Occurrence and migration study of chemicals from baking paper and aluminium foil

Elisa Sonego[a], Patrizia Di Filippo[b], Carmela Riccardi [b], Donatella Pomata[b], Angela Bannò[a], Giulia Simonetti [a*], Francesca Buiarelli [a]

[a]Sapienza University of Rome - Department of Chemistry, 00185 Rome, Italy;
[b]Italian Workers' Compensation Authority (INAIL) - DIT, 00143 Rome Italy;

ABSTRACT

The present work focused on the development of an analytical method suitable to study the presence and the release of organophosphate esters (OPEs) and perfluoroalkylated substances (PFASs) from food contact materials (FCMs), from baking paper and aluminium foil. Although these classes of compounds are attracting increasing attention due to their toxicity the knowledge is still insufficient. The extent of their migration from FCMs to food was estimated using different liquid simulants. Ethanol 95 % was used to simulate the contact with fatty food, whilst acetic acid 3% to mime contact with acidic aqueous-based food and the contact mode involved the use of the ultrasound-assisted technique. Preliminary results showed the higher migration for baking paper samples in contact with aqueous simulant with contaminations in the ranges 78.30 - 413.21 ng/dm2 and 1.43 -13.87 ng/dm2 for OPEs and PFASs respectively. These findings highlighting the need to monitor particularly OPEs in FCMs.

Keywords: baking paper, aluminium foil, food simulant, migration test, food contact material

1. Introduction

Food contact materials (FCMs) include all those materials in contact with food and beverages during several activities such as packaging, transport, storage, distribution, cooking etc. In more detail, these FCMs can include plastics, paper, paperboard, metal, glass, and rubber etc. They are used not only for packaging, but also for cutlery, bowls, dishes and various utensils. Several chemicals in FCMs are intentionally used or non-intentionally present and, under specific conditions, they might be transferred into food (Groh et al., 2021, Grob et al., 2007). Chemical migration is defined as the release of substances belonging to the material in contact with food, which can change the composition of the product and/or its organoleptic characteristics (EC Regulation 1935/04) and may be a hazard to human health, depending on the extent of migration and on the chemical toxicity (Elsa et al., 2019, Muncke et al., 2017).

In the last few years more and more attention has been focused on this topic. To establish the safety of the migrating substances ingestion, toxicological data must be combined with exposure data (EFSA, 2019). The regulation includes specific migration tests to be conducted on food simulants or on the actual product. In migration studies the food or food simulant is placed in contact with the FCM and the migration is assessed by quantifying the contaminant in food or food simulant. Simulants are food substitutes which reflect the properties of the foodstuffs.

*Address correspondence to this author at Department of Chemistry University "La Sapienza" P.le Aldo Moro 5 -00185 Rome-Italy
Tel:+39-06-49913810 Fax:+39-06490631
E-mail:giulia.simonetti@uniroma1.it

Due to the complexity of foods, the use of simulants is a useful tool to simplify analysis and to standardize food categories defined in Commission Regulation EU 2016/1416 (EU 1416/16). Three simulants (named A, B and C) represent foods with hydrophilic properties, covering aqueous, acidic and alcoholic foods. Two simulants (named D1 and D2) are relative to foods that have lipophilic properties, including both dairy and non-dairy fatty foods. The latter simulant (named E) is assigned for testing specific migration into dry food. In addition, isooctane and ethanol 95% v/v can be used as alternative simulants for fatty foods in migration tests conducted on plastic and paper FCMs (EU 1416/16). These alternatives have proven to be the worst possible use (Blanco-Zubiaguirre et al., 2021).

Migration tests, whether performed on food simulants or on the real product, can assess the quantity (mass fraction) of substances that may be released from the material, with or without providing a specific identification in the former case, the migration is compared with the maximum permitted amount of a specific substance according to the limit values sought in EFSA evaluations.

Among the substances of growing interest in recent years are organophosphate esters (OPEs) and perfluoroalkyl substances (PFASs). Due to their wide use and massive production, OPEs have been defined as emerging contaminants (EC). The use of OPEs as flame retardants and plasticisers has increased in recent years because they are used alternatively to the brominated flame retardants (BFRs), which are gradually being reduced due to their potential toxicity (Li et al., 2019). In addition, OPEs are widely used as catalysts, polymer additives (Caroline et al., 2010), lubricants and plasticisers (Martínez-Carballo et al., 2007). PFASs are widely used as surfactants and surface protectants in many goods including cookware, furniture, textiles, garments, carpets, building materials, paints, polishes, and food packaging. Due to their persistence in the environment and toxicity, two of the most widely used PFASs, perfluorooctanesulfonic acid (PFOS) and perfluorooctane carboxylic acid (PFOA), have been classified by the Stockholm Convention as Persistent Organic Pollutants (POPs) in 2009 and 2019 respectively. Thanks to the regulatory actions, human exposure to PFOA and PFOS is slowly decreasing, but in the meantime, the use of a new generation of PFASs to replace them is increasing. In the production of food packaging, paper is one of the most widely used materials, often treated with chemical compounds to improve its properties such as wettability, strength and resistance to fats (Poothong et al., 2012). PFAS are used in the paper industry to create a protective film against oils, fats and water in products such as paper plates, wrappers, envelopes, containers and food packaging. In January 2016, the Food and Drug Administration (FDA) banned the use of PFAS with chain lengths of 8 or more carbon atoms, however, they can also be present because of the use of recycled papers (containing PFAS) for packaging material. Several studies in the literature addressed the presence of PFASs in food packaging materials and the release of PFASs to food or simulants and PFOA and PFOS resulted the most frequently investigated compounds (Curtzwiler et al., 2021; Kotthoff et al., 2015; Zabaleta et al., 2020; Lerch et. al, 2022). On the other hand, literature data investigating OPEs in FMCs are rather scarce. (Wang & Kannan, 2018; Zhang et al., 2016). In order to fill this gap, in this study present a method to assess the migration of both these controversial substances from FMCs evaluating the differences in their release in different food categories. The method presented allow the investigation about OPEs and PFASs migration using the same extraction protocol and instrumental method, easily making the collection of data needed as a basis for exposure assessment studies.

