Screening of brominated and chlorinated additives in plastic pellets

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Stockholm Convention on Persistent Organic Pollutants (POPs)

	2001	COP4 2009	COP5 2011	COP6 2013	COP7 2015	COP8 2017	COP9 2019	COP10 2022	COP11 2023
Pesticides	Aldrin, Chlordane, DDT, Dieldrin, Endrin, Heptachlor, Mirex, Toxaphene	Chlordecone, HCH, lindane	Endosulfan		PCP		Dicofol		Methoxychlor
Fluorinated compounds		PFOS PFOSF					PFOA	PFHxS	
Brominated flame retardants		HBB POP-BDEs		HBCD		DecaBDE			
Chlorinated compounds	HCB PCB	PeCB			HCBD PCN PCP	SCCP			Dechlorane Plus
UV stabilizer									UV-328
Unintentional POPs	HCB PCB PCDD/DF	PeCB			PCN	HCBD			

Most of the newly added POPs for global elimination are plastic additives

Brominated additives

Chlorinated additives

POPs Used as Plastic Additives

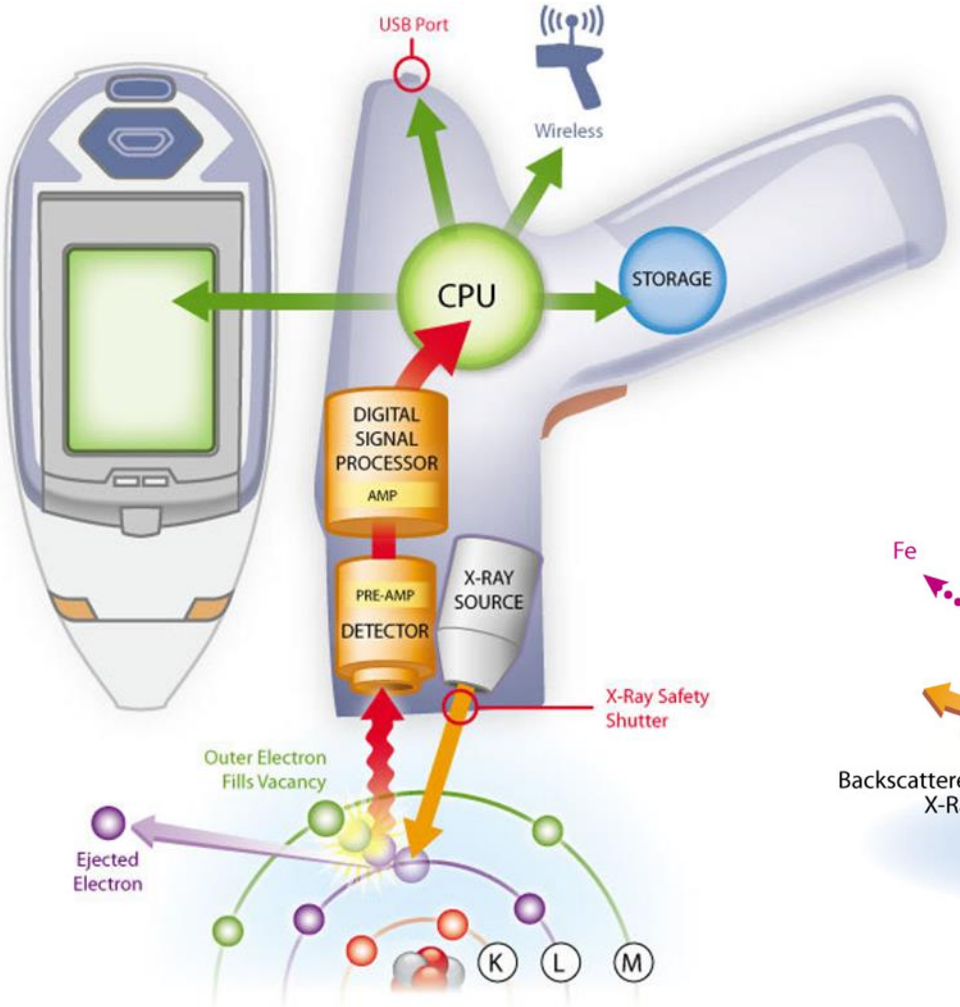
	Main use	Listing year to the Stockholm Convention	Contents added to products	Low POP content for waste under the Basel Convention
PentaBDE	Polyurethane foam, printed circuit board	2009 (tetra- to heptaBDEs)	Up to 40% by weight (1% = 10,000 mg/kg)	[50 mg/kg] or [500 mg/kg] or [1,000 mg/kg] as a sum
OctaBDE	Electronic casing			
DecaBDE	Electronic casing, textile coating, building insulation	2017 (decaBDE)		
HBCD	Textile, building insulation	2013	Up to 5% by weight in textile, ~0.5% in EPS, ~5% in XPS	100 mg/kg [or 500 mg/kg] or 1,000 mg/kg
SCCP	PVC, rubber, lubricant, *etc*.	2017	Up to 20% by weight	[100 mg/kg] or [1,500 mg/kg] or [10,000 mg/kg]
Dechlorane Plus	EEE, vehicles, building materials, *etc.*	2023	Up to 40% by weight	TBD

