

## **DMMP STATUS REPORT**

### **UPDATE ON PYRETHROID AND PBDE ANALYSIS**

Prepared by Stephanie Stirling (U. S. Army Corps of Engineers) and the RSET Chemical Analyte Subcommittee for the DMMP agencies.

The Regional Sediment Evaluation Framework Chemical Analyte Subcommittee is tasked with reviewing chemicals for potential listing as chemicals of concern for the regional Sediment Evaluation Framework. As part of that effort, the Subcommittee reviewed information on both pyrethroids and PBDEs and prepared white papers that document their findings. For pyrethroids the committee concluded that:

“The USGS found no evidence of permethrin (the most common pyrethroid) in comprehensive water monitoring programs conducted in the Willamette and Yakima watersheds, nor any record of significant agricultural applications of pyrethroids. While the use of these insecticides has grown in California, and toxicity to amphipods has been observed shortly after application and very close to the site of application (i.e. in small ditches and creeks dominated by irrigation return flows), similar conditions have not been shown to be prevalent in larger water courses. We therefore recommend continued monitoring of pyrethroids in regional monitoring programs, such as the USGS NAWQA program. Monitoring of pyrethroids in bed sediments of major waterways should be included. At this time, sufficient evidence does not exist to nominate pyrethroids for inclusion in the RSET program as “chemicals of special concern”.

For PBDEs, the subcommittee concluded:

Although we are concerned about the potential effects of PBDEs on biota, we are hesitant to recommend them as contaminants of special occurrence at this time because of the lack of a standardized analytical method for sediments and uncertainties about their effects on benthic organisms. We recommend that RSET participants should agree upon a standardized method for analysis of PBDEs, and that these chemicals should be incorporated into existing regional monitoring programs as funding allows to improve our knowledge base on their distribution and concentrations in regional sediments.”

The DMMP agencies are providing this information as part of the SMARM process to make stakeholders aware of the on-going consideration of new chemicals of concern.

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**RSET WHITE PAPER #33 – Evaluation of Pyrethroids in Sediments**

**CHEMICAL ANALYTE SUBCOMMITTEE**, T. Thornburg, Chair  
([tthornburg@anchorenv.com](mailto:tthornburg@anchorenv.com)) August 24, 2007

**QUESTION/ISSUE: Are significant sources of pyrethroids present in the Pacific Northwest? Are pyrethroids accumulating in sediments at potentially toxic levels? Should pyrethroids be listed as “chemicals of special occurrence”?**

**Discussion:** This Issue Paper provides a review of agricultural/commercial usage, environmental occurrence, chemical properties and toxicity of pyrethroids. This analysis is used to help prioritize the need for further study of these chemicals.

Because EPA recently phased out certain uses of organophosphorus pesticides due to their potential to cause toxicity in humans, especially children, some of these uses are being replaced by a class of insecticides called pyrethroids. Pyrethroids are synthetic derivatives of pyrethrins which are natural insecticides produced by certain species of chrysanthemum. Pyrethroids are neurotoxins which target insects' central nervous system (Oros and Werner 2005). Pyrethroids are primarily used for agricultural applications on orchards and row crops, structural pest control (to control ants and termites), and residential applications (pet products and lawn care).

Much of the recent research on the environmental effects of pyrethroids has occurred in California, in particular the Central Valley which is characterized by both intensive agricultural practices (the Central Valley produces more than half of the fruits, vegetables, and nuts grown in the U.S.) and rapid urban growth, both of which have encouraged increased pyrethroid usage in the last ten to fifteen years. The differences in land uses, cropping practices, climate, and other factors must therefore be considered when evaluating the applicability of these data to the Pacific Northwest.

**Chemicals of Interest:**

According to the California Department of Pesticide Regulation, the following pyrethroids received the highest applications in California in 2002 (in total pounds applied, including all applications) in decreasing order of importance (Zalom et al. 2005):

- Permethrin (41%)
- Cypermethrin (33%)
- Lambda-cyhalothrin (6%)
- Cyfluthrin (6%)
- Bifenthrin (5%)
- Fenpropathrin (4%)
- Esfenvalerate (3%)
- Deltamethrin (1%)

In particular, permethrin and cypermethrin accounted for about three-quarters of the total pyrethroid applications in California, at 41 percent and 33 percent of the total, respectively.

