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Concentrations of Select Commonly-Used Organic Ultraviolet Filters in San Francisco Bay Wastewater Effluent

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Executive Summary

Ultraviolet (UV) radiation filters 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. Widespread use of UV filters has led to extensive detections in the environment, and have raised concerns about impacts to aquatic ecosystems. In particular, several organic UV filters that are commonly used in sunscreen have been identified as neurotoxins and endocrine disruptors. To help understand the presence of organic UV filters and their potential to pose risks in San Francisco Bay, three of the most commonly used organic UV filters used in sunscreen (avobenzone, octinoxate, oxybenzone) as well as select metabolites were analyzed in municipal wastewater effluent from the six largest publicly-owned treatment works (POTWs) discharging into the Bay. Note that organic UV filters is a broad chemical class, and other constituents within this class were not included in this study.

Only two of the three organic UV filters analyzed were detected in effluent, avobenzone (detected in 70% of samples) and oxybenzone (83%), with median concentrations of 28 and 86 ng/L, and 90th percentile concentrations of 77 and 209 ng/L, respectively. Concentrations of avobenzone and oxybenzone varied widely across facilities, though there were no clear outlier values. The two POTWs utilizing advanced secondary treatment had the lowest concentrations of any facilities, which may indicate increased removal from these processes. Overall, these concentrations were higher than those reported in one other study of wastewater effluent in the US. An increasing body of literature will help to fully understand the occurrence and fate of organic UV filters in wastewater.

A hydrodynamic dilution model was used to estimate potential worst-case scenario concentrations in the Bay based on observed 90th percentile effluent levels. Of all the subembayments, the Lower South Bay showed the highest predicted (annual average) concentrations of avobenzone (5.0 ng/L) and oxybenzone (14 ng/L), which is consistent with the limited water exchange and longer water residence times in this area. All predicted concentrations for the Bay were under current method detection limits (MDLs) and available ecotoxicological thresholds, indicating dilution is an important factor mitigating potential adverse effects of organic UV chemicals.

Results from this study suggest limited need for immediate followup monitoring of avobenzone, octinoxate, and oxybenzone in the Bay at this time. Concentrations of avobenzone in effluent were well below available ecotoxicity thresholds. Most samples of effluent contained oxybenzone at levels exceeding the available marine predicted no effect concentration (PNEC), suggesting potential concern for organisms near effluent outfalls. However the hydrodynamic model indicated that dilution decreases the general concern for Bay water. Additionally, predicted diluted concentrations in the Bay are below current method detection limits. At present, we do not recommend that the Regional Monitoring Program for Water Quality in San Francisco Bay prioritize additional monitoring of avobenzone, octinoxate, oxybenzone in Bay matrices. We can

continue to track the developing science on these contaminants, especially improvements to analytical methods and toxicity testing, as new findings could influence future consideration of monitoring activities.

1. Introduction

Known predominantly for their use in sunscreens, ultraviolet (UV) radiation filters are a diverse class of compounds designed to absorb, reflect, and scatter harmful solar radiation. In addition to sunscreens, UV filters are also used in other personal care products including cosmetics, body wash, hair products, and toothpaste (NASEM, 2022). These chemicals are also found in other consumer and industrial applications including biocides, cleaning products, construction materials, electronics, paints and coatings, pharmaceuticals, plastics, textiles, and tires (ECHA, 2022a; NASEM, 2022; US EPA, 2022). Many of these uses are meant to mitigate the damaging effects of sunlight and extend product life.

There are two major categories of UV filters: those primarily consisting of inorganic particles (i.e., titanium dioxide and zinc oxide), and others consisting of organic chemicals, which are the focus of this study. Within the US, the Food and Drug Administration (FDA) has approved 14 organic UV filters for UV radiation protection, with most in regular production and use, especially in personal care products (FDA, 2016). Among the most commonly-used organic UV filters are avobenzone and benzophenones, including oxybenzone (or benzophenone-3, BP-3) and, to a lesser extent, dioxybenzone (or benzophenone-8, BP-8), which are present in many consumer products in the US and Europe (NASEM, 2022).

As a class, organic UV filters have a diverse range of physical and chemical properties. Organic UV filters largely consist of structures with an aromatic moiety, encompassing a variety of chemical groups such as benzophenones, cinnamates, and salicylates. Most in the class are hydrophobic and have a greater likelihood to partition into sediment in aquatic ecosystems or biosolids in a wastewater treatment process, though oxybenzone is moderately water soluble. These compounds also exhibit diverse biodegradation potential, with avobenzone showing low biodegradability and greater potential for persistence and bioaccumulation (NASEM, 2022). In contrast, oxybenzone is more biodegradable with an overall lower potential for bioaccumulation (NASEM, 2022).

Several organic UV filters, particularly those most commonly used, have been identified as potential neurotoxins and endocrine disruptors. These compounds have also been associated with induction of oxidative stress, an imbalance between the production of reactive oxygen species (free radicals) and antioxidant defenses, for a variety of biota (Carve et al., 2021; Du et al., 2017; Duis et al., 2022; Fivenson et al., 2021; Liu et al., 2021; Miller et al., 2021; NASEM, 2022; Vuckovic et al., 2022). Many of the aquatic toxicity studies to date have focused on coral bleaching; however, there is also growing evidence that organic UV filters may also have toxic effects on other aquatic species (Carve et al., 2021). For example, Liu et al. (2021) identified avobenzone as disrupting genetic pathways in zebrafish, affecting swimming performance. Recent work by Vuckovic et al. (2022) has highlighted the importance of also considering metabolites of oxybenzone and other organic UV filters, as metabolites may also be important contributors to oxidative stress from phototoxicity.

