Suspect screening of soot samples reveals the occurrence of emerging organophosphate ester: Tris(2,4-di-*tert*-butylphenyl) phosphate

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Introduction

- Organophosphite antioxidant (OPAs) refers to the group of anthropogenic chemicals that are commonly added to household products
- An example of OPA is Irgafos®-168 (tris(2,4-di-*tert*-butylphenyl)phosphite) (TDTBPPO) (Figure 1)
- Oxidation reaction, exposure to heat (e.g., UV and sunlight), and exposure to microwave leads to transformation reaction of TDTBPPO, which results in the formation of tris(2,4-di-*tert*-butylphenyl)phosphate (TDTBPP) (Figure 2), an organophosphate ester (OPE) compound
- Studies have suggested the potentially persistent nature of TDTBPP
- TDTBPP and 1,3,5-tripheylbenzene can also serve as atmospheric tracer for open-burning of domestic litter and refuse that contain plastic, but there is a limited knowledge with regard to the detection of TDTBPP for burning that occurs inside a house where materials that contain TDTBPPO and TDTBPP usually reside

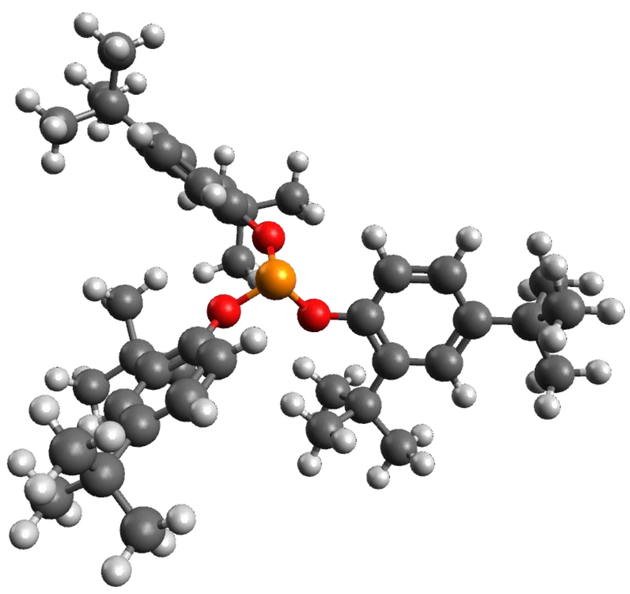

Figure 1. Chemical structure of TDTBPPO

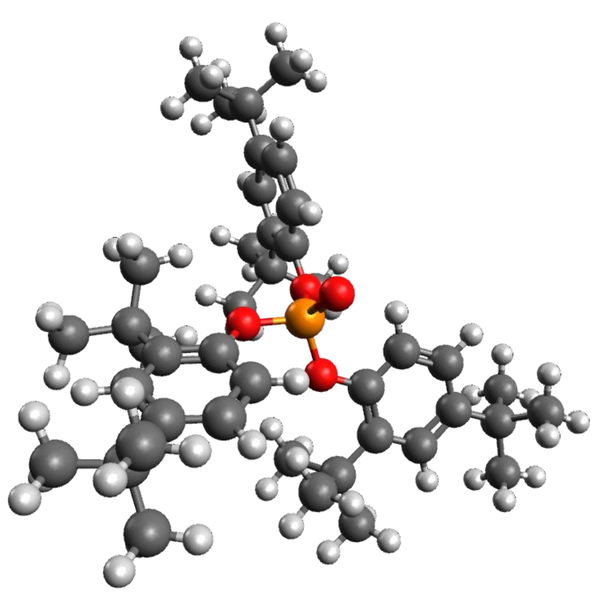

Figure 2. Chemical structure of TDTBPP

Research Objectives

1. *To detect the presence of TDTBPP and 1,3,5 triphenylbenzene using suspect screening analysis of gas and soot samples collected from a fire test that mimicked the burning of a living room*
2. *To screen for the presence of TDTBPPO, six OPEs, and two potential degradation products of TDTBPP (n = 11) in the gas and soot samples (Table 1)*

Table 1. List of compounds included in the suspect screening analysis of gas and soot samples from the fire test (adapted from Liu and Mabury, **2018**)