**Methods of Analysis:**

There are no regulatory approved methods for analysis of pyrethroids. EPA draft Method 1660 uses an HPLC method with MDLs of 1 to 2 ppb in water. It is generally recognized that these detection limits are insufficient to provide environmentally relevant data. The USGS, California Department of Food and Agriculture, and Caltest Analytical Lab in Napa generally follow a GC/MS-SIM procedure (modified EPA Method 8270) with MDLs of 1 to 5 ppt in water and 1 to 5 ppb in sediment. GC/ECD methods can provide similar levels of detection. Use of high-resolution GC/MS methods (HRGC/HRMS) can provide MDLs of 0.01 to 1 ppt in water (when coupled with high-volume sampling techniques) and 0.1 to 1 ppb in sediment (Woudneh and Oros 2006).

None of the regional analytical laboratories surveyed are presently set up for pyrethroid analysis. Pyrethroid analysis would therefore require internal method development, identification of a supplier and acquisition of laboratory standards, possibly new instrumentation, etc., and surcharges would be incurred by customers to cover some of these development costs. Preliminary cost estimates for GC/MS-SIM would likely be in the \$300 to \$500 range, and HRGC/HRMS in the \$800 to \$1,300 range.

**Environmental Sources, Occurrence, and Fate:**

Contaminant Sources. USGS studies conducted under the National Water Quality Assessment Program (NAWQA) provide excellent summaries of estimated pesticide use and application data in both western and eastern climates in the Pacific Northwest. In particular, NAWQA studies of the Willamette River watershed (Anderson et al. 1997) and Yakima River watershed (Ebbert and Embrey 2002) provide pesticide monitoring data representing large agricultural valleys and urban developments on the west side and east side of the Cascades, respectively. These NAWQA studies evaluated usage rates and environmental occurrence of 86 different pesticides, including the most commonly used pyrethroid – permethrin.

Pesticide application data in these watersheds was estimated on the basis of university publications (Oregon State University and Washington State University), statistics compiled by state and federal Departments of Agriculture, discussions with agricultural extension agents, and user/supplier surveys. Nonagricultural applications, such as construction, commercial, and residential uses, were not well quantified but the effects of these sources were nevertheless captured in runoff monitoring from urban areas (see below).

In the late 1990s, no agricultural applications of permethrin were reported in either the Willamette Basin or the Yakima Basin. Insecticide applications continued to be dominated by organophosphorus compounds (chlorpyrifos, diazinon, malathion, azinphos-methyl) and to a lesser extent other compounds (e.g. carbaryl, propargite) in the Pacific Northwest. This is in marked contrast with California practices, where pyrethroid usage peaked in the mid- to late-1990s and remains significant up to the present (Amweg 2005).

Environmental Occurrence (Water). The USGS conducted a comprehensive monitoring program for permethrin, an index pyrethroid, as well as numerous other pesticides in their

NAWQA studies of the Willamette River and Yakima River basins (Anderson et al. 1997; Ebbert and Embrey 2002). Although 36 different pesticides were detected in the Willamette basin, and 25 different pesticides were detected in the Yakima basin, permethrin was not detected in any samples from either basin at a detection limit of 0.005 µg/L. The detection frequencies were 0/94 and 0/98, respectively. The monitoring locations were targeted toward potential source areas, such as agricultural streams dominated by irrigation return flows (both basins), small urban streams (Willamette), and wastewater treatment plant discharges (Yakima). These results are consistent with the lack of reported agricultural pyrethroid applications in these basins.

Environmental Occurrence (Sediment). Sediment testing for pyrethroids is not available in the Pacific Northwest. Pesticide monitoring of sediments in the Central Valley of California provides the closest analogy. The California studies indicate pyrethroids are retained very close to their agricultural or urban source areas and are generally not mobilized into larger water courses. Concentrations are highest shortly after peak application periods and dissipate seasonally.

In 2002 and 2003, about 80 sediment samples were collected from small water bodies in the Central Valley comprised primarily of irrigation return flows, including tailwater ponds, irrigation canals, and small agricultural creeks. Many of the locations were specifically targeted toward areas of historically high pyrethroid use (Weston et al. 2004). In these areas, pyrethroids were detected in 75 percent of the samples. Permethrin was detected most frequently (66% of samples) with a median concentration of 2 µg/kg and maximum concentration of 130 µg/kg in an irrigation canal. Concentrations were greatest shortly after application during the peak summer months. Roughly one quarter of the samples in these agricultural source areas exhibited toxicity to the amphipod *Hyaella azteca*, a species particularly sensitive to pyrethroids. On the other hand, the few samples collected from major rivers showed low or undetectable pyrethroid concentrations which could not account for toxicity occasionally observed in the larger water courses.