The widespread usage of organic UV filters has led to detections across environmental matrices, including surface water, sediment, and wildlife including fish, birds, and

invertebrates (Gago-Ferrero et al., 2015; Liao & Kannan, 2014; Mao et al., 2018; Molins-Delgado et al., 2017; NASEM, 2022; Tsui et al., 2014, 2017). The extensive detections of organic UV filters, coupled with potential negative impacts to aquatic life, has led to growing interest in restricting their use. Hawai'i recently became the first state to ban the distribution and sale of products containing avobenzone, oxybenzone, octinoxate, and octocrylene due to exceedances of an ecological toxicity threshold for coral in water (*SB132 SD2 HD1*, 2021). The City of Key West, FL has similarly banned oxybenzone and octinoxate. At present, the FDA has stated that there is still insufficient safety information for the agency to determine whether avobenzene, dioxybenzone, oxybenzone, octinoxate, and eight other organic active ingredients are "generally recognized as safe and effective" (FDA, 2021).[1]

There are no published studies of organic UV filters commonly used in sunscreen in any environmental matrix in the Bay. The motivation for this study is to assess whether these commonly-used sunscreen ingredients may be of potential concern in the Bay, which might indicate the need to monitor Bay matrices and inform management actions. One main transport pathway of these contaminants to the Bay is through wastewater effluent (after down-the-drain washoff). Another relevant pathway is direct wash-off into surface waters during recreational activities (i.e., swimming). Considering the colder water temperature in the Bay compared to Hawai'i and Florida, direct wash-off in the Bay is likely to be more limited.

Stormwater is another potential pathway, though it remains unexplored at this time as "no studies have systematically measured stormwater for organic UV filters" (NASEM 2022). Several organic UV filters have outdoor uses that make them susceptible to transport via stormwater: octinoxate and octocrylene are used in paints and coatings, as well as long-life materials for outdoor use; dioxybenzone is used in long-life materials for outdoor use and automotive care products; and oxybenzone has uses in paints and coatings, vehicles, and long-life materials for outdoor use (NASEM 2022).

This study took a screening approach to assess potential risk by evaluating concentrations in effluent discharged to the Bay. We measured seven organic UV filters and metabolites. Observed concentrations in wastewater were used in combination with a hydrodynamic model to estimate potential worst-case scenario concentrations in the Bay from dilution of wastewater effluent. Additionally, contaminant concentrations in effluent, and estimated concentrations in Bay water, were compared to available ecotoxicity thresholds to inform future Bay monitoring priorities for this contaminant class.

[1] Inorganic compounds titanium dioxide and zinc oxide were "generally recognized as safe and effective."

2. Methods

2.1. Study Design and Sample Collection

Effluent samples were collected in August through October 2021 from six wastewater facilities in San Francisco Bay: Central Contra Costa Sanitary District (CCCSD), East Bay Dischargers Authority (EBDA), East Bay Municipal Utility District (EBMUD), Palo Alto Regional Water Quality Control Plant (PA), San Francisco Public Utilities Commision Southeast Treatment Plant (SEP [SFPUC]) and San José-Santa Clara Regional Wastewater Facility (SJ-SC). These six publicly-owned treatment works (POTWs) were selected because they are the largest POTWs based on discharge to the Bay, and combined represent approximately 70% of total wastewater effluent flow.

The chosen POTWs also represent a range of characteristics of Bay facilities, including service population, treatment type, and geographic location, as described in Table 1 and Figure A1. SJ-SC, the largest discharger in this study, and PA, the smallest, are both located in the Lower South Bay, an important area to monitor due to the greater impact of wastewater effluent relative to other subembayments. Both facilities incorporate advanced secondary treatment into their treatment trains, though SJ-SC utilizes the uncommon feature of biological nutrient removal (BNR), while PA uses the more common trickling filter and activated sludge (AS) treatment. EBDA is the second largest discharger by average dry water flow (ADWF) in 2020/2021 and is unique in that it discharges effluent coming from several POTWs including the City of San Leandro Water Pollution Control Plant, Oro Loma Sanitary District/Castro Valley Sanitary District Water Pollution Control Plant, City of Hayward Water Pollution Control Facility, Union Sanitary District Alvarado Treatment Plant, Dublin-San Ramon Sanitary District Wastewater Treatment Facility, and City of Livermore Water Reclamation Plant. This discharge allows us to capture a greater portion of discharges into the Bay, but provides no information on the potential effect of different treatment types.

Table 1. Characteristics of six wastewater facilities sampled for organic UV filters. Noted flows are in million gallons per day (MGD).

POTW	Estimated Population	Permitted ADWF[1] (MGD)	2020/2021 ADWF[1] (MGD)	Secondary Treatment Type	Advanced Secondary Treatment (Yes/No)
SJ-SC	1,400,000	167	76.1	AS/BNR	Yes
EBDA	1,000,000	107.8	60.2	AS, TF/AS, TF/Solids Contact	No
EBMUD	740,000	120	45.3	High Purity Oxygen	No
SEP (SFPUC)	580,000	85.4	42.2	High Purity Oxygen	No
CCCSD	500,000	53.8	31.4	AS	No
PA	236,000	39	17.1	TF/AS	Yes

ADWF: Average Dry Water Flow, AS: Activated Sludge, TF: Trickling Filter, BNR: Biological Nutrient Removal

[1] ADWF flows were obtained from BACWA, 2022

On opposite sides of the Central Bay, EBMUD and SEP (SFPUC) are similarly sized dischargers (in the middle of the sampled group) using the same treatment type, high purity oxygen in AS treatment. Further, these facilities, along with SJ-SC, represent the flows from the largest urban centers in the Bay. CCCSD, the largest POTW in the northern portion of the Bay, discharges at flows slightly below those at these Central Bay facilities and uses the common AS treatment.

Figure 1. Map of wastewater facilities sampled for this study.

