CHLORINATED ORGANOPHOSPHATE FLAME RETARDANTS IN WASTE FABRICS AND FOAMS: IMPLICATIONS FOR WASTE MANAGEMENT

by

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Abstract

The presence of some brominated flame retardants (BFRs) in food contact articles and childcare goods at levels lower than those allowed for flame retardancy is frequently linked to the recycling of flame retardant-treated plastics. In response to this, Low POP Concentration Limits (LPCLs) on the maximum permissible concentrations of some BFRs in waste have been established to ensure that waste plastics exceeding such limits are not recycled, hence limiting further contamination of the recycled plastic stream. Given that chlorinated organophosphate flame retardants (Cl-OPFRs) have similar toxicity and health impacts as BFRs, similar concentration limits are predicted to be adopted in the near future for Cl-OPFRs. This study measured Cl-OPFRs in fabrics and foams of waste furniture, end-life vehicle and childcare items from Ireland, the UK, and Saudi Arabia. Our investigation revealed that tris(1-chloro-2-propyl) phosphate (TCIPP) was the predominant Cl-OPFR detected in furniture and childcare items, while tris(1,3-dichloro-2-propyl) phosphate (TDCIPP) was the predominant Cl-OPFR detected in vehicles and childcare items intended for car use. Cl-OPFR concentrations in the UK and Ireland significantly exceeded those in Saudi Arabia likely because of international differences in fire safety regulations. In addition, this study evaluated the utility of X-ray fluorescence (XRF) as a screening tool for regulatory compliance. Specifically, we measured chlorine (Cl) and phosphorus (P) as a surrogate indicator of the presence of Cl-OPFRs in waste fabric and foam. Our investigation revealed that XRF was not a reliable tool for identifying articles containing levels of Cl-OPFRs exceeding the national limit of 1,000 mg/kg. This is because of the high incidence of false exceedances observed in our analyses in 81 %, 74 %, and 97 % of samples from Ireland, the UK, and Saudi Arabia, respectively, as well as the high positive slopes and y-intercepts of plots of XRF Cl

against GC/MS (gas chromatography/mass spectrometry) measurements of Cl-OPFRs. Finally, as human exposure to Cl-OPFRs via inhalation, dust ingestion, and dietary intake is crucial, this study assessed exposure to Cl-OPFRs via dermal contact with upholstered items. Our estimates of adult and toddler exposure to Cl-OPFRs via dermal uptake fall below the relevant health-based limit values.

Dedication

This thesis is dedicated to the memory of my brother

Ahmad Hassan Alghamdi

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List of Publications

Alghamdi, M., Abdallah, M.A.E. and 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. ***Emerging contaminants***, 8, pp.9-20.

Harrad, S., Drage, D., Sharkey, M., Stubbings, W., **Alghamdi, M.**, Berresheim, H., Coggins, M. and Rosa, A.H. (2023). Elevated concentrations of halogenated flame retardants in waste childcare articles from Ireland. ***Environmental Pollution***, 317, pp.120732-120738.

Harrad, S., Sharkey, M., Stubbings, W.A., **Alghamdi, M**., Berresheim, H., Coggins, M., Rosa, A.H. and 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***, 859, pp.160250-160256.

Conference presentations

Alghamdi, M., Abdallah, M.A.E. and Harrad, S. (2023). Chlorinated organophosphate flame retardants in childcare articles. 2023 Emerging Contaminants in the Environment Conference; Illinois, United States (Virtual presentation)

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Abbreviations

ABS	Acrylonitrile butadiene styrene
ANOVA	Analysis of variance
BAT/BEP	Best available technique and the best environmental practice
BFR	Brominated flame retardant
Br	Bromine
BSA	Body surface area
BW	Body weight
C&D	Construction and demolition
CHCC	Chemical of high concern to children
Cl	Chlorine
Cl-OPFR	Chlorinated organophosphate flame retardant
CDR	Chemical data reporting
CSF	Cancer slope factor
DED	Daily exposure dose
DCM	Dichloromethane
ECHA	European chemicals agency
EEE	Electrical and electronic equipment
EHFR	Emerging halogenated flame retardants
EI	Electron ionisation
ELV	End-of-life vehicle
EPA	Environemtal protection agency
EPS	Expanded polystyrene
EU	European commission
F	Fluorine
FA	fraction absorbed
FCA	Food contact article
FTIR	Fourier transform infrared spectrometers
GC/MS	Gas chromatography/ mass spectrometry
HBCDD	Hexabromocyclododecane
HBLV	Health-based limit value

HFR Halogenated flame retardant

HI Health index

HIPS High impact polystyrenes

HPLC High performance liquid chromatography

HPLC-MS/MS High Performance Liquid Chromatography- mass spectrometry

HQ Health quotient

I Iodine

IBM SPSS Statistical Package for the Social Sciences

IDL Instrument detection limit

IEF Indoor exposure fraction

IS Internal standard

K_{ow} n-octanol/water partition coefficient

LC/MS Liquid chromatography/ mass spectrometry

LOD Limit of detection

LOQ Limit of quantification

LPCL Low POP concentration limit

NOAEL No observed adverse effect level

OPFR Organic phosphorus flame retardant

PBDE Polybrominated diphenyl ether

PCB-62 2,3,4,6- tetrachlorobiphenyl

PFR Phosphorus flame retardant

POP Persistent organic pollutant

PUF Polyurethane foam

PVC Polyvinyl chloride

QA/QC Quality assurance/ quality control

RDS Recovery determination standard

REACH Registration, evaluation, authorisation and restriction of chemicals

RfD Reference dose

RoHS Restriction of hazardous substances

RRF Relative response factor

RSD Relative standard deviation

SAFER Screening of the Irish Waste Stream for Persistent Organic Chemicals

SCHER	Scientific committee on health and environmental risks
SF	Safety factor
SDL	Sample detection limit
SVHC	Substance of very high concern
TBBPA	Tetrabromobisphenol A
TBP	Tribromophenol
TCEP	Tris(2-chloroethyl) phosphate
TCIPP	Tris(1-chloro-2-propyl) phosphate
TDCIPP	Tris(1,3-dichloro-2-propyl) phosphate
TSCA	Toxic substances control act
UF	Uncertainty factor
UNEP	United nations environment programme
UTC	Unintentional trace contaminant
V6	Tetrakis (2-chloroethyl) dichloroisopentyl diphosphate
WAFER	Evaluation of hand-held XRF for screening waste articles for exceedances of limit values for brominated flame retardants
WEEE	Waste electrical and electronic equipment
XPS	Extruded polystyrene
XRF	X-ray fluorescence

Thesis structure and objectives

The thesis begins by providing a list of publications, abbreviations, and a table of contents, which ensures an informative and organised presentation of the research.

The thesis conducted analyses of waste fabric and foam samples from soft furnishing and childcare items from the UK, Ireland, and Saudi Arabia. Concentrations of chlorine (Cl) and phosphorus (P) were determined using XRF, while Cl-OPFRs concentrations were obtained through GC/MS analyses.

Chapter 1: The thesis begins with an introduction providing an overview of Cl-OPFRs, their physicochemical properties, applications, and occurrence in the environment. Furthermore, information regarding the toxicity of Cl-OPFRs and human exposure routes is included. Moreover, the chapter identifies existing knowledge gaps and outlines hypotheses as well as objectives.

Some sections in this chapter have been previously published in the critical review (as first- author), while additional sections were added particularly for the thesis, moreover, the chapter has been revised with recent research related to the same area.

Chapter 2: details the sampling procedure, chemical analyses, and QA/QC protocols followed to ensure accurate and precise measurements of Cl, P, and the three Cl-OPFRs. The employed techniques included XRF and GC/MS; in addition, the statistical analyses used to evaluate the data are described.

Chapter 3: presents concentrations of Cl-OPFRs in waste furniture and childcare items from three countries, alongside concentrations of Cl-OPFRs in ELV fabric and foam samples from Ireland and examines the implications of these data for waste management and legislation. The data of Cl-OPFRs in furniture and

childcare items waste from Ireland were co-authored and published in two separate publications.

Chapter 4: focuses on Cl and P concentrations in waste fabrics and foams from furniture, ELV, and childcare items from three countries, evaluating the efficiency of XRF as a screening technique to ensure compliance with regulatory limits exceeding 1,000 mg/kg for Cl-OPFRs. Additionally, it discusses potential explanations for false exceedances.

Chapter 5: explores the assessment of dermal exposure of adults and toddlers to Cl-OPFRs through contact with fabrics from furniture, childcare articles, and vehicles in Ireland and the UK. Finally, exposure estimates are compared with health-based limit values to determine if such exposure can pose risk to human health.

Chapter 6: summarises the thesis findings with reference to the thesis hypotheses and provides insights and recommendations for future research.

Thesis hypotheses

1. XRF is a viable tool for screening waste for compliance with potential limits on maximum permissible concentrations of Cl-OPFRs.

2. Cl-OPFRs have been extensively used in consumer products, and

3. the levels and relative abundance of Cl-OPFRs will be subject to international variation due to national differences in flame retardancy regulations and the means via which they are met.

4. The high concentrations of Cl-OPFRs in furniture and childcare items may lead to substantial exposure via the dermal pathway.

Thesis objectives

1. Compare XRF readings for Cl and P to the GC/MS results obtained for a wide range of plastic waste articles.

2. Enhance understanding of the causes of any false positive and false negative readings obtained.

3. Report for the first time on the concentrations of Cl-OPFRs in waste items including furniture and childcare items from three countries (Ireland, UK, and Saudi Arabia).

4. Estimate human exposure to Cl-OPFRs via dermal uptake following different scenarios.

Chapter 1: Introduction

This chapter contains sections some material taken verbatim from the following publications:

Alghamdi, M., Abdallah, M.A.E. and 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. ***Emerging contaminants***, 8, pp.9-20.

1.1 Overview

Chemicals used as flame retardants are additives incorporated into many flammable substances like plastics, furniture, textile, surface finishing and coatings to interrupt the ignition cycle either physically or chemically during one or more of the phases of heating, decomposition, ignition, or flame propagation (Khandual, 2014).

Flame retardants can be classified as either a reactive or an additive chemical. Additive flame retardants are only physically mixed with polymers but not chemically bound, and thus can be easily released from treated products to the surrounding environment. In contrast, reactive flame retardants are covalently bonded with polymers (Khandual, 2014; OEHHA, 2008) and are thus less easily emitted from the products within which they are incorporated. In 2003, more than 175 chemicals were classified as flame retardants. Of these, 50 %, 25 %, 20 % and 5 % are classified as inorganic, halogenated organic, organophosphorus, and nitrogen-based flame retardants, respectively (Figure 1.1) (Alaee et al., 2003).

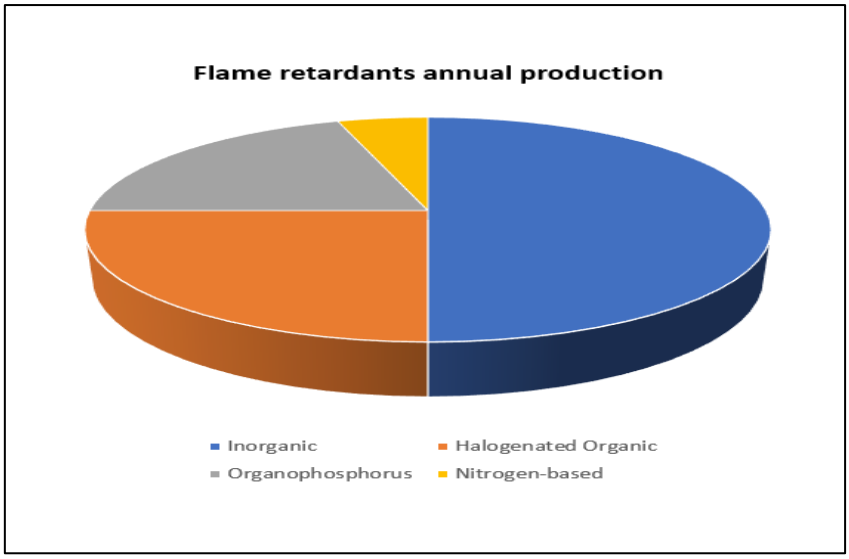


Figure 1. 1: Percentage of annual production of flame retardants according to chemical classification (Alaee et al., 2003)

The most diverse class of flame retardants are the halogenated flame retardants (HFRs) (Khandual, 2014). Four classes of HFRs may be defined, depending on whether they contain fluorine (F), chlorine (Cl), bromine (Br), or iodine (I). Brominated flame retardants (BFRs) are considered more effective than their chlorinated counterparts because their decomposition products are less volatile at elevated temperatures as bromine is heavier than chlorine (Segev et al., 2009). Despite these attributes with respect to flame retardancy, BFRs including polybrominated diphenyl ethers (PBDEs) have been found to be toxic, persistent, and capable of bioaccumulation in people and wildlife (Xu et al., 2017). As a result, several BFRs, including PBDEs, have been banned and phased out globally under the UNEP (United Nations Environment Programme) Stockholm Convention on Persistent Organic Pollutants (POPs). Consequently, there has been a growing demand for alternative flame retardants to comply with flammability regulations (Van der Veen and de Boer, 2012), some of which are referred to as emerging halogenated flame retardants (EHFRs) (Ekpe et al., 2020).

Phosphorus flame retardants (PFRs), which accounted for 20% of flame-retardant consumption in the EU in 2006, are often suggested as BFR alternatives (Xu et al., 2017). PFRs can be divided into three basic groups – i.e., inorganic, organic and halogenated organic phosphorus flame retardants (OPFRs) (Van der Veen and de Boer, 2012). According to the EU's Scientific Committee on Health and Environmental Risks (SCHER), chlorinated organophosphate flame retardants (Cl-OPFRs) are commonly used as potential alternatives for BFRs, including tris(1-chloro-2-propyl) phosphate (TCIPP), tris(1,3-dichloro-2-propyl) phosphate (TDCIPP), and tris(2-chloroethyl) phosphate (TCEP) (van der Veen, 2012).

1.2 Applications of Cl-OPFRs

In the commercial world, the use of Cl-OPFRs is widely spread across many industries, including flame retardants for plastics, electronics, textiles, building materials, lubricants, hydraulic fluids, paints, furniture, and automobiles; additionally, as stabilizers, plasticizers, antifoaming, and wetting materials.

TCEP is used in the manufacture of flexible and rigid polyurethane foams (PUFs), plastics, carpet, and textile back coatings (OEHHA, 2008), and is commonly applied as an additive flame retardant and plasticizer to polyesters and other polymers (e.g., Polyvinyl chloride (PVC) and polyisocyanurate), acrylic resins, adhesives, paints, varnishes, furniture (including upholstery) and construction (including roofing insulation). The main industrial sectors that use TCEP as a flame-retardant plasticizer are vehicles, railways, and aircraft (ECHA, 2008a; ECHA, 2010; cec.org, 2015). Paints containing TCEP were still being manufactured in Europe in 2004, although it was considered that these paints were intended for professional rather than consumer use (ECHA, 2010).

TCIPP is among the least costly and highest selling of the Cl-OPFRs, at least partly due to its use as an additive flame retardant in PUF (Khandual, 2014; ECHA, 2018a). The main use of TCIPP (more than 80 %) is in rigid PUF for building construction materials including adhesives, sealants, and roofing laminates (WHO, 2004; Danish EPA, 2016; EPA, 2018). The use in rigid PUF may be further sub-divided into blocks and spray systems for building insulation and for fridge casings. A smaller but still significant amount (about 17 %) of TCIPP is used in flexible furniture PUF as well as upholstery in the UK and Irish markets (WHO, 2004; Danish EPA, 2016). Due to its instability and fogging capacity, TCIPP appears not to be employed in flexible PUF for automobile industries (Danish EPA, 2016). TCIPP is also utilized as a flame retardant and plasticizer for manufacturing plastics, resins, fabrics, textile, leather, apparel, PVC, and electronics products (EPA, 2018). There is also moderate consumption of TCIPP in textile back-coating formulations (WHO, 2004).

TDCIPP is also used in the manufacture of flexible and rigid PUF. The more expensive TDCIPP is mostly employed in automobiles for moulded seat foam like seat cushions, seat, headrests, roofing, and fabric linen (ECHA, 2018a; Wang et al., 2020). In addition, TDCIPP is also added to a wide range of manufactured items like furnishings, textiles, coating, adhesives, electronics, construction materials, resins, plastics, as well as wires and cables (cec.org, 2015). TDCIPP and TCIPP commonly exist in the same market domain. However, because the price of TDCIPP is double that of TCIPP, it is employed only in those applications where a more effective flame retardant is needed to comply with more stringent fire retardancy standards (ECHA, 2008b) because in terms of oxidation and degradation by Cl attack, TDCIPP is more stable (Ekpe et al., 2020). Table 1.1 sums up the applications of Cl-OPFRs to show similarities and differences of these chemicals' utilisation (cec.org, 2015).

Table 1. 1: Cl-OPFR applications in intermediate and manufactured goods (cec.org, 2015)

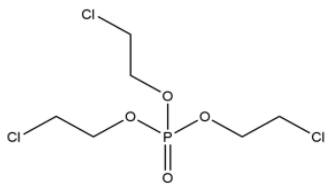
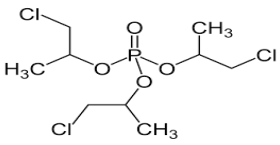
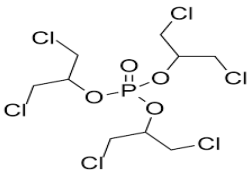
	TCEP	TCIPP	TDCIPP
Rigid & flexible PUF	●	●	●
Resin & Polyvinyl chloride (PVC)	●	●	
Rigid plastic & textiles	●	●	●
Flexible plastic/ rubber		●	
Spray foam	●	●	●
Furnishings, electronic, textiles, coatings & adhesives	●	●	●
Construction materials	●	●	
Automotive	●		●
Wires & cables			●

1.3 Physicochemical properties of Cl-OPFRs

The structures, as well as the physicochemical properties of TCEP, TCIPP, and TDCIPP display some similarities. However, there are significant variations in molecular weight, vapour pressure, water solubility and octanol/water partition coefficient between TCEP and TDCIPP. The similarity between TDCIPP and TCIPP is greater than that between TDCIPP and TCEP, although the water solubility and vapour pressure of TDCIPP and TCIPP differ by an order of magnitude (ECHA, 2018a) (Table 1.2).

TCEP was found as an impurity (4.5-10 % by weight) in the tetrakis (2-chloroethyl) dichloroisopentyl diphosphate (V6) commercial mixture, the least consumed Cl-OPFR (Ekpe at al., 2020). V6 is formed by the reaction of pentaerythritol, phosphorus trichoride, chlorine and ethylene oxide, which is frequently used in PUF for the furniture and automobile sectors (Ekpe et al., 2020).

Table 1. 2: Physicochemical properties of Cl-OPFRs

	TCEP	TCIPP	TDCIPP
CAS number	115-96-8	13674-84-5 6145-73-9	13674-87-8
Molecular weight (g/mol)	285.48	327.57	430.90
Physical State at Room Temperature	Liquid	Liquid	Liquid
Solubility	Soluble in most organic solvents. Insoluble in benzene	Soluble in most organic solvents	Soluble in most organic solvents
Molecular formula	$C_6H_{12}Cl_3O_4P$	$C_9H_{18}Cl_3O_4P$	$C_9H_{15}Cl_6O_4P$
Chemical structure			
Water solubility (mg/L)	7820	1080	18
Melting point	-55° C	-40° C	-58° C
Boiling point	Decompose at 320 °C	Decompose at 288 °C	Decompose at 326 °C
Vapour pressure (Pa) at 20 °C	1.14×10^{-3}	1.4×10^{-3}	5.6×10^{-6}
Log K_{ow} [c]	1.78	2.68	3.68
Density (g/cm^3) at 25° C	1.42	1.29	1.48
Odour	Slight	Moderate	Moderate
References	**(WHO, 1998; EPA, 2015; U.S. EPA, 2015a; ECHA, 2018a)**		

1.4 Mechanisms of action of Cl-OPFRs as flame retardants

Generally, halogenated OPFRs put together the features of both the halogen and the phosphorus (P) chemical group. The halogen acts directly on the flame, the core of the fire in the vapour phase, while phosphorus provides a char layer of solid phase to disturb the fire chemistry, and sometimes the effect can be synergetic (Van der Veen and de Boer, 2012; Khandual, 2014). In particular, the mechanism of Cl-OPFRs action relies on the chemicals included, for halogenated OPFR in the gas phase (OH. + H.) radicals are removed and replaced by the halogen (usually Cl) that increase the retention of the flame retardant in polymers due to their ability to reduce both vapour pressure and water solubility (Van der Veen and de Boer, 2012; Khandual, 2014), thereby slowing down the burning reaction and the spread of the fire. The advantage of this process is that both Cl and P atoms impart additional flame retardancy, as they both act independently in the polymer molecule (Van der Veen and de Boer, 2012).

1.5 Consumption of Cl-OPFRs

Worldwide consumption of PFRs in 1992, 1995, 2001, 2004, 2007, 2011 and 2015 was 100, 108, 186, 200, 341, 500, and 680 thousand tonnes per year, respectively (Ospina et al., 2018; Yang et al., 2019). More specifically, worldwide production of TCEP, TDCIPP and TCIPP in 2006 exceeded 50,000 tonnes (Xu et al., 2017). Also, the production volume of the three Cl-OPFRs increased from 14,000 to 38,000 tonnes per year in the mid-1980s to 2012 in the U.S.A (Ospina et al., 2018). In 2011, the worldwide demand for Cl-OPFRs was estimated to be approximately 180,000 tonnes and was anticipated to exceed 220,000 tonnes by 2017 (Papagni and Kerzic, 2015).

It is possible to make some observations about the production, current use, export and import of Cl-OPFRs in different countries over the years (Table 1.3). For instance, TCEP use in Finland has declined dramatically from 1598 tonnes in 2004 to 198.4

tonnes in 2008, which was attributed to the fact that TCEP is no longer manufactured in Europe and possibly replaced by TCIPP (OEHHA, 2008; Van der Veen and de Boer, 2012). Since the mid-1960s, TCIPP usage has increased, particularly in rigid and flexible PUF (Van der Veen and de Boer, 2012). TCIPP is a potential replacement for TCEP, and changes in TCIPP use are primarily related to a decrease in TCEP utilisation and a rise in the PUF market (EU RAR, 2008b). Under the Toxic Substances Control Act (TSCA) in the United States of America (U.S.A), the Chemical Data Reporting (CDR) rule requires manufacturers (including importers) to report to the Environmental Protection Agency (EPA) information on the production and use of chemicals in trade (U.S. EPA, 2015b). Therefore, production of TCEP was between 25,000 to 100,000 pounds (11.33 to 45.35 tonnes) as stated to the EPA during the 2016 CDR reporting period. Although the information is provided in ranges, TCEP production has typically declined over recent years (EPA, 2019). To illustrate, as reported to EPA, there was no shift in TCEP production from 1986 to 2002, before a fall between 2006 and 2013. TCEP production then increased and decreased in 2014 and 2015, respectively (EPA, 2019). Meanwhile, due to the higher cost of TDCIPP, the use of TCIPP in residential and workplace furniture foam is more prevalent in the UK to comply with Furniture and Furnishings Fire Safety (Amendment) Regulations 1989 (SI 1989 No. 2538) (EU RAR, 2008b). Meanwhile, the use of TDCIPP in Europe is generally restricted to applications needing a higher level of flame retardancy, such as the automotive industry (EU RAR, 2008a), while TCIPP appears to account for approximately 80 % of total Cl-OPFR use in Europe and is recognised as the most prominent Cl-OPFR in terms of volume (Leisewitz et al., 2001). On the contrary, the consumption of Cl-OPFRs in the U.S.A, mainly TDCIPP, has increased as illustrated by the study of Stapleton et al. (2012), which

revealed that only 24 % of couches purchased before 2005 were treated with TDCIPP, but the proportion of treated couches with TDCIPP increased to 52 % for those purchased after 2005 (Stapleton et al., 2012).

Table 1. 3: Cl-OPFR production, use, import and export volumes over various years in different countries

Chemicals	Produced, in use, imported and/ or exported volume (tonnes/year)	Country	Year	Reference
TCEP	>1 million to 10 million lbs* (>453.5 to 45359.2 tonnes) (produced and imported)	**U.S.A**	**1986, 1990, 1994 and 2002**	**(EPA, 2019) (OEHHA, 2008)**
	500-100 (produced/ in use)	**Germany**	**1977**	**(Brommer, 2014)**
	9000 (in use)	**Worldwide**	**1989**	**(WHO, 2004)**
	2040 (produced/ in use)	**EU**	**1995**	**(van der Veen and de Boer, 2012)**
	400 (produced/ in use)	**UK**	**1995**	**(van der Veen and de Boer, 2012)**
	4000 (in use)	**Worldwide**	**1997**	**(WHO, 2004)**
	2000 (produced)	**EU**	**1998**	**(ECHA, 2010)**
	143 (exported)	**EU**	**2002**	**(ECHA, 2010)**
	1007 (produced)	**EU**	**2002**	**(ECHA, 2010)**
	1286 (produced/ in use)	**Norway**	**2003**	**(van der Veen and de Boer, 2012)**
	798.5 (produced/ in use)	**Norway**	**2004**	**(van der Veen and de Boer, 2012)**
	1598 (produced/ in use)	**Finland**	**2004**	**(van der Veen and de Boer, 2012)**
	300-500 (produced)	**EU**	**2005**	**(ECHA, 2010)**
	300-400 (exported)	**EU**	**2005**	**(ECHA, 2010)**
	227-254 (produced/ in use)	**U.S.A**	**2006**	**(van der Veen and de Boer, 2012)**
	261.3 (produced/ in use)	**Norway**	**2008**	**(van der Veen and de Boer, 2012)**
	0.1 (produced/ in use)	**Denmark**	**2008**	**(van der Veen and de Boer, 2012)**
	198 (produced/ in use)	**Finland**	**2008**	**(van der Veen and de Boer, 2012)**
	400 (produced)	**EU**	**2009**	**(ECHA, 2010)**
	1000 (in use)	**EU**	**2009**	**(ECHA, 2010)**
	CBI** (imported)	**U.S.A**	**2011**	**(cec.org, 2015)**
	120 (produced/ in use)	**Australia**	**2011**	**(Brommer, 2014)**
	25,000 to 100,000 lbs (11.33 to 45.35 tonnes) (produced)	**U.S.A**	**2012-2013**	**(EPA, 2019)**

	79,364 lbs (35.99 tonnes) (imported)	**U.S.A**	**2012**	**(EPA CDR, 2016)**
	39,682 lbs (17.99 tonnes) (imported)	**U.S.A**	**2013**	**(EPA CDR, 2016)**
	158,728 lbs (71.99 tonnes) (imported)	**U.S.A**	**2014**	**(EPA CDR, 2016)**
	100,000 to 500.,000 lbs (45.35 to 226.7 tonnes) (produced)	**U.S.A**	**2014**	**(EPA, 2019)**
	25,000 to 100,000 lbs (11.33 to 45.35 tonnes) (produced)	**U.S.A**	**2015**	**(EPA, 2019)**
TCIPP	22,950 (produced/ in use)	**EU**	**1995**	**(van der Veen and de Boer, 2012)**
	2750 (produced/ in use)	**UK**	**1995**	**(van der Veen and de Boer, 2012)**
	40,000 (produced/ in use)	**Worldwide**	**1997**	**(WHO, 2004) (van der Veen and de Boer, 2012)**
	5000-6000 (produced/ in use)	**Germany**	**1997**	**(Brommer, 2014)**
	36,000 (produced)	**EU (Germany and UK)**	**2000**	**(ECHA, 2008c)**
	2,000 (imported)	**EU (Germany and UK)**	**2000**	**(ECHA, 2008c)**
	>40,000 (in use)	**EU**	**2000**	**(ECHA, 2008c)**
	50 (produced/ in use)	**Norway**	**2001**	**(van der Veen and de Boer, 2012)**
	812.9 (produced/ in use)	**Finland**	**2001**	**(Brommer, 2014)**
	704.2 (produced/ in use)	**Denmark**	**2001**	**(Brommer, 2014)**
	145 (produced/ in use)	**Sweden**	**2001**	**(Brommer, 2014)**
	290 (produced/ in use)	**Australia**	**2001**	**(Brommer, 2014)**
	50.5 (produced/ in use)	**Norway**	**2001**	**(Brommer, 2014)**
	42.7 (produced/ in use)	**Norway**	**2008**	**(van der Veen and de Boer, 2012)**
	177 (produced/ in use)	**Denmark**	**2008**	**(van der Veen and de Boer, 2012)**
	16,429 (produced/ in use)	**Finland**	**2008**	**(van der Veen and de Boer, 2012)**
	132 (produced/ in use)	**Sweden**	**2008**	**(van der Veen and de Boer, 2012)**
	>46,000 (in use)	**EU**	**2008**	**(ECHA, 2008c)**
	20 (imported)	**Mexico**	**2009**	**(cec.org, 2015)**
	40 (imported)	**Mexico**	**2010**	**(cec.org, 2015)**
	82 (imported)	**Mexico**	**2011**	**(cec.org, 2015)**

	160 (imported)	**Mexico**	**2012**	**(cec.org, 2015)**
	240 (imported)	**Mexico**	**2013**	**(cec.org, 2015)**
	199.5 (produced/ in use)	**Denmark**	**2010**	**(Brommer, 2014)**
	84 (produced/ in use)	**Sweden**	**2010**	**(Brommer, 2014)**
	43.3 (produced/ in use)	**Norway**	**2010**	**(Brommer, 2014)**
	19,600 (produced)	**U.S.A**	**2010-2011**	**(Kim et al., 2019)**
	24,800 (produced and imported)	**U.S.A**	**2011**	**(cec.org, 2015)**
	54,673,933 lbs (24799.6 tonnes) (produced)	**U.S.A**	**2012**	**(EPA, 2015) (EPA, 2018)**
	33341068 lbs (16670.534 tonnes) (produced) 3158099 lbs (1579.0495 tonnes) (imported)	**U.S.A**	**2012**	**(EPA CDR, 2016)**
	39112090 Ibs (19556.045 tonnes) (produced) 4119002 Ibs (2059.501 tonnes) (imported)	**U.S.A**	**2013**	**(EPA CDR, 2016)**
	40912198 Ibs (20456.099 tonnes) (produced) 3320734 Ibs (1660.367 tonnes) (imported)	**U.S.A**	**2014**	**(EPA CDR, 2016)**
	10-50 million Ibs (4535.9- 22679.6 tonnes) (produced)	**U.S.A**	**2012-2013**	**(EPA, 2018)**
	50-100 million Ibs (22679.6- 45359.2 tonnes) (produced)	**U.S.A**	**2014-2015**	**(EPA, 2018)**
TDCIPP	>8,000 (produced/ in use)	**Worldwide**	**1997**	**(WHO, 2004) (van der Veen and de Boer, 2012)**
	4,500-22,700 (produced/ in use)	**U.S.A**	**1998**	**(van der Veen and de Boer, 2012)**
	10,000 (produced)	**EU (Germany and UK)**	**2000**	**(EU RAR, 2008a) (van der Veen and de Boer, 2012)**
	132.8 (produced/ in use)	**Denmark**	**2000**	**(van der Veen and de Boer, 2012)**
	134.1 (produced/ in use)	**Denmark**	**2001**	**(van der Veen and de Boer, 2012)**
	134.1 (produced/ in use)	**Denmark**	**2002**	**(van der Veen and de Boer, 2012)**
	4500- 22,700 (produced/ in use)	**U.S.A**	**2002**	**(van der Veen and de Boer, 2012)**
	4500- 22,700 (produced/ in use)	**U.S.A**	**2006**	**(van der Veen and de Boer, 2012)**
	4,545–22,700 (unknown)	**U.S.A**	**2011**	**(cec.org, 2015)**
	10-50 million Ibs (4535.9- 22679.6 tonnes) (produced)	**U.S.A**	**2012**	**(Wang et al., 2020) (EPA, 2015)**
	2.2-22 million Ibs (1000- 10,000 tonnes) (produced)	**EU**	**2012**	**(Wang et al., 2020)**

	653,5267 Ibs (3267.6335 tonnes) (imported) 13273754 Ibs (6636.877 tonnes) (produced)	**U.S.A**	**2012**	**(EPA CDR, 2016)**
	2375226 Ibs (1187.613 tonnes) (imported) 11133363 Ibs (5566.6815 tonnes) (produced)	**U.S.A**	**2013**	**(EPA CDR, 2016)**
	10-50 million Ibs (4535.9- 22679.6 tonnes) (produced)	**U.S.A**	**2015**	**(Blum et al., 2019)**

*Ibs abbreviation for pounds unit
**CBI: (confidential business information)

1.6 Occurrence of Cl-OPFRs in the environment

Due to their extensive use as additives and consequent potential for emission from materials to which they are added, Cl-OPFRs are commonly observed in different environmental media (Marklund, 2005) like air and dust (Bergh et al., 2011; Ali et al., 2021), soil and sediment (Yadav et al., 2018), rain and snow (Kim and Kannan, 2018), and water (Zhang et al., 2019).

1.6.1 Cl-OPFRs in air

In various studies, TCEP and TCIPP were frequently detected in air at levels higher than TDCIPP; Also, TCIPP concentrations were often higher than TCEP. In air samples from houses in Japan, TCIPP was found at a maximum concentration of 14,320 ng/m^3 (Saito et al., 2001), while TCEP and TDCIPP were identified at levels up to 372 and 100 ng/m^3, respectively. In offices, TCIPP was detected at the highest median concentration 19.3 ng/m^3, with the TCEP median concentration 11.6 ng/m^3 (Saito et al., 2001).

Bergh et al. (2011) reported the concentration of Cl-OPFRs in air from private houses, day-care centres, and work environments (Bergh et al., 2011) in Sweden. TCIPP displayed the highest mean concentrations in homes (15 ng/m^3) and work environments (110 ng/m^3); while TCEP displayed the highest mean concentration in day care centres (47 ng/m^3). By comparison, TDCIPP was present at the lowest mean concentration in air from houses and day care centres (Bergh et al., 2011). In Switzerland, the highest concentration of TCIPP (260 ng/m3) was primarily observed in cars. TDCIPP, on the other hand, was below the limit of quantification in all samples (Hartmann et al., 2004).

1.6.2 Cl-OPFRs in indoor dust

Several studies have investigated the presence of Cl-OPFRs in indoor dust (Kanazawa et al., 2010; Bergh et al., 2011; Xu et al., 2016; Kim et al., 2019; Ali et al., 2021). The presence of Cl-OPFRs in dust samples could be attributed to the requirement to comply with fire-safety regulations in public buildings as well as a wider range of electronic devices and equipment. In Japan, the median concentration of Cl-OPFRs was significantly higher in multi-surface dust (83,000 ng/g) than in floor dust (30,200 ng/g) from household living areas (Kanazawa et al., 2010). Similarly, the median concentration of Cl-OPFRs in surface dust from homes in Norway (6,826 ng/g) was higher than in floor dust (2,829 ng/g) (Xu et al., 2016). In Sweden, high levels of Cl-OPFRs were mainly associated with work environment dust samples, where TCEP had the highest mean value of (36,000 ng/g) followed by TCIPP (32,000 ng/g) and TDCIPP (30,000 ng/g) (Bergh et al., 2011).

Higher concentrations of TCIPP were reported in dust from UK microenvironments like cars, classrooms, living rooms, and offices, where the median concentrations of TCIPP were 53,000, 16,000, 21,000 and 33,000 ng/g, respectively. The median TDCIPP concentration of 31,000 ng/g in cars was significantly higher than those found in the other examined samples (Brommer and Harrad, 2015). This is consistent with the use of TCIPP and TDCIPP in PUF in the UK. Also, in British homes, stores, and offices, TCIPP was the predominant Cl-OPFR (the median concentration in homes was 64,546 ng/g and in offices and stores was 25,751 ng/g) (Kademoglou et al., 2017). A large study investigated the presence of Cl-OPFRs in 341 house dust samples from 12 countries including China, Colombia, Saudi Arabia, Japan, India, Greece, Kuwait, Pakistan, Romania, the U.S.A, South Korea, and Vietnam. TCIPP was the most abundant of the measured Cl-OPFRs, found at a median of 222 ng/g and

a maximum concentration of 66,700 ng/g, followed by TCEP and TDCIPP at median concentrations 201 (maximum 45,900) and 79.6 (maximum 166,000) ng/g, respectively (Li et al., 2019a). The concentrations of Cl-OPFRs in indoor dust from more industrialized countries (South Korea: median, 3,291; Japan: 4,090; and the U.S.A: 5,150 ng/g) were one or two orders of magnitude higher than those from less industrialized countries (China: 365.4, Colombia: 68.6, Greece: 1,592, India: 42.4, Kuwait: 1,740, Pakistan: 5.05, Romania: 931, Saudi Arabia: 2,620, and Vietnam: 99 ng/g) (Li et al., 2019a).

1.6.3 Cl-OPFRs in water

Domestic and public sewers potentially are major sources of Cl-OPFRs to sewage treatment plants (STPs) (Marklund et al., 2005). To illustrate, concentrations of Cl-OPFRs in influent wastewater samples were 1,205 ng/L in Canada, 3,730 ng/L in Sweden, 6,220 ng/L in Norway, and 4,800 ng/L in China, exceeding those in effluent samples of 800 ng/L in Canada (Woudneh et al., 2015), 1,980 ng/L in Sweden (Marklund et al., 2005), 3,286 ng/L in Norway (Green et al., 2008) and 85 ng/L in China (Deng et al., 2018). TCIPP was usually the dominant compound, followed by TCEP and TDCIPP.

Cl-OPFRs in aqueous environments are affected by urban and industrial input sources significantly. For example, because of different degrees of anthropogenic activity, Cl-OPFR concentrations ranged from 33.8 to 103.7 ng/L for TCEP, 89.9 to 127.8 ng/L for TCIPP and 51.8 to110.5 ng/L for TDCIPP in surface water samples from the Elbe River in Germany (Wolschke et al., 2015), while median concentrations of 5 ng/L for TCEP and 47 ng/L for TCIPP were reported from northwest Spain (Rodil et al., 2012). The mean concentrations of TCEP and TDCIPP in river water in Spain were 136 and 120 ng/L, respectively, and 500 ng/L for TCIPP (García-López et al., 2010).

Similarly, the mean concentrations of TCEP and TDCIPP respectively were 189 and 184 ng/L, and 674 ng/L for TCIPP in water from the Danube, Schwechat and Liesig rivers in Austria (Martínez-Carballo et al., 2007). Meanwhile, the highest concentration of Cl-OPFRs was found in the River Aire in the UK. Concentrations of TCIPP, TCEP and TDCIPP ranged respectively from 113 to 26,050 ng/L, 119 to 316 ng/L, and 62 to 149 ng/L (Cristale et al., 2013a).

Concentrations of Cl-OPFRs in drinking water are typically several to hundreds of ng/L, down an order of magnitude from surface water. In tap water, the mean concentration of TCEP and TDCIPP found in China were respectively 48.5 and 43 ng/L (Ding et al., 2015), which was lower than those found in the U.S.A (150 and 220 ng/L) (Benotti et al., 2009), but higher than those in Spain (5 and 40 ng/L) (Rodil et al., 2012), Korea (25.3 and 10.7 ng/L) (Lee et al., 2016) and the UK (3 and 2.9 ng/L) (Gbadamosi et al., 2023). In bottled water, high mean concentrations of TCIPP (79.6 ng/L) and TCEP (16.4 ng/L) were identified in Korea and considered the result of contamination occurring during the purifying and bottling processes (Lee et al., 2016). However, lower concentrations of TCEP (0.5 ng/L) and TCIPP (0.6 ng/L) were observed in bottled water in China (Ding et al., 2015) and in the UK (TCEP 0.6 and TCIPP 1.1 ng/L) (Gbadamosi et al., 2023).

1.6.4 Cl-OPFRs in sediments

A study of Cl-OPFRs in sediment samples from Lake Shihwa in Korea found that the average concentration of TCIPP was highest (194 ng/g dw), followed by TDCIPP (43.6 ng/g), and TCEP (18.4 ng/g). Industrial activities are likely to contribute to the release of Cl-OPFRs into creek waters and their subsequent deposition in river sediments (Lee et al., 2018). River sediments from Spain (Cristale et al., 2013b) and Austria (Martínez-Carballo et al., 2007) have Cl-OPFR concentrations that fall within

a similar range, with those of TCIPP ranging from 4.5 to 365 ng/g and from 20 to 1,300 ng/g, in Spain and Austria respectively. In Nepal, TCIPP was the most prevalent Cl-OPFR in sediments at concentrations ranging from 1.69 to 892 ng/g with a median of 39 ng/g (Yadav et al., 2018), which is similar to the reported median concentration of TCIPP in sediment from Saudi Arabia (37.4 ng/g) (Picó et al., 2021). However, the concentrations of TCIPP in this Nepalese study (Yadav et al., 2018), was twenty times lower than those recorded in Norwegian river sediments of 63-16,000 ng/g (Green et al., 2008). TDCIPP was present at concentrations ranging from 4 to 9 ng/g in Nepal sediments (Yadav et al., 2018) and from 13 to 405 ng/g in Lake Shihwa- Creek in Korea (Lee et al., 2018). These TDCIPP concentrations are significantly exceeded by those in Norwegian river sediments (100 to 660 ng/g (Green et al., 2008)). Meanwhile, in sediments from the Adige River basin in Italy, the mean concentration of TCEP was 2.52 ng/g (range 0.33 to 19 ng/g), exceeding the reported mean of 0.79 ng/g of TCEP (range 0.07 to 2.32 ng/g) in sediments from the Sava River basin in Serbia (Giulivo et al., 2017)

1.6.5 Cl-OPFRs in soil

Concentrations of Cl-OPFRs in soil are influenced by land usage type. In locations such as parks (Cui et al., 2017; Lorenzo et al., 2018), a university campus (Mihajlović et al., 2011), farms (Wang et al., 2018), an airport (Li et al., 2019b), and rural sites (Fries and Mihajlović, 2011; He et al., 2017); Cl-OPFRs concentrations are usually below 100 ng/g. For instance, TCIPP and TCEP were detected in soil samples from a university campus in Osnabrueck, Germany (Mihajlović et al., 2011) at average concentrations of 1.23 and 4.96 ng/g, respectively, in line with another study conducted in the same location (Mihajlović and Fries, 2012), in which concentrations in soil varied from 5.07 to 23.48 and 6.16 to 19.82 ng/g for TCEP and TCIPP,

respectively. Interestingly, TDCIPP concentrations in soil samples in the same study were below the detection limit (<0.09 ng/g) which the authors attributed to the very low TDCIPP concentrations in snow and rain from the same location (Mihajlović and Fries, 2012). Soil samples collected from different sites in Frankfurt and Osnabrück, Germany, reported concentrations of TCEP and TCIPP ranging from <0.6 to 18.2 and from 0.59 to 8.33 ng/g, respectively (Fries and Mihajlović, 2011). In Asia, the mean concentrations of TCEP (11.3 ng/g), TCIPP (3.3 ng/g) and TDCIPP (5 ng/g) in soil samples collected from Chongqing, a metropolitan city in western China (He et al., 2017) were significantly lower than those in soils from an e-waste recycling workshop in northern Vietnam (mean concentration of TCEP 4 ng/g, TCIPP 19 ng/g, and TDCIPP 21 ng/g) (Matsukami et al. 2015); and in soils impacted by plastic waste treatment TCEP 92 ng/g and TCIPP 21 ng/g in China (Wan et al., 2016).

1.6.6 Cl-OPFRs in food and wildlife

Dietary exposure to Cl-OPFRs has been reviewed and found to be an important contributor to human exposure (Maddela et al., 2020; Gbadamosi et al., 2021; Gbadamosi et al., 2022). Moreover, Cl-OPFRs have been reported in multiple wildlife specimens. For example, TDCIPP was found in fish and mussels (Evenset et al. 2009; Green et al. 2008; Takahashi et al. 2013), in bird blood, plasma, and eggs (Leonards et al. 2011; Takahashi et al. 2013), and in herring gulls and their eggs (Greaves et al., 2016). TCEP, TCIPP, and TDCIPP were present in fish samples at levels ranging from< 0.6 to 26 ng/g wet weight in the Norwegian Arctic; although only TCEP and TCIPP were identified in seabird samples at a range of < 0.5 to 4.7 ng/g wet weight (Evenset et al., 2009). Cl-OPFRs were detected in all honeybee samples from Spain with TCIPP, TCEP and TDCIPP found in concentrations ranging from 9.6 to 64.8 ng/g, <0.9 to 8.4 ng/g, and ND to 7.8 ng/g, receptively (García-Valcárcel et al., 2016).

Food contamination with Cl-OPFRs could occur as result of food chain transfer, and through food industrial processing, packaging, canning, and drying (Maddela et al., 2020). A variety of foodstuffs have been investigated in various studies, including rice, cereal, vegetables, fruit, snacks, oil, beverages, meat, fish/seafood, dairy products, baby formula, and baby supplementary food (Zhang et al., 2016; Poma et al., 2017; Hyland et al., 2015; He et al., 2018; Chen et al., 2022; Wang et al., 2022). High concentrations of Cl-OPFRs were reported in rice samples from China (Zhang et al., 2016). Mean concentrations of TCEP and TCIPP were 24.6 and 14.1 ng/g dry weight, respectively; while TDCIPP displayed a lower mean concentration of 2.34 ng/g dry weight (Zhang et al., 2016). In Belgium, TCIPP was found in fat and oil samples at a mean concentration of 38.9 ng/g wet weight (Poma et al., 2017), which is higher than the reported geometric mean of TCIPP (0.35 ng/g wet weight) in cooking oil from China (Wang et al., 2022). In Sweden, the mean concentrations of TCEP, TDCIPP, and TCIPP in vegetables were 0.41, 0.37, and 0.18 ng/g wet weight, respectively (Poma et al., 2017). In fruit samples from Australia, the mean concentration of TCIPP was 1.29 ng/g wet weight (He at al., 2018a). Because TDCIPP has a higher fruit-to-shoot concentration factor (FSCF) it was found in strawberries in China at a mean concentration of 5.05 ng/g dry weight, thus exceeding the mean concentrations detected of TCEP (0.77 ng/g dry weight) and TCIPP (0.17 ng/g dry weight) (Hyland et al., 2015).

1.7 Human exposure to Cl-OPFRs

The evidence of the presence of Cl-OPFRs in air, dust, food, and consumer goods means that human exposure occurs to varying degrees via air inhalation, dietary intake, ingestion of dust and dermal contact with consumer goods containing such

flame retardants (Figure 1.2) (Wei et al., 2015; Yang et al., 2019; Wang et al., 2020; Ding et al., 2018).

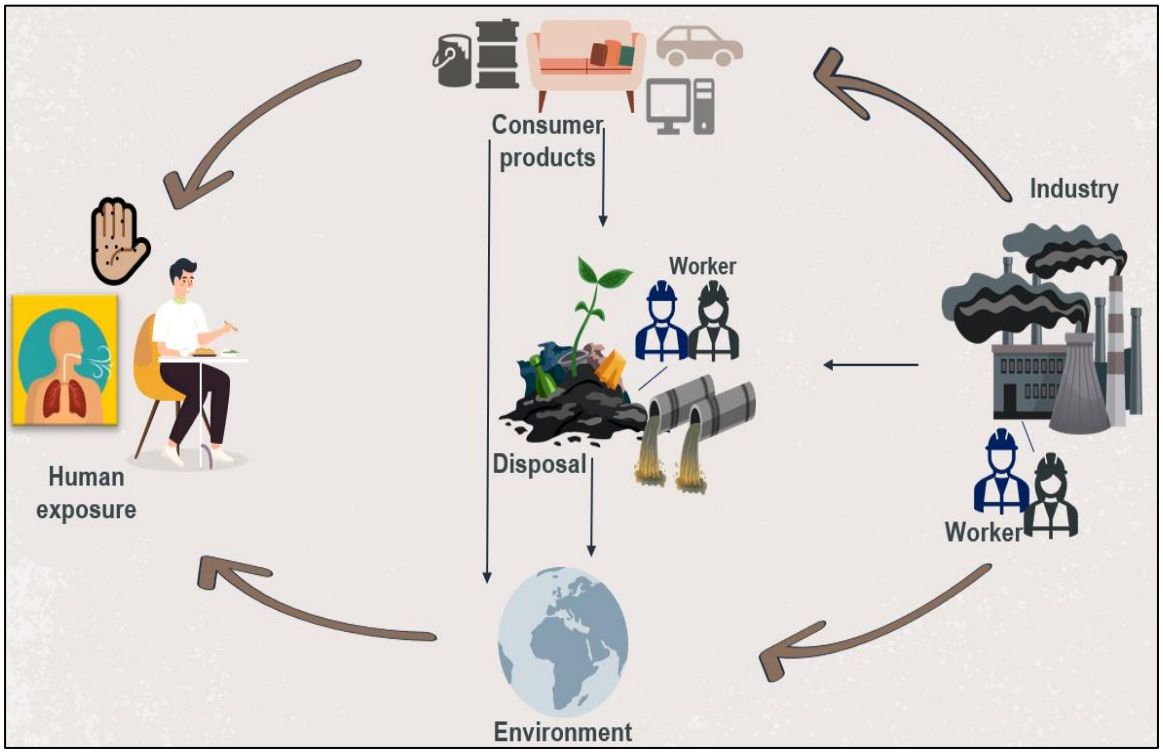


Figure 1. 2: Routes of exposure to Cl-OPFRs

1.7.1 Inhalation

In a study conducted in the U.S.A (Schreder et al., 2016), inhalation intakes of TCIPP, TDCIPP, and TCEP were calculated to be 4,540, 102, and 186 ng/day, respectively. These exceeded estimated exposure via dust ingestion of 145, 48.6, and 41.4 ng/day for TCIPP, TDCIPP, and TCEP, respectively (Schreder et al., 2016). Another study reported inhalation was a higher source of exposure to Cl-OPFRs than dust ingestion in Norway. The estimated median daily exposure doses (in ng/kg bw/day) via personal air were 0.53 for TCEP, 0.11 for TDCIPP, and 5.95 for TCIPP, exceeding those via ingestion of floor dust (TCEP 0.17, TDCIPP 0.07 and TCIPP 0.76 ng/kg bw/day) (Xu et al., 2016).