Weston et al. (2005) characterized sediments in small urban drainages in a suburb of Sacramento (Roseville) which experienced rapid population growth and expansive new construction on former open grassland. The primary source of water in these drainages was runoff from over-irrigation of landscapes and lawns. Pyrethroid concentrations as high as several hundred parts per billion were observed, affecting survival of *H. azteca* in localized areas near storm drain inputs. However, the main creek in the development—measuring 2 to 3 feet deep and 6 to 12 feet wide—remained largely unaffected. In the main creek, pyrethroid concentrations had decreased by one to two orders of magnitude (many below detection) and little toxicity was observed, indicating minimal transport of pyrethroids beyond the immediate influence of residential irrigation runoff.

Toxicity. Aquatic and sediment toxicity data are summarized in Table 1. Solomon et al. (2001) performed a distributional analysis of aquatic toxicity data to identify the lower tenth percentile LC50 values as defined by the most sensitive laboratory test species. Aquatic invertebrates, including crustaceans (e.g. amphipods) and insects, are generally the most sensitive species; fish are not quite as sensitive (typically by one or more orders of magnitude); and molluscs are

relatively insensitive (Oros and Werner 2005).

Amweg et al. (2005) used spiked sediment bioassays to develop median lethal concentrations (LC50) and growth lowest observable effects concentrations (LOEC) for pyrethroids based on 10-day *H. azteca* tests (Table 1). Toxicity data from Weston et al. (2004) suggest *H. azteca* is more sensitive to pyrethroid toxicity than *Chironomus tentans*.

**Table 1. Chemical Properties and Toxicity Data for Pyrethroids**

|                    | Relative Usage <sup>[1]</sup> | Koc <sup>[2]</sup> | Soil Aerobic Half Life <sup>[2]</sup> | Soil Anaerobic Half Life <sup>[2]</sup> | Water Aerobic Half Life <sup>[2]</sup> | Water LC50 <sup>[3]</sup> | Sediment LC50 <sup>[4]</sup> | Sediment LOEC <sup>[4]</sup> |
|--------------------|-------------------------------|--------------------|---------------------------------------|---|--|---------------------------|------------------------------|------------------------------|
|                    | (%)                           | (L/kg)             | (days)                                | (days)                                  | (days)                                 | (ng/L)                    | (µg/kg)                      | (µg/kg)                      |
| Permethrin         | 41%                           | 277,000            | 40                                    | 197                                     | --                                     | 76                        | 90                           | 59                           |
| Cypermethrin       | 33%                           | 310,000            | 28                                    | 55                                      | 7                                      | 10                        | --                           | --                           |
| Cyfluthrin         | 6%                            | 124,000            | 12                                    | 34                                      | --                                     | 12                        | 14                           | 7.5                          |
| Lambda-Cyhalothrin | 6%                            | 326,000            | 43                                    | --                                      | 22                                     | 10                        | 5.6                          | 2.2                          |
| Bifenthrin         | 5%                            | 237,000            | 96                                    | 425                                     | --                                     | 15                        | 4.5                          | 2.9                          |
| Fenpropathrin      | 4%                            | --                 | 22                                    | 276                                     | --                                     | --                        | --                           | --                           |
| Esfenvalerate      | 3%                            | --                 | 39                                    | 90                                      | 72                                     | 37                        | 24                           | 9.4                          |
| Deltamethrin       | 1%                            | 704,000            | 24                                    | 29                                      | 80                                     | 9                         | 9.9                          | 10.2                         |

Notes:

[1] California State-Wide Usage 2002, as reported in Zalom et al. 2005

[2] Laskowski 2002

[3] Solomon et al. 2001, 10th percentile value of species distribution

[4] Amweg et al. 2005, 10-day spiked-sediment bioassay, *H. azteca*

**Chemical Properties.** Pyrethroids are hydrophobic, with organic-carbon partitioning coefficients (Koc values) ranging from 124,000 to 704,000 L/kg (see Table 1; Laskowski 2002). Thus, pyrethroids will partition strongly to sediments and will tend to be transported primarily with suspended sediments rather than in solution.

