Final Report
Existing Data on PCB Concentrations of Nearshore Sediments and Assessment of Data Quality

Clean Estuary Partnership

Project 4.10a

Submitted to:

Clean Estuary Partnership
PCB Workgroup

Submitted by

Dane Hardin

APPLIED marine SCIENCES

October 28, 2005

Project History

11/2/02 Scope of Work approve by CEP Technical Committee.

1/8/03 Preliminary results were presented to CEP Technical Committee. Concerns were raised regarding method of selecting sites from historic datasets.

3/18/03 Additional guidance received from Water Board staff in a meeting to discuss project status and selection of sites from historic datasets.

8/17/03 Draft Report submitted to PCB Workgroup.

9/19/03 Report revised according to reviewers' comments.

3/19/04 Obtained NOAA-EMAP data collected in 2000-2001.

8/3/04 Submitted second draft report to Workgroup, which was based upon analysis of NOAA-EMAP data.

9/13/04 Sent report to Dr. Robert Smith for review and computation of tolerance intervals.

10/8/04 Report revised based upon Workgroup comments and Dr. Smith's analyses.

3/25/05 Report revised according to comments received at Workgroup meeting on 12/15/04.

6/05 Report sent to external peer reviewers.

8/05 Peer reviewers' comments received

10/3/05 Synopsis of peer reviewers' comments completed and sent to PCB Workgroup

10/05 Water Board staff stated they are not intending to set a PCB sediment target and will use a fish tissue target with linkage from the Food Web Model. PCB workgroup and Technical Committee agree to accept the 3/25/05 version with minor revisions.

10/28/05 Revised Final Report submitted to Technical Committee.

11/2/05 Revised Final Report approved by Technical Committee.

Table of Contents

Introduction

This report constitutes the final deliverable for Project 4.10a. As indicated by the project history presented on the cover page, several other draft reports were submitted to the PCB Workgroup before data from the NOAA and EMAP sampling programs became available. The NOAA-EMAP data required additional work that was justified by the fact that these samples were collected randomly, as compared to other available data that were collected to describe PCB hotspots in San Francisco Bay. Moreover, after this version was submitted to external peer review, staff of the San Francisco Regional Water Quality Control Board (Water Board) decided that they probably would not set a sediment target for PCBs, but rather they would use a fish-tissue target and use the sediment-tissue linkage from the Food Web Model developed by Frank Gobas and Jon Arnot (CEP Task #4.27) to set load allocations where appropriate. Consequently, the PCB Workgroup and the Technical Committee agreed that there was no need to revise the report according to peer reviewers' comments, which are included in Appendix D.

According to the approved Scope of Work for this project, this report was to be submitted to the PCB Workgroup to enable it to make a recommendation to the Technical Committee, based on its review of the report, as to whether samples needed to be collected to achieve the purposes of the project. The need for additional samples and further work on the project became moot with the decision by the Water Board to base PCB load allocations on fish tissue data, rather than on sediment data. The background of the study, the approach taken, and the findings that were submitted to the PCB Workgroup are presented in the following sections.

Background

On June 4, 2002, a draft PCB Workplan was submitted to the CEP Technical Committee (TC) that identified PCB concentrations in nearshore sediments as a significant information gap. Knowledge of upper bound concentrations of PCBs in ambient nearshore sediments would be useful for evaluating remedial options at hot spots (i.e., sites with especially elevated PCB concentrations) and to evaluate the potential for degradation of the Bay from discharges of sediments with elevated PCB concentrations. Specifically, the Water Board desired to focus on sediments offshore of areas that were affected by historically industrial activities, except for those areas considered to be hot spots. Between submittal of the initial draft of the PCB Workplan on June 4, 2002 and November 2002, a series of documents were written and revised according to comments from the PCB Workgroup and the TC, which provided the basis for a Scope of Work for this project that was approved by the TC on November 6, 2002.

The two project objectives stated in the approved Scope of Work are as follows:

1) Determine whether existing data are sufficient to quantify PCB concentrations in the sediment of the nearshore environment of central and south San Francisco Bay.
2) Collect additional monitoring data, if necessary, to quantify PCB concentrations in the nearshore sediments of central and south San Francisco Bay.

Achievement of the first objective involved gathering existing data, reviewing the quality of those data, and making an initial determination of PCB concentrations in the nearshore environment. Because of the several iterations of data analyses and reports on the sufficiency of existing data, as described in the Project History on the cover page, the second objective of this project, if deemed necessary by stakeholders, will be achieved with a subsequent and separate project.

Approach

Data from three sources initially were gathered and evaluated for quality and relevance to the objectives of the study. These sources were NOAA and EMAP samples collected in 2000 and 2001, Bay Protection and Toxic Cleanup Program (BPTCP) screening surveys conducted in San Francisco Bay in 1995 and 1996, and analyses by Dr. Robert Risebrough (Risebrough) of samples collected by the National Oceanic and Atmospheric Administration in 1990.

The goals and objectives of each of these programs were similar. The goal of the EMAP program is to take the pulse of the nation's ecological resources and produce a national environmental report card. This goal is reached through achievement of four operations objectives, as follows:

1. Estimate current status, trends, and changes in selected indicators of the nation's ecological resources on a regional basis with known confidence.
2. Estimate the geographic coverage and extent of the nation's ecological resources with known confidence.
3. Seek associations between selected indicators of natural and anthropogenic stresses and indicators of the condition of ecological resources.
4. Provide annual statistical summaries and periodic assessments of the nation's ecological resources.

The NOAA estuaries program is designed to answer the following questions:

1. Are environmental conditions improving or deteriorating? If so, where and during what time of year?
2. Are the changes related to human activities? Do some activities (e.g., agriculture, industry, sewage treatment) have a greater impact than others?
3. What actions can best correct existing problems or prevent future problems?

One of the goals of the BPTCP is to identify and characterize sediment toxic hot spots. To reach this goal, the program had four major objectives for sampling in San Francisco Bay, as follows:

1. To identify locations in enclosed bays, estuaries, or the ocean that are potential or candidate toxic hot spots,
2. To determine the extent of biological impacts in portions of enclosed bays and estuaries not previously sampled (areas of unknown condition),
3. To confirm the extent of biological impacts in enclosed bays and estuaries that have been previously sampled; and
4. To assess the relationship between toxic pollutants and biological effects.

The goal of the Risebrough program also was to help determine the relationship between toxicity and concentrations of pollutants in sediments. Although all three programs used a grab sampler to collect surficial sediments, the NOAA/EMAP program was the only program based exclusively on random sampling locations.

The quality of these data was evaluated by Jay Davis and Jon Leatherbarrow of the San Francisco Estuary Institute (SFEI) based upon the congeners that were reported in each study and the expected ratios of congeners, as observed in samples from the Regional Monitoring Program for Trace Substances (RMP). Memos from SFEI regarding their evaluation of each set of data are included in Appendix A to this report. Synopses of these evaluations are as follows:

BPTCP
Overall data quality was good. There was one sample that was potentially affected by contamination or coelution and it was collected near Kirker Creek, outside the regions of San Francisco Bay covered by our study.

Risebrough
Overall data quality was good with six samples potentially affected by contamination or coelution. The questionable congener values were not included in subsequent calculations of total PCBs for those samples.

NOAA/EMAP
Overall data quality was good and there were 8 samples with specific PCB congeners potentially influenced by contamination or coelution. NOAA/EMAP reported only 17 of the 40 congeners analyzed by the RMP and SFEI's memo on the evaluation of these data stated, "summation of the 17 EMAP congeners comprises approximately 60 to 90% of ΣPCBs reported by the RMP. Moreover, many of the values for congener 170/190 were qualified with matrix interference.

Random samples are necessary to estimate population parameters from a subsample. Consequently, of the three programs, the NOAA/EMAP samples were best suited to achieve the objectives of this study. The NOAA/EMAP data are included in Appendix C. Before they could be used to estimate nearshore sediment PCB concentrations, it was necessary to explore the relationship between sum of PCB concentrations for the 40 congeners measured by the RMP and the sum of PCB concentrations for the 16 congeners[1] for which consistent data were available in the NOAA/EMAP samples.

SFEI analyzed the relationship between the 40 RMP congeners and the 16 NOAA/EMAP congeners for different scenarios for RMP samples from 1993–2001. These included the following:

- all sediment samples with PCBs >10 μg/kg,
- all sediment samples with PCB concentrations between 10 μg/kg and 130 μg/kg,
- all sediment samples with PCB concentrations between 10 μg/kg and 50 μg/kg,
- all particulate water samples with PCB concentrations >50 pg/kg.

The first scenario was chosen as being most representative of the NOAA/EMAP sediment samples because they included 12 samples in which the sum of 16 congeners exceeded 70 μg/kg. This scenario determined that the 16 NOAA/EMAP congeners accounted for approximately 60%

[1] Excluding data for congener 170/190 for data quality issues discussed previously.

of the PCB mass in the sum of the 40 RMP congeners (see Appendix B; RMP = 1.72 x NOAA/EMAP). Moreover, the 16 congeners explained 99% of the variation in the 40 congeners.

According to the objectives of this project, determination of whether existing data are sufficient to quantify PCB concentrations in the sediment of the nearshore environment of central and south San Francisco Bay was based only on analysis of NOAA/EMAP samples south of Point San Pablo (Figure 1). A total of 167 samples were available from this area and all analyses were based on the estimated concentrations of the 40 RMP congeners.

Following the estimation of RMP congeners from the NOAA/EMAP data, Dr. Robert Smith applied his methods (Smith, 2001) to calculate tolerance intervals for nearshore PCBs. Tolerance intervals are intervals covering population percentiles or proportions with a specified level of confidence. In this case, tolerance intervals were calculated to estimate the upper bounds of the estimated sum of PCB concentrations for the 40 RMP congeners for various percentiles of the nearshore sample population, with a 95% probability. These analyses were intended to provide an estimate of the upper bounds of reference or background PCB concentrations in nearshore sediments. These analyses assume that the data are randomly sampled from a normal distribution.

Findings

An initial plot of PCB concentrations based upon estimates of the 40 RMP congeners in the NOAA/EMAP samples suggested that many sites within 500 meters of shore (mean higher high water = MHHW) had higher concentrations than sites greater than 500 meters from shore (Figure 2). Moreover, an analysis of variance (ANOVA) on log-transformed data (natural log) revealed that nearshore and offshore sites had significantly different PCB concentrations ($p < 0.0001$; Figure 3).

An important concern in determining the background concentrations of PCBs in nearshore sediments is whether samples used in the analysis might have come from hot spots, despite having been collected randomly. In order to avoid arbitrary decisions regarding which sites might represent hot spots, outlier box plots associated with distribution analysis in the JMP statistical software (SAS Institute, 2002) were used to identify nearshore samples that could be outliers. Outliers were defined as those sites whose PCB concentrations were more than 1.5 times above the interquartile range (Figure 4). This was an iterative process that required removal of identified outliers and reanalysis to determine whether additional outliers would be identified among the remaining samples.

Three iterations of outlier identification and removal resulted in a distribution of raw PCB concentrations in which no further outliers were identified (Figure 5). Nevertheless, this distribution was not normal, as confirmed with a Shapiro-Wilk test ($p = 0.0020$). Transformation of the remaining samples to their natural logarithms did produce a normal distribution (Figure 6) with a non-significant Shapiro-Wilk result ($p = 0.7754$).

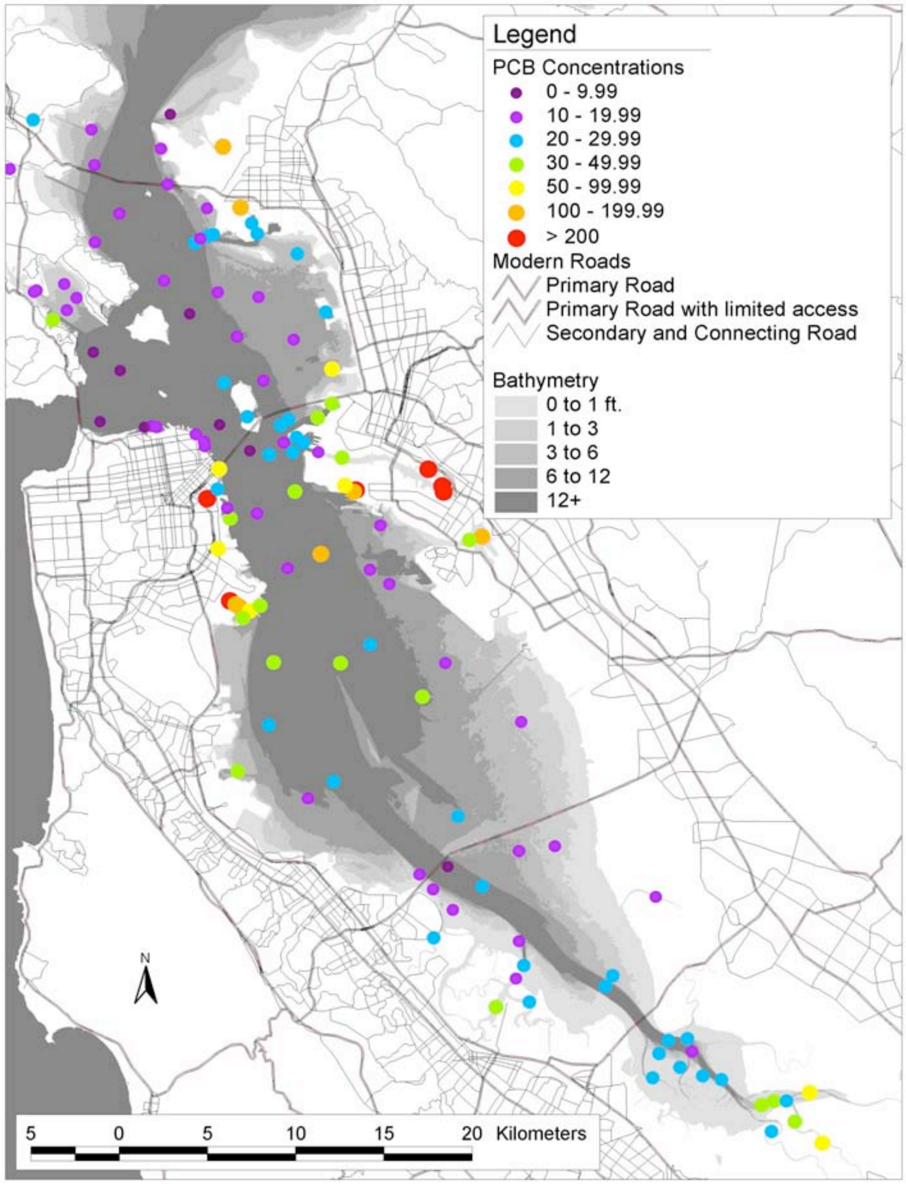

Figure 1. NOAA/EMAP sampling sites displayed according to the estimated sum of PCBs for 40 RMP congeners.