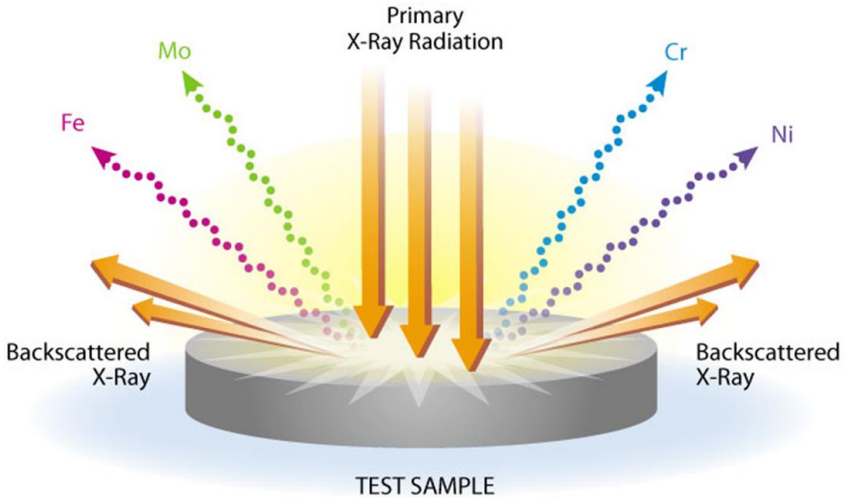
➔ Br or Cl contents as indicators of the presence of POPs in plastic

➔ Quick screening of Br and Cl by using a handheld X-ray fluorescence (XRF) analyzer

XRF screening of bromine (Br) and chlorine (Cl) contents

How Does XRF Work?





Notes on XRF Measurements

1. The sample should completely cover the measurement window.
2. The sample should be homogeneous.
3. The sample should be thick enough that additional material will not affect the result. For plastic samples, the thickness should at least 1.5 cm. Or the area to be measured should not be in contact with any other materials.
4. XRF analysis is limited to the detection of elements including Br and Cl in the test samples, without any capacity to identify the type of additives.

a non-destructive method

5 cm

5 cm

Validations of Element Contents (mg/kg) in Polymer Reference Samples by a Handheld XRF

	PE-Low		PE-High		PVC-Low		PVC-High	
Element	Certified value	Analytical value*	Certified value	Analytical value*	Certified value	Analytical value*	Certified value	Analytical value*
Cr	399	400	1,000	1,100	400	300	1,000	1,100
Br	499	500	1,100	1,000	500	400	1,100	1,000
Cd	101	<LOD	300	200	100	100	300	300
Hg	200	100	1,099	800	200	100	1,200	700
Pb	399	300	1,199	900	400	300	1,200	900

* Concentrations obtained by the handheld XRF analysis

PE: Polyethylene; PVC: Polyvinylchloride

XRF Instrument

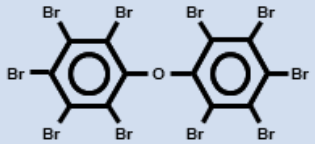
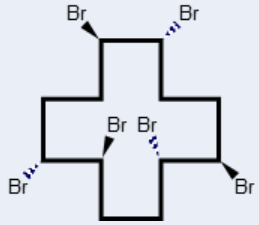
Innov-X Systems alpha6500

RoHS/WEEE mode

Analytical time: 30 sec

Kajiwara *et al* (2011) *J. Environ. Chem*. 21, 13–20.

Br Contents in BDE 209 and HBCD

	Molecular structure	Molecular formula	Molecular weight (g/mol)	Br content
BDE 209 (Decabromodiphenyl ether)		$C_{12}Br_{10}O$	959.2	83% = (79.9 x 10 / 959.2) x 100
HBCD (Hexabromocyclododecane)		$C_{12}H_{18}Br_6$	641.7	75% = (79.9 x 6 / 641.7) x 100

➔ For example, if the Br concentration measured by XRF was 1,000 mg/kg by weight, all derived from BDE 209 or HBCD, it corresponds to 1,200 mg/kg of BDE 209 and 1,300 mg/kg of HBCD, respectively.

