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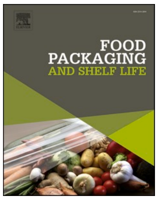

# MS-DIAL as efficient tool for the food safety assessment of volatile substances in disposable tableware

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## ABSTRACT

In this work, the food safety of disposable tableware with different compositions and uses has been studied. Migration tests of nine commercially disposable tableware made of polypropylene (PP), polystyrene (PS) and cardboard have been performed in four food simulants (ethanol 10 %, ethanol 95 %, acetic acid 3 % and Tenax ®) and analysed by direct-immersion solid-phase microextraction gas chromatography-mass spectrometry (DI-SPME-GC-MS). Mass Spectrometry Data Independent Analysis (MS-DIAL) software was used for identifying the volatile migrants and proved to be a huge step forward to perform non-target analysis in food contact material samples compared to traditional approaches. Our study detected a wide range of additives like plasticizers, lubricants, and inks and non-intentionally added substances (NIAS) like degradation products from polystyrene (oligomers) and polypropylene along with degradation products of antioxidants and UV stabilizers. More than 80 % of the compounds found were non listed substances (NLS) and their potential toxicological risk was estimated on the basis of Cramer's rules.

## 1. Introduction

The use of disposable tableware, a key subgroup of food contact materials (FCM), has experienced exponential growth in recent decades. This phenomenon has been driven by a more accelerated lifestyle as well as by its low cost and easy disposable. In addition, since the COVID pandemic, disposable tableware has been widely used by food delivery restaurants (Dybka-Stępień et al., 2021). However, this proliferation has raised significant food safety concerns due to the potential migration of chemical compounds from the packaging to the food.

FCMs regulation is mainly guided by Regulation (EC) Nº 1935/2004 of the European Parliament and Council. This regulation lays down general requirements for all materials and articles intended to come into contact with food (EC, 2004). According to this, FCMs must be manufactured in accordance with good manufacturing practices Regulation (EC) Nº 2023/2006 and "*must not transfer their components to food in quantities that could endanger human health, cause an unacceptable change in the composition of the food and deteriorate the organoleptic characteristics*".

In addition, the European Union has developed specific regulations for different types of materials, such as Regulation (EU) Nº 10/2011 for plastic materials, which sets specific migration limits for certain monomers and additives, and proposes guidelines for migration tests on these materials, specifying temperature, time and food simulants (Commission Regulation (EU) Nº 10, 2011). These limits are based on risk assessments carried out by the European Food Safety Authority (EFSA).

Migration of chemicals from FCMs to food can include a wide range of compounds such as plasticizers, lubricants, antioxidants, adhesives, printing inks, slip agents and others, which are intentionally added substances (IAS). In addition, other compounds might migrate like non-intentionally added substances (NIAS) that come from the degradation process, additive degradation, impurities, neoformed compounds and/or contaminants (Nerin et al., 2013; Nerín et al., 2022). The analysis of migrant compounds presents a considerable analytical challenge in the field of food safety, especially untargeted analysis, which is the most frequent.

Analytical instrumentation plays a crucial role in the identification

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and quantification of FCM migrant compounds by providing accurate, sensitive and efficient tools. Among the most prominent techniques are gas chromatography (GC) ideal for determination of volatiles and semi-volatile compounds (Kirchkeszner et al., 2022) and liquid chromatography (LC) for determination of non-volatile (Ubeda et al., 2018), both coupled to mass spectrometry (MS) (Nerín et al., 2022; Oldring et al., 2023).

However, it is not only an analytical challenge because of the variety of chemical compounds, but also because of the low detection levels required, as low as 10 μg per kg of simulant for non-intentionally added substances (NIAS) according to European legislation (Commission Regulation (EU) Nº 10, 2011). Moreover, although the listed substances (LS) are provided by this Regulation, there is a lack of commercially available standards for most of these substances and this issue is even more severe when it comes to oligomers.

In order to cover the wide range of different chemical compounds at low quantification levels, non-targeted analysis with solid-phase micro extraction coupled to gas chromatography-mass spectrometry (SPME-GC-MS) and ultrahigh-performance liquid chromatography coupled to quadrupole time of flight (UPLC-QTOF) have been used.

The use of these techniques generates a significant amount of data that must be processed with care to reliably identify all migrant compounds. Traditional analytical methods often struggle to efficiently identify and quantify the wide range of compounds present (Tsochatzis, 2021), particularly NIAS (Nerin et al., 2013; Nerín et al., 2022), which may arise from degradation, contamination, or by-products. In this context, MS-DIAL (Mass Spectrometry Data Independent Analysis) represents a significant advancement for FCM analysis and harmonization efforts across the industry.

MS-DIAL is an open-source software platform designed for the comprehensive analysis of mass spectrometry data, providing powerful tools for both targeted and untargeted analyses. Its capabilities include deconvolution of complex MS data, retention time alignment, and identification of a wide range of metabolites, including those present at low concentrations or with unknown structures. These features make MS-DIAL particularly valuable for FCM analysis, where the diversity of IAS and NIAS requires robust, high-resolution detection and interpretation (Tsugawa et al., 2015). However, the use of this type of software, focused on metabolomics and lipidomics, is not easy to use for a conventional user, although there is a comprehensive guide published (MS-DIAL Tutorial | Mtbinfo.Github.Io, 2020).

In this work, the food safety of disposable tableware has been analysed using techniques such as GC-MS and applying the MS-DIAL to also demonstrate its advantage over conventional identification methods. A detailed protocol for using MS-DIAL is also provided to help with the identification of volatile substances.

## 2. Material and methods

### 2.1. Chemicals and reagents

Ethanol absolute (HPLC quality) from Panreac (Barcelona, Spain), glacial acetic acid (technical grade) from Sigma-Aldrich Quimica S.A. (Madrid, Spain) and ultrapure water from a Mili-Q Ultramatric Wasserlab GR 216071 (Madrid, Spain) were used to prepare the aqueous simulants. Tenax ® (Poly (2,6-dipheyl-p-phenylene oxide)) with a particle size 60–80 mesh and a pore size 200 nm, was purchased from Sigma-Aldrich Química S.A. (Madrid Spain). Methanol was purchased from Panreac (Barcelona, Spain). Sodium hydroxide from Sigma-Aldrich (Madrid-Spain) was used to neutralize acetic acid extract.

Standards were purchased from Sigma-Aldrich (Madrid-Spain): C7-C40 alkanes solution, Benzaldehyde (100−52−7), D-limonene (5989–27–5), acetophenone (98−86−2), nonanal (124−19−6), nonanoic acid (112−05−0), hexadecane (544−76−3), 3,5-di-tert-butyl-4-hydroxybenzaldehyde (1620−98−0), 2,4-di-tert-butylphenol (96−76−4), 2,6-di-tert-butyl-1,4-benzoquinone (719−22−2), dioctyl phthalate (117−84−0), dibutyl phthalate (84−74−2), 2-tridecanone (593−08−8), benzophenone (119−61−9), diethylene glycol (111−46−6), heptane (142−82−5), isophorone (78−59−1), methyl salycilate (119−36−8), naphthalene (91−20−3), nonadecanoic acid (646−30−0), methyl palmitate (112−39−0), o-xylene (95−47−6), styrene (100−42−5), tridecanol (112−70−9), 2,6-diisopropyl naphthalene (24157−81−1) and toluene (108−88−3).

Stock solutions (concentration above 1000 mg/kg) of each analyte were prepared in methanol, except for hexadecane, naphthalene, nonadecanoic acid and 2,6-diisopropylnaphthalene that were prepared in hexane. Afterwards, they were grouped up to 6 standards per group, mixed and diluted to 10 mg/kg in both ethanol 10 % or neutralized acetic acid 3 % as working solutions. All standards and solutions were prepared under gravimetric control. Appropriate dilutions were obtained in each case for quantitative purpose.

### 2.2. Samples

Nine types of disposable plates were selected to be analysed as its composition was representative of the usual composition in disposable tableware. The samples were purchased from local supermarkets. Samples were categorized in three groups according to its composition: polypropylene (PP), polystyrene (PS) and carboard (C).

- Polypropylene: Blue (PPZ), yellow (PPA) and white (PPB)
- Polystyrene: Red (PSR), black (PSN) and white (PSB)
- Carboard (C): CL (Color L), CP (Color P) and CB (white)

### 2.3. Migration tests

Migration tests were carried out according to European Legislation (Commission Regulation (EU) Nº 10, 2011), with simulants under temperature and time to represent the intended use. In order to cover the worst scenario of use for this type of materials, 10 days at 40ºC were selected, which is intended for long term storage and/or heating up to 70ºC for up to 2 hours or heating up to 100ºC for up to 15 minutes.

Migration tests were performed with simulants: ethanol 10 % (Simulant A) for simulating hydrophilic foods, ethanol 95 % (Substitute for simulant D2, vegetable oil) for simulating high-fat foods, acetic acid 3 % (Simulant B) for simulating acidic foods and Tenax (Simulant E) for dry foods. With carboard samples, Tenax was exclusively used as liquid food simulants were not appropriate.

Tenax as a simulant entails prior purification by Soxhlet extraction with acetone for 6 hours and subsequent oven drying at 100ºC for at least 24 hours. The tests were carried out following optimized procedures described in the literature (Aznar et al., 2015; Vera et al., 2019).

The samples, cut into 4 × 2 cm, were covered on the food contact side with 0.32 g Tenax, according to the international standard (UNE-EN 14338, 2004) that established the ratio of 4 g Tenax per $dm^2$ ratio. Then, they were covered in aluminum foil and placed in Petri dishes. Three replicates of the samples were prepared for each test and placed in the oven under the conditions mentioned above. Additionally, several process blanks were prepared.

After the exposure, Tenax was extracted twice with 3 mL of ethanol. The total solution was centrifuged at 3000 rpm for 30 min (Microfuge®18 Centrifuge, Beckman Coulter TM, California USA) to remove the Tenax® residues. Then, an aliquot of 1.9 mL was diluted with water up to reach a 10 % ethanol and finally, it was analyzed by DI-SPME-GC-MS.

For liquid simulants, samples were cut into cut-offs of 10.8 $cm^2$ surface and were subjected to immersion contact with 18 g of each simulant to fulfil the legislative rate of 6 $dm^2$ per kg of food simulant. Additionally, pH adjustment to 7 of acetic acid 3 % migration extract was performed with sodium hydroxide solution.

### 2.4. DI-SPME-GC-MS method

DVB/CAR/PDMS 50/30 µm fibre was used due to its proven highly efficient extraction capacity for low and high molecular mass molecules (Chen et al., 2019). The CTC Analytics Pal RSI 85 from CTC Analytics AG (Zwingen, Switzerland) coupled to GC-MS equipment GC 8890 gas chromatograph from Agilent (Palo Alto, CA, USA) with an Agilent ultrainert liner (id = 0.75 and 4 mm for SPME) was used for the analysis of volatile compounds. HP-5 MS column from Agilent (30 cm×0.25 mm, 0.25 µm film thicknesses) was used to separate the compounds. The applied temperature ramp started at 50°C for 5 min and increased at a rate of 8°C min$^{-1}$ up to a 300°C and held for 10 min. The injector had a temperature of 250°C and splitless mode was used. Helium was the carried gas used with a flow of 1 mL/min. Temperature and adsorption time were 70°C and 55 min, respectively. Desorption time was set to 8 min and the stirring rate conditions were 600 rpm. An Agilent 5977B Mass Spectrometer in SCAN mode from 45 to 450 $m/z$ was used with a source temperature of 250ºC to perform the analysis of migrants.

These conditions are based on the optimised method for non-targeted screening of food contact materials developed (Su et al., 2020) with minor modifications to reduce instrumental noise. A quality control (QC) pool sample was made mixing the same amount of each sample, and then it was injected several times during the acquisition sequence. Agilent MassHunter software version 13.0 was used for acquisition.

### 2.5. MS-DIAL settings

Chromatograms were processed as described in the workflow of Fig. 1. (Further details can be found in the Supplementary Material Section 2). To identify, deconvolute and perform the alignment of characteristic peaks, final files were processed using MS-DIAL software version 4.9 (Tsugawa et al., 2015). MS-DIAL parameters were set as follows (recommended by Tsugawa et al.): a minimum detected peak height of 2000, a sigma window value of 0.5 and 10 Electronic Impact (EI) spectra cut off. Alignment was performed with a retention time tolerance of 0.075 min and an EI similarity tolerance of 70 %. Identification was carried out with NIST 20 modified library and retention index (RI) experimentally calculated, with a RI tolerance of 30. Additionally, peaks with a maximum/mean sample fold change of less than 5 and those that were not present in all three replicates were removed.

