Special Study Proposal: Bisphenols in Wastewater and Sediment; Sunscreens in Wastewater

Summary: Bisphenols are a class of widely used, synthetic, 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 included on California's Prop 65 List (OEHHA, 2019). Although production of BPA is still increasing, several BPA analogues are rapidly replacing BPA in industrial practices and consumer products. The ECWG classified bisphenols as Moderate Concern in the RMP tiered framework after reviewing results from 2017 Bay water samples; detections of both BPA and bisphenol S (BPS) were in the range of a protective toxicity threshold for BPA (60 ng/L). While only BPA and BPS were detected in Bay waters, some bisphenols have chemical properties that suggest they are more likely to favor other environmental matrices such as sediment. We propose a screening study to quantify levels of sixteen bisphenol compounds in the wastewater effluent pathway and in Bay sediment.

Additionally, recent qualitative work has indicated presence of one sunscreen active ingredient, oxybenzone, in Bay water and wastewater effluent. Oxybenzone and other sunscreen active ingredients have been shown to cause adverse effects, such as endocrine disruption in fish and bleaching on coral reefs. The City of San Francisco is considering a resolution to examine the occurrence and potential impacts of some of these compounds. This sunscreen screening study will help assess whether they may be a potential concern for the Bay.

This study is broken down into three tiered design options of increasing scale based on available project funding. Option 1 would only include a screening of bisphenols in effluent. Option 2 would leverage sample collection costs and would include analysis of both bisphenols and sunscreens in wastewater effluent. Option 3 would including bisphenols and sunscreen in effluent as well as analysis of bisphenols in archived sediment samples.

Estimated Cost:	Option 1: Bisphenols in effluent: $51,300 Option 2: Bisphenols and sunscreens in effluent: $83,800 Option 3: Bisphenols and sunscreen in effluent, plus bisphenols in sediment: $104,400
Oversight Group:	ECWG
Proposed by:	**Bisphenols:** Ila Shimabuku and Rebecca Sutton (SFEI) **Sunscreens:** William Mitch and Djordje Vuckovic (Stanford University); Meg Sedlak and Diana Lin (SFEI)
Time Sensitive:	No

Proposed Deliverables and Timeline

Deliverable	*Due Date*
Task 1. Field collection of effluent samples	Summer 2020
Task 2. Laboratory analysis of samples	Fall 2020–Winter 2021
Task 3. QA/QC and data management	Spring 2021
Task 4. Draft technical report(s)	Summer 2021
Task 5. Final technical report(s)	Fall 2021

Background

Bisphenols

Bisphenols are a class of high production, endocrine-disrupting chemicals that are used in the manufacturing of products such as polycarbonate plastics and epoxy resins. Bisphenol A (BPA), the most widely used and studied bisphenol, is one of the highest production volume chemicals in the world, at an estimated at 8 million tons per year. It is also listed on California's Prop 65 List for developmental and female reproductive toxicity (OEHHA, 2019).

Leading up to the 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 other bisphenols that are structural analogues to BPA. This increase in substitution and production of BPA analogues is expected to continue increasing (Rochester and Bolden, 2015).

Bisphenols are mobile and 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). A review conducted by Biomonitoring California in 2012 predicted that many of the alternatives such as 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). The European Union's marine predicted no effect concentration (PNEC) for BPA is 150 ng/L (Bakker et al. 2016), but is thought by some to be too high due to omission of a more sensitive species during derivation. In 2011, a new assessment established a PNEC for BPA of 60 ng/L, based on an assessment of 61 studies evaluating the ecotoxicological endpoints of survival, growth, development, and reproduction in 24 freshwater and marine organisms (Wright-Walters et al., 2011).

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 aquatic life. Empirical data on the toxicity and environmental fate of most alternative bisphenol compounds are scarce. In 2012, the State Water Resources Control Board's CEC Science Advisory Panel published a CEC monitoring guidance document that recommended monitoring BPA in wastewater effluent, stormwater, and ambient embayment waters (Anderson et al., 2012). This recommendation was based on the 60 ng/L PNEC, as well as high environmental concentrations previously measured in California.

