

https://dspace.org/

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

Nondumiso Mofokeng; L Madikizela; Luke Chimuka

https://hdl.handle.net/10539/46487
WOS

Downloaded from a DSpace repository. https://dspace.org/

Check for updates

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

AUTHORS:
Nondumiso N. Mofokeng[1,2]
Lawrence M. Madikizela[3]
Luke Chimuka[1]

AFFILIATIONS:
[1]Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Johannesburg, South Africa
[2]Mpact Operations Pty (Ltd), Innovation, Research & Development Division, Stellenbosch, South Africa
[3]Institute for Nanotechnology and Water Sustainability, College of Science, Engineering and Technology, University of South Africa, Johannesburg, South Africa

CORRESPONDENCE TO:
Nondumiso Mofokeng

EMAIL:
nmofokeng@mpact.co.za

DATES:
Received: 09 Nov. 2023
Revised: 14 Oct. 2024
Accepted: 13 Dec. 2024
Published: 27 Mar. 2025

HOW TO CITE:
Mofokeng NN, Madikizela LM, Chimuka L. Source apportionment and transport of pollutants within the South African paper recycling chain. S Afr J Sci. 2025;121(3/4), Art. #17228. https://doi.org/10.17159/sajs.2025/17228

ARTICLE INCLUDES:
☒ Peer review
☒ Supplementary material

DATA AVAILABILITY:
☐ Open data set
☒ All data included
☐ On request from author(s)
☐ Not available
☐ Not applicable

EDITORS:
Priscilla Baker
Philani Mashazi

KEYWORDS:
paper recycling, accelerated solvent extraction, gas chromatography, pollutants, emerging contaminants

FUNDING:
Mpact Operations Pty (Ltd)

Recycled paper is a valuable commodity that forms an intrinsic part of promoting sustainable resource utilisation. In this study, we aimed to investigate the possible sources and transport of semi-volatile organic pollutants in paper grades used in the recycled paperboard value chain. Accelerated solvent extraction followed by gas chromatography-mass spectrometry were employed for the analyses. The results show 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 sulfonamide 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 samples indicates 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:

To the best of our knowledge, this study is the first performed in South Africa on the identification of chemical constituents of different recycling paper grades, that considers the unique South African paper recycling chain. The pollutants identified indicate that the South African paper recycling chain has pollutants in common with those reported in Global North studies as well as unique pollutants. These included butylated hydroxytoluene, N-butylbenzene sulfonamide, tris (2,4-di-tert-butylphenyl) phosphite and its degradation product tris (2,4-di-tert-butylphenyl) phosphate.

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.[1] The United Nations Sustainable Development Goal 12.5 target is aimed at the substantial reduction of waste generation through prevention, reduction, recycling and reuse.[2] 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.[3-5] In 2023, the South African recovery rate of recyclable paper was 65%, which was equivalent to 1 825 944 metric tonnes.[5] 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.[6]

In this study, semi-volatile organic pollutants were quantified in pre-consumer, retail and post-consumer samples using the internal standard calibration method for 11 of the pollutants and semi-quantification of 1 pollutant. The study focused on the various paper grades used in the manufacture of recycled paperboard and corrugated board in the South African paper recycling chain. 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.

Literature review

The main stages of recycling are collecting, sorting and reprocessing of fibre into new products.[7] Apart from being sustainable, the collection and sorting of paper waste is a major source of job creation in South Africa.[8] In most developing countries, many of the poor and underprivileged rely on recycling for income generation and sustenance.[9] 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.[9] 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.[10] The majority of paper destined for recycling in South Africa makes use of commingled 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.[11] 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).[12] 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.

© 2025. The Author(s). Published under a Creative Commons Attribution Licence.

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.[13] Recycled paper is made by repulping collected wastepaper, followed by the removal of impurities.[14] 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 consisting of, amongst others, varnishes, waxes, coatings and printing inks; along with control additives in the form of biocides, defoamers, drainage aids and control agents.[15] Layers of paperboard are often held together by different types of adhesives to make corrugated boards or to form folding cartonboards.[16] The manufactured recycled paper may also contain reaction products, degradation products or by-products of chemical additives.[17] Extensive research in the Global North has identified several typical pollutants in recycled paper which include, amongst others, phthalates, phenols, benzophenone and naphthalenes.[10,18-22] For virgin, unconverted paper, the most prominent pollutants reported in the literature are anthraquinone[23], 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[24].

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.[25] 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[1,26-29] 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[30] 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, 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.[31] This study may therefore be important in understanding recycling in other developing countries.

Materials and methods

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 1) 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 sulfonamide (NBBS) and tris (2,4-di-tert-butylphenyl) phosphate (AO1680) 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.