All POTWs were sampled between August 17, 2021 and October 18, 2021 (dry season), with the goal of sampling during warmer months when more sunscreen use is expected. Each POTW was sampled twice, on separate dates with a duplicate collected concurrently, during this three month time period. The first samples were collected during the typical workweek (Tuesday through Friday), while the second was collected on the day following the weekend (Monday). This was done to evaluate potential variability, and identify whether organic UV filter effluent concentrations suggest

differences in weekday versus weekend usage. Effluent samples were 24 hour composite samples transferred from a larger automatic sampler bottle to 4 L pre-cleaned amber glass bottles (~3 L sample volume), kept on ice, and extracted within the day of collection. Along with each sample, a sample blank was collected in a separate 4 L container that was kept open for several minutes in the same location as the sample collection, and filled with laboratory deionized water.

2.2. Laboratory Analysis and Quality Control

All samples were analyzed under supervision of Dr. Djordje Vuckovic and Dr. William Mitch at Stanford University using a novel method for the analysis of organic UV filters in environmental samples. Once received at the laboratory, samples were filtered through 0.7 µm glass fiber filters with the filtrate divided into three equal aliquots (~1 L). Two aliquots were used for analysis (including a laboratory replicate) and the third used for matrix spike analysis. Aliquots were spiked with surrogate standards (including d_5-BP-3, ^{13}C-d_3-avobenzone, d_3-octinoxate, and d_3-BP-8), and subsequently extracted onto solid phase extraction cartridges. The concentrated extracts were analyzed by liquid chromatography mass spectrometry (LCMS) using a triple quadrupole MS system in the MRM mode. The analysis included the following organic UV filters: avobenzone, benzophenone-1 (BP-1), oxybenzone, dioxybenzone, octinoxate, oxybenzone-glucoside, and oxybenzone-glucuronide; method detection limits (MDLs) for each matrix are noted below in Table 2.

Table 2. Method detection limits (MDLs) for all analyzed organic UV filters.

Analyte	MDLs* (ng/L)
Avobenzone	14
Benzophenone-1 (BP-1)	11
Oxybenzone (benzophenone-3 or BP-3)	18
Dioxybenzone (benzophenone-8 or BP-8)	42
Octinoxate	14
Oxybenzone-glucoside	45
Oxybenzone-glucuronide	127

*Note: MDLs were calculated using 12 wastewater matrix spike samples in the following manner: The concentration of the 100 ng/L spike recovered (i.e., the difference between the concentration measured in the spiked sample compared to the average measured in the unspiked duplicate samples) was determined for each of the 12 samples. The standard deviation of this recovered concentration was multiplied by the two-sided Student's t-test critical value for n = 11 degrees of freedom and alpha = 0.05 (i.e., 2.201).

Area counts of oxybenzone, avobenzone, and octinoxate were normalized by their respective deuterated, ^{13}C and/or ^{15}N internal standards in all samples. Values of dioxybenzone were normalized by d_5-BP-3 in all samples from PA, EBDA, and SJ-SC. Samples from CCCSD, SEP (SFPUC), and EBMUD were normalized by d_5-BP-3 for the first round of samples, and by its own internal standard (d_3-BP-8) for the following round of samples.

A review of the laboratory results indicated acceptable method performance according to RMP QAPP standards (Yee et al., 2021). Average recoveries across five blank spikes and twelve matrix spikes (100 ng/L for all spikes) were within the target range of 50-150% for most analytes. However, BP-1 had very poor (<50%) recovery in matrix spikes, and thus may not be quantitative in wastewater samples. This may have contributed to the lack of detections in samples. Relative percent differences (RPDs) on matrix spike duplicates were generally below 10%. Analysis of five laboratory blanks showed avobenzone slightly over the MDL in a single sample (15.6 ng/L). All avobenzone results in that batch were not reported because concentrations fell below three times the standard deviation observed in laboratory blanks (2 of the 12 sites). All other analytes were not detected in any laboratory blanks.

All samples had replicates. Most duplicates at each sampling event showed a replicate percent difference (RPD) of less than 20%, though one set of samples had a 60% difference. The average of the duplicate samples was used to represent the concentration on a particular sampling date (Table A1).

2.3. Hydrodynamic Model

A Bay hydrodynamic dilution model calculation was conducted to produce an evaluation of worst-case scenario Bay concentrations of organic UV filters from diluted wastewater discharges. This modeling exercise was intended as a simple, screening-level effort to evaluate whether concentrations measured in wastewater suggest potential for concern in the Bay and inform future monitoring priorities.

The hydrodynamic model was previously developed to approximate the dilution of persistent and water soluble contaminants discharged into the Bay (Holleman et al., 2017; Lin et al., 2018), and estimated Bay concentrations are generally considered worst-case scenario because the model only simulates the dilution of discharges in Bay waters, and does not include degradation processes, sorption to sediment, or exchange with the atmosphere, which can significantly reduce concentrations of many contaminants in Bay waters. A spreadsheet version of the hydrodynamic model was developed for emerging contaminant applications, and condenses the Bay hydrodynamic model into a series of spreadsheets that summarize the relationship between concentrations in load streams and ambient concentrations in each subembayment of the Bay (Holleman et al., 2017; Lin et al., 2018). Model inputs require concentrations for each load stream, which includes 34 individual wastewater treatment plants and five refineries, as well as a single representative concentration for all local runoff and another single value for outflow from the Sacramento-San Joaquin river delta. The spreadsheet hydrodynamic model used for the present study simulates the

period from October 2012 to September 2013, and concentrations in the Bay are predicted over two-month periods (e.g. October to November, December to January).