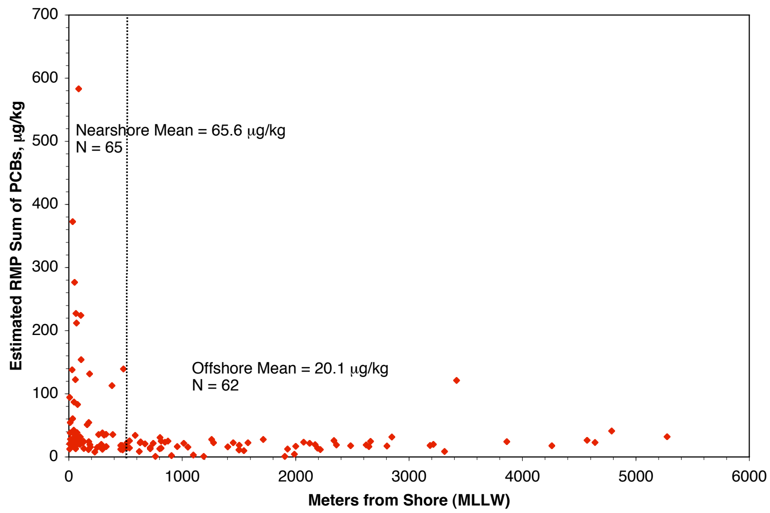

Figure 2. Sum of 40 RMP PCB congeners estimated from 16 NOAA/EMAP congeners versus distance from shore.

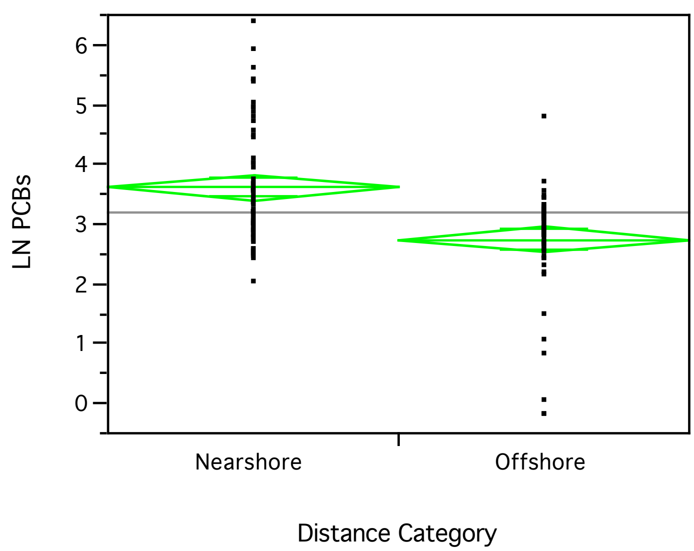

Figure 3. Distribution of PCB concentrations at nearshore and offshore sites. The horizontal line indicates the grand mean and the midline in each diamond indicates the category mean and the vertical extent of each diamond represents the 95% confidence intervals in each category.

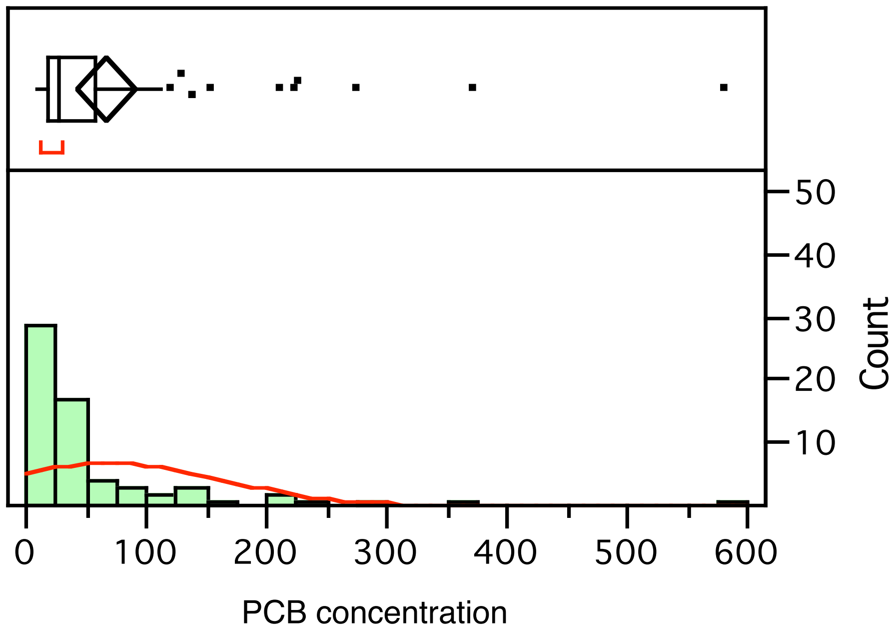

Figure 4. Distribution and outlier box plot of estimated raw PCB concentrations for all nearshore NOAA/EMAP sites before removal of any outliers. The red curve over the histogram indicates an approximately normal curve. The red bracket below the box plot indicates the densest 50% of the distribution. The box ends indicate the 25th and 75th quartiles and the vertical line in the box represents the sample median. The midpoint and ends of the diamond indicate the mean and the 95% confidence intervals, respectively. The whiskers extending from the ends of the box indicate 1.5 times the interquartile range. Points beyond the whiskers are defined as outliers.

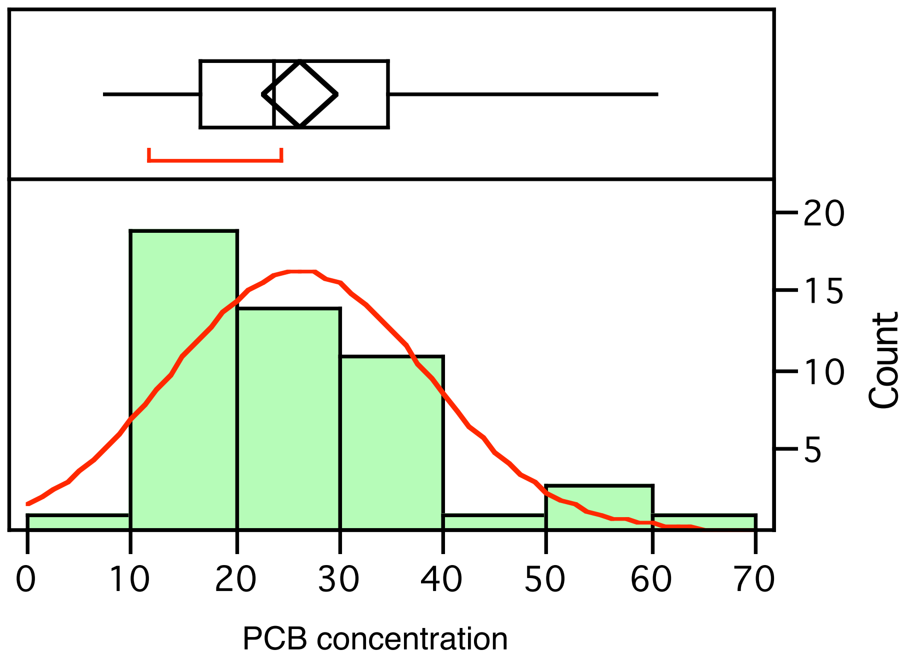

Figure 5. Distribution and outlier box plot of raw PCB concentrations for nearshore NOAA/EMAP sites following removal of all outliers. Figure description is as for Figure 4.

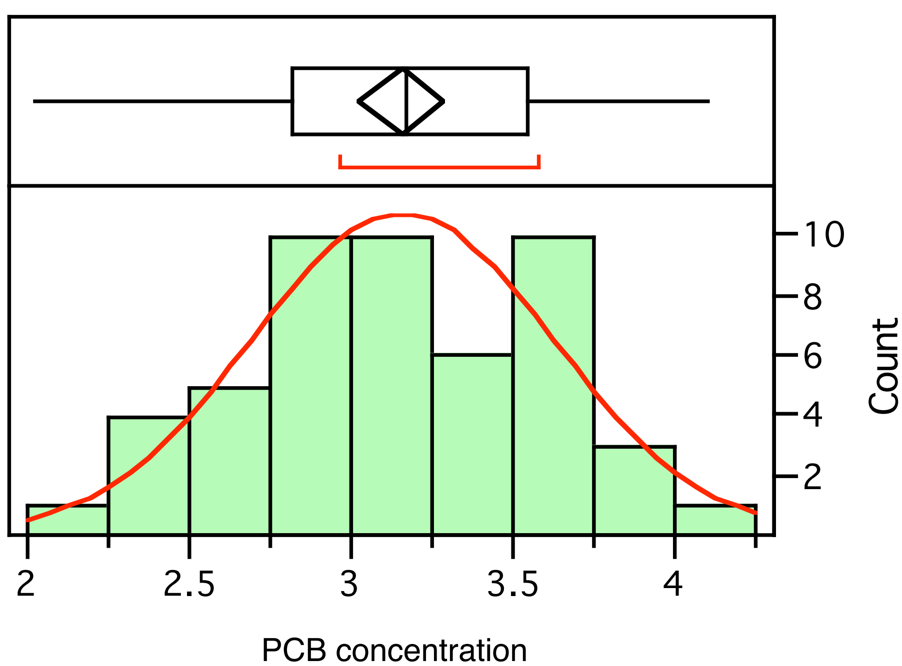

Figure 6. Distribution and outlier box plot of transformed (natural log) PCB concentrations for nearshore NOAA/EMAP sites following removal of all outliers. Figure description is as for Figure 4.

Sites that remained following removal of all high outliers in both the nearshore and offshore regions still differed in their PCB concentrations (Figure 7). There were no offshore sites with PCB concentrations exceeding 35 µg/kg and the nearshore category had 12 sites that exceeded 35 µg/kg. ANOVA on log-transformed (natural log) data after removal of outliers revealed significantly higher concentrations in the nearshore category than in the offshore category (p = 0.0007; Figure 8).

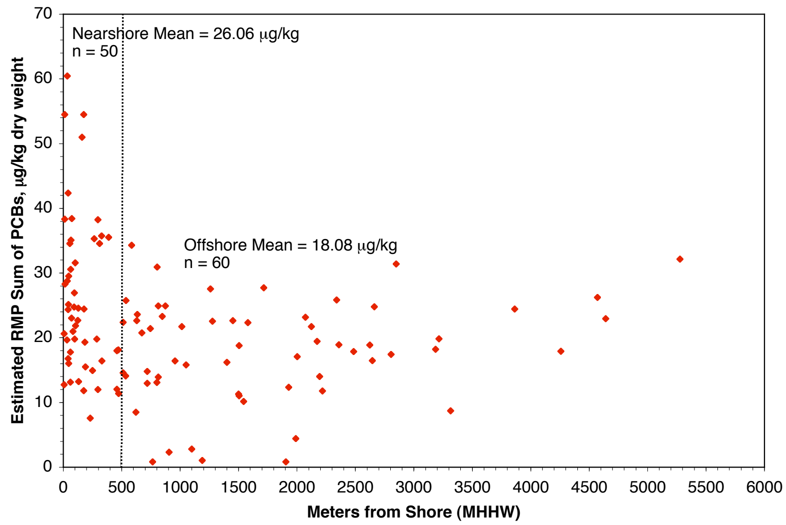

Figure 7. Sum of 40 RMP PCB congeners estimated from 16 NOAA/EMAP congeners versus distance from shore after all high outliers were removed.

