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Research Paper

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 also shown to 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.

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

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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 and 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.

2. Materials and methods

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).

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.

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 g 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.

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 C_{11}-C_{35} aliphatic chains (Biedermann et al., 2013; Biedermann and 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 h 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.

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

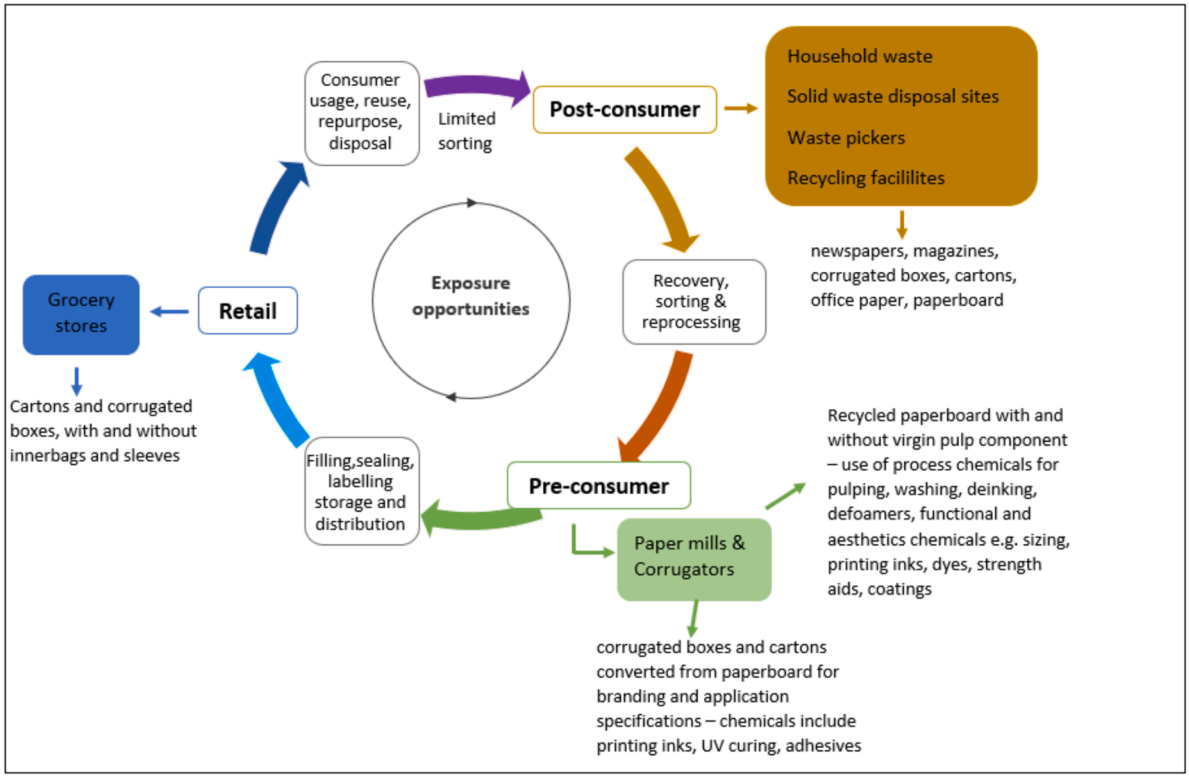

Fig. 1. Overview of paper recycling chain and stages of sample collection.

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 °C. The binary mobile phase comprised of 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.

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 h at 160 °C. For UAE, borosilicate glass vials were heat-treated in a furnace for 2 h 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.

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) 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).

$$Masstolerance(ppm) = \left|\frac{Theoreticalmassexpected - MassObserved(m/z)}{Theoreticalmassexpected(m/z)}\right| \times 10^6 \quad (1)$$

In high resolution mass spectrometry (HRMS), the mass tolerance is often used as an indication of an instrument's 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 and 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 confirmation of compound identity by certified reference standards, with a lack of structural evidence and molecular formula generation considered the lowest confidence level

(El-Deen and 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.

3. Results and discussion

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 comprised 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 organo-phosphonates, 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, gas chromatography coupled to mass spectrometry (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-di-*tert*-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's 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 C_{18} 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 to 3.5 g. This 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.

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.

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 C_{30}, 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 and 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.

