were the most prominent pollutants in pre-consumer samples. The results suggested possible latent compounds present in the pre-consumer samples. It was also possible that lower concentrations of pollutants could have been introduced during manufacturing process, leading to possible cumulative effects as the samples moved from retail to post-consumer. An increase in detected pollutants in the carton board at retail stage was attributed to pollutant exposure opportunities during transportation, packing and distribution of consumer goods as well as during converting processes. The difficulty in postulating this was that the original state of these particular retail samples was unknown. The fibre composition of the retail and post-consumer samples may have been virgin, recycled as well as a combination of these, which would also likely influence the detected concentrations. At the post-consumer level, additional pollution exposure may have arisen from the mingling of waste as well as from the leaching of phthalates from the goods packaged in paperboard materials. Clothing, plastic goods, personal care products and furnishings items (Li et al., 2018) often contain

phthalates which could adhere to paper packaging at the post-consumer stage, further influencing the various pathways. In general, paper packaging is often used as secondary packaging with goods in primary contact with plastic. This likely promotes the interaction of paper and plastic during storage and use.

5.4.3 Paper grade apportionment of pollutants

A plot of PLS-VIP scores, plotted using MetaboAnalyst 5.0, was used to identify the importance of each pollutant relative to the paper recycling grade, as shown in Fig. 3.

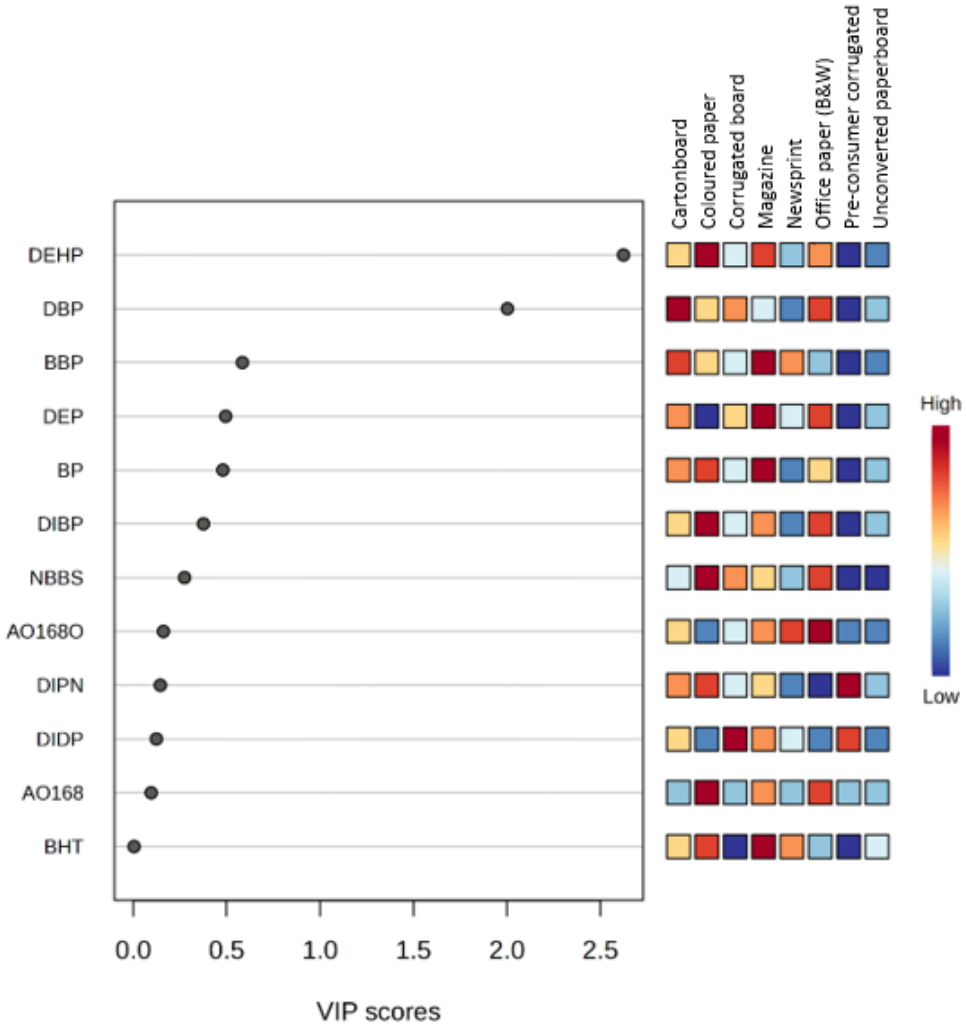


Fig. 3 Plot of PLS-VIP scores

The VIP scores were used to assess the prominence of each pollutant in the population and to project the likely source of pollutants based on the paper grades

using a heat map where ‘high’ indicated a strong correlation and ‘low’ indicated a weaker correlation. According to Galindo-Prieto et al. (2014), VIP scores larger than 1 indicate the most significant variables (Galindo-Prieto et al., 2014). From the plot, it was seen that DEHP and DBP were the most prominent pollutants in the samples, whilst AO168 and BHT were the least significant pollutants. This was probable because DEHP is a common phthalate found in paper and plastic goods. (Geueke et al., 2022). In paper-based packaging, phthalates are used in inks, lacquers and adhesives (Biedermann et al., 2013). The prominence of DEHP, DBP, DIBP, BBP, and DEP in the present study corresponded with literature (Biedermann et al. 2013; Pivnenko et al., 2016; Geueke et al., 2018) where the same phthalates have been identified in waste paper and recycled paper and board.

With respect to DIPN, Geueke et al. (2018) postulated that since DIPN was used in carbonless copy paper, the recycling of office paper grades would lead to its presence in recycled paper. DIPN was found in a large fraction of the pre-consumer samples which contained a recycled fibre component (Geueke et al., 2018). Moreover, DIPN was detected in other samples (Supplementary Table S4) including an egg carton, paperboard, cardboard, magazine, and newsprint. Although the fibre component of these was not known, it demonstrated that the sources of DIPN may not be limited to just the presence of office paper or recycled fibre in recycling paper grades. In the study by Guazzotti et al. (2015), it was detected mostly in pigmented, coated packaging samples (Guazzotti et al., 2015). This showed that in addition to a recycled fire component, the use of certain printing inks may influence the detection of DIPN. The presence of BHT and AO168, although not as significant, was possibly due to their use in chemical additives as well as exposure to different materials during packaging and recycling. Both BHT and AO168 are typically used as antioxidants and have been associated with plastic packaging and multi-materials (Geueke et al., 2022; Hermabessiere et al., 2020; Hanafi et al., 2019) as well as printing inks used in printed paper material (Liu & Mabury, 2021). BHT is also used as an antioxidant and stabilizer in cosmetics, as a food additive, jet fuels, rubber, plastics, animal feeds, paints and lacquers, adhesive hardeners, cleaning agents, printing products, pharmaceuticals and thinners (Andersen, 2002).

When apportioning pollutants to recycling paper grades in Fig 2., cartonboard samples were strongly associated with DBP. Cartonboards generally consist of paperboard shaped into folding boxes and held together by some sort of adhesive. The prominence of DBP may thereby be linked to the likely use of adhesives. DEHP, DIBP, NBBS and AO168 were associated with coloured paper whilst BBP, DEP and BP were linked to magazine samples. Black and white office paper was associated with AO168O. It was interesting to note that pre-consumer corrugated board was associated with DIPN whilst the unconverted paperboard had the least associated pollutants. This therefore indicated that pollutant prevalence could be projected based on the paper grade used.

5.4.4 The case of NBBS

NBBS, an organophosphate emerging contaminant (Eggen et al., 2013), has been reported as a wastewater contaminant (Pitarch et al., 2010). NBBS was not detected in any of the pre-consumer samples or the retail corrugated board. It was however detected in retail cartonboard as well as other grades of post-consumer samples, as shown in Fig. 4. When looking at the NBBS occurrence in the population, 87% were post-consumer samples, the majority of which were coloured paper and office paper. Neither coloured paper nor office paper were collected at pre-consumer and retail samples, it could thereby be possible that NBBS may be associated with the manufacture of these mechanical grades. The possibility of contamination from other sources was also possible based on its detection in groundwater (Pitarch et al., 2010) as well as use in cooking utensils (NIH, 2010). The possible removal of NBBS during repulping of recycled fibre could not be excluded as a possible reason for not being detected at pre-consumer level.

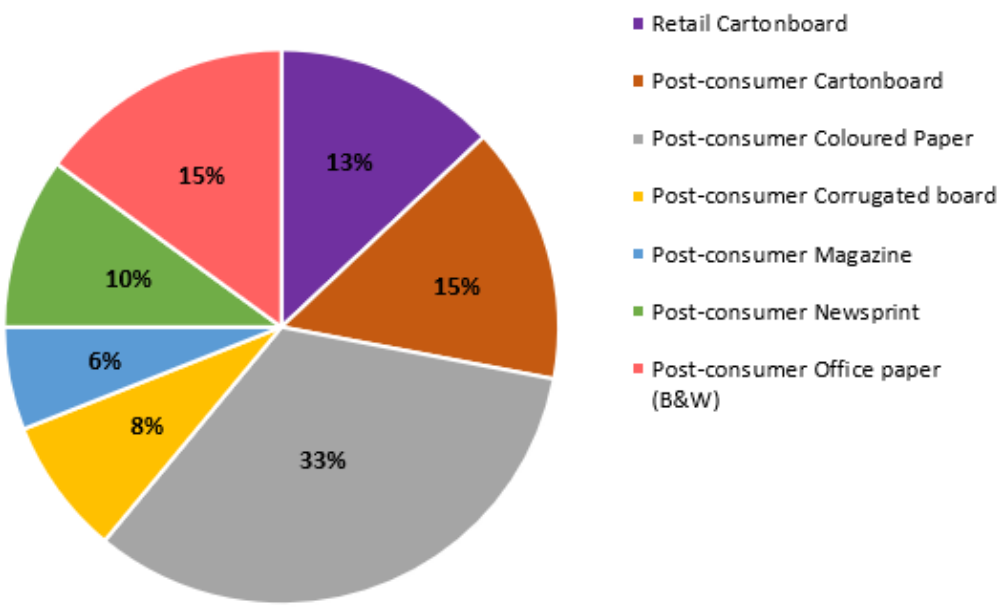


Fig. 4 Fraction of retail and post-consumer grades containing NBBS

5.4.5 The prevalence of AO168 and AO168O

The organophosphate ester AO168O, referred to as a novel pollutant (Liu & Mabury, 2021; Shi et al., 2020), was initially identified in e-waste dust (Shi et al., 2020) as well as indoor dust (Venier et al., 2018). The first reported instance of its presence in paper-based material was reported in 2021 in Liu and Mabury (2021) where it was linked to the use of printing inks in magazines and dry food paper packaging (Liu & Mabury, 2021). In this study, AO168O was predominantly detected at the recycling sites with the highest concentration found in a cereal cartonboard followed by a coffee cartonboard and newsprint insert (Fig. 5). AO168O was also detected in papers collected from household waste whilst AO168 was detected in samples from retail and solid waste sites. This suggested that over time AO168 degrades and can easily transfer during waste mingling. Common physical traits were noted in samples found to contain AO168 and/or AO1680. Most of the samples had a glossy or coated finish, were electronics packaging or had black printing. This suggested that AO168 may be used in paper packaging to prevent the possible fading of darker printing inks or to possibly maintain a gloss or coated finish (Lahimer et al., 2017). The detection and quantification of AO168 and AO168O highlighted how the mingling, use of chemical additives and chemical degradation may lead to the prevalence of certain pollutants. Neither AO168 nor A168O were detected in pre-consumer samples suggesting that there may be a

lower probability of these compounds circulating in the paper recycling chain, that current reprocessing of recycled fibre removes them and/or the concentrations of these compounds may be a very low concentration; beyond the detection limits of this study.

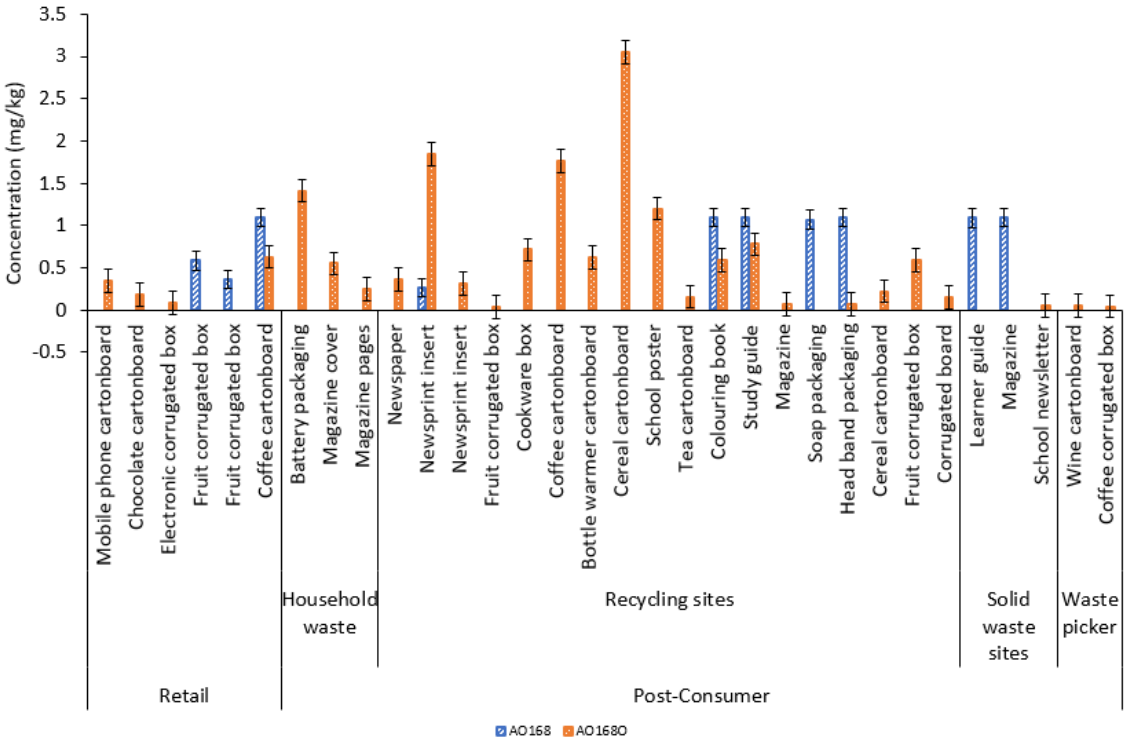


Fig. 5 The prevalence of AO168 and AO168O

5.4.6 The influence of paper recycling grades

The sorting of paper into various grades is important when it comes to the intended application of the subsequent recycled paper product and the quality required (Rahman et al., 2014). The interview participants for this study are shown in Supplementary Table S5. The interviews conducted indicated that for the participants, the average number of different recycling paper grades known was 5.25, with the five most identified grades being newspaper, cardboard, common mixed waste, magazine and office paper (Supplementary Table S6). This was 0.33 of the South African defined paper grades. Knowledge and awareness of the various paper recycling grades was expected to influence the sorting, collection and mingling of the various paper grades in the paper recycling chain. Socio-economic factors also likely influenced sorting and collecting; the most sought paper recycling grades were those with the highest value and general sorting involved

separating these out first (Supplementary Table S7). According to the South African recycling grades, post-consumer used newspapers and magazines fall into a single grade referred to as “Special News”. For the target compounds analysed in this study, newspapers and magazines were found to have different pollutant patterns (Fig 1 and Fig 2). The combination of these would thereby increase the probability of mingling of their typical pollutants.

The most diverse paper recycling grade was identified as “common mixed waste”. By definition, this grade included a mixture of grades of paper and board without restrictions on fibre content. Interview participants mentioned that sorting was generally performed by elimination where the valuable and known grades made from cardboard, white paper and office paper were removed first and the remaining recovered paper was deemed “common mixed waste” (Supplementary Table S8). This common mixed waste predominantly consists of used cartonboards (such as cereal boxes, fast food packaging, chocolate cartonboards, pharmaceutical packaging, etc.) as well as posters, miscellaneous papers and boards and could thus be considered an unsorted paper grade. Although a pre-consumer cartonboard grade exists in the form of “IMW” i.e., cartonboard cuttings, there is currently no designated post-consumer strictly designated for a post-consumer cartonboard grade. The two lowest combined concentrations of target pollutants in this group were a retail chocolate cartonboard with 0.377 mg/kg and a cereal cartonboard at 0.832 mg/kg; and the two highest were a toilet paper core (37.99 mg/kg) and pharmaceutical packaging (20.43 mg/kg), both obtained in household waste. Wide variations of concentrations were found at the different post-consumer sites making it difficult to fully predict the behaviour of this paper recycling grade. The drive for sustainable paper-based packaging in recent years (Oloyede & Lignou, 2021) means that packaging that was previously polymer-based is now manufactured from paper, including paper-based fruit punnets, confectionary products, paper straws and other fast-food packaging. These products form part of the common mixed grade when collected for recycling, further adding complexity to the mixed paper grade.

5.5 Concluding remarks

Paper and board pollutant prevalence was found to be influenced by external factors arising from exposure to undesirable pollutants during sorting, collecting and recycling as well as internal factors from the use of manufacturing and converting additives in the initial manufacturing and reprocessed fibre. The findings of the present study suggest that the South African recycled paper chain consists of pollutants prevalent in paper, plastic and multi-material goods and that the mingling of waste and/or use of additives containing such compounds may contribute to the prevalence of these pollutants in paper-based products. The further segregation of common mixed grades and special news could minimise contaminants entering product cycles from cartonboards, newspapers and magazines. The results emanating from this study are crucial for understanding the possible sources and the influence of recycling practices on the prevalence of pollutants in the recycling paper grades. Further, this study may serve as a critical baseline to grow the body of knowledge in this research area. More extensive evaluations of a wider scope of target analytes at much lower concentrations are needed.

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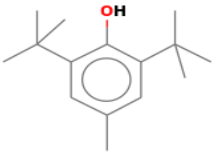
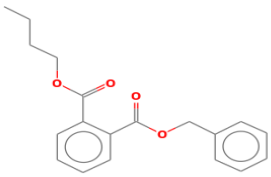
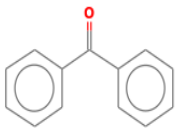
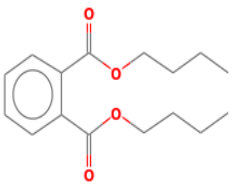
Supplementary material

Source apportionment and transport of semi-volatile organic pollutants within the South African paper recycling chain

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Table S1

Chemical structures and physicochemical properties of the target compound

Target Compound	Chemical structure	Boiling point (°C)	Molecular weight (g/mol)
1. Butylated hydroxytoluene CAS 128-37-0		265	220.3
2. Benzylbutyl phthalate CAS 85-68-7		408	312.3
3. Benzophenone CAS 119-61-9		305	182.2
4. Dibutyl phthalate CAS 84-74-2		340	278.3

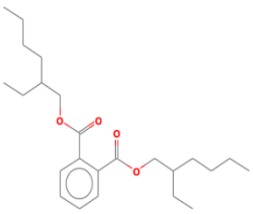
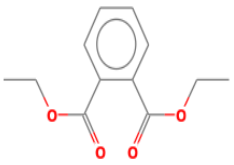
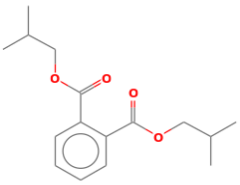
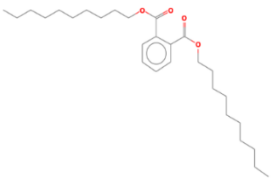
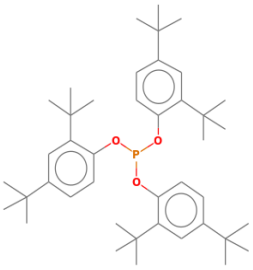
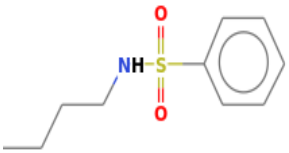
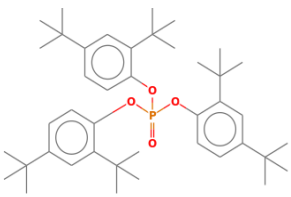
5. Diethylhexyl phthalate CAS 117-81-7		385	390.6
6. Diethyl phthalate CAS 84-66-2		295	222.2
7. Diisobutyl phthalate CAS 84-69-5		296	278.3
8. Didecyl phthalate CAS 84-77-5		261	446.7
9. Irgafos 168 (Tris (2,4-di-tert-butylphenyl) phosphite) CAS 31570-04-4		594	646.9
10. N-butylbenzene sulphonamide CAS 3622- 84-2		314	213.3
11. Tris (2,4-di-tert-butylphenyl) phosphate CAS 95906-11-9		609	662.9

Table S2

Sample overview

HOUSEHOLD WASTE 1						
 A1	 A2	 A3	 A4	 A5	 A6	 A7
 A8	 A9	 A10	 B1			
HOUSEHOLD WASTE 2						
 B2	 B5	 B6	 B7	 B8	 B9	 B10
 B11						
RECYCLING FACILITY 1						
 C1	 C2	 C3	 C4	 D1	 D2	 D3
 D4	 E1	 E3	 E4	 E5	 E6	 E7
 E8	 E9	 E10	 F1	 F2	 G1	 G3
RETAIL 1 & 2						
 H2	 H4	 H5	 H3	 H6	 J1	 J2
 J3						
SOLID WASTE 1						
 K1	 K2	 L2	 L3	 M1	 M2	 M3
 N1	 N3					
WASTE PICKER 1						
 O1	 O2	 O3	 O4			
MILLS						

 P1	 P2	 P3	 P4	 P5		
CORRUGATORS						
 Q1	 Q2	 Q3	 Q4			
RETAIL 3 & 4						
 R1	 R2	 R3	 S1	 S2	 S3	 S4
 S5						
WASTE PICKERS 2 & 3						
 T1	 T2	 T3	 U1	 U2	 U3	
RECYCLING FACILITY 2						
 V1	 V2	 V3	 W1	 W2	 W3	 X1
 X2	 X3	 Y1	 Y2			
RETAIL 5						
 Z1	 Z2	 Z3				
SOLID WASTE 2						
 AA1	 BB1	 BB2	 CC1	 DD1	 DD2	 DD3
 EE1	 EE2	 EE3				

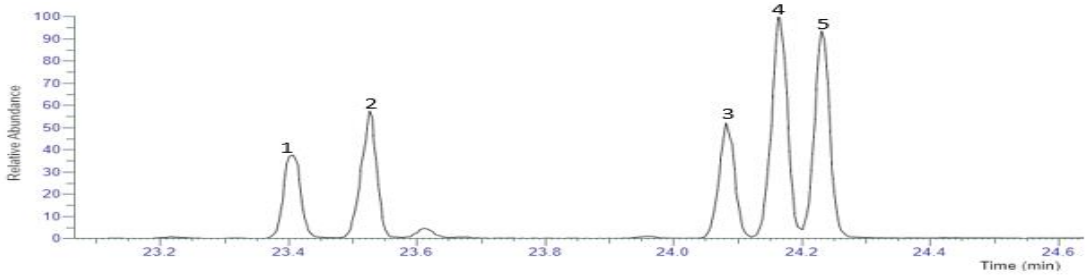


Fig. S1 A GC-MS chromatogram of relative abundance versus time showing the detected isomers of diisopropylnaphthalene isomers where peaks 1, 2, 3, 4, and 5 represent 1,3-DIPN, 1,7-DIPN, 2,6-DIPN, 2,7-DIPN and 1,6-DIPN, respectively.

Table S3

Performance of the analytical method for multi-residue analysis of semi-volatile pollutants in recycling paper grades

Compound	Retention Time (min)	SIM ion (m/z)	R^2	LOD (ηg/ g paper)	LOQ (ηg/ g paper)	RECOVERY ± %RSD					
						Paperboard (mg/kg)			Paper (mg/kg)		
d-DBP	27.12	153				**0.12**	**0.2**	**3**	**0.12**	**0.2**	**3**
BBP	30.22	149	0.9906	3.620	12.069	99±2.0	100±5.7	98±3.1	99±3.4	100±2.2	100±1.6
BHT	20.98	205	0.9966	2.050	6.832	73±4.2	83±5.3	91±3.4	82±2.0	90±5.6	98±2.33
BP	23.05	105	0.9904	4.488	14.962	84±4.4	93±1.5	96±3.2	87±6.7	98±5.3	97±2.4
DBP	27.14	149	0.9957	2.974	9.914	99±5.4	99±2.6	98±1.0	99±1.8	100±1.3	100±2.7
DEHP	33.58	149	0.9943	1.538	5.128	98±2.5	97±2.2	101± 3.4	101±2.9	100±1.9	100±1.5
DEP	22.41	149	0.9923	3.301	11.004	92±1.8	98±4.6	95±7.7	94±7.1	97±1.6	99±3.03
DIBP	25.98	149	0.9962	1.987	6.662	99±2.4	97±2.9	99±1.3	99±8.4	99±2.1	99±3.1
DIDP	39.21	149	0.9913	1.064	3.547	100±3.7	99±6.9	98±5.4	100±2.2	99±6.7	100±1.6
AO168	41.10	441	0.9979	0.944	3.147	99±2.1	98±1.9	98±1.8	99±3.7	100±2.0	87±1.9
NBBS	25.97	77	0.9992	0.964	3.212	100±2.7	100±1.6	104±5.4	98±2.85	99±3.9	99±3.5
AO168O	43.67	57	0.9927	1.161	3.872	98±2.4	100±5.7	99±1.5	99±3.3	101±1.7	100±2.0

Table S4
Detected Concentrations ± %RSD (mg/kg paper)

#		DBP	DIBP	DEHP	BBP	DEP	DIDP	BHT	BP	NBBS	AO168	AO168O	DIPN
1	A1	0.10±5.85	ND	37.12±6.72	ND	<LOQ	ND	ND	0.16±4.15	0.60±3.70	ND	ND	
2	A2	0.26±5.01	0.11±2.24	0.61±16.68	0.15±3.02	0.10±10.13	ND	0.11±36.46	0.14±18.96	ND	ND	ND	0.07±19.39
3	A3	ND	0.06±1.35	0.57±5.29	ND	0.01±24.45	0.73±12.81	ND	ND	ND	ND	ND	ND
4	A4	0.74±1.04	0.08±4.97	2.71±4.98	0.15±8.03	0.09±3.84	0.14±11.03	0.03±1.77	0.38±3.06	ND	ND	ND	0.15±3.10
5	A5	ND	0.06±6.70	0.62±9.20	0.51±11.15	<LOQ	0.13±10.61	ND	ND	ND	ND	ND	
6	A6	0.41±25.18	0.30±2.85	3.43±0.91	ND	0.10±11.04	ND	ND	0.20±6.22	ND	ND	ND	0.04±12.49
7	A7	0.75±7.20	0.14±11.98	1.61±8.30	ND	0.07±24.76	ND	ND	0.16±10.50	ND	ND	ND	ND
8	A8	2.55±6.25	0.07±1.27	0.35±2.02	16.84±9.39	0.61±12.53	ND	ND	ND	ND	ND	ND	ND
9	A9	1.60±0.31	0.36±2.14	12.43±6.83	ND	0.21±8.62	0.88±3.15	ND	ND	ND	ND	ND	0.03±6.82
10	A10	ND	ND	0.30±4.13	ND	0.88±6.25	ND	ND	ND	ND	ND	ND	ND
11	B1	3.47±4.63	0.24±1.26	3.38±3.25	ND	0.04±6.28	0.03±22.13	ND	1.71±8.57	ND	ND	ND	0.03±32.19
12	B2	ND	0.03±5.70	1.89±1.18	ND	0.07±24.76	ND	ND	0.16±10.50	ND	ND	ND	ND
13	B5	1.30±2.06	ND	1.40±1.99	ND	0.10±1.64	ND	ND	0.03±21.82	ND	ND	ND	0.08±4.41
14	B6	0.34±20.71	0.06±15.45	3.59±3.19	ND	0.01±24.05	ND	ND	ND	ND	ND	ND	ND
15	B7	ND	ND	5.12±27.32	4.80±37.19	0.03±21.59	ND	ND	0.72±7.25	1.08±23.90	ND	1.41±18.96	0.11±14.09
16	B8	0.08±3.70	0.07±5.13	1.18±12.34	ND	0.01±22.67	ND	0.05±41.32	1.77±28.41	ND	0.55±21.08	ND	ND
17	B9	ND	0.04±4.58	2.92±11.71	0.36±1.28	0.03±53.94	ND	0.04±6.01	7.69±4.23	0.05±2.39	ND	0.25±24.69	ND
18	B10	55.64±5.68	1.99±13.57	15.04±10.34	0.60±4.28	0.64±9.20	2.80±7.27	ND	3.43±9.20	ND	ND	ND	0.58±18.27
19	B11	2.65±1.14	2.10±1.86	8.51±3.67	ND	ND	ND	ND	0.18±15.99	ND	ND	ND	0.03±16.66
20	C1	ND	0.03±9.38	0.93±4.17	0.42±32.84	<LOQ	0.13±31.14	0.13±24.45	0.17±12.10	0.74±41.93	ND	0.36±38.06	ND
21	C2	2.27±3.11	0.16±14.46	2.06±17.81	ND	ND	ND	0.05±30.82	ND	ND	0.27±11.82	1.83±2.00	1.36±6.34
22	C3	ND	0.05±4.09	2.08±5.60	ND	ND	ND	ND	ND	0.57±12.66	ND	ND	ND
23	C4	ND	ND	9.11±12.21	ND	ND	ND	0.05±14.71	ND	0.49±15.22	ND	0.31±7.26	ND
24	D1	0.43±19.17	0.06±5.83	0.33±20.07	<LOQ	ND	ND	ND	0.46±19.97	ND	ND	0.04±5.73	ND
25	D2	ND	ND	1.67±19.14	ND	ND	ND	ND	24.71±0.57	ND	ND	ND	0.15±17.01
26	D3	1.24±2.31	0.10±2.25	2.58±3.44	0.61±16.93	ND	0.27±11.04	ND	ND	0.37±6.25	ND	ND	
27	D4	2.23±2.80	0.23±2.14	4.03±5.72	0.17±11.87	0.03±3.65	0.50±13.69	ND	4.53±9.64	ND	ND	0.71±7.58	0.04±1.17
28	E1	4.91±9.28	0.11±5.75	9.01±0.56	ND	ND	0.18±0.19	ND	0.91±6.38	ND	ND	1.76±3.99	0.08±3.55
29	E3	6.91±27.09	0.18±7.18	3.82±4.88	0.02±23.65	0.03±27.76	0.08±30.58	ND	0.60±13.70	0.04±1.86	ND	ND	1.03±10.94
30	E4	2.37±4.65	0.39±4.57	10.39±21.23	ND	0.11±18.22	ND	<LOQ	0.41±18.11	0.56±9.24	ND	0.62±15.19	0.14±7.99
31	E5	2.93±17.39	ND	ND	ND	ND	ND	ND	3.30±30.11	ND	ND	ND	0.02±38.26
32	E6	2.58±4.95	0.05±2.68	2.28±21.51	0.62±2.69	ND	ND	ND	0.37±3.40	0.57±46.62	ND	3.05±45.23	0.07±11.19
33	E7	0.66±5.86	0.57±27.10	13.90±16.59	ND	ND	ND	ND	ND	0.69±2.21	ND	1.20±15.00	ND

34	E8	2.51±2.64	0.14±18.00	1.22±4.64	ND	0.01±34.41	ND	ND	0.61±5.09	ND	ND	ND	0.11±24.13
35	E9	2.95±13.77	0.15±15.68	3.66±4.52	0.08±32.18	0.01±92.59	ND	0.03±2.56	ND	0.59±34.63	ND	0.16±9.29	0.58±7.50
36	E10	ND	0.06±20.75	2.80±15.67	ND	ND	ND	ND	0.43±25.24	0.95±27.82	ND	ND	ND
37	F1	5.42±0.55	0.39±8.22	2.96±22.45	ND	ND	ND	ND	0.12±7.77	0.74±20.61	1.10±0.06	0.59±23.17	ND
38	F2	ND	0.10±1.84	5.63± 9.45	ND	0.01±39.15	0.54±19.75	0.03±2.44	0.19±6.42	0.77±6.52	1.09±0.02	0.78±5.20	ND
39	G1	ND	ND	1.14±9.56	ND	0.01±19.79	1.14±9.56	0.03±1.28	14.16±7.50	0.59±11.68	ND	0.07±3.97	0.19±9.70
40	G3	ND	0.16±1.39	7.40±15.31	ND	ND	ND	ND	2.05±9.90	1.59±24.79	ND	ND	0.03±1.32
41	H2	0.65±19.42	0.14±21.66	5.63±18.46	ND	ND	ND	ND	0.09±19.11	0.88±16.66	ND	0.34±15.83	ND
42	H4	4.76±15.36	0.22±31.69	3.94±11.28	ND	ND	ND	ND	ND	ND	ND	ND	0.06±30.92
43	H5	ND	0.05±0.70	0.24±0.92	ND	ND	ND	0.09±2.29	ND	ND	ND	ND	ND
44	H3	ND	0.08±4.13	3.27±4.25	3.11±1.75	<LOQ	2.88±8.73	0.08±3.23	ND	0.39± 8.3	<LOQ	0.19±6.50	ND
45	H6	ND	0.15±18.08	1.20±3.33	ND	ND	ND	0.52±21.37	ND	ND	ND	ND	ND
46	J1	2.50±4.33	0.98±10.15	34.80±21.90	ND	0.89±20.97	ND	ND	0.70±26.34	ND	ND	ND	ND
47	J2	2.04±12.42		28.14± 5.69	2.16±17.32	0.05±29.93	ND	ND	0.80±23.70	2.48±9.58	ND	ND	ND
48	J3	1.94±13.73	0.92±25.37	1.84±40.20	<LOQ	0.56±34.06	1.18±31.11	0.05±21.42	22.02±24.02	0.52±22.25	ND	ND	0.04±30.35
49	K1	28.74±17.03	0.08±9.68	2.53±21.42	0.39±14.49	ND	ND	ND	0.21±15.53	0.31±39.58	ND	ND	0.01±16.12
50	K2	ND	ND	ND	ND	ND	ND	ND	0.58±11.30	0.52±9.19	ND	ND	0.02±9.67
51	L2	ND	ND	12.00±10.62	0.03±18.66	ND	ND	0.02±1.33	2.34±13.74	0.06±9.70	ND	ND	ND
52	L3	ND	0.20±12.98	4.53±26.14	ND	ND	ND	ND	2.58±12.54	0.42±18.77	ND	ND	ND
53	M1	0.52±5.81	0.19±6.45	5.13±1.55	ND	ND	ND	ND	ND	ND	<LOQ	0.06±12.27	ND
54	M2	0.53±11.46	0.11±5.77	36.13±2.89	ND	ND	ND	ND	ND	ND	ND	ND	ND
55	M3	1.82±3.80	0.12±4.51	0.08±7.40	ND	0.02±5.03	ND	ND	0.15±5.00	ND	ND	ND	ND
56	N1	ND	0.07±19.92	ND	2.12±9.71	0.04±14.90	ND	0.05±18.87	ND	0.12±2.87	ND	ND	ND
57	N3	ND	0.06±9.83	1.13±21.61	2.49±5.45		ND	ND	ND	0.12±12.72	ND	ND	ND
58	O1	ND	0.24±0.62	1.53±3.41	<LOQ	<LOQ	ND	ND	ND	ND	ND	ND	0.13±3.98
59	O2	0.34±4.17	0.42±9.98	0.65±3.51	0.16±23.75	0.05±22.03	ND	0.13±1.32	0.69±2.05	ND	ND	ND	0.05±5.96
60	O3	0.68±4.35	0.08±5.27	1.07±16.12	ND	ND	ND	ND	ND	ND	ND	0.06±3.91	0.03±5.33
61	O4	0.48±2.56	0.29±8.72	4.56±13.86	0.12±7.30	<LOQ	1.31±8.76	ND	0.33±15.36	ND	ND	0.04±20.25	0.36±2.18
62	P1	2.16±1.86	0.12±12.83	1.93±1.56	ND	ND	ND	ND	0.27±5.92	ND	ND	ND	0.05±2.09
63	P2	0.59±3.63	0.07±3.28	1.35±7.46	ND	<LOQ	ND	<LOQ	ND	ND	ND	ND	0.21±3.45
64	P3	ND	0.04±0.39	0.69±11.71	ND	ND	ND	ND	ND	ND	ND	ND	0.02±1.07
65	P4	0.16±3.19	ND	0.15±1.03	ND	ND	ND	ND	ND	ND	ND	ND	ND
66	P5	4.21±8.31	0.22±5.75	2.86±10.54	0.07±4.59	0.01±15.02	<LOQ	ND	0.26±2.79	ND	ND	ND	ND
67	Q1	0.25±7.92	0.04±5.15	0.52±4.77	ND	ND	ND	ND	ND	ND	ND	ND	ND
68	Q2	0.95±5.31	0.08±3.18	1.22±3.64	0.01±16.81	ND	0.18±3.93	ND	ND	ND	ND	ND	ND
69	Q3	ND	0.12±5.49	2.29±3.57	0.38±4.21	ND	0.62±6.59	ND	ND	ND	ND	ND	ND
70	Q4	1.59±8.16	ND	2.58±8.88	ND	ND	ND	ND	ND	ND	ND	ND	0.20±23.67

71	R1	ND	0.06±5.41	0.40±12.76	ND	0.06±29.89	ND	ND	0.32±8.55	ND	ND	ND	ND
72	R2	0.34±2.00	0.33±2.49	ND	ND	0.28±2.19	ND	0.04±0.49	0.64±1.66	ND	1.09±0.02	0.63±2.88	0.18±2.27
73	R3	ND	ND	ND	ND	ND	ND	ND	1.34±9.38	ND	ND	ND	ND
74	S1	0.28±1.42	2.14±3.70	3.89±6.87	0.04±32.20	0.01±18.12	ND	ND	0.61±2.16	ND	ND	ND	0.10±3.75
75	S2	0.26±5.14	0.17±6.86	3.63±3.22	0.93±51.92	0.01±26.15	ND	0.03±0.81	0.86±6.12	ND	ND	ND	0.89±7.36
76	S3	0.82±0.56	0.14±1.84	2.21±2.07	0.26±10.65	ND	ND	ND	0.61±11.29	ND	ND	ND	0.23±5.74
77	S4	7.19±14.07	0.10±2.34	1.23±0.75	ND	ND	ND	ND	ND	ND	ND	ND	0.29±2.63
78	S5	0.34±3.77	0.08±8.09	4.46±19.03	ND	0.01±16.63	ND	ND	0.45±5.59	ND	ND	0.08±9.09	0.62±19.22
79	T1	0.46±9.13	0.06±7.15	3.92±15.34	ND	ND	ND	0.03±0.27	ND	ND	ND	ND	ND
80	T2	2.19±8.50	0.16±18.30	8.73±9.71	0.30±4.37	<LOQ	ND	ND	ND	ND	ND	ND	0.17±3.87
81	T3	6.15±3.06	2.68±3.85	1.40±5.02	0.12±11.85	ND	0.24±11.36	ND	ND	ND	ND	ND	ND
82	U1	0.48±5.79	0.10±5.02	0.41±10.38	ND	ND	ND	ND	0.27±5.41	ND	ND	ND	ND
83	U2	3.62±2.19	0.19±4.44	2.96±2.67	0.07±7.82	ND	ND	ND	0.36±1.49	ND	ND	ND	0.05±18.88
84	U3	3.58±4.02	0.18±5.17	2.14±5.52	ND	ND	0.57±6.39	ND	0.54±5.45	ND	ND	ND	0.08±6.57
85	V1	0.13±4.47	0.07±7.74	0.61±10.15	0.42±46.62	<LOQ	ND	0.05±2.77	0.25±9.01	ND	ND	ND	0.01±9.44
86	V2	ND	0.09±24.57	0.56±5.79	0.10±5.93	ND	0.17±5.42	9.41±26.94	ND	ND	ND	ND	0.04±4.60
87	V3	ND	0.39±4.35	9.50±4.95	1.39±2.32	0.10±1.23	ND	0.05±2.77	0.25±9.01	ND	ND	ND	0.01±9.44
88	W1	0.33±19.28	0.18±5.63	2.49±4.08	0.47±44.20	<LOQ	ND	ND	0.52±0.58	ND	ND	ND	0.21±12.99
89	W2	ND	0.78±1.61	ND	0.17±4.75	3.81±25.35	ND	0.03±2.86	ND	ND	ND	1.07±1.31	
90	W3	0.74±5.82	0.07±7.66	0.62±1.31	ND	0.02±1.55	ND	ND	ND	ND	1.09±0.11	0.07±1.94	
91	X1	1.36±10.11	0.09±4.99	ND	0.16±20.90	ND	ND	ND	ND	ND	ND	0.22±36.09	0.22±4.23
92	X2	0.23±6.26	0.07±2.46	0.35±9.65	ND	ND	ND	0.11±19.35	0.38±13.05	ND	<LOQ	0.59±26.98	0.02±25.51
93	X3	0.03±6.85	0.15±67.80	3.96±17.41	0.46±8.37	<LOQ	7.99±17.78	ND	0.48±5.58	ND	ND	0.15±20.25	0.11±7.65
94	Y1	0.09±0.84	0.06±50.19	0.11±0.38	ND	ND	ND	ND	ND	ND	ND	ND	ND
95	Y2	0.16±5.54	0.18±38.47	0.26±2.08	ND	ND	ND	ND	ND	ND	ND	ND	ND
96	Z1	0.27± 6.05	0.05±5.45	0.02±21.76	ND	ND	0.02±21.76	ND	ND	ND	ND	ND	ND
97	Z2	11.08±28.61	ND	ND	ND	ND	ND	ND	ND	ND	0.58±20.79	ND	ND
98	Z3	ND	0.16±0.24	0.42±7.57	ND	<LOQ	ND	ND	ND	ND	0.36±15.38	ND	ND
99	AA1	ND	0.06±8.28	1.09±1.98	0.56±9.74	ND	ND	0.04±10.88	0.61±3.53	ND	ND	ND	ND
100	BB1	0.86±9.34	0.33±8.07	2.70±9.54	ND	ND	ND	ND	ND	ND	ND	ND	ND
101	BB2	0.16±14.53	0.14±12.90	0.66±15.50	ND	ND	ND	0.03±0.45	0.17±2.51	ND	1.09±0.02	ND	ND
102	CC1	0.07±1.95	0.12±2.27	0.24±1.51	0.21±0.47	ND	0.20±7.41	0.03±0.27	ND	ND	1.10±0.01	ND	ND
103	DD1	0.12±2.09	0.07±2.54	1.19± 2.81	ND	ND	ND	ND	0.49±2.44	ND	ND	ND	0.06±1.88
104	DD2	ND	ND	2.59±11.23	1.45±4.03	ND	ND	0.06±4.56	ND	ND	ND	ND	ND
105	DD3	ND	0.05±5.84	1.17±7.89	ND	ND	ND	0.05±55.42	ND	ND	ND	ND	ND
106	EE1	0.31±0.94	0.09±2.31	0.59±0.04	<LOQ	ND	ND	ND	0.08±2.00	ND	<LOQ	ND	ND
107	EE2	0.75±1.82	0.10±3.14	0.78±4.14	ND	0.01±7.17	ND	ND	0.65±1.42	ND	ND	ND	0.02±9.46

108	EE3	ND	0.08±31.61	0.82±3.56	0.36±7.66	0.01±3.27	0.02±29.23	ND	0.61±11.22	ND	ND	ND

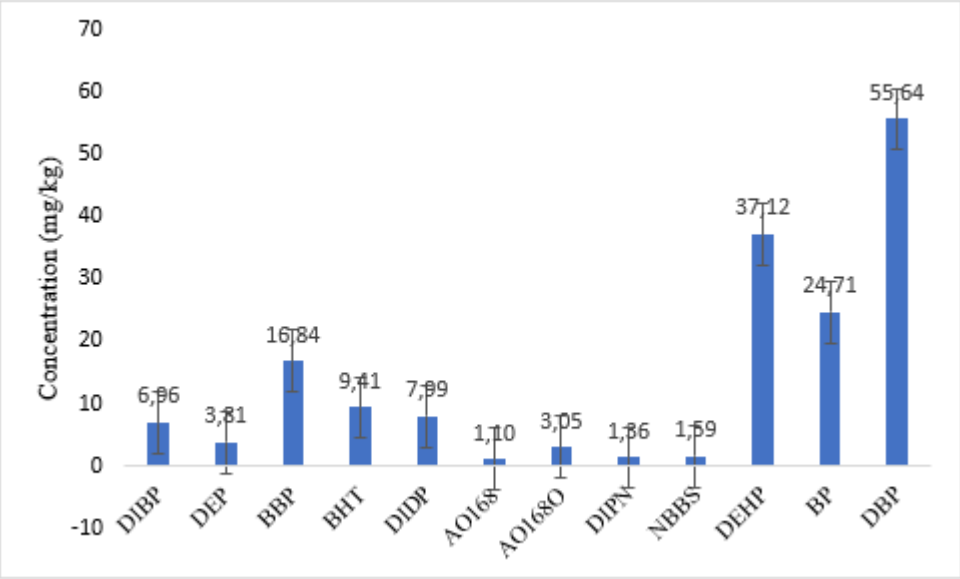


Fig. S2 Target compound ranges

Table S5

Interview Participants

#	Description
1	Formal sorter
2	Recycled materials specialist
3	Recycling middleman
4	Small business owner
5	Waste picker
6	Waste picker
7	Waste picker
8	Waste picker
9	Industry watchdog
10	Recycling research analyst
11	Recycling manager
12	Formal sorter
13	Recycling facility manager
14	Formal collector
15	Formal suburban recycling collector
16	Recycling site supervisor

Table S56

Responses: What is your understanding of the different paper grades used for recycling?