To improve the reliability of the identification, mass spectra and retention index (RI) of all the candidates were manually checked. Moreover, all tentatively identified compounds were assigned the corresponding identification levels (Schymanski et al., 2014).

Once the tentative identification was performed, suitable and available standards were prepared to quantify each compound. In absence of pure standard, the identified compounds were semi quantified with an alternative standard with similar chemical structure, in the result tables the quantification standard is detailed for each compound. Calibration curves were prepared in ethanol 10 % and neutralized acetic acid 3 %.

### 2.6. Data processing

Identification workflow described in the literature (Su et al., 2019) was used along with the identification confidence proposed (Schymanski et al., 2014). It contains 5 levels. Level 1: Confirmed by a reference standard with MS, MS/MS and retention index match (For GC); Level 2: Probable structure which is subdivided into 2a (MS and MS/MS or retention index) and 2b (No other structure fits the experimental information); Level 3: Tentative candidate where exists evidence for possible structure but insufficient information for one exact structure only; Level 4: Unequivocal molecular formula; and Level 5: Exact mass ($m/z$).

Migrants were classified by ClassyFire (Djoumbou Feunang et al., 2016) which uses a combination of classification rules and chemical ontologies to categorize chemical compounds in a well-defined hierarchy. Furthermore, migrants were classified according to whether they were listed (LS) or not listed (NLS) substances in European legislation (EC, 2011) which stablish a 10 µg/kg limit for NLS. Additionally, for NLS, their potential toxicological risk was tentatively classified using the Threshold of Toxicological Concern (TTC), based on Cramer's decision tree, calculated using Toxtree v3.1. ® software (Patlewicz et al., 2008). Cramer's classification system categorizes compounds according to their chemical structure into three toxicity classes: Class I (low toxicity), Class II (medium toxicity) and Class III (high toxicity). Considering the estimated daily exposure and a daily food intake of 1 kg per person, and an average bodyweight of 60 kg, the recommended maximum migration levels are 1.8 mg/kg for Class I, 0.54 mg/kg for Class II and 0.09 mg/kg for class III (Koster et al., 2011).

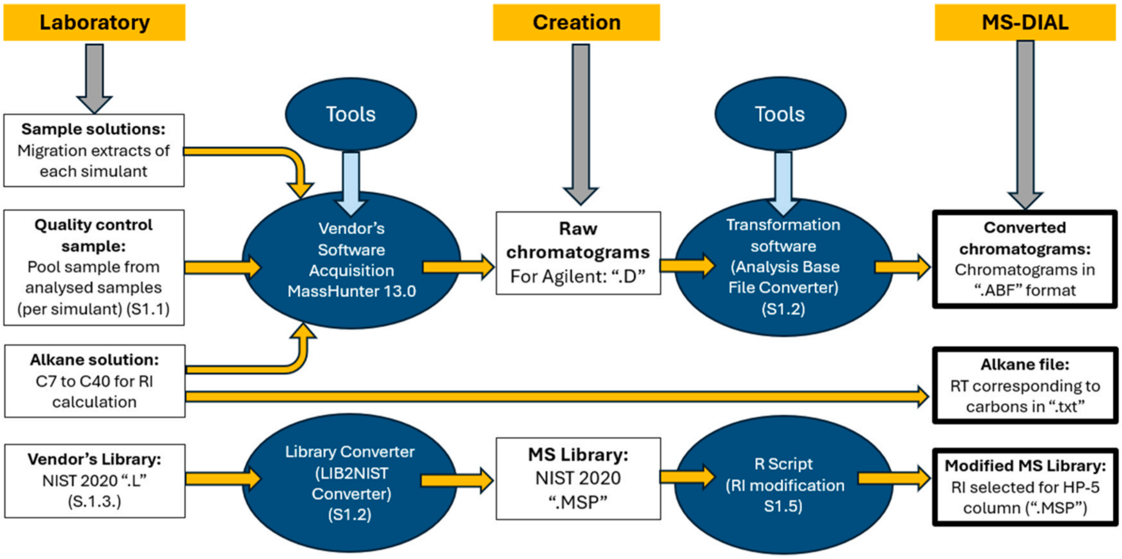

**Fig. 1.** Flow chart diagram of MS-DIAL processing process from the lab to the final files to use MS-DIAL. In brackets, Supplementary Material Sections are shown (i.e, S2.1) acquisition.

## 3. Results and discussion

### 3.1. Identification of volatile compounds with MS-DIAL

In FCM, a complex mixture of compounds can migrate from the material into food simulants. This results in chromatograms with a large number of peaks to process, which is commonly referred to as the "peak forest", as shown in Fig. 2(a). This scenario present challenges as overlapping peaks and varying intensities and baselines.

Once raw chromatograms are processed into acceptable format (.ABF format), MS-DIAL performs peak detection using a deconvolution algorithm. It separates overlapping peaks in the Total Ion Chromatogram (TIC) or Extracted Ion Chromatograms (EIC) by examining their unique mass spectral patterns. This step is vital for resolving co-eluted compounds and distinguishing between similar compounds as shown in Fig. 2(b), where a partial coeluting is present between benzaldehyde and 1-ethyl-3-methylbenzene. Without deconvoluting tools, total coelutions might be overlooked as shown in Fig. 2(c), where hexadecane and diethyl phthalate have the same retention times.

Additionally, MS-DIAL offers the blank removal filter, which is crucial in FCM, where trace contaminants are being studied. However, traditional approaches are likely to overlook blanks coeluting with actual analytes as shown in Fig. 2(d).

### 3.2. Volatile compounds

The results of the migration tests performed at different conditions in the 9 disposable plates are shown in Table 1 (PP), Table 2 (PS) and Table 3 (Carboard). Table S1 provides additional information on the compounds identified based on ClassyFire, Toxtree and LS or NLS. IAS such as antioxidants, plasticizers, slip agents, lubricants and NIAS from degradation processes and degradation of additives were identified and semi quantified using the standards descripted in Table S2 and identified with its corresponding code (Quantifier: QS, see Section 2.1. for more details).

Only five out of all compounds identified had specific migration levels (SML): 1-Hexanol, 2-ethyl-; 2,2,4-Trimethyl-1,3-pentanediol diisobutyrate; benzophenone; hexanedioic acid, bis(2-ethylhexyl) ester and bis(2-ethylhexyl) phthalate. For the remaining listed compounds (LS), that are described below, the overall migration limit of 60 mg/kg applies, what means that they were of no concern.

Concerning the IAS, two lubricants octadecanoic acid (Vera et al., 2018), or octadecanoic acid, ethyl ester (Estremera et al., 2024) were found in PSR and PSB respectively, and both in CP. None of them exceeded the legislated limits.

A variety of plasticizers were also detected in most of the samples, notably phthalates like diethyl phthalate, Diisobutyl phthalate, dibutyl phthalate and bis (2-ethylhexyl) phthalate (DEHP). Phthalates plasticizers, especially DEHP, have been shown to have adverse effects on human health (Benson, 2009). Furthermore, non-phthalate plasticizers like di-(2-ethylhexyl) adipate (DEHA) and acetyl tributyl citrate (ATBC) were found to be within legislative limits in all the samples.

In PP samples, degradation products like cyclooctane, 1,4-dimethyl-, trans- and nonane, 2-methyl-3-methylene- were found in concentration higher than 1 mg/kg. Other alkanes like decane, 2-methyl-; undecane; dodecane; dodecane, 4,6-dimethyl-tridecane which could be defined as PP oligomers, were also quantified.

Regarding PS plates, styrene, the monomer of polystyrene, was found in high amounts, especially in ethanol 95 % and Tenax ®, even exceeding 1 mg/kg. This would be alarming if only the consolidated version of the EU legislation (EU 10/2011) is considered. However, a change in the specific migration levels (SMLs) to 40 µg/kg (De Seze & Kriz, 2023) is foreseen as a precautionary measure in view of the European Commission's mandate for the assessment of its genotoxic potential.

In addition to styrene, several polymer degradation NIAS were found, including ethylbenzene, which is used for the synthesis of styrene by catalytic dehydrogenation and for the production of polystyrene copolymers (Tang et al., 2000), as well as styrene oligomers such as Benzene, 1,1′-(1,3-propanediyl)bis- and Cyclobutane, 1,2-diphenyl-

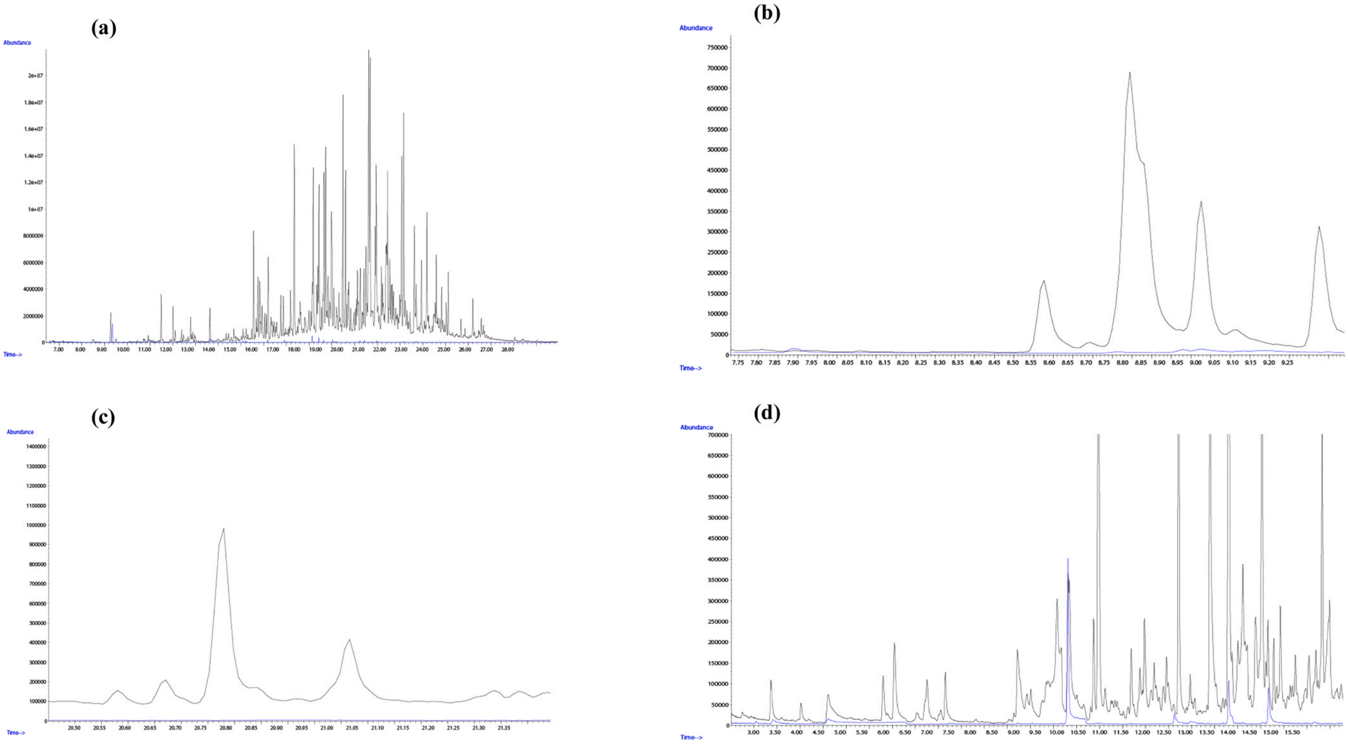

Fig. 2. Overlayed chromatograms of sample (black) and blank (blue) showing a general overview of migration extracts peak forest (a), partial coelution of benzaldehyde and 1-ethyl-3-methylbenzene (b), complete co-elution of diethyl phthalate and hexadecane (RT: 20,80) (c) and blank removal with peak differentiation (d).

