**Patmont Comments on April 2010 *Development of Benthic SQGs for Freshwater Sediments***

**May 17, 2010**
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Following up on my preliminary thoughts e-mailed to the Sediment Workgroup on May 2, provided below are my comments on the draft freshwater sediment quality guideline (SQG) report cited above. Overall, I think the SQGs developed in the draft report do a commendable job of developing reasonable reliability (~80%) and controlling false positives, and the document represents a strong step forward to develop freshwater sediment criteria. However, there are at least several issues that should be addressed more thoroughly in the final report, including:

- Organic carbon (OC) normalization;
- Chemical criteria for bis(2-ethylhexyl)phthalate;
- Use of reference samples for confirmatory biological determinations;
- Future incorporation of additional sediment data; and
- Other miscellaneous comments.

Each of these issues is discussed below.

**Organic Carbon-Normalization**

The draft report recommends use of dry weight-normalized SQGs based on the following:

- Dry weight SQGs have similar or potentially better reliability compared with OC-normalized values;
- OC-normalized SQGs can be difficult to understand and explain to the regulated community; and
- In some situations, anthropogenically derived organic carbon can complicate OC normalization.

However, I submit that a comprehensive weight-of-evidence evaluation would conclude that OC-normalization provides a more defensible and consistent set of SQGs for polar organic chemicals including polychlorinated biphenyls (PCBs), polynuclear aromatic hydrocarbons (PAHs), bis(2-ethylhexyl)phthalate and others. The weight-of-evidence evaluation would consider the following:

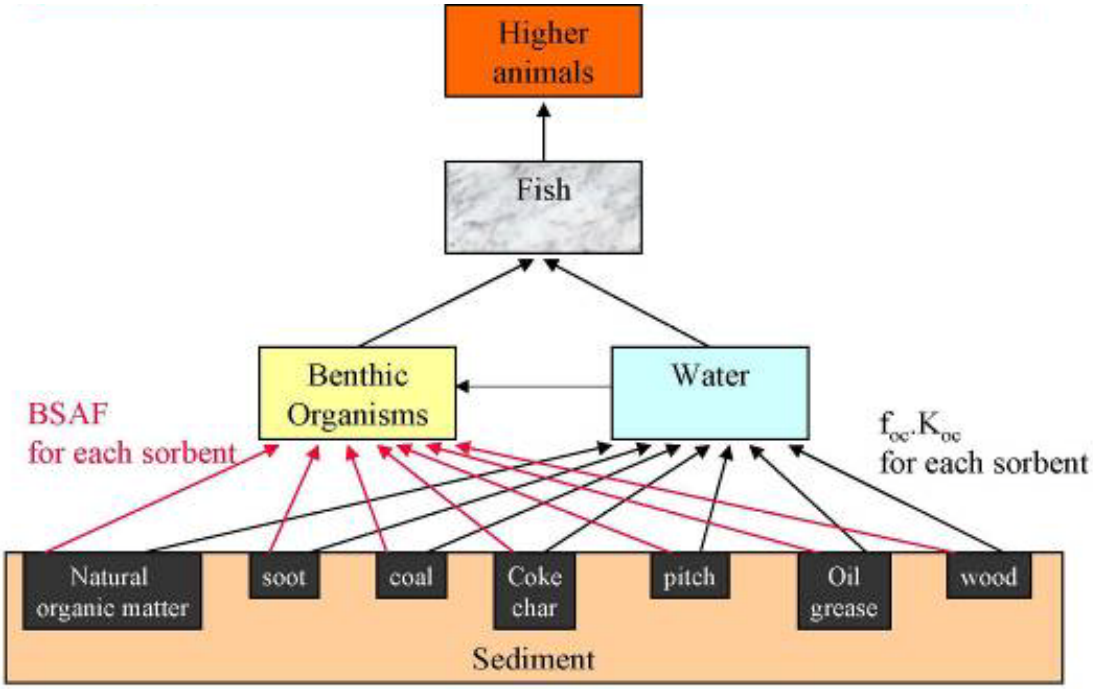
- The minor differences in reliability reported between dry weight and OC-normalized SQGs do not appear to be statistically significant and thus should not be used as a basis to select between these approaches;
- The scientific underpinnings supporting use of OC-normalization to assess the potential bioavailability of polar organic chemicals is now firmly established and widely supported in the