Participant	Known Paper Grades	Number of grades Identified
1	Newsprint, K4, White, SBM, Special News, HL1, HL2, CMW	9
2	Newsprint, K4, K3, SBM, HL1, HL2, CMW, sacks & bags,	8
3	Newspaper, cardboard, magazine, paper	4
4	Cardboard	1
5	Newspaper, boxes, magazine, white paper	4
6	News, magazine, white paper, common paper	4
7	Newspaper, cardboard, magazine, white paper, common paper	5
8	Not sure, newspaper, cardboard	2

9	K4 highest recycling, HL1 toilet paper, newspaper, CMW, FN, SN	6
10	In SA grouped according to end product, SN, K3, K4, HL1, HL2, CMW	6
11	Newspaper, K4, K3, SBM, HL1, HL2, CMW	7
12	Newspaper, catalogues, boxes, office paper, potato sacks, common waste	6
13	K4, White, CMW, special news, flat news	5
14	mainly cardboard, white, office, magazine	6
15	Newspaper, magazine, office, white paper, cardboard, mixed	5
16	Newspaper, white, CMW, IMW, K4, HL	6
	Average	**5.25**

CMW – common mixed waste

IMW – cartonboard cuttings

SN – special news

FN – unsold newspapers

SBM – unsold magazines

HL1 – white printed or unprinted paper

HL2 – pastel coloured printed or unprinted paper

K4 – post-consumer corrugated containers

K3 – pre-consumer corrugated

Table S7

Responses: What recycled paper grades do you consider as valuable and why?

Participant	**Valuable Grade**
1	Corrugated, most common
2	K4, HL1, highest demand
3	All grades
4	Cardboard
5	White paper

6	White paper, people like to use it
7	White paper, most expensive get most money
8	Office paper
9	K4- most recovered and most readily available, most efficiently broken down
10	Demand-dependent and driven by supply issues
11	K4-paper mills, HL1 & white paper -tissue paper
12	cardboard, can get the most from it and most collected
13	i.t.o. quantity K4 at R1.50 /kg, i.to. Value white paper R2.50-R3.50/kg
14	cardboard, office paper
15	every paper is used, newspaper to cardboard paper
16	white paper, used for toilet paper industry
	• K4 and white paper are the most valuable • Most valued are the ones with highest monetary value. Type collected driven strongly by money and influences collection. Demand, supply influences • Paper collecting and sorting influenced by buy-back value rate

Table S8

Responses: What methods or protocols do you apply when sorting and collecting recycled paper**?**

Participant	Sorting and Collecting Protocols
1	Sorting visually according to grade, coated and laminated not visually distinguishable, remove prohibited, check moisture
2	By look
3	Separate into different types
4	Collect only cardboard, mix rest
5	Separate into same types, remove non-paper
6	Separate carboard and paper, put unwanted in bin
7	Start by sorting for white paper then cardboard, then the rest put together

8	Separate papers, then remove plastics
9	Ensure correct grading of paper
10	Currently not using technology which could make sorting of paper more efficient. Sorting of paper could be based on physical and chemical properties not just visual
11	Loose material into relevant grades, avoid mixing of papers, white paper generally removed first
12	Paper collected and sorted in skips and bins outside retail shops then sorted into relevant grades again before baling
13	Train workers, visual sorting but not easy to distinguish visually when laminated or coated
14	Samples by type then remove unwanted or prohibited stuff e.g. fast food containers with food
15	Collect then put mixed together then sort cardboard and paper before baling
16	Usually comes in sorted, those that are sorted look at what can be pulped, laminated samples can’t be broken down as water doesn’t get into it

CHAPTER SIX

6 PAPER 3

This paper titled “Emerging Contaminants as Unintentional Substances in Paper and Board: A Case of Unexpected Pharmaceuticals Detection in the Paper Recycling Chain” was published in the **Journal of Hazardous Material**. **Journal of Hazardous Material** (2024) 472, 134419.
https://doi.org/10.1016/j.jhazmat.2024.134419.
This pioneering paper is to the authors’ knowledge, the first reported targeted and suspect screening of pharmaceuticals extracted from paper-based materials.

GRAPHICAL ABSTRACT



Emerging Contaminants as Unintentional Substances in Paper and Board: A Case of Unexpected Pharmaceuticals Detection in the Paper Recycling Chain

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Abstract

The contamination of paper products by various chemicals has been reported on a global level, but to date, no published research has investigated pharmaceutical contamination of paper-based products. In this study, pharmaceutical analysis was conducted on 42 samples collected from various points of the recycled paper chain in Cape Town, South Africa, which included the various grades that may be included in the manufacturing of recycled paperboard. The analysis was achieved by ultrasonic-assisted extraction of paper samples before detection by UHPLC-Q Orbitrap. Quantification limits ranged from 1.15 pg/g for ketoprofen to 46.07 pg/g for methocarbamol. Pharmaceuticals identified in newspaper samples were dexamethasone, ketoprofen, and 17β-estradiol. The latter was also detected in paper shopping bags (up to 697.49 ng/g), infant bathtub packaging (280.62 ng/g), battery packaging (137.43 ng/g), and an egg carton (170.47 ng/g). Carbamazepine was also prominent with its concentration reaching 13.02 ng/g in a vegetable box. Suspect screening tentatively identified 14 additional pharmaceuticals in paper samples, with minocycline, prazepam, and anabolic steroids appearing more prominently. This pioneering study indicated that unintentional pharmaceutical exposure had expanded beyond environmental media to consumer products.

Keywords: pharmaceuticals, recycled paper, emerging contaminants, liquid chromatography, high resolution, suspect screening

Environmental Implications

This study is the first reported pharmaceutical contamination of paper. Pharmaceuticals are emerging contaminants that have been detected in environmental media such as water, soil, and plants. Their detection in paper recycling is thereby important in showing the proliferation of pharmaceuticals beyond traditional sources and sinks. It identifies the need for further evaluations of exposure pathways in future risk assessments. The study highlights the intertwining linkages between consumer products, healthcare, waste management, environmental pollution, and the manufacturing industry.

6.1 Introduction

Pharmaceuticals have been detected in freshwater bodies (Madikizela, 2023) reclaimed wastewater (Abdallat et al., 2022), sewage sludge, soils (Camotti Bastos et al., 2020), marine organisms (Madikizela & Ncube, 2022), food products (Vaudin et al., 2022) as well as in plants and animals due to their uptake from the contaminated environment (Madikizela et al., 2022). The presence of pharmaceuticals in the environment has been attributed to poor sanitation (Madikizela et al., 2020), wastewater treatment plants (WWTPs) (Khulu et al., 2022), inaccessibility to modern ablution facilities, and improper disposal of expired or unused medications (Madikizela et al., 2020). On a global level, the complete elimination of pharmaceutically active compounds and their metabolites by WWTPs does not occur (Sharma et al., 2021; Vaudin et al., 2022). For this reason, pharmaceuticals are considered emerging environmental pollutants (Abdallat et al., 2022; Vaudin et al., 2022). In South Africa, different therapeutic classes of pharmaceuticals which include nonsteroidal anti-inflammatory drugs (NSAIDs), antiretroviral drugs, antibiotics, β-blockers, antidiabetics, lipid regulators, antidepressants, antipsychotics, muscle relaxants and anti-epileptics have been identified in the environment (Madikizela, 2023). Unintentional exposure to pharmaceuticals is associated with adverse environmental and human effects. For instance, the presence of antibiotics in the environment has been linked to altered bacterial compositions in stable ecosystems and to antibiotic-resistant bacteria (Polianciuc et al., 2020). Antiepileptics have been shown to modify electrical activities in the neurons (Kobayashi et al., 2020) while NSAIDs reportedly inhibit brain development in foetus (Vaudin et al., 2022).

Paper recycling involves extensive water use for pulping, fibre property development, dilution of pulp, paper web formation, and steam generation; often in closed-water systems (Han et al., 2021). Since pharmaceutically active compounds have been identified as water contaminants (Abdallat et al., 2022; Camotti Bastos et al., 2020; Madikizela, 2023), pharmaceuticals may thereby be introduced to the fibre lattice during the paperboard manufacturing process. Paper-based materials are also often used as secondary packaging for pharmaceutical products (Zadbuke et al., 2013), which could further promote pharmaceutical exposure opportunities.

The circular nature of paper recycling (Zhu et al., 2022) in itself means that pharmaceuticals may accumulate and propagate in the paper recycling chain; exacerbated by the sorting and collection protocols employed. The mingling of paper with other waste products during disposal, collecting, and sorting as well as consumer contact and usage has been shown to introduce contaminants (Blanco et al., 2013; Miranda et al., 2013) and may thus also lead to pharmaceutical contamination. Moreover, the interaction of post-consumer paper with the environmental media when disposed of in soil, water, and vegetation may inadvertently provide other opportunities for pharmaceutical contamination of waste paper intended for recycling; where no mechanisms are currently used to actively remove such compounds. In South Africa, the recycling paper chain includes paper recovered from unsorted domestic waste as well as paper collected at kerbsides, solid waste disposal sites, and landfills by informal waste collectors commonly referred to as waste pickers. This results in increased exposure opportunities to water, soil, plants, and leachates. Since pharmaceuticals are ubiquitous in environmental media (Waleng & Nomngongo, 2022) exposure to pharmaceuticals is highly probable in the paper recycling chain.

Cellulose fibres such as those present in paper pulps are hydrophilic (Keller, 2019) and are referred to as hygroscopic material with the ability to absorb, or desorb, water vapour in the air and liquid water from their surroundings (Bajpai, 2018). Paper is highly sensitive to gases and liquids which can diffuse through the highly porous material (Rovera et al., 2020) increasing opportunities for pharmaceutical contamination. To minimise and improve general barrier properties, non-cellulosic polymers, waxes, and aluminium are often added to the paper during manufacturing (Rovera et al., 2020). In more recent years, biopolymers (such as polycaprolactone and polylactic acids) and hydrocolloids (including starch, chitosan, and cellulose derivatives) (Rovera et al., 2020; Thitsartarn & Jinkarn, 2020, 2021) have been used to improve the functional performance of paper products, to introduce hydrophobicity and to reduce the introduction of contaminants (Wang et al., 2022). This thereby means that different paper products may adsorb or absorb chemical compounds differently depending on the barrier coating, retention aids and wet-strength additives used.

The contamination of paper products by various chemical compounds such as phthalates, benzophenone, phenols, and mineral oil has been reported (Ahmadkhaniha & Rastkari, 2017; Bengtström et al., 2016; Biedermann et al., 2013; Farzanehfar & Kobarfard, 2017; Geueke et al., 2022; Pivnenko et al., 2015; Vápenka et al., 2016), but to date, no published research has investigated pharmaceutical contamination of paper products. The lack of literature on the occurrence of pharmaceuticals in paper-based goods meant that the pharmaceuticals of interest were selected based on recent works on pharmaceuticals in water bodies and reported usage patterns of pharmaceuticals in South Africa. To this end, an anti-epileptic drug (carbamazepine), NSAID (ketoprofen), corticosteroid (dexamethasone), steroid hormone (17β-estradiol), antiretroviral (nevirapine), antidepressant (venlafaxine), muscle relaxant (methocarbamol) and cardiac stimulant (etilefrine) were selected as representative analytes of the main therapeutic classes of pharmaceuticals found in the South African environment (Khulu et al., 2022; Lees et al., 2016; Madikizela et al., 2020; Zunngu et al., 2017). The occurrence of these pharmaceuticals was investigated at key stages of the paper recycling chain; pre-consumer, retail, and post-consumer. The pre-consumer samples comprised of paperboard prior to exposure to consumers (with a recycled fibre component) whilst retail samples consisted of samples that had been packed and distributed to grocery stores. The post-consumer samples included the various grades of paper grades used to manufacture recycled paperboards, such as newspapers, magazines, and office paper. These were used post-consumer samples. The com-mingled paper collected for recycling in South Africa, like many developing countries such as Brazil, Argentina, Nigeria, and India (IAWP, 2022) includes paper recovered by informal waste pickers. Waste pickers collect waste from kerbsides, solid waste disposal sites, and landfills. Poorly managed waste systems have resulted in unrestricted waste collection and inappropriate disposal of waste (Omotoso, 2017). A portion of this wastepaper, destined for end-of-life incineration, ends up at recycling facilities along with waste paper collected from households, retailers, schools, businesses, and various industries before being manufactured into recycled paperboard. The analysis was achieved by ultrasonic-

assisted extraction before detection by ultra-high performance liquid chromatography – high resolution mass spectrometry (UHPLC-HRMS) Q Orbitrap.

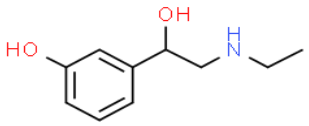
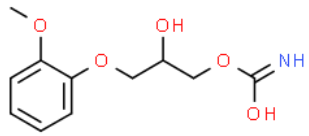
6.2 Materials and methods

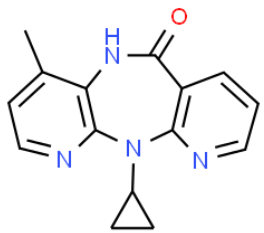
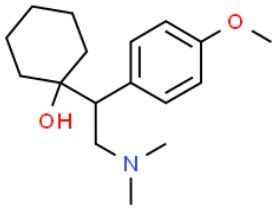
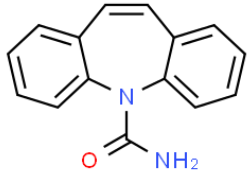
6.2.1 Chemicals and preparation of pharmaceutical standards

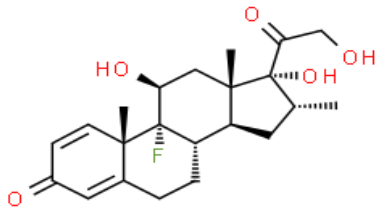
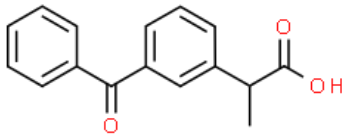
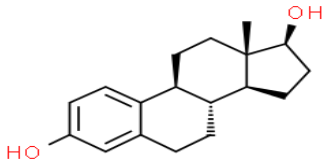
The analytical standards consisted of carbamazepine, dexamethasone, nevirapine, venlafaxine, methocarbamol, etilefrine, ketoprofen, and 17β-estradiol (Merck, Johannesburg, South Africa) as shown in Table 1. These were made up in LC-MS grade methanol (Merck, Johannesburg, South Africa) at a concentration range of 10 - 500 µg/L. Other solvents used in the study were ethanol (Merck, Johannesburg, South Africa) and water (Merck, Johannesburg, South Africa).

Table 1

Pharmaceutical standards

Pharmaceutical	**Chemical Formula**	**Chemical Structure**	**CAS #**	**Water solubility (mg/L)**	**LogP**	**LogD (pH 7.4)**	**Boiling Point (°C)**
Etilefrine	$C_{10}H_{15}NO_2$		709-55-7	18.9	0.5	-1.61	352
Methocarbamol	$C_{11}H_{15}NO_5$		532-03-6	29.9	0.61	-2.07	418

Nevirapine	$C_{15}H_{14}N_4O$		129618-40-2	100	2.5	2.10	415
Venlafaxine	$C_{17}H_{27}NO_2$		93413-69-5	572 x 10^3	3.2	1.43	398
Carbamazepine	$C_{15}H_{12}N_2O$		298-46-4	35.4	2.77	2.28	411

Dexamethasone	$C_{22}H_{29}FO_5$		50-02-2	89	1.87	1.92	568
Ketoprofen	$C_{16}H_{14}O_3$		22071-15-4	51	3.1	0.06	431
17β-estradiol	$C_{18}H_{24}O_2$		50-28-2	3.9	4	3.62	446

6.2.2 Sampling

A total of 42 paper and board samples were collected at solid waste sites, recycling facilities, retail stores, informal waste pickers, and household waste in Cape Town, South Africa (Fig. 1) and consisted of various grades in the paper recycling chain that go into the manufacture of recycled boards. Pre-consumer samples were sourced from various South African corrugators and paper mills situated outside the Cape Town district, with the samples collected from the paper machine, wrapped in foil, and dispatched. The retail samples were collected from South African grocery stores. The pre-consumer and retail samples consisted only of the board, whilst the post-consumer samples consisted of the paper grades typically used in the manufacture of recycled boards. These samples consisted of cartonboard, newsprint, corrugated board, office paper, and magazines.



Fig. 1. Sample Overview in Cape Town (Western Cape province, South Africa)[1]

[1] *adapted from* (Cooke, 2012)

6.2.3 Sample preparation

A sample of 1 g shredded paper was placed in a 20 mL solvent mixture consisting of water: ethanol: and methanol (2:1:1) inside a 60 mL glass vial and vortexed for 2 minutes. This was followed with ultrasonic-assisted extraction (UAE) at 60 ℃ for 2 hours in a sonic bath (Power Sonic 405, United Scientific, Cape Town). The extraction process strategically aimed for the release of target pharmaceuticals from the paper-based samples into an aqueous medium. The addition of methanol and ethanol was done to improve extraction efficiency as done elsewhere (Eloff, 1998) whilst remaining compatible with the UHPLC- Q Orbitrap solvent system. The selection of 60 ℃ was based on the boiling temperature of the solvents, to closely match typical pulping temperature (Chatrath & Durge, 2011) and to improve extraction that would otherwise be achieved at lower temperatures (Saien & Daliri, 2014). The boiling points of the target compounds were all above 350 ℃ (Table 1) and so were not expected to volatilise. The resulting supernatants were filtered into glass vials with a 0.22 µm regenerated cellulose filter (Stargate Scientific, Johannesburg, South Africa) before analysis using UHPLC-Q Orbitrap.

6.2.4 UHPLC-Q Orbitrap

UHPLC-HRMS analysis was performed using a Thermo Scientific Vanquish UHPLC^{+} Q Exactive Focus Orbitrap (Anatech, Cape Town, South Africa). Chromatographic separation was achieved using a Hypersil Gold aQ 100 mm x 2.1 mm x 1.9 µm column (Anatech, Cape Town, South Africa) at a column compartment temperature of 30 ^{o}C and autosampler temperature of 10 ^{o}C. The instrument method developed was guided by compound chemical characteristics and instrument capabilities [40-43] with the final optimised conditions consisting of solvent A as 0.1% formic acid in water (Merck, Johannesburg, South Africa) with 5 mM ammonium formate (Merck, Johannesburg, South Africa) and solvent B as 0.1% formic acid in methanol with 5 mM ammonium formate. The gradient method was initiated at 30% solvent B at 0.3 mL/min (hold 1 min) before increasing to 100% B with a curve set at 2 until 15 min. The flow rate was increased to 0.35 mL/min for 4 min before returning to 30% solvent B and 0.3 mL/min. A 10 µL injection volume was used. Tandem mass spectrometry was coupled to a heated electron spray ionisation spray in positive mode with the sheath gas flow rate at 40

aU, the aux gas flow rate at 10 aU, spray voltage at 3.20 kV, S-lens RF level at 55.0, 300 ºC capillary temperature and 400 ºC aux gas heater temperature. The full scan acquisition range was 83.4 to 1250 m/z at a resolution of 70 000, and data-dependent acquisition (dd-MS^2) in discovery at a resolution of 35 000. Stepped collision energy was selected at 15 and 30 eV with the AGC target set at 2E+04. The accurate mass analysis and retention times for the compounds were determined by equation (1).

$$Mass\ tolerance\ (ppm) = \left|\frac{Theoretical\ mass\ expected\ (m/z) - Mass\ Observed\ (m/z)}{Theoretical\ mass\ expected\ (m/z)}\right| \times 10^6 \quad (1)$$

For HRMS, a mass tolerance < 5 ppm indicates accurate mass detection (Knolhoff et al., 2014).

6.2.5 Quality assurance

To evaluate the external calibration curves, the coefficient of determination (R^2) was determined as the indicator of linearity. The limit of detection (LOD) and limit of quantification (LOQ), which were taken as the sensitivity indicators, were measured at signal-to-noise of 3 and 10, respectively at 10 µg/L. Virgin, unconverted, unprinted paperboard samples were used to evaluate the method performance by spiking the samples at two different concentrations in triplicate. Spiking was performed on virgin samples using standards made up in methanol which were allowed to dry for approximately 3 hours at 21 ºC prior to the extraction procedure. The relative recovery and %RSD were used to evaluate the accuracy and precision of the method.

6.2.6 Data analysis

Instrument data acquisition and analysis were performed using Thermo Scientific Xcalibur and TraceFinder 5.0. TraceFinder 5.0 was used for suspect screening where an unknown analysis method was developed for a minimum peak width of 0.21 minutes, maximum peak width of 0.74 minutes, and Retention Time window set at 35 seconds with alignment and gap filling selected for exhaustive searching. The mass tolerance for the screening was set at 10 ppm on the full scan using the

National Institute of Standards and Technology (NIST) 2020 library. The match factor gave an indication of the similarity of the unknown spectrum to the library spectrum at a scale of 0-1000 with the highest possible score of a perfect match being 999. General guidelines from NIST indicated that a match factor > 900 was considered an excellent match, 800-900 a good match, and 700-800 a fair match. In the reverse match the peaks of the unknown's spectrum that are not in the library's known reference spectrum were ignored. The threshold for positive identification was based on match factors and accurate mass tolerance where the similarity index (SI) was above 750 and the reverse similarity index (RSI) above 800.

6.3 Results and discussion

6.3.1 Method validation

Acceptable mass accuracy was achieved, as shown in Table 2, with mass tolerance < 5 ppm for all target compounds under investigation at the retention times stated using the confirmatory ions listed. The chromatogram obtained for the separation of target compounds is shown in Fig 2.

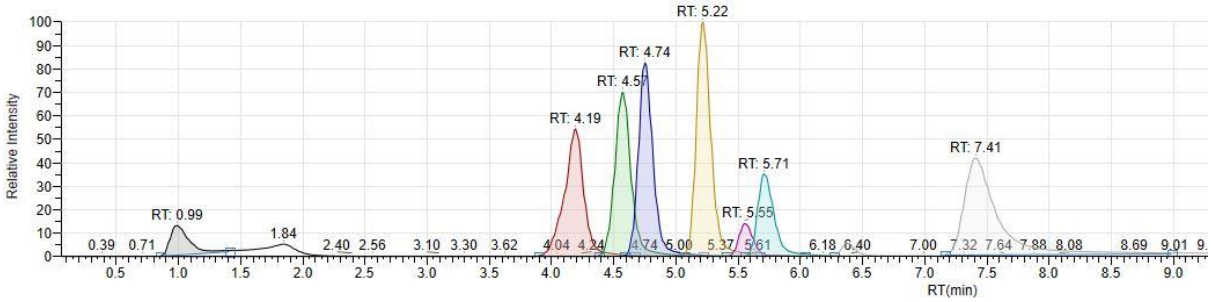


Fig. 2. A chromatogram demonstrating the separation of eight target pharmaceuticals, where RT represents the retention time (min) of each compound, with the elution order of etilefrine, methocarbamol, nevirapine, venlafaxine, carbamazepine, dexamethasone, ketoprofen, and 17β-estradiol at RT: 0.99, 4.19, 4.57, 4.74, 5.22, 5.55, 5.70, 7.41, respectively.

Method validation parameters were determined and are listed in Table 3. The R^2 of the calibration curves ranged from 0.97 to 0.99 indicating good overall linearity of the target compounds. The LODs were found to range from 1.15 pg/g for ketoprofen to 46.07 pg/g for methocarbamol whilst the LOQs ranged from 3.84 pg/g for

ketoprofen to 153.57 pg/g for methocarbamol. The recoveries of the paperboard were performed by spiking samples at 50 and 100 ng/g with the lowest recovery obtained for nevirapine being 52.63% at 50 ng/g and the highest for dexamethasone at 95.42% for 100 ng/g. The reduced recovery of nevirapine at the lower spiking level may have likely been influenced by poorer ionisation efficiency of the four nitrogen (bond acceptor) - containing nevirapine (Table 1) in the pH 2.7− 4.7 buffered mobile phase (Johnson et al., 2013).

The differences in the recoveries for the eight target compounds were likely due to differences in the solubility of the pharmaceuticals in the extraction solvent, the chemical structures, and the logP values (Table 1). The logP indicated how readily the pharmaceutical would partition between an aqueous and an organic phase (equation (1)) (Low et al., 2016). Better recovery was obtained from the pharmaceuticals having higher log P values. LogD, as defined in equation (2), is the measure of lipophilicity of ionisable compounds (Kah & Brown, 2008) and is often used to evaluate pharmaceutical partitioning in water (Kah & Brown, 2008; Landry & Crawford, 2020; Wells, 2006).

$$Log\ P\ = Log\ \frac{[neutral\ compound]_{oct.}}{[neutral\ compound]_{aq.}} \quad (1)$$

where [neutral compound] is the concentration of the compound in its neutral form at pH = 7 as a ratio in octanol (oct.) to aqueous (aq.) medium.

$$Log\ D\ = Log\ \frac{[neutral\ \ and\ ionised\ compound]_{oct}}{[neutral\ and\ ionised\ compound]_{aq}} \quad (2)$$

where [neutral and ionised compound] is the sum of the neutral and ionised concentration of the compound as a function of pH as a ratio in octanol (oct.) to aqueous (aq.) medium.

From Table 1, it was evident that for the 100 ng/g spiking concentration, the highest recovery was achieved for compounds with the highest LogD (dexamethasone and 17β-estradiol) whilst poorer recoveries were obtained for etilefrine and methocarbamol, which had significantly lower LogD values. When factoring the water solubility (Table 1), the results suggested that a fully organic extraction

solvent such as 100% methanol could improve the recoveries obtained. Another factor considered that may have influenced the recovery was suppression from matrix effects (Furey et al., 2013). The addition of sample clean-up steps would have likely reduced such matrix effects; however, it would have also introduced undesired selectivity to the suspect screening (Poole et al., 2016). The average recovery of the target analytes at the two spiking levels ranged from 70−89% for nevirapine and 17β-estradiol respectively. This was deemed analytically acceptable since the generally accepted range of recovery is 70−120% (European Commission, 2017). To date, there are no other studies on the quantification of pharmaceuticals in paper-based samples using UHPLC-Q Orbitrap HRMS, hence, the performance of the proposed analytical method could not be evaluated against another reported method. Further studies are required to expand and explore the prevalence and possible propagation of pharmaceuticals in the paper recycling chain.

Table 2

Pharmaceutical accurate mass detection

Compound	**Confirmatory Ion (m/z)**	**Monoisotopic Mass (amu)**	**$[M+H]^+$ Theoretical Mass expected**	**Observed Mass (m/z)**	**Mass tolerance (ppm)**
Etilefrine	164.1069	181.1103	182.1181	182.1176	2.77
Methocarbamol	118.0500	241.0950	242.1028	242.1023	2.23
Nevirapine	198.0147	266.1168	267.1246	267.1241	1.82
Venlafaxine	121.0649	277.2042	278.2120	278.2116	1.50
Carbamazepine	194.1175	236.0950	237.1028	237.1021	2.87
Dexamethasone	237.1272	392.1999	393.2077	393.2074	0.80
Ketoprofen	209.0961	254.0943	255.1021	255.1015	2.35
17β-estradiol	255.1372	272.1776	273.1854	273.1859	1.83

Table 3

Method validation

Compound	**R^2**	**LOD±%RSD (pg/g)**	**LOQ±%RSD (pg/g)**	**% RECOVERY ± %RSD (n = 3)**	
				Paperboard spiking level (ng/g)	
				50	**100**
Etilefrine	0.9921	14.44±11.8	48.15±11.8	86.05±1.5	68.19±9.0
Methocarbamol	0.9952	46.07±9.5	153.57±9.6	73.99±4.9	74.89±8.4
Nevirapine	0.9704	2.21±12.3	7.37±12.3	52.63±2.2	87.85±1.1
Venlafaxine	0.9988	3.27±0.4	10.90±0.4	88.49±6.9	87.55±2.7
Carbamazepine	0.9884	3.49±4.3	11.65±4.3	72.50±5.8	91.01±4.9
Dexamethasone	0.9988	31.80±7.1	105.99±7.1	83.15±1.9	95.42±2.8
Ketoprofen	0.9977	1.15±6.8	3.84±6.8	71.83±2.1	84.64±6.4
17β-estradiol	0.9985	1.91±0.5	6.37±0.5	84.20±5.9	94.48±4.6

6.3.2 Occurrence of pharmaceuticals in paper-based samples

Carbamazepine, dexamethasone, ketoprofen, and 17β-estradiol were detected and quantified in 15 of the 42 samples analysed (Fig. 3). 17β-estradiol was found to occur in the highest concentrations with its maximum level found in a paper shopping bag at 697.49 ng/g collected from a recycling facility followed by a recycling facility newspaper sample (498.28 ng/g) and an infant bathtub box from household waste (280.62 ng/g). From Fig. 3, it was evident that the target pharmaceuticals were detected more in post-consumer samples than in retail or pre-consumer samples. In this case, 58% of the target pharmaceuticals were detected in samples collected from recycling facilitates, 18% from solid waste disposal sites, and another 18% from household waste; in comparison, retail and pre-consumer samples constituted 6% and 0%, respectively. Dexamethasone was detected in a newspaper sample (241.48 ng/g) collected at a recycling facility. Carbamazepine was on the other hand, detected in retail store samples (toy box at 4.43 ng/g) and recycling facility samples (a vegetable box at 13.02 ng/g and a magazine at 2.12 ng/g). The detected pharmaceuticals were predominantly found at the household waste, recycling facilities, and solid waste disposal sites which suggested that pharmaceutical exposure likely occurred from exposure to consumers and the mingling of waste, as opposed to the use of pharmaceutical-contaminated water in the paper manufacturing process. The prominence of carbamazepine, dexamethasone, ketoprofen, and 17β-estradiol, over the other target compounds, may have also been due to their chemical properties allowing them to adhere well to paper fibre. The occurrence of 17β-estradiol could be possibly linked to naturally occurring oestrogens, oral contraceptives, and hormone therapy (Nazari & Suja, 2016). A study by Olatunji et al. (2017) reported that surface water from the city of Cape Town was found to contain estriol and 17β-estradiol with maximum concentrations of 45.5 µg/L and 15.7 µg/L, respectively (Olatunji et al., 2017). This indicated that 17β-estradiol prevalence or use in Cape Town may have contributed to higher concentrations in the samples under investigation. In recent years, 17β-estradiol has also been reported in food matrices (Pu et al., 2019; Wathudura et al., 2019). Pu et al. (2019) identified human and animal excreta, industrial waste, hospital waste, and animal residues as possible sources of 17β-estradiol in animal

and plant-derived foods (Pu et al., 2019). These same exposure pathways could interact with consumer goods such as paper and could have led to their occurrence in this study. The occurrence of ketoprofen was linked to its possible use as an anti-inflammatory drug in South Africa (Ngqwala & Muchesa, 2020). Overall, pharmaceuticals were identified in different types of paper recycling grades including newspaper, paperboard, corrugated board, and carton board, with newspaper samples found to contain three different pharmaceuticals (241.48 ng/g dexamethasone, 1.47 ng/g ketoprofen and 17β-estradiol at of maximum of 498.28 ng/g). This indicated that exposure to pharmaceuticals occurs in various paper grades with different barrier properties. Further, the identified compounds highlight that complex pathways exist between humans, consumer goods, food, industry, waste management, and the environment and that, practices such as packaging of goods and recycling of material could provide increased opportunities for contact.

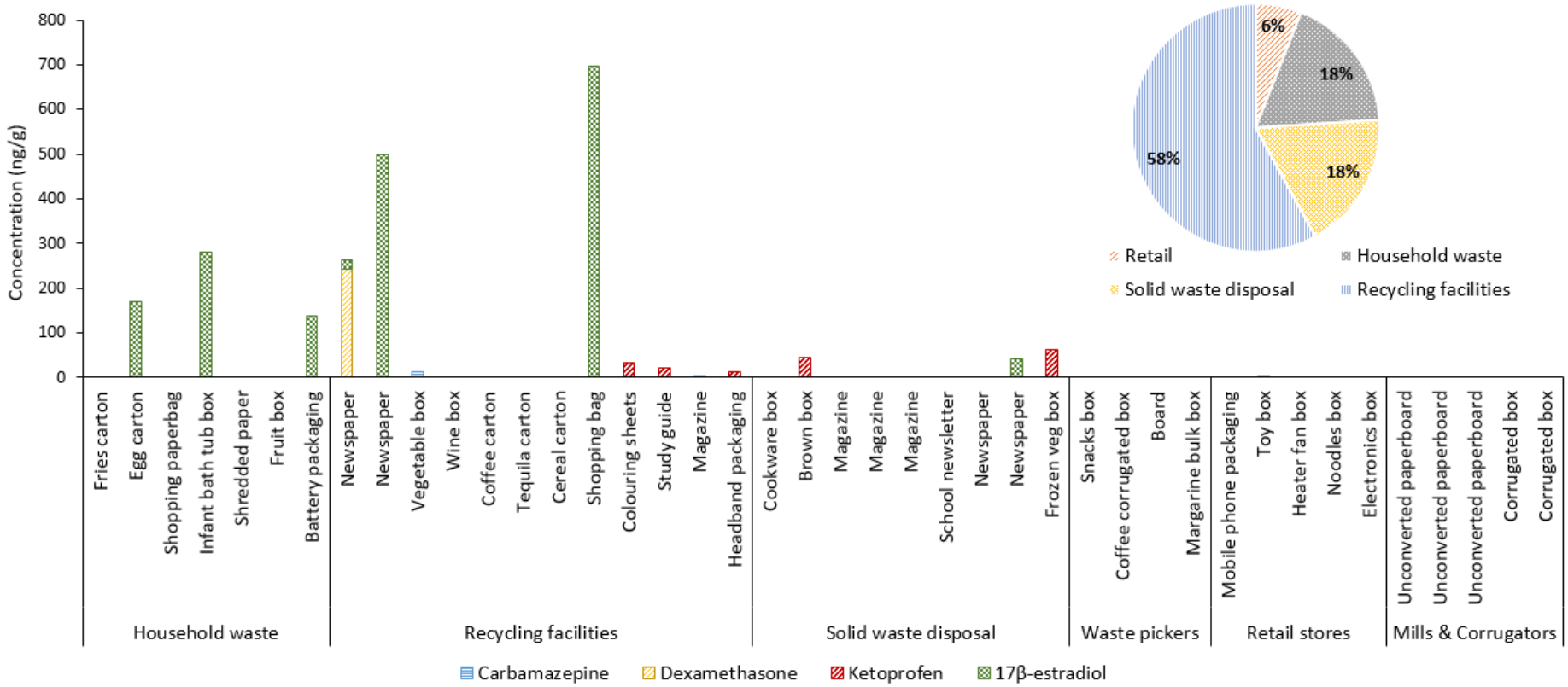


Fig. 3. Pharmaceutical occurrence in paper-based samples

6.3.3 Suspect screening of pharmaceuticals in paper-based samples

Suspect screening was performed in order to identify other possible pharmaceuticals that could be present in the paper-based samples under investigation as shown in Table 4. For this study, all other classes of compounds were not included. The suspect compounds reported were those having mass tolerance (ppm) < 10ppm, SI>700, and RSI>800, to increase the likelihood of correct identification. An illustration of the acquired extracted-ion-chromatograph (XIC) for the newspaper sample collected at a solid waste disposal site is shown in Fig. 4.