2. Materials and methods

2.1. Chemicals and reagents

A table providing the name and acronym, chemical formula and the structure of the single compounds monitored in this study is reported in supplementary material (Table S1).

OPEs standards were obtained from Sigma-Aldrich s.r.l. (Milan, Italy) (Tripropylphosphate (TPrP), Tris(2-cloroetil)phosphate, (TCEP), triphenyl phosphate (TPhP)) and Wellington Laboratories (Ontario, Canada) (Tris(2-ethylhexyl)phosphate (TEHP), Tris(2-butoxyethyl)phosphate (TBEP), Tris(1,3-dichloro-2-propyl)phosphate (TDCPP), 2-Ethylhexyl diphenyl phosphate (EHDPhP), Tri-m-tolyl phosphate (TMTP), Tris(1,3-dichloro-2-

propyl) phosphate (TCPP) and Triethyl phosphate (TEP)) as well the deuterated Tributyl-d27 phosphate (TBuP-d27), Triphenyl–d15 phosphate (TPhP-d15), and Tris(2-chloroethyl)-d12 phosphate (TCEP-d12) used as internal standards.

PFAC-PFAS mixture (containing perfluoroalkyl carboxylic acids with carbon chain length: 4-14, 16 and 18 together with perfluoroalkyl sulfonic acids with carbon chain length: 4-10 and 12), Cl-PFESA and MePFOSA were also obtained from Wellington Laboratories (Ontario, Canada); FOSA (perfluorottansolfonammide) and EtFOSA (N-ethyl perfluoro-1-ottansolfonamide), were purchased from Sigma-Aldrich s.r.l. (Milan, Italy); GenX was purchased from Apollo Scientific (UK). Mass-Labelled PFASs, PFBA, PFHxA, PFOA, PFNA, PFDA, PFUnDA, PFDoA, PFHxS, PFOS (mixture name: MPFAC-MXA) were purchased from Wellington Laboratories (Ontario, Canada). The standard materials purity in this work was higher than 97%

HPLC grade methanol, n-hexane, ethyl acetate, 2-propanol were purchased from Sigma-Aldrich (Milan, Italy), LC/MS Optima Acetonitrile was from Fisher Scientific (Geel, Belgium) and toluene was from Romil ltd (Cambridge, UK). Absolute anhydrous ethanol was from Carlo Erba Reagents S.r.l. (Val-de-Reuil, France). Milli-Q water (Millipore Corporation, Billerica, Massachusetts, USA) was used. Florisil 60-100 mesh was purchased from Sigma-Aldrich S.r.l. (Milano, Italia). Phenex-RC (Regenerated Cellulose) filters 15 mm with pore size 0.20 μm were from Phenomenex (Torrance, CA, USA) and the PDVF 4 mm filter (0.22 μm pore size) from Millex (Massachusetts, USA).

2.2. Sampling and sample pre-treatment

The FMC samples taken into account were baking paper and aluminium foil used for cooking and storing foods. 11 samples of aluminium foil and 11 samples of baking paper of different brands and production batches were collected from several supermarkets in Rome in the period between November 2020 and July 2021, including one baking paper sample produced before 2017 reported as paper-5A. The baking paper and aluminium foil samples were coded with the prefix "paper-" and "foil-" followed by a progressive number to discriminate the different brands, finally a progressive alphabetic letter was used to identify the different batch of the same producer.

Three aliquots of each sample, taken at the beginning, middle and end of the rolls, were analysed in triplicate by collecting 1 dm^2 of baking paper and aluminium foil, corresponding to an average weight of 0.415 g and 0.345 g respectively.

In addition, a sample of baking paper and a sample of aluminium foil were also subjected to heat treatment, to evaluate the variation of the concentration of analytes transferred to the simulant before and after a possible baking treatment of the contact materials at two different temperatures.

