

REVISED MODIFICATIONS TO HOLDING TIMES FOR PSDDA CHEMICAL ANALYSES

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The Management Plan Assessment Report for Dredged Material Management Year 1990 contained a clarification paper which recommended holding times for PSDDA chemical analyses for unfrozen (4 degrees C) sediment (see page A-5). Several laboratories provided feedback relative to some of these holding times. Letters received from laboratories are included as enclosures to these minutes. Comments were directed at holding times for: 1) semivolatiles, pesticides and PCBs; 2) total solids, total volatile solids and total organic carbon; and 3) mercury. In addition, the holding time for ammonia was raised as an issue, although no modification to the current holding time was recommended. As a result of this feedback, additional protocol documentation review, and coordination with the Department of Ecology's Manchester Lab, National Marine Fisheries Service's (NMFS) Northwest Fisheries Science Center, Skidaway Institute of Oceanography (SIO-Savannah Georgia), and EPA's Region 10 QA Branch were undertaken.

As a result of the comments received, the guidance available in protocol documentation and the additional coordination, the following holding times are recommended (see Table 1 for multi-source documented and recommended holding times and Table 2 for recommended PSDDA holding times):

Semivolatiles, Pesticides and PCBs: PSEP contains one reference to "fresh" sediments on page 18 of the December 1989 revision of "Recommended Guidelines for Measuring Organic Compounds" and specifies that 7 days is the appropriate holding time. Revision 2 (November 1990) of Table 2-29 in EPA SW846, however, which is more recent guidance than that provided in PSEP, recommends a holding time of 14 days for sediments at 4 degrees C. A 14 day holding time for semivolatiles, pesticides and PCBs would be consistent with the holding time currently used by PSDDA for volatile analytes. PSDDA will adopt this 14 day holding time.

Total Solids, Total Volatile Solids, Total Organic Carbon: The regulatory guidance cited for total solids (TS) and total volatile solids (TVS) is generally 7 days for both preserved aqueous and sediment samples. For total organic carbon (TOC), recommended holding times ranged from 1 to 28 days for aqueous samples. It was the general consensus among those experts contacted that, for these parameters, the holding time for aqueous samples is more critical than for sediments. The gravimetric fraction of these parameters is greater in sediment samples than in aqueous samples and this fraction in sediments is not as susceptible to change with holding time as it is in an aqueous sample. In this light, and to alleviate the burden the testing laboratories face with short holding times, it is recommended that the holding time for TS, TVS and TOC be set at 14 days for unfrozen samples.

Mercury: All of the regulatory guidelines for preserved aqueous samples list the holding time for mercury as 28 days. SW846 method 7470 (manual cold vapor-liquid wastes) states that non-aqueous samples should be analyzed as soon as possible. One protocol, Plumb 1981, recommends a 7-day holding time for mercury analysis on sediment samples held at 4 degrees C.

Subsequent coordination with trace metals experts Drs. Robert Clark (NMFS) and Herb Windom (SIO), revealed enough uncertainty relative to the stability of mercury samples to warrant care in adopting any holding time for unfrozen sediment. Mercury methylation by microbes can dramatically alter the quantitation of this chemical, and the rate of methylation varies with sediment type, organic loading and microbial community. These biological effects take place even at 4 degrees C. Freezing of sediments for mercury analysis was highly recommended as standard operating procedure.

Because of the uncertainty involved with mercury analysis, and until more definitive scientific evidence is gathered relative to holding times for unfrozen sediment, it is recommended that the current PSDDA guidelines be maintained: sediment samples for mercury analysis must be frozen and held for no more than 28 days.

Ammonia: It was suggested by AmTest that the holding time for ammonia was not as critical as the holding condition (i.e. in a moist state). This may be true and special care should be taken to ensure that sediment samples for ammonia analysis are prevented from losing moisture. A 7 day holding time for ammonia for unfrozen sediments is clearly stated in PSEP, however, and is recommended by Plumb as well. The ammonia protocol of Plumb is the accepted protocol for PSDDA analyses. Additional coordination with the Department of Ecology's Manchester Laboratory indicated that 7 days should be considered a maximum. It is recommended, therefore, that the current PSDDA holding time of 7 days be retained.

NOTE: The PSDDA agencies have attempted to establish rational holding times for sediments at 4 degrees C in response to the common laboratory practice of using unfrozen samples and the general unavailability of freezer capacity. It is still highly recommended that the PSEP protocols for sample storage be followed when possible, which means freezing of sediments at -18 degrees C for those analytes for which freezing is indicated. As stated previously, mercury samples must always be frozen.