

Response to Comments

Comments: Jean Brochi, EPA New England

MDL Verification Results:

General Comments:

1. The MDL studies for trace metals, dioxins/furans and dioxin-like PCBS in sediment and tissue were reviewed to determine if the resulting data would meet the sensitivity requirements outlined in the LIS QAPP. In most cases the MDLs do meet the project requirements for sensitivity but there are some exceptions. We know that MDLs change from instrument to instrument and from year to year. The MDL supports the Project quantitation limit or the reporting limit and must be at least three time below those limits. In some cases this is not demonstrated. The exceptions are in the following specific comments:

Specific Comments:

1. The 2002 MDLs for antimony, arsenic and beryllium are higher than expected but will support decisions to be made about sediment. Arsenic and lead values are higher than expected for tissue but support the reporting limits. Only metals detailed in Table #9b were checked.

Response – It appears that all metals meet the Project DL goals listed in table #9b of the QAPP (page 83 of 408).

Tissue Target Metal	Project DL Goal (µg/g dry wt.)	MSL 2002 MDL (µg/g dry wt.)
As	5	0.09 ICP-MS
Be	0.5	0.04 ICP-MS
Cd	0.5	0.01 ICP-MS
Cr	1	0.09 ICP-MS
Cu	5	0.03 ICP-MS
Pb	0.5	0.03 ICP-MS
Hg	0.1	0.002 CVAA\F
Ni	0.5	0.04 ICP-MS
Se	0.5	0.14 ICP-MS
Ag	0.25	0.01 ICP-MS
Zn	5	0.11 ICP-MS

2. The MDLs for Dioxin in tissue were checked against MDL versus RL/PQL requirements outlined in the QAPP . Several of the compounds are high and will not support the PQL and decisions to be made about risk. The compounds that appear to be most significant as far as risk calculations are 2,3,7,8-Cl4-Dibenzofuran(TEF=0.1), 1,2,3,4,6,7,8-Cl7-Dibenzofuran (TEF=0.01), and 1,2,3,4,6,7,8-Cl7-Dibenzodioxin (TEF=0.01). None of the MDLs here support the Project QL Goal. If these compounds are non detects there will be a risk using half the detection limit. The Octachloro dioxin and furan compounds do not meet the QAPP criteria but their effect on risk is minimal.

Response - No "Project QL Goals" were defined in the QAPP for the LIS Tissue Study for dioxin/furans or dioxin-like PCB congeners.

The actual "MDL" used to report and qualify dioxin/furan and PCB data quantified by methods 1613 and 1668, respectively, are not the MDLs determined using the 7-replicate MDL study reviewed here. The High Resolution methods of 1613 and 1668 calculate a sample specific detection limit based on signal to noise (S/N). This measurement is accomplished by integrating the noise level in the window where an analyte of interest would elute if it were present in the sample. This value (area or height) is multiplied by 2.5 (definition of a detectable signal, 2.5 X noise) and used in the same calculation as that used for detected analytes. Because the calculations in the High Resolution methods use labeled internal standards (a compound which is spiked prior to extraction and clean up), the sample recovery is taken into account and makes this MDL sample specific.

The traditional MDL calculation is based on the precision of 7 replicates of a clean spiked matrix at a level of 3 to 5 times the actual method MDL. This traditional MDL is performed annually and may or may not represent the ability of the laboratory to detect the calculated level of analyte at all times and in all matrices.

It is important to note that the major assumption for applying a detection limit determined using the S/N approach is that the calibration is somewhat linear in this very low concentration region where no calibration points are obtained. Keeping in mind that the MDL value is determined by extrapolation of a curve that may have a low point 10 to 100 times higher than the calculated MDL.

3. The MDLs in Biota for the Dioxin-like PCBs #105 and #118 are high but these compounds do not impart much of the risk and they are the most prevalent of the PCBs that are found in native samples. Most likely these two compounds will be detected above the reporting limits of the method thus one half the detection limit convention will not have to be evoked. 156/157 congeners are high but not so much that they will cause a risk problem.

Response - See discussion for comment 2. above in regards to the actual MDL used to report and qualify dioxin-like PCB congener results.

Finfish Report:

General comments: this data set is very much like the other data sets and has some of the same issues related to blanks and flagging. Flagging of data (B) that is essentially a non-detect due to method blank contamination does not help the data user in determining the comparability of reference location data to dredge spoils data. The analyses performed in this project are for trace levels of contaminants and must be free of interfering problems otherwise the data reviewers will not be able to use the data to make project decisions. Specific comments. 1. PAH contamination of the blanks needs to be explained in greater detail. The effect on the data usability should also be discussed. The use of the 10 X factor should also be discussed in relation to using the 5X factor used for all other parameters. The 10X factor nullifies more of the data for comparisons than does the 5X factor. 2. The Tributyl Tin results indicate that the method blank contamination renders the relatively low TBT results as non-detected. If the results do not correspond to any risk, then the blank problem is unimportant. Please clarify where this issue will be discussed. 3. The finfish results for dioxin-like congener specific PCBs and Dioxins/furans do not include the rerun method blank information discussed last week. The data here shows many "B" flags that indicate not detected results. The new method blanks generated on the Batch 2 data indicate much lower method blank results that would yield less "B" flags during validation and make more low concentration data usable. The most important question is: "If we only have Batch 2 rerun method blank data, what method blank data are we going to use for Batch 1 and Batch 3? This issue must be resolved. 4. Please clarify whether these reports are to be reissued with new tables and QC discussion or whether the database will be corrected, or both.

