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Bromine in plastic consumer products – Evidence for the widespread recycling of electronic waste

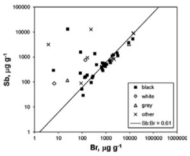
Andrew Turner [a,*], Montserrat Filella [b]

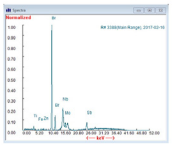
[a] School of Geography, Earth and Environmental Sciences, Plymouth University, Drake Circus, Plymouth PL4 8AA, UK
[b] Institute F.-A. Forel, University of Geneva, Boulevard Carl-Vogt 66, CH-1205 Geneva, Switzerland

HIGHLIGHTS

- XRF has been used to determine Br in 1000 plastic consumer products.
- Br was detected in 42% of electronic and 18% of non-electronic samples.
- Its presence is attributed to brominated flame retardants (BFRs).
- The results suggest that plastics from WEEE are widely recycled.
- The occurrence of BFRs in toys and food-contact items are of concern.

GRAPHICAL ABSTRACT





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ABSTRACT

A range of plastic consumer products and components thereof have been analysed by x-ray fluorescence (XRF) spectrometry in a low density mode for Br as a surrogate for brominated flame retardant (BFR) content. Bromine was detected in about 42% of 267 analyses performed on electronic (and electrical) samples and 18% of 789 analyses performed on non-electronic samples, with respective concentrations ranging from 1.8 to 171,000 μg g^{-1} and 2.6 to 28,500 μg g^{-1}. Amongst the electronic items, the highest concentrations of Br were encountered in relatively small appliances, many of which predated 2005 (e.g. a fan heater, boiler thermostat and smoke detector, and various rechargers, light bulb collars and printed circuit boards), and usually in association with Sb, a component of antimony oxide flame retardant synergists, and Pb, a heavy metal additive and contaminant. Amongst the non-electronic samples, Br concentrations were highest in items of jewellery, a coffee stirrer, a child's puzzle, a picture frame, and various clothes hangers, Christmas decorations and thermos cup lids, and were often associated with the presence of Sb and Pb. These observations, coupled with the presence of Br at concentrations below those required for flame-retardancy in a wider range of electronic and non-electronic items, are consistent with the widespread recycling of electronic plastic waste. That most Br-contaminated items were black suggests the current and recent demand for black plastics in particular is met, at least partially, through this route. Given many Br-contaminated items would evade the attention of the end-user and recycler, their disposal by conventional municipal means affords a course of BFR entry into the environment and, for food-contact items, a means of exposure to humans.

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[*] Corresponding author.
E-mail address: aturner@plymouth.ac.uk (A. Turner).

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1. Introduction

Plastic is the dominant component of waste electrical and electronic equipment (WEEE) and, having superior mechanical and thermal properties to plastics used in most other applications, is attractive for recycling. However, because a significant fraction of WEEE plastics contains brominated flame retardants (BFRs), there are constraints on how such materials are disposed of or reprocessed (Tange and Slijkhuis, 2009; Buekens and Yang, 2014). According to the 2001 Stockholm Convention and its various amendments, waste containing persistent organic pollutants (POPs) should be eliminated from the recycling stream and not intentionally diluted with compliant materials to prevent the reappearance of restricted chemicals in new products and minimise potential for release in to the environment (UNEP, 2011). BFRs classified accordingly include hexabromocyclododecane (HBCDD), hexabromobiphenyl, and the commercial polybrominated diphenyl ethers (PBDEs), penta-BDE and octa-BDE.

The discrimination between restricted and non-restricted BFRs in WEEE plastics by, for example, solvent extraction and gas chromatography, is timely and costly. Moreover, the number and variety of BFRs that have been employed in plastics means that many compounds may evade detection (Morf et al., 2005). The European Committee for Electrical Standardization (CENELEC) therefore stipulates that, in practice, waste containing (total) Br concentrations in excess of 2000 μg g^{-1} by weight should be removed and destroyed or depolluted (Stenmarck et al., 2017). Dismantling and subsequent sorting by polymer type and Br content is, nevertheless, labour-intensive, and many countries, including the US and EU, have elected to bale WEEE and ship it to China, India or Nigeria to be recycled or disposed of (Ni et al., 2013; Obaje, 2013; Haarman and Gasser, 2016).

Despite attempts to 'close the loop' on harmful BFRs, they have recently been detected in a variety of consumer products that do not require flame retardancy or at concentrations insufficient to provide fire protection, including children's toys (Ionas et al., 2015), kitchen utensils (Samsonek and Puype, 2013), beaded garlands (Miller et al., 2016) and flooring products (Votja et al., 2017). Thus, in many cases, recycled plastics from WEEE appear to have been used, in whole or in part, to manufacture contemporary electrical and non-electrical products that may not themselves be compliant.