Sample collection

Samples were collected from various points of the paper recycling chain in Cape Town, South Africa, as shown in Figure 1, making up a population of 108 samples (Supplementary figure 1 and Supplementary table 2). 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 cartonboards, 22 corrugated boards, 7 magazines, 10 office papers, 13 newsprint and 3 coloured papers were collected.

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 US Environmental Protection Agency (EPA)'s Method 3545A[32], which recommended the



Figure 1: Sample collection sites in the paper recycling chain.

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[33]. 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 °C. 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 °C[34,35], followed by filtration with a 0.45-µm syringe filter prior to GC-MS injection.

Gas chromatography-mass spectrometry analysis

Analysis was performed using a 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 × 0.25 mm ID × 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 ionisation 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 3) were then used in single ion monitoring (SIM) mode for quantification.

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 (R^2). Diisopropylnaphthalene (DIPN) was found to elute as a mixture of five isomers on the GC-MS. It had already been established that this compound exists as 10 isomers.[36] 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.[36] 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 figure 1). 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:

$$C_{sample} = \frac{C_{is}}{A_{is}} \times A_{sample} \qquad \text{Equation 1}^{37}$$

where C_{sample} represents the concentration in the sample, C_{is} is the concentration of the internal standard d-DBP, A_{is} is the area of the internal standard and A_{sample} is 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.

Data analysis

Data analysis was performed using Thermo Scientific XcaliburTM, Thermo Scientific Freestyle 1.8 SP2, MetaboAnalyst 5.0 and Microsoft® Excel. Partial least squares (PLS) discriminant analysis, a chemometrics tool, 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[38] using Equation 2:

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

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.[38]

Interviews

Interviews were conducted with role players involved in paper recycling in South Africa. The incorporation of qualitative interview data into the quantitative analysis results was important in gaining further insight into the factors that influence the collection and sorting of recyclable paper grades, given the limited South African research in this field of study. The 16 participants included both informal and formal waste collectors, sorters, as well as managers, research analysts and plant supervisors.

Results and discussion

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) and hexane:acetone (4:1) 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 obtained 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 the literature where the same hump was evident and could be attributed to unresolved alkane C_{11}–C_{25} chains.[18,39] 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 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.[19] 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.[33] 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 h at 160 °C.

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 3). The LODs and LOQs ranged from 0.944 to 3.147 ηg/g and 4.488 to 14.962 ηg/g, respectively, as shown in Supplementary table 3. The LOQs attained in the present study were comparable to those found in the literature[35,40,41] for the analysis of the same compounds in plastic and paper-based materials using GC-MS. Linearity was confirmed with a coefficient of determination (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 3), 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 more strongly than smaller grammage paper samples.

Overview of pollutant prevalence

The concentrations of the target compounds detected in pre-consumer, retail and post-consumer (Supplementary table 4) 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 figure 2). 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 figure 2). When comparing this finding to previous research, this concentration was within the ranges found in the literature.[35,40,42] The three highest combined concentrations were found in a corrugated box from household waste, which 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 4). This result indicates that consumer usage and exposure to different elements may influence the concentration. An overview of the average pollutants under investigation (Figure 2) showed considerably lower amounts of pollutants in pre-consumer samples than those from retail and post-consumer sites.

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 suggest possible latent compounds present in the pre-consumer samples. It is also possible that lower concentrations of pollutants could have been introduced during manufacturing processes, leading to possible cumulative effects as the samples moved from retail to post-consumer. An increase in detected pollutants in the cartonboard at the 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

