# Chlorinated organophosphate esters in Irish waste foams and fabrics

Harrad, Stuart; Sharkey, Martin; Stubbings, William A.; Alghamdi, Misbah; Berresheim, Harald; Coggins, Marie; Rosa, André Henrique; Drage, Daniel

*DOI:*
10.1016/j.scitotenv.2022.160250



*Citation for published version (Harvard):*
Harrad, S, Sharkey, M, Stubbings, WA, Alghamdi, M, Berresheim, H, Coggins, M, Rosa, AH & Drage, D 2023, 'Chlorinated organophosphate esters in Irish waste foams and fabrics: Concentrations, preliminary assessment of temporal trends and evaluation of the impact of a concentration limit value', *Science of the Total Environment*, vol. 859, no. 1, 160250. https://doi.org/10.1016/j.scitotenv.2022.160250

Science of the Total Environment 859 (2023) 160250

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

# Chlorinated organophosphate esters in Irish waste foams and fabrics: Concentrations, preliminary assessment of temporal trends and evaluation of the impact of a concentration limit value

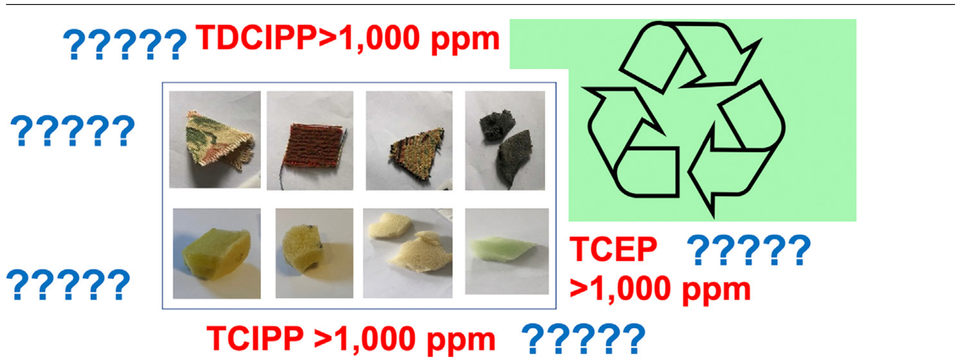
Stuart Harrad [a,*], Martin Sharkey [b], William A. Stubbings [a], Misbah Alghamdi [a], Harald Berresheim [b], Marie Coggins [b], André Henrique Rosa [a,c], Daniel Drage [a,d]

[a] School of Geography, Earth and Environmental Sciences, University of Birmingham, Edgbaston, West Midlands B15 2TT, United Kingdom
[b] School of Natural Sciences & Ryan Institute, National University of Ireland, Galway H91TK33, Ireland
[c] Institute of Science and Technology, São Paulo State University (UNESP), Av. Três de Março, 511, Alto da Boa Vista, 18087-180 Sorocaba, SP, Brazil
[d] Queensland Alliance for Environmental Health Sciences (QAEHS), The University of Queensland, 20 Cornwall Street, Woolloongabba, QLD 4103, Australia

## HIGHLIGHTS

- In 2019–20, 82 of 273 Irish waste foam and fabrics contained a Cl-OPE >1000 mg/kg.
- Mass of Cl-OPEs entering waste stream an order of magnitude higher than BFRs.
- Limit of 1000 mg/kg on Cl-OPEs will result in ~7200 t/yr unrecyclable waste.
- Same limit will remove 98 % (144,000 kg/yr) of Cl-OPEs from the recycling stream.
- TDCIPP and TCIPP significantly higher in ELV foam in 2019–20 than 2015–16.

## GRAPHICAL ABSTRACT




## ARTICLE INFO

Editor: Adrian Covaci

*Keywords:*
Plastics
TCIPP
TDCIPP
TCEP
Waste

## ABSTRACT

Concentrations of the chlorinated organophosphate esters (Cl-OPEs): tris(2-chloroethyl) phosphate (TCEP), tris(1-chloro-2-propyl) phosphate (TCIPP), and tris(1,3-dichloro-2-propyl) phosphate (TDCIPP) were measured in 273 waste synthetic foam and fabric articles collected in Ireland between 2019 and 2020. Articles examined comprised: polystyrene building insulation foam, as well as foam fillings and fabric coverings from furniture, mattresses, end-of-life vehicles, curtains, and carpets. Cl-OPEs were also measured in 156 samples from the same categories (except for building insulation foam) collected in 2015–16. Concentrations of TCIPP and TDCIPP in most samples exceeded those of TCEP; with those of TCIPP and TDCIPP generally and for some waste categories significantly ($p < 0.05$) higher in samples collected in 2019–20. Given potential future restrictions on use of these Cl-OPEs, we identified articles containing concentrations that exceeded 1000 mg/kg, in line with a similar limit that at the time of sample collection existed for some brominated flame retardants within the European Union. In 2019–20, 82 articles contained at least one Cl-OPE above 1000 mg/kg, with at least one article exceeding this concentration in each waste category examined. By comparison, only 28 samples collected in 2015–16, contained at least one Cl-OPE >1000 mg/kg, and articles exceeding this concentration were restricted to furniture and mattress foam, along with foams and fabrics from end-of-life vehicles. In the event of the introduction of such a limit on Cl-OPE concentrations in waste, it will result in 7200 t/year of such waste (24 % of the total) being rendered unrecyclable, while removing 98 % of the estimated ~147,000 kg/year of Cl-OPEs from the recycling stream.

