NATIONAL COUNCIL FOR AIR AND STREAM IMPROVEMENT, INC.
West Coast Regional Center
Mailing address: PO Box 458, Corvallis OR 97339
Street address: 720 SW Fourth Street, Corvallis OR 97333
Phone: (541)752-8801 Fax: (541)752-8806

Dr. Jeff Louch
Principal Scientist
JLouch@ncasi.org

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MEMO TO: Adriane Borgias
Bud Leber
Spokane River Regional Toxics Task Force

FROM: Jeff Louch

SUBJECT: LimnoTech Draft Sampling and Analysis and Quality Assurance Project Plans

NCASI has reviewed the Draft Sampling and Analysis Plan (SAP) and the Draft Quality Assurance Project Plan (QAPP) developed by LimnoTech and offers the following comments specific to measuring PCBs.

1. Blank Contamination Must be Evaluated in a More Rigorous Manner

The documents describe multiple types of blanks (e.g., method blanks, field blanks, equipment blanks, etc.) and give criteria defining acceptable blank results. However, no guidance is provided on how blank results should be reported. In addition, NCASI is concerned about how blank results will be used to qualify sample results.

As evidenced by results recently reported by the Washington State Department of Ecology[1], it can be anticipated that congener-specific results in blanks will be variable and that many of the associated sample results will be of the same magnitude as found in blanks. Under these circumstances it is often impossible to identify the real signal-to-background ratio (S/B), and thus the potential for reporting biased results. As examples:

- (From Table C-2 in Era-Miller, 2014) PCB-95 was reported as not detected at 13 pg/L in both the field blank and the method blank from the fall, 2012 PCB sampling. Associated reported sample concentrations ranged from 13.4 pg/L to 19.9 pg/L, with the results from two samples reported as non-detect at 13 pg/L. Because the reported sample concentrations are within a factor of 2 of the detection limit (DL) in the associated blanks they must be considered highly suspect, and more likely than not reflect laboratory contamination as opposed to presence of PCB-95 in samples prior to analysis.
- (From Table C-3 in Era-Miller, 2014) PCB-11 was reported as not detected at 35.2 pg/L in the method blank from the spring, 2013 PCB sampling. Results from two of the associated samples were reported as 34.3 pg/L and 60.4 pg/L, while the remaining four samples were reported as having non-detectable concentrations of PCB-11 at DLs ranging from 18.9 pg/L to 54.3 pg/L. Thus, the reported concentration of PCB-11 in one sample (#1305006-03) was actually less than

[1] Era-Miller, B., 2014. Draft Technical Memo: Spokane River Toxics Sampling 2012-2013 – Surface Water, CLAM and Sediment Trap Results. March 31, 2014. Available at http://srrttf.org/?p=2684

the DL from analysis of the associated method blank. As a consequence, absolutely nothing can be said about the measurement-specific S/B, so it's impossible to state with any authority that PCB-11 was actually present in this sample prior to it being brought into the analytical laboratory.

All this suggests the need to be more rigorous when evaluating the potential for contamination, and the following is suggested:

- All blank results should be reported without any censoring. This means that whenever a chromatographic peak is integrated the raw instrumental quantification is reported regardless of any censoring level. In those instances where no chromatographic peak is present the result should be reported as the estimated DL (based on chromatographic signal-to-noise).
- When evaluating an associated sample result against a single method or field blank, any result <5x the associated blank result should be reported as not detected (ND) at 5x the associated blank result regardless of whether the blank result was ND (at X pg/L) or not.

The above is inconsistent with Table 5 of the QAPP, which states that sample results <3x the associated blank result will be reported but flagged (JB-Flag) to indicate potential high-bias due to background contamination. This approach would not be unreasonable if the associated blank result was the mean from replicate blanks and the decision as to whether or not the sample result was <3x this mean was based on some statistical test (e.g., T-test). In fact, this is nominally equivalent to EPA's method detection limit/minimum level (MDL/ML) construct.

However, as currently outlined, the decision to apply the JB-Flag will be based on a simple ratio using a single batch-specific blank result. This approach is biased towards reporting false positives. Because the purpose of this study is to get an accurate picture of mass loadings there is no reason to add this kind of bias to results that will be used in calculating a mass balance. In fact, it would be counter productive to add this kind of noise.

Unless a systematic study of background contamination is performed and evaluation of blank contamination is based on some statistical methodology, the process outlined in these comments should be used to evaluate the impact of background contamination on sample results.