In detail, both matrices were baked at 180°C for 1 hour, simulating the cooking process in an oven and in addition only aluminium foil was heated at 120 °C for 20 minutes, to reproduce a mild heating. Samples subjected to these baked processes were reported with a suffix –T followed by a number (T1 = 180°C for 1 hour and T2 = 120 °C for 20 minutes). Ethanol 95% (v/v) simulated the contact with fatty food, whereas acetic acid 3% (v/v) mimed the contact with acidic aqueous-based food. The migration between the FMCs and food simulants involved the use of the ultrasound-assisted (US).

2.3. Migration tests

The migration tests were carried out using 1 dm^2 of each sample (in triplicate) cut into small pieces, placed in a glass centrifuge tube, and fortified with the internal standards mixture. The standards were allowed to interact with the matrices overnight and the tubes were not capped to allow the solvent evaporation. Then, 20 mL of simulant liquid (ethanol 95 % v/v (simulant 1) or acetic acid 3 % v/v (simulant 2) were chosen to carry out OPEs and PFASs migration tests from baking paper and aluminium foil and the following steps were performed: 15 minutes ultrasonic at 60° C; 5 minutes vortex 1500 RPM at room temperature; 5 minutes centrifugation at 4000 RPM at room temperature.

The extract was taken from the centrifuge tube and collected in an evaporation tube. The migration experiments were repeated twice and finally the two extracts were combined, resulting in a total volume of 40 mL. For the two simulants used, the evaporation and filtration procedure were different. For simulant 1 (ethanol 95 % v/v) the extracts were made up to small volume (1 mL) under nitrogen flow at 35 °C, filtered by 15 mm filters (pore size 0.20 µm, Phenex-RC) and evaporated to dryness under the same conditions.
For simulant 2 (3% acetic acid v/v), the extract, after filtration by a 15 mm filter (pore size 0.20 µm, Phenex-RC, Torrance, CA, USA), transferred to a glass flask and dried by low-pressure evaporation using a rotary evaporator (BÜCHI, Villebon sur yvette, France) at a temperature of 60 °C and pressure of 40 mbar. The dried extract was then re-solubilized with 4 mL of methanol, transferred in a glass vial and evaporated to dryness again at 35 °C with a gentle nitrogen flow.
In both cases the final evaporated extracts were solubilised with 50 µL of methanol and filtered a second time using a glass syringe fitted with a 4 mm and 0.22 µm porosity PVDE filter (Millex), before the instrumental analysis by HPLC-ESI-MS/MS.

2.4. Quantitative analysis by LC-ESI-MS/MS and data quality

The analysis of PFASs and OPEs was performed by HPLC-ESI-MS/MS in multiple reaction monitoring (MRM) using the method and the parameter described in the Sonego et al., 2022. The internal standard method was used to perform the quantitative analysis, using three deuterated OPEs and nine 13C-mass labelled PFASs as internal standards. The matrix-matched calibration curves were built and used for each simulant/matrix investigated. In particular, the standard additions method was applied to one sample of baking paper and one of aluminium foil; the curves obtained were translated to the origin and used for the quantification of all samples tested. For this purpose, five increasing concentration points were prepared spiking the sample aliquots before the extraction to achieving levels of final concentration between 5 to 40 ng/mL for PFAS 1 to 4 µg/mL for TEP, TBuP, TBEP and TEHP and 25 to 100 ng/mL for the remaining OPEs with a fixed concentration of internal standards (MPFAC-MXA, TPhP-d, and TCEP-d at 100 ng/mL and TBuP-d at 300 ng/mL). The linearity of the method was then evaluated considering the linear regression coefficient. Limit of detention and quantification (LOD and LOQ), repeatability (intra and inter day), matrix effect of the method was also assessed for the investigated analytes in each simulant after migration from aluminium foil and baking paper. The LOD and LOQ were evaluated using the replicate analysis of a blank analysed in triplicate and were calculated using the average background signals and the associate standard deviation using the following formula

$$LOD = \frac{Y_D - q}{m} \qquad LOQ = \frac{Y_Q - q}{m}$$

Where Y_D is the average background signal plus 3 times its standard deviation and Y_Q is the average background signal plus 10 times its standard deviation, while q and m are the intercept and the slope of the calibration curve respectively.
The repeatability was calculated by the relative standard deviation (RSD), calculated by performing repeated measurements obtained under the same operating conditions (same method on identical materials, same laboratory, same operator, same equipment). The RSD was assessed by measurements taken in triplicate on the same day (intra-day repeatability) and on different days (inter-day repeatability). RSD value < 25% was considered acceptable. The matrix effect was assessed in terms of signal suppression enhancement (SSE) by comparing the analyte signals between a fortified extract and a pure solvent solution at the same concentration. Due to the lack of blank samples, to assess the matrix effect, one of the least contaminated samples from each matrix was analysed to determine its contamination and then fortified. The obtained response was then subtracted from the endogenous contribution and compared to the pure solvent solution.

2.5. Left censored data management

If many of the data obtained in an analysis have values < LOQ (left-censored data), different approaches, involving substitution of these values, can be used to assay the exposure related to them. In this work, the middle-bound method was used to evaluate the migration of OPE and PFAS from packaging to food. The middle bound is one of the commonly used substitution methods, indicated by EFSA (European Food Safety Agency) (EFSA, 2015), in which the values of LOD/2 and LOQ/2 are assigned to the results "≃ LOD" and "between LOD and LOQ" respectively.

