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**Field-portable-XRF reveals the ubiquity of antimony
in plastic consumer products**

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Abstract

Very little systematic information exists on the occurrence and concentrations of antimony (Sb) in consumer products. In this study, a Niton XL3t field portable-x-ray fluorescence (FP-XRF) spectrometer was deployed in situ and in the laboratory to provide quantitative information on Sb dissipated in plastic items and fixtures (including rubber, textile and foamed materials) from the domestic, school, vehicular and office settings. The metalloid was detected in 18% of over 750 products analysed, with concentrations ranging from about 60 to 60,000 $\mu\text{g g}^{-1}$. The highest concentrations were encountered in white, electronic casings and in association with similar concentrations of Br, consistent with the use of antimony oxides (e.g. Sb_2O_3) as synergistic flame retardants. Concentrations above 1000 $\mu\text{g g}^{-1}$, and with or without Br, were also encountered in paints, piping and hosing, adhesives, whiteboards, Christmas decorations, Lego blocks, document carriers, garden furniture, upholstered products and interior panels of private motor vehicles. Lower concentrations of Sb were encountered in a wide variety of items but its presence (without Br) in food tray packaging, single-use drinks bottles, straws and small toys were of greatest concern from a human health perspective. These observations are consistent with the use of antimony compounds as catalysts in the production of polyethylene terephthalate but also suggest that electronic casings are widely recycled for the manufacture of a variety of consumer products. Further research is required into the mobility of Sb when dissipated in new, recycled and aged polymeric materials.

Keywords: FP-XRF; antimony; household; plastics; bromine; recycling

1. Introduction

One of the main features of the current use of chemical elements is their application in materials at small concentrations by weight but in a large variety of products. This results in ubiquity in the environment but strongly hinders the ready and routine determination of their presence. Measuring and monitoring trace elements in final products is necessary for different reasons, ranging from assessing their potential toxicological and ecotoxicological effects to an evaluation of in-use stocks for life-cycle assessments.

In this context, antimony (Sb) is a particularly interesting element for two reasons. Firstly, its use increased significantly in the first decade of the present century (total antimony consumption grew by about 40% and from 147,000 to 206,000 tonnes between 2000 and 2011; USGS, 2016) and, although global production has receded slightly since 2011, it is predicted to increase from 2015 to 2020 (Dupont et al., 2016). Secondly, the type of use of Sb has shifted from applications where it can be recovered (e.g., as an additive in lead alloys) to those where recycling is not possible because of its dissipation in the product (e.g., as a catalyst in polyethylene terephthalate (PET) manufacturing and as a synergistic flame retardant) (Zimmermann and Gößling-Reisemann, 2013; Talens Peiró et al., 2013; Ciacci et al., 2015). At present, Sb use as a catalyst and flame retardant accounts for about 60% of its total production while applications in metallurgy account for about 35% (Schwarz-Schampera, 2014).

Despite the cumulative toxicity of Sb and its similarity with As in many biological respects, the element was rather poorly studied until the mid-1990's. Specifically, a

possible link between sudden infant death syndrome (SIDS) and volatile antimony hydride generated via the biomethylation of antimony trioxide (Sb_2O_3) used as a flame retardant in cot mattress covers triggered a strong interest in the metalloid (Richardson, 1990, 1994). More recently, scientific and media attention has been diverted to the presence of measurable concentrations of antimony in bottled water (Shotyk et al., 2006; Westerhoff et al., 2008), fruit juices (Hansen et al., 2006) and ready-meals (Haldimann et al., 2013) arising from the leaching of Sb from PET containers. PET is a highly favourable and widely used material for food and drink packaging and oven-proof and reheatable meals because of its thermal and physical stability, low density and recyclability (Chapa-Martinez et al., 2016).

