

## Special Study Proposal: Sunscreens in Bay Area Wastewater Effluent

Summary: Ultraviolet (UV) radiation filters (sunscreens) are widely used in sunscreen lotions and other products such as cosmetics, paints, and plastics. In humans, it has been shown that many of these chemicals can be quickly absorbed through skin and circulated throughout the body. 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. Several sunscreens have been shown to cause adverse effects such as endocrine disruption in fish, and are responsible for significant coral reef bleaching. Hawaiian State Legislators just passed a ban on two chemicals commonly found in sunscreen lotions; the bill is currently pending the Governor's signature. The City of San Francisco is considering a resolution to examine the occurrence and potential impacts of some of these compounds. Recent nontargeted analyses conducted by the RMP have qualitatively identified oxybenzone, a UV filter, in Bay water and effluent. This study will quantify sunscreens in Bay Area effluents to assess whether they may be a potential concern for the Bay.

Estimated Cost: \$50,300

Oversight Group: Emerging Contaminant Workgroup

Proposed by: William Mitch and Djordje Vuckovic (Stanford University); Meg Sedlak and Diana Lin (SFEI)

### PROPOSED DELIVERABLES AND TIMELINE

<b>Deliverable</b>	<b><i>Due Date</i></b>
Task 1. Field collection of effluent samples	Summer/Winter 2019
Task 2. Laboratory analysis of samples	Fall/Winter 2019
Task 3. Review of data	Spring 2020
Task 4. Draft technical memorandum	June 2020
Task 5. Final technical memorandum	September 2020

### Background

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 to extend product life.

At present, the US Food and Drug Administration has approved 16 chemicals for sunscreen protection. UV sunscreen chemicals in over-the-counter sunscreen products are frequently combined to increase the efficacy of the product. 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 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).

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 great 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 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 and gonad maturation was observed (Kinneberg et al. 2015). Exposure to oxybenzone in another laboratory study of zebrafish caused mortality, unsuccessful hatching, and structural malformations such as deformed tails, impaired development of the jaw, and lack of swim bladder inflation (Balazs et al. 2016).

Due in part to the potential for endocrine disruption and other deleterious effects in fish, and the ability for these compounds to cause coral bleaching, there is currently regulatory interest in restricting their use. A bill was recently passed in Hawaii that bans oxybenzone 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 coral reef die-offs and potential endocrine disruption. City officials are interested in knowing whether these chemicals are detected in the Bay. 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

Management Question	Study Objective	Example Information Application
1) Which CECs have the potential to adversely impact beneficial uses in San Francisco Bay?	Quantify sunscreens that are detected in Bay effluent.	Identifying the presence of sunscreens in Bay Area effluent will be important for determining whether there is a potential problem for 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 discharge of effluent is a possible source of sunscreen chemicals to the Bay.	The study will provide information to help assess the need for pollution prevention activities.
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 study will provide baseline information that can be used to determine whether sunscreens may be an issue of concern to Bay organisms.
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?		

## Approach

We are proposing to collect effluent from eight wastewater treatment facilities to analyze for sunscreen chemicals including oxybenzone, octinoxate, and butylparaben. Based on a literature review, it appears that the removal of oxybenzone from treatment plants varies tremendously from 68 to 93 percent (Balmer et al. 2005).

Drs. William Mitch and Djordje Vuckovic of Stanford University, the analytical partners for this proposed study, have expertise in analyzing sunscreens in environmental samples. They are currently investigating the mechanisms by which sunscreens cause toxicity in anemones (which are similar to coral).

*Wastewater*

We are proposing to sample a variety of wastewater treatment facilities that are of different sizes, treatment type (e.g., secondary vs. tertiary), and sewersheds. We will collect 24-hour composites of effluent into glass containers that we will transport to the laboratory. We will collect samples mid-week to avoid variations that may occur during the weekend.

We are also interested in evaluating whether there are seasonal differences. We will undertake two sampling events during the summer months. After reviewing these dry weather results, we will sample four facilities having the highest concentrations twice during the winter months to assess whether there are seasonal differences.

*Sample Analysis*

The target analyte list will at a minimum include: oxybenzone, octinoxate, and butylparaben. At present, the laboratory is confirming the analyte list (Table 2). Oxybenzone is the priority analyte because it is one of the most widely used sunscreens and has significant ecotoxicity concerns.

*Data Analysis*

We will compare the effluent concentrations to literature values to determine whether the levels are of concern. Data will be reviewed by RMP data management staff and will not be uploaded to CEDEN.

**Table 2.** Potential Target Analytes

<b>Compound</b>	<b>Concerns</b>
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.
4-hydroxybenzophenone (4HB)	BP-3 metabolite.
Benzophenone-1 (BP-1)	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 Justification

**Table 3.** Proposed Budget.

<b>Personnel</b>	<b>SFEI</b>	<b>Stanford</b>
Sample design and site visit coordination	\$1,700	
Collection of effluent at 8 sites in summer (two events) and at 4 sites in the winter (two events)	\$9,800	
Laboratory Analyses (Stanford)		\$13,400
Reporting (literature and summary)	\$14,000	\$2,500
Data Technical Services	\$7,500	
Direct costs (field supplies, travel)	\$1,400	
<b>Total</b>	<b>\$50,300</b>	

### *Field Costs*

Field costs will consist of sampling eight facilities twice for effluent during the summer months. We will coordinate with other special study projects that are sampling effluent to optimize fieldwork.

### *Reporting Costs*

The reporting task will consist of a literature review to place the values in context and a short technical summary of the results. Depending on the results, it is possible that Stanford researchers will prepare a manuscript.

### *Laboratory Costs*

The laboratory costs are a fixed budget for the analysis of 24 wastewater effluent samples as well as 8 QA/QC samples.

### *Data Management Costs*

The data will be reviewed by RMP data management staff; however, it will not be uploaded to CEDEN.

## Reporting

Deliverables will be a short technical memorandum.

## References

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