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Alghamdi, Misbah; Abdallah, Mohamed Abou Elwafa; Harrad, Stuart

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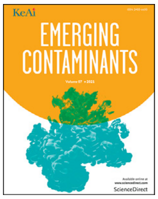

The utility of X-Ray fluorescence spectrometry as a tool for monitoring compliance with limits on concentrations of halogenated flame retardants in waste polymers: A critical review

Misbah Alghamdi, Mohamed Abou-Elwafa Abdallah, Stuart Harrad*

School of Geography, Earth, and Environmental Sciences, University of Birmingham, Birmingham, B15 2TT, UK

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ABSTRACT

This study reviews current knowledge about the presence of brominated and chlorinated organophosphate flame retardants (BFRs and Cl-OPFRs) in plastic consumer articles, with particular reference to the potential as a result of recycling, for such chemicals to unintentionally contaminate articles in which flame retardants are not required. To minimize such unintentional contamination, jurisdictions such as the EU (European Union) have introduced limits on concentrations of some BFRs in waste plastics, with articles exceeding such limits prevented from being recycled. Substantial technical and economic constraints associated with the conventional methods for determining compliance with such limit values exist, leading to less specific, but simpler, more rapid, and less expensive methods such as portable X-ray fluorescence (XRF) spectrometry being identified as possible alternatives. This paper thus examines the evidence that XRF offers a viable method for checking compliance with existing and possible future limits on BFRs and Cl-OPFRs in waste plastics and identifies future research priorities.

1. Introduction

Flame retardants (FRs) are chemical additives applied to a broad variety of consumer goods to mitigate fire risk [1]. Two widely used classes of organic flame retardants are brominated (BFRs) and organophosphate (OPFRs) [2]. Both classes have been widely applied to varying degrees in items such as electronics, cars, polyurethane foam (PUF), furniture and synthetic fabrics. However, most are environmentally persistent and can pose adverse health effects to humans and wildlife [3,4]. Moreover, as many BFRs and OPFRs are used as additives rather than chemically bonded to products, they are prone to emission from treated products via volatilisation, leaching, and abrasion, and are thus detected frequently in the indoor and outdoor environment [5,6]. Emissions of and consequent exposure of human and wildlife to such halogenated FRs, coupled with their potential to contribute to fire toxicity, have led to some studies expressing concern that these risks may outweigh their fire safety benefit [7,8].

Historically, the most widely used BFRs are tetrabromobisphenol A (TBBPA), polybrominated diphenyl ethers (PBDEs), and hexabromocyclododecane (HBCDD) [9]. However, the toxicity, persistence, ability to undergo long-range environmental transport, and capacity for bioaccumulation of PBDEs and HBCDD has led the United Nations Environment Programme (UNEP) to list these BFRs under the Stockholm Convention on Persistent Organic Pollutants (POPs) [10]. In 2009, tetra-, penta-, hexa-, hepta-, and octa-BDEs were added to Annex A of the Stockholm Convention [11]. Following this, HBCDD and deca-BDE were listed as POPs, in 2013 and 2017 respectively [12,13]. The listing of PBDEs and HBCDD as POPs identifies them as chemicals whose use and manufacture should be phased out. However, in recent years, evidence has mounted on the presence of such prohibited BFRs in consumer products which are not required to meet flame retardancy standards e.g., food contact articles (FCAs), plastic children's toys, children's hair accessories and other goods [14,15]. The presence of PBDEs and HBCDD at concentrations below those required to impart flame retardancy likely arises as a result of recycling of plastics that were flame-retarded in their first use. In response to this, the Stockholm Convention sets Low POP Concentration Limits (LPCLs) of 1000 mg/kg for PBDEs and HBCDD to ensure waste

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* Corresponding author.
E-mail address: S.J.Harrad@bham.ac.uk (S. Harrad).
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plastics exceeding these limits are not recycled [16,17]. Enforcement of these LPCLs is intended to prevent further contamination of the recycled plastic stream with PBDEs and HBCDD. In May 2017, the most recent Conference of Parties to the Basel and Stockholm Conventions proposed establishing a 50 mg/kg or 1000 mg/kg limit for POPs waste including PBDEs [18]. It is important to know that the LPCL is now being examined with the goal of implementing legislative limitations of less than 500 mg/kg as soon as possible, no later than 2021 [19]. Furthermore, the EU (European Union) has established a 100 mg/kg Unintentional Trace Contaminant (UTC) limit for HBCDD [17], with 10 mg/kg UTC limits for tetra-, penta-, hexa-, hepta-, and deca- BDEs being implemented in July 2021 [19]. The Restriction of Hazardous Substances (RoHS) directive promulgated by the European Commission, prohibits the sale on the EU market of electrical and electronic equipment (EEE) exceeding permitted concentrations (1000 mg/kg) of hazardous chemicals including the sum of PBDEs [20]. The goal of RoHS is to limit the generation of waste electrical and electronic equipment (WEEE) [21]. Based on the possible environmental and human health hazards, TBBPA is considered a prospective candidate for inclusion under RoHS [22].

As a consequence of restrictions on PBDEs, use of alternative BFRs as substitute has been mooted, but concerns have been expressed that the effects on human health and the environment of such alternative BFRs are not fully understood [23].

Both halogenated and non-halogenated OPFRs exist. Halogenated OPFRs are used as FRs in electronics, furniture, and textiles; while their non-halogenated counterparts are applied as plasticisers and antifoaming products, as well as FRs [24]. More specifically, chlorinated OPFRs (Cl-OPFRs) are applied to both rigid and flexible PUFs used in furniture and building insulation, PVC (polyvinyl chloride) plastic, and textiles. Recently, the use of OPFRs is thought to have increased [3], possibly related to the bans on PBDEs and HBCDD, accompanied by a rise in the usage of PUF, to which the Cl-OPFRs tris(1-chloro-2-propyl) phosphate (TCIPP) and tris(1,3-dichloro-2-propyl) phosphate (TDCIPP) are widely applied [25]. Moreover, in the EU, high usage of TCIPP has been linked to increased installation of building insulation in keeping with the Kyoto Protocol [26]. To illustrate the extent of the recent increase in OPFR manufacture; in 1992, the production of OPFRs (including Cl-OPFRs) was 100,000 tonnes worldwide, rising in 2007 to 341,000 tonnes [27], and 680,000 tonnes in 2015 [28]. More specifically, since the 1990s, global annual production of Cl-OPFRs has exceeded 50,000 tons [29]. Moreover, in 2011, the global market for Cl-OPFRs was anticipated to be 180,000 tonnes, with an expected increase by 2017 to about 220,000 tonnes (Papagni and Kerzic, 2015).