In a recent article, we demonstrated the ubiquity of Sb amongst polymeric consumer products by means of a portable Niton x-ray fluorescence (XRF) spectrometer configured in a low density mode and with thickness correction (Turner and Filella, 2017). The metalloid was often encountered with similar or greater concentrations of Br in both electrical-electronic goods or components and non-electronic products, indicative of the presence of BFRs in association with oxides of Sb as flame retardant synergists. Here, we employ XRF spectrometry to determine total Br amongst a wider range of plastic consumer products as a proxy for evaluating the abundance and distribution of BFRs in the indoor setting. The approach has been validated by independent analytical methods and with customized, polymeric standards containing specific BFRs (Guzzonato et al., 2016), and is gaining increasing application in the WEEE recycling industry as a practical solution to accurately and rapidly monitor for material compliance with limit concentrations (Löw, 2014; Gallen et al., 2014; Aldrian et al., 2015).

2. Materials and methods

2.1. Material access, collection and categorisation

A total of 1000 items and fixtures ('samples') of moulded hard and soft plastic construction (i.e. excluding foams, paints, rubbers, waxes and textiles) were accessed or sourced from domestic dwellings in Plymouth, offices and the nursery on the Plymouth University campus, a local primary school, a number of nationwide hardware stores and supermarkets, and a variety of local establishments serving fast and/or takeaway food and beverages.

Depending on their location and principal use, samples or distinct components thereof were categorised as electronic (encompassing both electronic and electrical items) and non-electronic. The former category embraces all items dependent on electric currents or electromagnetic fields in order to work, and includes small and large household appliances, IT equipment, lighting, toys and tools. The latter, broader category was further sub-categorised as food-hygiene (food packaging, drinks bottles, cutlery, flasks, lunch boxes, cosmetics, medicine blister packs), construction-storage (plumbing, worktops, fixtures, flooring, frames, cans, cases, hangers), tools-office (stationery, DIY, adhesive taping, book covers, noticeboards), leisure (toys, games, sports gear, hobbies, crafts, Christmas decorations, trophies) or clothing-accessories (raincoats, jewellery, straps, rucksacks, shoes, spectacles, hairbrushes, buttons). For each sample, and where evident, the place of manufacture and type of plastic were recorded, along with the colour of the area(s) to be measured (sometimes revealed below a layer of paint); electronic products were also categorised as historic or non-historic according to the original WEEE Directive relating to collection, recycling and recovery targets for electrical goods (European Parliament and of the Council, 2003). While the surface or casing of most samples was investigated, some end-of-life electronic goods were dismantled and interior components analysed separately.

2.2. XRF analysis

Samples were analysed by energy-dispersive field-portable-XRF using a Niton XL3t 950 He GOLDD + that was employed either in situ and hand-held or in the laboratory and housed in a 4000 cm^3 Thermo Scientific accessory stand. The Niton XL3t employs a miniature x-ray tube that operates at up to 50 kV of high voltage and 200 μA of current as the source of sample excitation, and is fitted with a geometrically optimised large area silicon drift detector to detect characteristic x-rays from the sample. The instrument was operated in a 'plastics' mode through a standardless, fundamental parameters-based alpha coefficient correction model that is capable of simultaneously compensating for a wide variety of geometric and fluorescent effects. Because plastics are composed of light elements that are weak absorbers and relatively strong scatterers of x-rays, a thickness correction algorithm down to 50 μm that employs a compensation for mass absorption based on Compton scattering was also applied. Although a suite of elements may be determined in this mode, the present study focuses on Br as an indicator of BFR content, as well as Sb as a measure of the retardant synergistic content, Cl for the discrimination of PVC- and non-PVC-based materials, and Pb as a hazardous heavy metal that is often encountered as an additive or contaminant in WEEE and consumer plastics (Wäger et al., 2012).

In practice, sample thickness was determined through the flattest or smoothest (measurement) surface using 300 mm Allendale digital callipers, and to increase the effective depth and flatness of thin or hollow samples analysed in the accessory stand, items were cut (with scissors, pliers or a blade), folded or layered. The corrective algorithm was employed for all samples whose measured thickness was <20 mm, while an estimated value was applied to objects and components whose interiors were inaccessible or that were fixed to or components of walls, floors, windows, doors and appliances.

In the laboratory, samples were placed on the stainless steel base plate of the accessory stand with the measurement surface above the XRF detector window or, for samples smaller than the 10 mm window diameter, on to a SpectraCertified Mylar polyester 3.6 m film that was carefully suspended above. On closing the stand shield, measurements with appropriate thickness correction and collimation (3 mm or 8 mm beam width) were activated through the laptop. Specifically, an initial, ~2-s matrix evaluation based on the measurement of characteristic chlorine peaks (and defining PVC as $Cl > 15\%$ by weight) was succeeded by counting periods equally distributed between a low energy range