

Revised Evaluation Guidelines for Benzyl Alcohol (BA) in Marine Sediments

May 4, 2016

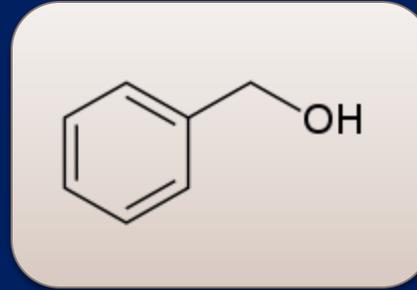
Heather Whitney Fourie (USACE)

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Current DMMP Guidelines

Benzyl Alcohol (BA)



Marine projects:

- Screening Level (SL) = 57 ug/kg
- Maximum Level (ML) = 870 ug/kg
- Toxicity testing required if SL is exceeded

The Problem

- BA has been detected more frequently in DMMP projects
- BA was the only COC to exceed SL in several recent DMMP projects:
 - 2011
 - Duwamish Navigation Channel O&M
 - 2012
 - Snohomish Navigation Channel O&M
 - 2014
 - Shelter Bay Marina
 - La Connor Marina
 - 2015
 - Bellingham Cold Storage

La Connor Marina 2014 sampling



The Problem: continued...

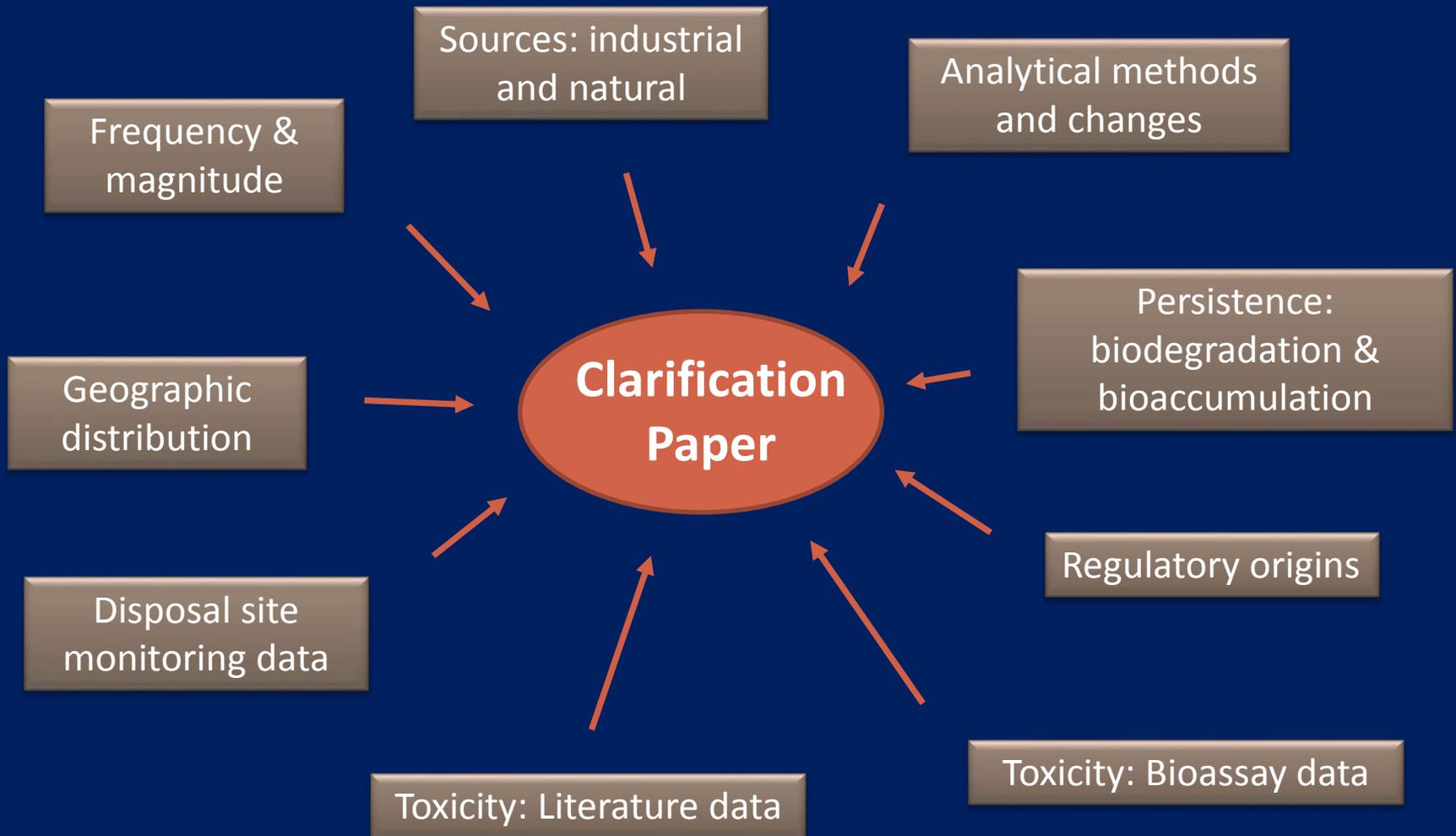
- BA has **both industrial** and **natural** sources
- BA is suspected to occur with leaf litter, small woody debris, terrestrial **plant-derived material**, etc.
- DMMP has been using **best professional judgement (BPJ)** to exempt some projects from the bioassay requirement when BA is the only SL exceedance

