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EVALUATION OF MERCURY AND PCB TRENDS IN SAN FRANCISCO BAY REGION STORMWATER

BACKGROUND

San Francisco Bay TMDLs seek reductions in stormwater loads of PCBs (90%) and mercury (50%) in the next ~20 years.

Stormwater concentrations and loads have varied considerably among years and individual storms in monitored watersheds.

Data from watersheds previously monitored were analyzed to evaluate potential for detecting trends toward meeting TMDL goals

METHODS

Whole water grab samples were collected and analyzed for suspended sediments (SSC), PCBs, mercury, and other contaminants between 2002 and 2014 (TABLE 1) in five watersheds (FIGURE 1).

Samples were collected across a range of flows, but focused on moderate to high flow storms, with multiple grabs (typically 4 to 5) collected each event.

FIGURE 1
Map of monitored watersheds used in this analysis.

WATERSHED	SIZE KM2	YEARS SAMPLED	SAMPLE COUNT HG	SAMPLE COUNT PCB
Guadalupe River	236	2003-2006, 2009-2010, 2012-2013	198	127
Lower Marsh Creek	99	2011-2014	37	35
San Leandro Creek	8.9	2010, 2012-2014	51	51
Sunnyvale East Channel	14.8	2011-2012, 2014	43	46
Zone 4 Line A Hayward	4.2	2006-2010	115	86

TABLE 1
Watersheds monitored and sampling effort

RESULTS

PCB (FIGURE 2A) and mercury (FIGURE 2B) concentrations varied widely among grab samples. To categorize samples collected, we divided them into quartiles based on flow at the time of collection at each site: low, moderate, and high.

- Concentrations were usually lowest at low (minimum to 25th percentile lowest) flows for a site, reflecting low concentrations of contaminated sediment in the water.
- In moderate (26 to 75th percentile) flows, concentrations usually increased, with increasing contaminated suspended sediments.
- For the highest (76th percentile to maximum) flows for a site, concentrations would sometimes decrease, reflecting a washout effect.

FIGURE 2A

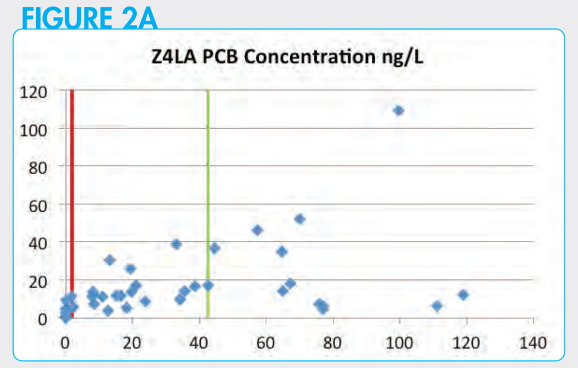
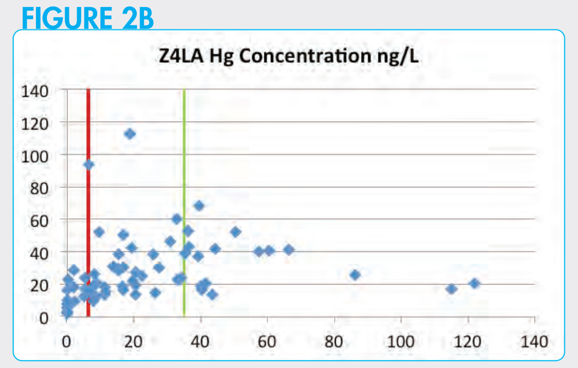


FIGURE 2B



FIGURES 2A and 2B
PCB (2A) and mercury (2B) whole water concentrations for Zone 4 Line A, 2006-2010. 25th (red) and 75th (green) percentile flows among grab samples collected shown as vertical lines.

Using calculated RSDs for particle ratios or concentrations, we can estimate grab sample counts needed to detect significant changes in PCBs and mercury for these watersheds.

- The "effect size" for a difference in population means is commonly expressed as Cohen's d statistic,

$$d = \frac{|\mu_1 - \mu_2|}{\sigma}$$

  the difference in population means sought (μ1-μ2) divided by the standard deviation (σ).
- Cohen's d for PCBs (for 90% decrease) and mercury (for 50% decrease) in the monitored watersheds is summarized in FIGURES 5A and 5B, with smaller d indicating more difficulty in detecting desired decreases.

