Appendix A: The memoranda prepared by ENTRIX and presented in this appendix are working review drafts which were not edited or finalized by the Trustees.

Appendix A-1:

- **A-1a**, "Regional background chemical concentrations for Castro Cove"
- **A-1b** "Estimation of historical sediment chemical concentrations in Castro Cove"

Original Author(s): ENTRIX

Distributed to the injury subcommittee in the cooperative NRDA process.

Trustee Comments: These memoranda address mercury data. Total polycyclic aromatic hydrocarbon (TPAH) concentrations used in the injury quantification were estimated from available data after these documents were written and therefore are not contained in these memoranda. The geometric mean of the TPAH concentration that was calculated in March 2006, based on data from the San Francisco Estuary Institute's samples from San Pablo Bay, was 722 µg/kg (see graph in appendix A-2c). The Castro Cove Injury Quantification is presented in Chapter 3.

E N T R I X

MEMORANDUM

WORKING REVIEW DRAFT

ENTRIX, Inc.
2701 1st Avenue
Seattle, WA 98121
206/269-0104

Date: February 23, 2006

Re: Regional background chemical concentrations for Castro Cove

Project No. **3054545**

PURPOSE

Calculation of ecological service loss in Castro Cove due to exposure to the chemicals of concern (COCs) requires estimation of the conditions (e.g., biota and ecological services from those biota) that would have been present *but for* the concentrations of those COCs attributable to Chevron's activities. This memorandum describes the method for estimating the background concentrations of those COCs by estimating a regional background level of mercury in sediment. It will be part of the text associated with Section 3.2 of the DARP outline, "Data Sources."

INTRODUCTION

It has been determined that concentrations of mercury in sediment can be used to adequately model potential injury and service loss to the benthic community of Castro Cove[1]. It is, therefore, the only COC considered below.

A data set of regional sediment samples for the COCs in Castro Cove was assembled from the San Francisco Estuary Institute (SFEI) data base. The SFEI is responsible for implementation of the Regional Monitoring Program (RMP) for Trace Substances, established by the San Francisco Regional Water Control Board (Board) in 1992. The

[1] See memorandum "Estimation of historical sediment chemical concentrations in Castro Cove."

RMP regularly monitors contaminant concentrations in water, sediment, fish and shellfish in San Francisco Bay. This monitoring program allows the Board to evaluate the effectiveness of its water quality programs in meeting its overarching goal of protecting the beneficial uses of the San Francisco Bay[2].

The concentrations of mercury in this samples are considered to to represent the typical, or *but for*, background conditions for this region of the Bay.

RESULTS

Sediment samples were selected from the SFEI reference data set for 18 locations in San Pablo Bay nearest to Castro Cove (Figure 1). The sediment samples were collected from 0-5 cm below surface, with the objective of monitoring current conditions. For 12 of these sampling locations, a single observation was available, while at the remaining six sampling locations, as many as 18 samples had been collected over time. .To eliminate any bias towards some sampling locations presented by this imbalance, the mercury sample values were averaged for each of these six sampling locations.

The 18 stations were not spatially weighted in any way-- *e.g.*, we did not use Voronoi tessellation[3] -- because the sampling locations are:

- generally dispersed throughout a large area of San Pablo Bay, and
- biased neither towards or away from any apparent or known gradients of mercury in San Pablo Bay (*i.e.*, a higher density of sampling preferentially located near a known or suspected source of mercury).

These resulting 18 values were then averaged, producing an estimate of **0.28** mg/kg for the regional mean mercury sediment concentration[4].

CONCLUSION

This estimate of the typical concentration of mercury (0.28 mg/kg) in sediments of the region is taken to represent *regional background*. This mean estimate will be used in estimating potential benthic injuries (and potential the benthic service losses) in Castro Cove from exposure to COC concentrations above regional background. It will also be used to define the spatial extent of Chevron's contribution to sediment mercury concentrations as one moves toward the mouth of Castro Cove.

[2] See memorandum "Sediment concentrations of mercury in regional (SFEI) and Castro Cove (Tier I) data – A basis for establishing reference or background conditions" for additional information about this database.
[3] These tessellations form what are also known as Thiessen polygons or Dirichlet cells.
[4] The standard deviation equals 0.06 mg/kg.

