

MEMORANDUM

September 25, 2008

To: Technical Review Committee

From: Katie Harrold, Meg Sedlak, and Jay Davis

Re: Results of Organics Reanalysis of 2005 Bivalve Samples and Rationale for Laboratory Change

This memorandum presents the results of the original organics analysis of 2005 bivalves by California Department of Fish and Game (CDFG), the results of reanalysis of archived 2005 bivalve samples by AXYS Analytical (AXYS), and the rationale for switching laboratories for future bivalve analyses.

Bivalve samples were collected annually through 2006 and have been collected biennially since 2006. Tissues are analyzed annually for organics (PCBs, organochlorine pesticides, PBDEs, and PAHs) and approximately every five years for inorganics (most recent analysis will be 2008). Since 2002, CDFG has conducted these organics analyses. However, due in part to decreasing concentrations of these organic contaminants, it has not been possible to quantify all analytes. In 2004, 10 of 12 PBDEs, 21 of 48 PCBs, and 26 of 29 organochlorine (OC) pesticides were below detection limits. Similarly, in 2005, 9 of 12 PBDEs, 18 of 40 PCBs, 23 of 29 OC pesticides were below detection limits. Therefore, in 2007, archived 2005 samples from seven sites were reanalyzed by AXYS to determine if lower detection limits, quantification of more analytes, and consistency with past data could be achieved. (Samples from the following seven sites were reanalyzed: Coyote Creek (BA10); Redwood Creek (BA40); Yerba Buena Island (BC10); San Pablo Bay (BD20); Pinole Point (BD30); San Joaquin River (BG30); and Bodega Head (T-0).) Additionally, in 2008, 3 archived 2005 samples (Redwood Creek (BA40); San Pablo Bay (BD20); and Pinole Point (BD30)) were reanalyzed by AXYS for PAHs using a different extraction method.

In general, the AXYS results are superior to CDFG results. AXYS was able to quantify most analytes and results are consistent with past data.

PCBs

The AXYS PCB ratios are consistent with past data, even at low concentrations suggesting that the method works well at low concentrations. AXYS was able to quantify all of the PCB congeners analyzed and the data are generally acceptable. The results of some PCBs were censored because of detection in blanks, but most were only censored at one site; PCB 008, 018, and 031 were each flagged and censored at three or four sites. However, there were no detection issues for the PCBs of interest.

CDFG had detection problems and was unable to quantify many of the congeners. Of the 47 congeners analyzed, 23 were not detected at any site and 13 were not detected at more than half of the sites. Additionally, of the top ten highest PCB congeners analyzed (180, 183, 187, 189, 194, 195, 200, 201, 203, and 206) only three (180, 183, and 187) were detected at more than half of the sites,

the other seven congeners were not detected at any site. The results of two PCB congeners were flagged and censored due to detection in blanks.

Pesticides

The AXYS pesticide results are also improved over CDFG results. CDFG was able to quantify dieldrin and two of the DDT isomers, but not the other pesticides. Aldrin, alpha-chlordane, and trans-nonachlor were detected, but not quantified, at some sites. AXYS quantified chlordanes in all samples; CDFG had detection limit problems with chlordanes and was only able to detect chlordanes at four of 13 sites and was not able to quantify these results. AXYS quantified all DDT isomers, in contrast to CDFG, which was unable to quantify p,p'-DDD and p,p'-DDE; this resulted in higher sums of DDT. AXYS's dieldrin results also looked good. AXYS did not detect heptachlor or delta-HCH at any sites and quantified hexachlorobenzene at 3 sites and mirex at 4 sites.

PBDEs

PBDEs results from AXYS were improved, more congeners were quantified and there was more consistency in the results from AXYS than from CDFG. AXYS is able to analyze for BDE-209, which CDFG currently cannot. AXYS quantified 39 of 49 congeners. AXYS was able to quantify all six of the congeners most often detected in biota (BDE-47, -99, -100, -153, -154, and -209). AXYS results were censored in a few cases: BDE-209 results were censored at one site based on professional judgment and BDE-183 results were censored at three sites due to blank contamination.

CDFG was able to quantify 10 and 9 of 12 PBDE congeners in 2004 and 2005, respectively. Of the six congeners detected most often in biota, CDFG was able to quantify results of one congener (BDE-47) at more than half the sites and detected BDE-99 and -100 at more than half of the sites, but was not able to quantify all the results. CDFG did not detect BDE-153 and -154 and BDE-209 was not included in the analyses.⁸

PAHs

AXYS analyzed the bivalve tissue using two different methods, by soxhlet extraction and base digestion followed by soxhlet extraction. The second method, base digestion, was conducted with samples from three sites to see if better results, especially for naphthalene, could be achieved. The base digestion PAH data from AXYS is consistent with past data. And, as CDFG was unable to quantify PAHs, the results are a significant improvement.

Average concentrations ranged 1-50 $\mu\text{g kg}^{-1}$ for individual PAHs, much higher than previous CDFG results (where half the compounds were near 100% non-detects), and more in line with previous Texas A&M Geochemical and Environmental Research Group (GERG) results (2000 – 2002), which generally averaged greater than 5 $\mu\text{g kg}^{-1}$ for individual PAHs. Only 1-methylnaphthalene was greater than 50% non-detect, and it also had elevated concentrations in the blank; perhaps in part due to low surrogate recovery (leading to overcorrection).

Summary

Based on these improved analytical results, we propose switching to AXYS for organics analysis of the as of yet unanalyzed 2006 bivalve samples and future bivalve samples. Additionally, we propose having AXYS reanalyze the archived 2004 bivalve samples. Due to analytical difficulties, the 2004 CDFG results have not been reported.