**Table 1**
Quantified compounds by SPME-GC-MS in PP plates along with the retention time (min), retention index, m/z of quantification, CAS and Quantifier (QS).

| Compound | RT (min) | RI | m/z Quant. | CAS | QS | Sample | Concentration ±s (μg/kg) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | EtOH 10% | EtOH 95% | HAcO 3% | Tenax |
| 2,4-Dimethyl-1-heptene | 5.62 | 783.5 | 70.1 | 19549-87-2 | A | PPA | ND | ND | ND | 462.51 ± 22.50 |
| | | | | | | PPB | ND | 42.20 ± 2.07 | 0.010 ± 0.001 | 4020.47 ± 585.88 |
| | | | | | | PPZ | ND | ND | ND | 495.07 ± 43.59 |
| Heptane, 2,3-dimethyl- | 6.06 | 812.4 | 84.1 | 3074-71-3 | A | PPB | ND | 5.33 ± 0.32 | ND | ND |
| Ethylbenzene | 6.26 | 825.3 | 91.1 | 100-41-4 | A | PPA | 0.05 ± 0.01 | ND | ND | 38.76 ± 1.84 |
| | | | | | | PPZ | 0.05 ± 0.01 | ND | ND | 33.02 ± 3.25 |
| Octane, 4-methyl | 6.30 | 828.4 | 85.1 | 2216-34-4 | A | PPA | ND | ND | ND | 756.20 ± 59.73 |
| | | | | | | PPB | ND | 19.19 ± 1.48 | ND | 2567.99 ± 335.25 |
| | | | | | | PPZ | ND | 5.02 ± 1.88 | ND | 843.28 ± 9.38 |
| p-Xylene | 6.51 | 842.0 | 91.0 | 106-42-3 | B | PPA | 0.09 ± 0.03 | ND | ND | 107.00 ± 15.85 |
| | | | | | | PPB | ND | ND | ND | 55.04 ± 21.76 |
| | | | | | | PPZ | 0.09 ± 0.01 | ND | ND | 80.65 ± 19.74 |
| o-Xylene | 7.19 | 886.8 | 91.1 | 95-47-6 | B | PPA | 0.09 ± 0.02 | ND | ND | ND |
| | | | | | | PPZ | 0.08 ± 0.02 | ND | ND | ND |
| Benzene, (1-methylethyl)- | 8.13 | 926.6 | 105.1 | 98-82-8 | A | PPZ | ND | 2.07 ± 0.16 | ND | ND |
| .alpha.-Pinene | 8.38 | 935.6 | 93.1 | 80-56-8 | C | PPA | ND | ND | ND | 394.09 ± 14.40 |
| | | | | | | PPB | ND | ND | ND | 153.20 ± 25.94 |
| | | | | | | PPZ | ND | 5.20 ± 2.23 | ND | 342.82 ± 52.88 |
| 2-Heptanone, 4-methyl- | 8.58 | 942.9 | 58.0 | 6137-06-0 | D | PPB | ND | ND | 0.26 ± 0.04 | ND |
| Propylbenzene | 8.95 | 956.6 | 91.1 | 103-65-1 | A | PPA | ND | ND | ND | 8.02 ± 2.10 |
| | | | | | | PPZ | ND | ND | ND | 8.30 ± 0.56 |
| β-Pinene | 9.54 | 978.0 | 93.1 | 127-91-3 | C | PPA | ND | ND | ND | 530.03 ± 24.03 |
| | | | | | | PPZ | ND | 7.21 ± 1.32 | ND | 378.78 ± 58.20 |
| 2-Octanol, 2-methyl- | 9.64 | 981.7 | 59.1 | 628-44-4 | F | PPB | ND | ND | 2.00 ± 0.06 | ND |
| Benzene, 1,2,4-trimethyl- | 10.00 | 994.5 | 120.1 | 95-63-6 | A | PPB | ND | ND | ND | 22.31 ± 6.65 |
| Benzene, 1-ethyl-3-methyl- | 10.21 | 1002.5 | 111.1 | - | A | PPA | ND | ND | ND | 104.26 ± 6.05 |
| Nonane, 2,6-dimethyl- | 10.46 | 1013.5 | 71.1 | - | G | PPB | ND | ND | ND | 6711.51 ± 862.89 |
| Nonane, 2-methyl-3-methylene- | 10.68 | 1022.8 | 56.1 | - | C | PPB | ND | ND | ND | 1113.59 ± 192.68 |
| p-Cymene | 10.77 | 1026.6 | 119.1 | 99-87-6 | C | PPA | ND | ND | ND | 389.51 ± 98.78 |
| | | | | | | PPB | ND | ND | ND | 119.24 ± 20.52 |
| | | | | | | PPZ | ND | ND | ND | 155.21 ± 11.08 |
| D-Limonene | 10.86 | 1030.5 | 68.1 | 5989-27-5 | C | PPB | ND | 2.84 ± 0.24 | ND | 190.14 ± 33.04 |
| | | | | | | PPZ | ND | 2.55 ± 0.45 | ND | ND |
| 1-Hexanol, 2-ethyl- | 10.88 | 1031.5 | 57.1 | 104-76-7 | F | PPA | ND | ND | 0.26 ± 0.11 | ND |
| | | | | | | PPB | ND | ND | 0.30 ± 0.03 | ND |
| | | | | | | PPZ | ND | ND | 0.55 ± 0.11 | ND |
| 1-Ethyl-2,2,6-trimethylcyclohexane | 10.99 | 1036.2 | 154.2 | 71186-27-1 | B | PPB | ND | ND | ND | 55.55 ± 11.01 |
| 2-Heptanone, 4,6-dimethyl- | 11.50 | 1058.0 | 84.1 | 19549-80-5 | D | PPB | ND | ND | 0.22 ± 0.01 | ND |
| Decane, 2-methyl- | 11.54 | 1059.4 | 71.1 | 6975-98-0 | D | PPA | ND | 6.30 ± 1.91 | ND | 794.63 ± 26.85 |
| | | | | | | PPB | ND | 12.56 ± 0.23 | ND | 975.97 ± 140.60 |
| | | | | | | PPZ | ND | 7.51 ± 1.55 | ND | 854.79 ± 10.70 |
| Acetophenone | 11.80 | 1070.6 | 105.0 | 98-86-2 | I | PPA | ND | ND | ND | 320.11 ± 150.79 |
| 1-Octanol | 11.85 | 1072.7 | 56.1 | 111-87-5 | F | PPA | ND | ND | 0.15 ± 0.01 | ND |
| | | | | | | PPB | ND | ND | 0.14 ± 0.04 | ND |
| | | | | | | PPZ | ND | ND | 0.11 ± 0.01 | ND |
| Cyclooctane, 1,4-dimethyl-, trans- | 12.04 | 1080.8 | 69.1 | 13151-99-0 | C | PPA | ND | ND | ND | 1196.21 ± 70.30 |
| | | | | | | PPZ | ND | ND | ND | 1109.41 ± 12.40 |

(*continued on next page*)

**Table 1** (*continued*)

| Compound | RT (min) | RI | m/z Quant. | CAS | QS | Sample | Concentration ±s (μg/kg) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | EtOH 10% | EtOH 95% | HAcO 3% | Tenax |
| Undecane | 12.54 | 1102.5 | 71.1 | 1120-21-4 | D | PPA | ND | 228.08 ± 101.61 | ND | 638.32 ± 37.62 |
| | | | | | | PPB | ND | 86.42 ± 35.69 | ND | ND |
| | | | | | | PPZ | ND | 4.83 ± 0.73 | ND | 609.80 ± 19.07 |
| Nonanal | 12.60 | 1105.6 | 57.1 | 124-19-6 | G | PPA | 1.94 ± 0.17 | ND | 0.13 ± 0.07 | 5473.84 ± 1737.28 |
| | | | | | | PPB | ND | ND | ND | 719.03 ± 14.28 |
| | | | | | | PPZ | 0.68 ± 0.17 | ND | ND | 6178.86 ± 197.83 |
| 1H-Indene, 2,3-dihydro-5-methyl- | 13.58 | 1153.5 | 117.1 | 1075-22-5 | H | PPB | ND | 0.75 ± 0.20 | ND | ND |
| Benzene, pentyl- | 13.71 | 1159.8 | 91.1 | 538-68-1 | A | PPB | ND | 2.81 ± 0.10 | ND | ND |
| Benzene, pentyl- | 13.71 | 1159.8 | 91.1 | 538-68-1 | A | PPZ | ND | ND | ND | 19.45 ± 5.78 |
| Naphthalene, 1,2,3,4-tetrahydro- | 13.82 | 1165.4 | 104.1 | 119-64-2 | H | PPB | ND | 0.31 ± 0.05 | 0.11 ± 0.02 | 72.50 ± 4.76 |
| Naphthalene | 14.30 | 1188.7 | 128.1 | 91-20-3 | H | PPA | ND | ND | 0.01 ± 0.00 | 175.29 ± 26.76 |
| | | | | | | PPB | ND | ND | 0.05 ± 0.01 | ND |
| | | | | | | PPZ | 0.25 ± 0.07 | 1.54 ± 0.46 | 0.19 ± 0.02 | 232.98 ± 17.96 |
| .alpha.-Terpineol | 14.42 | 1194.4 | 59.1 | 98-55-5 | C | PPA | ND | ND | 0.22 ± 0.02 | ND |
| Dodecane | 14.53 | 1200.2 | 57.1 | 112-40-3 | D | PPB | ND | 3.75 ± 0.31 | ND | 295.82 ± 30.92 |
| Decanal | 14.65 | 1206.3 | 57.1 | 112-31-2 | G | PPA | ND | ND | ND | 798.14 ± 78.20 |
| | | | | | | PPB | ND | ND | ND | 389.20 ± 135.27 |
| | | | | | | PPZ | ND | ND | ND | 663.79 ± 140.84 |
| Naphthalene, 1,2,3,4-tetrahydro-2-methyl- | 14.89 | 1219.4 | 146.1 | 3877-19-8 | H | PPB | ND | 0.96 ± 0.15 | ND | 291.96 ± 7.16 |
| Benzaldehyde, 3,4-dimethyl- | 14.93 | 1221.5 | 133.1 | 5973-71-7 | E | PPA | ND | ND | ND | 17.84 ± 4.56 |
| Benzene, 1-methyl-2-(1-ethylpropyl)- | 15.67 | 1261.0 | 105.1 | - | A | PPB | ND | ND | ND | 2178.80 ± 106.56 |
| Naphthalene, 1,2,3,4-tetrahydro-5-methyl- | 15.82 | 1269.4 | 131.1 | 1680-51-9 | H | PPB | 1.14 ± 0.64 | 32.12 ± 1.96 | 0.46 ± 0.04 | 2275.24 ± 69.33 |
| Dodecane, 2,6,11-trimethyl- | 16.01 | 1279.6 | 71.1 | 31295-56-4 | D | PPA | 0.11 ± 0.01 | ND | ND | 401.37 ± 39.18 |
| | | | | | | PPB | ND | 7.34 ± 1.39 | ND | 235.52 ± 40.34 |
| | | | | | | PPZ | ND | 8.24 ± 0.89 | ND | 521.06 ± 218.52 |
| Naphthalene, 1,2,3,4-tetrahydro-6-methyl- | 16.34 | 1297.5 | 131.1 | 1680-51-9 | H | PPB | ND | ND | 0.17 ± 0.02 | ND |
| Tridecane | 16.36 | 1298.4 | 57.1 | 629-50-5 | D | PPB | ND | 15.28 ± 0.35 | ND | 838.59 ± 84.60 |
| Undecanal | 16.51 | 1306.9 | 82.0 | 112-44-7 | G | PPZ | ND | ND | ND | 162.20 ± 34.84 |
| 1-Tridecene | 16.52 | 1307.5 | 69.1 | 2437-56-1 | D | PPA | ND | 1.90 ± 0.13 | ND | ND |
| | | | | | | PPZ | ND | 1.86 ± 0.14 | ND | ND |
| Naphthalene, 1-methyl- | 16.64 | 1314.7 | 142.1 | 90-12-0 | H | PPA | ND | ND | ND | 40.64 ± 4.65 |
| | | | | | | PPZ | ND | ND | ND | 89.66 ± 6.92 |
| Naphthalene, 1,2,3,4-tetrahydro-2,7-dimethyl- | 16.79 | 1323.1 | 118.1 | 13065-07-1 | H | PPB | ND | 17.87 ± 1.62 | ND | 1509.20 ± 22.06 |
| Dodecane, 4,6-dimethyl- | 16.82 | 1325.2 | 57.1 | - | D | PPA | ND | ND | ND | 228.17 ± 11.38 |
| | | | | | | PPZ | ND | ND | ND | 259.65 ± 118.01 |
| Tridecane, 5-methyl- | 17.12 | 1342.6 | 71.1 | - | D | PPA | ND | 3.13 ± 0.52 | ND | ND |
| | | | | | | PPZ | ND | ND | ND | 174.40 ± 75.98 |
| (3-Methylphenyl) methanol, n-butyl ether | 17.33 | 1354.6 | 106.1 | - | D | PPB | ND | ND | ND | 654.01 ± 48.92 |
| 1H-Indene, 2,3-dihydro-4-propyl- | 17.50 | 1364.7 | 91.1 | - | H | PPB | ND | 12.78 ± 1.27 | ND | ND |
| Decanoic acid, ethyl ester | 17.99 | 1393.3 | 88.1 | 110-38-3 | J | PPA | ND | ND | ND | 941.74 ± 65.38 |
| | | | | | | PPZ | ND | ND | ND | 884.81 ± 49.39 |
| Naphthalene, 1,2,3,4-tetrahydro-5,7-dimethyl- | 18.06 | 1397.4 | 71.1 | - | H | PPA | ND | ND | ND | 90.47 ± 16.60 |
| | | | | | | PPB | 1.11 ± 0.57 | 58.45 ± 4.81 | 0.25 ± 0.03 | 4122.46 ± 87.85 |
| Tetradecane | 18.06 | 1397.5 | 57.1 | 629-59-4 | D | PPZ | ND | ND | ND | 96.87 ± 29.18 |
| Dodecanal | 18.24 | 1408.1 | 57.1 | 112-54-9 | G | PPA | ND | ND | ND | 702.35 ± 143.09 |
| | | | | | | PPB | 2.57 ± 0.76 | ND | ND | 1313.63 ± 202.38 |
| | | | | | | PPZ | ND | ND | ND | 867.93 ± 395.72 |
| Naphthalene, 1,7-dimethyl- | 18.53 | 1426.1 | 156.1 | 575-37-1 | H | PPA | ND | ND | ND | 62.39 ± 8.71 |