➔ Conversely, for example, to ensure that PBDE and HBCD concentrations are below 1,000 mg/kg, Br concentrations should be below 830 mg/kg and 750 mg/kg, respectively.

Major Brominated Flame Retardants other than PBDE and HBCD

- Tetrabromobisphenol A (TBBPA) (CAS no. 79-94-7)
- Brominated bisphenol-A type epoxy resin (CAS no. 68928-70-1)
- TBBPA carbonate oligomer (CAS no. 71342-77-3)
- TBBPA bis(dibromopropyl ether) (CAS no. 21850-44-2)
- TBBPA-bis-(allyl ether) (CAS no. 25327-89-3)
- 1,2-Bis(2,3,4,5,6-pentabromophenyl)ethane (DBDPE) (CAS no. 84852-53-9)
- 1,2-Bis(2,4,6-tribromophenoxy)ethane (CAS no. 37853-59-1)
- 2,4,6-Tris(2,4,6-tribromophenoxy)-1,3,5-triazine (CAS no. 25713-60-4）
- Poly(2,6-dibromophenol oxide) (CAS no. 69882-11-7)
- Brominated polystyrene (CAS no. 57137-10-7)
- 1,2-Bis(tetrabromophthalimido) ethane (CAS no. 32588-76-4)
- Hexabromobenzene (CAS no. 87-82-1)
- Pentabromobenzyl Acrylate (CAS no. 59447-55-1)
- Poly(pentabromobenzyl acrylate) (CAS no. 59447-57-3)
- Octabromotrimethylphenylindan (CAS no. 155613-93-7)
- 1,2,3,4,5-pentabromobenzene (CAS no. 608-90-2)
- Pentabromophenol (CAS no. 608-71-9)

And many more…

➔ Br content is only an indicator of the presence of brominated compounds, not POP-BFRs

Cl as an Indicator for Chlorinated Additives?

	Main use	Contents added to products	Low POP content for waste under the Basel Convention
SCCP	PVC, rubber, lubricant, *etc*.	Up to 20% by weight	[100 mg/kg] or [1,500 mg/kg] or [10,000 mg/kg]
Dechlorane Plus	EEE, vehicles, building materials, *etc.*	Up to 40% by weight	TBD

1. The detection limit of Cl concentration in XRF measurements is several orders of magnitude higher than that of Br.
2. Since PVC originally contains a large amount of Cl (up to 70% by weight), it is difficult to determine the presence/absence of SCCP or Dechlorane Plus based on the XRF screening of Cl concentration.
   - XRF screening may be effective for polymer products that do not originally contain Cl.
   - Need to accumulate case studies of such cases in the future.

Some case studies applied to plastic samples

Recycling PBDEs to New Products including Toys and Consumer Products

Category	No of Items	No of Components
Giveaway toys	187	393
100-yen shop products	92	228
Cheap plastic products purchased overseas	261	518
Total	540	1,139

Kajiwara *et al* (2022) *Chemosphere*, 289, 133179.