In this study, we used the spreadsheet hydrodynamic model to calculate screening-level estimates of dilution factors for wastewater effluent compared to ambient concentrations in each subembayment. A normalized value of one was applied for all 34 wastewater effluent loads into the Bay to represent a simple worst-case scenario concentration for all wastewater discharges, while a value of zero was applied as the model input for all other load streams (i.e., refineries and stormwater discharges). The model was used to calculate dilution factors (ratio of subembayment concentration to wastewater effluent discharge concentration) for each subembayment averaged over each two-month period. Larger dilution factors represent a worst-case scenario where there is less dilution predicted, and therefore higher predicted ambient Bay concentrations. Selected dilution values were then multiplied by measured effluent concentrations to estimate potential subembayment concentrations.

3. Results and Discussion

3.1. Occurrence in Wastewater

Two organic UV filters, avobenzone and oxybenzone, of seven analytes were detected in wastewater effluent (Table 3; see Table A1 in the Appendix for all individual sample data, including analytes not detected). Avobenzone (range: <14–100 ng/L; median: 28 ng/L) was detected in 70% of samples while oxybenzone (range: <18–251 ng/L; median: 86 ng/L) was found in 83% of samples. The 90th percentile concentrations of avobenzone and oxybenzone were 77 ng/L and 209 ng/L, respectively (Table 3). Overall summary statistics showed little change for avobenzone and oxybenzone when NDs were substituted for the MDL with averages changing to 40 ng/L and 101 ng/L, respectively.

Table 3. Summary statistics (where ND = 0) of organic UV filters detected in Bay Area wastewater effluent. All concentrations are in ng/L.

	Avobenzone	**Oxybenzone**
Detection Frequency	70%	83%
n[1]	10	12
MDL	14	18
Minimum	ND (<14)	ND (<18)
Maximum	100	251
Median	28	86
Average	36	98
90th Percentile	77	209
Standard Deviation	33	77

[1]Only 10 samples were included for avobenzone analysis because 2 samples were not reported due to laboratory blank contamination.

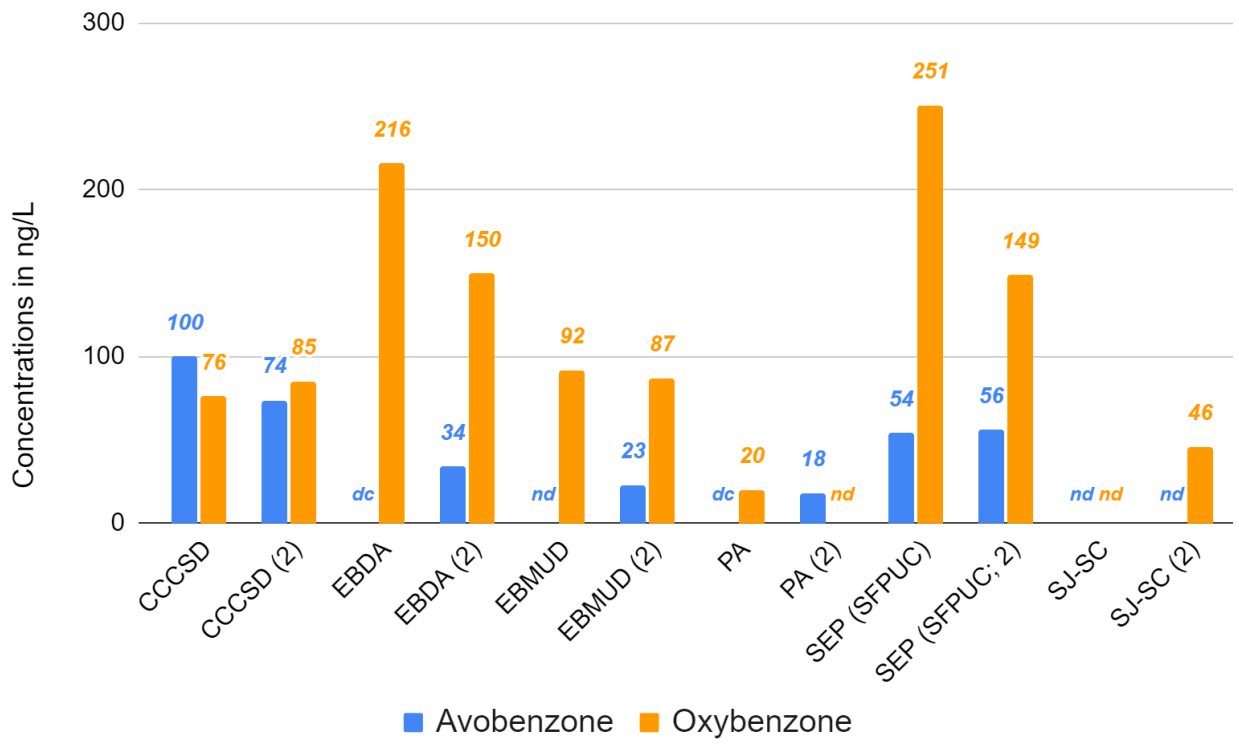

Figure 2. Concentrations of oxybenzone and avobenzone in wastewater effluent samples from participating POTWs from two sampling dates. Nondetects are indicated by “nd” and avobenzone samples that were not reported due to potential contamination are denoted by “dc”.

Avobenzone and oxybenzone concentrations in effluent varied among Bay wastewater facilities (Figure 2, Table 3), with the lowest (<14 ng/L) and highest detected values (100 ng/L) differing by an order of magnitude. A Shapiro-Wilks test indicated all the data for individual analytes were normally distributed with a Grubbs test further suggesting neither of the maximum concentrations were unusual or outlier detections, though this is a limited dataset.