(*continued on next page*)

**Table 1** (*continued*)

| Compound | RT (min) | RI | m/z Quant. | CAS | QS | Sample | Concentration ±s (μg/kg) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | EtOH 10% | EtOH 95% | HAcO 3% | Tenax |
| | | | | | | PPZ | ND | ND | ND | 208.65 ± 8.38 |
| Naphthalene, 1,2,3,4-tetrahydro-6-propyl- | 19.00 | 1455.4 | 106.1 | - | H | PPB | ND | 7.89 ± 1.22 | ND | 1028.23 ± 98.00 |
| Benzene, octyl- | 19.19 | 1467.2 | 92.1 | 2189-60-8 | A | PPB | ND | ND | ND | 889.48 ± 86.56 |
| 1-Dodecanol | 19.25 | 1470.9 | 55.1 | 719-22-2 | L | PPZ | ND | ND | ND | 320.68 ± 14.19 |
| 1,1’-Biphenyl, 3-methyl- | 19.55 | 1489.3 | 168.1 | - | K | PPB | ND | ND | ND | 474.32 ± 17.23 |
| Tetradecane, 6,9-dimethyl- | 19.61 | 1492.9 | 71.1 | - | D | PPA | 0.06 ± 0.01 | ND | ND | ND |
| | | | | | | PPZ | ND | 2.47 ± 0.34 | ND | ND |
| Pentadecane | 19.65 | 1495.5 | 57.1 | - | D | PPB | ND | ND | ND | 428.28 ± 174.76 |
| Tridecanal | 19.84 | 1507.9 | 82.1 | - | G | PPA | ND | ND | ND | 306.85 ± 42.23 |
| | | | | | | PPZ | ND | ND | ND | 230.63 ± 18.09 |
| 2,4-Di-tert-butylphenol | 19.87 | 1510.2 | 191.2 | 96-76-4 | M | PPA | 0.80 ± 0.05 | 0.61 ± 0.14 | ND | 1251.70 ± 88.04 |
| | | | | | | PPB | 10.45 ± 1.14 | 24.01 ± 6.51 | ND | 2299.15 ± 105.96 |
| | | | | | | PPZ | 0.85 ± 0.11 | 1.25 ± 0.22 | ND | 968.37 ± 152.30 |
| Bicyclo[4.2.0]oct-1-ene, exo-7-(1-cyclohexen-1-yl)- | 20.25 | 1535.6 | 131.1 | - | H | PPB | ND | ND | ND | 892.67 ± 69.42 |
| Naphthalene, 2,3,6-trimethyl- | 20.30 | 1538.7 | 170.1 | - | H | PPZ | ND | ND | ND | 176.87 ± 11.02 |
| Naphthalene, 6-butyl-1,2,3,4-tetrahydro- | 20.62 | 1560.1 | 145.1 | - | H | PPB | ND | 13.93 ± 1.65 | ND | 1088.10 ± 78.51 |
| 1,2,5,5,8a-Pentamethyl-1,2,3,5,6,7,8,8a-octahydronaphthalen-1-ol | 20.80 | 1572.1 | 135.1 | - | H | PPZ | ND | 14.37 ± 6.10 | ND | ND |
| 2-Cyclohexen-1-one, 4-methyl-4-phenyl- | 20.86 | 1576.0 | 144.1 | - | N | PPB | ND | 13.09 ± 1.39 | ND | ND |
| 3,3’-Dimethylbiphenyl | 21.13 | 1593.9 | 182.1 | - | K | PPB | ND | ND | ND | 453.99 ± 3.67 |
| Hexadecane | 21.15 | 1595.2 | 57.1 | - | D | PPB | 0.72 ± 0.33 | ND | ND | ND |
| 2,2,4-Trimethyl-1,3-pentanediol diisobutyrate | 21.19 | 1598.1 | 71.1 | 6846-50-0 | J | PPB | ND | ND | 0.13 ± 0.06 | ND |
| | | | | | | PPZ | ND | ND | 0.14 ± 0.03 | ND |
| Benzophenone | 21.73 | 1636.1 | 105.0 | 119-61-9 | K | PPA | 0.65 ± 0.29 | ND | 0.33 ± 0.12 | ND |
| | | | | | | PPB | ND | 4.63 ± 0.10 | ND | ND |
| | | | | | | PPZ | 19.40 ± 2.99 | 78.56 ± 13.61 | 29.43 ± 3.10 | 3788.56 ± 230.60 |
| Cyclopentaneacetic acid, 3-oxo-2-pentyl-, methyl ester | 22.01 | 1655.3 | 83.1 | 24851-98-7 | D | PPA | 0.11 ± 0.01 | ND | 0.48 ± 0.02 | ND |
| | | | | | | PPB | 0.17 ± 0.04 | ND | ND | ND |
| | | | | | | PPZ | 0.12 ± 0.01 | ND | 0.63 ± 0.11 | ND |
| Benzene, 1,1’-(1,3-propanediyl)bis- | 22.05 | 1658.1 | 92.0 | 1081-75-0 | A | PPA | ND | ND | ND | 38.76 ± 3.11 |
| | | | | | | PPB | ND | ND | ND | 21.98 ± 2.37 |
| | | | | | | PPZ | ND | ND | ND | 56.96 ± 3.13 |
| 8-Pentadecanone | 22.21 | 1669.1 | 127.1 | - | D | PPA | ND | ND | ND | 46.58 ± 3.24 |
| | | | | | | PPZ | ND | ND | ND | 52.93 ± 3.52 |
| 1-Tetradecanol | 22.24 | 1671.7 | 83.1 | - | F | PPA | ND | 2.61 ± 0.83 | ND | 189.79 ± 15.83 |
| | | | | | | PPZ | ND | 4.78 ± 1.94 | ND | 362.39 ± 30.30 |
| 1,1’-Biphenyl, 2,2’,5,5’-tetramethyl- | 22.43 | 1684.8 | 195.1 | 3075-84-1 | H | PPZ | ND | ND | ND | 1008.25 ± 118.47 |
| 1,7-di-iso-propylnaphthalene | 22.44 | 1685.3 | 197.2 | - | H | PPA | ND | 2.52 ± 0.75 | ND | 46.90 ± 12.79 |
| Heptadecane | 22.62 | 1697.9 | 58.1 | - | D | PPB | ND | ND | ND | 64.80 ± 32.40 |
| Pentadecanal- | 22.79 | 1711.1 | 82.1 | 2765-11-9 | G | PPA | ND | ND | ND | 363.24 ± 113.46 |
| 1H,2H,3H-Cyclopenta[a]naphthalen-5-ylmethane | 22.83 | 1714.1 | 165.1 | - | H | PPB | ND | ND | ND | 256.48 ± 7.74 |
| 2,6-Diisopropylnaphthalene | 22.99 | 1725.9 | 197.2 | 24157-81-1 | H | PPZ | ND | 17.16 ± 6.27 | ND | 874.54 ± 361.23 |
| Octanal, 2-(phenylmethylene)- | 23.32 | 1751.1 | 117.1 | 101-86-0 | G | PPA | ND | ND | ND | 367.38 ± 87.18 |
| | | | | | | PPZ | ND | ND | ND | 349.25 ± 133.34 |
| 3,5-di-tert-Butyl-4-hydroxybenzaldehyde | 23.60 | 1771.5 | 219.2 | 1620-98-0 | R | PPZ | 0.84 ± 0.27 | ND | ND | ND |
| n-Pentadecanol | 23.63 | 1773.9 | 83.1 | 629-76-5 | F | PPA | ND | 4.51 ± 0.71 | ND | ND |
| | | | | | | PPZ | ND | ND | ND | 67.19 ± 29.23 |
| 3-Hexadecanol | 23.95 | 1798.3 | 59.1 | 593-03-3 | F | PPA | ND | 16.63 ± 7.13 | ND | ND |
| | | | | | | PPB | ND | 18.19 ± 10.79 | ND | ND |

(*continued on next page*)