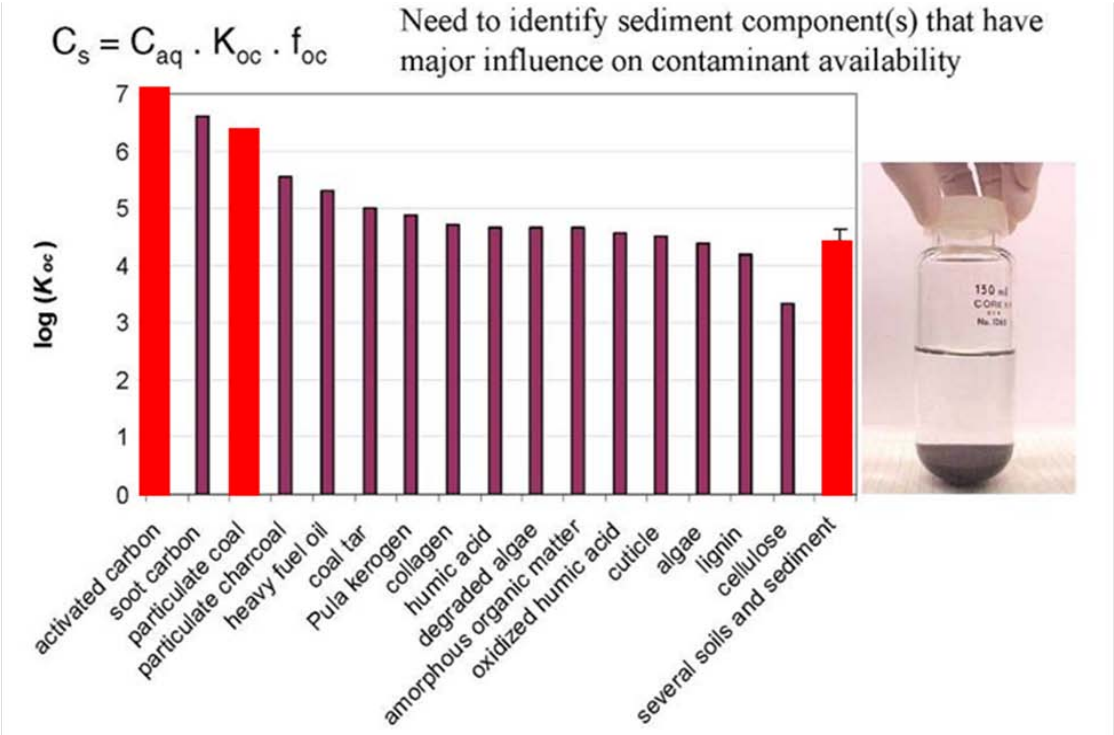
technical literature and other regulatory programs – e.g., EPA's current sediment quality benchmarks for PAHs and other polar chemicals are based on OC-normalization for this reason;

- The most recent EPA guidance on sediment bioavailability assessments for polar organics uses a two- or three-phase partitioning model consisting of the bioavailable dissolved phase and a generally non-bioavailable particulate OC phase (the generally non-bioavailable dissolved organic carbon phase can also be added as a further refinement) – consistency with these other regulatory programs should be maintained;

- In addition, Ecology and other state agencies recently collaborated to develop more detailed guidance on how to assess bioavailability of contaminants in sediment – consistency with this guidance can be achieved in part through incorporation of OC-normalization (the web link for this bioavailability report is as follows: http://www.js3design2.com/con_sed_web_jws);

- Within a given sediment site, OC-normalization has been demonstrated to strongly improve predictions of bioavailability for polar organics, but the variability in the types organic carbon between sites (e.g., soot versus wood) contributes to the observed variability in region-wide correlation analyses – the generally accepted bioavailability model for polar organics and a summary of variable sorption characteristics associated with different sediment materials for a representative PAH compound (phenanthrene) is depicted below (note that some forms of anthropogenic carbon such as coal, soot and activated carbon dramatically decrease the bioavailability of polar chemicals, further supporting the use of OC-normalization);






- The promulgated Sediment Management Standards (SMS) marine chemical criteria for polar organic chemicals are based on OC-normalization - regulatory consistency with the existing marine SMS chemical criteria should be maintained, as there are no clear or compelling reasons not to do so;

- While occasionally some of the lay public may be confused by OC-normalization, the vast majority of the regulated community readily understands this procedure, particularly since it is the basis for the existing SMS marine criteria, EPA benchmarks, and expanding federal and state guidance; and

- Though the presence of anthropogenically derived organic carbon can complicate OC-normalization, there are relatively straightforward approaches that are currently applied to address this situation, such as setting lower and upper bounds on organic carbon levels that can be used in the normalization calculations and excluding macroscopic woody materials from the organic carbon analysis.

Thus, OC-normalized SQGs for polar organic chemicals should be used in the final report as the basis for SQS and CSL chemical criteria for polar organic chemicals, similar to the promulgated marine criteria. There should also be a narrative provision included with the rule that further evaluations of bioavailability can be performed as necessary on a case-by-case basis (e.g., using current high resolution sediment porewater sampling and analysis methods) to provide a more direct assessment of bioavailability.

