

## Revised Evaluation Guidelines for Benzyl Alcohol in Marine Sediments

Prepared by Heather Whitney Fourie (U.S. Army Corps of Engineers) and David Fox (U.S. Army Corps of Engineers) for the DMMP agencies.

### Introduction

Benzyl alcohol is one of the standard Dredged Material Management Program (DMMP) chemicals of concern (COCs) required to be analyzed for dredging projects in marine waters. It has a screening level (SL) of 57 ug/kg and a maximum level (ML) of 870 ug/kg (DMMP, 2015b).

The DMMP evaluation guidelines require toxicity testing if one or more COC exceeds its SL. Toxicity testing consists of a suite of three bioassays: a 10-day amphipod mortality test; 48-hr bivalve or echinoderm larval development test; and a 20-day juvenile infaunal mortality and growth test using *Neanthes arenaceodentata*.

### Problem Identification

Since around 2011, benzyl alcohol has been much more frequently detected in dredged material characterization studies than in the years prior (1989-2010). More importantly, benzyl alcohol has been the only COC to exceed its SL in several recent DMMP projects, including the Duwamish Turning Basin and Navigation Channel O&M (2011), Snohomish Navigation Channel O&M (2012), Shelter Bay Marina (2014a), La Connor Marina (2014b), and Bellingham Cold Storage (2015a). Under the current DMMP guidance, biological testing of sediments is required for even a single exceedance of a marine SL. However, unlike other anthropogenic contaminants such as PCBs and organochlorine pesticides, benzyl alcohol has both industrial and natural sources, and has long been suspected of being associated with leaf litter, small woody debris or other herbaceous or ligneous material of terrestrial origin. This led the DMMP agencies to apply best professional judgment (BPJ) to eliminate the requirement for bioassays for four of the five projects listed above. Concurrent bioassays were conducted on all samples from the Duwamish O&M project, so use of BPJ was not necessary in that case.

Best professional judgment is used on a case-by-case basis to address analytical problems, ambiguous data or other project-specific issues that arise during dredged material characterization. However, the number of cases in which benzyl alcohol was the only COC exceeding SL reached a point where the DMMP agencies determined that a more rigorous evaluation was needed to validate the use of BPJ.

### Technical Evaluation

Seattle District conducted a multifaceted technical evaluation on behalf of the DMMP agencies, including an investigation into the increasing number of benzyl alcohol detections; a review of the sources of benzyl alcohol; research into its biodegradability; mapping of its distribution; a review of disposal site monitoring data; an evaluation of its toxicity; and a review of the origins of its regulation in the State of Washington.

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## ***Why the Increase in Detections of Benzyl Alcohol?***

### **Data trend**

Figure 1 displays the number of Dredged Material Management Units (DMMUs) with detects and non-detects of benzyl alcohol that exceeded the current SL of 57 ug/kg by biennial report year. Prior to 2005, benzyl alcohol was frequently reported as a non-detect above the SL in DMMP projects, but was only *detected* once above the SL. After 2005, the number of benzyl alcohol non-detects that exceed the SL drops off dramatically, and a significant increase in benzyl alcohol detections above the SL is observed starting around 2011.

Increased benzyl alcohol occurrence has not been limited to DMMP projects. A compilation of surface sediment benzyl alcohol data for the Lower Duwamish Waterway shows a dramatic increase in both detection frequency and the frequency of exceedance of the SL in the datasets collected after 2010 (S. McGroddy, Pers. Communication, 2016). Figure 2 summarizes the Lower Duwamish Waterway data.

The DMMP and Lower Duwamish data raise the question: are we really seeing an increase in benzyl alcohol concentrations in Washington State sediments, or could there be other factors at play? To answer this question, Seattle District reached out to local laboratories and consultants familiar with sediment sampling and the analysis of benzyl alcohol in sediments.

### **Analytical Improvements**

The primary analytical method used to measure benzyl alcohol is EPA Method 8270 for semi-volatile organic compounds. The basic underlying principles (gas chromatography and mass spectrometry) have not changed since DMMP sediment data collection began in earnest in the early 1990s. Historically, benzyl alcohol recoveries have been challenging for laboratories due to chromatographic interferences. In the 1990s, larger volumes of sediment were required for extraction; frequently these extracts contained high levels of humic materials and other interferents that required additional cleanup steps. Any materials that could not be removed could have affected chromatography and, more specifically, could have resulted in non-detect results for more reactive compounds such as benzyl alcohol<sup>1</sup> (S. McGroddy, personal communication, 2016).

Faced with demands for lower detection limits for many of the analytes of EPA Method 8270, laboratories have worked hard to increase the efficiency of their sample extraction and analysis methods including replacing or upgrading instruments, injectors, solvents, extraction procedures, and more. Increased efficiency enables the laboratory to reduce the sample mass required for analysis which is important because it reduces the amount of matrix interference in the sample. The cumulative effect of these numerous individual improvements is likely a contributing factor to the sudden recent increase in both the frequency and magnitude of detections of benzyl alcohol.

A recent (2015) sediment monitoring event at the Boeing Plant 2 Superfund Early Action Site clearly demonstrates the impact of laboratory improvements on analytical results for benzyl alcohol (AMEC, 2015). Benzyl alcohol was not detected in six sediment samples collected at +7 feet MLLW from the recently restored shoreline area at the site. The sample results were rejected due to low (less than 10%)

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<sup>1</sup> EPA Method 8270D Section 1.4.6 states: "Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, benzoic acid, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, 2-nitroaniline, 3-nitroaniline, 4-nitroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material." (EPA, 1998)

Laboratory Control Sample (LCS) recoveries. In response, the laboratory quickly and aggressively tackled the problem with internal extraction and methodological improvements. LCS recoveries were dramatically improved, and re-analysis of the six samples resulted in benzyl alcohol detections in three of the six samples, with a maximum concentration of 360 ug/kg (AMEC, 2015).

Our research into the increase in benzyl alcohol detections suggests that both the increase in frequency of detection of benzyl alcohol and the magnitude of the concentrations reported are due to improvements in analytical technologies and techniques. If this is true, then much of the historical benzyl alcohol data associated with sediment samples in Washington State may underestimate the frequency of detection and concentrations of benzyl alcohol. It is important to keep this caveat in mind when evaluating time trends in the distribution of benzyl alcohol, its co-occurrence with benzoic acid, and benthic toxicity associated with its presence.

### ***Sources – Industrial and Natural***

Benzyl alcohol is an aromatic organic alcohol produced and used industrially as a solvent, a preservative, and as feedstock for the manufacture of other chemicals. The chemical is commonly used in the soap, perfume and flavoring industries and as an ingredient in ointments and cosmetics; it is also frequently used in inks, paints, epoxy resins and paint strippers (HSDB, 2016; HPD, 2016). Benzyl alcohol is added as a carrier solvent for flavoring substances to some foods and beverages at a level up to 400 mg/kg (EC, 2002). In 2009, the FDA approved a 5% solution for treatment of head lice in patients 6 months of age and older (Concordia Pharmaceuticals, 2013; Buck, 2012; CDC, 2016). At lower concentrations (0.9%), benzyl alcohol is available for use as a bacteriostatic preservative in intravenous solutions (Hospira, 2016; Pediatrics in Review, 1984).

Benzyl alcohol is found naturally in a number of plants, including some edible fruits (up to 5 mg/kg) and in green and black tea (1-30 and 1-15 mg/kg respectively) (EC, 2002). It is also found in daffodils (165-330 mg/kg), hyacinths (64-920 mg/kg), jasmine (120-228 mg/kg), rosemary (7-32 mg/kg), tangerines (1-2 mg/kg), blueberries (0.01-0.08 mg/L in fruit juice).

In addition to improvements in analytical technologies and techniques, it is possible that some of the increase in detected benzyl alcohol in Puget Sound can be explained by a growing use of this chemical in consumer products such as food, cosmetics, solvents, etc. Seattle District attempted to address this possibility, but a significant amount of time and effort would be needed to investigate this question properly.

The available literature regarding natural sources of benzyl alcohol focused exclusively on food and flowers. Nothing was found that provided any insight into natural sources of benzyl alcohol in marine sediments.