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 hydrolyzed 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 (C_{35}) 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; German Federal Institute for Risk Assessment, 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 and 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 and 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 and 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 (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 cartons 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, paper packaging 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 (German Federal Institute for Risk Assessment, 2023; Höke and 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 and 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-di-*tert*-butylphenyl)phosphite or Irgafos 168. It is considered a ubiquitous plastic additive found in food packaging, dust, printing paper, and aquatic systems (Liu and Mabury, 2021; Shi et al., 2020; Zhang et al., 2021). Other organic phosphorus compounds detected, used as flame retardants, antioxidants, or plasticizers (Lowe et al., 2021; Sanchis et al., 2019; Sohn et al., 2011) 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-di-*tert*-butylphenyl) phosphate and 2,4-di-*tert*-butylphenol (Hermabessiere et al., 2020); although 2,4-di-*tert*-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.

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 and 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 pre-consumer 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 and 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.

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 %.

The number of classes identified 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.

The highest number of different chemical classes per site were 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

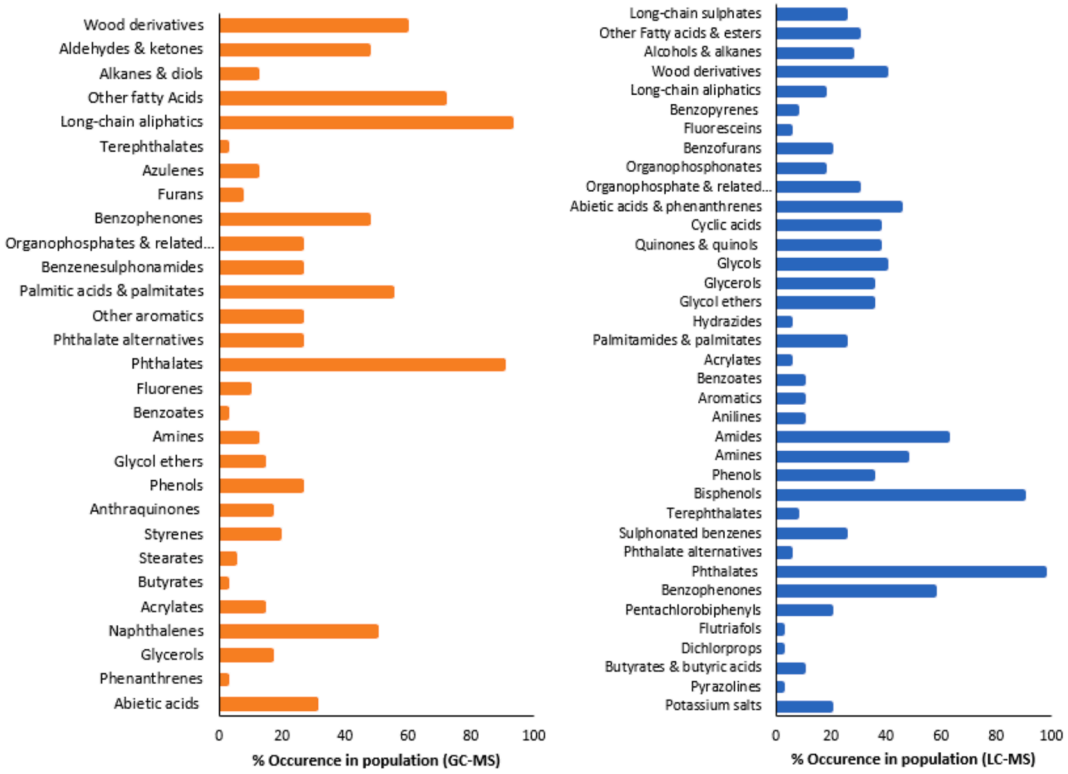

Fig. 2. Occurrence of chemical classes by GC-MS and LC-MS.

