SUPPORTING INFORMATION

A Novel Brominated Triazine-based Flame Retardant (TTBP-TAZ) in Plastic Consumer Products and Indoor Dust

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Commercial sources and uses of TTBP-TAZ

TTBP-TAZ (CAS number 25713-60-4; trade names FR 245; FR 368; GX 6145; Pyroguard SR 245; SR 245; TBPC; XZ-2300 or FR-245) was developed jointly by Dai-Ichi Kogyo Seiyaku (DKS, Japan) and ICL-Industrial Products (ICL-IP, Israel). TTBP-TAZ is widespread in Asian markets as appears from online trade platforms (e.g. *alibaba, gmdu*). It is also used in Europe as shown in the European Chemical Agency (ECHA) registered substances database (online available at http://www.echa.europa.eu/) by two individual submissions, one of them with a production of 1.000 – 10.000 tons per year. Since TTBP-TAZ is mainly used in acrylonitrile butadiene styrene (ABS) and high impact polystyrene (HIPS) polymers, it could be a possible replacement of the banned octaBDE mix in ABS and also for DecaBDE in HIPS. It may be also a replacement of hexabromocyclododecane (HBCDD) in HIPS, which constitute only a minor use of this flame retardant (approximately 1-7% of total HBCDD use). Regarding the UNEP evaluation reports for the replacement of certain flame retardants, TTBP-TAZ was not assessed as replacement for octaBDE (UNEP/POPS/POPRC.4/15/Add.1.) but it was considered a technically feasible replacement for HBCDD in HIPS (UNEP/POPS/POPRC.7/19/Add.1). The fact of not including TTBP-TAZ in the UNEP report of octaBDE could be due to its limited toxicity information at the time of reporting. TTBP-TAZ was also recently considered as a viable replacement for decaBDE in HIPS by the recent report of the Environmental Protection Agency (EPA) published in January 2014 "An Alternatives Assessment For The Flame Retardant Decabromodiphenyl Ether (DecaBDE)".

Currently, toxicological properties and data of environmental fate and pathways of exposure can be found in the ECHA database. A number of toxicological studies are provided with detailed protocols, most of them concluding with negative results or no observed adverse effects. In general, TTBP-TAZ is classified as a very persistent but not bioaccumulable neither toxic compound (according to the criteria established in Commission Regulation (EU) No 253/2011). This is probably due to its low water solubility (less than 1µg L^{-1} at 20°C) and consequently low bioavailability. However, it is controversial that under the CLP/GSH (classification, labeling and packaging)/ globally harmonized system of classification and labeling of chemicals) of REACH regulation (Registration, Evaluation, Authorization and Restriction of Chemicals) for the market of TTBP-TAZ, it is still determined as "not classified" since the toxicity and environmental fate assessment data is not considered sufficient. In the EPA report of 2014 about alternatives flame retardants for replacement of DecaBDE (cited above), the hazard of TTBP-TAZ for human health effects and acute toxicity is considered mainly low, but the persistence and bioaccumulation are considered very high and high, respectively. Further non-company funded toxicological and environmental fate studies are lacking in scientific literature and would be desirable.

Table S-1. Concentrations (percentage in weight material, % w/w) of TTBP-TAZ in different plastic parts of 26 consumer products