While no published scientific literature was found in which plant material from common Northwest species was analyzed for benzyl alcohol, there is strong evidence from a habitat restoration project at Boeing Plant 2 on the Duwamish Waterway. Organic matter approved for use at this project was chemically analyzed. The material was derived from a local source of “dark fines,” composed primarily of duff (i.e., leaves, branches, bark and stems from the forest floor) and other organic material cleared from forested areas. In two samples taken from fully-aged and partially-aged stockpiles of these dark

finest, benzyl alcohol concentrations were 3,910 and 450 ug/kg, respectively<sup>2</sup> (Floyd|Snider, 2013). Note that the benzyl alcohol concentration in the fully-aged sample was nearly an order of magnitude greater than that in the partially-aged sample, which may indicate that benzyl alcohol is generated by decaying plant matter.

Circumstantial evidence also exists from the four DMMP projects for which BPJ was used. Visible organic matter (leaves, twigs, roots, etc.) was noted in the core/sample logs for all of these projects. This observation was used as one line of evidence to justify waiving biological testing for these projects.

Based on the evidence in hand, we hypothesize that some or all of the benzyl alcohol found in many sediment samples has its origin in herbaceous or ligneous material from the terrestrial environment.

### ***Biodegradation***

Studies using the Organization for Economic Cooperation and Development biodegradation testing protocols has shown that benzyl alcohol is readily biodegradable, with 94% biodegradation measured in a standard 28-day test conducted under aerobic conditions (HSDB, 2016). A shorter 7-day test (also under aerobic conditions) produced the same percentage of biodegradation (92-96%) (HSDB, 2016). If released to water, benzyl alcohol is expected to undergo microbial degradation under aerobic and anaerobic conditions (EPA, 1993; Howard, 1993). Using sediment from an anoxic salt marsh, benzyl alcohol underwent degradation to carbon dioxide and methane after a 2-month incubation period (Howard, 1993).

Biodegradation also occurs readily in wastewater treatment facilities under both aerobic and anaerobic conditions. Benzyl alcohol underwent 70% biological oxygen demand in 5 days under aerobic conditions using an acclimated mixed microbial culture (Howard, 1993). Under anaerobic conditions, benzyl alcohol underwent 100% mineralization within two weeks when inoculated with municipal digester sludge (Howard, 1993). The fraction of benzyl alcohol removed by wastewater treatment plants in the Puget Sound region is unknown. While benzyl alcohol is readily biodegradable, the fraction removed depends on temperature and retention time, among other factors. If benzyl alcohol is not completely removed, it will appear in the effluent discharged to the receiving waters. For example, benzyl alcohol was detected in effluent samples from two of ten treatment plants in Illinois (Ellis, 1982)

Benzoic acid is a degradation product of benzyl alcohol and is structurally very similar. Benzoic acid biodegradability has been extensively studied with study results confirming that it too is readily biodegradable under both aerobic and anaerobic scenarios (HSDB, 2016).

Like benzyl alcohol, benzoic acid has many industrial uses in the preservative and flavor industry (Wibbertmann et al, 2000). It is also on the list of DMMP COCs for marine and freshwater sediments. The marine SL and ML for benzoic acid are 650 and 760 ug/kg, respectively.

Both benzyl alcohol and benzoic acid are of low concern for bioaccumulation. Benzyl alcohol's reported range of octanol-water partitioning coefficients ( $\log K_{ow}$ ) is relatively low: 1.00 to 1.16 (EPA, 1978; Montgomery, 2000). The reported range of  $\log K_{ow}$  values for benzoic acid is slightly higher: 1.69 to 2.18 (Montgomery, 2000). Chemicals with low octanol-water partitioning coefficients ( $\log K_{ow} < 2.7$ )

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<sup>2</sup> Benzoic acid concentrations were also elevated at 5,600 and 3,630 ug/kg for the fully aged and partially-aged stockpiles, respectively. The DMMP marine SL for benzoic acid is 650 ug/kg.

generally have low soil sorption, low bioaccumulative risk, high biodegradation rate, high solubility and greater mobility (Weiner, 2008).

Our hypothesis is that benzyl alcohol in dredged material disposed at the DMMP open-water sites is biodegraded to benzoic acid within a short time span and poses a low bioaccumulative risk to benthic organisms.

### ***Geographic Distribution***

If common Northwest tree and plant species do contain benzyl alcohol, and debris from these trees and plants is entering marine waters via riverine or other discharges, then this chemical would be expected to be found throughout Puget Sound, including non-urban areas, geographically removed from possible industrial sources or wastewater outfalls. And, since benzyl alcohol is readily biodegraded to benzoic acid, one would expect benzoic acid to co-occur with benzyl alcohol. These hypotheses were investigated by plotting benzyl alcohol and benzoic acid data from Ecology's Environment Information Management (EIM) database using ArcGIS. The time span covered by the data was 1984-2015.

Figures 3a-d show the detected occurrences of benzyl alcohol and benzoic acid in four non-urban embayments. The four embayments shown – Carr Inlet, Dabob Bay, Holmes Harbor and Samish Bay – were used during development of the DMMP dioxin guidelines as non-urban reference areas, and are considered to represent background conditions in Puget Sound. As can be seen from the figures, benzyl alcohol exceeded the DMMP SL in two of the reference embayments (Carr Inlet and Dabob Bay), with concentrations reaching as high as 281 ug/kg. Benzoic acid (BZA) exceeded its marine SL in three of the embayments (Carr Inlet, Dabob Bay and Samish Bay), with concentrations as high as 1,700 ug/kg.

Of note is the fact that benzyl alcohol and benzoic acid detections did not always co-occur in these reference areas. Possible explanations include the complete biodegradation of benzyl alcohol to benzoic acid at those locations where only benzoic acid was detected, or fresh inputs of benzyl alcohol with storm-deposited woody debris at stations where only benzyl alcohol was detected. Another possibility is that the analytical issues referred to earlier in this paper resulted in inaccurate measurements of one or both chemicals. To test this hypothesis, co-occurrence of benzyl alcohol and benzoic acid was examined for data generated in 2011 or later, which presumably was generated using more advanced technologies and techniques than older data. Figure 4 shows detected occurrences of benzyl alcohol and benzoic acid throughout Puget Sound since 2011. Several observations can be made from this figure. First, benzoic acid does co-occur at most stations where benzyl alcohol was detected. Second, benzyl alcohol was detected far less than benzoic acid and always near the shoreline. Third, benzoic acid was much more widely distributed than benzyl alcohol, and in some areas – such as the San Juan Islands and Discovery Bay – was the only one of the two chemicals detected. What this means in terms of sources and relative biodegradation rates of benzyl alcohol and benzoic acid will require additional investigation to understand.

### ***Disposal Site Monitoring Data***

The five non-dispersive DMMP disposal sites (Anderson-Ketron, Commencement Bay, Elliott Bay, Port Gardner, and Bellingham Bay) are monitored periodically to ensure that the DMMP disposal site management objectives are being met. Monitoring includes chemical analysis of sediment samples taken from on-site stations as well as samples taken from perimeter stations located one-eighth of a nautical mile outside of the disposal site boundary. Data from all 19 monitoring studies (DMMP, 2015c) conducted at the non-dispersive sites since establishment of the sites in 1988-89 were reviewed. Benzyl

alcohol was not detected at any of the on-site and perimeter sampling stations during any monitoring event except one. The non-detect reporting limits were below the SL in all cases. In the one study in which benzyl alcohol was detected – Commencement Bay monitoring in 2007 (SAIC, 2008) – the detected concentrations ranged from 4.7 to 21 ug/kg (at 8 stations), which is well below the SL. This finding is important, because it demonstrates that the evaluation procedures used by the DMMP agencies, including the use of BPJ for some projects, has not resulted in on-site benzyl alcohol concentrations exceeding the DMMP SL value (57 ug/kg).

While benzyl alcohol was rarely detected at the disposal sites, benzoic acid was frequently detected. This finding provides further support for the hypothesis that any benzyl alcohol in disposed sediments is rapidly biodegraded to benzoic acid which is more persistent in the marine environment. The last disposal event within a dredging year occurs at or before the end of the in-water work window, which is typically mid-February. Sampling for monitoring studies tends to occur in late spring or early summer. This would leave several months for biodegradation of benzyl alcohol to occur, which could explain why benzyl alcohol is usually not detected at the disposal sites, while benzoic acid is detected. It should be noted that while benzoic acid was found during many of the monitoring studies, it was never detected at concentrations exceeding its marine SL.

It is important to note that the majority of the monitoring data for the disposal sites was generated prior to 2011. Therefore, it is possible these data underestimate the sediment benzyl alcohol concentrations due to the analytical issues discussed earlier.