**Chemical Criteria for Bis(2-Ethylhexyl)Phthalate (BEHP)**

The proposed sediment quality standard (SQS) chemical criterion for BEHP (500 µg/kg dry weight basis; this should be recalculated using OC-normalized values as discussed above) deserves additional scrutiny. BEHP is a ubiquitous contaminant in urban stormwater that contributes to regional background conditions, and a contaminant that will likely be a focus of regional and municipal source control efforts in the years and decades to come. Therefore, it is critically important that a reliable sediment quality value for BEHP is selected carefully. The reliability of the current recommended BEHP SQS chemical criterion is suspect given the following observations:

- The currently proposed SQS chemical criterion for BEHP (500 µg/kg) is based on the floating percentile model (FPM) for *Hyalella* 10-day mortality, whereas the FPM for *Hyalella* 28-day mortality is almost 1,000 times higher (>440,000 µg/kg) – the longer-duration test should at least be as sensitive as the shorter-duration test;

- The currently proposed cleanup screening level (CSL) value for *Hyalella* 10-day mortality (22,000 µg/kg) is substantially higher than the SQS value for *Hyalella* 10-day mortality (500 µg/kg), suggesting that the test result is overly sensitive to the selection of the adverse effects level;

- The proposed SQS chemical criterion for BEHP of 500 µg/kg is likely above typical reference concentrations in urban areas (note that reference comparisons were not used to develop these SQGs), making this value particularly problematic;

- EPA does not list a chronic water quality criterion for BEHP in its National Recommended Water Quality Criteria because "*There is a full set of aquatic life toxicity data that show that BEHP is not toxic to aquatic organisms at or below its solubility limit*"; and

- EPA lists the water solubility of BEHP at approximately 340 µg/L - applying the average log $K_{oc}$ for this compound of approximately 5.1 and setting the criterion at 1 percent of the solubility limit to prevent development of non-aqueous phase liquids (similar to petroleum criteria) would result in a calculated solubility-based OC-normalized sediment criterion of roughly 400 mg/kg OC, which is somewhat higher than the current marine CSL chemical criterion of 78 mg/kg OC.

In consideration of the apparent inconsistencies in the sediment quality database, and the lack of demonstrated toxicity in water quality studies, it is likely that BEHP provides little or no contribution to sediment benthic toxicity. Thus, both the SQS and CSL chemical criteria for BEHP should either be eliminated or revised, also folding in the OC-normalization procedure discussed above as appropriate.

**Use of Reference Samples for Confirmatory Biological Determinations**

While control comparisons were used to reduce the noise in the database and to optimize the number of valid data pairs for the purpose of developing chemical screening criteria, it is crucial to clarify both in the final SQG report and in the rule that control comparisons should not be used for confirmatory biological testing evaluations. On page 7, the possibility of identifying reference sites for freshwater sites is discussed, and confounding factors such as the greater heterogeneity and changing conditions

associated with freshwater locations is noted. While this is an accurate summary of freshwater sediment reference characteristics, it also underscores the vital importance of developing appropriate "real world" reference data for confirmatory testing evaluations, since use of controls for such comparisons will result in a significant false positive bias. While this issue may be beyond the scope of the existing draft SQG report, the final report and the rule should nevertheless clarify that appropriate statistical procedures will be needed to properly interpret confirmatory bioassay data, including use of a reference envelope or pooled reference data approach (e.g., combining suitable reference data across studies, potentially with subsets to address different grain size categories).

**Future Incorporation of Additional Sediment Data**

The screening approached used in this evaluation may miss some important studies such as the Ecology Quendall/Baxter data for PAHs or upper Columbia data for metals. These data were apparently screened out based on the observation that "*toxicity would frequently occur in samples without adequate chemistry to explain it*". In many situations this conclusion may be erroneous (e.g., focused chemistry/bioassay analyses are often based on early screenings which determined that other chemicals of concern were not important). A step should be added that evaluates such cases so that in the future these robust datasets are included in the SQG updates.

**Other Miscellaneous Comments**

- The proposed SQS chemical criterion for naturally-occurring metals such as nickel (26 mg/kg) appears to be below the state-wide background (38 mg/kg per Ecology's reports), so this should be adjusted (reference concentrations of other metals should also be checked);
- The bulk (i.e., dry weight-based) SQGs for ammonia and sulfide should be removed, as bulk sediment concentrations of these chemicals are only very poorly correlated with the bioavailable dissolved fraction – development of SQGs for these naturally occurring chemicals should be based on porewater concentrations and should also explicitly consider reference conditions (similar to the BEHP discussion above); and
- The proposed SQGs for petroleum compounds are also problematic, in part because concentrations similar to the proposed SQS and CSL values are common in organic rich sediments, particularly within urban areas – the following additional steps should be included in any further application of the petroleum criteria, potentially resulting in removal of the criteria:
    - Verify that non petroleum organics were removed from the samples through appropriate cleanup steps in the analytical method
    - Verify with chromatograms or other chemistry review that samples actually contained petroleum rather than just other organics (e.g., wood can frequently give false positives)
    - Assess the different types of petroleum and consider parsing the bioassay data out further within the fractions (toxicity can vary greatly with different sub fractions or weathering of petroleum)