Sample No.	Sample type		[a]Purchase or [b]manufacture year	TTBP-TAZ % w/w	[c]BFRs	[c]PFRs
1	Electrical power boards	1	[a]2012	0.8	TBBPA (7), BDBPE (1), BDE209	TPHP, PBDPP, BPA-BDPP
2		2	[a]2012	0.1	BTBPE, DBDPE	-
3	Electrical adaptors	1	[a]2012	0.3	TBBPA (6), BTBPE, DBDPE, BDE209	TPHP, PBDPP, BPA-BDPP
4		2	[a]2012	0.01	TBBPA (7), BDBPE, BDE209 (2), BTBPE	TPHP, PBDPP, BPA-BDPP
5	[d]Plastic parts of children toys	1	[a]2012	n.d.	TBBPA (16)	TBOEP
6		2	[a]2012	n.d.	TBBPA, BTBPE, DBDPE	-
7		3	[a]2012	n.d.	TBBPA (14)	PBDPP, BPA-BDPP
8		4	[a]2012	n.d.	TBBPA	-
9	Vacuum cleaner		[a]2012	n.d.	TBBPA	-
10	Electrical plastic adorn		[a]2012	0.3	TBBPA, BTBPE, DBDPE (1)	TPHP, TMPP, PBDPP, BPA-BDPP
11	Heat sealer		[a]2012	0.6	TBBPA (7), BTBPE, DBDPE, BDE209	TPHP, TMPP, PBDPP, BPA-BDPP
12	Televisions	1	[a]2012	1.9	DBDPE (16)	-
13		2	[a]2012	0.06	TBBPA, BTBPE, DBDPE, BDE209 (9)	TPHP, TCEP,TMPP, PBDPP, BPA-BDPP
14		3	[b]2002	n.d.	n.a.	n.a.
15		4	[b]2006	n.d.	n.a.	n.a.
16		5	[b]2002	n.d.	n.a.	n.a.
17		6	[b]2005	n.d.	n.a.	n.a.
18		7	[b]2000	n.d.	n.a.	n.a.
19		8	[b]2006	n.d.	n.a.	n.a.
20	PC monitor		[b]2000	n.d.	n.a.	n.a.
21	Scanners	1	[b]2004	n.d.	n.a.	n.a.
22		2	[b]1998	n.d.	n.a.	n.a.
23		3	[b]2002	n.d.	n.a.	n.a.
24	Printers	1	[b]2000	n.d.	n.a.	n.a.
25		2	[b]2000	n.d.	n.a.	n.a.
26		3	[b]1998	n.d.	n.a.	n.a.

[c]Percentage values in brackets are given only for flame retardants with concentrations equal or higher than 1% w/w (values are only estimated or semi-quantitative and calculated by external calibration)

[d]Children toys: plastic dolls (samples No 1 and 4), plastic wagon train (sample No 2), racing train track (sample No 3)

Abbreviations: non detected, n.d.; non analyzed, n.a.; tetrabromobisphenol A, TBBPA; decabromodiphenylethane, DBDPE; 1,2-bis(2,4,6-tribromophenoxy)ethane, BTBPE; BDE209, decabrominated diphenyl ether; tris(phenyl) phosphate, TPHP; resorcinol bis(biphenylphosphate, PBDPP; bisphenol A bis(bisphenylphosphate, BPA-BDPP; tris(2-butoxyethyl) phosphate, TBOEP; tris(methylphenyl) phosphate, TMPP

Table S-2. Concentrations (ng g^{-1}) of TTBP-TAZ in house dust collected in the Netherlands

Sample No.	House	Location	Electronic/electrical equipment (if applicable)	TTBP-TAZ (ng g^{-1})
1	1	On electronics	Television and video game console	15100
2	1	Around electronics	Television and video game console	470
3	2	On electronics	Desk PC	7240
4	2	Around electronics	Desk PC	1300
5	3	On electronics	Television and video game console	1070
6	3	Around electronics	Television and video game console	220
7	4	On electronics	Television	n.d.
8	4	Around electronics	Television	n.d.
9	5	On electronics	Television	n.d.
10	5	Around electronics	Television	n.d.
11	6	On electronics	Desk PC	22150
12	6	Around electronics	Desk PC	3950
13	7	On electronics	Television	n.d.
14	7	Around electronics	Televison	n.d.
15	8	On electronics	Television	n.d.
16	8	Floor	-	n.d.
17	9	Floor	-	160

Abbreviations: n.d., non detected; computer, PC

Samples were collected on and around the same electronic/electrical equipment in each house

Table S-3. APCI source parameters and MS parameters (positive acquisition mode) for the analysis of TTBP-TAZ

APCI source	**HR-TOF-MS**
Capillary -1000 V	Capillary exit: ±160 V
End plate offset -500	Skimmer1: ±59 V
Corona +5000 nA	Hexapole 1: 23 V
Dry gas 2 L min^{-1}	Hexapole RF: 700 V
Nebulizer 2 bar	Transfer time: 70
Dry Heater 220 °C	Puls storage time: 15
Vaporizer temperature at 240°	