Given the properties and applications of Sb, there are reasons to suspect that the presence of the element in our daily lives may be more widespread than is implied from current or past research. However, outside of the grey literature, systematic, quantitative information on the occurrence of Sb in the domestic and consumer setting appears to be limited to a few measurements performed on PET bottles (Chapa-Martinez et al., 2016) and other food-contact polymers (Puype et al., 2015), toys (Korfali et al., 2013) and end-of-life televisions (Saphores and Milovantseva, 2011). To this end, we describe the use of field-portable-x-ray fluorescence (FP-XRF) spectrometry to determine the presence, distribution and concentrations of Sb in products from the indoor environment. The focus is on synthetic, polymeric materials (plastics), where the element is most likely to be present as a catalyst or added as a flame retardant, that are encountered in the household, office, school and vehicular environments. Simultaneous measurements of Br and Cl are also performed in order

to determine the type of materials and flame retardants that Sb is associated with in different products.

2. Materials and methods

2.1. Material access, collection and categorisation

Antimony considered in the present study was bound to moulded plastics, rubbers, textiles, foams, fibres and waxes, or incorporated into paints and coatings applied to various products, structures and surfaces. A total of 750 items and fixtures (‘samples’) were accessed or sourced from a variety of domestic dwellings in Plymouth, three private vehicles registered between 2004 and 2016, offices around the Plymouth University campus, a local primary school and nursery, and a hardware chain store.

Depending on their location and principal use, samples were categorised according to the list given in Table 1. However, it must be appreciated that several of the categories are not mutually exclusive (for example, electronic toys, constructed versus upholstered flooring, storage for food and for sports equipment) and that some samples comprised distinct components that were analysed and categorised separately. While the surface or coating of most samples was targeted, occasional end-of-life electronic products were dismantled and interior components analysed individually.

2.2. XRF analysis

Samples were analysed energy-dispersive FP-XRF using a Niton XL3t 950 He GOLDD+ that was employed handheld and in situ or configured in the laboratory in an accessory-stand. The Niton XL3t employs a miniature x-ray tube with a silver

transmission anode that operates at up to 50 kV of high voltage and 200 μ A of current as the source of sample excitation, and is fitted with a geometrically optimised large area silicon drift detector to detect fluorescent x-rays from the sample. The concentrations of Sb, based on characteristic peaks at 26.359 KeV ($K\alpha$) and 3.604 KeV ($L\alpha$) (Figure 1), were determined in a ‘plastics’ mode through a standardless, fundamental parameters-based alpha coefficient correction model. This iterative approach accounts for background matrix effects by describing characteristic x-ray intensities using mathematical equations that tie together the physics of the interaction of x-rays with sample components, and has a wide dynamic range that is independent of the size and shape of the surface (Bosco, 2013). Concentrations of Br and Cl were also recorded during sample analyses, as indicators of the presence of halogenated flame retardants and polymer chlorination (and polyvinyl chloride, PVC).

Because plastics are composed of light elements that are weak absorbers and relatively strong scatterers of x-rays, below a critical thickness the measured intensity of characteristic x-rays will be dependent on both the analyte concentration and the depth of the sample. For polyethylene, for example, the critical thickness is about 9 mm while for PVC the presence of chlorine results in a corresponding thickness of around 5 mm; for polymers containing heavier elements, including Sb and Br, critical thickness depth is reduced compared with that of the pure material. In the plastics mode, the Niton XL3t incorporates a thickness correction algorithm down to 50 μ m that employs a compensation for mass absorption based on Compton scatter so that variations in density are factored in. Although the corrective algorithm is embedded in the fundamental parameters code and inaccessible to the user, it has been empirically

defined for various elements (including Sb, Br and Cl) in a variety of plastics elsewhere (Turner and Solman, 2016).

In the present study, 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 less than 30 mm, while an estimated value was applied to all objects and components whose interiors were inaccessible or that were fixed to or components of walls, floors, windows, doors and appliances. A thickness of 0.05 mm was assumed when analysing painted surfaces or paints and cosmetics that had been applied to and oven-dried on glass slides.