### ***Evaluation of Toxicity***

Our investigation supports the hypotheses that a natural source exists for at least some of the benzyl alcohol found in Puget Sound waters and that, regardless of the source, benzyl alcohol rapidly biodegrades to benzoic acid, which has a much higher SL. Nevertheless, the DMMP agencies agreed that Seattle District should investigate the toxicity of benzyl alcohol to ensure that the disposal site management objective (Site Condition II – minor adverse effects) was not being exceeded, even for short periods, at the disposal sites.

Two lines of investigation were pursued. First, bioassay data from Ecology's EIM, Seattle District's Dredged Analysis Information System (DAIS), and Ecology's Puget Sound Ambient Monitoring Program<sup>3</sup> (PSAMP) database that were associated with detected benzyl alcohol concentrations above the SL were reviewed. Second, a literature review was conducted for ecotoxicity results associated with benzyl alcohol.

### **Bioassay Data Findings**

The DMMP bioassays include the 10-day amphipod mortality test; 48-hour sediment larval development test; and the 20-day *Neanthes* mortality and growth test. An additional bioassay, the sea urchin fertilization test, has been used in PSAMP. Bioassay data for sediment samples with detected concentrations of benzyl alcohol above the DMMP SL were compiled from several sources in order to assess the relationship between benzyl alcohol concentrations and bioassay results. These included Ecology's EIM system and PSAMP database; Seattle District's DAIS database; and the data report from a Lower Duwamish subsurface investigation conducted in 2012 (USACE, 2013).

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<sup>3</sup> PSAMP is now known as the Puget Sound Ecosystem Monitoring Program (PSEMP)

Bioassay results were evaluated for two subsets of samples – DMMP and PSAMP. These subsets were evaluated separately because the PSAMP samples were all subjected to the sea urchin fertilization test, while the DMMP samples were subjected only to bioassays used within DMMP. It should be noted that two of the studies (EBCHEM and HYLWD99-1) in the “DMMP” subset were not actually DMMP projects, but *were* subjected to DMMP bioassays only. Toxicity was evaluated for DMMP samples by comparing bioassay results against the DMMP interpretation guidelines (DMMP, 2015b). For the PSAMP samples, the toxicity interpretations assigned by PSAMP scientists were used. The DMMP samples are discussed first, followed by the PSAMP samples.

The ability to demonstrate sediment toxicity depends on the number of tests being run and the sensitivity of the organisms used. The following sections present the bioassay data available for sediment samples with concentrations of benzyl alcohol exceeding the SL. This dataset is relatively small and for many samples includes only a single bioassay. Therefore, conclusions drawn from an evaluation of the data must be used with some degree of caution.

**DMMP samples.** For marine dredging projects evaluated by the DMMP agencies, two levels of biological response are defined for each bioassay. A “2-hit” response is a minor response. A 2-hit response is required in two or more bioassays in order for the sample to fail biological testing. A “1-hit” response is a higher-intensity response. Only one bioassay needs to exhibit a 1-hit response for a sediment sample to fail biological testing.

DMMP samples with a detected benzyl alcohol concentration greater than the DMMP SL of 57 ug/kg and for which one or more DMMP bioassays were run were compiled. This included 26 samples from six individual studies (Table 1).

Of the 17 samples subjected to the entire suite of DMMP bioassays and passing, the highest concentration of benzyl alcohol was 290 ug/kg (sample LDW18 0-2.8C). For this sample, there was a hit under the 2-hit rule for the larval test, but no corroborating hit in another bioassay. Therefore, this sample passed biological testing. Sample 1C06, with a concentration of 150 ug/kg, exhibited no hits at either hit-level for any of the DMMP bioassays. One sample (EBCHEMEW-12), with a benzyl alcohol concentration of 870 ug/kg, was only subjected to the amphipod test, but exhibited neither a 1-hit nor 2-hit level of response in that bioassay.

The assessment of toxicity potentially attributable to benzyl alcohol was complicated by the fact that many of the samples also had one or more other co-occurring chemicals of concern exceeding SL. Table 2 lists the 10 samples that were subjected to the full suite of DMMP bioassays and for which the only chemical exceeding SL was benzyl alcohol. All 10 samples passed biological testing. There was only one sediment sample that failed bioassay testing for which the only chemical exceeding the screening level was benzyl alcohol. This sample (EBCHEMWW-02) had a benzyl alcohol concentration of 8,800 ug/kg (Table 1), which is two orders of magnitude above the DMMP SL. Only the amphipod test was run on this sample, but it exhibited a hit under the 1-hit rule.

In summary, results from the DMMP samples support the hypothesis that benzyl alcohol alone is not toxic enough to cause DMMP bioassay testing failures at or near the current screening level.

**PSAMP samples.** Table 3 includes all the PSAMP records for which the sea urchin fertilization assay was conducted on samples with detected concentrations of benzyl alcohol above the DMMP SL. Five of the 15 sediment samples listed in Table 3 were also subjected to the amphipod test. The highest

concentration of benzyl alcohol (678 J ug/kg) occurred for sample UWI2007-202, which was found to be non-toxic in the fertilization test.

The three samples that exhibited toxicity in the fertilization test had co-occurring chemicals of concern other than benzyl alcohol that were highly elevated, including phthalates, PAHs, phenolic compounds and dibenzofuran. The one sample that exhibited toxicity in both the fertilization test and the amphipod test had a concentration of bis (2-ethylhexyl) phthalate of 8,300 ug/kg, which is equal to the DMMP maximum level. Due to the multiple SL exceedances associated with cases of demonstrated toxicity in the fertilization test, nothing can be concluded about the contribution of benzyl alcohol to the toxicity observed in these three samples.

The PSAMP sea urchin fertilization data provide further evidence that benzyl alcohol is not likely toxic at the DMMP SL. Concentrations as high as 678 ug/kg were demonstrated to be non-toxic in this test, despite the presence of other COCs.

### Ecotoxicity Literature Data

Benzyl alcohol is generally considered to be of relatively low toxicity to humans at low- to moderate-concentrations (HSDB, 2016). In many mammals (including humans), benzyl alcohol is quickly oxidized to benzoic acid, conjugated with the amino acid glycine in the liver, and excreted as hippuric acid. However, this metabolic pathway may not be well developed in premature infants and is thought to be a factor in benzyl alcohol's known toxicity in premature infants (Pediatrics in Review, 1984; HSDB, 2016).

A survey of EPA's online EcoTox database was performed to evaluate the aquatic ecotoxicity of benzyl alcohol. Relevant aquatic toxicity studies for benzyl alcohol are limited to a few primary studies conducted prior to 2000 that exposed test species to various aqueous concentrations of benzyl alcohol. Attachment 1 contains a summary of the findings for studies with defined endpoints such as LC50 or EC50. Benzyl alcohol concentrations for the observed LC, EC, or IC50 endpoints ranged from 10 mg/L (in fish) up to 892 mg/L (protozoa).

Using the aqueous concentrations reported in the literature and the equilibrium partitioning model, the predicted sediment concentration ( $C_{sed}$ ) of a non-ionizable organic compound required to produce the measured aqueous concentration ( $C_w$ ) can be calculated using the following equation:

$$C_{sed} = C_w \times (K_{oc} \times f_{oc}) \times (\text{mg}/1,000 \text{ ug})$$

Where

$K_{oc}$  = soil-water partition coefficient in terms of soil organic carbon (L/kg)

$f_{oc}$  = decimal fraction of organic carbon (unitless)

$C_{sed}$  = soil/sediment concentration (ug/kg)

$C_w$  = aqueous concentration (mg/L)

The above equilibrium partitioning model equation can be used to relate aqueous and bulk sediment concentrations for non-ionic organics. Benzyl alcohol, a weak acid with a  $pK_a$  of 15.4, is expected to behave predominantly as a non-ionic species in the pH range (pH = 8.0 - 8.1) typically encountered in the marine environment. The parameters in the formula were assigned the following values:

$$K_{oc} = 27 \text{ L/kg (Gerstl, 1990}^4\text{)}$$
$$f_{oc} = 0.01 \text{ (1\%)}$$

Using the minimum (10 mg/L) and maximum (770 mg/L) effective concentrations for invertebrates and vertebrates in Attachment 1, the calculated equilibrium sediment concentrations are 2,700 ug/kg and 208,000 ug/kg, respectively. The minimum calculated equilibrium sediment concentration (2,700 ug/kg) is nearly two orders of magnitude greater than the current DMMP SL (57 ug/kg) and suggests that the current SL may be overly conservative.

Note that in a sediment-porewater-water column scenario in which the sediment is the assumed primary source of the contaminant to the system, porewater concentrations are expected to exceed water column concentrations. Thus, a higher sediment concentration may be required to produce toxic water column concentrations for the pelagic species listed in Attachment 1.