Although pyrethroids are hydrophobic and thus lipophilic and fat soluble, they are easily degraded and are not known to be stored in the body nor excreted in milk. They have multiple sites in their structures that can be readily attacked in biological systems (Oregon State University 2006). Depuration is rapid and bioaccumulation through the food web is not a significant route of exposure (Oros and Werner 2005).

**Environmental Persistence.** Degradation half lives for pyrethroids in water range from a several days to several weeks (Laskowski 2002; Table 1). Degradation half lives in aerobic sediments are typically a few weeks to a few months, and half lives in anaerobic sediments range from a few months to approximately one year. Based on these rates, significant degradation is likely to occur between one application season and the next. These rates are similar to those of other modern pesticides which also degrade relatively quickly in the environment, especially compared to legacy pesticides such as DDT and chlordane which can persist for decades.

**CONCLUSION AND RECOMMENDATION:**

The USGS found no evidence of permethrin (the most common pyrethroid) in comprehensive water monitoring programs conducted in the Willamette and Yakima watersheds, nor any record of significant agricultural applications of pyrethroids. While the use of these insecticides has grown in California, and toxicity to amphipods has been observed shortly after application and very close to the site of application (i.e. in small ditches and creeks dominated by irrigation return flows), similar conditions have not been shown to be prevalent in larger water courses. We therefore recommend continued monitoring of pyrethroids in regional monitoring programs, such as the USGS NAWQA program. Monitoring of pyrethroids in bed sediments of major waterways should be included. At this time, sufficient evidence does not exist to nominate pyrethroids for inclusion in the RSET program as “chemicals of special concern”.

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**DRAFT RSET WHITE PAPER #4 – Evaluation of PBDEs as a contaminant of concern in Sediments and tissues**

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**QUESTION/ISSUE: Are brominated fire retardants (PBDEs) accumulating in sediments at potentially toxic levels? Should they be listed as “chemicals of special occurrence” to be considered for evaluation in urban areas where potential sources are located? Should sediment and tissues guidelines be developed for PBDEs?**

**DISCUSSION:** Polybrominated diphenyl ethers (PBDEs) are flame retardants that are added to many consumer products, including clothing, furniture, and electronic equipment for fire protection. Structurally these compounds are similar to PCBs, and are persistent in sediments with the potential for bioaccumulation and biomagnification. The toxicity of PBDEs, especially to aquatic organisms, is not fully understood, but there is evidence that they may disrupt thyroid function and cause neurodevelopmental problems (ASTDR 2004; Ecology 2006). Regional monitoring studies have documented the presence of PBDEs in aquatic environments throughout the Pacific Northwest, with elevated levels at urban and industrial sites. This White Paper provides a review of usage rates, environmental occurrence, chemical properties, and toxicity of PBDEs, which may be used to evaluate the need for their inclusion as a contaminant of concern in the Pacific Northwest. After sufficient data have been collected (including synoptic chemistry and bioassay data), these chemicals may be evaluated to determine whether they contribute to sediment toxicity, and if so, whether the observed effects are predictable enough to support the development of screening levels.

**Chemicals of Interest:**

Commercial PBDEs are manufactured by bromination of diphenyl ethers resulting in a mixture of diphenyl ethers containing tetra-, penta-, hepta-, octa-, and deca-congeners in various percentages (ATSDR 2004). There are three commercial products as Penta-, Octa- and Deca-brominated diphenyl ethers. There are 209 individual congeners that can be divided into 10 homologue groups from mono- to deca-BDE. Of these, the tri- to hexa-BDEs are the most lipophilic. The most persistent congener is PBDE-47. The most commonly detected congeners in biological and environmental samples are PBDE-47, PBDE-99, and PBDE-153. PBDE-209 is also found at high concentrations in house dust (Ecology 2006). Higher brominated commercial mixtures (e.g., decaBDE) are concentrated in soils and sediment near industrial point sources.

The second Chemical Action Plan developed under the Washington state PBT Initiative focuses on PBDEs (Ecology, 2006). The PBDE levels in Washington’s fish tissue samples and water samples are currently assessed and the results will be used to establish baseline PBDE conditions in Washington freshwater area (Johnson and Seiders, 2005). There are no regulatory criteria for PBDEs for the protection of human health and the

environment. Diet, especially food with high fat content like fatty fish, is the main exposure pathway for the adults in the general public.