Slipsheet for figure 1

E N T R I X

MEMORANDUM

WORKING REVIEW DRAFT

ENTRIX, Inc.
2701 1st Avenue
Seattle, WA 98121
206/269-0104

Date: February 23, 2006

Re: Estimation of historical sediment chemical concentrations in Castro Cove

Project No. **3054545**

PURPOSE

This memorandum addresses the development of representative chemical concentrations in Castro Cove for use in the calculation of estimated service loss for the period of interest, using available data.

APPROACH

We address this question by the comparison of chemical concentrations in samples collected from surface sediment to samples collected from sediment cores. The steps in that comparison are a description of relevant data; an examination of accretion studies in Castro Cove; the selection of representative chemicals; and an analysis of the concentration gradients with sediment depth.

BACKGROUND

An important component of the calculation of discounted service-acre-years (DSAYs) in Castro Cove is the estimation of representative concentrations of certain chemicals in the Cove throughout the period of interest (1981 through 2006). Most of the available data for chemical concentrations – both in Castro Cove and the region – are from surficial sediment samples (upper 5 cm or 2 inches, depending upon the survey) collected within

the past ten years. Investigations suggest that sediments from San Pablo Bay at large are being borne into and deposited in Castro Cove. These newer surface sediments are burying older sediments, with deposition at a rate suggesting that surficial sediments from the 1980's are now sequestered.

SEDIMENT DATA INVENTORY

Samples were collected from 13 locations throughout Castro Cove in the Tier I investigation (Dames & Moore 1999) (Figure 1). In the northern portion of the Cove, the chemical concentrations in Tier I samples were low, and indistinguishable from regional background[5][6]. In the southern portion of the Cove, chemical concentrations were higher. Based on those results, additional samples were collected in the southern portion of the Cove in the Tier II investigation (URS June 2002).

In the Tier II study, samples were collected from 43 locations (including 2 reference locations). In all of these locations, samples were collected from 0 to 2 inches below the sediment's surface. In 24 of those 43 locations, co-located core samples were collected from 0 to 1 foot and 1 to 2 feet below the sediment's surface (Figure 1).

In a separate ecological risk assessment of the area of Castro Cove surrounding Skeet Hill, sediment samples were collected at 15 locations at 0 to 6 inches and 6 to 12 inches depth below surface. These samples were only analyzed for lead concentration and number of lead shot present (URS March 2002).

SEDIMENT ACCUMULATION RATE STUDY

As part of the Tier II investigation, sediment accumulation rates were estimated, to determine the rate at which sediment deposited in various areas of Castro Cove was burying contaminated sediments (URS 2002; Dr. Ian Austin, pers. comm.).

Four cores were collected, one each from the middle of the Area of Concern (AOC), the northern edge of the AOC, the weir at the end of the 250-foot channel, and just offshore of the Rod and Gun Club Lagoon. Based on measurements of isotope decay for Pb-210 and Cs-137, it was estimated that accumulation rates varied from 4.3 inches/year at the weir to 0.2 inches/year at the northern edge of the AOC. Accumulation rates in the middle of the AOC and offshore of the Rod and Gun Club Lagoon were approximately 0.5 inches/year. These estimates do not take into account the effects of bioturbation, chemical diffusion, and the apparent non-steady state sediment deposition at some of the core sites, all of which contribute uncertainty to both the accuracy and precision of the estimated accumulation rates.

RELATIONSHIPS BETWEEN CHEMICALS IN SEDIMENT

In URS's Tier II report, sample concentrations of arsenic, mercury, and PAHs were compared to ERL and ERM criteria. For all samples except one, where any chemical

[5] Also see memorandum "Spatial extent of service losses in Castro Cove attributable to Chevron"
[6] These samples were excluded from the remainder of the analyses in this memorandum.

other than mercury exceeded its ERL, so did mercury. In the one exception, the surface sample at DM-36, arsenic was reported at 8.5 mg/kg, compared to its ERL of 8.2 mg/kg (Figure 1). In the same sample, mercury was 0.11 mg/kg, compared to its ERL of 0.15 mg/kg. Using EPA/NOAA's logistic regression model (LRM) approach (EPA 2005), P values for mercury are almost always higher than P_Max[7] for mercury plus PAHs.