### ***Basis of Regulatory Guidelines for Benzyl Alcohol***

#### **PSDDA/DMMP**

Benzyl alcohol was among the COCs for which apparent effects thresholds (AETs) were established in the 1980s to make clean-up decisions for contaminated sediment in Commencement Bay. The database used to develop the AETs was later expanded to include chemical and biological data from areas outside of Commencement Bay. The AETs derived from the larger database became the basis for the PSDDA chemical evaluation guidelines. The AET approach identified concentrations of contaminants that were associated with adverse biological effects. However, the empirical relationships used to establish AETs did not prove a cause-and-effect relationship between contaminants and effects (Tetra Tech, 1986). This was primarily due to the multiple COCs present in sediment samples and the potential for synergistic effects.

The highest AET (HAET) for four biological indicators was used to establish a PSDDA maximum level (ML) for most, but not all, of the COCs. For the majority of the COCs with an ML, the SL was initially set equal to 10% of the ML or to the lowest AET (LAET), whichever was lower. For some chemicals, such as benzyl alcohol, 10% of the ML was lower than the concentration in sediment from a reference area. In those cases, the SL was set equal to the reference concentration. The original SL and ML for benzyl alcohol were 10 and 73 ug/kg respectively (PSDDA, 1988). The 10 ug/kg value likely represented a reporting limit, although documentation for this could not be found. The SL for benzyl alcohol was raised to 25 ug/kg in 1994, likely due to difficulties routinely achieving lower analytical reporting limits. In 1997, the AETs were recalculated and the SL and ML for benzyl alcohol were set at their current concentrations of 57 and 870 ug/kg respectively (DMMP, 1997). The practice of setting the SL equal to 10% of the ML was abandoned at that time and the SL for benzyl alcohol was set equal to the LAET instead. Attachment 2 lists the AETs used to select the current benzyl alcohol SL and ML.

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<sup>4</sup> Gerstl (1990) reported an empirically derived log  $K_{oc}$  of 1.43 for benzyl alcohol. This was the only empirically-derived log  $K_{oc}$  found in the literature survey. For comparison, the log  $K_{ow}$  for benzyl alcohol in the literature ranges from 1.00 to 1.16 (EPA, 1978; Montgomery, 2000). Using Di Toro's equation ( $\log K_{oc} = 0.983 \log K_{ow} + 0.00028$ ) for non-ionizable, semivolatile organic compounds and a log  $K_{ow}$  of 1.1 (EPA, 1978), a log  $K_{oc}$  of 1.08 can be computed. This equates to a  $K_{oc}$  of 12.07 L/kg. Using this value for  $K_{oc}$ , calculated sediment concentrations for the range of toxicity concentrations reported in the literature for invertebrates and vertebrates range from 1,200 to 93,900 ug/kg.

## SMS

The State of Washington also adopted the AET approach for development of its Sediment Management Standards (SMS). The SMS rule was originally adopted in 1991, with subsequent amendments in 1995 and 2013. Under the current SMS, the sediment quality standard (SQS) and cleanup screening level (CSL) for benzyl alcohol are 57 and 73 ug/kg respectively (Ecology, 2013). Both the DMMP SL and SMS SQS are set equal to the LAET. However, unlike DMMP, which set the ML equal to the HAET, the CSL was set equal to the second lowest AET.

### The Role of Benzyl Alcohol in Development of the AETs

There is evidence that the early developers of the 1988 AETs were aware that, unlike metals and PAHs, benzyl alcohol was not a major chemical player driving AET sensitivity. Barrick (1988; page 57) states (bold emphasis added):

“The following chemical groups do not uniquely account for predicted impacts for either the amphipod bioassay or benthic infauna AET:

- Miscellaneous organic compounds including pentachlorophenol, resin acids, organic bases (e.g., N-nitrosodiphenylamine), and several Hazardous Substance List compounds including 2-methylnaphthalene, dibenzofuran, benzoic acid, **benzyl alcohol** (low detection limits for the latter two compounds are sometimes difficult to attain but may not be essential).”

### Other State and Federal Guidelines

A survey of other state and federal agency guidelines for the regulation of contaminants in marine sediments indicates that benzyl alcohol appears to be of little or no concern outside of Washington State. Of four states identified with marine sediment quality evaluation criteria (Alaska, California, New York, and Florida), none included a screening level for benzyl alcohol (ADEC, 2001, 2013; NJDEP, 2009, 2015; CDWR, 1995; MacDonald, 1994; NYSDEC, 2014). Among federal agencies, the well-known National Oceanic and Atmospheric Administration (NOAA) Effects Range-Low (ERLs) and Effects Range-Median (ERMs) sediment quality guidelines also do not include values for benzyl alcohol (NOAA, 1999; 2008).

## Summary

In the past few years, the DMMP agencies have seen an increase in the number of projects with detected benzyl alcohol concentrations that exceed the SL. Evidence exists that this phenomenon may be tied to recent improvements in analytical technologies and techniques. Multiple lines of evidence suggest the occurrence of benzyl alcohol is not a significant cause of concern to the DMMP agencies:

- Benzyl alcohol likely occurs naturally in plant-derived material in marine sediment.
- Benzyl alcohol is likely readily biodegraded in the marine environment.
- Benzyl alcohol detections are widespread in Washington State and have been found in both urban and non-urban areas.

- Benzyl alcohol has seldom been detected at the DMMP non-dispersive disposal sites during monitoring<sup>5</sup>.
- Bioassay data indicate that benzyl alcohol has low toxicity.
- Sediment benzyl alcohol concentrations derived from aquatic toxicity data using equilibrium partitioning are more than two orders of magnitude greater than the current SL.

### Proposed Action/Modification

On the basis of the above lines of evidence, the DMMP agencies do not believe that benzyl alcohol is a chemical of significant concern at the concentrations found in many dredging projects. The DMMP agencies recommend re-evaluation of the current SL for benzyl alcohol, including possible recalculation of the AETs or use of other benthic toxicity modeling tools, to update the DMMP evaluation guidelines for this COC. In the meantime, the information presented in this paper will be used to inform any future use of best professional judgment to determine the need for biological testing when benzyl alcohol is the only COC exceeding SL.

### Implication for other DMMP COCs

Other chemicals that are known to occur or are suspected of occurring naturally include benzoic acid, phenol, 2-methylphenol (o-cresol), 4-methylphenol (p-cresol), and 2,4-dimethylphenol. These chemicals have occasionally been the only COCs exceeding SL for DMMP projects but, so far, this has not occurred with the frequency seen for benzyl alcohol. However, given the evidence provided in this paper of the wide distribution of benzoic acid, and detections of benzoic acid in reference embayments at concentrations exceeding the SL, it is very possible that such cases will be encountered in the future, especially for benzoic acid. The DMMP agencies will continue to investigate these COCs to determine the appropriateness of using best professional judgment as has been proposed here for benzyl alcohol. Results of further investigations will be presented in SMARM papers as necessary.

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<sup>5</sup> Caveat: the majority of the monitoring data for the disposal sites was generated prior to 2011. Therefore, it is possible these data underestimate the sediment benzyl alcohol concentrations due to the analytical issues discussed in this paper.

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Figure 1. Benzyl Alcohol Detects and Non-detects Greater than the SL by Biennial Report Year

