In response to results from a new survey of alternative flame retardants, the use of some chemicals found in lower concentrations than those detected in San Francisco Bay (RMP) has been suggested to have endocrine-disrupting properties. Known about many of the diverse array of organophosphate flame retardants (PBDE) flame retardants, including diphenyl ether (PBDE) flame retardants during nationwide phase-outs of polybrominated diphenyl ethers (PBDEs). Some of these chemicals have been in use for decades, while others are newer and have not been shown to have endocrine-disrupting properties. In recent studies, the Regional Monitoring Program for Water Quality in San Francisco Bay has detected some of these alternative flame retardants in samples of Bay water, sediment, and biota. Typically, they are found in lower concentrations than PBDEs. The levels observed have been far below the thresholds that would be of concern for a few of these compounds, but for most of these chemicals the potential risks are unknown. Starting in 2014, changes in California’s flammability standards may lessen the use of bromine-containing compounds that have replaced PBDEs. Some of these chemicals have been in use for decades, while others are newer and have not been shown to have endocrine-disrupting properties.

The state of California has implemented unique flammability standards for consumer products and other common goods. In response to nationwide phase-outs of polybrominated diphenyl ether (PBDE) flame retardants, manufacturers began to substitute other flame retardant chemicals in their products. Little is known about many of the diverse array of bromine-, chlorine-, and phosphorus-containing compounds that have replaced PBDEs. Some of these chemicals have been in use for decades, while others are newer and have not been shown to have endocrine-disrupting properties.

The potential for impacts caused by exposure to mixtures of flame retardants and other endocrine-disrupting contaminants must be thoroughly assessed risks to wildlife. Some South Bay samples exhibited levels of TBP approaching the marine aquatic toxicity threshold of 370 ng/L (predicted no effect concentration (PNEC), ECHA 2014).

Phosphate flame retardants enter the Bay via stormwater and effluent runoff and fate of organophosphorus flame retardants and plasticizers in aquatic organisms, including zebrafish embryos/larvae to TDCPP alters concentrations of thyroid hormones and other endocrine disrupting contaminants must be explored to thoroughly assess risks to wildlife. Some South Bay samples exhibited levels of TBP approaching the marine aquatic toxicity threshold of 370 ng/L (predicted no effect concentration (PNEC), ECHA 2014).

An analyses conducted on 4 L grab samples:

- **AMBIENT BAY WATER**: Discrete grab samples from 12 locations, eight collected in July (dry season), four collected in October, and two collected in November (beginning of wet season).
- **STORMWATER**: Two grab samples collected during each of two storm events from two different urban, industrial settings.
- **WASTEWATER**: Discrete grab samples of effluent from three WWTPs.

Samples were filtered to allow analysis of both particulate and dissolved phases. Some phosphate flame retardants are used as plasticizers, so exposure to plasticized objects.

Analyses were conducted on tri-water phosphate flame retardants (TBP) using liquid chromatography-electrospray ionization-high performance liquid chromatography (LC-ESI-HPLC) and gas chromatography-mass spectrometry (GC-MS) (Klosterman et al. 2013). Labeled phosphorus flame retardants (POCIS) deployed in the Bay in 2010 also suggested that many of these compounds may not adequately characterize less polar phosphate flame retardants.

**RESULTS**

Analytical data from an array of alternative flame retardants in San Francisco Bay. **Phosphate flame retardants were widely detected in San Francisco Bay**.

- **TCP** was typically the most abundant contaminant, followed by TBP and TPhP. TCPP, TCP, and TBP were also widely detected.
- Qualitative data from polar organic chemical integrative samplers (POCIS) deployed in the Bay in 2010 also suggested the presence of these compounds.
- In contrast, there were few detections of TBP and TPhP (Klosterman et al. 2013). Because POCIS are designed to survey polar compounds.
- Contaminants were more concentrated in southern parts of the Bay, where surface waters experience the least amount of mixing with non-estuarine flow, particularly in the dry season. However, the highest hydraulic residence times compared to other segments. The average total concentration of phosphate flame retardants in the South and Lower South Bay was 4 times higher than in the rest of the Bay. Averages of all individual phosphate flame retardants were higher in south-eastern parts of the Bay.
- **San Francisco Bay has higher levels of contamination for most phosphate flame retardants relative to other estuarine or marine regions** (Table 2).
- **Previous monitoring has detected some of these contaminants in Bay sediment, biota, and aquatic bird eggs** (Klosterman et al. 2013).

![Phosphate Flame Retardants in San Francisco Bay](Image)

**Table 1** Potential Endocrine Activity of Phosphate Flame Retardants

<table>
<thead>
<tr>
<th>Phosphate Flame Retardant</th>
<th>Antiandrogenic</th>
<th>Thyroid Disruptor</th>
<th>Possible Thyroid Disruptor</th>
<th>Antiestrogenic</th>
<th>Antiandrogenic</th>
<th>Thyroid Disruptor</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBP</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>TPhP</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>TCPP</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>TDCPP</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

**Table 2** Phosphate Flame Retardants in Estuarine/Marine, Stormwater, and WWTP Effluent Samples (ng/L)

<table>
<thead>
<tr>
<th>Location</th>
<th>Year</th>
<th>TCEP</th>
<th>TCPP</th>
<th>TDCPP</th>
<th>TPhP</th>
<th>TBP</th>
<th>TCrP</th>
<th>TBEP</th>
<th>TEHP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estuarine/Marine</td>
<td>2013</td>
<td>6.2</td>
<td>300</td>
<td>32</td>
<td>2,900</td>
<td>5.9</td>
<td>450</td>
<td>15</td>
<td>300</td>
</tr>
<tr>
<td>Stormwater</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WWTP Effluent</td>
<td>2014</td>
<td>190</td>
<td>1,900</td>
<td>120</td>
<td>85</td>
<td>22</td>
<td>14</td>
<td>2,500</td>
<td>17</td>
</tr>
<tr>
<td>WWTP Effluent</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**CONCLUSIONS**

- **Phosphate flame retardants enter the Bay via stormwater and effluent runoff**.
- **TCP was typically the most abundant contaminant in stormwater, followed by TBP, TCP, TCPP, and TBP** were also widely detected.
- **Bay stormwater contamination is generally similar to that reported in Frankfurt, Germany, with higher levels of TDCPP and TPhP**.
- **TCP** was typically the most abundant contaminant in WWTP effluent, followed by TBP, TCP, TCPP, TBP, and TBP were also widely detected.
- **Bay WWTP effluent contaminant levels were similar to or less than those reported in other regions** (Table 2).
- **Phosphate flame retardants may pose potential risks to Bay wildlife**.
- **In sites and in situ analyses indicate phosphate flame retardants can produce a wide range of endocrine disrupting effects** (Table 1).
- **Studies in fish show measurable endocrine-related impacts at exposure levels of at least 100 times higher than found in San Francisco Bay** (Liu et al. 2012, 2013a,b; Wang et al. 2013).
- **The potential for impacts caused by exposure to mixtures of these and other endocrine disrupting contaminants must be explored to thoroughly assess risks to wildlife**.
- **Some South Bay samples exhibited levels of TBP approaching the marine aquatic toxicity threshold of 370 ng/L (predicted no effect concentration (PNEC), ECHA 2014)**.

**METHODS**

**Analyses were conducted on 4 L grab samples**:  
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