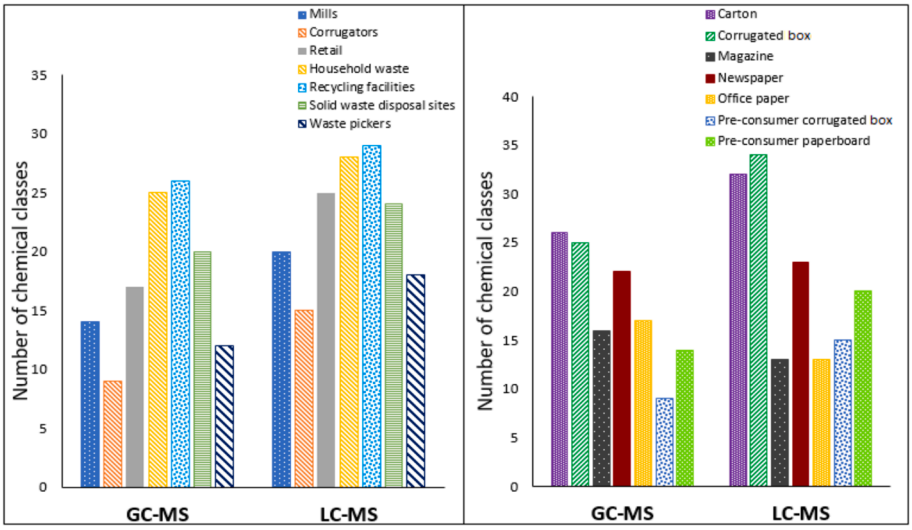

Fig. 3. Chemical classes identified by a) sample collection site b) paper recycling grade.

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.

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 recycling grades, it is thus important to understand what impact 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 (Fig. 5), in this case, chemical classes, that occurs in each paper grade according to

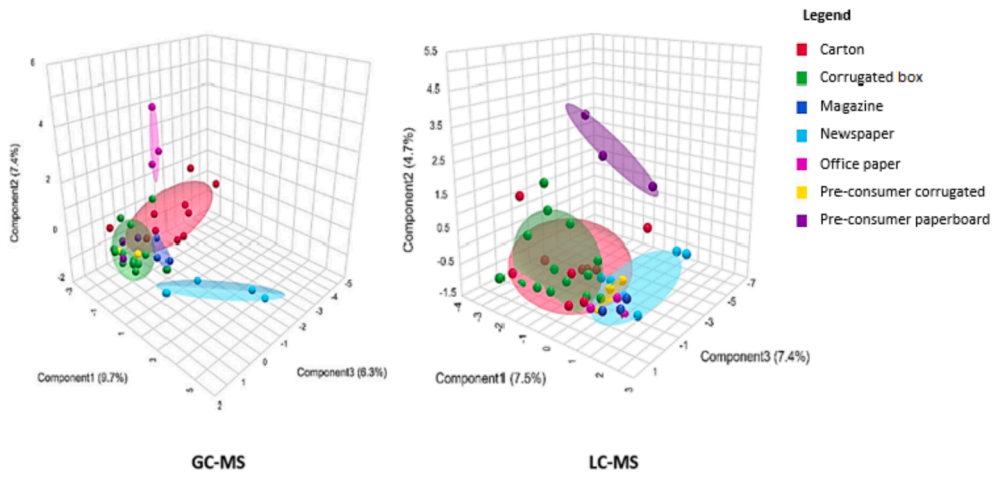

Fig. 4. Spls-da scores plot for GC-MS and LC-MS by paper grade.

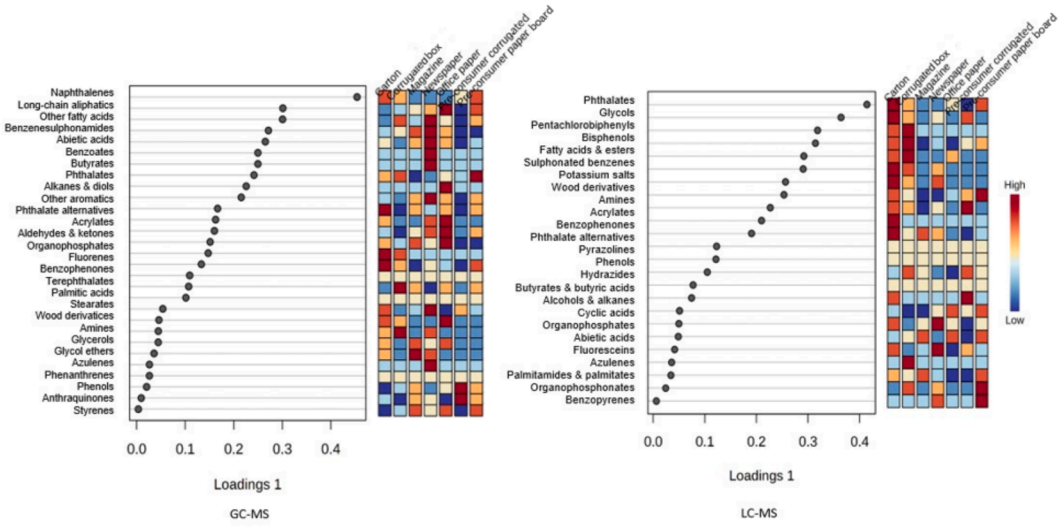

Fig. 5. Spls-da loadings plot for GC-MS and LC-MS by paper grade.