The URS ecological risk assessment at Skeet Hill addressed lead contamination, with the primary concern impacts on feeding birds. The ecological risk assessment concluded that the concentrations of lead (in shot or adsorbed to sediment particles) in the sediments of Castro Cove are unlikely to result in substantial riskto either the benthic community or to higher level organisms via bioaccumulation (URS March 2002).

Lead concentrations (after lead shot were sieved out) collected from 0 to 6 inches in Skeet Hill sediments ranged from 16 to 42 mg/kg, with a mean of 31 mg/kg. Lead concentrations in sediment samples collected from 6 to 12 inches ranged from 8.1 to 51 mg/kg, with a mean of 34 mg/kg. These concentrations never exceeded the ERM (218 mg/kg), and exceeded the ERL (46.7 mg/kg) in only one sample[8] (URS March 2002).

The NOAA/EPA P value from the average mercury concentration in Tier I and II samples[9] collected in surface sediments near Skeet Hill was higher (46%) than for the average lead concentrations from the 0-6 inches Skeet Hill samples (21%) (Table 1). As with arsenic and PAHs, the probability of significant toxicity for observed lead concentrations is less than for mercury. Based on the LRM evaluation, lead is unlikely to contribute any additional risk (which is used here as a conservative surrogate measure of service loss) to the Castro Cove benthic community beyond that present from the baseline or reference values.

These results, taken together, demonstrate that mercury alone is sufficient to represent the area where sediment concentrations of contaminants might result in a loss of benthic services I beyond baseline levels in Castro Cove.

CHANGES IN MERCURY CONCENTRATIONS IN SEDIMENT WITH CHANGING DEPTH

Mercury concentrations in 0-1 foot core samples are, on average, higher than in surface (0-2 inches) sediment samples (URS June 2002). However, this average value obscures the fact that mercury concentrations in 0-1 foot samples and in co-located surface (upper 2 inches) samples are typically comparable throughout most of Castro Cove (Figure 2).

Three sample locations (DM-18, 23, and 43) have mercury concentrations in 0-1 foot samples that are substantially higher than in co-located surface samples. If these three samples are removed from the data set, the Pearson correlation coefficient between log-transformed surface and 0-1 foot sample concentrations increases from 0.51 to 0.73 and their linear regression is not significantly different ($p = 0.05$) from a 1:1 relationship (Figure 3), which indicates these three samples are statistical outliers (Figure 1)[10].

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[7] In four surface sediment and two subsurface samples, P_Max was 4-5% higher than P for mercury. In one subsurface sample (DC/DM-36), the difference was greater (9%), but those P values were low: 9% *vs.* 18%.

[8] SH-2 at 51 mg/kg

[9] DM-8, 13, 28, and 29.

In addition, mercury concentrations in 1-2 feet sediment samples were almost always lower than in co-located surface samples and co-located 0-1 foot samples (24 of 27 of locations sampled).

CONCLUSION

These analyses support the conclusion that for the majority of the Cove, mercury concentrations do not increase substantially at greater depths, and that in a relatively small portion of Castro Cove, accretion may have buried older sediments, which contained higher mercury concentrations. This result supports the use of the larger data set of surface sediment results for the estimation of service loss in Castro Cove. Doing so removes the substantial uncertainties associated with attempting to estimate mercury concentrations in older, deeper sediments, using newer, surface sediment samples where deeper samples were not collected. It also allows a direct comparison of sediment chemical concentrations in samples from Castro Cove to concentrations in reference samples throughout San Pablo Bay.

For those three sampling locations noted above (DM-18, 23, and 43) where sediment mercury concentrations are clearly higher in deeper sediments, an alternative approach could be implemented. The 0-1 foot cores are a physical average of sediments representing the chemical concentrations at 6 inches depth; similarly, the 0-2 inches surface samples represent the 1 inch depth. Using an accretion rate of 0.2 inches/year,[11] we can estimate the year of deposition for a given sediment depth. For example, sediments at 3 inches depth correspond to 1985 (based on samples collected in 2000). Mercury concentrations for each depth (or year) of interest could be estimated by linear interpolation (or extrapolation) of concentrations between the sampled depths of 1 and 6 inches in a given location. This method could be used to estimate the potential additional service loss that might be associated with higher mercury concentrations found in deeper (older) sediments at these four locations.