3. Results and discussion

3.1. Optimization parameter for migration test

The food simulants used to study the migration of OPE and PFAS from baking paper and aluminium foil are 95% v/v ethanol (simulant 1) and 3% v / v acetic acid (simulant 2). As suggested from EC Regulation 1416/16 Commission Regulation EU 2016/1416 (EU 1416/16), isooctane or ethanol 95% v/v can be used alternatively to vegetable oil, while acetic acid 3 % v/v for simulating acidic aqueous foods with pH ≤ 4.5.
In accordance with Annex III of the Ministerial Decree of 21/03/73 and amendments (DM 21.3.73), the simulant and the food packaging sample must be placed in contact at 40 °C for 24 hours for the static contact release test. Starting from this point, different contact conditions were used to force the migration of FMC components and additives to simulants, in order to mime the worst scenario with a significant time saving.
The tests (Table 1) were carried out by different conditions in triplicate, using 1 dm^2 of baking paper or aluminium foil (cut in small pieces) spiked with a standard mixture of all the analytes at a concentration within the calibration range.
Thereafter, the sample was centrifuged for 10 minutes at 4000 RPM at room temperature and the supernatant was transferred to another vial. After dryness, the residue, resuspended in 50 µL of methanol and filtered, was analysed by HPLC-ESI-MS/MS in MRM mode.
Fig. 1 shows the sums of the analyte amounts extracted, normalised to the higher migration. As it can be seen both for baking paper that for aluminium foil, test 1 yielded the greatest number of transferred analytes.
Other authors (Guart et al., 2011, Fasano et al., 2012) used the ultrasonic extraction method as an accelerated method to force the migration of FMC components and additives to simulants. Although the use of the ultrasound may produce an overestimation in the evaluation of the extent of chemical transfer from packaging into food, this contact condition was considered the best suitable to provide precautionary approach for consumer health, by reproducing the worst possible food contamination scenario.
Subsequently the efficiency of migration was assessed in terms of number of ultrasound cycles. For this purpose, the samples were subjected to three subsequent extraction cycles and then analysed by HPLC-ESI-MS/MS in MRM mode. The results (supplementary material Fig. S1) for both the contact materials, showed the third extraction not significantly contributing to the overall migration. For this reason, the optimised method involved the use of two ultrasound cycles for migration experiments.

3.2. Matrix-matched calibration curves and validation data

The matrix-matched calibration curves were built for both the simulants fortifying prior the extraction 5 aliquots of a baking paper and aluminium foil using the standard addition method. Table 2 shows synthetically the linearity, repeatability inter and intra-day, matrix effect (SSE), LOD and LOQ for simulant 1 relatively to both the materials, the data relative to the single compounds are reported in the supplementary material Table S2.
As it can be seen R^2 correlation coefficients were worse for OPEs than for PFASs, because of the OPEs presence in working solvents and laboratory consumables leading to contamination of procedural blanks that negatively

influenced the linearity. The SSE strongly affected the response of both the classes under consideration due to the to the chemical and physical characteristics of the analysed compounds.

The evaluation of the matrix effect showed the need to perform a quantitative analysis using a matrix-matched calibration curve. Due to the high concentration of TEP, TBuP and TBEP in the sample used for construction of the matrix matched calibration curves, these analytes were not quantified in the real samples. As reported in section 2.4, LOD and LOQ were evaluated using triplicate analysis of a procedural blank, because of the lack of a sample without any contamination. For the PFASs, LODs and LOQs were in the range 0.01-3.17 and 0.01-3.70 ng/dm^2 respectively. As regard OPEs in simulant 1, their LOD and LOQ ranged from 0.02 to 3.17 ng/dm^2 and from 0.05 to 8.55 ng/dm^2 respectively.

In contrast to simulant 1, which can be easily evaporated at 35 °C with a gentle flow of N_2, simulant 2 was aqueous and therefore its evaporation was not performed under the same conditions as simulant 1. For this reason, specific tests were carried out in order to choose the suitable condition and obtaining the better compromise in term of time and evaporation yields. The use of the rotary vacuum evaporation at 60 °C and 40 mbar was the best choice. Unfortunately, among the PFASs, MeFOSA and EtFOSA were completely lost in the evaporation step; TPrP, TEP, PFOA, PFNA, Cl-PFONS and TBuP showed a yield of about 30%. For all other analytes, there was no appreciable loss in evaporation. In addition, due to the different contamination of the solvents and materials used, TCEP, TDCPP, TPhP, TBuP, TEHP and PFBA were not quantifiable because of their variable presence in the procedural blanks. In Table 3 all the investigated validation parameters for simulant 2 are reported synthetically, the data specific for each analyte are reported in supplementary material Table S3.

Simulant 2 showed a very heterogeneous suppression/enhancement effect, able to interfere with the analytical determination of the compounds in study. However, it should be highlighted that, since the quantitative analysis was carried out using the internal standard method and the matrix matched calibration curve, also for these analytes, the SSE contribution was automatically corrected on the obtained results. LODs and LOQs parameters were higher for OPEs than PFASs in simulant 2. In particular, LOD and LOQ were in the range 0.01-0.80 ng/dm^2 0.02-1.73 ng/dm^2 for PFAs and 0.40-13.67 ng/dm^2, 0.50-14.62 ng/dm^2 for OPEs.