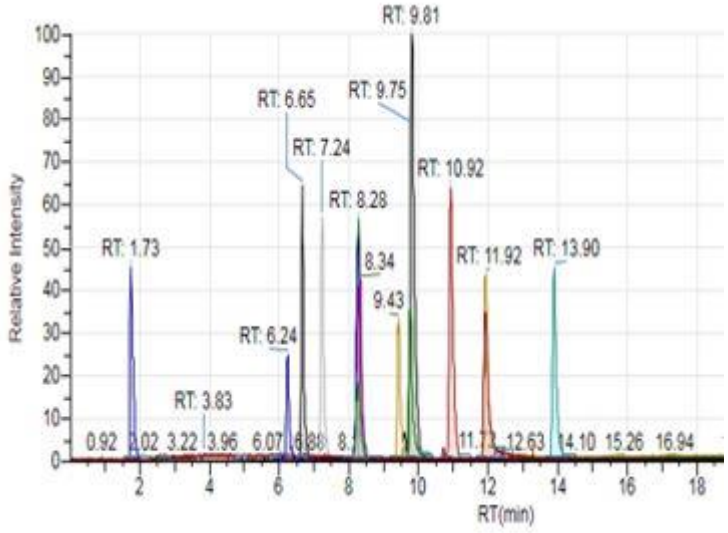


Fig. 4. XIC for newspaper sample

The therapeutic class of the suspected pharmaceutical was included in order to apportion to a possible source of contamination. A total of 14 pharmaceuticals (Table 4 and Fig. 5) belonging to different therapeutic classes were tentatively identified in 17 of the 42 investigated samples. The majority of the screened pharmaceuticals were detected from samples collected from recycling facilitates (24%) and household waste (24%). The paper grade with the most prevalent suspected occurrence of pharmaceuticals was corrugated boxes (41%), followed by cartonboard (18%). Both corrugated boxes and cartons are used extensively for packaging goods and are also integral elements of the paper recycling chain, which would likely have increased exposure opportunities. When looking beyond the therapeutic classes to the application, pharmaceuticals related to skin disorders such

as trioxsalen (Manga & Arowojolu, 2014), chlorphenoxamine (Hassan et al., 2008) and bufexamac (Aquino & Rosner, 2019) were tentatively identified. This suggested that dermal contact could have resulted in the transfer of these pharmaceuticals to paper materials. The identification of several different anabolic steroids such as 17β-nandrolone decanoate, androsterone sulphate, and boldenone at recycling facilities, solid waste sites, and in a mill, sample suggest that certain pharmaceuticals may be more well retained in the fibre lattice of paper throughout the paper recycling chain. Integrated peak areas in the acquired chromatograms were used as measures of the response function of the UHPLC corresponding to the unknown concentrations (Asnin, 2016) of the suspected pharmaceuticals. In the absence of chemical standards, the peak areas of the suspected pharmaceuticals were plotted to give an indication of the possible prevalence (Fig. 5). The highest peak area was for tamoxifen (2.19E+08) detected in a study guide collected at a recycling facility. The bufexamac detected in the margarine bulk box from a waste picker had the lowest detected area in the suspect screening with a peak area of 3.12E+07. Samples collected from recycling facilities, waste pickers, and household waste were found to have the highest areas in the suspect pharmaceuticals. The higher prevalence of suspect pharmaceuticals in post-consumer samples correlated with the quantified data (Fig. 3) where the highest concentrations were detected in samples collected from recycling facilities and household waste. Although the peak area gave an indication of possible concentration differences for the same compound differentiation, analytical standards would be necessary for accurate comparisons.

Table 4

Suspect screening of pharmaceutical compounds

Pharmaceutical	Therapeutic Class	Sample Description	Site	RT (min)	Chemical Formula	Monoisotopic Mass (amu)	Expected Mass (m/z)	Observed Mass (m/z)	Mass tolerance (ppm)	SI	RSI
Minocycline	Antibiotic	Fries carton board	Household waste	8.29	$C_{23}H_{27}N_3O_7$	457.1849	458.1927	458.1964	1.17	737	998
		Heater corrugated box	Retail					458.1964	8.09	743	999
		Cookware box	Solid waste site					458.1963	7.84	725	999
		Coffee corrugated box	Waste picker					458.1967	8.75	747	997
Trioxsalen	Psoralen	Egg carton	Household waste	4.59	$C_{14}H_{12}O_3$	228.0735	229.0813	229.0817	2.28	871	999
		Snacks box	Waste picker					229.0798	6.72	867	999

Bufexamac	NSAID	Margarine bulk box	Waste picker	2.32	$C_{12}H_{17}NO$	223.1207	224.1283	224.1278	3.22	985	985
Flunixin	NSAID	Shopping paperbag	Household waste	7.96	$C_{14}H_{11}F_3N_2O_2$	296.1345	297.1423	297.1418	1.81	737	815
Triflupromazine	Antipsychotic	Shredded paper	Household waste	9.10	$C_{18}H_{19}F_3N_2S$	352.1584	353.1662	353.1656	1.52	758	984
		Coffee corrugated box	Waste picker					353.1657	1.43	788	990
Donepezil	Psychiatric	Newspaper	Solid waste	9.81	$C_{24}H_{29}NO_3$	379.2143	380.2221	380.2199	5.56	765	993
Prazepam	Psychotropic	Shopping paper bag	Recycling facility	4.69	$C_{19}H_{17}ClN_2O$	324.2199	325.2277	325.2272	1.65	925	937
		Coffee corrugated box	Waste picker					325.2272	1.65	927	927
		Noodles box	Retail					325.2272	1.65	951	955
		Colouring sheets	Recycling facility					325.2271	1.96	940	949

Tamoxifen	Hormonal	Study guide	Recycling facility	6.29	$C_{26}H_{29}NO$	371.2255	372.2333	372.2328	1.44	702	985
Chlorphenoxamine	Antihistamine	Tequila carton	Recycling facility	4.07	$C_{18}H_{22}ClNO$	303.1381	304.1459	304.1468	3.05	901	999
Beclomethasone	Corticosteroid	Newspaper	Solid waste	5.65	$C_{22}H_{29}ClO_5$	408.1642	409.1720	409.1715	1.31	772	998
17β-Nandrolone decanoate	Anabolic-androgenic steroid	Shopping paperbag	Recycling facility	11.72	$C_{28}H_{44}O_3$	428.3650	429.3728	429.3722	1.25	775	929
Androsterone sulphate		Study guide	Recycling facility	10.45	$C_{19}H_{30}O_5S$	370.1814	371.1892	371.1896	1.06	716	928
		Newspaper	Solid waste					371.1899	1.95	769	922
Boldenone		Newspaper	Solid waste	6.79	$C_{19}H_{26}O_2$	286.1933	287.2011	287.2002	3.04	795	870
		Unconverted paperboard	Mill					287.2005	1.87	767	867
Theobromine	Vasodilator	Margarine bulk box	Waste picker	2.65	$C_7H_8N_4O_2$	180.0647	181.0725	181.0732	3.65	902	999

	Fries cartonboard	Household waste		181.0732	3.65	898	999

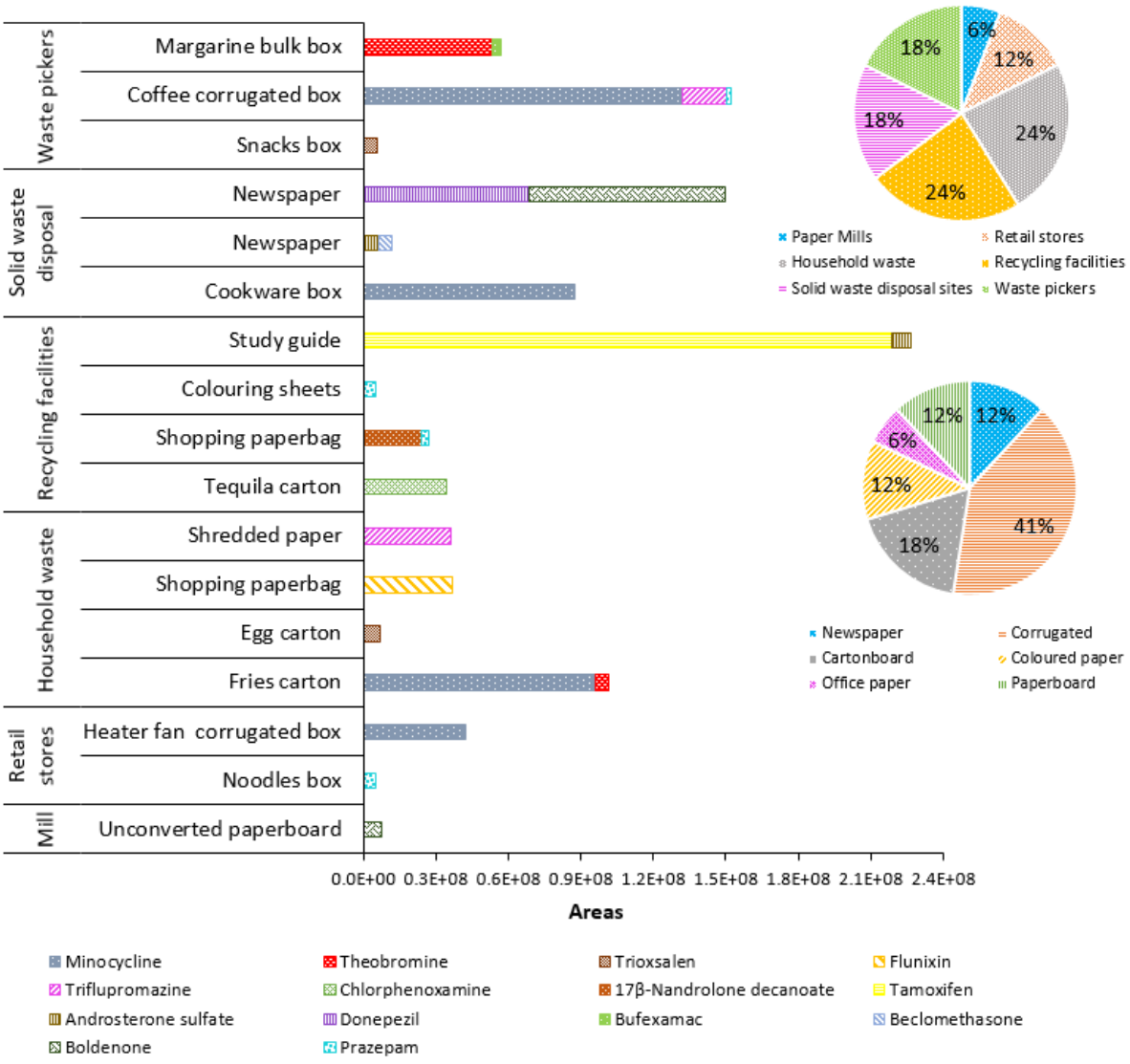


Fig. 5. Possible pharmaceutical prevalence in investigated samples.

6.4 Conclusion

Overall, this study reported a suitable analytical method that proved to be useful in the analysis of both targeted pharmaceuticals and suspect screening of the same compound classes in paper-based samples. The analytical approach was based on UAE of pharmaceuticals followed by the analysis with UHPLC-HRMS. This work highlighted the importance of understanding the chemical interface between industry, consumers, and the environment. Waste management protocols used for the recovery, collection, sorting, and co-mingling of waste material likely influenced the presence of pharmaceuticals in the paper samples. The highest

concentration of pharmaceuticals was identified in post-consumer samples in household waste and at recycling facilities with 17β-estradiol being the most prevalent pharmaceutical. The absence of the target pharmaceuticals in pre-consumer samples suggested that pharmaceutical contamination may not be as substantial in the paper manufacturing and converting stages. Suspect screening enabled tentative identification using the power of HRMS. The suspect screening indicated the need for accurate quantification with the use of reference standards. Although trace-level concentrations of pharmaceuticals were identified, more work is needed to understand the risk posed by pharmaceuticals, the possible effects on human health, the different exposure pathways, and how consumer usage and contact patterns affect the prevalence of these compounds. This study indicated the proliferation of pharmaceutical contamination beyond environmental media. It further emphasized the importance of building more knowledge into emerging contaminants that may be present in paper-based material and the crucial need to influence policy driven towards proper waste management protocols that can improve the quality of recycled material for consumers and the environment.

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Declaration of interests

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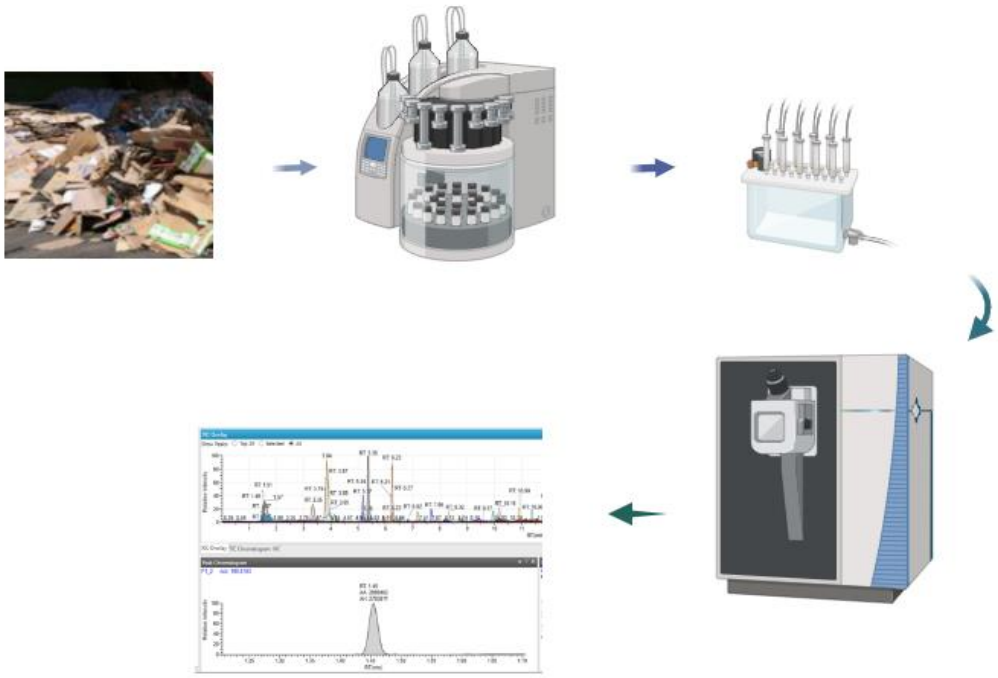
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CHAPTER SEVEN

7 PAPER 4

This paper titled “Determination of per- and polyfluoroalkyl compounds in paper recycling grades using ultra-high performance liquid chromatography – high resolution mass spectrometry” was published in **Environmental Science and Pollution Research** 2024) 31:30126–30136. https://doi.org/10.1007/s11356-024-33250-9. A validated targeted analysis method was developed for the quantification of perfluorocarboxylic acids, perfluorosulphonic acids and telomer sulphonates.

GRAPHICAL ABSTRACT



Determination of per- and polyfluoroalkyl compounds in paper recycling grades using ultra-high performance liquid chromatography – high resolution mass spectrometry

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Abstract

Globally, PFAS-related research on paper products has focused on food packaging with less consideration on the presence of PFAS at different stages of the paper recycling chain. This study analysed the prevalence of per- and polyfluoroalkyl substances (PFAS) in paper grades used for the manufacture of recycled paperboard. The presence of PFAS was attributed to the use of PFAS-containing additives, consumer usage, exposure to packed goods as well as contamination during mingling, sorting, collection, and recovery of paper recycling material. Q Orbitrap mass spectrometry was used to analyse the paper samples after accelerated solvent extraction and solid phase extraction. The distribution and possible propagation of 22 PFAS were determined in pre-consumer, retail, and post-consumer paper products. Post-consumer samples had the highest combined average concentration (ΣPFAS) at 213 ng/g whilst the ΣPFAS in retail (159 ng/g) and pre-consumer samples (121 ng/g) was detected at lower concentrations. This study showed that waste collection and recycling protocols may influence PFAS propagation and that measures must be developed to minimise and possibly eliminate exposure opportunities.

Keywords: PFAS; recycled paper; pollutant prevalence; ultra trace analysis; waste management; analytical method

7.1 Introduction

Over the past five years, more than 50 million tons of paper products were recycled annually, with almost half of these being used to manufacture corrugated boxes (WEF, 2022). In the same period, the global paper recycling rate was 68% (Van Ewijk et al., 2021), with South Africa having an average five-year paper recovery rate of 67% (PAMSA, 2022). The growing emphasis on circular economy and thereby paper recycling (Semple et al., 2022) means that it is imperative to investigate how potentially toxic substances such as per- and polyfluoroalkyl substances (PFAS) propagate across the paper recycling value chain. PFAS may be introduced during the initial manufacture of packaging if they are applied as moisture and grease repellents (Schultes et al., 2019). In addition to the manufacturing stage, PFAS exposure may occur during transportation, storage, use, and disposal of paper products as well as from the mingling of recovered paper with other waste materials during collection, sorting, and repulping (Reinhart et al., 2023). In addition, PFAS present in the soil, air, and water (Solan et al., 2023) may interact with paper destined for recycling. PFAS have been shown to be present at waste disposal sites and landfills (Helmer et al., 2022), and can thereby be present at recycling facilities where recycling includes paper recovered from solid waste disposal sites and landfills. The true contribution of PFAS from paper recycling processes is currently not fully understood in developed and developing countries (Geueke et al., 2018).

PFAS, often referred to as “forever chemicals”, are classified as very persistent, bioaccumulative, and toxic (Cousins et al., 2020; Chambers et al., 2021; Liu & Sun, 2021; Brunn et al., 2023). Long-chain PFAS, which typically contain fluoroalkyl chains of six or more carbons (Baldwin et al., 2023; Chambers et al., 2021), possess extremely stable carbon-fluorine bonds, making them more resistant to degradation (Chambers et al., 2021). These longer-chain PFAS have increased hydrophobicity which promotes their retention in paper’s organic, cellulose lattice (Liu & Sun, 2021). Initial research into PFAS suggested that PFAS compounds with alkyl chain lengths of five carbons or less were significantly less bioaccumulative and less toxic (Quinete et al., 2010). This led manufacturers to a shift towards shorter-chain PFAS which have now also been shown to be very stable, (Brendel et al. 2018), toxic (Lu

et al., 2017; Solan et al., 2023) and persistent in the environment (Vierke et al., 2014; Brendel et al., 2018). These short-chain PFAS often have a higher mobility in aqueous environments owing to their higher solubility (Vierke et al., 2014). Since paper manufacturing is associated with high water use (Blanco et al., 2013), PFAS may easily circulate during the manufacture of recycled paper.

The analysis of PFAS in different paper grades used in the manufacture of recycled paper is important to further understand the global occurrence of PFAS. Globally, PFAS-related research on paper products has been focused on food packaging (Trier et al., 2011; Rosenmai et al., 2016; Curtzwiler et al., 2021; Timshina et al., 2021) with less focus on other grades of paper such as newspapers, magazines, and packaging used for non-food applications (Glüge et al., 2020). This study aimed to fill this gap in understanding the possible presence of PFAS in different paper recycling grades used to manufacture recycled paperboard. This investigation is crucial as it addresses the challenges of paper recycling processes by pinpointing the possibility of PFAS circulation through the mechanisms employed in solid waste management. The findings of the present study are important for showcasing a need to develop measures that could assist in minimising and eliminating PFAS exposure opportunities.

7.2 Materials and methods

7.2.1 Chemicals and buffers

The chemicals and buffers used were LC-MS grade methanol (Anatech, Cape Town, South Africa), water (Merck, Johannesburg, South Africa), ammonium formate (Merck, Johannesburg, South Africa), HPLC grade toluene (Merck, Johannesburg) and analytical grade ammonium hydroxide (Merck, Johannesburg, South Africa). Certified reference standards made up in methanol were obtained from AccuStandard (Stargate, Johannesburg, South Africa), the details of which are shown in Table S1. The mixture standard contained both short- and long-chain per- and polyfluorocarboxylic acids (PFCAs) and sulphonic acids (PFSAs). Perfluorohexanesulphonic acid (PFHxS) and Perfluorooctanesulphonic acid (PFOS) were present as linear & branched isomers with both isomers considered in the calibration standards and quantification. The calibration standards were made

up in methanol in two concentration ranges, from 0.2 - 120 µg/L and from 30 - 450 µg/L.

7.2.2 Sampling

Thirty-nine paper samples were collected from Cape Town, South Africa, and consisted of various grades of paper used for recycling (Fig. 1 and Table S2). The pre-consumer and retail samples consisted only of boards, while the post-consumer samples consisted of paper grades typically used in the manufacture of recycled boards. These included cartonboards, newspapers, corrugated boards (boxes), office paper, and magazines. The pre-consumer samples were sourced directly from paper mills and paper conversion sites, whereas retail samples were collected from South African grocery stores. Post-consumer samples were collected at recycling facilities, solid waste disposal sites, household waste, and informal waste pickers.



Fig. 1. Overview of paper recycling chain sample collection sites

7.2.3 Sample preparation

Paper samples were prepared in triplicate (1 g each), followed by accelerated solvent extraction (ASE) using a Dionex 350 ASE system (Anatech, Cape Town, South Africa). The extraction method was optimised for ethanol: methanol solvent combination (Table S3), with the final optimised conditions being a 3:2 ethanol: methanol combination at 70°C oven temperature for 3 cycles at 12 min each (MacLennan et al.2019). After extraction, the sample was evaporated to 1 mL under nitrogen at 40 °C using a Biotage TurboVap (Anatech, Cape Town, South Africa) in preparation for SPE clean-up. The SPE process was based on weak ionic exchange (WAX) mechanism. The SPE steps were guided by the United States (U.S) Environmental Protection Agency (EPA) Draft Method 1633, EPA Method 533 and Barola et al. (2020) (Barola et al., 2020; EPA, 2021; Wendelken & EPA, 2018). For this study, 500 mg sorbent bed/ 6 mL Enviro-Clean WAX SPE cartridges (Stargate Scientific, Johannesburg, South Africa) were used. The cartridges were mounted on a SPE manifold (Stargate Scientific, Johannesburg, South Africa) and operated under vacuum using a DryVac 400 vacuum pump (Air & Vacuum Technologies, Johannesburg, South Africa). The SPE was initiated by conditioning the cartridges with 3 mL of methanol followed with 5 mL of 0.1 M ammonium formate buffer. This was followed by loading 500 µL of sample and elution of analytes using 6 mL of 1% methanolic ammonium hydroxide. The eluted compounds were concentrated to 1 mL under 40 °C nitrogen and filtered into a polypropylene vial with 0.22 µm filter (Stargate Scientific, Johannesburg, South Africa) before analysis by UHPLC-HRMS.

7.2.4 Instrumentation

High resolution LC-MS analysis was achieved using a Thermo Scientific Vanquish UHPLC^{+} Q Exactive Focus Orbitrap (Anatech, Cape Town, South Africa). A Hypersil Gold aQ 100mm x 2.1mm x 1.9 µm column and Hypersil Gold 50mm x 3 mm x 1.9 µm delay column (Anatech, Cape Town, South Africa) were used at 35 ^{o}C. The autosampler temperature was set to 7 ^{o}C. The instrument operating method was adapted from (Curtzwiler et al., 2021; Silva et al., 2021; Zhu & Walker, 2020) with the final optimised conditions consisting of solvent A as 0.1% formic acid in

water and 10 mM ammonium formate in methanol as solvent B (Curtzwiler et al., 2021; Silva et al., 2021; Zhu & Walker, 2020). The initial flowrate was 0.400 mL/min in 30% solvent B which increased to 100% solvent B at 13 min (at 1 mL/min), held until 17 min, before returning to 30% solvent B at 21.1 min (Table S4). The acquisition mode was full scan with Data Dependent acquisition (ddMS^2) in negative mode. The PFAS transitions and retention times are tabled in Table S5.

7.2.5 Quality assurance

PFAS are ubiquitous compounds (Evich et al., 2022) and are used extensively in analytical chemistry laboratory items such as PTFE-lined reagent bottle caps, O-rings, septa linings and syringe filters. It was therefore important to investigate latent PFAS contamination in the PFAS analysis workflow. The necessary steps were included to measure the possible contamination from sample collection (Table S6) and the UHPLC-HRMS system (Table S7). Preparation blanks were analysed to subtract the analyte concentrations found in the blanks from the detected concentrations in the samples (Table S8). Additionally, a stringent washing and cleaning protocol was established using toluene, 1% methanolic ammonium hydroxide, and methanol. The target compounds absent in the preparation blanks were quantified using external calibration quantification, whereas those found to be present were semi-quantitatively determined by subtracting the preparation blank from the detected concentration. PFBA, PFPeA, PFDoA, PFTeDA, PFBS, PFOS, PFNS, PFDS, and 4:2FTS were identified as system contaminants and were semi-quantitatively determined. To evaluate the external calibration curves, the coefficient of determination (R^2) was used as an indicator of linearity. The limit of detection (LOD) and limit of quantification (LOQ), which were used as sensitivity indicators, were measured at signal-to-noise ratios of 3 and 10, respectively. Relative recovery and %RSD were used to evaluate the accuracy and precision of the method, respectively. Virgin, unconverted, unprinted paper and paperboard samples were used to evaluate the method performance by spiking the samples at three different concentrations in triplicate. The data was corrected for the relative recoveries obtained by considering the unspiked paper and paperboard samples. Due to the use of external standards and expected variability, the quantified concentrations were reported with their associated uncertainty using equation (1):

$$U = \sqrt{s^2 + u_{matrix}^2 + u_{recovery}^2 + u_{prep.\ blanks}^2} \qquad (1)$$

where s^2 is the variance of the sample, u_{matrix} is the uncertainty of the sample repeatability due to matrix effects, $u_{recovery}$ is the uncertainty of the recovery of the target compound, and $u_{prep.\ blank.}$ is the uncertainty related to the preparation blanks (Rasul et al. 2017; Ellison & Williams, 2012). The equations related to each term are shown in equations (S1) to (S4).

7.2.6 Data analysis

Instrument data analysis was performed using Thermo Scientific Xcalibur™. Further data analysis was performed using Microsoft Excel, MetaboAnalyst 5.0, and TIBCO Statistica 14.0. The statistical analysis aimed to identify possible correlations between the target analytes. TIBCO Statistica 14.0. was used to determine if the data followed normal or non-normal distributions. For normally distributed data, the Pearson correlation coefficient would be employed, while the Spearman rank correlation, a non-parametric correlation, would be used for non-normal data that contains outliers (Leon, 1998). Once established, the Spearman correlation was plotted using MetaboAnalyst 5.0. The Spearman rank equation is defined as

$$r_s = 1 - \frac{6\sum d^2}{n(n^2-1)} \qquad (2)$$

where the Spearman rank coefficient r_s is calculated by determining the sum of the squared differences in distance (d^2) for n observations. A value of $r_s = 1$ indicates a linear positive relationship, while a value *of* $r_s < 0$ indicates a negative relationship between two variables, where an increase in the value of one variable would be associated with a decrease in the second variable (Leon, 1998). Hierarchical clustering analysis was performed in conjunction with Spearman correlation. Hierarchical clustering allows for similarity analysis of one sample to the entire dataset and can provide insight into any heterogeneity or homogeneity present in different groups (Kumar et al., 2014).

7.3 Results and discussion

7.3.1 Method validation

The R^2 of the calibration curves ranged from 0.98 for PFHpA to 0.99 for PFDS, indicating acceptable overall linearity of the target compounds (Table S9). The relative recoveries of paper and board were determined by spiking samples at 10, 20, and 100 ng/g, 20, 40, and 200 ng/g, and 40, 80, and 400 ng/g, depending on the concentration present in the standard mixture**.** Relative recoveries ranged from 55% for PFHxA to 139% for PFOA (except for 6:2 FTS) (Table S9). For the target PFAS investigated, 19 of the 22 fell within the generally accepted range of 70–130 % (Srivastava et al.2022). PFHxA (10 ng/g paperboard spike), PFOA (10 ng/g paperboard spike), and 6:2 FTS showed poor recovery. This may have been due to the lack of isotopically labelled internal standards that would have likely corrected any matrix effects that would have resulted in changes in ionisation. According to Harris et al. (2022) and Rawn et al. (2022), the use of isotopically labelled internal standards is critical in ensuring absolute quantification and correcting for matrix effects (Harris et al., 2022; Rawn et al., 2022). Other factors, such as SPE interaction, the influence of the buffer solvent system, interaction with other PFAS compounds present, and salts, ions, and organic matter in the paper samples, may have further influenced the recovery of these target PFAS (Zabaleta et al., 2016; Kaiser et al., 2020; Harris et al., 2022). The %RSD for the relative recoveries ranged from 1.0 to 9.8%, indicating acceptable precision (Srivastava et al., 2022). The method LODs and LOQs were found to be generally lower for the compounds present in the lower concentration in the calibration standard mix with LODs ranging from 1.47 pg/g for PFDA to 10.1 pg/g for PFUnA for compounds present as 2 µg/mL in methanol (Table 1). For the compounds present in larger concentrations, the LODs ranged from 11.2 pg/g for PFPeA to 53.1 pg/g for PFBA. In addition to differences in carbon chain lengths and chemical structures, the stability and possible interactions of the different PFAS compounds in methanol may also have contributed to the differences found in the LOQs and LODs. To date, there have been limited studies on the quantification of paper-based samples using UHPLC Orbitrap HRMS. However, most studies have focused on the use of LC-MS/MS or LC-QTOF-MS (Zabaleta et al., 2016; Zabaleta et al., 2020; Blanco-

Zubiaguirre et al., 2021; Boisacq et al., 2023; Vera et al., 2024).The LODs in this study were thus compared with the analysis of PFAS in food matrices and landfill leachate, where the instrument of analysis was an HRMS Q Orbitrap. This study achieved more sensitive detection limits for common PFAS (Rawn et al., 2022; Rehnstam et al., 2023). Rawn et al. (2022) reported LOQs ranging from 18 g/g food for L-PFDS to 12.4 ng/g PFBA food (Rawn et al., 2022). In this study, the limits of quantification ranged from 0.0049 ng/g paper for PFDA to 0.18 ng/g paper for PFBA, further highlighting the sensitivity achieved in this study.

7.3.2 Occurrence of PFAS

The combined sum of average concentrations (ΣPFAS) of the 22 analysed PFAS compounds was highest for post-consumer samples (213 ng/g), followed by retail samples (159 ng/g) and pre-consumer samples (121 ng/g), as shown in Fig. 2. Overall, PFAS contamination increased from pre-consumer to post-consumer, with the highest concentration associated with post-consumer samples where recovered material had likely interacted with the environment and possibly mingled with other waste materials. The pre-consumer samples analysed consisted of samples made with a recycled fibre component, whereas the retail and post-consumer samples were expected to contain virgin, mixed, and/or recycled fibre. The occurrence of PFAS in these samples was strongly related to PFAS intentionally and/or unintentionally used in manufacturing, retained PFAS from recycling; and in retail samples, exposure from transport, distribution, and packed goods. When looking at the categorical box and whiskers chart plotted using Statistica ® (Table S10), it was further evident that more PFAS were detected in post-consumer samples, with the categorical data being found to statistically follow normal distributions (Fig. S1 to Fig. S22). In terms of the PFAS compounds, 6:2 FTS was the most prevalent target analyte with the highest average concentration of 55.2 ng/g for post-consumer samples, 34.3 ng/g for retail and 22.1 ng/g for pre-consumer samples. This 6-fluoroalkyl chain telomer has become a predominant polymer processing alternative to PFOS and PFOA (Lu et al., 2017; Schwartz-Narbonne et al., 2023; Solan et al., 2023) In a study by Dueñas-Mas et al. (2023) on food packaging in fast-food restaurants in France, 6:2 FTS and PFHxA were detected in all 47 samples analysed (Dueñas-Mas et al., 2023). It has also been reported in fast-food packaging

in the U.S. (Schaider et al., 2017). This corroborated the prevalence of 6:2 FTS in this study. It is important to note that matrix enhancement effects may have given results that were biased high due to the high 6:2 FTS recovery rate obtained. Along with 6:2 FTS, PFBA, PFHxA, PFDoA, and PFTeDA were also frequently detected in the samples. This highlighted the possible circulation of short-chain PFAS. According to Palma et al. (2022) and Rehnstam et al. (2023), shorter-chain PFAS such as PFPeA, PFHxA and PFBA are the main degradation products of both PFOA and PFOS in the environment (Palma et al., 2022). PFPeA and PFHxA are common breakdown products of stain- and grease-proof coatings in food packaging and household products (Liu & Liu, 2016).

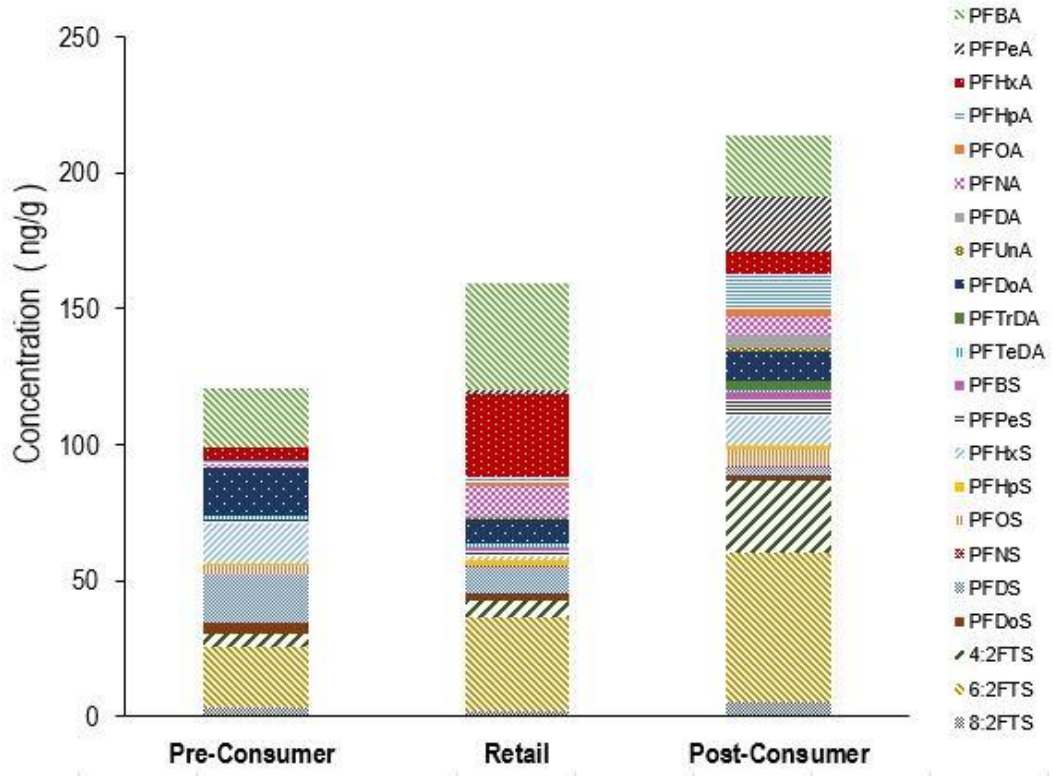


Fig. 2. Overview of ΣPFAS in pre-consumer, retail and post-consumer samples

The PFAS range was plotted to compare the ranges of the detected PFAS (Fig. 3). The smallest range was for PFNS from (0 - 0.04 ng/g) and the largest was for 6:2 FTS (0 – 354.5 ng/g). The majority of the PFAS compounds detected were below 50 ng/g; with PFDoA (58.3 ± 0.5 ng/g for a recycling facility coffee box), PFPeA (70.4 ± 3.1 ng/g for a waste picker corrugated box), PFHxA (156.9 ± 9.6 ng/g for a

retail chocolate box) and 4:2FTS (164.79 ± 7.1 ng/g for the same waste picker corrugated box) all being higher than 50 ng/g. In comparison, the PFAS concentrations reported in Dueñas-Mas et al. (2023) were considerably lower in food packaging with concentrations detected found to be less than 10 ng/g (Dueñas-Mas et al., 2023).

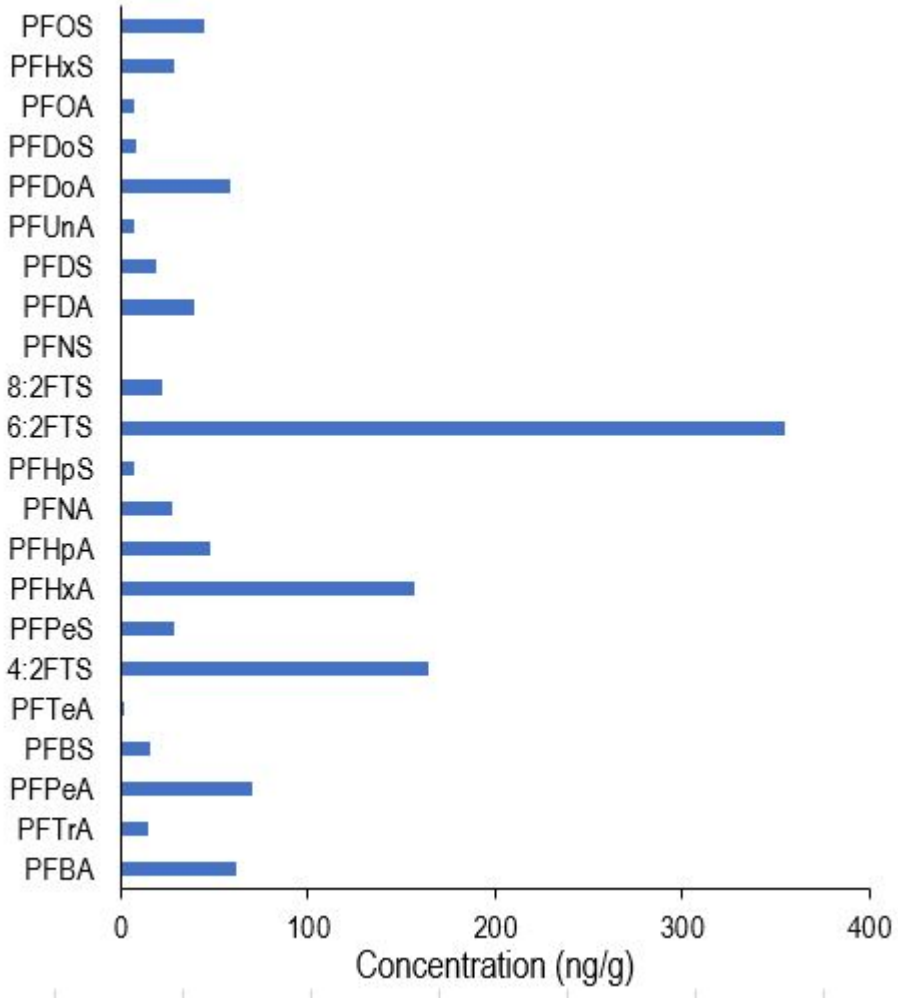


Fig. 3. Target PFAS concentration range

7.3.3 PFAS profile of samples

The PFAS profiles of the samples are plotted in Fig. 4 for the detected concentrations (Tables S11 and S12). When examining the individual PFAS in specific samples, the three highest ΣPFAS was found in post-consumer samples; namely a recycling facility tequila carton (ΣPFAS of 647.9 ng/g), a recycling facility newspaper (ΣPFAS of 400.2 ng/g) and a waste picker corrugated food box

(ΣPFAS of 548.0 ng/g). The corrugated food box had the highest number of different PFAS detected with 21 of the 22 quantified PFAS detected. An egg carton collected from household waste was found to contain 18 of the 22 quantified PFAS detected, albeit in smaller combined concentrations (ΣPFAS of 127.6 ng/g) than the waste picker corrugated food box. The lowest concentration of combined PFAS concentration samples was found in a newsletter collected at a solid waste disposal site (ΣPFAS of 2.6 ng/g), a recycling facility cereal carton (ΣPFAS = 14.5 ng/g), a colouring book cover (ΣPFAS = 17.2 ng/g) and a recycling facility corrugated fruit box (ΣPFAS 31.9 ng/g). Among the retail samples, a chocolate carton had the highest combined PFAS concentration (ΣPFAS = 235.1 ng/g) with PFHxA being the dominant PFAS. Across the paper recycling chain, the average ΣPFAS in the corrugated boxes increased from pre-consumer (99 ng/g) to retail (102 ng/g) to post-consumer (145 ng/g). All samples analysed in this study were found to contain PFAS, further demonstrating the prevalence of PFAS compounds. This differed Zabaleta et al. (2020) and other findings related to targeted quantification (Zafeiraki et al. 2014; Zabaleta et al. 2016), where the majority of the food packaging material was found to contain PFAS at very low concentrations or not detected at all. However, it correlated with Dueñas-Mas et al. (2023) and Sapozhnikova et al. (2023). In the study by Sapozhnikova et al. (2023), PFHpA, PFDA, 6:2 fluorotelomer phosphate diester, and PFHxS were the most frequently detected PFAS (Sapozhnikova et al. 2023). These comparisons showed that the detection of PFAS may be dependent on the region, circulating PFAS, exposure pathways, analysis protocols, and analytical method sensitivity.