1.7.2 Dietary intake

Dietary intake of contaminated food and drinking water with Cl-OPFRs is another significant exposure pathway; most foods have been found to contain trace quantities of these flame retardants (Ding et al., 2018; Zhao et al., 2019; Maddela et al., 2020; Gbadamosi et al., 2022) and drinking water (Rodil et al., 2012; Gbadamosi et al., 2023).

In addition, dietary intake was the most significant exposure pathway for TCEP (4.1 ng/kg bw/day) and TCIPP (25 ng/kg bw/day) compared to dust ingestion and inhalation in an Australian study (He et al., 2018). In another study both adults and children (3 to 12 years old) were exposed to TCEP (8.7 ng/kg bw/day for adult; 12.8 ng/kg bw/day for children) and TCIPP (6.4 ng/kg bw/day for adult; 11.4 ng/kg bw/day for children) through consumption of food, mainly cereals and vegetables in China (Ding et al., 2018). Another study reported high concentrations of TCEP in rice from different areas of China. Rice consumption exposed men and women respectively to 162 and 182 ng/kg bw/day of TCEP, 72 and 82 ng/kg bw/day of TCIPP, and 37 and 42 ng/kg bw/day of TDCIPP (Zhang et al., 2016).

Infants' exposure to Cl-OPFRs via breastfeeding, consumption of formulae and supplementary food have been reported (Chen et al., 2021; Chen et al., 2022). Intake of TCEP, TDCIPP, and TCIPP for nursing infants via human milk were estimated respectively at values of 25.8, 5.88 and 86.1 ng/kg bw/day (Chen et al., 2021); in addition, estimated daily intakes of Cl-OPFRs via baby formula were calculated as 31.66, 44.72, and 51.12 ng/kg bw/day for TCEP, TDCIPP, and TCIPP respectively for infants aged from 0 to 36 months. Regarding baby supplementary food consumption, estimated daily intakes of TCEP, TDCIPP, and TCIPP were

respectively: 77.5, 82.3, and 342 ng/kg bw/day, for infants aged 7 to 36 months (Chen et al., 2022).

1.7.3 Dermal uptake

Adults and toddlers in the UK were estimated to have been exposed to Cl-OPFRs by skin contact with indoor dust. Dermal uptake estimates for toddlers under a median exposure scenario for TCEP, TCIPP, and TDCIPP were respectively 1.5, 32.9, and 1.6 ng/kg bw/day, and for adults 0.1, 3.8, and 0.2 ng/kg bw/day (Abdallah et al., 2016). A recent UK study reported that the dermal uptake of Cl-OPFRs in summer would exceed that in winter. This is partly because of increased perspiration in summer leading to more efficient dermal uptake when skin is wet. Moreover, in summer, there is more dermal contact with furniture fabrics because of the larger skin surface area exposed than in winter. Therefore, estimated dermal uptakes of TCEP, TCIPP, and TDCIPP for adults were: 3.1, 37.2, and 5.3 ng/kg bw/day respectively; exceeding the corresponding values in winter of: 0.6, 6.7, and 2.3 ng/kg bw/day (Abdallah and Harrad, 2022).

1.7.4 Dust ingestion

Many studies have estimated exposure to Cl-OPFRs via dust ingestion (Xu et al., 2016; Li et al., 2019a). A study involving indoor dust from 12 countries (including China, Columbia, Greece, India, Japan, Korea, Kuwait, Pakistan, Romania, Saudi Arabia, the U.S.A, and Vietnam) showed that average estimated daily intakes of Cl-OPFRs via dust ingestion for children from these countries were in the ranges of 0.01 to 5.15 for TCEP, 0 to 5.76 for TCIPP, and 0 to 3.28 for TDCIPP ng/kg bw/day. By comparison for adults, exposures ranged from 0 to 1.19 for TCEP, 0 to 1.15 for TCIPP, and 0 to 0.71 for TDCIPP ng/kg bw/day (Li et al., 2019a). The highest exposures were for TDCIPP in Japan, TCIPP in the U.S.A, and TCEP in Korea (Li et

al., 2019a). Another study in Norway compared the exposure of adults to Cl-OPFRs from dust ingestion via surface dust with that via ingestion of floor dust (Xu et al., 2016). The median estimated daily intake of TCEP (0.21), TDCIPP (0.58), and TCIPP (2.31) ng/kg bw/day derived for surface dust exceeded those based on ingestion of floor dust TCEP (0.17), TDCIPP (0.18), and TCIPP (0.76 ng/kg bw/day) (Xu et al., 2016).

1.7.5 Cl-OPFRs in human tissues samples

Several previous studies have reported the presence of Cl-OPFRs in human tissues samples including blood, hair, urine, breast milk, and nails (Sundkvist et al., 2010; Liu et al., 2015; Dodson et al., 2014; Zhao et al., 2016).

Median concentrations of TCEP, TCIPP and TDCIPP in breastmilk samples were respectively 4.9, 45, and 4.3 ng/g lipid weight in Sweden (Sundkvist et al., 2010) and 5.59, 18.6 and 1.27 ng/g lipid weight in China (Chen et al., 2021). In human hair and nail samples obtained from the public on the Bloomington campus of Indiana University; TCEP, TCIPP, and TDCIPP concentrations in hair samples ranged from <75 to 1,950, 290 to 1,190 and <75 to 970 ng/g dry weight, respectively (Liu et al., 2015). However, in fingernail samples, TCEP, TCIPP, and TDCIPP concentrations ranged from <150, <150, and 280 to 630 ng/g dry weight, respectively (Liu et al., 2015). In Norway, in hair from female adults, the TDCIPP median concentration was 30 ng/g and ranged from <9 to 3,744 ng/g, while the TCEP median concentration was 72 ng/g and ranged from <33 to 163 ng/g (Kucharska et al., 2015).

Mean concentrations of TCEP, TCIPP, and TDCIPP metabolites in urine from 16 residents living in Northern California were 0.76, 0.17, and 0.46 ng/mL, respectively (Dodson et al., 2014). Similarly, TDCIPP was detected at 100 % in urine samples

(n=181) of US children, at a geometric mean of 1.29 ng/mL, while the geometric mean concentration of TCIPP was 0.43 ng/mL (Phillips et al., 2018). In the same study, in hand wipes of children (n=202), the geometric mean value for TDCIPP was 143.6 ng/wipe, while those for TCIPP and TCEP were 89.8 and 27.5 ng/wipe, respectively (Phillips et al., 2018).

In blood samples obtained from 327 residents in Shenzhen, China, TCIPP, TCEP and TDCIPP concentrations ranged from not detected (ND) to 21.61, ND to 2,438, and ND to 3.41 ng/mL, respectively (Zhao et al., 2016). Similarly, TCEP was the most abundant OPFR in human serum at a median concentration of 214 ng/g lipid weight in North Carolina, U.S.A (Gao et al., 2020) and a median of 142 ng/g lipid weight in human placenta samples obtained in eastern China (Ding et al., 2016).

1.7.6 Toxicity and health effects of Cl-OPFRs

Cl-OPFRs including TCEP, TDCIPP, and TCIPP are suspected carcinogens (Baril et al., 1998; Crawford et al., 2012). Both TDCIPP and TCEP have been designated as carcinogens under Proposition 65 by the State of California, U.S.A (OEHHA, 2011), while TCEP was identified as a Substance of Very High Concern (SVHC) by the European Chemicals Agency (ECHA) because of its reproductive toxicity, suspected carcinogenicity, and chronic and acute impact on aquatic life (ECHA, 2017). TCEP has shown adverse developmental effects in rats and is carcinogenic to animals (van der Veen and de Boer, 2012). Indoor dust containing high concentrations of TCEP has been related to an increased risk of papillary thyroid cancer (Hoffman et al., 2017), and reduced cognitive abilities in children (ECHA, 2009). In addition, an increased rate of atopic dermatitis was associated with concentrations of TDCIPP in floor dust (Araki et al., 2014). Moreover, TDCIPP was related to health problems like increasing prolactin levels, as well as decreasing thyroid hormone levels and sperm quality in

men (Meeker and Stapleton, 2010). TCEP has been associated with kidney and thyroid tumour development, while TDCIPP has been associated with brain, liver, and testes tumour formation (Baril et al., 1998).

Cytotoxicity, endocrine dysfunction, neurotoxicity, developmental toxicity, and interference with reproductive functions are all reported toxicological consequences of exposure to Cl-OPFRs like TCEP, TCIPP, and TDCIPP (Yang et al., 2019; Saillenfait et al., 2018). Cl -OPFRs have been known to accumulate in human adipose tissue and seminal fluid. For example, TCIPP can accumulate in body organs like liver and kidneys (Reemtsma et al., 2008); while TDCIPP can pass quickly into blood, liver, kidneys, and male reproductive organs and stimulate cancer-cell growth (Yang et al., 2019).

1.8 Legislation relating to the use and manufacture of Cl-OPFRs

Over the years, owing to evidence of substantial human exposure and adverse health effects, the manufacture and use of Cl-OPFRs has come under increasing scrutiny. To illustrate, the European Commission (EU) proposed in 2018 that all organohalogen chemicals be banned from electronic display enclosures and stands starting April 1, 2021 (European Commission, 2019a). TCEP is classified as a Substance of Very High Concern (SVHC) under the REACH legislation (Registration, Evaluation, Authorisation and Restriction of Chemicals), and REACH (Annex XIV Authorisation List) prohibited the use of TCEP in 2015 (ECHA, 2015). TCEP is also known as a Chemical of High Concern to Children (CHCC) (Bergen and Stone, 2021). Inclusion on the SVHC list is the first step in the authorisation process, which controls chemical use and can eventually lead to their prohibition. For the phase-out of TCEP, a proposal for a ban was issued (ECHA, 2009; ECHA, 2018a). Alongside REACH, another EU directive, the European Commission's Toy Directive, limited the

concentrations of TCEP, TDCIPP, and TCIPP in children's toys to 5 mg/kg in 2014 after identifying TCEP as a category 2 carcinogen and classifying it as a toxic for reproduction type 1B chemical (European Commission, 2014). In 2018, ECHA (European Chemicals Agency) proposed restriction of TCEP, TDCIPP, and TCIPP in all childcare goods and residential upholstered furniture to a maximum concentration of 0.1 % (1,000 mg/kg=1,000 ppm) by weight because of the carcinogenic risk to infants exposed to these compounds (ECHA, 2018a). This proposal was paused pending the publication of the US National Toxicology Program's study of the carcinogenicity of TCIPP. Notwithstanding such uncertainties, the Environmental Protection Agency of Denmark has placed TCIPP on its List of Undesirable Substances (Danish EPA, 2009).

In Canada, the Consumer Product Safety Act in 2010 prohibited the selling of foam padded children's products with TCEP (Government of Canada, 2014). Also, in 2016, the Children's Sleepwear Regulations in Canada prohibited the use of flame retardants that could pose specific hazards like gene mutation and tumorigenicity in loose fitting sleepwear for children (Government of Canada, 2016).

In the U.S.A, the Children's Safe Product Act in 2011 demanded that TCEP, TDCIPP, and TCIPP in children's products be reported by manufacturers, also in 2017 restricted the concentration of TCEP and TDCIPP to 0.1% (1,000 mg/kg) in juvenile's products and residential furniture (Blum et al., 2019). California's proposition 65 listed TCEP (in 1992) and TDCIPP (in 2011) as carcinogenic substances (OEHHA, 1992; OEHHA, 2011) and some states have passed legislation banning TDCIPP use in children's goods (Massachusetts, 2016). Moreover, Washington DC B210143 law in 2016 limited the concentration of TCEP and TDCIPP to 0.1 % (1,000 mg/kg) in children's' products and residential furniture (LegiScan, 2016). In 2017, the California

Safer Consumer Products Program rule required manufacturers to report the presence of TCEP and TDCIPP in children's foam padded sleeping products (Blum et al., 2019). The California Assembly Bill 2998 in 2018 sets limits to all OPFRs of 0.1 % (1,000 mg/kg) in children's goods, furniture, and mattresses. On or after January 1, 2020; any of the mentioned products including flame retardants above specified levels are prohibited from being sold or distributed in commerce (Quirk et al., 2018). The Minnesota (MN) HF 1627 legislation in 2018, prohibited the production or selling of children's goods, upholstered residential furniture and textile, or mattress including more than 0.1 % (1,000 mg/kg) of TCEP, TDCIPP, and TCIPP (Minnesota Legislature, 2018). Moreover, in New York, Vermont, and Maryland, products for children under the age of 3 to 12 are prohibited from including more than 0.1 % (1,000 mg/kg) of TDCIPP, TCEP or TCIPP (Vermont, 2013; New York, 2013; Maryland, 2014).

In addition, under the Toxic Substances Control Act (TSCA) in the U.S.A, TCEP has been designated as high priority or is undergoing risk assessment to determine whether they pose an unreasonable risk to public health or the environment in 2019 (U.S. EPA, 2022).

1.9 Recycled plastics as a source of Cl-OPFRs in new consumer products

Considering that Cl-OPFRs must be present in treated products in concentrations over 1–2% (10,000-20,000 mg/kg) to impart flame retardancy, articles with concentrations below 0.1 % (1,000 mg/kg) of Cl-OPFRs may be unintentionally contaminated by recycled polymers. Recent studies have found that materials including Cl-OPFRs have been recycled in the production of articles for which no flame retardancy is required including food contact articles (FCAs) and children’s toys (Borling et al., 2006; Glensvig and Ports, 2006; SCHER, 2012; Ionas et al., 2014; Health Canada,

2020). Toy and childcare products were found to contain low levels (less than 50 mg/kg) of TCEP in Denmark (Borling et al., 2006) as well as of TCEP, TDCIPP, and TCIPP in Belgium (Ionas et al., 2014). In contrast, higher levels of TCEP were detected in one soft cube textile (160 mg/kg) and foam (6,500 mg/kg) (SCHER, 2012).

This demonstrates that the flow of flame retardant-based plastics for recycling is not well regulated, and that materials containing Cl-OPFRs are combined with non-flame-retarded polymers to create products with sensitive end uses (Figure 1.3). As a result, the use of recycled plastic can be substantially more hazardous than the initial application in some situations (for example, recycling a printer housing into a toy that a child can chew or food contact articles).

Products containing Cl-OPFRs at levels exceeding 1,000 mg/kg like upholstered furniture (Stubbings et al., 2016; Stapleton et al., 2009; Stapleton et al., 2012; Hammel et al., 2017), juvenile items (Bergen and Stone, 2021; Stapleton et al., 2011; Wu et al., 2018; Danish EPA, 2016), and plastics will remain in use for a certain period. At end of life, these materials move into the waste and recycling stream, where such flame retardants can pose risks; for example, by being recycled into new products that might contain Cl-OPFRs, albeit at lower concentrations.

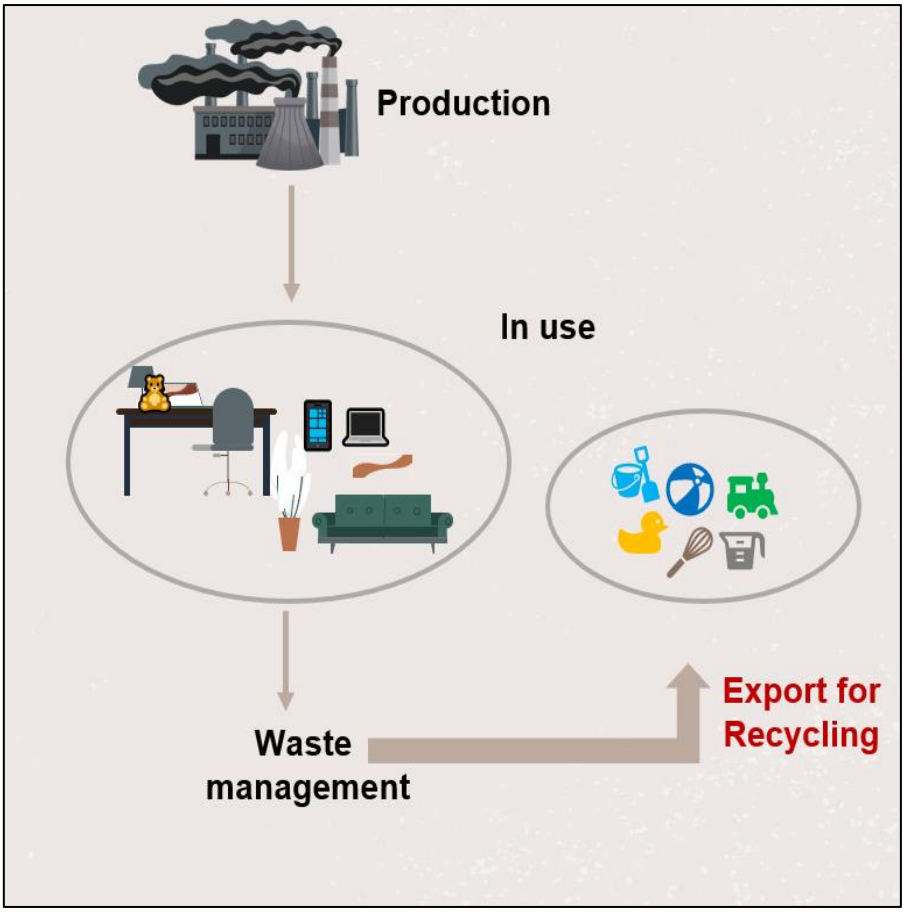


Figure 1. 3: Schematic diagram of the life cycle of Cl-OPFRs and potential hazardous recycling

1.10 X-ray fluorescence spectroscopy as a tool for screening compliance with limits on concentrations of flame retardants in waste items

In developed countries, especially in the EU, the circular economy and zero-waste principles are gaining popularity (European Commission, 2015). In a circular economy, waste is seen as a resource that is reused and/or recycled wherever possible. The circular economy is projected to generate many jobs, preserve environmental resources, and add value to waste materials (European Commission, 2015). Mixing household items with toxic chemicals, such as HFRs, makes reuse and recycling challenging. It will be crucial to design and implement waste processing methods that identify and eliminate dangerous chemicals before recycling (Kral et al., 2013; UNEP,

2017a). Hazardous additives should be minimized or removed as much as possible, as this not only minimizes or eliminates risks during product use, but it also lowers challenges to healthy recycling and product reuse.

Historically, the most utilized BFRs were PBDEs, tetrabromobisphenol A (TBBPA), and hexabromocyclododecane (HBCDD) (Gallen et al., 2014). The UNEP has listed PBDEs and HBCDD under the Stockholm Convention on POPs due to their toxicity, persistence, ability to undergo long-range environmental transport, and bioaccumulation capacity (UNEP, 2013). Annex A of the Stockholm Convention was updated in 2009 to include tetra-, penta-, hexa-, hepta-, and octa-BDEs (UNEP, 2009). Following this, in 2013 and 2017, HBCDD and deca-BDE (also known as BDE-209) were respectively listed as POPs (UNEP, 2013; UNEP, 2017b). PBDEs and HBCDD are listed as POPs, which means that they should no longer be used or manufactured. Despite their prohibited status, such BFRs have been detected in consumer products which are not required to meet flame retardancy standards, for example, food contact articles (FCAs), juvenile toys and items, and other products (Gallen et al., 2014; Digangi et al., 2017; Kuang et al., 2018; Straková et al., 2018; Li et al., 2019c; Kajiwara et al., 2022; Lestido-Cardama et al., 2022), When plastics that were flame-retarded in their first use are recycled, they are likely to contain PBDEs and HBCDD at concentrations below those required for flame retardancy. Consequently, the Stockholm Convention sets Low POP Concentration Limits (LPCLs) for PBDEs and HBCDD of 1,000 mg/kg to prevent waste plastics exceeding this limit from being recycled (European Commission, 2011). With the enforcement of these LPCLs, it is intended that recycled plastics will no longer be contaminated by PBDEs and HBCDD. A proposal was made in May 2017 to set limits for POP waste, including PBDEs, at 50 mg/kg or 1,000 mg/kg by the Basel and Stockholm Conventions

Conference of Parties (Basel Convention, 2017). To protect consumer health, the Unintentional Trace Contaminant (UTC) limit was established at 10 mg/kg for all substances placed on the market (including tetra-, penta-, hexa-, hepta-, and deca-BDEs), as well as 500 mg/kg for the total amount of PBDEs, and 100 mg/kg for HBCDD, regardless of whether the products are made from recycled materials (European Commission, 2016; European Commission, 2019b). The European Commission adopted the Restriction of Hazardous Substances (RoHS) directive that prohibits the sale of electrical and electronic equipment (EEE) with hazardous chemical concentrations exceeding the permitted doses (1,000 mg/kg), including PBDEs (European Commission, 2011; European Commission, 2012). In addition, the goal of RoHS is to limit the generation of waste electrical and electronic equipment (WEEE) (European Commission, 2012).

In terms of Cl-OPFRs, there are no restrictions on the management of waste containing Cl-OPFRs at the current time; however, they are likely to arise in the near future, given the EU's aim to ban the use of all HFRs in some applications and the European Chemicals Agency's (ECHA) proposal to limit the use of TCEP, TCIPP, and TDCIPP in flexible PUF used in childcare goods and domestic furniture (ECHA, 2018a).

Although effective implementation of LPCLs has been shown to significantly reduce the amount of PBDEs and HBCDD entering the recycling stream (Harrad et al., 2019), an efficient and quick technology to screen waste is required due to the vast amount of generated waste. "Gold standard" techniques such as conventional GC/MS (gas chromatography/ mass spectrometry) and LC/MS (liquid chromatography/ mass spectrometry) are accurate and precise in terms of BFRs and Cl-OPFRs analyses; however, the costs, time, and skill involved in these techniques make them unfeasible

for waste handling or recycling facilities to employ. Hence, given the huge amount of waste materials that must be evaluated, there is an urgent need for faster, cheaper, and more user-friendly technologies capable of immediately evaluating compliance with LPCL values at trash and recycling facilities.

Several studies have investigated the use of X-ray fluorescence (XRF) as an alternative tool for screening consumer products for HFRs (Aldrian et al., 2015; Miller and Gearhart, 2015; Guzzonato et al., 2016; Sharkey et al., 2018; Lestido-Cardama et al., 2022). Furthermore, a number of studies have demonstrated that XRF can be used to monitor flame retardant containing wastes at waste-recycling facilities, in compliance with RoHS and WEEE regulations (Sindiku et al., 2011; Naturvårdsverket, 2012; Sharkey et al., 2018; Kajiwara et al., 2022).

XRF is widely applied for qualitative and quantitative analyses of the material composition as well as for non-destructive chemical analyses. This technique is based primarily on monitoring the emission of characteristic "secondary" (or fluorescence) X-rays from a material after stimulation with high energy X-rays or gamma rays (Figure 1.4). A strong X-ray (greater than the bonding energy of an atom's K or L shell) can dislodge an electron from an atom's inner orbital shell (Figure 1.4). An electron from one of the atom's higher energy orbital shells fills the vacancy in the inner orbital shell, restoring the atom's stability. By emitting a fluorescent X-ray, the electron falls to a lower energy state. The energy of this X-ray is equivalent to the difference in energy between two electron quantum states. The determination of this energy is the foundation of XRF analysis (Thermofisher Scientific, 2020).

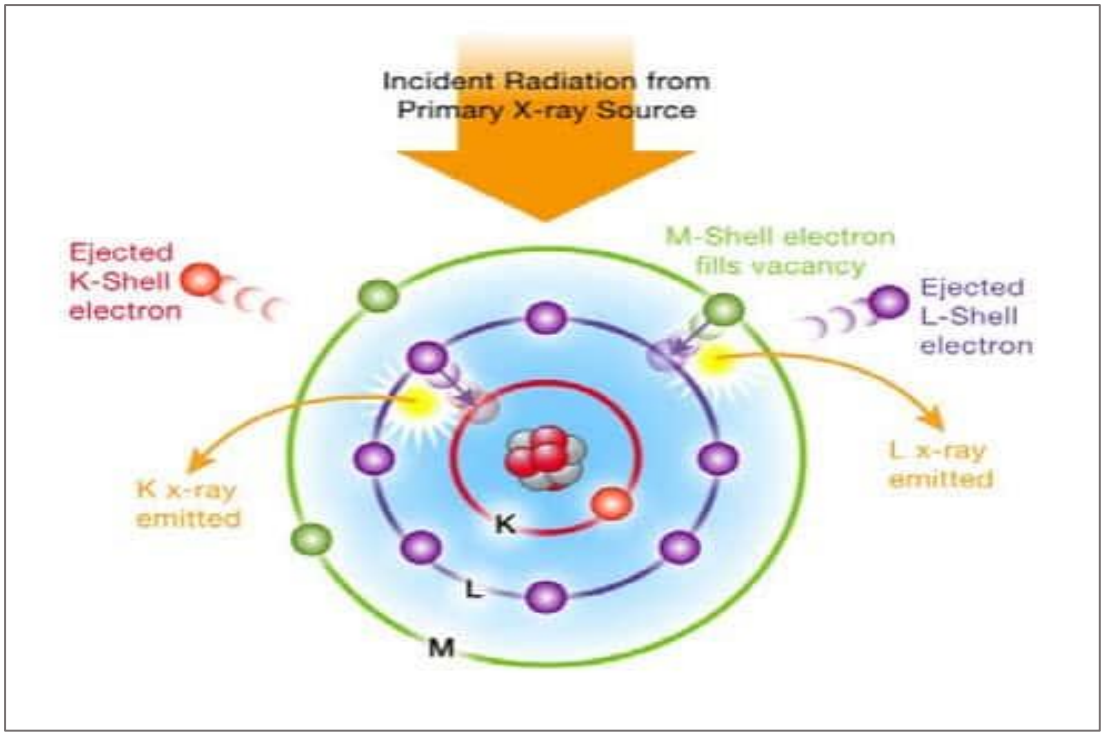


Figure 1. 4: Principle of XRF analyses (Thermofisher Scientific, 2020)

The XRF technique does not need to replicate GC/LC-MS measurements in order to be effective as a tool for screening for compliance with concentration limit values like LPCLs. Instead, it only needs to correctly identify whether the LPCL value has been exceeded. Several studies have compared XRF data with conventional GC/MS and LC/MS determined concentrations of BFRs and Cl-OPFRs (Kajiwara et al., 2011; Sindiku et al., 2011; Naturvårdsverket, 2012; Aldrian et al., 2015; Guzzonato et al., 2016; UNEP, 2017a; Sharkey et al., 2018; Drage et al., 2018; Harrad et al., 2019; Turner and Filella, 2017; Fatunsin et al., 2020; Knutsen and Arp, 2021; Chaine et al., 2022; Kajiwara et al., 2022; Jang et al., 2022). These studies screened materials for Br, Cl, and P content as a proxy for the presence of BFRs and Cl-OPFRs. One study reported that the accuracy of XRF with respect to Br was enhanced by use of polymeric standards including specific BFRs (BDE-209) incorporated within acrylonitrile butadiene styrene (ABS) and high impact polystyrene (HIPS) (Guzzonato et al., 2016). According to the study, XRF was a feasible instrument for

determining if WEEE complied with LPCLs (Guzzonato et al., 2016). Also, XRF has proven to be an effective "pass/fail" screening method for monitoring compliance with LPCLs for PBDEs and HBCDD in Ireland (Drage et al., 2018; Harrad et al, 2019; Sharkey et al., 2018). In a large-scale study, XRF Br readings were compared to GC/MS and liquid chromatography – tandem mass spectrometry (LC/MS/MS) measurements of BFRs (Harrad et al., 2019). XRF was determined to be over 90% effective based on these data for determining compliance with LPCLs for PBDEs and HBCDD in wastes including EPS (expanded polystyrene), XPS (extruded polystyrene), and C&D (construction and demolition), ELV (end-of-life vehicle), and furniture (Harrad et al., 2019). However, in 26 (11%) of the 237 tested WEEE objects, XRF measurements of Br mistakenly identified the items as exceeding the LPCL (this false exceedance was attributed to factors such as the presence of non-regulated BFRs like TBBPA). There were no reported false negatives (defined as instances where Br was not detected by XRF, but the concentration of POP-BFRs exceeds the LPCL) (Harrad et al., 2019). Similarly, a study in Norway using XRF measurements of Br in EPS foam (n=120) waste found that XRF was a successful pass/fail technique for evaluating whether the LPCL was exceeded, and no false negative readings were obtained (Knutsen and Arp, 2021).

In Austria, XRF proved to be a useful technology for rapid monitoring of large volumes of waste plastics for compliance with legislative limits on POP-BFR concentrations (Aldrian et al., 2015). Likewise, a recycling facility in Sweden stated that the quality and precision of the sorting process was sufficient to abide by EU regulations after using XRF to separate plastics from electronic equipment that include POP-BFRs (Naturvårdsverket, 2012; UNEP, 2017a). A Nigerian study employed XRF to screen waste goods containing Br and Cl to ensure compliance with

RoHS legislation (Sindiku et al., 2011). According to Schlummer et al. (2015), XRF measurements of Br in waste polystyrene foam can be used as a surrogate indicator for BFRs such as HBCDD. In fact, XRF was found to be the commonly used tool to segregate plastics containing BFRs from a mixed plastic waste stream (Wagner et al., 2019; Wagner and Schlummer, 2020).

The use of XRF to detect BFRs in various products, including FCAs and juvenile items, has also been successful in Japan (Kajiwara et al., 2022), Spain (Lestido-Cardama et al., 2022), China (Li et al., 2019c), Australia (Gallen et al., 2014), and the UK (Kuang et al., 2018). In Spain, a study investigated the occurrence of BFRs (like TBP (Tribromophenol), TBBPA, and BDE-209 in 21 black FCAs purchased in Spain (Lestido-Cardama et al., 2022). The Br content of these articles was screened using XRF, and BFRs quantified using HPLC-MS/MS (High Performance Liquid Chromatography- mass spectrometry). No false negatives were detected, but a false exceedance occurrence of 5 % was obtained (that could be due to the presence of brominated substances different to the targeted BFRs). In fact, 4 out of 5 samples (80%) detected by HPLC-MS/MS were also detected by XRF when compared as a confirmatory technique, which suggests both techniques should be used to improve the detection of contaminated samples. The study found that the fundamental limitation of XRF is that it cannot identify individual compounds, making it unable to identify brominated substances (Lestido-Cardama et al., 2022). Another study goal was to assess the current state of international circulation of PBDE-containing waste plastics. The study measured the concentrations of Br (by XRF) and PBDEs (by GC/MS/MS) in a variety of 540 plastic objects (1,139 samples), including children's toys, purchased in Japan and 17 other Asian, European, and Canadian nations (including India, Belgium, Serbia, Taiwan, Thailand, Vietnam, Canada, Brazil,

Myanmar, Cameroon, Korea, Argentina, Hong Kong, Sri Lanka, Kenya, Indonesia, and Malaysia) (Kajiwara et al., 2022). Approximately 219 samples (20 %) contained Br at levels >30 mg/kg and 109 samples (10 %) included PBDEs at concentrations ranging from 35 to 10,000 mg/kg. In 34 plastic components from cheap toys and consumer products, PBDE concentrations exceeded 1,000 mg/kg. Black clothes hangers from Hong Kong had the highest concentration (10,000 mg/kg). Usually, plastics need at least 3 % (30,000 mg/kg)–5 % (50,000 mg/kg) of BFR by weight to be flame retardant, which is equal to at least 20,000 mg/kg Br. Therefore, this study was unable to identify any intentional use of BFRs, and instead assumed that the BFRs in e-waste plastics were recycled, and that BFRs can be determined effectively with XRF (Kajiwara et al., 2022). Another study aimed to provide an overview of recycling procedures and material flows of end-of-life vehicles (ELVs) in South Korea towards a circular economy. When XRF Br readings exceeded 100 mg/kg, quantitative analyses by GC/MS were employed to identify PBDEs. 10 out of 46 seat cover and foam samples (21.7%) contained PBDEs at an average of 3,559 mg/kg, and 12 out of 16 automobile shredder residue samples (75 %) contained PBDEs at an average of 1,247 mg/kg (Jang et al., 2022). According to Kuang et al. (2018), XRF has been used successfully to identify BFRs in new and used kitchen utensils in the UK. Also, XRF was found as a quick and non-destructive testing technique for finding BFRs in objects. Repeat measurements of Br were possible due to XRF's ease of use (Gallen et al., 2014). Furthermore, XRF has been demonstrated to be a useful screening method for detecting BFRs in new children's items and recycled electronics (Furl et al., 2012), and in children's toys manufactured from BFR-containing recycled materials (Digangi et al., 2017), recycled foam carpet padding (Digangi and Strakova, 2011), toys, décor, and many other goods (Miller et al., 2016). According to Petreas et

al. (2016), XRF measurements of Br and Sb are a rapid, feasible and excellent methodology to screen for BFRs in upholstered furniture in compliance with California's new labelling law (SB1019). Moreover, XRF can detect Br down to 5 mg/kg in plastics, electronics, furniture, metals, and textiles (Allen et al., 2008; Takigami et al., 2009; Sindiku et al., 2014), and at levels of 8 and 20 mg/kg in EPS and XPS (Sharkey et al., 2018; Knutsen and Arp, 2021). A concentration of 10 mg/kg Br was detected in upholstery, textiles, and PUF, HIPS, and ABS polymeric materials (Allen et al., 2013; Sharkey et al., 2018).

The use of XRF to screen objects for the presence of Cl-OPFRs has also been examined albeit to lesser degree than has been the case for BFR. A study in the U.S.A investigated the presence of BFRs and Cl-OPFRs in various products like childcare items, electronics, and furniture by using XRF to screen Br, Cl, and P (Stapleton et al., 2011). Overall, there was a significant correlation ($p < 0.001$) between XRF and GC/MS results for detection of Br and BFRs, respectively. In contrast, the correlation between Cl and Cl-OPFRs was not significant. XRF measurements of Cl did not correlate with GC/MS Cl-OPFRs measurements possibly due to the presence of both V6 and the hitherto unreported flame retardant, 2,2-bis(chloromethyl)propane-1,3-diyl tetrakis(1-chloropropan-2-yl) bis(phosphate), which the authors could not quantify in the absence of reliable reference standards. Exclusion of these compounds from the Cl-OPFRs measurements used in the correlation, yielded a higher but still not statistically significant correlation coefficient ($P=0.33$). The author proposed that XRF Cl readings surpassing those attributed to GC/MS measurements of Cl-OPFRs potentially could be caused by chlorinated impurities in toluene diisocyanate, a chemical used to manufacture PUF, and suggested further studies to examine the effectiveness of XRF as a screening technique for Cl-OPFRs (Stapleton et al., 2011).

According to similar studies, XRF was a suitable screening method for Br and Sb but not for Cl and P since XRF is insensitive to light elements such as Cl and P (Kajiwara et al., 2011; Petreas et al., 2016). For instance, when elemental phosphorus P measurements by Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES) and XRF results were compared, it was discovered that the latter had poorer predictive ability and produced false negative results when the elemental phosphorus concentration surpassed 50 mg/kg (Petreas et al., 2016). XRF, on the contrary, was successfully used to demonstrate the existence of Cl-OPFRs in products used for childcare, according to two studies in the U.S.A (Mathieu, 2014; Miller and Gearhart, 2015). The first of these utilised XRF to screen purchased childcare items and furniture in Washington State, and successfully identified TCEP, TCIPP, and TDCIPP in foam components (Mathieu, 2014). Furthermore, there was good agreement between the data obtained by XRF and GC/MS analyses of Cl-OPFRs for foam and fabrics of baby's car seats with GC/MS confirming the occurrence of TDCIPP and TCIPP in samples. Depending on the sample matrix, BFRs and Cl-OPFRs could successfully be identified when XRF Br and Cl readings exceeded 400 mg/kg and 3,500 mg/kg, respectively (Miller and Gearhart, 2015). More recently, light elements like Cl and P have been reported to be detectable at lower detection limits using advanced handheld XRF analysers like the Niton XL2 GOLDD and Niton XL3t GOLDD+ (Thermo Scientific Niton, 2016). For example, Cl can be detected at levels of 50 and 200 mg/kg respectively using an advanced XRF (Margalit, 2010). The Niton XL3t GOLDD Series XRF analyser can detect Cl at levels as low as 80 mg/kg for consumer goods screening (Thermo Scientific Niton, 2013). Aside from Cl, P can be detected at a level of 350 mg/kg using a Niton XL2 GOLDD series (Thermo Scientific Niton, 2010b), and at lower levels of 250 mg/kg using a Niton XL3t

GOLDD+ Series (Thermo Scientific Niton, 2010a). In the same context, Cl can be detected at levels of 75 and 60 mg/kg respectively by using Niton XL2 GOLDD and Niton XL3t GOLDD+ Series (Thermo Scientific Niton, 2010b; Thermo Scientific Niton, 2010a). By comparison, when Cl levels exceed 50,000 mg/kg, Fourier transform infrared spectrometers (FTIR) can successfully detect PVC polymer in high concentrations (Miller et al., 2016). Also, FTIR can measure PBDEs in plastic and distinguish deca-BDE from its commercial substitute (decabromodiphenylethane) in terms of BFRs (Kajiwara and Matsukami, 2019).

Overall, XRF is a screening approach that is quick, in-situ, portable, non-destructive, simple to use, reliable and cost effective. It can also measure elements individually or in a mixture and is capable of screening large numbers of items in a short period of time without the need for sample preparation or a skilled operator (Bezati et al., 2011; Furl, 2011; Aldrian et al., 2015; Sharkey et al., 2018; Ravansari et al., 2020). Samples of dark or black colour have no effect on the detecting process of XRF (Bezati et al., 2011; Kajiwara et al., 2022; Lestido-Cardama et al., 2022). XRF has been recognised as the best available technique and the best environmental practice (BAT/BEP) for screening plastic waste for Br (Li et al., 2019c), and positively correlated with conventional techniques like GC/MS for identifying regulated BFRs (Stapleton et al., 2011; Sharkey et al., 2018; Aldrian et al., 2015; Miller and Gearhart, 2015). XRF, however, has drawbacks. The main limitations of XRF are its lack of compound specificity, which means it cannot be used to identify specific brominated (or chlorinated) compounds (Lestido-Cardama et al., 2022), and poor sensitivity to light elements like P (Kajiwara et al., 2011; Petreas et al., 2016). Improvements to such inherent limitations are not possible.

According to various studies, other issues related to XRF could perhaps be improved (Figure 1.5). For example, measurements by XRF that are of insufficient duration can generate inaccurate readings (Sharkey, 2020). For that, XRF reading errors can be reduced by 4-8 % with sufficient testing times of up to 30 seconds (Aldrian et al., 2015). Interestingly, another study found that 28 out of 210 WEEE samples screened were false exceedances based on a 60-second measurement interval (Sharkey et al., 2022). There were no additional false exceedances when the measurement time was reduced to 10 s, and one only additional false exceedance when it was reduced to 5 s. In the same study, 86.7 % of WEEE was successfully screened for LPCL compliance using a 60 s screening time, and 86.2 % for a 5 s screening time (Sharkey et al., 2022).

Because XRF is a technology for surface screening, the distance between the sample, the source of radiation, and the detector has a significant impact on the X-ray signal (Aldrian et al., 2015). Therefore, the operator should provide the best possible contact between the XRF instrument and the sample to minimize geometric changes and enhance the accuracy of readings (Aldrian et al., 2015). Also, XRF findings can be less reliable, because of the heterogeneity, size, and surface topography and texture of samples (Furl, 2011; Aldrian et al., 2015). To minimise such inaccuracies, the sample surface should be free of contamination and coating (Aldrian et al., 2015), and repeated scanning for different areas of the sample can help to mitigate the effect of sample non-homogeneity effect (Sharkey, 2019). Finally, because thin samples are easily penetrated by X-rays and produce background interference from other components, controlling sample thickness improves XRF reading accuracy (Sharkey et al., 2018). A thickness of 12 mm has been established as the ideal minimum sample thickness in this regard (Jeannerat et al., 2016).

False exceedances and false negatives are potential drawbacks of using XRF to screen for adherence with permissible limits on concentrations of BFRs and Cl-OPFRs. To clarify, XRF can only identify the elemental composition of a sample rather than its molecular components. Thus, false exceedances occur when XRF measurements of Br indicate exceedance of the LPCL, but conventional techniques like GC/MS show POP-BFRs concentrations below the permissible limits. This was reported to occur due to the presence of different nonregulated BFRs like TBPPA or emerging BFRs (Harrad et al., 2019; Knutsen and Arp, 2021; Kajiwara et al., 2022; Lestido-Cardama et al., 2022). Also, false exceedances reading can happen when the sample thickness is not sufficient to prevent or avoid screening unwanted backscatter from substrate materials (Stapleton et al., 2011; Gallen et al., 2014). The widespread use of non-regulated BFRs like TBBPA has been identified as a major contributory factor to the observed XRF false exceedances in 9.7% (Harrad et al., 2019), 7% (Stapleton et al., 2011), 17% (Gallen et al., 2014), 13% (Knutsen and Arp, 2021), and 5% (Lestido-Cardama et al., 2022) of tested samples in different studies. Similarly, in terms of Cl-OPFRs, impurities in toluene diisocyanate and the presence of PVC are potential causes of false positive readings for Cl via XRF in 3 of 76 and 4 of 47 of foam samples (Stapleton et al., 2011; Petreas et al., 2016; Strobl et al., 2021).

A false negative, on the other hand, can also be generated by XRF if PBDE and HBCDD concentrations exceed LPCL levels, but XRF is unable to detect them (Sharkey et al., 2018; Sharkey et al., 2022). As opposed to false exceedances, false negatives would allow controlled flame retardants to be recycled into new items (Gallen et al., 2014; Petreas et al., 2016; Sharkey et al., 2018; Kajiwara et al., 2022). There were no false negative readings in studies conducted in Ireland (Sharkey et al., 2018; Harrad et al., 2019), Spain (Lestido-Cardama et al., 2022), and Norway

(Knutsen and Arp, 2021). However, among the 468 samples of plastics, textiles, and foams tested in a recent study in Ireland, nine (1.9 %) were false negatives; seven in furniture and ELV foam samples, and two in upholstery fabric samples. It is likely that some of these false negatives were related to the inhomogeneous mixing of BFRs in mixed materials or the low density of samples (Sharkey et al., 2022). In terms of Cl-OPFRs, a study attributed false negative readings for Cl and P elements in 2 of 47 samples due to density and texture issues of the examined samples (Petreas et al., 2016) and to Br element in 12.5% (6 out of 48) of samples where TBBPA concentrations found at 150 mg/kg (Gallen et al., 2014).

To enhance the accuracy and precision of XRF, the use of reference materials or matrix matched control standards was recommended (Aldrian et al., 2015; Schlummer et al., 2015; Guzzonato et al., 2016). Also, repeated sample measurements can be used to enhance XRF precision (Aldrian et al., 2015). Figure 1.5 provides tips to enhance XRF performance.

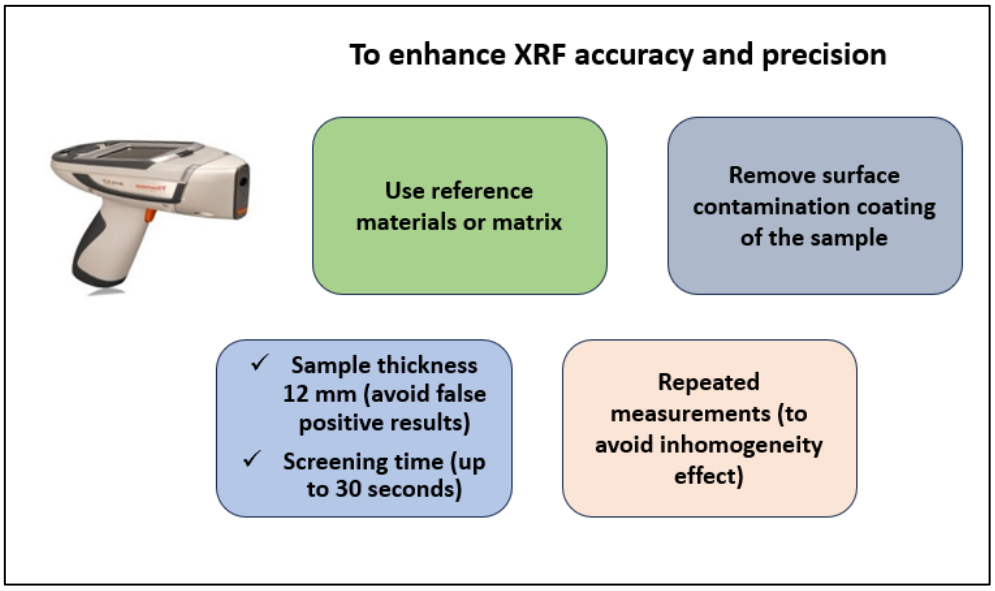


Figure 1. 5: Approaches for improvement of XRF performance

1.11 Current knowledge gaps

Flame retardants have been found in plastic objects that are not obliged to comply with fire safety regulations, such as children's toys, FCAs and packaging materials. There is substantial evidence that this is due to the use of recycled polymers that were flame retarded in their first application. In response to this, jurisdictions like the EU have introduced limits on the concentration of some flame retardants in waste plastics, which prevent such items from being recycled if exceeded. To date, such limits are established for a small number of BFRs, but similar limits are anticipated to be set for Cl-OPFRs in the near future. These limit values can substantially reduce contamination in recycling if they are implemented effectively. Successful implementation of legislative limits on halogenated chemicals in waste, however, faces several obstacles, including the large number of items that require checking and the high cost and time involved in GC-LC/MS analyses. Consequently, an inexpensive, quick, and accurate screening technique is urgently needed.

According to the literature, even though XRF cannot measure specific Cl-OPFRs or BFRs accurately, it is a fast, simple, and cost-effective method of determining whether such BFR concentrations are exceeding LPCLs. The only requirement in this context is that XRF identifies whether the LPCL value is exceeded correctly. However, the causes of false exceedances recorded by XRF need to be investigated in more detail. Moreover, while the use of XRF as a screening tool for BFRs has been the subject of numerous studies, there have been very few studies on the suitability of XRF to verify compliance with possible limits on the concentrations of Cl-OPFRs in plastics. Also, there is currently little to no evidence in the literature on the presence of Cl-OPFRs in waste soft furnishings, building insulation foam, and childcare goods. Indeed, there are only a few data points on the topic of Cl-OPFRs concentrations in

goods, and their levels in items that do not require fire retardancy like juvenile goods and toys, FCAs and others, which potentially indicate contamination from recycled materials. The lack of data on these topics creates significant research gaps.

1.12 Hypotheses and objectives

The hypotheses of this thesis are:

1. XRF is a viable tool for screening waste for compliance with potential limits on maximum permissible concentrations of Cl-OPFRs;
2. Cl-OPFRs have been extensively used in consumer products, and
3. the levels and relative abundance of Cl-OPFRs will be subject to international variation due to national differences in flame retardancy regulations and the means via which they are met.
4. The high concentrations of Cl-OPFRs in furniture and childcare items may lead to substantial exposure via the dermal pathway.

To test these hypotheses, the principal objectives are thus to:

1. Compare XRF readings for Cl and P to the GC/MS results obtained for a wide range of plastic waste articles.
2. Enhance understanding of the causes of any false positive and false negative readings obtained by XRF.
3. Report for the first time on the concentrations of Cl-OPFRs in waste items including furniture and childcare items from three countries (Ireland, UK, and Saudi Arabia).
4. Estimate human exposure to Cl-OPFRs via dermal uptake following different scenarios.