1. PAH contamination of the blanks needs to be explained in greater detail. The effect on the data usability should also be discussed. The use of the 10 X factor should also be discussed in relation to using the 5X factor used for all other parameters. The 10X factor nullifies more of the data for comparisons than does the 5X factor.

Response – PAHs are often found in procedural blanks at levels above the MDL. Because the levels are variable, the exact source is unknown. Air coming into the lab, reagents, and contamination from other samples, urban dust, could all be possible sources of contamination. Contamination could be an accumulation of all these variables, or others, adding trace amounts of PAH through out the sample preparation process. Battelle strives to achieve a PAH free lab, baking reagents and lab glass before use, rinsing glassware with extraction solvents etc, but unfortunately PAHs (especially the volatile naphthalenes) are ubiquitous and may still be detected above the ultra-low MDLs. Currently, Battelle is switching to a new alumina used for extract clean up, in an attempt to curb PAH contamination of future projects.

Because of the PAH contamination associated with the blanks processed and the anticipated use and interpretation of the data generated for this project, action limits have been reduced from what was stated in the original QAPP. Any sample data that is not greater than 5X the concentration found in the blank (as opposed to 10X as stated in the original QAAP) will be flagged with a "U".

2. The Tributyl Tin results indicate that the method blank contamination renders the relatively low TBT results as non-detected. If the results do not correspond to any risk, then the blank problem is unimportant. Please clarify where this issue will be discussed.

Response – TBT contamination is discussed in both the QA/QC summary and section 4.3 of the finfish analytical results report. Additional information will be added to section 4.3 to address the issues mentioned above.

3. The finfish results for dioxin-like congener specific PCBs and Dioxins/furans do not include the rerun method blank information discussed last week. The data here shows many "B" flags that indicate not detected results. The new method blanks generated on the Batch 2 data indicate much lower method blank results that would yield less "B" flags during validation and make more low concentration data usable. The most important question is: " If we only have Batch 2 rerun method blank data, what method blank data are we going to use for Batch 1 and Batch 3? This issue must be resolved.

Response – Dioxin/furan and dioxin-like PCB data reported in the draft finfish analytical result report was not qualified against the "new" blank data. PSC has re-run blanks from all batches, not batch 2 exclusively. The data will be reflagged using the appropriate blanks for the final report.

4. Please clarify whether these reports are to be reissued with new tables and QC discussion or whether the database will be corrected, or both.

Response – Final reports will have updated tables, using the "5x" rule, "U" qualifiers, new PCDD/F and dioxin-like PCB blanks, and the associated requalified data, as decided in discussions with the USACE. This correct data will be entered in the database.

Comments: Forrest Knowles

Metals

1. In the method blanks, Cu and Zn, are > 5x MDL; Ni and Se are < 5x MDL in batch 5, and As, Cd, and Zn are detected in batch 6.

Response – Addressed in narrative.

2. In batch 5, the % difference for Zn was exceeded in one of the SRMs, Zn was in control for the remaining SRMs.

Response – Correct, addressed in narrative.

3. Is Se sometimes found in the blanks? I don't recall this for any other projects.

Response – Se is not usually found in the blanks. One of the two method blanks was not detected for Se, while the other contained Se at 0.136 ppm wet wt. The mean of the MDL (0.034 ppm) and the detectable concentration was used to flag sample results that were detected at < 5x that concentration. Only a few sample concentrations fell below the blank action limit.

4. Was detectable Se expected in the tissue?

Response – The Se concentrations were generally between 0.3 and 0.7 ppm wet wt. in all fillet samples. This represents a relatively low range of Se tissue concentrations.

5. Some of the As concentrations for winter flounder tissue seem higher than the others, namely 1767-165 and 168. Are these concentrations within the expected range? Winter flounder concentrations seem higher overall than the other fish.

Response - The Winter Flounder As concentrations appeared to be consistently higher than the other species. The quality of the data is acceptable based on results of QC samples, therefore, the validity of the numbers is not in question. The issue of relative concentrations among species and relative to other areas of the North East Atlantic will be addressed in the Environmental Consequences section of the EIS.

PCB/Pesticides

1. Many recoveries exceeded acceptable ranges – background sample mislabeled. Fillets rerun, 3 MSD recoveries and 6 of 43 RPDs exceeded limits.

Response – Correct, addressed in narrative.

2. Surrogates were out of range for one sample.

Response – Correct, addressed in narrative.