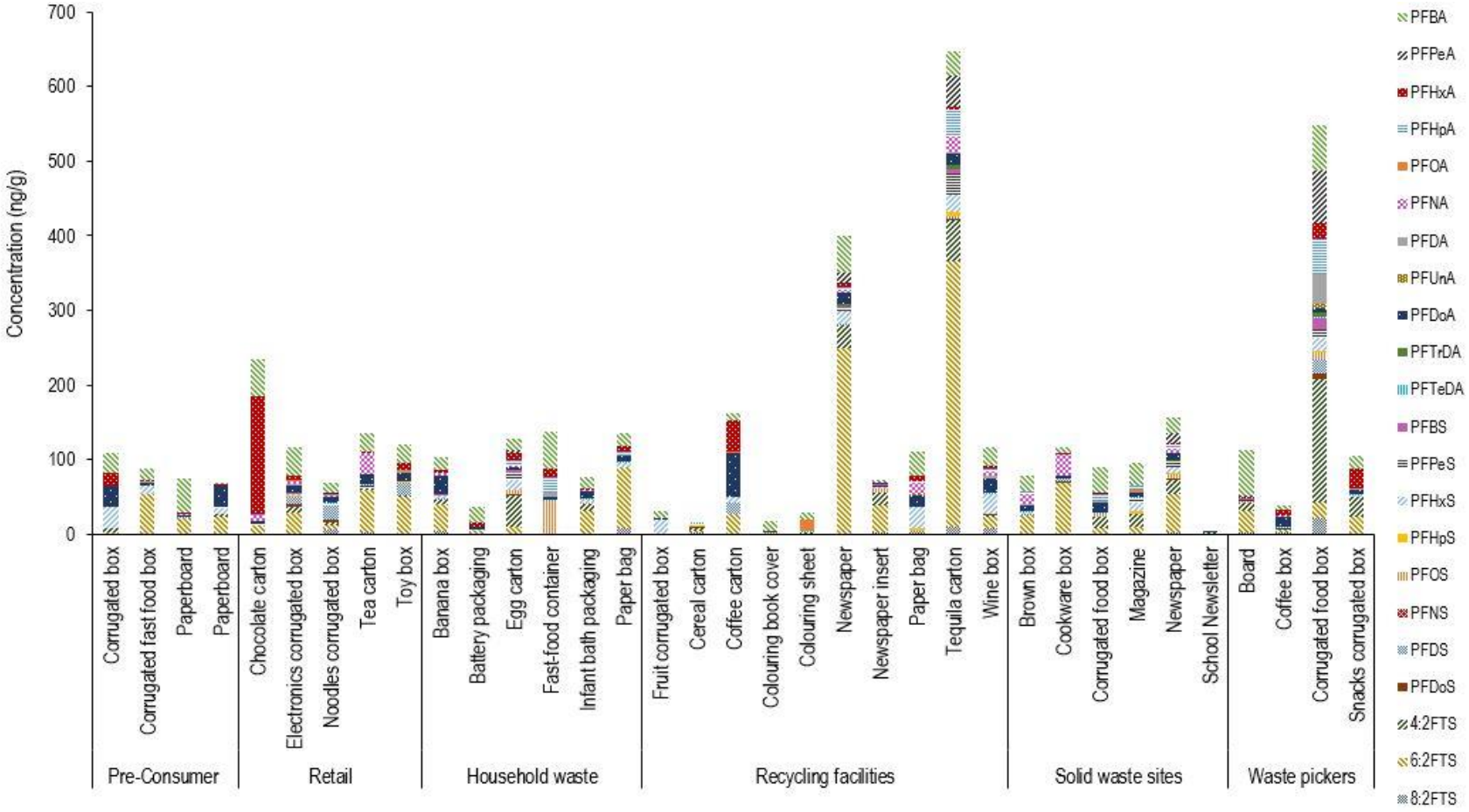


Fig. 4. ΣPFAS concentration profile of samples

The uncategorised data followed non-normal distributions with outliers (Fig. S23). Spearman rank correlation (Equation (1)) was used as the distance measure for the correlation heat map which was constructed with its associated dendrogram using MetaboAnalyst 5.0. In Fig. 5, a correlation of 1 (shown in dark red) represented a directly proportional relationship and -0.4 indicated the most negative correlation, shown in dark blue. The correlation between the different PFAS under investigation showed that the strongest correlation was between PFPeA and PFTrDA (0.69) and between 8:2 FTS and PFDoS (0.30). This indicated that the presence of PFPeA was accompanied by the detection of PFTrDA in the same sample. Furthermore, the detection of PFTeDA was associated with the presence of PFDA and PFUnA. The PFAS found to likely co-occur to some extent were PFNA, PFHpS, PFDS, PFBS, 8:2 FTS, and PFDoS. Conversely, PFTeDA and PFHpS had a strong negative correlation at -0.261. A hierarchical clustering dendrogram as shown in Fig. 6. was based on the principle that variables with similar numerical values would also be close to each other in space (Kumar et al., 2014). The dendrogram indicated distinct clustering in the presence of several target PFAS in various papers. For instance, it could be seen that PFTeDA, PFDA, PFUnA, PFOA and PFDoA clustered together when compared to the remaining target analytes. In addition, further clustering was evident between PFTeDA and PFDA with PFUnA compared to PFOA and PFDoA. The investigation of such clustering was beneficial for understanding the detection of numerous types of poly- and perfluorocarboxylic and sulphonic acids in different paper samples and environmental media (Trier et al., 2011; Zabaleta et al., 2020; Bai & Son, 2021; Kurwadkar et al., 2022; Bugsel et al., 2022). This further suggested that it would be difficult to isolate a single PFAS compound for targeted removal, for instance, without determining all possible co-occurrences.

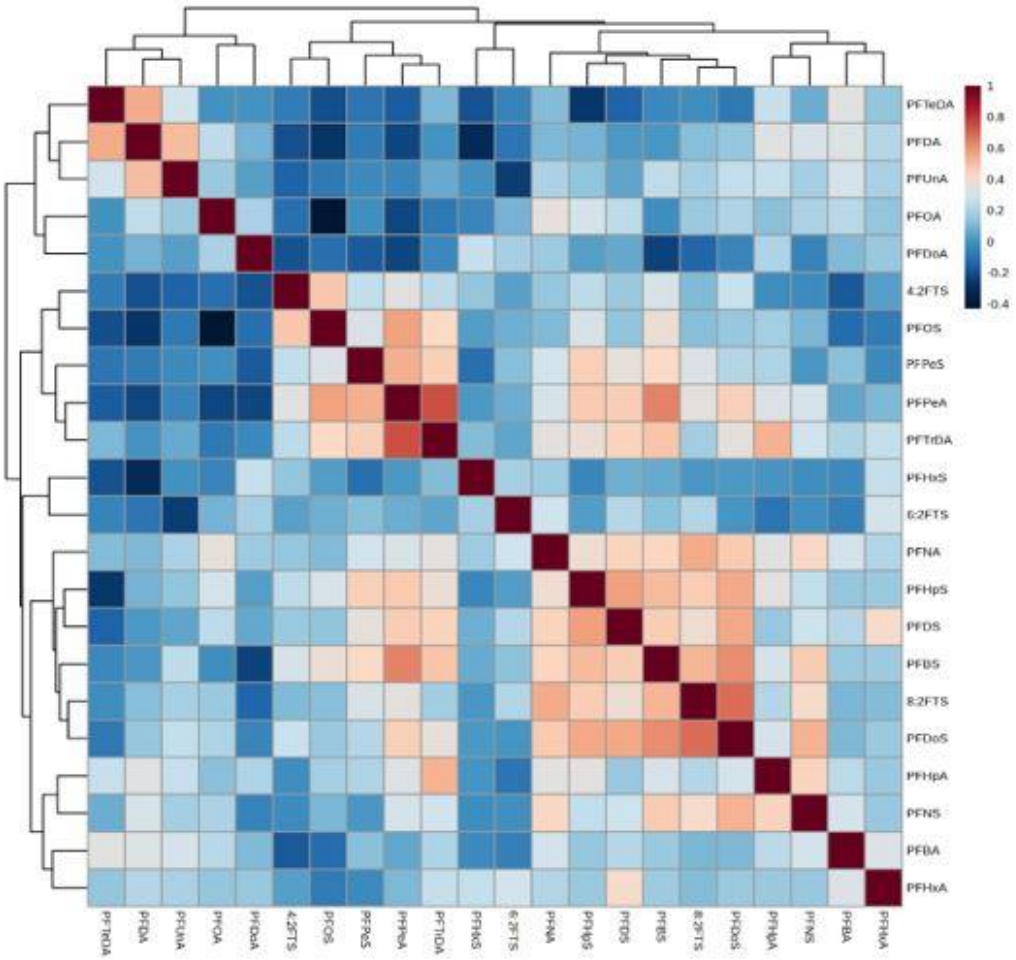


Fig. 5. PFAS compounds correlation heat map

7.3.4 Stockholm-listed PFAS

In 2009, PFOS and its salts were the first PFAS to be listed in the United Nations Stockholm Convention list of persistent organic pollutants. The listing of PFOA followed in 2019, with PFHxS formally listed most recently in 2022 (UNEP, 2019b). When looking specifically at the Stockholm Convention-listed PFAS, the highest detection was at 19.9±2.1 ng/g for PFHxS in a pre-consumer corrugated board. PFHxS was the most prevalent PFAS in the Stockholm Convention-listed PFAS, followed by PFOS and PFOA (as shown in Fig. 6). Sapozhnikova et al. (2023) reported that PFHxS was one of the most frequently detected PFAS in their study of globally sourced food packaging (Sapozhnikova et al. 2023). PFHxS is used as a surfactant in various applications, including firefighting foams, metal plating, and textiles (Boucher et al., 2019). PFHxS and its related compounds have also been associated with paper production (Langberg et al., 2021; UNEP, 2019a), which could

explain their detection in this study. In addition, PFHxS has been found to form from perfluoroalkyl sulphonamide derivatives during chlorination and chloramination in water disinfection (Li et al., 2023) and bioaccumulate in the environment (Zhong et al., 2021), which may be another exposure pathway in the paper recycling chain. When examining the other listed PFAS in this study, PFOS was more prominent in the household waste samples with the highest concentration detected in a fast food container (44.4±1.6 ng/g). PFOA on the other hand, was less prominent in household waste and pre-consumer samples but was more prevalent in post-consumer solid waste disposal and recycling facility samples, in the colouring sheet sample (14.3±0.7 ng/g) and magazine sample (7.0±1.4 ng/g), respectively. This shows that these longer-chain PFAS of concern may be circulating in the environment and consumer-good value chains. Many developing countries are guided by the Stockholm Convention and the ratification thereof. The co-occurrences shown in this study are therefore important for the Global South as they open avenues for further research that can be used to motivate for legislation that is driven towards the restriction of all PFAS.

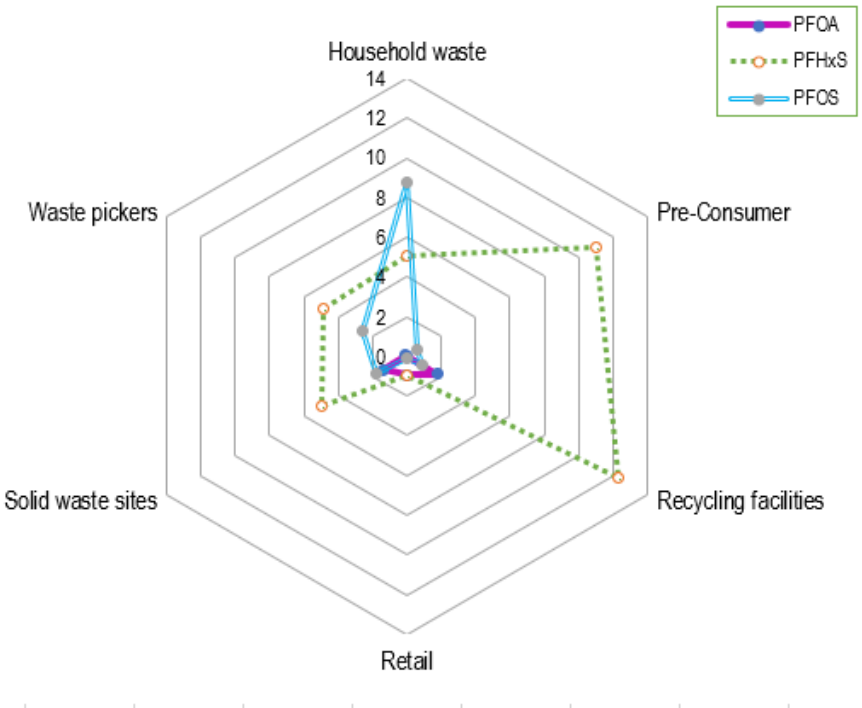


Fig. 6. Stockholm Listed PFAS radar chart

7.4 Concluding remarks

The analysis of PFAS using UHPLC-HRMS highlighted the difficulty of PFAS analysis given the ubiquitous nature of PFAS in the samples as well as in laboratory ware, solvents, and instrumentation. Blank samples were largely able to account for contamination issues; however, the lack of internal standards meant that the matrix effects could not be accounted for. When comparing the results obtained, it was shown that the combined average concentration of PFAS was lowest in the pre-consumer samples and highest in the post-consumer samples. This study further showed that the co-mingling, sorting, and collection protocols may influence PFAS propagation, as the highest PFAS concentrations were detected at post-consumer sites. When considering paper recycling and the circular economy, this study illustrated the need to further understand and investigate activities in the entire paper recycling chain. The initial manufacturing, usage, sorting, collection, disposal, recovery, and remanufacturing design protocols for recycled paper are key to ensuring minimal PFAS circulation in the paper recycling chain. Research on different exposure pathways is still required to further unpack PFAS contamination, exposure, and propagation to fully evaluate the safety and impact of PFAS in paper recycling.

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Competing Interests

Nondumiso Nomonde Mofokeng and Ineke Tiggelman declare employment at Mpact Operations Pty (Ltd). Lawrence Mzukisi Madikizela, Edmond Sanganyado and Luke Chimuka declare they have no competing interests.

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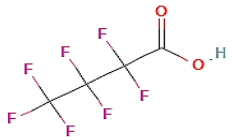
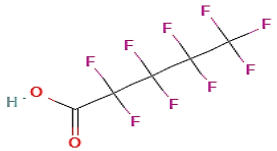
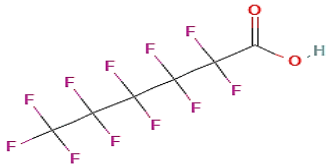
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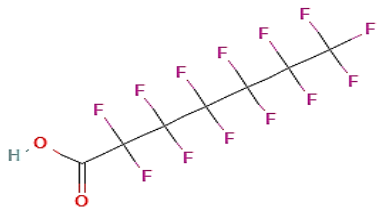
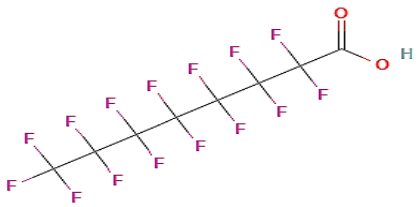
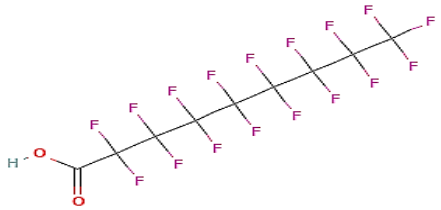
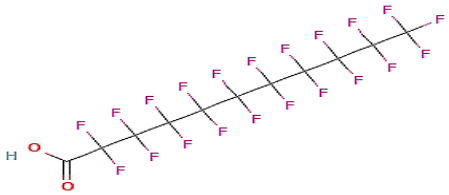
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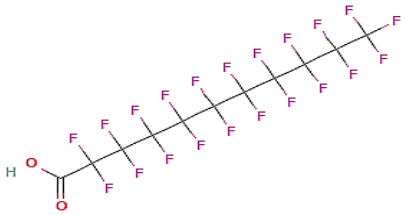
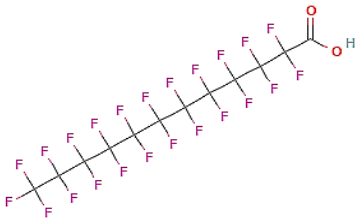
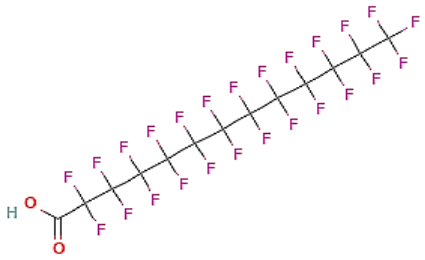
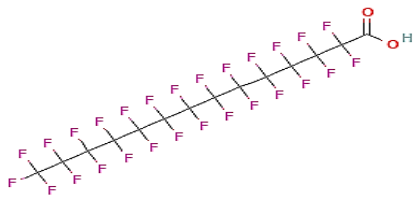
Determination of per- and polyfluoroalkyl compounds in paper recycling grades using ultra-high performance liquid chromatography - high resolution mass spectrometry

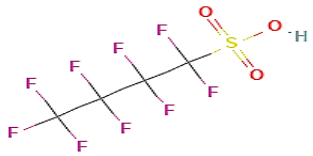
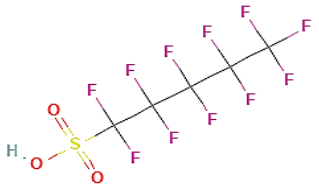
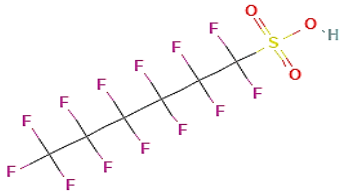
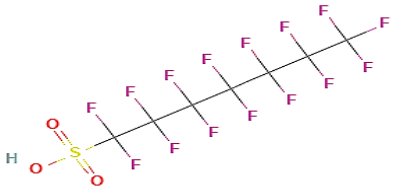
Nondumiso N. Mofokeng, Lawrence M. Madikizela, Ineke Tiggelman, Edmond Sanganyado, Luke Chimuka

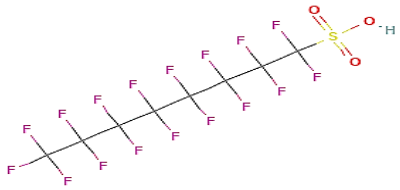
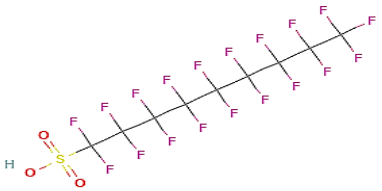
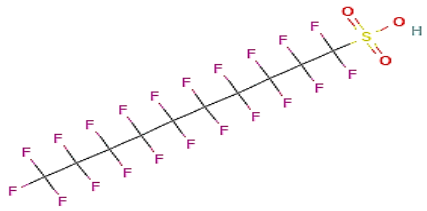
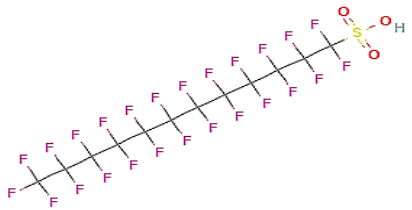
Table S1
Certified reference standard mixture

Compound	Chemical formula	Compound name	Chemical structure	CAS #	Concentration in standard mixture (µg/mL) in methanol
PFBA	$C_4HF_7O_2$	Perfluoro-n-butanoic acid		375-22-4	8
PFPeA	$C_5HF_9O_2$	Perfluoro-n-pentanoic acid		2706-90-3	4
PFHxA	$C_6HF_{11}O_2$	Perfluoro-n-hexanoic acid		307-24-4	2

PFHpA	$C_7HF_{13}O_2$	Perfluoro-n-heptanoic acid		375-85-9	2
PFOA	$C_8HF_{15}O_2$	Perfluoro-n-octanoic acid		335-67-1	2
PFNA	$C_9HF_{17}O_2$	Perfluoro-n-nonanoic acid		375-95-1	2
PFDA	$C_{10}HF_{19}O_2$	Perfluoro-n-decanoic acid		335-76-2	2

PFUnA	$C_{11}HF_{21}O_2$	Perfluoro-n-undecanoic acid		2058-94-8	2
PFDoA	$C_{12}HF_{23}O_2$	Perfluoro-n-dodecanoic acid		307-55-1	2
PFTrDA	$C_{13}HF_{25}O_2$	Perfluoro-n-tridecanoic acid		72629-94-8	2
PFTeDA	$C_{14}HF_{27}O_2$	Perfluoro-n-tetradecanoic acid		376-06-7	2

PFBS	$C_4HF_9O_3S$	Perfluorobutane-1-sulphonic acid		375-73-5	2
PFPeS	$C_5HF_{11}O_3S$	Perfluoropentanesulphonic acid		2706-91-4	2
PFHxS (linear & branched)	$C_6HF_{13}O_3S$	Perfluorohexane-1-sulphonic acid		355-46-4	2
PFHpS	$C_7HF_{15}O_3S$	Perfluoroheptanesulphonic acid		375-92-8	2

PFOS (linear & branched)	$C_8HF_{17}O_3S$	Perfluorooctane-1-sulphonic acid		1763-23-1	2
PFNS	$C_9HF_{19}O_3S$	Perfluorononanesulphonic acid		68259-12-1	2
PFDS	$C_{10}HF_{21}O_3S$	Perfluorodecane-1-sulphonic acid		335-77-3	2
PFDoS	$C_{12}HF_{25}O_3S$	Perfluorododecanesulphonic acid		79780-39-5	2

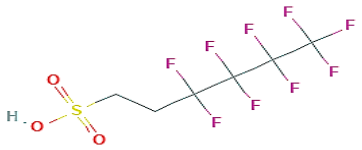
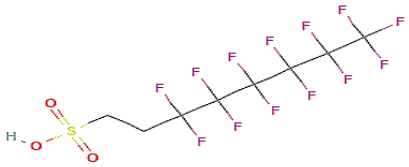
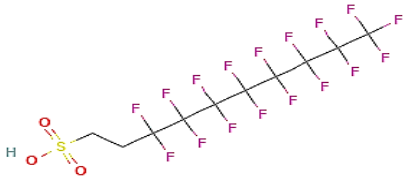
4:2 FTS	$C_6H_5F_9O_3S$	1H,1H,2H,2H-Perfluorohexanesulphonic acid		757124-72-4	8
6:2 FTS	$C_8H_5F_{13}O_3S$	1H,1H,2H,2H-Perfluorooctanesulphonic acid		27619-97-2	8
8:2 FTS	$C_{10}H_5F_{17}O_3S$	1H,1H,2H,2H-Perfluorodecanesulphonic acid		39108-34-4	8

Table S2
Sample description

Site	Recycling Paper Grade	Number of Samples
Mills	Unconverted paperboard	3
Corrugators	Corrugated board	2
Recycling facilities	Cartonboard	4
	Coloured paper	1
	Corrugated board	2
	Newspaper	2
	Black & white office paper	1
Retail	Cartonboard	2
	Corrugated board	4
Solid waste disposal sites	Corrugated board	3
	Magazine	2
	Newspaper	2
	Black & white office paper	1
Waste pickers	Cartonboard	1
	Corrugated board	3
Household waste	Cartonboard	4
	Corrugated board	2

ASE Extraction

A literature survey indicated the two most commonly used solvents in paper-based and solid samples were ethanol. acetonitrile. water and methanol. MacLennan et al. (2019; 2021) used oven temperature 100 °C Static cycle. time 300 s Solvent 80:20 methanol/ acetonitrile with 50 mL volume in 3 cycles 3 whilst Silva et al. (2021) focused ultrasonic liquid extraction (FUSLE) procedure using ethanol. (Trier et al.. 2011) compared extraction of PFAS at room temperatures in ethanol water where 10% ethanol was negligible whilst 50% ethanol and 95% ethanol gave similar results. Ethanol and methanol extractions of 1g of the same unspiked cardboard sample were compared in this study for optimisation of solvent.

Table S3

Solvent comparison

where red- highest value, yellow- middle value, green – lowest value.

EtOH: MeOH Solvent Ratio	Concentration (µg/L)															
	PFBA	PFPeA	PFHxA	PFHpA	PFNA	PFDA	PFBS	PFUnA	PFDoA	PFTrDA	PFTeDA	PFHxS	PFOS	4:2 FTS	6:2 FTS	8:2 FTS
1:1	23.64	4.09	4.13	7.27	2.79	0.40	0.37	0.50	6.66	0.52	0.93	0.93	0.53	6.73	29.11	0.76
2:3	24.99	3.59	3.50	7.11	3.16	0.39	0.29	0.49	8.51	0.48	0.94	1.26	0.24	6.01	23.87	0.83
3:2	27.79	4.37	3.67	8.58	3.99	0.40	0.39	0.49	5.15	0.54	0.91	0.70	0.65	6.93	34.74	0.76
%RSD	8.30	9.81	8.59	10.53	18.66	1.38	14.13	1.47	24.86	6.16	1.38	29.27	44.85	7.40	18.60	4.92

From Table S3, the 3:2v/v ethanol: methanol was found to give the highest detected concentrations and was selected as the extraction solvent. The oven temperature was selected as 70°C. based on modification of MacLennan et al. (2019).

Thermo Scientific Q Exactive Focus UHPLC$^+$ Orbitrap HRMS Instrument Parameters

Solvent A: LC-MS grade water with 10mM Ammonium formate 0.1% formic acid

Solvent B: LC-MS grade methanol

Table S4

Orbitrap LC-HRMS flow gradient

	Time	Flow (mL/min)	%B	Curve
1	0.00	0.400	30	5
2	1.00	0.400	30	5
3	13.00	1.00	100	3
4	17.00	1.00	100	5
5	17.10	0.500	60	5
6	21.1	0.500	50	5
7	21.10	0.500	30	5

Table S5 PFAS transitions and Retention Times

Compound	Precursor ion (m/z)	Product ions (m/z)	RT (min)

PFBA	212.9786	168.9883; 118.8934	2.67
PFPeA	262.9759	218.9859; 80.3690	4.35
PFBS	298.9456	98.9545; 79.9560	4.54
4:2 FTS	326.9744	306.9677; 80.9639	4.99
PFHxA	312.9730	268.9830; 91.0208	5.07
PFPeS	348.9398	118.9392; 98.9542	5.16
PFHxS	398.9387	218.9736; 79.9575	5.65
PFHpA	362.9695	318.9799; 168.9882	5.67
6:2 FTS	426.9674	406.9639; 80.9639	6.06
PFOA	412.9661	168.9884; 118.9911	6.11
PFHpS	448.9331	112.9842; 75.4488	6.19
PFNA	462.9634	218.9850; 168.9882	6.56
PFOS	498.9714	318.9456; 112.9843	6.56
8:2 FTS	526.9605	606.955-; 80.0639	7.00
PFDA	512.9613	468.9704; 218.9854	6.99
PFNS	548.9269	412.8763; 112.9842	7.03
PFDS	598.9269	229.9752; 112.3167	7.48
PFUnA	562.9562	268.9828; 168.9882	7.50
PFDoA	612.9535	568.9627; 268.9828	7.97

PFDoS	699.9198	290.9486; 112.9847	8.40
PFTrDA	662.9497	268.9824; 218.9854	8.44
PFTeDA	712.9467	268.9824; 218.9854	8.89

Contamination Considerations for PFAS Workflow

Table S6 Other possible contamination sources: PFAS concentrations (pg/µL)

	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTrDA	PFTeDA	PFBS	PFPeS	PFHxS	PFHpS	PFOS	PFNS	PFDS	PFDoS	4:2 FTS	6:2 FTS	8:2 FTS
Black PE bag	7.840	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.396	0.492	<LOD	<LOD	0.004	0.644	0.192	0.262	<LOD	2.938	<LOD	<LOD
Clear PE	8.005	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.383	0.477	<LOD	0.022	<LOD	0.747	0.205	0.281	<LOD	0.831	<LOD	<LOD
Clear PP sachet	7.995	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.371	1.045	<LOD	0.08	0.041	1.168	0.238	0.565	<LOD	2.156	<LOD	<LOD
Aluminium Foil	7.771	<LOD	<LOD	<LOD	1.097	<LOD	<LOD	<LOD	<LOD	<LOD	0.410	0.221	<LOD	0.131	<LOD	0.556	0.193	0.254	<LOD	0.863	16.946	<LOD
Blender Rinse	7.231	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.356	0.211	<LOD	<LOD	0.082	2.184	0.192	0.246	<LOD	0.197	<LOD	<LOD
Nitrile Gloves	6.526	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.368	<LOD	<LOD	0.375	0.246	<LOD	<LOD	0.072	8.26	0.205	0.234	<LOD	0.107	<LOD	<LOD

Table S7 Unfiltered solvent blank concentrations (pg/µL)

Solvent Blank (not filtered)	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTrDA	PFTeDA	PFBS	PFPeS	PFHxS	PFHpS	PFOS	PFNS	PFDS	PFDoS	4:2 FTS	6:2 FTS	8:2 FTS
Blank 1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.393	0.351	<LOD	<LOD	<LOD	0.532	0.193	0.256	<LOD	<LOD	<LOD	<LOD
Blank 2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.387	0.221	<LOD	<LOD	<LOD	0.532	0.193	0.256	<LOD	<LOD	<LOD	<LOD
Blank 3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.386	0.379	<LOD	<LOD	<LOD	0.434	0,192	0,247	<LOD	<LOD	<LOD	<LOD
Blank 4	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.378	0.379	<LOD	<LOD	<LOD	0.434	0.191	0.247	<LOD	<LOD	<LOD	<LOD
Blank 5	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.378	0.230	<LOD	<LOD	<LOD	0.521	0.192	0.258	<LOD	<LOD	<LOD	<LOD
Blank 6	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.370	0.380	<LOD	<LOD	<LOD	0.521	0.192	0.251	<LOD	<LOD	<LOD	<LOD
Blank 7	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.371	0.270	<LOD	<LOD	<LOD	0.449	0.190	0.238	<LOD	<LOD	<LOD	<LOD
Blank 8	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.389	0.380	<LOD	<LOD	<LOD	0.497	0.191	0.233	<LOD	<LOD	<LOD	<LOD
Blank 9	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.382	0.380	<LOD	<LOD	<LOD	0.477	0.191	0.23	<LOD	<LOD	<LOD	<LOD
Blank 10	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.381	0.381	<LOD	<LOD	<LOD	0.531	0.189	0.244	<LOD	<LOD	<LOD	<LOD
Blank 11	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.382	0.251	<LOD	<LOD	<LOD	0.530	0.187	0.243	<LOD	<LOD	<LOD	<LOD
Blank 12	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.3817	0.381	<LOD	<LOD	<LOD	0.518	0.192	0.249	<LOD	<LOD	<LOD	<LOD
Blank 13	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.378	0.359	<LOD	<LOD	<LOD	0.400	0.197	0.29	<LOD	<LOD	<LOD	<LOD
Blank 14	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.368	0.380	<LOD	<LOD	<LOD	0.472	0.189	0.262	<LOD	<LOD	<LOD	<LOD
%RSD											1.99	18.7				9.17	1.01	5.90				
Average											0.380	0.337				0.489	0.192	0.251				

Table S8 Workflow preparation blanks concentration (pg/µL)

	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTrDA	PFTeDA	PFBS	PFPeS	PFHxS	PFHpS	PFOS	PFNS	PFDS	PFDoS	4:2 FTS	6:2 FTS	8:2 FTS
Preparation Blank 1	8.951	1.605	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.548	<LOD	0.399	0.277	<LOD	<LOD	<LOD	0.573	0.190	0.229	<LOD	0.795	<LOD	<LOD
Preparation Blank 2	8.645	1.624	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.550	<LOD	0.394	0.382	<LOD	<LOD	<LOD	0.490	0.188	0.243	<LOD	0.742	<LOD	<LOD
Preparation Blank 3	8.218	1.713	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.552	<LOD	0.389	0.381	<LOD	<LOD	<LOD	0.415	0.175	0.234	<LOD	0.622	<LOD	<LOD
Preparation Blank 4	8.237	1.691	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.547	<LOD	0.377	0.250	<LOD	<LOD	<LOD	0.413	0.186	0.242	<LOD	0.622	<LOD	<LOD
Preparation Blank 5	7.961	1.644	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.549	<LOD	0.337	0.381	<LOD	<LOD	<LOD	0.388	0.218	0.214	<LOD	0.836	<LOD	<LOD
Preparation Blank 6	7.866	1.648	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.548	<LOD	0.387	0.365	<LOD	<LOD	<LOD	0.410	0.194	0.225	<LOD	0.854	<LOD	<LOD
Preparation Blank 7	7.973	1.641	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.547	<LOD	0.384	0.282	<LOD	<LOD	<LOD	0.490	0.154	0.253	<LOD	0.895	<LOD	<LOD
Preparation Blank 8	6.820	1.319	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.561	<LOD	0.370	0.389	<LOD	<LOD	<LOD	0.583	0.174	0.253	<LOD	0.756	<LOD	<LOD
Preparation Blank 9	7.833	1.622	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.447	<LOD	0.386	0.339	<LOD	<LOD	<LOD	0.586	0.217	0.241	<LOD	0.743	<LOD	<LOD
Preparation Blank 10	7.811	1.554	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.548	<LOD	0.367	0.382	<LOD	<LOD	<LOD	0.218	0.142	0.242	<LOD	0.678	<LOD	<LOD
Average	8.032	1.606							0.540		0.379	0.343				0.457	0.184	0.238		0.754		
%RSD	7.06	7.26							6.08		4.70	15.46				24.89	13.14	5.17		12.44		

Equations for the determination of uncertainty

Equation S1:

$$s^2 = \frac{\sum(x_i - \bar{x})^2}{n-1} \quad \text{(S1)}$$

where x_i concentration determined for i^{th} replicate, $\bar{x}$ is the sample mean and n is the number of replicates.

Equation S2:

$$u_{matrix} = \frac{\%RSD_x}{n} \quad \text{(S2)}$$

where *%RSD* is the percent relative standard deviation of the determined sample concentration and *n* is the number of replicates.

Equation S3:

$$u_{recovery} = \frac{SD_{rec}}{n_{rec}} \quad \text{(S3)}$$

where SD_{std} is the standard deviation of the recoveries obtained for the target compound in the spiked for the number of replicates, $n_{rec.}$

Equation S4:

$$u_{prep.\ blaks} = \frac{\sum(b_i - \bar{b})^2}{n_b - 1} \quad \text{(S4)}$$

where *bi* is the concentration determined for each target compound in the preparation blank replicates, n_b and $\bar{b}$ is the mean.

Table S9 Method validation table

Compound	R^2 Calibration Range 1	R^2 Calibration Range 2	LOD±%RSD (pg/g)	LOQ±%RSD (pg/g)	%RELATIVE RECOVERY ± %RSD Paperboard (ng/g)			Paper (ng/g)		
					10	20	100	10	20	100
PFBS	0.9875	0.9959	4.896±7.30	16.319±7.30	89±6.5	100±2.4	101±2.6	98±1.1	95±3.4	88±2.8
PFHxA	0.9959	0.9846	4.891±8.85	16.302±8.85	55±4.7	82±5.2	87±3.0	79±2.0	80±1.1	88±1.1
PFPeS	0.9861	0.9920	8.746±6.60	29.155±6.60	97±2.6	98±1.0	102±1.4	105±1.2	103±2.1	90±4.6
PFHxS	0.9882	0.9982	4.757±7.81	15.857±7.81	85±3.4	99±5.4	91± 1.9	103±1.9	102±1.6	101±2.3
PFHpA	0.9840	0.9919	2.898±3.22	9.661±3.22	69±1.9	70±1.6	109±3.9	99±1.0	97±2.0	89±1.2
PFOA	0.9887	0.9912	2.346±5.013	7.821±5.013	139±1.3	116±3.6	130±2.9	98±1.0	105±2.9	124±1.3
PFHpS	0.9875	0.9956	4.458±5.19	14.861±5.19	104±3.1	100±5.2	100±1.3	103±2.3	102±2.2	96±2.7
PFNA	0.9903	0.9930	4.048±5.48	13.495±5.48	92±1.5	93±4.7	103±1.7	98±9.8	96±2.9	97±1.1

PFOS	0.9855	0.9916	3.037±10.20	10.124±10.20	91±2.2	96±1.5	91±2.5	99±4.4	100±2.0	97±3.0
PFDA	0.9935	0.9930	1.465±3.90	4.885±3.90	92±1.7	90±2.7	97±1.9	111±1.8	119±4.5	111±2.3
PFNS	0.9930	0.9936	4.497±5.26	14.991±5.26	100±4.6	102±1.1	102±2.6	103±5.6	103±1.8	105±1.4
PFDS	0.9992	0.9922	3.667±1.54	12.222±1.54	80±1.5	73±1.4	75±1.1	76±2.5	75±2.1	79±1.8
PFUnA	0.9917	0.9914	10.067±7.55	33.557±7.55	95±3.2	97±1.0	104±1.0	77±3.8	76±7.5	79±2.6
PFDoA	0.9968	0.9968	5.097±5.98	16.991±5.98	102±1.3	102±2.9	103±3.6	89±5.2	92±3.2	87±3.4
PFDoS	0.9990	0.9928	3.925±5.39	13.082±5.39	78±1.7	86±1.1	83±1.9	78±1.7	84±2.4	83±2.7
PFTrDA	0.9959	0.9919	5.700±6.00	19.002±6.00	77±3.9	80±1.9	106±3.0	90±1.1	81±1.9	93±2.0
PFTeDA	0.9916	0.9959	4.329±9.85	14.429±9.85	84±1.5	88±2.3	88±2.3	86±3.6	84±7.5	88±1.3
					Paperboard (ng/g)			**Paper (ng/g)**		
					20	**40**	**200**	**20**	**40**	**200**
PFPeA	0.9922	0.9968	11.177±6.55	37.258±6.55	85±1.1	101±2.2	104±1.2	87±1.1	99±3.2	81±2.9

					40	**80**	**400**	**40**	**80**	**400**
PFBA	0.9922	0.9938	53.069±8.98	176.899±8.98	111±2.7	105±3.1	103±1.3	103±1.9	89±3.4	106±3.5
4:2 FTS	0.9889	0.9985	38.935±11.11	129.782±11.11	98±2.8	109±2.4	105±4.0	76±3.6	83±3.1	113±2.1
6:2 FTS	0.9898	0.9918	50.968±9.68	169.894±9.68	226±1.4	198±2.1	211±3.2	190±4.1	196±3.9	197±2.2
8:2 FTS	0.9938	0.9977	15.378±9.06	51.259±9.06	97±2.0	102±2.0	111±2.8	103±1.9	103±2.4	110±3.1

Table S10 Categorical box and whisker plots category definitions

Stage Description	Assigned Number	Site Description	Assigned Number	Paper Recycling Grade Description	Assigned Number
Pre-Consumer	1	Domestic waste	1	Cartonboard	1
Retail	2	Recycling facilities	2	Newsprint	2
Post-Consumer	3	Solid waste sites	3	Corrugated board	3
		Waste Pickers	4	Black & white paper	4
		Paper Mills	5	Magazine	5
		Corrugators	6	Unconverted pre-consumer board	6
		Retail	7	Corrugated pre-consumer	7
				Coloured paper	8