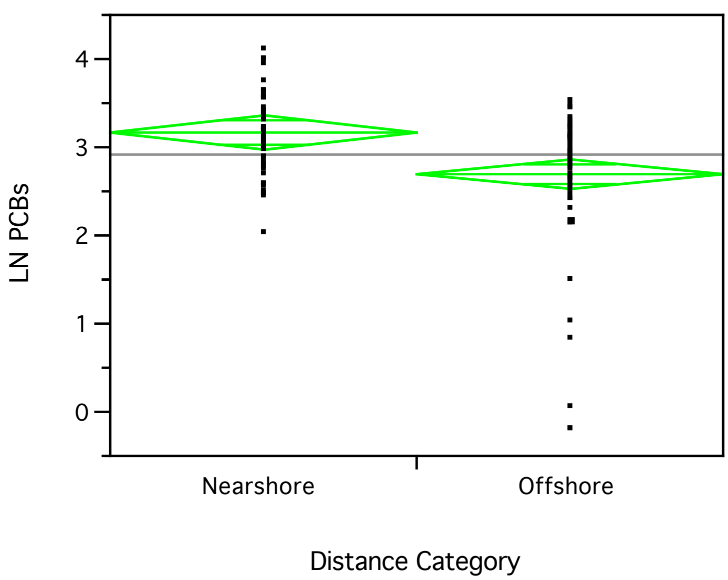

Figure 8. Distribution of PCB concentrations at nearshore and offshore sites following removal of high outliers. Figure description is as for Figure 3.

It is possible that contaminated onshore sites influenced our estimate of nearshore background PCB concentrations, even after removal of statistical outliers. Comparison of the spatial distribution and PCB concentrations of sites remaining after outlier removal (Figure 9) with those for all sites (Figure 1) suggests that, while sites with higher concentrations were removed, the remaining sites with the highest concentrations of PCBs are still found primarily along the urbanized shores of San Francisco, Emeryville, and Lower South Bay.

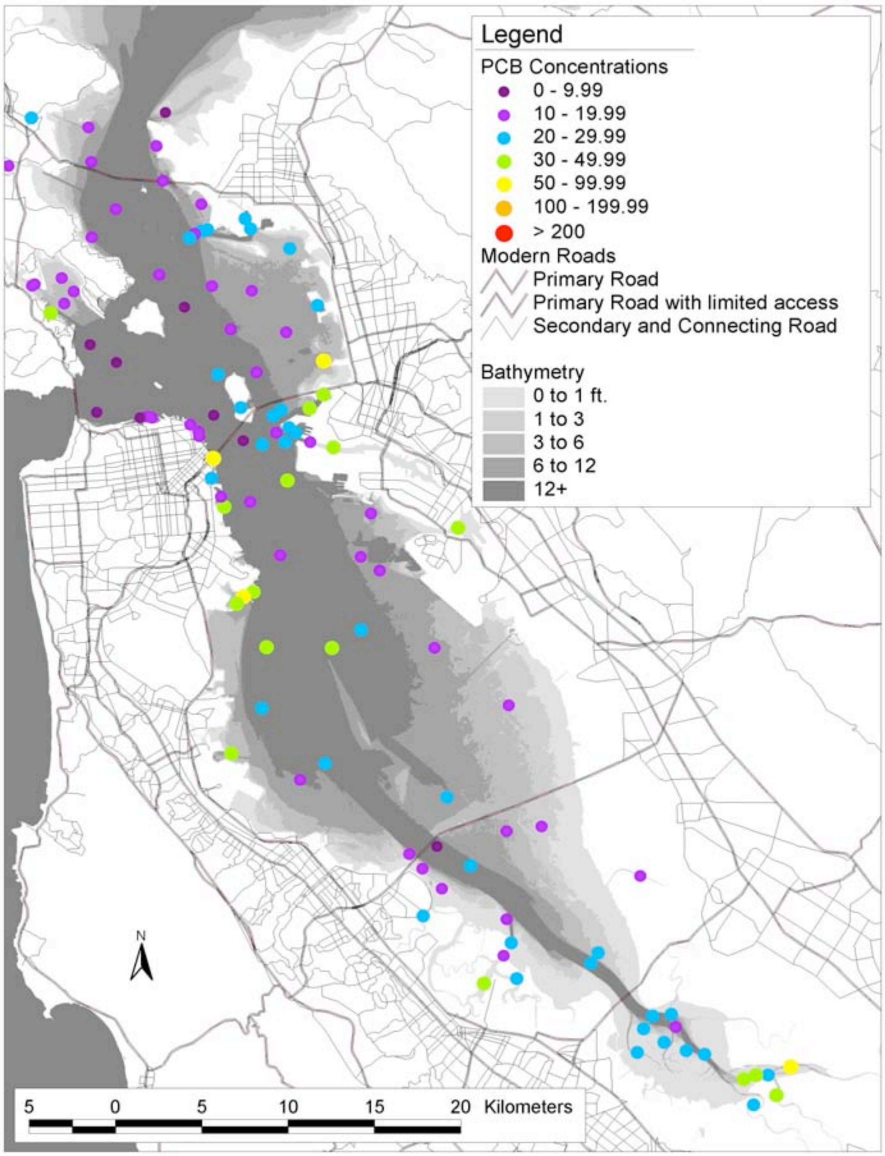

Figure 9. NOAA/EMAP sampling sites, with statistical outliers removed, displayed according to the estimated sum of PCBs for 40 RMP congeners.

Calculation of tolerance intervals for several percentiles of the nearshore PCB concentrations following removal of outliers revealed high upper bounds of nearshore background sediments (Table 1). To be considered outside the upper bounds of the 80th percentile of nearshore background samples, a sample would have to have a PCB concentration greater than 53.5 µg/kg.

To be considered outside the upper bounds of the 99th percentile of nearshore background samples, a sample would have to have a PCB concentration greater than 331 μg/kg. If the 80th percentile were selected as the designation of background, three of the samples remaining after removal of outliers would have been considered outside of background.

Table 1. Tolerance interval bounds for several percentiles (P values) of the nearshore background PCB distribution. The tolerance interval bounds were computed with log-transformed data, but the bounds shown have been back-transformed to the original raw units (μg/kg).

P	Tolerance Interval Bound
1	1.84
5	5.72
10	7.90
20	11.39
30	14.76
70	41.22
80	53.41
90	76.98
95	106.35
99	330.86

If data for grain size or total organic carbon had been available for the NOAA/EMAP samples, it is possible that the calculated tolerance intervals would have been lower. Smith and Riege (1999) found a strong correlation between grain size and PCB concentrations in sediments from across all of San Francisco Bay. When they stratified sediments according to grain size, their tolerance intervals for the sum of PCBs for the 40 RMP PCB congeners were substantially lower than those reported in this study (Table 2 versus Table 1). Assuming that the percent fines in the NOAA/EMAP samples was similar to the average percent fines in RMP sediment samples collected from Central Bay, South Bay and Lower South Bay from 1995–2002 (i.e., 72%), the tolerance intervals reported here are approximately four times higher than those reported by Smith and Riege (1999), although some of this difference could be due to higher PCB concentrations in nearshore regions, as compared to the Bay average.

Table 2. Tolerance interval bounds for several percentiles (P values) of PCB concentrations in San Francisco Bay sediments, as shown in Smith and Riege (1999).

	P					
% Fines	0.70	0.75	0.80	0.85	0.90	0.95
5	0.68	0.83	0.98	1.08	1.53	1.77
25	3.38	4.14	4.88	5.40	7.63	8.83
50	6.76	8.28	9.77	10.81	15.26	17.66
72	9.74	11.92	14.07	15.56	21.98	25.43
75	10.14	12.42	14.66	16.21	22.90	26.49
100	13.52	16.56	19.54	21.62	30.53	35.32

All sediments in San Francisco Bay undoubtedly have been influenced by historic discharges of PCBs. Advection patterns of PCB-containing sediments from the numerous likely discharge points are poorly described and overlapping dilution fields from these discharges, which probably confounded the estimation of nearshore background concentrations, also have partially contributed to the high tolerance limits reported here. In an effort to estimate the nearshore area influenced by potential hot spots, all sites from all three programs (i.e., NOAA/EMAP, BPTCP and Risebrough) were plotted together (Figure 10). As this figure includes a high density of sites that were specifically sampled in areas with known high PCB concentrations, the differences in colors of nearby sites can be used to infer the spatial influence of hot spots. Using the Hunters Point area as an example, the concentrations of PCBs attenuate within approximately 2 km of the highest concentrations (i.e., >200 μg/kg) to near the overall average of nearshore and offshore samples in the NOAA/EMAP dataset, with outliers removed (i.e., 21.7 μg/kg).

Data from additional samples from areas less affected by terrestrial sources also might reduce the variation in nearshore PCB concentrations, which could reduce the tolerance limits. One possible source of additional samples is the RMP. Eighty-four random sediment samples were collected by the RMP in the study area from 2002–2004, for which data will be available sometime in 2005. It is estimated that approximately 10% of those samples could fall within the nearshore region. While more samples are always beneficial, an additional eight samples might not substantially reduce calculated tolerance limits for the nearshore region. Nevertheless, it also is conceivable that data from additional samples could contradict the finding of a statistical difference between the nearshore and offshore regions.

The first objective of this project has been at least partly achieved. Existing data were sufficient to quantify PCB concentrations in the sediment of the nearshore environment of central and southern San Francisco Bay, within the constraints of variation caused by complex spatial patterns of discharge and advection and tolerance intervals were calculated. Stakeholders have several decisions to make based upon these results. They can decide either to accept the reported tolerance intervals or obtain data from additional samples. If they accept the reported tolerance intervals, they must choose the percentile beyond which sediments will be considered polluted. Collection of additional data, if necessary, should be accomplished by a future project.

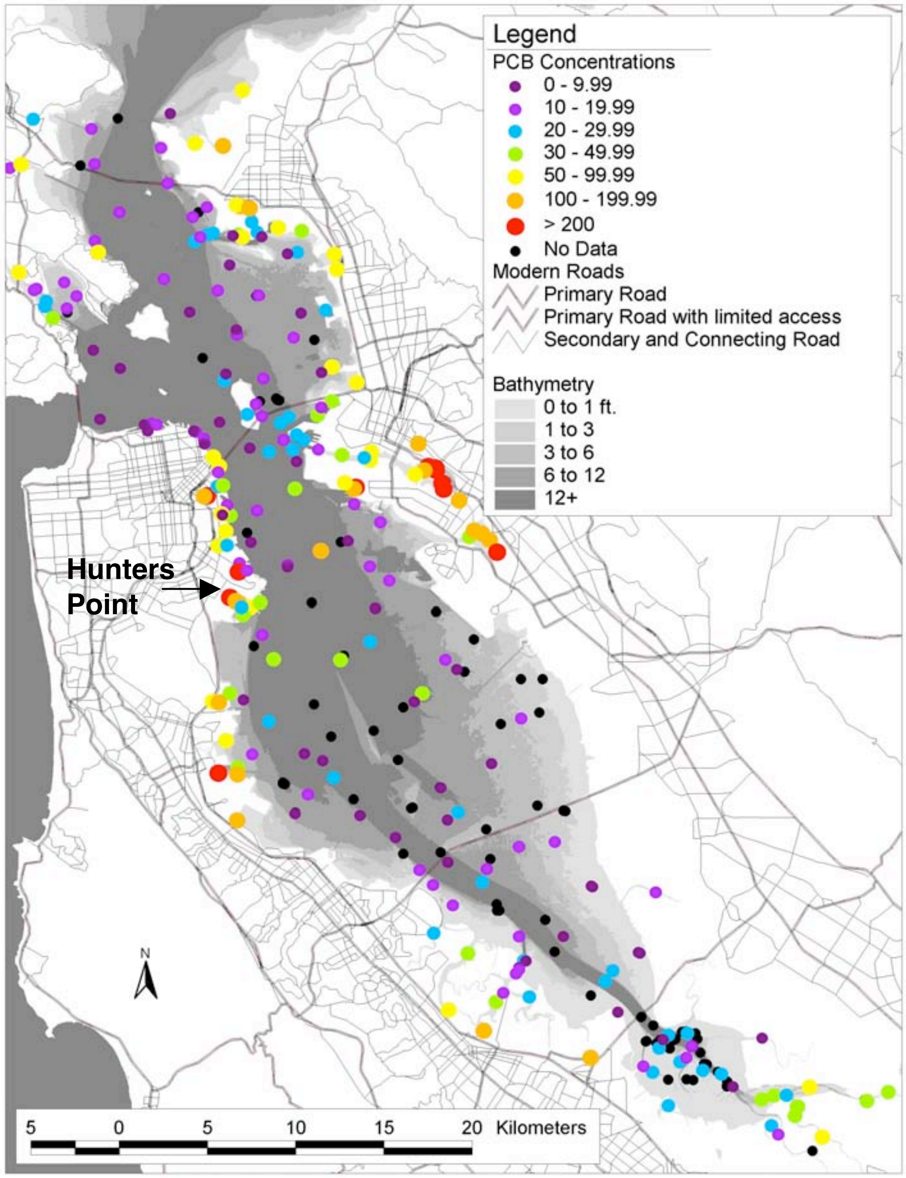

Figure 10. All sites from NOAA/EMAP, BPTCP and Risebrough sampling programs displayed according to the sum of PCBs. Sum of PCBs for NOAA/EMAP sites are estimated for 40 RMP congeners. Sites with no data (black dots) are sites sampled by the RMP in 2002–2004.