The RMP previously analyzed open Bay water for BPA and 15 analogues in samples collected in 2017 (Shimabuku et al., 2019). BPA and BPS were detected in many samples with total water concentrations ranging from 1.5-35 ng/L and <1-120 ng/L, respectively. Most other bisphenol analogues were not detected in Bay water in the previous study (below method detection limits of 0.7-2.7 ng/L; Shimabuku et al., 2019). However, some of these analogues are more hydrophobic and likely to be more bioaccumulative or may partition to sediment (log K_{OW}s range from 1.2 (BPS) to 7.2 (BPPH); OEHHA 2012; Wang et al. 2017). Ambient Bay water monitoring alone may not provide a comprehensive screening for the presence of various bisphenols in the ecosystem. It may be more appropriate to examine other matrices as well as likely pathways to assess presence in the Bay.

This proposal outlines a study to monitor BPA and 15 alternative bisphenol compounds in wastewater effluent and archived Bay sediment. Concurrent analysis of bisphenols stormwater is underway as part of the multi-year stormwater CECs study. Sport fish samples from 2019 will be archived for potential future analysis of bisphenols. The results from this study will be used to further inform and/or refine the placement of bisphenols in the RMP's tiered risk framework. Findings may also suggest the need for additional ecotoxicity or human-health thresholds.

Sunscreens

Ultraviolet (UV) radiation filters (sunscreens) are chemicals designed to absorb or reflect harmful solar radiation, and are used in products as diverse as personal care products (e.g., sunscreens, lotions, and cosmetics) and industrial products (e.g., insecticides, plastics, and paints) to mitigate deleterious effects of sunlight and extend product life.

At present, the FDA has approved 16 chemicals for sunscreen protection. UV filter sunscreens are also additives to plastic. These chemicals are widely detected in the environment, and some may biomagnify (Gago-Ferrero et al., 2018). These chemicals are also potential endocrine disruptors (Balazs et al., 2016), and there is increasing concern about their ecotoxicity (Kunz et al., 2006; Balmer et al., 2005; Downs et al., 2016), particularly for oxybenzone.

Oxybenzone (also known as benzophenone-3 or BP-3) is of high concern due to its wide use in the U.S., detection in the environment, and its potential for endocrine disruption. In a recent study of personal care products, oxybenzone was detected in over 80 percent of the products analyzed (Liao and Kannan, 2014). Oxybenzone is a high production volume chemical that is manufactured or imported into the U.S. in amounts greater than one million pounds per year. Oxybenzone has been detected in surface water, treated wastewater, invertebrates, fish, bird eggs, and coral tissue (Liao and Kannan, 2014; Mao et al., 2018; Fent et al., 2010; Kim et al., 2014). It has been identified as an endocrine disruptor in fish, causing vitellogenin induction in male fish, among other effects (Coronado et al., 2008; Kunz et al., 2006; Kim et al., 2014). In a laboratory study of zebrafish, a significant skewing of the sex ratio towards females and effects on gonad maturation were observed (Kinnberg et al., 2015).

For aquatic organisms, the main exposure route is through direct wash-off into surface waters during recreational activities, and indirect discharge of these chemicals from wastewater treatment facilities to surface waters.

Due in part to the potential for endocrine disruption and other deleterious effects in fish, and the potential for these compounds to cause coral bleaching, there is currently regulatory interest in restricting their use. The State of Hawai'i and the City of Key West, FL, recently banned the sale of sunscreens containing oxybenzone and octinoxate due to exceedances of an ecological toxicity threshold for coral in water. The City of San Francisco is considering a resolution stating concerns about sunscreen chemicals oxybenzone, octinoxate, and butylparaben (a preservative) that are implicated in potential endocrine disruption of fish. City officials are interested in knowing whether these chemicals are detected in the Bay. Meanwhile, newly proposed sunscreen regulations from the FDA indicate there is insufficient safety information for the agency to determine whether oxybenzone, octinoxate, and ten other active ingredients are "generally recognized as safe and effective." This project will provide information on an important pathway by which sunscreens may be introduced into the Bay.

Study Objectives and Applicable RMP Management Questions

Table 1. Study objectives and questions relevant to CEC management questions. Bisphenols objective and examples are shown in plain text whereas sunscreen objectives and examples are shown in italics.