In the laboratory, the XRF was used in a collapsible bench-top accessory stand (Thermo Scientific SmartStand, with internal dimensions of 20 cm x 20 cm x 10 cm; PN 420-017) and was connected to a laptop computer via USB and a remote trigger. Samples were placed on the stainless steel base plate of the accessory stand above the detector window or, for samples smaller than the 8 mm window diameter, on to a SpectraCertified Mylar polyester 3.6 μm film that was carefully positioned centrally above the window. On closing the shield of the stand, measurements with appropriate thickness correction and collimation (3 mm or 8 mm beam width) were activated through the laptop. Specifically, an initial, ~ 2-second matrix evaluation based on the measurement of characteristic chlorine peaks (and defining PVC as Cl > 15% by weight) was succeeded by an analysis time of between 60 and 200 seconds,

comprising counting periods equally distributed between a low energy range (20 kV and 100 μ A) and main energy range (50 kV and 40 μ A). Spectra were quantified by fundamental parameter coefficients to yield elemental concentrations on a dry weight basis (in μ g g⁻¹) and with a counting error of 2 σ (95% confidence). Polyethylene reference discs supplied by the manufacturer and certified for Sb (PN 180-619, LOT#T-18) and Br (PN 180-554, batch SN PE-071-N) were analysed at the beginning and end of each 1-4 h sample measurement session, and spectra and elemental concentrations arising from each session were subsequently downloaded to the laptop using Niton data transfer (NDT) PC software.

For in situ measurements of permanent fixtures and objects too large to be contained by the laboratory accessory stand, the XRF was used handheld and in situ. Here, the nose was pressed firmly against the measurement surface, ensuring that the detector window was completely covered and that there was sufficient shielding and/or distance behind. The instrument was activated by the operator using the trigger mechanism and the touch-screen control panel, and where possible a Thermo Scientific backscatter collar shield was clipped on to the nose of the instrument. The shield consists of tungsten-impregnated PVC that extends and tapers outwardly from the propagation axis to a radius of about 10 cm and, while designed to lie proximate to the material being inspected, has some degree of flexibility to conform to the contours of irregularly-shaped surfaces. As above, reference discs were analysed at the beginning and end of each measurement session while placed on a solid surface and data were subsequently downloaded to the laptop via the NDT software.

2.3. Sample digestion and analysis by ICP

In order to validate the XRF approach, an independent measure of the Sb content of synthetic, polymeric materials was performed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) following digestion in Fisher Scientific TraceMetal grade acids. Specifically, 50 to 100 mg offcuts or slices of 14 samples of varying characteristics (in terms of colour, use-origin, thickness, density and Sb content as retuned by the FP-XRF) were prepared with a stainless steel blade and a pair of pliers before being accurately weighed into individual 100 ml borosilicate Tecator tubes. Three ml of concentrated sulphuric acid was added to each tube and the contents heated to 300°C for 2 h in an aluminium digestion block before concentrated HNO₃ was added dropwise until solutions became pale yellow or colourless. Digests were then allowed to cool overnight before being transferred to 50 ml glass volumetric flasks and diluted with 2% HNO₃. To any digests containing a visible precipitate, concentrated ammonia solution was added dropwise until the solids cleared. Procedural controls were undertaken in triplicate likewise but in the absence of solid material.

Digests were analysed for Sb at a peak emission wavelength of 206.833 nm by ICP-OES using a Thermo Scientific iCAP 7400. The instrument was calibrated using four standards and a blank prepared by serial dilution of a CPI International standard in 2% HNO₃, with settings as follows: exposure time = 2 s; RF power = 1150 W; nebuliser, coolant and auxiliary gas flows = 0.50, 12 and 0.5 L min⁻¹, respectively; viewing height = 12 mm; uptake time = 50 s; wash time = 15 s.

