

UCSC Special Studies
on
Methylmercury and Reactive Mercury
in
San Francisco Bay Estuarine Sediments

Introduction

Studies on San Francisco Bay sediments and those of its drainage basins will be conducted to (1) determine the potential effects on sample handling on subsequent measurements of methylmercury (MeHg) concentrations; (2) determine the effect of different pretreatment techniques on those MeHg concentrations; and (3) characterize the reactive mercury concentrations of those sediments. Sampling is reported to be the most important factor influencing the accuracy and uncertainty of MeHg in coastal marine sediments (Horvat et al., 2004). The transformation and degradation of MeHg can also occur during sample storage and pretreatment, so that the MeHg present in the analyzed sample may differ markedly from the original sample, as demonstrated in a recent comparison of different extractions on MeHg concentrations in sediments (Liang et al., 2004). The accurate characterization of the concentration of reactive mercury is now considered the most important need for environmental regulation and remediation in the estuarine system, based on discussion at the recent Fourth Annual SF Bay Mercury Coordination Meeting (February 22, 2007). Therefore, the following special studies are proposed, with the relative amount of effort for each study shown in parentheses.

Special Studies

1. Effects of handling on MeHg measurements in sediments (40%).

The San Francisco Bay Regional Monitoring Program (RMP) sampling protocol (David et al., 2001) may affect the MeHg concentrations in sediment samples, so that the analysed sample concentrations may be significantly different than the sample site. The RMP collects sediment samples with a Van Veen grab sampler, which is designed to collect large samples in soft sediment with a penetration depth up to 25 cm. The top 5 cm of two separate grabs are scooped and homogenized with aliquots distributed into sample containers for different analyses. The MeHg sample homogenates are placed in polyethylene (PE) jars and frozen on dry ice. Prior to 2005, sample processing and collection previously could take up to 45 minutes, but procedures instituted in 2005 require freezing of MeHg samples within 20 minutes of collecting the first grab.

The MeHg concentration of a sediment sample may be changing at each step during the sample collection and processing. Light exposure while scooping sample from the grabs, and disturbance while mixing samples under ambient temperature and atmosphere may alter the redox conditions. Redox changes may slow once the sample is placed on dry ice, but they may not halt until the samples are thoroughly frozen. In addition, by homogenizing a 5cm sediment layer from two grabs, the maximum MeHg exposure to

biota in narrow sediment zones may be underestimated. It is important to understand various possible artifacts and biases of the sampling and handling procedures utilized.

Therefore, the effects of sampling on MeHg concentration in sediments will be assessed by comparing aspects of sampling and storage methods, including scooping vs. coring, immediate freezing vs. cold until freezing later, and compositing vs. discrete layer sampling. A Van Veen grab will be used to collect benthic sediments from sites in San Francisco Bay to obtain a range of representative estuarine sediment types. Sediment MeHg analyses will be performed using KBr/H₂SO₄/CuSO₄ digestion, CH₂Cl₂ back-extraction followed by aqueous phase ethylation, volatile organic trapping, and detection by CVAFS (Horvat et al., 1993).

2. Effects of extraction techniques on MeHg measurements in sediments (10%)

As previously indicated, different extraction techniques were found to yield different amounts of MeHg measured in sediments (Liang et al., 2004). Since the sediments were from other systems, and possibly quite different than the sediments in the San Francisco Bay estuarine system, a similar comparison of those different techniques will be conducted using sediments from the estuary. The methodologies will be comparable to those delineated in that report, which are also comparable to those used by different groups measuring MeHg in San Francisco Bay sediments.

3. Reactive mercury in sediments (50%).

We will develop a method for determining the chemical availability of mercury in sediment from the estuary and its tributaries. As previously noted, the need to determine the relatively bioavailable mercury in sediments with differing total mercury concentrations was recently emphasized at the Fourth Annual San Francisco Bay Mercury Coordination Conference. To address this, we have evaluated the use of a sequential extraction method (Bloom et al., 2003) in resolving the relative chemical availability of mercury in the sediments of the system. Our preliminary results suggest that this method may be useful (Kerin et al., 2004), and the preliminary results of others suggests that the method may provide information similar to 'reactive' mercury in sediment (Bloom et al., 2006). However, due to concerns on the applicability of this method to estuarine sediments (Mikac et al., 2003), the method must be further developed and tested in its application. We will develop and apply this extraction method to investigate the relative chemical availability of mercury from various parts of the estuary and tributaries. Sediments from the Guadalupe River watershed will receive priority, and an attempt will be made to characterize ancillary sediment lithology. The expected results of this study will be the development of a chemical extraction method to evaluate important fractions of mercury that can be potentially transported to the estuary.

References

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