Due to their extensive and widespread use and emission from products, Cl-OPFRs are frequently detected in various environmental media [30] such as air [31–33], soil [34], water [35,36], indoor dust [33,37,38], sediments [4,39,40], and biological samples [38,41–43]. While Cl-OPFRs are not listed as POPs under the Stockholm Convention, it has been suggested that they are of similarly concern as persistent mobile organic compounds (PMOCs) [44].

Inhalation has been identified as an important route of human exposure to Cl-OPFRs owing to their relatively high vapour pressures [25]. Additionally, food intake, dermal absorption, and inadvertent dust ingestion have also been reported as major pathways of human exposure to Cl-OPFRs [3]. Such evidence of human exposure is of concern owing to evidence of adverse health effects arising from such exposure. Specifically, Cl-OPFRs have been associated with several toxicological effects, including cytotoxicity, neurotoxicity, carcinogenicity, endocrine disruption, developmental toxicity, and interference with reproductive functions [27,45,46]. Exposure to TDCIPP in indoor dust has been related to an increase in prolactin levels, as well as a decrease of thyroid hormone levels and sperm quality in men [27,46]. In addition, TDCIPP can pass quickly into blood, liver, kidneys, and male reproductive organs and stimulate cancer-cell growth [27]. Moreover, both TCEP (tris(2-chloroethyl) phosphate) and TDCIPP were proven as cytotoxic [46] and listed as carcinogenic substances under California's proposition 65 [47]. The U.S. Environmental Protection Agency (EPA) identified TDCIPP as an environmentally persistent chemical that can possibly disturb the function of human reproductive, genetic, and developmental systems [27]. Furthermore, Austrian research found indoor dust containing TCEP to be associated with reduced cognitive abilities in children [48].

2. Legislation relating to the manufacture, use, and disposal 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, within the EU, inclusion of a chemical on the SVHC (Substances of Very High Concern) list is the first phase in the authorisation process, which regulates the usage of chemicals and may contribute to a prohibition/restriction of their use. TCEP was suggested for phase-out by 2015 with only approved uses permitted after that date [48,49].

Furthermore, under the European Commission's Toy Directive, the maximum permissible concentration of TCEP, TDCIPP, and TCIPP in toys allowed onto the EU market was restricted to 5 mg/kg in 2014 [49]. A summary of legislative restrictions on the manufacture and use of Cl-OPFRs is provided in Table 1.

In terms of BFRs, as previously mentioned, RoHS establishes the maximum PBDE concentration (1000 mg/kg) in goods intended for daily use. The Toy Safety Directive (2009/48/EC) is a related regulation that mandates producers to conduct risk analysis before releasing a toy on the market, as well as examining the potential exposure of children to such hazards [58].

3. Recycled plastics as a source of FRs in new products

There is substantial evidence of BFRs entering goods containing recycled plastics. Numerous studies (Table 2) have found BFRs (e.g. PBDEs, HBCDD and/or TBBPA) in newly purchased, recycled, and in use products including children's items (toys and hair accessories) [14,15,61–66], carpet padding foam [59], kitchen utensils (Kuang at al., 2018; [14], FCAs [60,63], and polystyrene packaging materials [67]. Also, an extensive study in the U.S. provided evidence of the recycling of hazardous BFRs into new products such as toys, décor and much more [68]. In these studies, BFRs were identified at a wide range of concentrations where some were lower than the LPCL and others were significantly higher, as a result of their intentional or unintentional incorporation in consumer products through recycling (Table 2).

As illustrated by Table 2, numerous reports exist about the presence of BFRs in consumer and children's products containing recycled materials. Conversely, there is a relative paucity of data about the presence of Cl-OPFRs in recycled products.

Table 3 summarises data on the presence of Cl-OPFRs in products and furniture. Such data provide a surrogate for identifying Cl-OPFRs used in goods with potential to be recycled later into new products. As concentrations of Cl-OPFRs need to exceed ~1–2% in treated products in order to impart flame retardancy, the presence in articles of concentration of <0.1% (1000 ppm; or 1000 mg/kg) of Cl-OPFRs is likely, a result of unintentional contamination arising from use of recycled polymers [74]. Indeed, a number of studies have identified Cl-OPFRs in children's and FCAs possibly as a result

Table 1
Summary of legislative restrictions on the manufacture and use of Cl-OPFRs.

Country	Directive	Regulation	Year	Reference
Canada	Consumer Product Safety Act	Prohibited the sale of foam padded children's products with TCEP.	2010	[50]
USA	Children's Safe Product Act	Required manufacturers to report the presence of TCEP, TDCIPP and TCIPP in children's products. Limited the concentration of TCEP and TDCIPP to 1000 mg/kg in children's' products and residential furniture.	2011 2017	[44]
	California's proposition 65	Respectively, TCEP and TDCIPP were listed as carcinogenic substances.	1992 2011	[51,52]
	Washington DC B210143 law	TDCIPP and TCEP required to be limited to 0.1% in children's products and furniture.	2016	[53]
	CA Safer Consumer Products Program rule	Manufacturers of children's foam padded sleeping goods required to report if including TCEP and TDCIPP.	2017	[44]
	CA Assembly Bill 2998	Limits all OPFRs to 1000 mg/kg in children's goods, furniture, and mattresses.	2018	[54]
	Minnesota (MN) HF 1627	Prohibits the sale or production of children's goods, upholstered residential furniture and textile, or mattress containing more than 1,000 mg/kg of TCEP, TDCIPP and TCIPP.	2018	[55]
EU	Commission's Toy Directive (2009/48/EC)	Concentrations of TCEP, TDCIPP and TCIPP in children's toys are limited to 5 mg/kg after identifying TCEP as carcinogenic category 2 and toxic for reproduction type 1B.	2014	[56]
	REACH (Annex XIV Authorisation List)	Prohibits TCEP use.	2015	[57]
	ECHA	Proposed restriction of TCEP, TCIPP and TDCIPP in all childcare goods and residential upholstered furniture to 1000 mg/kg by weight because of identified risk of carcinogenicity for exposed infants.	2018	[49]

of recycling [61,69,70,80–86].