3. Results

3.1. Detection limits

The limits of detection (LODs) of FP-XRF spectrometers are dependent on the response of specific elements to primary x-rays and the energies of their characteristic x-rays, detector resolution, mode of application (or current, peak voltage and beam filtration), counting time, sample thickness, and physical and chemical characteristics of the material. The Niton XLT3t series of analysers define LODs from counting errors as three standard deviations ($1.5 \times 2\sigma$, or 99.7% confidence interval), and concentrations are delivered in the NDT output only where they exceed this threshold with calculated detection limits returned otherwise. LODs stated by the manufacturer for Sb in pure polyethylene and in PVC (both of unspecified thickness) and for a 30-second total counting time configured in plastics mode are $22 \mu\text{g g}^{-1}$ and $25 \mu\text{g g}^{-1}$, respectively; the respective LODs for Br are $3 \mu\text{g g}^{-1}$ and $8 \mu\text{g g}^{-1}$, and for Cl in polyethylene the LOD is $40 \mu\text{g g}^{-1}$.

Under the operating conditions of the instrument described above, LODs for Sb were highly variable, reflecting the diverse and complex nature of the samples. Respective minimum and maximum LODs were about $19 \mu\text{g g}^{-1}$ and $400 \mu\text{g g}^{-1}$, with increasing values generally related to decreasing thickness and counting time. By comparison, LODs for Br and Cl ranged from about $3 \mu\text{g g}^{-1}$ to $50 \mu\text{g g}^{-1}$ and about $45 \mu\text{g g}^{-1}$ to $200 \mu\text{g g}^{-1}$, respectively.

3.2. Accuracy and precision

Table 2 shows the results of multiple analyses of the two reference discs manufactured by Niton. Regarding the disc impregnated with Sb, concentrations measured by the XRF both in the accessory stand and handheld are close to the certified concentration, with marginally better accuracy and precision achieved when

the instrument was employed in the stand. With respect to the disc impregnated with Br, mean measured concentrations are within the 95% confidence interval of certified values, with a marginally lower accuracy but greater precision achieved in the stand. Multiple analyses of various samples revealed precisions for Sb and Br that improved with absolute concentration and thickness but that were always better than 20% (as relative standard deviation) in both types of instrument application.

A comparison of the concentrations of Sb in various samples of plastic, paint and foam returned by FP-XRF and by ICP-OES following acid digestion is shown in Figure 2. (Note that in the six cases where Sb was not detected by the XRF, ICP measurements did not exceed the corresponding LOD of the XRF.) The best fit line forced through the origin reveals a gradient of 1.3, indicating that, on average, the XRF returns a concentration of Sb that is about 30% higher than that delivered by the ICP. The discrepancy may be attributed to spatial heterogeneity of Sb within samples (XRF will determine elemental concentrations at a specific location while ICP relies on digestion and analysis of whole sections), incomplete acid digestion or partial loss of volatile Sb compounds in some samples, and, with respect to XRF, inaccuracies in thickness estimation and spectral interferences arising from material below or within the target surface. Regardless of the causes of such a discrepancy, however, the statistically significant proportionality between Sb concentrations returned by the FP-XRF and those delivered by an independent method, coupled with a correlation coefficient exceeding 0.9, meet the definitive level criterion according to US EPA validation guidelines (Environmental Protection Agency, 2007).

3.3. Occurrence and distribution of Sb

Table 3 provides a summary of the number of XRF analyses performed in each sample category. Also shown is the number of cases in which Sb was detected, along with the number of cases in which Sb was encountered in PVC or co-associated with either Br or (non-PVC-based) Cl or with both Br and Cl. Overall, Sb was detected in 150 cases, or in about 18% of all analyses, and relative abundance was greatest in vehicle interiors (37%) and lowest in the cleaning-storage category (8%). Its occurrence in PVC was greatest in vehicle interiors and in electronic casings or components, with no Sb detected in PVC products in the food-drink, toys-hobbies or office-stationery categories. Association with Br was most frequent on both a number and percentage basis in the electronics category while no co-existence was detected in the food-drink category. Association of Sb with Cl occurred in fewer cases overall but across all sample categories, while association with both Br and Cl was observed in only 17 samples among six categories.