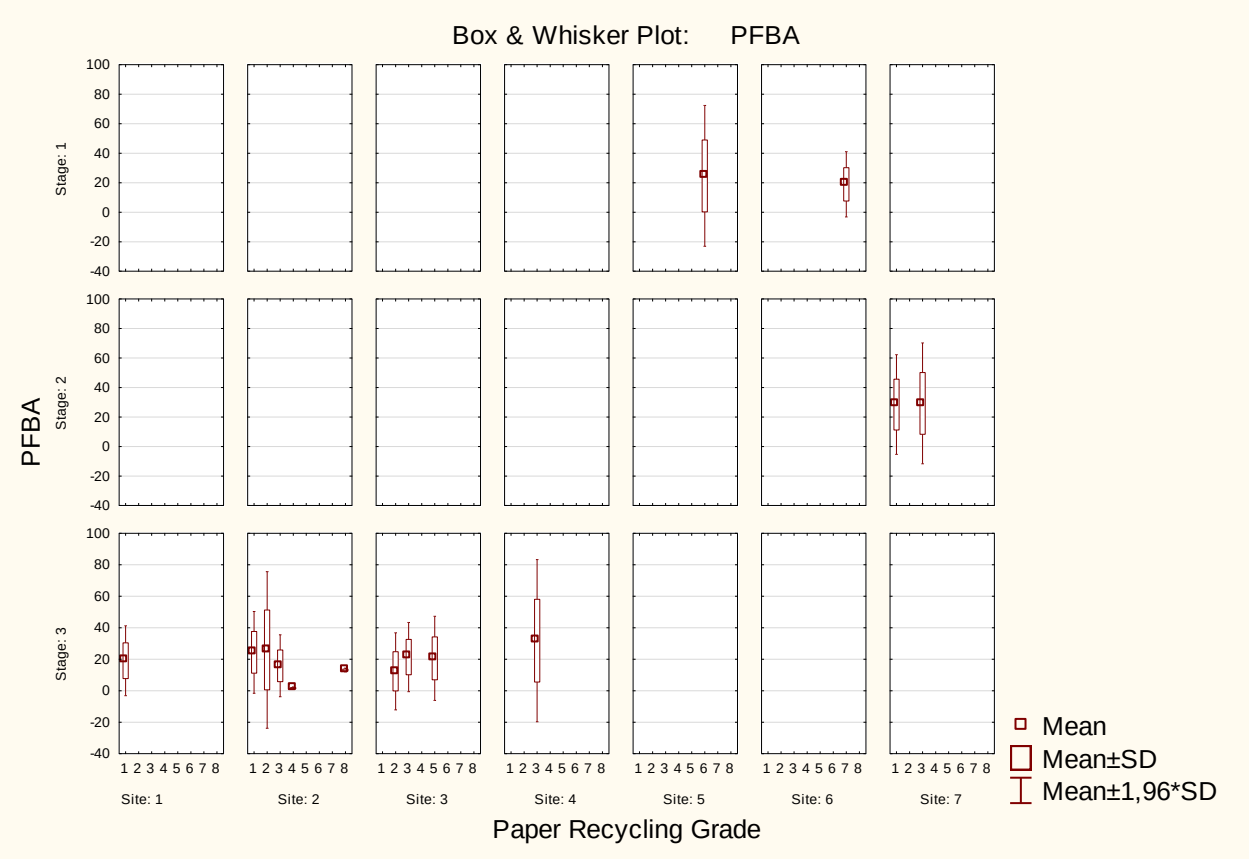


Fig. S1 PFBA box and whisker plot

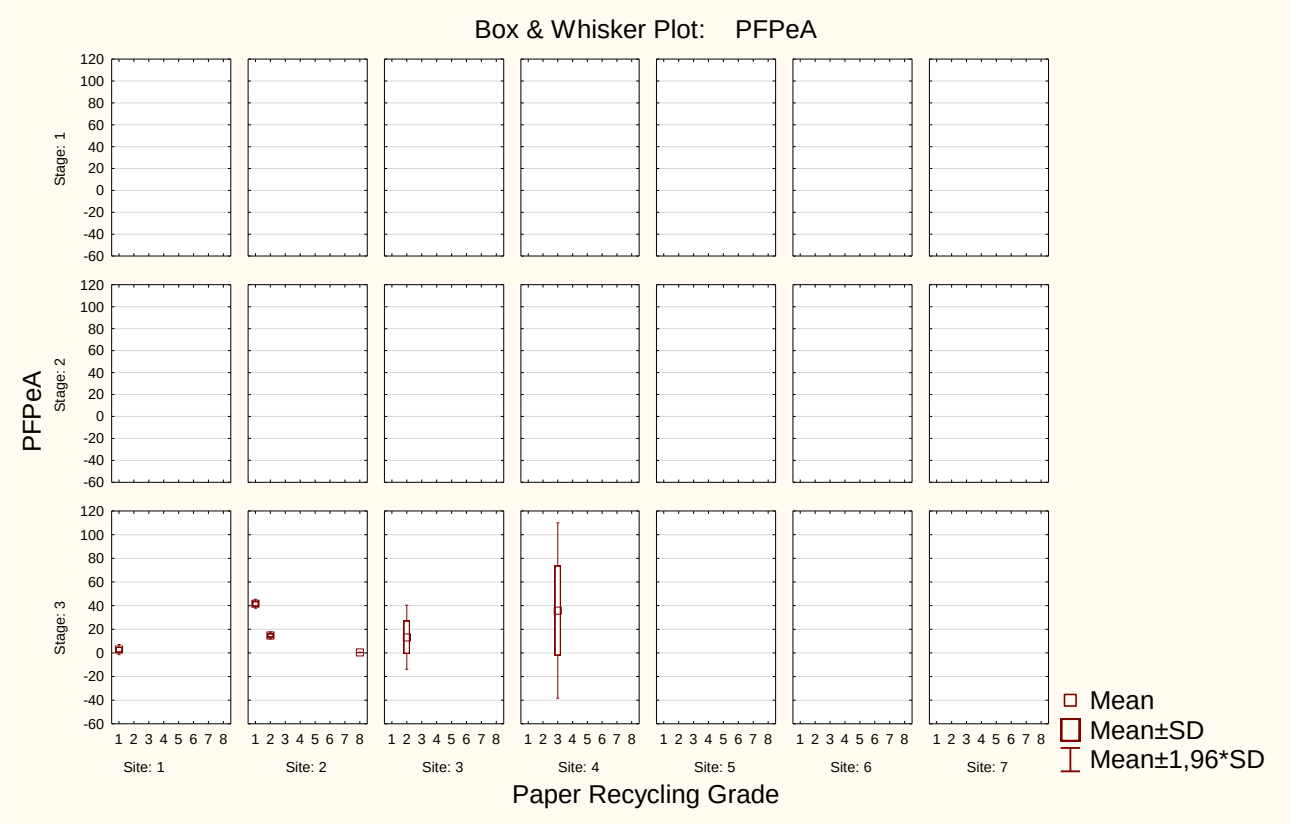


Fig. S2 PFPeA box and whisker plot

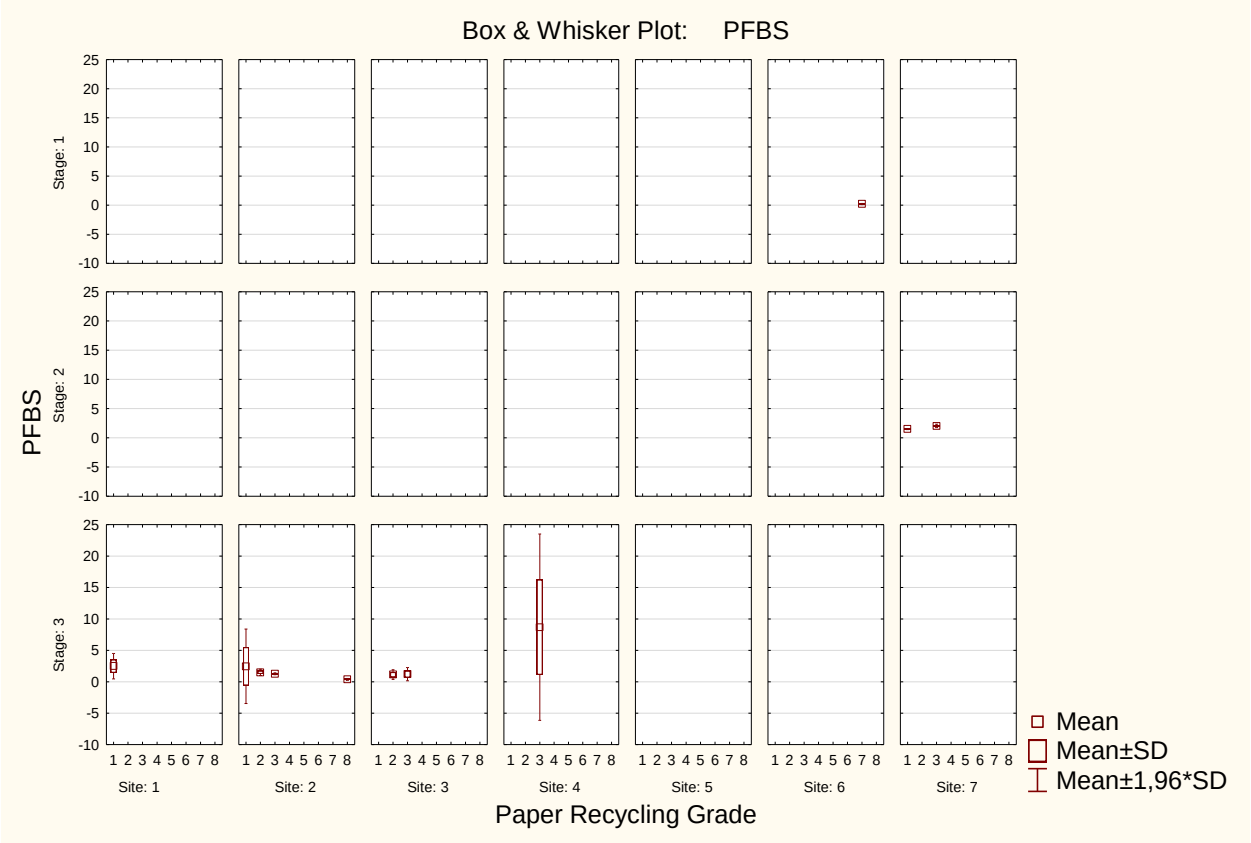


Fig. S3 PFBS box and whisker plot

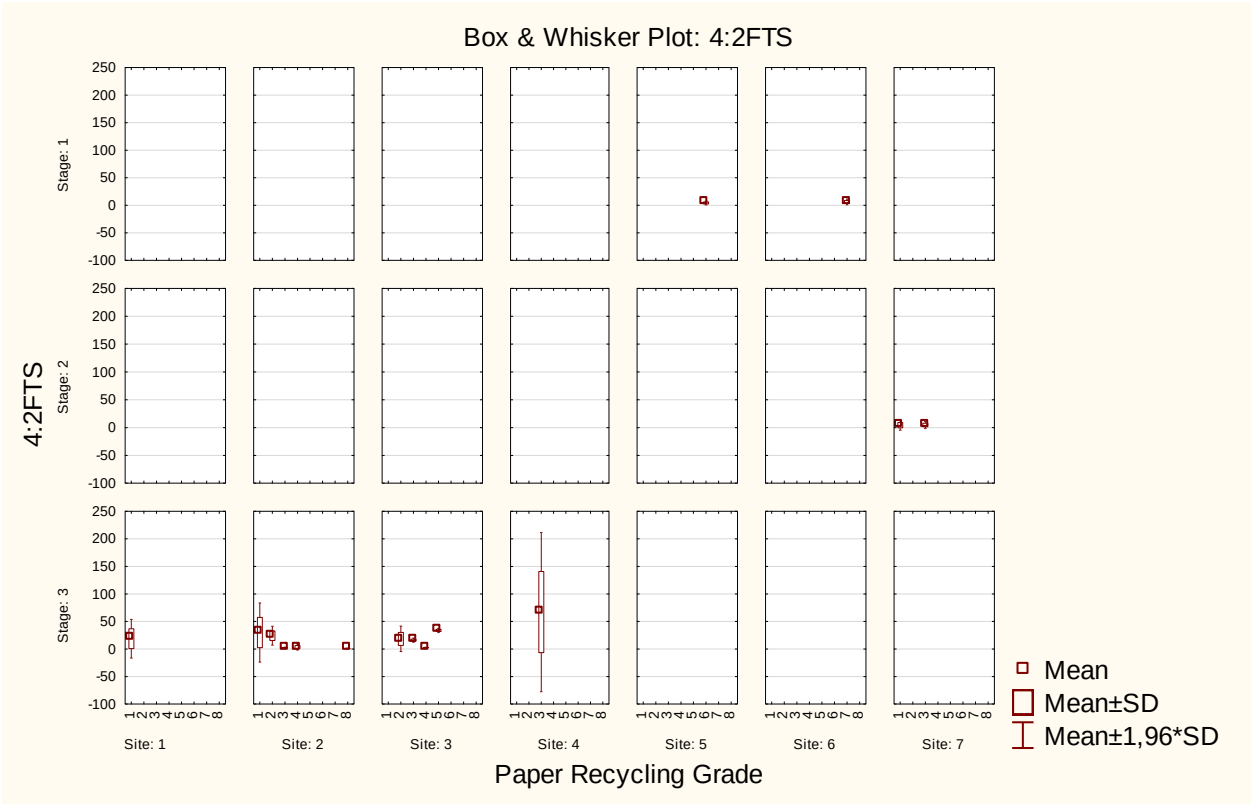


Fig. S4 4:2 FTS box and whisker plot

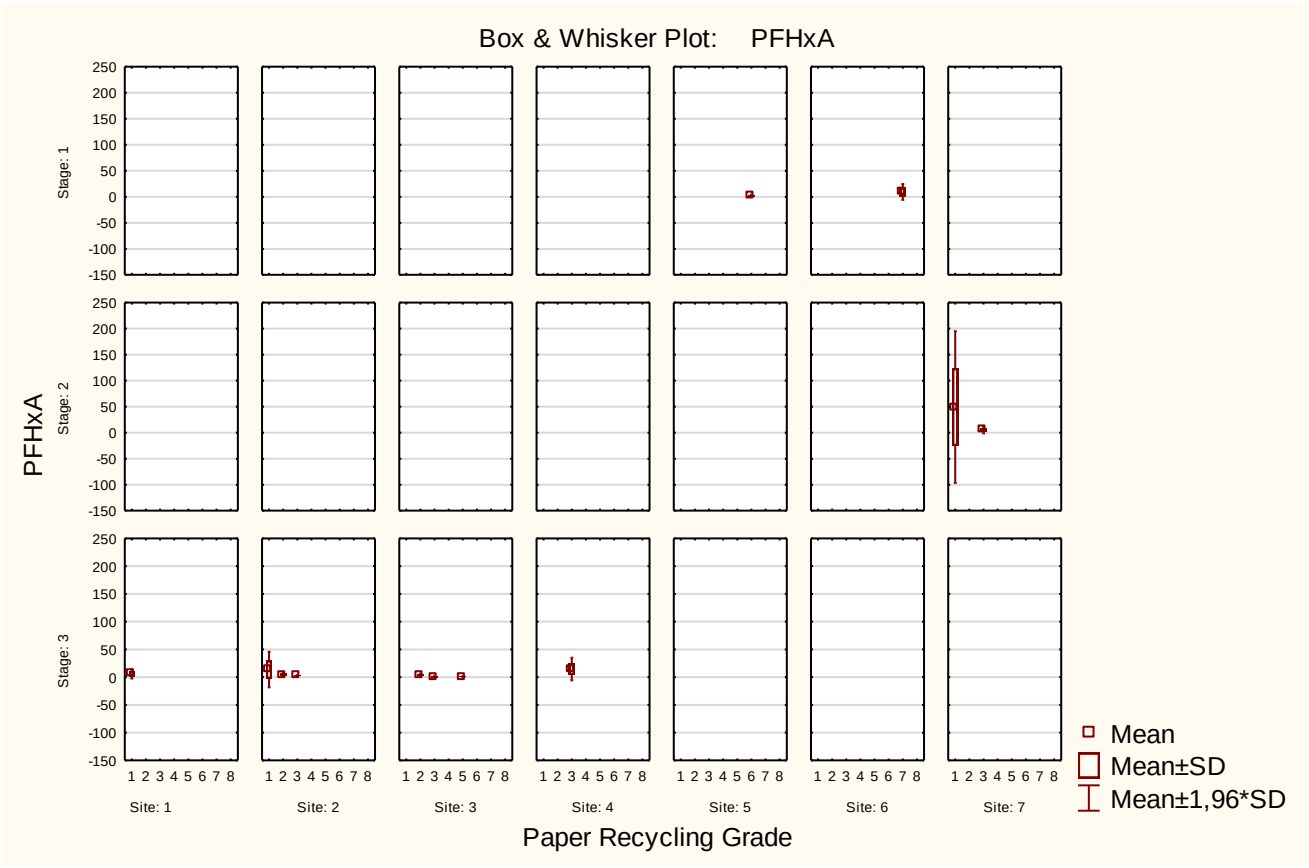


Fig. S5 PFHxA box and whisker plot

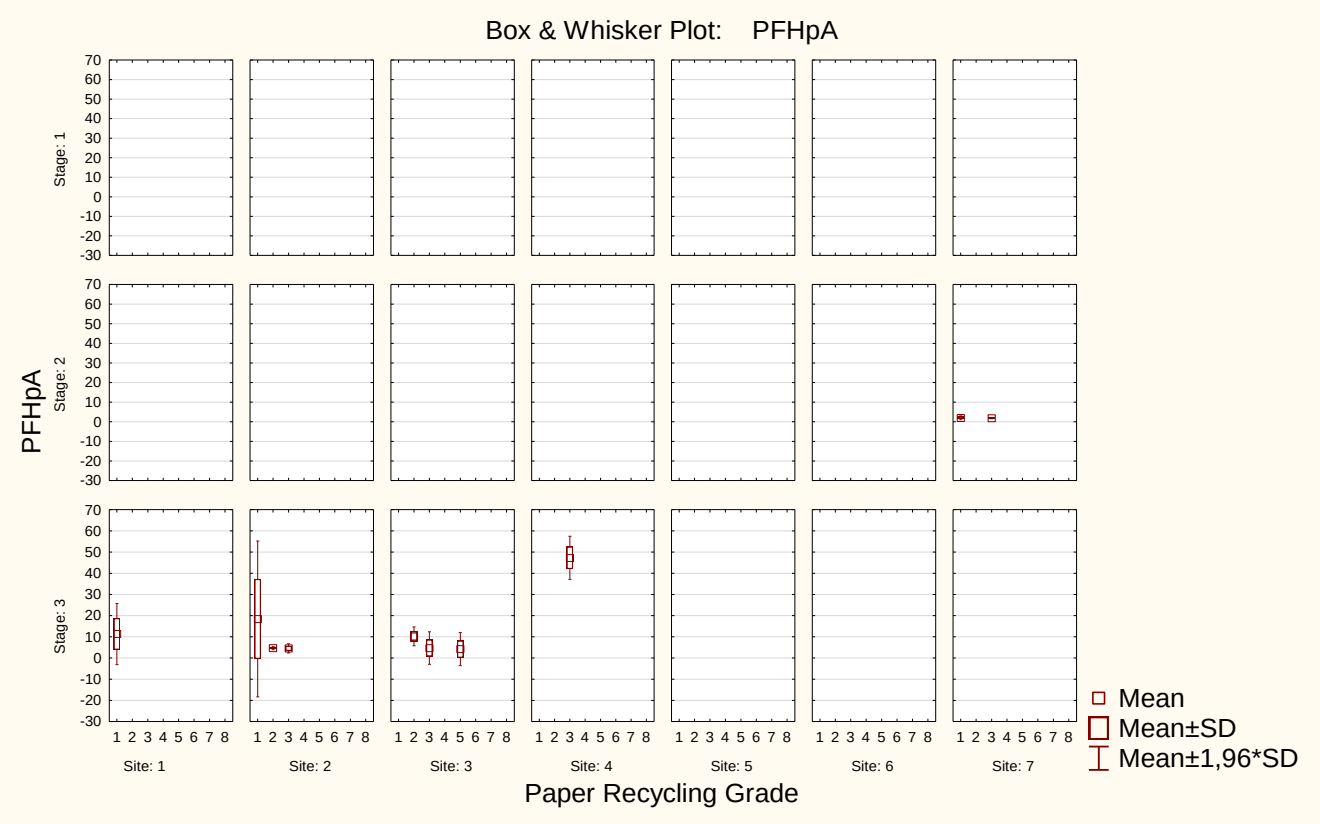


Fig. S6 PFHpA Box and Whisker Plot

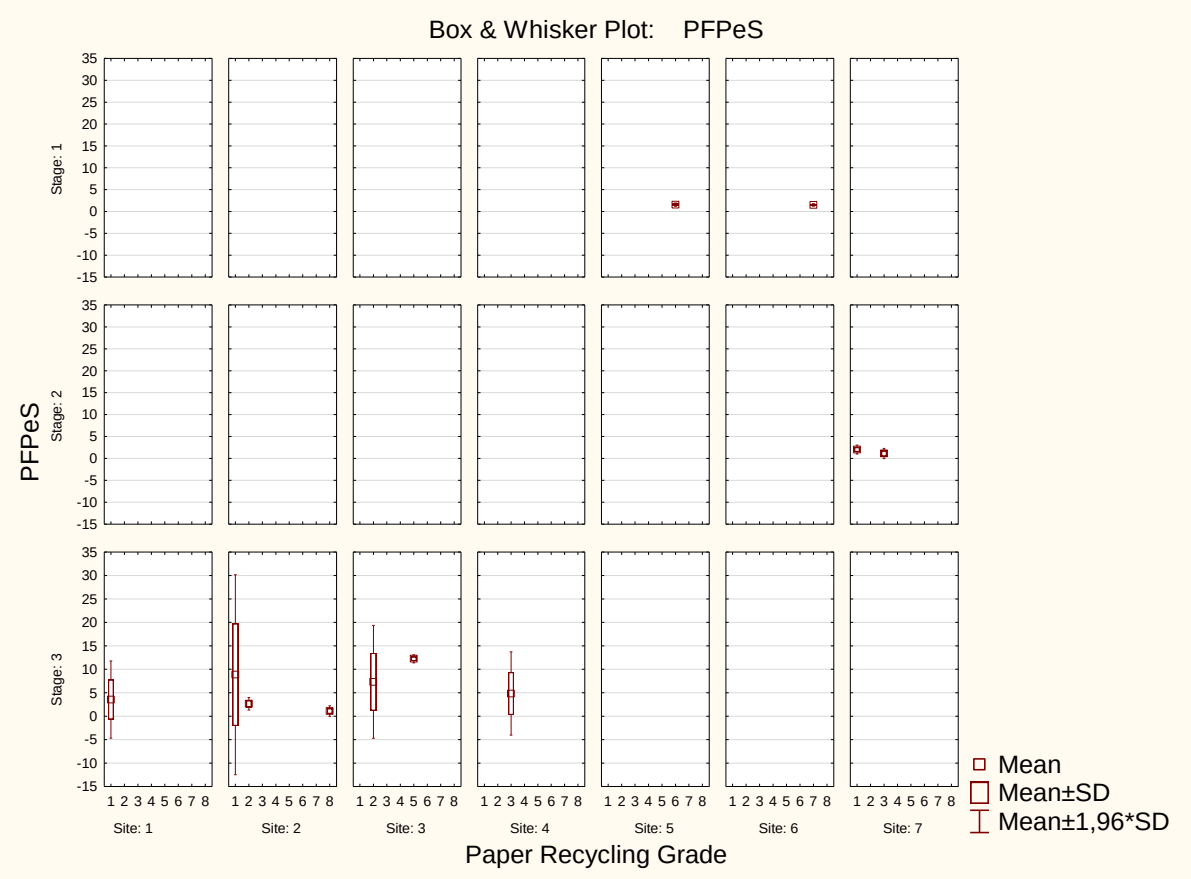


Fig. S7 PFPeS box and whisker plot

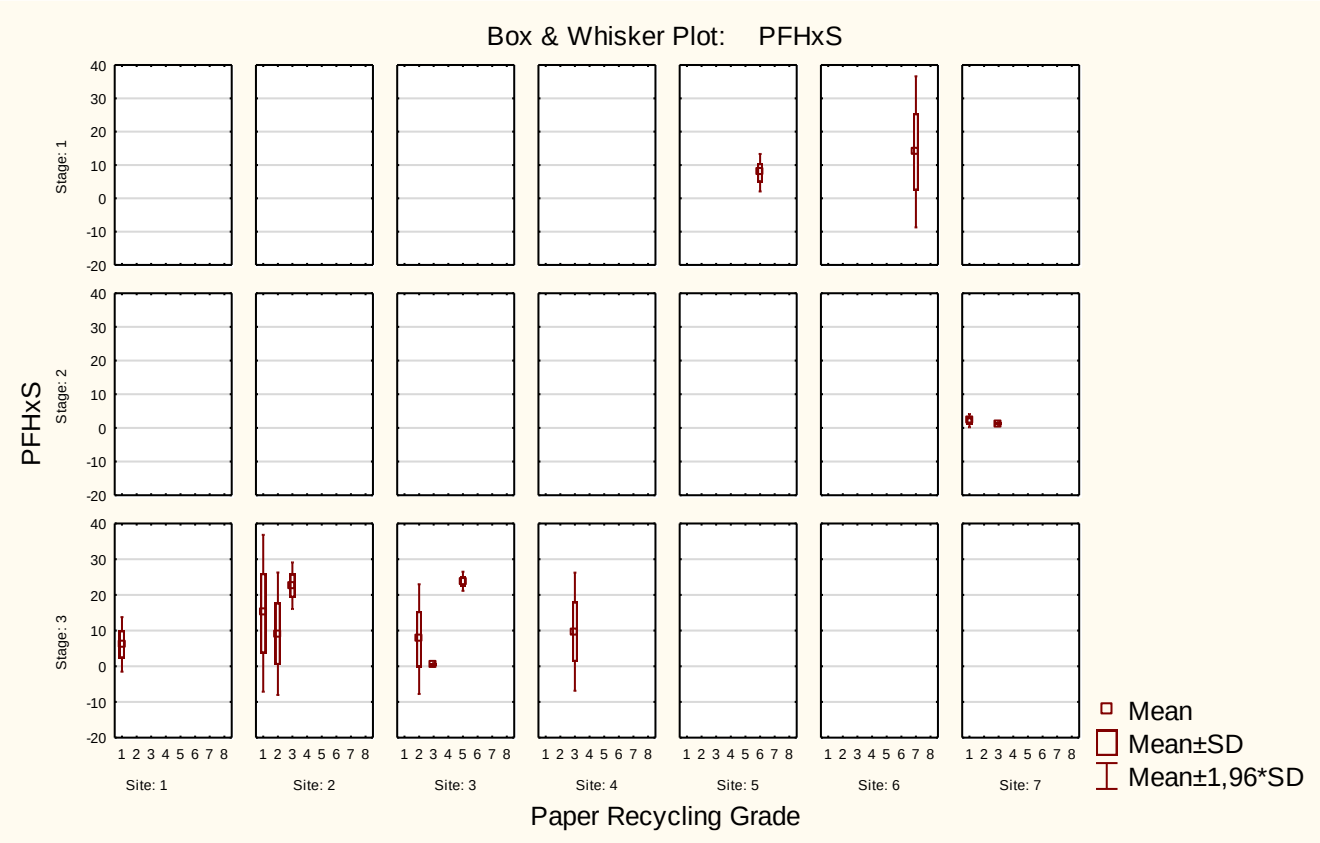


Fig. S8 PFHxS box and whisker plot

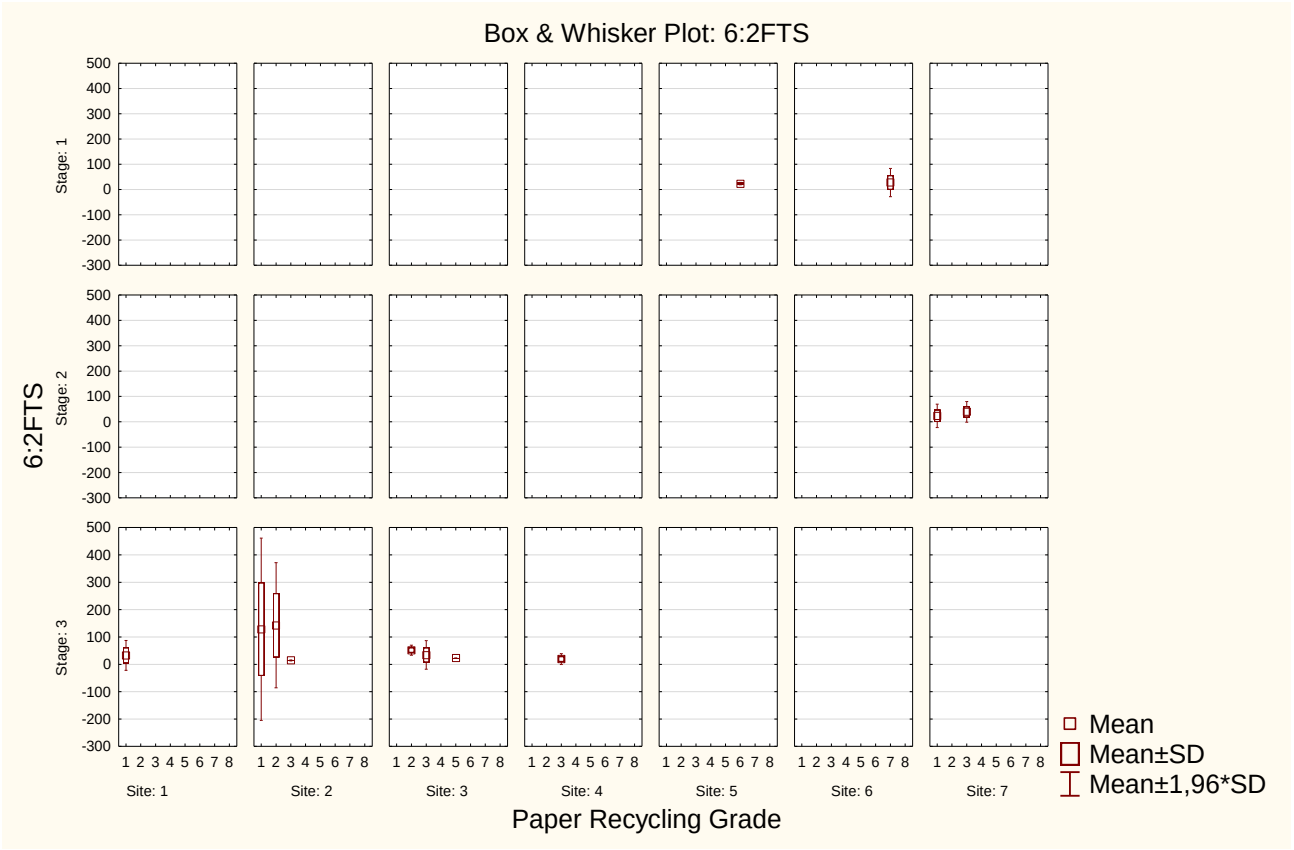


Fig. S9 6:2 FTS box and whisker plot

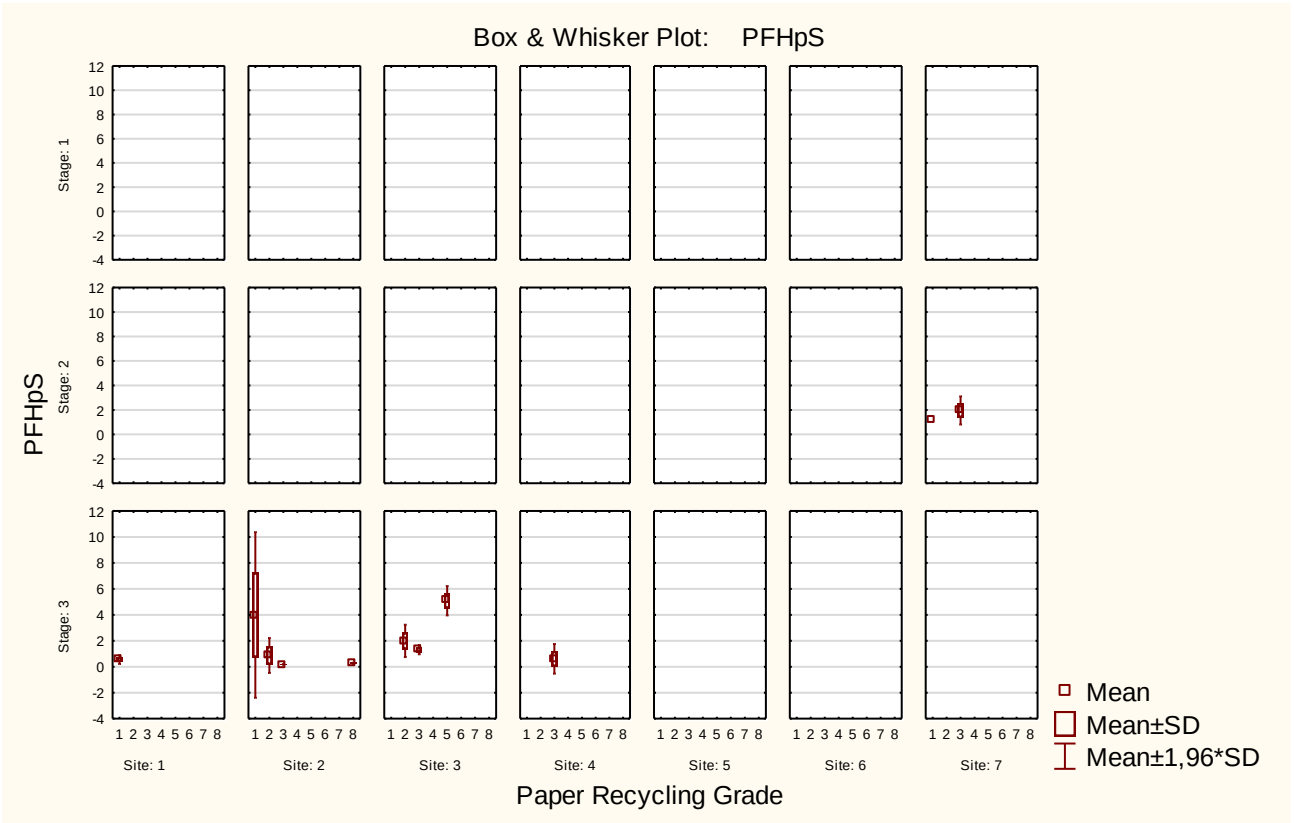


Fig. S10 PFHpS box and whisker plot

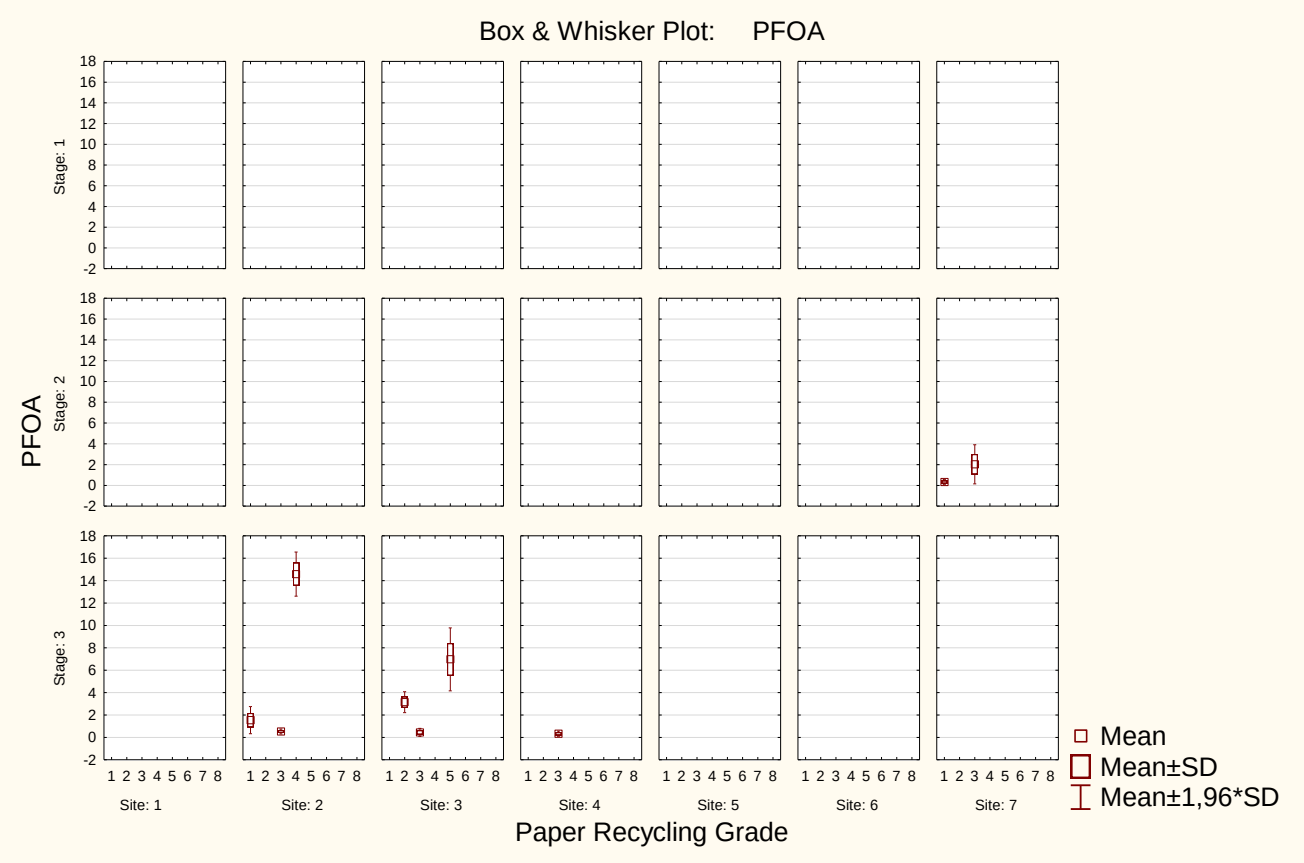


Fig. S11 PFOA box and whisker plot

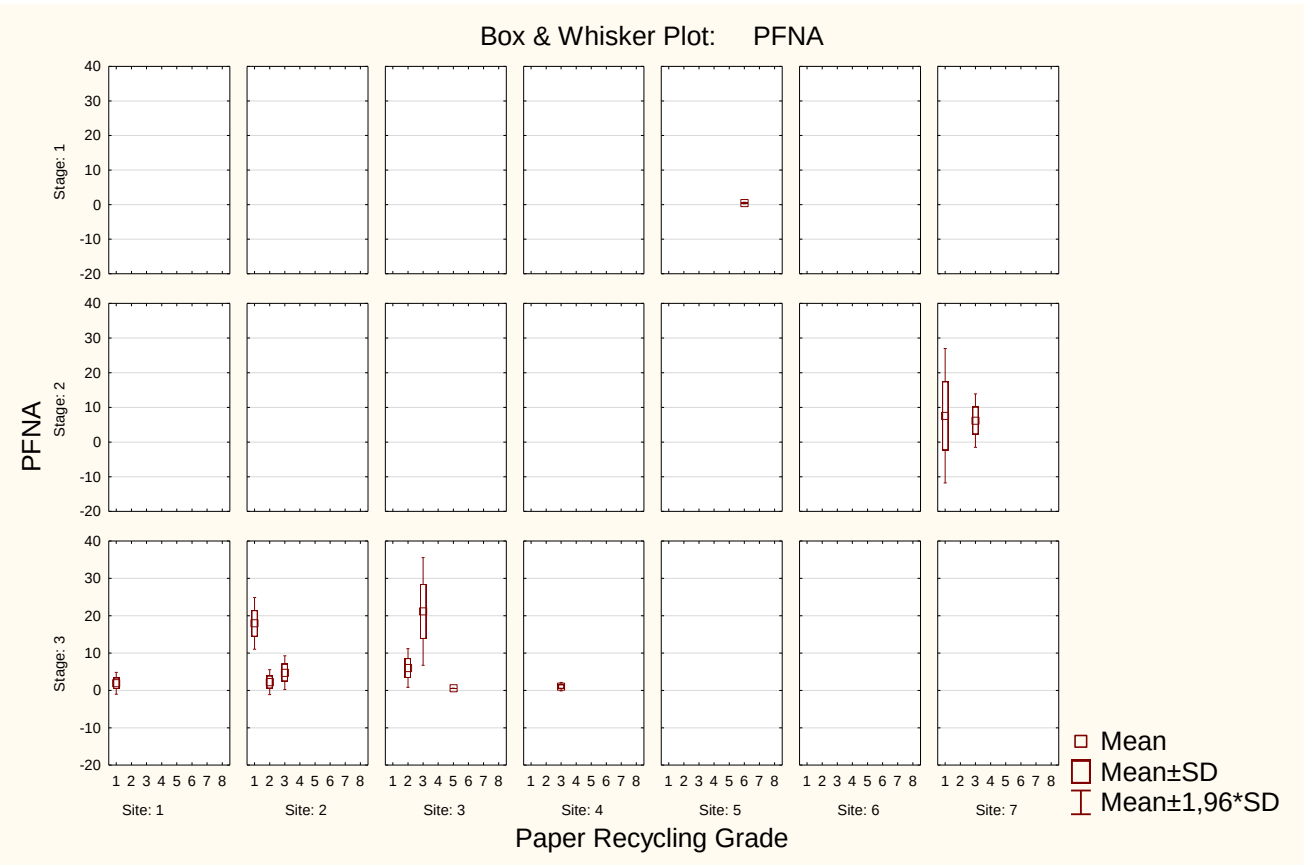


Fig. S12 PFNA box and whisker plot

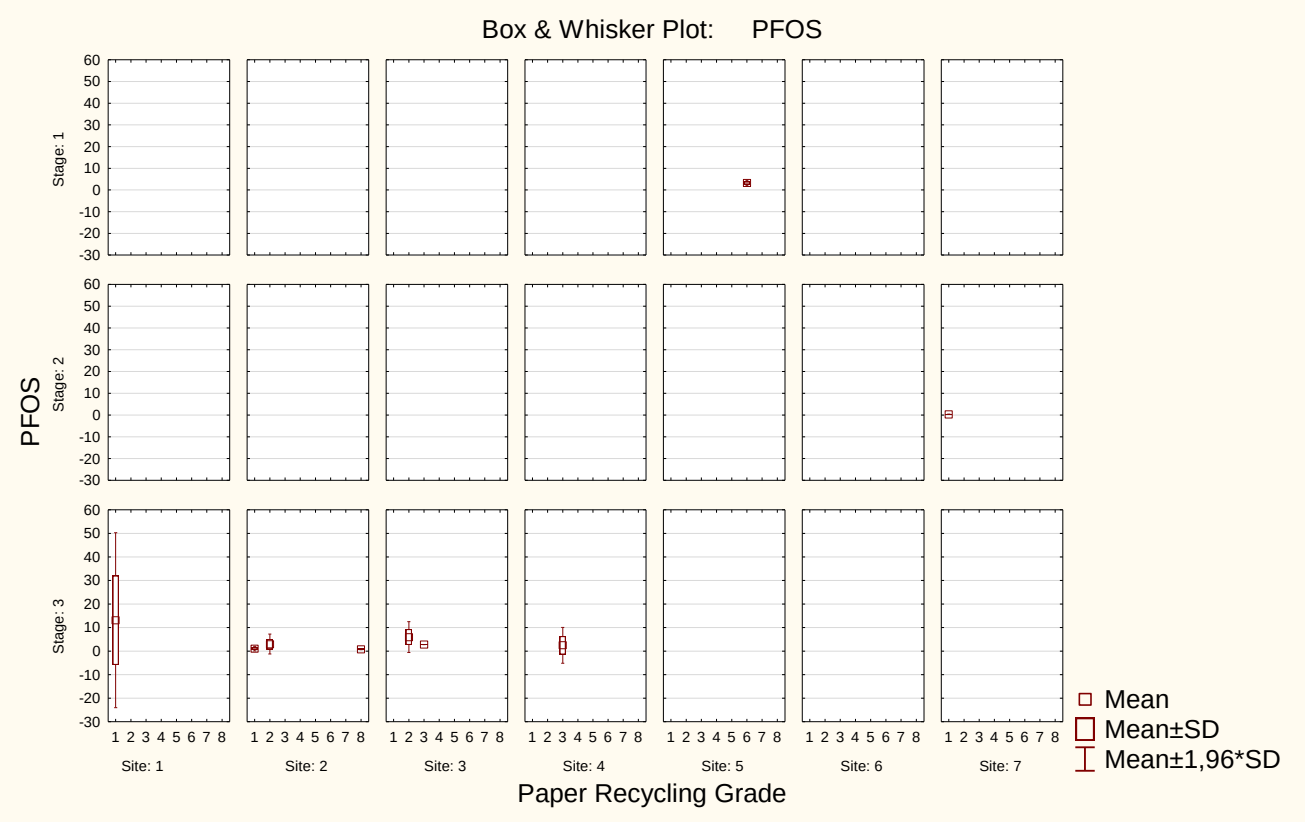


Fig. S13 PFOS box and whisker plot

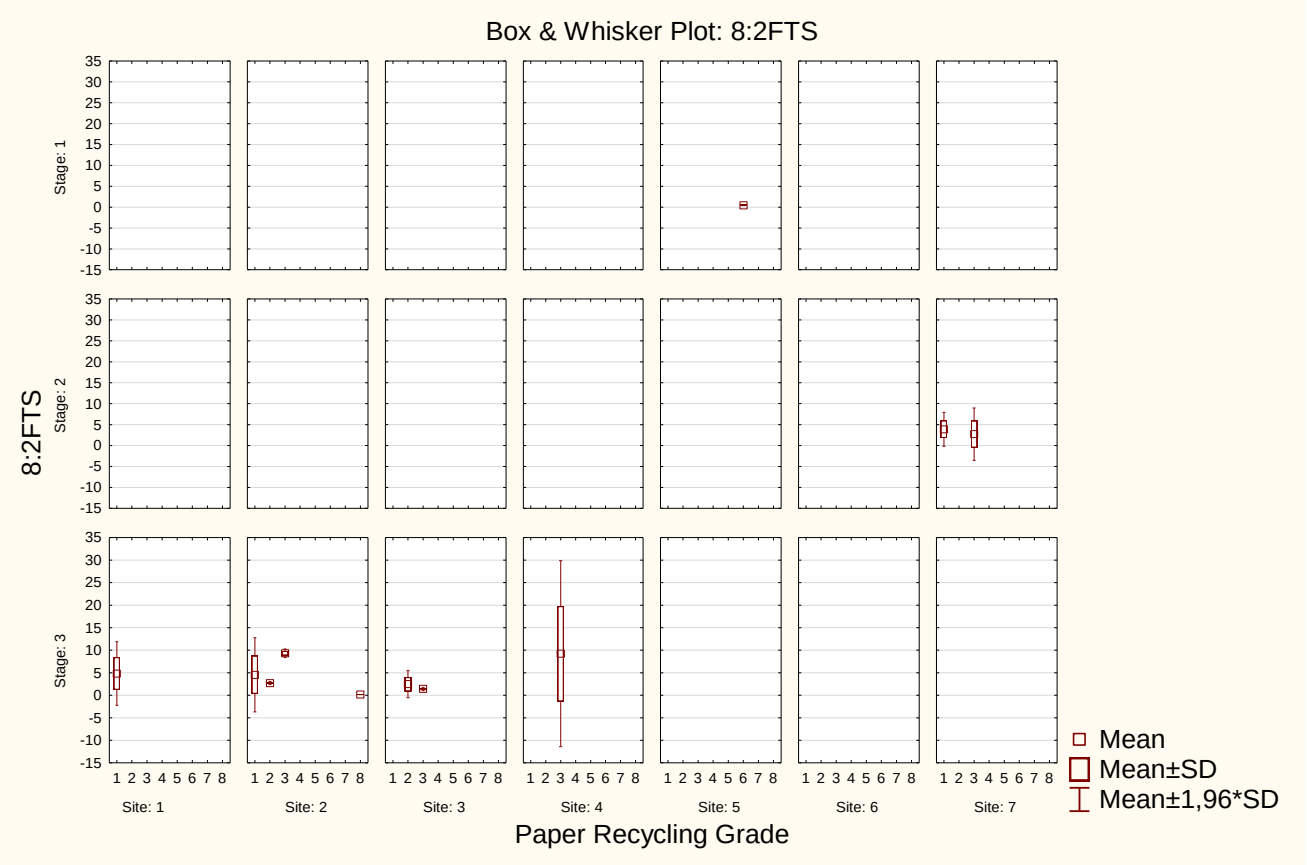


Fig. S14 8:2 FTS box and whisker plot

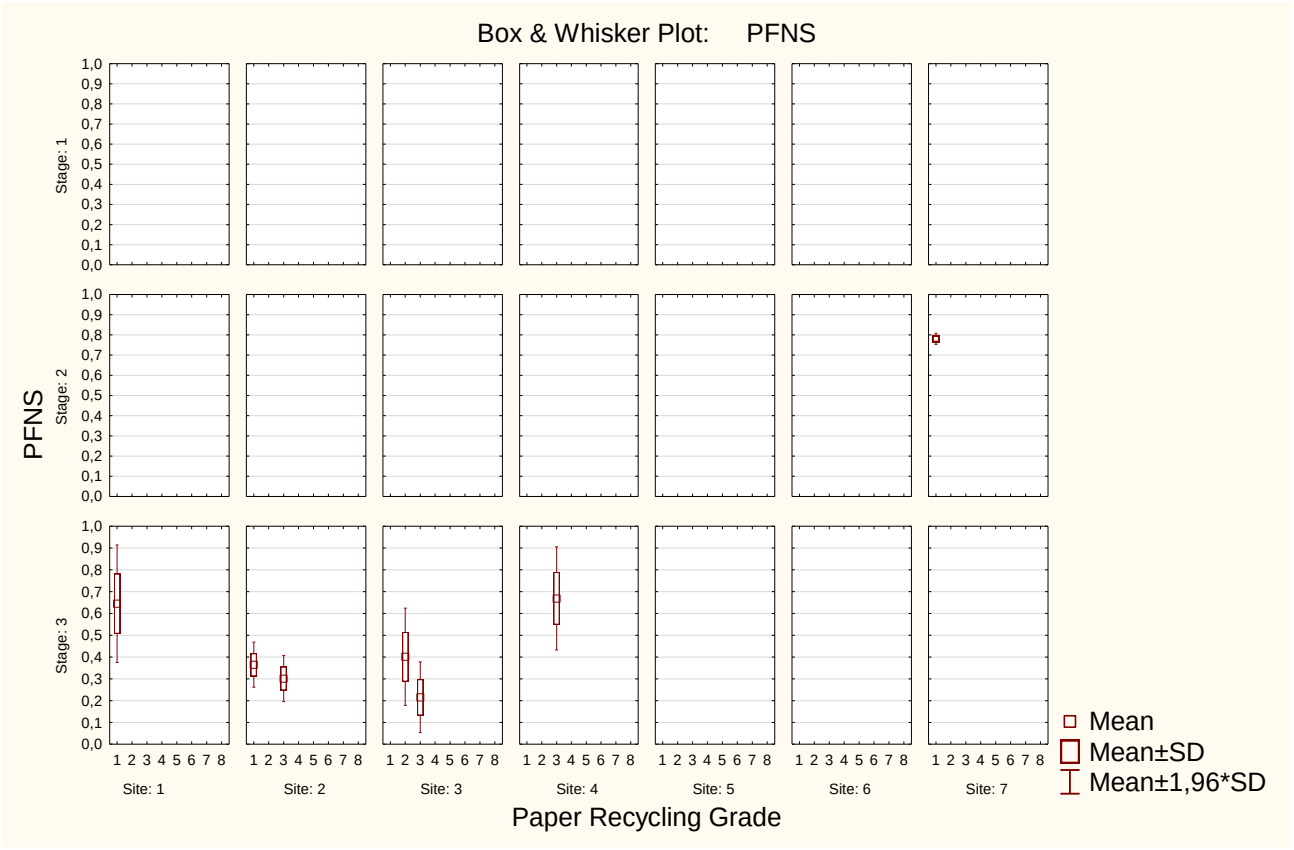


Fig. S15 PFNS box and whisker plot

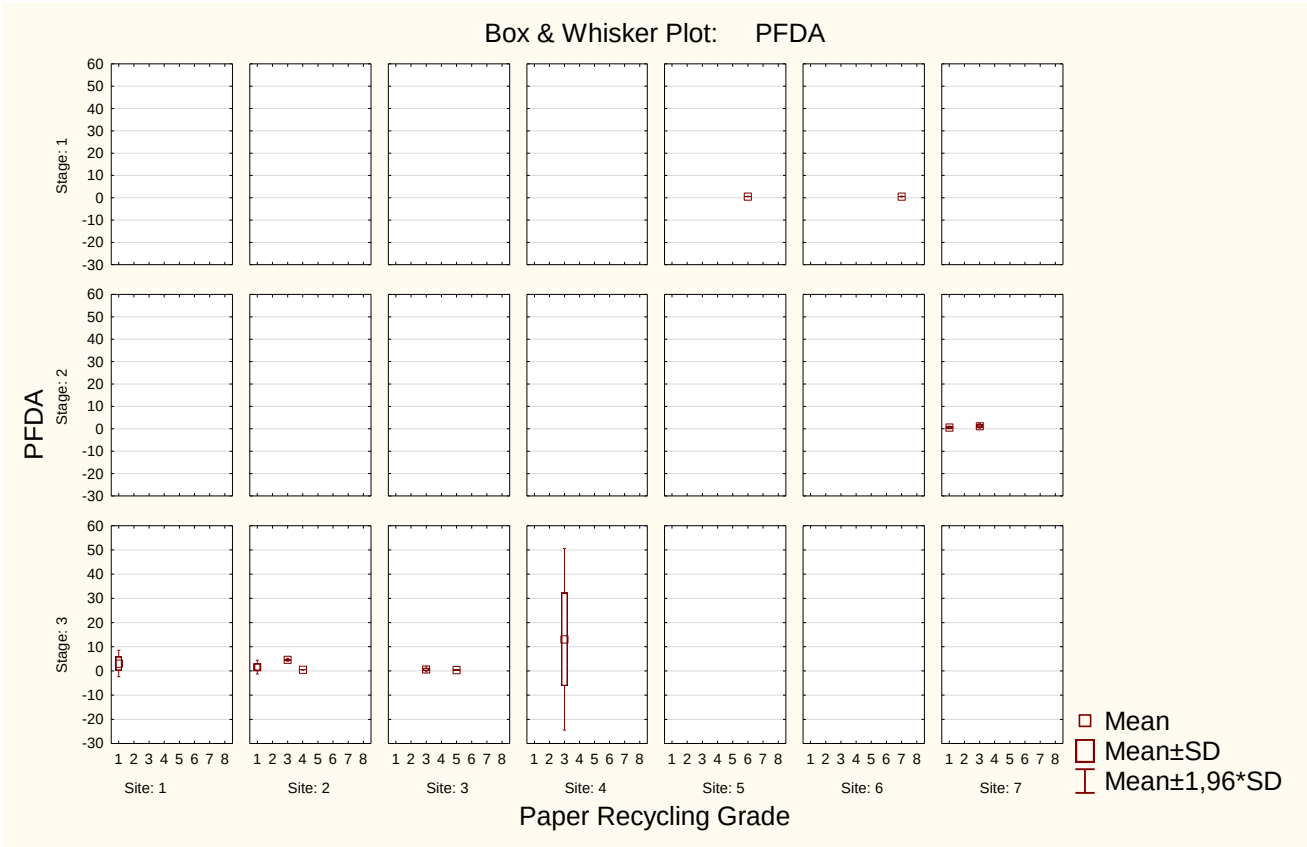


Fig. S16 PFDA box and whisker plot



Fig. S17 PFDS box and whisker plot

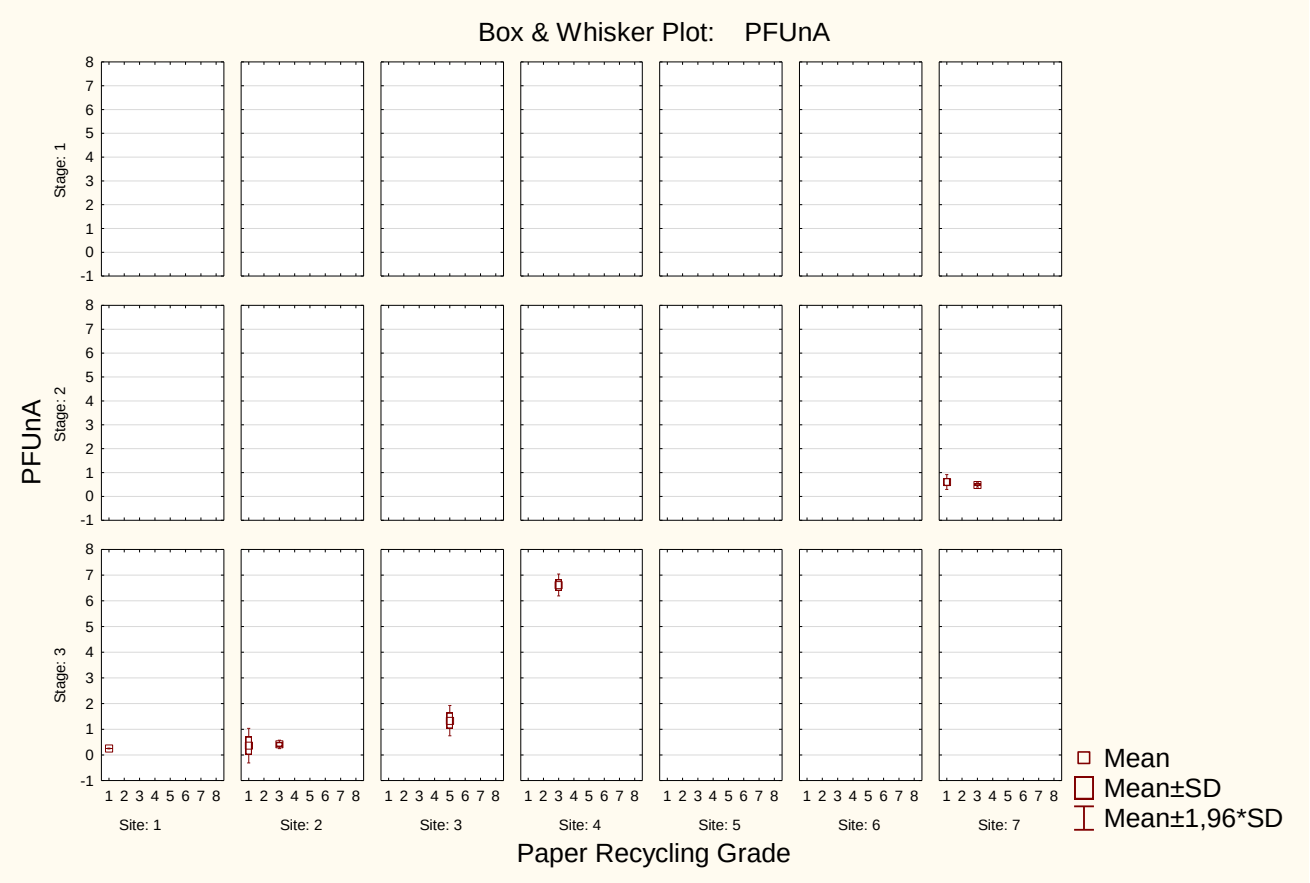


Fig. S18 PFUnA box and whisker plot

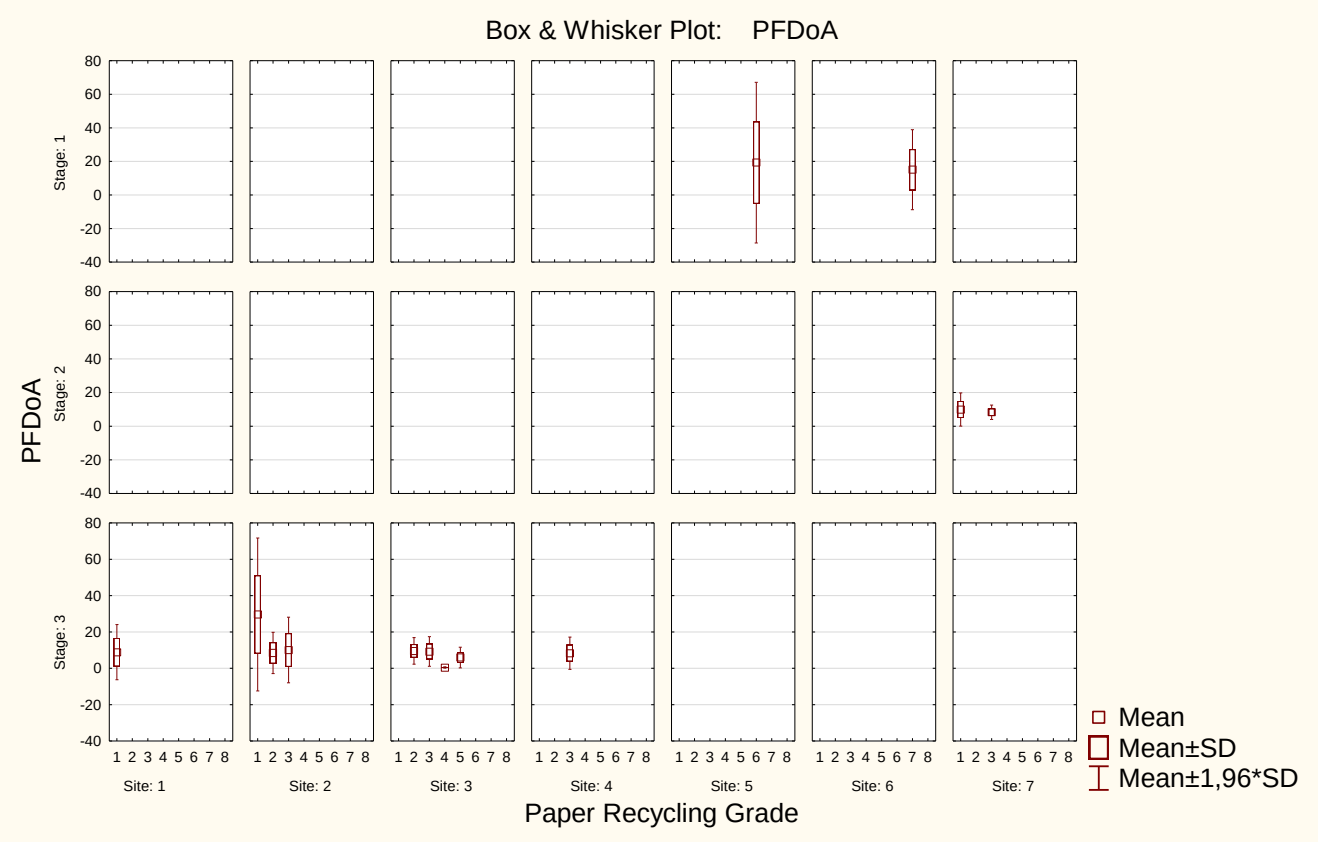


Fig. S19 PFDoA box and whisker plot

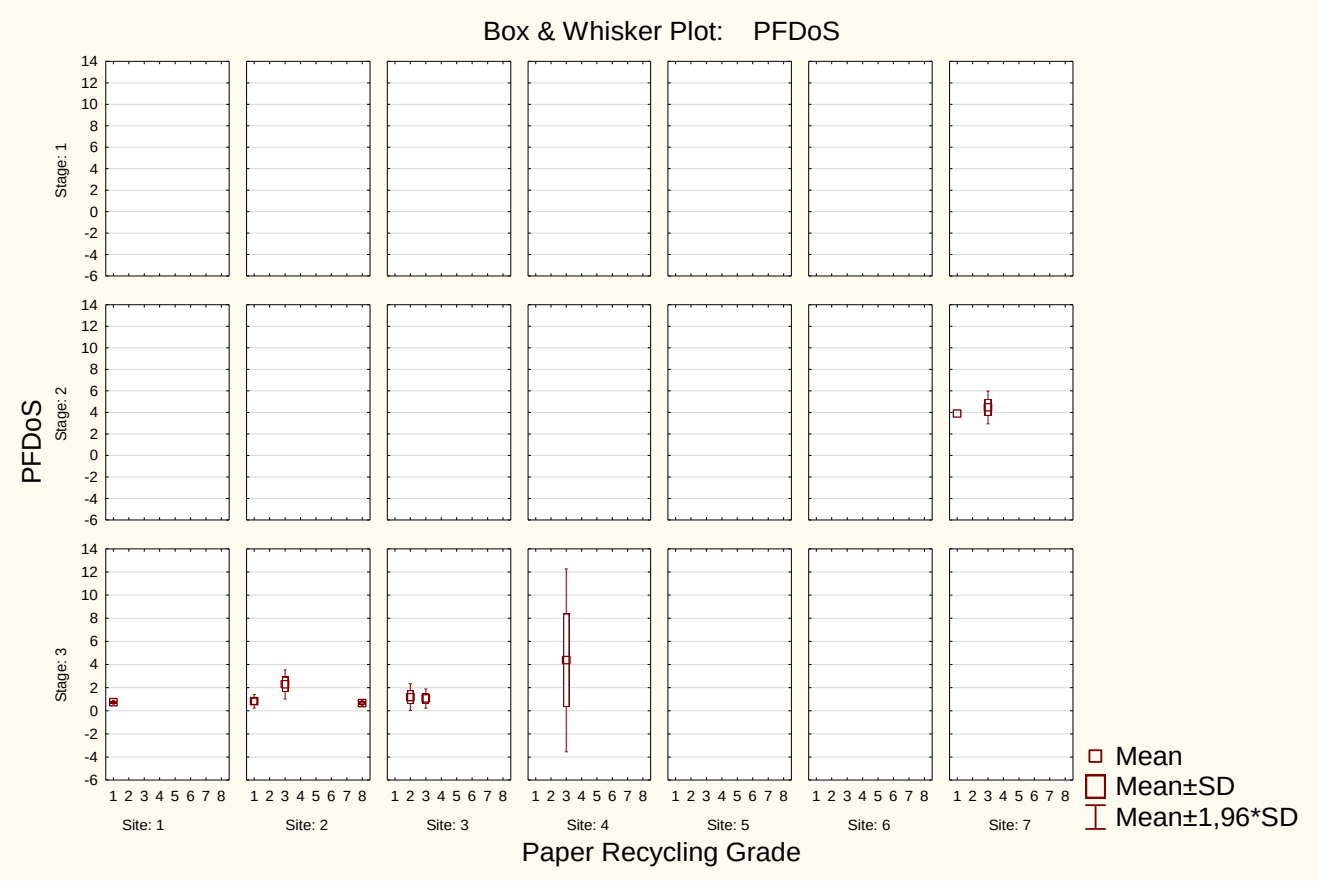


Fig. S20 PFDoS box and whisker plot

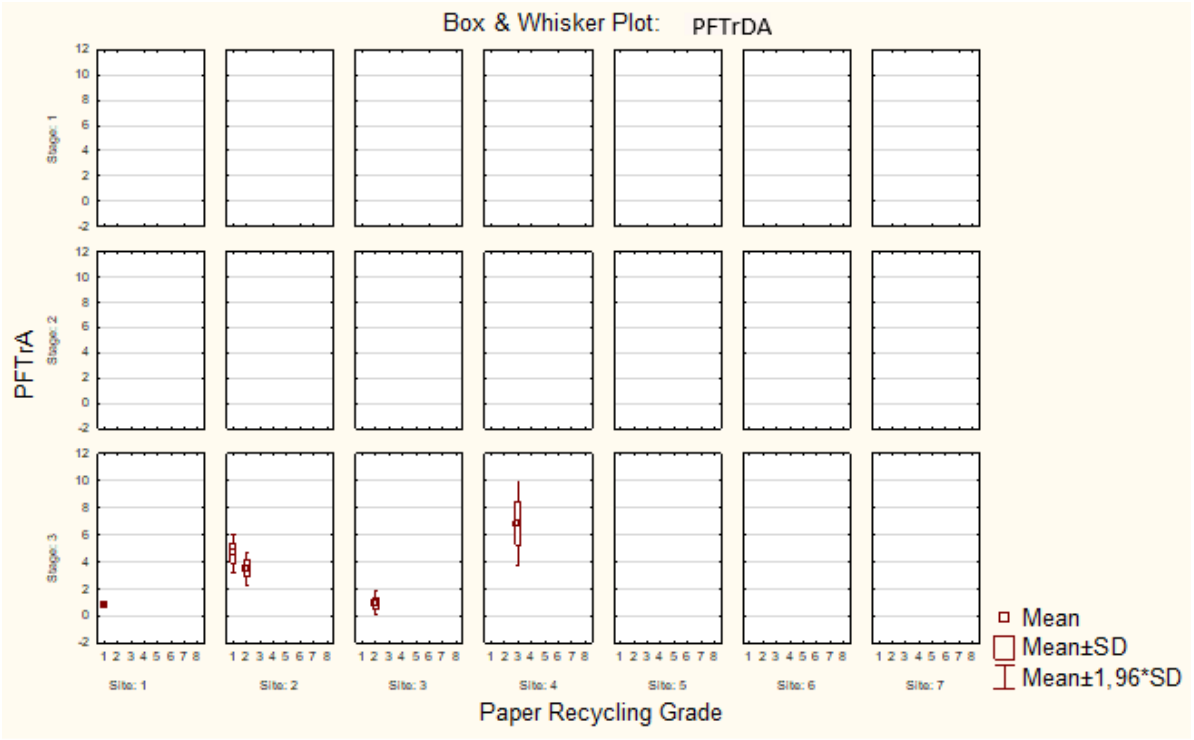


Fig. S21 PFTrDA box and whisker plot

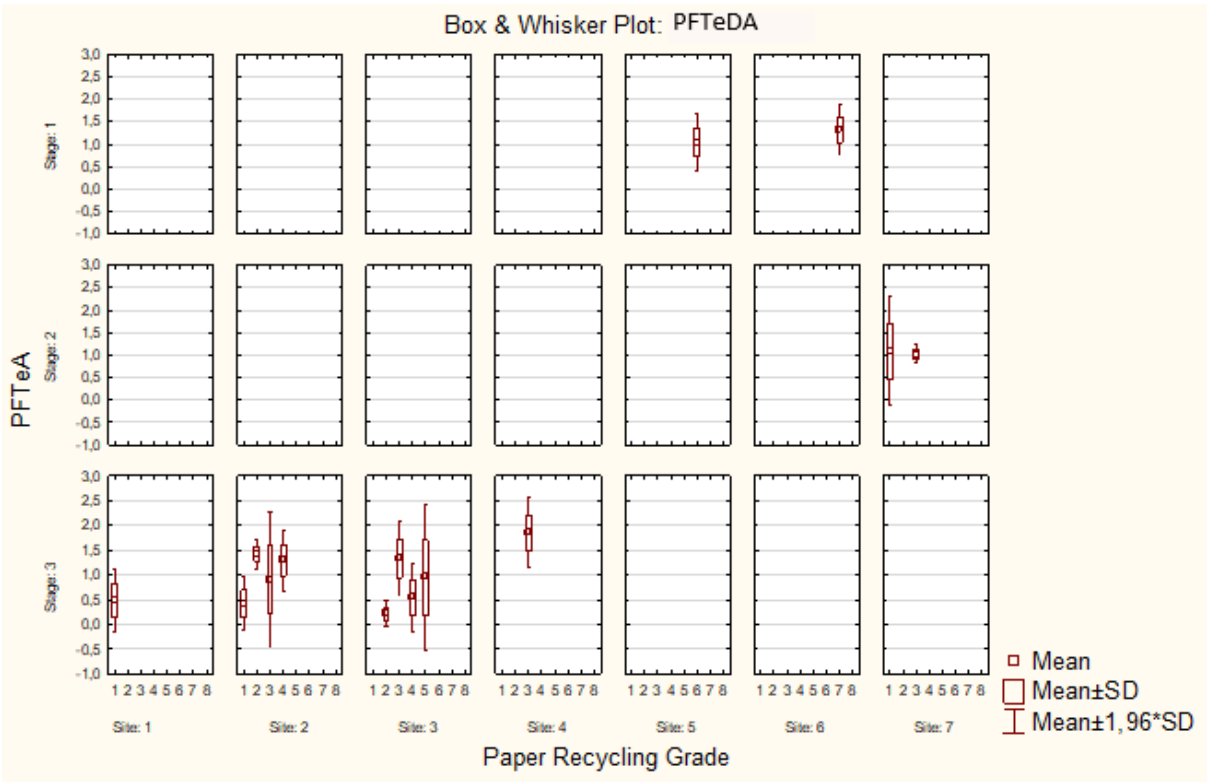


Fig. S22 PFTeDA box and whisker plot

Table S11 Detected concentrations of PFCAs ± U (ng/g)

	Description	PFBA	PFPeA	PFHxA	PFHpA	PFDA	PFDoA	PFUnA	PFTrDA	PFTeDA	PFNA	PFOA
Pre-Consumer	Paperboard	0	0	<LOD	<LOD	<LOD	4.14±0.36	<LOD	<LOD	0	<LOD	<LOD
	Paperboard	2.43±0.9	0	2.87±0.9	<LOD	<LOD	51.66±5.3	<LOD	<LOD	0.76±0.3	0.41±0.2	<LOD
	Paperboard	46.81±5.6	0	1.48±0.9	<LOD	0.58±0.2	2.05±0.3	<LOD	<LOD	1.33±0.1	0.55±0.2	<LOD
	Corrugated box	27.81±3.1	0	16.41±2.5	<LOD	0.54±0.2	26.02±3.2	<LOD	<LOD	1.03±0.3	<LOD	<LOD
	Corrugated fast food box	16.02±1.9	0	2.01±0.1	<LOD	0.05±0.02	4.17±0.4	<LOD	<LOD	1.09±0.3	<LOD	<LOD
Retail	Tea box	25.42±1.6	0	2.36±0.3	<LOD	0.35±0.3	12.44±0.2	0.58±0.2	<LOD	1.54±0.1	27.20±2.8	0.25±0.1
	Chocolate box	50.65±12.6	0	156.90±8.6	2.26±10.6	0.83±0.2	3.11±0.9	<LOD	<LOD	1.07±0.4	5.89±0.9	0.37±0.2
	Toy box	25.19±1.1	0	9.43±1.2	<LOD	1.11±0.5	10.64±1.4	<LOD	<LOD	0	<LOD	2.4±0.6
	Electronics box	60.99±2.4	0	6.85±1.3	<LOD	1.67±0.2	6.02±0.2	0.05±9.91	<LOD	0.94±0.1	9.07±0.4	2.60±0.4
	Noodles box	13.91±1.8	0	1.46±0.2	1.62±0.6	0.76±0.3	7.88±0.3	<LOD	<LOD	1.14±0.4	1.77±0.2	0
	Electronics box	14.51±2.0	0	4.14±1.9	<LOD	<LOD	14.17±0.9	<LOD	<LOD	0.28±0.4	0.09±0.05	<LOD
Household	Fast-food container	47.72±3.4	0	13.09±2.1	20.62±2.8	5.59±0.5	4.13±0.4	<LOD	<LOD	0.21±0.1	<LOD	<LOD
	Egg carton	14.27±1.2	4.71±0.7	7.92±2.6	8.90±1.3	<LOD	3.65±0.3	<LOD	0.88±0.4	0.04±0.02	0.89±0.4	<LOD
	Paper bag	17.22±1.1	0	7.36±0.9	4.51±0.6	0.54±0.2	8.12±0.5	<LOD	<LOD	1.08±0.4	0.30±0.1	<LOD
	Infant bath packaging	15.64±4.7	0	0.90±0.3	<LOD	<LOD	9.90±2.0	<LOD	<LOD	0.04±0.02	2.49±0.3	<LOD
	Banana box	15.75±1.1	0.84±0.1	3.23±0.9	<LOD	<LOD	24.72±0.6	<LOD	<LOD	0.21±0.08	3.96±0.8	<LOD
	Battery box	21.46±3.8 (	0	6.38±1.1	<LOD	<LOD	2.84±0.8	<LOD	<LOD	0.06±0.03	<LOD	<LOD

Recycling Site	Newspaper	48.78±2.6	14.65±1.6	5.31±1.7	4.63±0.3	<LOD	13.72±1.0	<LOD	3.50±0.8	1.28±0.4	3.73±0.6	<LOD
	Newspaper insert	2.77±0.6	0	<LOD	<LOD	<LOD	3.08±0.2	<LOD	<LOD	0	0.70±0.2	<LOD
	Avocado box	10.08±1.2	0	<LOD	<LOD	<LOD	1.68±7.7	<LOD	<LOD	0.30±0.2	<LOD	<LOD
	Wine box	24.59±1.5	0	2.91±0.9	4.31±0.9	4.61±0.4	18.5±0.2	0.41±0.2	<LOD	1.05±0.3	4.63±2.5	0.53±0.3
	Coffee box	10.17±2.9	0	41.66±1.8	<LOD	<LOD	58.30±0.5	<LOD	<LOD	0	<LOD	1.54±0.5
	Tequila box	33.12±1.2	41.54±2.0	4.66±1.0	35.40±4.3	2.85±0.6	15.42±0.9	<LOD	4.37±1.2	0.20±0.2	20.67±2.7	<LOD
	Cereal box	0	0	<LOD	<LOD	<LOD	0	<LOD	<LOD	0.06±0.05	<LOD	<LOD
	Paper bag	32.79±1.8	0	6.98±2.9	1.44±0.8	0.33±0.2	15.26±8.8	0.13±0.2	<LOD	0	15.23±1.3	1.31±0.5
	Colouring sheet	10.62±0.6	0	<LOD	<LOD	0.45±0.2	0	<LOD	<LOD	1.29±0.4	<LOD	14.26±0.7
	Colouring box cover	12.62±0.7	0.37±0.2	<LOD	<LOD	<LOD	0	<LOD	<LOD	0	<LOD	<LOD
Solid Waste Site	Cookware box	8.10±4.4	0	0.96±0.2	<LOD	0.09±0.1	4.99±0.1	<LOD	<LOD	0.93±0.1	27.72±2.8	0.60±0.3
	Brown box	22.25±1.9	0	0.19±0.1	2.39±0.5	0.12±0.01	8.52±0.4	<LOD	<LOD	1.04±0.1	14.54±2.43	0.29±0.1