Literature Cited

SAS Institute, Inc. 2002. JMP Statistical Software, version 5.0.1.2.

Smith, R.W.. 2001. The use of random-model tolerance intervals in environmental monitoring and regulation. Journal of Agricultural, Biological and Environmental Statistics. 7:74-94

Smith, R.W. and L. Riege. 1999. San Francisco Bay Sediment Criteria Project Ambient Analysis Report. Report prepared for San Francisco Bay Regional Water Quality Control Board.

Appendix A
Data Evaluation Memos from SFEI

San Francisco Estuary Institute

7770 Pardee Lane, 2nd Floor
Oakland, CA 94621-1424
Office (510) 746-SFEI (7334)
Fax (510) 746-7300

November 13, 2002

To: Paul Salop, AMS
From: Jon Leatherbarrow and Jay Davis, SFEI
RE: PCB Data Evaluation for NOAA/EMAP Summer 2000 Sampling

Hi Paul,

As requested by Applied Marine Sciences, SFEI staff conducted an evaluation of data quality for NOAA/EMAP PCB data from Summer 2000 sampling in San Francisco Bay. Data quality was evaluated by comparing NOAA PCB congener profiles among 92 NOAA/EMAP samples (including duplicates) and to profiles in RMP samples collected from 1993 through 2000.

Based on expected contributions of individual congeners to the sum of PCBs (ΣPCBs), the preliminary evaluation indicates that the overall data quality is good with relatively few questionable reported PCB concentrations (Table 1). These samples are potentially affected by contamination or coelution that have artificially inflated the reported concentrations. We recommend qualifying these values and not using them in sums. Profiles indicative of Aroclor 1260 were determined in two samples: NOAA33-5 and CA00-0001.

Table 1. Samples with specific PCB congeners potentially influenced by contamination or coelution.

Sample ID	PCB congeners
CA00-0006	128
CA00-0013	180
CA00-0017	66
NOAA29-2	209
NOAA32-3	52
NOAA35-2	128
NOAA43-3	52
NOAA46-4	44, 52

The 21 congeners that comprise ΣPCBs in the NOAA/EMAP study consist of 17 RMP/SFEI PCB congeners (out of 40 RMP/SFEI PCBs) that make up approximately 87 to 100% of ΣPCBs in the NOAA/EMAP samples. An analysis of RMP sediment data from 1993 to 2000 indicates that the 17 NOAA/EMAP in common with RMP/SFEI congeners comprise approximately 65 ± 4.2% of ΣPCBs greater than 50 ppb (n = 8) in RMP samples and 70 ± 10% of ΣPCBs greater than 10 ppb (n = 101). Therefore, summation of only the 17 NOAA/EMAP congeners would underestimate ΣPCBs reported by the RMP by approximately 60 to 90%. Congeners that may provide substantial portions of ΣPCBs that were not reported in the current study include PCB 110 and PCB 149. For example, PCB 110 typically comprises 5 to 20% of total PCBs in RMP sediment.

Please feel free to contact me by phone (510) 746-7387 or email jon@sfei.org for further questions or comments.

Sincerely,

Jon Leatherbarrow

San Francisco Estuary Institute

7770 Pardee Lane, 2nd Floor
Oakland, CA 94621-1424
Office (510) 746-SFEI (7334)
Fax (510) 746-7300

December 9, 2002

To: Dane Hardin, AMS
From: Jon Leatherbarrow and Jay Davis, SFEI
RE: PCB Data Evaluation of Bay Protection Toxic Cleanup Program Data from 1995

Hi Dane,

As requested by Applied Marine Sciences, SFEI staff conducted an evaluation of data quality for PCB concentrations in San Francisco Bay sediment measured by the Bay Protection Toxic Cleanup Program in 1995. Data quality was evaluated by comparing PCB congener profiles among study samples and to typical profiles in RMP samples collected from 1993 through 2000.

Based on expected contributions of individual congeners to the sum of PCBs (ΣPCBs), the preliminary evaluation indicates that only one sample from Dow Chemical-Kirker Creek was potentially affected by contamination or coelution (Table 1). We recommend qualifying this value and not using it in the sum of PCBs.

Table 1. PCB congeners potentially influenced by contamination or coelution.

Sample ID	Site ID	Station Name	PCB Congener	Concentration
1529	21049	DOW CHEMICAL- KIRKER CREEK	PCB151	2.64

Please feel free to contact me by phone (510) 746-7387 or email jon@sfei.org for further questions or comments.

Sincerely,

Jon Leatherbarrow

San Francisco Estuary Institute

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Fax (510) 746-7300

December 6, 2002

To: Dane Hardin, AMS
From: Jon Leatherbarrow and Jay Davis, SFEI
RE: PCB Data Evaluation of Risebrough data from 1991

Hi Dane,

As requested by Applied Marine Sciences, SFEI staff conducted an evaluation of data quality for PCB concentrations in San Francisco Bay sediment measured by Dr. Robert Risebrough in 1991. Data quality was evaluated by comparing PCB congener profiles among study samples and to typical profiles in RMP samples collected from 1993 through 2000.

Based on expected contributions of individual congeners to the sum of PCBs (ΣPCBs), the preliminary evaluation indicates that the overall data quality is good with relatively few questionable reported PCB concentrations (Table 1). These samples are potentially affected by contamination or coelution. We recommend qualifying these values and not using them in sums.

Table 1. Samples with specific PCB congeners potentially influenced by contamination or coelution.

Sample ID	**Site ID**	**Station Name**	**PCB Congeners**	**Concentration**
10C	91-0071	Emeryville	15	1.115
23C	91-0073	Islais Creek	49	8.894
24C	91-0046	Islais Creek	153	0.027
25C	91-0050	India Basin	15, 141/179	2.267, 6.662
29C	91-0077	Sierra Point	15	0.445
42C	91-0037	Redwood Creek	138	1.498

Please feel free to contact me by phone (510) 746-7387 or email jon@sfei.org for further questions or comments.

Sincerely,

Jon Leatherbarrow

San Francisco Estuary Institute

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March 17, 2004

To: Dane Hardin, AMS
From: Jon Leatherbarrow and Jay Davis, SFEI
RE: PCB Data Evaluation for NOAA/EMAP 2001 Sampling

Hi Dane,
As requested by Applied Marine Sciences, SFEI staff conducted an evaluation of data quality for NOAA/EMAP PCB data from 2001 sampling in San Francisco Bay. Data quality was evaluated by comparing PCB congener profiles in 56 individual NOAA/EMAP samples to PCB profiles in RMP samples collected from 1993 through 2000.

Based on expected contributions of individual congeners to the sum of PCBs (ΣPCBs), the preliminary evaluation indicates that the overall data quality is good with relatively few questionable reported PCB concentrations (Table 1). These samples are potentially affected by contamination or coelution that have artificially inflated the reported concentrations. We recommend qualifying these values and not using them in sums. In sample NOAA_01_22-5, congeners 128 and 138 had the same concentration (2.166 ppb), which may be the result of a formatting error. We recommend checking the original files to determine if a formatting error occurred during the reporting process.

Table 1. PCB congeners potentially influenced by contamination or coelution.

Sample ID	PCB congeners
NOAA_01_45-2	52
NOAA_01_22-5	128
NOAA_01_46-5	52
NOAA_01_37-3	128
NOAA_01_20-4	128
NOAA_01_24-1	128
NOAA_01_37-1	128

Please feel free to contact me by phone (510) 746-7387 or email jon@sfei.org for further questions or comments.

Sincerely,

Jon Leatherbarrow

Appendix B
Comparison of NOAA/EMAP and RMP PCB Datasets by SFEI

San Francisco Estuary Institute

7770 Pardee Lane
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MEMORANDUM

Date:	July 6, 2004
To:	Dane Hardin, AMS
From:	John Ross and Jay Davis, SFEI
Subject:	Comparison of NOAA and RMP PCB Datasets

Introduction

The San Francisco Estuary Institute (SFEI) was asked to establish a defensible conversion between the RMP sediment PCB data, and the 2000-2001 sediment PCB data collected by the partnership of the National Oceanographic and Atmospheric Administration and the U.S. Environmental Protection Agency through its Environmental Monitoring and Assessment Program (NOAA-EMAP).

Method

It was decided to develop a factor from the RMP sediment data to be used in converting the sum of PCB congeners measured in the NOAA-EMAP sediment samples to the RMP "equivalent". The RMP measures 40 PCB congeners in San Francisco Estuary sediments, but only 17 of these are reported in the NOAA-EMAP study. The conversion factor was estimated by first calculating the sum of the 40 PCB congener concentrations in each of the 1993-2001 RMP sediment samples and then comparing it to the sum of the 16 PCB congeners shared in common between the RMP and NOAA-EMAP studies. The sum of the 17 PCB congeners in common was not used, as the NOAA-EMAP data for PCB 170/190 were qualified as having matrix interference.

The relationship between the two sums was examined using linear regression analysis. Sediments having a sum of 40 PCB congeners less than 10 ppb were excluded as not enough congeners were quantified at these lower concentrations. At concentrations less than 10 ppb the sum of 40 PCB congeners is really only a sum of 16 or less congeners because only 16 or fewer are actually detected. The conversion factor developed from the higher concentrations should apply just as well to concentrations < 10 ppb. The same comparison was conducted using the 1993-2001 RMP water particulate PCB data to provide another line of evidence in potential support of the conversion factor.

Results

All regressions, with or without the high concentration samples, had similar slopes, were highly significant, and explained from 92% to 99% of the variation in the data (Figures 1, 2, 3 and 4).

Conclusions

Enough sediment data are available to support a defensible factor for the conversion of all NOAA-EMAP PCB sums to RMP sums, even for those NOAA-EMAP samples with low concentrations. This conversion factor is estimated to be 1.72 suggesting that the sum of the 16 PCB congeners accounts for approximately 60% of the sum of the 40 PCB congeners. The similarity of the relationship for the 1993-2001 RMP water particulate PCB data supports this conclusion.

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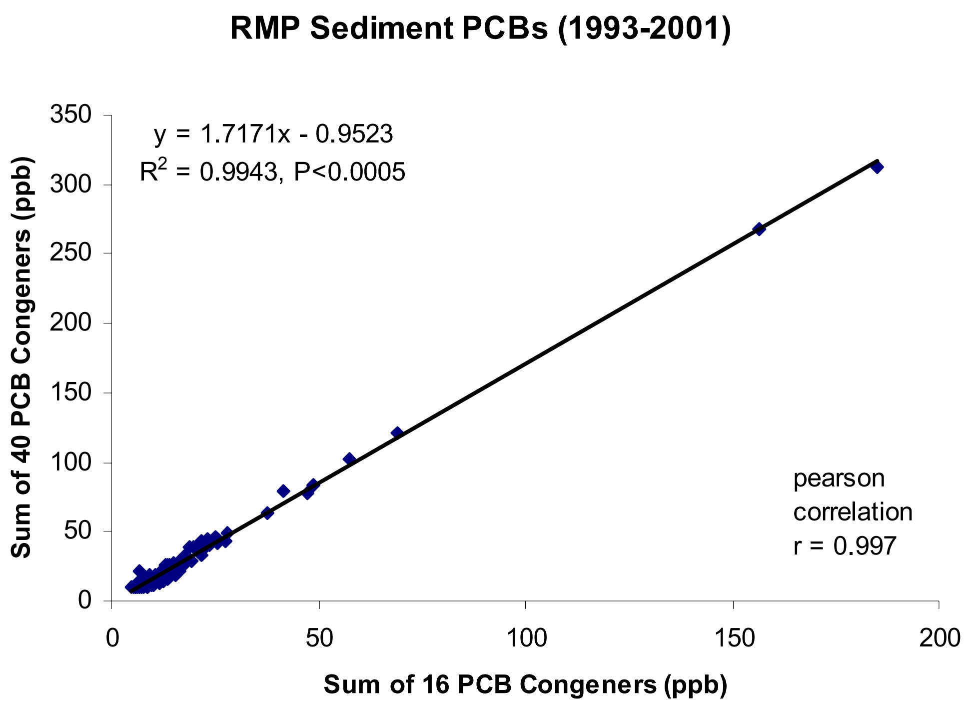

Figure 1. Relationship between PCB congener sums for all sediment samples with a sum of 40 PCB congeners > 10 ppb.