Kajiwara et al. [71], investigated new products in the Japanese market such as curtains, wallpaper, and electronics and found Cl-OPFRs (TCEP, TCIPP and TDCIPP) at low concentrations up to 15 mg/kg. In another study, Cl-OPFRs were measured in samples of waste domestic, and office soft furnishing products collected in the UK in 2011 and 2012 [87]. Samples analysed included carpets, curtains, mattress fabrics, furniture foam, and upholstery textiles. TCIPP was found in 7 of 9 furniture PUF samples with a mean concentration of 19,000 mg/kg by weight. In foam samples, concentrations of TCIPP ranged from 8,400–38,000 mg/kg, while in one office chair foam, TDCIPP and TCEP were detected at 11,000 mg/kg and 5,000 mg/kg respectively. No other samples contained TDCIPP and TCEP above detection limits [87]. Additionally, the Danish Environmental Protection Agency in 2016 reported Cl-OPFRs in child car seats and textiles from other children's articles. For example, TDCIPP was found in a sample of carrycot foam at 89,700 mg/kg, and in car seat foam at 42,600 mg/kg [79].

In an Austrian study of infant car seats, TCIPP, TDCIPP and TCEP were also identified. A car seat (head cover filling) contained 9,200, 4,700, and 580 mg/kg of TDCIPP, TCIPP, and TCEP respectively. In one pillow filling, TDCIPP was found at 8,700 mg/kg; while in contrast, it was found at 68 mg/kg in a push chair cover filling. Moreover, the textile of a changing mat contained low concentrations of TCIPP and TDCIPP of 67 and 14 mg/kg, respectively [79]. It is not clear whether these lower concentrations arose as a result of the use of recycled foam.

Several studies in the USA investigated the presence of Cl-OPFRs in consumer products. In a study of OPFRs in furniture foam and U.S. home dust, 15 out of 26 furniture foams samples contained TDCIPP at concentrations varying from 10,000–50,000 mg/kg, with 4 of the 26 foam samples containing TCIPP at concentrations varying from 5,000–22,000 mg/kg [37]. Two years later, Stapleton et al. [72] analysed 101 foam samples including children's products such as car seats, strollers, changing pads, pillows, mattresses, and infant sleep positioners to identify OPFRs. TDCIPP was the predominant Cl-OPFR detected with an average concentration of 39,000 mg/kg. In contrast, TCEP was detected only at very low levels. Likewise, TCIPP was measured at appreciable concentrations in only 2 samples (5,000 and 800 mg/kg respectively) [72]. One year later, TDCIPP was the most frequently identified FR in 42 of 102 samples of PUF from residential couches in a 2012 study. The average concentration of TDCIPP in foam was 43,500 mg/kg with a range from 1,600 to 110,000 mg/kg in couches purchased in 1999 and 2009 respectively [73].

Carignan et al. [38] found 56,000 mg/kg of TDCIPP in foam of one pit cube used in gymnastic equipment that was advertised as a FR free product. A study conducted also in the U.S. examined 169 products including furniture and children's articles to identify the flame retardants present. TCEP, TDCIPP, and TCIPP were detected in 27 components from 224 products (1 plastic, 5 fabrics, and 21 foams). To illustrate, Cl-OPFRs were found in all samples of carpet padding (n = 1), chair pad (n = 1), seat cushion (n = 1), and tent fabric (n = 2) [38].

Keller et al. [88] detected TDCIPP at ~ 10,000 mg/kg in tent textiles [88]. Similarly, Bergen and Stone, [74]; conducted a study of flame retardants in consumer items from Washington State, USA, including foam from children's goods and furniture, as well as tent fabric. TDCIPP was frequently detected in foam samples and tent textiles [74]. In fact, TDCIPP, TCEP, and TCIPP were detected at concentrations exceeding 2000 mg/kg in many samples. TDCIPP and TCIPP were the two Cl-OPFRs frequently detected in textiles and PUF from children's car seats [89].

Another study in the U.S., found TDCIPP was the most frequently detected FR in 24% of 1,411 PUF samples from sofas, chairs, mattresses, car seats, and pillows at concentrations that in some samples exceeded 10,000 mg/kg by weight. TDCIPP and TCIPP were the most frequently found combination of FRs and were respectively found in 47 and 50 children's car seats purchased between 2014 and 2016 [90]. TDCIPP and TCIPP were frequently detected at percent levels in fabrics and foams [75,76]. In a gymnastic studio, TDCIPP was detected in a new foam block at 2.2 mg/kg, likely indicative of incidental contamination rather than an intentional ingredient [77].

TCEP was the most abundant OPFR detected in U.S. children's car seats with a detection frequency of 25% and a maximum concentration of 0.16 mg/kg. In contrast, TCIPP and TDCIPP were detected at lower frequencies of 8.3% and 19% respectively, with each detected in fabrics, but only TCIPP in foam [78].

To summarise, Cl-OPFRs have been detected in consumer products and furniture at a range of concentrations (Table 3), so it is reasonable to hypothesise that recycled products derived from these items will contain Cl-OPFRs, albeit at lower concentrations. It is pertinent to mention recycling of PUF, which is undertaken in the

Table 2
Summary of concentrations of restricted BFRs in consumer articles.

