Special Study Proposal: Bisphenol Compounds in Ambient Bay Water

Summary: Bisphenols are a class of widely used endocrine-disrupting compounds, commonly found in polycarbonate plastics and epoxy resins and frequently detected in many environmental matrices. Bisphenol A (BPA) is a high-production volume compound, and use volumes of several BPA alternatives have increased in recent years. This study would screen ambient water samples from San Francisco Bay for 16 bisphenol compounds. The results of this initial screening will inform the classification of bisphenols within the RMP's tiered risk framework for contaminants of emerging concern (CECs).

Estimated Cost: $50,000

Oversight Group: ECWG

Proposed by: Jennifer Sun and Rebecca Sutton (SFEI)

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	*Due Date*
Task 1. Project Management (manage subcontracts, track budgets)	2017-2018
Task 2. Develop detailed sampling plan	Spring 2017
Task 3. Field sampling – ambient Bay water	Summer 2017
Task 4. Lab analysis	Fall-Winter 2017
Task 5. QA/QC and data management	Spring 2018
Task 6. Draft technical report	9/30/18
Task 7. Final technical report	12/31/18

Background

Bisphenols are a class of widely produced endocrine-disrupting chemicals that are used in the manufacturing of polycarbonate plastics and epoxy resins, as well as various other products, including as developers applied on thermal receipt paper. Bisphenol A (BPA), the most widely used and studied bisphenol, is one of the highest production volume chemicals in the world (4.6 million tons in 2012), and can be found in products ranging from automotive and electrical equipment, linings for food containers and drinking water pipes, and thermal paper used in receipts such as those used at ATMs, gas stations, restaurants, and grocery stores (MRC, 2014; EPA Action Plan, 2010).

Leading up to California state and federal bans on BPA in certain feeding containers for children and babies in the early 2010s, several major manufacturers began replacing BPA in their products with alternative compounds – most commonly, Bisphenol S (BPS) and bisphenol F (BPF), two of the most structurally similar bisphenols to BPA. Measured concentrations of BPS and BPF in human urine in the United States appear to reflect that use volumes of these alternative bisphenol compounds have been increasing in recent years (Ye et al., 2015).

At the same time, concentrations of BPA use in other materials remain high. Recent studies have found high concentrations of both BPA and BPS (for example, 14 mg of BPA on a 3.125 x 12 in receipt) on thermal receipt papers, on which these compounds are used as developers (Apfelbacher, 2014). Bisphenols applied to the surface of the receipt paper are not bound to a polymer, and thus are very transferrable both to humans and the environment. Studies have shown that concentrations of BPA can be up to 10 times higher in the urine of humans that have handled BPA-coated receipt paper for just four minutes (Hehn, 2015; Hormann et al., 2014).

These compounds have been linked to a variety of potential negative health impacts in humans and wildlife, including estrogenic and genotoxic effects (Rosenmai et al., 2011; OEHHA, 2012; Lee et al. 2013). In 2011, a new aquatic hazard assessment lowered an aquatic health threshold (Predicted No Effects Concentration (PNEC)) for BPA from 100 ug/L to 0.06 ug/L, based on an assessment of 61 studies evaluating the ecotoxicological endpoints of survival, growth, development and reproduction in freshwater and marine organisms (Wright-Walters et al., 2011). This suggests that many previous measurements of BPA with method detection limits (MDLs) higher than 0.06 ug/L may no longer be adequate for assessing the risk of BPA toxicity.

Empirical data on the toxicity and environmental fate of most alternative bisphenol compounds are scarce, but a 2015 USEPA review of BPA and 4 bisphenol alternatives (BPS, BPF, BPC, BPAP, BPPH) in thermal paper gave the alternatives "Moderate" or "High" hazard designations for most human health or aquatic toxicity endpoints, and identified no clearly safer alternatives to BPA (US EPA, 2015). A review conducted by Biomonitoring California (a joint program of the California Department of Public Health, Department of Toxic Substancse Control, and Office of Environmental Health Hazard Assessment) in 2012 also predicted that many of the alternatives such as Bisphenol A-diglycidyl ether (BA-DGE), Bisphenol AF (BPAF), Bisphenol AP (BPAP), Bisphenol B (BPB), Bisphenol C (BPC), Bisphenol F (BPF), and Bisphenol PH (BPPH) were likely to be toxic or very toxic to aquatic organisms, according to US EPA criteria (OEHHA, 2012).