* Corresponding author.
*E-mail address:* S.J.Harrad@bham.ac.uk (S. Harrad).

http://dx.doi.org/10.1016/j.scitotenv.2022.160250
Received 29 July 2022; Received in revised form 11 November 2022; Accepted 14 November 2022
Available online 16 November 2022

## 1. Introduction

To help meet flame retardancy regulations in various jurisdictions, chlorinated OPEs (Cl-OPEs i.e., tris(2-chloroethyl) phosphate (TCEP), tris (chloropropyl) phosphate (TCIPP) and tris(1,3-dichloro-2-propyl) phosphate (TDCIPP)) have found extensive application (Wei et al., 2015). For example, in 2000, total TCIPP production in Europe was 36,000 t, in applications such as rigid foams used in construction blocks and panels used for building insulation purposes, and in flexible polyurethane foam (PUF) for sofas, chairs, vehicle seating, and mattresses (Cooper et al., 2016; European Union, 2008; Stubbings et al., 2016). Similar applications have also been identified for both TDCIPP and TCEP (Marklund et al., 2003). While now suspended awaiting evaluation of the carcinogenicity of TCIPP by the United States (US) Toxicology Program (ECHA, 2019); in 2018 the European Chemicals Agency (ECHA) identified a risk to children from exposure to TCEP, TCIPP, and TDCIPP (ECHA, 2018); highlighting that the principal driver for use of such Cl-OPEs in these applications within Europe was to meet the flammability standards for such goods in the United Kingdom (UK) and Ireland (ECHA, 2018). Owing to evidence that restricted brominated flame retardants (BFRs) are present in food contact articles and children's toys made from recycled plastics (Guzzonato et al., 2017; Puype et al., 2015); the European Union (EU) introduced low persistent organic pollutant (POP) concentration limits (LPCLs) on concentrations of polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD) in waste articles, such that articles exceeding 1000 mg/kg of these BFRs cannot be recycled (EU, 2019). Moreover, in June 2022, the Council of the EU announced that provisional agreement was reached to lower this limit for both PBDEs and HBCDD to 500 mg/kg (Council of the EU, 2022). Given evidence that Cl-OPEs are also entering new articles as unintentional contaminants (Alghamdi et al., 2022), combined with ECHA's restriction proposal (ECHA, 2018), it is not unrealistic to anticipate that a similar limit will be placed on concentrations of TCEP, TCIPP, and TDCIPP in waste.

In the current study (the SAFER - *S*creening of the Irish *WA*ste Stream *F*or P*ER*sistent Organic Chemicals - project), we tested the hypothesis that use of Cl-OPEs to meet flame retardancy regulations in Ireland has been extensive and that this has resulted in a high proportion of soft furnishings and building insulation foam containing concentrations of Cl-OPEs that exceed 1000 mg/kg. Moreover, given that in the US, the detection frequency of TDCIPP in domestic sofas increased significantly from 24 % in items bought before 2005 to 52 % in those purchased post-2005 (Stapleton et al., 2012); we also hypothesised that Cl-OPE use in such applications has increased following restrictions on use of PBDEs and HBCDD. Our final hypothesis was that introduction of a limit of 1000 mg/kg on concentrations of Cl-OPEs above which waste cannot be recycled would provide a highly effective instrument via which such chemicals may be removed from the recycling stream. To test our hypotheses, between 2019 and 2020, as part of the SAFER project we determined concentrations of Cl-OPEs in 273 samples of waste building insulation foam, as well as foam and fabrics from end-of-life vehicles (ELV), and domestic soft furnishings. We also measured Cl-OPEs in 156 articles from a similar range of applications collected in Ireland between 2015 and 16 as part of the WAFER (Identification and Treatment Options for *WA*ste Streams of Certain Bromine Containing *F*lam*E R*etardants) project. In this paper, we compare data on Cl-OPE concentrations and exceedances of limit values from the two projects to test our hypotheses. While we acknowledge that comparing data collected at just two points in time carries some uncertainty; we believe our comparison provides a baseline against which future evaluations of concentrations of Cl-OPEs in waste plastic articles may be assessed.

## 2. Materials & methods

### 2.1. Sample collection

Samples from those waste categories considered possibly treated with our target Cl-OPEs were collected from several waste handling facilities located in the Republic of Ireland between 2019 and 2020. Overall, 273 samples were collected from 3 broad categories of waste: building insulation specifically, construction and demolition (C&D) extruded/expanded polystyrene foam (EPS/XPS) (n = 25); soft furnishings (n = 137), as well as ELV fabrics and foams (n = 111). Table 1 provides further details.

All samples in the SAFER project were collected from waste collection or waste transfer sites within the County Galway region. These comprised: three ELV scrapyards; two major recycling/waste transfer sites that process household, commercial, and C&D wastes; and some C&D sites where some EPS/XPS samples were collected. Fabrics/upholstery and directly underlying PUF along with any other cushioning materials (wool, additional fabrics etc.) were taken from ELV, furniture, and mattress samples.

As part of this study, we also measured concentrations of Cl-OPEs in archived samples collected in 2015–16 as part of the WAFER project for which sufficient material remained available for analysis. Note that the archived WAFER project samples analysed had been stored in sealed containers at 4 °C. The numbers of WAFER project samples analysed are provided in Table 1. Note that no archived building insulation foam samples were available for analysis.

### 2.2. Chemicals and standards

HPLC grade n-hexane, dichloromethane (DCM) and Optima grade methanol (MeOH) (Fisher Scientific, Loughborough, UK) were used for extraction and analysis of all samples. Reference standards of native TCEP, TCIPP, TDCIPP, $d_{12}$-TCEP, and $d_{15}$-TDCIPP were obtained from Wellington Laboratories (Guelph, ON, Canada). Both TCEP and TDCIPP were quantified relative to their corresponding deuterated analogue, with deuterated TCEP used to quantify TCIPP.