Chapter 2: Methodology

To address the hypotheses and objectives of this thesis, sampling methodology and analytical techniques were developed and adjusted from previous studies (Abdallah et al., 2017; Drage et al., 2018; Wu et al., 2018) to measure concentrations of Cl-OPFRs in samples of furniture and childcare products, and to facilitate the assessment of the main factors affecting human exposure to Cl-OPFRs via dermal uptake. This chapter provides a detailed discussion of the materials and methods used for collecting samples of furniture and childcare items, as well as the extraction, and analysis of Cl-OPFRs in these samples. Also, this chapter describes the validation of analytical procedures, as well as the quality assurance/quality control measures used to ensure the accuracy and consistency of the generated data.

2.1 Sampling

For this PhD study, samples were collected from soft furnishing and childcare items in 3 countries, Ireland, Saudi Arabia, and the UK. In all, 525 samples were obtained (Figure 2.1) including fabrics, foams, extruded polystyrene (XPS), expanded polystyrene (EPS), leather, and wool from soft furnishing and childcare goods. A 16-24 cm^2 surface area aliquot of each sample was collected by cutting or tearing from the main sample body, wrapped in aluminum foil, and sealed in a small Ziploc bag for later laboratory analyses. Details of sampling locations, numbers and categories are provided in the following sections.

In the process of sample selection and collection in Saudi Arabia, it is important to acknowledge the potential for bias, as the sourcing of fabric and items mostly relied on contributions from family and friends. It is worth noting that a similar pattern may be observed in the UK and Ireland samples, where connections with friends,

collaborators, and local networks may have influenced the selection process. Certainly, this approach facilitated accessibility and cooperation, but its impact with respect to bias is unknown. We do not, however, consider it likely that sample donors will have specifically sought out samples that they considered likely to be more (or less) contaminated with Cl-OPFRs, as donors were rarely environmental chemists.

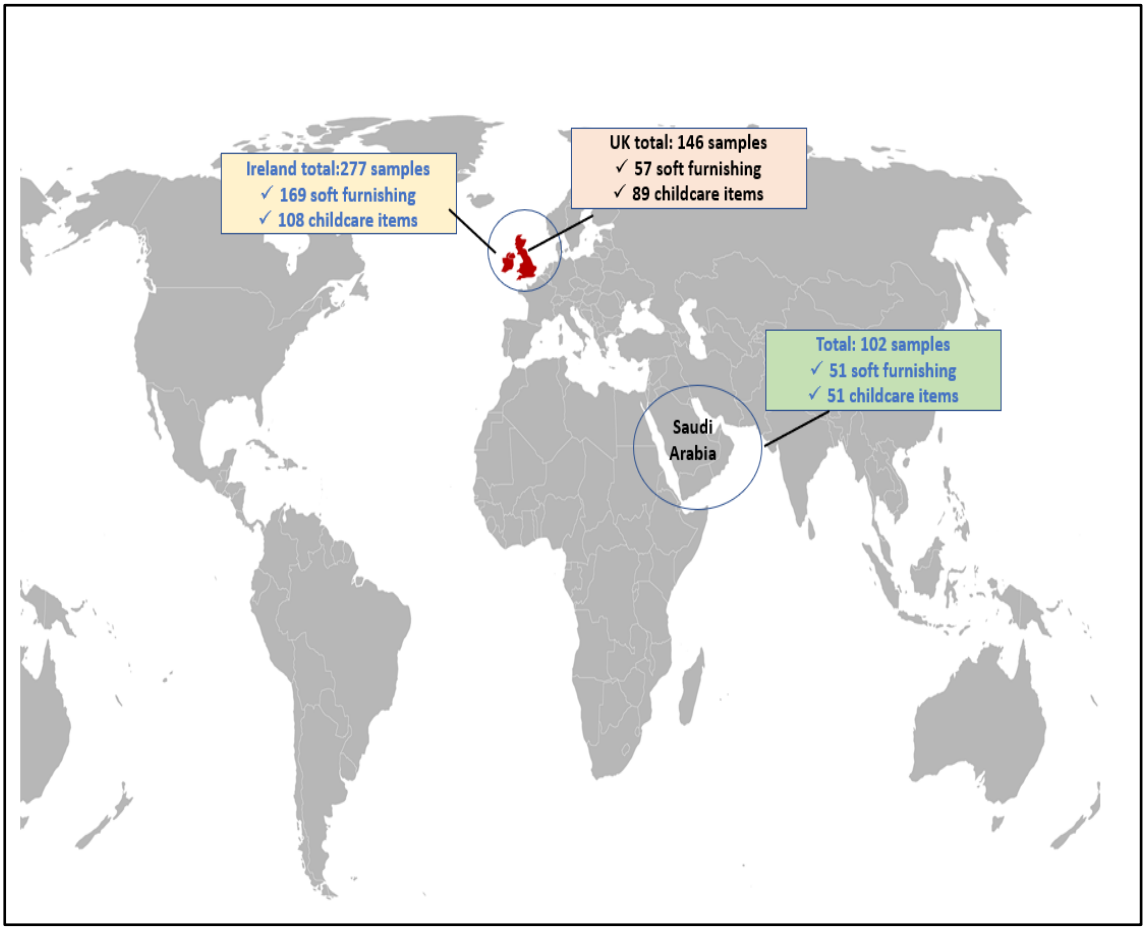


Figure 2. 1: Sample locations and numbers

2.1.1 Furniture, end of life vehicle, and childcare article samples from Ireland

For this PhD study, archived samples collected previously in Ireland as part of two projects (WAFER and SAFER) were obtained. WAFER is an abbreviation of "Evaluation of Hand-held XRF for Screening Waste Articles for Exceedances of Limit Values for Brominated Flame Retardants", while SAFER is an abbreviation of "Screening of the Irish Waste Stream for Persistent Organic Chemicals". WAFER

project samples were collected from waste sites in Ireland between October 5th 2015, and May 18th 2016 (Harrad et al., 2019), while the SAFER project samples were collected from waste collection or waste transfer sites within the County Galway region in Ireland between 2019 and 2020.

2.1.1.1 End of life vehicle and soft furnishing samples from Ireland

Samples from 169 ELV (end-of-life vehicle) and soft furnishing waste were available to be studied in this thesis. The ELV samples (n=97) were collected in Ireland from cars that were intended to be scrapped or recycled and consisted of seat upholstery (n=34), seat PUF (n=35) fillings, roof trim (n=13), floor mats (n=10), and ceiling padding (n=5). For each sample, the vehicle make, model, and manufacture year were recorded whenever possible. On the other hand, soft furnishings (n=72) were divided into three waste sub-categories, specifically comprising: carpets and curtains, furniture fabrics and foam fillings, and mattresses. The numbers of archived WAFER project samples studied are provided in Table 2.1.

Table 2. 1: Categories and subcategories of soft furnishng and ELV waste from Ireland analysed in this study (2015-2016)

Category	**Sub-category**	**Number of samples**
End of life vehicle (ELV) articles	Foams	35
	Fabrics	34
	Floor mat	10
	Padding	5
	Roof trim	13
Total ELV	-	97
Soft furnishings	Carpets	22
	Curtains	7
	Furniture fabrics	15

	Furniture foam filling	12
	Mattress foam filling	10
	Mattress fabric covering	6
Total soft furnishings	-	72

2.1.1.2 Childcare articles

Regarding samples of childcare articles, 108 samples were collected (Table 2.2). Samples include fabric, foam, and wool of childcare goods from car seats (n=62), changing mat foams (n=14), pushchairs (n=15), and a mix of other samples (n=17) from items like play mats, child couches, prams, baby seats, and cot mattress.

Table 2. 2: Categories and subcategories of waste childcare items from Ireland analysed in this study (collected in 2019-2020)

Category	**Sub-category**	**Number of samples**
Child car seat n=62	Foams	19
	Fabrics	15
	XPS	2
	EPS	5
	Wool	21
play mat n=3	Fabric	2
	Wool	1
Baby seat n=6	Fabric	4
	Wool	1
	Foam	1
Pram n=2	Wool	2
Child couch n=3	Fabric	2
	Foam	1
Cot mattress n=3	Fabric	1

	Foam	2
Changing mat foam n=14	Wool	14
Pushchair n=15	Fabric	5
	Wool	9
	XPS	1
Total	-	108

2.1.2. Furniture and childcare articles from Saudi Arabia

2.1.2.1 Soft furnishing samples

Samples were taken from items donated by residents of Jeddah and Riyadh, Saudi Arabia (Table 2.3). Regarding the furniture fabric, PUF and fillings, in May 2019 about 48 samples were taken from sofas, ottomans, cushions, bed frames, pillows, and related other products. Also, carpet and rug samples were obtained. Household furniture samples included: fabrics (n=19), PUFs (n=15), wool (n=10), and fillings (XPS n=1 and EPS n=3). The other samples included carpet and carpet padding (polypropylene wool and XPS n=2) and rug (polypropylene wool n=1) (Table 2.3). Information about the sample providers and year of purchase are not available due to the nature of samples.

Table 2. 3: Categories and subcategories of soft furnishing waste from Saudi Arabia analysed in this study (2019)

Category	**Sub-category**	**Number of samples**
Sofa n=6	Fabric	7
	PUF	6
	Wool	2
Ottoman n=2	Fabric	2
	PUF	1

	Wool	1
Cushion n=3	Fabric	3
	PUF	2
	Wool	3
Pillow n=2	Fabric	2
	Wool	2
Carpet and carpet padding n=2 **Rug n=1**	Polypropylene wool and XPS Polypropylene wool	2 1
Bed frame n=2	Fabric PUF Wool	1 1 1
Mix of household items n=10	Fabric PUF Wool EPS XPS	4 5 1 3 1
Total	-	51

2.1.2.2 Childcare articles

In June 2021, Saudi women volunteered to donate unused childcare goods to be examined in this PhD study. The samples in total (n=43) included fabric (n=23), foam (n=4), wool (n=5), XPS (n=1), and PUF (n=10) from about 16 items of 4 children's car seats, 2 baby walkers, 2 bouncers, Moses' baskets, carrycots, 4 soft play foams, a child mattress, and a changing mat. In February 2022, an additional 8 samples (5 fabrics, 2 wool, and 1 PUF) were collected from 6 items consisting of a stroller, a pushchair, 2 toys, and 2 baby chairs. Table 2.4 shows the number, category, and subcategories of childcare items samples from Saudi Arabia.

Table 2. 4: Categories and subcategories of waste childcare articles from Saudi Arabia analysed in this study (2021-2022)

Category	**Sub-category**	**Number of**

		samples
Car seat n=4	Fabric	7
	PUF	3
	Wool	1
	XPS	1
Child mattress n=1	Fabric	1
	PUF	1
Baby walker n=2	Fabric	4
	PUF	3
Stroller and pushchair n=2	Fabric	3
Baby chair n=2	PUF	1
	Wool	1
Bouncer n=2	Fabric	4
	Wool	2
Moses' basket n=1	Fabric	2
	Wool	1
Changing mat n=1	Fabric	1
	PUF	1
Carrycot n=1	Fabric	4
	PUF	2
	Wool	1
Soft play foam n=4	Foam	4
Teddy bear toy and toy holder n=2	Fabric Wool	2 1
Total	-	51

2.1.3. Furniture and childcare goods samples from the UK

2.1.3.1 Soft furnishing samples

Regarding samples of soft furnishings from the UK, we analysed 51 samples collected as part of a separate project led by WRc plc (Water Research Centre) on behalf of the Environment Agency in 2022. The items collected were sofas, chairs, armchairs, and others (like footstools). Thirty-four samples were in their original status and comprised: leatherette covers (n=23), lining (n=2), leather covers (n=5), textile covers (n=2), foam (n=1), and miscellaneous (n=1). In addition to these, 17 samples were provided for analysis as ground powder obtained by grinding samples rendered brittle via immersion in liquid nitrogen. These pre-ground samples consisted of 4 textile and 1 leather cover, along with 6 foam fillings from sofas: 1 leather and 3 textile armchair covers, as well as 1 foam sample from a footstool and another from a chair. Finally, fabric, PUF, lining, and wool samples were collected from unused two sofas in Birmingham. Table 2.5 shows the number, category, and subcategories of soft furnishing samples from UK.

Table 2. 5: Categories and subcategories of UK soft furnishing waste samples analysed in this study (2022)

Category	Sub-category	Number of samples
Sofa n=18	Cover (leatherette)	10
	Cover (leather)	4
	Lining	2
	Foam	1
	Miscellaneous	1
Armchair n=8	Cover (leatherette)	6
	Cover (leather)	1

	Cover (textile)	1
Chair n=6	Cover (leatherette)	6
Other n=2	Cover (leatherette)	1
	Cover (textile)	1
Sofa n=2 (Birmingham)	Fabric	3
	PUF	1
	Wool	1
	Lining	1
Total	-	40
Ground powder samples		
Category	**Sub-category**	**Number of samples**
Sofa n=10	Cover (textile)	3
	Foam	6
	Cover (leather)	1
Armchair n=5	Cover (textile)	3
	Foam	1
	Cover (leather)	1
Chair n=1	Foam	1
Other (footstool) n=1	Foam	1
Total	-	17

2.1.3.2 Childcare articles

A total of 11 items were collected following a call for donations in Birmingham, UK in March 2022, yielding 52 sub-samples. The 11 items were: a baby bed, two pushchairs, a baby feeding seat, a liner for a car seat pushchair, a sample of soft play foam, a baby walker, a play mat, a sleeping bag, a car seat head holder, and a baby mattress. In April 2022, another 5 items including a child booster seat, 2 baby carriers,

changing mat, and Moses' basket were obtained, and 37 samples were collected from these goods. Overall, samples were fabric (n=57), PUF (n=12), wool (n= 15), XPS (n=3), foam (n=1) and leather (n=1) from all 16 items, which summarized in Table 2.6. The brands of the goods were noted as much as possible.

Table 2. 6: Categories and subcategories of UK waste childcare articles analysed in this study (2022)

Category	**Sub-category**	**Number of samples**
Baby bed n=1	Wool	1
Pushchair n=2	Fabric	9
	PUF	2
	Wool	2
	Leather	1
Baby mattress n=1	Fabric	1
	PUF	1
Baby feeding seat n=1	Fabric	4
	Wool	2
Liner for car seat and pushchair n=1	Fabric	4
	Wool	2
Soft play foam n=1	Foam	1
Baby walker n=1	Fabric	3
	PUF	1
Baby play mat n=1	Fabric	6
	Wool	2
	XPS	1
Baby sleeping bag n=1	Fabric	4

	Wool	2
Car seat head holder n=1	Fabric	1
	PUF	1
	Wool	1
Child booster seat n=1	Fabric	2
	PUF	2
Baby carrier n=2	Fabric	11
	PUF	2
	Fabric with PUF	3
	Wool	2
	XPS	2
Changing mat n=1	Fabric	4
	PUF	2
Moses' basket n=1	Fabric	5
	PUF	1
	Wool	1
Total	-	89

2.2. Chemicals

Native (TCEP, TCIPP and TDCIPP), and isotopically labelled (d_{12}-TCEP and d_{15}-TDCIPP) standards were purchased from Wellington Laboratories Inc. Guelph, Canada as stock solutions in toluene. The recovery determination standard (RDS) 2,3,4,6- tetrachlorobiphenyl (PCB-62) was purchased from Dr. Ehrenstorfer GmbH. Augsburg, Germany as a stock solution in isooctane. The isotopic purity of all standards was > 98%. The chemical properties of all reference standards are summarised in (Table 2.7).

Table 2. 7: Details of native, internal, and recovery determination standards used in this thesis.

Compound name and abbreviation	Molecular formula	Molecular weight	Isotopic Purity	Concentration
Internal standards				
deuterated-tris (1, 3-dichloro-2-propyl) phosphate (d_{15}-TDCIPP)	$C_9D_{15}Cl_6O_4P$	446.0	98 %	50 µg/mL
deuterated-tris(2-chloroethyl) phosphate (d_{12}-TCEP)	$C_6D_{12}Cl_3O_4P$	297.56	98 %	50 µg/mL
Native standards				
Tris(2-chloroethyl) phosphate (TCEP)	$C_6H_{12}Cl_3O_4P$	285.5	98 %	50 µg/mL
Tri (2-chloroisopropyl) phosphate (TCIPP)	$C_9H_{18}Cl_3O_4P$	327.57	98 %	50 µg/mL
Tri (1,3-dichloropropyl) phosphate (TDCIPP)	$C_9H_{15}Cl_6O_4P$	430.9	98 %	50 µg/mL
Recovery Determination Standard				
2,3,4,6-Tetrachlorobiphenyl (PCB-62)	C_{12} H_6 Cl_4	291.99	98%	100 µg/mL

2.2.1 Internal and calibration standards preparation

Two internal standards (ISs), d_{15}-TDCIPP and d_{12}-TCEP, each at a concentration of 50 µg/mL were used to prepare the IS mixture used to spike samples. To prepare 1 µg/mL of IS, 20 µL of each of the two above mentioned standards were added to a GC/MS vial, diluted with 960 µL of toluene then vortexed for 2 minutes. To prepare 5 µg/mL of native standard mix, 100 µL of each of the three native standards (TCEP, TCIPP, and TDCIPP each at 50 µg/mL) were added to GC/MS vial, diluted with 700 µL of toluene then vortexed for 2 minutes.

In order to prepare 5 calibration standards, a mixed solution of d_{15}-TDCIPP and d_{12}-TCEP, as well as TCEP, TCIPP, and TDCIPP, was prepared by dissolving all the above-mentioned mixes of internal and native standards in toluene as described in Table 2.8. Each of the stock standards used were at a concentration of 50 µg/mL. After preparing each calibration standard, the solution was vortexed for 3 minutes.

Table 2. 8: Concentrations of native Cl-OPFRs in the five-point calibration standard mixtures

Concentrations of natives in each calibration standard mixture pg/ µL	Volume (µL) of each 5 µg/mL native solution added (n=3)	Volume (µL) of each 50 µg/mL IS solution added (n=2)	Volume (µL) of toluene added
50	10	30	960
100	20	30	950
250	50	30	920
500	100	30	870
1000	200	30	770

2.2.2 Recovery Determination Standard (RDS)

To prepare 250 pg/µL of PCB-62 (RDS), 10 µL was taken from the stock concentration of 100 µg/mL and diluted with 3990 µL of toluene then vortexed for 2 minutes. After that, to prepare internal-recovery standards, 10 µL of IS mix plus 10 µL of prepared RDS were added to a clean GC/MS vial, and eventually diluted with 190 µL of toluene and vortexed for 2 minutes.

For sample preparation prior to GC/MS analyses, solvents such as acetone, hexane, toluene, ethyl acetate, dichloromethane (DCM), and methanol were HPLC (high performance liquid chromatography) grade supplied by Fisher Scientific UK Ltd.

2.3. Extraction and clean up procedure

Prior to the extraction process, it was important to minimise contamination of laboratory tools like glassware, tweezers, and scissors; to do so, they were rinsed twice with hexane: acetone (3:1 v/v), then rinsed twice with acetone.

For subsequent extraction, 50 mg of sample was accurately weighed, and transferred to a sterile 15 mL Greiner Bio-One™ CELLSTAR™ test tube. For extraction, 5 mL of hexane; methanol; DCM (1:2:1) was added to the sample, then vortexed for 2 minutes and sonicated for 20 minutes (three times). From the extraction, 50 µL was

transferred to a new sterile Greiner Bio-One™ CELLSTAR™ test tubes, spiked with 10 µL of IS (1 ng/µL), then evaporated under a gentle stream of nitrogen until incipient dryness, and finally resolubilised with 200 µL of toluene and transferred to GC/MS vial. 10 µL of the RDS PCB-62 (250 pg/µL) was added as well to the same GC/MS vial then vortexed for 10 seconds. The extraction procedure was carried out in a clean fume hood to prevent contamination. The extraction/clean up method is summarised in Figure 2.2 and 2.3.

Cleaning: rinse the glassware, tweezers, and scissors twice with Hexane: Acetone (3:1) Then rinse twice with Acetone
Weighing: weight 50 mg of sample + transfer it to a 15 mL Greiner Bio-One™ CELLSTAR™ test tubes
EXTRACTION & CLEAN UP
Add 5 mL hexane: methanol: DCM (1:2:1) vortex 2 min sonicate for 20 minutes **(Repeat the vortex and sonication step 3 times)**
Transfer 50 µL of the above extract to a new sterile Greiner Bio-One™ CELLSTAR™ test tube spike with 10 µL of IS (1 ng/µL) blow down under N_2 until incipient dryness add 200 µl of toluene + vortex 2 minutes transfer to GC/MS vial then add 10 µL of the RDS PCB-62 (250 pg/µL) and vortex ready for injection

Figure 2. 2: Summary of Cl-OPFRs extraction and clean up method for GC/MS analyses

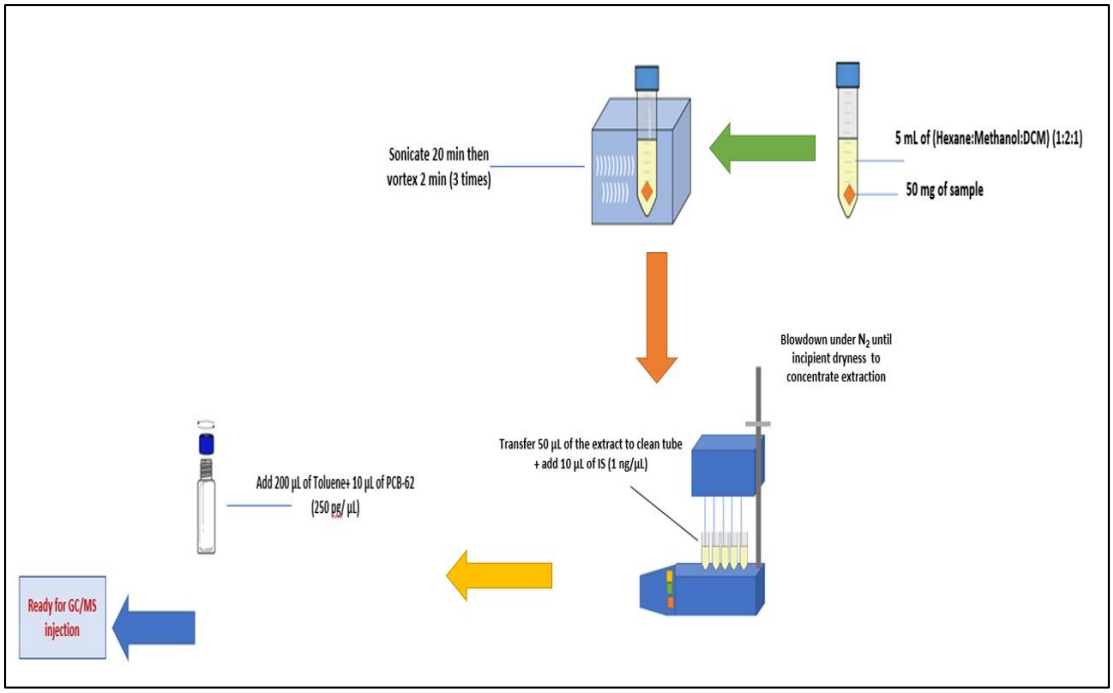


Figure 2. 3: Cl-OPFR extraction and clean up method for GC/MS analyses

2.4. Instrumental analysis

2.4.1. X-ray fluorescence (XRF)

The XRF is thoroughly confirmed for accuracy before screening samples, undergoing annual calibration by the instrument manufacturer (Niton). Such regular calibration checks, using certified reference materials, was essential to maintain the accuracy and repeatability of XRF measurements over time.

A new dedicated test-stand approach was created, which uses a configuration that eliminates interference from other materials, resulting in more accurate results, particularly when dealing with thinner samples like fabrics and in situations where the presence of air within the samples may affect results – as is the case with PUF, EPS, and XPS foams. The employed Niton XL3t GOLDD+ XRF analyser can identify chlorine (Cl) and phosphorus (P) at levels as low as 60 mg/kg and 250 mg/kg, respectively.

To determine concentrations of chlorine (Cl), phosphorus (P), bromine (Br) and antimony (Sb), a small piece was cut from each sample (1 to 3 cm^2) to get a suitable size for the XRF measurement chamber. The XRF measuring chamber (portable XRF test stand) (Figure 2.4) was pre-cleaned by wiping with an ethanol-impregnated clean tissue prior to using it. The XRF test stand contains radiation and minimises interfering factors such as, change of the distance or angle of the measuring device of XRF and the sample, and unintentional measurement of the surrounding area or other components.

Figure 2. 4: Portable XRF test stand

To screen samples for elemental analyses, a hand-held XRF spectrometer (Niton^{TM} XL3t GOLDD^{+} XRF Analyser, Thermo Fisher Scientific) was occupied (Figure 2.5). First, the XRF analyser must be grasped by the handle. Through the measurement window, primary radiation was produced by the analyser and emitted out to screen the sample by pulling the trigger and initiating sample analyses (Figure 2.5).

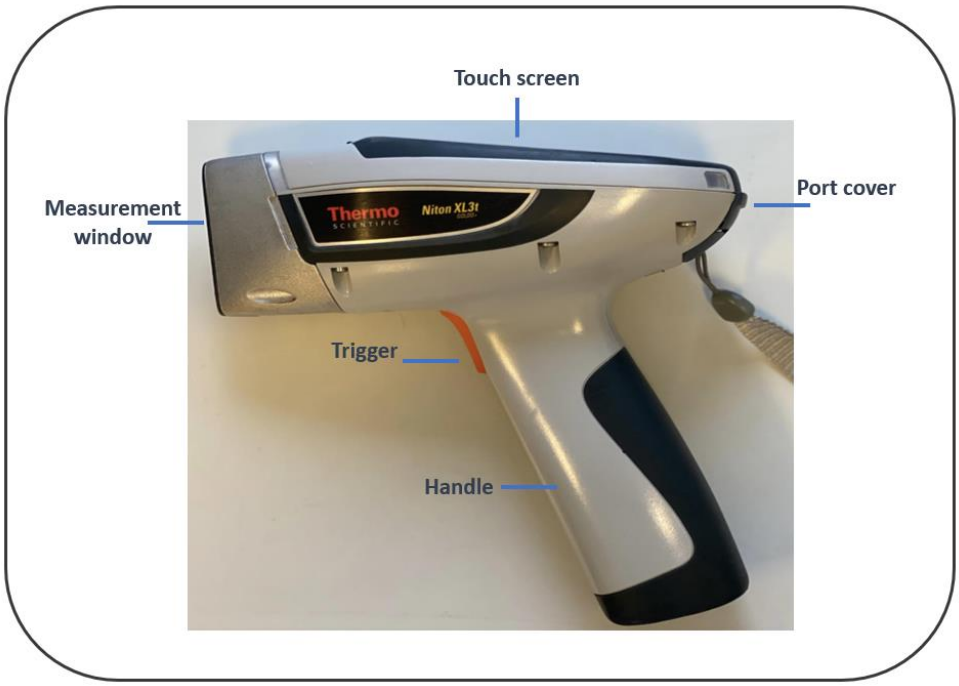


Figure 2. 5: XRF NitonTM XL3t GOLDD+ XRF Analyser, Thermo Fisher Scientific overview

The touch screen is part of the XRF control panel, which allows to access all screens and menus of the analyzer (Figure 2.6). On/Off Button controls power to analyzer and pressing enter button will lead to radiation warning screen then to password screen (Figure 2.9). The 4-way touch pad has four buttons, right, left, up, and down to highlight the system icon.

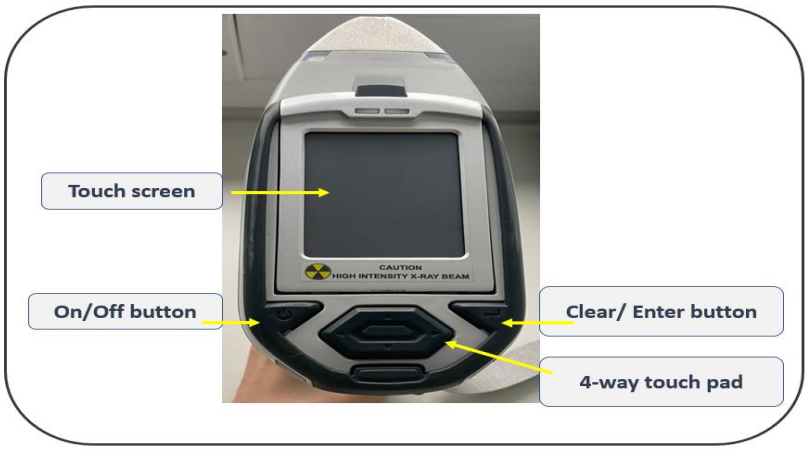


Figure 2. 6: XRF control panel

The port cover part includes (USB port, power port and remote trigger port) those employed when connected the XRF to portable test stand for remote work while connected to the computer (Figure 2.7).

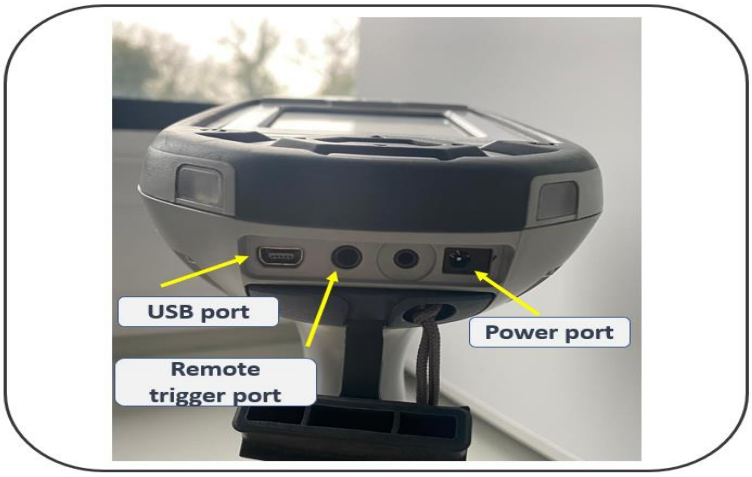


Figure 2. 7: XRF data ports

The Remote Trigger Port controls the analyzer's trigger function when its cable is attached to the portable test stand and to the XRF. This allows the analyser to detect if the protective lid is closed or open, and thus whether it is safe to initiate a test. If the instrument is unplugged, it will not be able to initiate a reading.

The USB Port is a communications and control port used to upload and download data, configuration files, and software from the analyzer, which requires the plug of the USB cable into the computer's USB port and other end plugged into the test stand's USB port.

Once the portable test stand was completely set up, the XRF front part was placed into the cone-shaped opening under the top half of the stand's floor and pushed gently until recoginsed by the software (Figure 2.8).

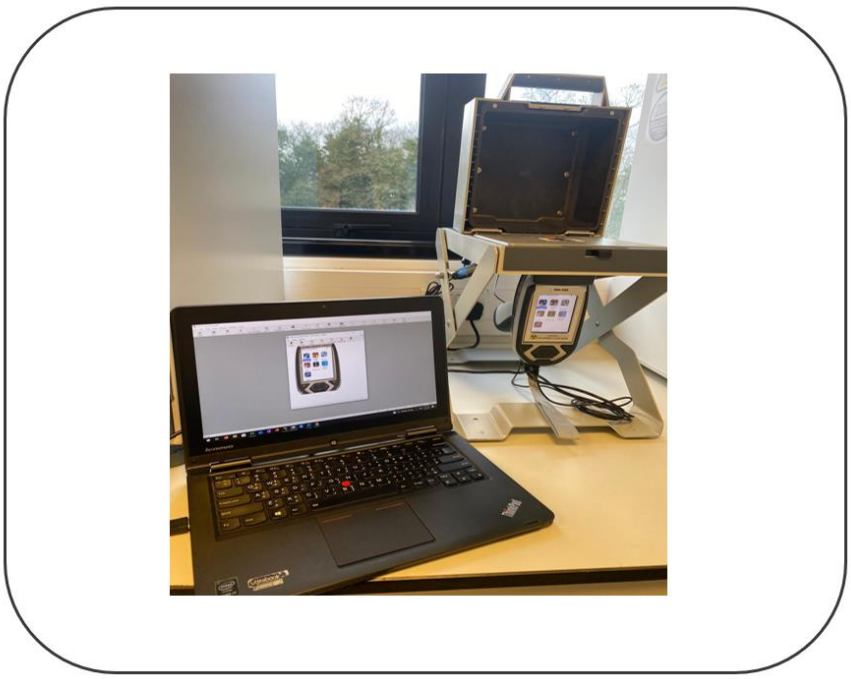


Figure 2. 8: Full set up and life screen

To turn on the XRF, on the operating panel, the on/off power button was pressed, the radiation warning was acknowledged and the security 4 digit code entered (Figure 2.9).

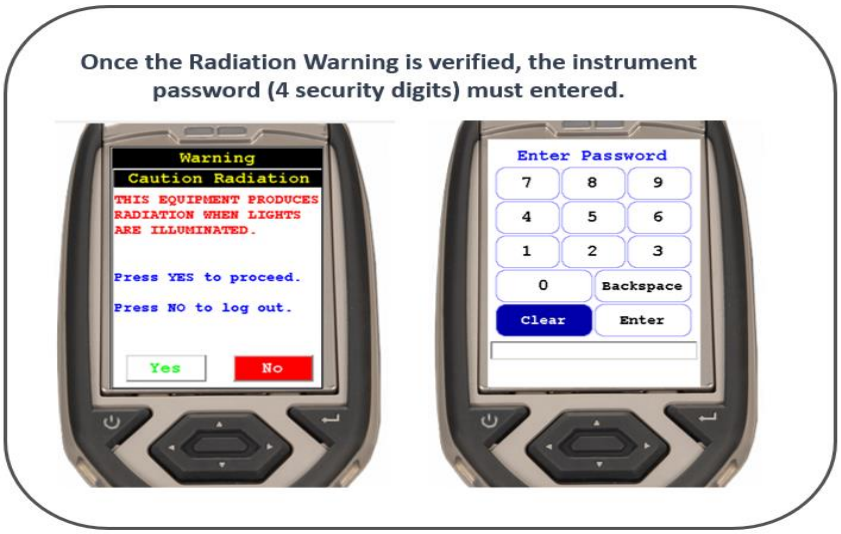


Figure 2. 9: Warning screen and virtual numeric keypad for log on

After positioning the sample on the designated area of the portable test stand, the (analyze) icon was clicked, then "user sample" and finally selected the user-installed methods for Cl and P analyses were choosen (Figure 2.10). Then, the remote trigger was clicked to initiate screening and the Cl and P readings were acquired on the screen (Figure 2.11 and 2.12). To avoid heterogeneity and measurement error, three replicates were applied for samples from different areas and the average of these calculated. The methods installed for Cl and P screening are shown in (Figure 2.13 and 2.14).

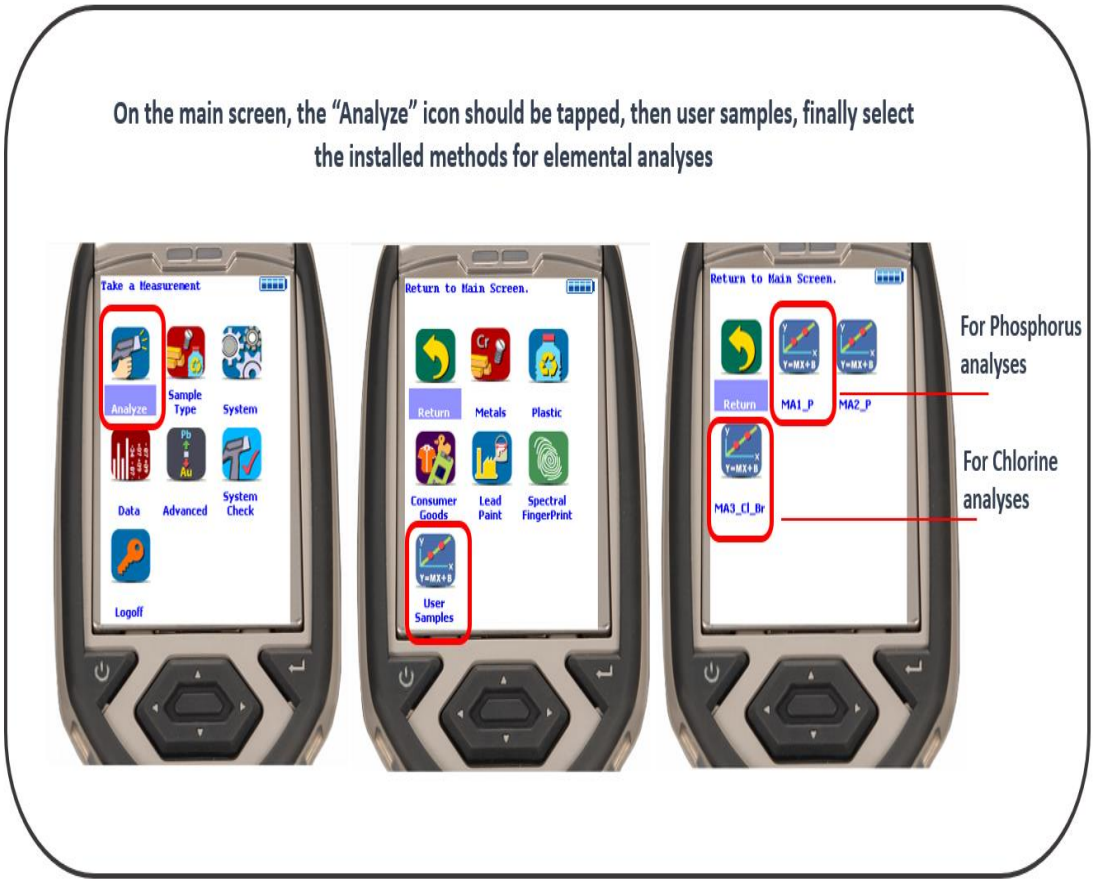


Figure 2. 10: The XRF system menu

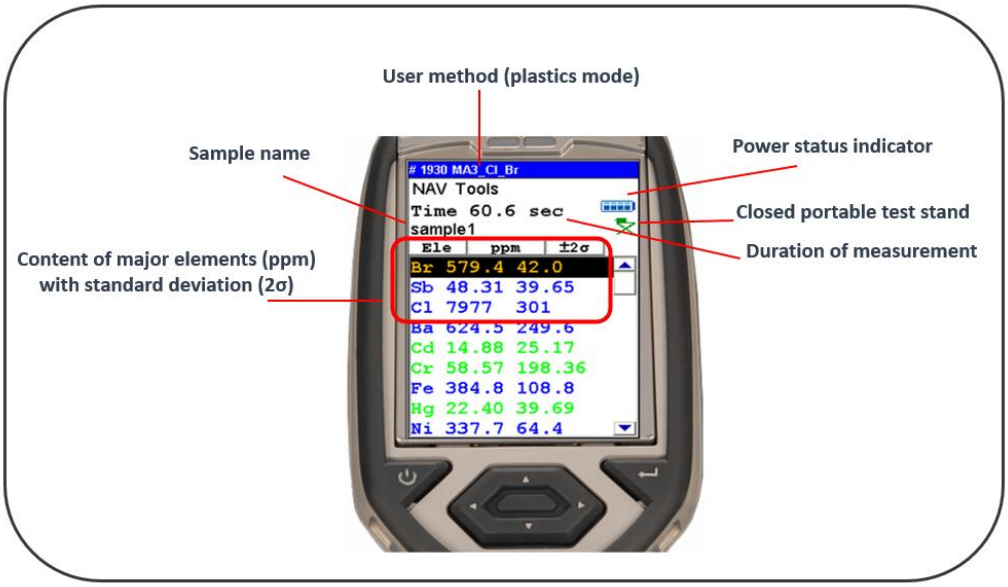


Figure 2. 11: Interpretation of XRF Chlorine results

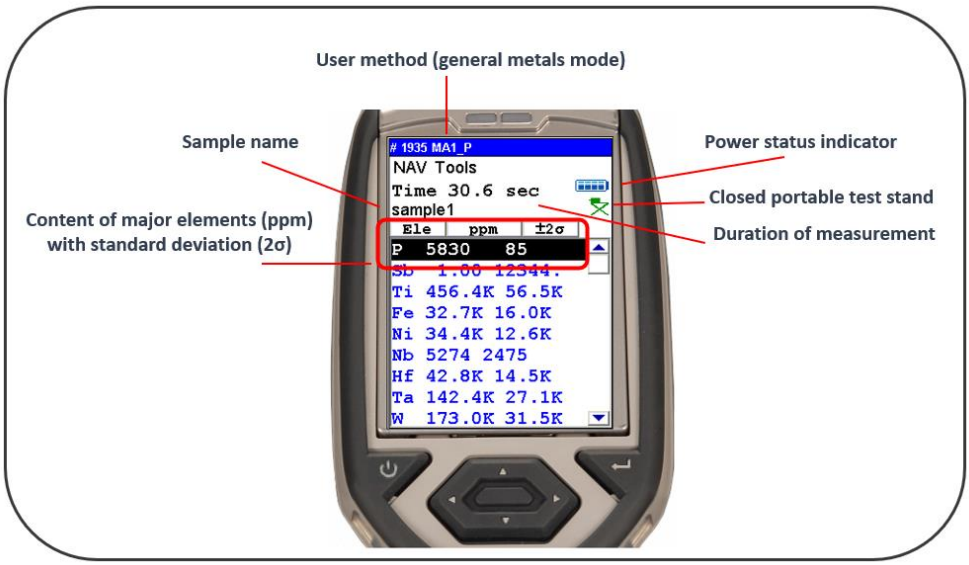


Figure 2. 12: Interpretation of XRF phosphorus results

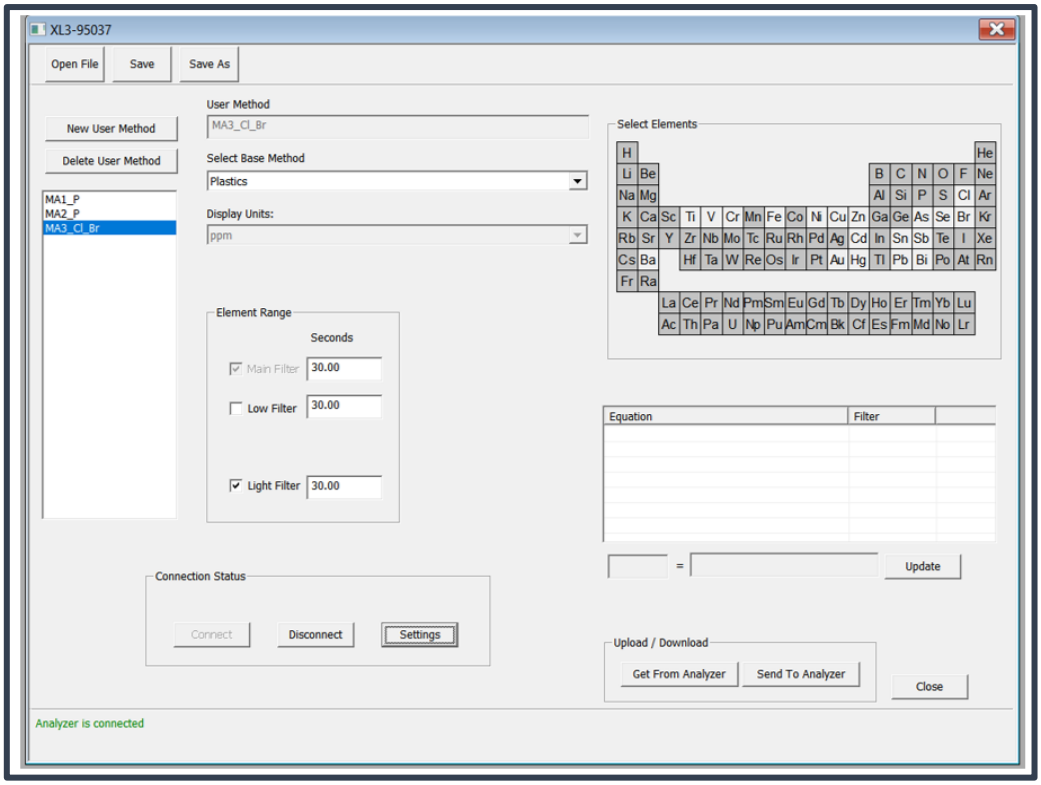


Figure 2. 13: Analytical method for measuring Chlorine

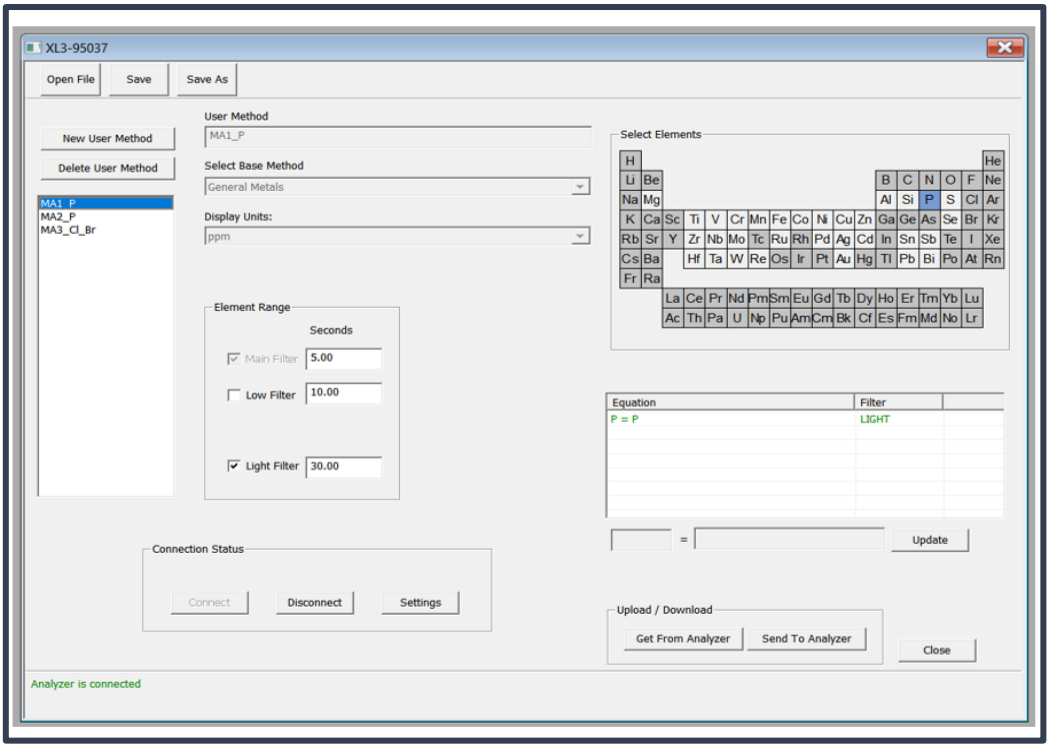


Figure 2. 14: Analytical method for measuring Phosphorus

To obtain the XRF readings, the Thermo Scientific NDT (Niton Data Transfer) software program includes a download icon that can provide such readings besides the image of the screened sample. An Excel data sheet can be generated that shows measured concentrations (and standard deviations, n=3) of Br, Sb, Cl, and P in individual samples, besides unit of concentrations measured (ppm=mg/kg), sample name, and the applied method of screening. Other information like sample description, size, and other potentially important notes can be added to the data sheet (Figure 2.15).