2. The Impact of Spatial Heterogeneity in Concentration Needs to be Accounted For

Although the study explicitly acknowledges the potential impact of temporal variability, neither document acknowledges that both flow and concentration are heterogeneous in space as well as time. Thus, measurements (of flow and/or concentration) reflecting one point in the Spokane River will be interpreted as reflecting the river *in toto;* i.e., results (flow and concentration) reflecting one mid-river sampling location at River Mile (RM) X will be used to calculate the mass flux of PCBs at RM X.

Collection of samples at USGS gaging stations should, to some extent, mitigate the impact on results due to spatial heterogeneity in flow. However, the study plan ignores the potential impact of concentration heterogeneity. This is a significant gap that will cast doubt on any resulting mass balance. Even if the study cannot be modified to account for this under all circumstances (i.e., at every river mile), some work should be performed to evaluate the potential impact of concentration heterogeneity on any mass balance ultimately attempted. Thus, at one in-river location at least, multiple grab samples should be collected at different depths at multiple points across the river and the results used to assess spatial variability in

concentration. Without this level of detail is will be essentially impossible to identify when apparent closure of any mass balance is real or simply a matter of luck.

3. The Process Used to Generate Composite Samples Needs to be Detailed, and Must Specify Generation of Associated "Compositing Blanks"

Both documents state that composite samples will be generated from the multiple grab samples collected as part of the synoptic survey, but provide no rationale why this is being done other than to suggest that composites might be analyzed as a means of reducing cost. Regardless, generation of composites, whether done in the laboratory or the field, increases the potential for contamination. Thus, an associated "compositing blank" should be generated every time samples are composited, and this blank should be analyzed with the associated composite samples (in addition to a standard method blank). If all composites are generated in one batch, two composite blanks should be generated to provide some measure of variability.

4. The Process Used to Generate Sample Splits Needs to be Detailed, and Must Specify Generation of Associated "Splitting Blanks"

The documents describe collection of replicate samples and state that analysis of these replicates will be used to characterize variability. When these replicates are unique samples collected one after the other there is no need to perform any additional QA. However, the documents imply that these replicates will be splits, and that these splits will be generated in the field. If splits are going to be generated the procedure for doing so should be described. This procedure should specify generation of a processing blank ("splitting blank") concurrent with sample splitting, and the resulting blank should be analyzed along with the splits.

5. The Specified Detection Limits are Unreasonable

Table 5 of the QAPP specifies a uniform DL of 10 pg/L for all PCB congeners. This is absolutely unrealistic even when considering analysis of blank water spikes, and expecting that a 10 pg/L DL will be achieved for every congener (or group of co-eluting congeners) in every sample is even more unrealistic. If this criterion is fully enforced a significant portion of the analytical data will be rejected due to the inability to achieve the 10 pg/L DL.

6. Additional Detail on how Results Will be Flagged is Required

Table 11 of the QAPP gives the proposed data validation qualifiers ("data flags"). This table needs additional detail.

JB-Flag: Table 5 of the QAPP indicates that sample results <3X the associated blank result will be JB-flagged, so this flag should be included in Table 11. However, given the discussion concerning background contamination (Comment #1), this flag should be unnecessary.

J-Flag: The circumstances under which a result will be J-flagged need to be clarified; e.g., a quantification greater than 5x the blank level, above the nominal DL, but less than the lower calibration level (LCL) is a circumstance clearly consistent with a J-Flag, while a quantification greater than 5x the blank level but less than the nominal DL is not (this quantification should be reported as not detected and flagged U).

UJ-Flag: If an analyte was analyzed for but was not detected there is no basis for estimating a concentration, so the reported result should be ND at the appropriate DL. The only time a UJ flag might be appropriate is when the associated DL is an estimated DL, e.g., as is obtained from graphical evaluation of chromatographic S/N (as opposed to a statistical analysis of pooled blank or low-level spike data). The circumstances under which this flag will be applied need to be clarified.

NJ-Flag: The circumstances under which this flag will be applied need to be clarified, and should explicitly exclude quantifications of any chromatographic peak failing both retention time and abundance ratio criteria (this circumstance is a true non-detect).

Please do not hesitate to contact me if you have any questions or concerns about these comments.

Sincerely,

Jeff Louch

Jeff Louch
Principal Scientist

ec: Doug Krapas, Inland Empire Paper Company
Christian McCabe, Northwest Pulp & Paper Association
Steve Stratton, NCASI
Paul Wiegand, NCASI