### 2.3. Sample extraction & clean-up

In brief, aliquots of samples (around 50 mg) were accurately weighed into a 15 mL glass tube, before extraction via vortexing (for 2 min) and ultrasonication (for 20 min) with 5 mL n-hexane:MeOH:DCM (1:2:1, v/v ratio) – vortexing and ultrasonication were repeated three times in total. Aliquots (50 μL) of extracts were transferred to a separate glass tube containing internal standards (50 ng each of $d_{12}$-TCEP and $d_{15}$-TDCIPP), prior to concentration to incipient dryness and precipitation of polymer matrix by addition of n-hexane (1 mL) and concentration to 200 μL. These extracts were vortexed for 20 s and transferred into inserted autosampler vials ready for gas chromatographic/mass spectrometric (GC/MS) analysis.

### 2.4. Instrumental analysis

Quantitative analysis of Cl-OPEs was undertaken on a Thermo Fisher Trace 1310 gas chromatograph coupled to a Thermo Fisher ISQ mass spectrometer (MS). The MS was operated in electron ionisation mode using selective ion monitoring (SIM). The ions (*m/z*) monitored for quantification/

**Table 1**
Categories and subcategories of waste products analysed in this study (2019–2020) and in 2015–2016.

| Category | Sub-category | Number of samples (2019–20) | Number of samples (2015–16) |
|---|---|---|---|
| Construction and demolition | EPS | 12 | 0 |
| | XPS | 13 | 0 |
| End of Life Vehicle (ELV) articles | Foams | 49 | 35 |
| | Fabrics | 62 | 35 |
| Soft furnishings | Carpets | 20 | 29 |
| | Curtains | 25 | 14 |
| | Furniture fabrics | 16 | 15 |
| | Furniture foam | 16 | 12 |
| | Mattress foam | 40 | 10 |
| | Mattress fabric covering | 20 | 6 |

qualification of Cl-OPEs were 249/251 (TCEP), 261/263 ($d_{12}$-TCEP), 277/279 (TCIPP), 381/379 (TDCIPP), 396/394 ($d_{15}$-TDCIPP). One μL of the purified extract was injected for analysis using a programmable temperature vaporiser (PTV) onto a Restek Rxi-Rtx-1614 MS column (15 m × 0.25 mm × 0.1 μm film thickness). Helium was used as the carrier gas at a flow rate of 1.0 mL/min. At the start of the program the GC was set at an initial temperature of 80 °C and held for 2 min. The oven was then ramped at 20 °C/min to 170 °C and held for 5.5 min. The GC was then ramped to 320 °C at 25 °C/min and held for 10 min, resulting in a total run time of 28 min.

### 2.5. Quality control

A reagent blank consisting of 100 mg of anhydrous sodium sulfate was analysed with every batch of 11 samples. Low masses of Cl-OPEs were detected in blank samples. Where the concentration in the blank associated with a given batch was 5–25 % of the sample concentration, the latter was corrected by subtracting the blank concentration. Where the concentration in the blank was >25 % of the sample concentration, then the sample was reported as <LOQ (limit of quantification). LOQs for Cl-OPEs were reported as the average blank concentration (0.02 mg/kg for TCEP and TCIPP; and 0.25 mg/kg for TDCIPP). In addition, we evaluated the accuracy of our method via analysis of matrix spikes. Matrix spikes (of pre-extracted PUF) were performed at 50 mg/kg (n = 5) and 1000 mg/kg (n = 5). All measured values were found to be within 80–120 % of the spiked concentrations with a relative standard deviation of <15 % (Table SD1). Matrix spikes of native target analytes were also performed with every other batch of samples analysed. For a batch to be accepted, the measured concentration for each compound was required to be within 80–120 % of the spiked concentration.

**Table 2**
Summary of concentrations (mg/kg) of TCEP, TCIPP, and TDCIPP and percentage of samples exceeding 1000 mg/kg limit value in samples from waste streams in Ireland collected in 2019–2020 (this study) and 2015–2016 (WAFER study).