REFERENCES

Dames & Moore. May 1999. Draft sediment characterization and Tier I ecological risk assessment for Castro Cove.

EPA. 2005. Predicting toxicity to amphipods from sediment chemistry. National Center for Environmental Assessment, Washington, DC; EPA/600/R-04/030

URS. March 2002. Additional sediment characterization and risk evaluation: Skeet Hill

URS. June 2002. Tier II sediment characterization and ecological risk assessment: Castro Cove

		N	Average	Maximum
Skeet Hill[1]	Lead (mg/kg)	14	31	42
	P value from LRM		0.21	0.28
Castro Cove[2]	Mercury (mg/kg)	4	0.41	
	P value from LRM		0.46	

Notes:
[2] Sediment samples from 0-6 inches, collected near Skeet Hill in 2001 as part of ecological risk assessment
[2] Sediment samples from 0-2 inches, collected near Skeet Hill in 1999 and 2000 as part of Tier II study

Table 1. Comparison of P values from LRMs for lead and mercury near Skeet Hill.

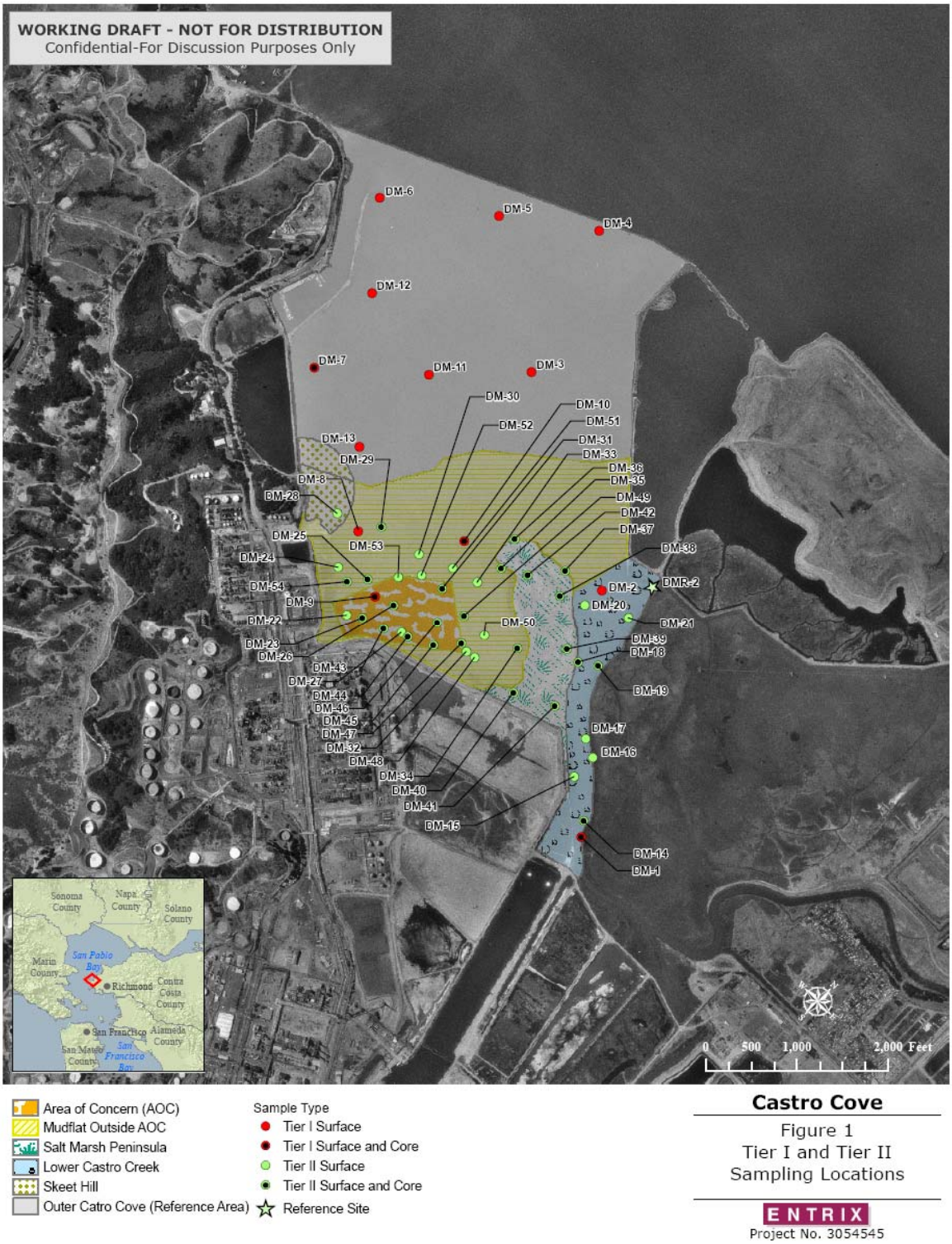

Figure 1. Castro Cove with Area of Concern and Sample Sites.

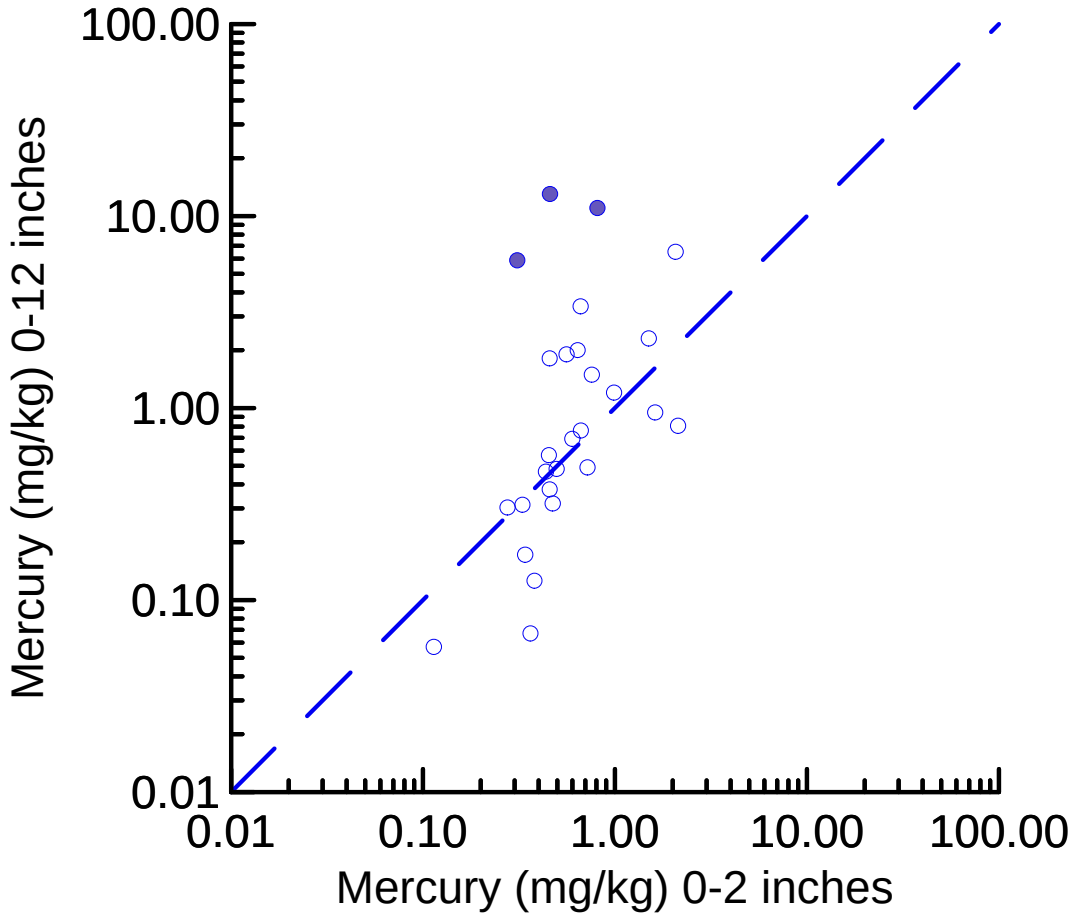

Figure 2. Scatter plot comparing mercury concentrations in samples collected from surface sediments (0 to 2 inches) and co-located sediment cores (0 to 1-foot depth) in Castro Cove. The dashed line represents the 1:1 relationship in concentration. The four symbols filled in black represent sample locations DM-18, 23, and 43, which are noted in the text.