Methods

XRF Instrument
Olympus DELTA
RoHS/WEEE mode
Analytical time: 30 s

Screening of Br Contents in Components by a Handheld XRF

Br <30 mg/kg

No further chemical analysis

Br >30 mg/kg

Pulverization by a Freezer Mill

Ultrasonic Extraction

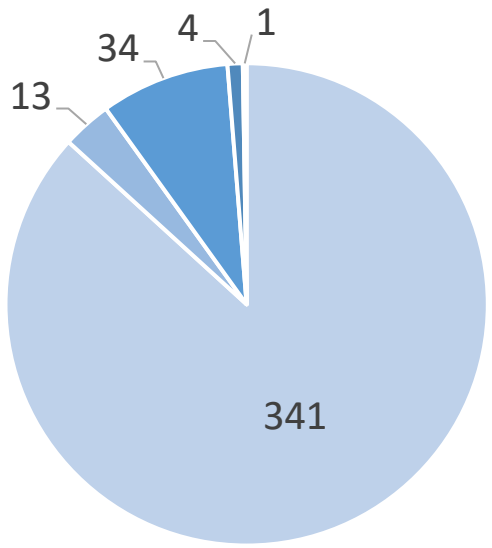
Cleanup

PBDEs analysis by GC-MS/MS

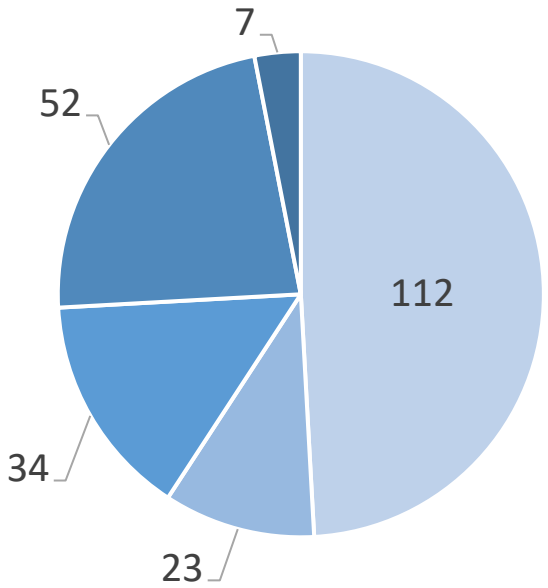
Agilent 7000D

Br Contents in Plastic Components (*n* = 1139)

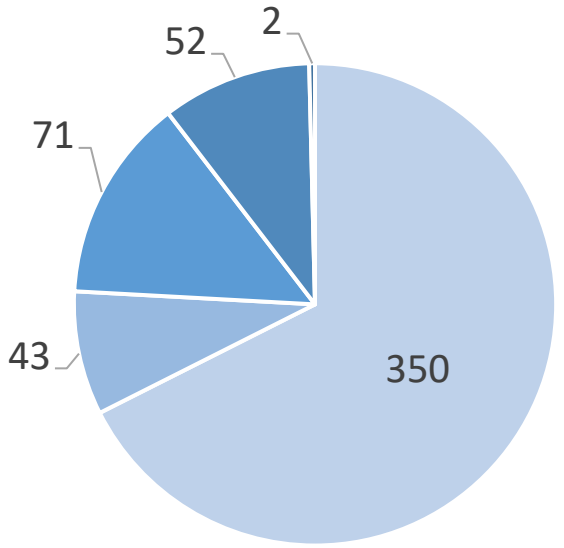
Giveaway toys (*n*=393)

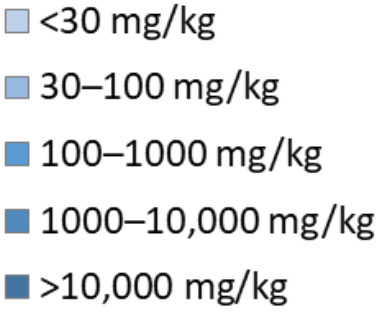


100-yen shop products (*n*=228)



Cheap overseas products (*n*=518)