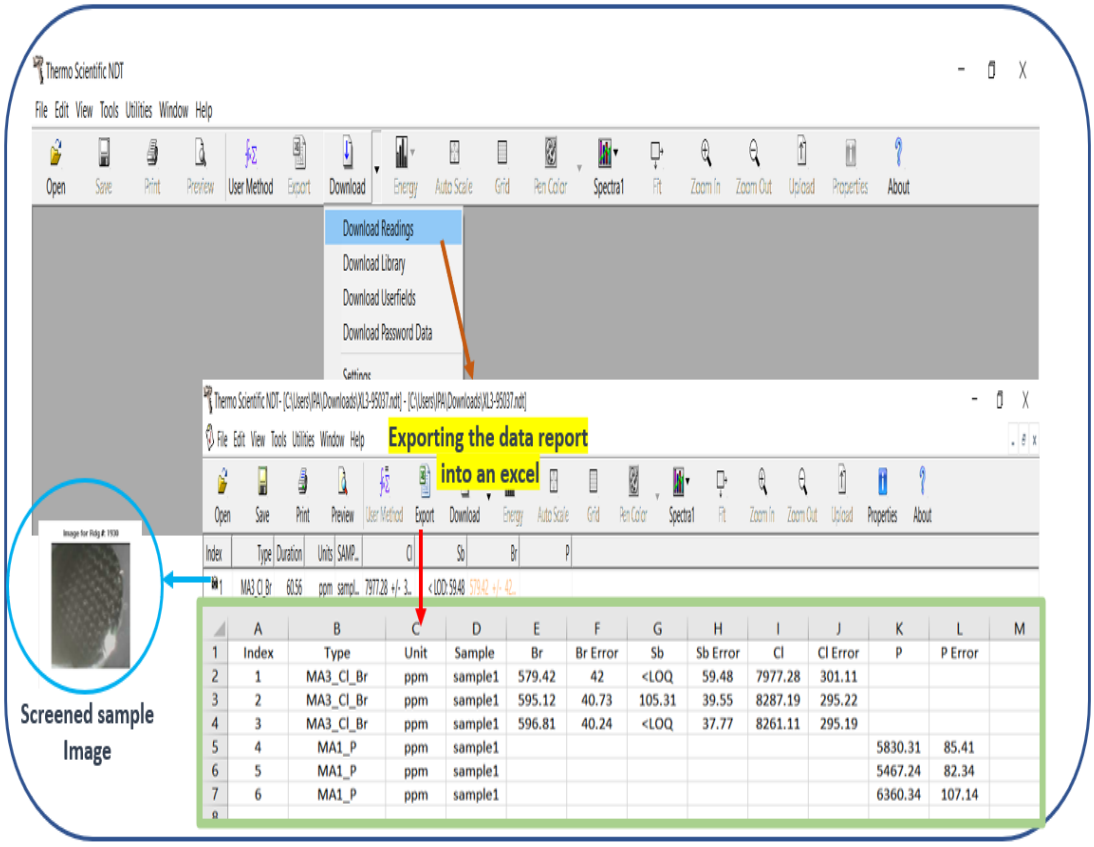


Figure 2. 15: Sample XRF reading report

2.4.2. GC/MS

The analysis of Cl-OPFRs was carried out using a method developed on an Agilent 5975C GC/MS equipped with a 30 m DB-5 MS column (0.25 mm id, 0.25 m film

thickness) with the MS operated in electron ionisation (EI) mode. Helium was employed as the carrier gas, and the flow rate was kept constant at 1.0 mL/min. Under splitless injection mode, the injector temperature was adjusted to 290 °C, and the MS ran with a solvent delay of 5 minutes. The temperatures of the ion source, quadrupole, and interface were respectively set to 230 °C, 150 °C, and 300 °C. The GC temperature programme was 65°C, hold for 0.75 min, ramp 20°C/min to 250˚C, hold for 1 min, ramp 5 °C/min to 260 °C, and hold for 0 min, ramp 30 °C/min to 305 °C, and hold for 1 min ((Figure 2.16 to Figure 2.19). Total run time was 15 min.

Table 2.9 provides an overview of the ions monitored for identification and quantification of target compounds, internal standards (IS) and the recovery determination standard (RDS). TDCIPP was quantified against d_{15}-TDCIPP, while d_{12}-TCEP was used to quantify TCEP and TCIPP.

Table 2. 9: Ion (m/z) monitored and retention time monitored for target compounds, internal standards (IS) and recovery determination standard (RDS)

Analyte	Quantification Ion	Identification Ion	Retention time (min)
TCEP	249	251	8.91
TCIPP	277	279	9.09
TDCIPP	381	383	12.20
d_{12}-TCEP	261	263	8.85
d_{15}-TDCIPP	394	396	12.08
PCB-62	292	294	10.13

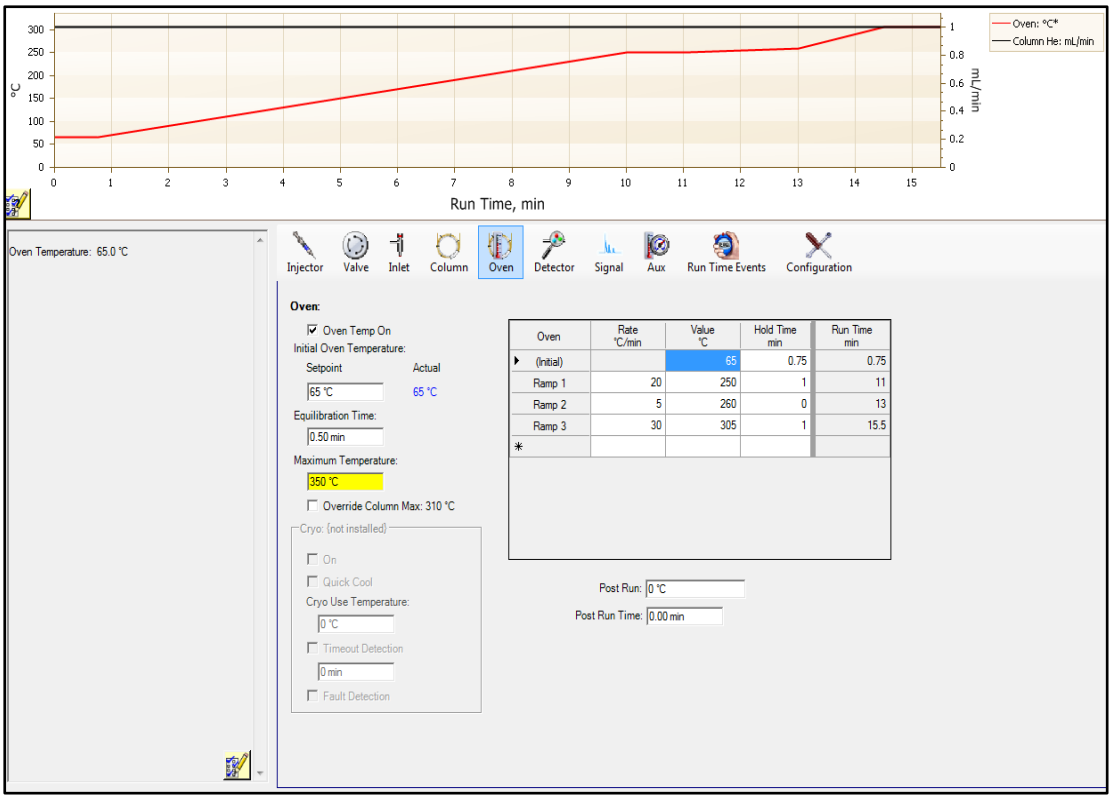


Figure 2. 16: GC temperature programme for Cl-OPFRs

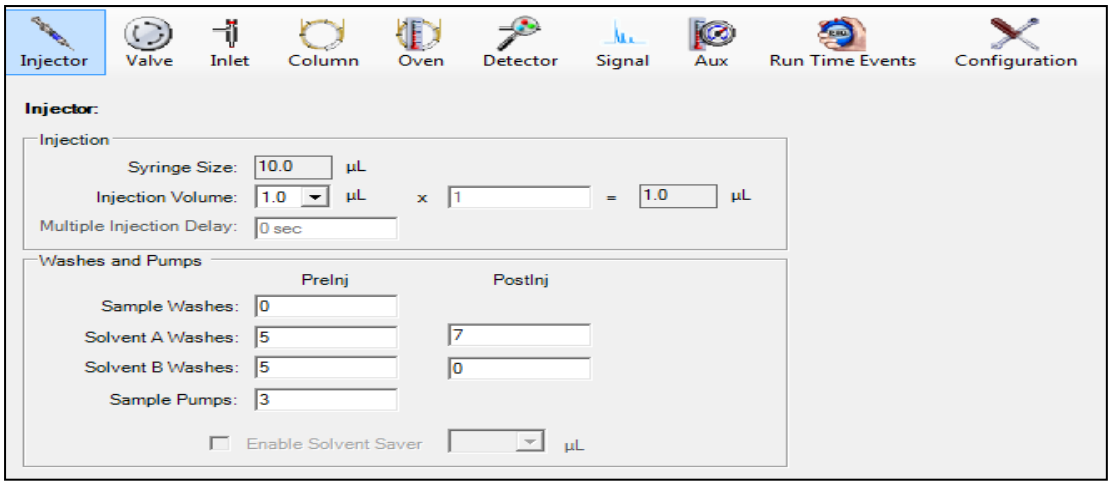


Figure 2. 17: Cl-OPFRs GC/MS method showing injector settings

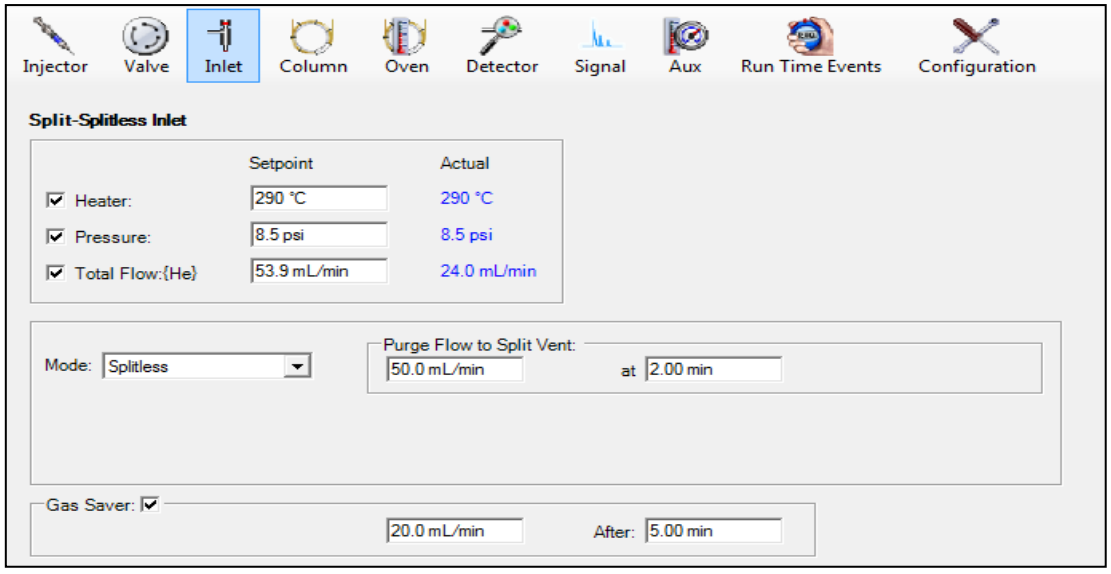


Figure 2. 18: Cl-OPFRs GC/MS method showing inlet settings

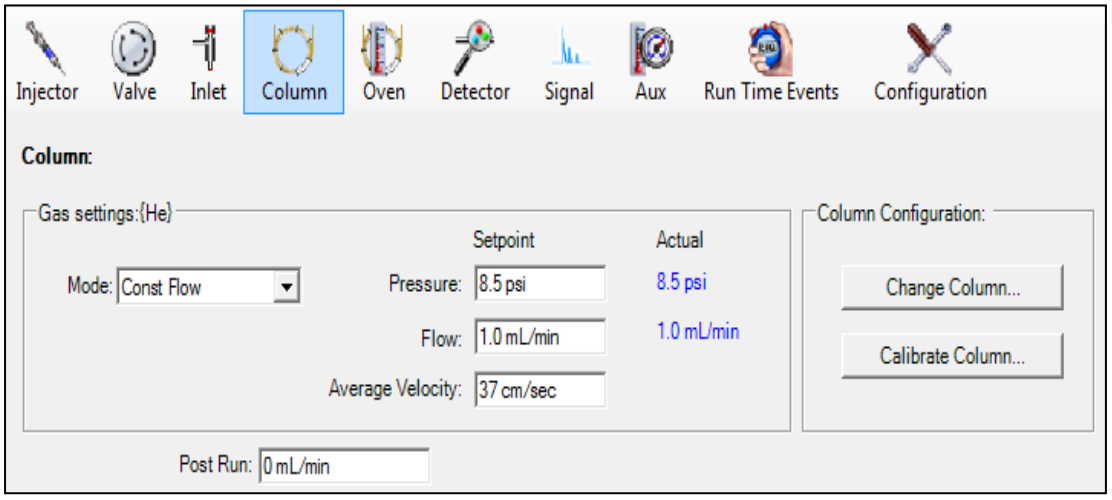


Figure 2. 19: Cl-OPFRs GC/MS method showing column flow rate

2.5. Validation and Quality Assurance/ Quality Control (QA/QC) criteria

New and used glassware and tools like scissors and tweezers were used in this project. For cleaning used glassware, they were soaked overnight in detergent solution, before rinsing sequentially with tap and distilled water; then heated to 470 ˚C for 5 hours. Because Cl-OPFRs have been frequently detected in indoor air and dust (Bergh et al., 2011; Cao et al., 2014; Du et al., 2019; Chupeau et al., 2020), pre-cleaning of all glassware and tools with solvents like hexane or acetone before covering them with aluminum foil is essential because Cl-OPFRs could easily contaminate samples and

glassware. Greiner Bio-One™ CELLSTAR™ test tubes were all new and sterile when used for sample extraction. The research was conducted in a clean laboratory environment, and the extraction was carried out in a clean fume hood to minimise contamination.

2.5.1. Instrumental calibration

A set of five calibration standards containing all native Cl-OPFRs at 50, 100, 250, 500, and 1000 pg/µL as well as the RDS and ISs in each calibration standard was performed to assess the linearity of the GC/MS response.

The data from the five calibration standards were used to calculate relative response factors (RRFs) for each target compound (Table 2.8). RRFs were calculated using Equation 1.

$$RRF = \frac{A\ NAT}{A\ IS} x \frac{C\ IS}{C\ NAT} \qquad \textit{(Equation 1)}$$

Where A_{NAT} and A_{IS} are the peak areas for the "native" and internal standards, respectively. C_{IS} and C_{NAT} are the concentrations of the internal standard and native compound in the standard, respectively.

The relative standard deviation (RSD) of RRFs obtained for a specific target chemical in the 5 calibration standards should not exceed 10%. Table 2.10 displays the RRF values acquired for each standard in a typical full five-point calibration, with the average and relative standard deviation (%RSD).

Table 2. 10: RRFs for five-point calibration standards

Analyte	RRF-A	RRF-B	RRF-C	RRF-D	RRF-E	Average	%RSD
TCEP	0.80	0.77	0.77	0.74	0.84	0.78	4.88
TDCIPP	1.29	1.39	1.34	1.34	1.34	1.34	2.52

TCIPP	0.59	0.50	0.48	0.52	0.51	0.52	8.05

Figure 2.20 displays chromatograms of Cl-OPFRs with IS in the calibration standard (500 pg/µL).

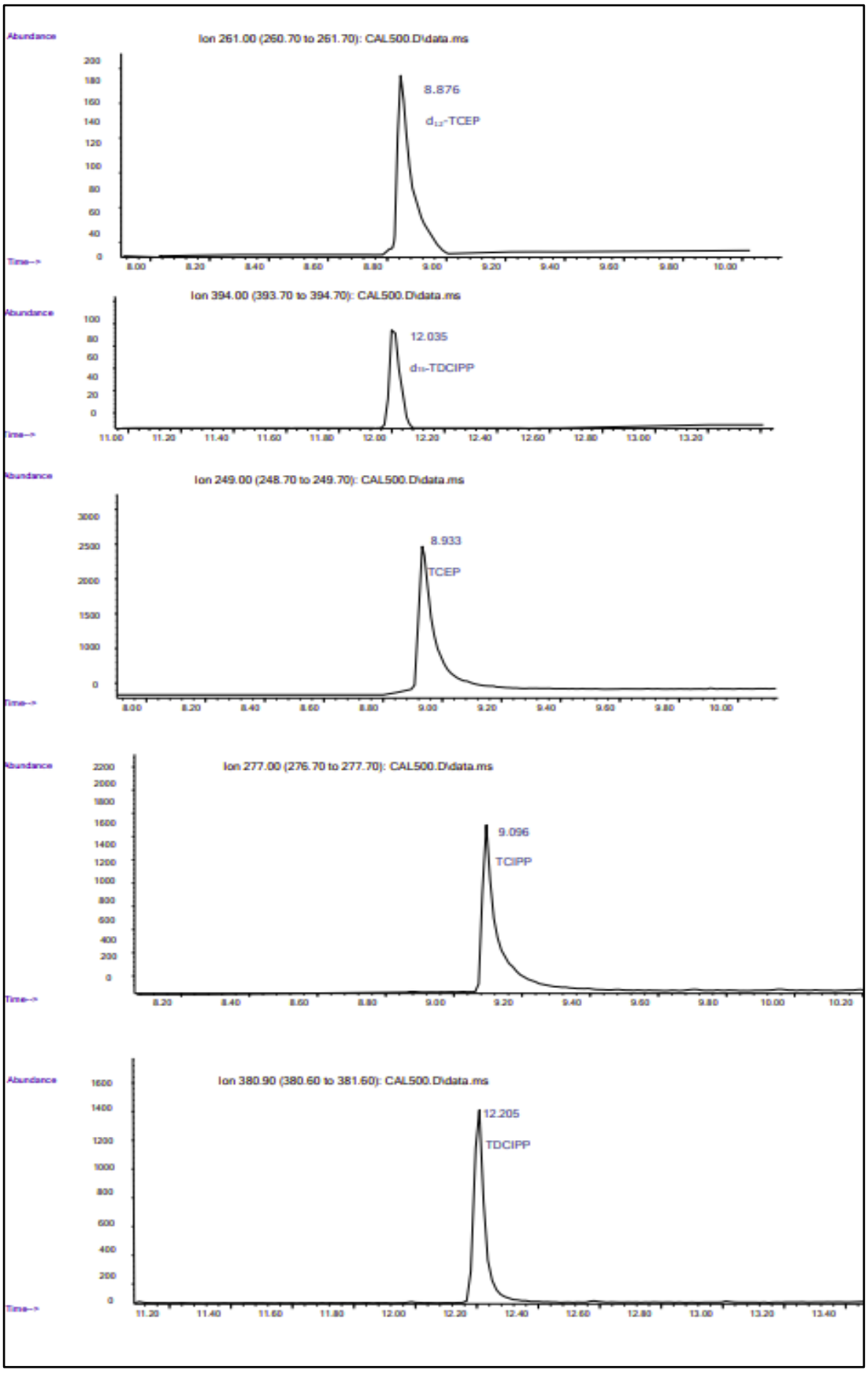


Figure 2. 20: GC/MS chromatograms of calibration standard (500 pg/µL)

2.5.2. Determination of internal standard recoveries

Internal standard (IS) recoveries were calculated by adding a recovery determination standard (RDS) to the final extract before injection into the GC/MS. These calculations were conducted to determine the overall loss of IS during the extraction and clean-up methods, assuming a zero loss of RDS (PCB-62) as it was added at the end. IS recoveries were calculated according to Equation 2.

$$\%IS\ Recovery = \left[\left(\frac{A_{IS}}{A_{RDS}}\right)_S \times \left(\frac{A_{RDS}}{A_{IS}}\right)_{STD} \times \left(\frac{C_{IS}}{C_{RDS}}\right)_{STD} \times \left(\frac{C_{RDS}}{C_{IS}}\right)_S\right] x100 \qquad \textit{(Equation 2)}$$

In which $(A_{IS}/A_{RDS})_S$ represents the ratio of internal standard peak area to recovery determination standard peak area in the sample; $(A_{RDS}/A_{IS})_{STD}$ represents the ratio of recovery determination standard peak area to internal standard peak area in the calibration standard; $(C_{IS}/C_{RDS})_{STD}$ indicates the ratio of concentration of internal standard to concentration of recovery determination standard in the calibration standard; and $(C_{RDS}/C_{IS})_S$ indicates the ratio of concentration of recovery determination standard to concentration of internal standard in the sample. In general, satisfactory recoveries should be around 70% and could range from 30% to 150%. A statistical summary of the internal standard recoveries is listed in Table 2.11.

Table 2. 11: Summary of internal standard recoveries obtained for samples in this study

Standard	Average	Median	Minimum	Maximum	SD	%RSD
d_{12}-TCEP	95.7	94.7	73.4	117.9	10.9	11.3
d_{15}-TDCIPP	98.5	98.2	72.1	118.9	11.3	11.5

2.5.3. Evaluation of method accuracy and precision

Due to the absence of certified or indicative values for Cl-OPFRs in the matrices studied in this thesis, the accuracy and precision of the analytical method applied in this study was validated by analysing archived samples (fabric and foam) that have

been analysed previously by our research group using different methods of extraction and other GC/MS instrument. Good agreement was found between the Cl-OPFRs concentrations determined previously by our group and those recorded in the same samples in this study, with no significant difference (p=0.61) found when assessed using a paired t-test for the comparison of data (Table 2.12).

Table 2. 12: Concentrations (mg/kg) of Cl-OPFRs reported in archived samples and analysed in our study

Sample	**Reported**	**This study**	**Reported**	**This study**	**Reported**	**This study**	**Reported**	**This study**
	TCEP	**TCEP**	**TDCIPP**	**TDCIPP**	**TCIPP**	**TCIPP**	**∑Cl-OPFRs**	**∑Cl-OPFRs**
Pushchair 5.2 (PUF)	4	8	20000	32693	2900	6684	22904	39386
Pushchair 7.3 (Fabric)	<0.02	1	17	11	6	22	23	34
Pushchair 11.2 (Fabric)	3	5	19	11	110	114	132	130
Pram 3.3 (PUF)	67	54	33000	33804	13000	13576	46067	47434
Pram 4.3 (PUF)	4	5	42000	52234	9400	15891	51404	68130
Office 2 (PUF)	<0.0006	<0.01	<0.0011	<0.02	38000	24653	38000	24653
Domestic 2 (PUF)	<0.0006	<0.01	<0.0011	<0.02	17000	14969	17000	14969
Office 1 (PUF)	<0.0006	<0.01	<0.0011	<0.02	17000	13031	17000	13031

2.5.4. Determination of blank concentrations

To further assess the quality of the method or any contamination contributed to sampling, as well as sample transport, storage, extraction, and clean-up, one reagent blank was run on the GC/MS per five samples. The blank contains no sample but is extracted and cleaned as a real sample treated for GC/MS injection (Table 2.13). Whenever the blank concentration was 5-25% of the concentration detected in any samples in the same batch, concentrations in all samples from that batch were corrected by subtracting the blank concentration. When blanks contained less than 5% of the target compounds, the data were not blank corrected. However, in cases where

contamination exceeds 20%, samples were reported <LOQ. Figure 2.21 shows chromatograms of a typical blank.

Table 2. 13: Summary of blank concentrations (mg/kg) assuming 50 mg of sample analysed

Blank (n=106)	TCEP	TDCIPP	TCIPP
Average/Mean	0.05	0.09	0.03
Median	0	0	0
Min	0	0	0
Max	1.31	1.25	1.72
SD	0.15	0.28	0.20

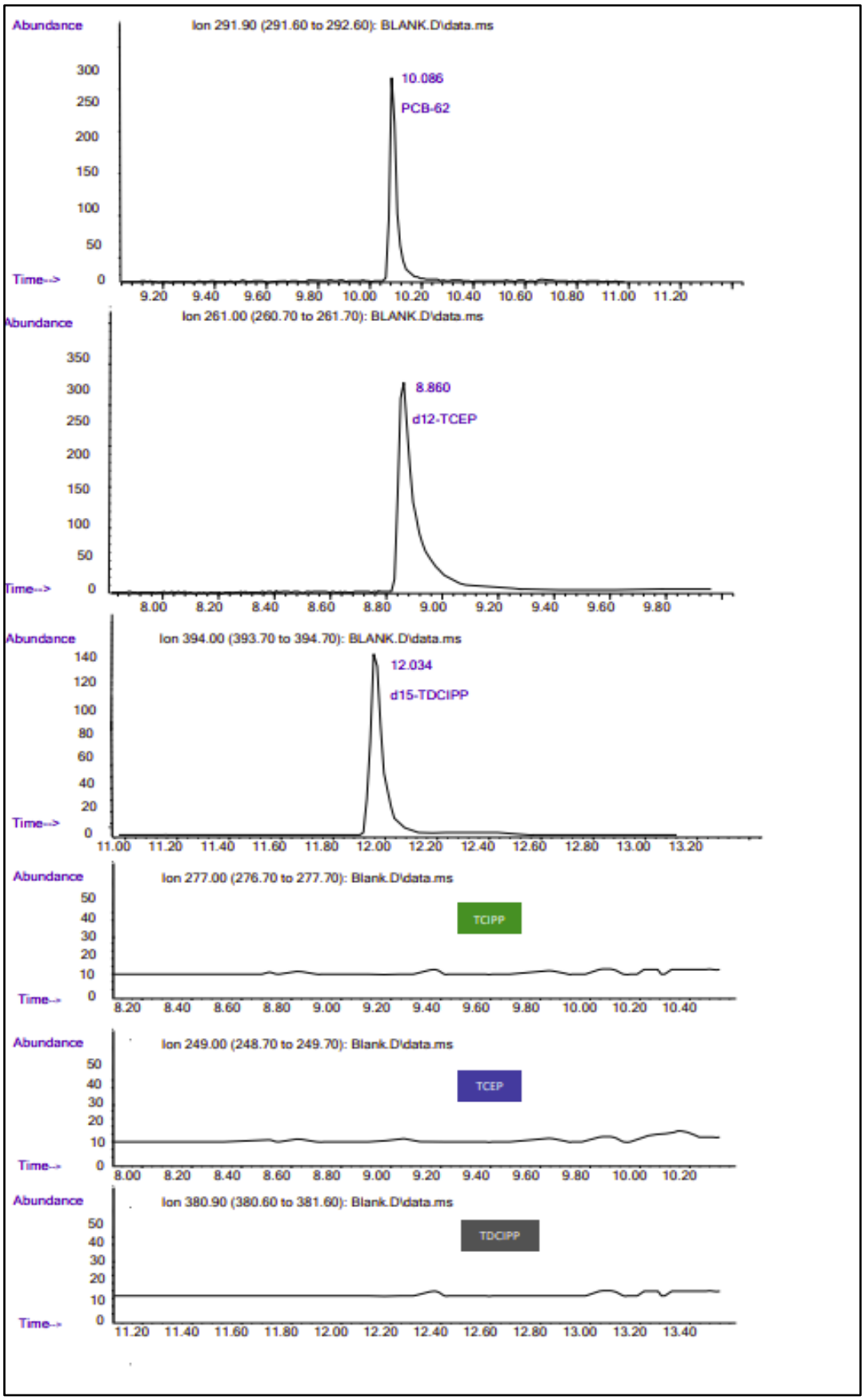


Figure 2. 21: GC/MS chromatograms of blank sample with IS (1 ng/µL) and RDS (250 pg/µL)

2.5.5. Determination of detection limits

Instrument detection limit (IDL) and sample detection limit (SDL)

The instrumental detection limit (IDL) or limit of detection (LOD) of an analyte is defined as the lowest mass of an analyte that yields a signal-to-noise ratio of 3:1 on the instrument. The limit of quantification (LOQ) is defined as the smallest amount of an analyte that can be quantified with acceptable precision and accuracy, which was calculated as the mass generating a 10:1 signal to noise ratio.

Sample detection limits (SDLs) were calculated based on the LOD, final extract volume (FEV) of 210 µL, volume of final extract injected (VFEI) of 1 µL, sample size (SS) of 50 mg and percentage of internal standard recovery (% IS Rec) (95.7 for d_{12}-TCEP and 98.5 for d_{15}-TDCIPP) using Equation 3. Calculated method SDL for each analyte is listed in Table 2.14.

$$SDL = \frac{IDL \times FEV}{VFEI \times SS} \times \frac{100}{\%IS\ Recovery} \qquad \textit{(Equation 3)}$$

Table 2. 14: Calculated values of LOD and LOQ for Cl-OPFRs in this study

Analyte	LOD or IDL (ng/injection)	LOQ or SDL (mg/kg)
TCEP	0.002	0.01
TDCIPP	0.006	0.02
TCIPP	0.001	0.007

2.5.6. Calculation of concentrations in samples

Concentrations of Cl-OPFRs in samples were calculated using Equation 4.

$$\textit{Concentration} = \frac{A_{NAT}}{A_{IS}} \times \frac{1}{RRF} \times \frac{M_{IS}}{SS} \qquad \textit{(Equation 4)}$$

Where A_{IS} = peak area of internal standard in sample; A_{NAT} = peak area of target pollutant in sample; RRF = relative response factor for the target pollutant (calculated using equation 1); M_{IS} = mass of internal standard added to sample (pg) and SS = sample size (g).

2.6. Statistical analyses

A variety of statistical tests were performed to assess the data generated by this study. The main statistical tools utilised to analyse the data in this study were Excel (Microsoft Office 365) and IBM SPSS (Statistical Package for the Social Sciences) statistics software version 28. Mean, median, minimum, and maximum parameters were used to describe quantitative levels and distribution patterns. Means were compared to examine differences between dependent variables. SPSS was used to evaluate the distribution of concentrations for target pollutants, and the data were log transformed to ensure normal distribution. The t-test is used to compare the means of two datasets, while ANOVA (analysis of variance) was used to compare the differences among three or more datasets. Pearson correlations (for the normally distributed data) and spearman correlation (for the non-normally distributed data) were used when needed to examine potential correlations between generated data, with a p- value of 0.05 established as the level of statistical significance. Concentrations below the detection limit were always assumed to equal half of the limit of quantification.

Chapter 3: Cl-OPFR concentrations and exceedances of 1,000 mg/kg "limit" for waste fabrics and foams from Ireland, UK, and Saudi Arabia

This chapter contains sections of some material taken verbatim from the following publications:

Harrad, S., Sharkey, M., Stubbings, W.A., **Alghamdi, M.**, Berresheim, H., Coggins, M., Rosa, A.H. and Drage, D. (2022). 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***, pp.160250-160256.

Harrad, S., Drage, D., Sharkey, M., Stubbings, W.A., **Alghamdi, M.**, Berresheim, H., Coggins, M. and Rosa, A.H. (2022). Elevated concentrations of halogenated flame retardants in waste childcare articles from Ireland. ***Environmental Pollution***, pp.120732-120762.

3.1 Introduction

This chapter reports the concentrations of Cl-OPFRs (TCEP, TDCIPP, and TCIPP) in wastes foams and fabrics from furniture, vehicle, and childcare articles from Ireland, the UK, and Saudi Arabia.

The hypothesis tested in this chapter is that Cl-OPFRs have been used extensively in the UK and Ireland for compliance with fire safety regulations and are thus widely present at concentrations above 1,000 mg/kg in waste fabrics and foams from furniture, vehicles, and childcare items. To test this hypothesis, Cl-OPFRs were measured in 169 samples of waste fabrics and foams from furniture and vehicles, as well as in 108 samples of waste fabrics and foams from childcare items from Ireland. In addition, in the UK, 57 samples of waste furniture fabrics and foams and 89 samples of fabrics and foams from waste childcare items were analysed to test this hypothesis.

The other hypothesis tested in this chapter is that because of national variations in flame retardancy regulations and their implementation methods, Cl-OPFR levels and relative abundance will vary internationally. To test this hypothesis, data on Cl-

OPFRs via GC/MS were generated for 51 samples of waste fabrics and foams from furniture, as well as in 51 samples of fabrics and foams from waste childcare items in Saudi Arabia.

3.2. Results and discussion

3.2.1 Cl-OPFR concentrations in waste furniture from Ireland, UK, and Saudi Arabia

Table 3.1 provides a statistical summary of the target Cl-OPFRs concentrations in furniture waste from Ireland, UK, and Saudi Arabia. Overall, the average concentration of Cl-OPFRs in waste furniture from Ireland and the UK exceeded those in Saudi Arabia (Figure 3.1). In addition, the maximum Cl-OPFR concentration as well as the number of samples exceeding 1,000 mg/kg in the UK was higher than in Ireland. Moreover, the concentration of Cl-OPFRs in the waste furniture examined from Saudi Arabia was lower than in either the UK and Ireland and was below levels deemed necessary to meet fire safety regulations since no Saudi Arabian sample contained >1,000 mg/kg. A Kruskal-Wallis test revealed ∑Cl-OPFR concentrations in samples from Saudi Arabia, UK, and Ireland were significantly different ($P<0.01$).

Table 3. 1: Statistical summary of concentrations (mg/kg) of Cl-OPFRs in fabrics and foams from Ireland, UK, and Saudi Arabia waste furniture and percentage of samples exceeding 1,000 mg/kg

	TCEP	**TDCIPP**	**TCIPP**	**∑Cl-OPFRs**
Ireland furniture n=72				
Average	230	200	2,100	2,500
Range	0.13-8,900	<LOQ-13,000	2.6-25,000	4.8-25,000
No. (%>1,000 mg/kg)	4 (6%)	2 (3%)	11 (15%)	11 (15%)
UK furniture n=57				

Average	52	570	2,600	3,200
Range	<LOQ-2400	<LOQ-31,000	1.2-13,000	1.7-35,000
No. (%>1,000 mg/kg)	1 (2%)	1 (2%)	36 (63%)	36 (63%)
Saudi Arabia furniture n=51				
Average	2.8	2.2	12	17
Range	<LOQ-130	<LOQ-91	<LOQ-330	<LOQ-330
No. (%>1,000 mg/kg)	0	0	0	0

The detection frequency of TCEP, TDCIPP, and TCIPP in Ireland was 100 %, 99 %, 100 %, in the UK it was 72 %, 74 %, and 100 %; and in Saudi Arabia it was 16 %, 12 %, and 20 %, respectively. The percentage of furniture samples exceeding the limit of 1,000 mg/kg was 15 % in Ireland and 63 % in the UK, but none in Saudi Arabia.

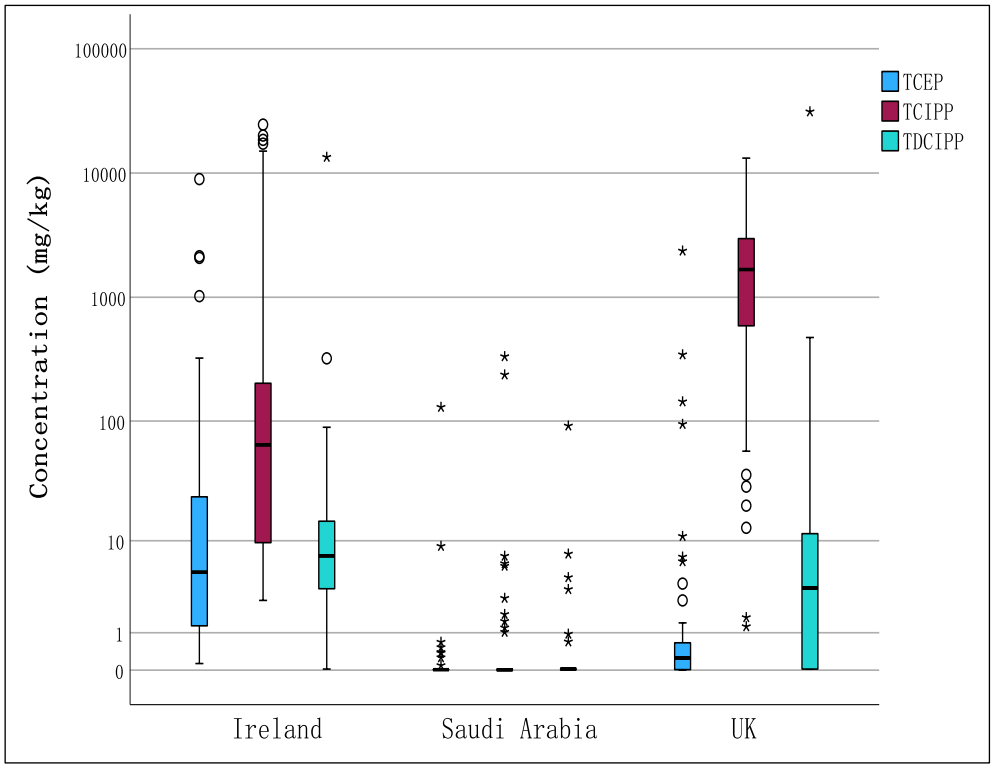


Figure 3. 1: Box and whisker plots of Cl-OPFRs in waste furniture in Ireland, UK, and Saudi Arabia (the middle line of the box is the median Cl-OPFRs concentrations, the top and bottom lines of the box represent the 75th percentile and 25th percentile Cl-OPFRs concentrations, while the top and bottom lines of the y-error bars represent the maximum and minimum Cl-OPFRs concentrations excluding outliers. Circles are the outliers and asterisks are the extreme outliers).

Comparison of Cl-OPFR concentrations in similar furniture goods between the three countries was carried out. As an illustration, the average Cl-OPFR concentration in sofas was 6,500 mg/kg in Ireland, 3,500 mg/kg in the UK, and 1.6 mg/kg in Saudi Arabia. For armchairs, the average of Cl-OPFRs was 2,500 mg/kg in the UK, i.e. lower than the average 9,000 mg/kg observed in Ireland. For cushions, Cl-OPFR concentrations were on average 72 mg/kg in Saudi Arabia, which was lower than the average of 3,800 mg/kg detected in Ireland. In Ireland and Saudi Arabia, carpets appeared to be not treated with Cl-OPFRs to resist fire as the average concentrations were 29 mg/kg and 73 mg/kg, respectively.

Generally, the average concentrations of Cl-OPFRs in foams exceeded those in fabrics. For instance, the average concentrations of ∑Cl-OPFRs in furniture fabrics

were respectively 1,600 mg/kg in the UK, 180 mg/kg in Ireland, and 1 mg/kg in Saudi Arabia. These were exceeded by corresponding average ∑Cl-OPFR concentrations in foams, i.e. 11,000 mg/kg in the UK, 7,900 mg/kg in Ireland and 43 mg/kg in Saudi Arabia. When compared to reported concentrations of Cl-OPFRs in foams from other studies in different countries (Figure 3.2), higher levels of TCIPP were reported in the UK (Stubbings et al., 2016), France (Lounis et al., 2019), and Germany (Kemmlein et al, 2003), as well as of TDCIPP and TCEP in the U.S.A (Stapleton et al., 2012; Bergen and Stone, 2021; Cooper et al., 2016; Petreas et al., 2016; Hammel et al., 2017). For instance, the average concentration of ∑Cl-OPFRs in PUFs was 16,667 mg/kg in the UK (Stubbings et al., 2016), 26,220 (Hammel et al., 2017), 20,487 mg/kg (Petreas et al., 2016), 40,000 mg/kg (Bergen and Stone, 2021) in the U.S.A, and 55,000 mg/kg in Germany (Kemmlein et al, 2003).

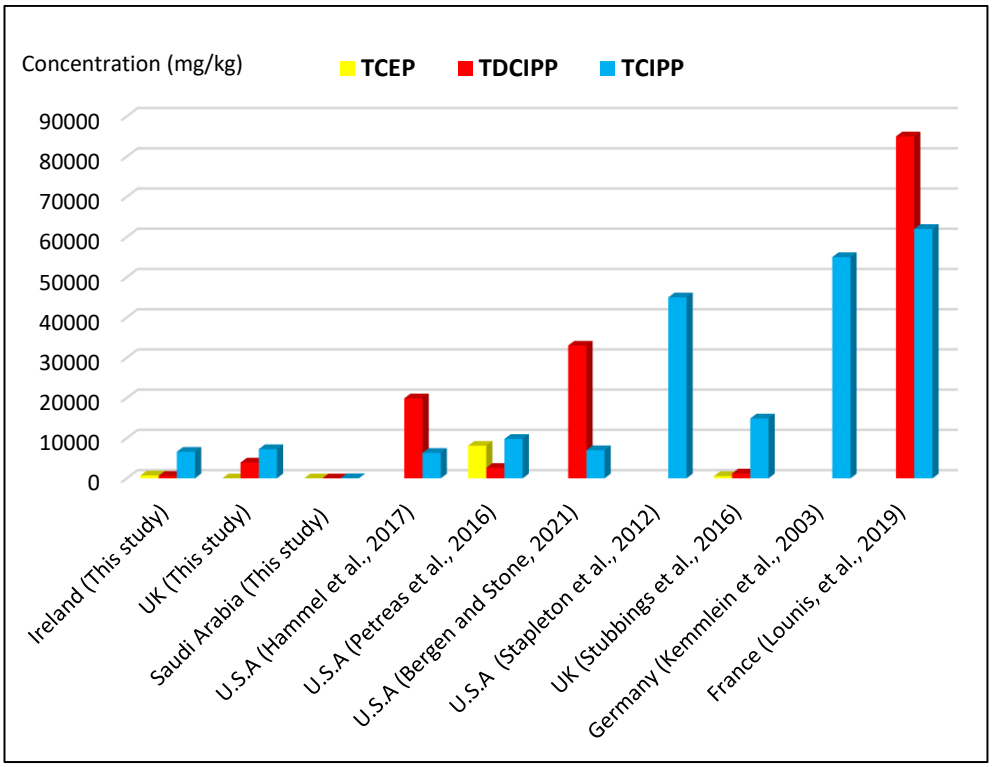


Figure 3. 2: Average concentrations (mg/kg) of ∑Cl-OPFRs in furniture PUF from various studies

3.2.1.1 Cl-OPFR concentrations in furniture waste from Ireland

Table 3.2 provides a statistical summary of the concentrations of Cl-OPFRs (TCEP, TDCIPP, and TCIPP) in furniture waste from Ireland. In addition, the concentrations of Cl-OPFRs in our Irish furniture are compared with those reported in other studies in Table 3.3.

Except for 1 mattress foam sample; curtain, carpet, mattress upholstery, and mattress foam waste analysed in this study contained trace amounts of Cl-OPFRs below <1 % by weight, consistent with other studies that analysed curtains from Japan (Kajiwara et al., 2011), Belgium (Ionas et al., 2015), and the UK (Stubbings et al., 2016) as shown in Table 3.3. However, analyses of 40 flame retarded curtains collected in 2014 in Japan revealed TDCIPP was present in two polyester curtains at levels of 3,900 and 4,310 mg/kg (Miyake et al., 2017).

Table 3. 2: Statistical summary of Cl-OPFR concentrations (mg/kg) in fabrics and foams from Irish waste furniture and percentage of samples exceeding 1,000 mg/kg

Waste category	TCEP				TDCIPP				TCIPP				Cl-OPFRs			
	Average	Median	Range	No. (%>1,000 mg/kg)	Average	Median	Range	No. (%>1,000 mg/kg)	Average	Median	Range	No. (%>1,000 mg/kg)	Average	Median	Range	No. (%>1,000 mg/kg)
Soft furnishings n=72	230	5.2	0.13-8,900	4 (6%)	200	7.3	<LOQ-13,000	2 (3%)	2,100	64	2.6-25,000	11 (15%)	2,500	90	4.8-25,000	11 (15%)
Soft furnishings >1,000 mg/kg n=11	1,400	250	100-8,900	4 (36%)	1,200	13	7.1-13,000	2 (18%)	13,000	12,000	1,900-25,000	11 (100%)	16,000	15,000	6,400-25,000	11 (100%)
Curtain n=7	5.7	6.4	1.3-10	0	2	2.4	0.84-3.1	0	63	68	12-150	0	71	77	15-160	0
Carpet n=22	1.3	0.64	0.13-9.7	0	11	6.7	3.2-48	0	17	8.5	6.7-140	0	29	17	11-140	0
Mattress upholstery n=6	36	7.6	1.4-110	0	2	0.51	<LOQ-10	0	40	24	2.6-130	0	78	32	4.8-230	0
Mattress foam n=10	14	3.4	2-100	0	14	4.4	2.1-88	1 (10%)	1,700	180	28-15,000	1 (10%)	1,700	210	45-15,000	1 (10%)
Furniture	61	19	2.5-	0	37	8.3	6.5-320	0	130	130	11-330	0	230	230	21-540	0

upholstery n=15			320													
Furniture foam n=12	1,300	240	2.3-8,900	4 (33%)	1,100	13	2.8-13,000	1 (8%)	11,000	9,500	11-25,000	10 (83%)	13,000	13,000	16-25,000	10 (83%)

The average concentration of Cl-OPFRs in 15 samples of furniture upholstery from armchairs, cushions, and couches was 230 mg/kg. The maximum concentrations of TCEP and TCIPP were 320 and 330 mg/kg in couches, while the maximum concentration of TDCIPP was 320 mg/kg in a cushion. Overall, it seems like these upholstery samples were not treated with Cl-OPFRs to resist fire like those reported in the UK that contained minimal concentrations of Cl-OPFRs (Stubbings et al., 2016), and furniture fabrics in the U.S.A in which the maximum Cl-OPFR concentration was 990 mg/kg for TCIPP (Petreas et al., 2016).

The average concentration of Cl-OPFRs in mattress foams (n=10) was 1,700 mg/kg, which was predominantly due to TCIPP (1,700 mg/kg) as opposed to TCEP (14 mg/kg) and TDCIPP (14 mg/kg). Of all foam samples, only one sample contained TCIPP (15,000 mg/kg) and TDCIPP (15,000 mg/kg) at levels above 1,000 mg/kg. In the U.S.A, a similar concentration of TDCIPP (12,000 mg/kg) was found in a mattress pad foam sample (Stapleton et al., 2009). Analysis of 71 mattress foam samples in the U.S.A showed that TCIPP (9 samples) was more often detected than TDCIPP (5 samples) (Cooper et al., 2016); however, in mattress pad foam TDCIPP was detected in 9 samples while TCIPP was found in only 4 samples (Cooper et al., 2016).

In PUF samples from armchairs, cushions, and couches, concentrations of Cl-OPFRs exceeded 1,000 mg/kg in all 10 samples (4 TCEP, 1 TDCIPP, and 10 TCIPP). The average ∑Cl-OPFR concentration in these samples was 16,000 mg/kg, with a maximum of 25,000 mg/kg. Trace concentrations of Cl-OPFRs were found in two wool samples, one from a couch (14 mg/kg) and the other from an armchair (104 mg/kg).

In the 8 couch foam samples, the average TCIPP concentration was 12,000 mg/kg, 1,570 mg/kg for TCEP and 15 mg/kg for TDCIPP. By comparison, higher concentrations of TCIPP and TDCIPP were reported in the U.S.A in 24 foam samples from couches, mattress pads, pillows, and other furniture goods. Specifically, these contained high levels of TDCIPP (range 10,000-50,000 mg/kg) in 14 samples and TCIPP (range 5,000-22,000 mg/kg) in 4 samples (Stapleton et al., 2009). In addition, another study in the U.S.A that examined 958 foam samples from furniture obtained between 2014 and 2016 found that among 415 sofa and love seat foam samples, TDCIPP and TCIPP was detected in 113 and 21 of them at concentration >10,000 mg/kg, respectively. Also, among 130 chair foam samples, TDCIPP was detected in 35 and TCIPP in 14 at concentration >10,000 mg/kg (Cooper et al., 2016). Examining 115 foam samples from sofas purchased before 2005 in the U.S.A revealed that TCIPP was detected in 7 samples with a geometric mean of 6,320 mg/kg and maximum of 46,000 mg/kg (Hammel et al., 2017). TDCIPP was detected in 22 samples with geometric mean of 19,900 mg/kg and maximum of 88,100 mg/kg. Although most of these sofas were purchased before 2005, others were acquired second hand or passed down; thus, the original manufacturer and date of purchase were unknown (Hammel et al., 2017). The Cl-OPFR concentrations reported in our Irish samples were consistent with those reported for similar samples obtained in the UK (Table 3.3) (Stubbings et al., 2016).