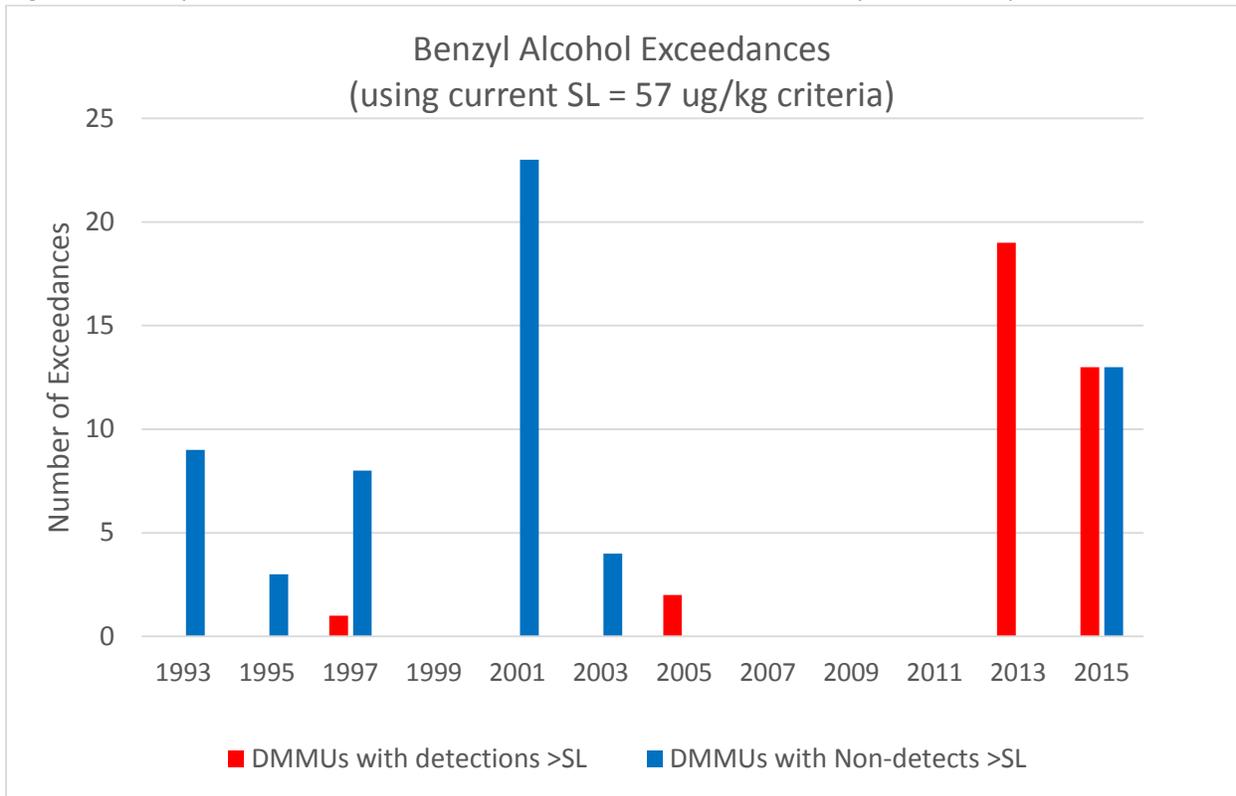
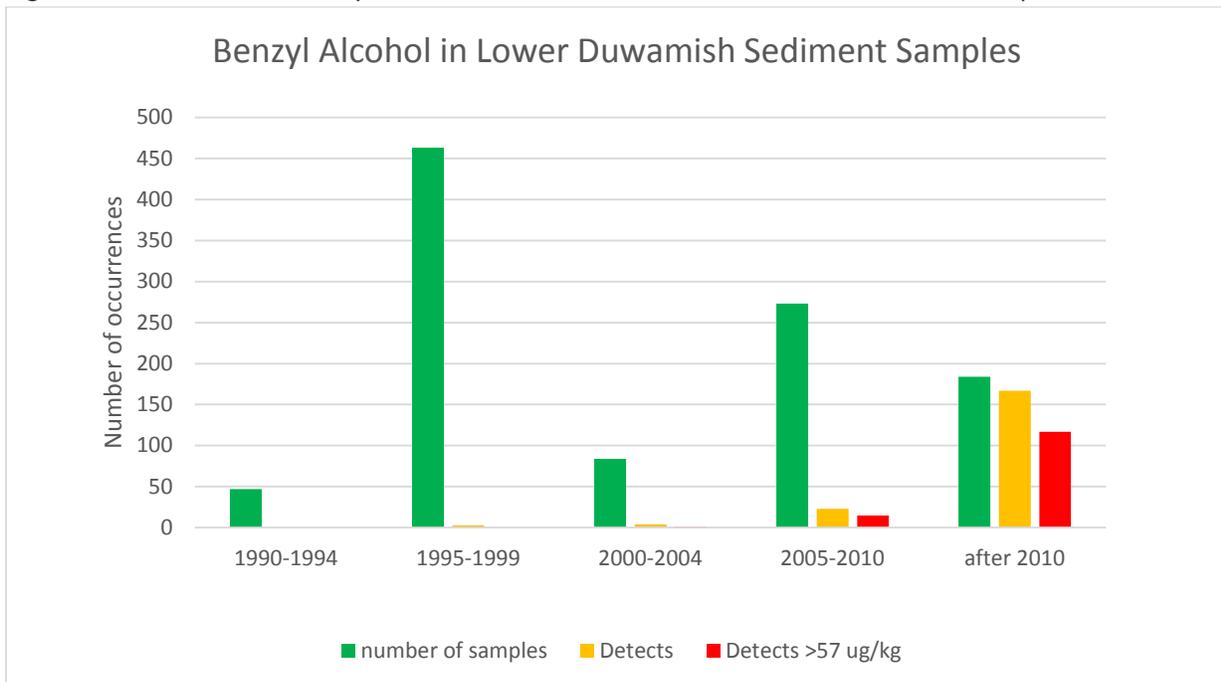


Figure 2. Occurrence of Benzyl Alcohol Detections in Lower Duwamish Sediment Samples



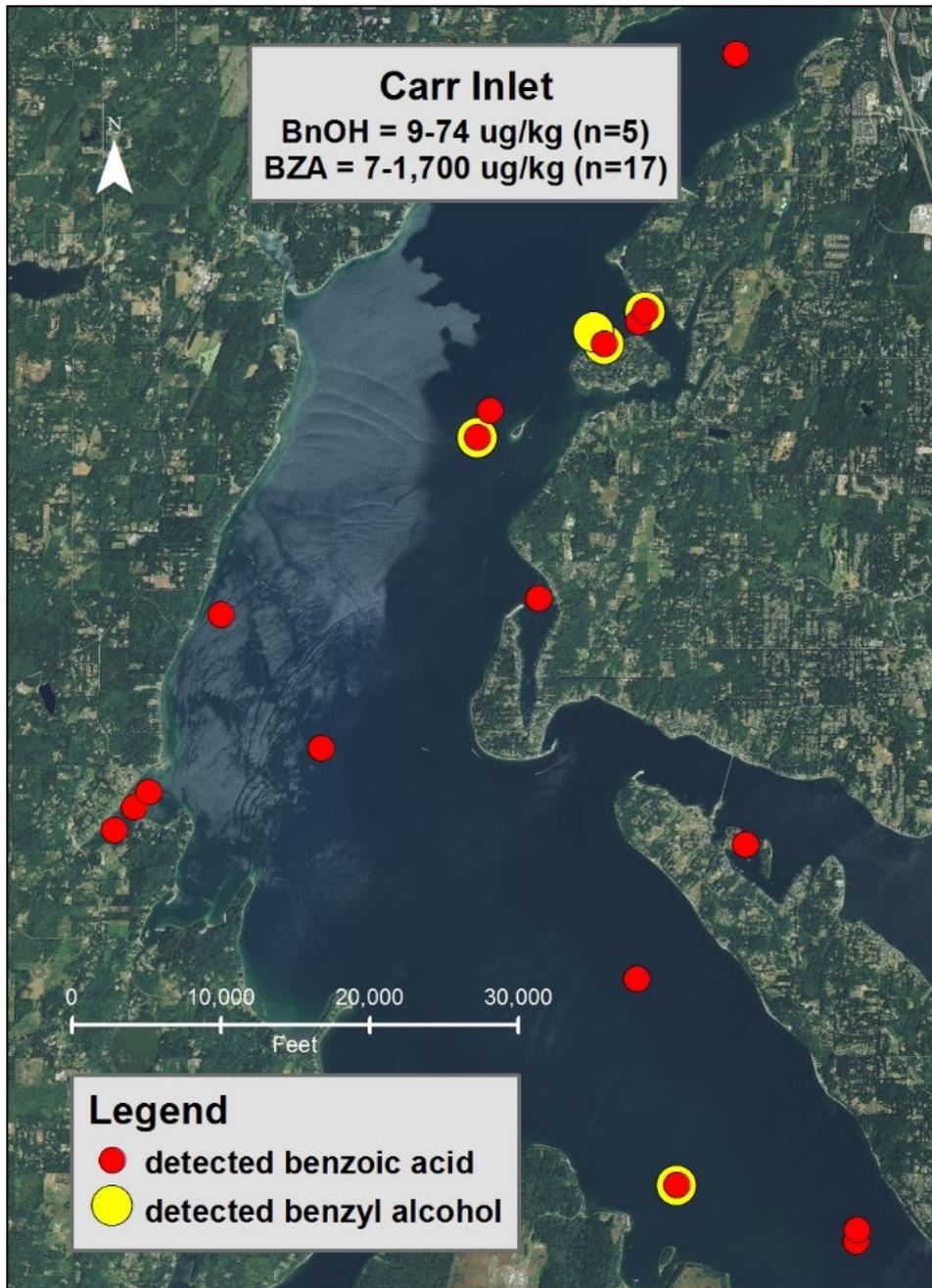


Figure 3a. Detected Benzyl Alcohol and Benzoic Acid in Carr Inlet (data from EIM)