**Table 1** (*continued*)

| Compound | RT (min) | RI | m/z Quant. | CAS | QS | Sample | Concentration ±s (μg/kg) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | EtOH 10% | EtOH 95% | HAcO 3% | Tenax |
| | | | | | | PPZ | ND | 10.49 ± 5.75 | ND | ND |
| 2-Ethylhexyl salicylate | 24.10 | 1809.8 | 120.0 | 118-60-5 | O | PPA | ND | 86.58 ± 10.14 | ND | 6286.52 ± 779.72 |
| | | | | | | PPB | ND | ND | ND | 1868.04 ± 1026.24 |
| | | | | | | PPZ | ND | 97.00 ± 25.88 | ND | 7011.06 ± 2592.46 |
| Isopropyl myristate | 24.25 | 1821.8 | 228.2 | 110-27-0 | J | PPA | ND | ND | ND | 1031.05 ± 206.41 |
| | | | | | | PPZ | ND | ND | ND | 1349.83 ± 611.38 |
| 4,8,12-Tetradecatrienal, 5,9,13-trimethyl- | 24.48 | 1840.2 | 69.1 | - | G | PPA | ND | ND | ND | 2144.86 ± 697.21 |
| | | | | | | PPB | ND | ND | ND | 1103.65 ± 125.71 |
| | | | | | | PPZ | ND | ND | ND | 2234.69 ± 545.14 |
| Pentadecanoic acid | 24.67 | 1855.7 | 73.0 | 1002-84-2 | Q | PPA | 1.23 ± 0.23 | ND | ND | ND |
| | | | | | | PPB | ND | 33.53 ± 7.18 | ND | ND |
| | | | | | | PPZ | ND | 80.62 ± 38.41 | ND | 2740.97 ± 1174.69 |
| Phthalic acid, diisobutyl ester | 24.87 | 1871.6 | 149.0 | 84-69-5 | P | PPA | 5.58 ± 0.17 | ND | 0.80 ± 0.06 | 88.75 ± 32.79 |
| | | | | | | PPZ | 4.42 ± 0.64 | ND | 0.51 ± 0.15 | 140.38 ± 12.99 |
| 1-Hexadecanol | 24.94 | 1877.0 | 83.1 | 36653-82-4 | F | PPA | ND | ND | ND | 693.02 ± 117.65 |
| Nonadecane | 25.16 | 1894.3 | 57.1 | 629-92-5 | D | PPB | 0.12 ± 0.03 | ND | ND | ND |
| 9-Hexadecenoic acid | 25.71 | 1940.7 | 55.1 | 57-10-3 | Q | PPA | 0.78 ± 0.25 | ND | ND | 335.58 ± 89.86 |
| | | | | | | PPZ | 0.78 ± 0.25 | ND | ND | ND |
| Dibutyl phthalate | 26.05 | 1969.5 | 149.0 | 84-74-2 | P | PPA | ND | ND | 3.85 ± 0.75 | 8301.08 ± 609.78 |
| | | | | | | PPB | 0.83 ± 0.34 | ND | 4.84 ± 2.86 | 278.77 ± 87.02 |
| | | | | | | PPZ | 2.11 ± 0.43 | 148.19 ± 14.50 | 7.64 ± 0.80 | 752.28 ± 46.35 |
| 3,5-di-tert-Butyl-4-hydroxyphenylpropionic acid | 26.43 | 2001.5 | 263.2 | 20170-32-5 | R | PPA | 0.25 ± 0.02 | ND | ND | ND |
| | | | | | | PPZ | 0.56 ± 0.03 | ND | ND | ND |
| 1-Octadecanol | 27.41 | 2086.4 | 83.1 | 112-92-5 | F | PPA | ND | ND | ND | 172.63 ± 37.31 |
| | | | | | | PPB | ND | ND | ND | 40.03 ± 7.96 |
| cis-9-Hexadecenoic acid, isobutyl ester | 27.69 | 2111.5 | 85.0 | - | J | PPA | ND | 56.19 ± 19.53 | ND | ND |
| | | | | | | PPB | ND | 61.07 ± 29.11 | ND | ND |
| Oxacyclohexadecan-2-one | 28.02 | 2140.6 | 55.1 | 106-02-5 | D | PPA | 0.11 ± 0.01 | 2.97 ± 1.16 | ND | ND |
| | | | | | | PPB | ND | 1.88 ± 0.46 | ND | ND |
| | | | | | | PPZ | ND | 6.38 ± 2.39 | ND | 166.08 ± 43.17 |
| Octadecanamide | 28.53 | 2186.2 | 59.1 | 124-26-5 | D | PPB | ND | 0.78 ± 0.37 | ND | ND |
| | | | | | | PPZ | ND | 1.42 ± 0.35 | ND | ND |
| Octadecanoic acid, ethyl ester | 28.64 | 2196.2 | 88.1 | 111-61-5 | J | PPA | 11.74 ± 3.30 | ND | ND | ND |
| [1,1’:3’,1’’-Terphenyl]-2’-ol | 29.23 | 2249.8 | 246.1 | 2432-11-3 | I | PPA | ND | ND | ND | 224.74 ± 100.97 |
| Tetradecanoic acid, 2-hydroxy-1-(hydroxymethyl) ethyl ester | 29.80 | 2303.5 | 211.2 | 3443-83-2 | J | PPA | 6.85 ± 0.44 | ND | ND | ND |
| | | | | | | PPZ | 3.51 ± 1.59 | ND | ND | ND |
| Methyl dehydroabietate | 30.42 | 2363.7 | 239.2 | 1235-74-1 | J | PPA | ND | 11.04 ± 5.23 | ND | ND |
| Hexanedioic acid, bis(2-ethylhexyl) ester | 30.83 | 2403.8 | 129.1 | 103-23-1 | J | PPB | ND | ND | ND | 909.81 ± 442.61 |
| | | | | | | PPZ | ND | ND | ND | 1487.63 ± 370.19 |
| n-Octylpentaoxyethylene | 31.28 | 2449.3 | 45.1 | 19327-40-3 | J | PPA | ND | ND | ND | 7985.94 ± 4444.52 |
| Hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl) ethyl ester | 31.93 | 2509.3 | 98.1 | 23470-00-0 | J | PPA | 167.06 ± 3.11 | ND | ND | ND |
| | | | | | | PPZ | 97.64 ± 50.15 | ND | ND | ND |
| Bis(2-ethylhexyl) phthalate | 32.33 | 2535.7 | 149.0 | 117-81-7 | P | PPB | ND | ND | ND | 25.05 ± 6.34 |
| | | | | | | PPZ | ND | ND | ND | 91.55 ± 27.73 |
| Docosane, 1-iodo- | 33.79 | 2631.2 | 57.1 | 62127-53-1 | J | PPA | 9.70 ± 0.57 | ND | ND | ND |
| | | | | | | PPZ | 5.83 ± 3.29 | ND | ND | ND |
| Heptacosane | 34.54 | 2680.6 | 85.1 | 593-49-7 | J | PPZ | 2.84 ± 1.16 | ND | ND | ND |

**Table 2**
Quantified compounds by SPME-GC-MS in PS plates along with the retention time (min), retention index, m/z of quantification, CAS and Quantifier (QS).

| Compound | RT (min) | RI | m/z Quant. | CAS | QS | Sample | Concentration ±s (μg/kg) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | EtOH 10% | EtOH 95% | HAcO 3% | Tenax |
| Ethylbenzene | 6.26 | 825.8 | 91.1 | 100-41-4 | A | PSB | 0.72 ± 0.04 | 11.41 ± 0.62 | 1.20 ± 0.03 | 59.11 ± 9.10 |
| | | | | | | PSN | 11.91 ± 1.46 | 116.73 ± 2.19 | ND | 1261.27 ± 76.55 |
| | | | | | | PSR | 8.82 ± 0.71 | 120.21 ± 1.51 | 14.97 ± 0.42 | 716.43 ± 219.09 |
| p-Xylene | 6.50 | 841.6 | 91.1 | 106-42-3 | B | PSB | 0.41 ± 0.01 | 4.75 ± 0.40 | 0.06 ± 0.01 | ND |
| | | | | | | PSN | 2.02 ± 0.20 | 15.37 ± 1.63 | ND | ND |
| | | | | | | PSR | 3.77 ± 0.34 | 45.29 ± 1.25 | 4.92 ± 0.12 | 259.53 ± 106.62 |
| Styrene | 7.15 | 884.1 | 104.1 | 100-42-5 | A | PSB | 81.28 ± 2.78 | 889.22 ± 7.06 | ND | 4624.83 ± 409.36 |
| | | | | | | PSN | 181.80 ± 9.99 | 1533.76 ± 75.28 | 15066.14 ± 789.20 | ND |
| | | | | | | PSR | 110.93 ± 5.17 | 1104.80 ± 11.44 | 86.88 ± 2.28 | 6428.66 ± 844.12 |
| o-Xylene | 7.20 | 887.3 | 91.1 | 95-47-6 | B | PSB | 0.31 ± 0.03 | ND | 0.07 ± 0.02 | ND |
| | | | | | | PSN | 0.74 ± 0.15 | ND | ND | ND |
| | | | | | | PSR | 3.02 ± 0.29 | 24.01 ± 0.43 | 4.73 ± 0.13 | 159.45 ± 43.48 |
| Benzene, (1-methylethyl)- | 8.13 | 926.7 | 105.1 | 98-82-8 | A | PSB | 0.51 ± 0.06 | 5.13 ± 0.49 | ND | ND |
| | | | | | | PSN | 3.63 ± 0.66 | 25.78 ± 1.22 | ND | 315.81 ± 102.24 |
| | | | | | | PSR | 1.92 ± 0.85 | 12.91 ± 0.71 | ND | ND |
| Benzene, (1-methylethyl)- | 8.13 | 926.7 | 105.1 | 98-82-8 | A | PSR | 1.21 ± 0.05 | ND | ND | ND |
| Benzene, 2-propenyl- | 8.73 | 948.5 | 117.1 | 300-57-2 | A | PSR | ND | ND | 0.06 ± 0.01 | ND |
| Propylbenzene | 8.95 | 956.4 | 91.1 | 103-65-1 | A | PSB | 0.47 ± 0.02 | 10.14 ± 1.05 | ND | 22.95 ± 11.32 |
| | | | | | | PSN | 3.39 ± 0.44 | 48.63 ± 1.73 | ND | 684.80 ± 58.76 |
| | | | | | | PSR | 1.72 ± 0.13 | 31.24 ± 0.93 | 1.20 ± 0.03 | 219.14 ± 68.28 |
| Benzaldehyde | 9.16 | 964.2 | 105.1 | 100-52-7 | E | PSB | ND | ND | 13.91 ± 0.81 | ND |
| | | | | | | PSR | ND | ND | 9.89 ± 0.66 | ND |
| Benzene, 1-ethyl-2-methyl- | 9.18 | 964.8 | 105.0 | 611-14-3 | A | PSN | 0.85 ± 0.18 | 0.65 ± 0.11 | ND | ND |
| Benzene, 1-ethenyl-2methyl | 9.96 | 993.1 | 117.1 | 611-15-4 | A | PSR | ND | 4.09 ± 0.14 | 0.08 ± 0.01 | ND |
| Benzene, (1-methylpropyl)- | 10.42 | 1011.7 | 105.1 | 135-98-8 | A | PSN | 0.76 ± 0.10 | 10.63 ± 1.16 | ND | ND |
| | | | | | | PSR | 1.50 ± 0.17 | 17.22 ± 1.40 | 0.67 ± 0.02 | 172.15 ± 37.10 |
| Indane | 10.81 | 1028.4 | 117.1 | 496-11-7 | H | PSR | ND | 1.04 ± 0.11 | ND | ND |
| D-Limonene | 10.86 | 1030.5 | 68.1 | 5989-27-5 | C | PSB | ND | 4.42 ± 0.23 | ND | ND |
| | | | | | | PSN | ND | 4.16 ± 1.76 | ND | ND |
| | | | | | | PSR | ND | 5.02 ± 0.55 | ND | ND |
| 1-Hexanol, 2-ethyl- | 10.88 | 1031.5 | 57.1 | 104-76-7 | F | PSR | ND | ND | 0.10 ± 0.01 | ND |
| Decane, 2-methyl- | 11.55 | 1059.8 | 71.1 | 6975-98-0 | D | PSB | ND | ND | ND | 13.87 ± 6.44 |
| Acetophenone | 11.80 | 1070.4 | 105.0 | 98-86-2 | I | PSR | ND | ND | 2.21 ± 0.27 | ND |
| Undecane | 12.53 | 1102.0 | 71.1 | 1120-21-4 | D | PSB | ND | ND | ND | 36.58 ± 12.27 |
| Nonanal | 12.60 | 1105.5 | 57.1 | 124-19-6 | G | PSN | 1.04 ± 0.49 | ND | ND | ND |
| Nonanal | 12.60 | 1105.5 | 57.1 | 124-19-6 | G | PSR | 1.61 ± 0.73 | ND | ND | ND |
| Benzene, pentyl- | 13.71 | 1159.8 | 91.1 | 538-68-1 | A | PSN | ND | ND | ND | 22.85 ± 0.50 |
| Naphthalene | 14.31 | 1189.2 | 128.0 | 91-20-3 | H | PSB | 0.16 ± 0.06 | ND | ND | ND |
| | | | | | | PSR | 0.22 ± 0.03 | ND | 0.15 ± 0.02 | 13.16 ± 6.54 |
| Dodecane | 14.54 | 1200.5 | 57.1 | 112-40-3 | D | PSB | 0.13 ± 0.06 | ND | ND | ND |
| | | | | | | PSR | ND | 2.08 ± 0.04 | ND | 21.95 ± 8.49 |

(*continued on next page*)