Product	Detected FR	Concentration (range) in mg/kg	Country	Reference
Carpet backing foam	Penta-BDE, Octa-BDE, Deca-BDE, ∑PBDEs	0-1130, 0–263, 0–100, and 0-1316	Canada	[59]
Carpet backing foam	Penta-BDE, Octa-BDE, Deca-BDE, ∑PBDEs	12, 1, 5, and 18	Hungary	
Carpet backing foam	Penta-BDE, Octa-BDE, Deca-BDE, ∑PBDEs	0-1033, 0–65, 0–166, and 0-1128	USA	
Thermo-cup	Deca-BDE	10–740	Czech market	[60]
Thermo-cup	Deca-BDE & TBBPA	398–1922	European market: Sweden, Belgium, Germany and Slovakia	
Egg cutter	Deca-BDE & TBBPA	18		
Apple cutter	TBBPA	172		
Thermo-cup	TBBPA	26–300		
Toys	PBDEs	0.01–143*	Belgium	[61]
	TCEP	65*		
	TCIPP	80*		
	TDCIPP	5*		
Toys and hair accessories	Octa-BDE, Deca-BDE	0-95, and 1-121	Czech Republic	[62]
FCA (Food contact article):(Thermo-cup)	Octa-BDE, Deca-BDE	3, and 6	Czech Republic	
Toys	Octa-BDE, Deca-BDE	1, and 3-4	Germany	
Toys	Octa-BDE, Deca-BDE	6, and 58	Hungary	
Toys	Octa-BDE, Deca-BDE	0-51, and 0-79	Poland	
Toys	Octa-BDE, Deca-BDE	26, and 98	Slovakia	
Toys	Octa-BDE, Deca-BDE, HBCDD	0-95, 1–23, and 0-375	Czech Republic	(Digangi at al., 2017)
FCA(Food contact aricles) (Thermo-cup)	Octa-BDE, Deca-BDE	3, and 6	Czech Republic	
Kid's headdress	Octa-BD, Deca-BDE, HBCDD	9-107,33–195, and 0-24	Czech Republic	
Toys	Octa-BD, Deca-BDE, HBCDD	4-89, 8–145, and 0-21	Netherlands	
Kid's headdress	Octa-BDE, Deca-BDE	7, and 17	Slovakia	
Toys	Deca-BDE, TBBPA	210.5–9225.8, and 208.4–7747.1	European market: Italy, Czech Republic and Germany	[63]
FCA	Deca-BDE, TBBPA	775.2–778.8, and 442.8–471.3		
Radio back panel	Deca-BDE	5118.8		
Hair accessories	∑PBDEs, HBCDD	7.94–1623.44, and <0.01–7.71	Czech Republic	[64]
Toys	∑PBDEs, HBCDD	8.14–2614.34, and <0.01–91.07	Czech Republic	
EPS (Expanded Polystyrene)	∑HBCDD	<0.7–91050	UK	(Abdallah et al., 2018)
XPS (extruded polystyrene)	∑HBCDD	0–14354	UK	
EPS	∑HBCDD	36–5897342	Ireland	
XPS	∑HBCDD	<0.7–1009162	Ireland	
Kitchen utensils	Penta- BDE (47, 99)	(<0.0002–1), (<0.0002–0.33)	Birmingham, UK	(Kuang at al., 2018)
	Octa-BDE (183)	(<0.001–13)		
	Deca-BDE (209)	(<0.0026–140)		
Toys	Octa-BDE, Deca-BDE, ΣPBDEs, HBCDD	0-161, 3–3310, 4–3318, and <LOQ[a]- 25	Austria, Belgium, Czech Republic, Denmark, France, Germany, Poland, Portugal, Spain, Belarus, Bosnia and Hercegovina, Macedonia, Montenegro, Russia & Serbia	(Straková at al., 2018)
Hair accessories	Octa-BDE, Deca-BDE, ΣPBDEs, HBCDD	<LOQ-70, <LOQ-2491, <LOQ-2526, and <LOQ-207		

Table 2 (*continued*)

Product	Detected FR	Concentration (range) in mg/kg	Country	Reference
Toys	Octa-BDE, Deca-BDE, ΣPBDEs	5-9, 28−41, and 33-50	Armenia	
Hair accessories	Octa-BDE, Deca-BDE, ΣPBDEs	<LOQ-57, <LOQ-1048, and <LOQ- 1105	Albania, Belgium, Denmark & Czech Republic	
Others (waste bin, massage roller)	Octa-BDE, Deca-BDE, ΣPBDEs	13-42, 165−178, and 178-221	Germany	
Others (eyeglasses, coat hanger &stapler)	Octa-BDE, Deca-BDE, ΣPBDEs, HBCDD	0-62, 1−652, 1−675, and <LOQ-15	Czech Republic	
Toys	PBDEs, HBCDD	593- 2614, and 1- 91	Argentina, Czech Republic, India & Nigeria	[65]
Toys	PBDEs, HBCDD, TBBPA	169-3318, 0.2−2, and 8-314	Brazil, Czechia & Portugal	
Hair accessories	PBDEs, HBCDD, TBBPA	358, 0.3, and 10	Cambodia	
Hair accessories	PBDEs, TBBPA	718-1623, and 1-8	Canada & Czech Republic	
Key fob	PBDEs, HBCDD, TBBPA	511, 2, and 307	Germany	
Smart phone holder	PBDEs, HBCDD, TBBPA	693, 0.5, and 37	Japan	
Toys	BDE-209 (deca-BDE), TBBPA, HBCDD	<LOQ-3100, <LOQ-3100, <LOQ-840	UK	(Fatunsin et al., 2020)

[a] Limit Of Quantification.

U.S [91]. And the EU [92]. This can occur through mechanical (PUF is reused in its original form) and chemical (PUF is converted to its different constituents) recycling [93]. Because PUF is a cross linked polymer [94], mechanical recycling seems the simplest and most basic method of reusing PUF that entails converting solid waste into flakes, granules, or powder [93]. The products of mechanical recycling can be used directly as pillow and toy fillers [93], or eventually turned into carpet underlay, sports mats, cushioning, furniture, and similar goods [95,96].

Several studies have reported the incidence of Cl-OPFRs in baby goods and toys, raising concerns about the increased exposure of infants to FRs by putting such products in their mouths. In Belgium, Ionas et al. [61] reported that in children's toys, concentrations of OPFRs were 10,000 times higher than those of PBDEs. Specifically, Cl-OPFRs were found in 114 samples of toys, where TCEP, TDCIPP and TCIPP account for 28%, 33% and 42% of samples, receptively [61]. In the same study, however, toys were classified according to the material from which the analysed toys were made, revealing that Cl-OPFRs were found in each category of hard and soft plastics, rubber, wood, as well as textile and foam products. Except for TDCIPP, toys produced in China contained concentrations of Cl-OPFRs that were 1−2 orders of magnitude higher than those originating elsewhere. Median concentrations of TCEP, TDCIPP, and TCIPP were: 4, 1, and 5 mg/kg respectively. As these amounts are too low to provide flame retardancy, it appears such chemicals were unintentionally introduced into toys through the process of recycling [61].

In a survey conducted to identify the presence of FRs in eight toys and childcare articles produced from foam plastic on the Danish market, TCEP was not detected above the limit of detection of 50 mg/kg [69].

