Comunicaciones

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BROMINATED FLAME RETARDANTS (BFRS) IN HONEY SAMPLES FROM SPAIN

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Introduction

Brominated Flame Retardants (BFRs) are used to protect people from fires by reducing the flammability of combustible materials. The exposure to these compounds may occur in many situations in daily life, once they have been used in products such computers, mobile phones, textiles, plastic, among others.[1]

Polybrominated Diphenyl Ethers (PBDEs) are BFRs that are included in the list of the Persistent Organic Pollutants (POPs) and have been present in the environment for decades, leading their residual contamination to the food chain. Similar to other POPs, they can be toxic and have teratogenic, mutagenic, and carcinogenic effects in wildlife.[2] Consequently, the European Community introduced new regulations to restrict or ban the usage of the commercial PBDE mixtures (Deca, Octa and Penta-BDE).[3,4] After the phase-out of these mixtures, many new and alternative BFRs has been used as replacements for the banned formulations, such as decabromodiphenylethane (DBDPE) and 1,2-*bis*(2,4,6-tribromophenoxy)ethane (BTBPE), called as "novel" brominated flame retardants (NBFRs). DBDPE is structurally similar to decabromodiphenyl ether (BDE-209) and is marketed as an alternative for technical Deca-BDE,[5] while BTBPE has been announced as a potential replacement for technical Octa-BDE.[6] Their presence in the environment has been already reported,[7,8] but their potential sources and environmental behaviors are still not clear.[9]

Honey is a natural product consumed by many people around the world. Several studies have been used bees and honey as indicators of environmental pollution,since honeybees are greatly affected by industrial chemicals and transport them to the colony, which ends as a contaminated honey.[10] Residues of some POPs have been found in honey samples, such as organochlorine pesticides and Polychlorinated Biphenyls (PCBs).[11,12] No data was found in respect to contamination of honey by BFRs.

This work reports, for the first time, the concentration levels of 17 BFRs, including 15 PBDE congeners and two "novel" BFRs (BTBPE and DBDPE), found in honey samples collected in Spain between 2006 and 2012.

Materials and Methods

A total of 10 honey samples, collected between 2006 and 2012, were purchased in different supermarkets from Spain. The samples were of different botanical origin, transported to the laboratory and stored at room temperature in a fresh and dark place before analysis.

All reagents used for the analysis were of trace analysis grade. A total of fifteen individual PBDE congeners were determined: 17, 28, 47, 66, 85, 99, 100, 153, 154, 183, 184, 191, 196, 197 and 209. Two NBFRs (BTBPE and DBDPE) were also included in the analysis.

The sample preparation was based on Blasco et al. (2004)[13], with some modifications. After a liquid-liquid extraction of the honey samples (10 grams approximately) with a mixture of ethyl acetate and petroleum ether (9:1, v/v), the organic phase was cleaned-up in a multilayer column filled with activated neutral silica gel, silica gel activated and modified with sulfuric acid (44% and 22%, w/w) and anhydrous sodium sulfate, eluted with *n*-hexane.

The sample extracts were concentrated and analyzed by GC-QqQ-MS/MS on a TRACE GC Ultra (Thermo Fisher Scientific, Milan, Italy) coupled to a TSQ Quantum XLS triple quadrupole mass spectrometer (Thermo Fisher Scientific, Bremen, Germany), operating in EI mode (40 eV electron energy). Injections were performed in the PTV mode and a capillary VF-5ht column (15 m, 0.25 mm i.d., 0.10 µm film thickness) purchased from Varian, Inc. (Palo Alto, CA, USA) was used for the separation. The temperature program was as follows: initial temperature of 90 °C (held for 2 min), first ramp at 15 °C min^{-1} to 160 °C, second ramp at 4 °C min^{-1} to 225 °C, third ramp at 7 °C min^{-1} to 290 °C and the final ramp was 10 °C min^{-1} to 310 °C, which was held constant for 10 min. Helium was used as the carrier gas at a constant flow rate of 1.2 mL min^{-1}. The mass spectrometer was operated in multiple reaction monitoring (MRM), with two transitions monitored using argon as the collision gas, which was set to 1 mTorr for all the