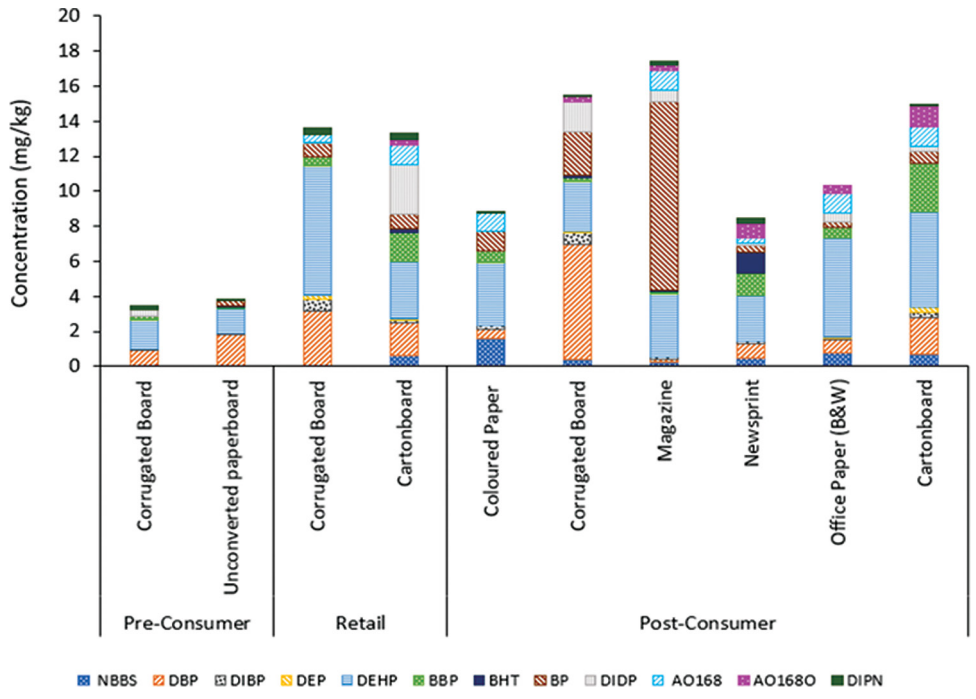


Figure 2: Overview of the concentrations of target compounds in different sources.

samples may have been virgin, recycled or 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[42] 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.

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 Figure 3.

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., VIP scores larger than 1 indicate the most significant variables.[38] From the plot, it is 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.[21] In paper-based packaging, phthalates are used in inks, lacquers and adhesives.[18] The prominence of DEHP, DBP, DIBP, BBP, and DEP in the present study corresponded with findings reported in the literature[18,25,43] in which the same phthalates have been identified in waste paper and recycled paper and board.

With respect to DIPN, Geueke et al.[25] postulated that, because 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. Moreover, DIPN was detected in other samples (Supplementary table 4), including an egg carton, paperboard, cardboard, magazine and newsprint. Although the fibre component of these was not known, its presence demonstrates 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., DIPN was detected mostly in pigmented, coated packaging samples.[44] This shows that, in addition to a recycled fibre 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[21,45,46] as well as printing inks used in printed paper material[47]. BHT is also used as an antioxidant and stabiliser in cosmetics, as a food additive, jet fuels, rubber, plastics, animal feeds, paints and lacquers, adhesive hardeners, cleaning agents, printing products, pharmaceuticals and thinners.[48]

When apportioning pollutants to recycling paper grades in Figure 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