Projects with BA
as sole
exceedance



→ More rigorous evaluation of BPJ use needed

What We Investigated



Outcome

- 22-page clarification paper
- More details and references than can be covered in this talk

PUBLIC REVIEW DRAFT: DMMP Clarification Paper

April 2, 2016

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

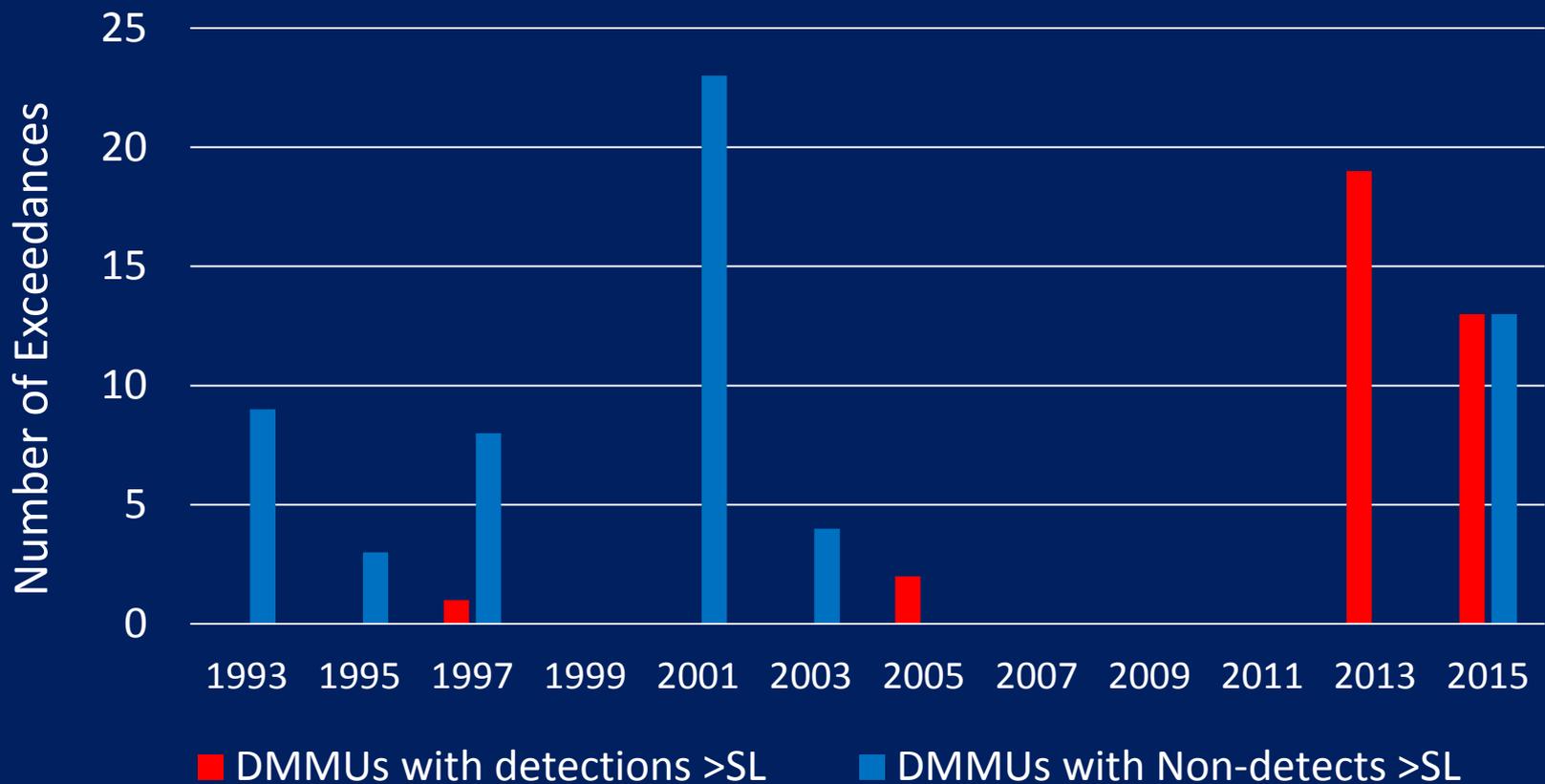
Since around 2011, benzyl alcohol has been much more frequently detected in dredged material characterization studies than in the years prior (1989-2010). More importantly, benzyl alcohol has been the only COC to exceed its SL in several recent DMMP projects, including the Duwamish Turning Basin and 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.