**Methods of Analysis:**

Brominated fire retardants may be analyzed by GC/MS or GC/ECD using methods similar to those used for measurement of PCBs and organochlorine pesticides.

EPA has developed a draft method 1614 for analysis of PBDE congeners in water, soil, sediment, biosolids and tissue by high resolution GC/MS (HRGC/HRMS), which measures all 209 PBDE congeners. The method detection limits and practical quantitation limits (PQLs) for EPA Method 1614 are typically in the 1-10 ppt range for sediment and tissue and 20 – 100 ppq range for water. A similar method is GC/HRMS method for analysis of tissues is described Alae et al (2001).

However, this level of detail may not be necessary for initial screening analyses. Alternatively, the Washington Department of Ecology Manchester Environmental Laboratory (MEL) has the standard operating procedure (SOP) 730002 for “Analysis of Water/Soil/Sediment/Fish Tissue Samples for Organochlorine Pesticides, PBDEs and PCBs by GC/ECD. The PQLs for SOP 73002 are in the 0.0033 – 0.1 ppb range for water and 1.0 – 100 ppb range for tissue. The MEL also has the SOP based on the EPA method 8270 to identify low level PBDEs in water, soil, sediment, sludge, oil samples, and tissue by GC/MS with PQLs of 2 – 5 ppb for all congeners except congener 209, Deca-BDE (Ecology 2005). NOAA’s Northwest Fisheries Science Center uses a similar GC/MS method (not high resolution) for quantitation of a subset of the most common PBDE congeners (BDEs 28, 47, 49, 66, 85, 99, 100, 153, 154, and 183) in sediment and tissue samples (Sloan et al. 2005), in conjunction with PCBs (40 congeners) and organochlorine pesticides. Method detection limits and practical quantitation limits for the NOAA method are typically in the 1-5 ppb range, depending on sample size.

Commercial laboratories are beginning to offer PBDE analyses by EPA Method 1614 and modified versions of EPA Method 8270. The approximate cost for commercial analysis of sediment by EPA Method 1614 is \$1000 or more; the modified EPA Method 8270 would be less expensive. If method 8270 were used, the PBDE analyses could be potentially be incorporated into analyses for organochlorine compounds and phthalates by Method 8270 that are already routinely required under the SEF.

**Evaluation Criteria:**

Use Rates. PBDEs occur in three technical mixtures: Penta-BDE used mainly in foam for furniture and upholstery, Octa-BDE used in plastics for business machine, and Deca-BDE used in electronic closures and textiles. Of the three mixtures, Penta-BDE is the most bioaccumulative. In 2001, the total market demand for PBDEs within the Americas was 33,100 metric tons, with deca-BDE accounting for 74% of the total (ATSDR 2004). There are 141 facilities that produce or process Deca-BDE in the United States, including one facility in Washington State with between 10,000 and 100,000 lbs of the material on site (ATSDR 2004). Production of Penta and Octa-BDEs was phased out voluntarily in the USA by the end of 2004 (ATSDR 2004). Therefore Deca-BDE currently accounts for 100

% of PBDE production. The amount of PBDEs used in consumer products usually ranges between 5 and 30% by weight (Alaee et al 2003).

Detection in Water. There information on PBDE concentrations in Pacific Northwest waters is limited. In a study in San Francisco Bay, PBDE concentrations in water samples ranged from 0.3 to 513 pg/L, with highest concentrations at sites with high inputs of wastewater treatment plant effluent (Oros et al. 2005). The Washington DOE measured PBDEs in the water column in Washington State river and lakes using SPMDs (Johnson et al. 2006). Estimated water column concentrations, based on the SPMD data ranged from 1-926 pg/L in the fall and from 8-146 pg/L in the spring, with highest concentrations in the Spokane River. The highest total PBDE concentrations observed in other water bodies were 80 pg/L in Lake Washington, 50-57 pg/L in the Columbia River, and 40 pg/L in the Yakima River. The USGS also measured PBDEs in the Lower Columbia and Lower Willamette Rivers using SPMDs, and found concentrations similar to those reported in the Columbia by Washington DOE (LCREP 2007; Morace 2006). Levels were highest in the Lower Willamette, near Portland, OR.