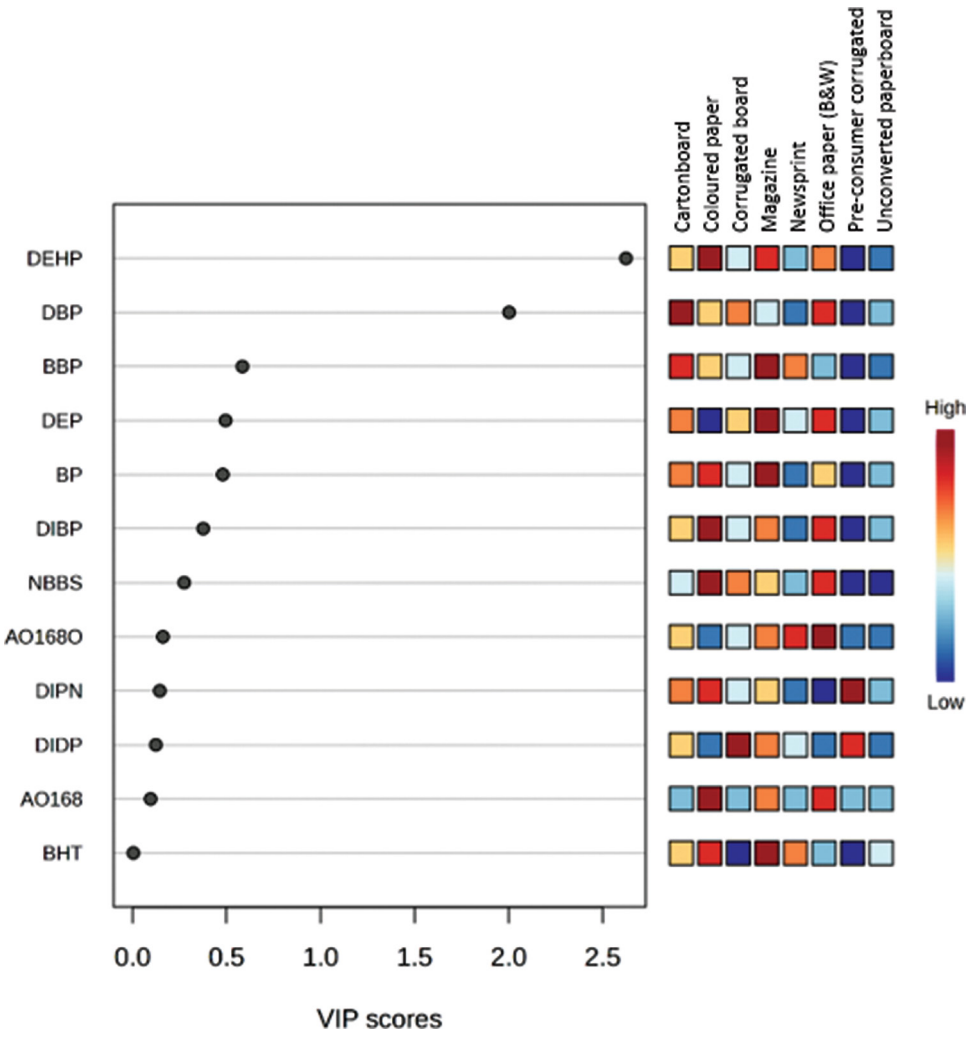


Figure 3: Plot of PLS-VIP scores.

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.

The case of NBBS

NBBS, an organophosphate emerging contaminant[49], has been reported as a wastewater contaminant[50]. 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 Figure 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 sample sites; it could therefore be possible that NBBS may be associated with the manufacture of these mechanical grades. The possibility of contamination from other sources is also probable based on its detection in groundwater[50] as well as its use in cooking utensils.[51] 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.

The prevalence of AO168 and AO168O

The organophosphate ester AO168O, referred to as a novel pollutant[47,52], was initially identified in e-waste dust[52] as well as indoor dust[53]. The first report of its presence in paper-based material was in 2021 by Liu and Mabury, who linked to the use of printing inks in magazines and dry food paper packaging.[47] 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 (Figure 5). AO168O was also detected in papers collected from household waste whilst AO168 was detected in samples from retail and solid waste sites. This suggests that, over time, AO168 degrades and can easily transfer during mingling of waste. Common physical traits were noted in samples found to contain AO168 and/or AO168O. Most of the samples had a glossy or coated finish, were electronics packaging or had black printing. This suggests that AO168 may be used in paper packaging to prevent the possible fading of darker printing inks or to possibly maintain

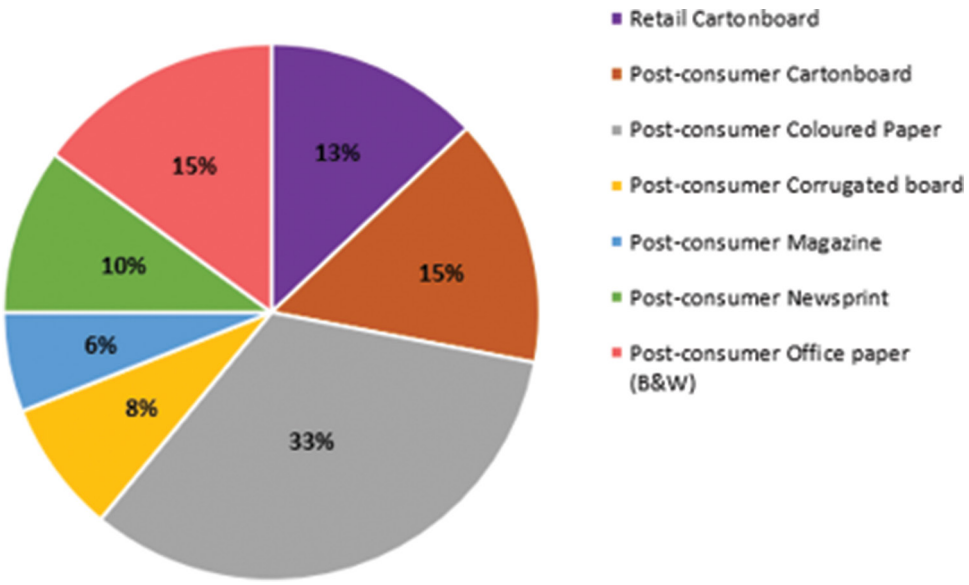


Figure 4: Fraction of retail and post-consumer grades containing NBBS.

