

# Reverse Osmosis Concentrate Treatment Research Results and Context for San Francisco Bay

Prepared by:  
University of California Berkeley  
Stanford University  
San Francisco Estuary Institute

April 21, 2020



Santa Clara Valley  
Water District



ReNUWit

Re-Inventing the Nation's Urban Water Infrastructure



Stanford  
University

SFEI

AQUATIC  
SCIENCE  
CENTER

# Executive Summary

This Technical Memorandum summarizes the design of the pilot open-water engineered treatment cells and the results of the research testing the efficacy of ozone and the treatment cell at removing contaminants from reverse osmosis concentrate (ROC). It also identifies key water quality and baylands habitat concerns regarding ROC for San Francisco Bay, as well as alternatives to current discharge locations.

Chapter 1 provides the results of measurements conducted by researchers at the University of California Berkeley and Stanford University to test the effectiveness of ozone and open-water treatment cells to remove nutrients, organic contaminants, and metals from ROC. The researchers tested the individual effects of ozone and open-water treatment cells, as well as the combined effect. The results showed that the combination of ozone and open-water treatment cells for ROC partially removed nutrients and organic contaminants, with enhanced removal of many contaminants using the combined treatment system. Nitrate was partially removed by the open-water treatment cells in the summer, but there was little to no removal in the winter. Removal of some trace organics was enhanced by the combined system, whereas others were primarily removed either by ozone or open-water cells, and some compounds were not removed by the hybrid system. Perfluorinated compounds (PFOS and PFOA) were not removed by the hybrid system. Nickel and copper were not well removed by the combined treatment system. Although the ozone and open-water treatment cells did not remove all contaminants, they did reduce concentrations below current wastewater effluent levels for many of them. Additional ozonation, longer hydraulic residence time, and alternative treatment technologies used in tandem could increase the efficacy of this treatment for ROC.

Chapter 2 provides the results from a set of laboratory experiments conducted by researchers at the University of California at Berkeley and Stanford University to assess the transferability of findings from the pilot-scale treatment system to RO concentrate treatment sampled from five facilities throughout the state of California. This study evaluated the ability of ozone and open water wetland treatment to degrade organic contaminants (e.g. pesticides), metals (in the form of EDTA chelates), and nutrients. Ozone and open water wetlands were complementary for the removal of a set of organic contaminants. Additionally, ozone pre-treatment facilitated the removal of nickel and copper, although excessive sludge was generated during precipitation treatment. Open water wetland microcosms partially removed nitrate and organic contaminants, but there were differences in efficiency depending on the nitrogen species present in the wastewater sample. Trace organic contaminant removal was consistent across concentrate samples, indicating that bio- and phototransformation processes in open-

water wetlands may be similarly effective across a range of RO concentrates. Additional studies are recommended to identify technologies capable of removing liberated metals and nutrients.

Chapter 3 assesses the potential toxicological impacts of ROC discharge in San Francisco Bay. The concentrations of nutrients, organic contaminants, and metals present in ROC after treatment were compared to regulatory limits and protective toxicity thresholds by scientists at the San Francisco Estuary Institute (SFEI) to assess the possible effects to the San Francisco Bay ecosystem, particularly near the discharge location. The overall reduction of nutrient loads to the Bay from this treatment train could be an important piece of the nature-based solutions needed to reduce nutrient input and related impacts to the Bay. Additionally, the treatment train removed significant amounts of several unregulated organic contaminants in ROC, which would reduce potential impacts to wildlife near the point of discharge. ROC treatment can complement management actions for specific contaminants, including source control measures designed to reduce environmental contamination and limit risks to Bay wildlife. Some contaminants, specifically metals and PFAS, showed limited removal from the treatment train; additional management options for these contaminants should be considered. Development of a monitoring strategy to assess water quality changes and potential toxicity concerns associated with ROC discharge is recommended.