| Waste category | Sub-category | Statistical parameter | TCEP 2015–16 | TCEP 2019–20 | TCIPP 2015–16 | TCIPP 2019–20 | TDCIPP 2015–16 | TDCIPP 2019–20 |
|---|---|---|---|---|---|---|---|---|
| Construction & demolition | EPS | Average* | – | <LOQ | – | 1.0 | – | 750 |
| | | Median | – | <LOQ | – | 0.32 | – | 75 |
| | | Range | – | <LOQ | – | <LOQ-3.8 | – | 5.2–6100 |
| | | % > limit value | – | 0 | – | 0 | – | 17 |
| | | P value[a] | – | | – | | – | |
| | XPS | Average | – | 0.04 | – | 7000 | – | 51 |
| | | Median | – | <LOQ | – | 7500 | – | 4.0 |
| | | Range | – | <LOQ-0.43 | – | <LOQ-22,000 | – | <LOQ-150 |
| | | % > limit value | – | 0 | – | 62 | – | 0 |
| | | P value | – | | – | | – | |
| End-of-Life Vehicles | Foams | Average | 220 | 370 | 170 | 5900 | 1000 | 30,000 |
| | | Median | 26 | 14 | 130 | 630 | 25 | 250 |
| | | Range | 1.2–2400 | 2.0–8400 | 3.6–570 | 61–100,000 | 6.7–15,000 | <LOQ-340,000 |
| | | % > limit value | 8.6 | 6.1 | 0 | 37 | 14 | 43 |
| | | P value | 0.51 | | 0.03 | | 0.004 | |
| | Fabrics | Average | 110 | 10 | 60 | 99 | 880 | 2300 |
| | | Median | 7.2 | <LOQ | 60 | 27 | 62 | <LOQ |
| | | Range | 1.0–1200 | <LOQ-220 | 5.6–150 | <LOQ-1200 | 7.5–6300 | <LOQ-17,000 |
| | | % > limit value | 2.9 | 0 | 0 | 1.6 | 26 | 26 |
| | | P value | 0.03 | | 0.12 | | 0.04 | |
| Soft furnishings | Carpets | Average | 1.0 | <LOQ | 9.1 | 91 | 13 | 32 |
| | | Median | 0.58 | <LOQ | 6.3 | <LOQ | 8.3 | <LOQ |
| | | Range | <LOQ-10 | <LOQ | 0.39–48 | <LOQ-1600 | <LOQ-140 | <LOQ-350 |
| | | % > limit value | 0 | 0 | 0 | 5.0 | 0 | 0 |
| | | P value | 0.01 | | 0.32 | | 0.36 | |
| | Curtains | Average | 2.9 | 1.1 | 35 | 60 | 1.0 | 210 |
| | | Median | 0.80 | <LOQ | 13 | <LOQ | 0.45 | 36 |
| | | Range | <LOQ-10 | <LOQ-3.1 | 0.39–150 | <LOQ-1500 | <LOQ-3.1 | <LOQ-2700 |
| | | % > limit value | 0 | 0 | 0 | 4.0 | 0 | 4.0 |
| | | P value | 0.25 | | 0.69 | | 0.08 | |
| | Furniture fabrics | Average | 61 | 53 | 130 | 540 | 37 | 340 |
| | | Median | 19 | 0.39 | 130 | 300 | 8.3 | 110 |
| | | Range | 2.9–320 | <LOQ-700 | 12–330 | <LOQ-3400 | 6.5–320 | <LOQ-1600 |
| | | % > limit value | 0 | 0 | 0 | 6.3 | 0 | 13 |
| | | P value | 0.97 | | 0.09 | | 0.04 | |
| | Furniture foam | Average | 1300 | 940 | 11,000 | 5400 | 1100 | 5700 |
| | | Median | 240 | 4.7 | 9500 | 220 | 13 | 24 |
| | | Range | <LOQ-9000 | <LOQ-14,000 | 0.35–25,000 | 1.8–40,000 | 1.1–13,000 | 4.8–44,000 |
| | | % > limit value | 33 | 6.3 | 83 | 38 | 8.3 | 19 |
| | | P value | 0.76 | | 0.16 | | 0.23 | |
| | Mattress foam | Average | 5.5 | 2.3 | 1700 | 3900 | 14 | 50 |
| | | Median | 4.7 | <LOQ | 180 | 67 | 4.4 | <LOQ |
| | | Range | <LOQ-13 | <LOQ-54 | 29–15,000 | <LOQ-41,000 | 2.1–88 | <LOQ-1100 |
| | | % > limit value | 0 | 0 | 10 | 18 | 0 | 2.5 |
| | | P value | 0.12 | | 0.31 | | 0.24 | |
| | Mattress fabric covering | Average | 36 | 1.2 | 40 | 330 | 2.0 | 360 |
| | | Median | 8.1 | <LOQ | 24 | 300 | 0.51 | 140 |
| | | Range | 1.9–110 | <LOQ-8.4 | 2.9–130 | <LOQ-1200 | <LOQ-10 | <LOQ-2200 |
| | | % > limit value | 0 | 0 | 0 | 5.0 | 0 | 10 |
| | | P value | 0.14 | | 0.001 | | 0.14 | |

* When calculating averages, concentrations below limit of quantification (LOQ) were assumed to be equal to LOQ*0.5.
[a] P value derived from independent *t*-test comparing concentrations in 2015–16 samples with those in 2019–20.

## 3. Results & discussion

### 3.1. Concentrations of Cl-OPEs and exceedances of the LPCL in Irish waste plastic samples collected in 2019–20 compared to 2015–16

Table 2 summarises the concentrations of TCEP, TCIPP, and TDCIPP detected in samples collected in 2019–2020. A full list of concentrations of each target Cl-OPE in every sample analysed is provided as supporting data (Tables SD-2 and SD-3). Table 2 also provides the percentage of samples for which concentrations of any individual Cl-OPE exceeded 1000 mg/kg. Where available, the same information for archived samples obtained in 2015–16 is provided and Fig. 1 compares the percentage of samples >1,000 mg/kg for each Cl-OPE in different waste categories in 2015-16 and 2019-20. Table 2 also gives the p value obtained for an independent *t*-test comparison of means for concentrations in samples from each waste category in 2019–20 with those in 2015–16.