	Magazine	27.97±2.3	0	1.26±0.4	1.09±0.5	0.37±0.3	3.27±0.6	1.31±0.3	<LOD	1.57±0.2	<LOD	<LOD
	Magazine	30.96±0.3	0	<LOD	9.73±1.0	<LOD	8.57±0.6	<LOD	<LOD	0.10±0.1	0.56±0.2	6.96±1.4
	School Newsletter	0	0	<LOD	<LOD	<LOD	0.05±0.05	<LOD	<LOD	<LOQ	<LOD	<LOD
	Newspaper	11.03±3.6	0.63±0.5	<LOD	<LOD	<LOD	12.97±0.8	<LOD	<LOD	0	3.56±0.6	<LOD
	Newspaper	28.61±7.4	25.84±1.0	4.46±0.9	10.20±2.3	<LOD	6.03±0.5	<LOD	0.8±0.5	0.21±0.3	8.11±1.1	3.15±0.5
	Corrugated food box	33.94±1.0	0	1.53±0.7	10.14±0.7	<LOD	13.37±1.6	<LOD	<LOD	1.68±0.3	<LOD	<LOD
Waste Pickers	Snacks box	16.31±1.8	0	28.04±4.3	<LOD	0.47±0.3	6.51±3.8	<LOD	<LOD	1.53±0.1)	<LOD	<LOD

	Coffee box	6.62±1.0	0	7.67±0.3	<LOD	0.12±0.2	14.18±0.9	<LOD	<LOD	1.90±0.3	0.54±0.2	0.33±0.3
	Board	60.56±1.3	1.13±0.2	3.35±0.2	<LOD	<LOD	0	<LOD	<LOD	0	<LOD	<LOD
	Corrugated food box	61.51±2.8	70.37±3.1	19.58±2.1	47.29±5.2	38.67±0.2	4.30±0.9	6.61±0.2	6.8±1.7	1.93±0.4	1.50±0.4	<LOD

Table S12 Detected concentrations of PFSAs ± U (ng/g)

	Description	PFBS	PFOS	PFPeS	PFHxS	PFHpS	4:2FTS	6:2FTS	8:2FTS	PFNS	PFDS	PFDoS
Pre-Consumer	Paperboard	0	0	1.57±0.2	9.96±1.0	<LOD	0	23.03±9.2	<LOD	0	0	<LOD
	Paperboard	0	3.22±0.8	<LOD	5.16±0.8	<LOD	4.27±1.8	26.33±13.0	<LOD	0	0	<LOD
	Paper	0	0	<LOD	<LOD	<LOD	0	22.16±11.2	0.46±0.2	0	0	<LOD
	Corrugated box	0	0	1.46±0.2	19.87±2.1	<LOD	6.17±2.7	2.00±1.4	<LOD	0	0	<LOD
	Corrugated fast food box	0.18±0.1	0	<LOD	11.06±0.1	<LOD	0	53.83±16.0	<LOD	0	0	<LOD
Retail	Tea box	1.50±0.6	0	2.11±0.1	1.39±0.7	<LOD	1.17±0.99	57.21±18.8	2.89±0.8	0	0	<LOD
	Chocolate box	0	0	1.70±0.4	<LOD	<LOD	0	11.51±4.5	<LOD	0.78±0.1	0	<LOD
	Toy box	0	0	1.22±0.5	<LOD	2.47±0.2	1.40±0.5	50.71±23.4	<LOD	0	16.68±1.2	<LOD
	Electronics box	2.04±0.3	0	0.42±0.3	1.26±0.4	1.94±0.5	7.30±3.3	49.84±15.1	0.41±0.2	0	4.35±1.3	4.67±0.7
	Noodles box	0	0.36±0.2	1.63±0.1	<LOD	1.18±0.1	5.04±0.3	5.46±5.9	6.14±1.7	0	17.58±3.2	3.88±0.5
	Electronics box	0	0	<LOD	2.96±0.6	<LOD	10.50±1.8	7.30±5.10	<LOD	0	17.54±1.6	<LOD
Household	Fast-food container	0	44.36±1.6	0.51±0.1	<LOD	0.74±0.3	0	<LOD	<LOD	0	0	<LOD
	Egg carton	3.43±0.2	5.46±0.6	9.10±0.7	13.06±0.7	0.40±0.1	42.35±5.9	10.10±1.5	0.62±0.2	0	1.16±0.1	0.70±0.4
	Paper bag	0	0	<LOD	6.50±0.4	<LOD	0	80.88±22.5	8.66±0.3	0	0	<LOD
	Infant bath packaging	0	2.09±0.7	<LOD	5.31±0.6	<LOD	7.90±1.4	32.23±13.3	<LOD	0	0	<LOD
	Banana box	1.34±0.3	0.49±0.4	0.96±0.4	3.36±0.3	0.54±0.1	5.63±0.4	35.39%±12.9	4.87±0.3	0.06±0.1	0.89±0.1	0.76±0.5
	Battery box	0	0	<LOD	2.12±0.3	<LOD	0	4.97±2.6	<LOD	0	0	<LOD

Recycling Site	Newspaper	1.70±0.1	0.99±0.1	3.24±0.4	16.85±2.2	0.25±0.1	31.12±6.6	249.33±42.7	<LOD	0	1.16±0.7	<LOD
	Newspaper insert	1.27±0.1	4.95±0.6	2.08±0.1	1.27±0.6	1.11±0.1	17.09±2.9	36.44±9.7	2.70±0.4	0	0	<LOD
	Avocado box	0	0	<LOD	19.81±0.2	<LOD	0	<LOD	<LOD	0	0	<LOD
	Wine box	1.27±0.2	0	<LOD	25.34±2.2	0.02±0.1	2.04±0.7	14.44±7.6	9.34±0.5	0.30±0.1	0	1.98±0.5
	Coffee box	0	0	<LOD	8.08±0.8	<LOD	0	28.04±11.7	<LOD	0	14.51±1.5	<LOD
	Tequila box	6.22±0.3	0.72±0.3	28.40±11.5	21.94±1.8	7.19±0.2	54.85±0.3	354.51±88.1	11.33±1.0	0	3.06±18.7	1.14±0.6
	Cereal box	0.40±0.2	1.13±0.2	1.28±0.2	1.22±0.3	0.16±0.1	4.60±0.9	2.45±2.1	2.43±0.9	0	0	0.72±0.5
	Paper bag	0.46±0.2	0	<LOD	28.17±0.3	4.43±1.7	0	<LOD	2.80±0.5	0.38±0.1	1.11±0.1	0.60±0.4
	Colouring sheet	0	0	<LOD	<LOD	<LOD	3.60±2.8	<LOD	<LOD	0	0	<LOD
	Colouring box cover	0.38±0.2	0.80±0.2	1.05±0.7	<LOD	0.28±0.1	0.90±0.8	<LOD	0.17±0.2	0	0	0.66±0.5
Solid Waste Site	Cookware box	0	0	<LOD	<LOD	<LOD	0	68.83±26.6	1.50±0.3	0.18±0.1	1.24±0.4	1.44±0.4
	Brown box	1.70±0.2	0	<LOD	0.68±0.5	1.13±0.1	0	24.19±12.6	1.32±0.2	0.17±0.1	0.47±0.1	0.68±0.5
	Magazine	0	0	<LOD	<LOD	<LOD	0	<LOD	<LOD	0	0	<LOD
	Magazine	0	0	12.21±0.4	23.82±1.4	5.09±0.6	33.65±3.3	22.78±10.5	<LOD	0	0	<LOD
	School Newsletter	0	0	<LOD	<LOD	<LOD	2.52±2.8	<LOD	<LOD	0	0	<LOD
	Newspaper	1.19±0.6	2.80±0.8	1.73±0.2	0.55±0.3	1.65±0.7	11.39±2.9	43.20±17.9	0.98±0.2	0	0.32±0.2	
	Newspaper	1.01±0.2	8.71±0.3	12.91±0.7	14.67±2.1	2.30±0.5	28.45±11.1	60.28±16.1	3.80±0.3	0	0	0.92±0.5
	Corrugated food box	0.67±0.2	2.81±0.2	<LOD	<LOD	<LOD	14.87±4.2	9.38±6.0	<LOD	0.28±0.1	0	<LOD
Waste Pickers	Snacks box	0	0.17±0.2	<LOD	2.02±1.7	0.44±0.1	25.97±3.0	24.08±8.1	<LOD	0	0	<LOD
	Coffee box	0	0	2.02±0.1	<LOD	0.19±0.1	0	3.45±2.4	2.49±0.2	0	0.32±0.3	<LOD
	Board	1.82±0.2	0.43±0.3	1.58±0.2	<LOD	0.25±0.1	10.13±1.0	29.07±11.0	3.15±0.5	0	0.47±0.3	0.69±0.4
	Corrugated food box	15.55±1.2	9.75±1.0	10.60±2.5	17.34±1.2	1.56±0.1	164.79±7.1	20.84±11.5	22.05±6.6	0.60±0.1	18.30±2.1	8.03±7.7