3.3. Sample migration results

3.3.1.Simulant 1

The migration results relative to simulant 1 are reported in Fig 2. Data are presented as the sum of the amount of each OPEs (blue histogram) and PFASs (orange histogram); baking paper is on the left panel, whereas aluminium foil is on the right one. As described above, the middle-bound approach was applied for the left censored data. Based on the results of baking paper, the migration of OPEs (Fig. 2a) ranged from about 4.25 ng/dm^2 to 27.78 ng/dm^2. Baking paper-1B, 3 and 1A showed the highest value of OPE migration.

In particular, the predominant OPEs were TDCPP (detected in 7 samples of 12), found at concentrations between 0.72-7.33 ng/dm^2, TEHP (detected in 7 samples of 12), found at concentrations between 0.57-4.47 ng/dm^2 followed by TMTP (detected in 6 samples of 12), found at concentrations between 0.93-11.97 ng/dm^2. The migration of both these contaminants in simulant 1 is also confirmed by different investigations present in literature. TDCPP is one of the most investigated OPEs in food samples (such as cheese, potatoes, and meat) due to its presence in food packaging materials and its ability to migrate to food (Wang et al., 2020) whereas TMTP, thanks to its characteristics of hydrophobic and insolubility in water, is expected to show a good migration in simulant 1 (fatty food). In addition, the analysis of different batches of baking paper allowed us to evaluate how different years of production may give different information about the extent of migration to simulants. Data showed as the migration from different batches was not overlapped, especially for the brand 5 whom batch A was produced before 2017. Despite the need to collect more data about it, this preliminary result could suggest that the use of OPEs has decreased in packaging material during the last years.

As for PFASs, Fig. 2b highlights that the highest amount among all the samples tested is in paper-9, a recyclable and compostable baking paper, whereas the baked paper-1A-T1 did not show significant migration variation after heating. Based on the results the migration of PFASs ranged from about 2.07 ng/dm^2 to 5.21 ng/dm^2 and t~~T~~he PFASs mostly frequently found in baking paper samples was PFBA, found into the simulant 1 at concentrations ranging between 0.10 and 1.68 ng/dm^2. This is a short-chain (4 carbon atoms) perfluoroalkyl carboxylic acid, and it belongs to the new generation of short-chain PFAS used alternatively to PFOS and PFOA. This result agrees with those of Zabaleta et al. (Zabaleta et al., 2020). These results highlighted the inadequacy of the producer to finding alternatives to these banned compounds. On the other hand, the lowest migration of both OPEs and PFASs to simulant 1 was estimated for paper-4.

As for aluminium foil, the histograms in Fig. 2 shows in the right panel c) and d) the sum of the concentrations of OPEs, PFASs transferred to simulant 1. In detail the sum of OPEs was always >35 ng/dm^2, among the detected OPEs the TDCPP was the most frequently detected in 6 samples of 13 with a migration range from 1.51 to 2.75 ng/dm^2, lower value than found in the baking paper, followed by TCEP detected in 4 samples of 13 with a migration range from 0.76 to 3.36 ng/dm^2.

Furthermore, the distribution of OPEs in aluminium foils showed more homogeneous values in all the investigated samples probably due to the presence of this class of pollutants in the upstream materials before the migration. In addition, the higher presence of TDCPP in aluminium foils confirms once more the findings reported by Wang et al., 2020 about its presence in FCM and probably to its more tendency ability to migrate to food/simulants More studies should be carried out about TDCPP presence in FCM considering its negative effects on human health from exposure to this chemical.

Also, in PFASs the migration test in aluminum foil showed a more homogeneous results for almost all the samples except for foil 8A which showed a maximum around 4.93 ng/dm^2.

The most prevalent perfluoroalkyl substance was PFOA in concentrations between 0.10 and 0.26 ng/dm^2, despite the Food and Drug Administration (FDA) have banned the use of PFAS with chains of 8 to more carbon atoms since 2016, in the aluminium foils. In this case, the greater presence of long-chain PFAS in aluminium foil, compared to baking paper samples, demonstrates that much work will still have to be done and new formulations devised to comply with FDA directives. The extent of contaminant migration was comparable (about 2.80 ng/dm^2) between two different batches from the same manufacturer in aluminium foil (foil-8B and foil 8C), but different from sample foil-8A, because of the wrapped structure (having a bigger surface), which showed the highest migration of PFAS (around 5 ng/dm^2). Moreover, the Foil-8C was subjected to two different baking procedures: baking at 180 °C for 1 hour and baking at 120 °C for 20 minutes (foil-8C-T1 and foil-8C-T2 respectively).

In contrast to the oven paper, both OPEs and PFAS concentrations do not change with baking. These results would suggest a greater resistance of the aluminium foil to temperatures, not affecting the analyte migration.