While no previous data exist on concentrations of Cl-OPEs in Irish waste articles, our data are broadly consistent with those for a preliminary study of FRs in waste office furniture in the UK, in which 7 out of 9 furniture foam samples contained TCIPP at an average concentration of 19,000 mg/kg,

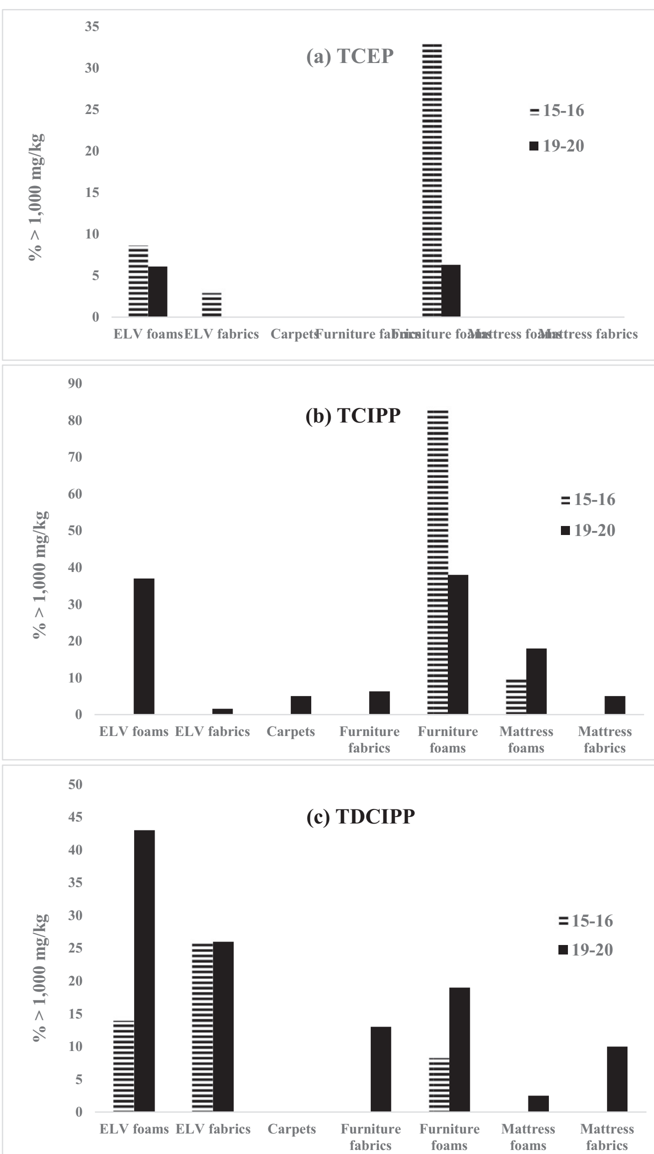



**Fig. 1.** Percentage of samples from different waste categories >1000 mg/kg in 2015–16 and 2019–20 for: (a) TCEP, (b) TCIPP, and (c) TDCIPP.

with a further foam sample containing both TDCIPP and TCEP at 11,000 and 5000 mg/kg respectively (Stubbings et al., 2016). Data reported in this study are also within the range of those reported for soft furnishing samples like sofas, chairs, mattresses etc. collected in the US, in which e.g. 25 % of sofas/love seats contained TDCIPP and 4.6 % contained TCIPP at a concentration >10,000 mg/kg (Cooper et al., 2016).

#### 3.1.1. C&D EPS/XPS waste

No archived C&D EPS or XPS building insulation foam samples were available for analysis. However, in the samples collected in 2019–20, while concentrations were below or only just above LOQs for TCEP in both EPS and XPS, for TCIPP in EPS, and for TDCIPP in XPS; 8/13 (62 %) of XPS samples and 2/12 (17 %) of EPS samples contained >1000 mg/kg of TCIPP and TDCIPP respectively. The maximum concentration of TCIPP was 22,000 mg/kg in XPS, while that of TDCIPP was 6100 mg/kg EPS respectively. This is consistent with the reported application of these Cl-OPEs in building insulation foam (European Union, 2008).

#### 3.1.2. ELV waste fabrics and foams

Out of the ELV fabric (n = 62) and foam (n = 49) samples collected in 2019–20, concentrations of TCEP exceeded 1000 mg/kg in 3 foam samples (6.1 %), with no such exceedances observed in any of the ELV fabric samples. The proportion of samples containing >1000 mg/kg of TCEP was greater in the samples collected in 2015–16, at 3 (8.6 %) of foam and 1 (2.9 %) fabric samples. While this did not translate into a significant difference between the two studies for ELV foams; TCEP concentrations were significantly lower in ELV fabrics collected in 2019–20. In contrast, for both TCIPP and TDCIPP, concentrations and the proportion of samples >1000 mg/kg are significantly higher in foam samples collected in 2019–20, for which maximum concentrations are 340,000 mg/kg and 100,000 mg/kg for TDCIPP and TCIPP respectively. By comparison, in ELV foam samples collected in 2015–16, maximum concentrations were 15,000 mg/kg for TDCIPP and 570 mg/kg for TCIPP. The situation is less clear for ELV fabrics, as there is no significant difference between TCIPP concentrations in samples collected in different years, and while concentrations of TDCIPP samples are higher in ELV fabric samples collected in 2019–20, the proportion >1000 mg/kg is the same, whichever year of samples were collected.

As we were able to identify the year of manufacture of most of the cars from which the ELV samples were derived in our 2019–20 samples (see Table SD-2), we examined our data for any relationship between vehicle date of manufacture and concentration of Cl-OPEs in ELV samples. We tested first for any linear relationship via Pearson's correlation, with no significant relationship found between vehicle age and concentration of any Cl-OPE. We also conducted a *t*-test comparison of means between samples derived from vehicles manufactured between 1999 and 2003, with those manufactured between 2004 and 2007. No significant differences were observed for any of our target Cl-OPEs, although concentrations of TCIPP in PUF (but not fabric) samples from the more recent vehicle group (average = 8800 mg/kg) exceeded those in the older group (average = 1400 mg/kg), with a near significant p value of 0.08.