In another study, concentrations of TCEP in foam cubes used in children's soft play areas were determined by the Danish EPA. The cubes consisted of textile, plastic, and foam rubber, and contained 160 mg/kg TCEP in the textile, and up to 6,500 mg/kg in the foam [70].

In 2014, Health Canada performed testing of 23 children goods including PUF chairs, nursing pillows, and toys bought from retail shops in Ottawa, Canada. In a foam toy, TDCIPP was found at a mean concentration of about 7% w/w; however, TCIPP was not identified in any of the foam samples above the limit of quantification of 0.3% w/w [82].

Health Canada performed an additional study in 2015 on 21 PUF-containing baby products like toys and cushions. TCIPP concentrations were observed to range between 0.02 and 3.4% w/w (LOQ = 0.013% w/w), with the highest concentration detected in bath toys. In the same samples, concentrations of TDCIPP varied from 0.012 to 7.3% w/w (LOQ = 0.012 w/w) [82].

Evidence also exists of the presence of Cl-OPFRs in FCAs or equipment used for food wrapping, packing and canning, where there is no regulatory requirement for flame retardancy. A study conducted in Australia analysed 92 different samples of food from various groups [85]. The study found low concentrations of OPFRs including Cl-OPFRs in food samples, indicating that in addition to bioaccumulation - packaging materials may be a possible source of contamination of foodstuffs with Cl-OPFRs. That Cl-OPFRs can contaminate foodstuffs via their presence in food packaging, as well as via industrial processes like packing, canning, drying, and handling has been suggested elsewhere [86,97].

To summarise, uncontrolled recycling can unintentionally transfer FRs into consumer goods and materials that do not require them, like children's toys, FCAs etc. To prevent this within the EU, low POP concentration limits (LPCLs) have been set for certain BFRs in wastes, above which waste cannot be recycled until the BFRs are removed or irreversibly destroyed [16,17]. This is at odds with the growing moves worldwide towards a Circular Economy, where waste is regarded as a resource, rather than a problem. Although equivalent limits on permissible concentrations of Cl-OPFRs in waste do not yet exist, they may emerge in the foreseeable future given the EU's intention to ban the use of all halogenated FRs in some applications, and the proposal of the European Chemicals Agency (ECHA) to restrict the use of TCEP, TCIPP, and TDCIPP in flexible PUFs used in childcare products and residential furniture [49].

While evidence suggests that LPCLs could be highly effective at preventing PBDEs and HBCDD entering the recycling stream [98]; real and very substantial issues exist regarding their enforcement. For both BFRs and Cl-OPFRs, the conventional GC/MS (gas

Table 3
Concentrations of Cl-OPFRs in consumer products.

Product	Cl-OPFRs detected	Concentration (mg/kg unless otherwise stated)	Region	Reference
Child's toys (sword, floor puzzle 1, floor puzzle 2, mask, surfboard, activity carpet, ball and book)	TCEP	≤50	Denmark	[69]
Child's toy (Soft cube- textile)	TCEP	160	Denmark	[70]
(Soft cube-PUF (polyurethane foam))	TCEP	3300, 5200, and 6500		
Wallpaper	TCIPP, TCEP, TDCIPP	0.078–0.100, <0.004–0.08, <0.002-<0.02	Japan	[71]
Curtain	TCIPP, TCEP, TDCIPP	<0.003, 0.004–0.006, <0.002		
Electronic outlet	TCIPP, TCEP, TDCIPP	0.012, <0.008, <0.005		
Insultation board	TCIPP, TCEP, TDCIPP	0.028–0.087, 0.009–0.01, <0.002–0.006		
Laptop	TCIPP, TCEP, TDCIPP	0.004–0.15, <0.004–0.12, <0.002–0.035		
LCD-TV	TCIPP, TCEP, TDCIPP	0.004–0.052, <0.004–0.009, <0.002		
Furniture (domestic soft furniture)	TDCIPP	<0.0011	UK	(Stubbings at al., 2016)
	TCEP	<0.00067		
	TCPP	<0.00044–8,600		
Furniture (office soft furnishing)	TDCIPP	<0.0011–11,000		
	TCEP	<0.00067–5,000		
	TCPP	<0.00044–38,000		
Children car seat	TCEP	580	Austria	(Uhl et al., 2010)
	TDCIPP	9,200		
	TCIPP	4,700		
Children pillow filling	TDCIPP	8,700		
	TCIPP	10		
Children push chair cover filling	TDCIPP	68		
PUF (furniture and baby products)	TDCIPP and TCIPP	10,000–50,000 and 5,000–22,000	U.S.	[37]
Baby products PUF	TDCIPP	400-124,000 (average 39,220)	U.S.	[72]
	TCEP	1,080–5,940 (average 5,910)		
	TCIPP	1,100–14,400 (average 5,490)		
Couch PUF	TDCIPP	44.87 mg/g (average)	U.S.	[73]
Child's chair (foam)	TDCIPP	<96–29,000	U.S.	[74]
	TCIPP	1800–23,000		
	TCEP	<96–3,400		
Child's chair (accessory)	TDCIPP	7,000		
	TCIPP	890		
	TCEP	<98		
Child's changing pad (foam)	TDCIPP	370- 25,000		
	TCIPP	4,900–5,000		
	TCEP	<87- <93		
Child's changing mat (foam)	TDCIPP	15,000		
	TCIPP	2,800		
	TCEP	270		
Child's crib wedge (foam)	TDCIPP	25,000		
	TCIPP	7,700		
	TCEP	<93		
Child booster seat- for car (foam)	TDCIPP	44,000		
	TCIPP	15,000		
	TCEP	550		
Child's portable crib pad (foam)	TDCIPP	16,000		
	TCIPP	9,700		
	TCEP	<92		
Child's pee protector (foam)	TDCIPP	270		
	TCIPP	<98		
	TCEP	<98		
Child's tablet (plastic)	TDCIPP	250		
	TCIPP	<92		
	TCEP	<92		
Baby carrier (fabric)	TDCIPP	<97		
	TCIPP	640–870		
	TCEP	510- 2,700		
Carpet padding (foam)	TDCIPP	1,800–84,000		
	TCIPP	180–990		
	TCEP	<96- 150		
Tent (fabric)	TDCIPP	12,000–19,000		
	TCIPP	<98- <100		
	TCEP	130–160		
Tent floor liner (fabric)	TDCIPP, and TCEP	4,300, and 180		
Seat cushion (foam)	TDCIPP	33,000		