3.3.2.Simulant 2

The histograms of Fig. 3 show the concentration of OPEs and of PFASs after migration to simulant 2. Data are presented as the sum of the amount of each OPEs (blue histogram) and PFASs (orange histogram); baking paper is on the left panel, whereas aluminium foil is on the right one. As described above, the middle-bound approach was applied for the left censored data. Based on the results of baking paper, the migration of OPE (Fig. 3a) ranged from about 78.30 ng/dm^2 to 413.21 ng/dm^2.

The higher migration of OPEs was registered from paper-1A and paper-5A, while paper 4 and paper-5B showed less contamination. Overall, the sum of the migrated OPEs from baking paper to simulant 2 were considerably higher than to simulant 1.

This result could suggest a greater exposure of consumers to this class of compounds with acidic aqueous food compared to fatty food.

In particular, the predominant OPEs were TEP (detected in all the sample), found at concentrations between 47.03-327.37 ng/dm^2, and TBEP (detected in 10 samples of 12), found at concentrations between 14.69-83.21 ng/dm^2.

The higher migration of TEP in this aqueous simulant is probably due to its smaller molecule size compared to the class under investigation. Regarding PFASs, the migration ranged from about 1.43 to 13.87 ng/dm^2 showing overall a higher migration of this class of compounds in simulant 2 compared to simulant 1 and confirming the trend, already known, of PFAS to migrate in aqueous solvents. Fig. 3b shows paper-1A the oven paper releasing the highest quantity of PFAS. Cl-PFESA, (detected in all the sample) was found at concentrations between 0.13-3.14 ng/dm^2, whereas PFDA (detected in 8 sample of 12) was found at concentrations between 0.11-3.16 ng/dm^2 and PFNA (detected in 11 samples of 12) migrated in a concentration range between, 0.53-6.01 ng/dm^2 respectively. In overall, all the baking papers showed higher migration of OPEs than PFASs, in agreement with the results obtained in the case of simulant 1.

Considering aluminium foils (panel right), the OPEs estimated migration ranged from 13.19 to 61.52 ng/dm^2. The sample releasing the highest amount of OPEs to simulant 2 was the foil-8A (Fig. 3c). TEP and TBEP were detected in 5 samples of 12 in a range of concentration between 15.41-54.26 ng/dm^2 and 15.22-34.48 ng/dm^2 respectively. As regards PFASs in aluminium foils the overall migration accounted ranged from 1.17 to 7.83 ng/dm^2, in Fig. 3d, the foil-7 was the sample with the highest amount of PFASs migrated. On this foil, the main contribution to contamination was due to PFDS with a concentration of 7.01 ng/dm^2; for the other samples the PFASs migration was below 1 ng/dm^2. In general, OPEs migrated more than PFASs from the aluminium foils, in agreement with the data obtained in the case of simulant 1 and, also in this case, the heated foil did not show a decrease in contaminants released.

To sum up, the two simulants tested showed interesting differences in the migration of the investigated compounds. TEP was the OPEs with a higher migration in simulant 2, compared to simulant 1, probably due to the high solubility of this molecule into water (log K_{ow} = 0.8) (van deer Veen & de Boer, 2012). It was also found that PFUnDA, PFDoA, PFDoS, PFTrDA, PFTeDA, PFHxDA, PFODA, being characterised by high hydrophobicity due to their long aliphatic chain, do not migrate to the aqueous-based simulant as also reported by Paseiro-Cerrato (Paseiro-Cerrato et al., 2021). The results showed in addition, the presence of banned PFASs at not-negligible concentrations, highlighting that the ban of the use is not enough to assure consumer protection, but more should be done in order to find/develop and propose safer alternatives on the marked.

3.4. Comparison between matrices and simulants

For a global comparison of the migration for exposure purpose, two classes of compounds were summed and evaluated by the middle-bound approach, considering the data for each matrix and simulant (Fig. S2).

As for baking paper (panel left), compounds migration to simulant 2 was up to 10 times higher than to simulant 1 (approximatively 425 ng/dm^2 and 40 ng/dm^2 respectively). In particular, the baking papers presenting the greatest migration in simulant 2 are paper 1A and 5A. In addition, the baking paper baked at 180°C for one hour (paper-1A-T) showed a decrease in the concentration of analyte migration in both the simulants, highlighting the loss or degradation of contaminants at high temperature.

At the opposite, in aluminium foil samples (panel right) the release to simulant 1 and 2 was in the same magnitude order and it was not highlighted a particular tendency to migrate in one simulant versus the other (approximatively 41 ng/dm^2 and 33 ng/dm^2 for simulant 1 and 2 respectively).

Overall, from this data can be assessed that the worst scenario is caused using baking paper in contact with aqueous acidic foods (simulant 2). On the other hand, it is well known that the aluminium foil is not recommended for this kind of food either (Ojia et al. 2007), due to aluminium migration, therefore it should be encouraging the use of more inert material in cooking/storing them.