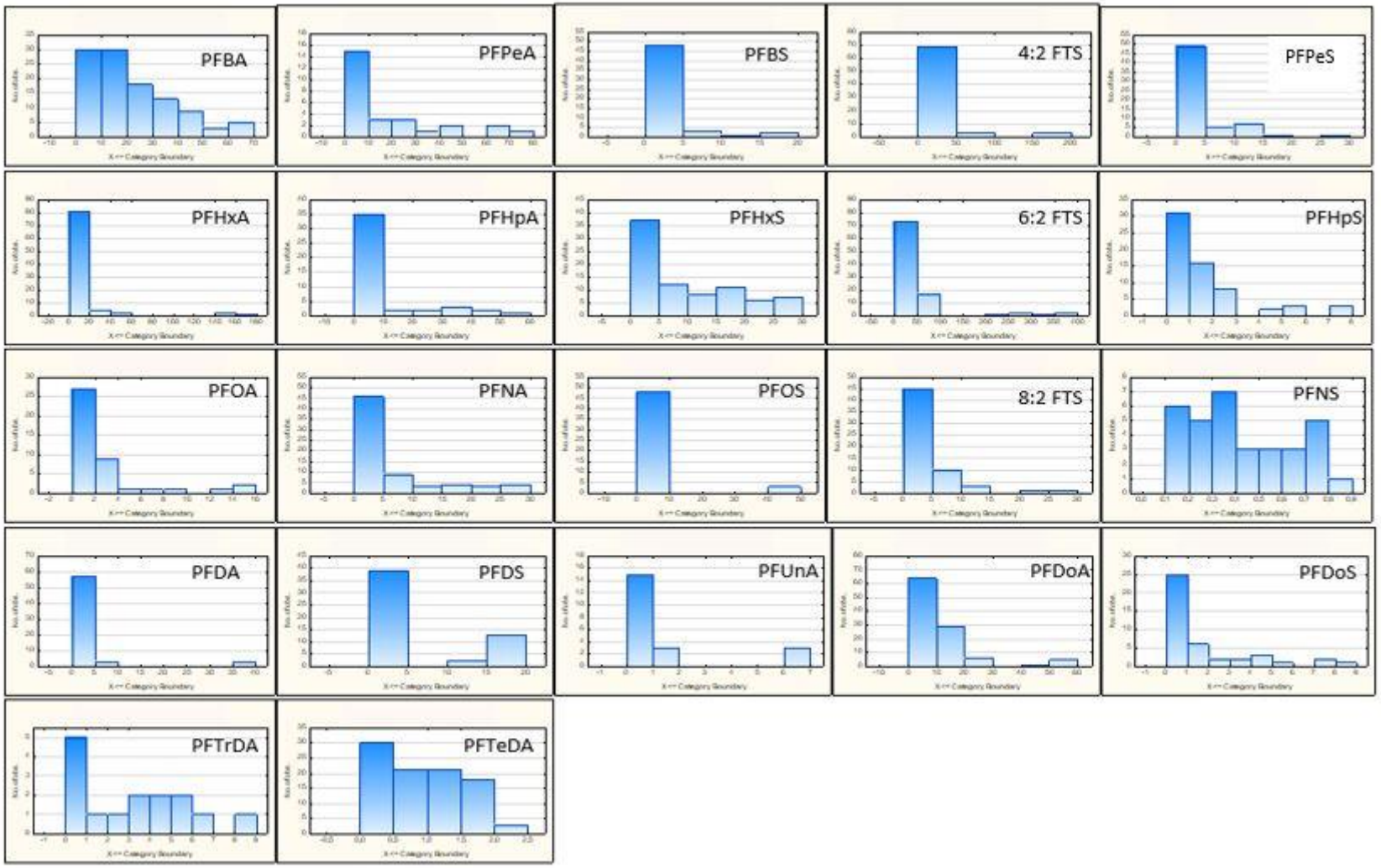


Fig. S23 Uncategorised distribution plots

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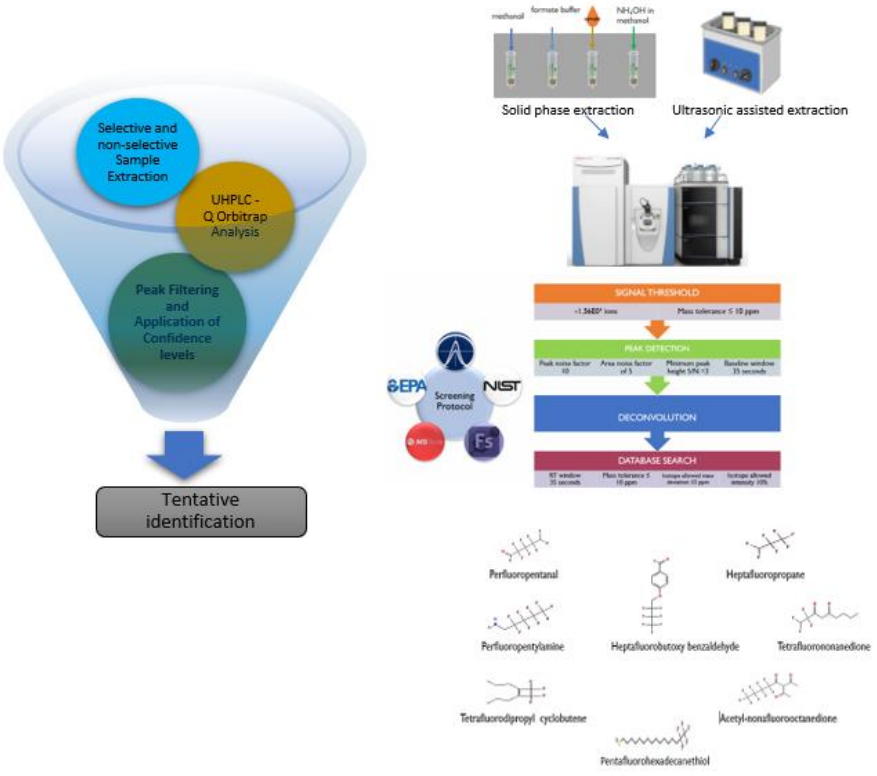
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CHAPTER EIGHT

8 PAPER 5

This paper titled **"**Suspect screening of per- and polyfluoroalkyl substances in paper by selective and non-selective extraction with UHPLC-Q Orbitrap MS**"** was published in **Chemosphere** (2024) 363, 142904. https://doi.org/10.1016/j.chemosphere.2024.142904.

The importance of sample pre-treatment techniques was explored in this paper with the tentative identification of various PFAS compounds reported against a confidence level.



Suspect screening of per- and polyfluoroalkyl substances in paper by selective and non-selective extraction with UHPLC-Q Orbitrap MS

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Abstract

Non-targeted analysis and suspect screening of per- and polyfluoroalkyl substances (PFAS) in various matrices have gained traction with advancements in accurate mass analytical instruments. This study employed ultra-high performance liquid chromatography coupled to quadrupole orbitrap high-resolution mass spectrometry for PFAS suspect screening of paper grades used in the paper recycling chain. The samples were prepared using two extraction techniques; selective accelerated solvent extraction with weak anionic exchange solid-phase extraction and non-selective ultrasonic-assisted extraction. A suspect screening protocol was established to tentatively identify suspected PFAS against spectral databases using a systematic approach of peak filtering and study-specific thresholds for reporting, linked to a confidence level. The possible prevalence of previously unreported PFAS in several paper materials across the various collection sites in the paper recycling chain was inferred by the common detection of short-chain polyfluoroalkyl ketones and diketones in the paper recycling chain. The suspect screening tentatively identified 41 unique PFAS, with 3 common to both pre-treatment techniques. The detection of unique PFAS by the two sample pre-treatment techniques highlighted the significance of both selective and non-selective extraction in PFAS screening endeavours. Further, it showed the importance of understanding the acquisition mechanisms employed in mass spectrometry where data-dependent acquisition triggered fragmentation in certain identified compounds, and not in others. The tentatively identified PFAS indicated that there were several previously unreported PFAS in the paper recycling chain and that additional studies were required to investigate their abundance, possible persistence, bioaccumulation and toxicity, in relation to their functional groups and carbon chains.

Keywords: untargeted analysis; high resolution mass spectrometry; solid phase extraction; ultrasonic; chromatography; recycled paper

8.1 Introduction

The analysis of per- and polyfluoroalkyl substances (PFAS) in various samples has become synonymous with the detection of perfluoroalkyl carboxylic acids and sulfonic acids (Al Amin et al., 2020). However, PFAS include a wide range of chemical classes and functional groups, including esters, betaines, hydrofluoroethers, chlorofluoro olefins, fluoropolymers, fluorotelomers, aromatics, amines, ethers, and benzamides (Berhanu et al., 2023; Bugsel et al., 2023). The need for further exploration of a wider range of compounds has led to an increasing need for screening and non-targeted approaches (Houtz et al., 2018; Liu et al., 2022; Liu et al., 2019; Wang et al., 2022; Bugsel et al., 2023; Zweigle et al., 2023). Such an exploration is often hindered by several challenges associated with PFAS analysis. The first challenge is the large number of compounds in this class. PFAS consist of over 10 000 compounds (Tang et al., 2023), when defined as any fluorinated compound with at least one fully fluorinated methyl group and including a broad range of compounds from small molecules to complex aromatics and polymers (Wang et al., 2021). These are manufactured for numerous applications (Glüge et al., 2020) using various undisclosed and unreported synthesis pathways that result in intermediates, precursors, and degradation products (Shen et al., 2023). The number of PFAS that have been identified thus far pales in comparison to the number of analytical standards available (Bugsel et al., 2023; Manojkumar et al., 2023). Ubiquitous PFAS contamination and instrument capabilities (Manojkumar et al. 2023) are other challenges associated with untargeted PFAS detection. High-resolution mass spectrometry (HRMS) is a powerful tool for addressing some of these challenges to identify known, novel, and/or emerging PFAS (Manojkumar et al., 2023; Strynar et al., 2023). In the absence of reference standards, confidence intervals have been used to assess the tentatively identified compounds (Charbonnet et al., 2022). Charbonnet et al. (2022) proposed a confidence scheme for screening and non-target analysis of PFAS from Levels 1 to 5, where Level 1 indicates the greatest confidence (by reference standard and MS2) and Level 5 the least confident identification (validated by comparison with exact mass (Charbonnet et al., 2022). In the case of suspected screening, matching the

expected exact mass, isotope pattern formation, and product ions strengthens the probability of correct identification (Hajeb et al., 2022).

For liquid chromatography in tandem with mass spectrometry, the quality of the results obtained in PFAS screening often lies in the extraction and ionization efficiency. Complex materials, such as paperboard, consist of a complex matrix of chemicals used in manufacturing and conversion processes. These chemicals include organic and inorganic compounds, salts, and polymeric compounds. These compounds influence the resultant sample matrix constituents and can significantly affect the detection of PFAS (Dickman and Aga, 2022). Matrix effects influence the ionization efficiency and signal response (Shen et al., 2023). To reduce these effects, pre-treatment or purification procedures are employed to influence both the selectivity and sensitivity of the analyses (Hajeb et al., 2022). For suspect screening, the sample pre-treatment steps should ideally extract a wide range of PFAS compounds while minimizing interfering matrix elements that may adversely impact identification. HRMS has been found to significantly reduce interference from matrices, allowing for a degree of flexibility in enhancing the sensitivity of ultra-trace PFAS analysis (Al Amin et al., 2020). Supported liquid extraction (SLE), pressurized liquid extraction (PLE) (also referred to accelerated solvent extraction (ASE)), ultrasonic-assisted extraction (UAE), and solid phase extraction (SPE) are common extraction techniques for PFAS detection in solid matrices, such as soil, sediment, food packaging, and sludge (Al Amin et al., 2020; Hajeb et al,. 2022). Suspected PFAS screening has been undertaken on various food packaging matrices (Hajeb et al., 2022; Boisacq et al., 2023; Sapozhnikova et al., 2023); however, reports on non-food packaging are limited. The circularity of paper recycling means that unknown PFAS may propagate among recycled paper manufacturing, paper recycling, waste mingling, consumers, and the environment. Therefore, it is important to explore the nature of PFAS that may be present and generate new knowledge in the research area.

In this study, suspected screening of recycling paper grades was investigated using two sample pre-treatment techniques; ASE with SPE and UAE in order to compare the detection and chemical properties of the resulting tentatively identified PFAS.

Various grades of paper were sourced from paper mills and conversion sites (pre-consumer), grocery store (i.e., supermarket store with both food and non-food packaging) (retail), domestic waste sites, solid waste disposal sites, waste pickers, and recycling facilities (post-consumer) in Cape Town, South Africa. Analysis was performed using ultra-high-performance liquid chromatography – high-resolution mass spectrometry (UHPLC-HRMS) Orbitrap.

8.2 Materials and methods

8.2.1 Chemicals and sampling

LC-MS-grade methanol, ethanol, and water, as well as HPLC-grade formic acid, toluene, ammonium formate, and analytical grade ammonium hydroxide solution were purchased from Merck (Johannesburg, South Africa) and Anatech (Cape Town, South Africa). These chemicals and buffers were used as received without further purification (Table S1). Thirty-nine paper samples were collected from Cape Town, South Africa, consisting of various grades of paper used for recycling. The pre-consumer and retail samples consisted only of paperboard, whereas the post-consumer samples consisted of paper grades typically used in the manufacture of recycled boards. These included cartons, newspapers, corrugated boxes, office paper, and magazines. Pre-consumer samples were sourced directly from paper mills and paper conversion sites, whereas retail samples were collected from South African grocery stores. Post-consumer samples were collected from recycling facilities, solid waste disposal sites, household waste, and informal waste pickers. The collected samples were placed in polypropylene (PP) sleeves and polyethylene (PE) bags prior to sample pre-treatment.

8.2.2 Sample pre-treatment

The samples were first shredded using a kitchen blender to a dry pulp consistency for the two pre-treatment techniques: ASE with SPE and UAE. Paper samples were prepared in triplicate (0.5 g each) using an analytical balance (Table S2) and extracted using a Dionex 350 ASE system (Anatech, Cape Town, South Africa). The extraction conditions consisted of a 3:2 ethanol: methanol solvent combination at 70 °C oven temperature for three cycles of 12 min each. After extraction, the

sample was evaporated to approximately 1 mL under nitrogen at 40 °C using a Biotage TurboVap (Anatech, Cape Town, South Africa) in preparation for SPE clean-up. Selectivity and specificity were expected to be enhanced based on pH-controlled weak anionic exchange. The selective sample pre-treatment was developed for perfluorocarboxylic acids (PFCAs), perfluorosulfonic acids (PFSAs), and telomeric sulfonates. Enviro-Clean WAX SPE cartridges with a 500 mg sorbent bed (Stargate Scientific, Johannesburg, South Africa) were mounted on an SPE manifold (Stargate Scientific, Johannesburg, South Africa) and operated under vacuum using a DryVac 400 vacuum pump (Air & Vacuum Technologies, Johannesburg, South Africa). The SPE was initiated by conditioning the cartridges with 3 mL of methanol followed by 5 mL of 0.1 M ammonium formate buffer. The supernatant was then loaded (500 µL) before elution with 6 mL of 1% methanolic ammonium hydroxide. The eluent was concentrated to approximately 1 mL under nitrogen at 40 °C using the Biotage TurboVap and filtered into a vial with a 0.22 µm regenerated cellulose syringe filter (Stargate Scientific, Johannesburg, South Africa) filter before analysis by UHPLC-HRMS. The UAE technique aims for less selectivity for a broader class of compounds present in paper-based materials that are generally soluble in polar environments. For sample pre-treatment, 1 g of shredded paper was placed in a 20 mL of 2:1:1 water: ethanol: methanol solution inside a 60 mL glass vial and vortexed for 2 min prior to indirect UAE at 60 °C for 2 h in a sonic bath (Power Sonic 405, United Scientific, Cape Town). The resulting extract was filtered through a 0.22 µm regenerated cellulose syringe filter before analysis by UHPLC-HRMS. Blanks were prepared for both extraction techniques to eliminate any latent PFAS from the suspect screening.

8.2.3 UHPLC-HRMS parameters

The UHPLC-HRMS was achieved using a Thermo Scientific Vanquish UHPLC+ Q Exactive Focus Orbitrap (Anatech, Cape Town, South Africa) equipped with a Hypersil Gold aQ 100 mm x 2.1 mm x 1.9 µm column and Hypersil Gold 50 mm x 3 mm x 1.9 µm delay column (Anatech, Cape Town, South Africa). Instrument data acquisition was performed using Thermo Scientific Xcalibur and TraceFinder. For the ASE pre-treatment, a binary solvent system was used which consisted of solvent A as 0.1% formic acid in water and 10 mM ammonium formate and methanol as

solvent B. The initial flow rate was 0.4 mL min-1 in 30% solvent B, which increased to 100% solvent B at 13 min (at 1 mL min-1), held for 17 min, before returning to 30% solvent B at 21.1 min (0.5 mL min-1) (Table S3). The acquisition mode was a full scan with data-dependent acquisition (DDA or ddMS2) in negative mode. The sample injection volume was 5 µL. The full scan acquisition range was set at 150-750 m/z at a resolution of 70 000 with DDA at a resolution of 35 000 (Stroski and Sapozhnikova, 2023). The stepped collision energies were selected as 15 and 30 eV. For the UAE-extracted samples, solvent A consisted of water in 0.1% formic acid with 5 mM ammonium formate, and solvent B as methanol in 0.1% formic acid with 5 mM ammonium formate. The gradient method was initiated at 30% solvent B at 0.3 mL min-1 (hold 1 min) before increasing to 100% B, with a curve set at 2 until 15 min. The flow rate was increased to 0.35 mL min-1 for 4 min before returning to 30% solvent B and 0.3 mL min-1 (Table S3). A 10 µL injection volume was used. The acquisition mode was a full-scan DDA in the negative mode. The full scan acquisition range was 83.4 to 1250 m/z at a resolution of 70 000 and DDA at a resolution of 35 000. The stepped collision energy was selected as 15 and 30 eV.

8.2.4 Suspect screening methodology

Data analysis was performed using Thermo Scientific Xcalibur TraceFinder 5.0. and FreeStyle 1.8. Two PFAS databases were used for suspect screening: the National Institute of Standards and Technology (NIST) PFAS Suspect List (Place, 2021) and the U.S Environmental Protection Agency (EPA) PFAS Chemicals database (EPA, 2022) containing 4969 and 10988 PFAS compounds, respectively. Both databases include unique entries that would otherwise be neglected (Bugsel et al, 2023) and allow for increased matching opportunities. The limitation of the NIST suspect list is that it is not a validated list (Place, 2021). An Unknown screening data-processing method was developed using TraceFinder. Freestyle was used for mass defect and isotopic pattern verification. Five main factors were used for tentative identification: library database match percentage, accurate mass of the molecular ion, mass tolerance, isotopic pattern match, and MS2 fragmentation. The accurate mass, mass tolerance, and isotopic pattern match were based on the full-

scan acquisition of the molecular ion, taking charge and adduct into consideration. Mass tolerance was defined using Equation (1).

$$Mass\ tolerance\ (ppm) = \left|\frac{Theoretical\ mass\ expected - Mass\ Observed\ (m/z)}{Theoretical\ mass\ expected\ (m/z)}\right| \times 10^6 \quad (1)$$

A mass tolerance criterion of ≤ 10 ppm indicated an accurate mass for suspect screening. The isotopic pattern match was based on a comparison of the theoretical isotopic distribution with the acquired spectrum (Bugsel et al., 2023). This instrument-generated tool was imported to assess the confidence of molecular formula identification by HRMS (Charbonnet et al., 2022). In this study, an acceptable isotopic pattern score was ≥80%, with the number of isotopes matched being ≥ n-1, where n represents all theoretically possible fragments. The MS^2 fragments obtained were used to further enhance the confidence interval for qualitative identification. A confirmatory MS^2 ion was identified for assenting purposes using Thermo Scientific FreeStyle and MStools. Charbonnet et al. (2022) proposed categories for confidence in identifying PFAS using HRMS, where most confidence was categorized as level 1 for most confident matching using a reference standard to least confident identification at level 5, where accurate mass was the only required match criterion. This study aimed for Level 3 identification confidence that considered accurate mass, mass defect, consistent retention time, and isotopic pattern matching with at least one MS2 fragment linked to a subclass (Charbonnet et al., 2022). The use of mass defects as a PFAS criterion has been extensively used in non-target PFAS analyses (Trier et al., 2011; Baduel et al., 2017; Wang et al., 2018; Liu et al., 2019). However, this filtering process results in false positives for compounds containing other heteroatoms such as sulfur, chlorine, and oxygen (Liu et al., 2018). Getzinger et al. (2021) found that mass defect filtering, although beneficial for filtering out non-PFAS compounds, could also eliminate a large number of potential PFAS. This study showed that PFAS containing nitrogen resulted in higher positive mass defect values than typical PFAS compounds. In this study, the mass defect was therefore used for verification and was not a strict requirement. The mass defect was determined using Thermo

Scientific Freestyle, which subtracted the nominal mass from the exact molecular mass (Getzinger et al., 2021).

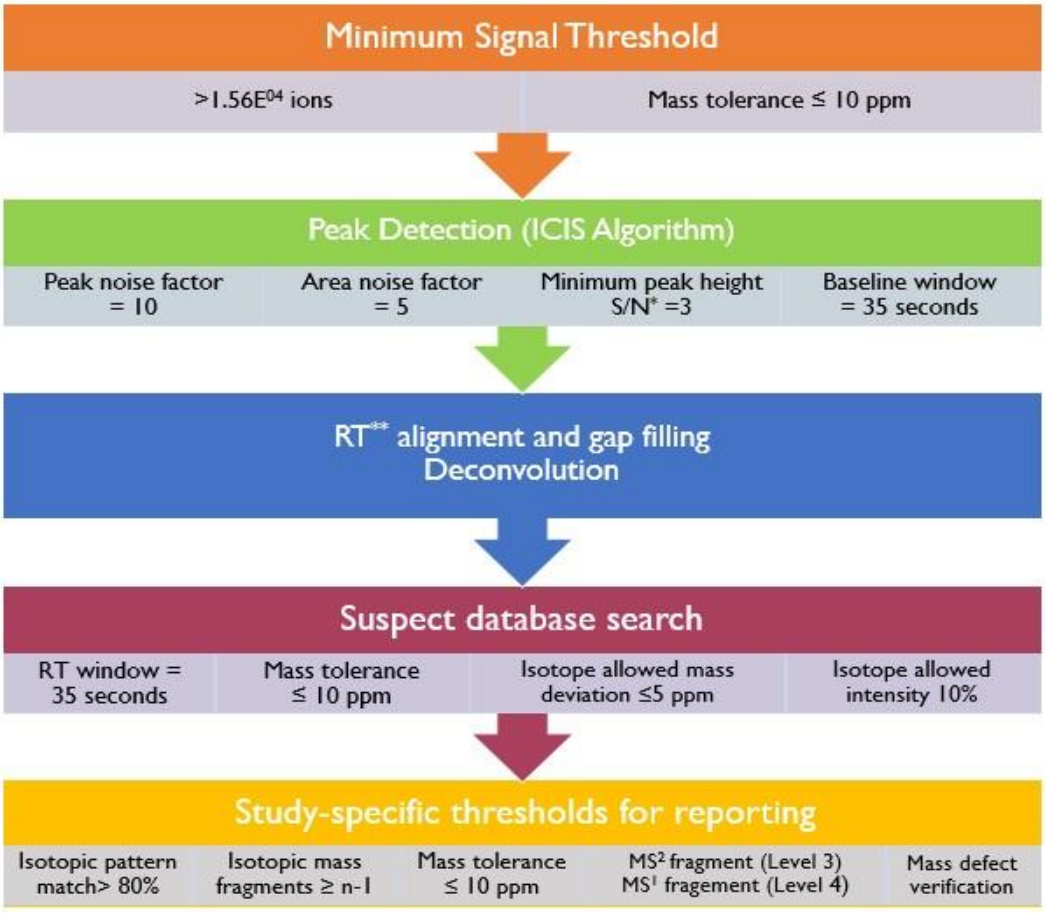
8.2.5. Quality assurance

Preparation blanks of both extraction workflows were prepared to account for any possible PFAS that may have been present in the analytical equipment, solvents and general laboratory consumables. The delay column was fitted between the solvent mixer and autosampler to trap any possible system PFAS. In addition, solvent blanks were inserted between each triplicated sample run to minimise any carry-over. To minimise cross-contamination, prior to each sample the blender was meticulously washed with warm water and detergent, then thoroughly rinsed with deionised water followed by an ethanol rinse before air drying. The stainless-steel ASE cells were washed in warm water, rinsed with 1:1 methanol: ethanol, and then placed in an oven for 4 hours at 160 °C. The 60mL borosilicate vials were single-use and discarded after each use. After each use, the vacuum manifold, worktop and laboratory ware used were cleaned with toluene, 1% methanolic ammonium hydroxide followed by methanol.

8.3 Results and Discussion

8.3.1 Suspect PFAS identification workflow

The suspect screening protocol developed in this study is shown in Fig. 1. An unknown analysis data processing method was developed using TraceFinder for a minimum peak width of 0.21, maximum peak width of 0.84, and RT window set at 35 seconds, with retention time alignment and gap filling selected for exhaustive searching. Peak detection was performed by using an instrument-automated isotope cluster integration system (ICIS) algorithm. The mass tolerance for screening was 10 ppm in the full-scan mode. Thermo Scientific Freestyle was used for mass defects and isotopic pattern verification.



* S/N – signal-to-noise **RT – retention time

Fig.1 Suspect screening protocol

The in-built deconvolution feature of TraceFinder resulted in an extracted ion chromatogram (XIC), the illustration of which is shown in Fig. 2 for a magazine sample.

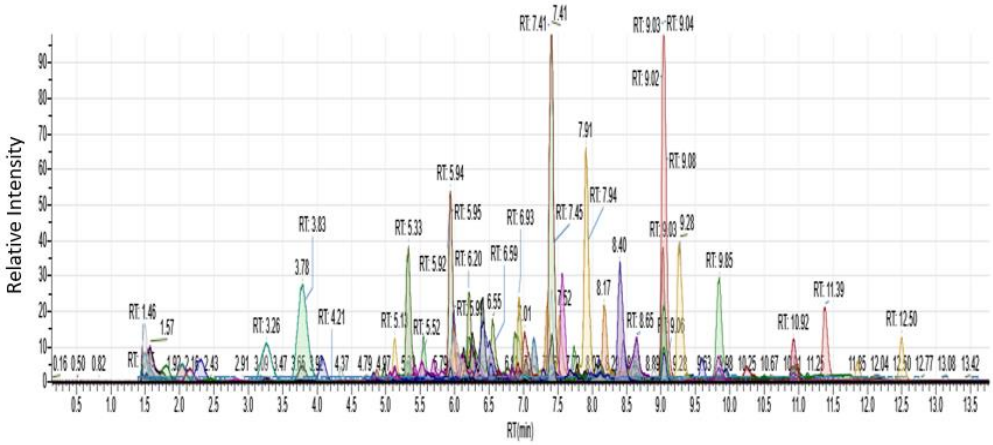


Fig. 2 XIC for magazine sample

In suspect screening, XICs are important for removing background noise and baseline correction; in addition, they can assist in correcting repeating matrix effects. Deconvolution and background correction are also important when attempting to identify the PFAS present at trace levels (Liu et al., 2019). The Orbitrap MS^1 scan produced a forest of peaks that could be attributed to different types of organic chemical compounds present in the paper samples. In this study, PFAS compounds were of interest, and all other chemical classes were disregarded. Because the database libraries used were MS^1 level, it was important to be able to remove all background signals and matrix interferences from the full scan prior to database searching. A process of elimination or peak filtering was then employed to report the detected PFAS at as high a confidence level as possible. The advantage of advanced high-resolution accurate mass analysis is that the software can generate a monoisotopic mass, chemical formula, and isotopic mass pattern based on the acquired signal. The software further evaluates the observed isotopic pattern against the theoretically expected isotopic pattern based on the monoisotopic mass. The isotopic pattern observed for the tentatively identified 1,1,2,2-Tetrafluorononane-3,5-dione is shown in Fig. 3, where all four possible isotopic fragments were observed for the [M-H] adduct as a molecular mass (M) of 227.0701 m/z at 5.93

min. Isotopic pattern matching is an important feature-filtering tool used to further increase the confidence of the identified compounds.

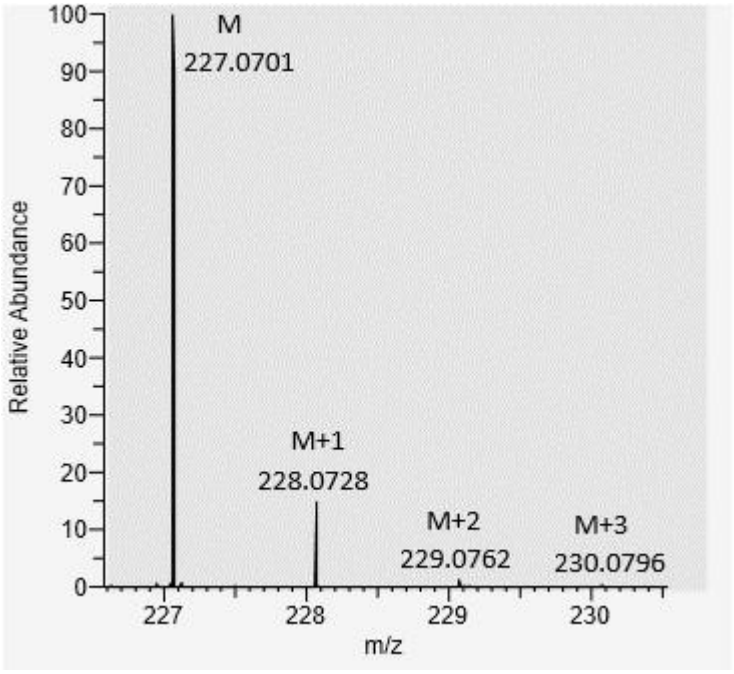


Fig. 3 Isotopic pattern for [M-H] 227.0701 m/z

8.3.2 Tentatively identified PFAS

The suspected PFAS identified in this study are shown in Tables 1 and 2 for ASE with SPE and UAE-extracted samples, respectively. It is important to add that the ASE sample pre-treatment has already been shown to identify and quantify perfluorocarboxylic acid, perfluorosulphonic acids, and fluorotelomers in a targeted PFAS study (Mofokeng et al., 2024). The reported compounds all had isotopic pattern scores of ≥80%, with number of isotopes matched being ≥ n-1. Suspect screening was conducted on the premise of [M-H] adduct prominence. The compounds presented in Tables 1 and 2 were those obtained through the suspect screening workflow in Fig. 1 and were tentatively considered identification confidence level 3 according to (Charbonnet et al., 2022). The majority of the suspected compounds were found to have mass tolerances of less than 5 ppm, showing overall high accuracy and increased probability of positive identification. Five of the tentatively identified compounds were found to have a mass tolerance of less than 1 ppm, namely (1,1,1,3,3,3-hexafluoro-2-phenylpropan-2-yl) 2-phenylsulphanylbenzoate, 1-[4-(1-methylpropyl)phenoxy]-3-(2,2,3,3-tetrafluoro

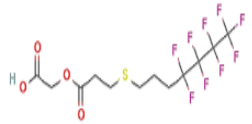
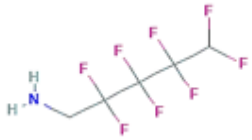
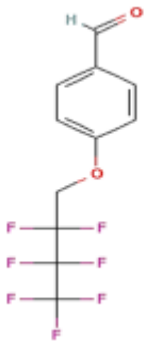
propoxy)-2-propanol, 1-(2,2,3,3-Tetrafluoropropyl)-1H-1,2,4-triazol-3-amine, N'-(benzenesulphonyl)-2,2,3,3,3-pentafluoro propanimido hydrazide and 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8,8-dimethoxyoctane. MS^2 adds an additional layer of identification confidence. MS^2 fragments were acquired by DDA, in which abundant ions automatically initiated MS^2 fragmentation in the higher-energy collision-induced dissociation cell (HCD) with the instrument switching between full scan and MS^2 in one run (Martinez-Bueno et al., 2019). Product ions were automatically assigned to the relevant precursor ions (Bugsel et al, 2023). The collision energy was stepped for ASE with SPE- and UAE-derived extracts at 15 and 30 eV. This indicated that the HCD energy switched between the two collision energies for each ion undergoing MS^2 fragmentation. The three most prominent MS^2 fragments are listed in Tables 1 and 2, respectively. The collision energy was not optimised for individual compounds; therefore, there was a strong possibility of insufficient collision energy. To illustrate, 4-(2,2,3,3,4,4,4-Heptafluorobutoxy) benzaldehyde with an MS^1 precursor ion at 303.0269 m/z fragmented to m/z 80.9976, 222.7641, and 302.6823 (Table 1).

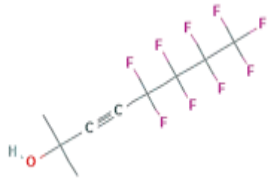
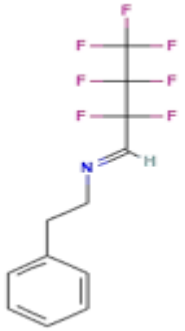
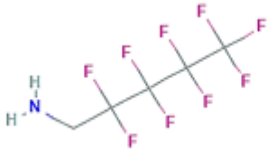
The presence of 302.6823 m/z suggested insufficient fragmentation of the molecular ion. Although the use of DDA allowed for an automated link between the product ions and their associated precursor ions, the intensity threshold for fragmentation indicated that not all compounds triggered MS^2 fragmentation. This was also seen in Table 2, where ten identified PFAS MS^1 signals did not trigger MS^2 fragmentation. The lack of clean-up in the UAE-prepared samples meant that the sample matrix consisted of various classes of compounds that underwent full-scan acquisitions. The different ions present in each duty cycle could be present at higher intensities than the PFAS compounds, and would therefore be the preferred fragmentation candidates (Dickman & Aga, 2022). According to Furey et al. (2013), the analyte of interest in matrix components competes for the available charge, leading to either ion suppression or ion enhancement of the PFAS compounds (Furey et al., 2013). The specificity and selectivity of WAX SPE reduced the complexity of the samples and improved the intensities of MS^2 fragmentation, where all tentatively identified PFAS triggered fragmentation. For the MS^2 fragments, a confirmatory ion was identified using FreeStyle MS^2. The

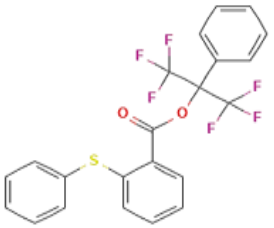
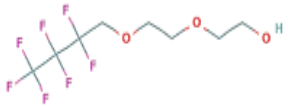
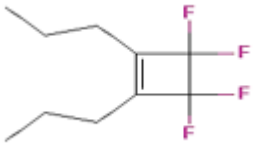
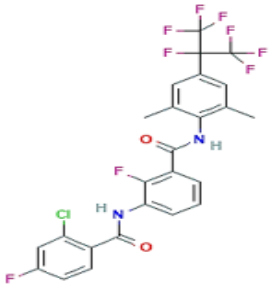
MS/MS Fragment generator of MStools was then used to identify the possible chemical composition of the fragments acquired, followed by a mass tolerance evaluation in order to further strengthen the confidence level of the tentative identification and to confirm that the compounds were of PFAS origin. The selected MS^2 ion and aligned retention time were then used to evaluate the presence of PFAS in the paper samples analysed. The majority of mass tolerances on MS^2 were less than 15 ppm for a majority of the compounds; however, a number of compounds had mass tolerances close to 30 ppm. In contrast, all MS^1 mass tolerances were less than 10 ppm. This indicated that analytical standards analysed under the same analytical conditions were required to truly optimize and confirm the ionization and fragmentation of the different PFAS compounds.

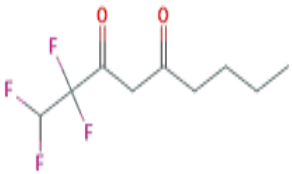
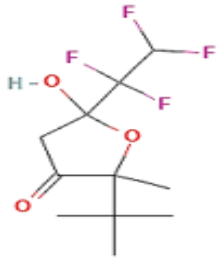
Thermo FreeStyle was used to assess mass defect ranges as a possible data filtering step (Bugsel et al., 2023) using a relative mass defect filter of 50 mmu for a charge of -1 and hydrogen as the species. The premise of using mass defect filtering is the prominence of carbon and fluorine in typical PFAS compounds leading to an expected mass defect range of – 0.25 Da from the negative fluorine contribution and +0.1 Da from the positive carbon contribution. The mass defect filter was outside the expected range for several compounds. This was attributed to the relatively short -CF_2 chains and the different heteroatoms present in the identified compounds, where carbon and hydrogen were associated with positive mass defects and the remaining chlorine, fluorine, iodine, nitrogen, and sulphur were associated with negative mass defects (Liu et al., 2022; Sleno, 2012). These results indicate that filtering compounds by mass defects could potentially result in overlooking the PFAS compounds. In this study, it was therefore employed for the purpose of verification and not as a data eliminating feature, as in non-target screening (Dickman & Aga, 2022; Koelmel et al., 2020; Bugsel & Zwiener, 2020; Liu et al., 2022; Liu et al., 2019).