analyses. The transfer line and source temperatures were both set at 300 °C. The MS/MS collision energy and the ion transitions monitored were optimized for each compound individually. Isotope dilution technique was used as quantification method.
All analyses such as blanks, recoveries, and parallel analyses were complied with analytical standards as recommended by the EU Commission in the directive for measuring dioxins in food. A method blank in each set of analysis (three samples and a blank) was carried out. To eliminate interferences in blanks, all the glassware, chemicals, solvents, and equipment used during extraction and clean-up procedures as well as the instrumentation used have been routinely checked. Recoveries of the labeled congeners in samples and in spiked blanks were always higher than 98%. The laboratory has participated in different international inter-laboratory studies and several international quality control studies for the analysis of PBDEs in different food matrices. The results were consistent at all times with the consensus means given by the inter-laboratory organization.

Results and discussion
Concentrations of BFRs in the honey samples are presented in Table 1.

Table 1. BFR concentrations in honey samples from Spain (*n*=10). Values are median concentration of positive samples, expressed in pg g^{-1} w.w.

Compound	Positive samples	Median	Range
BDE 17	40%	0.010	n.d. - 0.028
BDE 28	90%	0.020	n.d. - 0.075
BDE 47	90%	1.498	n.d. - 2.451
BDE 66	50%	0.019	n.d. - 0.047
BDE 85	0%	n.d.	-
BDE 99	80%	0.179	n.d. - 0.460
BDE 100	80%	0.034	n.d. - 0.075
BDE 153	50%	0.111	n.d. - 0.150
BDE 154	10%	0.029	n.d. - 0.003
BDE 183	0%	n.d.	-
BDE 184	0%	n.d.	-
BDE 191	20%	0.280	n.d. - 0.512
BDE 196	0%	n.d.	-
BDE 197	0%	n.d.	-
BDE 209	40%	3.210	n.d. - 9.062
BTBPE	60%	0.096	n.d. - 0.493
DBDPE	30%	0.137	n.d. - 2.526
∑BDEs		**5.390**	
∑NBFRs		**0.233**	

Regarding PBDEs, five BDE congeners were not detected in any of the samples: BDE-85, -183, -184, -196 and -197. Generally speaking, residue levels in honey were quite low. BDE-209 presented the highest median concentration (3.210 pg g^{-1}), followed by BDE-47 (1.498 pg g^{-1}). These results agree with those previously found in other samples of foods marketed in Spain in which BDEs 47 and 209 were always the most abundant PBDEs.[1,14] BDE-47 was also one of the most frequently detected congener, together with BDE-28 (90%), followed by BDE-99 and -100 (80%), all of them present in the Penta-BDE technical mixture.
In relation to NBFRs, DBDPE is exhibiting the highest median concentration (0.137 pg g^{-1}), while BTBPE is more frequent in the samples (60% of positive samples). The presence of DBDPE has already been reported in sewage sludge samples from Spain by De la Torre et al. (2012)[15] and Gorga et al. (2013),[8] but at much lower concentrations than those found for PBDEs. These results indicate that the replacement of Deca-BDE technical mixture by DBDPE in Spain is still quite slow.
To our knowledge, no previous studies have been performed to investigate concentrations of BFRs in honey samples. So, it is difficult to compare the results presented here with those of other monitoring programmes. Many investigators have employed honeybees or honeybee products (honey, wax, pollen) as tools for assessing environmental pollution in agricultural and industrial areas, but it has being performed mainly with pesticides.

Conclusions

Those are the first data regarding the honey contamination by PBDEs, BTBPE and DBDPE. Although the results indicate a low concentration of BFRs in the honey samples analyzed,further and more extensive studies are necessary, including more samples and areas to confirm the results obtained.

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