4. Conclusions

The FMCs represents a route of exposure to different substances, sometimes toxic, for humans. OPEs, PFASs are compounds used in the production and processing of materials and consequently found in FCMs, causing possible

migration into food. In this work, the migration of these substances from backing paper and aluminium foil samples to food simulants was verified, developing and optimising a method suitable for studying their release. The contact mode between FMCs samples and food simulants involved the use of the ultrasound-assisted technique to evaluate the migration of analytes in a time-saving manner, reproducing the worst-case scenario of food contamination. Overall, comparing all the migration tests, the matrix showing the highest release of contaminants is baking paper to simulant 2 (acetic acid 3 % to mime aqueous-based acid food) one order of magnitude higher than the other combinations of matrix/simulant, with migrations in the ranges 78.30-413.21 ng/dm^2 and 1.43-13.87 ng/dm^2 for OPEs and PFASs respectively. This first result would show a greater exposure of consumers to the contaminants, consuming aqueous-based acid food compared to fatty food for the two FCMs under consideration.
In addition, the obtained data showed that, in all the cases, the simulant contamination was mainly due to OPEs release. This study underlines the need to better estimate and evaluate the contribution of OPEs, in particular TDCPP migration especially in fatty food in FMCs, because of the negative potential human health effects deriving from exposure to this chemical. As concern migration test results to simulant 2, TEP and TBEP are the OPE detected almost in all samples reaching high values up to 327.37 ng/dm^2 and 83.21 ng/dm^2 respectively.
Further studies should be conducted in the future to confirm their presence and concentration in FMC as well as performing in-depth epidemiological studies to fully understand the real exposure risks of consumers to these molecules.

Supplementary data Supplementary data associated with this article can be found in the online version

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.

Funding This research was funded by Sapienza University of Rome project “Research Starter Projects - Type 2” 2021, protocol num. AR22117A89D62AE0.

References

Blanco-Zubiaguirre, L., Zabaleta, I., Prieto, A., Olivares, M., Zuloaga, O., & Elizalde, M. P. (2021). Migration of photoinitiators, phthalates and plasticizers from paper and cardboard materials into different simulants and foodstuffs. *Food Chemistry*, 344. https://doi.org/10.1016/j.foodchem.2020.128597

Caroline, B., Ralf, T., & Conny, Ostman. (2010). Simultaneous selective detection of organophosphate and phthalate esters using gas chromatography with positive ion chemical ionisation tandem mass spectrometry and its application to indoor air and dust. *Rapid Communications in Mass Spectrometry*, 24, 2859–2867. https://doi.org/10.1002/rcm

Curtzwiler, G. W., Silva, P., Hall, A., Ivey, A., & Vorst, K. (2021). Significance of Perfluoroalkyl Substances (PFAS) in Food Packaging. *Integrated Environmental Assessment and Management*, 17(1), 7–12. https://doi.org/10.1002/ieam.4346

DM 21.3.73 Italian Ministerial Decree of 21/03/1973 “Hygienic regulation of packaging, containers, tools, intended to come into contact with the food substances or substances for personal use.” Minister of Health and published on official gazette No. 104 of 04/20/1973 https://www.gazzettaufficiale.it/eli/id/2016/07/26/16G00154/sg

EU 1416/16 - Commission Regulation (EU) 2016/1416 of 24 August 2016 amending and correcting Regulation (EU) No 10/2011 on plastic materials and articles intended to come into contact with food. Published in *Official Journal of the European Union*. L230/22. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32016R1416&from=EN

EFSA, 2015 – European Food Safety Agency (2013). Scientific Opinion on the risks to public health related to the 4 presence of bisphenol A (BPA) in foodstuffs – Part: exposure assessment 1. *European Food Safety Agency Journal*. https://doi.org/10.2903/j.efsa.2015.3978

EFSA, 2019 - European Food Safety Agency (2019). Safety assessment of the substance phosphorous acid, triphenyl ester, polymer with alpha-hydroxy omega hydroxypoly[oxy(methyl-1,2-ethanediyl)], C10-16 alkyl esters, for use in food contact materials. *European Food Safety Agency Journal*. https://doi.org/10.2903/j.efsa.2019.5679

Elsa, O., Emmanuelle, B., Sébastien, H., Anne-Lise, R., Fabrice, M., Hélène, G., Paul, H., Gérald, R., Gaud, D. P., Cariou, R., & Bruno, L. B. (2019). Toward the characterisation of non-intentionally added substances migrating from polyester-polyurethane lacquers by comprehensive gas chromatography-mass spectrometry technologies. *Journal of Chromatography A*, 1601, 327–334. https://doi.org/10.1016/j.chroma.2019.05.024

Fasano, E., Bono-Blay, F., Cirillo, T., Montuori, P., & Lacorte, S. (2012). Migration of phthalates, alkylphenols, bisphenol A and di(2-ethylhexyl) adipate from food packaging. *Food Control*, 27(1), 132–138. https://doi.org/10.1016/j.foodcont.2012.03.005

Grob, K., Pfenninger, S., Pohl,W., Laso, M., Imhof, D., & Rieger, K. (2007). European legal limits for migration from food packaging materials: 1. Food should prevail over simulants; 2. More realistic conversion from concentrations to limits per surface area. PVC cling films in contact with cheese as an example. *Food Control*, 18(3), 201-210. https://doi.org/10.1016/j.foodcont.2005.09.015

Groh, K. J., Geueke, B., Martin, O., Maffini, M., & Muncke, J. (2021). Overview of intentionally used food contact chemicals and their hazards. *Environment International*, 150, 106225. https://doi.org/10.1016/j.envint.2020.106225

Guart, A., Bono-Blay, F., Borrell, A., & Lacorte, S. (2011). Migration of plasticizer phthalates, bisphenol A and alkylphenols from plastic containers and evaluation of risk. *Food additives and contaminants*, 28(5), 676-685. https//doi.org/ 10.1080/19440049.2011.555845.