Management Question	Study Objective	Example Information Application
1) Which CECs have the potential to adversely impact beneficial uses in San Francisco Bay?	Characterize levels of bisphenols in wastewater effluent and Bay sediment. *Characterize levels of sunscreens in wastewater effluent.*	Are detections observed previously in Bay water (BPA, BPS) capturing all bisphenols in the Bay environment? Is there a need to develop ecotoxicity or human health toxicity thresholds for bisphenols other than BPA? *Are there detectable loads of sunscreen chemicals in Bay effluent? Do sunscreen chemicals warrant monitoring in Bay waters to evaluate potential risk to the Bay?*

2) What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?	This study will assess whether effluent discharge is a possible pathway of bisphenols to the Bay. *This study will assess whether effluent discharge is a possible pathway of sunscreen chemicals to the Bay.*	The study will provide information to help assess the need for pollution prevention activities, and whether wastewater is an important pathway for bisphenols. *The study will provide information to help assess the need for pollution prevention activities, and whether wastewater is an important pathway for sunscreens.*
3) What are the physical, chemical, and biological processes that may affect the transport and fate of individual CECs or groups of CECs in the Bay?		
4) Have the concentrations of individual CECs or groups of CECs increased or decreased?		This bisphenols study will provide baseline information that can be used to evaluate loading trends. *This sunscreen study will provide baseline information that can be used to evaluate loading trends for sunscreen chemicals.*
5) Are the concentrations of individual CECs or groups of CECs predicted to increase or decrease in the future?		
6) What are the effects of management actions?	*This study will assess whether discharge of effluent is a possible source of sunscreen chemicals to the Bay.*	*Could management actions addressing sunscreen ingredients have a measurable impact on loadings to the Bay?*

Approach

Sample Selection:

Wastewater Effluent (Bisphenols & Sunscreens):

The primary goal will be to assess dominant effluent flows to the Bay. We propose to do this by collecting effluent from the six largest wastewater treatment facilities: Central Contra Costa Sanitary District, East Bay Dischargers Authority, East Bay Municipal Utility District, San Jose-Santa Clara Regional Wastewater Facility, Palo Alto Wastewater Treatment. These facilities combined discharge a combined ~70% of wastewater effluent flows to the Bay.

We will collect 24-hour composites of effluent into glass containers that we will be shipped to analytical laboratories. Facilities will be sampled twice during the summer months for two samples per analyte group (bisphenols and sunscreen chemicals). We will collect samples mid-week to avoid variations in product use that may occur during the weekend.

Sediment (Bisphenols Only):

Archived margin sediment samples will be analyzed for bisphenols so no additional resources are needed for the collection of sediment samples. Site selection will be biased towards those likely to be more highly contaminated due to proximity to pathways.

Analytical Methods

Bisphenols:

Samples will be analyzed by members of Dr. Da Chen's laboratory at Jinan University, the laboratory that previously analyzed the Bay water samples collected in 2017. Scientists will conduct the analysis in the U.S. while occupying guest positions within the laboratory of Dr. Rob Hale at the Virginia Institute of Marine Science.

Dr. Da Chen's team will use their existing, highly sensitive water method, which uses liquid chromatography-electrospray ionization(-)-triple quadrupole mass spectrometry (LC-ESI(-)-QQQ-MS/MS) for effluent samples and will modify the same method for analysis of sediment samples. This method will include analysis of bisphenol A, as well as a suite of bisphenol analogues, including bisphenols B, C, AF, AP, BP, M, E, P, F, PH, Z, G, TMC, and C-dichloride.

Sunscreens:

Drs. William Mitch and Djordje Vuckovic of Stanford University, the analytical partners for this proposed study, have expertise in analyzing sunscreens in environmental samples. The target analyte list is shown in Table 3. Currently, the first six compounds in Table 3 are confirmed as part of the analytical method. The last four compounds in the table are expected to be added to the analytical method. Oxybenzone is the priority analyte because it is one of the most widely used sunscreens and has significant ecotoxicity concerns. We will compare the effluent concentrations to literature values to determine whether the levels are of concern.

Table 3. Potential Target Sunscreen Analytes

Compound	**Concerns**
Oxybenzone (Benzophenone-3, BP-3)	Wide use; frequent detection; ecotoxicity concerns. ECHA classified as very toxic to aquatic life. Prioritized by City of San Francisco.
oxybenzone-glucuronide	BP-3 major metabolite
4-hydroxybenzophenone (4HB)	BP-3 metabolite
Benzophenone-1 (BP-1)	BP-3 metabolite
BP-8	BP-3 metabolite
Benzophenone-2 (BP-2)	

Benzophenone-12 (BP-12)	
4-Methylbenzophenone	
Octinoxate (Ethylhexyl methoxycinnamate, EHMC)	Wide use; frequent detection; ecotoxicity concerns. Prioritized by City of San Francisco.
Butylparaben	Wide use. Prioritized by City of San Francisco.