Although BPA and several of its alternatives photo- and biodegrade relatively quickly under aerobic conditions, degradation for BPA, BPE, BPB, and BPS has been shown in laboratory experiments to be slow under anaerobic conditions, such as in anoxic estuarine sediments (Voordeckers et al., 2002; Ike et al., 2006). Biodegradation of BPS in particular has also been shown in laboratory experiments to be slow in both artificial and field-collected seawater (no degradation detected in 30 days; Danzl et al., 2009). Several bisphenol alternatives evaluated by the US EPA's Persistent, Bioaccumulative and Toxic (PBT) Profiler are predicted to be "persistent" or "very persistent" in water (BA-DGE and BPAF) and sediment (BA-DGE, BPAF, BPAP, BPB, BPC, BPF, BPAP, BPS) according to US EPA criteria (OEHHA, 2012). Furthermore, regardless of degradation potential, the high production volume of these compounds suggests a constant source entering the environment, which may render even those compounds that degrade quickly a potential exposure concern for wildlife. Bisphenols are regularly detected in estuarine and marine waters, wastewater effluent and sludge, stormwater runoff, wildlife, sediment, freshwater bodies, groundwater, rainfall, air, and other environmental matrices (Flint et al., 2012; Huang et al., 2011; Cargheni, 2015), as well as human urine samples (BPA, BPS, BPF, and BPAF) (Ye et al., 2015; Liao et al., 2012).

The RMP had previously analyzed ambient Bay water samples for BPA (but no alternatives) as part of a broader pharmaceuticals scan in 2010 (Klosterhaus et al., 2013), but the detection limit used in the analysis was 2.5 ug/L, well above the more recently established 0.06 ug/L PNEC (Wright-Walters et al., 2011), because the method is not specifically optimized for BPA detection. As a result, bisphenols are currently classified as an emerging contaminant of Possible Concern (Tier 1) in the RMP's CEC risk and management action framework, due to a lack of monitoring information (Sutton and Sedlak 2015). In 2014, the Emerging Contaminants Workgroup suggested that staff prepare a proposal to monitor for a broader panel of analytes that would include all possible bisphenols in production and amenable to analysis.

RMP has been working with laboratories to support better method detection limits for bisphenols and we believed that the methods are now robust enough to conduct a study to evaluate this class of compounds in the Bay. Most recently, the RMP participated in a pro-bono collaboration with Dr. Da Chen at Southern Illinois University to support development of a method for analyzing for a suite of bisphenol compounds in ambient Bay water samples. Method development is now complete, and provides the broadest assessment of bisphenols available.

This proposal outlines a study to monitor for BPA and 15 alternative bisphenol compounds in ambient Bay water. The results from this study will help indicate the level of risk posed by BPA and alternative bisphenols to wildlife in the Bay.

Study Objectives and Applicable RMP Management Questions

This study will provide data essential to determining the placement of bisphenols in the RMP's tiered risk framework, which guides monitoring and management actions on emerging contaminants in San Francisco Bay (Sutton et al. 2013; Sutton and Sedlak 2015). While limited monitoring data on bisphenols in the Bay is available, use volumes suggest that bisphenols are ubiquitous in the environment. Management questions to be addressed by this study are the same as those of the overall RMP program, as shown in Table 1.

Table 1. Study objectives and questions relevant to RMP management questions.

Management Question	Study Objective	Example Information Application
1) Are chemical concentrations in the Estuary at levels of potential concern and are associated impacts likely?	Compare measured concentrations to toxicity thresholds.	Do findings suggest BPA and other bisphenols should be classified as moderate concern, low concern, or possible concern emerging contaminant within the RMP's tiered risk framework? Do the data indicate a need for management actions?
2) What are the concentrations and masses of contaminants in the Estuary and its segments? 2.1 Are there particular regions of concern?	Compare levels in different embayments.	Do specific embayments or regions appear to have greater levels of contamination?
3) What are the sources, pathways, loadings, and processes leading to contaminant-related impacts in the Estuary? 3.1. Which sources, pathways, etc. contribute most to impacts?		
4) Have the concentrations, masses, and associated impacts of contaminants in the Estuary increased or decreased? 4.1. What are the effects of management actions on concentrations and mass?		
5) What are the projected concentrations, masses, and associated impacts of contaminants in the Estuary?		