**Table 2** (*continued*)

| Compound | RT (min) | RI | m/z Quant. | CAS | QS | Sample | Concentration ±s (μg/kg) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | EtOH 10% | EtOH 95% | HAcO 3% | Tenax |
| Tetradecane | 18.06 | 1397.3 | 57.1 | 629-59-4 | D | PSR | 0.16 ± 0.06 | 2.59 ± 0.04 | ND | 29.09 ± 3.32 |
| Diphenyl ether | 18.22 | 1407.2 | 170.1 | 101-84-8 | K | PSB | ND | ND | ND | 38.03 ± 3.05 |
| | | | | | | PSR | ND | ND | ND | 38.08 ± 2.41 |
| Decanal | 19.30 | 1480.4 | 57.1 | 112-31-2 | G | PSR | 0.29 ± 0.08 | ND | ND | ND |
| 2,4-Di-tert-butylphenol | 19.88 | 1510.6 | 191.2 | 96-76-4 | M | PSN | 0.31 ± 0.15 | ND | ND | ND |
| Benzophenone | 21.72 | 1635.3 | 105.0 | 119-61-9 | K | PSR | ND | 1.85 ± 0.27 | ND | ND |
| Benzene, 1,1'-(1,3-propanediyl)bis- | 22.03 | 1656.9 | 92.1 | 1081-75-0 | A | PSB | 0.44 ± 0.02 | 58.37 ± 12.56 | ND | 249.35 ± 53.39 |
| | | | | | | PSN | ND | 54.72 ± 1.90 | ND | 578.53 ± 173.04 |
| | | | | | | PSR | 0.42 ± 0.04 | 43.53 ± 0.35 | ND | 237.64 ± 28.28 |
| 1-Tetradecanol | 22.24 | 1671.7 | 83.1 | - | F | PSR | ND | ND | ND | 95.63 ± 53.49 |
| Amberonne (isomer 3) | 22.27 | 1673.7 | 191.2 | - | N | PSB | 0.20 ± 0.05 | ND | ND | ND |
| | | | | | | PSN | 0.11 ± 0.04 | ND | ND | ND |
| 2,6-Piperidinedione, 3-phenyl- | 22.68 | 1702.5 | 104.1 | 14149-34-9 | H | PSB | 3.17 ± 0.15 | 77.46 ± 9.76 | ND | 224.38 ± 41.21 |
| | | | | | | PSN | 18.86 ± 0.61 | 742.23 ± 27.59 | ND | 5381.64 ± 1003.38 |
| | | | | | | PSR | 6.05 ± 0.57 | 145.68 ± 8.11 | 3.68 ± 0.12 | 467.40 ± 72.76 |
| Tetradecanoic acid | 23.39 | 1756.1 | 73.0 | 544-63-8 | Q | PSR | ND | ND | ND | 6265.50 ± 930.01 |
| Cyclobutane, 1,2-diphenyl- | 23.43 | 1759.2 | 104.1 | 3018-21-1 | A | PSB | 27.26 ± 0.78 | 1694.04 ± 381.82 | ND | 6013.21 ± 839.13 |
| | | | | | | PSN | 55.94 ± 1.83 | 7188.81 ± 223.68 | ND | 50236.21 ± 12164.22 |
| | | | | | | PSR | 36.48 ± 2.61 | 2361.20 ± 137.45 | 6.01 ± 0.09 | 8786.49 ± 901.15 |
| 3,5-di-tert-Butyl-4-hydroxybenzaldehyde | 23.59 | 1771.3 | 219.2 | 1620-98-0 | R | PSB | 1.35 ± 0.22 | ND | ND | ND |
| | | | | | | PSR | ND | ND | ND | 794.42 ± 438.28 |
| n-Pentadecanol | 23.63 | 1773.9 | 83.1 | 629-76-5 | F | PSR | ND | 1.90 ± 1.00 | ND | 165.37 ± 27.11 |
| Naphthalene, 1,2,3,4-tetrahydro-1-phenyl- | 23.71 | 1780.3 | 208.1 | 3018-20-0 | H | PSB | 0.07 ± 0.01 | 12.90 ± 4.27 | ND | ND |
| | | | | | | PSN | 0.29 ± 0.00 | 48.89 ± 1.84 | ND | 270.84 ± 76.70 |
| | | | | | | PSR | 0.03 ± 0.01 | 11.31 ± 1.00 | 0.03 ± 0.00 | ND |
| 3-Hexadecanol | 23.96 | 1798.9 | 59.1 | 593-03-3 | F | PSR | ND | ND | ND | 792.47 ± 251.65 |
| Naphthalene, 1,2-dihydro-4-phenyl- | 24.01 | 1802.9 | 206.1 | 7469-40-1 | H | PSN | 0.15 ± 0.05 | 39.64 ± 0.17 | ND | 205.35 ± 62.91 |
| | | | | | | PSR | 0.11 ± 0.05 | 12.53 ± 0.15 | 0.08 ± 0.00 | ND |
| Isopropyl myristate | 24.25 | 1821.8 | 228.2 | 110-27-0 | J | PSB | 2.47 ± 1.13 | ND | ND | 494.97 ± 255.03 |
| 4,8,12-Tetradecatrienal, 5,9,13-trimethyl- | 24.48 | 1840.3 | 69.1 | - | G | PSN | ND | ND | ND | 809.22 ± 358.60 |
| | | | | | | PSR | ND | ND | ND | 1343.15 ± 398.59 |
| Pentadecanoic acid | 24.67 | 1855.7 | 73.0 | 1002-84-2 | Q | PSB | 4.42 ± 0.81 | ND | ND | ND |
| | | | | | | PSR | 6.85 ± 3.72 | ND | ND | 1575.01 ± 448.90 |
| Phthalic acid, diisobutyl ester | 24.87 | 1871.2 | 149.0 | 84-69-5 | P | PSB | 1.40 ± 0.48 | ND | ND | ND |
| | | | | | | PSR | ND | 3.48 ± 1.71 | ND | ND |
| 9-Hexadecenoic acid | 25.71 | 1940.7 | 55.1 | 57-10-3 | Q | PSB | 2.47 ± 0.39 | ND | ND | ND |
| | | | | | | PSN | ND | 13.67 ± 3.68 | ND | ND |
| | | | | | | PSR | 5.43 ± 2.50 | ND | ND | ND |
| Dibutyl phthalate | 26.03 | 1968.3 | 149.0 | 84-74-2 | P | PSR | 87.99 ± 52.18 | ND | ND | ND |
| n-Hexadecanoic acid | 26.16 | 1978.6 | 73.1 | 57-10-3 | Q | PSR | ND | 11301.14 ± 6065.35 | ND | 301880.69 ± 57162.75 |
| Hexadecanoic acid, ethyl ester | 26.35 | 1995.4 | 88.1 | 628-97-7 | J | PSR | ND | ND | ND | 2282.27 ± 734.44 |
| Eicosane | 26.51 | 2008.8 | 57.1 | - | D | PSR | 0.18 ± 0.01 | ND | ND | ND |
| 1(2H)-Naphthalenone, 3,4-dihydro-4-phenyl- | 26.54 | 2011.3 | 165.1 | - | H | PSR | ND | ND | 0.34 ± 0.01 | ND |
| Heptadecanolide | 26.88 | 2041.0 | 55.1 | 67701-03-5 | D | PSB | 0.46 ± 0.05 | ND | ND | ND |
| | | | | | | PSR | 0.53 ± 0.20 | ND | ND | ND |

(*continued on next page*)

**Table 2** (*continued*)

| Compound | RT (min) | RI | m/z Quant. | CAS | QS | Sample | Concentration ±s (μg/kg) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | EtOH 10% | | | EtOH 95% | | | HAcO 3% | | | Tenax | | |
| Cyclohexyl 4-cyclohexylthiocyclohexyl hydrodisulfide | 27.62 | 2105.1 | 83.1 | 17796-82-6 | K | PSR | | ND | | | ND | | | ND | | 81.92 | ± | 17.83 |
| cis-9-Hexadecenoic acid, isobutyl ester | 27.70 | 2112.1 | 85.0 | - | J | PSN | | ND | | | ND | | | ND | | 1191.16 | ± | 253.45 |
| | | | | | | PSR | | ND | | | ND | | | ND | | 5550.86 | ± | 962.67 |
| Oxacyclohexadecan-2-one | 28.03 | 2141.6 | 55.1 | 106-02-5 | D | PSB | 2.55 | ± | 0.21 | | ND | | | ND | | 103.34 | ± | 25.46 |
| | | | | | | PSN | | ND | | 6.30 | ± | 1.23 | | ND | | 287.02 | ± | 127.87 |
| | | | | | | PSR | 1.81 | ± | 0.61 | 5.29 | ± | 2.07 | | ND | | 213.26 | ± | 68.06 |
| Phthalic acid, neopentyl pentyl ester | 28.25 | 2161.5 | 149.0 | - | P | PSR | | ND | | 0.94 | ± | 0.13 | | ND | | | ND | |
| Octadecanoic acid | 28.34 | 2169.0 | 73.0 | 57-11-4 | Q | PSR | | ND | | | ND | | | ND | | 40891.99 | ± | 12342.80 |
| Octadecanamide | 28.53 | 2186.1 | 59.0 | 124-26-5 | D | PSN | | ND | | 4.90 | ± | 0.84 | | ND | | 240.51 | ± | 61.34 |
| Octadecanoic acid, ethyl ester | 28.64 | 2196.1 | 88.1 | 111-61-5 | J | PSB | | ND | | | ND | | | ND | | 707.03 | ± | 365.62 |
| 3,5,5-trimethyl-6,6a-dihydroisoindolo[2,1-a]quinolin-11(5H)-one | 28.96 | 2225.3 | 262.2 | - | S | PSR | | ND | | | ND | | | ND | | 34.20 | ± | 10.84 |
| (2E,6E,10E)-3,7,11,15-Tetramethylhexadeca-2,6,10,14-tetraen-1-yl formate | 29.93 | 2315.5 | 69.1 | - | J | PSN | | ND | | | ND | | | ND | | 819.39 | ± | 176.25 |
| | | | | | | PSR | | ND | | | ND | | | ND | | 1995.37 | ± | 519.75 |
| 9-Octadecenamide, 12-hydroxy-, [R-(Z)]- | 30.47 | 2368.4 | 59.1 | 35732-94-6 | J | PSN | | ND | | | ND | | | ND | | 13898.65 | ± | 5668.89 |
| Cyclopentene-1-carboxylic acid, 4-[2-(diphenylmethyl)-2-propen-1-yl]-, methyl ester | 32.54 | 2549.4 | 207.1 | 10436-08-5 | J | PSB | 4.89 | ± | 1.85 | 4324.54 | ± | 1024.65 | | ND | | 23002.03 | ± | 4924.64 |
| | | | | | | PSN | | ND | | 15367.61 | ± | 1993.52 | | ND | | 75212.12 | ± | 17983.01 |
| | | | | | | PSR | 6.37 | ± | 2.58 | 5911.03 | ± | 568.77 | | ND | | 33670.55 | ± | 3688.08 |
| 2-Phenyl-1,2-dihydrobenzo[g]indazol-3-one | 33.57 | 2617.2 | 260.1 | - | J | PSB | | ND | | | ND | | | ND | | 17618.83 | ± | 1614.91 |

(Nakai et al., 2014). These oligomers, which are NLS and are classified as high toxicity (III) according to Cramer rules, exceed the 10 μg/kg limit according to European legislation, in all polystyrene samples. In addition, they greatly exceed the TCC limit for migration of 90 μg/kg in the D2 and E simulants.

Furthermore, Naphthalene, 1,2,3,4-tetrahydro-1-phenyl-, which was identified as print-related contaminant and reported as co-monomer (Lago & Ackerman, 2016), is a NLS and was found in higher concentrations than 10 μg/kg in cardboard and PS plates. Even surpassing the TTC value of 1.8 mg/kg in PP samples.

A recycled paper and printing ink marker (Jaén et al., 2022) like 2, 6-diisopropylnaphthalene (DIPN) (Nerín et al., 2002) was found at concentrations surpassing the TTC values in cardboard samples.

NIAS additives degradation products like 3,5-di-tert-Butyl-4-hydroxybenzaldehyde, which is a derived from phenolic antioxidants (Vera et al., 2018), exceeds limit concentrations. NIAS like benzene, 1,2,4-trimethyl-, which is a dye solvent and paint thinner (1,2,4-Trimethylbenzene | PubChem, 2024), was found in PP plates slightly exceeding 10 μg/kg.

Fig. 3. shows the classification by chemical of key compounds. Aldehydes (nonanal; decanal; undecanal and dodecanal), Aromatics (ethylbenzene and p-xylene), and Phathalates (phthalic acid, diisobutyl ester, dibutylphthalate and bis(2-ethylhexyl)phthalate). The concentration of each compound in its corresponding group was summed for each of the samples.

It is observed that PP dishes had the highest aldehyde content, followed by cardboard. PS trays hardly had any aldehyde, phthalates or terpenoids migrated as could be expected. However, they showed the highest content of aromatic compounds. No major differences in terpenoids were observed between paperboard and PP.

### 3.3. *Comparison between different materials*

The aim of food safety is to ensure that the materials we use are in accordance with the established standards. From this work, we can compare the differences between the three materials analysed with respect to volatile compounds that can migrate into the food.

Fig. 4(a) shows the number of migrants identified and quantified for each material according to the simulants used in the migration tests. In the case of cardboard, it is limited to simulant E (Tenax). There are considerable differences between materials for each simulant. In the case of PP, the highest number of compounds migrated to simulant A, while for PS they were found in the tests with simulant E. The highest number of compounds found in liquid simulants appeared in migration from the PP plates. The difference between the compounds found in simulant E for PS and the other simulants was minimum. For cardboard, the compounds appearing in simulant E exceed those found in the other two materials.

About 75 % of the total migrants were NLS and were not covered by European legislation. This can be seen in Fig. 4(b) where LS compounds were the minority. According to Cramer's rules, most of the identified compounds (around 70 %) had low toxicity (Class I) as can be seen in Fig. 4(c). However, compounds found with high toxicity (class III) were twice those of medium toxicity (class II).