Table 3. 3: Statistical summary of concentrations (mg/kg) of target Cl-OPFR in soft furnishing waste from this study and other countries

Location (collection year)	Sample type and number	TCEP				TDCIPP				TCIPP				Reference
		Mean	Median	Min	Max	Mean	Median	Min	Max	Mean	Median	Min	Max	
Ireland (2015-2016)	**Curtain=7**	**5.7**	**6.4**	**1.3**	**10**	**2**	**2.4**	**0.84**	**3.1**	**63**	**68**	**12**	**150**	**This study**
Japan (2008)	Curtain n=2	0.005	0.005	0.004	0.006	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	(Kajiwara et al., 2011)
Belgium (2013)	Curtain n=47	0.030	<LOQ	<LOQ	0.71	<LOQ	<LOQ	<LOQ	<LOQ	0.084	0.01	<LOQ	1	(Ionas et al., 2015)
UK (2011-2012)	Curtain n=4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	(Stubbings et al., 2016)
Japan (2014)	Curtain=40	8.38	<LOQ	<LOQ	92.2	195.16	<LOQ	<LOQ	4,300	5.21	<LOQ	<LOQ	47.5	(Miyake et al., 2017)
Ireland (2015-2016)	**Carpet=22**	**1.3**	**0.64**	**0.13**	**9.7**	**11**	**6.7**	**3.2**	**48**	**17**	**8.5**	**6.7**	**140**	**This study**
Belgium (2013)	Carpet n=14	0.288	0.085	<LOQ	1.8	<LOQ	<LOQ	<LOQ	<LOQ	0.045	0.023	<LOQ	0.39	(Ionas et al., 2015)
UK (2011-2012)	Carpet n=7	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	(Stubbings et al., 2016)
Ireland (2015-2016)	**Mattress upholstery n=6**	**36**	**7.6**	**1.4**	**110**	**2**	**0.51**	**<LOQ**	**10**	**40**	**24**	**2.6**	**130**	**This study**
UK (2011-2012)	Mattress upholstery n=1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	(Stubbings et al., 2016)
Ireland (2015-2016)	**Furniture upholstery n=15**	**61**	**19**	**2.5**	**320**	**37**	**8.3**	**6.5**	**320**	**130**	**130**	**11**	**330**	**This study**
U.S.A (-)	Furniture upholstery n=25	-	-	<LOQ	12.2	-	-	<LOQ	12	-	-	25.2	990	(Petreas et al., 2016)
U.S.A (2017-2020)	Furniture upholstery n=108	0.005	0.001	<LOQ	0.16	0.006	<0.0002	<LOQ	0.202	2.88	0.014	<LOQ	360	(Zhu et al., 2020)

Ireland (2015-2016)	**Furniture foam n=12**	**1,300**	**240**	**2.3**	**8,900**	**1,100**	**13**	**2.8**	**13,000**	**11,000**	**9,500**	**11**	**25,000**	**This study**
U.S.A (2002-2007)	Furniture foam n=24	-	-	-	-	-	-	10,000	50,000	-	-	5,000	22,000	(Stapleton et al., 2009)
U.S.A (2015)	Furniture foam n=11	-	-	<LOQ	92,500	-	-	<LOQ	21,000	-	-	<LOQ	96,500	(Petreas et al., 2016)
U.S.A (-)	Furniture foam n=115	-	-	-	-	19,900*	-	534	88,100	6320*	-	768	46,000	(Hammel et al., 2017)
UK (2011-2012)	Furniture foam n=9	556	<LOQ	<LOQ	5,000	1,222	<LOQ	<LOQ	11,000	14,889	16,000	<LOQ	38,000	(Stubbings et al., 2016)

*Geometric mean

3.2.1.2 Cl-OPFR concentrations in furniture waste from the UK

Cl-OPFR concentrations were determined in fabrics and foams of furniture from the UK, including sofas, armchairs, chairs, stools, and other furniture items. Overall, the concentrations of Cl-OPFRs in all UK furniture items (foams and fabrics combined) ranged from 1.7 to 35,000 mg/kg (average 3,200 mg/kg and median 1,800 mg/kg) (Table 3.4). Approximately 72 % of samples contained TCEP up to a maximum concentration of 2,400 mg/kg, while 74 % of samples had TDCIPP at up to 31,000 mg/kg. Finally, all samples contained TCIPP with a maximum concentration of 13,000 mg/kg. Cl-OPFRs were detected in all 41 UK furniture fabric samples (average 1,600 mg/kg, median 1,200 mg/kg, range from 1.7 to 7,500 mg/kg). Of these fabric samples, 23 (56 %) contained Cl-OPFRs at concentrations >1,000 mg/kg. The samples in questions comprised: 11 sofas, 7 armchairs, 3 chairs, and 2 other items. In previous studies, Cl-OPFRs were detected in fabrics used in childcare articles such as car seats (Danish Environmental Protection Agency, 2016) and carriers (Bergen and Stone, 2021) with the maximum concentrations of TCIPP and TDCIPP respectively being 19,000 mg/kg and 148,000 mg/kg. Additionally, baby carrier fabric in the U.S.A has been reported to contain 2,700 mg/kg of TDCIPP (Bergen and Stone, 2021). The presence of Cl-OPFRs was identified in all 11 of our UK furniture foams from 8 sofas and one chair, armchair and stool each. The average concentration of Cl-OPFRs in foams was 11,000 mg/kg and ranged from 1,400 to 35,000 mg/kg. While TDCIPP was only present in one sofa foam, the concentration detected 31,000 mg/kg was the maximum found in our UK samples of any individual Cl-OPFR. TCIPP was the main Cl-OPFR detected in our UK samples.

Table 3. 4: Statistical summary of Cl-OPFR concentrations (mg/kg) in fabrics and foams from waste furniture from the UK and percentage of samples exceeding 1,000 mg/kg

Waste category	TCEP				TDCIPP				TCIPP				Cl-OPFRs			
	Average	Median	Range	No. (%>1,000 mg/kg)	Average	Median	Range	No. (%>1,000 mg/kg)	Average	Median	Range	No. (%>1,000 mg/kg)	Average	Median	Range	No. (%>1,000 mg/kg)
Furniture n=57	52	0.25	<LOQ-2,400	1 (2%)	570	3.6	<LOQ-31,000	1 (2%)	2,600	1,700	1.2-13,000	36 (63%)	3,200	1,800	1.7-35,000	36 (63%)
Furniture >1,000 mg/kg n=36	66	0.28	<LOQ-2,400	1 (2%)	890	3.6	<LOQ-31,000	1 (2%)	4,000	2,400	1,100-13,000	36 (100%)	4,900	2,500	1,100-35,000	36 (100%)
Sofa n=34	14	0.22	<LOQ-340	0	940	3.7	<LOQ-31,000	1 (3%)	2,600	1,600	1.2-10,000	21 (62%)	3,500	1,600	2.7-35,000	21 (62%)
Sofa cover leatherette n=10	0.24	0.10	<LOQ-1.3	0	10	<LOQ	<LOQ-56	0	1,300	1,300	74-3,100	6 (60%)	1,300	1,300	93-3,100	6 (60%)
Sofa cover leather n=5	89	7.1	0.07-340	0	7.8	9.1	1.5-12	0	1,000	470	130-2,500	2 (40%)	1,100	580	230-2,500	2 (40%)
Sofa fabric n=6	2	0.21	<LOQ-11	0	84	3.9	1.2-470	0	940	970	13-1,900	3 (50%)	1,000	980	29-2,200	3 (50%)
Sofa foam n=8	0.35	0.29	<LOQ-1.4	0	3,900	7.7	<LOQ-31,000	1 (13%)	7,300	8,400	1,400-10,000	8 (100%)	11,000	8,700	1,400-35,000	8 (100%)
Sofa lining n=3	0.27	0.15	<LOQ-	0	4.4	4.33	1.9-7.1	0	1,800	2,300	29-	2 (67 %)	1,800	2,400	33-	2 (67 %)

			0.66								3,000				3,000	
Sofa wool and other miscellaneous n=2	<LOQ	<LOQ	<LOQ	0	0.74	0.74	<LOQ-1.5	0	19	19	1.2-36	0	20	20	2.7-36	0
Armchair n=13	180	0.30	<LOQ-2,400	1 (8%)	12	2.3	<LOQ-72	0	2,300	1,100	1.7-13,000	8 (62%)	2,500	1,400	1.7-13,000	8 (62%)
Armchair cover leatherette n=6	390	0.15	<LOQ-2,400	1 (17%)	22	2.8	<LOQ-72	0	1,200	730	1.7-4,500	3 (50%)	1,600	760	1.7-4,500	3 (50%)
Armchair cover leather n=2	2.1	2.1	0.16-4	0	5.1	5.1	<LOQ-10	0	1,600	1,600	1,400-1,800	2 (100%)	1,600	1,600	1,400-1,800	2 (100%)
Armchair cover textile n=4	1.9	0.62	0.06-6.5	0	0.47	<LOQ	<LOQ-1.9	0	1,500	1,300	780-2,600	2 (50%)	1,500	1,300	780-2,600	2 (50%)
Armchair foam n=1	0.58*				11*				13,000*				13,000*			
Chair cover leatherette n=6	24	0.42	<LOQ-140	0	4.3	4.3	<LOQ-11	0	2,600	1,700	590-7,500	4 (67%)	2,700	1,700	620-7,500	4 (67%)
Chair foam n=1	1.2*				12*				5,300*				5,300*			

***Actual concentration (mg/kg)**

Of the 57 samples of UK furniture tested, 36 samples (63 %) had Cl-OPFRs at levels greater than 1,000 mg/kg. There was only one sample (2 %) of leatherette cover and foam that contained TCEP and TDCIPP at >1,000 mg/kg, respectively. However, TCIPP was found in 36 samples (63 %) at concentrations greater than 1,000 mg/kg. These comprised 13 leatherette covers, 4 leather covers, 11 foams, 6 textiles, and 2 lining samples. In Europe, the lower cost of TCIPP makes it popular in many consumer goods (EU RAR, 2008) in comparison with TDCIPP that is primarily found in furniture in the U.S.A. Consistent with this, there are previous reports of furniture and childcare articles found to be treated with TCIPP in the UK (Stubbings et al., 2016), Germany (Kemmlein et al, 2003), Denmark (Danish Environmental Protection Agency, 2016) and France (Lounis et al., 2019). By comparison, furniture foam samples in the U.S.A appear more frequently treated with TDCIPP (Stapleton et al., 2011; Stapleton et al., 2012; Bergen and Stone, 2021; Cooper et al., 2016; Petreas et al., 206; Hammel et al., 2017).

The concentration of TCIPP in sofa foam samples (n=8) ranged from 1,400 to 10,000 (average 7,300) mg/kg, which is lower than the average concentration we found in Ireland of 12,000 mg/kg (range 2,000 to 25,000 mg/kg) as well as lower than the reported in a previous study of four sofa foams in the UK (average 17,000 mg/kg; range 16,000 to 17,000 mg/kg - Stubbings et al., 2016). Additionally, 115 foams from sofas in the U.S.A contained TCIPP and TDCIPP ranged from 768 to 46,000 mg/kg and from 534 to 88,100 mg/kg, respectively (Hammel et al., 2017). Tests on 451 foams from sofas and loveseats in the U.S.A. found that 25 % had TDCIPP and 5 % had TCIPP at levels exceeding 1,000 mg/kg (Cooper et al., 2016).

Our analyses determined average concentrations of TCEP, TDCIPP and TCIPP in chair foam to be 1.2, 12, and 5,300 mg/kg, respectively. By comparison, TCEP and

TDCIPP were reported in desk chair foam in the UK at concentrations of 5,000 and 11,000 mg/kg, respectively as well as for TCIPP of 8,400, 17,000 and 38,000 mg/kg in one dining chair and two desk chairs (Stubbings et al., 2016). A study of 130 chair foams in the U.S.A. revealed 27 % had TDCIPP and 11 % had TCIPP at concentrations exceeding 1,000 mg/kg (Cooper et al., 2016).

3.2.1.3 Cl-OPFR concentrations in furniture waste from Saudi Arabia

Concentrations of Cl-OPFRs in waste furniture samples from Saudi Arabia ranged between <LOQ to 330 mg/kg (median <LOQ mg/kg; average 17 mg/kg) (Table 3.5). Approximately 20 % of samples contained TCIPP up to 330 mg/kg. Meanwhile, 16 % of samples had TCEP at concentrations up to 130 mg/kg. Finally, TDCIPP was identified in 12 % of the samples at up to 91 mg/kg. None of the sofa, cushion, bed frame, ottoman, pillow fabric and PUF contained any of our target Cl-OPFRs at concentrations above 1,000 mg/kg.

Table 3. 5: Statistical summary of Cl-OPFR concentrations (mg/kg) in fabrics and foams from Saudi Arabian waste furniture and percentage of samples exceeding 1,000 mg/kg

Waste category	TCEP				TDCIPP				TCIPP				Cl-OPFRs			
	Average	Median	Range	%>1,000 mg/kg	Average	Median	Range	%>1,000 mg/kg	Average	Median	Range	%>1,000 mg/kg	Average	Median	Range	%>1,000 mg/kg
Furniture n=51	2.8	<LOQ	<LOQ-130	0	2.2	<LOQ	<LOQ-91	0	12	<LOQ	<LOQ-330	0	17	<LOQ	<LOQ-330	0
Sofa (composite) n=15	0.16	<LOQ	<LOQ-0.68	0	0.59	<LOQ	<LOQ-7.6	0	0.74	<LOQ	<LOQ-7.3	0	1.5	<LOQ	<LOQ-16	0
Ottoman (composite) n=4	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	1.5	<LOQ	<LOQ-5.9	0	1.5	<LOQ	<LOQ-5.9	0
Cushion (composite) n=8	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	72	0.91	<LOQ-330	0	72	0.94	<LOQ-330	0
Pillow (composite) n=4	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0
Bed frame (composite) n=3	0.037	<LOQ	<LOQ-0.090	0	0.020	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	0.064	<LOQ	<LOQ-0.12	0

Carpet (n=3)	43	<LOQ	<LOQ-130	0	31	0.69	<LOQ-91	0	<LOQ	<LOQ	<LOQ	0	73	0.71	<LOQ-720	0
Mix products n=14	0.65	<LOQ	<LOQ-8.9	0	0.59	<LOQ	<LOQ-4.6	0	0.45	<LOQ	<LOQ-6.2	0	1.7	<LOQ	<LOQ-12	0

The average Cl-OPFR concentration in Saudi Arabian furniture fabric in this study was 0.43 mg/kg (range <LOQ to 12 mg/kg), which is considerably lower than our findings in samples from Ireland and the UK and lower than those reported in the U.S.A of 272 mg/kg (Petreas et al., 2016) and 2.9 mg/kg (Zhu et al., 2020) in two separate studies of 25 and 108 furniture fabrics, respectively.

The average concentration of Cl-OPFRs in Saudi Arabian furniture foam was also far lower than we detected in samples from Ireland and the UK. Average concentrations of TCEP, TDCIPP, and TCIPP in the two Saudi Arabian cushion foams were 280 mg/kg for TCIPP and <LOQ for TCEP and TDCIPP. This is in stark contrast to the 12,500 mg/kg of TDCIPP found in one cushion foam collected in the U.S.A. in 2012 (Keimowitz et al., 2016).

The findings of our analyses of that TCEP, TDCIPP, and TCIPP were present at only low concentrations in Saudi Arabian furniture samples, suggest that there might be another source of Cl-OPFRs in indoor dust in Saudi Arabia (Table 3.6). For example, in dust of house floor, air condition (AC) filter, car, mosque and hotel, all three TCEP, TDCIPP, and TCIPP were identified and possibly were in the dust because of other source rather than furniture (Ali et al., 2016; Ali et al., 2018; Ali et al., 2021).

Table 3. 6: Cl-OPFRs concentrations (mg/kg for furniture and ng/g for dust) in different environments in Saudi Arabia

Location	Sample type	Cl-OPFR												Unit	Reference
		TCEP				TDCIPP				TCIPP					
		Median	Mean	Min	Max	Median	Mean	Min	Max	Median	Mean	Min	Max		
Jeddah and Riyadh	Household furniture n=**51**	**<LOQ**	**2.8**	**<LOQ**	**130**	**<LOQ**	**2.2**	**<LOQ**	**91**	**<LOQ**	**12**	**<LOQ**	**330**	**mg/kg**	**This study**
Jeddah and Riyadh	Childcare goods n=**51**	**<LOQ**	**2.7**	**<LOQ**	**97**	**<LOQ**	**2.6**	**<LOQ**	**65**	**9.7**	**160**	**<LOQ**	**3,000**	**mg/kg**	**This study**
Jeddah	Dust (House floor) n=15	410	560	125	1650	500	1770	150	8700	1650	1600	200	3700	ng/g	(Ali et al., 2016)
Jeddah	Dust (AC filter) n=15	820	2650	120	16,500	7800	14,300	1000	61,234	2000	3300	200	11,500	ng/g	(Ali et al., 2016)
Jeddah	Dust (car) n=15	1200	7020	30	52,300	2700	8850	100	45,600	1650	16,250	100	92,000	ng/g	(Ali et al., 2016)
Jeddah	Dust (Mosque) n=30	420	600	270	3470	2490	2960	970	6945	2055	2420	1570	4820	ng/g	(Ali et al., 2018)
Makkah & Madinah	Dust (Hotel) n=10	750	920	250	1750	2360	3625	1150	9050	3315	4585	375	12,620	ng/g	(Ali et al., 2018)
Jeddah	Dust (AC filter) n=20	14,480	16,100	<LOQ	58,200	5950	6500	650	19,700	1750	2500	670	5850	ng/g	(Ali et al., 2021)
Jeddah	Dust (Hotel floor) n=10	<LOQ	800	<LOQ	3370	660	1600	400	5650	2650	2900	150	7800	ng/g	(Ali et al., 2021)
Jeddah	Dust (House floor) n=20	280	2500	<LOQ	25,500	1530	42,700	<LOQ	613,000	1300	4100	25	17,300	ng/g	(Ali et al., 2021)

3.2.2 Cl-OPFR concentrations in waste childcare articles from Ireland, UK, and Saudi Arabia

A statistical summary of the concentrations of our target Cl-OPFRs concentrations in samples of waste childcare items from Ireland, UK, and Saudi Arabia is provided in Table 3.7. Overall, the average concentration of Cl-OPFRs in waste childcare items from Ireland and the UK were higher than in Saudi Arabia (Figure 3.3). In addition, the range of Cl-OPFR concentrations as well as the number of samples exceeding the limit of 1,000 mg/kg in Ireland was higher than in the UK and Saudi Arabia.

Based on the ∑Cl-OPFR levels of waste childcare items collected from these three countries, the Kruskal–Wallis test was used to determine whether there was a significant difference among them. The difference in Cl-OPFR concentrations between Saudi Arabia, the UK, and Ireland was significant ($P<0.01$).

Table 3. 7: Statistical summary of Cl-OPFR concentrations (mg/kg) in fabrics and foams from Ireland, UK, and Saudi Arabia waste childcare articles and percentage of samples exceeding 1,000 mg/kg

	TCEP	**TDCIPP**	**TCIPP**	**Cl-OPFRs**
Ireland childcare articles n=108				
Average	22	4,800	1,100	5,900
Range	0.31-1,600	<LOQ-68,000	<LOQ-44,000	0.52-68,000
No. (%>1,000 mg/kg)	1 (1%)	12 (11%)	8 (7%)	22 (20%)
UK childcare articles n=89				
Average	0.15	1,100	660	1,800
Range	<LOQ-4.4	<LOQ-49,000	<LOQ-10,000	<LOQ-50,000
No. (%>1,000 mg/kg)	0	3 (3%)	10 (11%)	13 (15%)

Saudi Arabia childcare articles n=51				
Average	2.7	2.6	160	170
Range	<LOQ-97	<LOQ-65	<LOQ-3,000	<LOQ-3,000
No. (%>1,000 mg/kg)	0	0	2 (4%)	2 (4%)

TCEP, TDCIPP, and TCIPP detection frequencies in samples from Ireland respectively were 100 %, 74 %, and 98 %, compared 45 %, 16 %, and 92 % in the UK and 14 %, 16 %, and 80 % in Saudi Arabia. The percentage of furniture samples exceeding the limit of 1,000 mg/kg was 20 % in Ireland, 15 % in the UK, and 4% in Saudi Arabia.

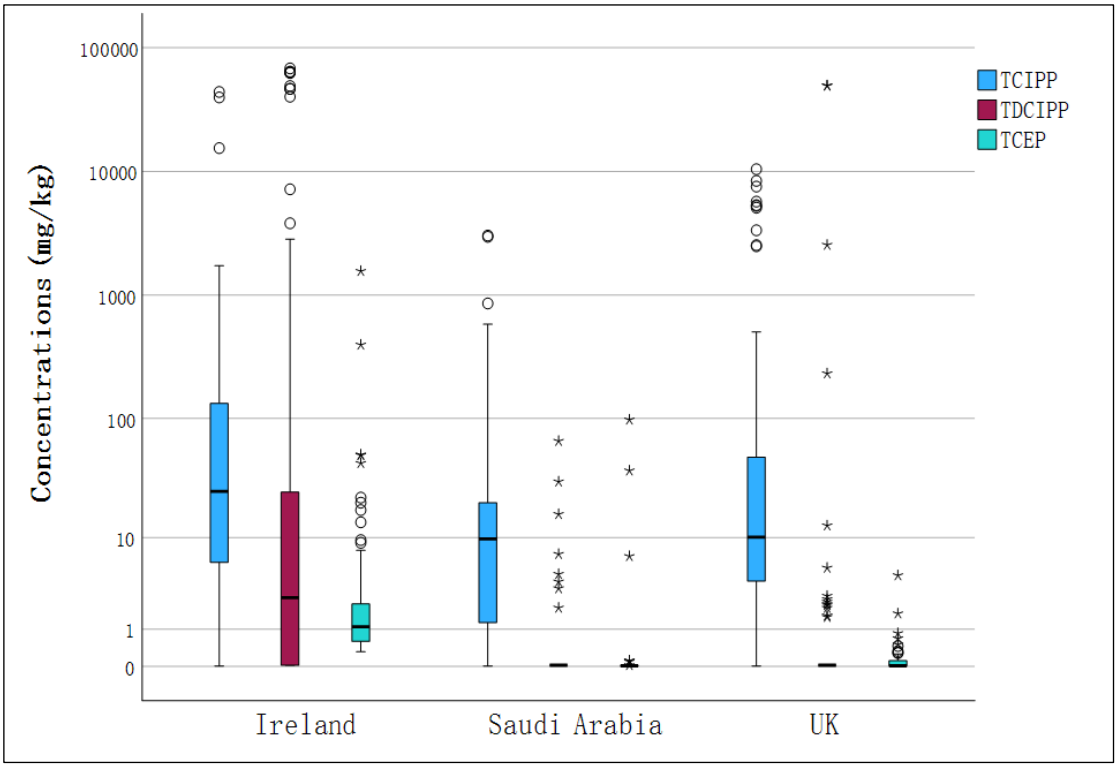


Figure 3. 3: Box plots of Cl-OPFRs in waste childcare articles in Ireland, UK, and Saudi Arabia (the middle line of the box is the median Cl-OPFRs concentrations, the top and bottom lines of the box represent the 75th percentile and 25th percentile Cl-OPFRs concentrations, while the top and bottom lines of the y-error bars represent the maximum and minimum Cl-OPFRs concentrations excluding outliers. Circles are the outliers and asterisks are the extreme outliers).

A comparison of Cl-OPFRs concentrations detected in similar childcare items was conducted between the three countries in Table 3.8 as well as with appropriate data from previous studies. Car seats, couches, and carrycot from Ireland, for instance, contained higher concentrations than those from Saudi Arabia. Cl-OPFR concentrations in changing mats were the highest in the UK, this was followed by Saudi Arabia, and then Ireland. While concentrations in pushchairs were also the highest Cl-OPFRs in the UK, this was followed by Ireland, and then Saudi Arabia. Pretty similar concentrations of Cl-OPFRs were found in baby walkers, Moses' basket, and soft play foams from the UK and Saudi Arabia, as well as in play mats from the UK and Ireland. However, higher concentrations of Cl-OPFRs were found in mattresses from the UK than the in mattress analysed from Saudi Arabia.

Table 3. 8: Comparison of Cl-OPFR concentrations (mg/kg) in childcare articles in our study with other studies

Item	Statistical parameter	TCEP	TDCIPP	TCIPP	Location	Reference
Car seat (composite)* n=34	Average	66	15,000	590	**Ireland**	**This study**
	Range	0.37-1,600	1.4-68,000	3.5-15,000		
Car seat (composite) n=12	Average	2.7	2.6	160	**Saudi Arabia**	**This study**
	Range	<LOQ-97	<LOQ -65	<LOQ - 3,000		
Car seat (composite) n=10	Average	440	17,000	3,700	Denmark	(Danish Environmental Protection Agency, 2016)
	Range	41-840	2,700-42,600	46-18,100		
Car seat (textile) n=40	Range	173	20-148,000	5.6-19,000		
Car seat (textile pads) n=40	Range	255	26-56,900	5.7-12,000		
Car seat (composite) n=20	Range	-	2,600-9,300	-		
Car seat (composite) n=15	Range	-	29	21-3,800		
Car seat (composite)	Actual	590	9,200	4,700	Austria	
Car seat (composite) n=16	Range	<LOQ-0.12	<LOQ	<LOQ-0.94	U.S.A	(Wu et al., 2018)
Cot mattress (composite) n=3	Maximum	1.1	2.9	40,000	**Ireland**	**This study**
Carrycot (composite) n=7	Maximum	<LOQ	<LOQ	66	**Saudi Arabia**	**This study**
Cot mattress (composite) n=1	Maximum	-	89,700	-	Denmark	(Danish Environmental

						Protection Agency, 2016)
Baby seat (composite) n=6	Range	0.44-0.86	0.82-13	18-1,600	**Ireland**	**This study**
Children couch (composite) n=3	Range	0.46-0.60	38-570	1,700-44,000	**Ireland**	**This study**
Children chair (foam and wool) n=2	Range	<LOQ-97	<LOQ-65	<LOQ-580	**Saudi Arabia**	**This study**
Children chair (foam) n=6	Range	<96–3,400	<96–29,000	1,800–23,000	U.S.A	(Bergen and Stone, 2021)
Play mat (fabric and wool) n=3	Range	0.36-0.52	<LOQ-3	15-91	**Ireland**	**This study**
Play mat (composite) n=9	Range	<LOQ-0.25	<LOQ	<LOQ-13	**UK**	**This study**
Play mat n=41 (composite)	Range	0.0026-0.0068	0.00033-0.04	0.017-0.23	China	(Peng et al., 2020)
Pram (wool) n=2	Range	0.44-0.53	<LOQ-77	44-58	**Ireland**	**This study**
Pram (composite) =6	Range	<LOQ- 320	44-3,300	6.9-23	Denmark	(Danish Environmental Protection Agency, 2016)
Baby walker (composite) n=4	Average	0.14	<LOQ	11	**UK**	**This study**
Baby walker (composite) n=7	Average	<LOQ	<LOQ	10	**Saudi Arabia**	**This study**
Changing mat (foam) n=14	Average	2	0.35	35	**Ireland**	**This study**
Changing mat (composite) n=6	Average	0.44	<LOQ	5,400	**UK**	**This study**
Changing mat (composite) n=2	Average	<LOQ	<LOQ	430	**Saudi Arabia**	**This study**
Changing mat (foam) n=3	Maximum	270	25,000	5,000	U.S.A	(Bergen and Stone, 2021)
Changing mat (foam) n=6	Maximum	-	-	48,300	U.S.A	(Gloekler et al., 2021)
Child mattress (composite) n=2	Average	<LOQ	1.1	4,000	**UK**	**This study**
Child mattress (composite) n=2	Average	<LOQ	<LOQ	<LOQ	**Saudi Arabia**	**This study**
Moses' basket (composite) n=7	Average	<LOQ	<LOQ	3.7	**UK**	**This study**
Moses' basket (composite) n=3	Average	<LOQ	<LOQ	15	**Saudi Arabia**	**This study**
Soft play foam n=1	Actual	<LOQ	<LOQ	8.5	**UK**	**This study**
Soft play foam n=4	Average	<LOQ	<LOQ	7.1	**Saudi Arabia**	**This study**
Pushchair (composite) n=15	Average	1.9	1.7	75	**Ireland**	**This study**
Pushchair (composite) n=14	Average	0.41	1.5	1,200	**UK**	**This study**
Pushchair (fabrics) n=2	Average	<LOQ	0.99	7.7	**Saudi Arabia**	**This study**
Pushchair (fabric) n=1	Actual	<LOQ	68	<LOQ	Austria	(Danish Environmental Protection Agency, 2016)

*Composite (both fabric and foam)

3.2.2.1 Cl-OPFR concentrations in waste childcare items from Ireland

Table 3.9 provides a statistical summary of the concentrations of target Cl-OPFRs found in waste childcare articles from Ireland.

Table 3. 9: Statistical summary of Cl-OPFR concentrations (mg/kg) in fabrics and foams from Irish waste childcare items and percentage of samples exceeding 1,000 mg/kg

Waste category	TCEP				TDCIPP				TCIPP				Cl-OPFRs			
	Average	**Median**	**Range**	**No. (%>1,000 mg/kg)**	**Average**	**Median**	**Range**	**No. (%>1,000 mg/kg)**	**Average**	**Median**	**Range**	**No. (%>1,000 mg/kg)**	**Average**	**Median**	**Range**	**No. (%>1,000 mg/kg)**
Car seats n=62	36	0.77	0.13-1,600	1 (2%)	8,400	6.5	<LOQ-68,000	12 (19%)	340	17	<LOQ-15,000	1 (2%)	8,800	34	0.52-68,000	15 (24%)
Car seat (fabric) n=15	4.3	0.67	0.37-50	0	560	10	1.4-3,800	2 (13%)	47	25	3.5-270	0	620	41	13-3,900	3 (20%)
Care seat (foam) n=19	110	9	1.3-1,600	1 (5%)	27,000	7,200	3-68,000	10 (53%)	1,000	130	48-15,000	1 (5%)	28,000	15,000	130-68,000	12 (63%)
Car seat >1,000 n=15	140	4.6	0.45-1,600	1 (7%)	35,000	46,000	11-68,000	12 (80%)	1,200	130	14-15,000	1 (7%)	36,000	47,000	1,300-68,000	15 (100%)
Mix of childcare items n=46	1.4	1.5	0.36-7.5	0	26	<LOQ	<LOQ-570	0	2,000	32	2-44,000	7 (15%)	2,100	38	3.3-44,000	7 (15%)
Play mat n=3	0.45	0.48	0.36-0.52	0	1.2	0.73	<LOQ-3	0	43	22	15-91	0	45	23	19-92	0
Baby seat n=6	0.61	0.58	0.44-0.86	0	4.6	2.9	0.82-13	0	710	640	18-1,600	3 (50%)	720	650	19-1,600	3 (50%)
Pram n=2	0.48	0.48	0.44-	0	38	38	<LOQ-	0	51	51	44-58	0	90	90	58-120	0

			0.53				77									
Child couch n=3	0.53	0.52	0.46-0.60	0	360	470	38-570	0	16,000	1,700	1,700-44,000	3 (100%)	16,000	2,300	2,200-44,000	3 (100%)
Cot mattress n=3	0.62	0.41	0.36-1.1	0	1.8	1.5	0.95-2.9	0	14,000	580	410-40,000	1 (33%)	14,000	580	420-40,000	1 (33%)
Change mat foam n=14	2	2	1.5-2.6	0	0.35	<LOQ	<LOQ-4.6	0	35	9.6	3.9-250	0	37	12	5.5-50	0
Pushchair n=15	1.9	1.5	1.1-7.5	0	1.7	<LOQ	<LOQ-15	0	75	28	2-290	0	78	34	3.3-300	0
Mix of childcare items >1,000 n=7	0.55	0.52	0.41-0.85	0	160	13	1.5-570	0	13,000	1,700	1,000-44,000	7 (100%)	13,000	2,200	1,100-44,000	7 (100%)

In fabrics, foams, wools, XPS and EPS from child car seats, the average concentrations of TDCIPP are an order of magnitude higher than TCEP and TCIPP. To illustrate, in the 62 samples from child car seats, the average concentration of TDCIPP was 8,400 mg/kg compared to 36 mg/kg for TCEP and 340 mg/kg for TCIPP. Moreover, the concentrations of Cl-OPFRs in foam exceed those in fabric samples. For example, the average concentration of TCEP, TDCIPP and TCIPP in fabric samples was 4.3, 560, and 47 mg/kg, respectively: compared to 110, 27,000, and 1,000 mg/kg, respectively in foam samples. Wool samples contained lower concentrations of Cl-OPFRs than those found in fabrics and foams. Specifically, in wool samples, the average concentration of TDCIPP, TCIPP, and TCEP were: 30, 37, and 0.69 mg/kg, respectively. EPS and XPS samples contained the lowest concentration of Cl-OPFRs among all car seat samples. The average concentrations of TCEP, TDCIPP, and TCIPP in such samples were 0.6, 4.87, and 3.46 mg/kg, respectively. Out of the 62 childcare article samples analysed, 15 samples (24%) contained Cl-OPFRs at levels exceeding 1,000 mg/kg. These 15 samples comprised 12 PUFs and 3 fabrics. TCEP was detected at >1,000 mg/kg in one PUF sample, TDCIPP in 12 samples (2 fabrics and 10 PUFs), with TCIPP >1,000 mg/kg in one PUF sample. Concentrations of Cl-OPFRs in our study are compared to those reported in previous relevant studies in Table 3.8. Danish researchers conducted a survey investigating the chemical composition of child car seats and other childcare products (Danish Environmental Protection Agency, 2016). They found that such products contained Cl-OPFRs. One car seat in Austria contained high levels of TDCIPP (9,200 mg/kg), TCIPP (4,700 mg/kg) and TCEP (590 mg/kg). In addition, there was a concentration of 840 mg/kg of TCEP, 18,100 of TCIPP and 6,700 of TDCIPP found in a car seat of unspecified country of manufacture. The concentration

of TCIPP and TDCIPP in car seat both foam and fabric made in China and Italy were 810 and 3,700 mg/kg and 4,800 and 21,100 mg/kg, respectively. Interestingly, two car seats made in France had both the highest TDCIPP level of 42,600 mg/kg, and the lowest TCIPP of 46 mg/kg (Danish Environmental Protection Agency, 2016). The reported concentrations of Cl-OPFRs in our study indicates the widespread use of such chemicals in car seats in Ireland. This contrasts with recent studies in the U.S.A that report much lower concentrations of Cl-OPFRs than detected in our study (Miller and Gearhart, 2016; Bloom et al., 2022; Miller et al., 2018; Wu et al., 2018).

In the different childcare items, i.e., play mats, baby seats, prams, couches, cot mattresses, and pushchairs analysed in this study, TCIPP was frequently detected at concentrations higher than TCEP and TDCIPP. To clarify, the average concentration of TCIPP was 2,000 mg/kg, compared to those of TCEP (1.4 mg/kg) and TDCIPP (26 mg/kg). Among the different childcare items, the average concentration of TCIPP was highest in child couches (16,000 mg/kg), followed by 14,000 mg/kg in cot mattresses, 710 mg/kg in baby seats, 75 mg/kg in pushchairs, 35 mg/kg in change mat foam, and 46 mg/kg in prams and play mats. The average concentration of TDCIPP was lowest at 0.35 mg/kg in change mat foam and highest at 360 mg/kg in child couch. Meanwhile, the average concentration of TCEP was lowest at 0.46 mg/kg in playmats and prams, but highest at 2 mg/kg in change mat foam. Seven of 46 samples (15%) contained Cl-OPFRs at levels exceeding 1,000 mg/kg, comprising 4 fabrics and 3 PUFs from baby seats, couches, and cot mattresses. All these exceedances were attributable to TCIPP. Other studies in the U.S.A and Denmark have also found Cl-OPFRs in childcare items (Table 3.8) like cot mattress, prams, and children's chairs (Danish Environmental Protection Agency, 2016; Bergen and Stone, 2021). In China, Cl-OPFRs in 41 play mats were found at an average concentration (0.069 mg/kg)

inadequate for imparting flame retardancy, which suggests that they were not purposefully added (Peng et al., 2020).

Because Cl-OPFRs have been identified as potentially carcinogenic and to exert adverse effects on children, the European Chemical Agency (ECHA) has proposed to restrict the use of Cl-OPFRs in certain products like childcare items and residential upholstered furniture (ECHA, 2018b). However, our findings indicate the widespread use of TDCIPP in children's car seats and TCIPP in other childcare articles.

3.2.2.2 Cl-OPFR concentrations in waste childcare items from UK

Table 3.10 provides a statistical summary of the concentrations of target Cl-OPFRs found in waste childcare articles from the UK. The concentration of ∑Cl-OPFRs ranged from <LOQ to 50,000 mg/kg with an average of 1,800 mg/kg. The detection frequencies for TCEP, TDCIPP, and TCIPP were 45 %, 16 %, and 92 %, respectively, based on examination of 89 fabrics and foams from childcare goods. Out of the 89 tested samples, 13 (15 %) contained Cl-OPFRs at a concentration greater than 1,000 mg/kg including 6 foams and 7 fabrics from mattresses, pushchairs, booster car seats, and changing mats.

Table 3. 10: Statistical summary of Cl-OPFR concentrations (mg/kg) in fabrics and foams from waste childcare articles from the UK and percentage of samples exceeding 1,000 mg/kg

Waste category	TCEP				TDCIPP				TCIPP				Cl-OPFRs			
	Average	Median	Range	No. (%>1,000 mg/kg)	Average	Median	Range	No. (%>1,000 mg/kg)	Average	Median	Range	No. (%>1,000 mg/kg)	Average	Median	Range	No. (%>1,000 mg/kg)
Childcare articles n=89	0.15	<LOQ	<LOQ-4.4	0	1,100	<LOQ	<LOQ-49,000	3 (3%)	660	10	<LOQ-10,000	10 (11%)	1,800	11	<LOQ-50,000	13 (15%)
Childcare articles >1,000 mg/kg n=13	0.57	<LOQ	<LOQ.4.4	0	7,800	<LOQ	<LOQ-49,000	3 (23%)	4,300	5,100	13-10,000	10 (77%)	12,000	5,300	2,500-50,000	13 (100%)
Childcare articles (fabric) n=57	0.09	<LOQ	<LOQ-.68	0	49	<LOQ	<LOQ-2,500	1 (2%)	620	11	<LOQ-10,000	6 (11%)	670	13	<LOQ-10,000	7 (12%)
Childcare articles (foam) n=13	0.56	<LOQ	<LOQ-4.4	0	7,600	<LOQ	<LOQ-49,000	2 (15%)	1,800	90	7.8-7,500	4 (31%)	9,300	500	7.8-50,000	6 (46%)
Mattress n=2	<LOQ	<LOQ	<LOQ	0	1.1	1.1	<LOQ-2.1	0	4,000	4,000	430-7,500	1 (50%)	4,000	4,000	430-7,500	1 (50%)
Pushchair n=14	0.41	0.10	<LOQ-4.4	0	1.4	<LOQ	<LOQ-13	0	1,200	54	6.2-5,700	3 (21%)	1,200	54	6.3-5,700	3 (21%)
Booster car	<LOQ	<LOQ	<LOQ	0	25,000	26,000	230-	3 (75%)	53	52	3.6-100	0	25,000	26,000	240-	3 (75%)

seat n=4							49,000								50,000	
Changin mat n=6	0.44	0.055	<LOQ-1.7	0	<LOQ	<LOQ	<LOQ	0	5,400	4,300	2,500-10,000	6 (100%)	5,400	4,300	2,500-10,000	6 (100%)
Childcare articles (wool, XPS& leatherette) n=19	0.07	<LOQ	<LOQ-0.26	0	0.26	<LOQ	<LOQ-2.7	0	11	3.4	<LOQ-65	0	11	3.9	<LOQ-65	0

Certain childcare articles, such as beds, pushchairs, feeding seats, car seat and pushchair liners, soft play foam, baby walkers, play mats, sleeping bags, car seat head holders, infant carriers, and Moses' baskets appear to not have been treated with Cl-OPFRs for flame retardancy, as the concentration of Cl-OPFRs in these products ranged from <LOQ to 77 mg/kg. These findings agreed with the findings of other studies concerning concentrations of Cl-OPFR in playmats from China and pushchairs in Austria (Table 3.8). In contrast, infant carriers, baby walkers, changing pads, and mattresses in the U.S.A contained TDCIPP at concentrations exceeding 1,000 mg/kg (Stapleton et al., 2011; Bergen and Stone, 2021). Also, out of six baby slings in Denmark, three of them contained TCEP, TCIPP, and TDCIPP up to 75, 160, and 340 mg/kg, while two slings contained higher concentrations up to 4,700, 13,000, and 16,300 mg/kg, respectively. One sling manufactured in Latvia was free of Cl-OPFRs (Danish Environmental Protection Agency, 2016). In addition, in two baby carrier fabrics in the U.S.A, the maximum concentrations of TCEP and TCIPP were respectively 2,700 mg/kg and 870 mg/kg - higher than the reported in our study (Bergen and Stone, 2021).

In this study, few childcare items appeared to be treated for with TCIPP for fire resistance like mattress, pushchair, and changing mat, while TDCIPP was detected in a booster car seat manufactured in France. As an example, a mattress foam contained 7,500 mg/kg of TCIPP, and two fabrics and one foam from pushchairs contained average of 5,700 and 5,200 mg/kg of TCIPP, respectively. In changing mat fabrics, the average concentration of TCIPP was 6,000 mg/kg and 4,300 mg/kg in foams. Also, child mattresses and changing mats were found to be treated with Cl-OPFRs in the U.S.A as they contained such flame retardants at levels exceeding 1,000 mg/kg -

10,000 mg/kg (Table 3.8) (Stapleton et al., 2011; Cooper et al., 2016; Bergen and Stone, 2021; Gloekler et al., 2021).

The concentration of TDCIPP was 2,500 mg/kg in one fabric and an average of 49,000 mg/kg in two foams of booster car seat. Similarly, TDCIPP was identified in a booster seat from the U.S.A (Miller and Gearhart, 2015; Bergan and Stone, 2021) at 44,000 mg/kg, with concentrations of TCIPP (15,000 mg/kg) and TCEP (550 mg/kg) also reported (Bergan and Stone, 2021). Moreover, one of five booster seats manufactured in the U.S.A in 2014 was treated with TCIPP and TCIPP in fabric and foam (Miller and Gearhart, 2015); however, none of nine booster seats manufactured in 2016 contained detectable concentrations of Cl-OPFRs (Miller and Gearhart, 2016).

The main driver for the addition of such flame retardants into these items is likely the UK fire safety regulations (FIRA, 2011) Furniture and Furnishings (Fire Safety) Regulations 1988 (as amended in 1989 and 1993). Childcare items containing upholstery that are intended to contain a baby or small child are subject to the Regulations, including mattresses, baby walkers, baby seats, car seats, Moses' baskets, pushchairs, and upholstery liners that come with these items. The regulations do not apply to play mats, changing mats, and carriers (FIRA, 2011).

Interestingly, some articles (changing mats) contained Cl-OPFRs at concentrations over 1,000 mg/kg, despite such articles not being subject to fire safety regulations.

3.2.2.3 Cl-OPFR concentrations in waste childcare items from Saudi Arabia

In childcare articles from Saudi Arabia, concentration of Cl-OPFRs ranged from <LOQ to 3,000 mg/kg (median 12 mg/kg; average 170 mg/kg) (Table 3.11). Among the 51 samples analysed, TClPP was the most abundant Cl-OPFR with a detection

frequency of 80 %, while TDCIPP and TCEP appeared in 16 % and 14 % of samples, respectively. Only TCIPP was found at a concentration above 1,000 mg/kg (specifically 3,000 mg/kg in each sample), with this in the foam and fabric of a single child car seat.

Table 3. 11: Statistical summary of Cl-OPFR concentrations (mg/kg) in fabrics and foams from Saudi Arabian waste childcare items and percentage of samples exceeding 1,000 mg/kg

Waste category	TCEP				TDCIPP				TCIPP				Cl-OPFRs			
	Average	Median	Range	%>1,000 mg/kg	Average	Median	Range	%>1,000 mg/kg	Average	Median	Range	%>1,000 mg/kg	Average	Median	Range	No. (%>1,000 mg/kg)
Childcare items n=51	2.7	<LOQ	<LOQ-97	0	2.6	<LOQ	<LOQ-65	0	160	9.7	<LOQ-3,000	2 (4%)	170	12	<LOQ-3,000	2 (4%)
Car seat (composite) n=12	3.7	<LOQ	<LOQ-37	0	5.4	1.6	<LOQ-30	0	540	18	<LOQ-3,000	2 (17%)	550	42	<LOQ-3,000	2 (17%)
Car seat (fabric) n=7	1	<LOQ	<LOQ-6.8	0	4	3.3	<LOQ-16	0	470	9.7	<LOQ-3,000	1 (14%)	470	15	<LOQ-3,000	1 (14%)
Car seat (foam) n=3	12	<LOQ	<LOQ-37	0	12	7.1	<LOQ-30	0	1000	25	11-3,000	1 (33%)	1000	79	31.79-3,000	1 (33%)
Changing mat n=2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	430	430	11-860	0	430	430	11.51-860	0
Child chair n=2	49	49	<LOQ-97	0	33	33	<LOQ-65	0	290	290	<LOQ-580	0	370	370	<LOQ-740	0
Mix of childcare items n=35	0.012	<LOQ	<LOQ-0.090	0	0.075	<LOQ	<LOQ-2	0	11	8.4	<LOQ-66	0	11	8.5	<LOQ-66	0

Higher concentrations of TCEP, TDCIPP, and TCIPP were found in car seats in the current study from Ireland, as well as in other studies like in the U.S.A and Denmark (Table 3.8).

The fabrics and foams of toy holders, child mattresses, and teddy toys from Saudi Arabia did not contain Cl-OPFRs. This is consistent with a study conducted in the U.S.A., in which Cl-OPFRs were not detected in samples of toy stuffing and fabrics, baby mattress fabrics and foams, or bath toy foam (Bergen and Stone, 2021). However, in other studies in the U.S.A., child mattress and toys were found to be treated with Cl-OPFRs. For example, among 13 portable mattresses for babies, one contained TCEP, two contained TCIPP, and one contained TDCIPP (Stapleton et al., 2011) at levels above 1,000 mg/kg. Cooper et al (2016) found that among 36 child mattresses in the U.S.A, TDCIPP was found in 5 and TCIPP in 3 at concentrations exceeding 1,000 mg/kg. Interestingly, PUFs from bath products (used to hold baby during bathing) contained TCIPP concentrations of 18,700 and 21,600 mg/kg (Gloekler et al., 2021). In contrast, there have been reports of very low concentrations of TCEP (<50 mg/kg) in fabric and foam used for toys and childcare articles in Denmark (Borling et al., 2006) and of Cl-OPFRs in Belgium (Ionas et al., 2014) and China (Zhang et al., 2022).

In this study, the remaining samples of fabric, foam, and wool from two baby walkers, two bouncers, a stroller, Moses's basket, changing mat, carrycot and soft play foam contained only TCIPP at concentrations that were mostly higher in foam than fabric but not exceeding 1,000 mg/kg in any such samples.

3.2.3 Cl-OPFR concentrations in waste ELV from Ireland

Cl-OPFRs were detected in all ELV samples examined, at concentrations ranging from 4.8 to 15,000 mg/kg. Table 3.12 is a statistical summary of concentrations of Cl-OPFRs in ELV waste sample analysed. TDCIPP was the Cl-OPFR found at the highest levels. To illustrate, in ELV samples comprising fabrics, foams, padding, floor mats and roof trim, the average and maximum concentration of TDCIPP was 750 mg/kg and 15,000 mg/kg, respectively. Average and maximum concentrations in the same samples were TCEP (120 and 2,400 mg/kg) and TCIPP (95 and 570 mg/kg), respectively. Information about the fabric, foam, padding, floor mat and roof trim samples obtained from ELV like car model and year of manufacture were obtained successfully for 62 samples. However, for 35 of 97 samples, such information was not available.

In ELV fabric, foam, and roof trim samples, TDCIPP was detected at higher levels than TCEP and TCIPP. To clarify, in 34 ELV fabric samples, the average concentration of TDCIPP was 910 mg/kg, followed by TCEP at 100 mg/kg and TCIPP at 60 mg/kg. Similarly, in 35 ELV foam samples, the average concentration of TDCIPP was 1,000 mg/kg, followed by TCEP at 220 mg/kg and TCIPP at 170 mg/kg. Finally, in 13 roof trim samples, average concentrations were 530 mg/kg for TDCIPP, 56 mg/kg for TCIPP and 7.2 mg/kg for TCEP. However, in ELV padding and floor mat samples, TCIPP was detected at higher levels than TDCIPP and TCEP. Specifically, in 5 padding and 10 floor mat samples, the average concentration of TCIPP was 56 and 19 mg/kg, respectively; compared to 4.4 and 6 mg/kg for TCEP and 4.8 and 2.3 mg/kg for TDCIPP, respectively.

Table 3. 12: Statistical summary of Cl-OPFR concentrations (mg/kg) in fabrics and foams from Irish waste ELV and percentage of samples exceeding 1,000 mg/kg

Waste category	TCEP				TDCIPP				TCIPP				Cl-OPFRs			
	Average	Median	Range	No. (%>1,000 mg/kg)	Average	Median	Range	No. (%>1,000 mg/kg)	Average	Median	Range	No. (%>1,000 mg/kg)	Average	Median	Range	No. (%>1,000 mg/kg)
ELV[a] (fabric, foam, padding, floor mat and roof trim) n=97	120	7.4	<LOQ-2,400	4 (4%)	750	17	<LOQ-15,000	15 (15%)	95	68	<LOQ-570	0	960	210	4.8-15,000	20 (21%)
ELV >1,000 mg/kg n=20	370	18	1.3-2,400	4 (20%)	3,300	2,400	14-15,000	15 (75%)	160	120	25-570	0	3,800	2,600	1,100-15,000	20 (100%)
ELV (fabric and foam) n=69	160	14	1.2-2,400	4 (6%)	950	59	6.7-15,000	13 (19%)	120	82	3.6-570	0	1,200	410	12-15,000	18 (26%)
ELV (fabric) n=34	100	6.8	1.2-1,200	1 (3%)	910	67	7.5-6,300	8 (24%)	60	60	5.6-150	0	1,100	400	22-6,400	9 (26%)
ELV (foam) n=35	220	26	1.2-2,400	3 (9%)	1,000	25	6.7-15,000	5 (14%)	170	130	3.6-570	0	1,400	410	12-15,000	9 (26%)
ELV (padding) n=5	4.4	4.9	<LOQ-9.1	0	4.8	2.3	2.-15	0	56	11	<LOQ-170	0	66	18	4.8-180	0
ELV (roof	7.8	7	0.83-31	0	530	7.2	1.3-	2 (15%)	56	58	1.8-130	0	590	82	11-	2 (15%)

trim) n=13							4,000								4,000	
ELV (floor mat) n=10	6	1.9	0.94-42	0	2.3	0.98	<LOQ-8.8	0	19	16	1.9-54	0	27	19	8.2-100	0

[a] ELV= end of life vehicle

Table 3.13 lists the average concentrations of TCEP, TDCIPP, and TCIPP in all ELV samples according to the year of vehicle manufacture (where known). TDCIPP is more expensive than other Cl-OPFRs and used mostly for automotive applications, where it is preferred for its low fogging potential (lower risk of forming thin films on windshields) (ECHA, 2018b). This could explain the frequent detection of TDCIPP at higher levels in ELV samples than TCEP and TCIPP. Figure 3.4 shows temporal trends in Cl-OPFRs concentrations in ELV waste and manufacture year of vehicle. Between 1999 and 2012, there is no clearly discernible trend, though analysis of more samples may prove instructive - while the highest concentration was in a vehicle made in 2009, this is only one sample.