#### 3.1.3. Waste soft furnishings

As shown in Table 1, soft furnishing samples collected in 2019–20 were a mix of fabric coverings and PUF fillings for chairs, mattresses, and sofas, as well as carpets and curtains. Of all the waste categories examined in this study, average concentrations and the proportion of samples containing >1000 mg/kg were highest for all three target Cl-OPEs in furniture foam, with at least one sample in each sub-category containing >1000 mg/kg for one or more Cl-OPEs. Most strikingly, 6 (37 %), 3 (19 %), and 1 (6.3 %) furniture foam samples contained >1000 mg/kg TCIPP, TDCIPP, and TCEP respectively, with maximum concentrations of 44,000 mg/kg TCIPP, 25,000 mg/kg TDCIPP, and 9000 mg/kg TCEP. Average concentrations of all Cl-OPEs were lowest for curtains and carpets.

With respect to possible temporal trends; while average concentrations and the proportion >1000 mg/kg were greater for all three Cl-OPEs in

**Table 3**
Estimated annual masses[a] of different categories of waste generated in Ireland in 2019 and mass[a] of TCEP, TCIPP, and TDCIPP associated with such waste.

| Category | t waste/yr[b] | TCEP (kg/yr) | TCIPP (kg/yr) | TDCIPP (kg/yr) | ΣCl-OPEs (kg/yr)[c] |
|---|---|---|---|---|---|
| C&D insulation foam | 5500 | 0.15 | 20,000 | 2100 | 22,000 |
| ELV foams and fabrics | 3800 | 630 | 10,000 | 55,000 | 66,000 |
| Carpets | 7600 | 0.08 | 690 | 240 | 930 |
| Curtains | 740 | 0.8 | 44 | 150 | 200 |
| Furniture foam | 2600 | 2400 | 14,000 | 15,000 | 31,000 |
| Furniture fabrics | 880 | 47 | 470 | 300 | 810 |
| Mattress foam | 6100 | 14 | 24,000 | 310 | 24,000 |
| Mattress fabrics | 2500 | 3.0 | 830 | 910 | 1700 |
| Total[b] | 30,000 | 3100 | 70,000 | 74,000 | 147,000 |

[a] Rounded to two significant figures.
[b] For detailed explanation of how these figures are derived, see Table SD-4.
[c] Totals may differ due to rounding.

furniture foam samples collected in 2015–16 – most notably 10 (83 %) of such samples contained >1000 mg/kg TCIPP in 2015–16; no significant differences were found with concentrations detected in 2019–20 samples. Indeed, while *t*-test comparison of data for 2015–16 and 2019–20 samples revealed concentrations of: TCEP to be higher in 2015–16 for carpets, those of TDCIPP to be higher in furniture fabrics in 2019–20, and those of TCIPP in mattress fabric coverings in 2019–20 to exceed those in 2015–16; there were very few of any such samples that contained >1000 mg/kg of the Cl-OPEs in question, and the temporal trends observed are unlikely to reflect a meaningful trend in the application of Cl-OPEs.

*3.1.4. Preliminary estimation of mass of products exceeding limit values and mass of Cl-OPEs annually entering the waste streams studied in Ireland*

We derived estimates of the mass of our target waste materials generated in Ireland in 2019 (Table SD-4). By multiplying these data on the mass of a given waste category generated annually by the average concentration of each Cl-OPE in that waste category, we generated preliminary estimates of the mass of TCEP, TCIPP, and TDCIPP annually entering our target waste streams in Ireland (Table 3). We provide two illustrative examples. First, Table SD-4 gives an estimate of the mass of waste furniture foam entering the Irish waste stream in 2019 of 2600 t. Multiplying this by the average concentration of TDCIPP in our 2019–20 furniture foam samples (Table 2) of 5700 mg/kg, yields an estimate (rounded to two significant figures) of 15,000 kg/year of TDCIPP. Second, our estimate of the mass of ELV foams and fabrics entering the Irish waste stream in 2019 is 3800 t (Table SD-4). Multiplying this by the average concentration of TCIPP in ELV foam and ELV fabric samples combined in our study (2700 mg/kg – this is the average of both ELV foam and fabric samples – and a similar approach was taken to derive a single average concentration for C&D EPS and XPS), results in an estimated 10,000 kg/year of TCIPP associated with ELV foams and fabrics. We emphasise the preliminary nature of these estimates, and acknowledge the uncertainties inherent in them. For example, estimating the mass of waste materials generated annually involves substantial uncertainty – for example, direct estimates of waste furniture foam for Ireland are unavailable, and we have thus extrapolated from estimated UK arisings of waste furniture and applied our own judgement to estimate how much of this is foam (see Table SD-4). Coupled with this, while this study is to the authors' knowledge one of the most extensive of its kind to date anywhere; the degree to which the samples analysed are representative of such articles in Ireland is uncertain. Regardless of these caveats, we believe our estimates constitute an informative overview of the presence of Cl-OPEs in the Irish waste stream.

Particularly notable is that the mass of Cl-OPEs (principally TCIPP and TDCIPP) entering the Irish waste stream in 2019, is – at ~147,000 kg – an order of magnitude greater than the ~10,200 kg PBDEs, HBCDD, and tetrabromobisphenol-A (TBBP-A) estimated to be entering the Irish waste stream in 2019 (Drage et al., 2022). Of the ~74,000 kg TDCIPP; 74 % were associated with ELV foams/fabrics, with most of the rest (20 %) present in furniture foams. TCIPP contamination is more evenly distributed; 34 % of the ~70,000 kg entering the Irish waste stream in 2019, is found in mattress foam, with 29 %, 20 %, and 14 % associated with: building insulation foam, furniture foam, and ELV foams and fabrics respectively. Meanwhile, of the ~3100 kg TCEP entering the Irish waste stream in 2019, most (77 %) is associated with furniture foam, with the bulk of the remainder (20 %) found in ELV foams and fabrics. These data regarding the distribution of Cl-OPEs across different waste categories may assist in directing monitoring resources towards those waste categories most contaminated with Cl-OPEs. Specifically, where monitoring resources are limited, focusing on those waste categories carrying most of the Cl-OPE burden is recommended.