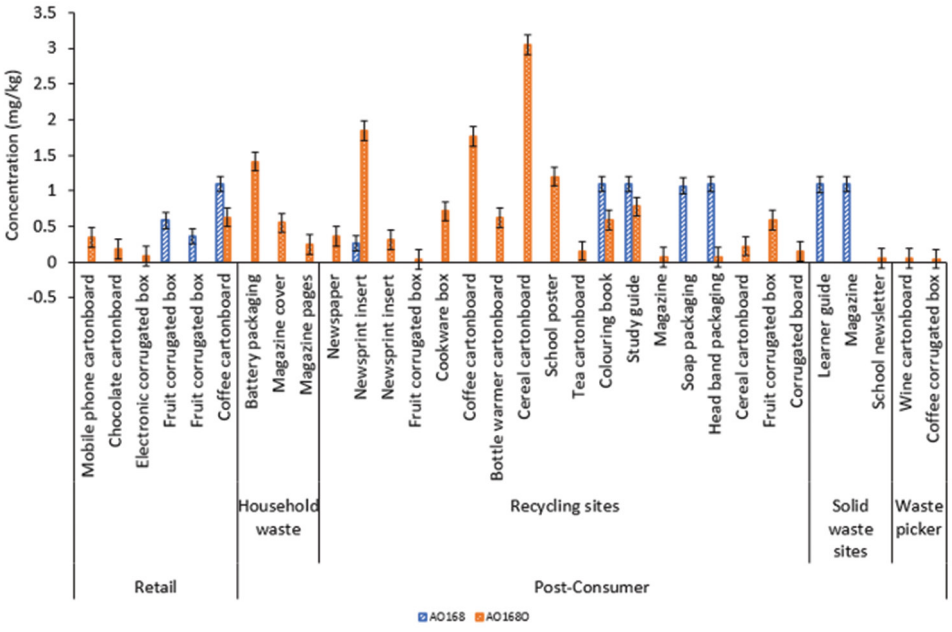


Figure 5: The prevalence of AO168 and AO168O.

a gloss or coated finish.[54] The detection and quantification of AO168 and AO168O highlight how the mingling, use of chemical additives and chemical degradation may lead to the prevalence of certain pollutants. Neither AO168 nor AO168O 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 that the concentrations of these compounds may be very low and beyond the detection limits of this study.

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.[14] The roles of the participants interviewed in this study are shown in Supplementary table 5. 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 6). This figure represents 0.33 of the South African defined paper grades. Knowledge and awareness of the various paper recycling grades were 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-after paper recycling grades were those with the highest value, and general sorting involved separating these out first (Supplementary table 7). 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 (Figures 1 and 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 includes a mixture of grades of paper and board without restrictions on fibre content. Interview participants mentioned that sorting is generally performed through elimination, whereby the valuable and known grades made from cardboard, white paper and office paper are removed first and the remaining recovered paper is deemed 'common mixed waste' (Supplementary table 8). This common mixed waste predominantly consists of used cartonboards (such as cereal boxes, fast-food packaging, chocolate cartonboards and pharmaceutical packaging) 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', that is, 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 at 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 from household waste. Wide variations in 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[55] means that packaging that was previously polymer-based is now manufactured from paper, including paper-based fruit punnets, confectionery products packaging, 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.

Concluding remarks

A validated analytical method was developed using accelerated solvent extraction and gas chromatography. Quantification of semi-volatile pollutants in conjunction with interview data, available literature and chemometrics were then used to investigate the possible sources and propagation of these compounds within the paper recycling chain. Paper and board pollutant prevalence was found to be influenced by external factors arising from exposure to undesirable pollutants during sorting, collecting and recycling. This was shown by the higher combined concentrations of the target analytes in the paper material collected at post-consumer sites. The use of manufacturing and converting additives in the initial manufacturing and reprocessed fibre, as well as the possible retention of chemical compounds in recycled fibre were also identified as important factors in the prevalence of the study analytes. 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 with the detection of known plasticisers, antioxidants and photoinitiators. Further, 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 cartons, 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. Moreover, 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.

Acknowledgements

We thank Ms Ineke Tiggelman of Mpact Operations Pty (Ltd), Research and Development Division for advising us and sharing her valuable experience regarding the paper recycling and paper manufacturing processes in South Africa.

Funding

This study was supported financially through the Innovation, Research and Development Division of Mpact Operations Pty (Ltd), a paper and plastics packaging manufacturing business in southern Africa.

Data availability

All the data supporting the results of this study are included in the article itself and the supplementary material.

Declarations

N.N.M. is employed by Mpact Operations Pty (Ltd). Ethical clearance was obtained from the University of the Witwatersrand (H21/07/29). We have no AI or LLM use to declare.

Authors' contributions

N.N.M.: Conceptualisation, methodology, analysis, writing – original draft, project administration, visualisation, funding acquisition. L.M.M.: Supervision, validation, visualisation, writing – reviewing and editing, project administration. L.C.: Conceptualisation, supervision, validation, writing – reviewing and editing, project administration. All authors read and approved the final manuscript.