The identifications according to the Schymanski levels showed that only 7–12 % of the compounds were confirmed and quantified with their corresponding standard. Less than 50 % of the compounds were identified at level 2 A and more than 50 % at level 3. This fact highlights the complexity of the analysis due to both the difficulty of identifying compounds with high confidence and the variety of analytical standards needed to adequately quantify migrants.

The trends described for LS, Cramer's classification and Schymasnki levels are common to all samples analysed. However, they are differentiated by the different IAS and NIAS found in each sample type.

Migrant grouping by ClassyFire can be found in Supplementary Material (Fig. S1). In all materials there was a clear predominance of

**Table 3**
Quantified compounds by SPME-GC-MS in cardboard plates along with the retention time (min), retention index, m/z of quantification, CAS and Quantifier (QS).

| Compound | Average RT (min) | Average RI | m/z Quant | CAS | QS | Sample | Concentration ±s (μg/kg) |
|---|---|---|---|---|---|---|---|
| Styrene | 7.19 | 886.3 | 104.1 | 100-42-5 | A | CL | 35.05 ± 16.01 |
| .alpha.-Pinene | 8.39 | 936.0 | 93.1 | 80-56-8 | C | CB | 121.29 ± 17.46 |
| | | | | | | CL | 138.32 ± 9.54 |
| | | | | | | CP | 157.28 ± 31.87 |
| 3-Carene | 10.40 | 1011.0 | 93.1 | 13466-78-9 | C | CP | 109.47 ± 15.48 |
| D-Limonene | 10.87 | 1030.8 | 68.1 | 5989-27-5 | C | CL | 85.72 ± 13.05 |
| | | | | | | CP | 97.45 ± 16.46 |
| Decane, 2-methyl- | 11.55 | 1059.8 | 71.1 | 6975-98-0 | D | CP | 27.88 ± 3.96 |
| Acetophenone | 11.79 | 1070.4 | 105.0 | 98-86-2 | I | CL | 661.62 ± 264.06 |
| | | | | | | CP | 1108.25 ± 474.42 |
| Nonanal | 12.59 | 1105.3 | 57.1 | 124-19-6 | G | CB | 411.33 ± 85.80 |
| | | | | | | CL | 458.85 ± 136.97 |
| | | | | | | CP | 897.17 ± 192.14 |
| Decanal | 14.65 | 1206.5 | 57.1 | 112-31-2 | G | CL | 124.46 ± 47.40 |
| | | | | | | CP | 406.16 ± 97.26 |
| Undecanal | 16.52 | 1307.6 | 82.1 | 112-44-7 | G | CP | 56.77 ± 15.75 |
| Diphenyl ether | 18.21 | 1406.3 | 170.1 | 101-84-8 | K | CL | 79.31 ± 8.21 |
| Dodecanal | 18.24 | 1408.1 | 57.1 | 112-54-9 | G | CP | 321.38 ± 104.88 |
| 5,9-Undecadien-2-one, 6,10-dimethyl-, (E)- | 18.96 | 1452.7 | 69.1 | 3796-70-1 | D | CB | 42.38 ± 8.04 |
| 2-Tridecanone | 19.17 | 1466.1 | 58.1 | 593-08-8 | D | CB | 35.35 ± 15.82 |
| | | | | | | CP | 55.46 ± 10.19 |
| 2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)- | 19.26 | 1471.4 | 177.1 | 719-22-2 | L | CB | 51.39 ± 1.99 |
| Tridecanal | 19.84 | 1508.2 | 82.1 | - | G | CB | 65.89 ± 19.13 |
| | | | | | | CL | 167.51 ± 80.22 |
| | | | | | | CP | 391.86 ± 134.97 |
| 2,4-Di-tert-butylphenol | 19.87 | 1510.1 | 191.2 | 96-76-4 | M | CB | 1099.90 ± 55.78 |
| | | | | | | CL | 979.05 ± 228.24 |
| | | | | | | CP | 1069.60 ± 353.50 |
| Benzoic acid, 2-hydroxy-, pentyl ester | 20.89 | 1577.9 | 120.0 | - | O | CL | 1004.89 ± 190.63 |
| Diethyl Phthalate | 21.16 | 1596.2 | 149.0 | 84-66-2 | P | CL | 18.65 ± 1.98 |
| | | | | | | CP | 17.68 ± 0.89 |
| Benzene, 1,1'-(1,3-propanediyl)bis- | 22.04 | 1657.6 | 92.1 | 1081-75-0 | A | CB | 5.81 ± 1.92 |
| | | | | | | CL | 26.84 ± 5.21 |
| | | | | | | CP | 16.63 ± 2.28 |
| 1-Tetradecanol | 22.24 | 1671.7 | 83.1 | - | F | CB | 75.37 ± 8.66 |
| | | | | | | CL | 199.77 ± 14.84 |
| | | | | | | CP | 367.80 ± 75.32 |
| 2-Pentadecanone | 22.57 | 1694.3 | 58.1 | - | D | CB | 28.31 ± 11.91 |
| Pentadecanal- | 22.79 | 1711.1 | 82.1 | 2765-11-9 | G | CB | 55.68 ± 15.67 |
| | | | | | | CL | 382.80 ± 139.30 |
| | | | | | | CP | 1076.08 ± 265.10 |
| 2,6-Diisopropylnaphthalene | 22.99 | 1725.8 | 197.2 | 24157-81-1 | H | CB | 121.07 ± 72.37 |
| | | | | | | CP | 360.25 ± 97.96 |
| Octanal, 2-(phenylmethylene)- | 23.32 | 1751.1 | 117.1 | 101-86-0 | G | CL | 642.21 ± 114.76 |
| | | | | | | CP | 420.78 ± 81.92 |
| Tetradecanoic acid | 23.39 | 1756.1 | 73.0 | 544-63-8 | Q | CP | 4716.18 ± 2460.50 |
| n-Pentadecanol | 23.63 | 1773.9 | 83.0 | 629-76-5 | F | CL | 99.44 ± 44.25 |
| | | | | | | CP | 75.04 ± 24.57 |
| Naphthalene, 1,2,3,4-tetrahydro-1-phenyl- | 23.71 | 1780.4 | 208.1 | 3018-20-0 | H | CL | 56.03 ± 23.77 |
| | | | | | | CP | 38.90 ± 13.97 |
| Tetradecanoic acid, ethyl ester | 23.83 | 1789.1 | 88.1 | 124-06-1 | J | CL | 1410.83 ± 289.42 |
| | | | | | | CP | 1962.06 ± 755.89 |
| 3-Hexadecanol | 23.96 | 1798.7 | 59.1 | 593-03-3 | F | CL | 251.01 ± 113.90 |
| 2-Ethylhexyl salicylate | 24.10 | 1810.3 | 120.0 | 118-60-5 | O | CB | 1378.68 ± 596.70 |
| | | | | | | CL | 7349.30 ± 984.96 |
| | | | | | | CP | 5659.94 ± 1491.11 |
| Isopropyl myristate | 24.25 | 1821.8 | 228.2 | 110-27-0 | J | CP | 1230.58 ± 720.75 |
| 4,8,12-Tetradecatrienal, 5,9,13-trimethyl- | 24.48 | 1840.2 | 69.1 | - | G | CB | 2923.50 ± 720.31 |
| | | | | | | CL | 1880.50 ± 99.72 |
| | | | | | | CP | 1655.45 ± 153.61 |
| Pentadecanoic acid | 24.67 | 1855.9 | 73.0 | 1002-84-2 | Q | CB | 2684.92 ± 1256.75 |
| | | | | | | CP | 1191.06 ± 260.39 |

(*continued on next page*)

**Table 3** (*continued*)

| Compound | Average RT (min) | Average RI | m/z Quant | CAS | QS | Sample | Concentration ±s (µg/kg) | | |
|---|---|---|---|---|---|---|---|---|---|
| Phthalic acid, diisobutyl ester | 24.87 | 1871.3 | 149.0 | 84-69-5 | P | CL | 198.33 | ± | 38.76 |
| | | | | | | CP | 117.64 | ± | 44.61 |
| 1-Hexadecanol | 24.94 | 1877.0 | 83.1 | 36653-82-4 | F | CB | 206.08 | ± | 11.41 |
| | | | | | | CL | 431.50 | ± | 84.68 |
| | | | | | | CP | 558.07 | ± | 110.56 |
| 9-Hexadecenoic acid | 25.71 | 1940.7 | 55.1 | 57-10-3 | Q | CB | 706.90 | ± | 286.10 |
| | | | | | | CL | 187.80 | ± | 22.89 |
| Dibutyl phthalate | 26.04 | 1968.9 | 149.0 | 84-74-2 | P | CL | 3076.97 | ± | 336.48 |
| | | | | | | CP | 2213.70 | ± | 1193.01 |
| 7-Acetyl-6-ethyl-1,1,4,4-tetramethyltetralin | 26.24 | 1985.7 | 243.2 | - | H | CL | 740.69 | ± | 166.21 |
| 4b,8-Dimethyl-2-isopropylphenanthrene, 4b,5,6,7,8,8a,9,10-octahydro- | 26.40 | 1998.8 | 241.2 | - | H | CL | 38.65 | ± | 20.52 |
| 1H-Naphtho[2,1-b]pyran, 3-ethenyldodecahydro-3,4a,7,7,10a-pentamethyl-, [3S-(3.alpha.,4a.alpha.,6a.beta.,10a.alpha.,10b.beta.)]- | 26.60 | 2016.3 | 275.2 | 1227-93-6 | H | CP | 46.11 | ± | 20.50 |
| 10,18-Bisnorabieta-8,11,13-triene | 27.13 | 2062.8 | 227.2 | 32624-67-2 | H | CL | 508.98 | ± | 131.83 |
| 1-Octadecanol | 27.40 | 2086.2 | 83.1 | 112-92-5 | F | CB | 375.97 | ± | 135.88 |
| | | | | | | CP | 150.71 | ± | 37.25 |
| s-Indacen-1(2H)-one, 3,5,6,7-tetrahydro-3,3,4,5,5,8-hexamethyl- | 27.45 | 2090.0 | 241.2 | - | H | CL | 60.65 | ± | 33.39 |
| Oxacyclohexadecan-2-one | 28.01 | 2140.2 | 55.1 | 106-02-5 | D | CB | 514.48 | ± | 130.97 |
| | | | | | | CL | 106.02 | ± | 28.39 |
| | | | | | | CP | 109.88 | ± | 16.00 |
| Oleic Acid | 28.04 | 2142.5 | 55.1 | 112-80-1 | Q | CB | 9254.22 | ± | 2380.99 |
| trans-13-Octadecenoic acid | 28.17 | 2154.2 | 177.2 | 693-71-0 | Q | CB | 2934.89 | ± | 1336.28 |
| Octadecanoic acid | 28.32 | 2167.6 | 73.0 | 57-11-4 | Q | CP | 19886.41 | ± | 7522.42 |
| Octadecanoic acid, ethyl ester | 28.64 | 2196.2 | 88.1 | 111-61-5 | J | CP | 1356.53 | ± | 796.91 |
| Tributyl acetylcitrate | 29.43 | 2269.0 | 185.1 | 77-90-7 | I | CB | 839.20 | ± | 272.22 |
| 1-Phenanthrenecarboxaldehyde, 1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-, [1R-(1?,4a?,10a?)]- | 29.71 | 2294.4 | 269.2 | 13601-88-2 | H | CB | 168.94 | ± | 91.24 |
| Isopimarol | 30.19 | 2340.9 | 257.3 | 1686-64-2 | J | CB | 798.63 | ± | 260.46 |
| Methyl dehydroabietate | 30.42 | 2363.4 | 239.2 | 1235-74-1 | J | CB | 15102.77 | ± | 3078.21 |
| 9-Octadecenamide, 12-hydroxy-, [R-(Z)]- | 30.47 | 2368.3 | 59.1 | 35732-94-6 | J | CL | 16558.62 | ± | 8435.45 |
| | | | | | | CP | 18760.25 | ± | 8075.40 |
| 1-Phenanthrenemethanol, 1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-, [1R-(1.alpha.,4a.beta.,10a.alpha.)]- | 30.71 | 2391.5 | 72.1 | - | J | CB | 3364.86 | ± | 325.63 |
| Hexanedioic acid, bis(2-ethylhexyl) ester | 30.83 | 2403.8 | 129.1 | 103-23-1 | J | CB | 768.92 | ± | 314.09 |
| | | | | | | CP | 789.19 | ± | 332.66 |
| Docosanol | 31.72 | 2492.7 | 125.1 | 30303-65-2 | J | CB | 450.21 | ± | 218.09 |
| Bis(2-ethylhexyl) phthalate | 32.33 | 2535.7 | 149.0 | 117-81-7 | P | CB | 18.09 | ± | 2.12 |
| | | | | | | CL | 18.26 | ± | 2.73 |
| | | | | | | CP | 23.30 | ± | 6.25 |