Kotthoff, M., Müller, J., Jürling, H., Schlummer, M., & Fiedler, D. (2015). Perfluoroalkyl and polyfluoroalkyl substances in consumer products. *Environmental Science and Pollution Research*, 22(19), 14546–14559. https://doi.org/10.1007/s11356-015-4202-7

Li, J., Zhao, L., Letcher, R. J., Zhang, Y., Jian, K., Zhang, J., & Su, G. (2019). A review on organophosphate Ester (OPE) flame retardants and plasticizers in foodstuffs: Levels, distribution, human dietary exposure, and future directions. *Environment International*, 127 (October 2018), 35–51. https://doi.org/10.1016/j.envint.2019.03.009

Lerch, M., Nguyen, K. H., & Granby, K. (2022). Is the use of paper food contact materials treated with per- and polyfluorinated alkyl substances safe for high-temperature applications? – Migration study in real food and food simulants. Food Chemistry, 133375. https://doi.org/10.1016/j.foodchem.2022.133375

Martínez-Carballo, E., González-Barreiro, C., Sitka, A., Scharf, S., & Gans, O. (2007). Determination of selected organophosphate esters in the aquatic environment of Austria. *Science of the Total Environment*, 388(1–3), 290–299. https://doi.org/10.1016/j.scitotenv.2007.08.005

Muncke, J., Backhaus, T., Geueke, B., Maffini, M., Martin, O., Myers, J.P., Soto, A., Trasande, L., Trier, X. & Scheringer, M. (2017). Scientific challenges in the risk assessment of food contact materials. *Environment Health Perspectives*, 125 (9), 095001. https://doi.org/10.1289/EHP644

Ojha, P., Ojha, C.S. & Sharma, V.P. (2007) Influence of physico-chemical factors on leaching of chemical additives from aluminium foils used for packaging of food materials. *Journal of Environmental Engineering and Science*. 49(1), 62-6. PMID: 18472563.

Paseiro-Cerrato, R., De Jager, L., & Begley, T. H. (2021). Migration of phenolic brominated flame retardants from contaminated food contact articles into food simulants and foods. *Food Additives and Contaminants - Part A*, 38(3), 464–475. https://doi.org/10.1080/19440049.2020.1871082

Poothong, S., Boontanon, S. K., & Boontanon, N. (2012). Determination of perfluorooctane sulfonate and perfluorooctanoic acid in food packaging using liquid chromatography coupled with tandem mass spectrometry. *Journal of Hazardous Materials*, 205–206, 139–143. https://doi.org/10.1016/j.jhazmat.2011.12.050

van der Veen, I., & de Boer, J. (2012). Phosphorus flame retardants: Properties, production, environmental occurrence, toxicity and analysis. *Chemosphere*, 88(10), 1119–1153. https://doi.org/10.1016/j.chemosphere.2012.03.067

Sonego, E., Simonetti, G., Di Filippo, P., Riccardi, C., Buiarelli, F., Fresta, A., ... & Pomata, D. (2022). Characterization of organophosphate esters (OPEs) and polyfluoralkyl substances (PFASs) in settled dust in specific workplaces. *Environmental Science and Pollution Research*, 1-15. https://doi.org/10.1007/s11356-022-19486-3

Wang, Y. & Kannan, K. (2018). Concentrations and dietary exposure to organophosphate esters in foodstuffs from Albany, New York, United States. *Journal of Agricultural and Food Chemistry*, 66, 13525-13532. https://doi.org/10.1021/acs.jafc.8b06114

Wang, C., Chen, H., Li, H., Yu, J., Wang, X. & Liu, Y. (2020) Review of emerging contaminant tris (1,3 dichloro-2-propyl) phosphate: Environmental occurrence, exposure, and risks to organisms and human health. *Environment International*, 143, 105946. https://doi.org/10.1016/j.envint.2020.105946

Zabaleta, I., Blanco-Zubiaguirre, L., Baharli, E. N., Olivares, M., Prieto, A., Zuloaga, O., & Elizalde, M. P. (2020). Occurrence of per- and polyfluorinated compounds in paper and board packaging materials and migration to food simulants and foodstuffs. *Food Chemistry*, 321(April), 126746. https://doi.org/10.1016/j.foodchem.2020.126746

Zhang, X., Zou, W., Mu, L., Chen, Y., Ren, C., Hu, X. & Zhou, Q. (2016) Rice ingestion is a major pathway for human exposure to organophosphate flame retardants (OPFRs) in China. *Journal of Hazardous Materials*, 318, 686-693. https://doi.org/10.1016/j.jhazmat.2016.07.055