Detection in Sediment. Information on PBDE concentrations in the Pacific Northwest sediments is limited, but detections have been reported. Rayne et al. (2003) measured PBDE concentrations ranging from 2.7 to 91 ppb dry wt in 11 surficial sediments collected from several sites along the Columbia River system in Southeastern British Columbia in 2001. The concentrations of PBDEs in sediments from San Francisco Bay ranged from below detection limits to 212 ppb dry wt (Oros et al. 2005). In 2004-2005, the Washington State Department of Ecology surveyed Puget Sound sediments for a subset of common PBE congeners, and found concentrations ranging from < 1 to ~13 ppb, somewhat lower levels than in San Francisco Bay (Dutch and Assen 2007). The USGS and the Lower Columbia Estuary Partnership detected PBDEs on suspended sediments at a site near the mouth of the Lower Columbia River, at a concentration of 84 ppb (LCREP 2007; Morace 2006). Overall, concentrations of PBDEs in sediments from California and the Pacific Northwest are fairly typical of concentrations ranges for other sites in the United States, with Puget Sound in the lower end of the range (ATSDR 2004).

Detection in Tissues of Aquatic Organisms. Bioaccumulation of PBDEs in the aquatic food web is inversely related to the degree of bromination (Burreau et al. 2000b; Jansson et al. 1993). Thus, higher brominated congeners are rarely detected in biota. This is a result of their low solubility and high log Kow values (Hardy 2000). In contrast, tetra- to hexaBDE homologs are most frequently detected in biota (Burreau et al. 1997), which would be expected due to their greater water solubility and relatively high Kow values. Concentrations of PBDEs in biota are related to the trophic level of the species. For example, Haglund et al. (1997) examined the concentrations of PBDEs in herring, salmon muscle, and gray and ringed seals collected along the Swedish coast of the Baltic sea between 1981-1988. PBDE concentrations were found to increase with trophic level. (ATSDR 2004)

Concentrations of PBDEs have been measured in tissues of several types of organisms at

Pacific Northwest sites, including invertebrates, fish, birds, and marine mammals. NOAA Fisheries and the Lower Columbia Estuary Partnership (LCREP) detected PBDEs at concentrations ranging from < 1 to 66 ng/g ww (wet wt) in stomach content samples of juvenile Chinook salmon from the Lower Columbia River and Estuary, which contained of chironomid larvae and other aquatic insects. Highest PBDE levels were found in salmon collected in the Portland and Vancouver area (LCREP 2007). The US Army Corps of Engineers has detected PBDEs in a similar concentration range (up to ~180 ng/g ww) in freshwater clams (*Corbicula* sp.) collected from Columbia River sites from Bonneville to the mouth of the estuary. These concentrations are comparable to those reported for oysters, mussels, and clams from San Francisco Bay (Oros et al. 2005). Similarly, Ikonomou et al. (2002) found PBDE concentration ranging from 0.6-52 ng/g ww in hepatopancreas of Dungeness crab (*Cancer magister*) from British Columbia coastal sites.

The Washington State Department of Ecology analyzed freshwater fish samples from various locations in Washington State, and found PBDE concentrations ranging from 1.4 ng/g ww in rainbow trout from Douglas Creek in Eastern Washington to 1,250 ng/g ww in mountain whitefish from the Spokane River (Johnson and Olson 2001; Johnson et al. 2006). The highest PBDE concentrations were found in fish from areas draining urbanized watersheds (Spokane, Yakima and Snake Rivers); concentrations were much lower in undeveloped watersheds (Douglas Creek, Rock Island Creek, and Soleduck River). Tetra and penta isomers were the major congeners present, in ratios similar to the commercial formulation Penta-BDE. PBDEs have also been detected in adult salmon and several species of marine fish in Puget Sound (O'Neill et al. 2005), at concentrations up to about 30 ng/g ww, and in juvenile salmon from the Lower Columbia River and Puget Sound at concentrations as high as 93 ng/g ww (LCREP 2007). Rayne et al. (2003) found comparable concentrations of PBDEs in Mountain whitefish from the Columbia River, British Columbia (0.726 – 131 ng/g ww), while Ikonomou et al. (2002) found PBDE concentration ranging from 2-17 ng/g ww in liver of English sole (*Pleuronectes vetulus*) from coastal British Columbia sites.