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.

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.

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 most 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

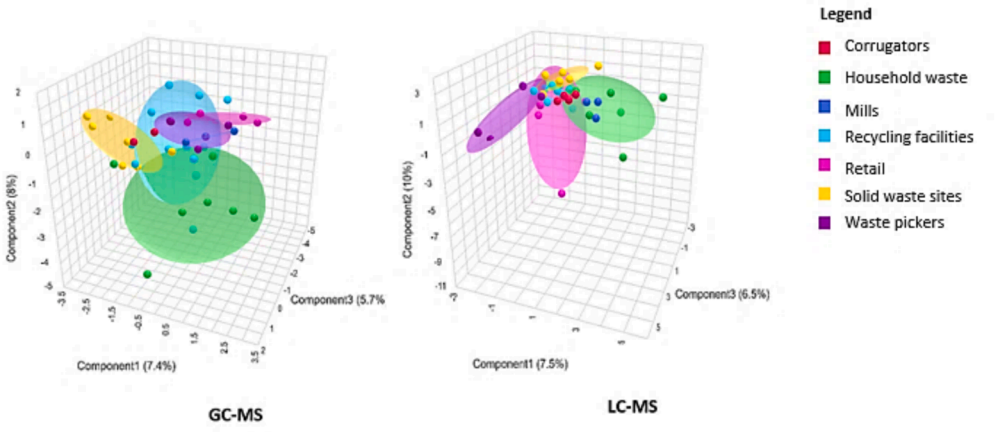

Fig. 6. Spls-da scores plot for GC-MS and LC-MS by collection site.

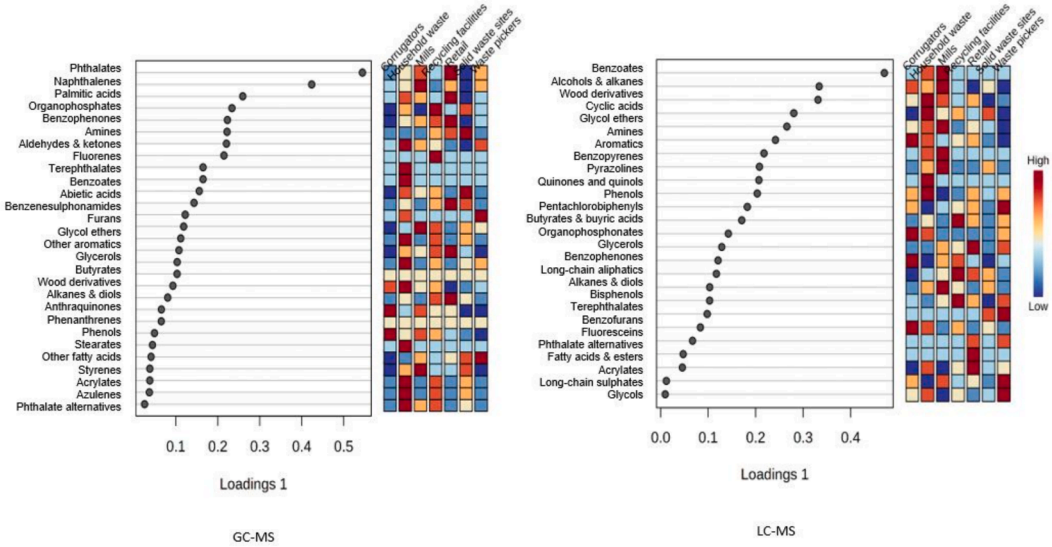

Fig. 7. Spls-da loadings plot for GC-MS and LC-MS analysis by collection sites.

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.

4. Conclusions

A unique approach was employed to understand 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 recycling 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 investigate how they influence the recyclability of both food and non-food paper materials.

CRediT authorship contribution statement

Nondumiso N. Mofokeng: Conceptualization, Methodology, Project administration, Formal analysis, Writing – original draft preparation. **Lawrence M. Madikizela:** Writing – review & editing, Validation, Supervision, Project administration, Data curation. **Ineke Tiggelman:** Writing – review & editing, Validation, Supervision, Funding acquisition, Data curation. **Luke Chimuka:** Writing – review & editing, Validation, Supervision, Project administration, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data is available in the supplementary material.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.wasman.2024.08.014.

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