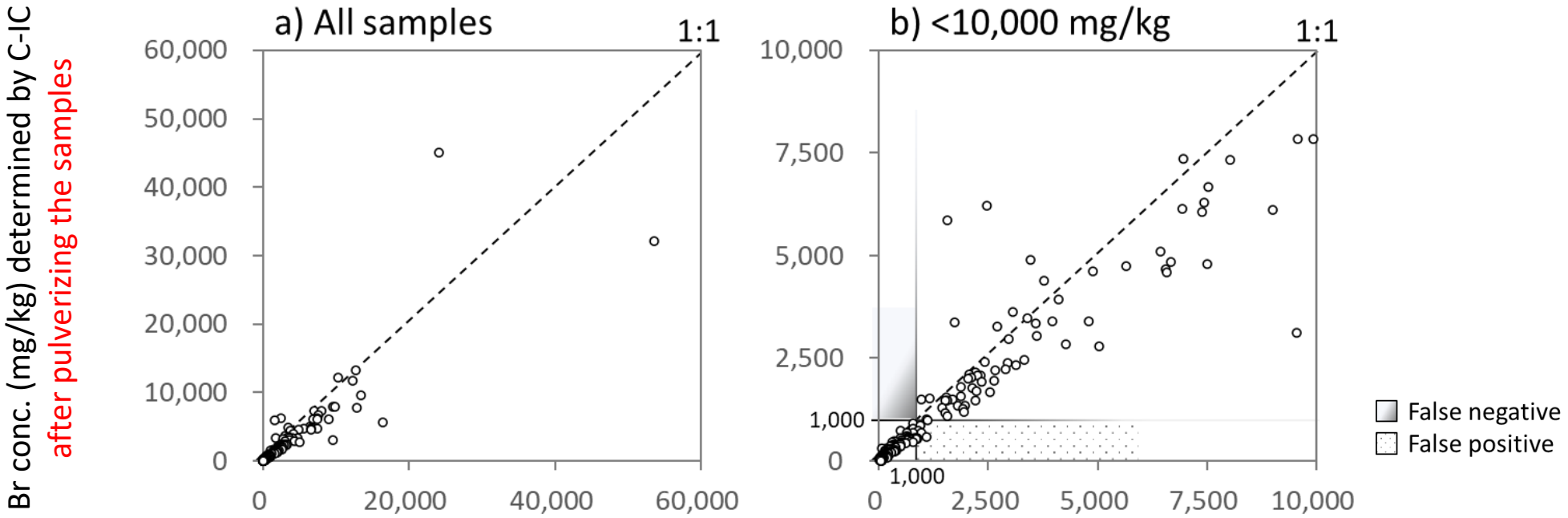


➔ *219 components with >30 mg/kg Br were pulverized (20% of the original samples):*

1. *PBDE analysis by GC/MS for confirmation*
2. *More accurate determination of Br conc. by combustion ion chromatography (C-IC)*

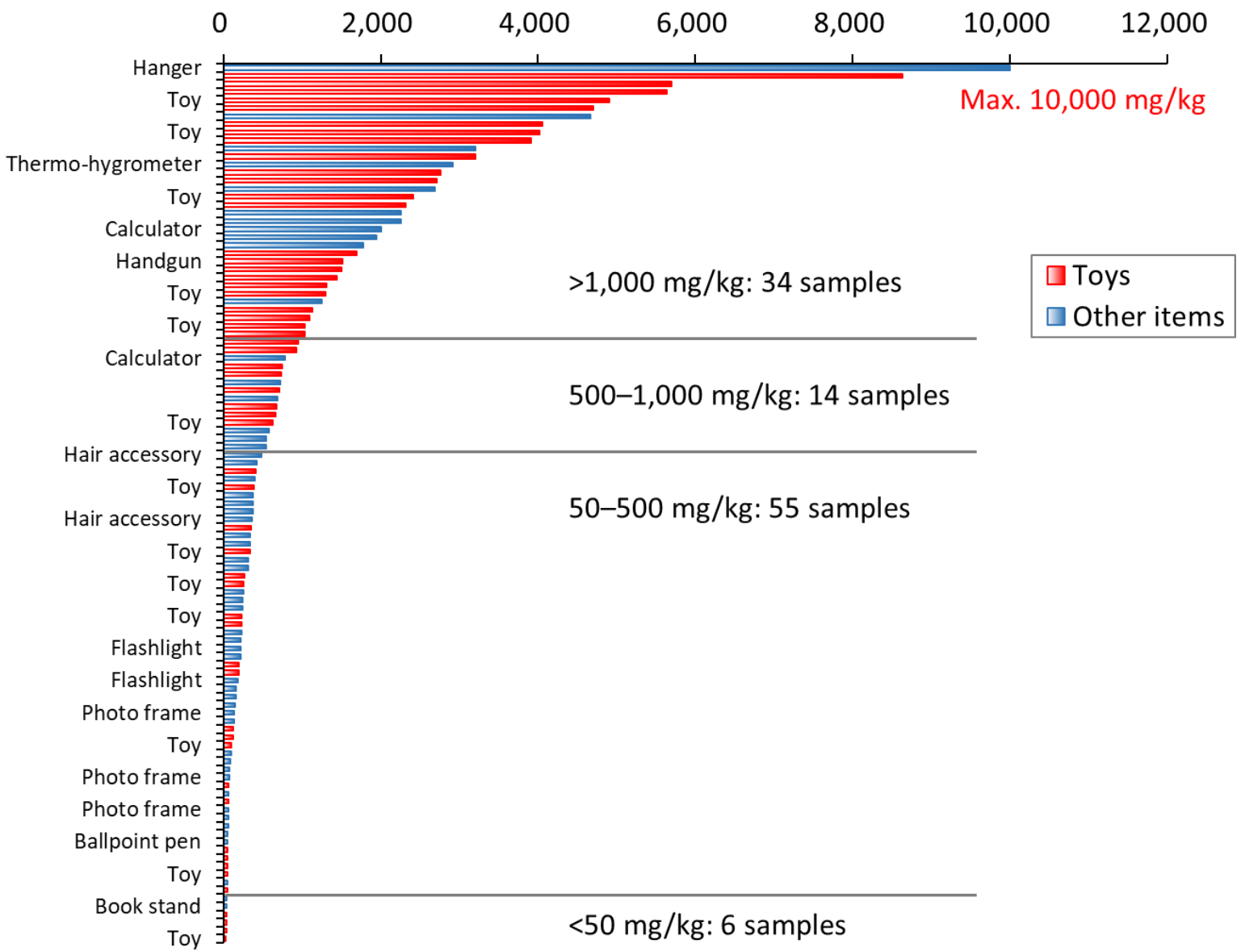
Kajiwara *et al* (2022) *Chemosphere*, 289, 133179.