PBDEs also appear to be accumulating in fish-eating birds and mammals. Buck et al. (2005) measured total PBDEs in bald eagle eggs collected along the Lower Columbia River in Washington and Oregon states at 446 to 1,206 ng/g wet weight. Reported PBDE concentrations in Heron eggs from British Columbia ranged from 1-288 ng/g ww (citation?). High levels of PBDEs have been reported in sea otters from the California coast (up to 26,800 ng/g lipid in sea otter liver; Kannan et al. 2007) and orca whales from Puget Sound and Georgia Basin (Rayne et al. 2004). Ikonomou et al. (2002) found PBDE concentration ranging from 240-2200 ng/g ww in blubber of harbor porpoise (*Phocoena phocoena*) from coastal British Columbia sites.

Hydrophobicity. The octanol-water partitioning coefficient ( $K_{ow}$ ) is a measure of the hydrophobicity. The Log  $K_{ow}$  values for PBDEs are relatively high, typically in the 7-12 range for mixtures and different individual congeners (e.g., Log  $K_{ow}$  = 12.1 (EPIWIN). Log  $K_{ow}$  = 6.27 (measured) (EU Risk Assessment, 2002). Log  $K_{ow}$  = 6.77 (tetra-BDE), Log  $K_{ow}$  = 7.66 (penta-BDE), Log  $K_{ow}$  = 8.55 (hexa-BDE) (ASDTR 2004; Ecology 2006). These values are in the same range as persistent, bioaccumulative contaminants

such as PCBs and DDTs. In general, PBDEs are hydrophobic, and will exhibit a strong tendency to adsorb to sediments

Environmental Persistence. PBDEs are quite persistent in the environment. For Deca-hexa, penta, and tetra-BDE congeners, estimated half-lives are: 180 days in water; 360 days in soil; 1600 days in sediment (EPA PBT Profiler); for Deca-BDE, a half-life has also been estimated of 460 days in air (EPA PBT Profiler). Recent studies indicate that Deca-BDE can be broken down into lower brominated PBDEs through exposure to sunlight or biodegradation.

The lower-brominated PBDEs have an especially high potential for bioconcentration. For Deca-BDE, the estimated bioconcentration factor (BCF) is 3.16 (EPIWIN), but the BCFs of potential breakdown products are much higher (e.g., 32,000 for tetra-BDE; 8,100 for penta-BDE; and 490 for hexa-BDE, estimated with the EPA PBT Profiler). A BCF of ~27,400 has been determined for the Penta commercial product in carp (EU Risk Assessment for Penta-BDE, 2000). Juvenile carp given Deca-BDE in feed contained no detectable amount of the parent compound, but several ethers containing five to eight bromines were found (Stapleton et al., 2004). Deca-BDE has been found in food, indoor dust, human fat, blood, and breast milk (Ecology 2006).

Toxicity. Structurally, PBDEs, are very similar to PCBs, and may have some of the same toxic properties. In mammals, PBDE exposure has been linked to imbalances in thyroid hormone levels and disruption in thyroid function, and exposure to PBDEs during early development can lead to neurological abnormalities and subtle impacts on learning and behavior (Gill et al. 2004, Danerud 2003, McDonald 2002). Effects on neural development and thyroid function occur at doses as low as 0.6-2 mg/kg body weight in rats and mice (Danerud 2003).

Research on the toxicity of PBDEs to aquatic organisms is more limited, although some of the effects reported in mammals have been induced in fish exposed to PBDEs in the laboratory. Depressed plasma thyroid hormone levels have been reported in juvenile lake trout (*Salvelinus namaycush*) exposed to dietary PBDE at concentrations ranging from 32.5 to 325 ng/g wet wt in the laboratory for 56 days (Tomy et al. 2006), concentrations that are within the range reported in invertebrate species that are representative of fish prey. There is also some evidence for neuro-developmental impacts of PBDEs in fish. Timme-Laragy et al. (2006) found changes in activity level, fright response, predation rates, and learning ability in killifish (*Fundulus heteroclitus*) exposed to a PBDE mixture at water concentrations from 0.001 to 100 ug/L during embryonic development (day 0-7 post fertilization). At concentrations from 0.001-0.1 ug/L, which are within the reported environmental range, fish showed reduced activity and changes in feeding behavior, while at 1 ug/L, there were effects on learning behavior. Delays in hatching time were seen at concentrations as low as 0.1 ug/L. Lema et al. (2007) observed neural defects and cardiac arrhythmia, and reduced survival in larval zebrafish exposed to PBDE 47, but at relatively high concentrations (>100 ug/L in water and > 3400 ng/g wet wt in zebrafish tissue). Dietary exposure to PBDEs in the 1000 ug/g wet wt range disrupts metamorphosis in frogs (Carlsson et al. 2007; Balch et al. 2006).