References

1. Godfrey L, Oelofse S. Historical review of waste management and recycling in South Africa. Resources. 2017;6(4):57. https://doi.org/10.3390/resources6040057
2. Ghafari D. Sustainable Development Goals (SDG) Waste Indicators [document on the Internet]. c2022 [cited 2023 Aug 10]. Available from: https://wesr.unep.org/sites/default/files/2022-02/Waste_Methodologies.pdf
3. Bezuidenhout D. Aluminium cans and metal packaging: MetPac-SA sets its sights high [document on the Internet]. c2017 [cited 2023 Aug 20]. Available from: https://www.metpacsa.org.za/wp-content/uploads/2019/11/Metals-recycling-final_July-2017.pdf
4. CEPI. European Declaration on Paper Recycling 2016–2020 [webpage on the Internet]. c2020 [cited 2023 Aug 24]. Available from: https://www.cepi.org/eprc-monitoring-report-2019/
5. Paper Manufacturers Association of South Africa (PAMSA). Recycling stats [document on the Internet]. c2023 [cited 2024 Aug 24]. Available from: https://thepaperstory.co.za/wp-content/uploads/2024/07/243470-PAMSA-Recycling-facts-2023-final.pdf
6. Cudjoe D, Zhu B, Nketiah E, Wang H, Chen W, Qianqian Y. The potential energy and environmental benefits of global recyclable resources. Sci Total Environ. 2021;798, Art. #149258. https://doi.org/10.1016/j.scitotenv.2021.149258

7. Yavini D, Chia I, Jen D. Environmental sustainability through chemical wastes recycling techniques in the socio-economic context of sub-Saharan countries. J Environ Sci Resour Manag. 2014;6(2):22–39.

8. Viljoen JMM, Schenck CJ, Blaauw PF. The role and linkages of buy-back centres in the recycling industry: Pretoria and Bloemfontein (South Africa). Acta Commercii. 2012;12(1), a125. https://doi.org/10.4102/ac.v12i1.125

9. Omotoso KO. Informal waste recycling activities: Implications for livelihood and health. Afr J Sci Technol Innov Dev. 2017;9(6):785–793. https://doi.org/10.1080/20421338.2017.1380584

10. Pivnenko K, Eriksson E, Astrup TF. Waste paper for recycling: Overview and identification of potentially critical substances. Waste Manag. 2015;45:134–142. https://doi.org/10.1016/j.wasman.2015.02.028

11. Miranda R, Monte MC, Blanco A. Analysis of the quality of the recovered paper from commingled collection systems. Resour Conserv Recycl. 2013;72:60–66. https://doi.org/10.1016/j.resconrec.2012.12.007

12. FibreCircle. Paper grade definitions for recycling [webpage on the Internet]. c2020 [cited 2023 Aug 01]. Available from:https://fibrecircle.co.za/paper_categories.html

13. Knapp J, Allesch A, Müller W, Bockreis A. Methods to estimate the transfer of contaminants into recycling products – A case study from Austria. Waste Manag. 2017;69:88–100. https://doi.org/10.1016/j.wasman.2017.08.035

14. Rahman MO, Hussain A, Basri H. A critical review on waste paper sorting techniques. Int J Environ Sci Technol. 2014;11(2):551–564. https://doi.org/10.1007/s13762-013-0222-3

15. Bajpai P, editor. Biermann's handbook of pulp and paper. Vol 1. 3rd ed. Amsterdam: Elsevier; 2018. https://doi.org/10.1016/B978-0-12-814240-0.00002-1

16. Blanco A, Miranda R, Monte MC. Extending the limits of paper recycling: Improvements along the paper value chain. For Syst. 2013;22(3):471–483. https://doi.org/10.5424/fs/2013223-03677

17. Muncke J, Andersson AM, Backhaus T, et al. Impacts of food contact chemicals on human health: A consensus statement. Environ Health. 2020;19(1):25. https://doi.org/10.1186/s12940-020-0572-5

18. Biedermann M, Ingenhoff JE, Zurfluh M, Richter L, Simat T, Harling A, et al. Migration of mineral oil, photoinitiators and plasticisers from recycled paperboard into dry foods: A study under controlled conditions. Food Addit Contam Part A Chem Anal Control Expo Risk Assess. 2013;30(5):885–898. https://doi.org/10.1080/19440049.2013.786189

19. Bengtström L, Rosenmai AK, Trier X, Richter L, Simat T, Harling A, et al. Non-targeted screening for contaminants in paper and board food-contact materials using effect-directed analysis and accurate mass spectrometry. Food Addit Contam Part A Chem Anal Control Expo Risk Assess. 2016;33(6):1080–1093. https://doi.org/10.1080/19440049.2016.1184941

20. Ahmadkhaniha R, Rastkari N. Identification of suspected hazardous chemical contaminants in recycled pastry packaging. Acta Sci Pol Technol Aliment. 2017;16(1):33–41. https://doi.org/10.17306/J.AFS.2017.0444

21. Geueke B, Groh KJ, Maffini MV, Martind OV, Boucher JM, Chiang Y-T, et al. Systematic evidence on migrating and extractable food contact chemicals: Most chemicals detected in food contact materials are not listed for use. Crit Rev Food Sci Nutr. 2022;63(28):9425–9435. https://doi.org/10.1080/10408398.2022.2067828

22. Farzanehfar V, Faizi M, Naderi N, Kobarfard F. Development of an analytical method for dibutyl phthalate determination using surrogate analyte approach. Iran J Pharm Res. 2017;16:140–145. https://www.researchgate.net/publication/315773021

23. Vápenka L, Vavrouš A, Votavová L, Kejlová K, Dobiáš J, Sosnovcová J. Contaminants in the paper-based food packaging materials used in the Czech Republic. J Food Nutr Res. 2016;55(4):361–373.