Table 3 (*continued*)

Product	Cl-OPFRs detected	Concentration (mg/kg unless otherwise stated)	Region	Reference
	TCIPP	7,000		
	TCEP	<98		
Chair pad (foam)	TDCIPP	21,000		
	TCIPP	3,000		
	TCEP	<96		
Toys	TCEP	4 (median)	Belgium	[61]
	TCIPP	1 (median)		
	TDCIPP	5 (median)		
PUF (furniture)	TCIPP, and TDCIPP	6,320 (geometric mean), and 19,900 (geometric mean)	U.S.	[75]
Nap mat (childcare center)	TDCIPP	68,000 (mean)	U.S.	[76]
New block foam (gym studio)	TDCIPP	2.2	U.S.	[77]
Children car seat	TCEP	0.012 (median)	U.S.	[78]
	TCIPP	0.036 (median)		
	TDCIPP	0.11 (median)		
Children car seat (textile & foam)	TCEP	41–840	Denmark	[79]
	TCIPP	46-18.,000		
	TDCIPP	2,700–42,600		
Children car seat (black plastic)	TCIPP, and TDCIPP	300 and 14		
Children car seat (black rubber)	TDCIPP	23		
Carrycots (textile & foam)	TDCIPP	92- 89,700		
Baby sling (textile, foam and felt)	TCEP	20-4,700		
	TCIPP	17-16,300		
	TDCIPP	23-13,000		

chromatography/mass spectrometry) and LC/MS (liquid chromatography/mass spectrometry)-based approaches to their measurement are expensive, time-consuming, require skilled operators, and cannot easily be conducted at waste handling or recycling facilities. Given the vast quantity of waste materials requiring to be checked; this has generated an urgent need for faster, cheaper, and more user-friendly methods capable of evaluating compliance with LPCL values directly at waste and recycling facilities.

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

Several researchers have investigated the application of X-ray fluorescence (XRF) as an alternative technique to screen consumer products for the presence of halogenated FRs [89,99–101]. In addition, there have been several studies reporting the use of XRF as a screening tool for FR-containing wastes in waste-recycling facilities, in order to comply with the EU RoHS and WEEE Directives [101,102].

XRF is a useful spectroscopic technique to identify and quantify many elements. The technique relies mainly on measuring the emission of characteristic "secondary" (or fluorescent) X-rays from a material following excitation by bombarding with high energy X-rays or gamma rays [103]. It is based on the principle that when individual atoms are exposed to an appropriate source of energy, if sufficient energy is provided, it can knock an orbital electron out of its inner electron shell of the exposed atom. Electrons from higher energy levels fill the vacancies of the knocked-out electrons by losing energy, which is emitted in the form of X-ray photons specific to the excited element atoms. So, by counting the photons of each energy transition emitted from a sample, the elements can be identified and quantified [103].

To be an effective LPCL enforcement technique, XRF does not have to fully replicate GC/LC-MS measurements; instead, all that is required is to correctly determine whether the LPCL value has been exceeded. To date, several studies have screened materials for bromine (Br), chlorine (Cl), and phosphorus (P) content using XRF, and compared these data with conventional GC/MS and LC/MS derived concentrations of BFRs and Cl-OPFRs [98,102,104,105]. Guzzonato et al. [100] showed that using custom-made solid reference standards containing Deca-BDE, enhanced the accuracy of XRF measurements of Br in acrylonitrile butadiene styrene (ABS) and high impact polystyrene (HIPS), and concluded that XRF was a feasible tool for screening WEEE for compliance with LPCLs. As a "pass/fail" screening method for enforcement of LPCLs for PBDEs and HBCDD, XRF proved an effective tool in a study of ~550 waste plastic articles conducted in Ireland [98,101,105]. The concentration of Br in each sample obtained via XRF was compared to GC/MS and liquid chromatography – tandem mass spectrometry (LC/MS/MS) measurements of BFRs in the same sample. Based on these data, XRF was found to be an accurate method for checking compliance with LPCLs for PBDEs and HBCDD for: C&D (construction and demolition) EPS/XPS waste, ELV (End-of-Life Vehicle) waste, and waste soft furnishings [98]. The same study, however, concluded that XRF measurements of Br incorrectly identified articles of waste electrical and electronic equipment (WEEE) as exceeding the LPCL in 26 (11%) of the 237 WEEE articles tested. Such "false exceedances" of the LPCL values were identified as being due to the presence of elevated concentrations of other BFRs not covered by the LPCLs, such as TBBPA.

In Austria, XRF proved an effective tool for rapid monitoring of the Br content of large volumes of waste plastics as an indicator of their POP-BFR concentrations [99]. In Sweden, a recycling facility used XRF to separate electronic equipment's plastics contain POP-BFRs and reported that the quality and accuracy of sorting approach is sufficient to comply with EU legislation [104]. To comply with RoHS legislatives, a Nigerian study used XRF to screen waste items containing Br and Cl [102], while Austrian e-waste dismantlers used XRF as the Austrian Waste Treatment Obligation Ordinance includes the control of WEEE where plastic components of that WEEE will be recycled [99]. Aldrian et al. [99] suggested XRF is a reliable screening tool for Br content in WEEE that can determine whether samples comply with regulatory obligations for BFRs. Also, Schlummer et al. [106] recommended the use of XRF to measure Br as a surrogate indicator of the presence of regulated

BFRs like HBCDD in waste polystyrene foam.

XRF has also been used successfully to detect BFRs in products in Japan [71], China [107], and the UK [108]. In the UK, XRF proved a useful method for identifying the presence of BFRs in new and used kitchen utensils [108]. According to an Australian review, XRF is a non-destructive and fast testing method for detecting BFRs in items. XRF was simple to use and allowed repeat measurements of Br [9]. In addition, XRF has been shown as an important screening method for detecting BFRs in new children's products and recycled electronics [109], as well as in children's toys made of recycled materials that contain BFRs [15], in recycled foam carpet padding [59], and in toys, décor, and other products [68]. Similarly, Petreas et al. [110] proposed XRF as an excellent and feasible tool for measuring concentrations of Br and Sb (antimony) (the latter often used in conjunction with BFRs like PBDEs) in furniture to support the enforcement of the new California law (SB1019). Several studies concluded that XRF is a quick and suitable technique for detecting Br in various consumer products with limits of detection of 5 mg/kg in plastics [111–113], electronics [111], furniture [111], metals and textiles [112]. During the analysis of EPS and XPS, a conservative limit of detection of 5 mg/kg [106], 8 mg/kg [114], and 20 mg/kg [101] were reported for XRF analyses. For other polymeric materials, such as PUF, HIPS, ABS, upholstery, textiles, Br concentrations were detected at 10 mg/kg [101,115].