Comparison of Br concentrations Determined by XRF or C-IC



Kajiwara *et al* (2022) *Chemosphere*, 289, 133179.

PBDE Contents (mg/kg) in Plastic Components (n = 109)



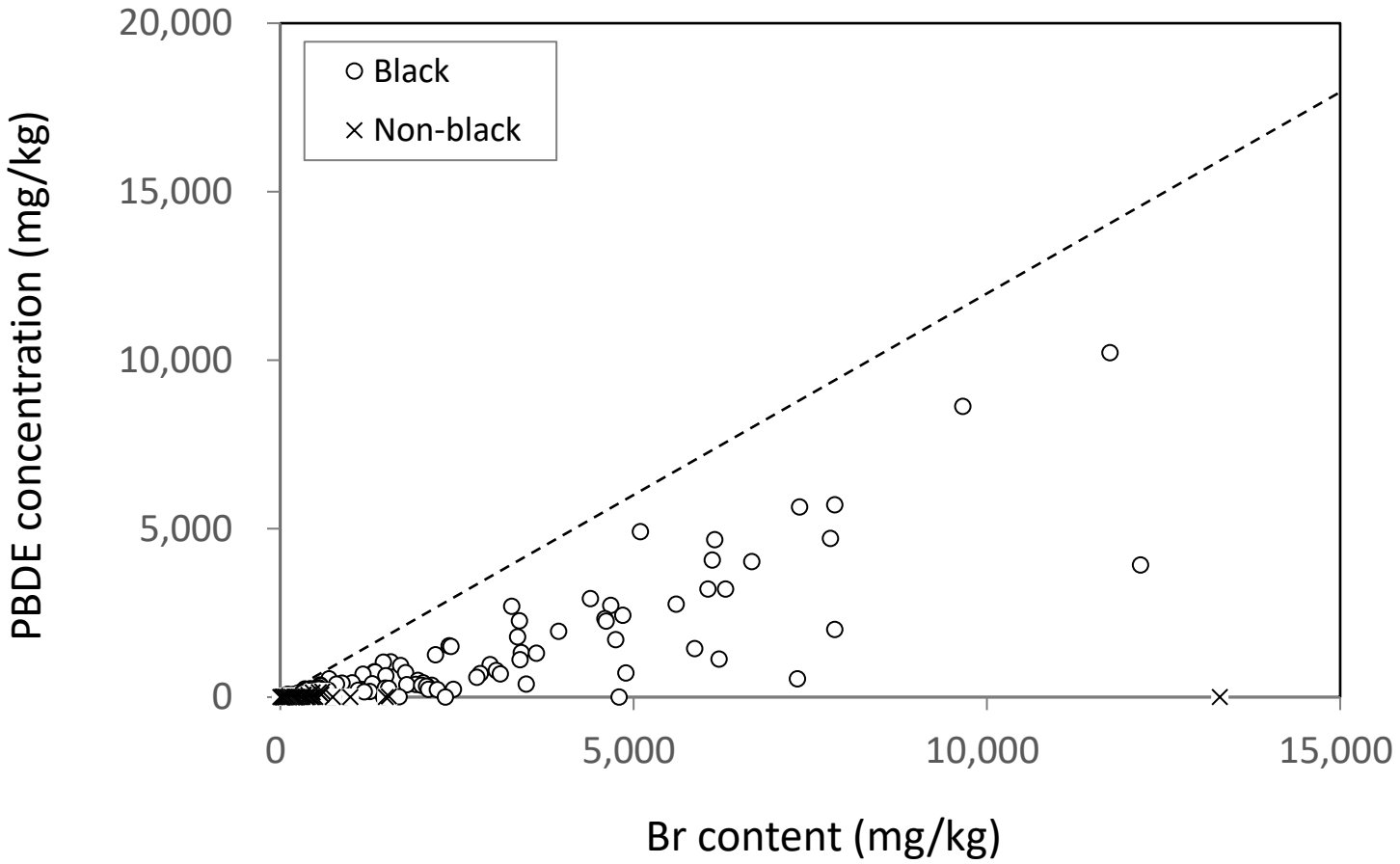
Kajiwara *et al* (2022) *Chemosphere*, 289, 133179.