24. Peters RJB, Groeneveld I, Sanchez PL, Gebbink W, Gersen A, de Nijs M, et al. Review of analytical approaches for the identification of non-intentionally added substances in paper and board food contact materials. Trends Food Sci Technol. 2019;85:44–54. https://doi.org/10.1016/j.tifs.2018.12.010

25. Geueke B, Groh K, Muncke J. Food packaging in the circular economy: Overview of chemical safety aspects for commonly used materials. J Clean Prod. 2018;193:491–505. https://doi.org/10.1016/j.jclepro.2018.05.005

26. Muzenda E. Recycling situation in South Africa: A discussion. Int J Biol Ecol Environ Sci. 2013;2(4):79–82.

27. Dlamini SQ. Solid waste management in South Africa: Exploring the role of the informal sector in solid waste recycling in Johannesburg [MSc paper]. Johannesburg: University of the Witwatersrand; 2017. http://hdl.handle.net/10539/22736

28. Godfrey L. Quantifying economic activity in the informal recycling sector in South Africa. S Afr J Sci. 2021;117(9–10), Art. #8921. https://doi.org/10.17159/sajs.2021/8921

29. Nell CM, Schenck C, de Waal J. Waste characterisation in Stellenbosch Local Municipality, South Africa. S Afr J Sci. 2022;118(Special issue: Waste as a Resource), Art. #12795. https://doi.org/10.17159/sajs.2022/12795

30. Seyring N, Dollhofer M, Weißenbacher J, Bakas I, McKinnon D. Assessment of collection schemes for packaging and other recyclable waste in European Union-28 Member States and capital cities. Waste Manag Res. 2016;34(9):947–956. https://doi.org/10.1177/0734242X16650516

31. IAWP. Countries with prospective affiliates [webpage on the Internet]. c2022 [cited 2023 Aug 24]. Available from: https://globalrec.org/where-are-we/

32. EPA. Method 3545A (SW-846): Pressurized fluid extraction (PFE) Revision 1 [webpage on the Internet]. c2007 [cited 2023 Aug 24]. Available from: https://www.epa.gov/esam/method-3545a-sw-846-pressurized-fluid-extraction-pfe

33. Boccacci Mariani M, Giannetti V, Mannino P, Ceccarelli V. Enhanced quality control of recycled paperboard for food packaging. Anal Lett. 2015;48(11):1720–1737. https://doi.org/10.1080/00032719.2014.999271

34. Wang X, Sun X, Wang X, Qi X, Wang D, Jiang J, et al. Determination of 15 phthalic acid esters based on GC-MS/MS coupled with modified QuEChERS in edible oils. Food Chem X. 2022;16, Art. #100520. https://doi.org/10.1016/j.fochx.2022.100520

35. Anggarkasih MG, Yuliana ND, Regiyana Y, Massijaya MY, Budijanto S. Analysis of Di-N-Butyl phthalate (DBP) residue in commercial food packaging from recycled paper and its migration into food simulant I. J Teknol Ind Pert. 2018;28(2):171–179. https://doi.org/10.24961/j.tek.ind.pert.2018.28.2.171

36. Brzozowski R, Skupiński W, Jamróz MH, Skarzyński M, Otwinowska H. Isolation and identification of diisopropylnaphthalene isomers in the alkylation products of naphthalene. J Chromatogr A. 2002;946(1–2):221–227. https://doi.org/10.1016/S0021-9673(01)01571-0

37. Karabagias IK. HS-SPME/GC-MS metabolomic analysis for the identification of exogenous volatile metabolites of monofloral honey and quality control suggestions. Eur Food Res Technol. 2022;248(7):1815–1821. https://doi.org/10.1007/s00217-022-04007-w

38. Galindo-Prieto B, Eriksson L, Trygg J. Variable influence on projection (VIP) for orthogonal projections to latent structures (OPLS). J Chemom. 2014;28(8):623–632. https://doi.org/10.1002/cem.2627

39. Biedermann M, Grob K. On-line coupled high performance liquid chromatography-gas chromatography for the analysis of contamination by mineral oil. Part 1: Method of analysis. J Chromatogr A. 2012;1255;56–75. https://doi.org/10.1016/j.chroma.2012.05.095