Table 3. 13: Average concentration (mg/kg) of TCEP, TDCIPP, and TCIPP for ELV waste samples according to vehicle manufacture year

Vehicle manufacture year	no. of samples	Fabric	Foam	Padding	Roof trim	Floor mat	TCEP	TDCIPP	TCIPP
1999	2	1	1	0	0	0	19	8	116
2000	8	3	3	0	1	1	410	94	169
2001	5	1	1	0	1	2	29	1,043	59
2002	9	3	6	0	0	0	548	25	143
2003	8	4	4	0	0	0	120	121	87
2004	10	2	2	1	3	2	10	1,642	87
2005	5	1	1	1	1	1	121	577	77
2006	6	3	2	0	1	0	34	2,234	152
2007	3	2	1	0	0	0	16	232	96
2008	3	1	2	0	0	0	8	385	51
2009	1	0	1	0	0	0	31	10,243	380
2012	2	1	1	0	0	0	342	14	65
Unknown	35	12	10	3	6	4	8	593	64

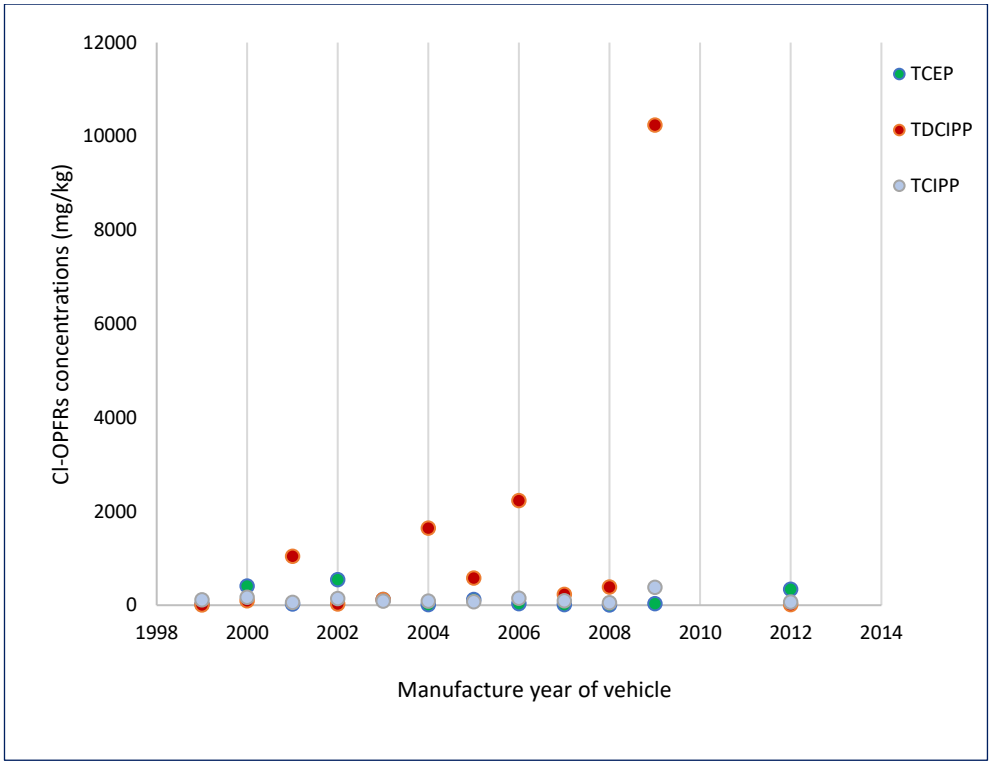


Figure 3. 4: Cl-OPFR concentrations (mg/kg) in ELV waste depending on the year of vehicle manufacture

Additionally, the presence of Cl-OPFRs in ELV samples may reveal their use as alternatives to BFRs. For example, some of the ELV waste samples from our study have been analysed previously for BFRs (Harrad et al., 2019). Out of 119 ELV samples studied, the average HBCDD concentration was 45 mg/kg, while that of ∑PBDEs (mainly BDE-209) was 840 mg/kg. The percentage of samples exceeding 1,000 mg/kg were 1.5% and 3.7% for HBCDD and ∑PBDEs (mainly BDE-209), respectively (Harrad et al., 2019); however, in our investigation, there were 20 samples out of 97 (21%) with Cl-OPFR concentrations above 1,000 mg/kg, which implies Cl-OPFRs were more commonly used than BFRs in vehicle fabrics and foams.

We examined whether Cl-OPFRs applied to foam transfers during use to the overlying fabric covering. Using a paired t-test for all paired foam and fabric samples (n=52) to see if Cl-OPFR concentrations in foams are significantly higher than those

in the associated fabric coverings, showed no significant difference between fabric and foam Cl-OPFRs concentrations (P >0.61). Focusing on those samples (n=20) where Cl-OPFRs exceeding 1,000 mg/kg (implying a likelihood that such samples had been intentionally treated with Cl-OPFRs) also showed no significant difference (P>0.38). This might be because Cl-OPFRs in a few fabric samples (n=3) were higher than in the corresponding foam sample (contrary to reports that Cl-OPFRs are more usually applied to foam rather than fabric). Excluding these 3 samples led to a significant difference (P >0.03) with Cl-OPFRs higher in foams than the corresponding fabrics. This suggests transfer of Cl-OPFRs from foam to fabric could occur over time during product use. Also, our findings imply that Cl-OPFRs have been found previously in fabrics of car seats in Denmark and carrier in the U.S.A (Danish Environmental Protection Agency, 2016; Bergen and Stone, 2021), where TCEP, TDCIPP, and TCIPP concentrations were up to 2,700, 19,000, and 148,000, respectively.

3.2.4. Comparing Cl-OPFR concentrations across countries for the same product categories

This study involved making a statistical analysis of the concentrations of Cl-OPFRs in the same product categories across Ireland, UK, and Saudi Arabia, such as furniture fabrics and foams, as well as child car seat fabrics. However, due to the study's design, not all three countries had access to the same product categories, limiting the scope of the comparison, but it is still valuable.

A statistical comparison of the concentrations of Cl-OPFRs in Ireland, UK, and Saudi Arabia for sofa fabrics and foams was carried out (Table 3.14). Following log transformation of Cl-OPFRs concentrations (mg/kg), one-way repeated measures

ANOVA tests were applied to compare means of TCEP, TDCIPP, and TCIPP concentrations.

For sofa foams and fabrics, there was a statistically significant difference for ∑Cl-OPFRs and for TCEP, TDCIPP, and TCIPP individually between the three countries as determined by one-way ANOVA ($p < 0.01$). A Tukey post hoc test revealed that Cl-OPFRs concentrations were significantly lower in Saudi Arabia than in Ireland and the UK ($P<0.01$). However, there was no statistically significant difference between Ireland and the UK. A significant difference observed for TDCIPP and TCIPP concentration between Saudi Arabia and the UK and between Saudi Arabia and Ireland, but not between UK and Ireland. In addition, a significant difference was evident for TCEP between Ireland and UK and between Ireland and Saudi Arabia, but not between the UK and Saudi Arabia.

Table 3. 14: ANOVA test results with post hoc Tukey tests comparing concentration of Cl-OPFRs in furniture fabrics and foams from Ireland, UK, and Saudi Arabia

Chemical compound	F	Significant differences	P value
Sofa fabric			
Cl-OPFR	77.062	Saudi Arabia < UK	<0.01
		Ireland < UK	>0.13
		Ireland > Saudi Arabia	<0.01
TCEP	13.482	Saudi Arabia > UK	>0.20
		Ireland > UK	<0.01
		Ireland > Saudi Arabia	<0.01
TDCIPP	9.973	Saudi Arabia < UK	<0.05
		Ireland > UK	>0.05
		Ireland > Saudi Arabia	<0.01
TCIPP	91.515	Saudi Arabia < UK	<0.01
		Ireland < UK	>0.06
		Ireland > Saudi Arabia	<0.01

Sofa foam			
Cl-OPFR	51.670	Saudi Arabia < UK	<0.01
		Ireland < UK	>0.91
		Ireland > Saudi Arabia	<0.01
TCEP	35.047	Saudi Arabia < UK	>0.80
		Ireland > UK	<0.01
		Ireland > Saudi Arabia	<0.01
TDCIPP	7.735	Saudi Arabia < UK	<0.01
		Ireland > UK	>0.99
		Ireland > Saudi Arabia	<0.01
TCIPP	47.805	Saudi Arabia < UK	<0.01
		Ireland < UK	>0.93
		Ireland > Saudi Arabia	<0.01

P values highlighted red are significant.

For child car seat fabrics, an independent t-test was applied to evaluate variation in concentrations of TCEP, TDCIPP, and TCIPP between Ireland and Saudi Arabia. This revealed concentrations of TCEP and TDCIPP (but not TCIPP) in Ireland significantly exceeded those in Saudi Arabia (Table 3.15).

Table 3. 15: p values obtained from the T-test comparison of concentrations of Cl-OPFRs in child car seat fabrics between Ireland and Saudi Arabia

T test (childcare items- car seats fabrics) (**Ireland and Saudi Arabia**)		
Chemical compound	**F**	**P value**
TCEP	4.435	<0.01
TDCIPP	0.565	<0.01
TCIPP	14.574	>0.18
Cl-OPFR	0.393	>0.23

P values highlighted red are significant.

3.2.5 Estimation of mass of Cl-OPFRs annually entering the waste streams studied in Ireland, UK, and Saudi Arabia

The estimated mass of the waste materials considered in this study that are generated annually in Ireland, UK, and Saudi Arabia are provided in Table 3.16. As with all estimates, it is important to note that these are only preliminary estimates, and there are uncertainties involved. For example, one area of uncertainty is regarding the amount of waste materials produced each year in Ireland and Saudi Arabia, particularly waste curtains, carpets, and mattresses that were not available directly; thus, we have extrapolated from UK waste furniture data and used our own judgement.

Table 3. 16: Estimated annual masses (t/year) generated in Ireland, UK, and Saudi Arabia for each waste category examined in this study

Waste Category	**Estimated Annual Mass Generated in Ireland (t/year)**	**Source***
Ireland		
ELV foam & fabrics	3,000	We assume that out of the 126,000 t ELVs generated in Ireland in 2020 (EPA, 2022a), 2.4% of those will be foam and fabrics.
Carpets	7,600	Assuming Ireland's waste generation is proportional to the UK's 103,972 t generation of carpet in 2010-11 (WRAP, 2012a).
Furniture foam	2,600	We assume that out of the 100,890 t households generated in Ireland in 2020 (EPA, 2022a), 17.5% of those will be furniture and 15% will be foam.
Furniture fabric	880	We assume that out of the 100,890 t households generated in Ireland in 2020 (EPA, 2022a), 17.5% of those will be furniture and 5% will be fabric.
Curtains	730	We estimated that about 50% of the 20,000 t of all other bulky textiles (WRAP, 2012a) generated in the UK in 2010-11 is curtain waste, and assuming that the waste generated in Ireland is proportional to the population of the UK and Ireland.
Mattress foam	6,100	We estimated that about 50% of the 166,474 t (WRAP, 2012a) mattress generated in the UK in 2010-11 is foam waste, and assuming that the waste generated in Ireland is proportional to the population of the UK and Ireland.
Mattress fabrics	2,400	We estimated that about 20% of the 166,474 t (WRAP, 2012a) mattress generated in the UK in 2010-11 is fabric waste, and assuming that the waste generated in Ireland is proportional to the population of the UK and Ireland.

Total	23,310	
UK		
Furniture foam	36,000	We estimate that 15% of the 237,516 t of waste arisings from sofas, armchairs, and chairs in the UK in 2010-11 (WRAP, 2012b) will be foam.
Furniture fabric	12,000	We estimate that 5% of the 237,516 t of waste arisings from sofas, armchairs, and chairs in the UK in 2010-11 (WRAP, 2012b) will be fabric.
Total	48,000	
Saudi Arabia		
Carpet	53,000	Assuming waste generation in Saudi Arabia is proportional to the UK's 103,972 t generation of carpet in 2010-11 (WRAP, 2012a).
Furniture foam	20,000	We assume that out of the 1,976,834 t households generated in Saudi Arabia in 2020 (Radwan et al., 2021), 6.8 % of those will be furniture and 15% will be foam.
Furniture fabric	6,700	We assume that out of the 1,976,834 t households generated in Saudi Arabia in 2020 (Radwan et al., 2021), 6.8 % of those will be furniture and 5% will be fabric.
Total	79,000	

In this analysis, proportions were calculated based on the estimated 2020 populations for the UK of 67,886,011, Ireland of 4,937,786, and Saudi Arabia of 34,813,871 (Worldometer, 2023)

Our preliminary estimate of the mass of TCEP, TCIPP, and TDCIPP entering the waste streams (Table 3.17) was generated by multiplying the mass of a given waste category annually by the average concentration of each Cl-OPFRs in that waste category. To illustrate, according to Table 3.16, about 2,600 tonnes of waste furniture foam entered the Irish waste stream every year. Taking this into account and multiplying it by the average TCIPP concentration in our furniture foam samples (Table 3.2) of 11,000 mg/kg gives us a 28,600 kg/year estimate of TCIPP.

Table 3. 17: Estimated annual masses (ton/year) of different categories of waste generated in Ireland, UK, and Saudi Arabia, and mass of TCEP, TCIPP, TDCIPP, and ∑Cl-OPFRs (kg/year) associated with such waste.

Waste Category	**Estimated Annual Mass Generated in Ireland (t/year)**	**TCEP (kg/yr)**	**TDCIPP (kg/yr)**	**TCIPP (kg/yr)**	**Cl-OPFRs (kg/yr)**

Ireland					
ELV foam & fabrics	**3,000**	480	2,850	360	3600
Carpets	**7,600**	10	84	129	220
Furniture foam	**2,600**	3,380	2,860	28,600	33,800
Furniture fabric	**880**	54	33	114	202
Curtains	**730**	4	1	46	52
Mattress foam	**6,100**	85	85	10,370	10,370
Mattress fabrics	**2,400**	86	5	96	187
Total	**23,310**	4,100	5,918	39,716	48,432
UK					
Furniture foam	**36,000**	17	102,934	276,624	379,576
Furniture fabric	**12,000**	851	241	17,123	18,216
Total	**48,000**	868	103,175	293,747	397,791
Saudi Arabia					
Carpet	**53,000**	2,279	1,643	4	3,869
Furniture foam	**20,000**	5	26	32	62
Furniture fabric	**6,700**	1	1	2	4
Total	**79,700**	2,285	1,670	37	3,935

The mass of Cl-OPFR estimated to enter waste streams of Ireland, UK, and Saudi Arabia was compared to that of ∑POP-BFRs and BDE-209 and ΣBFRs (PBDEs, HBCDD, and TBBP-A) entering the Irish waste stream in Table 3.18 for the same waste categories (Drage et al., 2018; Drage et al., 2022). The estimated mass of Cl-OPFRs entering the Irish waste stream annually is 48,432 kg, which exceeds the estimated amount of POP-BFRs and BDE-209 (Drage et al., 2018) and BFRs (PBDEs, HBCDD, and TBBP-A) in 2019 in Ireland (Drage et al., 2022). However, the amount of Cl-OPFRs estimated in the UK is 397,791 kg, which is higher than the amount we estimated in Ireland, and even higher than the mass of POP-BFRs and BDE-209 and BFRs (PBDEs, HBCDD, and TBBP-A) entering the Irish waste stream

in 2019 for furniture fabrics and foams (Drage et al., 2018; Drage et al., 2022). Finally, the mass of Cl-OPFR entering the waste stream in Saudi Arabia of 3,935 kg is lower than our estimates in the UK and Ireland, also lower for the same waste ∑POP-BFRs and BDE-209 in Ireland (Drage et al., 2018) but higher than ΣBFRs (PBDEs, HBCDD, and TBBP-A) in 2019 in Ireland (Drage et al., 2022).

Table 3. 18: Estimated annual mass (kg/year) of POP-BFRs and BDE-209 and ΣBFRs associated with Irish waste categories.

	Waste categories			
Chemical compound	**ELV, curtain, carpet, furniture foam and fabric, and mattress fabric and foam (kg/year)**	**Furniture fabrics and foam (kg/year)**	**Carpet and furniture fabrics and foam (kg/year)**	**Reference**
∑POP-BFRs and BDE-209	24,208	19,148	21,016	(Drage et al., 2018)
ΣBFRs (PBDEs, HBCDD, and TBBP-A)	5,032	2,400	2,510	(Drage et al., 2022)

In Ireland, 48 % of 5,918 kg TDCIPP was attributed to ELV foams and fabrics, and an equivalent percentage (48 %) was related to furniture foam. The distribution of TCIPP contamination is more even; 72 % of the 39,716 kg that entered the Irish waste stream related to furniture foam, and 26 % to mattress foam. In contrast, the majority (82 %) of the 4,231 kg of TCEP that entered the Irish waste stream was linked to furniture foam, with the majority of the remaining (11 %) detected in ELV foams and fabrics. In the UK, 98 % of TCEP was associated with furniture fabrics. TCIPP was mostly related to furniture foam 94 % and 6 % to furniture fabrics, and 99.8 % of

TDCIPP was related to furniture foam and 0.2 % to fabrics. In Saudi Arabia, 99.7 % of TCEP and 98.3 % of TDCIPP were respectively associated with carpet while 86.4 % of TCIPP was related to furniture foam.

These findings on the distribution of Cl-OPFRs among waste categories should help target monitoring efforts to the waste categories most polluted with Cl-OPFRs. Where monitoring resources are limited, it is advisable to concentrate on waste types that carry the majority of the Cl-OPFRs load.

3.2.6 The impact of regulations on Cl-OPFRs in waste furnishings

We detected far lower concentrations of Cl-OPFRs in our Saudi Arabian samples than in those from the UK and Ireland. This might be because in Saudi Arabia and other countries, flame retardants are regulated differently.

To clarify, in Saudi Arabia, the Saudi Standards, Metrology and Quality Organization (SASO) governs standards, metrology, and quality, which manages the Saudi Product Safety Program, or "SALEEM," to ensure imported and locally manufactured goods meet important safety and quality requirements (SASO, 2018). In 2018, SASO published new technical regulations that apply to all textile products including furniture and childcare items on the Saudi market such that they must meet the requirements of safety, consumer health and environment conservation. Therefore, products should be labelled with any applied hazardous chemicals like flame retardants that can be carcinogenic, mutagenic, toxic chemical for reproduction, and adversely affect people and environment health. It is not a requirement in this regulation for furniture and childcare products to be fire-resistant (SASO, 2018). Perhaps this could explain why most of our analysed furniture and childcare items from Saudi Arabia were not treated with Cl-OPFRs (Figure 3.3).

Meanwhile, in countries such as U.S.A. and EU (like UK, Ireland, France, Czech Republic, Finland, Sweden, and Norway), there are different regulations for fire resistance than in Saudi Arabia. In the UK, use of flame retardants in furniture is influenced by the Furniture and Furnishings (Fire) (Safety) (Amendment) Regulations 1989 (SI 1989 No. 2538) (FIRA, 2011). In the absence of regulations specifying which flame retardants can be used in a product, and since product labels do not have to specify which flame retardants were used, it is unclear which chemicals were used and at what concentrations. The regulation is also applied to the upholstery and foam of nursery furniture and upholstered items (FIRA, 2011). There is an equivalent Fire Safety Regulation in Ireland, the 316/1995, which requires upholstered furniture to comply with specific fire safety requirements (eISB, n.d). That might explain why furniture and childcare items from the UK (49 of 146 samples) and Ireland (33 of 180 samples) in the current study were treated with Cl-OPFRs.

California Furniture Flammability Standard, Technical Bulletin 117 (TB117), was implemented in 1975 in the U.S.A. To comply with the standard, North American furniture and childcare products must contain flame retardants. Products sold in California, regardless of where they were manufactured, must conform to the standard (State of California, 2013). TB 117 has been replaced by TB 117-2013 in 2014 in response to potential human harm associated with flame retardant exposure. As a result, manufacturers no longer must make their products resistant to an open flame ignition source; they must only resist cigarette smoulder. The law allows manufacturers to use methods other than flame retardants to meet the flammability standard; however, the use of flame retardants is not prohibited. Furthermore, the California 1019 Senate Bill requires that furniture is labelled if the concentration of flame retardants in any component is above 1,000 mg/kg (State of California, 2013).

Due to the lack of a specific chemical list in the law, manufacturers, distributors, and retailers of furniture and childcare items are responsible for deciding whether their products contain flame retardants, and if so, to mark the product label accordingly (Petreas et al., 2016). Generally, product flame retardancy is not considered if its total content of flame retardants is below 1,000 mg/kg (0.1 %). Samples of furniture components collected before 2015 (when the SB1019 law took effect) were from items manufactured between 2000-15. In about 5 of 11 furniture foams, the maximum concentration of TCEP, TDCIPP and TCIPP was 92,500, 21,000 and 96,500 mg/kg, respectively (Petreas et al., 2016). A total of 1411 foam samples taken from furniture and childcare products between 2014-16 and 42 % contained flame retardants at concentration greater than 1,000 mg/kg. The most detected flame retardant was TDCIPP (in 24 %) while TCIPP was found in 7 % of tested samples, of which some samples had a concentration of 1,000 mg/kg (Cooper et al., 2016). During the testing of 102 PUFs of American couches purchased between 1985 and 2010, 85 % of the samples had flame retardants, with TDCIPP found in 41 % of the couches at an average concentration of 44,870 mg/kg (Stapleton et al., 2012). As a result of the testing of 15 car seats in 2016, no flame retardants (including Cl-OPFRs) were found for the first time (Miller and Gearhart, 2016) in contrast to those car seats tested in 2014, which contained either one or both of TDCIPP or TCIPP (Miller and Gearhart, 2015).

European Union countries like France, Czech Republic, Finland, Norway, and Ireland require that domestic upholstered furniture not be ignitable by lighted cigarettes and matches due to legal fire safety regulations (Table 3.19) (Guillaume et al., 2020). For instance, a French study investigated the presence of flame retardants in upholstered furniture, found that TCIPP was found in 5 of 7 foams at concentration ranged from

3,000 to 87,000 mg/kg and in one coating of 5 in combination with other flame retardant (Tetraphenyl resorcinol) at concentration of 250,000 mg/kg. Only in one foam of 7, TDCIPP was found at concentration of 85,000 mg/kg (Lounis et al., 2019).

National regulations and standards in Saudi Arabia, Europe, and U.S.A towards the ignitability of domestic upholstered furniture are presented in Table 3.19.

Table 3. 19: National regulations and standards in Saudi Arabia, Europe, and USA towards the ignitability of domestic upholstered furniture

Country	Furniture type	Reference regulation	Requirement	Test method	Classification	Reference
Saudi Arabia	Upholstered furniture	No regulation	Prohibited	-	-	(SASO, 2018)
U.S.A	Upholstered Furniture	The standard (Technical Bulletin 117, or TB117) and (TB 117-2013)	No ignition by cigarette and match	Smolder Resistance Testing (UFAC/NFPA 260)	Pass/fail	(State of California, 2013)
France	Bedding	No. 2000-164	No ignition by cigarette	EN ISO 12952-1 and 2	Pass/fail	(Guillaume et al., 2020)
UK	Seat, mattress, and filling	Furniture and furnishing Regulations No. 1324	No ignition by cigarette, match, and crib five	EN 1021–1 EN 1021-2 BS 5852	Pass/fail	
Ireland	Seat and mattress	S.I. No. 316/1995	No ignition by cigarette and match	I.S. 419:1988	Pass/fail	
Czech Republic	Seat and mattress	Statutory Instrument N°23 – Notice on technical requirement fire safeguard	No ignition by match	EN1021-2	Pass/fail	

		building				
Finland	Seat	No. 743/1990 No. 479/96	No ignition by cigarette	EN1021-2	Pass/fail	
Sweden	Seat and mattress	No regulations only recommendation from consumer agency	No ignition by cigarette	EN1021-2 EN 597-1	Pass/fail	
Norway	Seat and mattress	Crown Prince Regent's Decree September 7, 1990	No ignition by cigarette	EN1021-2 EN 597-1	Pass/fail	

3.3 Conclusions

To test the hypothesis that Cl-OPFRs have been extensively used in furniture, vehicle, and childcare items, about 53 out of 277 samples (19%) from Ireland and 49 of 146 samples (35%) from the UK contained Cl-OPFRs at concentrations exceeded 1,000 mg/kg. The elevated concentrations of Cl-OPFRs indicating that they have been used in the UK and Ireland. With respect to the hypothesis that levels of Cl-OPFRs in different countries could vary because of national variations in flame retardancy regulations; we found that Cl-OPFR concentrations in a country like Saudi Arabia where there are no furniture fire safety regulations were significantly lower than in the UK and Ireland which both have furniture fire safety regulations. In furniture and childcare items from Saudi Arabia, only 2 of 102 samples tested (2 %) contained Cl-OPFR at level up to 3,030 mg/kg, while the concentration of Cl-OPFRs in the remaining 100 of 102 samples (98 %) were < 1,000 mg/kg. The absence of furniture fire safety regulations in Saudi Arabia removes the regulatory imperative to use chemical flame retardants.

A statistical comparison of concentration of Cl-OPFRs (TCEP, TDCIPP, and TCIPP) in sofa's fabrics and foams from Ireland, UK, and Saudi Arabia was conducted, which revealed a statistically significant difference for Cl-OPFR ($p < 0.01$). In addition,

TCEP and TDCIPP (but not TCIPP) concentrations in child car seat fabrics were significantly higher in Ireland than in Saudi Arabia.

The mass of Cl-OPFR estimated enter waste streams of Ireland and the UK each year were 48,432 kg and 397,791 kg, respectively. When comparing the amount of the mass of Cl-OPFRs entering the waste stream in Ireland with the restricted BFRs (24,208 kg for ∑POP-BFRs and BDE-209 and 5,032 kg for PBDEs, HBCDD, and TBBP-A), our Cl-OPFRs estimations were higher.

Finally, our investigation demonstrates that Cl-OPFRs are extensively prevalent in childcare items, raising possible exposure concerns for children using these items, which will be discussed in Chapter 5.

Chapter 4: Concentrations of Cl and P in waste foam and fabrics from Ireland, UK, and Saudi Arabia; efficiency of XRF as screening tool for regulatory compliance

4.1. Introduction

This chapter tests the hypothesis that XRF is a viable tool for screening waste for compliance with a proposed concentration limit for Cl-OPFRs of 1,000 mg/kg. Therefore, XRF readings for Cl and P were compared to the GC/MS Cl-OPFRs results obtained for a wide range of waste articles.

To test this hypothesis, Cl and P concentrations were determined using XRF and Cl-OPFR concentrations obtained using GC/MS for

- 72 furniture samples, 97 ELV, and 108 childcare articles from Ireland
- 40 furniture and 89 childcare articles from the UK
- 51 furniture and 51 childcare articles from Saudi Arabia

4.2. Sampling and analytical methods

Analyses of waste fabrics and foams with GC/MS and portable XRF were conducted to determine the concentrations of Cl-OPFRs, Cl, and P. Screening for Cl and P was performed using a hand-held XRF spectrometer (Niton^{TM} XL3t GOLDD^{+} XRF Analyser, Thermo Fisher Scientific). The entire sample was placed in a clean XRF test stand and repeated measurements (of three at least) were taken from different spots for the homogeneity of the sample, then the average of these measurements was calculated. XRF was programmed to collect measurements with 60 seconds for Cl and 30 seconds for P. The sampling and analytical methods used are described in detail in Chapter 2, sections 2.1 and 2.4.1, respectively.

4.3. Results and discussion

4.3.1. Total Cl and P concentrations determined by XRF in waste from Ireland

Table 4.1 provides a statistical summary of the concentrations of Cl and P determined via XRF in waste articles from the various sample categories. Generally, the average Cl and P concentrations exceed those of Cl-OPFRs reported in Table 3.2 and 3.9. The highest Cl measurements (exceeding 90,000 mg/kg) in each waste category were found in furniture and mattress foam, ELV floor mats, fabrics of pushchairs and baby seat and foams from car seats, child couches and cot mattresses. Lower concentrations of Cl were detected in ELV up to 80,000 mg/kg, as well as in soft furnishing and childcare articles (up to 30,000 and 5,000 mg/kg, respectively). In one sample (pushchair PVC fabric), the Cl reading was the highest (920,000 mg/kg = 92 %) among all Irish waste. Given that the Cl content of PVC is typically 67 % (Walsh, 2011), our data for this pushchair fabric indicates that XRF accuracy is questionable at highly elevated Cl concentrations.

Table 4. 1: Statistical summary of Cl and P concentration (mg/kg) in Irish soft furnishing, ELV, and childcare article waste samples

	Chlorine			Phosphorus		
Waste category	**Average concentration**	**Median concentration**	**Range**	**Average concentration**	**Median concentration**	**Range**
Soft furnishing n=72	**16,000**	**3,000**	**450-110,000**	**21,000**	**12,000**	**3,800-110,000**
Soft furnishing >1,000 mg/kg n=11	73,000	71,000	20,000-110,000	56,000	64,000	19,000-77,000
Curtain n=7	2,200	1,500	550-8,700	5,400	5,400	4,200-6,600
Carpet n=22	3,200	850	450-29,000	14,000	13,000	5,900-32,000
Mattress upholstery n=6	14,000	6,500	3,800-30,000	35,000	24,000	6,100-110,000
Mattress foam n=10	14,000	2,400	1,500-110,000	19,000	13,000	8,600-68,000
Furniture upholstery n=15	7,800	7,000	1,800-24,000	15,000	11,000	6,400-41,000
Furniture foam n=12	58,000	64,000	530-110,000	46,000	51,000	3,800-77,000
ELV (all) n=97	**16,000**	**8,100**	**220-95,000**	**15,000**	**9,400**	**3,900-74,000**
ELV >1,000 mg/kg n=20	31,000	24,000	5,300-74,000	22,000	15,000	7,700-54,000
ELV (fabric and foam) n=69	18,000	13,000	1,500-84,000	17,000	12,000	3,900-74,000

ELV (fabric) n=34	22,000	19,000	1,600-84,000	21,000	15,000	5,600-74,000
ELV (foam) n=35	15,000	9,000	1,500-63,000	14,000	8,200	3,900-54,000
ELV (padding) n=5	5,400	5,400	2,500-8,100	6,100	6,000	5,100-7,000
ELV (roof trim) n=13	10,000	5,000	1,600-37,000	11,000	7,700	5,700-24,000
ELV (floor mat) n=10	16,000	3,700	220-95,000	13,000	9,200	5,900-31,000
Childcare articles n=108	**35,000**	**4,300**	**1,200-920,000**	**35,000**	**5,500**	**3,400-460,000**
Car seats n=62	38,000	5,100	1,400-240,000	27,000	5,600	3,400-110,000
Car seat (fabric) n=15	12,000	6,300	3,600-35,000	17,000	5,700	3,800-83,000
Car seat (foam) n=19	110,000	87,000	3,300-240,000	67,000	70,000	5,800-110,000
Car seat >1,000 n=15	140,000	190,000	10,000-240,000	52,000	58,000	7,900-80,000
Mix of childcare items n=46	32,000	3,500	1,200-920,000	46,000	5,300	3,600-460,000
Play mat n=3	3,000	2,500	2,400-4,100	4,100	3,900	3,900-4,600

Baby seat n=6	20,000	5,100	3,400-94,000	170,000	87,000	3,900-460,000
Pram n=2	3,400	3,400	3,200-3,500	6,600	6,600	5,600-7,700
Child couch n=3	52,000	12,000	12,000-130,000	31,000	12,000	12,000-70,000
Cot mattress n=3	55,000	14,000	9,500-140,000	30,000	6,700	6,100-76,000
Mattress foam n=14	2,300	1,900	1,200-5,100	5,200	4,500	3,600-9,900
Pushchair n=15	67,000	5,800	1,500-920,000	52,000	5,400	3,600-190,000
Mix of childcare items >1,000 n=7	57,000	12,000	3,600-140,000	110,000	70,000	5,200-400,000

4.3.2. Total Cl and P concentrations determined by XRF in waste from the UK

Table 4.2 provides a statistical summary of the concentrations of Cl and P determined via XRF in furniture and childcare items waste from the UK. Average Cl and P readings those of Cl-OPFRs provided in Tables 3.4 and 3.10. Highest Cl readings were observed in PVC changing mat fabrics that ranged between 600,000 mg/kg and 900,000 mg/kg. Furniture fabrics and foams, as well as foams from pushchairs, changing mats, and booster seats, also contained high Cl concentrations, with some such samples > 100,000 mg/kg. Of the remaining furniture and childcare items tested, concentrations of Cl were lower, ranging from 1,000 to 70,000 mg/kg.

Table 4. 2: Statistical summary of Cl and P concentration (mg/kg) in furniture and childcare article waste samples from the UK

	Chlorine			Phosphorus		
Waste category	**Average concentration**	**Median concentration**	**Range**	**Average concentration**	**Median concentration**	**Range**
Furniture n=40	**67,000**	**16,000**	**1,100-370,000**	**53,000**	**25,000**	**4,200-400,000**
Furniture >1,000 mg/kg n=21	99,000	60,000	1,800-310,000	60,000	43,000	7,000-200,000
Sofa n=24	65,000	8,100	1,500-370,000	58,000	24,000	4,200-400,000
Sofa cover leatherette n=10	130,000	65,000	3,000-370,000	70,000	60,000	12,000-200,000
Sofa cover leather n=4	6,400	5,400	1,700- 13,000	28,000	26,000	19,000-41,000
Sofa fabric n=3	2,300	2,200	1,800- 2,900	140,000	7,000	5,900-400,000
Sofa foam n=2	100,000	100,000	75,000-130,000	60,000	60,000	46,000-73,000

Sofa lining n=3	13,000	14,000	7,900- 16,000	8,800	9,100	5,700- 12,000
Sofa wool and other miscellaneous n=2	1,700	1,700	1,500- 1,900	4,900	4,900	4,200- 5,600
Armchair n=8	37,000	22,000	1,100- 100,000	38,000	28,000	13,000- 120,000
Armchair cover leatherette n=6	46,000	26,000	1,100- 100,000	41,000	28,000	16,000- 120,000
Armchair cover leather* n=1	3,100	-	-	49,000	-	-
Armchair cover textile* n=1	22,000	-	-	13,000	-	-
Chair cover leatherette n=6	130,000	87,000	1,800- 300,000	67,000	70,000	9,700- 120,000
Childcare articles n=89	**54,000**	**5,900**	**840- 940,000**	**21,000**	**5,400**	**3,300- 220,000**
Childcare articles >1,000 mg/kg n=13	330,000	157,000	18,000- 940,000	91,000	51,000	8,500- 220,000
Childcare articles (fabric) n=57	69,000	7,200	1,100- 940,000	23,000	5,400	3,900- 220,000
Childcare articles (foam) n=13	64,000	6,700	840- 180,000	34,000	34,000	5,100- 96,000

Childcare articles (wool, XPS& leatherette) n=19	3,800	4,100	1,900- 6,100	4,300	4,000	3,300- 7,600
Changing mat n= 6	600,000	750,000	98,000- 940,000	150,000	170,000	48,000- 220,000
Booster car seat n=4	93,000	87,000	16,000- 180,000	24,000	23,000	8,200- 43,000
Pushchair n=14	31,000	14,000	2,600- 120,000	28,200	7,300	4,600- 180,000

*Actual Cl concentration (mg/kg)

4.3.3. Total Cl and P concentrations determined by XRF in waste from Saudi Arabia

Table 4.3 provides a statistical summary of the concentrations of Cl and P found in waste articles from furniture and childcare items. Concentrations of Cl and P exceed those of Cl-OPFRs shown in Tables 3.5 and 3.11. In furniture, the highest Cl reading was observed in a sample of PVC fabric from door insulation, which was 260,000 mg/kg. Lower Cl concentrations up to 26,000 mg/kg were found in fabrics from ottomans, pillows, bedframes, wool from cushions, and carpets, as well in PUFs from sofas. In childcare items, the highest Cl concentration was recorded in a sample of PVC fabric from a car seat of 240,000 mg/kg. Foams from baby walkers and car seats contained Cl concentrations up to 21,000 mg/kg and 47,000 mg/kg, respectively.

Table 4. 3: Statistical summary of Cl and P concentrations (mg/kg) in Saudi Arabian soft furnishing and childcare article waste samples

	Chlorine			Phosphorus		
Waste category	**Average concentration**	**Median concentration**	**Range**	**Average concentration**	**Median concentration**	**Range**
Furniture n=51	9,300	3,300	480-260,000	8,500	4,800	3,500-100,000
Sofa (composite) n=15	5,600	3,500	490-26,000	6,300	4,900	3,700-12,000
Ottoman (composite) n=4	6,900	5,800	2,000-14,000	8,000	8,500	4,700-10,000
Cushion (composite) n=8	3,400	3,400	1,000-7,300	4,400	4,200	3,800-5,600
Pillow (composite) n=4	3,600	2,900	1,300-7,100	4,500	4,700	3,700-4,900
Bed frame (composite) n=3	3,000	2,900	2,100-4,100	15,000	13,000	7,600-25,000
Carpet n=3	920	790	480-1,500	15,000	18,000	7,500-20,000
Mix products n=14	22,000	3,800	1,400-260,000	12,000	4,800	3,500-100,000
Childcare items n=51	12,000	5,300	250-240,000	14,000	6,400	3,500-87,000
Car seat (composite)	31,000	9,000	2,500-	15,000	6,600	5,200-52,000

n=12			240,000			
Car seat (fabric) n=7	43,000	9,600	4,300- 240,000	14,000	6,400	5,200-52,000
Car seat (foam) n=3	22,000	14,000	5,300-47,000	11,000	6,100	5,200-22,000
Changing mat n=2	5,600	5,600	3,700-7,500	24,000	24,000	18,000- 31,000
Child chair n=2	1,400	1,400	250-2,600	4,800	4,800	3,500-6,100
Mix of childcare items n=35	6,100	4,700	430-21,000	14,000	6,200	3,600-87,000

4.3.4 Efficiency of handheld XRF as a screening tool for compliance with anticipated concentration limits for Cl-OPFRs in waste soft furnishing

To determine the suitability of Cl and P as an Cl-OPFR-qualifier, a Spearman rank correlation was used to evaluate the relationship between the variables (because the population distribution was not normal). It was used to determine the degree of correlation between concentrations of Cl and P and those of ∑Cl-OPFRs (concentration of the Cl-OPFR as measured by the GC/MS) in the same samples. In addition, concentrations of Cl-OPFRs were converted into an equivalent Cl concentration by multiplying the GC/MS determined TCEP, TDCIPP and TCIPP concentrations by their respective molar fractions that are Cl, i.e.: 106/285=0.373, 213/430=0.494, and 106/327= 0.325, respectively. A comparison between GC/MS Cl equivalent TCEP, TDCIPP and TCIPP concentration with those of elemental Cl measured in the same samples using XRF was conducted.

The Cl-equivalent concentrations that equate to 1,000 mg/kg for TCEP, TDCIPP, and TCIPP are: 373 mg/kg, 494 mg/kg, and 325 mg/kg, respectively. We thus examined our data to see whether the XRF measurements of Cl correctly identified samples containing >1,000 mg/kg of one or more Cl-OPFRs. Instances where XRF-Cl incorrectly indicated the Cl-OPFR concentration to exceed 1,000 mg/kg are referred to as “false exceedances”, while cases where XRF-Cl measurements failed to identify samples where Cl-OPFRs >1,000 mg/kg are called “false negatives”. The following sections first describe the correlation between XRF and GC/MS data, followed by discussion of the extent to which XRF correctly identifies articles containing >1,000 mg/kg Cl-OPFRs.

4.3.4.1. Correlation of quantified Cl-OPFRs and Cl and P concentrations in furniture, ELV, and childcare articles waste from Ireland

Table 4.4 summarises correlations between concentrations of Cl and P and the concentration of the actual Cl-OPFR as measured by the GC/MS in waste soft furnishing, ELV, and childcare articles. Taken as a whole, the Irish waste articles examined in this study show significant correlation between both Cl and Cl-OPFRs and between P and Cl-OPFRs.

Table 4. 4: Overview of the corresponding Spearman correlation (R), P value, slope, and y intercept for soft furnishing, ELV, and childcare items waste from Ireland

	Chlorine				**Phosphorus**			
Waste category	**R value**	**p-value**	**Slope**	**y-intercept**	**R value**	**p-value**	**Slope**	**y-intercept**
Irish waste n=277	0.67	<0.01	3.4418	12316	0.56	<0.01	1.0047	21172
Soft furnishing n=72	0.59	<0.01	4.1082	5323.1	0.32	<0.01	2.6113	14570
Curtain n=7	-0.17	0.70	-12.815	3139.5	0.42	0.33	9.8795	4691.4
Carpet n=22	-0.07	0.73	-24.217	3957.3	-0.36	0.09	-65.343	15572
Mattress upholstery n=6	-0.46	0.35	-69.017	19008	-0.29	0.57	-166.12	47823
Mattress foam n=10	0.24	0.48	7.1643	1436.8	-0.01	0.96	3.6192	12926
Furniture upholstery n=15	0.52	<0.05	11.29	5279.9	0.17	0.53	11.455	12569
Furniture foam n=12	0.73	<0.01	3.4829	12516	0.83	<0.01	2.867	8702.8
Upholstery (furniture & mattress) n=21	0.14	0.53	-6.386	10657	-0.07	0.73	-35.134	27075
Foam (furniture & mattress) n=22	0.86	<0.01	4.1034	5382.3	0.86	<0.01	2.7527	12105
ELV (all) n=97	0.60	<0.01	4.5186	12083	0.38	<0.01	1.9171	13540
ELV (fabric and foam) n=69	0.65	<0.01	4.4152	13055	0.38	<0.01	1.7951	15067

ELV (fabric) n=34	0.63	<0.01	5.9532	15804	0.29	0.08	0.7436	19924
ELV (foam) n=35	0.69	<0.01	4.096	9225.6	0.55	<0.01	2.2454	10818
ELV (padding) n=5	0.10	>0.87	8.1573	4858.2	0	>1	1.9187	5990.4
ELV (roof trim) n=13	0.74	<0.01	4.9527	7094.8	0.42	0.14	0.3154	10319
ELV (floor mat) n=10	-0.03	0.93	-91.071	18470	0.02	0.94	17.147	12835
Childcare articles n=108	0.78	<0.01	3.3344	15784	0.67	<0.01	0.7154	30681
Car seats (Fabric, foam, wool, XPS, and EPS) n=62	0.85	<0.01	3.5461	6711.8	0.70	<0.01	0.8736	19190
Car seat (fabric) n=15	0.62	<0.05	7.4365	7499.4	0.59	<0.05	-1.7732	17988
Car seat (foam) n=19	0.87	<0.01	3.4338	12764	-0.23	0.34	0.0294	66303
Mix of childcare items n=46	0.73	<0.01	2.6504	26931	0.63	<0.01	0.7924	44141
Play mat, baby seat, pram, child couch, cot mattress n=17	0.84	<0.01	3.0323	10079	0.66	<0.01	-0.0126	73769
Mattress foam n=14	0.10	0.71	1.576	2237.5	0.43	0.12	-3.9435	5382.4
Pushchair n=15	0.76	<0.01	1502.8	-50586	0.66	<0.01	493.11	13426

Cl-OPFR concentrations did not exceed 1,000 mg/kg in any of our curtain, carpet, mattress upholstery and foam samples. Analysis of curtain, carpet, mattress upholstery and foam data showed no correlation between Cl-OPFRs measurements as well as Cl and P readings as provided in Table 4.4. However, furniture upholstery data showed significant correlation between Cl-OPFRs and Cl but not significant correlation between Cl-OPFRs and P measurements (Table 4.4).

For soft furnishing waste, a statistically significant correlation was observed between Cl and P and ∑Cl-OPFRs (Figure 4.1 and 4.2), as well as for furniture foam (Figure 4.3 and 4.4) and furniture and mattress foam (Figure 4.5 and 4.6).