Br Content vs. PBDE Concentrations in Consumer Products

10,000 mg/kg in a clothes hanger

4,700 mg/kg in a flashlight

1,500 mg/kg in a toy gun

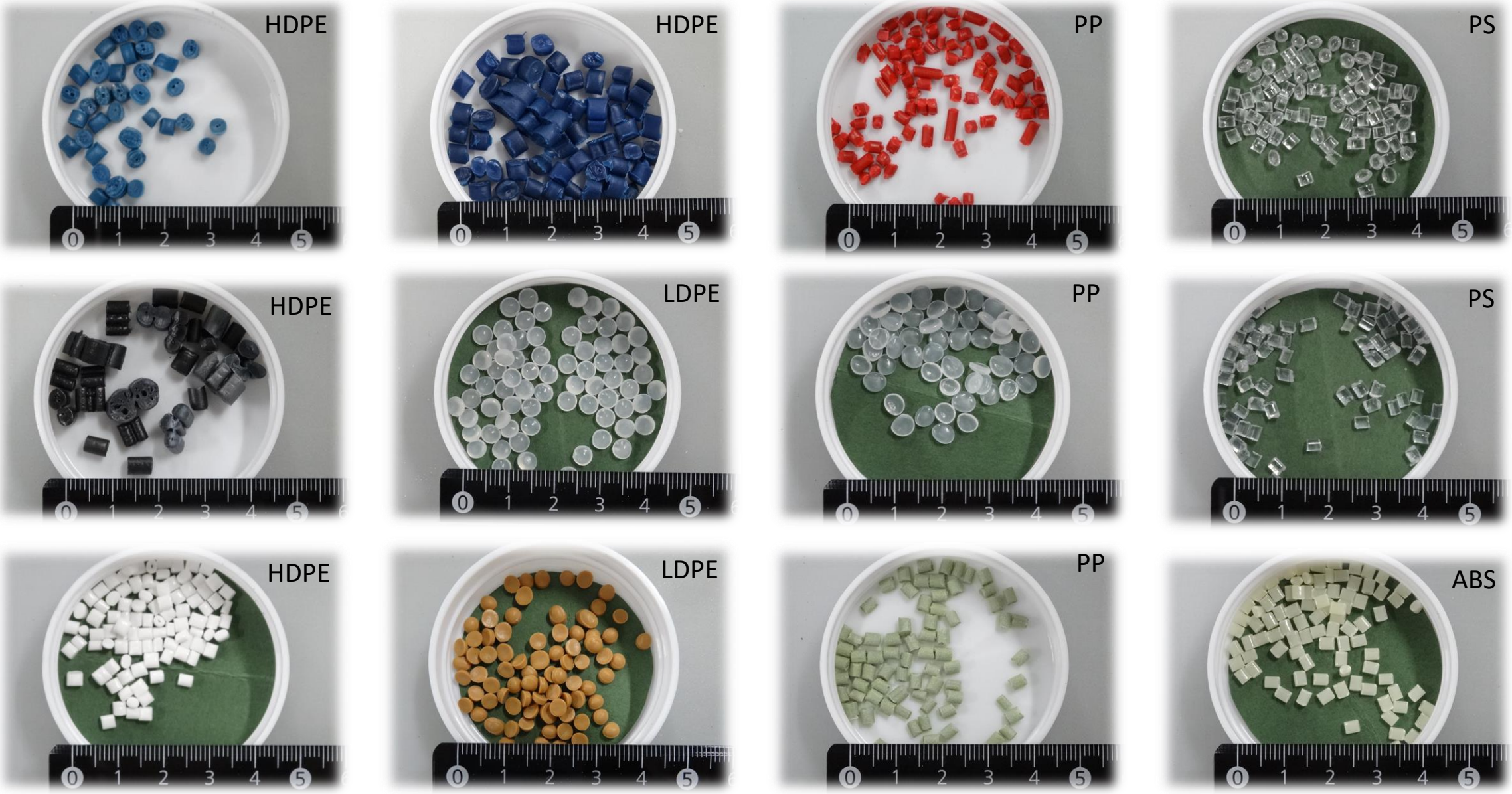


❖ Large contribution from brominated flame retardants other than PBDEs

Kajiwara *et al* (2022) *Chemosphere*, 289, 133179.