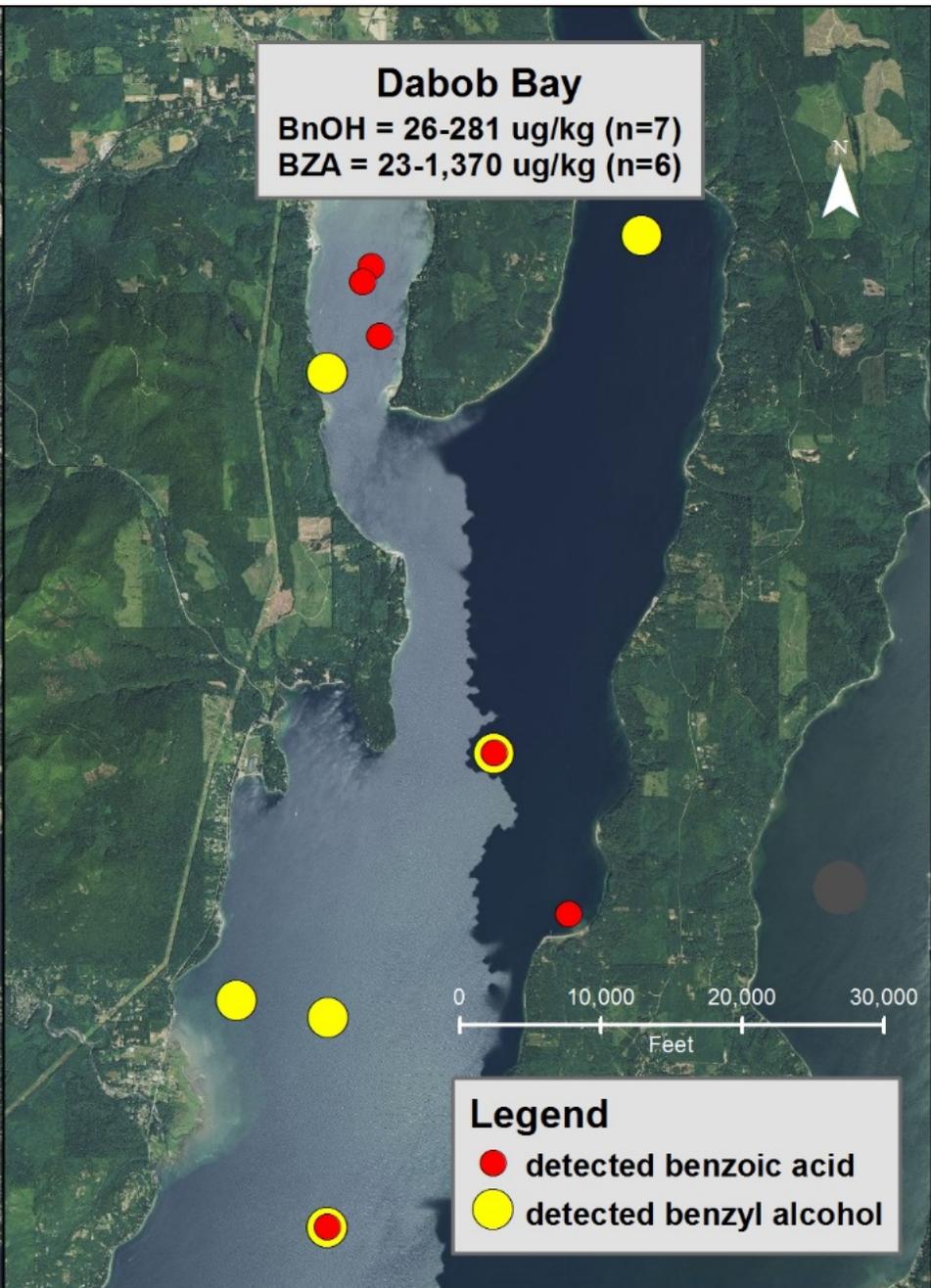


Figure 3b. Detected Benzyl Alcohol and Benzoic Acid in Dabob Bay (data from EIM)



Figure 3c. Detected Benzyl Alcohol and Benzoic Acid in Holmes Harbor (data from EIM)

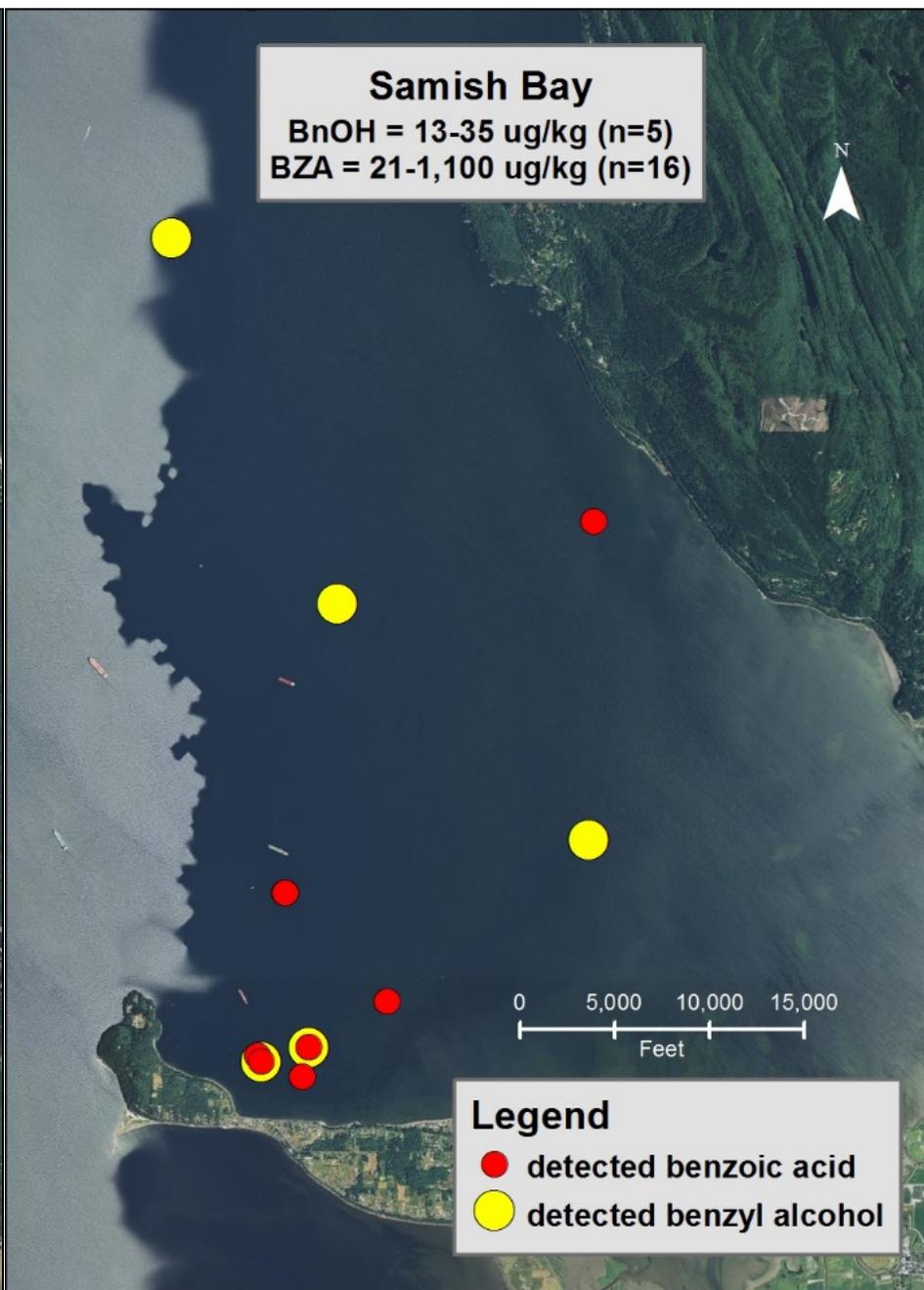


Figure 3d. Detected Benzyl Alcohol and Benzoic Acid in Samish Bay (data from EIM)

Figure 4. Distribution of Benzyl Alcohol and Benzoic Acid in Puget Sound (Since 2011)