Budget

Table 4. Proposed Budget for the following options:

- Option 1: Bisphenols in Effluent
- Option 2: Bisphenols and Sunscreen in Effluent
- Option 3: Bisphenols and Sunscreen in Effluent, Bisphenols in Sediment

Expense	Option 1	Option 2	Option 3
Labor			
Project Staff			
Sample Design Collection	14,000	14,000	15,000
Reporting	20,000	35,000	40,000
Data Technical Services	5,200	9,900	14,200
Subcontracts			
Da Chen, Jinan University	10,200	10,200	19,800
Bill Mitch, Stanford University		12,500	12,500
Direct Costs			
Equipment	300	300	300
Travel	1,000	1,300	1,200
Shipping	1,200	1,200	2,000
Grand Total	51,900	84,500	105,000

Budget Justification

The added cost necessary to fund the sunscreens add-on is $32,500. As a stand-alone study, the costs associated with analyzing sunscreens in wastewater effluent are estimated at $47,000.

Labor: Field Costs

Field costs for Option 1 and 2 are associated with collecting effluent samples from the six largest wastewater treatment plants twice. Funds are leveraged to combine sample collection at wastewater treatment facilities for bisphenols and sunscreens.

Labor: Reporting

Two separate reports will be developed for bisphenols and sunscreen chemicals. Depending on the results from the sunscreen analysis, it is possible that Stanford researchers will prepare a manuscript.

Labor: Data Technical Services Costs

To minimize data management costs, data for the bisphenols project and the sunscreens will undergo RMP QA/QC and be formatted for CEDEN but not uploaded. Combining efforts saves anywhere from $500-$2,000 in data management costs.

Subcontracts: Laboratory Costs

Bisphenols:

For wastewater effluent, analytical costs are estimated to be $600 per sample. For 16 samples, including two field replicates and three field blanks, the total analytical costs for wastewater effluent will be $10,200. For sediment, analytical costs are estimated at $800 per sample. For twelve samples (and no additional QA samples), analytical costs are $9,600. For both effluent and sediment efforts, the grand total for analytical costs is $19,200.

Sunscreens:

The laboratory analysis costs of $10,000 are a fixed budget for the analysis of 12 wastewater effluent samples as well as approximately four QA/QC samples. An extra $2,500 was added in for the lab to help with reporting.

Reporting

Two separate reports will be written for the bisphenols and the sunscreens. Each will have the same timeline: results will be provided to the RMP committees in a technical report. A draft of the report will be provided for review in summer 2021. Comments will be incorporated into the final report by fall 2021.

References

Anderson PD, Denslow ND, Drewes JE, Olivieri AW, Schlenk D, Scott GI, Snyder SA 2012. Monitoring Strategies for Chemicals of Emerging Concern (CECs) in California's Aquatic Ecosystems. Southern California Coastal Water Research Project: Technical Report 692. Available at: http://www.waterboards.ca.gov/water_issues/programs/swamp/cec_aquatic/docs/cec_ecosystems_rpt.pdf

Bakker J, Hakkert BC, Hessel EVS, Luit RJ, Piersma AH, Sijm DTHM, Rietveld AG, van Broekhuizen FA, van Loveren H, Verhoeven JK. 2016. Bisphenol A (No. 2015– 0192), Part 2. Recommendations for risk management. National Institute for Public Health and the Environment: Ministry of Health, Welfare and Support.

Balazs A, Krifaton C, Orosz I, Szoboszlay S, Kovacs R, Csenki Z, Urbanyi B, Balazs K. 2016. Hormonal activity, cytotoxicity, and developmental toxicity of UV Filters. Ecotoxicology and Environmental Safety, 131:45-53.

Balmer M, Buser HR, Muller M, Poiger T. 2005. Occurrence of some organic UV filters in wastewater, surface waters, and in fish from Swiss Lakes. Environ. Sci. Technol., 39:953-962.

Coronado M, Haro H, Deng X, Rempell M, Lavado R, Schlenk D. 2008. Estrogenic activity and reproductive effects of the UV-filter oxybenzone (2-hydroxy-4-methoxyphenyl-methanone) in fish. Aquatic Toxicology, 90:182-187.