Ongoing project on recycled plastic pellets

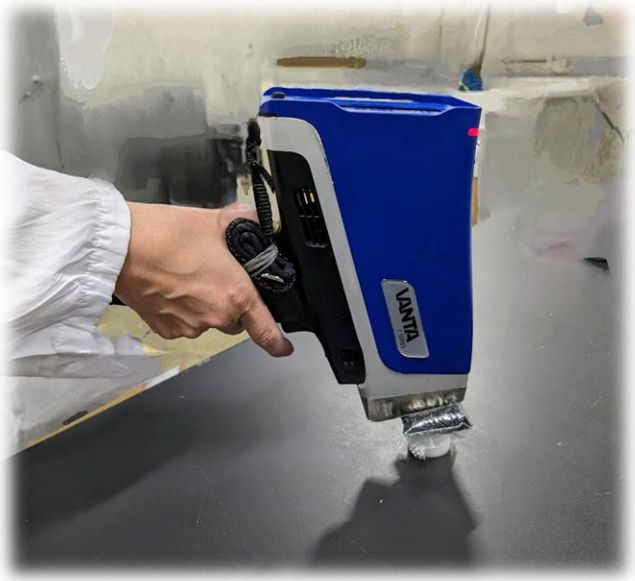
Recycled Plastic Pellets from Various Countries



HDPE: High density polyethylene; LDPE: Low density polyethylene; PP: Polypropylene; PS: Polystyrene; ABS: Acrylonitrile butadiene styrene

Variation of Br Concentrations (mg/kg) in Plastic Pellets

	n	Average	Range	CV (%)
Pellet A	5	110,000	110,000–110,000	1.2
Pellet B	6	84	77–89	5.5
Pellet C	6	30	27–32	5.9



➔ Br concentration in pellet sample can be considered homogeneous

Methods

XRF Instrument
Olympus VANTA
RoHS/WEEE mode
Analytical time: 30 s

Screening of Br Contents in Pellet Samples by a Handheld XRF

Br <15 mg/kg

No further chemical analysis

Br >15 mg/kg

Pulverization by a Freezer Mill

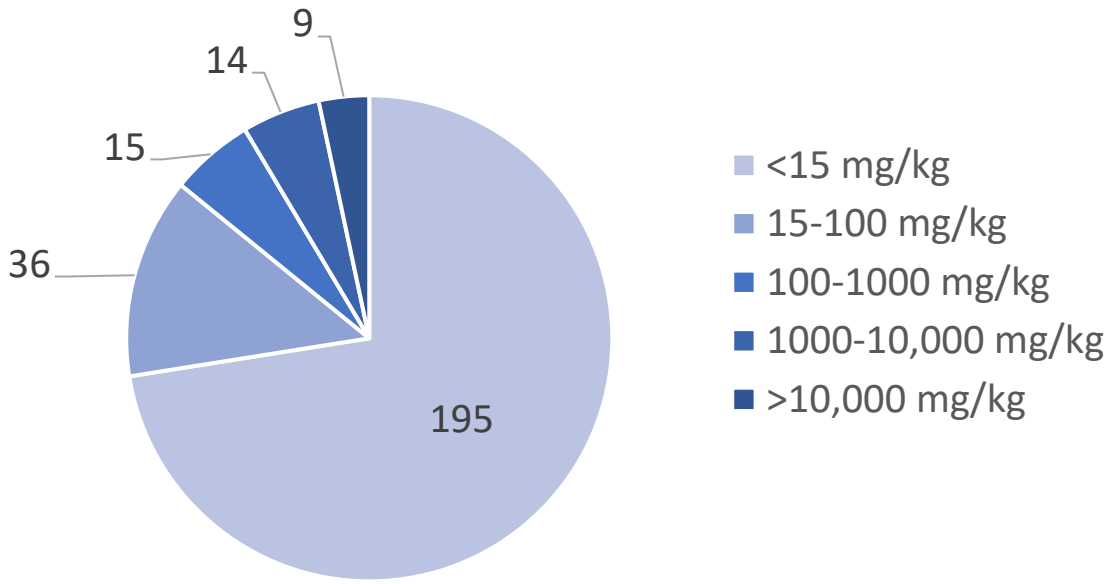
Ultrasonic Extraction

Cleanup

PBDEs analysis by GC-MS/MS

Agilent 7000D

Br Contents in Pellet Samples (*n* = 269)



➔ *74 pellet samples with >15 mg/kg Br (28% of the original samples) were selected for further PBDE analysis*

Thank you very much for your kind attention!

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