PS/SS: Pentachlorophenol in San Francisco Bay tributary water and sediments: Implications for dioxin loading

Estimated Cost: $7,200-17,850
Oversight Group: Emerging Contaminants Work Group
Proposed by: Don Yee and Susan Klosterhaus, SFEI

Background

Pentachlorophenol (PCP) was one of the most widely used biocides in the U.S. prior to regulatory actions in 1987 to cancel and restrict uses aside from wood preservation. Current commercial uses of PCP include pressure or thermal treated wood used for utility poles, fences, shingles, walkways, building components, piers, docks and porches, and flooring and laminated beams. Agricultural PCP uses include wood protection treatment for buildings/products and fencerows/hedgerows. There are currently no registered residential uses. PCP enters the environment through evaporation from treated wood surfaces, industrial spills, and disposal at uncontrolled hazardous waste sites. It has been detected in air, stormwater, and sediment/soil and is characterized as a moderately persistent chemical. PCP has also been detected in fish and humans but tissue concentrations are usually low. The EPA has determined that PCP is a probable human carcinogen.

Because polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are impurities in PCP technical mixtures, PCDD/F contamination as a result of PCP use is a potential concern. Samples of technical-grade PCP manufactured during the mid to late 1980s contained about 1.7 mg TEQ/kg, with PCDD/F concentrations in the mixtures ranging 290-3,200 mg/kg. The TEQ content of PCP manufactured since 1988 is estimated to be about 0.6 mg TEQ/kg. A recent study found that dioxins can be formed from PCP in clay (Gu et al 2008), while another study linked dioxin formation with the presence of PCP and other pesticide-derived dioxin precursors in soil samples (Holt et al. 2008). In both studies octachlorodibenzodioxin (OCDD) was formed -- this is also the congener that typically dominates the dioxin profile in water and sediment samples. Understanding the contribution of PCP-associated dioxin to the total dioxin concentrations in the environment would assist in efforts to reduce dioxin exposure to wildlife and people.

Applicable RMP Management Questions (MQ) and Study Objectives

MQ1. Are chemical concentrations in the Estuary at levels of potential concern and are associated impacts likely?

- A: Which chemicals have the potential to impact humans and aquatic life and should be monitored?
- B: What potential for impacts on humans and aquatic life exists due to contaminants in the Estuary ecosystem?

MQ2. What are the concentrations and masses of contaminants in the Estuary and its segments?

- A: Do pollutant spatial patterns and long-term trends indicate particular regions of concern?

MQ3. What are the sources, pathways, loadings, and processes leading to contaminant-related impacts in the Estuary?

- A: Which sources, pathways, and processes contribute most to impacts?

The primary objective of this study is to assess the contribution of PCP-associated dioxin to the total dioxin concentrations in Bay surface waters and sediments (MQ3A). This study will also provide information on whether PCP concentrations in Bay sediments and surface water are within range of effects concentrations and if spatial patterns exist (MQ1A, B and MQ2A).

Relationship of the Study to the ECWG Priority Question

The Emerging Contaminant workgroup is focused on answering the question: "What emerging contaminants have the greatest potential to adversely impact beneficial uses in the Bay?" PCP was not detected in a previous analysis of Bay surface waters (Yee 2003) though detection limits were high (1 and 10 µg/L). PCDD/Fs have been detected in Bay surface waters, sediment, and fish (Yee 2003; Connor et al. 2004). The USEPA placed dioxins in San Francisco Bay on the California list of impaired waters and determined they are a high priority to address. The San Francisco Regional Water Quality Control Board has subsequently begun the process to develop a water quality attainment strategy (e.g. a TMDL), which will include an assessment of dioxin sources. An SFEI report (Connor et al. 2004) previously found that PCP-treated utility poles may constitute the largest source of dioxin releases and reservoir of dioxins in the Bay Area. Estimation of the significance of PCP-associated dioxin as a source of dioxin will provide valuable information useful for managing dioxin sources and subsequent transfer to the Bay.

Approach

Planned monitoring of PCDD/Fs in tributary and bay surface waters and sediment as part of the RMP Dioxin Strategy provides an opportunity to concurrently assess the potential contribution of PCP use to dioxin concentrations in the Bay. Analysis of PCP and PCDD/Fs in the same samples allows chemical comparisons. In coordination with the Dioxin Strategy sampling plan, 16 tributary water samples collected in winter 2009-2010 will be analyzed for both PCP and PCDD/Fs.

Using the PCDD/F congener profile of a technical PCP formulation as a guideline, PCP and PCDD/F concentrations in Bay samples will be compared to estimate the potential contribution of PCP-associated dioxin to the total PCDD/F concentrations locally. AXYS Analytical can analyze PCP in samples combined with organochlorine pesticides (OCPs), or PCBs at a cost of $825 per sample. For samples already being analyzed for PCBs or OCPs by LRMS, the lab estimated incremental cost to add PCP is $50/sample, but we likely require HRMS which would add $150-200/sample. A proposed budget is presented below. Funding for PCDD/F analysis in these samples is already allocated as part of the RMP Dioxin Strategy.

Optionally, some or all (47) of the Bay sediment samples planned for PCDD/F analysis can be analyzed for PCP, but because AXYS is not the primary RMP laboratory for organics analysis in sediment, PCP could not be added onto existing PCB/OCP analyses. Costs would therefore be ~$450/sample for PCP alone by LRMS, or ~$500/sample for PCP combined with PCBs or OCPs. PCP combined with PCBs or OCPs by HRMS would cost ~$950-1000/sample. Potentially, EBMUD could be encouraged to develop a HRMS method to quantitate PCP with other organochlorines they already report (whether PCBs or OCPs). Although the final cost of adding this analyte is unknown, it is likely around ~$150/sample. Including sediment analysis

increases project and data management costs (another lab/contract, and more sample results) but does not proportionally increase work in data analysis and reporting.

Deliverable

The product of this pilot study would be a short report or technical memo (<10 pages) evaluating the likely bounds of PCP derived PCDD/Fs, estimating likely maximum and minimum results expected, and implications for PCP as being either a large or small portion of total PCDD/F sources.

Proposed Budget

Task	**Estimated Cost**
Tributary water PCP analysis (16 sites) x $150 (samples already analyzed for PCB/OCP)	$ 2400
Project Management (20 hrs)	$ 2400
Data Management (20 hrs)	$ 1200
Data analysis and reporting (10 hrs added to dioxin reporting))	$ 1200
Shipping, miscellaneous expenses (none for PCB/OCP samples)	$
Total	**$ 7200**
Optionally	
Sediment PCP analysis (47 sites) x $150 (samples for PCB/OCP if done by EBMUD)	*+$ 7050*
Project/Data Management+Reporting	*+3600*

References

Gu et al. 2008. Octachlorodibenzodioxin Formation on Fe(III)-Montmorillonite Clay. Environ. Sci. Technol. 42:4758-4763.

Holt et al. 2008. Assessing Dioxin Precursors in Pesticide Formulations and Environmental Samples As a Source of OCDD in Soil and Sediment. Environ. Sci. Technol. 42:1472-1478.

Connor et al. 2004. San Francisco Estuary Institute . Dioxins CMIA report prepared for the Clean Estuary Partnership.

Yee, D. 2003. California Toxics Rule Monitoring Report San Francisco Estuary Institute.