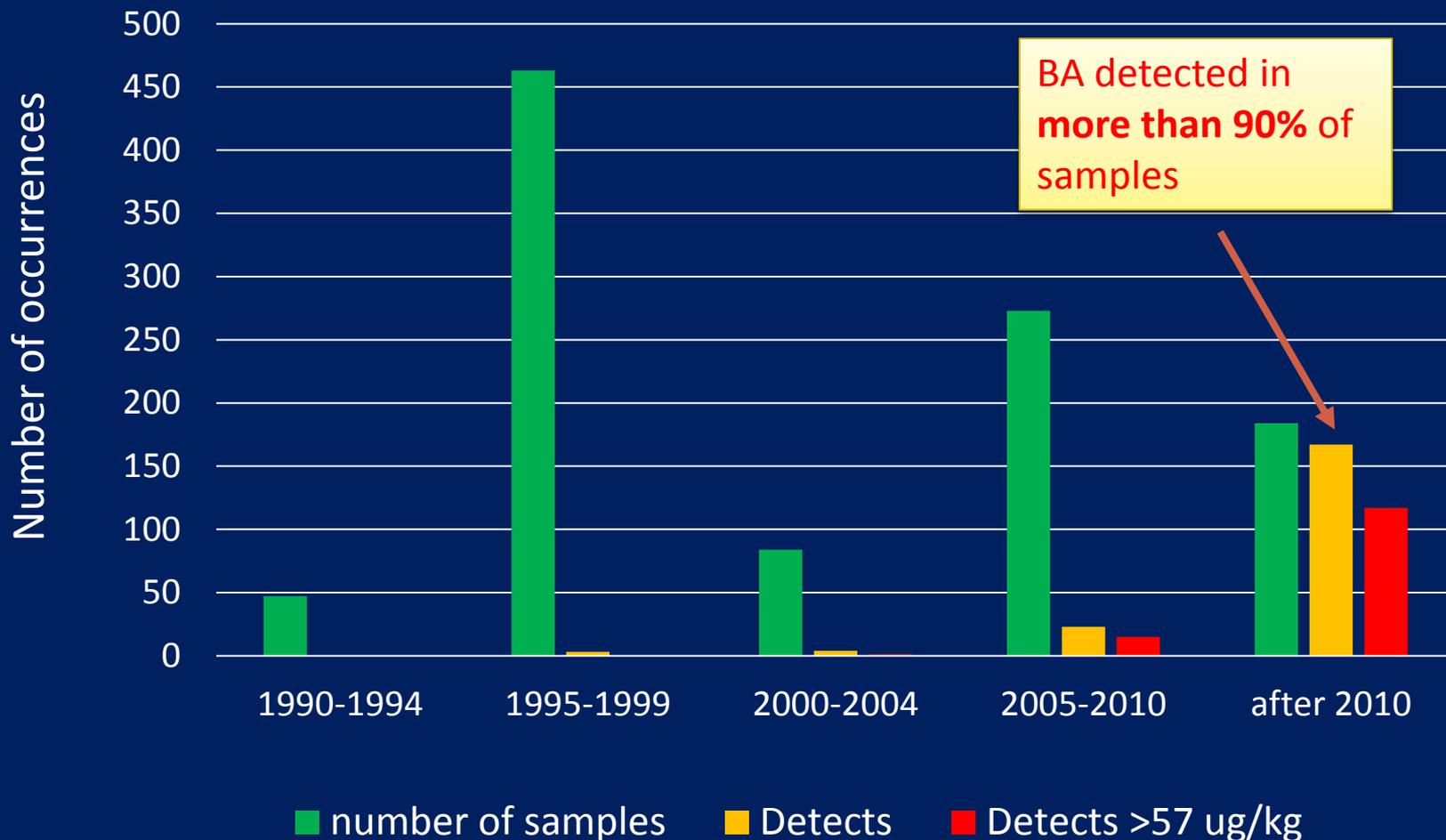
BA SL exceedances in DMMP projects have increased since ~2011