In addition to addressing questions 1 and 2, the study will address the established emerging contaminants priority question: What emerging contaminants have the potential to adversely impact beneficial uses of the Bay? BPA is currently listed as a contaminant of possible concern (Tier 1) in RMP's tiered risk and management action framework due to a lack of information; findings will allow the ranking of this chemical to be reevaluated.

Approach

Ambient Bay Water Sampling

BPA and other bisphenols have been detected in ambient estuary water from urbanized estuaries around the world, where they may pose a threat to both human and wildlife health. BPA concentrations in Puget Sound, a comparably urbanized estuarine system relative to the San Francisco Bay, were found to range from 0.0028 – 0.0043 ug/L. At these concentrations, BPA was shown to accumulate up to concentrations of 0.041 ug/g (wet weight) in salmon and 0.0045 ug/g in sculpin that use the estuary (Meador et al., 2015). Ambient water concentrations measured in the Yangtze River Estuary and East China Sea ranged from 0.00098 to 0.043 ug/L during the wet season (Shi et al., 2013). These results suggest that while ambient Bay water concentrations would be expected to be low relative to source concentrations, estuary water BPA concentrations have been measured on the same order of magnitude as the 0.06 ug/L BPA PNEC in other urban estuary systems, and it is possible that such levels of bisphenol pollution are present in the Bay as well.

Bay water sample collection will take place in the summer of 2017 as part of the RMP's regular Status and Trends water monitoring cruise. Grab samples of ambient Bay water (4 L, amber glass, 3 day hold time) will be collected at 22 Bay sites, including the 5 historical fixed sites and 17 random sites (three or four samples in each segment of the Bay). One field replicate and one field blank will also be collected.

Analytical Methods

BPA is moderately hydrophilic and bioaccumulative (log Kow = 3.4). In measurements of surface water and wastewater samples, BPA has been predominantly measured in the dissolved water fraction compared to particulates (Kalmykova et al. 2013). However, other BPA alternatives are predicted to more strongly adhere to sediments (log Kows: BPAF 4.47; BPB 4.13; BPAP 4.86; BPC 4.73) (OEHHA 2012). Thus, water samples will be collected and analyzed in total phase, including separate analyses for the dissolved and particulate fractions. Findings from this study may suggest whether or not future monitoring of sediment is warranted.

Total water samples will be analyzed by Dr. Da Chen of Southern Illinois University using a highly sensitive liquid chromatography–electrospray ionization(-)-triple quadrupole mass spectrometry (LC–ESI(-)-QQQ-MS/MS) based analysis method. This method will include analysis of bisphenol A, as well as suite of alternative bisphenol compounds, including bisphenols B, C, AF, AP, BP, M, E, P, F, PH, Z, G, TMC, and C-dichloride, as well as bisphenol A diglycidyl ether (BPA-DGE). Limits of detection are typically in the range of 0.1-0.5 ng/L, except for BPA-DGE (0.8 ng/L) and BPA-dichloride (1.0 ng/L). Per sample analytical costs are estimated to be $500.

Reporting

The following budget represents estimated costs for this proposed special study (Table 2). Efforts and costs can be scaled back by reducing the number of sites or matrices sampled.

Table 2. Proposed Budget

Task	Estimated Cost
Labor*	
Project Planning	$2,000
Field Work – 2017 Status & Trends Water Cruise	$0
Data Management	$2,000
Analysis & Reporting	$31,500
Subtotal	**$35,500**
Subcontracts	
Southern Illinois University – 25 samples @ $500/sample	$12,500
Subtotal	**$12,500**
Direct Costs	
Equipment	$100
Shipping	$1.700
Travel	$200
Subtotal	**$2,000**
Grand Total	**$50,000**

Budget Justification

Field Costs
Field costs are minimized through sample collection during the RMP's 2017 Status and Trends water sampling cruise.

Laboratory Costs
Analytical costs per sample are estimated to be $500. For 24 samples, including one field replicate and one field blank, the total analytical cost will be $12,000.

Data Management Costs
To minimize data management costs, data will undergo QA/QC by the laboratory and project PI, but will not formatted and uploaded to CEDEN. If bisphenol compounds are incorporated into standard RMP sampling events, this data may be added to CEDEN at a later date.

Reporting

Results will be provided to the RMP committees in a technical report, which will be distributed for internal RMP review only prior to the publication of a peer-reviewed journal manuscript. A draft of the report will be provided for review by 9/30/18. Comments will be incorporated into the final report by 12/13/18.

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