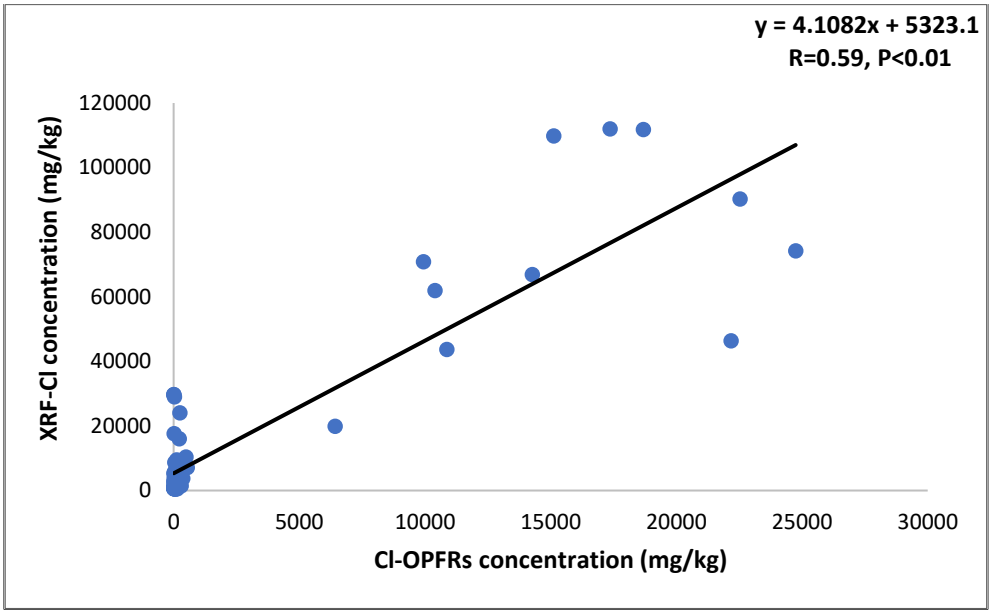


Figure 4. 1: Plot of Cl versus Cl-OPFRs concentrations (mg/kg) for waste soft furnishing from Ireland

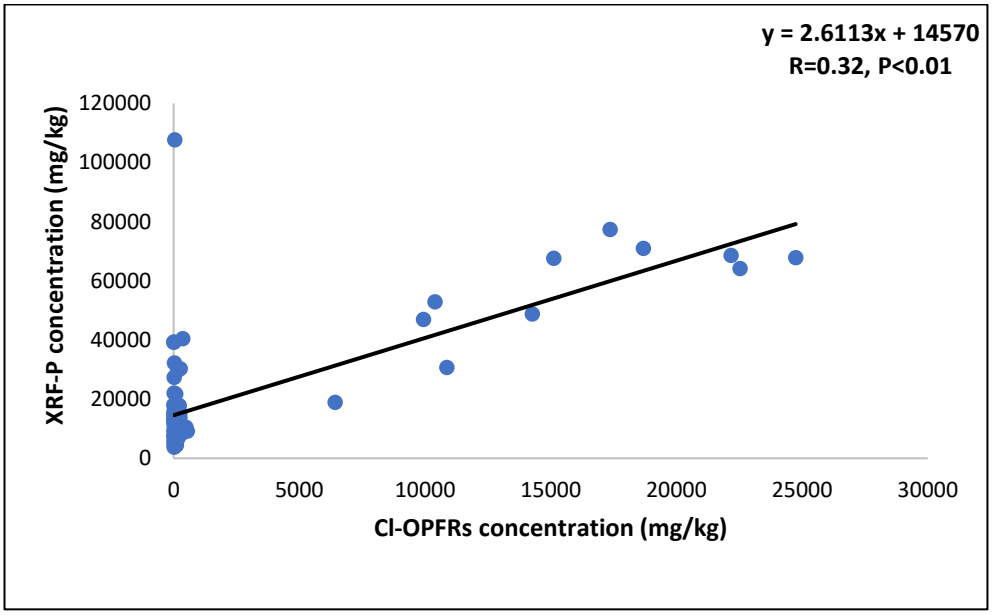


Figure 4. 2: Plot of P versus Cl-OPFRs concentrations (mg/kg) for waste soft furnishing from Ireland

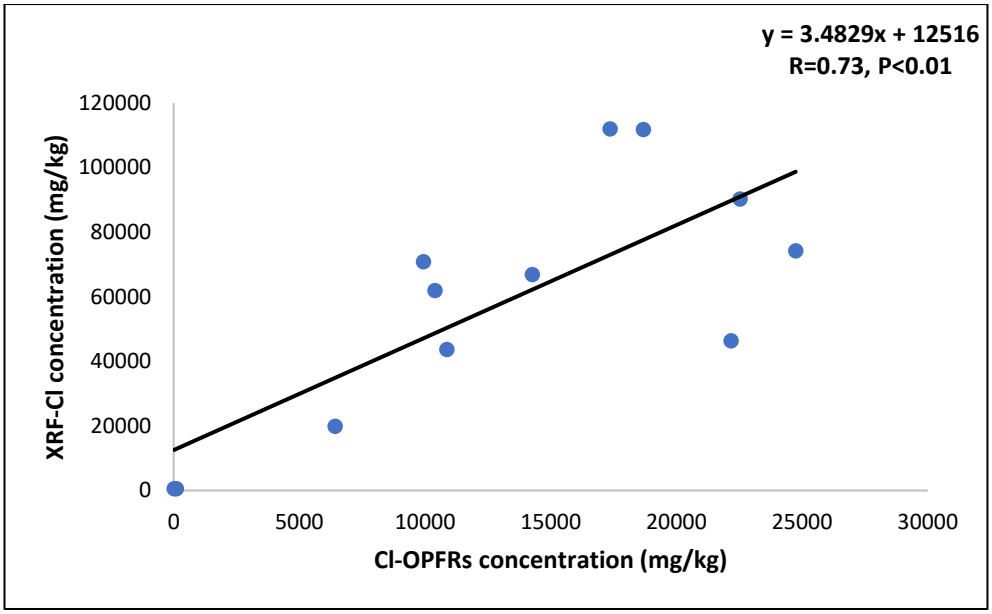


Figure 4. 3: Plot of Cl versus Cl-OPFRs concentrations (mg/kg) for waste furniture foam from Ireland

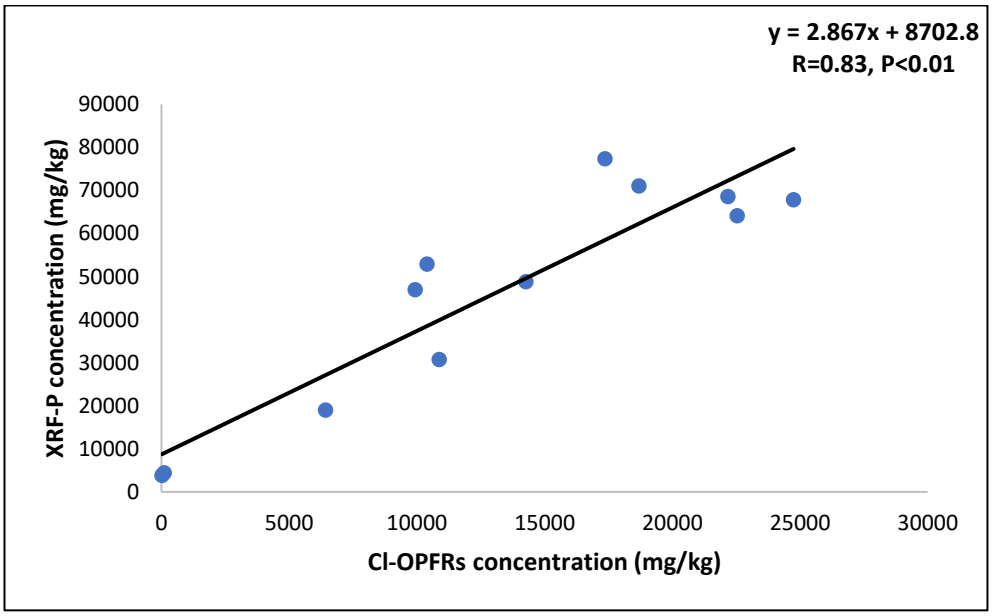


Figure 4. 4: Plot of P versus Cl-OPFRs concentrations (mg/kg) for waste furniture foam from Ireland

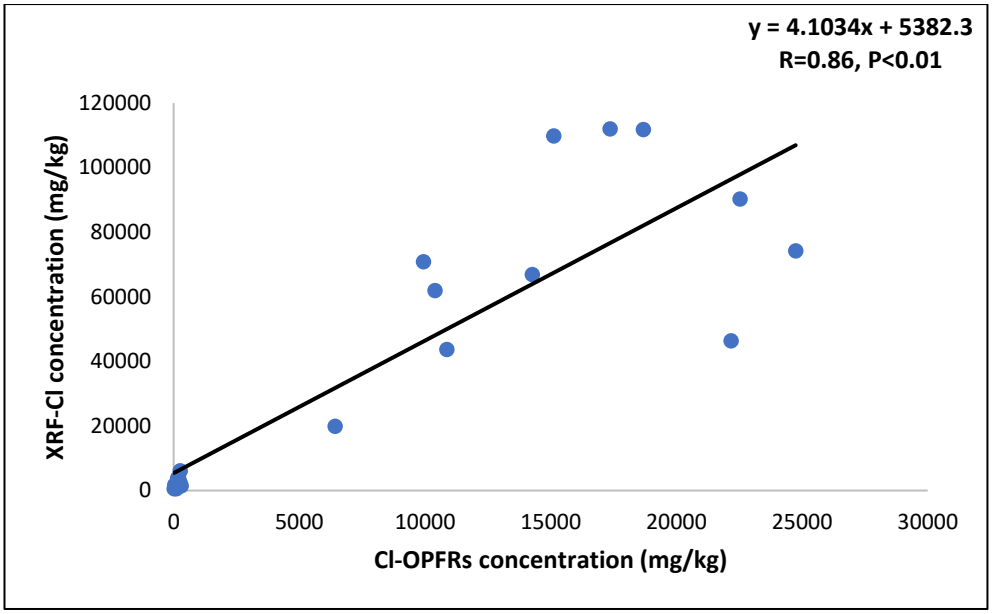


Figure 4. 5: Plot of Cl versus Cl-OPFRs concentrations (mg/kg) for waste furniture and mattress foam from Ireland

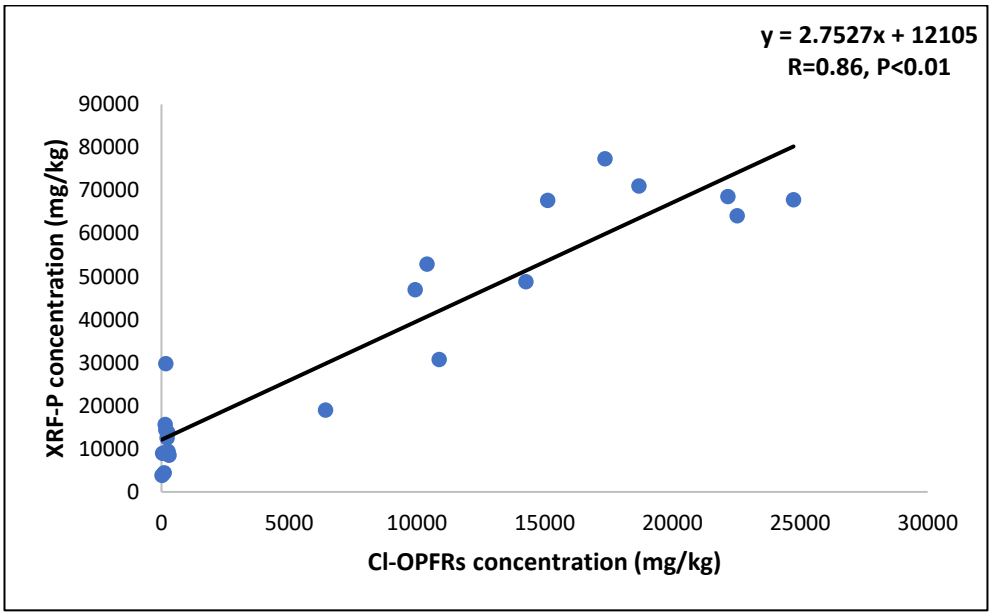


Figure 4. 6: Plot of P versus Cl-OPFRs concentrations (mg/kg) for waste furniture and mattress foam from Ireland

ELV waste showed a statistically significant correlation between Cl and Cl-OPFRs (Figure 4.7) and between P and Cl-OPFRs (Figure 4.8).

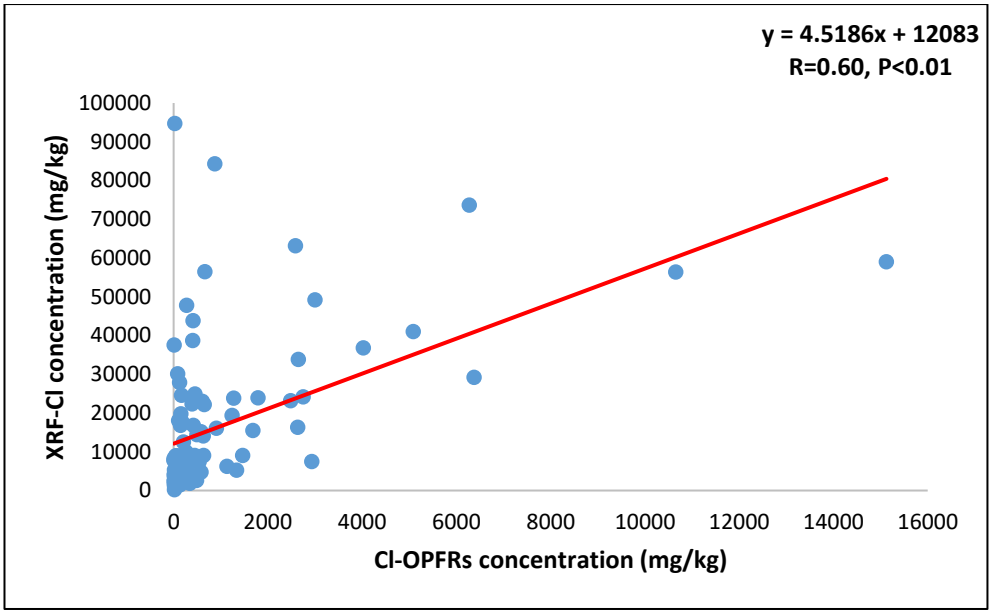


Figure 4. 7: Plot of Cl versus Cl-OPFRs concentrations (mg/kg) for waste ELV from Ireland

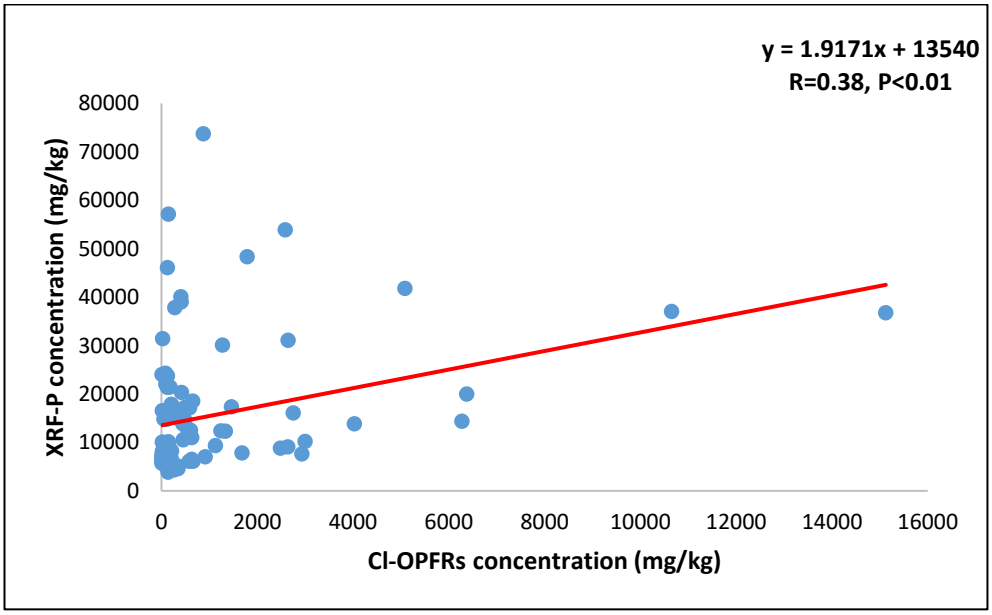


Figure 4. 8: Plot of P versus Cl-OPFRs concentrations (mg/kg) for waste ELV from Ireland

Table 4.4 shows the correlation strength (R value) and p value for childcare articles including car seats and a mix of waste childcare items. A statistically significant correlation was found between Cl and Cl-OPFRs (Figure 4.9) as well as between P and Cl-OPFRs (Figure 4.10).

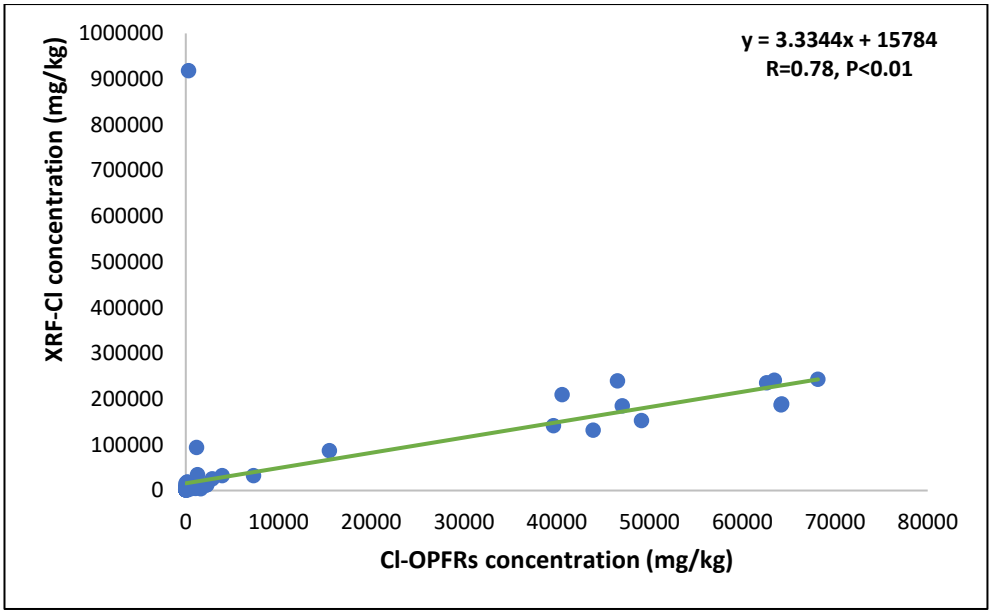


Figure 4. 9: Plot of Cl versus Cl-OPFRs concentrations (mg/kg) for Irish waste childcare articles

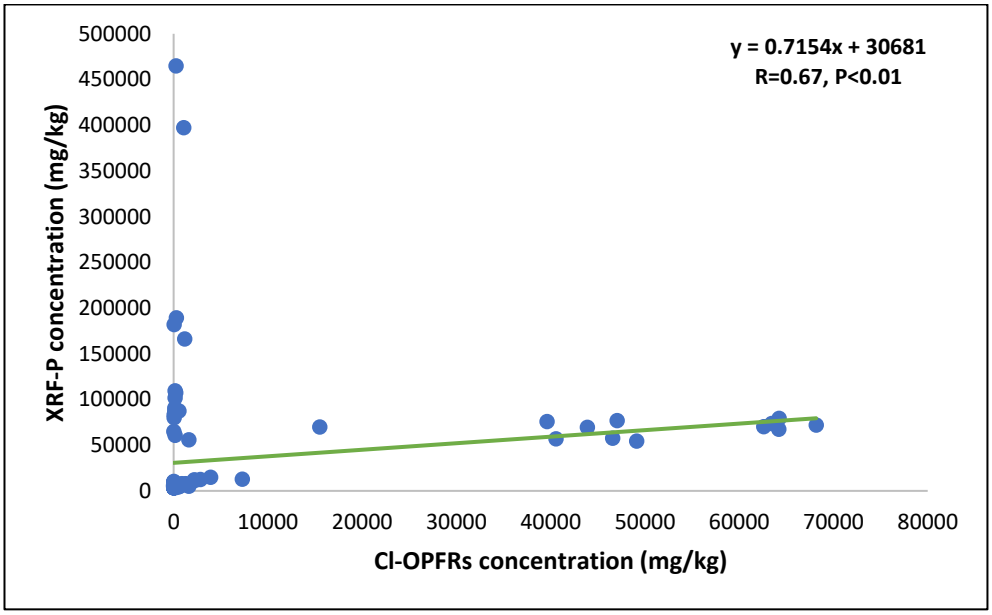


Figure 4. 10: Plot of P versus Cl-OPFR concentrations (mg/kg) for Irish waste childcare articles

A correlation analysis of child car seat data showed significant correlation between Cl and Cl-OPFRs measurements (Figure 4.11) and between P and Cl-OPFRs measurements (Figure 4.12).

For child car seat fabric samples, the correlation between Cl and Cl-OPFRs was significant, and similarly between P and Cl-OPFRs. However, for child car seat foams, a significant correlation between Cl and Cl-OPFRs was observed but no correlation between P and Cl-OPFRs.

According to Table 4.4, there is a statistically significant correlation between Cl and Cl-OPFRs and between P and Cl-OPFRs for childcare items that include play mats, seats, couches, prams, cot mattresses, and pushchairs, but no significant correlation was found for mattress foams.

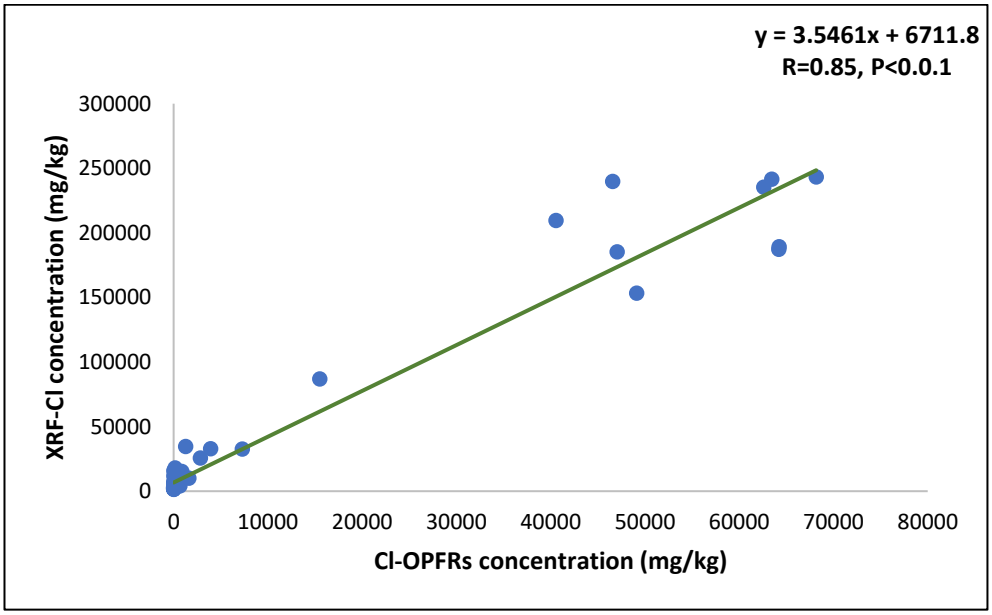


Figure 4. 11: Plot of Cl versus Cl-OPFRs concentrations (mg/kg) for waste child car seat from Ireland

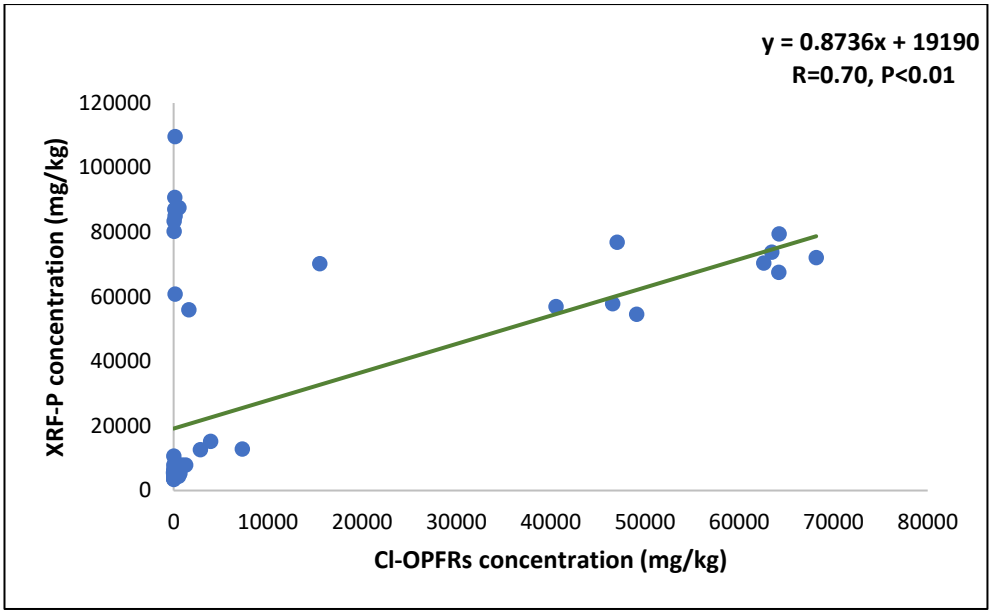


Figure 4. 12: Plot of P versus Cl-OPFRs concentrations (mg/kg) for waste child car seat from Ireland

A significant correlation was observed between Cl and GC/MS Cl concentrations for waste soft furnishings (Figure 4.13), ELV (Figure 4.14), and childcare articles (Figure 4.15). The slope and y-intercept values indicate that other sources of Cl rather than Cl-OPFRs are present in the tested samples.

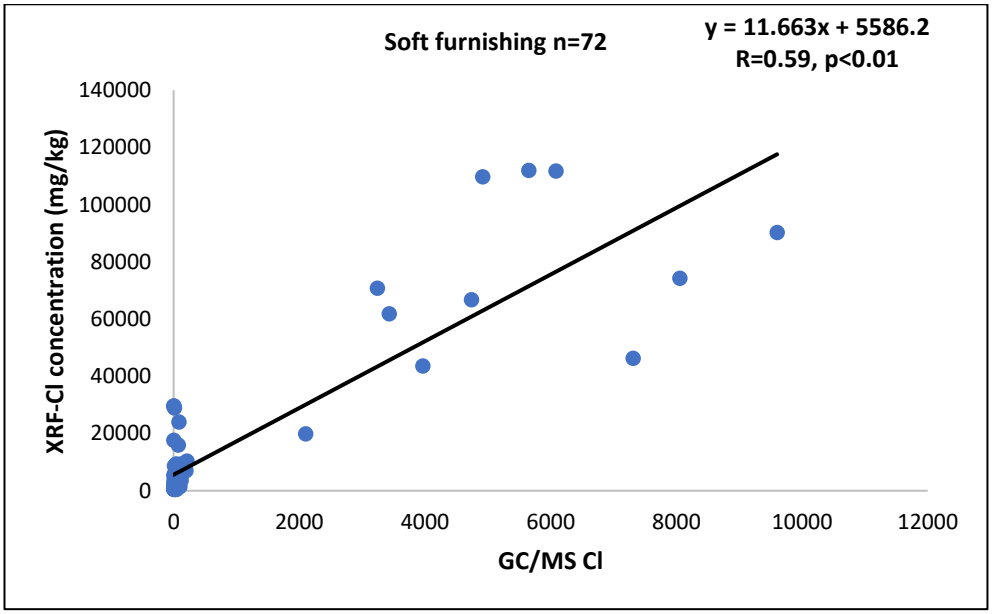


Figure 4. 13: Plot of Cl versus GC/MS Cl concentrations (mg/kg) for waste soft furnishing (n=72) from Ireland

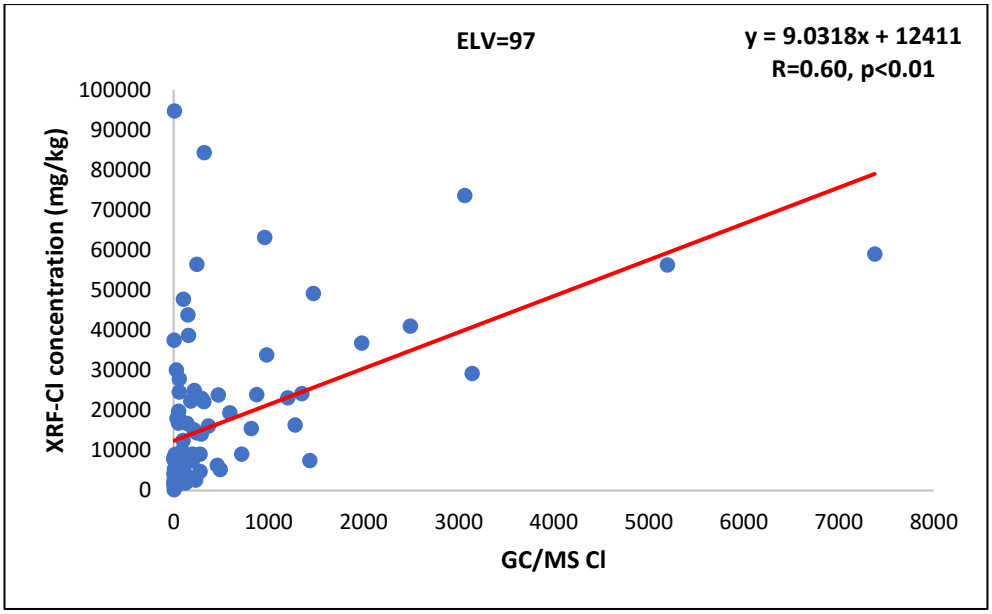


Figure 4. 14: Plot of Cl versus GC/MS Cl concentrations (mg/kg) for waste ELV (n=97) from Ireland

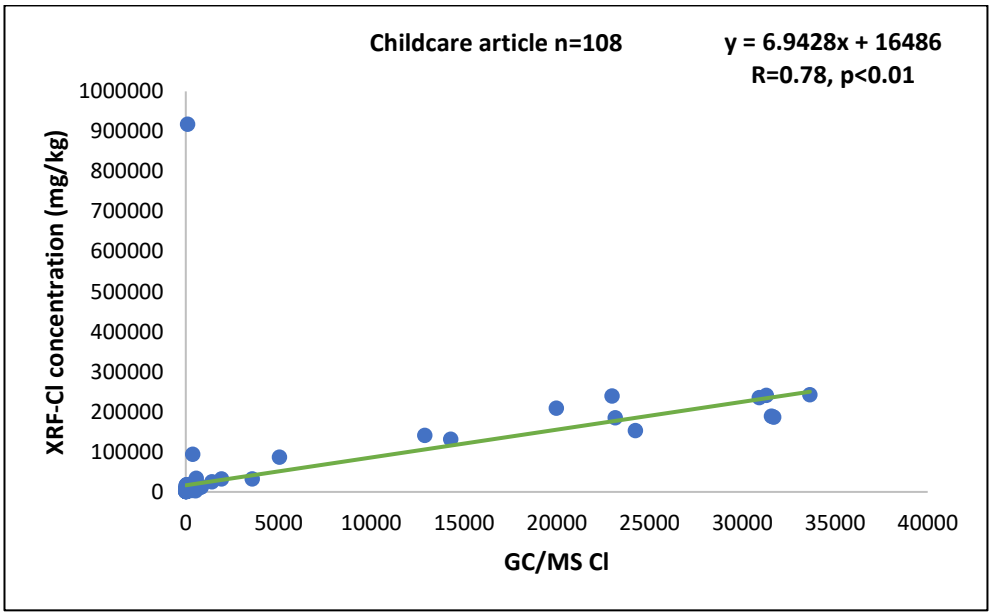


Figure 4. 15: Plot of Cl versus GC/MS Cl concentrations (mg/kg) for waste childcare article (n=108) from Ireland

Although the correlation coefficient appears to be mathematically significant in many instances, the straight line on a scatter plot (represented by a linear equation) shows that the high positive intercept that constantly surpasses 1,000 mg/kg in all correlation values and high slope values (greater than one) are concerning. The high positive

intercept means that the XRF is measuring more than 1,000 mg/g of Cl and P when GC/MS Cl-OPFR value equals 0.

A circumstance like this shows a fundamental issue that prevents the proposed usage of XRF as screening tool for compliance with limit when used as a guideline to decide if a substance or material is safe or appropriate for a given application. Essentially, the continuously high positive intercept and high slope values in all correlation graphs demonstrate that XRF produces false exceedances, in this case. The false exceedances evident in section 4.3.4.4 will be discussed in section 4.3.4.7.

If XRF measurements of Cl were a perfect indicator of, for example, concentrations of TCEP, TDCIPP, and TCIPP, then the intercept would be zero and the slope would be respectively 0.285, 0.430, and 0.327 (106/373, 212/494, and 106/325), which indicates that XRF and the reference method, such as GC/MS, agree and generate consistent measurements, as well as no systematic bias or disparity between the two approaches when analysing the correlation between XRF Cl readings and Cl-OPFRs levels. In other words, XRF would detect and measure Cl-OPFR accurately without causing false exceedances. However, it is crucial to remember that reaching a zero intercept is not always achievable due to a variety of circumstances that can induce uncertainties and restrictions in measurement procedures, such as interferences from other Cl elements or compounds (Miller and Gearhart, 2015; Stapleton et al., 2011) and limitations of the XRF technique itself to light elements like Cl and P (Kajiwara et al., 2011; Petreas et al., 2016).

4.3.4.2. Correlation of quantified Cl-OPFRs and Cl and P concentrations in furniture and childcare articles waste from the UK

Table 4.5 summarises the correlations between concentrations of Cl and P and the concentration of the Cl-OPFR as measured by the GC/MS in furniture and childcare

articles. In general, a significant correlation was found between Cl and concentration of the Cl-OPFR as measured by the GC/MS and P and concentration of the Cl-OPFR as measured by the GC/MS for all UK waste including furniture and childcare items.

Table 4. 5: Overview of the corresponding Spearman correlation (R), P value, slope, and y intercept for furniture and childcare items waste from the UK

	Chlorine				Phosphorus			
Waste category	**R value**	**P value**	**Slope**	**y-intercept**	**R value**	**P value**	**Slope**	**y-intercept**
UK waste n=129	0.70	<0.01	5.4184	47509	0.81	<0.01	1.3414	28262
Furniture waste n=40	0.57	<0.01	2.4587	61240	0.48	<0.01	0.3888	52475
Furniture cover n=33	0.49	<0.01	26.596	34285	0.46	<0.01	5.6804	51542
Furniture foam, lining, wool, and other n=7	0.85	<0.05	2.1259	20371	0.92	<0.01	1.243	13630
Childcare article waste n=89	0.71	<0.01	6.1075	43355	0.71	<0.01	1.4597	18215
Childcare article waste (fabrics) n=57	0.75	<0.01	75.931	17867	0.65	<0.01	18.977	10619
Childcare article waste (foams) n=13	0.92	<0.01	2.9672	36254	0.74	<0.01	0.3349	30718
Childcare article waste (wools and XPSs) n=19	0.23	0.33	-0.1552	3777.5	0.40	0.08	20.343	4045.7

In furniture waste, there was a significant correlation between Cl and Cl-OPFRs and P and Cl-OPFRs. In furniture fabrics, the correlation was statistically significant between both Cl-OPFRs and Cl and P; as well as in furniture foams, linings, wools, and other samples (Table 4.5).

For childcare items, correlation between Cl and Cl-OPFRs and between P and Cl-OPFRs was significant. For all fabrics and foams, XRF Cl and P measurements

showed a statistically significant correlation with GC/MS Cl-OPFRs; however, no significant correlation observed for wools and XPSs waste (Table 4.5).

For furniture, a significant correlation was found between Cl and GC/MS Cl concentrations (R=0.56, P<0.01, Slope =3.7) (Figure 4.16). Similarly, in childcare articles, a significant correlation was found (R=0.71, P<0.01, Slope= 10) between XRF and GC/MS Cl concentrations (Figure 4.17).

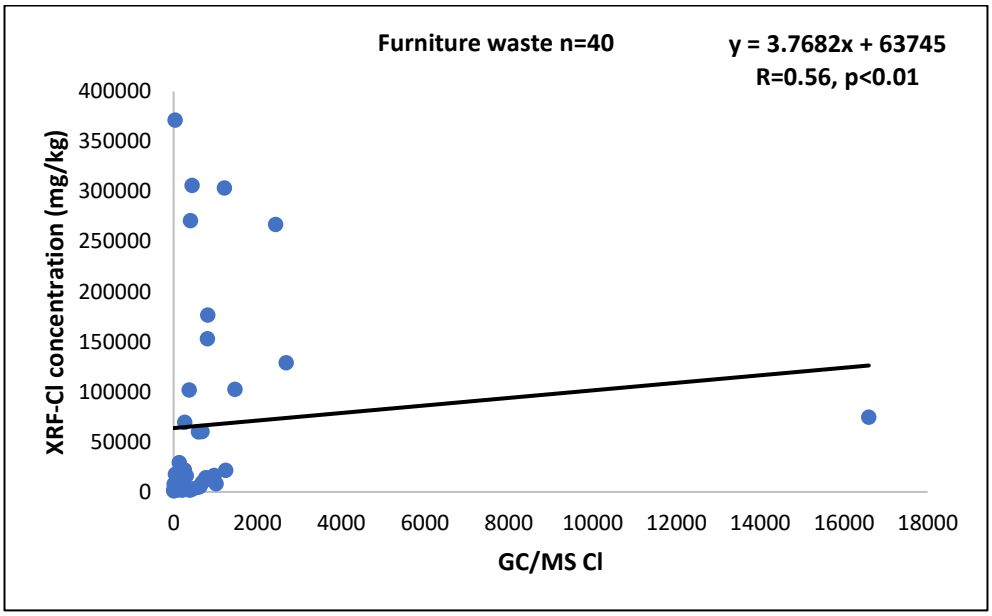


Figure 4. 16: Plot of Cl versus GC/MS Cl concentrations (mg/kg) for UK waste furniture (n=40)

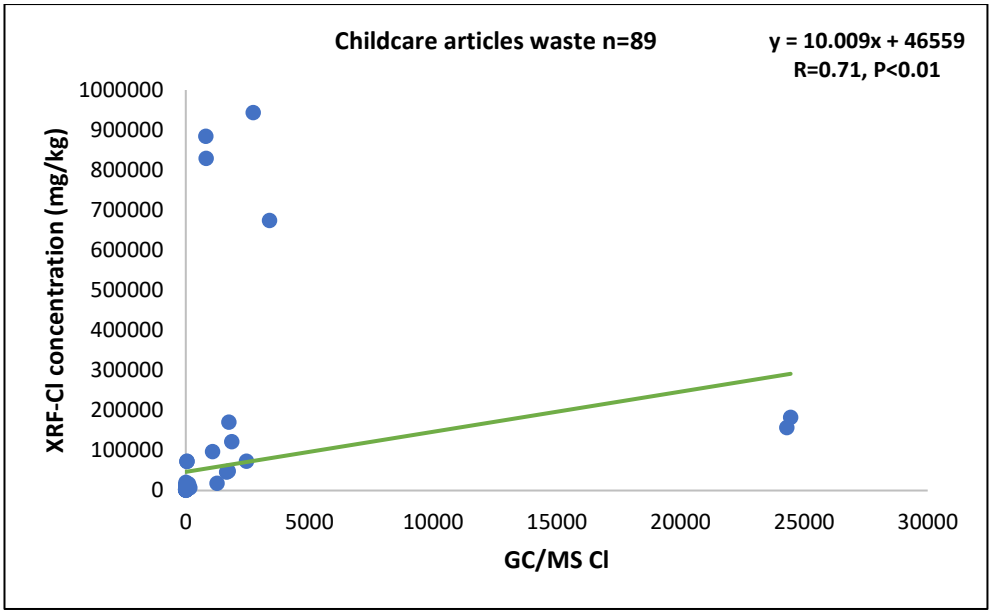


Figure 4. 17: Plot of Cl versus GC/MS Cl concentrations (mg/kg) for UK waste childcare articles (n=89)

The high positive intercept and high slope values in XRF measurements of Cl and P (Table 4.5) indicate a concern about their reliability. The high positive intercept indicates that XRF is measuring more than 1,000 mg/kg of Cl and P when GC/MS Cl-OPFR value equals 0. False exceedances, such as higher Cl levels, are also evident in section 4.3.4.5 and discussed in section 4.3.4.7.

4.3.4.3. Correlation of quantified Cl-OPFRs and Cl and P concentrations in furniture and childcare articles waste from Saudi Arabia

No waste furniture samples from Saudi Arabia contained Cl-OPFRs above 1,000 mg/kg. Moreover, no correlation was observed between concentration of the Cl-OPFR as measured by the GC/MS and XRF Cl ($R=-0.14$, $P>0.30$) and between concentration of the Cl-OPFR as measured by the GC/MS and XRF P ($R=0.09$, $P>0.51$) for furniture waste. Similarly, there was no correlation observed between concentration of the Cl-OPFR as measured by the GC/MS and XRF Cl concentrations ($R=0.16$, $P>0.24$) or between concentration of the Cl-OPFR as measured by the GC/MS and XRF P concentrations ($R= 0.15$, $P>0.26$) for childcare item waste. A

summary of the correlations between XRF Cl and P and concentration of the Cl-OPFR as measured by the GC/MS measurements for furniture and childcare waste from Saudi Arabia is provided in Table 4.6. The high values for the slope and intercept in Table 4.6 suggest that XRF produces false exceedances, which will be reported in section 4.3.4.6 and discussed in section 4.3.4.7.

Table 4. 6: Overview of the corresponding Spearman correlation (R), P value, slope, and y intercept for furniture and childcare item waste from Saudi Arabia

	Chlorine				**Phosphorus**			
Waste category	**R value**	**P value**	**Slope**	**y-intercept**	**R value**	**P value**	**Slope**	**y-intercept**
Saudi Arabia waste n=102	0.17	0.08	41.979	6639.5	0.28	<0.01	9.0118	10592
Furniture waste n=51	-0.14	0.30	-26.404	9766	0.09	0.51	0.8284	8441.6
Furniture fabric n=15	0.03	0.89	-190.32	5497.2	-0.11	0.68	-1363.4	8691.9
Furniture foam n=10	0.38	0.27	-5.2117	5479.1	0.33	0.34	-2.6729	5503.2
Mix products n=17	-0.68	<0.01	-96.111	19852	0.39	0.11	32.687	11698
Childcare articles waste n=51	0.16	0.24	43.616	4373.6	0.15	0.26	8.1111	13030
Car seat (fabrics and foams) n=10	0.47	<0.05	45.823	7350.9	0.61	0.06	10.239	6586.4
Car seat (fabrics) n=7	0.64	0.11	76.803	6405.2	0.78	<0.05	14.906	6949.5
Car seat (foams) n=3	1	<0.01	12.995	9045.5	1	<0.01	5.64	5307
Mix of childcare items n=39	-0.01	0.92	-2.3673	5932.7	0.01	0.93	7.6302	13797

Comparing Cl and P measurements with Cl-OPFRs from furniture (Figure 4.18) and from childcare articles (Figure 4.19) suggest the presence of other sources of Cl and P rather than Cl-OPFRs.

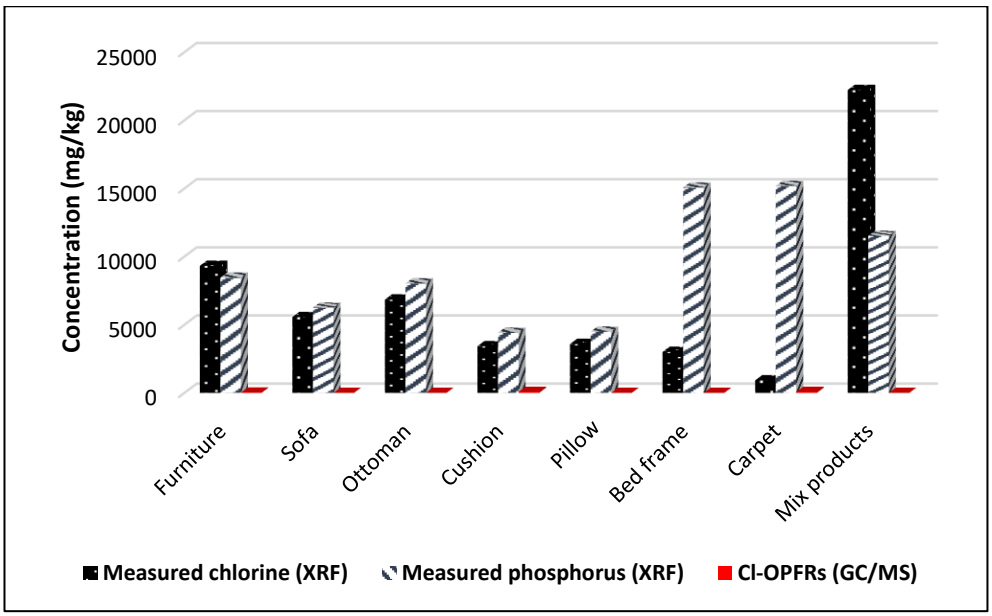


Figure 4. 18: Chlorine and phosphorus content in waste furniture from Saudi Arabia (measured by XRF) and Cl-OPFRs content (measured by GC/MS)

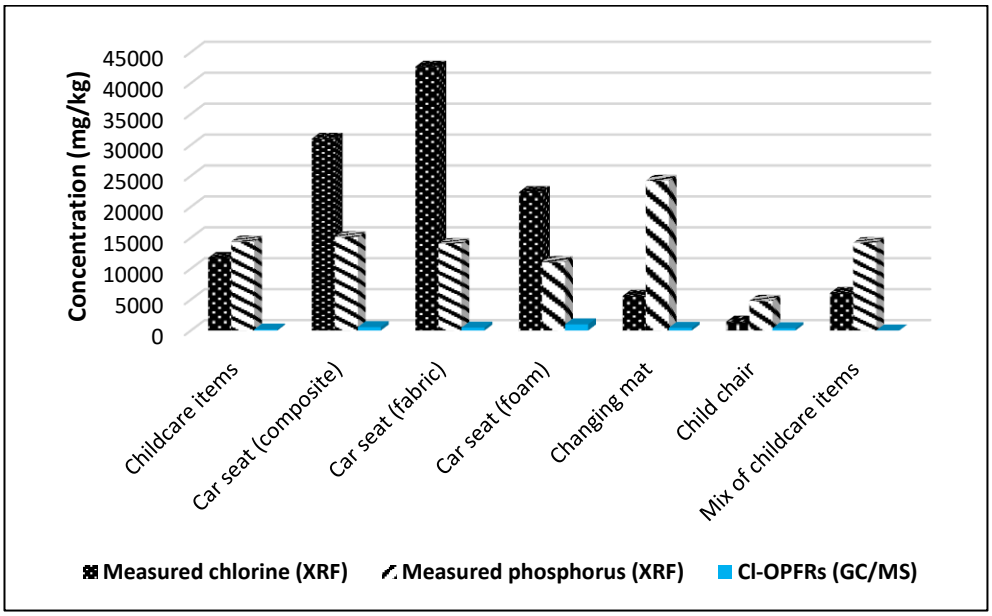


Figure 4. 19: Chlorine and phosphorus content in waste childcare articles from Saudi Arabia (measured by XRF) and Cl-OPFRs content (measured by GC/MS)

4.3.4.4. Proportion of samples from Ireland containing Cl-OPFRs >1,000 mg/kg and correctly identified by XRF Cl

The percentage of Irish soft furnishing and ELV waste where ∑Cl-OPFR concentrations exceeded 1,000 mg/kg were 15 % for soft furnishing (as indicated in section 3.2.1.1) and 21 % for ELV (as indicated in section 3.2.3) waste. For childcare articles, 20 % contained Cl-OPFRs at levels exceeding 1,000 mg/kg as mentioned in section 3.2.2.1. Overall, out of 277 Irish waste (soft furnishing, ELV and childcare articles), 53 samples (19 %) contained Cl-OPFRs >1,000 mg/kg.

In contrast, Cl-OPFRs concentrations did not exceed 1,000 mg/kg in any of the Irish samples of curtains, carpets, mattresses, and furniture upholsteries, ELV paddings and floor mats, baby play mats, prams, mattress foams, and pushchairs.

Table 4.7 shows the number of samples identified as exceeding 1,000 mg/kg for the ∑Cl-OPFRs alongside the proportion of the same samples that XRF Cl falsely indicated to exceed 1,000 mg/kg for each waste category in Ireland.

Overall,

- 85 % (61 samples) of the soft furnishing samples (n=72) were false exceedances, while 15 % (11 samples) were correctly identified by XRF as containing Cl-OPFRs >1,000 mg/kg.
- For ELV waste, 78 % (76 of 97) were false exceedances, while 21 % (20 samples) were correctly identified by XRF Cl as containing Cl-OPFRs >1,000 mg/kg.
- 80 % (86 of 108) of waste childcare articles were found to be false exceedances, with the remaining 20 % (22 samples) correctly identified by XRF Cl to contain >1,000 mg/kg Cl-OPFRs.

- No false negatives were reported for waste from Ireland.

In summary, it seems that XRF Cl is a poor predictor of whether Cl-OPFR concentrations exceed 1,000 mg/kg due to a high incidence of false exceedances.

Table 4. 7: The number of samples correctly identified by XRF to contain > 1,000 mg/kg ∑Cl-OPFRs and false exceedances for each waste category in Ireland

Waste category	Total number of samples	Number of samples correctly identified as containing > 1,000 mg/kg Cl-OPFRs	Number of samples identified as false exceedances
Furniture waste			
Curtain	7	0	7
Carpet	22	0	22
Mattress upholstery and foam	16	1	15
Furniture upholstery and foam	27	10	17
ELV waste			
ELV fabrics and foams	69	18	51
ELV padding, floor mat and roof trim	28	2	25
Childcare items waste			
Car seat	62	15	47
Play mat, seat, couch, mat foam, cot mat, and pushchair	46	7	39

4.3.4.5. Proportion of samples from the UK containing Cl-OPFRs >1,000 mg/kg and correctly identified by XRF Cl

The percentage of furniture and childcare article waste containing Cl-OPFR concentrations > 1,000 mg/kg were respectively 63 % and 15 % as mentioned in section 3.2.1.2 and 3.2.2.2.

There were no Cl-OPFRs concentrations exceeding 1,000 mg/kg in fabrics and wool from sofas, chairs, and armchairs as well as in childcare items like bed, pushchair, feeding seat, car seat and pushchair liner, soft play foam, baby walker, play mat, sleeping bag, car seat head holder, carrier, and Moses' basket. The number of samples identified as exceeding 1,000 mg/kg for the total of ∑Cl-OPFRs as well as false exceedances are presented in Table 4.8 for each waste category from the UK.

Overall,

- For furniture, 19 of 40 samples (47 %) were identified as false exceedances. The remaining 21 samples (53 %) were correctly identified by XRF Cl as containing >1,000 mg/kg Cl-OPFRs.
- For childcare items, 76 of 89 samples (85 %) were identified as false exceedances. The remaining 13 of 89 samples (15 %) were correctly identified by XRF Cl as containing >1,000 mg/kg Cl-OPFRs.
- None of waste from the UK was reported as a false negative.

The high incidence of false exceedances suggests that XRF Cl is a poor predictor of Cl-OPFR concentrations exceeding 1,000 mg/kg.

Table 4. 8: The number of samples correctly identified by XRF to contain > 1,000 mg/kg ∑Cl-OPFRs and false exceedances for each waste category in the UK

Waste category	Total number of	Number of samples	Number of samples

	samples	correctly identified as containing > 1,000 mg/kg Cl-OPFRs	identified as false exceedances
Furniture waste			
Sofa	24	12	12
Armchair	8	4	4
Chair	6	3	3
Other	2	2	0
Childcare items waste			
Mattress, pushchair, booster seat, and changing mat	26	13	13
Bed, feeding seat, liner for car seat and pushchair, baby walker, play mat, sleeping bag, car seat holder, carriers, and Moses' basket	63	0	63

4.3.4.6. Proportion of samples from Saudi Arabia containing Cl-OPFRs >1,000 mg/kg and correctly identified by XRF Cl

According to our results in section 3.2.1.3 and 3.2.2.3, 0 % of furniture waste and 2 % of childcare article waste contained concentrations of Cl-OPFR exceeding 1,000 mg/kg. Comparing Cl and P measurements with those of Cl-OPFRs in furniture and childcare items revealed that:

- 100 % of furniture waste (51 samples) were identified as false exceedances.

- 94 % of childcare item waste articles (51 samples) were identified as false exceedances, while only 2 samples (4 % - one fabric and one car seat foam) were correctly identified by XRF Cl as exceeding the limit of 1,000 mg/kg Cl-OPFRs.
- No false negatives were reported.