PBDEs may also have reproductive effects; Muirhead et al. (2006) observed disrupted egg laying, reduced condition factor, and reduced sperm production in fathead minnows exposed to dietary PBDE 47, but tissue concentrations where these effects were produced were substantially higher than levels reported in the field studies cited above; the PBDE body burden in the males was 15,000 ng/g ww, while that in the females was 60,000 ng/g ww.

Exposure to PBDEs does not appear to induce CYP1A activity (Boon et al. 2002, Timme-Laragy et al. 2006); nor does it appear to have estrogenic activity, based on its ability to induce vitellogenin or zona radiata proteins in Atlantic salmon (Boon et al. 2002). Their immunotoxicity seems to be weak. Birchmeier et al. 2006 found reduced viability of immune cells of lake trout exposed to PBDE 47, but only concentrations well above those reported in the environment (100 g/L). Similarly, there are few reports of immunotoxic effects of PBDEs in mammals except at high exposure concentrations (Gill et al. 2004).

Additional toxicity data are available for water and dietary exposures from several bioassays (Ecotoxicity Data excerpted from Ecology 2006 Appendix F):

- Crustaceans, based on the Daphnia assay (21 days exposure), the NOEC = 2 ug/l (solubility limit for Deca- BDE) (EU Risk Assessment, 2002).
- Fish (killifish) LC50 (48 hours) > 500 mg/l (above water solubility limit). Fish (rainbow trout; 16, 49 or 120 day exposures) LOEL = 7.5 – 10 mg/kg body weight/day (120 day exposures). (EU Risk Assessment, 2002).
- Algae EC50 (72 or 96 hours) > 1 mg/l (EU Risk Assessment, 2002).
- Activated sludge microorganisms, NOEC .>= 15 mg/l (EU Risk Assessment, 2002).

Human toxicity data excerpted below are from ATSDR 2004:

- An MRL of 0.006 mg/m<sup>3</sup> has been derived for intermediate-duration inhalation exposure (15–364 days) to lower brominated BDEs.
- An MRL of 10 mg/kg/day has been derived for intermediate-duration oral exposure (15–364 days) to decabromodiphenyl ether.
- An MRL of 0.03 mg/kg/day has been derived for acute-duration oral exposure (14 days or less) to lower brominated diphenyl ethers.
- An MRL of 0.007 mg/kg/day has been derived for intermediate-duration oral exposure (15–364 days) to lower brominated BDEs.

As yet, few human health or aquatic life criteria have been developed for PBDEs. In 2005, the State of North Carolina, based on guidance from EPA, recommended a threshold concentration of 2,000 ug/Kg in fish tissue for fish consumption warnings.

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**RECOMMENDATION:** PBDEs have been detected in biota and to a lesser extent in sediments from Pacific Northwest sites at concentrations comparable to those measured in other urbanized river and estuaries in the United States. These compounds may pose a risk to organisms because of their persistence in media and their bioaccumulation into fish, wildlife, and humans. In these higher order receptors, PBDEs appear to have effects on thyroid function and neurological development, based on studies conducted primarily with mammals. However, little information is available on their direct sediment toxicity to benthic organisms. Because toxicity data on the effects of PBDEs on fish and benthic organisms are limited, it is difficult to offer recommendations for screening level guidelines for either sediments or fish tissues. Also, although various methods have been used to measure PBDEs, as yet there is no standardized method for their analysis and no standard list of congeners available to recommend to commercial labs.

Although we are concerned about the potential effects of PBDEs on biota, we are hesitant to recommend them as contaminants of special occurrence at this time because of the lack of a standardized analytical method for sediments and uncertainties about their effects on benthic organisms. We recommend that RSET participants should agree upon a standardized method for analysis of PBDEs, and that these chemicals should be incorporated into existing regional monitoring programs as funding allows us to improve our knowledge base on their distribution and concentrations in regional sediments. Bioassay, animal and epidemiological studies are also needed to determine NOELs, LOELs, and safe human health and ecological health risk based concentrations for PBDEs. We strongly encourage additional research to better characterize toxic responses of fish and aquatic invertebrates to PBDEs, as well as more extensive agency monitoring of PBDE concentrations in the environment.

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