

**Assessment of the
Demonstration of Capability Package for
High Resolution Mass Spectrometer
Submitted by East Bay Municipal Utility District (EBMUD)
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Introduction

East Bay Municipal Utility District (EBMUD) acquired a high resolution gas chromatograph/high resolution mass spectrometer (HRGC/HRMS) in the Fall of 2004 that will be used to analyze Regional Monitoring Program for Trace Substances (RMP) sediment samples. The impetus for purchasing this equipment was the change in sediment sampling methodology that was initiated in 2002 (“the RMP sampling redesign”). As a result of the randomized sampling design, sediment samples in the San Francisco Estuary were observed to contain very low concentrations of contaminants, so low that they could not be characterized by gas chromatograph/electron capture detector. To mitigate this problem, EBMUD purchased a HRGC/HRMS to enable the laboratory to lower its detection limits. Prior to commencing with the analyses of RMP samples, RMP staff requested that EBMUD submit a demonstration of capability for the compounds of particular interest to the RMP, specifically polychlorinated biphenyls (PCBs) and pesticides. This report presents an assessment of the demonstration capability package submitted by EBMUD.

The demonstration package included the following components: a detection limit study for organochlorine (OC) pesticides, PCBs, and polybrominated diphenyl ethers (PBDEs); validation of three 2003 samples for OC pesticides and PCBs; a comparison of this data to data from a second laboratory, AXYS Analytical; and analysis of a standard reference material (NIST 1941a). The detection limit study was performed by EBMUD, and results are being compiled, although modifications to the EBMUD method have been made in the interim (~10-fold decrease in the final extract volume for a given mass of sediment sample). Because of the ongoing method development, EBMUD is using the software calculated signal to noise ratio for each sample to report the LOD and LOQ in lieu of the traditional MDL. EBMUD aims to generate more current MDLs through control chart information (for lab calibration standards) over the longer term to verify that the software calculated MDLs are appropriate and seen in control samples. The remainder of this report discusses the demonstration package by chemical.

Polychlorinated Biphenyls

Three 2003 samples were analyzed for PCBs: BC11S, SB013S, and LSB013S. The initial results submitted in January had several deficiencies including relatively high detection limits, poor recovery of the labeled surrogate recoveries, and poor agreement with the AXYS data. Because congeners elute slightly differently on different columns, EBMUD switched from a DB-5 column to an Octyl Supelco column to be consistent with

the method that AXYS is using (USEPA Method 1668A). In April, EBMUD resubmitted the PCB data. This data is located on the SFEI shared drive at S:Research\RMP\2003\Source\2003-08_Sediment\EBMUD_2003-08s_SedimentOrgsHRGCMStest. A brief discussion of the data is presented.

Sensitivity

Software generated sample specific MDLs ranged from 0.08 to 1.2 ng/kg and are within a range that is acceptable for the expected concentrations observed in the Estuary.

Blank Contamination

EBMUD and SFEI agreed to an acceptance criteria of less than 5 ng/kg. A review of the data indicates that all but one of the 40 congeners were below this criteria. In the method blank, congener 110 contained 6.54 ng/kg. Because this occurred in only one congener and the exceedance was very close to the criteria, this issue is not deemed significant to result in rejection of the data package.

Accuracy

EBMUD and SFEI agreed to recoveries of matrix spikes of +/- 30 percent for 95 percent of the analytes. Recoveries of the matrix spikes ranged from 83.9 percent to 121 percent and were within the accepted range.

Precision

Relative standard deviation (RSD) among replicate measurements was generally good and well within the target of less than 35 percent RSD, except for third analysis of sample LSB013S. The RSD were significantly greater than 35 percent in the third analysis; however, it was noted that the recoveries of the laboratory surrogates were poor in this sample (i.e., <30 percent), which suggests that there were quality control issues with this analysis. If this sample analysis was eliminated from the calculation, then the RSDs were acceptable.

Agreement with NIST data

EBMUD analyzed one reference sample, NIST 1941b. EBMUD and SFEI agreed to an acceptance criteria of +/- 35 percent of the certified value for 70 percent of the analytes, +/- 50 percent of the certified value for 90 percent of the analytes and the remainder within +/- 70 percent. Six of the 40 congeners had values exceeding the +/- 35 percent value of the standard, indicating that 80 percent of the analytes were within the acceptable range.

Agreement with AXYS data

The three RMP samples were split and sent to AXYS Analytical Laboratory for analyses. EBMUD and SFEI agreed to an acceptance criteria similar to the standard reference material as described above. For the first sample (L116625-4) the EBMUD data agrees very well with AXYS data (i.e. 11.1 ug/kg vs. 12.1 ug/kg). Approximately 80 percent of the congeners have RPDs less than 35 percent. Agreement between the AXYS and EBMUD results for remaining two samples (L11625-5 and L11625-6) was not as good.