Samples from the same facility collected on different days of the week generally had a RPD of less than 35%. Several RPDs between data pairs from the same facility from different days of the week were above 100% for oxybenzone due to one of the samples being low or ND (Figure 2). However, there was no clear observable or consistent trend in weekday versus weekend levels (Tues-Fri, Mon). SJ-SC and PA, which use advanced secondary treatment, had the lowest reported concentrations, possibly indicating improved removal through these treatment processes. Wastewater treatment has been shown to degrade or remove, through adsorption to sewage solids, some UV filters detected in influents (NASEM, 2022).

Occurrence data for organic UV filters in wastewater effluent are extremely limited with oxybenzone and its derivatives the most widely-studied in the class. The only comparable study in the US collected wastewater influent, effluent, and biosolids from

two POTWs in Albany, NY in 2013 to examine oxybenzone and four derivatives including BP-1 and dioxybenzone (Wang & Kannan, 2017). This study found relatively low levels of oxybenzone in wastewater effluent (range: <0.5–33 ng/L; median: <0.5) compared to the sum of its derivatives (range: 5.4–43 ng/L; median: 7–17 ng/L). The levels of oxybenzone in Albany POTWs were generally lower than in our study, although they detected more derivatives, which could be due to their lower detection limits and additional analytes targeted. The Albany study also investigated oxybenzone transformation and transport through the treatment process and found 75–83% of oxybenzone and its derivatives were transformed or lost, likely through biodegradation and volatilization, with an additional 13–16% adsorbing onto biosolids. Biosolids showed relatively high levels of oxybenzone (median: 1200–1290 ng/g dw) and BP-1 (median: 1370–1510 ng/g dw).

3.2. Estimated Concentrations in San Francisco Bay

A hydrodynamic dilution model was used to estimate the concentrations of avobenzone and oxybenzone in Bay water from dilution of wastewater effluent. Modeled concentrations in the Bay were conservative (i.e., worst case scenario), only simulating the dilution of discharges in Bay waters, and not including degradation processes, sorption to sediment, or exchange with the atmosphere, which can significantly reduce concentrations of many contaminants in Bay waters. Many of these analytes are hydrophobic enough that they may partition to a surface microlayer or sediment, leading to high uncertainty in aqueous concentrations, particularly in marine systems. Still, this model provided a reasonable upper-bound estimate of ambient Bay water concentrations.

Dilution factors were derived from the hydrodynamic model by applying a single normalized value of one to represent wastewater effluent flows from all 34 wastewater discharge points into the Bay. The calculated ambient Bay concentrations are estimates of a two-month average in each subembayment based on dilution factors, or ratio of ambient subembayment concentrations to wastewater effluent concentration. The dilution factors representing the sampled dry season period (August to September) ranged from the lowest value of 0.008 in Suisun Bay to 0.06 in Lower South Bay (Table 4). Annual average dilution factors were in a similar range (Table 4). This is explained by dilution in the Bay being mostly driven by tides rather than seasonal stormwater discharges. Modeled wastewater effluent discharge rates are also higher during the wet season, negating substantial dilution influence that could be expected from higher stormwater flows in the wet season.

To estimate a conservative (upper-bound) ambient Bay concentration, the derived dilution factors were multiplied by the 90th percentile wastewater concentration for avobenzone and oxybenzone (77 ng/L and 209 ng/L, respectively). The measured 90th percentile wastewater effluent concentrations were used due to the large and variable concentrations of avobenzone and oxybenzone observed in Bay wastewater effluent.

Estimated concentrations (2-month average and annual average) in the Lower South Bay of both avobenzone (4.6 and 5.0 ng/L) and oxybenzone (13 and 14 ng/L) were the

highest of any subembayment. The higher levels of organic UV filters in Lower South Bay, relative to the rest of the Bay, reflects the relatively long residence times in this region. Still, all concentrations modeled in the Bay were below noted MDLs for this study (<14 ng/L for avobenzone, <18 ng/L for oxybenzone).

Table 4. Conservative (upper-bound) concentration estimates for Bay water calculated by multiplying 90th percentile concentrations of UV filters detected in Bay wastewater effluent and dilution factors for each subembayment.

			Avobenzone		Oxybenzone	
	Dilution Factors (Aug. to Sept.)	Dilution Factors (Annual Avg.)	Aug. to Sept. (ng/L)	Annual Average (ng/L)	Aug. to Sept. (ng/L)	Annual Average (ng/L)
Suisun Bay	0.008	0.008	0.6	0.6	1.7	1.7
San Pablo Bay	0.004	0.005	0.3	0.4	0.8	1.0
Central Bay	0.006	0.006	0.5	0.5	1.2	1.2
South Bay	0.018	0.019	1.4	1.5	3.8	4.0
Lower South Bay	0.06	0.065	4.6	5.0	13	14

3.3. Risk Evaluation for San Francisco Bay

Detected Analytes

Avobenzone has been shown to cause no adverse effects in water-only toxicity tests of a variety of organisms at concentrations up to its limit of solubility, so no predicted no effect concentration (PNEC) has been derived for this compound (Duis et al., 2022). Similarly, in sediment toxicity tests, avobenzone concentrations up to approximately 50 mg/kg dry weight had no chronic effects on freshwater oligochaetes, insects, and snails (Duis et al., 2022). The detected concentrations of this compound in wastewater effluent entering the Bay (90th percentile: 77 ng/L) therefore likely represent very low risk to Bay organisms.