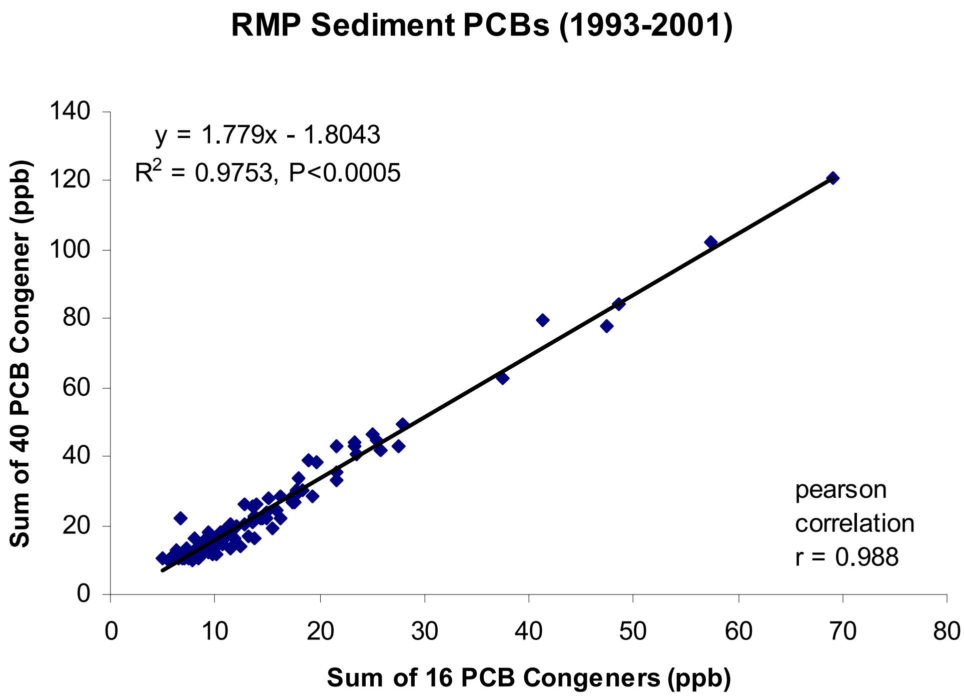

Figure 2. Relationship between PCB congener sums for sediment samples with a sum of 40 PCB congeners > 10 ppb, excluding the two highest concentrations.

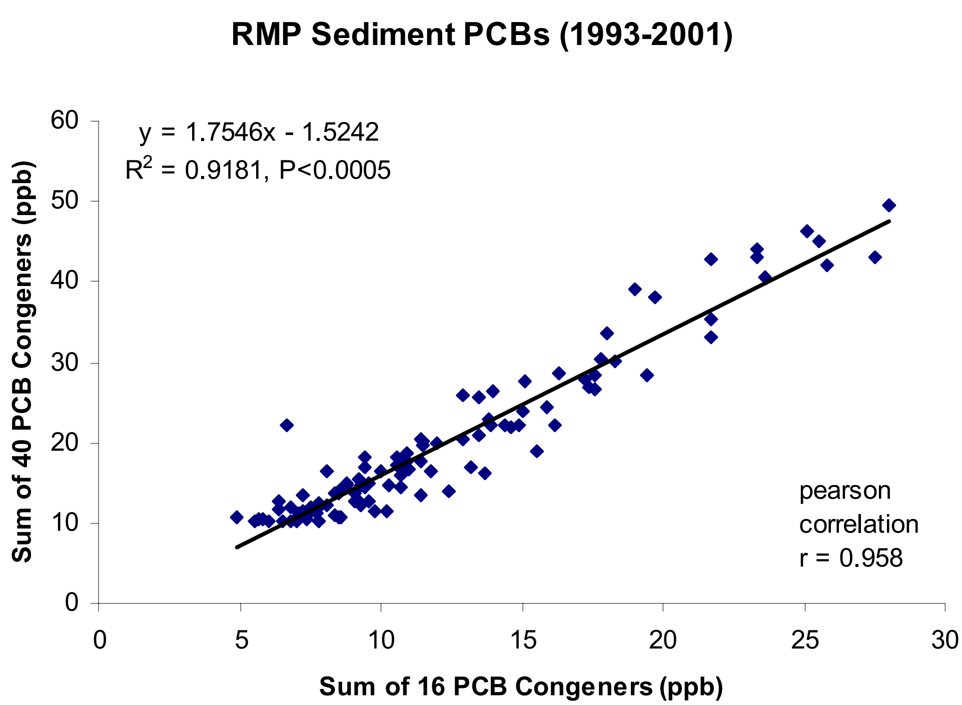

Figure 3. Relationship between PCB congener sums for all sediment samples with a sum of 40 PCB congeners < 50 and > 10 ppb.

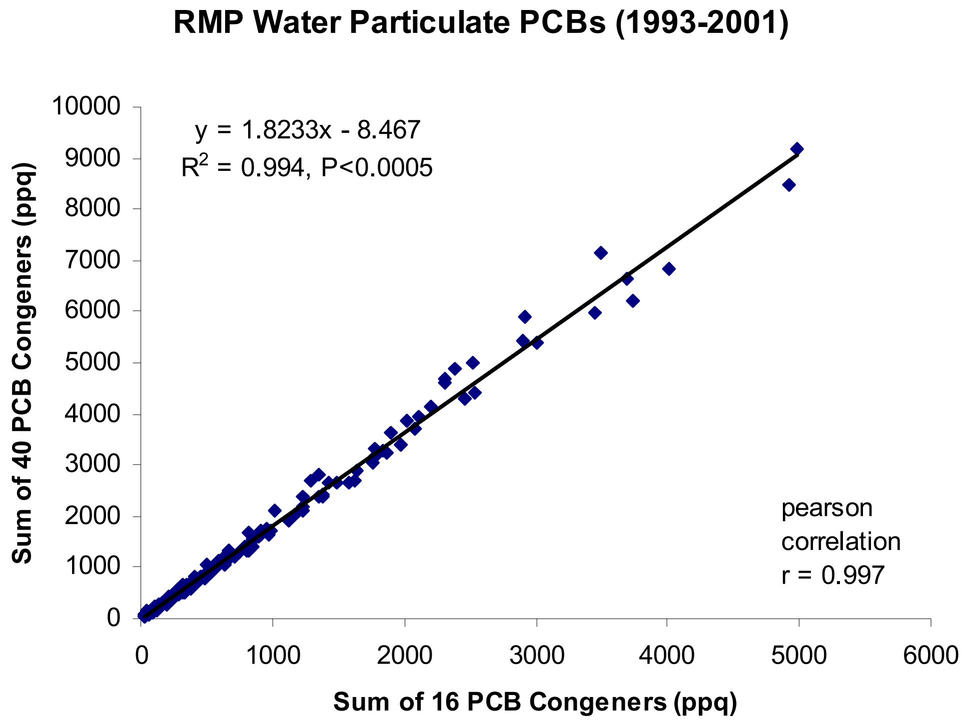

Figure 4. Relationship between PCB congener sums for all water particulate samples > 50 ppq.

Appendix C
NOAA/EMAP 2000-2001 San Francisco Bay Data Analyzed for this Project

Appendix C. NOAA-EMAP samples used for data analysis.

STATION	Depth, m	Distance, m	Distance Category	Year Sampled	Latitude	Longitude	SUM PCBs	SUM minus 170/190	RMP estimate
NOAA_01_44-3B	0	7.31	Nearshore	2001	37.4407	-122.0035833	57.097	54.97	94.5484
NOAA46-1	0	7.85	Nearshore	2000	37.96726	-122.50533	14.4	11.99	20.6228
NOAA_01_25-2	0	7.87	Nearshore	2001	37.80251667	-122.3965333	7.849	7.42	12.7624
NOAA26-1	0	12.29	Nearshore	2000	37.78806	-122.38685	32.56	31.68	54.4896
NOAA_01_26-3	0	12.89	Nearshore	2001	37.76298333	-122.3799667	23.397	22.273	38.30956
NOAA_01_33-1	0	13.87	Nearshore	2001	37.77783333	-122.3879833	18.502	16.455	28.3026
NOAA_01_19-1C	0	30.05	Nearshore	2001	37.92178333	-122.3718333	83.891	80.337	138.17964
NOAA_01_46-5	0	31.23	Nearshore	2001	37.94236667	-122.52055	14.05	11.428	19.65616
NOAA_01_33-2	0	32.58	Nearshore	2001	37.77318333	-122.3947833	220.439	216.663	372.66036
CA00-0017	0	32.89	Nearshore	2000	37.86799	-122.31753	41.06	16.72	28.7584
NOAA_01_47-5A	1.22	34.37	Nearshore	2001	37.83893333	-122.3137833	36.862	35.152	60.46144
NOAA_01_47-1	0.61	42.07	Nearshore	2001	37.88018333	-122.5036	10.372	9.763	16.79236
NOAA_01_45-1	0	42.17	Nearshore	2001	37.54751667	-122.2512333	15.042	14.158	24.35176
CA00-0015	0	42.29	Nearshore	2000	37.45201	-122.02087	25.67	24.62	42.3464
NOAA19-2	10.97	44.30	Nearshore	2000	37.91365	-122.36464	15.35	14.62	25.1464
NOAA_01_45-5	0	44.92	Nearshore	2001	37.44696667	-122.0358667	18.645	17.163	29.52036
NOAA25-1	0	45.58	Nearshore	2000	37.80613	-122.40181	9.82	9.32	16.0304
NOAA_01_33-3	0	46.37	Nearshore	2001	37.74723333	-122.3879167	57.82	50.605	87.0406
NOAA32-2	1.52	49.46	Nearshore	2000	37.78727	-122.25236	167.64	160.8	276.576
CA00-0016	0	55.98	Nearshore	2000	37.86489	-122.49351	22.27	20.09	34.5548
NOAA_01_29-3	5.18	56.82	Nearshore	2001	37.7761	-122.3002833	72.36	71.202	122.46744
NOAA_01_45-4	0	60.99	Nearshore	2001	37.56768333	-122.1086	8.053	7.642	13.14424
NOAA25-3	0	61.04	Nearshore	2000	37.80007	-122.3961	10.84	10.33	17.7676
NOAA32-3	1.52	61.96	Nearshore	2000	37.77875	-122.24359	205.21	132.04	227.1088
NOAA_01_32-1	11.58	64.17	Nearshore	2001	37.7936	-122.3079	19.181	17.774	30.57128
NOAA_01_31-1	11.58	65.84	Nearshore	2001	37.82135	-122.3141333	21.57	20.397	35.08284
NOAA29-2	2.13	67.11	Nearshore	2000	37.77688	-122.2991	141.67	123.3	212.076
NOAA_01_31-3	3.96	70.67	Nearshore	2001	37.8041	-122.3367667	14.379	13.395	23.0394
NOAA_01_27-2	8.53	71.77	Nearshore	2001	37.71818333	-122.3611833	23.696	22.338	38.42136
NOAA_01_29-1	4.88	76.26	Nearshore	2001	37.77935	-122.3061833	50.588	48.417	83.27724
NOAA18-1	11.89	83.46	Nearshore	2000	37.90727	-122.39386	14.52	12.2	20.984
NOAA_01_33-4	0	85.83	Nearshore	2001	37.72078333	-122.3806333	368.939	339.015	583.1058

STATION	Depth, m	Distance, m	Distance Category	Year Sampled	Latitude	Longitude	SUM PCBs	SUM minus 170/190	RMP estimate
NOAA_01_45-2	3.05	92.29	Nearshore	2001	37.5143	-122.19015	18.066	14.401	24.76972
CA00-0014	0	95.80	Nearshore	2000	37.46252	-122.0261	16.29	15.67	26.9524
CA00-0002	10.97	98.14	Nearshore	2000	37.79648	-122.32285	12.24	11.52	19.8144
NOAA40-3	8.53	102.10	Nearshore	2000	37.51198	-122.21182	18.99	18.37	31.5964
NOAA_01_18-3	8.53	105.47	Nearshore	2001	37.90815	-122.3896333	13.75	12.721	21.88012
NOAA_01_32-4	8.84	105.69	Nearshore	2001	37.7757	-122.2425	136.749	130.418	224.31896
NOAA_01_33-6	1.22	109.27	Nearshore	2001	37.71771667	-122.3742833	97.878	89.565	154.0518
NOAA19-3	10.67	123.80	Nearshore	2000	37.90843	-122.36127	13.68	13.19	22.6868
NOAA_01_31-5	6.40	129.29	Nearshore	2001	37.80135	-122.3323167	15.403	14.277	24.55644
NOAA_01_24-1	11.89	131.78	Nearshore	2001	37.81041667	-122.4304	10.155	7.702	13.24744
CA00-0001	1.83	160.42	Nearshore	2000	37.71544	-122.36781	31.91	29.65	50.998
NOAA_01_24-3	5.79	173.89	Nearshore	2001	37.80988333	-122.4268833	7.167	6.88	11.8336
NOAA_01_43-1	0	175.21	Nearshore	2001	37.46665	-122.0115167	32.791	31.683	54.49476
NOAA_01_21-2	6.71	176.90	Nearshore	2001	37.81468333	-122.3684833	15.285	14.212	24.44464
NOAA33-5	0.91	182.38	Nearshore	2000	37.71874	-122.37682	83.51	76.43	131.4596
NOAA26-2	9.75	185.54	Nearshore	2000	37.76828	-122.38172	11.73	11.23	19.3156
NOAA_01_47-2	0.30	189.34	Nearshore	2001	37.87941667	-122.5052667	9.508	9.005	15.4886
NOAA24-2	10.67	229.42	Nearshore	2000	37.8098	-122.43466	4.6	4.41	7.5852
NOAA_01_17-3	1.52	249.54	Nearshore	2001	37.92168333	-122.39365	9.365	8.69	14.9468
NOAA43-3	2.44	263.30	Nearshore	2000	37.46264	-122.03411	29.78	20.52	35.2944
CA00-0013	7.32	285.60	Nearshore	2000	37.5266	-122.19878	17.24	11.51	19.7972
NOAA_01_34-2	0.91	296.01	Nearshore	2001	37.63348333	-122.3763	23.15	22.23	38.2356
NOAA17-1	0.61	296.79	Nearshore	2000	37.95231	-122.42291	7.29	6.98	12.0056
NOAA31-2	11.58	311.69	Nearshore	2000	37.81413	-122.32335	21.16	20.09	34.5548
NOAA_01_32-5	1.83	327.13	Nearshore	2001	37.75098333	-122.2262667	21.748	20.787	35.75364
CA00-0037	1.52	330.08	Nearshore	2000	37.87638	-122.47797	10.51	9.56	16.4432
CA00-0004	0	381.46	Nearshore	2000	37.75267	-122.21803	68.06	65.67	112.9524
NOAA_01_27-3	1.83	388.09	Nearshore	2001	37.71191667	-122.3723333	22.313	20.656	35.52832
CA00-0003	11.58	457.92	Nearshore	2000	37.80168	-122.34532	7.36	7.01	12.0572
CA00-0032	3.96	458.64	Nearshore	2000	37.90475	-122.46583	12.8	10.47	18.0084
NOAA_01_18-2	11.28	469.62	Nearshore	2001	37.90631667	-122.3980833	11.385	10.535	18.1202
NOAA_01_37-1	0.30	473.81	Nearshore	2001	37.57261667	-122.2514833	9.876	6.631	11.40532
NOAA46-4	0	481.33	Nearshore	2000	37.95286	-122.38292	117.57	81.02	139.3544
CA00-0033	1.83	511.67	Offshore	2000	37.93411	-122.41868	10.33	8.47	14.5684