40. Carlos KS, de Jager LS, Begley TH. Determination of phthalate concentrations in paper-based fast food packaging available on the U.S. market. Food Addit Contam Part A Chem Anal Control Expo Risk Assess. 2021;38(3):501–512. https://doi.org/10.1080/19440049.2020.1859623

41. Altuntaş U, Hitay V, Özçelik B. Development and validation of a rapid method for identification and quantitation of benzophenone and related 17 derivatives in paper and cardboard packaging materials by gas chromatography-mass spectrometry. Packag Technol Sci. 2016;29(10):513–524. https://doi.org/10.1002/pts.2234

42. Li X, Huo L, Liu C. Study on phthalates plasticizers detection of food paper packaging. In: Zhao P, Ouyang Y, Xu M, Yang L, Ren Y, editors. Applied sciences in graphic communication and packaging. Lecture Notes in Electrical Engineering vol 477. Singapore: Springer; 2018. p. 597–601. https://doi.org/10.1007/978-981-10-7629-9_73

43. Pivnenko K, Olsson ME, Götze R, Eriksson E, Astrup TF. Quantification of chemical contaminants in the paper and board fractions of municipal solid waste. Waste Manag. 2016;51:43–54. https://doi.org/10.1016/j.wasman.2016.03.008

44. Guazzotti V, Giussani B, Piergiovanni L, Limbo S. Screening for chemicals in paper and board packaging for food use: Chemometric approach and estimation of migration. Packag Technol Sci. 2015;28(5):385–395. https://doi.org/10.1002/pts.2109

45. Hermabessiere L, Receveur J, Himber C, Mazurais D, Huvet A, Lagarde F, et al. An Irgafos® 168 story: When the ubiquity of an additive prevents studying its leaching from plastics. Sci Total Environ. 2020;749, Art. #141651. https://doi.org/10.1016/j.scitotenv.2020.141651

46. Hanafi H, Nurdiani N, Melati Sirait S, Nurani Widyahapsari DA, Irawan C. Migration test of polylactic acid packaging that modified with (Butyl hydroxy toluene) and (Tert butyl hydroxy quinon) synthetic antioxidant in food simulant. Oriental J Chem. 2019;35(2):552–556. https://doi.org/10.13005/ojc/350207

47. Liu R, Mabury SA. Printing ink related chemicals, including synthetic phenolic antioxidants, organophosphite antioxidants, and photoinitiators, in printing paper products and implications for human exposure. Environ Int. 2021;149, Art. #106412. https://doi.org/10.1016/j.envint.2021.106412

48. Final report on the safety assessment of BHT. Int J Toxicol. 2002;21 (2_suppl):19–94. https://doi.org/10.1080/10915810290096513

49. Eggen T, Heimstad ES, Stuanes AO, Norli HR. Uptake and translocation of organophosphates and other emerging contaminants in food and forage crops. Environ Sci Pollut Res. 2013;20(7):4520–4531. https://doi.org/10.1007/s11356-012-1363-5

50. Pitarch E, Portolés T, Marín JM, Ibáñez M, Albarrán F, Hernández F. Analytical strategy based on the use of liquid chromatography and gas chromatography with triple-quadrupole and time-of-flight MS analyzers for investigating organic contaminants in wastewater. Anal Bioanal Chem. 2010;397(7):2763–2776. https://doi.org/10.1007/s00216-010-3692-x

51. NIH. Chemical information review document for N-Butylbenzenesulfonamide [document on the Internet]. c2010 [cited 2023 Aug 24]. Available from: https://ntp.niehs.nih.gov/sites/default/files/ntp/htdocs/chem_background/exsumpdf/n_butylbenzensulfonamide_508.pdf

52. Shi J, Xu C, Xiang L, Chen J, Cai Z. Tris(2,4-di-tert-butylphenyl)phosphate: An unexpected abundant toxic pollutant found in PM2.5. Environ Sci Technol. 2020;54(17):10570–10576. https://doi.org/10.1021/acs.est.0c03709

53. Venier M, Stubbings WA, Guo J, Romanak K, Nguyen LV, Jantunen L, et al. Tri(2,4-di-tert-butylphenyl) phosphate: A previously unrecognized, abundant, ubiquitous pollutant in the built and natural environment. Environ Sci Technol. 2018;52(22):12997–13003. https://doi.org/10.1021/acs.est.8b02939

54. Lahimer CM, Ayed N, Horriche J, Belgaied S. Characterization of plastic packaging additives: Food contact, stability and toxicity. Arab J Chem. 2017;10:S1938–S1954. https://doi.org/10.1016/j.arabjc.2013.07.022

55. Oloyede OO, Lignou S. Sustainable paper-based packaging: A consumer's perspective. Foods. 2021;10(5), Art. 1035. https://doi.org/10.3390/foods10051035