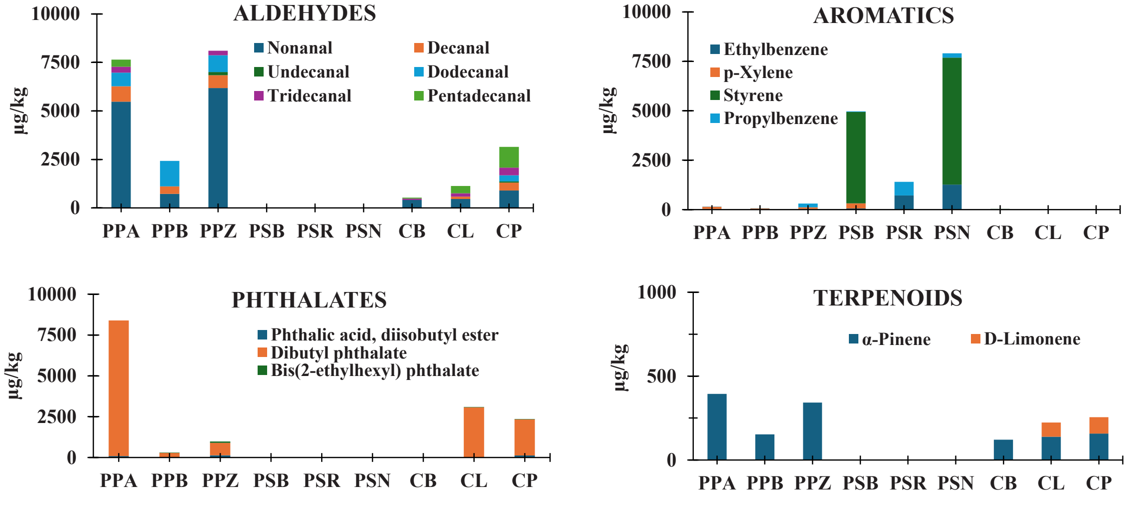

**Fig. 3.** Bar chart of total concentration of migrants (µg/kg) grouped in aldehydes, aromatics, phthalates and terpenoids for each sample.

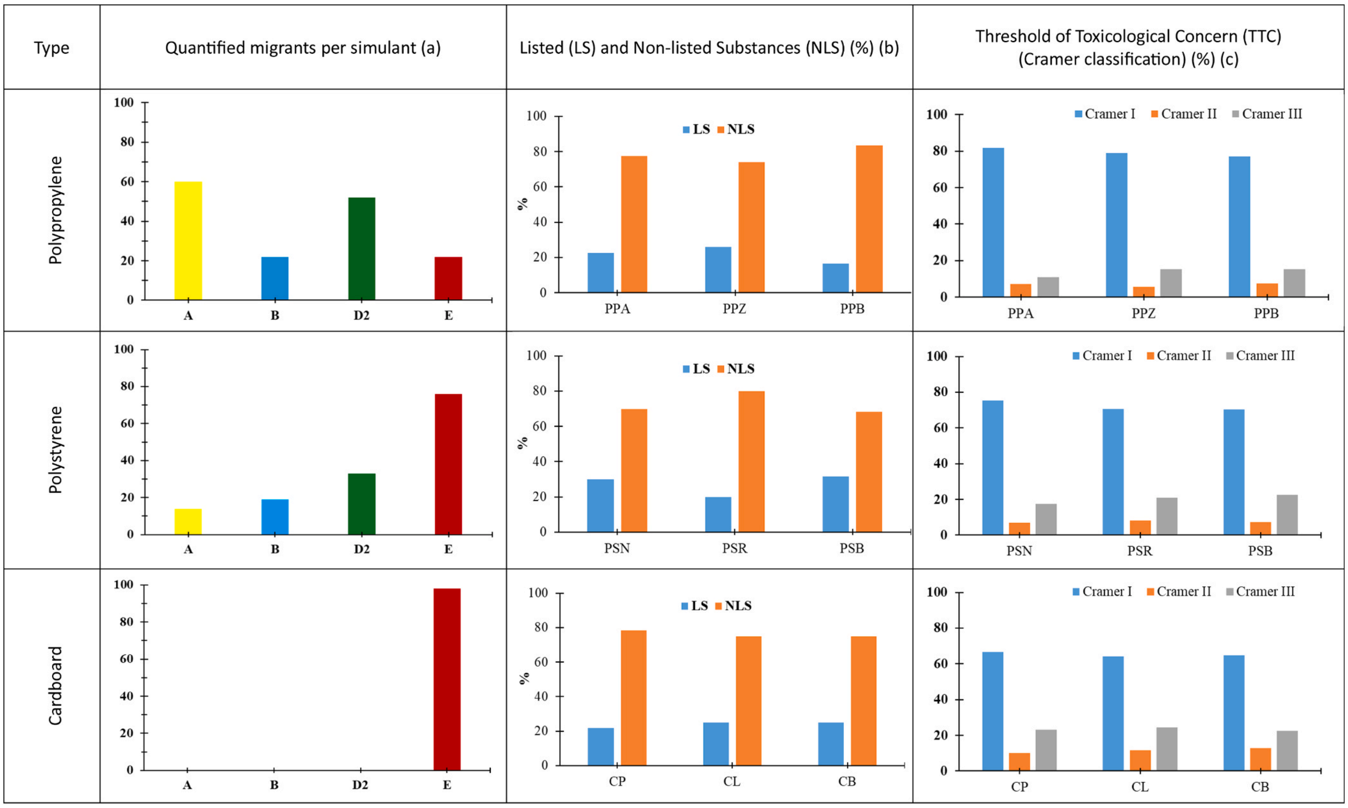

**Fig. 4.** Bar charts showing the quantified migrants per simulant (A, B, D2 and E) (a), percentage of listed (LS) and non-listed substances (NLS) (b) and % of migrants according to threshold of toxicological concern (TTC) by Cramer classification (c) for polypropylene, polystyrene and paperboard.

benzene-derived compounds. They were also more present in Tenax than in the other simulants. The PP plates showed a high number of alkanes and alkenes compared to the other materials, due to the degradation of the PP structure and release of oligomers.

The behaviour of esters, ketones and carboxylic acids was similar among all the samples, with PPB standing out as the one with the lowest number of carboxylic acids.

### *3.4. MS-DIAL vs traditional approach analysis*

Non target analysis seeks to detect and characterise as many compounds as possible present in a sample without having prior knowledge of them. A traditional approach, especially in FCM, involves a detailed inspection of each individual peak in the chromatograms. This procedure is very laborious and time-consuming, especially when handling large data sets or complex samples.

The researcher must visually identify the peaks, verify their intensities and associate them with possible compounds which may be subjected to human error, especially when there are coelutions or when peaks are of low intensity. Reproducibility of analyses may also be compromised because subjective judgement may vary between operators or between different analyses of the same data set. Although this variation is difficult to completely disappear due to the complexity of assigning compounds to certain unknowns, this type of software reduces it significantly. In addition, the contribution of human expertise in the field, which is incalculable, can be also applied.

Therefore, it would be worthwhile to monitor the improvement with the use of this software in the FCM analysis applied to this disposable tableware. Six chromatograms corresponding to the same sample with different simulants were selected to be analysed by two groups. The ‘Trainees’ group consists of undergraduate students who have completed their training in the laboratory, and the ‘Experts’ group consists of researchers and technicians with at least two years of experience specifically in FCM analysis. The seven participants analysed the chromatograms by collecting the identification of each compound with MS-DIAL and with the traditional approach. The identifications made with each method and the time taken by each analyst in each group of participants were compared. As shown in Fig. 5 there was an increase in the number of compounds identified and a notable decrease in the time required in each of the groups. Considering that the differences between individuals within the same group were negligible, the data can be treated as representative of the groups and perform a *t*-test for independent samples to assess whether the differences observed between the two groups (Trainees and Experts) were significantly different.

Test t for independent samples revealed p values well below 0.05 ($p < < 0.05$) so the null hypothesis can be rejected and conclude that the groups showed significant differences in their results.

The experiment showed an increase of up to 33 % in compound identification in the ‘expert’ group and up to 79 % in the ‘trainee’ group. At the same time, a large decrease in time to complete data analysis of up to 71 % for the ‘expert’ group and up to 80 % for the ‘trainees’ was observed.

## 4. Conclusions

The complexity of identifying, quantifying and assessing the presence of a large number of compounds requires a tool that facilitates the work in order to draw conclusions. MS-DIAL represents a step forward in the analytical capabilities of FCM safety assessments. Its ability to handle complex data sets, identify a wide range of substances and provide a standardised approach to analysis makes it an essential tool for the future of food contact materials regulation and harmonisation.

The results obtained in the study underline the importance of monitoring both IAS and NIAS to ensure consumer safety and the ongoing challenge of understanding the potential health risks posed by

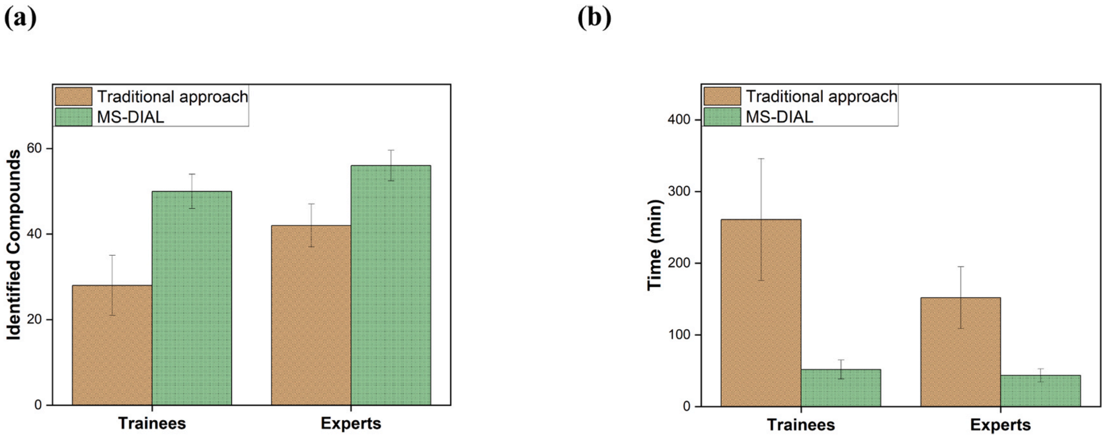

**Fig. 5.** Bar chats representing the total correctly identified compounds (a) and the amount of time required in minutes (b) for each group for seven participants and a total of 6 chromatograms analyzed per participant.

these substances. A number of IAS was detected, mainly consisting of regulatory approved additives commonly used in FCM such as phthalates. However, the majority presence of NIAS highlighted the difficulty in assessing the safety of food packaging. The NIAS detected include degradation products and contaminants, some of which have not yet been fully characterised in terms of their toxicological profile, nor are they present in the legislation. Among them, PS and PP oligomers have been found, as well as others such as antioxidants and UV stabilisers.

After reviewing the results, the tested disposable tableware does not comply with EU regulation 10/2011 due to the high concentration of IAS and NIAS. However, it is important to note that many of the identified compounds have been semi-quantified and the calculated values should be carefully considered.

The use of MS-DIAL has allowed comparison with the traditional approach and has shown an increase in the number of identifications ranging from 33 % to 79 % and a reduction in the time required of up to 80 %, even for analysts with little experience in the field.

## CRediT authorship contribution statement

**Carlos Estremera:** Writing – review & editing, Writing – original draft, Supervision, Software, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Margarita Aznar:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Methodology, Investigation. **Javier Blazquez-Martín:** Writing – review & editing, Writing – original draft, Supervision, Software, Methodology, Investigation, Formal analysis. **Celia Domeño:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Software, Resources, Methodology, Investigation, Formal analysis, Conceptualization. **Nerin Cristina:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Project administration, Funding acquisition.

## 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.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.fpsl.2025.101528.

## Data Availability

Data will be made available on request.

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