

# POLYBROMINATED FLAME RETARDANTS - POSTERS

## DISTRIBUTION OF DECABROMODIPHENYL OXIDE IN THE ENVIRONMENT

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### Introduction

Brominated flame retardants (BFRs) comprise about 25% of the volume of flame retardants (FR) used on a global scale. They are used in applications requiring high FR performance or in resins needing a FR active in the gas phase of a fire. Examples of applications requiring high FR performance (e.g. the ability to meet V0 or FR4 requirements) are electronic equipment and printed circuit boards.<sup>1</sup> Resins requiring gas phase flame retardancy are those which melt, drip, and depolymerize to form volatile monomers, dimers and trimers when exposed to heat (e.g. styrenic polymers). Styrenic polymers include polystyrene (PS), acrylonitrile-butadiene-styrene (ABS), polyphenylene oxide/polystyrene blends (modified PPO) and polycarbonate/ABS blends.<sup>2</sup>

Gas phase FR act as free radical scavengers by competing with oxygen for free radicals formed by the combustion process.<sup>2</sup> This competition interrupts and terminates the combustion reaction. To do this, the FR must form a gaseous component and must produce this component at the decomposition temperature of the polymer. Halogens are some of the few chemical elements with the ability to form gaseous compounds in this manner. Further, very few halogens are able to form effective FR compounds. The halogens' order of reactivity as free radical scavengers is I>Br>Cl>F. I is the most effective scavenger, but is very expensive and lacks the thermal and photolytic stability required for most thermoplastic applications. Br is the next most effective scavenger and is the element most widely used in gas phase FR. Cl is considerably less effective than Br as a scavenger, because Cl only marginally competes with oxygen for hydrogen radicals and the aromatic C-Cl bond is too stable. F has virtually no activity as a FR due to the stability of C-F and H-F bonds. Because of these limitations, there are very few gas phase FR, and BFRs are the most effective gas phase FR available. Further, these limitations mean that the most suitable substitute for one BFR is another BFR, and that a switch to an entirely different resin system is usually required if a BFR cannot be utilized in a particular application.

BFRs as a class are structurally diverse and include aromatic diphenyl oxides (a.k.a. ethers), cyclic aliphatics, phenolic derivatives, aliphatics, phthalic anhydride derivatives and others. Recent years have seen a proliferation of papers reporting the detection of "brominated flame retardants" or "polybrominated diphenyl ethers" (a.k.a. polybrominated diphenyl oxides, PBDPO, PBDE) in various environmental samples.<sup>3,4</sup> In fact, the "PBDE" have been called ubiquitous environmental contaminants in several of these papers.<sup>4</sup>

In spite of the sweeping nomenclature used in these publications, the majority report only the detection of tetra- and pentaBDPO. Approximately 70% of the "PBDE" detected in biological samples collected in the environment is related to a single BFR isomer: 2,2',4,4'-TetraBDPO.<sup>5</sup> The next most frequently detected "BFR" is 2,2',4,4',5-PentaBDPO. These two isomers are major

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components of the commercial PBDPO product known as pentabromodiphenyl oxide (PeBDPO). PeBDPO is one of three commercial PBDPO products marketed; the other two PBDPO products are known as decabromodiphenyl oxide (DBDPO) and octabromodiphenyl oxide (OBDPO). DBDPO together with Tetrabromobisphenol A makes up approximately 50% of all BFR usage globally. The remaining 50% of the global volume of BFRs is composed of a number of different BFR structural types and includes OBDPO and PeBDPO. OBDPO and PeBDPO are produced and used in substantially smaller quantities than DBPDO. This paper reviews reports of the environmental detection of the second largest volume BFR in use today, DBPDO.

## Predicted Environmental Distribution

DBDPO has extremely low water solubility and vapor pressure,  $< 0.1 \text{ ug/L}$  and  $4.63 \times 10^{-6} \text{ Pa}$ , respectively.<sup>6</sup> These measured values can be used to predict DBDPO's probable environmental distribution.