FIGURE 5A

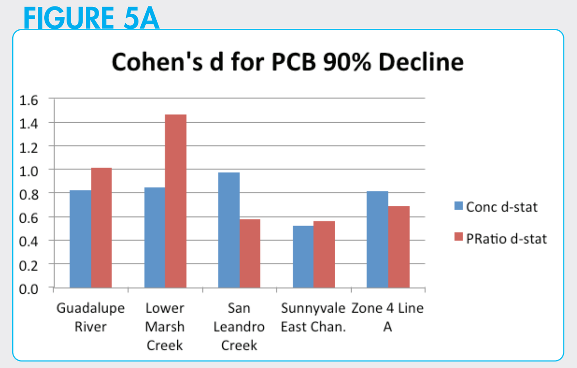
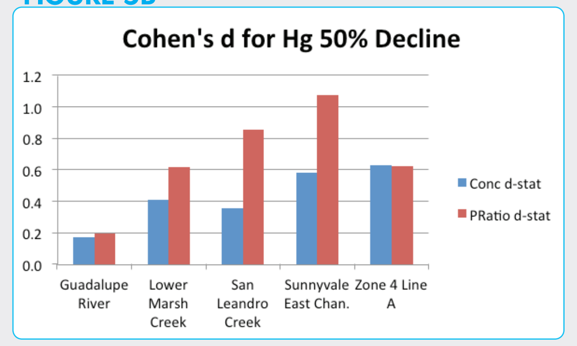


FIGURE 5B



FIGURES 5A and 5B
Cohen's d for PCBs and Mercury in Studied Watersheds. A higher d-statistic indicates greater potential for detecting differences. For PCBs, the d-statistic was moderate (over 0.5) to high (over 0.8) for both water concentration and particle ratio, assuming detection of a 90% decline desired. For mercury, a smaller decline of 50% yielded d-statistics of over 0.5 for particle ratio, except at Guadalupe.

Particle ratios (PCB (FIGURE 3A) or mercury (FIGURE 3B) concentrations, divided by SSC) provided an estimate of the contaminant concentration on the sediment particles in runoff assuming little of these occurred in dissolved phase during storm flow conditions.

- At low flows, particle ratios were highly variable due to a higher proportion of contaminants in the dissolved phase compared to particulate phase.
- Particle ratios were relatively stable at moderate flows, indicating transport of similarly contaminated sediment.
- At high flow rates, particle ratios often decreased, perhaps reflecting washout or dilution with less contaminated sediments.
- Particle ratios often varied less (lower relative standard deviation, RSD = stdev/mean) than water concentrations for any given location (FIGURES 4A and 4B).

FIGURE 3A

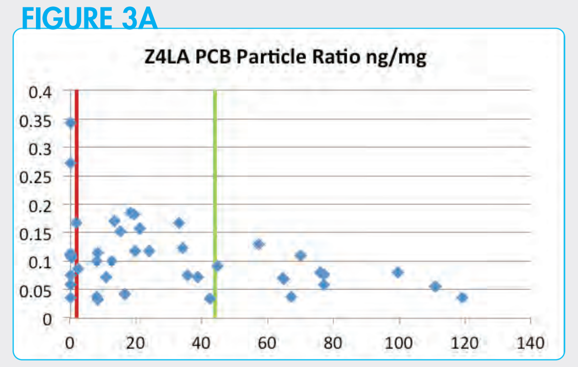
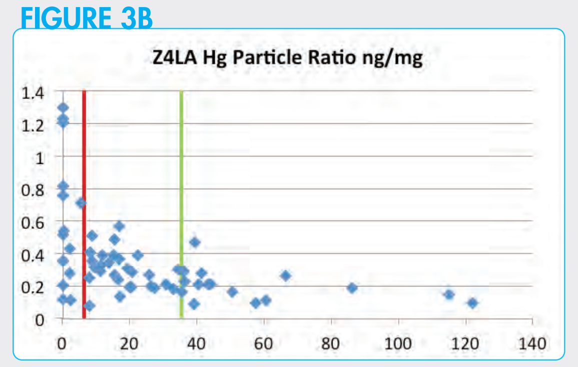


FIGURE 3B



FIGURES 3A and 3B
PCB (3A) and mercury (3B) particle ratios for Zone 4 Line A, 2006-2010. 25th (red) and 75th (green) percentile flows among grab samples collected shown as vertical lines.

FIGURE 4A

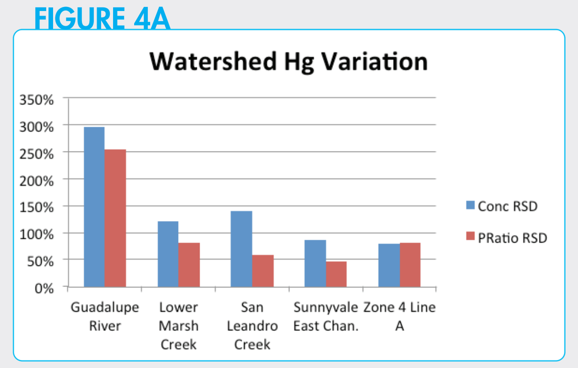
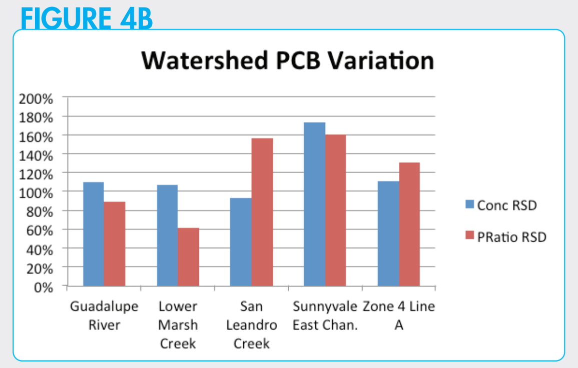


FIGURE 4B



FIGURES 4A and 4B
Variation in PCBs and Mercury in Studied Watersheds. For PCBs, particle ratios were sometimes more variable than water concentrations, but for mercury, particle ratios were almost always less variable.