STATION	Depth, m	Distance, m	Distance Category	Year Sampled	Latitude	Longitude	SUM PCBs	SUM minus 170/190	RMP estimate
NOAA42-1	6.40	512.57	Offshore	2000	37.49403	-122.10141	13.89	13.02	22.3944
NOAA_01_30-2	1.83	534.21	Offshore	2001	37.75888333	-122.2834667	8.542	8.189	14.08508
NOAA_01_22-5	6.71	535.54	Offshore	2001	37.8322	-122.3832833	17.8	14.968	25.74496
NOAA_01_43-2	2.44	584.51	Offshore	2001	37.46061667	-122.0422167	21.739	19.941	34.29852
NOAA_01_12-3	0.61	621.76	Offshore	2001	37.96973333	-122.4166667	5.267	4.929	8.47788
CA00-0036	11.58	629.09	Offshore	2000	37.81033	-122.34713	13.72	13.17	22.6524
NOAA20-6	3.66	632.28	Offshore	2000	37.81329	-122.34175	15.52	13.72	23.5984
NOAA30-1	6.40	671.55	Offshore	2000	37.79641	-122.3393	12.78	12.06	20.7432
NOAA_01_37-2	0	717.62	Offshore	2001	37.56193333	-122.2387667	8.954	8.619	14.82468
NOAA_01_34-4	1.22	717.86	Offshore	2001	37.58016667	-122.26	7.954	7.542	12.97224
NOAA00-BA21	2.13	744.10	Offshore	2000	37.49483333	-122.089	12.97	12.46	21.4312
NOAA_01_22-4B	16.76	764.39	Offshore	2001	37.81265	-122.4631833	0.518	0.481	0.82732
NOAA_01_23-1	0.61	801.04	Offshore	2001	37.88338333	-122.4858	8.132	7.614	13.09608
NOAA_01_28-3	13.11	803.67	Offshore	2001	37.77645	-122.33835	19.134	17.969	30.90668
NOAA_01_23-3	1.22	812.64	Offshore	2001	37.87011667	-122.4842	8.863	8.087	13.90964
NOAA_01_45-3	0.30	812.94	Offshore	2001	37.47503333	-122.1116833	16.197	14.493	24.92796
NOAA_01_16-2	7.62	847.91	Offshore	2001	37.90386667	-122.4014333	14.364	13.543	23.29396
NOAA_01_20-2	1.52	873.40	Offshore	2001	37.89798333	-122.33545	15.072	14.48	24.9056
NOAA22-1	22.86	904.73	Offshore	2000	37.84814	-122.46741	1.34	1.34	2.3048
CA00-0035	9.14	956.34	Offshore	2000	37.83337	-122.35784	10.04	9.55	16.426
NOAA_01_40-1	9.14	1013.27	Offshore	2001	37.53303333	-122.1936333	14.152	12.623	21.71156
NOAA_01_15-2	3.35	1050.80	Offshore	2001	37.94418333	-122.4658167	9.972	9.183	15.79476
NOAA28-1	17.98	1098.50	Offshore	2000	37.79745	-122.36685	1.64	1.64	2.8208
NOAA22-6	28.65	1188.99	Offshore	2000	37.81077	-122.3864	0.61	0.61	1.0492
NOAA42-3	4.57	1259.99	Offshore	2000	37.47373	-122.06752	16.62	16.02	27.5544
NOAA_01_41-1	0	1276.51	Offshore	2001	37.48741667	-122.10745	14.501	13.105	22.5406
CA00-0031	0.91	1400.94	Offshore	2000	37.96239	-122.46772	10.72	9.43	16.2196
NOAA_01_28-2	12.80	1449.89	Offshore	2001	37.79538333	-122.35435	14.089	13.168	22.64896
NOAA_01_16-3	13.11	1499.56	Offshore	2001	37.88483333	-122.4216	6.951	6.569	11.29868
NOAA_01_42-2	3.66	1503.55	Offshore	2001	37.48835	-122.0861833	11.596	10.93	18.7996
NOAA28-4	17.37	1503.60	Offshore	2000	37.76553	-122.36269	6.82	6.43	11.0596
NOAA28-5	15.85	1543.62	Offshore	2000	37.7373	-122.34322	6.3	5.91	10.1652
CA00-0011	12.19	1578.73	Offshore	2000	37.52201	-122.14155	13.62	12.98	22.3256
CA00-0005	5.18	1714.25	Offshore	2000	37.65713	-122.35584	16.87	16.13	27.7436

STATION	Depth, m	Distance, m	Distance Category	Year Sampled	Latitude	Longitude	SUM PCBs	SUM minus 170/190	RMP estimate
NOAA22-3	23.47	1904.12	Offshore	2000	37.83879	-122.45016	0.48	0.48	0.8256
NOAA_01_30-4	2.74	1929.35	Offshore	2001	37.72903333	-122.2778167	7.539	7.185	12.3582
CA00-0010	13.41	1989.24	Offshore	2000	37.58382	-122.24165	2.75	2.58	4.4376
NOAA20-5	2.74	2001.91	Offshore	2000	37.85431	-122.33817	10.51	9.92	17.0624
NOAA_01_41-2	0	2071.00	Offshore	2001	37.4803	-122.0941167	14.775	13.468	23.16496
NOAA_01_39-3	0.91	2122.99	Offshore	2001	37.52746667	-122.1366333	13.194	12.632	21.72704
CA00-0006	3.66	2172.44	Offshore	2000	37.61961	-122.33133	12.87	11.3	19.436
NOAA16-1	10.67	2193.98	Offshore	2000	37.91938	-122.44992	9.32	8.16	14.0352
CA00-0012	0.61	2216.76	Offshore	2000	37.59417	-122.17296	7.13	6.86	11.7992
NOAA_01_41-3	0	2338.26	Offshore	2001	37.47566667	-122.07955	16.594	15.023	25.83956
NOAA_01_37-3	0.30	2358.55	Offshore	2001	37.54556667	-122.19665	13.263	11.009	18.93548
CA00-0007	2.44	2484.55	Offshore	2000	37.68818	-122.24239	10.88	10.38	17.8536
NOAA30-3	2.74	2623.11	Offshore	2000	37.7363	-122.29039	11.5	10.98	18.8856
NOAA_01_20-4	4.27	2645.18	Offshore	2001	37.856	-122.3748833	11.342	9.586	16.48792
NOAA_01_38-2	11.58	2660.54	Offshore	2001	37.57371667	-122.2196333	15.255	14.409	24.78348
CA00-0009	0.91	2804.68	Offshore	2000	37.6579	-122.19392	10.49	10.14	17.4408
NOAA35-2	7.92	2849.30	Offshore	2000	37.68912	-122.35265	21.22	18.25	31.39
NOAA_01_20-3	2.13	3186.56	Offshore	2001	37.87605	-122.3606833	11.451	10.606	18.24232
CA00-0034	3.05	3214.89	Offshore	2000	37.87874	-122.38702	12.82	11.54	19.8488
NOAA_01_22-2	18.90	3313.56	Offshore	2001	37.86758333	-122.4049667	5.397	5.066	8.71352
NOAA00-BB70	8.84	3418.59	Offshore	2000	37.74433333	-122.3216667	73.24	70.42	121.1224
NOAA_01_35-4	9.75	3861.85	Offshore	2001	37.62786667	-122.3145667	15.145	14.217	24.45324
NOAA_01_39-2	1.83	4258.31	Offshore	2001	37.59188333	-122.1960333	11.043	10.409	17.90348
NOAA_01_35-1	7.01	4570.19	Offshore	2001	37.69771667	-122.2905667	16.987	15.247	26.22484
NOAA_01_36-4	3.05	4640.12	Offshore	2001	37.60968333	-122.2350333	14.416	13.353	22.96716
CA00-0008	3.66	4786.05	Offshore	2000	37.67103	-122.25744	25.13	23.96	41.2112
NOAA35-3	8.53	5276.10	Offshore	2000	37.68845	-122.30964	19.71	18.7	32.164

Appendix D
Synopsis of Peer Reviewers' Comments

Synopsis of Peer-review Comments And Recommendations for Concluding Task #4.10a

Introduction

Task #4.10a has a long history marked by several changes in analytical direction. Four distinctly different reports have been submitted for this task between August 14, 2003 and March 25, 2005. These different iterations have been in response to changes in analytical approaches based upon input from Water Board staff and the PCB Workgroup, as well as reviewers' comments on various drafts. One of the major shifts in project direction and analytical effort was based upon availability of the NOAA/EMAP dataset, which had previously been deemed unsuitable for the project and unavailable for our use. The project history is shown in the following table.

Project History

11/2/02 Scope of Work approve by CEP Technical Committee.

1/8/03 Preliminary results were presented to CEP Technical Committee. Concerns were raised regarding method of selecting sites from historic datasets.

3/18/03 Additional guidance received from Water Board staff in a meeting to discuss project status and selection of sites from historic datasets.

8/17/03 Draft Report submitted to PCB Workgroup.

9/19/03 Report revised according to reviewers' comments.

3/19/04 Obtained NOAA-EMAP data collected in 2000-2001.

8/3/04 Submitted second draft report to Workgroup, which was based upon analysis of NOAA-EMAP data.

9/13/04 Sent report to Dr. Robert Smith for review and computation of tolerance intervals.

10/8/04 Report revised based upon Workgroup comments and Dr. Smith's analyses.

3/25/05 Report revised according to comments received at Workgroup meeting on 12/15/04.

6/05 Report sent to external peer reviewers.

The latest report (Final Report Existing Data on PCB Concentrations of Nearshore Sediments and Assessment of Data Quality, March 25, 2005) was sent to three external reviewers in June 2005 and all comments were received from them by early August. The three reviewers were Roger Green (Professor Emeritus, University of Western Ontario), Don Stevens (Research Associate Professor, Oregon State University) and William Warren-Hicks (EcoStat, Inc.). The reviewers were given four focusing questions, which each answered, and two also provided specific comments on the content of the report. The following sections provide an overview of the specific comments and synopses of the responses to each focusing question. The verbatim comments from reviewers are included as an attachment.

Specific Comments

In general, the specific comments reflect a lack of clarity in several areas of the report. For example, the reviewers were uncertain of the objectives and questions being addressed by the study. Some of this confusion is due to the fact that the report assumed knowledge by the reader about the sources of data and history of the project. Much of the confusion, however, could be alleviated by more explicitly presenting the objectives and questions, along with their historic or regulatory bases. Many of the specific comments can be addressed editorially, while others related to the technical approach and content of the report and are discussed in the following sections.

Peer Review Focusing Questions

1. ***Is the distinction between nearshore and offshore sediments supported by the data and associated analyses?***

The reviewers were divided on their opinions regarding whether the distinction between nearshore and offshore were supported by the data and analyses. Two of the reviewers either denied a difference between nearshore and offshore or suggested such a distinction should be based on different analyses.

- Green agreed that there appeared to be differences between nearshore and offshore, but suggested that hypothesis testing was unnecessary and misplaced.
- Stevens disagreed that distance from shore was the major variable controlling PCB concentrations in surficial sediments. He provided detailed and compelling analyses using all NOAA/EMAP samples that suggested geographic location was a more important determinant of PCB concentration than distance from shore.
- Warren-Hicks also disagreed that the analyses were appropriate for determining whether there are differences between nearshore and offshore PCB concentrations and recommended comparison of PCB distributions between nearshore and offshore regions, rather than comparison of mean values. Such an approach would, of course, require establishment of an *a priori* distinction between nearshore and offshore regions. He also disagreed with the application of the regression model to convert NOAA/EMAP PCBs into RMP PCBs.