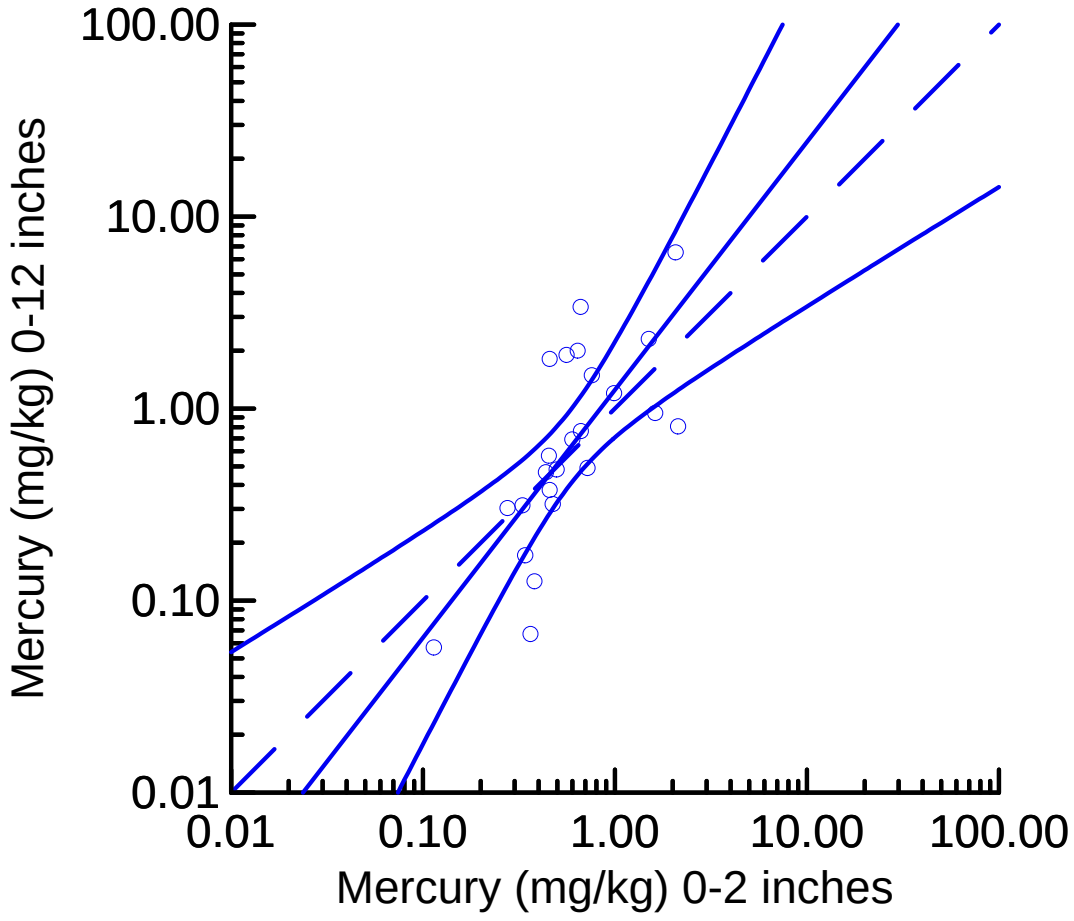

Figure 3. Scatter plot comparing mercury concentrations in selected samples collected from surface sediments (0 to 2 inches) and co-located sediment cores (0 to 1-foot depth) in Castro Cove. The dashed line represents the 1:1 relationship in concentration. The solid straight line represents a linear regression of the log-transformed data; the curved solid lines enclose the 95% confidence limit around the linear regression.