The distribution and summary statistics for Sb concentrations among the different categories are shown in Table 4, while figure 3 illustrates some of the specific products in which the XRF returned concentrations of the metalloid. Electronic samples exhibited the highest mean and median concentrations and a concentration range that spanned nearly three orders of magnitude. The highest individual concentrations of about 50,000 $\mu\text{g g}^{-1}$ were encountered in a variety of white products, including a multi-plug adaptor, telephone-modem connector, fan heater, central heating thermostat and a number of collars around connectors of long-life light bulbs. All of these items were associated with concentrations of Br that were in excess of but less than double the respective concentrations of Sb, but none of the items was PVC-based and only one contained detectable Cl. Other products containing Sb at

concentrations in excess of 10,000 $\mu\text{g g}^{-1}$ included a number of plugs and television casings, a printed circuit board, several PVC wire insulators and a USB-connector cover. These products did not always contain measurable Br and were a variety of colours, but principally black or white. Items that contained concentrations of Br in excess of 10,000 $\mu\text{g g}^{-1}$ but no measurable Sb included a games consol, several printed circuit boards, remote controls and extension leads, and components of various computer mice.

In the food-drink category, measurable concentrations of Sb, ranging from about 200 to 900 $\mu\text{g g}^{-1}$, were encountered in packaging trays for vegetables, confectionary, fish and ready meals, and in straws, single-use drink bottles and a cool bag. While Br was not detected in these products, Cl often occurred at concentrations lower than corresponding levels of Sb.

With a mean Sb concentration of about 1600 $\mu\text{g g}^{-1}$ and a concentration range spanning two orders of magnitude, Sb was detected in a wide variety of products from the clothing-upholstery category. The highest concentrations (of several thousand $\mu\text{g g}^{-1}$) were encountered in combination with similar or higher corresponding concentrations of both Br and Cl in a futon cover and in cushioning from a garden chair and dressing table stool. Items of clothing in which Sb was detected at several hundred $\mu\text{g g}^{-1}$ included a safety jacket, raincoats, sports shirts and items of fancy dress, most of which contained similar concentrations of either Br or Cl and one of which was PVC-based.

Antimony was detected in three products classified as cleaning-storage and with a mean concentration of $355 \mu\text{g g}^{-1}$; specifically, a watering can, a PVC door-stop and, in association with both Br and Cl, a luggage tag. In the construction-plumbing category, mean, minimum and maximum concentrations of Sb were about 1600, 100 and $13,000 \mu\text{g g}^{-1}$, respectively. The majority of cases and the highest concentrations were associated with plumbing (PVC-hosing, radiator caps, piping and pipe insulation), although Sb was also detected in wall and door paints, PVC-flooring and a window frame. In most products in this category, either Br or Cl was also detected at concentrations similar to corresponding Sb concentrations. With respect to toys-hobbies, Sb was detected with a mean and range of concentrations similar to respective values for the construction-plumbing category, with concentrations of several thousand $\mu\text{g g}^{-1}$ encountered in Christmas beads, artists' paints and contemporary Lego bricks. Co-association with similar concentrations of Br was found in various Christmas decorations and a toy car and with variable levels of Cl in a variety of products that included 35 mm negative slides, soft toys, game counters and the plastic sleepers of an electric railway track.

The office-stationery and leisure-sport categories exhibited similar occurrences and concentration distributions of Sb, with mean values of around $800 \mu\text{g g}^{-1}$ and ranges from about 100 to $2500 \mu\text{g g}^{-1}$. Among items with the highest concentrations recorded were a foot pump, the seating of an exercise bike and the plastic top of a trophy, all of which contained Br at concentrations exceeding those of Sb, and, in the absence of Br (and Cl), PVC adhesive taping, two whiteboards and a document carrier.

Regarding vehicle interiors, the mean concentration of Sb was about 1700 $\mu\text{g g}^{-1}$, with a concentration range that spanned two orders of magnitude. Concentrations greater than 1000 $\mu\text{g g}^{-1}$ were measured in panels, armrests and seats that were non-PVC-based, but Br and Cl were only detected in two cases each (and at concentrations exceeding the corresponding Sb concentrations). Where Br was detected in the absence of measurable Sb, however, concentrations were always less than 10 $\mu\text{g g}^{-1}$.