2. ***Are the methods used to remove outliers, in order to account for hot spots, adequate or are there other, better methods?***

The reviewers were unanimous in their criticism of either the method or value of removing outliers. In particular, the iterative process of successive outlier identifications and outlier removal before transforming the data were criticized. Moreover, all of the reviewers suggested that it is best to analyze the entire data set without removing outliers or using geographic criteria to reduce the effect of "hotspots" on the estimate of background PCB concentrations.

- Green disagreed with the iterative outlier identification and the use of untransformed data and also questioned the need to remove outliers.
- Stevens also favored using the entire data set and disagreed with the outlier identification using untransformed data. He conceded that, if hotspot removal was necessary, geographic criteria should be used to support such data removal.
- Warren-Hicks also favored using the entire data set and disagreed with the iterative outlier identification.

3. Are there ways of reducing variation in nearshore sediments other than through analysis of additional samples or stratification according to grain size or total organic carbon?

The reviewers were divided in their opinions regarding whether reduction in variation was necessary. Two of them suggested that use of other physical variables, such as grain size and total organic carbon (TOC), could help inform selection of sample strata and, as a result, assist in determining whether distinctions between nearshore and offshore are real.

- Green suggested using grain size or TOC and collecting more samples as ways to reduce variation.
- Stevens, as indicated in his response to Question #1, suggested defining spatial strata, probably based upon geography, rather than distance from shore. He also emphasized the value of being able to support the identification of spatial strata with physical characteristics, such as grain size and TOC.
- Warren-Hicks was uncertain of the need to reduce variation and suggested, as for Question #1, that comparisons of PCB distributions would be a better way to set sediment criteria.

4. Is Smith's method of defining upper bound concentrations adequate or are there other, better methods?

Again, the reviewers were divided or uncertain in their opinions of the efficacy of Smith's method for defining upper bound concentrations to help set sediment guidelines. One of the reviewers agreed with the method, one disagreed with the method and the third was not familiar with the method.

- Green supported the use of Smith's method.
- Stevens questioned the use of Smith's method in this context, because of its reliance on assumed population normality. Moreover, he suggested tolerance intervals may not be the best metric and recommended using confidence limits on a particular population percentile. He stated that the EMAP program "summarizes a population distribution and its associated uncertainty via a cumulative distribution function, or cdf" and recommended consideration of that method.
- Warren-Hicks was not familiar enough with the approach to offer an opinion.

Response to Comments

If the reviewers' comments were applied to a manuscript submitted for publication, the editor probably would suggest that the manuscript be reconsidered for publication after major revisions. Consequently, the PCB workgroup should evaluate the following responses to comments and recommendations for project completion with consideration for whether the evaluation of differences between offshore and nearshore background PCB concentrations and estimation of the nearshore concentration would still be useful, within the context of current CEP priorities and resources.

We agree with Stevens that analysis of the full dataset suggests that spatial factors, other than distance from shore, appear to be important determinants of PCB concentration. The analysis provided by Stevens and John Oram's recent kriging analysis of sediment PCBs and the reviewed report all clearly point to higher PCB concentrations along the eastern San Francisco and the Berkeley–Oakland shorelines, which suggest major sources of PCBs in those areas. If the Water Board is still interested in determining nearshore background concentrations of PCBs, the question becomes "How do we account for the major sources in estimating background PCBs?" Regardless of the reviewers' general aversion to removal of outliers, some method is needed for discounting samples obviously influenced by nearby sources or "hotspots". Moreover, with the benefit of hindsight, we suggest that the analytical procedures should have been applied in a different order. Such outliers, identified by whatever method is chosen, should be removed before determining whether distance from shore affects PCB concentrations. We originally suggested the use of the outlier analysis in JMP because it is objective and does not require decisions regarding what constitutes a source or "hotspot." While some of the reviewers questioned whether the iterative process would continue to find outliers, ad infinitum, this clearly was not the case in our results. Nevertheless, if such a method is performed again, we agree entirely with the reviewers that outliers should be determined using transformed data and we would agree to not use an iterative process. Geographical criteria also could be used to remove outliers by excluding samples within certain latitudinal or longitudinal ranges.

Reduction in sample variation is important to provide the tightest possible tolerance intervals or confidence limits on the selected population parameter. Based upon reviewers' comments, we could pursue obtaining NOAA/EMAP grain size and TOC data. Following outlier or "hotspot" removal, distance from shore, water depth, grain size and TOC could be tested for their effects on PCB concentrations using stepwise regressions and/or partial correlations.

The method used for determining sediment guidelines clearly requires further consideration. While there is a precedent for use of Smith's tolerance interval method in the San Francisco Bay area, it was not broadly supported by the reviewers.

Recommendations

We recommend a sequential process for completion of Task #4.10a.

1. First, the Water Board should determine whether an estimate of nearshore background PCB concentrations is still useful for implementation of the PCB TMDL.
    a. If not, then we recommend closing out Task #4.10a by making minor revisions to the project history and introduction to mention the peer review and the decision to not revise the report. This synopsis of peer reviewers' comments would be attached as an appendix.
2. If the Water Board determines that an estimate of nearshore background PCB concentrations is still useful, then two options are offered for consideration.
    a. Close out Task #4.10a and recommend another project to make use of analyses performed by Don Stevens as part of his peer review and the kriging analyses of John Oram, and/or
    b. Complete Task 4.10a by including RMP data since 2002 to increase the number of samples for determining nearshore PCB concentrations in areas that have been relatively unaffected by onshore sources, obtaining NOAA/EMAP grain size and TOC data and applying whatever "hotspot" removal procedure is chosen.

If Option 2b is chosen, we propose to retain Don Stevens to provide input for this discussion. For example, we need to know whether his analyses have determined conclusively that there is no difference between nearshore and offshore PCB concentrations or whether the recommendations merit consideration. If additional analyses are warranted, his input also would be helpful to support a discussion and decision by the PCB Workgroup regarding the method that should be used to remove the effects of "hotspots" on the dataset. As we see it, there are two choices, removal according to either geography or PCB concentration. Once that decision is made, the identified outliers should removed and the remaining data analyzed to determine whether PCB concentrations are related to any of the variables for which we can obtain data. These include distance from shore, water depth, sediment grain size and TOC. If distance from shore is not an important variable, there would be no need to proceed with further discussion or analyses and the report could be completed. If distance from shore is an important variable, the Workgroup could discuss whether to investigate the use of confidence limits for establishing sediment guidelines, instead of tolerance intervals. We estimate that revision of the report according to Option 2b could be completed within six–eight weeks at a cost of approximately $9,000, within the remaining funds for this task.

Attachment 1 – Reviewers' Comments

Review of **"Final Report: Existing Data on PCB Concentrations of Nearshore Sediments and Assessment of Data Quality"** , March 25 2005, by Roger H. Green

General

- It would have been nice to see the RFP or Scope of Work, in order to have seen where these objectives came from.
- In several places this report needs more clarity, explanation &/or justification for statements. I have tried to note those.
- I have reviewed the document and drafted comments before addressing the "peer review questions" that were provided. My answers to those questions are at the end of this review.

Specific

- **Introduction**
  When you say the *NOAA* and *EMAP* data were collected randomly, I assume this means an initial random site allocation and then sampling at those sites at any subsequent times.

- **Background**

  - 3rd sentence, l.6-8, (Specifically - - spots."): This is not clear, both re. what is meant and re. why.

  - 4th sentence, l.9: Is "submittal" correct? Should it be "submission"?

- **Approach**

  - p.2, 1st sentence, l.3: Why is "Risebrough" in parentheses after "Risebrough"?

  - p.2, general re. *NOAA* and *EMAP*: Are these two different programs or one program? It isn't clear. I think it's two but in the 2nd last paragraph there is a reference to "the *NOAA*/*EMAP* program" as if it is one program. This is done subsequently as well, e.g. top of p.3.

  - p.3, 1st par. ("**NOAA/EMAP**"), last sentence ("Moreover - - interference"): This needs more explanation.

  - p.3, 4th par., 1st sentence ("Random - - subsample."): This is true but it is out of any context. Why do we need to estimate population parameters from samples? Why isn't it sufficent to estimate the expected values for arbitrarily chosen sites? [I know what the argument is likely to be, but my point is that for many readers this statement will be an out of context declaration from the heavens.]

- p.3, 4th par., 3rd (last) sentence ("Before - - samples."): This needs explanation and clarification. *Why* is it necessary? And why the *sums* of the concentrations? Some explanation is needed here.

- **Findings**

  - p.5, 1st paragraph: Is this question an *a priori* one? For example, did it come out of the Scope of Work? (It isn't one of the stated project objectives.) As described here it sounds like an arbitrary question based on noticing a difference in the initial plot of the data. And why 500 m? That seems arbitrary too, and also apparently based on looking at the data. OK, there is nothing wrong with noting what you think you see in the data, e.g. in the initial plot, but a statistical test implies an *a priori* hypothesis that you collected the data to test – and it doesn't sound like that's what you have here.

  - p.6, 1st paragraph: There is no justification given for doing this as an "iterative process". I have never heard of it being done this way or seen it in a publication. If the author has, it should be cited. Boxplots are very Tukey'ish of course, and I don't remember this from Tukey. Might this process tend to keep re-creating "outliers"? I am not sure what one would end up with. How about trying it with simulated data? See next comment.

  - p.6, last paragraph: Why was it done in this order i.e. remove outliers and then log transform? I would have done it the other way around. If, as you say, the normal distribution without outliers is "in there" after log transformation then the "outlier box plots" should have been done on the log-transformed data, shouldn't they? Otherwise points at the extreme of the long right-hand tail of the skewed distribution (that will become normal after log transformation) will look like outliers. I'll bet. Try it. Simulate some normally distributed data X and try the "outlier box plots". Then "back-transform" by $Y=e^{bX}$. Then apply your "outlier box plots" on those data. I'll bet you find more "outliers" this time.

  - p.9, 1st paragraph: As I get to the end of this paragraph I have a vague sense of circular reasoning. Let me try to summarize the logic. There are lots of sites with lots of variation among them in PCB concentrations. A frequency distribution of concentrations suggests that some of them are outliers, in the sense that they are affected by "hot spots". Some are demonstrably from more impacted areas (external evidence). The relationships and patterns that you want to establish are best established using the data set with these "outliers" omitted. So you select the ones to be removed by an iterative outlier box plots process. The remaining data, log-transformed, are normally distributed. In these data you can still see geographic pattern, e.g. nearshore vs. offshore and especially where the nearshore are urban-influenced. OK, but I think that what is wanted is a clear explanation of why all this was necessary. Exactly what would have gone wrong if you had left all these "outliers" in the data? The closest to this that I can find is the first sentence at the top of p.6, which is that you want "background concentrations". But in the end, after all of the filtering and tweaking of the data, you still have sites ("the urbanized shores of San Francisco, Emeryville, and Lower South Bay") that are hot spots in the sense of having the highest concentrations and being near probable contaminant sources. So is this different in any conceptual way from what you started with? Of course you have shaved off the *most* extreme values, but that's just a matter of degree. It reminds me a bit of Garrison Keiller's Lake Wobegon where the children are all above average.

- p.10, mid-page paragraph: Yes there is a lot of evidence out there that adjusting for grain size or TOC (either by stratifying or by using ANCOVA) will reduce variation of organic (or organically bound) contaminant concentrations. Be careful about possible confounding though. Sediments typically get finer and higher in TOC with distance from shore (and increasing depth), and - as you have shown – contaminant concentrations are higher closer to shore. So there will be some correlations in there which have nothing to do with the tendency of fines to have more organics and thus more organic contaminants. You might artificially "adjust out" the distance from shore contaminant gradient. Or artificially enhance it. The bottom line is that the variation you should try to reduce by adjusting for grain size or TOC should be local variation (within the same distance from shore).

<u>Peer review questions</u>

- **Is the distinction between nearshore and offshore sediments supported by the data and associated analyses?** Well, the data certainly suggest a difference, and a descriptive presentation of the data helps show that. But I would stay away from hypothesis-testing statistics to show it – unless it is made clear (can legitimately be made clear) that this was a question/hypothesis to be tested from the beginning. It doesn't sound like it as presently written.

- **Are the methods used to remove outliers, in order to account for hot spots, adequate or are there other, better methods?** I have a lot of questions on this subject. See my specific comments.

- **Are there ways of reducing variation in nearshore sediments other than through analysis of additional samples or stratification according to grain size or TOC?** As I mention in my specific comments ANCOVA with TOC (or % silt) as a covariate could be done instead of stratifying. I didn't mention it but another way to reduce variation might be to take more samples (e.g. along a distance from shore contour) and physically pool them before analysis.

- **Is Smith's method of defining upper bound concentrations adequate or are there other, better methods?** I don't know of any better method.

Date: July 19, 2005
To: Paul Salop, Applied Marine Sciences, Inc.
From: Don Stevens
Subj: Review of "Final Report: Existing Data on PCB Concentrations of Nearshore Sediments and Assessment of Data Quality"

Your request for a review asked me to address several questions:

- Is the distinction between nearshore and offshore sediments supported by the data and associated analyses?
- Are the methods used to remove outliers, in order to account for hot spots, adequate or are there other, better methods?
- Are there ways of reducing variation in nearshore sediments other than through analysis of additional samples or stratification according to grain size or total organic carbon?
- Is Smith's method of defining upper bound concentrations adequate or are there other, better methods?

I'll address these points in turn.