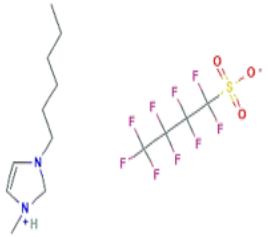
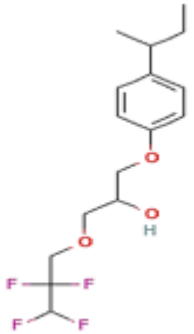
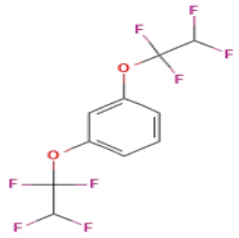
Table 1
PFAS identified by ASE with SPE

Chemical name	Chemical Formula	Chemical Structure*	RT	Monoiso-topic Mass (amu)	$[M-H]^-$ Theoretical Mass m/z	$[M-H]^-$ Observed Mass (m/z)	MS^1 Mass tolerance (ppm)	Mass defect range (amu)	Confirmatory MS^2 fragments	Theoretical Mass m/z	MS^2 Mass tolerance (ppm)
4:2 fluorotelomer thia propanoyl oxy propanoic acid	$C_{12}H_{13}F_9O_4S$		1.48	424.0391	423.0312	423.0333	4.96	-0.018 to 0.082	99.9945 $[C_2F_4]^-$	99.9936	9.00
5H-Perfluoropentanal	$C_5H_2F_8O$		1.49	229.9978	228.9899	228.9887	5.24	0.941 to 1.041	80.9956 $[C_2F_3]^-$	80.9952	4.94
2,2,3,3,4,4,5,5-Octafluoropentan-1-amine	$C_5H_5F_8N$		1.49	231.0294	230.0215	230.0218	1.30	-0.028 to 0.072	78.0177 $[C_2H_2F_2N]^-$	78.0155	28.20
4-(2,2,3,3,4,4,4-Heptafluorobutoxy)benzaldehyde	$C_{11}H_7F_7O_2$		1.52	304.0334	303.0255	303.0269	4.62	-0.024 to 0.076	80.9976 $[C_2F_3]^-$	80.9952	29.63

5,5,6,6,7,7,8,8,8-Nonafluoro-2-methyloct-3-yn-2-ol	$C_9H_7F_9O$		1.52	302.0353	301.0274	301.0289	4.98	-0.022 to 0.078	68.9971 $[CF_3]^-$	68.9952	27.54
Difluoro(1,1,2,2-tetrafluoroethoxy)acetyl fluoride	$C_4HF_7O_2$		2.72	213.9865	212.9786	212.979	1.88	0.929 to 1.029	168.9884 $[C_3F_7]^-$	168.9888	2.37
1H-Heptafluoropropane	C_3HF_7		2.75	169.9966	168.9894	168.9887	3.96	0.939 to 1.039	68.9940 $[CF_3]^-$	68.9952	17.39
(1E)-2,2,3,3,4,4,4-Heptafluoro-N-(2-phenylethyl)butan-1-imine	$C_{12}H_{10}F_7N$		2.85	301.0701	300.0622	300.0639	5.67	0.013 to 0.113	115.0054 $[C_2HF_4N]^-$	115.0045	7.8
1H,1H-Perfluoropentylamine	$C_5H_4F_9N$		3.95	249.0200	248.0121	248.0115	2.42	-0.037 to 0.063	79.0211 $[C_2H_3F_2N]^-$	79.0234	29.11

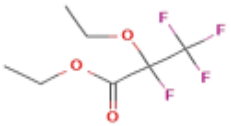
(1,1,1,3,3,3-hexafluoro-2-phenylpropan-2-yl) 2-phenylsulphanylbenzoate	$C_{22}H_{14}F_6O_2S$		3.88	456.0619	455.0540	455.0537	0.66	0.005 to 0.105	80.9955 $[C_2F_3]^-$	80.9952	3.70
1-(ethoxymethyl)-3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)urea	$C_{12}H_{11}F_{15}N_2O_2$		4.05	500.0581	499.0502	499.0526	4.81	0.001 to 0.101	106.0051 $[C_4HF_3]^-$	106.0030	19.81
2-[2-(2,2,3,3,4,4,4-Heptafluorobutoxy)ethoxy]ethan-1-ol	$C_8H_{11}F_7O_3$		4.31	288.0596	287.0517	287.0541	8.36	0.002 to 0.102	121.0108 $[C_4H_3F_2O_2]^-$	121.0101	5.78
3,3,4,4-tetrafluoro-1,2-dipropylcyclobutene	$C_{10}H_{14}F_4$		4.32	210.1032	209.0953	209.0947	2.68	0.046 to 0.146	118.0041 $[C_5HF_3]^-$	118.0030	9.32
3-(2-Chloro-4-fluorobenzamido)-2-fluoro-N-[4-(1,1,1,2,3,3,3-heptafluoropropan-2-yl)-2,6-dimethylphenyl]benzamide	$C_{25}H_{16}ClF_9N_2O_2$		5.32	582.0756	581.0677	581.0671	1.03	0.018 to 0.118	198.0588 $[C_{10}H_7F_3N]^-$	198.0531	28.78

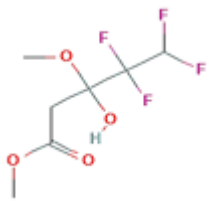
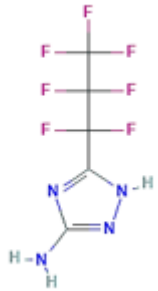
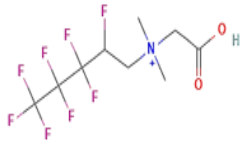
3-Acetyl-5,5,6,6,7,7,8,8,8-nonafluorooctane-2,4-dione	$C_{10}H_7F_9O_3$		5.37	346.0251	345.0172	345.0164	2.32	0.032 to 0068	80.9956 $[C_2F_3]^-$	80.9952	4.94
1,1,2,2-Tetrafluorononane-3,5-dione	$C_9H_{12}F_4O_2$		5.93	228.0773	227.0694	227.0701	2.95	0.02 to 0.12	80.9956 $[C_2F_3]^-$	80.9952	4.94
2-Tert-butyl-5-hydroxy-2-methyl-5-(1,1,2,2-tetrafluoroethyl)oxolan-3-one	$C_{11}H_{16}F_4O_3$		6.12	272.1036	271.0957	271.0978	7.89	0.046 to 0.146	80.9955 $[C_2F_3]^-$	80.9952	3.70
15,15,16,16,16-Pentafluorohexadecane-1-thiol	$C_{16}H_{29}F_5S$		6.53	348.1910	347.1831	347.1863	9.22	0.134 to 0.243	197.1361 $[C_{12}H_{21}S]^-$	197.1364	1.52

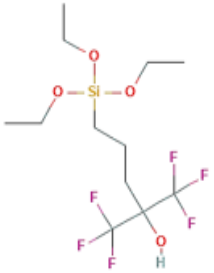
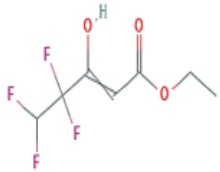
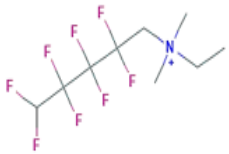
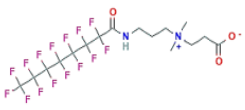
3-Hexyl-1-methyl-1H-Imidazolium perfluorobutane sulphonate	$C_{14}H_{21}F_9N_2O_3S$		6.82	468.1129	467.1050	467.1032	3.85	0.056 to 0.156	79.9556 $[SO_3]^-$	79.9568	15.01
1-[4-(1-methylpropyl)phenoxy]-3-(2,2,3,3-tetrafluoropropoxy)-2-propanol	$C_{16}H_{22}F_4O_3$		8.38	338.1505	337.1426	337.1429	0.89	0.093 to 0.193	94.0249 $[C_3H_4F_2O]^-$	94.0230	20.21
1,3-Bis(1,1,2,2-tetrafluoroethoxy)benzene	$C_{10}H_6F_8O_2$		9.09	310.0240	309.0161	309.0175	4.53	-0.033 to 0.067	96.9889 $[C_2F_3O]^-$	96.9901	12.37

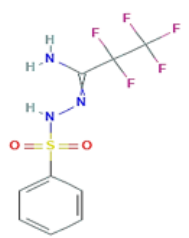
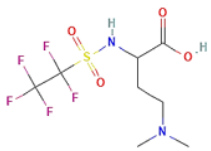
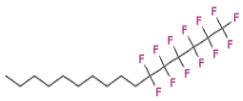
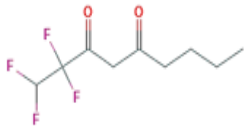
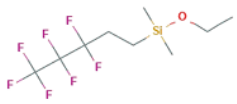
* Chemical structures are representative and do not show any branching.

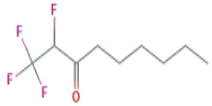
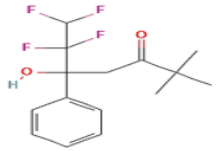
Table 2
PFAS identified by UAE

Chemical name	Chemical Formula	Chemical Structure*	RT	Monoisotopic Mass (amu)	[M-H]- Theoretical mass (m/z)	[M-H]- Observed Mass (m/z)	Mass tolerance (ppm)	Mass defect filtering range (Da)	MS^2 fragments acquired	Theoretical Mass m/z	MS^2 Mass tolerance (ppm)
Pentafluoropropane peroxoic acid	$C_3HF_5O_3H$		1.68	179.9846	178.9767	178.9773	-3.35	0.935 to 1.035	118.9958 $[C_2F_5]^-$	118.9920	31.93
4,4,5,5,6,6,7,7,8,8,8-Undecafluoro-2-iodooctan-1-ol	$C_8H_6F_{11}IO$		1.72	453.9288	452.9209	452.9215	-1.32	0.871 to 0.971	-		
ethyl 2-ethoxy-2,3,3,3-tetrafluoropropanoate	$C_7H_{10}F_4O_3$		1.75	218.0566	217.0487	217.0480	3.23	-0.001 to 0.099	68.9948 $[CF_3]^-$	68.9952	5.80
1-(2,2,3,3-Tetrafluoropropyl)-1H-1,2,4-triazol-3-amine	$C_5H_6F_4N_4$		2.62	198.0529	197.0450	197.0451	-0.51	0.004 to 0.096	-		

Methyl 4,4,5,5-tetrafluoro-3-hydroxy-3-methoxypentanoate	$C_7H_{10}F_4O_4$		4.08	234.0515	233.0436	233.0454	-7.72	-0.006 to 0.094	162.0134 $[C_6H_4F_2O_3]^-$	162.0129	3.09
1-(ethoxymethyl)-3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)urea	$C_{12}H_{11}F_{15}N_2O_2$		4.15	500.0581	499.0502	499.0527	-5,01	0.001 to 0.101	-		
3-(Heptafluoropropyl)-1H-1,2,4-triazol-5-amine	$C_5H_3F_7N_4$		4.16	252.0246	251.0167	251.0183	-6,41	-0.033 to 0.067	-		
N-Carboxymethyl-N,N-dimethyl-2-(perfluoropropyl)-2-fluoroethan-1-aminium	$C_9H_{12}F_8NO_2$		4.31	318.0740	317.0661	317.0665	-1,26	0.017 to 0.117	-		

1,1,1-trifluoro-5-(triethoxysilyl)-2-(trifluoromethyl)- 2-pentanol	$C_{12}H_{22}F_6O_4Si$		4.50	372.1192	371.1113	371.1138	-6,74	0.062 to 0.162	97.9995 $[C_2HF_3O]^-$	97.9979	16.33
Ethyl 4,4,5,5-tetrafluoro-3-hydroxypent-2-enoate	$C_7H_8F_4O_3$		5.03	216.0409	215.0330	215.0346	-7.44	-0.016 to 0.084	-		
N-Ethyl-N,N-dimethyl-(3-(difluoromethyl)perfluoropropyl)methan-1-aminium	$C_9H_{14}F_8N$		5.16	288.0998	287.0919	287.0925	-2.09	0.043 to 0.143	-		
N-Propyl-N,N-dimethyl-(3-(difluoromethyl)perfluoropropyl)methan-1-aminium	$C_{10}H_{16}F_8N$		5.16	302.1155	301.1076	301.1082	-1.99	0.058 to 0.158	99.9918 $[C_2F_4]^-$	99.9936	18.00
(2-Carboxylatoethyl)dimethyl[3-(perfluorooctanamido)propyl]ammonium	$C_{16}H_{17}F_{15}N_2O_3$		5.28	570.0999	569.0920	569.0945	-4.39	0.043 to 0.143	-		

N'-(Benzenesulphonyl)-2,2,3,3,3-pentafluoropropanimidohydrazide	$C_9H_8F_5N_3O_2S$		5.32	317.0257	316.0178	316.0178	0.95	-0.032 to 0.068	111.9921 $[CF_4]^-$	111.9936	13.39
N-dimethylammoniocarboxypropyl perfluoroethane sulphonamide	$C_8H_{13}F_5N_2O_4S$		5.53	328.0516	327.0437	327.0444	-2.14	-0.006 to 0.094	158.9648 $[C_2F_3NO_2S]^-$	158.9602	28.94
1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluoro-8,8-dimethoxyoctane	$C_{10}H_9F_{13}O_2$		5.75	408.0395	407.0316	407.0319	-0.74	-0.018 to 0.082	-		
1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluorohexadecane	$C_{16}H_{21}F_{13}$		5.75	460.1436	459.1357	459.1340	3.70	0.086 to 0.186	-		
1,1,2,2-Tetrafluorononane-3,5-dione	$C_9H_{12}F_4O_2$		5.83	228.0773	227.0694	227.0710	-7.05	-0.001 to 0.099	-		
Ethoxydimethyl (3,3,4,4,5,5,5-heptafluoropentyl) silane	$C_9H_{15}F_7OSi$		5.84	300.0780	299.0701	299.0716	-5.02	0.02 to 0.12	255.0506 $[C_7H_{10}F_7Si]^-$	255.0440	25.88

2-Tert-butyl-5-hydroxy-2-methyl-5-(1,1,2,2-tetrafluoroethyl)oxolan-3-one	$C_{11}H_{16}F_4O_3$		5.92	272.1036	271.0957	271.0977	-7.53	0.021 to 0.121	99.9918 $[C_2F_4]^-$	99.9936	18.00
1,1,1,2-Tetrafluorononan-3-one	$C_9H_{14}F_4O$		6.03	214.0981	213.0902	213.0917	-7.04	0.046 to 0.146	197.0601 $[C_8H_9F_4O]^-$	197.0590	5.58
3,3,4,4,5,5,6,6,7,7-Decafluorooctyl 2-methylprop-2-enoate	$C_{12}H_{12}F_{10}O_2$		6.10	378.0677	377.0598	377.0604	-1.59	0.041 to 0.141	80.9940 $[C_2F_3]^-$	80.9952	14.82
6,6,7,7-Tetrafluoro-5-hydroxy-2,2-dimethyl-5-phenylheptan-3-one	$C_{15}H_{18}F_4O_2$		6.37	306.1243	305.1185	305.1164	-6.88	0.01 to 0.11	111.9917 $[C_3F_4]^-$	111.9936	16.97

8.3.3 Influence of selectivity on chemical characteristics of identified PFAS

In this study, various classes of PFAS were identified in the different paper samples. These PFAS compounds include perfluoroalkyl amines (2,2,3,3,4,4,5,5-octafluoropentan-1-amine and 1H,1H-perfluoropentylamine), polyfluoroalkyl diketones (1,1,2,2-tetrafluorononane-3,5-dione and 3-Acetyl-5,5,6,6,7,7,8,8,8-nonafluorooctane-2,4-dione), esters ((1,1,1,3,3,3-hexafluoro-2-phenylpropan-2-yl) 2-phenylsulphanylbenzoate ethyl 2-ethoxy-2,3,3,3-tetrafluoropropanoate), and fluorotelomer betaines (N-ethyl-N,N-dimethyl-(3-(difluoromethyl) perfluoro propyl) methan-1-aminium N-propyl-N,N-dimethyl-(3-(difluoromethyl) perfluoro propyl) methan-1-aminium). PFAS containing other halogens, (3-(2-chloro-4-fluorobenzamido)-2-fluoro-N-[4-(1,1,1,2,3,3,3-heptafluoropropan-2-yl)-2,6-dime thylphenyl] benzamide, 4,4,5,5,6,6,7,7,8,8,8-undecafluoro-2-iodooctan-1-ol) as well as silyl alcohols, 1,1,1-trifluoro-5-(triethoxysilyl)-2-(trifluoromethyl)-2-pentanol, were also identified. The different classes of PFAS detected were strongly influenced by the applied extraction technique. UAE was observed to extract more nitrogen-containing compounds than ASE with the SPE. This was attributed to the pH selectivity caused by the weak anionic exchange mechanism (Taniyasu et al. 2023) targeting acidic carboxylic and sulphonic acids at pH < 6. UAE extraction was considered a generally more neutral extraction at pH ~ 7, which may have been more favourable for quaternary ammonium compounds (fluorotelomer betaines). Confirmation with certified reference material would be important in further understanding this observation, reiterating the need for a broader range of commercially available PFAS standards. In addition to the pH-controlled sample pre-treatment, the mobile phase pH and matrix had a strong influence on the ionisation efficiency. In the ASE with SPE, the mobile phase consisted of a buffered water system of 0.1 % formic acid with 10 mM ammonium formate, which resulted in a pH of 3.5 with a buffering range of 2.7 – 5.7. UAE sample preparation included buffering of both the aqueous phase and organic modifier to provide a consistent ionic state of the components in the complex matrix where no SPE had been performed. Stronger intensities were seen in ASE prepared samples which triggered MS^2 fragmentation indicating better ionisation; however, this may have been due to less matrix interference after SPE. UAE allowed for the detection of different

functional groups which inferred that the selectivity of SPE excluded some functional groups which could be important for suspect screening.

Concerns regarding PFAS have often been associated with the length of carbon chains present in PFAS. For PFCAs, carbon chains shorter than seven carbons and for PFSAs those less than six carbons, are considered short-chain PFAS and are believed to be less persistent than their longer chain counterparts (Grgas et al., 2023). The persistence of PFAS is associated with an extremely stable synthetic C-F bond (Berhanu et al., 2023). The PFAS identified from both extraction techniques were evaluated according to the length of the carbon chain and the length of the fluoroalkyl chain (Fig. 4). Significant differences were noted for 15,15,16,16,16-pentafluorohexadecane-1-thiol (C-chain of 16 carbons, CF-chain of 2), 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorohexadecane (C-chain 16 and CF-chain 6) and 3-hexyl-1-methyl-1H-imidazolium perfluorobutane sulfonate (C-chain 10 and CF-chain of 4). Although these compounds would be considered short-chain PFAS (Ateia et al., 2019), their associated aliphatic chains were greater than the nine carbons chain long which suggested that further understanding of their overall stability in the paper recycling chain is required. This is especially important when considering the other functional groups present such as esters, ethers, amines, exposure pathways and related toxicity (McKee et al., 2018; Grgas et al., 2023).

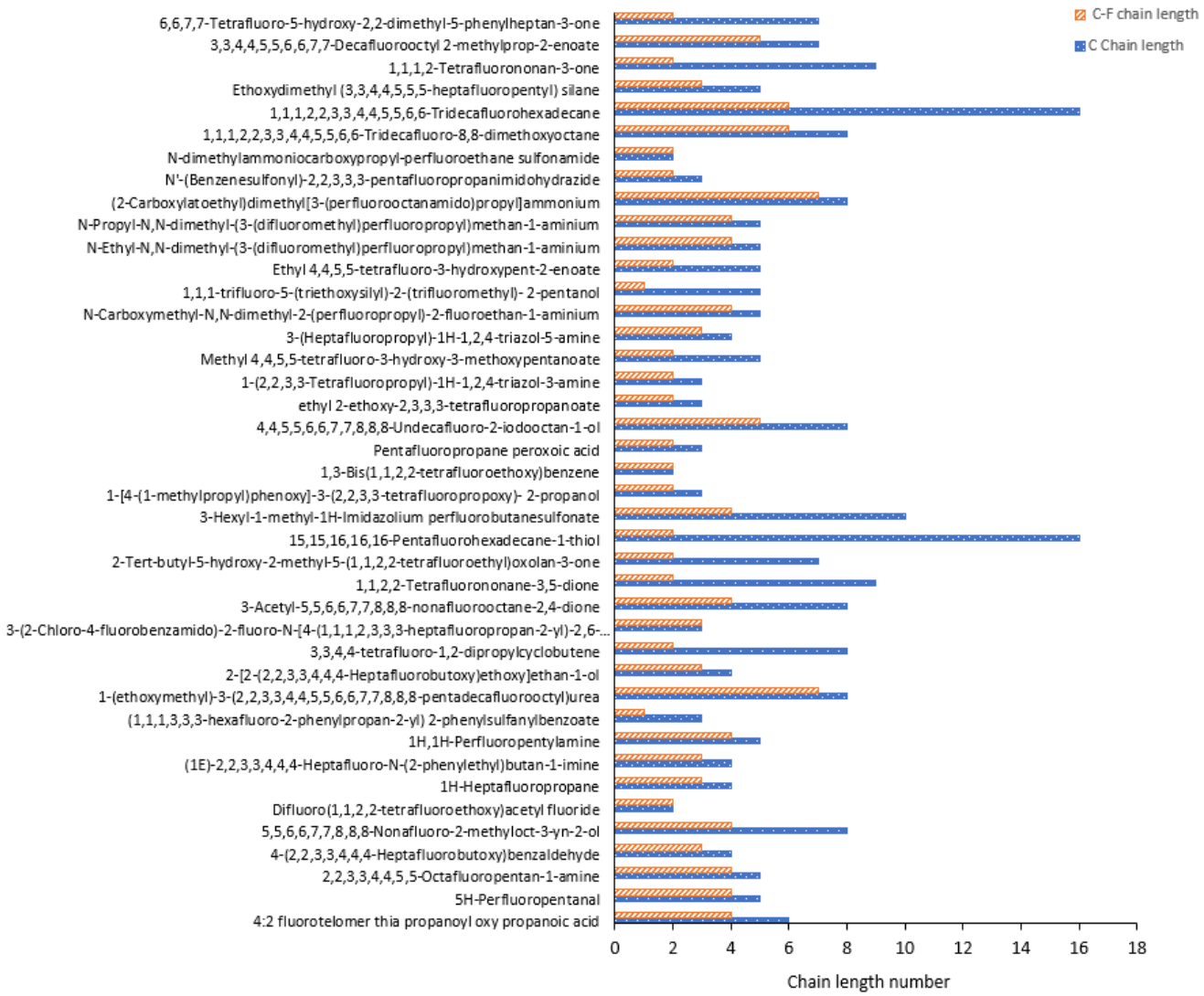


Fig. 4. Carbon chain lengths of identified PFAS

It must be highlighted that the reported PFAS in this study were those that met the confidence interval threshold discussed in section 3.1. Although the advantage of having higher confidence intervals increases the probability of correct identification, the limitation is that it may exclude chemical compounds that may not act in the theoretically expected manner, further emphasizing the need for PFAS reference material. Illustratively, if the threshold for accurate mass were set to accurate mass threshold < 15 ppm instead of the set < 10 ppm and the isotopic mass fragment increased to > n-2 instead of the set > n-1, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl isobutyrate ($C_{12}H_{11}F_{13}O2$) detected in the corrugated box collected at a recycling facility by UAE would then be included in this tentative identification study. It can thus be said that the balance between explorative untargeted analysis and the corroborative features selected for confident tentative identification is important in expanding PFAS knowledge on occurrences. More importantly, it indicated that the absence of the required evidence for identification may not, at this stage, mean that the PFAS in question was not detected; it merely meant that it could not be confidently reported on.

8.3.4 Distribution of identified PFAS in samples

The PFAS detected in the paper samples were compared to evaluate the distribution of PFAS from the combined pre-treatment methods (Tables 3 and 4). 2-tert-butyl-5-hydroxy-2-methyl-5-(1,1,2,2-tetrafluoroethyl)oxolan-3-one was detected in the highest number of samples across various sites. This suggests a possible prevalent use in paper manufacturing, which has not been previously reported. In contrast, 3-(2-chloro-4-fluorobenzamido)-2-fluoro-N-[4-(1,1,1,2,3,3,3-heptafluoropropan-2-yl)-,6-dimethylphenyl]benzamide was detected in household waste, recycling, and waste picker samples suggesting prevalence in or exposure related to post-consumer usage, waste collection, and recovery. Only 3 common PFAS were identified in both ASE and UAE prepared samples. These were 2-tert-butyl-5-hydroxy-2-methyl-5-(1,1,2,2-tetra fluoroethyl)oxolan-3-one, 1,1,2,2-tetrafluorononane-3,5-dione and 1-(ethoxymethyl)-3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro octyl) urea. This suggested that method specificity and selectivity are highly influenced by the method of extraction, implying the need for applying both methods when conducting suspect screening of PFAS. This would not only be

relevant to analytical identification but would be influential in how certain PFAS are removed in recycled material and process waters. The corrugated electronics box sourced from retail had the most tentatively identified PFAS (10 of the 45 PFAS) detected when both sample preparation results were considered in conjunction.

The sources of most PFAS are difficult to establish as the research field is emerging, and information from chemical manufacturers in the form of disclosures and patents is limited (Glüge et al., 2020). Different functional groups have been studied to determine their occurrence. Fluorinated aldehydes are oxidation products of alcohols and can form from the reduction of carboxylic acid; microbial degradation of fluorotelomers is known to generate aldehydes and PFCAs under aerobic conditions (Berhanu et al., 2023). Fluoro ether substances, on the other hand, are among the current alternatives to long-chain perfluoroalkyl acids (Munoz et al., 2019) whereas perfluoroalkyl butoxy ethoxy ethanols are used as fluorinated surfactants (Paborn & Caport, 2002). Perfluoroalkylethyl iodides can be readily converted to their corresponding alcohols, thiols, and sulfonyl chlorides, which are used as intermediates for fluorinated surfactants (Paborn & Caport, 2002). Interestingly, UAE extraction led to the detection of fluorotelomer betaines, which have been previously detected in samples of different origins, including aqueous film-forming foams and fluoro surfactants, as well as soil and groundwater (Li et al., 2019; Liu et al., 2023; Munoz et al., 2016). This class of PFAS has also been detected in biosolids, composts, and organic wastes (Munoz et al., 2022). The exposure of paper to similar organic wastes could be a possible reason for its detection in this study. It is difficult to apportion PFAS prevalence to a specific source, as PFAS undergo diverse transformations, transport, partitioning, and degradation processes (Grgas et al., 2023). Further studies are required to fully explore various exposure pathways, mechanisms, and transformations that may occur in the paper recycling chain.

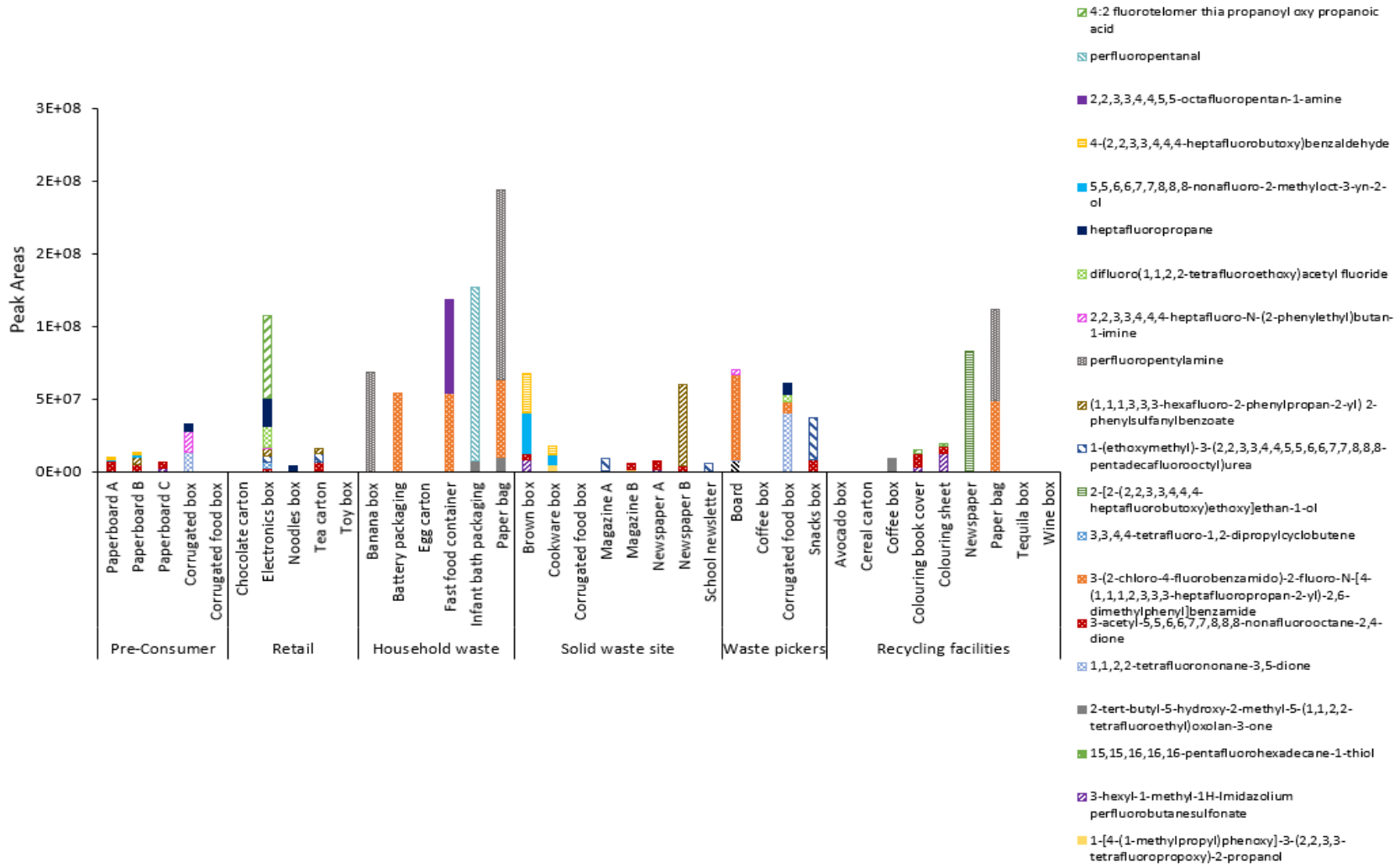


Fig. 5 Peak areas of identified PFAS from ASE with SPE sample pre-treatment

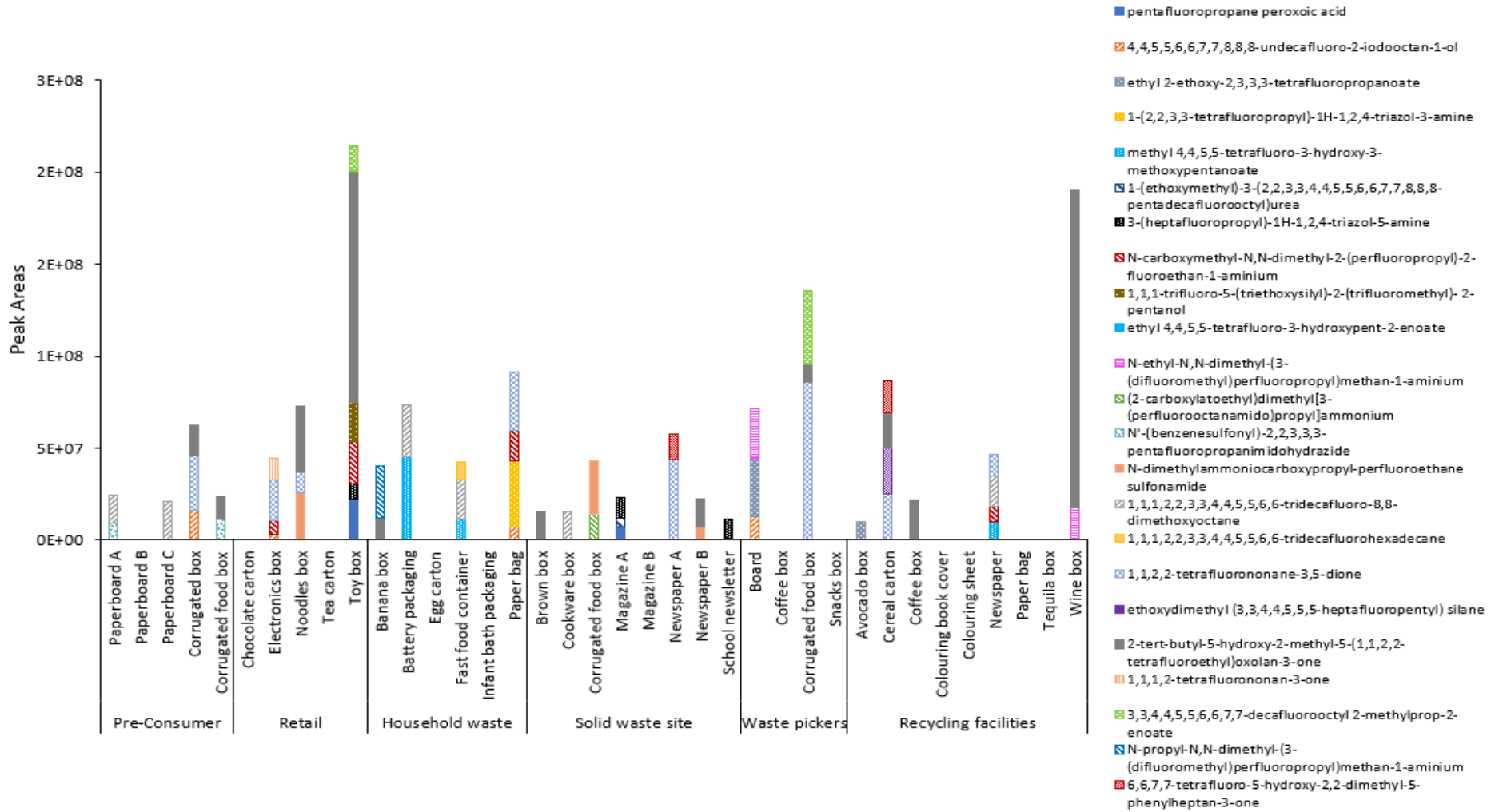


Fig. 6 Average peak areas of identified PFAS from UAE sample pre-treatment

The average integrated peak areas were used as indicators of the general abundance. For PFAS, it must be noted that the instrument response is dependent on matrix effects and ionisation efficiency (Tang et al., 2023). Another challenge associated with PFAS quantitation is poor recovery (Tang et al., 2023). The influence of the type of pre-treatment used is evident in Figs 5 and 6 for the PFAS identified by ASE with SPE and UAE, respectively. The commonly detected 2-tert-butyl-5-hydroxy-2-methyl-5-(1,1,2,2-tetra fluoroethyl)oxolan-3-one and 1,1,2,2-tetrafluorononane-3,5-dione were detected more frequently in pre-treatment by UAE than by ASE with SPE whilst 1-(ethoxymethyl)-3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl) urea was detected more in ASE with SPE than UAE.

This was influenced by the slight differences in solvents used in the pre-treatment techniques as well as the selectivity introduced by SPE. The possible prevalence of certain PFAS in the paper recycling chain was inferred by the common detection of 3-acetyl-5,5,6,6,7,7,8,8,8-nonafluorooctane-2,4-dione by ASE with SPE (in Fig 5) as well as 2-tert-butyl-5-hydroxy-2-methyl-5-(1,1,2,2-tetra fluoroethyl)oxolan-3-one and 1,1,2,2-tetrafluorononane-3,5-dione detected by UAE (Fig. 6) across the collection sites. Their abundance in this study implied the possible prevalence of short-chain polyfluoroalkyl ketones and diketones in the paper recycling chain. On the other hand, certain PFAS such as perfluoropentanal, detected in an infant bath packaging household sample from ASE with SPE, were unique in their identification. When comparing the number of different PFAS identified for both sample pre-treatment techniques, more types of PFAS were identified in an electronics box and toy box, both collected at retail. This suggested that sources of PFAS could also be related to the goods packed in paper-based packaging; in addition to activities related to the use of chemical additives, as well as handling, transport and distribution exposure opportunities. Overall, the tentatively identified PFAS indicated that there were several common previously unreported PFAS in the paper recycling chain as well as those that were unique to different collection sites and samples. Further research and the availability of analytical standards are needed

to accurately quantify these PFAS and understand their occurrence in paper-based material and possibly environmental media.

8.4 Conclusion

This study developed a systematic approach to suspect screening linked to confidence level. The peak filtering and thresholds employed increased the probability of correct identification while reducing false-positive reporting. This study highlighted the importance of extraction techniques, acquisition mechanisms, and data processing in PFAS screening. ASE with SPE sample preparation identified 21 suspected PFAS with MS2 fragmentation. UAE was able to tentatively identify 23 PFAS; however, not all suspected PFAS were able to trigger MS2 fragmentation, as a result of DDA acquisition. Fluoroalkyl amines, diketones, betaines, and silyl alcohols are among the different functional groups identified. The study highlighted that further exploration is required to understand the complexities of PFAS, their risks, and their applications.

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Supplementary material

Suspect screening of per- and polyfluoroalkyl substances in paper by selective and non-selective extraction with UHPLC-Q Orbitrap MS

Table S1

Purities of chemical solvents and buffers

Chemical Name	Manufacturer	Supplier	Specified purity
Methanol	Honeywell	Anatech	ChromaSolv™ LC-MS Ultra ≥ 99.9%
Methanol	Supelco	Merck	LiChrosolv® hypergrade for LC-MS ≥ 99.97%
Ethanol	Supelco		LiChrosolv® gradient grade for liquid chromatography ≥ 99.9%
Water	Sigma-Aldrich		HPLC-Plus ≥99.99%
Formic acid	Supelco		EMSURE ACS Reag., Ph. Eur ≥ 98%
Toluene	Honeywell		HPLC grade ≥ 99.8%
Ammonium formate	Sigma-Aldrich		LiChropur™ eluent additive for LC-MS ≥99%
Ammonium hydroxide solution	Sigma-Aldrich		Puriss. pa, Ph. Eur ~25% NH3 basis

Table S2

Analytical Balance Details

Make	Radwag
Model	As220 X2 Plus analytical balance
Supplier	United Scientific (Cape Town, South Africa)
Readability	0.1 mg
Repeatability (σ)	0.0002

Thermo Scientific Q Exactive Focus UHPLC^{+} Orbitrap HRMS Instrument Parameters

Table S3

Orbitrap LC-HRMS Flow Gradient for ASE with SPE

Solvent A: LC-MS grade water with 10mM Ammonium formate 0.1% formic acid

Solvent B: LC-MS grade methanol

	Time	Flow (mL/min)	%B	Curve
1	0.00	0.400	30	5
2	1.00	0.400	30	5
3	13.00	1.00	100	3
4	17.00	1.00	100	5
5	17.10	0.500	60	5
6	21.00	0.500	50	5
7	21.10	0.500	30	5

Table S4

Orbitrap LC-HRMS Flow Gradient for UAE

Solvent A: LC-MS grade water with 5mM Ammonium formate 0.1% formic acid

Solvent B: LC-MS grade methanol with 5mM Ammonium formate 0.1% formic acid

	Time	Flow (mL/min)	%B	Curve
1	0.00	0.300	30	5
2	1.00	0.300	30	5
3	15.00	0.300	100	2
4	19.00	0.350	100	5
5	19.10	0.300	60	5
6	21.00	0.300	50	5
7	21.10	0.300	30	5

CHAPTER NINE

9 CONCLUSIONS & RECOMMENDATIONS FOR FUTURE WORK

This study was able to successfully develop, validate and apply analytically sound methods for the quantification of various chemical compounds in the paper recycling chain. Tentative identification of various emerging contaminants and pollutants was achieved through the development of suspect screening protocols. Analytical exploration was achieved through the optimisation of sample pre-treatment techniques and analysis using both gas chromatography and liquid chromatography, in tandem with mass spectrometry. This study extended beyond typical food packaging migration studies and investigated the holistic extraction of both food and non-food paper-based materials. These included newspapers, office paper, magazines, corrugated boxes, and cartons which go into the manufacture of recycled paperboard. The use of chemometrics in the data analysis indicated that various paper grades and collection sites had unique features that must be considered in the subsequent product life. The presence of pollutants was linked to the use of chemical additives in the manufacturing process, retail activities, consumer usage and waste mingling during the collecting, sorting and recycling processes.

Overall, this study achieved three important discoveries: (1) the first occurrence of pharmaceuticals in paper-based materials, thereby, revealing important information about the fate of these emerging contaminants in the paper recycling chain, (2) the detection of new pharmaceutically active compounds not reported in the South African environment and (3), the infiltration of numerous polymer-associated chemicals such as plasticizers, antioxidants, flame retardants and polymer degradants; previously not associated with paper-based materials. In addition, the comparison of pre-consumer, retail and post-consumer paper recycling chain sites allowed for the investigation of possible propagation of emerging contaminants and pollutants, their possible sources and their fate within the paper recycling cycle.

This study thereby showed that to improve paper recycling practices, the cumulative effects of certain chemicals from various exposure pathways, their existing persistence in the paper recycling chain, and their associated breakdown products should be considered in promoting sustainable waste management that minimises the circulation of potentially harmful contaminants. This study also showcased new compounds that should be monitored in the environment, alongside investigating their removal strategies. To further grow this field of research in South Africa, sampling at different geographical locations in South Africa and quantification of the compounds identified in the suspect screening analyses would assist in evaluating any possible risks, occupational hazards and toxicological effects of paper-based material in the recycled paper value chain. There is also a need for further evaluations of exposure pathways in future risk assessments as well as the prevention and minimisation of exposure opportunities. To improve waste management and associated sorting and collection protocols, it is highly recommended that legislation and standardised operations be developed in line with actual practices and through collaborations between industry and government. This study thereby highlights the intertwining linkages between consumer products, healthcare, waste management, environmental pollution, and the manufacturing industry and may thus be a critical baseline to build the South African body of knowledge in this untapped research area.

APPENDIX

UNIVERSITY OF THE WITWATERSRAND, JOHANNESBURG

Research Office

HUMAN RESEARCH ETHICS COMMITTEE (NON-MEDICAL)
R14/49 Mofokeng

CLEARANCE CERTIFICATE	**PROTOCOL NUMBER: H21/07/29**
PROJECT TITLE	Source Apportionment, transport and fate of pollutants in the paper recycling chain- An analytical exploration of the South African context
INVESTIGATOR(S)	Mrs N Mofokeng
SCHOOL/DEPARTMENT	Chemistry/
DATE CONSIDERED	23 July 2021
DECISION OF THE COMMITTEE	Approved Risk Level: Minimal
EXPIRY DATE	22 August 2024

DATE 23 August 2021 **CHAIRPERSON** _____
(Professor J Knight)

cc: Supervisor : Dr L Chimuka

DECLARATION OF INVESTIGATOR(S)

To be completed in duplicate and **ONE COPY** returned to the Secretary at Room 10004, 10th Floor, Senate House, University. Unreported changes to the application may invalidate the clearance given by the HREC (Non-Medical)

I/We fully understand the conditions under which I am/we are authorized to carry out the abovementioned research and I/we guarantee to ensure compliance with these conditions. Should any departure to be contemplated from the research procedure as approved I/we undertake to submit an amendment of the protocol to the Committee. **I agree to completion of a regular progress report. For Minimal and Low studies, this is due annually on 31 December. For Medium and High Risk studies, this is due twice annually on 30 June and 31 December.**

_____ 24 / 08 / 2021
Signature **Date**

PLEASE QUOTE THE PROTOCOL NUMBER ON ALL ENQUIRIES