Downs C, Kramarksky-Winter E, Segal R, Fauth J, Knutson S, Bronstein O, Ciner F, Jeger R, Lichtenfeld Y, Woodley C, Pennington P, Cadenas K, Kushmaro A, Loya Y. 2016 Toxicopahtological effects of the sunscreen UV filter, Oxybenzone (Benzophenone-3) on coral planulae and cultured primary cells and its environmental contamination in Hawaii and the US Virgin Islands. Archives of Environmental Contamination and Toxicology. P 265-288.

Fent K, Zenker A, Rapp M. 2010. Widespread occurrence of estrogenic UV-filters in aquatic ecosystems in Switzerland. Environ. Pollution, 158(5):1817-24.

Gago-Ferrero P, Diaz-Cruz M, Barcelo D. 2015. UV filters bioaccumulation in fish from Iberian river basins. Science of the Total Environment, 518-525.

Kim S, Jung D, Kho Y, Choi K. 2014. Effects of benzophenone-3 exposure on endocrine disruption and reproduction of Japanese medaka (Oryzias latipes)--a two generation exposure study. Aquatic Toxicology, 155:244-52.

Kinnberg KL, Petersen GI, Albrektsen M, Minghlani M, Awad SM, Holbech BF, Green JW, Bjerregaard P, Holbech H. 2015. Endocrine-disrupting effect of the ultraviolet filter benzophenone-3 in zebrafish, Danio rerio. Environ Toxic Chem., 34(12):2833-40.

Kunz P, Galicia H, Fent K. 2006. Comparison of in vitro and in vivo estrogenic activity of UV filters in fish. Toxicological Science, 90(2):349-361.

Lee S, Liu X, Takeda S, Choi K. 2013. Genotoxic potentials and related mechanisms of bisphenol A and other bisphenol compounds: A comparison study employing chicken DT40 cells. Chemosphere, 93:434-440.
https://www.researchgate.net/profile/Kyungho_Choi/publication/241691440_Genotoxic_potentials_and_related_mechanisms_of_bisphenol_A_and_other_bisphenol_compounds_A_comparison_study_employing_chicken_DT40_cells/links/53dd25670cf2a76fb667c749.pdf

Liao C, Kannan K. 2014. Widespread occurrence of benzophenone-type UV light filters in personal care products from China and the US: An assessment of human exposure. Environ. Sci Technol., 48:4103-4109.

Mao F, You L, Reinhard M, He Y, Gin K. 2018. Occurrence and Fate of Benzophenone-Type UV Filters in a Tropical Urban Watershed. Environ Sci Technol., 52:3960-3967.

Office of Environmental Health Hazard Assessment (OEHHA). 2012. Preliminary Screen for Possible Future Consideration as Potential Designated Chemicals for Biomonitoring California. Some Bisphenol A Substitutes and Structurally Related Compounds. Materials for March 16, 2012 Meeting Scientific Guidance Panel (SGP). Available at: http://www.oehha.ca.gov/multimedia/biomon/pdf/031612PrelimScreen2.pdf

Office of Environmental Health Hazard Assessment (OEHHA). 2019. The Proposition 65 List. Available at: https://oehha.ca.gov/proposition-65/proposition-65-list

Rochester, JR, Bolden, AL, 2015. Bisphenol S and F: A Systematic Review and Comparison of the Hormonal Activity of Bisphenol A Substitutes. Environmental Health Perspectives 123:643–650. https://doi.org/10.1289/ehp.1408989

Rosenmai AK, Dybdahl M, Pederson M, Medea B, van Vugt-Lussenburg A, Wedebye EB, Taxvig C, and Vinggaard AM. 2014. Are Structural Analogues to Bisphenol A Safe Alternatives? Toxicological Sciences., 139:35-47.

Shimabuku I, Sutton R, Chen D, Wu Y, Sun J. 2019. Flame retardants and plastic additives in San Francisco Bay: a targeted monitoring of organophosphate esters and bisphenols. (in progress)

Wang Q, Chen M, Shan G, Chen P, Cui S, Yi S, Zhu L. 2017. Bioaccumulation and Biomagnification of Emerging Bisphenol Analogues in Aquatic Organisms from Taihu Lake, China. Sci. Total Environ., 598:814–820.

Wright-Walters M, Volz C, Talbott E, Davis D. 2011. An updated weight of evidence approach to the aquatic hazard assessment of Bisphenol A and the derivation of a new predicted no effect concentration (PNEC) using a non-parametric methodology. Sci. Total Environ., 409:676-685.