**Legend**

- detected benzoic acid
- detected benzyl alcohol

0 5 10 20 30 40 Miles

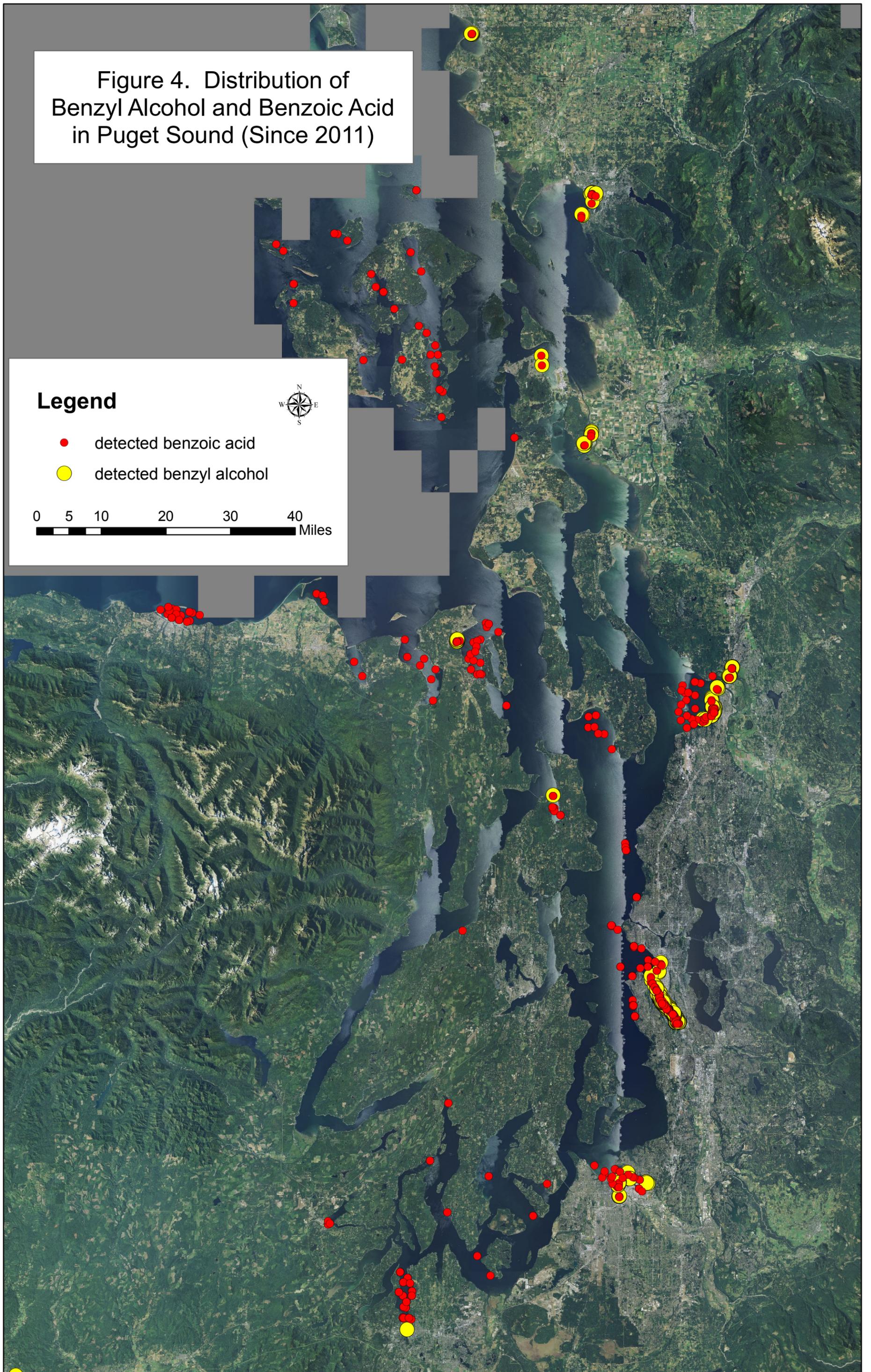


Table 1. DMMP Bioassay Results for Benzyl Alcohol Concentrations Greater than the Screening Level (57 ug/kg)

	Study_ID	Year	Sample ID	Location	Benzyl Alcohol Value (ug/kg)	LQ	Amphipod	Larval	Neanthes	Overall Interpretation	Other SL exceedances
full suite of DMMP bioassays	DUW111BF308	2011	DMMU 4	DNC - Section A	60		Pass	Pass	Pass	Pass	none
	DUW111BF308	2011	DMMU 12	DNC - Section B	66		Pass	Pass	Pass	Pass	none
	DUW111BF308	2011	DMMU 17	DNC - Section B	68		Pass	2-hit	Pass	Pass	none
	DUW111BF308	2011	DMMU 11	DNC - Section B	72		Pass	2-hit	Pass	Pass	DDT
	HYLWD99-1	1999	HYLWD99S15	Hylebos Waterway	75	J	no data	Pass	Pass	Pass	BBP, PCBs
	DUW111BF308	2011	DMMU 5	DNC - Section A	82		Pass	2-hit	Pass	Pass	none
	LDSI	2012	LDW07 2-4C2	Lower Duwamish	84		Pass	2-hit	Pass	Pass	PCBs
	LDSI	2012	LDW08 0-4C1	Lower Duwamish	84	J	Pass	2-hit	Pass	Pass	PCBs
	DUW111BF308	2011	DMMU 7	DNC - Section A	86		Pass	2-hit	Pass	Pass	none
	DUW111BF308	2011	DMMU 10	DNC - Section B	91		Pass	Pass	Pass	Pass	none
	LDSI	2012	LDW09 0-2.1C	Lower Duwamish	120		Pass	2-hit	Pass	Pass	PCBs
	LDSI	2012	LDW11 0-3.2C	Lower Duwamish	130		Pass	2-hit	Pass	Pass	PCBs
	DUW111BF308	2011	DMMU 8	DNC - Section B	140		Pass	Pass	Pass	Pass	none
	DUW111BF308	2011	DMMU 9	DNC - Section B	140		Pass	Pass	Pass	Pass	none
	PST181BF112	1996	1C06	Seattle Harbor EW	150	D	Pass	Pass	Pass	Pass	TBT, numerous PAHs, dibenzofuran, PCBs
	DUW111BF308	2011	DMMU 6	DNC - Section A	200		Pass	2-hit	Pass	Pass	none
	LDSI	2012	LDW07 0-2C1	Lower Duwamish	200		Pass	2-hit	Pass	Pass	PCBs
	LDSI	2012	LDW18 0-2.8C	Lower Duwamish	290		Pass	2-hit	Pass	Pass	none
EWSIA1CF181	2002	S1A-CMP-3	Seattle Harbor EW	92	J	1-hit	Pass	Pass	Fail	Hg, TBT, fluoranthene, pyrene, PCBs	
LDSI	2012	LDW13 2-7.2C2	Lower Duwamish	100		Pass	1-hit	Pass	Fail	PCBs	
LDSI	2012	LDW16 0-2.5C	Lower Duwamish	130		Pass	1-hit	Pass	Fail	PCBs	
LDSI	2012	LDW17 0-3.5C	Lower Duwamish	160		Pass	1-hit	Pass	Fail	PCBs	
amphipod test only	EBCHEM	1985	EBCHEMWW-08	Elliott Bay	140	J	2 pass/2 fail <sup>1</sup>	no data	no data	ND	BBP, Hg
	EBCHEM	1985	EBCHEMEW-12	Elliott Bay	870	J	Pass	no data	no data	ND	chrysene
	EBCHEM	1985	EBCHEMSS-03	Elliott Bay	1300	J	1-hit	no data	no data	Fail	numerous metals and PAHs
	EBCHEM	1985	EBCHEMWW-02	Elliott Bay	8800	J	1-hit	no data	no data	Fail	none

<sup>1</sup>There were four reference sediment samples run. The pass/fail interpretation of this sample depends on which reference it is compared to.