Based on DBPDO's measured water solubility and vapor pressure, its calculated Henry's Law Constant is  $2.76 \times 10^{-9} \text{ atm-m}^3/\text{mole}$ .<sup>7</sup> Likewise, DBDPO's calculated soil adsorption coefficient is  $1.79 \times 10^6$ , its  $\log K_{oc}$  is 6.254, and is expected to adsorb strongly onto soil and sediment. Volatilization from water is estimated to be  $1.93 \times 10^{-8} \text{ atm-m}^3/\text{mole}$ .<sup>7</sup> Removal by a sewage treatment plant is expected to be high (~93% removal), primarily by adsorption to sludge.<sup>7</sup>

A Level III Fugacity Model predicts the following distribution for DBPDO in the environment: Air, 0.132%, Water, 1.8%, Soil 46%, and Sediment, 52.1%.<sup>7</sup> Therefore, DBPDO is predicted to distribute primarily to soil and/or sediment. Further, due to its strongly adsorption to soil/sediment and extremely low water solubility, DBDPO is expected to be relatively immobile in soil and is unlikely to leach into groundwater. The SAMS soil model, run for a 2 year period and assuming an initial DBDPO concentration of  $1 \text{ kg/m}^3$  at a depth of 1 cm in the soil with no degradation and a  $K_{oc}$  of  $1.59 \times 10^6 \text{ l/kg}$ , predicted the majority of DBDPO to be in the top few centimeters of the soil with an insignificant amount (zero) leaching into the groundwater.<sup>5</sup> Actual environmental monitoring results are consistent with these predictions.

## Environmental Monitoring Results and Discussion

DBDPO has been infrequently detected in biological, sediment, or water samples collected from the environment in the European Union (EU), Japan, and the United States. The majority of reports of DBDPO's detection are in sediment near point sources of release.<sup>5</sup>

*Sediments.* In the EU, DBDPO sediment levels of up to  $1.2 \text{ mg/kg}$  wet wt were detected near U.K. sites using or storing DBDPO. The measured levels are generally below those predicted for these areas by the USES Modeling Software.<sup>5</sup> This indicates that the actual releases at sites using DBDPO are lower than estimated by the model.

Levels of DBDPO in sediments in the U.K. near possible sources of release ranged from  $<$  the detection limit (DL,  $0.6 \text{ ug/kg}$  dry wt) to  $3190 \text{ ug/kg}$  dry wt.<sup>8</sup> Results from 11 out of 24 of these samples were reported as  $<$  the DL. Sediments from two streams, collected downstream of landfills receiving brominated wastes, also reported results as  $<$  the DL.<sup>8</sup> Ten out of 11 samples collected in a second study in the U.K. near possible sources of release reported all values  $< 200$  or  $500 \text{ ug/kg}$  dry wt, which are the presumed detection limits. One sample was reported to possibly

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contain DBPDO at ~850 ug/kg, but interference in the analysis did not allow confirmation.<sup>9</sup>

A recent survey of marine sediments in estuaries discharging in to the North Sea has been carried out.<sup>10</sup> DBDPO concentrations in 22 samples ranged from < the DL (0.51 ug/kg dry wt) to 1700 ug/kg dry wt. The highest level, 1700 ug/kg dry wt, was detected in the Mersey estuary, a site used formerly for dumping sewage sludge. The next highest level, 200 ug/kg, was detected in the Schelde estuary. The lowest levels reported in this survey were samples collected 100 km off Terschding (<DL of 0.51 ug/kg dry wt), from the Glomma estuary (<DL of 0.52 ug/kg), from the Otria estuary (0.71 ug/kg), and from the Elbe estuary (0.83 ug/kg dry wt).

DBDPO levels up to 0.2 mg/kg wet wt in sediment collected in Sweden were reported.<sup>11</sup> Surface sediment (0-2 cm) collected at 8 locations in the River Viskan and other nearby water systems ranged from <1.1 to 241 ug DBDPO/kg wet wt. Five of the 9 samples analyzed had DBPDO concentrations <1.7 ug/kg wet wt. All samples were collected in an area thought to be using FR.