In contrast, oxybenzone has been shown to exert toxic effects on corals, freshwater algae, and, at higher concentrations, daphnids and fish (Coronado et al., 2008; Du et al., 2017; Miller et al., 2021). EU REACH registration requires aquatic toxicity testing as part of the chemical safety assessment of substances manufactured, imported, or used in quantities above 10 metric tons per year, with chronic testing required for substances above 100 metric tons (ECHA, 2006). These testing requirements often lead to the derivation of PNECs for fresh and marine water. The freshwater PNEC for oxybenzone is 670 ng/L, and the marine PNEC is 67 ng/L (ECHA, 2022c). These PNECs have a relatively large uncertainty, as they are derived from short-term algae growth values with

large assessment (safety) factors used to adjust the effect concentration from a limited dataset and intended to account for uncertainties and extrapolations such as intra- and inter-species variation; the extrapolation of short term toxicity to long term toxicity; and the extrapolation of laboratory results to the field. Recent studies using other algal species have found oxybenzone causes growth and chlorophyll synthesis inhibition down to 22.8 ng/L concentrations (Zhong et al., 2019), indicating the marine PNEC of 67 ng/L may not be protective of all species, especially considering algae appear to be less sensitive than anemones (Vuckovic et al., 2022). Most individual effluent samples and the 90th percentile concentration of oxybenzone in effluent, 209 ng/L, exceed the marine threshold for oxybenzone, which indicates this compound may pose a risk to Bay organisms near effluent outfalls, before sufficient dilution. However, once diluted in Bay water, conservative (upper-bound) concentrations are predicted to be up to 14 ng/L, well below the noted marine PNEC, but approaching the concentration of 22.8 ng/L found to inhibit chlorophyll synthesis in more sensitive algal species.

Analytes That Were Not Detected

Of the analytes not detected, BP-1, dioxybenzone, and octinoxate have available toxicity information indicating method detection limits are sufficiently low. The EU freshwater and marine PNECs for BP-1 are 33,000 ng/L and 3,000 ng/L, respectively, based on chronic algal growth values (ECHA, 2022b). EU PNECs are not available for BP-8 or octinoxate. However, PNECs have been proposed in the literature. Carve et al. derived freshwater and marine PNECs for BP-8 of 3,550 ng/L and 5,300 ng/L, respectively, based on *Daphnia magna* and *Seriatopora caliendrum* toxicity (Carve et al., 2021). Carve et al. derived a freshwater PNEC for octinoxate of 400 ng/L, and Carve et al. and Miller et al. both derived a marine PNEC for octinoxate of 300 ng/L, based on long-term zebrafish no observable adverse effect concentrations (Carve et al., 2021; Miller et al., 2021).

The oxybenzone metabolites (glucoside and glucuronide) have not undergone toxicity testing. However, recent research suggests that glucoside metabolites may be the driver of oxybenzone toxicity to corals (Vuckovic et al., 2022). Although oxybenzone itself protected against UV-induced photo-oxidation, both anemone and mushroom coral species formed oxybenzone-glucoside conjugates that were strong photo-oxidants. Animal mortality correlated with conjugate concentrations, but algal symbionts sequestered these conjugates and helped reduce toxicity, indicating oxybenzone-glucoside is not as toxic to at least some species of algae. Oxybenzone-glucoside toxicity to other organisms is unknown.

Glucuronidation is a common metabolic fate for a variety of xenobiotics and their oxidative metabolites and is generally a detoxification reaction. Thus, these metabolites are generally less toxic than the parent compound. One exception is acidic compounds containing a carboxyl group, which may form acyl glucuronides, many of which are associated with liver or gut toxicity (Bradshaw et al., 2020). Although oxybenzone does not contain a carboxyl group, it may be another exception to the rule that glucuronidation leads to a decrease in toxicity, as it appears to be as potent a photosensitizer as oxybenzone-glucoside (Vuckovic et al., 2022).

Organic UV filters have also been shown to have mixture effects with other potentially co-occurring contaminants; mixtures of bisphenols and organic UV filters exhibit synergistic and antagonistic effects on bioluminescent bacteria (Microtox assay) and human cells (Kudłak et al., 2022). Complex mixture effects are currently not possible to predict accurately, and are not incorporated into traditional toxicity threshold derivation or risk assessment methods.

Finally, these compounds react readily with chlorine, which is commonly used in wastewater disinfection. Wastewater therefore may also provide a possible pathway for additional unknown and unmeasured sunscreen transformation products with unknown toxicity.

Summary

The RMP classifies emerging contaminants within a tiered risk-based framework when concentration data for Bay matrices are available (Sutton et al., 2017). The present study provides data for three organic UV filters commonly used in sunscreen (avobenzone, oxybenzone, octinoxate, and select metabolites) in the wastewater pathway, and only estimates worst-case scenario concentrations in Bay water; as a result, we do not formally classify these contaminants in the framework. With the currently limited information on toxicity, we would predict these select organic UV filters would likely be classified as Low Concern for the Bay, although that could change as more toxicological information becomes available, or if new pathways to the Bay (such as recreational uses or stormwater) are quantified. This is generally consistent with past evaluations of other personal care product ingredients in Bay matrices (Lin et al., 2023)

4. Conclusion

This study responds to management questions about whether organic UV filters widely used in sunscreens and other personal care products pose a potential risk in the Bay, and whether the wastewater pathway is important. Avobenzone and oxybenzone were widely detected in Bay wastewater effluent. Concentrations of octinoxate and select oxybenzone metabolites were below detection limits.

Overall, the methods used to detect these select organic UV filters appear sufficiently sensitive compared to available ecotoxicological thresholds, although toxicity data are limited and more data are needed for some compounds, particularly metabolites. Only oxybenzone was detected in wastewater effluent at levels above toxicity thresholds, and conservative upper-bound estimates of regional concentrations of oxybenzone in wastewater effluent diluted in ambient Bay waters were below available toxicity thresholds. Yet, concentrations of oxybenzone could pose a risk near effluent outfalls in SF Bay.

We do not currently prioritize additional monitoring for these select organic UV filters in the Bay because predicted ambient Bay concentrations are below the method detection limits used in this study and due to their predicted limited risk to the Bay. Still, continued interest and study of organic UV filters, especially improvement of detection methods

and additional toxicity testing, could lead to future consideration of monitoring in Bay water to further inform their classification and potential future management actions to protect water quality and beneficial uses.