DNC = Duwamish Navigation Channel

EW = East Waterway

LDSI = Lower Duwamish Subsurface Investigation

ND = no determination

LQ = lab qualifier

D = diluted sample

J = estimate

ug/kg = micrograms/kilograms

BBP = butyl benzyl phthalate

Hg = mercury

PAHs = polyaromatic hydrocarbons

PCBs = polychlorinated biphenyls

TBT = tributyltin

Table 2. Samples Subjected to Full Suite of DMMP Bioassays and for which Benzyl Alcohol was the only SL Exceedance

Study ID	Year	Sample ID	Benzyl Alcohol			Amphipod	Larval	Neanthes	Overall	other SL exceedances
			Value (ug/kg)	LQ						
DUW111BF308	2011	DMMU 4	60			Pass	Pass	Pass	Pass	none
DUW111BF308	2011	DMMU 12	66			Pass	Pass	Pass	Pass	none
DUW111BF308	2011	DMMU 17	68			Pass	2-hit	Pass	Pass	none
DUW111BF308	2011	DMMU 5	82			Pass	2-hit	Pass	Pass	none
DUW111BF308	2011	DMMU 7	86			Pass	2-hit	Pass	Pass	none
DUW111BF308	2011	DMMU 10	91			Pass	Pass	Pass	Pass	none
DUW111BF308	2011	DMMU 8	140			Pass	Pass	Pass	Pass	none
DUW111BF308	2011	DMMU 9	140			Pass	Pass	Pass	Pass	none
DUW111BF308	2011	DMMU 6	200			Pass	2-hit	Pass	Pass	none
LDSI	2012	LDW18 0-2.8C	290			Pass	2-hit	Pass	Pass	none

LDSI = Lower Duwamish Subsurface Invest.

LQ = lab qualifier

ug/kg = micrograms/kilograms

Table 3. PSAMP Bioassays

Sample ID	Location	PSAMP stratum	Benzyl Alcohol Value (ug/kg)	LQ	Amphipod ( <i>E. estuarius</i> )	sea urchin fertilization	Overall interpretation	other SL exceedances
UWI2007-183	Elliott Bay, Pier 54	Harbor	58	J	Not Tested	Non-Toxic	Non-Toxic	2,4-dimethylphenol (53 J ug/kg); benzoic acid (1,160 J ug/kg)
PSAMP_SP-41	Port Angeles	Urban	66	J	Non-Toxic	Non-Toxic	Non-Toxic	phenol (1,230 ug/kg)
PSAMP_SP-323	Coon Bay	Basin	70	NJ	Not Tested	Non-Toxic	Non-Toxic	benzoic acid (966 J ug/kg)
PSAMP_SP-55	Possession Sound	Rural	81	J	Not Tested	Non-Toxic	Non-Toxic	2,4-dimethylphenol (39 J ug/kg)
UWI2010-53	Bellingham Bay	Urban	89	J	Moderate Toxicity	Moderate Toxicity	Moderate Toxicity	bis (2-ethylhexyl) phthalate (8,300 ug/kg)
PSAMP_SP-177	Discovery Bay	Rural	100	J	Non-Toxic	Non-Toxic	Non-Toxic	none
PSAMP_SP-405	Boundary Bay	Basin	108	J	Non-Toxic	Non-Toxic	Non-Toxic	2,4-dimethylphenol (86 J ug/kg); 2-methylphenol (76 ug/kg)
PSAMP_SP-128	Sisters Point	Rural	112	J	Not Tested	Non-Toxic	Non-Toxic	phenol (1,480 ug/kg)
PSAMP_SP-224	Mosquito Point	Basin	120	J	Not Tested	Non-Toxic	Non-Toxic	di-n-butyl phthalate (1,760 ug/kg); phenol (1,340 ug/kg)
PSAMP_SP-118	Shoofly Creek	Rural	128	J	Not Tested	Non-Toxic	Non-Toxic	di-n-butyl phthalate (1,980 ug/kg); phenol (1,780 ug/kg)
PSAMP_SP-83	South Port Townsend	Urban	141	J	Non-Toxic	Non-Toxic	Non-Toxic	phenol (1,200 J ug/kg)
PSAMP_SP-367	Middle Everett Harbor	Harbor	171	J	Not Tested	High Toxicity	High Toxicity	chrysene (1,910 ug/kg); dibenzofuran (888 ug/kg); fluoranthene (4,300 ug/kg); 2-methylphenol (104 ug/kg); pyrene (3,250 ug/kg)
PSAMP_SP-96	Sund Creek	Basin	210	J	Not Tested	Moderate Toxicity	Moderate Toxicity	di-n-butyl phthalate (2,990 ug/kg); phenol (1,180 ug/kg)
UWI2007-203	Duwamish River, North	Harbor	371	J	Not Tested	Non-Toxic	Non-Toxic	2,4-dimethylphenol (181 ug/kg); 2-methylphenol (212 J ug/kg)
UWI2007-203	Duwamish River, North	Harbor	382	J	Not Tested	Non-Toxic	Non-Toxic	2,4-dimethylphenol (181 ug/kg); 2-methylphenol (212 J ug/kg)
UWI2007-202	East Waterway, South End	Harbor	678	J	Not Tested	Non-Toxic	Non-Toxic	2,4-dimethylphenol (330 ug/kg); benzoic acid (2,040 J ug/kg); butyl benzyl phthalate (86 J ug/kg); bis (2-ethylhexyl) phthalate (2,150 ug/kg); fluoranthene (1,110 ug/kg); 2-methylphenol (372 J ug/kg); PCBs (574 ug/kg)

ug/kg = micrograms/kilograms

LQ = lab qualifier

PCBs = polychlorinated biphenyls

J = estimate

N = there is evidence that the analyte is present in the sample

## Attachment 1

### Benzyl Alcohol Aquatic Toxicity Literature Summary

Compilation of relevant aquatic toxicity data available from EPA's EcoTox database\*

	Special features	Effect	Endpoint	Effective Concentration Mean	Units	Reference	Notes	
<b>Cyanobacteria</b>								
Anabaena inaequalis	blue-green algae		3-h EC50	>100,000	ug/L	Stratton & Corke (1982)	photosynthesis reduction	
Anabena variabilis	blue-green algae	Population	2-h EC50	>100,000	ug/L	Stratton & Corke (1982)	photosynthesis reduction	
Anabaena cylindrica	blue-green algae		3-h EC50	>100,000	ug/L	Stratton & Corke (1982)	photosynthesis reduction	
<b>Algae</b>								
Scenedesmus quadricauda	green algae	Population	3-h EC50	>100,000	ug/L	Stratton & Corke (1982)		
Chlorella pyrenoidosa	green algae	Population	3-h EC50	>100,000	ug/L	Stratton & Corke (1982)		
<b>Protozoa</b>								
Tetrahymena pyriformis	Ciliate	pH 7.35	Population	2-day IC50	891,880	ug/L	Schultz et al (1996)	Cell multiplication inhibition test. Inhibition concentration to 50% of test organisms
				2-day IC50	853,470	ug/L	Schultz et al (1996)	Life stage unknown
<b>Invertebrates: Crustacea</b>								
Daphnia magna	Water flea		Behavior	24-hr EC50	55,000	ug/L	Bringman & Kuhn (1982)	
<b>Vertebrata: Fish</b>								
Pimephales promelas	Flathead minnow	juveniles	Mortality	4-day LC50	460,000	ug/L	Mattson et al (1976)	
			Mortality	24-h LC50	770,000	ug/L	Mattson et al (1976)	
			Mortality	1-h LC50	770,000	ug/L	Mattson et al (1976)	
			Mortality	2-day LC50	770,000	ug/L	Mattson et al (1976)	
			Mortality	3-day LC50	480,000	ug/L	Mattson et al (1976)	
			Mortality	45-min LC100	1,050,000	ug/L	Terhaar et al (1972)	100% mortality or 0% survival of organism
Lepomis macrochirus	Bluegill	pH 7.6 - 7.9	Mortality	4-day LC50	<b>10,000</b>	ug/L	Dawson et al (1977)	
Leuciscus idus	Ide		Mortality	LC50	646,000	ug/L	Knie et al (1983)	exposure duration not reported
Menidia beryllina	Inland silverside	pH 7.6 - 7.9	Mortality	4-day LC50	<b>10,000</b>	ug/L	Dawson et al (1977)	

Notes:

\*Accessed February 2016

EC = Effective Concentration

LC = Lethal Concentration

IC = Inhibitory Concentration

Lowest LC50 or EC50 in **bold**.

## Attachment 2

### Benzyl Alcohol AETs

Gries, 1997 states:

"Agencies are using 1994 amphipod, 1988 benthic, 1986 Microtox, and 1986 oyster AETs to determine LAETs."

	Amphipod	Oyster	Benthic	Microtox
1986 AETs	73	73	73	57
1988 AETs	870	73	870	57
1994 AETs	73	na	na	na

	LAET	HAET	Current SL	Current ML
Benzyl Alcohol	57	870	57	870