*The TOF-MS parameters for the first segment of the LC chromatogram (1.0-16 min) were optimal for a lower *m/z* range (250-700 *m/z*) in order to detect other flame retardants with lower *m/z* values in the samples. These values were as follows: capillary exit 100 V, skimmer 1: 33 V, hexapole 1: 23 V, hexapole RF: 250V, transfer time: 50 and pulse storage time 10. These same TOF-MS values were used for the negative APCI mode in the time segment for confirmation of TTBP-TAZ, with a value of hexapole RF of 400 instead

Figure S-1. Correlation between the concentration of 2,4,6-TBP (*x axis*) and TTBP-TAZ (*y axis)* in the plastic samples. The Pearson correlation coefficients (r) and significance values (P) were calculated with Minitab program. Linear regression lines are also included.

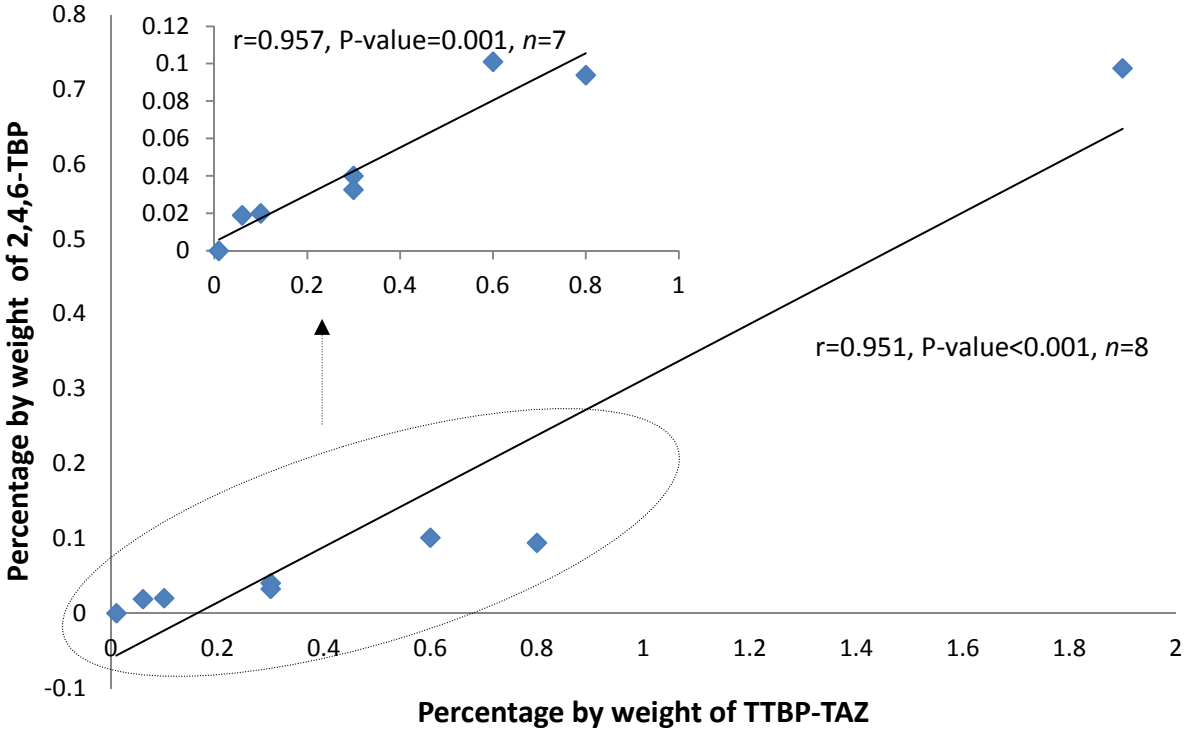

Figure S-2. Correlation between 2,4,6-TBP (*x axis*) and other major brominated flame retardants found in the plastic samples(*y axis)*(only those samples containing 2,4,6-TBP are shown)