No.	Compound	CAS No.	Molecular formula	Molecular weight (g/mol)	Note
1.	Tris(2-chloroethyl) phosphate	115-96-8	$C_6H_{12}Cl_3O_4P$	285.482	OPE
2.	Tris(1,3-dichloro-2-propyl) phosphate	13674-87-8	$C_9H_{15}Cl_6O_4P$	430.889	OPE
3.	Triphenyl phosphate	115-86-6	$C_{18}H_{15}O_4P$	326.288	OPE
4.	Tricresyl phosphate	1330-78-5	$C_{21}H_{21}O_4P$	368.369	OPE
5.	2-Ethylhexyl diphenyl phosphate	1241-94-7	$C_{20}H_{27}O_4P$	362.406	OPE
6.	Tris(2-ethylhexyl) phosphate	78-42-2	$C_{24}H_{51}O_4P$	434.642	OPE
7.	Tris(2,4-di-tert-butylphenyl)phosphite	31570-04-4	$C_{42}H_{63}O_3P$	646.937	TDTBPPO (OPA)
8.	Tris(2,4-di-tert-butylphenyl)phosphate	98906-11-9	$C_{42}H_{63}O_4P$	662.936	TDTBPP (OPE)
9.	Bis(2,4-di-tert-butylphenyl)phosphate	69284-93-1	$C_{28}H_{43}O_4P$	474.622	TDTBPP breakdown product
10.	2,4-di-tert-butylphenol	96-76-4	$C_{14}H_{22}O$	206.329	TDTBPP breakdown product
11.	1,3,5-triphenylbenzene	612-71-5	$C_{24}H_{18}$	306.408	Atmospheric tracer for open-burning

Experimental Design and Analysis

- Fire tests were conducted in 20 ft. containers placed outdoor
- Soot samples were collected on a stainless steel plate mounted in the container door, while gas samples were collected with active sampling using ORBO 609 Amberlite XAD-2 (20/50) 400/200 mg
- Samples were extracted using Soxhlet extraction and extracts were analyzed with fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS) in electron ionization (EI) mode at 70 eV

Results

- TDTBPP was detected in all replicates of all soot samples (representative MS spectrum of TDTBPP from one replicate of the soot samples is shown in Figure 3)
  - *similarity to the MS spectrum of TDTBPP obtained from the NIST Library database (Figure 4)*
- TDTBPP was tentatively identified in two replicates of the samples (representative MS spectrum of TDTBPP from one of the two replicates of the soot samples is shown in Figure 5)
  - *presence of the 181, 271, and 419 m/z ions potentially suggested the detection of a different compound that is not TDTBPP; or that TDTBPP may have mixed with another compound*
- TDTBPPO, any of the six OPEs, the two potential degradation products of TDTBPP, or 1,3,5-triphenylbenzene were not found in any of the samples
  - *for any TDTBPPO that was contained in the furniture and electronic equipment placed inside the room, some may have been completely transformed into TDTBPP and some may have been completely eliminated during the fire*
  - *breakdown products of TDTBPP, as well as OPEs, that may have been contained in furniture and electronic equipment were likely to be eliminated during the fire*
  - *absence of 1,3,5 triphenylbenzene in any of the samples was hypothesized to be from the difference in the profile of plastics in this experiment (i.e., primarily polyvinyl chloride) and what may be found in open-burning of domestic litter and refuse (i.e., primarily polyethylene and polyethylene terephthalate), where the presence of 1,3,5-triphenylbenzene was detected*