- FIGURE 6 shows parameters with effect sizes of around 0.5 (green line) will likely require 50 grab samples per period (before and after) to detect reductions with 80% power (power is probability of detecting a true reduction for a given sample count and effect size). This represents 10 to 12 storms each period, if collecting 4 to 5 samples per event.
- For PCBs, the Cohen's d estimates were generally above 0.5, largely due to the proportionally large (90%) reduction desired, so less than 50 grab samples each period may be needed to get 80% or higher power.
- For most watersheds, mercury effect sizes were also moderate (around d=0.5) or higher, requiring 50 samples or less each period to detect a 50% decrease with at least 80% power.
- However, for mercury in the Guadalupe River, approximately 100 samples in each period would be needed to detect the desired 50% change with 80% power, due to highly variable characteristics within and among storms.

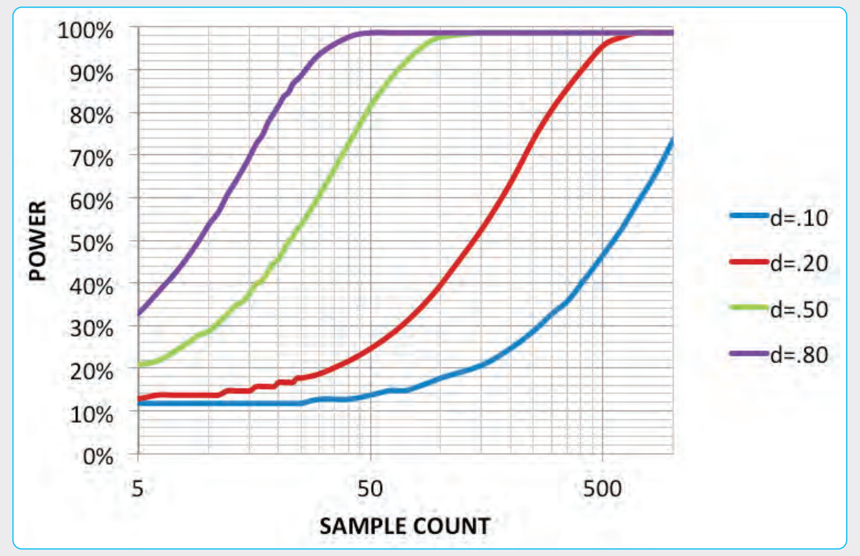


FIGURE 6
*Statistical power curves for a two-sample 1-tailed comparison of means (a = 0.05), plotted for a range of effect sizes (d statistic). For PCBs (for either concentration or particle ratio), the majority of cases fall between the moderate (green line) and high (purple line) effect size curves (d statistic >0.5 from **FIGURE 5A**). Mercury particle ratios are similarly above the green or purple line (d between 0.6 and 1.1 from Figure 5B), aside from Guadalupe, which is nearer the red line (d=0.2)*

SUMMARY

This preliminary analysis of previously collected data on water concentrations and particle ratios suggests that desired decreases of 90% for PCB loads and 50% for mercury loads may be detectable for most watersheds with a moderate level of effort. The effect sizes (Cohen's d statistic) for these PCB and mercury indicators suggest 50 or fewer grab samples collected over about a dozen events each for before and after periods may be enough to detect the desired changes.

FUTURE WORK

A number of other trends indicators are also being considered for evaluation of management effectiveness including loads and bed sediment concentrations. Indicators will be evaluated for the potential to identify trends at three scales: the region as a whole, single watersheds, and areas of management focus.To increase the potential for detecting a trend while limiting monitoring costs, a number of constraining factors may be evaluated, including selecting specific flow characteristics, various composite designs across storms and seasons, land use groupings, and other methods. For example, a constraint considering only grab samples collected during moderate (25th to 75th percentile) flows resulted in moderate improvements in detection power (~25 to 50% increase in Cohen's d for Z4LA).

Future analyses will also evaluate alternative designs for trends monitoring, depending on the types and timing of management actions planned, and expected resultant watershed responses (e.g., monitoring at a prescribed periodicity, reactionary (after meeting some rainfall or runoff thresholds), before and after management implementation, and other considerations.

REGIONAL MONITORING PROGRAM FOR WATER QUALITY IN SAN FRANCISCO BAY
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