References

BACWA. (2022). *Nutrient Watershed Permit Annual Report*. Bay Area Clean Water Agencies.

Bradshaw, P. R., Athersuch, T. J., Stachulski, A. V., & Wilson, I. D. (2020). Acyl glucuronide reactivity in perspective. *Drug Discovery Today*, *25*(9), 1639–1650. https://doi.org/10.1016/j.drudis.2020.07.009

Carve, M., Nugegoda, D., Allinson, G., & Shimete, J. (2021). A systematic review and ecological risk assessment for organic ultraviolet filters in aquatic environments. *Environmental Pollution*, *268, Part B*. https://doi.org/10.1016/j.envpol.2020.115894

Coronado, M., De Haro, H., Deng, X., Rempel, M. A., 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*(3), 182–187. https://doi.org/10.1016/j.aquatox.2008.08.018

Du, Y., Wang, W.-Q., Pei, Z.-T., Ahmad, F., Xu, R.-R., Zhang, Y.-M., & Sun, L.-W. (2017). Acute Toxicity and Ecological Risk Assessment of Benzophenone-3 (BP-3) and Benzophenone-4 (BP-4) in Ultraviolet (UV)-Filters. *International Journal of Environmental Research and Public Health*, *14*(11), 1414. https://doi.org/10.3390/ijerph14111414

Duis, K., Junker, T., & Coors, A. (2022). Review of the environmental fate and effects of two UV filter substances used in cosmetic products. *Science of The Total Environment*, *808*, 151931. https://doi.org/10.1016/j.scitotenv.2021.151931

ECHA. (2006). *C1 Regulation (EC) No 1907/2006 of the European Parliament and of the Council*. European Chemicals Agency (ECHA). https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:02006R1907-20161011&from=EN

ECHA. (2022a). *Registered Substances Factsheets*. https://echa.europa.eu/information-on-chemicals/registered-substances

ECHA. (2022b). *Registered Substances Factsheets—2,4-dihydroxybenzophenone*. https://echa.europa.eu/registration-dossier/-/registered-dossier/12687

ECHA. (2022c). *Registered Substances Factsheets—Oxybenzone*. https://echa.europa.eu/registration-dossier/-/registered-dossier/5515

FDA. (2021). *Over-the-Counter Monograph M020: Sunscreen Drug Products for Over-the-Counter Human Use* (No. OTC000006).

FDA. (2016, September 6). *Safety and Effectiveness of Consumer Antiseptics; Topical Antimicrobial Drug Products for Over-the-Counter Human Use*. Federal Register. https://www.federalregister.gov/documents/2016/09/06/2016-21337/safety-and-effectiveness-of-consumer-antiseptics-topical-antimicrobial-drug-products-for

Fivenson, D., Sabzevari, N., Qiblawi, S., Blitz, J., Norton, B. B., & Norton, S. A. (2021). Sunscreens: UV filters to protect us: Part 2-Increasing awareness of UV filters and their potential toxicities to us and our environment. *International Journal of Women's Dermatology*, *7*(1), 45–69. https://doi.org/10.1016/j.ijwd.2020.08.008

Gago-Ferrero, P., Díaz-Cruz, M. S., & Barceló, D. (2015). UV filters bioaccumulation in fish from Iberian river basins. *Science of The Total Environment*, *518–519*, 518–525. https://doi.org/10.1016/j.scitotenv.2015.03.026

Holleman, R. C., Nuss, E., & Senn, D. (2017). *San Francisco Bay Interim Model Validation report* (SFEI No. 850). San Francisco Estuary Institute.

Kudłak, B., Jatkowska, N., Liu, W., Williams, M. J., Barcelo, D., & Schiöth, H. B. (2022). Enhanced Toxicity of Bisphenols Together with UV Filters in Water: Identification of Synergy and Antagonism in Three-Component Mixtures. *Molecules*, *27*(10), 3260. https://doi.org/10.3390/molecules27103260

Liao, C., & Kannan, K. (2014). Widespread Occurrence of Benzophenone-Type UV Light Filters in Personal Care Products from China and the United States: An Assessment of Human Exposure. *Environmental Science & Technology*, *48*(7), 4103–4109. https://doi.org/10.1021/es405450n

Lin, D., Hamilton, C., Hobbs, J., Miller, E., & Sutton, R. (2023). Triclosan and Methyl Triclosan in Prey Fish in a Wastewater‐Influenced Estuary. *Environmental Toxicology and Chemistry*, etc.5557. https://doi.org/10.1002/etc.5557

Lin, D., Sutton, R., Shimabuku, I., Sedlak, M., Wu, J., & Holleman, R. (2018). *Contaminants of Emerging Concern in San Francisco Bay: A Strategy for Future Investigations 2018 Update* (No. 873). San Francisco Estuary Institute. https://www.sfei.org/documents/contaminants-emerging-concern-san-francisco-bay-strategy-future-investigations-2018-update

Liu, Y., Wang, Y., Ling, X., Yan, Z., Wu, D., Liu, J., & Lu, G. (2021). Effects of Nanoplastics and Butyl Methoxydibenzoylmethane on Early Zebrafish Embryos Identified by Single-Cell RNA Sequencing. *Environmental Science & Technology*, *55*(3), 1885–1896. https://doi.org/10.1021/acs.est.0c06479

Mao, F., You, L., Reinhard, M., He, Y., & Gin, K. Y.-H. (2018). Occurrence and Fate of Benzophenone-Type UV Filters in a Tropical Urban Watershed. *Environmental Science & Technology*, *52*(7), 3960–3967. https://doi.org/10.1021/acs.est.7b05634