Note: All comparisons use current SL = 57 ug/kg

BA detections are also increasing in non-DMMP projects

Benzyl Alcohol in Lower Duwamish Sediment Samples



Why the increase?



Analytical techniques have improved

- BA measured via EPA Method 8270 (GC/MS)
 - Historically, low detection limits have been difficult to attain
- Laboratories have made significant upgrades to instruments, injectors, solvents, extraction procedures, etc.
- Example: In 2015, non-detect sediment samples from Boeing Plant 2 were re-analyzed due to poor QC sample recoveries
 - BA detected in 3 of 6 re-analyzed samples
 - Maximum detection (360 ug/kg) > SL

Cumulative effect: Analytical improvements may be a contributing to observed sudden increase in BA detections (frequency and magnitude)

Benzyl alcohol has industrial and natural sources

- Used industrially as a solvent, preservative, and as a feedstock for other chemicals
- Consumer products: food, cosmetics, soap, perfume, flavoring industries, and medical treatments
- Occurs naturally in a number of plants and edible fruits
- Found at high levels (**>3,000 ug/kg**) in Pacific Northwest “dark fines” used on a Duwamish Waterway habitat restoration project
- Visible organic matter was noted in sample logs for DMMP projects for which BPJ was used

Persistence: Benzyl alcohol degrades quickly

- Aerobic and anaerobic tests: BA readily degrades
 - However, Puget Sound wastewater treatment facility efficiencies unknown
- Natural degradation product: benzoic acid
 - Also readily biodegradable
 - Many industrial uses
 - Has DMMP screening level
 - BA in dredged material will likely biodegrade to benzoic acid within a short time span
- Low concern for bioaccumulation
 - Low log K_{ow}