*3.1.5. Implications of enforcement of notional limit values on mass of Cl-OPEs removed from the waste stream and mass of waste rendered unrecyclable*

While there is presently no legislation preventing waste from being recycled due to its Cl-OPE content, as highlighted in the introduction, the currently suspended restriction proposal of ECHA on Cl-OPE use (ECHA, 2019), led us to consider the impact should in future a 1000 mg/kg limit (i.e. equivalent to that in place for PBDEs and HBCDD at the time of sample collection and analysis) be introduced on concentrations of TCEP, TCIPP, and TDCIPP.

To do so, in Table 4 we show: (a) the mass of each waste category containing Cl-OPE concentrations >1000 mg/kg and that therefore would – should such a limit be enforced – not be able to be recycled; and (b) the percentage of Cl-OPEs associated with this unrecyclable material and thus removed from the waste stream. To illustrate, 8/16 (50 %) of furniture foam samples contain at least one Cl-OPE at a concentration >1,000 mg/kg;

**Table 4**
Estimated Annual Mass (t/year[a]) of material in each waste category studied that exceeds limit value of 1000 mg/kg and annual mass of Cl-OPEs (kg/year[a]) associated with such material.

| Category | *t* > 1000 mg/kg/yr | TCEP associated with material > 1000 mg/kg (kg/yr) | TCIPP associated with material > 1000 mg/kg (kg/yr) | TDCIPP associated with material > 1000 mg/kg (kg/yr) | ΣCl-OPEs associated with material > 1000 mg/kg (kg/yr) |
|---|---|---|---|---|---|
| C&D insulation foam | 2200 | 0.12 | 20,000 | 1600 | 22,000 |
| ELV foams and fabrics | 1600 | 580 | 9600 | 55,000 | 65,000 |
| Carpets | 380 | 0.01 | 610 | 0 | 610 |
| Curtains | 59 | 0.79 | 44 | 79 | 120 |
| Furniture foam | 1300 | 2300 | 14,000 | 15,000 | 31,000 |
| Furniture fabrics | 170 | 0.02 | 280 | 200 | 480 |
| Mattress foam | 1100 | 8.0 | 24,000 | 220 | 24,000 |
| Mattress fabrics | 380 | 0.92 | 270 | 450 | 720 |
| Total[b] | 7200 | 2900 | 68,000 | 72,000 | 144,000 |
| % captured by Limit implementation | | 93 | 98 | 98 | 98 |
| % > 1000 mg/kg | 24 | | | | |

[a] Rounded to 2 significant figures.
[b] Totals may differ due to rounding.

thus of the 2600 t of waste furniture foam generated annually, 1300 t would not be able to be recycled if a 1000 mg/kg limit was enforced. Multiplying the average concentration of TCIPP in those 8 samples that contain >1000 mg/kg of 1 or more Cl-OPEs (10,800 mg/kg), by 1300 t; reveals them to contain a total of 14,000 kg of TCIPP. Table 4 shows that enforcement of a limit value of 1000 mg/kg for each of TCEP, TCIPP, and TDCIPP as an individual contaminant, will result in ~24 % (~7200 t) of the estimated ~30,000 t per year of the waste materials studied generated in Ireland in 2019 exceeding these limit values. Balanced against this, this material containing one or more of our target Cl-OPEs >1000 mg/kg contains ~144,000 kg or 98 % of the total mass of these Cl-OPEs (~147,000 kg) associated with the waste materials studied. Clearly, notwithstanding the reduction in the quantity of waste recycled and the technical, logistical, and economic issues associated with implementing a 1000 mg/kg limit on Cl-OPEs in waste; its implementation would likely be very effective in removing Cl-OPEs from the recycling stream. Moreover, should a lower limit value – e.g. in line with the recently (i.e. June 2022) agreed lower limit for PBDEs and HBCDD of 500 mg/kg – be set for Cl-OPEs; an even greater mass of these HFRs would be removed from the recycling stream.

It is important to note at this juncture, that currently it is likely that most (if not all) of the waste falling into the categories studied here, is not recycled and is instead either incinerated or landfilled. However, this study provides valuable information given potential moves towards increasing recycling of soft furnishings, ELV waste, and building insulation foam. Given the vast mass of waste involved and the economic costs of measuring Cl-OPEs via GC–MS on such a scale; in practice, procedures for checking compliance of waste with any future limits on Cl-OPE concentrations, are likely to be screening methods (e.g. X-ray fluorescence or density flotation) which anecdotal reports indicate are used by waste handlers to verify compliance with similar limits on PBDEs and HBCDD.

## 4. Conclusions

Enforcement of a 1000 mg/kg limit on each of TCEP, TCIPP, and TDCIPP in waste such that items exceeding this value were not permitted to be recycled, would result in removal of ~98 % of the sum of these Cl-OPEs from the Irish recycling stream. While this would also result in ~7200 t/year of such waste (24 % of the ~30,000 t/year generated in 2019) being rendered unrecyclable; the effectiveness of such a limit in removing Cl-OPEs from the recycling stream is clear.