4. Discussion

This study has revealed the presence of Sb in a wide range of polymeric products and components from the indoor environment. The highest concentrations, and exceeding 1% by weight, are largely restricted to electronic casings, and an association with Br or Cl is consistent with use of Sb as a synergistic, free radical-quenching flame retardant in the presence of halogenated compounds (including PVC, which itself exhibits inherent flame retardant properties). The majority of the highest concentrations of Sb in non-electronic samples were encountered in upholstered products or fixtures in the home and vehicular environments, and, as above, their association with Br or Cl is consistent with the use of Sb as a flame retardant synergist in soft furnishings.

Where Sb occurs at concentrations below 1000 $\mu\text{g g}^{-1}$ and without Br or Cl, the metalloid is most likely present as catalytic residue from the manufacture of PET (typical concentrations of Sb in the polyester are a few hundred $\mu\text{g g}^{-1}$; Bach et al., 2012). Most single-use food and drink items containing Sb were labelled as PET, and we suspect that this polymer has widespread use across all sample categories considered. Where Sb is encountered at concentrations of several thousand $\mu\text{g g}^{-1}$ (i.e.

exceeding levels in PET products) and in the absence of Br or Cl, it is possible that the metalloid is used as a pigment for plastics and paints. For example, the occurrence of Sb in white wall paints and whiteboards is consistent with the use of Sb_2O_3 as a moderately opaque white pigment (Abel, 2000), while its occurrence in red products may reflect the use of one or more antimony sulphide compounds (Eastaugh et al., 2008).

In a diversity of samples, including game mats, soft toys, rucksacks, ink cartridges, football shirts, safety jackets, insulating foam, currency and picture frames, concentrations of Sb of a few hundred $\mu\text{g g}^{-1}$ occurred in combination with similar concentrations of Br or Cl. A recent study by Puype et al. (2015) has also reported comparable concentrations of both Sb and Br in a number of black, polymeric food-contact articles purchased on the European market. Since concentrations of both elements are too low to offer adequate flame retardancy, it would appear that many polymeric household items that have no reason to be fire-resistant are constructed, at least in part, from end-of-life electronic products.

Critical to the human health risks posed by Sb encountered in polymeric materials are the extents of mobilisation of the metalloid from the matrix. Regarding non-occupational dermal exposure, so little is known that the National Research Council (2000) assumed that ionised antimony trioxide permeates the skin at the same rate as water, ($10^{-3} \text{ cm h}^{-1}$). A maximum dermal exposure level of $20 \mu\text{g kg}^{-1} \text{ d}^{-1}$ was then derived for an individual spending 25% of their time on Sb-treated upholstered furniture. Of more general significance for human Sb exposure, however, is the leachability of the metalloid from both food contact products and toys. In water and

juices bottled in PET containers, leaching of Sb has been shown to be a function of time, temperature, pH and insolation. Resulting aqueous concentrations are typically well below admissible levels for the European Union ($5 \mu\text{g L}^{-1}$) and the US EPA ($6 \mu\text{g L}^{-1}$) (Hansen and Pergantis, 2006; Shotyk et al., 2006; Greifenstein et al., 2013; Chapa-Martinez et al., 2016) but are closer to a $1 \mu\text{g L}^{-1}$ limit recently updated as a Public Health Goal (PHG) for Californian drinking water (Qiao, 2016). Mobilisation of Sb into pre-packaged food from PET trays heated by microwave and oven has also been documented, with quantities of the metalloid in cooked meals of up to about $35 \mu\text{g}$ (Haldimann et al., 2007). Although higher than quantities of Sb in many litres of bottled water, consumption of several of the most contaminated ready meals by an individual would still be below tolerable daily intake limits for the element ($360 \mu\text{g}$ for an adult of 60 kg) (WHO, 2003).