Based on the high incidence of false exceedances, XRF Cl is not a reliable method of predicting Cl-OPFR concentrations over 1,000 mg/kg.

4.3.4.7 Applicability of XRF as screening technique and possible reasons for false exceedances

Even when our analyses showed statistically significant correlations between Cl and P and Cl-OPFRs measurements for some waste from Ireland and the UK (not in Saudi Arabia), the false exceedances and consistent overestimation of Cl and P levels were issues found that indicated XRF is not a reliable screening measure for Cl-OPFR concentrations > 1,000 mg/kg.

In addition, for chlorine, the elevated values of the y-intercept (Table 4.4, Table 4.5, and Table 4.6) obtained for correlations between Cl and Cl-OPFRs, indicate that Cl measurements are impacted by additional non-Cl-OPFRs sources of Cl in many samples.

Possible explanations for these issues are that:

- There are other flame retardants including Cl and P that we did not measure in our study, like V6 (2,2-bis(chloromethyl)propane-1,3-diyl-tetrakis(2-chloroethyl) bis(phosphate)), which has been identified in items like furniture and childcare products in the U.S.A (Stapleton et al., 2012; Bergen and Stone,

2021; Cooper et al., 2016). In the automotive industry, V6 is mainly used as a flame retardant for polyurethane foams (SCHER, 2007).

- Toluene diisocyanate, a reagent used to make PUF, may contain chlorinated impurities that can cause high Cl concentrations (Stapleton et al., 2011; Strobl et al., 2021).
- Another chlorine source is PVC which has been shown previously by XRF to lead to Cl concentrations of up to 150,000 mg/kg (Turner, 2018). According to many studies, PVC is present in a variety of consumer goods like furniture fabrics, PUF, carpets, curtains, and automotive components (Chivas et al., 2009; Lounis, et al., 2019; Haines et al., 2020; Kumar et al., 2021; Strobl et al., 2021; Yu et al., 2016; Begum et al., 2020; Bertham et al., 2021), with PVC suggested to be used as a flame retardant in some instances (Chivas et al., 2009**;** Khan and Malvi, 2016; Begum et al., 2020).

It appears plausible that PVC is responsible for at least some of the very high Cl measurements reported here in curtains, carpets, upholsteries, and ELV (Table 4.1 to 4.3). For example, the highest Cl reading (8,685 mg/kg) observed for curtain waste from Ireland was in a sample of a back cover of curtain. It has been reported that polyester fabric curtains coated with PVC may be used as acoustic window treatments to reduce outdoor noise and light (Kumar et al., 2021; Bulut et al., 2022).

In similar fashion, XRF Cl readings (29,024, 17,629 and 5,329 mg/kg) were high in samples of carpet backing that potentially could be made of PVC (Haines et al., 2020; Sotayo et al., 2016; Jaiswal et al., 2022).

In upholstered furniture, some samples contain PUF with a covering based on fabric coated with PVC (Lounis, et al., 2019). In addition, the leatherette material used for furniture covers is known to be made of PVC and polyurethane (Zou et al., 2021).

In automobile industries, high performing materials are needed, which protect the occupants, reduce cost, produce cleaner, more energy efficient vehicles, and are durable. PVC is widely used in automotive components such as interior trims (like sun visors), coated fabrics (seat covering and upholstery), headlining, floor coverings and other parts (Yu et al., 2016). It is also applied in the fabrication of internal linings, bottom flooring protection, and vehicle coatings (Begum et al., 2020). Indeed, according to a study of automotive plastics aimed to develop a more circular economy, PVC (12.2 %) was one of the most common polymers found in vehicles (Bertham et al., 2021). This could explain the high Cl readings observed in our ELV waste from Ireland due to the presence of PVC.

It's worth noting that chlorine compounds sometimes are not applied directly in furniture manufacturing, but they are used in several stages of making polyester fibers that used in upholstery fabric and foams eventually. This may be a potential source of non-Cl-OPFR chlorine in upholstered furniture. Terephthaloyl chloride (TCl), for example, is an applied chlorine containing compound in the polymerization process to produce polyester fabrics for upholstery (Kent, 2015) and to produce foams when reacting with toluene diisocyanate (Morsi and Mohamed, 2017). In addition, titanium tetrachloride that often used as a catalyst during the polymerization reaction which help polyester fibre achieve the required molecular weight and polymer structure (Montazer and Pakdel, 2011). Polyester fabrics also can be treated with antimicrobial agents including such as sodium hypochlorite to suppress the growth of bacteria and fungi, making the fabrics resistant to odour-causing germs, improving their hygienic

features, and giving polyester fabrics lighter or white appearance (Jain et al., 2014; Mao and Russell, 2015). Overall, adding chlorine compounds to polyester fabric and foams gives them the needed strength and antibacterial resistance; nevertheless, during XRF screening items for Cl-OPFRs, interference with the measurements from other Cl sources can lead to higher XRF-Cl readings. The accuracy of XRF measurements can also be questioned when events such as the screening of PVC fabric result in data that exceed the predicted values. In this case, the XRF measurement of 920,000 mg/kg for Cl concentration in the PVC fabric of pushchair from Ireland is greater than the typical Cl content observed in PVC, which is around 670,000 mg/kg (Walsh, 2011). This difference raises questions regarding the XRF accuracy and reliability in determining the chemical composition of PVC fabric. The measurement may indicate Cl presence but not accurately reflect its content. This could be owing to an XRF instrument constraint; while its examination is rapid and non-destructive, it does not always produce precise quantitative results (Stapleton et al., 2011; Petreas et al., 2016).

For phosphorus, there appears to be a complete lack of correlation and persistent overestimation of phosphorus in our data, as well as no real association with anticipated mass balance with Cl that was mentioned in Section 1.3 of Chapter 1 about the physicochemical properties of Cl-OPFRs. To illustrate, the mass balance of phosphorus to chlorine in TCEP, TDCIPP and TCIPP can be represented by their chemical formulas of $C_6H_{12}Cl_3O_4P$, $C_9H_{15}Cl_6O_4P$, and $C_9H_{18}Cl_3O_4P$, respectively (ECHA, 2018a). There is one phosphorus atom (P) present that is covalently bonded to three chlorine atoms (Cl) in TCEP and TCIPP, and to six chlorine atoms in TDCIPP. Therefore, the ratio of phosphorus to chlorine in TCEP and TCIPP is 1:3 and in TDCIPP is 1:6. The atomic number of the element and the energy of the X-rays

released are two criteria that affect how sensitive an element is to XRF (Kikongi et al., 2017; Ravansari et al., 2020). Since lighter elements like phosphorus have fewer atoms (atomic number 15) than heavier ones, emitting X-rays with lower energy. When light elements emit low-energy X-rays, the sample material can absorb or scatter them more readily as well as possess peaks closer to each other (due to an overlapped spectrum), which reduce the intensity of the X-rays that reach the detector (Lim, 2013; Ravansari et al., 2020). As a result, the detection and quantification of light elements like phosphorus become less accurate and more challenging compared to heavier elements. The primary cause of this is the intrinsic limitations of the XRF technique, especially when it comes to detecting light elements like phosphorus (P) that falls on the borderline between light and heavy elements, making it challenging or impossible to accurately detect with XRF (U.S. EPA, 2007). In general, XRF is capable of detecting and quantifying atoms with atomic numbers of 16 or higher (U.S. EPA, 2007) that might explain the uncertainty and overestimation observed for XRF phosphorus P measurements.

This drawback has been emphasised in previous studies, highlighting the fact that XRF is neither a reliable nor preferred screening tool for light elements like phosphorus (Kajiwara et al., 2011; Petreas et al., 2016; Young et al., 2021). To overcome this limitation, XRF was merely employed as a direct qualitative determination technique to screen the presence of phosphorus in consumer products (Kajiwara et al., 2011; Petreas et al. 2016). In addition, an alternative analytical technique with higher sensitivity such as Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES) was used to identify and measure the actual concentration of phosphorus (Petreas et al. 2016).

Perhaps the need for quick and reliable technique to analyse light elements such as phosphorus for environmental application was a key driver for the development of new XRF analysers that can detected phosphorus at lower limits of detection. For example, new XRF instruments such as Niton XL^{3t} $GOLDD^{+}$ and the Niton XL2 GOLDD analysers (Thermo Scientific Niton, 2016) are capable of detecting phosphorus at low detection limits of 250 mg/kg and 350 mg/kg, respectively (Thermo Scientific Niton, 2010a; Thermo Scientific Niton, 2010b) in only one operational mining mode. However, our data and those reported by Young et al. (2021) showed the lack of accuracy of the phosphorus measurements when employing the same XRF instrument model as used in our study (Niton XL^{3t} $GOLDD^{+}$) possibly due to instrument constraints, leads to the conclusion that phosphorus is not a reliable indicator of Cl-OPFRs when screening consumer products.

Although XRF-measured phosphorus (P) as a surrogate for Cl-OPFRs has not been as studied or well-established as bromine, those few studies that have been conducted, found that XRF measurements of phosphorus were not reliable and only used XRF as qualitative determination technique even when XRF instrument with more advanced features was employed, and used alternative techniques when precise quantification of phosphorus was required (Kajiwara et al., 2011; Petreas et al., 2016; Young et al., 2021).

Overall, despite the fact that significant mathematical correlations were observed in some instances between XRF Cl and P and GC/MS Cl-OPFRs measurements for certain waste categories in Ireland and the UK, XRF provides very high Cl levels in waste items with low concentrations of Cl-OPFRs (demonstrated by the high y-axis intercept) as well as consistently overestimating P in all samples and has no genuine connection with the predicted mass balance for Cl. This might occur because of the

presence of other sources of Cl in the examined samples rather than Cl-OPFRs and the inherent limitations of XRF when screening light elements like P. The high false exceedance rate we observed indicated that XRF is not a suitable technique for screening waste for compliance with limits on Cl-OPFRs.

4.4. Conclusions

To test the hypothesis that XRF can be an effective tool to screen wastes exceeding anticipated LPCL limit of 1,000 mg/kg Cl-OPFRs, 53 samples (19 %) of Irish waste and 34 sample from the UK (26 %) were correctly identified by XRF Cl as containing >1,000 mg/kg Cl-OPFRs. However, XRF generates false exceedance in 223 samples (81 %) from Ireland and in 95 sample (74 %) from the UK. Among 102 samples from waste furniture and childcare items from Saudi Arabia, 2 % (n=2) were found to exceed the LPCL, while 97 % were identified as false exceedances. Correlation between XRF measurements of Cl and P and GC/MS ∑Cl-OPFRs was absent for waste from Saudi Arabia.

Our data demonstrate a significant correlation between XRF Cl and ∑Cl-OPFR concentrations in several groupings of waste samples, with P also exhibiting a correlation in some situations. However, the high y-intercept of such correlations suggests that many samples have Cl sources other than Cl-OPFRs and overestimation of P measurements is potentially related to the intrinsic limitation of XRF for such light elements. This strongly implies that XRF is not a reliable instrument for for predicting Cl-OPFR concentrations exceeding 1,000 mg/kg. This conclusion is further supported by the high rate of false exceedances reported in this study. Based on these data, it is concluded that XRF cannot be utilised to screen waste for compliance with any future limit on Cl-OPFR concentrations.

Chapter 5: Assessment of dermal exposure to Cl-OPFRs via contact with fabrics associated with furniture, childcare articles, and vehicles from Ireland and the UK

5.1 Introduction

This chapter uses data on Cl-OPFR concentrations in fabric samples to generate estimates of human exposure via dermal uptake through contact with such fabrics. This chapter tests the hypothesis that the high concentrations of Cl-OPFRs in furniture and childcare items may lead to substantial exposure via the dermal pathway. Exposure estimates are subsequently compared with health-based limit values (HBLVs) (Table 5.5) to determine if they pose a health risk.

We assume that such exposure will be insignificant for fabrics taken from articles where Cl-OPFRs have not been used. Consequently, our exposure estimates are based only on fabric samples for which the concentration in a given sample of one or more of TCEP, TDCIPP, and TCIPP exceeds 1,000 mg/kg; a concentration assumed to be an indicator of Cl-OPFR use.

Dermal exposure was estimated using the following equation.

$$\mathbf{DED}_{\mathbf{dermal\ uptake}} = \frac{C \times BSA \times FA \times IEF}{BW} \qquad \text{(U.S. EPA, 2011)}$$

where $DED_{dermal\ uptake}$ = daily exposure dose (ng/kg bw/day) through dermal uptake, C = Cl-OPFR (TCEP, TDCIPP and TCIPP) concentration in fabric (ng/cm^2), BSA = body surface area exposed (cm^2) (outdoor and indoor respectively was 876 and 1370 cm^2 for toddler, and 2971 and 4351 cm^2 for adult) (Table 5.1), FA = fraction absorbed by the skin (unitless) (Abdallah et al., 2016), IEF = indoor exposure fraction (hours spent over a day in contact with fabric) (unitless), BW = body weight (kg).

Exposure via dermal uptake was evaluated for two groups: a) adults, and b) toddler in Ireland and the UK. The focus of calculating estimation was only on these two countries because fabrics containing concentrations of Cl-OPFRs at levels exceeding 1,000 mg/kg were only observed in:

- Fabrics of vehicles and childcare articles from Ireland
- Fabrics of furniture and childcare articles from the UK.

In contrast, only one sample (from child car seat fabric) from Saudi Arabia contained >1,000 mg/kg of Cl-OPFRs; therefore, exposure was not estimated for Saudi residents.

The exposure parameters used in the dermal exposure equation for adults and children were acquired from the U.S. EPA exposure factors manual (Table 5.1) (U.S. EPA, 2011). The following listed scenarios were used to estimate adults and toddlers' dermal exposure:

A. **Vehicle**: adults back of forearms, palms of hands, half the back of thighs and legs were exposed to fabrics of vehicles. Toddlers were excluded from this scenario since they would be sitting in vehicles in booster seats and car seats and would not be in close contact with the fabric of the vehicle.
B. **Furniture**: both adults and toddlers back of forearms, palms of hands, half the back of thighs and legs, and feet were exposed to fabrics of furniture.
C. **Childcare items**: toddlers back of forearms, palms of hands, half the back of thighs and legs were exposed to fabrics of childcare items used in cars or outdoors (feet were not exposed as we assume the toddler is wearing shoes), while feet were included for items used at home like changing mat, seats, and couches as toddlers might not be wearing socks (bare feet). Since childcare

items are primarily intended for child usage, adults were excluded from this scenario because any adult contact with the fabric of these items would be unintentional.

Table 5. 1: Human dermal exposure parameters applied in the current study

Surface area (cm^2) *	**Adult**	**Toddler**
Back/forearms	730	212.8
Palms of the hands	535	182.4
Back/half-thighs	1028.25	285
Back/ half lower legs	677.5	195.7
Feet	1380	494
Body Weight (kg)*	70	15
Exposure time (h) per day	1 hour at home and 1 hour in car and outdoors	

*Body weight (BW) and surface area (SA) obtained from U.S. EPA's Exposure Factors Handbook (U.S. EPA, 2011).

5.2 Results

Estimated human dermal exposure (ng/kg bw/day) to TCEP, TCIPP & TDCIPP in fabrics is illustrated in Figure 5.1 for adults and Figure 5.2 for toddlers. Generally, average estimated toddlers' daily exposure to Cl-OPFRs through dermal uptake in the UK (via contact furniture fabrics) exceeded that for adults likely due to toddlers' higher body surface area relative to body weight. In addition, our estimates indicate that adults and toddlers were exposed to higher doses of TCEP and TCIPP in the UK but to lower levels of TDCIPP than in Ireland. Dermal exposure to TCEP in Ireland was principally via contact with vehicle fabrics and via furniture fabrics in the UK. Exposure to both TDCIPP and TCIPP were primarily through contact with childcare

articles from the UK and Ireland, and to TDCIPP via contact with vehicle fabrics in Ireland, whereas exposure to TCIPP was related to UK furniture fabrics.

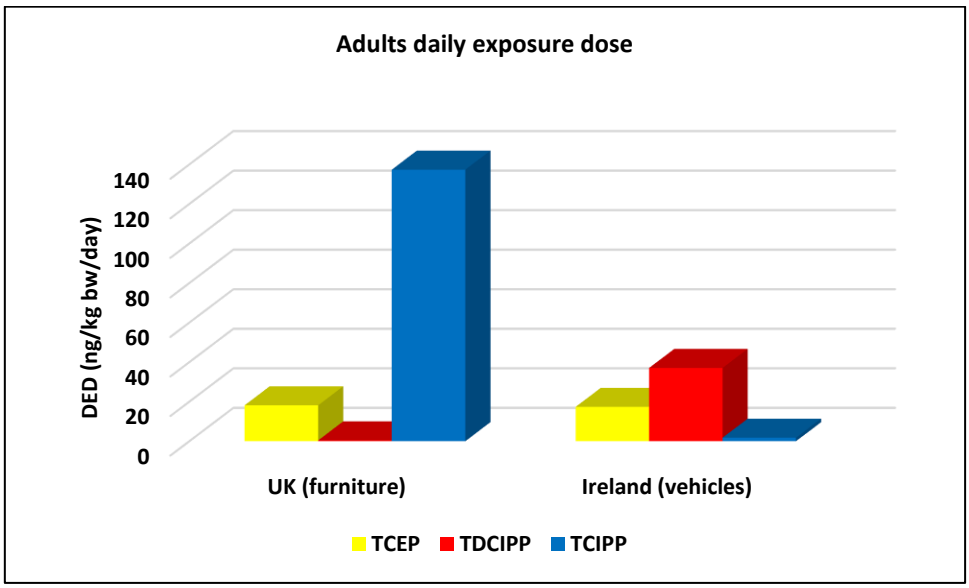


Figure 5. 1: Average estimated daily dermal uptake (ng/kg bw/day) of Cl-OPFRs for adults resulting from contact with fabrics from vehicles in Ireland and furniture in the UK

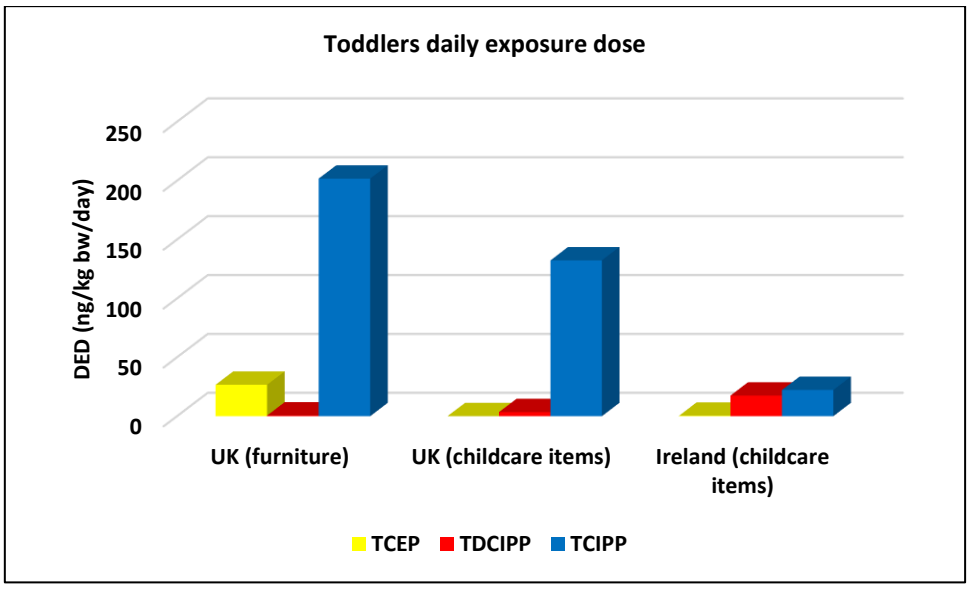


Figure 5. 2: Average estimated daily dermal uptake (ng/kg bw/day) of Cl-OPFRs for toddlers resulting from contact with fabrics from furniture in the UK and childcare items in the UK and Ireland

5.2.1 Human exposure to Cl-OPFR via dermal uptake in the UK and Ireland

To determine the likely range of exposure to TCEP, TDCIPP, and TCIPP through dermal uptake, three scenarios were evaluated separately. The three scenarios were low-end, median, and high-end, where 5th, median, and 95th percentile concentrations respectively were used in these calculations (in addition to the average scenario exposures shown in Figs 5.1 and 5.2). The resultant daily exposure estimates in ng/kg bw/day for TCEP, TDCIPP, and TCIPP are provided in Table 5.2 for both UK and Irish adults and toddlers via dermal uptake.

Adults are exposed to similar doses of TCEP through dermal contact with fabrics of vehicles and furniture in the UK and Ireland. For TDCIPP, adults are estimated to be exposed to higher doses in Ireland through contacting vehicle fabrics than in the UK. However, adults in the UK are exposed to higher levels of TCIPP through contacting furniture fabrics than in Ireland. Toddlers in Ireland are exposed to higher levels of TCEP and TDCIPP through contact fabrics of childcare items than those in the UK, but to higher TCIPP doses when contacting fabrics of furniture and childcare items in the UK.

Table 5. 2: Estimated adult and toddler daily exposure (ng/kg bw/day) to target Cl-OPFRs via dermal uptake through contact fabrics of vehicles, furniture, and childcare item in Ireland and the UK

Compound	**Adult**			**Toddler**		
	Exposure scenario			**Exposure scenario**		
	Low-end	**Median**	**High-end**	**Low-end**	**Median**	**High-end**
UK (furniture)						
TCEP	0.00066	0.036	62.13	0.00097	0.053	91.29
TDCIPP	0.00022	0.14	2.19	0.00036	0.22	3.23
TCIPP	53.54	106.15	290.97	78.67	155.98	427.56

Ireland (vehicles)						
TCEP	0.065	0.50	90.75	-	-	-
TDCIPP	4.20	31.31	82.66	-	-	-
TCIPP	0.47	0.84	6.35	-	-	-
UK (childcare items)						
TCEP	-	-	-	0.0002	0.00043	0.013
TDCIPP	-	-	-	0.00013	0.00023	17.23
TCIPP	-	-	-	23.15	91.15	288.79
Ireland (childcare items)						
TCEP	-	-	-	0.024	0.035	1.80
TDCIPP	-	-	-	0.092	8.12	50.04
TCIPP	-	-	-	0.96	21.40	47.76

5.2.1.1 Comparison of adult exposure to Cl-OPFR via dermal uptake in the UK and Ireland with other routes of exposures in different countries

First, focusing on dermal uptake via direct contact with fabrics of furniture, we compared our estimates to those reported in other studies in a similar context. To illustrate, we compared our median estimates of UK adult dermal exposure with those reported in previous studies in the UK, U.S.A, and China. Our median daily estimations for TCEP, TDCIPP, and TCIPP were 0.036, 0.14, and 106.15 ng/kg bw/day, respectively, where TCIPP was significantly higher than those estimations for contacting fabrics of sofa in the UK and chair cushions in the U.S.A., as well as for dermal absorption from indoor dust in China (Abdallah and Harrad, 2022; Black et al., 2019; Cao et al., 2019). The average estimation of adult exposure to TCEP, TDCIPP, and TCIPP in the UK was respectively 1.55, 2.65, and 18.6 ng/kg bw/day (Abdallah and Harrad, 2022) and 0.47, 0.027, and 0.51 ng/kg bw/day in China (Cao et al., 2019), and in the U.S.A was 67 ng/kg bw /day for TDCIPP (Black et al., 2019).

Second, to assess the importance of dermal uptake of Cl-OPFRs through contact with UK furniture fabrics, we compared our results to previous studies assessing adult exposure to Cl-OPFRs through other exposure routes in the UK like dust ingestion, food intake, drinking water, and inhalation. The estimated daily intakes of TCEP, TDCIPP, and TCIPP for adult were respectively 0.03, 0.07, and 0.92 ng/kg bw/day via dust ingestion (Brommer and Harrad, 2015), 2.34, 3.73, 4.16 ng/kg bw/day via food intake (Gbadamosi et al., 2022), 0.06, 0.0002, and 0.08 ng/kg bw/day via drinking water (Gbadamosi et al., 2023), and 174, 0.04, and 9.25 ng/kg bw/day via inhalation (Ortiz-Carrizales, 2018).

Finally, we compared the median and high exposure scenario of the estimated daily uptake for TCEP, TDCIPP, and TCIPP for UK and Ireland adults in our study with the identical values obtained from previous studies (Table 5.3). This allows us to directly compare our findings to previous studies that examined the identical Cl-OPFRs. Our estimates for TCEP, TDCIPP, and TCIPP were significantly lower than those reported in the U.S.A via air inhalation and dust ingestion (Schreder et al., 2016) (Table 5.3).

Adults in both Ireland and the UK were estimated to be exposed to lower levels of TCEP than those reported via dust ingestion in South Korea and Saudi Arabia, via drinking water in Korea, via dermal uptake of dust in Nepal, and via inhalation in Germany. However, our estimates for TCEP were higher than through dust ingestion in Belgium, Nepal, and Germany, as well as through inhalation in Nepal and through dermal uptake of dust in Germany as reported in Table 5.3.

Our adult estimates of TDCIPP exposure via dermal uptake exceeded those reported through dust ingestion in South Korea, Belgium, Nepal, and Germany, as well as via

inhalation in Nepal and Germany and via dermal uptake of dust in Germany; but were lower than through dust ingestion in Saudi Arabia and dermal uptake of dust in Nepal (Table 5.3). Our estimates for adult exposure to TCIPP in both Ireland and the UK were higher than exposure estimated through other pathways such as: dust ingestion, drinking water, inhalation, and dermal uptake (via contact dust and fabrics) in different countries (Table 5.3).

Our high-end exposure estimates for TCEP, TDCIPP, and TCIPP were higher than those reported in other studies via dust ingestion, drinking water, and food intake (Table 5.3), but lower than those reported through air inhalation and dust ingestion in the U.S.A.

It is worth noting that all dermal exposure estimations in our study are based on uptake (that included percentage absorption), whereas reports of dust ingestion, inhalation, and other estimates of dermal absorption from dust assume 100% absorption of intake (Kim et al., 2013; Ali et al., 2016; Yadav et al., 2017; Zhou et al., 2017). Also, we assumed the exposure time to fabric over a day was only one hour, which is a relatively short duration of exposure. This may lead to an underestimation of the daily exposure to Cl-PFRs through dermal contact with fabrics.

Table 5. 3: The estimated median and high-end uptake of Cl-OPFRs (ng/kg bw/day) for adults via different exposure routes in different countries

	TCEP		**TDCIPP**		**TCIPP**		**Country**	**Reference**
Exposure pathway	**Median**	**95%**	**Median**	**95%**	**Median**	**95%**		
Dermal uptake	0.07	112.84	0.37	65.45	74.95	254.67	Ireland and UK	This study
Dermal uptake from fabrics [a]	1.55	-	2.65	-	18.6	-	UK	(Abdallah and Harrad, 2022)
Dust ingestion (home)	0.16	3.3	0.07	0.89	0.26	1.2	South Korea	(Gown et al., 2021)

Inhalation (home)	186	1260	102	1370	4540	19,000	U.S.A	(Schreder et al., 2016)
Dust ingestion (home)	41.4	771	48.6	191	145	2480	U.S.A	
Drinking water	0.20	3.39	-	-	0.87	7.85	Korea	(Lee et al., 2016)
Dust ingestion (car, home, and classroom)	0.03	1.3	0.07	3.1	0.92	13	UK	(Brommer and Harrad, 2015)
Food intake [a]	2.34	9.07	3.73	15	4.16	16.1	UK	(Gbadamosi et al., 2022)
Drinking water [a]	0.06	0.37	0.002	0.01	0.06	0.39	UK	(Gbadamosi et al., 2023)
Dust ingestion [a]	0.43	1.1	-	-	-	-	Philippines	(Kim et al., 2013)
Dust ingestion (home)	0.1	1	0.1	0.5	0.5	4.8	Belgium	(Van den Eede et al., 2011)
Dust ingestion (hotel)	0.36	0.85	1.12	4.30	1.58	6	Saudi Arabia	(Ali et al., 2018)
Dust ingestion (home)	0.3	2.5	2	12	1.5	3	Saudi Arabia	(Ali et al., 2016)
Inhalation	0.062	-	0.012	-	0.115	-	Nepal	(Yadav et al., 2017)
Dust ingestion	0.007	-	0.009	-	0.025	-	Nepal	(Yadav et al., 2017)
Dermal uptake (dust)	0.329	-	0.462	-	1.223	-	Nepal	(Yadav et al., 2017)
Inhalation	0.09	-	0.16	-	3.6	-	Germany	(Zhou et al., 2017)
Dermal uptake (dust)	0.08	-	0.12	-	0.59	-	Germany	(Zhou et al., 2017)
Dust ingestion	0.05	-	0.04	-	0.19	-	Germany	(Zhou et al., 2017)

a: Mean estimations because median estimations were not available

5.2.1.2 Comparison of toddler exposure to Cl-OPFR via dermal uptake in the UK and Ireland with other routes of exposures in different countries

We compared our median toddler estimates of dermal uptake via contact with furniture fabrics to those reported in previous studies in the same scenario. We found that toddlers in the UK are exposed to 0.053, 0.22, and 155.98 ng/kg bw/day of TCEP, TDCIPP, and TCIPP, respectively. By comparison, toddlers were found to be exposed to 1.2 and 14.2 ng/kg bw/day of TCEP and TCIPP, respectively via

contacting sofa fabrics in the UK (Abdallah and Harrad, 2022) and to 415 ng/kg bw/day of TDCIPP through contacting fabrics of chair cushions in the U.S.A. (Black et al., 2019). In addition, to evaluate the significance of Cl-OPFRs dermal uptake via contact with UK furniture, we compared our toddler median estimations (ng/kg bw/day) in the UK via dermal uptake to those reported in the UK through other routes of exposure. For instance, toddlers are estimated to be exposed to 12.5, 20.5, and 19.4 ng/kg bw/day of TCEP, TDCIPP, and TCIPP respectively via food intake (Gbadamosi et al., 2022), to 0.09, 0.003, and 0.10 ng/kg bw/day via drinking water (Gbadamosi et al., 2022), to 210, 0.05, and 4.11 ng/kg bw/day via inhalation (Ortiz-Carrizales, 2018), and to 1.7, 4, and 43 ng/kg bw/day via dust ingestion (Brommer and Harrad, 2015).

The median and high-end exposure estimates of toddlers via dermal uptake when contacting fabrics of furniture and childcare items in both the UK and Ireland were calculated to compare with other studies in Table 5.4. Our median estimations showed higher TCIPP exposure than reported for toddler daily exposure estimations from toys in China via dermal uptake (via contact with plastic, rubber, stuffed, and foam toys), hand to mouth ingestion, and mouthing (5.88 for TCEP, 2.43 for TDCIPP, and 12.8 for TCIPP ng/kg bw/day) (Zhang et al., 2022) and via ingestion and dermal absorption of indoor dust, and inhalation of air in China of (5.8 for TCEP, 0.79 for TDCIPP, and 12 ng/kg bw/day for TCIPP) (Cao et al., 2019).

Moreover, our toddler median daily estimates for TCEP and TDCIPP were lower than those reported in previous studies via dust ingestion in South Korea, the UK, Belgium, Saudi Arabia, Philippines, and Germany; but higher (only for TDCIPP) than via drinking water in Korea (Table 5.4). Also, our TCEP and TDCIPP estimate was lower than those reported in Germany through dermal uptake (via contact with dust), and in the UK via food intake. For TCIPP, our estimates exceeded those reported via

dermal uptake, inhalation, and hand to mouth ingestion in China (via contact with fabrics) and Germany (via contact with dust), as well as being higher than through dust ingestion in South Korea, the UK, Belgium, Saudi Arabia, and Germany (Table 5.4).

Our high-end exposure estimate for TCEP was higher than drinking water in the UK but lower than through other routes of exposure like dust ingestion, drinking water, and food intake. TDCIPP high-end exposure estimate was lower than via dust ingestion and food intake in the UK, as well as via dust ingestion in Saudi Arabia, but higher than via drinking water and dust ingestion in the UK and Belgium, respectively. For TCIPP, our high-end exposure estimate was higher than via all other routes except those estimated to occur via dust ingestion in the UK (Table 5.4).

Table 5. 4: The estimated median and high-end uptake of Cl-OPFRs (ng/kg bw/day) for toddlers via different exposure routes in different countries

	TCEP		**TDCIPP**		**TCIPP**		**Country**	**Reference**
Exposure pathway	**Median**	**95%**	**Median**	**95%**	**Median**	**95%**		
Dermal uptake	0.02	1.95	0.18	33.41	109.80	367.39	Ireland and UK	This study
Dermal uptake from fabrics [a]	1.2	-	-	-	14.2	-	UK	(Abdallah and Harrad, 2022)
Dermal uptake from fabrics	-	-	-	-	0.0097	0.022	China	(Peng et al., 2020)
Inhalation	-	-	-	-	0.042	0.1	China	(Peng et al., 2020)
Hand to mouth ingestion	-	-	-	-	0.068	0.16	China	(Peng et al., 2020)
Dust ingestion	3.7	77	1.7	21	6.2	28	South Korea	(Gown et al., 2021)
Drinking water	0.28	4.76	-	-	1.22	11	Korea	(Lee et al., 2016)
Dust ingestion [a]	1.5	5.9	-	-	-	-	Philippines	(Kim et al., 2013)
Dust ingestion	1.7	45	4	170	43	740	UK	(Brommer and Harrad, 2015)

Food intake [a]	12.5	41.6	20.5	74.2	19.4	71.5	UK	(Gbadamosi et al., 2022)
Drinking water [a]	0.09	1.1	0.01	0.04	0.21	1.2	UK	(Gbadamosi et al., 2023)
Dust ingestion	1	19.8	1.5	9.8	5.6	92.7	Belgium	(Van den Eede et al., 2011)
Dust ingestion (home)	2	35	12	170	7	40	Saudi Arabia	(Ali et al., 2016)
Inhalation	0.08	-	0.16	-	1.10	-	Germany	(Zhou et al., 2017)
Dermal uptake (dust)	0.87	-	1.2	-	6.1	-	Germany	(Zhou et al., 2017)
Dust ingestion	3.3	-	2.5	-	14	-	Germany	(Zhou et al., 2017)

a: Mean estimations because median estimations were not available

5.2.2 Comparison of exposure estimates with health-based limit values (HBLVs)

To assess the health risks of Cl-OPFRs through dermal uptake in Ireland and the UK, the ∑DED values for ∑Cl-OPFRs for toddlers and adults were compared to the corresponding health-based limit values (HBLVs) listed in Table 5.5.

The median and high exposure DED values for ∑Cl-OPFRs for toddlers in Ireland were respectively (29.56 and 99.62 ng/kg bw/day) and in the UK (247.41 and 828.13 ng/kg bw/day), and for adults in Ireland (32.65 and 178.26 ng/kg bw/day) and in the UK (106.34 and 355.31 ng/kg bw/day) that were several orders of magnitude below the HBLVs provided in Table 5.5.

Table 5. 5: Median daily dermal uptake (ng/kg bw/day) (high end exposure scenario in parentheses) for individual Cl-OPFRs, corresponding reference doses (RfDs), and cancer slope factor (SFO) values

	TCEP	**TDCIPP**	**TCIPP**	**Reference**
Adults (Ireland & UK)	0.07 (112.84)	0.37 (65.45)	74.95 (254.67)	This study
Toddlers (Ireland & UK)	0.02 (1.95)	0.18 (33.41)	109.80 (367.39)	This study
RfD (ng/kg bw/ day)	7,000	20,000	10,000	(U.S. EPA, 2017)

RfD (ng/kg bw/ day)	2,200	1,500	8,000	(Van den Eede et al., 2011)
RfD (ng/kg bw/ day)	22,000	15,000	80,000	(Ali et al., 2012)
RfD (ng/kg bw/ day)	-	-	3,600	(Saito et al., 2007)
SFO (ng/kg bw/ day)$^{-1}$	$2x10^{-8}$	-	-	(Li et al., 2018)

The HBLVs for Cl-OPFRs listed in Table 5.5 refer to the determined thresholds to protect human health from probable detrimental effects associated with such chemical exposure. These values indicate the highest possible amount of Cl-OPFR that a human can be exposed to on a daily basis without harm (U.S. EPA, 2017).

Furthermore, these values can be expressed in different way, such as reference dose (RfD) (ng/kg bw/day) that is calculated by dividing the chronic no observed adverse effect level (NOAEL) (mg /kg /day) by a safety factor (SF) of 1,000 (Li et al., 2018).

Because the uncertainty factor (UF) incorporates more parameters for calculating the RfD from experimental data than the SF, it has been used in place of SF since 2002 (U.S. EPA, 2002). The hazard quotient (HQ) and hazard index (HI) are two other important indicators for evaluating the risk of Cl-OPFRs to human health. These are quantitative metrics utilised for evaluating the potential health impacts of exposure to a certain chemical or mixture (Ding et al., 2018). The HQ compares the estimated daily exposure level with a RfD value, which is calculated by dividing the daily exposure level by the limit value. The HI is an overall assessment that takes into account different chemical exposures. It is calculated by adding the HQs of each

chemical or compound (Ding et al., 2018). Whenever the HQ value is greater than one, it indicates that the potential exposure is greater than the safe limit, indicating a possibility of harmful effects (Ding et al., 2018).

The RfD and the cancer slope factor (CSF) are important metrics in assessing the health risks of hazardous chemical exposure in humans. RfD is used to assess a toxic substance's non-carcinogenic risk (non-CR) through environmental exposure (Li et al., 2018). On the other hand, the CSF is a risk assessment measure that estimates the probable cancer risk associated with exposure to a specific substance, in this instance, flame retardants. It quantifies the link between a substance's exposure and the chance of cancer development (Li et al., 2019d).

When research on Cl-OPFRs and its effects on human health was just beginning in 2011 and 2012, there was no information available on the compound's additive or synergistic toxicity (Van den Eede et al., 2011). Because of this, Van den Eede et al. (2011) and Ali et al. (2012) used NOAELs to derive the RfD values using the scant data that was available. The goal was to find out more about the possible risks to health that Cl-OPFRs cause to people (Li et al., 2019d). After these RfD values were published, many researchers used them for assessing human exposure risk to Cl-OPFRs (Abdallah and Covaci, 2014; Brommer and Harrad, 2015; Yadav et al., 2017) until a set of updated RfD values were made available to the scientific community by the U.S. EPA (Table 5.5) in response to findings from several toxicological studies (U.S. EPA, 2017). Before that in 2007, an RfD value for TCIPP was calculated by dividing chronic NOAEL by a SF of 10,000 (Saito et al., 2007). According to Table 5.5, there is a one-order-of-magnitude difference between the RfD values of the Cl-OPFRs from Van den Eede et al. (2011) and Ali et al. (2012). This discrepancy is caused by the authors' use of different UFs of 10,000 and 1,000 for Van den Eede et

al. (2011) and Ali et al. (2012), respectively. Nevertheless, the difference between the RfDs proposed by Ali et al. (2012) and the updated RfDs established by U.S. EPA (2017) tend to be limited, with a maximum difference of threefold (Li et al., 2018). There are several possible reasons for this observation. Firstly, in 2015, data on laboratory animal exposure and hazard assessments of Cl-OPFRs became available, enabling the computation of organ/system-specific RfDs. These assessments covered immunological effects like decreased thymus weight and serum immunoglobulin M (IgM) levels, reproductive impacts like decreased ovary weight and ovarian follicles, and developmental effects like neurodevelopmental deficits (U.S. EPA, 2015a; Li et al., 2018). Furthermore, the different calculation equations used by U.S. EPA (2017) and Ali et al. (2012) could account for a portion of the small discrepancy in RfD values. The calculation equations for RfD have been updated because of improvements in toxicological science throughout time (Bhat et al., 2014; U.S. EPA, 2014).

5.3. Conclusions

This chapter tests the hypothesis that the high concentrations of Cl-OPFRs in furniture and childcare items may lead to substantial exposure via the dermal pathway. According to the findings of this study, dermal exposure of adults and toddlers to TCEP occurs primarily via contact with vehicle fabrics in Ireland and furniture fabrics in the UK, respectively; to TDCIPP through vehicle fabrics and childcare item fabrics in Ireland, respectively; and to TCIPP through furniture fabrics and childcare item fabrics in the UK, respectively. Our daily estimates fall in a similar range and with findings of other studies of exposure to Cl-OPFRs through dust ingestion, drinking water, inhalation, dermal uptake, food intake, and hand to mouth ingestion. When normalised to body weight, toddlers are exposed to higher levels of Cl-OPFRs than

adults. Reassuringly, the calculated exposure estimates in this study were several orders of magnitude below the HBLVs reported in the literature. Finally, a comparison of our estimates of dermal uptake exposure with data on different routes of exposure reveals that dermal uptake is most likely a significant pathway of exposure to Cl-OPFRs.

Chapter 6: Conclusions and recommendations

Cl-OPFRs are a class of chemicals that are often added as flame retardants (as well as as plasticisers) to plastics, textiles, furniture, childcare items, and electronics. However, the presence and potential risks associated with Cl-OPFRs have raised concerns among researchers that have led to investigation into their presence in the environment. As a result of the paucity of information about the existence of Cl-OPFRs in furniture and childcare products, there are considerable research gaps. Also, there is a need for a quick, cost effective and feasible tool to screen waste for limit compliance with possible future regulatory limits on concentrations of Cl-OPFRs was needed. For that, this thesis aims are to

- Report for the first time the concentrations of Cl-OPFRs in waste plastics including furniture, vehicle, and childcare items from Ireland, the UK, and Saudi Arabia.
- Investigate the utility of handheld XRF as a tool for measuring compliance of waste items with proposed regulatory limits for Cl-OPFRs. This was achieved by comparing XRF measurements for Cl and P to the GC/MS results obtained for a wide range of plastic waste articles, and to enhance understanding of the causes of any false exceedance and false negative readings obtained.

The main achievements and outcomes of this research are summarised below:

6.1 Hypothesis 1 (Chapter 3): Cl-OPFRs are widely used in consumer products, and their concentrations will vary depending on national fire safety regulations.

- **Furniture, ELV, and childcare item samples from Ireland:**

In furniture, 11 foam samples from mattress, chair, couch, and armchair were found to contain >1,000 mg/kg Cl-OPFRs. TCIPP was the most abundant Cl-OPFR found in these samples, while TCEP and TDCIPP were only observed in four and two samples,

respectively. For childcare items, particularly car seats, TCEP and TCIPP were only found in one foam sample, while TDCIPP was the most abundant Cl-OPFR observed at levels exceeding 1,000 mg/kg in 12 samples (10 foams and 2 fabrics). For other childcare items like seats, prams, pushchairs, and others, only TCIPP was found at a concentration >1,000 mg/kg. For ELV samples, 20 samples contained Cl-OPFRs exceeding 1,000 mg/kg. TDCIPP was the most prevalent Cl-OPFR in 15 samples (8 fabrics, 5 foams, and 2 roof trims) and TCEP was only found in 4 samples (3 foams and 1 fabric).

- **Furniture and childcare item samples from the UK:**

For furniture, 36 samples (cover leatherette, leather, lining, and foam) contained TCIPP at concentrations >1,000 mg/kg, while only one sample contained TCEP (armchair cover leatherette) and TDCIPP (sofa foam). For childcare items, 13 samples (7 fabrics and 6 foams) contained Cl-OPFRs at levels above 1,000 mg/kg. TCIPP was the most prevalent Cl-OPFR found in childcare items except in booster car seat, TDCIPP was the dominant.

- **Furniture and childcare item samples from Saudi Arabia:**

No samples of furniture and childcare items from Saudi Arabia were found to contain Cl-OPFRs at levels exceeding 1,000 mg/kg (except one car seat fabric and foam).

In Saudi Arabia, the absence of national furniture fire safety laws removes the legislative requirement to employ chemical flame retardants in contrast to countries like the UK and Ireland where fire safety regulations are in place.

- In countries like Ireland and the UK, where fire safety regulations are implemented, the concentration of Cl-OPFRs was determined in fabrics and

foams from vehicles, furniture, and childcare item. We found that 19% of samples in Ireland and 35% of samples in the UK containing >1,000 mg/kg Cl-OPFR and this variation in percentage was affected by non-identical samples categories in both countries. TCIPP dominates in furniture and childcare item samples, while TDCIPP dominates in samples from vehicle and children car/booster seats.

- In Saudi Arabia, concentrations of Cl-OPFRs were below <1,000 mg/kg and were significantly lower (<0.01) than those we found in the UK and Ireland. This is likely because there are no furniture fire safety regulations in Saudi Arabia, so chemical flame retardants are not required.
- In addition, Cl-OPFRs concentrations were significantly different (P<0.01) in furniture and childcare item samples of the same category from Saudi Arabia, the UK, and Ireland.
- Vehicle fabric and foam samples contained higher TDCIPP concentrations than TCIPP and TCEP. Due to its low fogging potential and high cost, TDCIPP is preferred in automotive applications over other Cl-OPFRs.
- Estimated amounts of Cl-OPFRs annually entering the waste stream in the UK and Ireland were higher than that reported elsewhere for restricted BFRs (Drage et al., 2018; Drage et al., 2022).

6.2 Hypothesis 2 (Chapter 4): XRF is a useful technology for screening waste for compliance with expected limits on maximum allowable Cl-OPFR concentrations.

- Comparison of the XRF readings for Cl and P with the GC/MS results of TCEP, TDCIPP, and TCIPP, we found that a statistically significant correlation was observed between XRF and GC/MS measurements for waste

from Ireland and the UK, but not for waste from Saudi Arabia. We observed high y-intercept and slopes for such correlations between XRF Cl and GC/MS ∑Cl-OPFRs readings, suggesting that many samples have Cl sources other than Cl-OPFRs.

- XRF generated false exceedances in 81% of samples from Ireland, 74% of samples from the UK, and 97% of samples from Saudi Arabia; however, no false negatives were identified. Combined with the evidence from our correlation analyses above, this strongly suggests that XRF is not a reliable tool to screen waste for compliance with any future limit on Cl-OPFR concentrations.
- False exceedances observed in this study indicating that Cl measurements might be impacted by additional non-Cl-OPFR sources like V6, PVC, and impurities present in toluene diisocyanate (Chivas et al., 2009; Stapleton et al., 2011; SCHER, 2007) that could be applied to fabric and foam samples of furniture and childcare items as well as in vehicle floor mat samples.

6.3 Hypothesis 3 (chapter 5): The high concentrations of Cl-OPFRs in furniture and childcare items may lead to substantial exposure via the dermal pathway.

- Estimates of dermal uptake exposure were derived for the populations of Ireland and the UK. Both adults and toddlers were subjected to two separate exposure scenarios (median and high). According to these estimates, dermal uptake significantly contributes to human exposure to Cl-OPFRs. However, our exposure estimates for all Cl-OPFRs were significantly lower than currently published HBLVs.

6.4 Recommendations for future work

- Human dermal exposure to Cl-OPFRs must be assessed especially in those at risk like children.
- More knowledge about the source of Cl in samples that cause high readings by XRF is required.
- It is necessary to investigate the concentration of Cl-OPFRs in childcare items since such flame retardants can negatively affect children's health.
- Investigating waste is necessary to control the presence of Cl-OPFRs in waste streams and their recycling into new items.
- More research is needed to determine the presence of Cl-OPFRs in childcare items that are not required to be treated for fire resistance.
- Cl-OPFRs restrictions may vary by country, so more research comparing global variations in Cl-OPFRs concentrations using the same sampling and analysis techniques is required.
- Evaluate the use of Fourier Transform Infrared Spectroscopy (FTIR) as a screening technique to identify and quantify PVC in waste streams.
- Examine new methods and strategies to improve the precision, accuracy, and application of XRF in many research contexts. Develop and improve the experimental design of XRF to gain a deeper understanding of its capabilities and limitations.
- Research into the human toxicology, uptake, and metabolism of Cl-OPFRs.
- Evaluation of dermal exposure to Cl-OPFRs workers engaged in "high-risk" occupations, specifically within waste and recycling facilities.
- Measure concentrations of Cl-OPFRs in both indoor air and dust of waste/recycling facilities.

- Research into the emissions of Cl-OPFRs into the environment during disposal of waste furniture.
- Further understanding of the transfer of Cl-OPFRs into indoor air and dust from consumer products like furniture and vehicles.
- Improve knowledge regarding the possible negative health impacts and toxicity of Cl-OPFRs to support the risk assessment of these compounds for human health, facilitating the determination of Reference Doses (RfDs).
- Investigate the bioaccessibility of Cl-OPFRs to humans by means of different exposure routes, including dust ingestion, inhalation, and dermal contact. To improve predictions of the accumulation of these compounds in various human organs, investigate pharmacokinetic data as well, such as compound half-lives.
- More biomonitoring studies for Cl-OPFRs based on human milk, serum, hair, saliva, urine, and skin swabs are desirable for adults as well as for infants and children.

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