Is the distinction between nearshore and offshore sediments supported by the data and associated analyses?

Response: No. The analysis tools that were used consist of a scatter plot of concentration versus distance, and an ANOVA based on splitting at 500m. While it is true that mean value for the nearshore concentrations are less than the offshore concentrations, that difference seems to be much more related to geographical location than distance from shore. Figure 1 is a plot of concentration versus distance, similar to Figure 2 in the report, except it's on a log-log scale. I've identified three groups of point in the figure; high pcb (green), low pcb (magenta), and really close to shoe (blue). (The point at 7.3 meters and concentration 95 is colored green, but belongs to both the blue & green groups.) The black line is a non-parametric fit of all the data, and shows little or no relationship between distance from shore and pcb concentration. The green line is a fit to the data omitting the blue and magenta points, and the blue line is a fit to data omitting the green and magenta points. The green line is the only one that suggests a relationship between distance and concentration. However, if we examine the

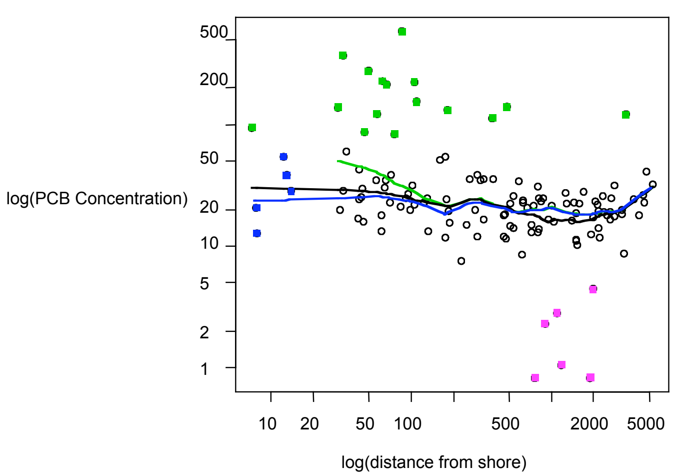

Figure 1

locations (Figure 2) of those three groups of points (the blue, green, and magenta), several features seem striking: (1) the low concentrations (magenta points) are primarily near the mouth of the Bay; (2) the high concentrations are primarily in a band a bit to the south of the Bay Bridge, and (3) the blue points seem to be marina/Fisherman's Wharf area of San Francisco. All three groups show substantial geographical clumping, as well as being identifiable clumps on the distance- concentration plot. To me, this suggests strongly that the significance of the nearshore versus offshore mean concentration is being driven largely by the group of green points, and has little to do with the distance from shore. The concentrations seem to be much more strongly related to geographic factors (or, rather, influences that are tied to location, such as industrial sites).

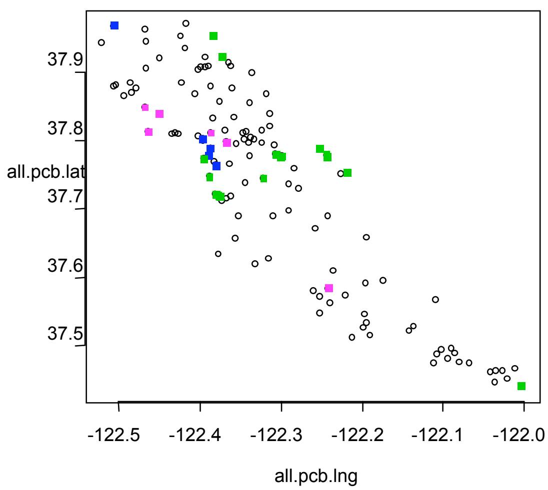

Figure 2

Are the methods used to remove outliers, in order to account for hot spots, adequate or are there other, better methods?

In general, I am not in favor of identifying and removing data points solely on the basis of their distance from the main body of data. Such automated procedures should be used to identify suspect points, and then be backed up by reference to ancillary data, e.g., location in an area near a known source. In particular, outlier removal should be used with extreme caution for concentration data, which tend to have long tails.

The expressed intent of the outlier removal exercise was to eliminate data points associated with "hot spots". As noted above, there is an identifiable area that contains an inordinate number of high pcb concentrations. The grouping of the high values strongly suggests that they are generated by a different process than the remainder of the observations. The outlier removal was carried out in the original scale, but all subsequent analyses were carried on in the log scale. I think it would make far more sense to do the entire analysis in the log scale. The results will likely be different.

The outlier removal method seemed to be partly driven by the desire to force the data to have a normal distribution. There is no particular reason to believe that pcb concentrations should have a normal (or log normal) distribution. The usual justification (that the observations are the sum (or product, for log normal) of a number of independent influences) doesn't seem to hold.

I realize that the Smith's tolerance interval procedure relies on having an underlying normal distribution, but I don't think that's justification for throwing out data until one gets a distribution such that the Shapiro test fails to label as non-normal.

Are there ways of reducing variation in nearshore sediments other than through analysis of additional samples or stratification according to grain size or total organic carbon?

The pcb data set has substantial spatial structure. I would think that the best way to better characterize the distribution of pcb concentration would be to define spatial strata. Nearshore/Offshore is one way of doing that, but I see little evidence that those strata are in fact related to concentration. To illustrate what I mean, Figure 3 is a histogram of all 127 pcb values. The distribution appears to be mixture of 3 distributions: one of low pcb values, a central, more or less symmetric distribution, and a distribution of high pcb values. That observation by itself would not be especially helpful; however, the high & low groups correspond to the high & low groups identified in Figure 2. In particular, they are, for the most part, spatially cohesive groups, so that there is some justification for identifying them as distinct population. A histogram of the remaining pcb values is shown Figure 4. The data conforms very well to a log normal distribution The distributions of the Nearshore & Offshore values are shown in Figure 5. The distributions show considerable overlap, although the Nearshore does have a higher mean values (mean log 3.16 versus 2.95). The distinguishing feature is really the difference in variance (0.22 versus 0.12, respectively). If the spatial strata can be linked to some physical characteristic (grain size, depth, deposition zones, industrial activity), so much the better.

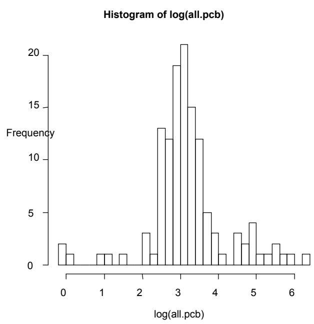

Figure 3

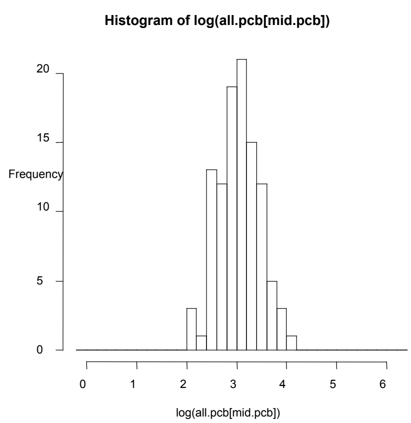

Figure 4

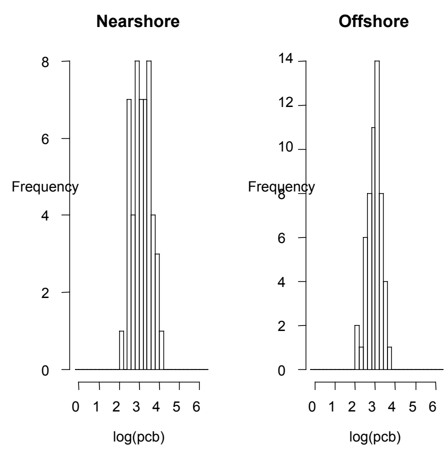

Figure 5

Is Smith’s method of defining upper bound concentrations adequate or are there other, better methods?

Smith's method relies on tolerance intervals, which don't seem to be quite the right concept. A *tolerance interval* is an interval that covers a fixed portion of a population with a specified level of confidence, which is not the same as a confidence limit on a particular population percentile.

For example, the USEPA's EMAP program routinely summarizes a population distribution and its associated uncertainty via a cumulative distribution function, or cdf. The EMAP cdf estimate gives estimates of population percentiles and the associated confidence intervals. One of the characteristics of the cdf estimator is that it will not return estimates that are outside the range of the data. Since the edited data set has only 50 points, an estimate of a 99th percentile would have little meaning. Software to calculate cdf's and associated confidence intervals is available for free download form EPA's Aquatic Resource Monitoring website at http://www.epa.gov/nheerl/arm/

Smith's method, in contrast, relies heavily on the assumed normality of the population. Under that assumption, it can produce estimates and confidence bounds for any percentile, even with small data sets. However, the validity of those estimates and bounds rests entirely on the normality assumption, and in this case, I think they are extremely conservative.

Review of:

Final Report
Existing Data on PCB Concentrations of Nearshore Sediments and Assessment of Data Quality
Project 4.10a

William Warren-Hicks

The following comments are provided on the above referenced report. Also, I have provided responses to the specific peer-reviewer charges.

Specific comments on the report

1. I suggest that clear statements of the issues and questions assessed within the report be provided early in the document. There seem to be several issues addressed by the report. And, each issue may require different data and associated statistical approaches. For example, I believe that the report attempts to address the following:

   (a) differences in PCB concentrations found in nearshore and offshore sites,
   (b) determination of baseline PCB concentrations, and
   (c) appropriate PCB discharge levels.

2. p. 3: I believe that a regression model is used to convert the 16 congener NOAA/EMAP sediment PCB concentrations into 40 congener equivalents. The report states that the NOAA/EPA data only is analyzed (i.e., the NOAA/EPA data are not combined with the RMP data). The report does not defend the need for this step, and I wonder why it is necessary. For example, for issue (a) above, the regression model conversion is not required. Furthermore, the use of a model adds an additional source of uncertainty (i.e., model prediction error) to the problem. For at least the analyses supporting issue (a), I would not convert the data. And, for other issues addressed by the report, I would justify the need for this step in the analysis.

3. p. 4: Tolerance intervals are calculated for specific population percentiles. The report does not justify this step, and again I'm wondering why this approach was chosen. Also, the report states that the tolerance interval calculations require normally distributed data. The data are clearly not normally distributed. Without further information on the method and procedures, I cannot comment on the tolerance interval calculations themselves. I wonder whether this approach provides sufficient answers to the issue under evaluation. If the issue is finding a PCB concentration such that a certain percentage of sites have lower values, then I suggest a probabilistic approach using all of the available data. I don't see the need to calculate 95% upper bounds on percentiles when there is a wealth of data that can be incorporated into a direct analysis of the issue.

4. p. 5: I agree that hypothesis testing of the PCB data (estimated or observed) should be conducted on the log-transformed data. The data are clearly log normal. Also, I think the box-and-whisker plot is effective. I would, however, provide an interpretation of the large degree of overlap between the nearshore and offshore site-specific PCB concentrations shown in the plot.

5. p. 6: I believe that the report switches issues and attempts to find a background PCB concentration. Unfortunately, the method used to eliminate outliers for the purpose of identifying a background concentration is highly flawed and should be avoided. There is an old adage in statistics: *never throw away data*. You may need to build a different probability model, but quality assured data are always valuable. The method itself is illogical. A data point that is not an outlier at round one could be an outlier in round two. With enough rounds, the investigator should eventually throw away most if not all of the available information.

   This issue is best attacked using reference site information. Or, develop a distribution of PCB concentrations and choose a cutoff to represent background.

   Again, the report incorrectly states that the data are normal.

6. p. 10: The information in Table 2 concerning tolerance intervals calculated for levels of %fines supports my earlier question about the appropriateness of the tolerance interval method.

Questions for peer-reviewers

1. Is the distinction between nearshore and offshore sediments supported by the data and associated analyses?

   No. However, it is difficult to know whether the changes suggested above will result in different findings. I suspect that, based on the graphics, that nearshore and offshore sites will have different mean PCB concentrations. However, I recommend that additional expanded statistical analysis be undertaken. For example, the investigators could examine the differences in PCB distributions between the two areas, rather than focus only on differences in the mean values.

2. Are the methods used to remove outliers, in order to account for hot spots, adequate or are there other, better methods?

   No. The method used to remove outliers is unacceptable.

3. Are there ways of reducing variation in nearshore sediments other than through analysis of additional samples or stratification according to grain size or total organic carbon?

   The question is a bit confusing. Statistical measures of variation simply reflect the data under analysis. And, generating new data many times simply increases the variation found in a specific data set because both high and low concentrations occur less frequently, and are identified with increased sampling effort. I recommend separating the notion of variance in the data from variance in a sufficient statistic of the sampling distribution. For example, the standard deviation around the mean value of a normally distributed random variable decreases as the square root of the sample size. However, the variance in the data can easily become larger with increasing sample size. The degree of uncertainty associated with the sample mean is interesting from several perspectives, for example, hypothesis testing on the means of two populations. But, for the purpose of setting PCB criteria, I believe that the distribution of PCB concentrations across sites is a better metric.

4. Is Smith's method of defining upper bound concentrations adequate or are there other, better methods?

The report does not provide enough information to judge this approach. I think that the method may be appropriate for some issues. However, since the report does not clearly state the question under evaluation, and no information is provided on the method or procedure, I can't judge the usefulness of the method nor suggest other approaches.