Results for L11625-5 were 10.1 ug/kg (EBMUD) and 6.5 ug/kg (AXYS) and for L11625-6 were 12.3 ug/kg (EBMUD) and 7.5 ug/kg (AXYS). The RPDs for these samples were in many cases above 35 percent. Because the internal QA/QC data for the EBMUD samples are good and because it is not known what the “true” value of the samples are, it was decided that the EBMUD results were acceptable.

Consistency with Historical Data and Observed Weathering Patterns

The three data sets were then reviewed to determine whether the congener patterns were typical of those historically observed in the Estuary. The relative percents (i.e. congener divided by the sum of congeners) were typical of those observed in previous years.

Pesticides

The samples analyzed for PCBs were also analyzed for pesticides as well. However, because of poor agreement on a set of replicates within that group, we suggested that rather than reanalyze all the samples in triplicate, steps be taken to reduce possible sources of variability to only those that are introduced by the laboratory analysis. One 2003 sample was analyzed for pesticides in a resubmitted data set (see data spreadsheet for complete list of compounds). That data was generated by extracting a single large sediment sample, then splitting the raw extract 6 ways to be cleaned up and analyzed separately. In addition to the field sample data, two standard reference materials were also analyzed (NIST 1941b) and a commercially available standard, ERA 720. The initial submittal was made on April 13th, 2005. Nine pesticides are included in the standard reference material (NIST 1941a), cis-chlordane, trans-chlordane, 4,4'-DDD, 2,4'-DDE, 4,4-DDT, hexachlordane, cis-nonachlor and trans-nonachlor. Five of the nine pesticides had surrogate recoveries that were unacceptably low (i.e., the recoveries were less than 50 percent of the reference value and frequently 30 percent of the reference value). Based on a review of the results reported for the NIST sample, it was agreed that the pesticide analyses need further refinement. The pesticide data was resubmitted on May 12, 2005. At that time, EBMUD evaluated whether using copper in the cleanup resulted in a cleaner sample with better quantitation. It did not as recoveries for some analytes were negatively impacted by the copper treatment, so EBMUD will perform future analyses for pesticides without copper.

Sensitivity

Pesticide MDLs (in the latter submission) ranged from 0.09 to 15.3 ng/kg and are within a range that is acceptable for the expected concentrations observed in the Estuary.

Blank Contamination

EBMUD and SFEI agreed to an acceptance criteria of less than the limit of quantitation for pesticides. A number of pesticides were found at concentrations above the MDL, but below concentrations found in the field samples (below 1/3 of the FS result).

Accuracy

EBMUD and SFEI agreed to recoveries of matrix spikes of +/- 30 percent for 95 percent of the analytes. Recoveries for matrix spikes were within a range of 80.1 to 129 for all but two analytes. Mirex had a recovery of 157 percent and delta BHC had a low recovery

of 57 percent. Low recoveries for two of the 42 analytes is acceptable (e.g., 95 percent are +/- 30 percent).

Precision

Relative standard deviation (RSD) among replicate measurements was generally good for samples after the corrective actions to reduce sample variability were introduced (i.e. replicates for the large composite sediment sample); performance was almost within the target of <35 percent RSD for 90 percent of the analytes in samples. Eighty-eight percent of the results reported had an RSD <35 percent. Five of the 42 pesticides had RSDs that were greater than 35 percent, delta and gamma BHC, gamma chlordane, heptachlor and hexachlorbenzene.

Agreement with NIST data

EBMUD analyzed two reference samples, NIST 1941b and a commercially available reference standard ERA 720. EBMUD and SFEI agreed to an acceptance criteria of +/- 35 percent of the certified value for 70 percent of the analytes, +/- 50 percent of the certified value for 90 percent of the analytes and the remainder within +/- 70 percent. Based on a review of the data, only 40 percent of the data was within 35 percent of the certified value and 60 percent of the data was +/- 50 percent of the certified value. However, the agreement with the ERA 720 certified reference material was very good with the results being between 84 percent and 119 percent of the certified value. Although the performance on NIST reference materials is somewhat out of the target range, EBMUD will be participating in the next round of NIST's interlab comparison exercise, and results more specifically compared to other laboratories using HRMS methods as well to minimize variability from labs using multiple methods.

Agreement with AXYS data

In the initial data submittal (March 2005), EBMUD included results from split samples sent to Axys. EBMUD's results for pesticides ranged from ~60-200% of the Axys result, with a 15 of 22 analytes falling within 80-120% of the Axys result. Given the variability seen among aliquots for a single sample, this was considered adequate correspondence to the Axys results.

Consistency with Historical Data and Observed Weathering Patterns

The data set were then reviewed to determine whether the concentrations and patterns were typical of those historically observed in the Estuary. The data were found to be consistent with previous results.