Antimony is one of eight elements for which migratable limits, based on extractability in dilute HCl (pH 1.8) at 37°C for two hours, exist in toys and other objects mouthable by young children (e.g. pens and crayons). The original European toy safety standard on the migration of certain elements (EN71-3: 1994 or BS EN71-3: 1995; British Standards Institution, 2006) defined a limit for Sb of $60 \mu\text{g g}^{-1}$, a value that was subsequently adopted as a maximum soluble concentration by the US Consumer Product Safety Commission (Cobb, 2015). Under this classification, products analysed by XRF and returning a concentration of Sb exceeding the threshold would require subsequent extraction in HCl in order to evaluate migratability. More recently, however, a revised version of the European standard (EN71-3: 2009) outlines migratable limits that are dependent on the characteristics of the material. Thus, $45 \mu\text{g g}^{-1}$ is adopted for brittle or pliable items, $11.3 \mu\text{g g}^{-1}$ for liquid or sticky products and

560 $\mu\text{g g}^{-1}$ for scraped off materials, including paints and plastics (European Parliament and the Council of the European Union, 2009). In the present study, all samples in the toys-hobbies categories in which Sb was detected by XRF ($n = 24$) were in the latter European material classification, with concentrations exceeding 60 $\mu\text{g g}^{-1}$ in all cases and exceeding 560 $\mu\text{g g}^{-1}$ in 13 samples. Although the migratability of Sb was not determined in these samples, Ciu et al. (2015) provide a mean HCl-extraction of Sb from various newly purchased toys and jewellery of 13.4%. Applying this figure to the current results, two samples (red and gold Christmas beads) would exceed the current European limit for migratable Sb in plastic products.

From an environmental perspective, Sb is a concern because of its potential mobilisation from polymeric waste items that are disposed of by landfill or incineration or that are dismantled-recycled. Although regulations exist in Europe limiting air-stack emissions of Sb (2000/76/EC; European Parliament and the Council of the European Union, 2000) and concentrations of leachable Sb in inert waste acceptable as landfill (Council of the European Union, 2003a), there does not appear to be an unawareness of the ubiquity of Sb in everyday items that the present study has highlighted. The high proportion of Sb in current use as a flame retardant synergist in electronic products and components should ensure that a significant fraction of waste containing Sb is reused, recycled or recovered in accordance with the requirements of the European Waste Electrical and Electronic Equipment (WEEE) Directive (2002/96/EC; European Parliament and the Council of the European Union, 2003). However, unlike many other heavy metals and flame retardants, Sb was not included in the original Restriction of Hazardous Substances (RoHS) Directive (2002/95/EC; Council of the European Union, 2003b) that limits use in electrical and

electronic equipment. Moreover, according to a subsequent investigation into substances not regulated by the RoHS Directive, it was concluded that, despite concerns about potential impacts on the marine environment and on sediment from flame-retardant back-coated products, the limited data available on Sb precluded justification for its inclusion (Groß et al., 2008). A consequence of this is that when electronic plastic waste is recycled, there is no consideration of the subsequent use and fate of Sb dissipated within the polymeric matrix.

5. Conclusions

FP-XRF has revealed that Sb is encountered in a wide range of polymeric consumer products in the household, school, vehicular and office settings, principally as either a catalyst in the production of PET or a synergistic flame retardant with halogenated compounds. In association with Br, concentrations are highest and a few percent on a weight basis in plastic electronic casings, but from a health perspective, the presence of lower quantities of catalytic Sb in food packaging and small toys is of greatest concern. Aside from these sources, it appears that an increasing, indirect source of the metalloid is related to the recycling of electronic plastic casings and housings. Further research into the toxicity of Sb and its mobility when dissipated in the polymeric matrix is required, while reconsideration of the means of disposal and recycling of Sb-rich electronic plastic waste is called for.