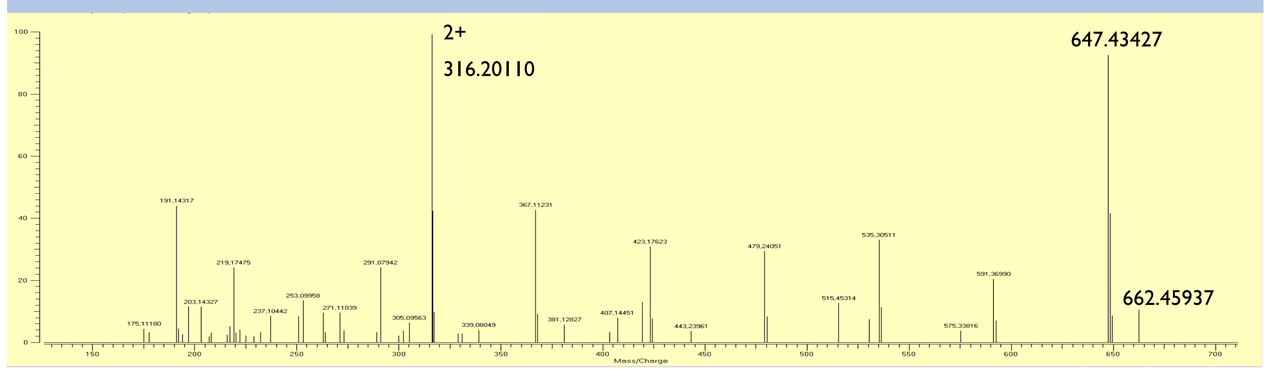

Figure 3. Representative MS spectrum of TDTBPP detected in one of the replicates of the soot samples

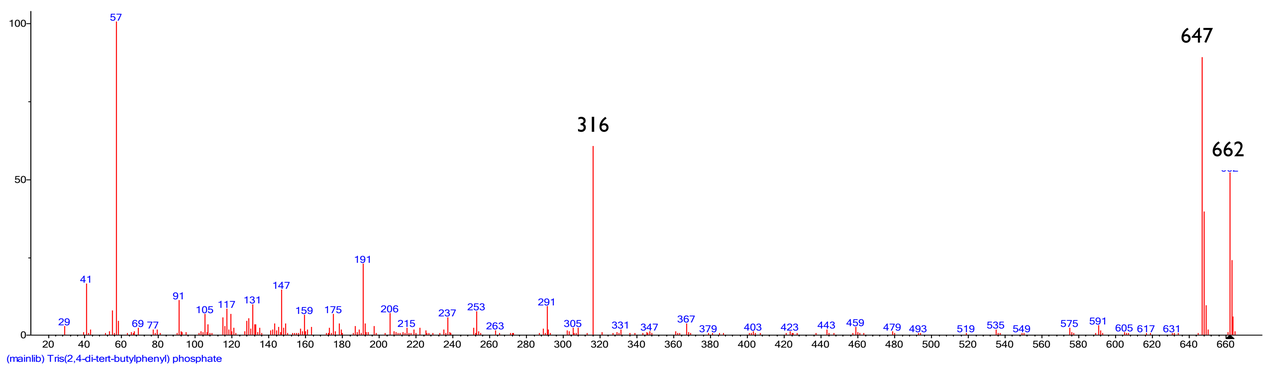

Figure 4. MS spectrum of TDTBPP obtained from the NIST Library database

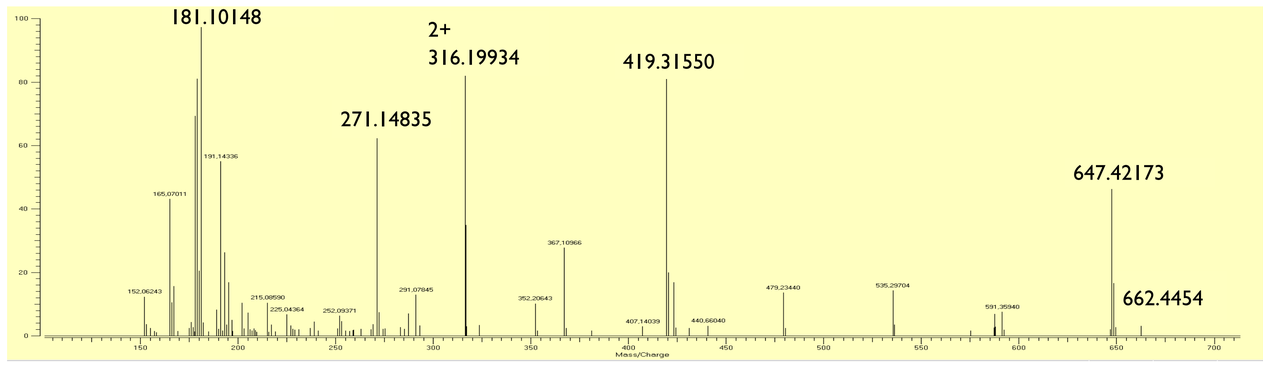

Figure 5. Representative MS spectrum of TDTBPP in a replicate of a gas sample. Note the high abundance of m/z 181, 271, and 419

Conclusions

1. *TDTBPP is formed from indoor burning of a room that contains household furniture and materials*
2. *TDTBPP is potentially an emerging contaminant that requires further screening in the future*

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