A number of sediment monitoring studies were conducted in Japan between 1977 and ~1989.<sup>12,13,14,15</sup> In 15 sediment samples collected in Japan in 1977, DBPDO was not detected (DL=25-870 ug/kg dry wt).<sup>12</sup> Marine, estuarine and river sediment samples were collected at different locations in Japan in 1981-83; DBPDO was detected in 7 out of 15 samples in the range of 20-375 ug/kg dry wt. DBDPO was identified at 20 ug/kg dry wt in one of 3 estuarine sediment samples from Osaka, but was not detected in samples from Tokyo, Matsuyama, or Hiroshima. DBDPO was detected in 16 out of 60 sediment samples at concentrations ranging from 10 to 1370 ug/kg in 1987 and was detected in 39 out of 129 samples collected at 43 locations at concentrations ranging from 4-6000 ug/kg in 1988-89 in Japan.<sup>12</sup> The upper sediment layer of the Second Neya River in Osaka, Japan was found to contain ~0.2 mg DBPDO/kg dry wt in 1983. Twenty sediment samples from the Kino River in Japan contained DBPDO ranging from 0.003-11.6 mg/kg dry wt.<sup>13</sup>

Near its manufacture in the U.S. in 1978, sediment levels of DBDPO were reported to range from not detectable up to 14 mg/kg.<sup>16</sup>

*Water.* DBPDO has not been reported in water samples which is consistent with its extremely low water solubility (<0.1 ug/L).<sup>12,13</sup> DBDPO was not detected in 15 water samples collected in Japan in 1977 (DL= 0.2-2.5 ug/L). DBDPO was not detected in 75 water samples collected in 1987 (DL= 0.1 ug/L) and was not detected in 141 samples collected in 47 locations in 1988-89 in Japan (DL= 0.06 ug/L). DBDPO was not detected in 12 samples from the Kino River water in Japan (DL= 0.1 ug/L). The samples were taken from several industrial, urban and rural areas of Japan and are thought to be representative of the country as a whole.<sup>5</sup>

*Air.* Data from 1977 identified DBDPO in air samples collected in the vicinity of two manufacturing facilities in the U.S.<sup>16</sup> The concentrations were between 0.016 and 26 ug/m<sup>3</sup> and DBPDO was present mainly in the particulate phase which likely reflects dust release. It is not clear from the report if these levels were taken on the manufacturing site or outside the site, and therefore these results are not useful in understanding DBPDO's environmental behavior.

*Biota.* Over 270 biological samples collected in the environment (fish, marine mammals) have

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been analyzed for DBPDO. DBPDO was detected in only one of these 270 samples at a level of 0.001 mg/kg wet wt. In the EU, DBPDO was not detected in dab,<sup>8</sup> whiting,<sup>8</sup> flounder,<sup>8</sup> plaice,<sup>8</sup> winkles,<sup>8</sup> mussels,<sup>8</sup> pike,<sup>11</sup> sperm whale,<sup>17</sup> dolphin,<sup>17</sup> minke whale,<sup>17</sup> harbour seal,<sup>17</sup> mackerel,<sup>8,17</sup> or mussels<sup>8,17</sup>. In Japan, DBPDO was not detected in 229 samples from different aquatic species, but was detected at 0.001 mg/kg wet wt in 1 mussel.<sup>12,18</sup> These results are consistent with the lack of biocentration in fish in a 6 week study, DBPDO's pharmacokinetic behavior in mammals, and DBPDO's physical/chemical properties. DBPDO's bioconcentration factor was <5 at a water concentration of 60 ug/L and <50 at a water concentration of 6 ug/L in a 6 week study conducted in carp.<sup>19</sup> Pharmacokinetic studies performed in the rat have shown DBPDO is poorly absorbed (<0.3% oral dose), has a short half life (<24 hr), is rapidly eliminated in the feces (>99% in 72 hr), and can be metabolized.<sup>20,21</sup> These results are likely related to DBPDO's large molecular weight (959 g/m) and size which limit its ability to pass through biological membranes.

The available monitoring data do not indicate widespread distribution of DBPDO in the environment away from sources of release. DBPDO's environmental detection is essentially limited to sediments near point sources of release. DBPDO is not being detected in biological samples collected from the environment. These monitoring data are consistent with DBPDO's physical/chemical properties and DBPDO's predicted environmental distribution.

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