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Table 1: Categorisation of the items and fixtures considered in the present study.

electronics	food-drink	clothing-upholstery	cleaning-storage	construction-plumbing	toys-hobbies	office-stationery	leisure-sport	vehicle interiors
fridges, freezers laptops, keyboards radios televisions, screens cables alarms plugs, adaptors phones cameras chargers hairdryers, irons light switches light bulbs headphones	packaging utensils plates mugs bottles ice packs straws lunch boxes trays tablet strips coffee pods	clothing sofas, cushions carpets, rugs shoes, boots rucksacks handbags wallets table cloths mattresses, pillows curtains	cans, canisters drawers bottles, tubes, lids polystyrene bags, sacks buckets boxes cartridges tools pegs paints brushes suitcases coathangers	doors, windows vinyl flooring drainage pipes hosing insulating foam baths and showers coving construction board worktops panels painted walls	figures cars, trains games, puzzles bath toys book covers fake jewellery building blocks musical instruments book covers pens, paints, crayons marbles, counters	pens adhesives document cases office equipment marker boards printing equipment lanyards stands, trays packaging	exercise bikes balls racquets, bats garden furniture cycle helmets tape trophies sports bags bike accessories bodyboards cosmetics sunglasses currency, cards CDs, DVDs	dashboards panels radios steering wheels seats, belts armrests flooring visors roof upholstery footplates chargers toll tags mats

Table 2: A comparison of reference and measured concentrations ($\mu\text{g g}^{-1}$) of Sb and Br in polyethylene discs of 31 mm diameter and 13 mm depth supplied by Niton. Note that reference concentrations are given with estimates of errors at the 95% confidence level arising from an unspecified number of analyses while measured concentrations are shown as the mean with one standard deviation ($n = 20$).

Reference disc	reference concentration	measured concentration in stand	measured concentration handheld
Sb (PN 180-619)	94 ± 10	93 ± 11	91 ± 16
Br (PN 180-554)	495 ± 20	500 ± 30	511 ± 19

Table 3: Number of analyses performed on samples from each category, and the number of cases in which PVC, Sb, Br and (non-PVC) Cl were detected together with the number of cases in which Sb was detected in PVC, and with Br or Cl and with Br and Cl.

	analyses	PVC	Sb	Br	Cl	Sb-PVC	Sb-Br	Sb-Cl	Sb-Br-Cl
electronics	194	16	47	75	59	8	32	10	5
food-drink	108	2	14	6	36	0	0	7	0
clothing-upholstery	76	10	14	18	28	1	8	8	4
cleaning-storage	44	3	3	2	12	1	1	3	1
construction-plumbing	56	15	14	11	8	2	6	4	0
toys-hobbies	162	12	24	14	74	0	7	16	4
office-stationery	55	7	9	9	14	0	2	2	1
leisure-sport	85	13	11	13	22	1	6	3	2
vehicle interiors	38	5	14	9	13	3	4	2	0
total	818	83	150	157	266	16	66	55	17

Table 4: Summary statistics and distributions of Sb concentrations (in $\mu\text{g g}^{-1}$) detected in the different sample categories.

	$< 10^2$	$10^2\text{-}10^3$	$10^3\text{-}10^4$	$>10^4$	mean	median	min.	max.
electronics	2	16	14	15	12,300	2620	80	58,900
food-drink	0	14	0	0	410	369	179	893
clothing-upholstery	1	10	3	0	1570	317	90	9922
cleaning-storage	0	3	0	0	355	342	229	495
construction-plumbing	0	11	2	1	1560	407	103	13,000
toys-hobbies	1	17	6	0	1490	571	72	9190
office-stationery	0	6	3	0	855	319	119	2720
leisure-sport	0	7	4	0	775	494	122	2470
vehicle interiors	1	6	7	0	1710	975	61	6020
total	5	90	39	16	4710	559	61	58,900

Figure 1: The spectrum generated by the NDT software for red Christmas beads, illustrating the principal peaks for Sb and Br below 30 keV.

Figure 2: A comparison of the concentrations of Sb in various samples as returned by the FP-XRF and by ICP-OES following acid digestion. Annotated are the best fit line through the data and statistical parameters defining the relationship.