Comparison of Cl-OPE concentrations in samples collected in 2019–20 with those in samples from the same waste categories collected in 2015–16 revealed few significant differences, with the principal feature being significantly higher concentrations in ELV foams of both TDCIPP and TCIPP in 2019–20. Further monitoring of Cl-OPEs in the waste stream is recommended to facilitate elucidation of temporal trends.

## Funding

This project (SAFER, reference 2018-RE-LS-3) is funded under the EPA Research Programme 2014–2020. The EPA Research Programme is a Government of Ireland initiative funded by the Department of Communications, Climate Action, and Environment. A.H. Rosa thanks the São Paulo Research Foundation (FAPESP, grants 2019/06800-5; 2022/00985-6) for fellowship and financial support. M. Alghamdi acknowledges her PhD scholarship award from the Department of Laboratory Medicine, Faculty of Applied Medical Sciences, Umm al-Qura University, Mecca, Saudi Arabia. Scholarship decision reference 4001065578.

## CRediT authorship contribution statement

**Stuart Harrad:** Supervision; Writing - Original manuscript preparation; Funding acquisition.

**Martin Sharkey**: Investigation; Writing - Review & Editing.

**William Stubbings:** Investigation; Writing - Review & Editing.

**Misbah Alghamdi:** Investigation; Writing - Review & Editing.

**Harald Berresheim:** Supervision; Writing - Review & Editing; Funding acquisition.

**Marie Coggins:** Supervision; Writing - Review & Editing.

**André Henrique Rosa:** Investigation; Writing - Review & Editing.

**Daniel Drage**: Investigation; Writing - Review & Editing.

## Data availability

Data will be made available on request.

## 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.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2022.160250.

## References

Alghamdi, M., Abdallah, M.A.E., Harrad, S., 2022. The utility of X-ray fluorescence spectrometry as a tool for monitoring compliance with limits on concentrations of halogenated flame retardants in waste polymers: a critical review. Emerg. Contam. 8, 9–20.

Cooper, E.M., Kroeger, G., Davis, K., Clark, C.R., Ferguson, P.L., Stapleton, H.M., 2016. Results from screening polyurethane foam based consumer products for flame retardant chemicals: assessing impacts on the change in the furniture flammability standards. Environ. Sci. Technol. 50, 10653–10660.

Council of the EU, 2022. Council and Parliament agree to reduce limit values for the presence of persistent organic pollutants in waste. https://www.consilium.europa.eu/en/press/press-releases/2022/06/21/council-and-parliament-agree-to-reduce-limit-values-for-the-presence-of-persistent-organic-pollutants-in-waste/?utm_source=dsms-auto&utm_medium=email&utm_campaign=Council+and+Parliament+agree+to+reduce+limit+values+for+the+presence+of+persistent+organic+pollutants+in+waste accessed 11th November 2022.

Drage, D., Sharkey, M., Al-Omran, L.S., Stubbings, W.A., Berresheim, H., Coggins, M., Rosa, A.H., Harrad, S., 2022. Halogenated flame retardants in Irish waste polymers: concentrations, legislative compliance, and preliminary assessment of temporal trends. Environ. Pollut. https://doi.org/10.1016/j.envpol.2022.119796.

ECHA, 2018. Draft screening report – an assessment of whether the use of TCEP, TCPP, and TDCP in articles should be restricted.Available at https://echa.europa.eu/documents/10162/df7715f2-e413-8396-119b-63f929bcde0c accessed 11th July 2022.

ECHA, 2019. Registry of restriction intentions until outcome. https://echa.europa.eu/registry-of-restriction-intentions/-/dislist/details/0b0236e1829a30b8 accessed 11th July 2022.

European Union, 2008. European Union Risk Assessment Report, Tris (2-chloro-1 methylethyl) phosphate (TCPP) risk assessment. Available at https://echa.europa.eu/documents/10162/13630/trd_rar_ireland_tccp_en.pdf/315063b0-593d-4703-9519-562c258506e6 accessed 19th July 2022.

European Union, 2019. Regulation (EU) 2019/1021 of the European Parliament and of the Council of 20 June 2019 on persistent organic pollutants.Available atOff. J. Eur. Union 169/45 accessed 19th July 2022.

Guzzonato, A., Puype, F., Harrad, S., 2017. Evidence of bad recycling practices: BFRs in children's toys and food-contact articles. Environ. Sci.: Processes Impacts 19, 956–963.

Marklund, A., Andersson, B., Haglund, P., 2003. Screening of organophosphorus compounds and their distribution in various indoor environments. Chemosphere 53, 1137–1146.

Puype, F., Samsonek, J., Knoop, J., Egelkraut-Holtus, M., Ortlieb, M., 2015. Evidence of waste electrical and electronic equipment (WEEE) relevant substances in polymeric food-contact articles sold on the European market. Food Addit. Contam., Part A 32, 410–426.

Stapleton, H.M., Sharma, S., Getzinger, G., Ferguson, P.L., Gabriel, M., Webster, T.F., Blum, A., 2012. Novel and high volume use flame retardants in US couches reflective of the 2005 PentaBDE phase out. Environ. Sci. Technol. 46, 13432–13439.

Stubbings, W.A., Drage, D.S., Harrad, S., 2016. Chlorinated organophosphate and "legacy" brominated flame retardants in UK waste soft furnishings: a preliminary study. Emerg. Contam. 2, 185–190.

Wei, G.L., Li, D.Q., Zhuo, M.N., Liao, Y.S., Xie, Z.Y., Guo, T.L., Li, J.J., Zhang, S.Y., Liang, Z.Q., 2015. Organophosphorus flame retardants and plasticizers: sources, occurrence, toxicity and human exposure. Environ. Pollut. 196, 29–46.