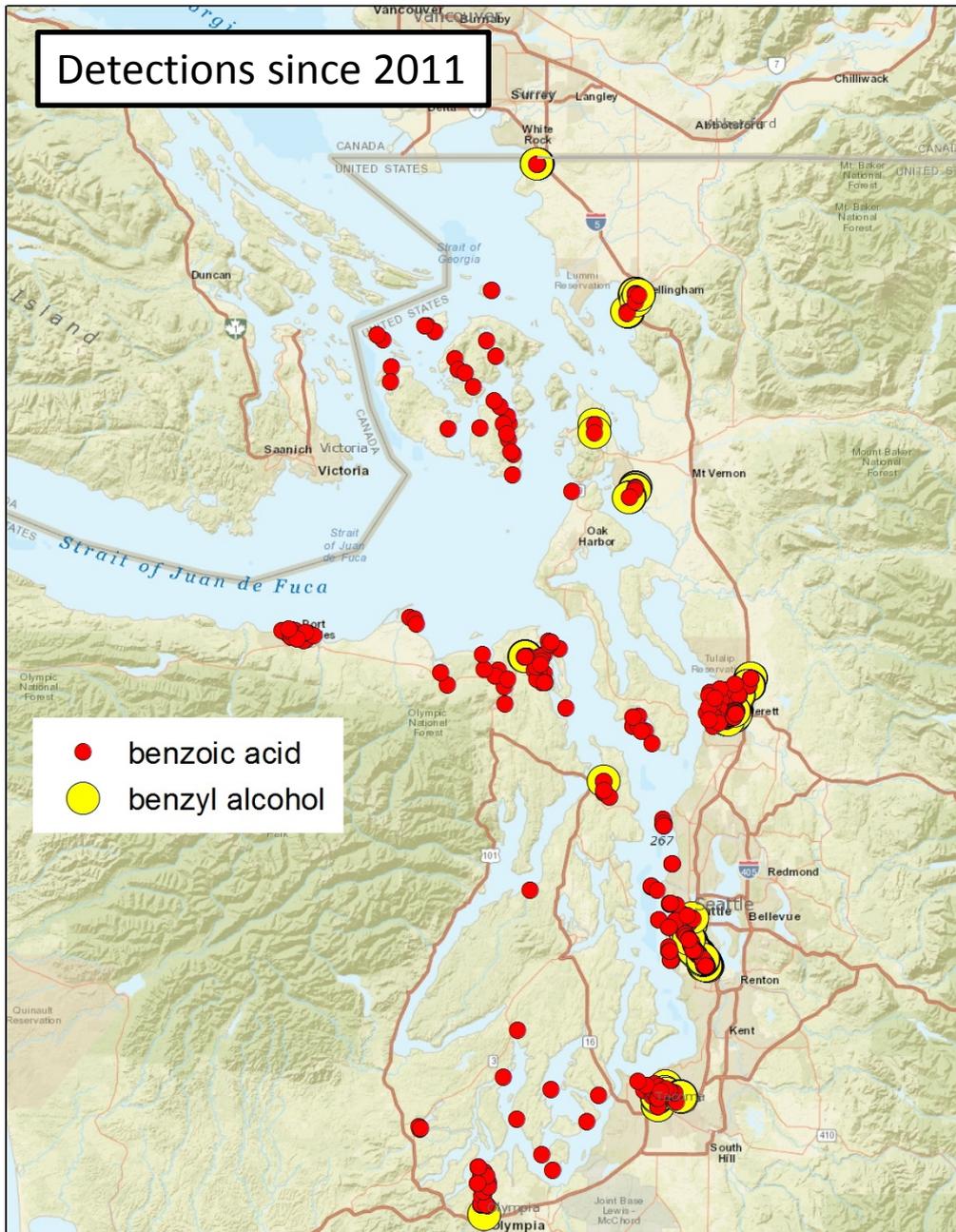
Geographic Occurrence & Distribution

BA found in excess of SL at non-urban reference sites

- Carr Inlet, Holmes Harbor, Dabob Bay, and Samish Bay
- BA exceeded the DMMP SL in 2 of 4 reference areas
- Maximum BA = 281 ug/kg

Recall: current SL = 57 ug/kg!

Detections since 2011



BA is widespread and frequently co-occurs with benzoic acid

- Urban and non-urban areas
- Benzoic acid detected even more often than BA

BA generally not found at disposal sites

- BA primarily non-detect at non-dispersive sites possibly due to biodegradation
- All BA detections < SL
- Benzoic acid frequently detected (at less than SL)
- Current DMMP evaluation procedures (including BPJ) are environmentally protective

Bioassay data indicate low toxicity at SL

- DMMP bioassay data: 26 samples from 6 studies
- PSAMP bioassay data: 15 samples
- Data are complicated by co-occurring chemicals
- Both datasets provide evidence that BA alone is likely not toxic enough to cause DMMP bioassay test failures at or near the SL

Literature ecotoxicity data also indicates low toxicity

- Surveyed EPA's EcoTox database
- Limited number of studies exposed test species to aqueous concentrations of BA
- Using Equilibrium Partitioning (EqP) relationship, the predicted sediment concentration associated with the lowest effective concentration (EC50) would be:

2,700 ug/kg

Recall: current SL = 57 ug/kg!

Summary

- Benzyl alcohol
 - Likely occurs naturally in plant-derived material in marine sediment
 - Likely readily biodegraded in the marine environment
 - Detections are widespread in WA; found in both urban and non-urban areas
 - Seldom detected at DMMP non-dispersive disposal sites
- Bioassay and literature toxicity data indicate
 - BA has low toxicity at/near the current SL

Proposed Action/Modification

- BA is not a chemical of significant concern to the DMMP agencies
- When BA is the only COC exceeding its SL, continued use of BPJ is justifiable to determine need for biological testing
- Re-evaluation of the current SL (and possible re-calculation of the AETs or use of other benthic toxicity modeling tools) is recommended

Implications for other DMMP COCs

- Other chemicals that are known or suspected to occur naturally include
 - Benzoic acid
 - Phenol
 - Methyl phenols
- More BPJ?
- More investigation?
 - Potential future SMARM papers

Questions?

Send comments to
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By June 4th.