Also pertinent is the use of XRF to screen items for the presence of Cl-OPFRs. Several studies in the U.S. have used XRF to screen children's products, furniture, and EEE to measure the presence of Cl-OPFRs and BFRs in such products. Stapleton et al. [72] used XRF to quantify the levels of Br and Cl in foam from baby products. In brief, XRF proved a good screening tool for the detection of BFRs in foam with a significant correlation of ($p < 0.001$) with GC/MS analysis results, but no significant correlation was reported between Cl and Cl-OPFRs. A contributing factor to this poor correlation between XRF and GC/MS measures of Cl and Cl-OPFRs respectively was the presence of both 2,2-bis(chloromethyl)trimethylene bis(bis(2-chloroethyl)phosphate) (V6) and the hitherto unreported flame retardant, 2,2-bis(chloromethyl)propane-1,3-diyl tetrakis(1-chloropropan-2-yl) bis(phosphate), that could not be quantified in the absence of authentic reference standards. Exclusion of these compounds from the $\sum$Cl-OPFR measurements used in the correlation, yielded a higher but still not statistically significant correlation coefficient ($P = 0.33$) [72]. This discrepancy between measurements of Cl and Cl-OPFRs were exemplified by the fact that while XRF-measured Cl varied from 1.2% to 3.3% by weight in three samples, GC/MS reported only BFRs to be present. The author suggested that chlorinated impurities in toluene diisocyanate, a reagent used to make PUF, could be at least partly responsible for XRF Cl readings exceeding those attributable via GC/MS measurements of Cl-OPFRs [72]. The study recommended further research to investigate the efficient use of XRF as a screening method for Cl-OPFRs [72].

A similar study reported that XRF was a good screening tool for Br and Sb but was not a good indicator for Cl and P [110] as XRF is poorly sensitive to light elements like phosphorus [71]. Based on Petreas et al.'s, (2016) comparison of XRF results with elemental phosphorus P analyses by Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES), it was found that XRF results lacked accuracy when the P concentration exceeded 50 mg/kg leading to poor predictive performance and false negative results; thus, care is recommended when interpreting XRF results for Cl and P. On the other hand, a study by Miller and Gearhart [89], showed an excellent agreement between XRF and GC/MS detection of Cl-OPFRs in both foams and textiles of children's car seats, with GC/MS and XRF agreeing on the presence of TDCIPP and TCIPP in samples. Miller and Gearhart [89] reported that XRF may successfully be used to measure halogenated FRs by detecting Cl at levels exceeding 3,500 mg/kg, depending on the sample matrix. This relatively high detection limit for Cl was obtained by using high definition XRF from XOS (X-Ray Optical Systems, Inc) [116]. A similar Cl limit of detection was reported using a DELTA handheld XRF from Olympus [117]. Interestingly, light elements such as Cl and P can be detected at lower limits of detection by handheld XRF analyser enhanced with Geometrically Optimized Large Area Drift Detector (GOLDD) technology, such as Niton XL3t GOLDD+ and the Niton XL2 GOLDD analysers [118]. To illustrate, screening of restricted elements, such as Cl, in polymers using Niton XL3t 700 Series and Niton XL3t 700 GOLDD XRF analysers were reported at detection limits of 200 mg/kg and 50 mg/kg, respectively [119]. For screening of consumer goods, Niton XL3t GOLDD Series XRF analysers can detect Cl at limits of 80 mg/kg [120]. Similarly, P could be detected by Niton XL2 GOLDD series at detection limit of 350 mg/kg [121], and at a lower detection limit of 250 mg/kg [122] by a Niton XL3t GOLDD + Series in the mining mode. In the same context, Cl can be detected by Niton XL2 GOLDD series at 75 mg/kg [121] and at 60 mg/kg [122] using Niton XL3t GOLDD + Series.

Interestingly, for high concentrations of Cl, greater than 50,000 ppm, Fourier transform infrared (FTIR) spectrometer was found to be a suitable alternative to determine the presence Cl in PVC [68]. For BFRs, FTIR has been used to determine PBDEs in plastics and was found capable of differentiating deca-BDE from its potential substitute decabromodiphenylethane [123].

Also in the U.S., purchased products in Washington State including children's products and furniture, were examined by XRF as a screen for Cl-OPFRs. The study successfully found TCEP, TCIPP, and TDCIPP in many foam components of baby goods [124].

Overall, a number of studies have concluded that XRF is widely applicable because it is a rapid, in situ, portable, non-destructive, easily operated, and reliable screening technique. For the screening of Br in plastics, XRF is an effective tool and has been identified as best available technique and the best environmental practice (BAT/BEP) for screening plastic waste [107]. Also, XRF measurements of Br have been shown to display positive correlation with those of regulated BFRs like PBDEs derived using conventional techniques such as GC/MS [72,89,99,101]. However, these findings are tempered by limitations on the use of XRF that are summarised in Table 4.

False exceedances and false negatives are potential limitations of XRF use as a tool for screening for compliance with limit values for BFRs and Cl-OPFRs. False exceedances occur where the Br concentration measured by XRF indicates exceedance of the LPCL, but GC/MS or LC/MS measurements reveal that concentrations of PBDEs or HBCDD are below the limit value. Such false exceedances can be generated due to background interference, or the presence of unknown Br compounds [9,72]. BFRs other than PBDEs and HBCDD, such as TBBPA, are commonly used on a wide range of products, resulting in false exceedances based on XRF measurements of Br for 9.7% [98],7% [72], and 17% [9] of tested products in different studies [72,110]. reported that impurities in toluene diisocyanate are a potential cause of false positives in 3 of 76 and 4 of 47 of foam samples for XRF readings of Cl. Another reason for high Cl levels in plastic may be the presence of PVC [128].