3. In the SRM for Batch 02-142, PCB 180 exceeded the PD limit.

Response – Correct, addressed in narrative.

4. MS/MSD not labeled in the data for individual results.

Response – Not entirely clear on the intent of this comment. There was a discrepancy in batch 02-142 (fish fillet Batch 2) where the MS/MSD recoveries were extremely high; it appears that the background sample may have been identified incorrectly and the native sample was re-spiked and re-run in a separate batch w/ better results. This is detailed in the QA/QC narrative.

5. Did you expect the PCB results to be as high as this?

Response – PCB results are especially high for the striped bass fillet, which were much larger fish and have somewhat higher lipid content than the other species. Otherwise, winter flounder and scup concentrations are relatively low.

6. Page 3 of 3 in the QC summary for batches 02-176 etc. – PCB34 recovered at 31%

Response – This omission will be corrected in the final data report.

PAH

1. In the method blank for batch 02-176, there is one instance of a detectable analyte >MDL but <RL

Response – Correct, addressed in analyte.

2. Benzo[g,h,i]perylene recoveries low in MS/MSD for 02-203.

Response – Correct addressed in narrative.

3. Surrogate Phenanthrene-d10 was below acceptable range in one sample.

Response – Correct, addressed in narrative.

4. For the triplicate data 2-Methylnaphthalene in Batch 02-203 and Benzo[g,h,i]perylene exceeded limits.

Response – 2-Methylnaphthalene in batch 02-203 had an exceeding RSD in batch 02-203. However, Benzo[g,h,i]perylene had no RSD exceedences in either the fillet or liver data, but in Batch 02-176 Bis(2-ethylhexyl)phthalate had a calculated RSD of 76.4%. This was correctly documented in the narrative.

5. SRM exceedences were found in batch 02-176 and 02-203.

Response – Batch 02-176 and 02-203 both had PD exceedences, however both exceedences in batch 02-176, and 7 of the exceedences from batch 02-203 met contingency criteria. This is documented in the narrative.

6. With very low MDLs some traces of PAH in the blanks are not surprising. Was anything established as to the causes of the batch 176 blank contamination?

Response – See response to Jean Brochi, EPA New England, comment number 1.

Dioxin/Furans and Dioxin-like PCBs

1. In the method blank didn't 10 analytes exceed the RL for batch 1?

Response – This is correct, the narrative from the original report was not correct. Narratives will be corrected for the final report.

2. In the MS/MSD 6 recoveries were outside the limits for batch 2C0693; some PCB MS/MSD recoveries were outside limits in Batches 2C0682 and 2C0693.

Response – Correct, addressed in narrative.

3. For surrogates, no PCB exceedences were in batch 2C0693, 7 for batch 699, 27 in 2C0692-most were not associated with target analytes. For dioxins:6 exceedences for 2C0692 and 5 for 693.

Response – Correct, this is addressed in the narratives. For the final report surrogates not associated with target PCB analytes will not be reported or noted in the data tables and narratives.

4. In triplicate analysis one analyte slightly exceeded the RSD in Batch 2C0699.

Response – Correct, the RSD for 2,3,7,8-C14-Dibenzofuran was calculated to be 27% for batch 2C0699 (winter flounder livers). This was addressed in the narrative.

5. One exceedence was noted for the PCB SRM, and 2 for the Dioxin data pertaining to finfish fillet analysis.

Response – Correct, addressed in narrative.

6. Batches identified as 1 and 2 in the sample data section. Should it be according to Submission #? Or should the submission number not be used in the QA/QC summary?

Response – Both identifications will be used in the report but it will be what batch is what will be clarified in the final report.

7. I find the PCB/dioxin section hard to follow: Ex. MS/MSD not clearly labeled.

Response – PCB/Dioxin data sections will be clearly labeled and presented in a more logical fashion in the final report.

8. The very low detection limits here can result in the blank spiking up trace quantities. Has the lab established if the trace amounts come from the reagent or possible cross contamination.

Response – PSC suspected blank contamination was a result of carryover observed by running the Method Blanks immediately after the ongoing precision and recovery (OPR) standard as required by the method. To test this hypothesis, archived fractions of the PCB and Dioxin/Furan Method Blanks were re-run along with two representative samples from each SDG, with a solvent blank separating them from the OPR. Results of this study were submitted on July 8, 2002. Target analyte concentrations for Method Blank re-runs were lower, in some cases by an order of magnitude, while field sample concentrations remained practically the same. These results help support the belief that carryover was the cause of contamination and that it was isolated in only the Method Blanks, which immediately followed the OPR.

Lipids

1. 34% RPD was found in batch 181. Triplicate determinations were run and in control.

Response – Correct, addressed in narrative.

Introductory Text

1. 1.1 Background: second paragraph, third sentence- “finfish”, last sentence – “striped”.

Response – The typos mentioned above will be corrected in the final report.

2. Page 9 of 12 in section 4.2 of the QC Summary line 3 reported “from”

Response – The typos mentioned above will be corrected in the final report.