Miller, I. B., Pawlowski, S., Kellermann, M. Y., Petersen-Thiery, M., Moeller, M., Nietzer, S., & Schupp, P. J. (2021). Toxic effects of UV filters from sunscreens on coral reefs revisited: Regulatory aspects for “reef safe” products. *Environmental Sciences Europe*, *33*(1), 74. https://doi.org/10.1186/s12302-021-00515-w

Molins-Delgado, D., Máñez, M., Andreu, A., Hiraldo, F., Eljarrat, E., Barceló, D., & Díaz-Cruz, M. S. (2017). A Potential New Threat to Wild Life: Presence of UV Filters in Bird Eggs from a Preserved Area. *Environmental Science & Technology*, *51*(19), 10983–10990. https://doi.org/10.1021/acs.est.7b03300

NASEM. (2022). *Review of Fate, Exposure, and Effects of Sunscreens in Aquatic Environments and Implications for Sunscreen Usage and Human Health*. The National Academies Press. https://doi.org/10.17226/26381.

SB132 SD2 HD1, 2021 Reg. Sess. (Hawaii 2021) (2021). https://www.capitol.hawaii.gov/session/archives/measure_indiv_Archives.aspx?billtype=SB&billnumber=132&year=2021

Sutton, R., Sedlak, M., Sun, J., & Lin, D. (2017). *Contaminants of Emerging Concern in San Francisco Bay: A Strategy for Future Investigations 2017 Revision* (p. 78). San Francisco Estuary Institute.

Tsui, M. M. P., Lam, J. C. W., Ng, T. Y., Ang, P. O., Murphy, M. B., & Lam, P. K. S. (2017). Occurrence, Distribution, and Fate of Organic UV Filters in Coral Communities. *Environmental Science & Technology*, *51*(8), 4182–4190. https://doi.org/10.1021/acs.est.6b05211

Tsui, M. M. P., Leung, H. W., Wai, T.-C., Yamashita, N., Taniyasu, S., Liu, W., Lam, P. K. S., & Murphy, M. B. (2014). Occurrence, distribution and ecological risk assessment of multiple classes of UV filters in surface waters from different countries. *Water Research*, *67*, 55–65. https://doi.org/10.1016/j.watres.2014.09.013

US EPA. (2022). *Chemical Data Reporting under the Toxic Substances Control Act*. https://www.epa.gov/chemical-data-reporting

Vuckovic, D., Tinoco, A. I., Ling, L., Renicke, C., Pringle, J. R., & Mitch, W. A. (2022). Conversion of oxybenzone sunscreen to phototoxic glucoside conjugates by sea anemones and corals. *Science*, *376*(6593), 644–648. https://doi.org/10.1126/science.abn2600

Wang, W., & Kannan, K. (2017). Mass loading and emission of benzophenone-3 (BP-3) and its derivatives in wastewater treatment plants in New York State, USA. *Science of The Total Environment*, *579*, 1316–1322. https://doi.org/10.1016/j.scitotenv.2016.11.124

Yee, D., Wong, A., & Weaver, M. (2021). *2021 Quality Assurance Program Plan for the Regional Monitoring Program for Water Quality in San Francisco Bay* (SFEI Contribution No. 1048). San Francisco Estuary Institute.

Zhong, X., Downs, C. A., Che, X., Zhang, Z., Li, Y., Liu, B., Li, Q., Li, Y., & Gao, H. (2019). The toxicological effects of oxybenzone, an active ingredient in suncream personal care products, on prokaryotic alga Arthrospira sp. And eukaryotic alga Chlorella sp. *Aquatic Toxicology*, *216*, 105295. https://doi.org/10.1016/j.aquatox.2019.105295

Appendix

Table A1. Concentrations of analyzed organic UV filters in San Francisco Bay wastewater effluent. All values are in ng/L with averages of two samples representing noted concentration values for each sampling event. Second samples were taken within two months of the first. The value <MDL is considered non-detect. Data censored due to lab blank contamination are labeled "dc."

	Avobenzone	BP-1[1]	Oxybenzone	Dioxybenzone[2]	Octinoxate	Oxy-glucoside	Oxy-glucuronide
Detection Frequency	70%	0%	83%	0%	0%	0%	0%
n	10	12	12	12	12	12	12
MDL	14	11	18	42	14	45	127
CCCSD	100	*<11*	76	*<42*	*<14*	*<45*	*<127*
CCCSD (2)	74	*<11*	85	*<42*	*<14*	*<45*	*<127*
EBDA	*dc*	*<11*	216	*<42*	*<14*	*<45*	*<127*
EBDA (2)	34	*<11*	150	*<42*	*<14*	*<45*	*<127*
EBMUD	*<14*	*<11*	92	*<42*	*<14*	*<45*	*<127*
EBMUD (2)	23	*<11*	87	*<42*	*<14*	*<45*	*<127*
PA	*dc*	*<11*	20	*<42*	*<14*	*<45*	*<127*
PA (2)	18	*<11*	*<18*	*<42*	*<14*	*<45*	*<127*
SEP (SFPUC)	54	*<11*	251	*<42*	*<14*	*<45*	*<127*
SEP (SFPUC; 2)	56	*<11*	149	*<42*	*<14*	*<45*	*<127*
SJ-SC	*<14*	*<11*	*<18*	*<42*	*<14*	*<45*	*<127*
SJ-SC (2)	*<14*	*<11*	46	*<42*	*<14*	*<45*	*<127*

[1]Only 10 samples were included for avobenzone analysis due to censoring of 2 samples due to laboratory blank contamination.

[2]The first round of samples from CCCSD, SEP (SFPUC), and EBMUD were normalized by d_5-BP-3 while its own internal standard, d_3-BP-8, was used for the second round.