In the context of false exceedances, it is important to know that Sb_2O_3 is usually used to improve flame retardancy in conjunction with BFRs and is, therefore, considered as a synergist for such flame retardants [129]. Consequently, Guzzonato et al. [63] suggested that simultaneous detection of concentrations of Sb and Br in WEEE samples for which the Br concentration indicated an LPCL exceedance at ratios between ~1:2 and 1:4, would provide confirmatory evidence that the Br detected was due to the presence of PBDEs and thus that the exceedance was genuine. The hypothesis

Table 4
XRF strengths, weaknesses and actions that may mitigate weaknesses.

Strengths
Detects elements quickly, individually or as a mixture [125].
Results of analyses are available in real-time [99,125].
Simple, portable, non-destructive, in situ, economic, and comprehensive elemental analysis approach to screening [99,101,125,126].
Continuous screening of large number of items with minimal inter-sample calibration and down-time [99]; Furl, 2011).
Minimal sample preparation resulting in low analysis cost [126].
Black-dark pigment samples do not impact the detecting procedure [125].

Weaknesses	Mitigation
Can only detect elemental rather than molecular composition of the screened item [99]. This can lead to "false exceedances" of LPCL values in which the XRF measurement of Br indicates the LPCL is exceeded for the POP-BFR but the POP-BFR concentration is lower than the LPCL and the false exceedance is found to be due to the presence of elevated concentrations of one or more other brominated compounds such as TBBPA [101].	As this is an intrinsic weakness of XRF, improvement not possible
Poorly sensitive to light elements, including phosphorus (P) [71].	As this is an intrinsic weakness of XRF, improvement not possible
XRF is a surface scanning technique. The X-ray signal is highly reliant on the distance between sample, source of radiation, and detector [99].	Operators should minimize change in geometric measurements and provide the best instrument/sample contact [99]
Sample measuring time (short time) can lead to inconsistencies of XRF readings [99].	Adequate time of measurement (5–30 s) can raise XRF readings accuracy [99,127].
XRF findings can be less reliable, because of heterogeneity, particle size, and physical structure of sample surface that tend to skew the XRF findings adversely [99]; Furl, 2011).	Removing surface contamination from the scanning area [99].
X-ray penetration depth can negatively affect the XRF readings [99].	Optimizing sample thickness enhance the accuracy of XRF readings because thin sample can easily penetrate by X-ray and cause background interference from other components [127].
Challenges exist in accurately measuring elements in non-homogenous, large or coated samples because individual XRF measurements cover only a small area of a sample (Furl, 2011).	XRF readings can be affected by inhomogeneity of polymer matrices; so, two or more measurements around the material surface for average element-counts is recommended [127].
"False negatives" identified when the POP-BFR concentration exceeds the LPCL but this is not indicated by the XRF measurements of Br [101].	False negatives appear rare but actions to minimize them include making XRF measurements at multiple points to minimize the influence of heterogeneity in POP-BFR concentrations [127].
XRF measurements of elements influenced by chemical nature of polymer analysed	To maximise XRF accuracy and precision, use reference materials or matrix-matched control standards [99,100,106]. XRF precision can be assessed by repeated sample measurements [99].

was based on their data showing variable Sb:Br ratios in hard plastic articles containing recycled polymers and reports that Sb_2O_3 was used in such articles in an approximately 1:3 ratio alongside PBDEs, but was used less frequently alongside other non-regulated-BFRs used as reactive flame retardants (i.e. covalently bonded to the polymer, rather than additively (i.e. quasi-dissolved in the polymer matrix) like PBDEs) such as TBBPA [130,131].

On the other hand, false negatives could be generated by XRF when concentrations of PBDEs and HBCDD in articles exceed LPCL values but XRF fails to identify such items [101]. False negative readings would arguably be more problematic than false exceedances because the former would allow controlled FRs to be recycled into new items [9,101,110]. [101]'s study in Ireland found no false negative readings whereby the LPCL of 0.1% PBDE/HBCDD was exceeded but was not indicated by the XRF measurement of Br. In contrast to some extent [9], reported 6 out of 48 samples to be false negatives whereby concentrations of Br were below the detection limit of XRF (1 mg/kg), despite containing TBBPA at up to 150 mg/kg. Moreover, with respect to Cl and P [110], reported false negative readings for these elements in 2 of 47 samples that they attributed to issues related to sample density and texture.

To improve XRF efficiency and minimize errors, it is important to be aware that short measurement durations are likely a key factor influencing XRF accuracy [127]. Adequate testing times of up to 30 s can reduce reading errors by 4–8% [99]. In addition, XRF accuracy can be reduced by up to 4% through the inhomogeneous distribution of flame retardants in the sample. Consequently, repeat measurements at different areas of the sample surface can reduce the impact of such heterogeneity [127]. Sample thickness correction can also improve XRF accuracy since the radiation easily penetrates very thin samples leading to undesirable backscatter from substrate materials [101]. In this respect, a thickness of 12 mm has been recommended as the optimum minimum sample thickness [132].

5. Conclusions and recommendations for future studies

FRs have been detected in plastic goods that are not required to meet fire safety regulations like children's toys as well as FCAs and packaging. Substantial evidence exists that this results from the use of recycled plastics that were flame retarded before their first use.

This issue has prompted jurisdictions like the EU to introduce limits on concentrations of some FRs in waste plastics, which if exceeded, prevent such items being recycled. To date, such limits are confined to a small number of BFRs, but similar limit values for Cl-OPFRs are anticipated to follow. Effective implementation of these limit values has the capacity to largely eliminate such contaminants from the recycling stream. However, such successful implementation faces several hurdles, including the vast number of items requiring to be checked and the cost/time involved with conventional GC-LC/MS techniques. Therefore, a rapid, inexpensive, yet accurate screening technique is urgently required.

The literature to date shows that while XRF cannot accurately quantify specific Cl-OPFRs and BFRs, it is potentially a cost-effective, rapid, and effective method for identifying whether concentrations of such BFRs exceed LPCL limits. This reflects the fact that the only requirement in this context is that XRF correctly recognises whether the LPCL value is exceeded. However, more research is required to determine and eliminate the causes of false exceedances recorded by XRF with respect to compliance with limit values for BFRs. While the situation for BFRs is reasonably clear, far less research has been conducted on the suitability of XRF as a tool for checking compliance with possible limits on concentrations of Cl-OPFRs in plastics. We, therefore, identify such research as a priority. Parallel to this, studies are needed to identify the extent to which Cl-OPFRs are present in plastic articles as a result of the use of recycled materials. This is especially pressing for children's toys and FCAs.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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