Chapter 4 explores the opportunities and constraints associated with local discharge of treated ROC into bayland marshes. This preliminary review by SFEI scientists sets the stage for future research investigating the impacts of ROC discharge to bayland habitats through mesocosm studies, pilot projects, and monitoring. Opportunities exist to restore historical salinity gradients and their corresponding habitat mosaics to the Lower South Bay using treated wastewater, including treated ROC. Discharges at the San Jose, Sunnyvale, and Palo Alto WWTPs could be designed to include “creek mouths” or horizontal levees (“wet meadows”) in addition to dilution through outfalls, which could restore diffuse freshwater flows and enhance tidal marsh-terrestrial transition zone habitat in a region where this habitat has been severely degraded. If these new types of bayland discharges are implemented, a robust monitoring system will be needed to allow managers to track restoration progress and identify unforeseen consequences. Effect monitoring implemented prior to discharge changes can help detect impacts caused by the additional discharge of ROC. There are some constraints that must be taken into account when designing bayland discharges. Adding ROC discharges will decrease salinity at new outfall locations, and care must be taken not to convert high-quality salt marsh to brackish marsh. Contaminants present in ROC are another constraint to consider due to the concentrated mix in ROC and toxicological concerns. Shifting discharges to bayland habitats rather than open water

could result in impacts to marsh habitats, and greater connectivity to terrestrial food webs, potentially resulting increased exposure to nutrients and organic contaminants. Appropriate dilution will be required to mitigate these effects. Other constraints to consider in design of discharges include mosquito abatement and invasive species management. Open-water ROC treatment cells may also provide habitat for wildlife; further research could inform the development of designs for these treatment systems that maximize benefit and minimize harm to species.

Chapter 5 provides an overview of the open-water treatment cell project, the rationale for choosing target analytes, and the study design, and the quality assurance methods used for the project. The chapter also includes design schematics of the pilot treatment project.

# **Chapter 1: Treatment of Reverse Osmosis Concentrate by Pilot-Scale Ozone and Open-Water Engineered Treatment Cells**

March 2020

Prepared by:

Rachel Scholes<sup>1</sup>, Jack King<sup>2</sup>, William Mitch<sup>2</sup>, David Sedlak<sup>1</sup>

<sup>1</sup>University of California, Berkeley

<sup>2</sup>Stanford University

## **1. Introduction**

As part of the Reverse Osmosis Concentrate Management Project (ROCMP), ozone and open-water engineered treatment cells were tested at pilot scale to assess their ability to remove contaminants from reverse osmosis concentrate. Reverse osmosis concentrate (ROC) generated during water reuse contains many wastewater-derived contaminants at concentrations that may adversely affect aquatic organisms. While the overall loading of contaminants from untreated ROC will not differ from current wastewater effluent, concentrated discharge could contribute to local effects near the discharge points. In particular, elevated nutrient concentrations in ROC could contribute to eutrophication, while trace organic contaminants and metals in some cases exceed USEPA aquatic toxicity benchmark values and site-specific water quality criteria, respectively. As part of this study, a team of researchers from UC Berkeley, Stanford University, and the San Francisco Estuary Institute collaborated with Valley Water to evaluate the removal of nutrients, organic, and inorganic contaminants in a pilot-scale treatment system operated at the Silicon Valley Advanced Water Purification Center in San Jose, California. We also evaluated the effects of ozone and open-water treatment cells individually and in combination for removal of contaminants from ROC.

Ozone and open-water cells were selected for the pilot-scale study because they showed promise for efficiently removing contaminants from ROC. Ozone is widely used for polishing municipal wastewater and can efficiently remove trace organic contaminants from ROC (Benner et al., 2008). Open-water treatment cells have previously been implemented to remove nutrients and trace organic contaminants from

municipal wastewater effluent. Open-water cells combine biological treatment of nutrients and organic contaminants with photochemical transformation of trace organic contaminants. A shallow water column facilitates the growth of a biofilm comprised of photosynthetic diatoms and associated bacteria, and the shallow depth allows for phototransformation of contaminants throughout the water column (Jasper et al., 2013; Jasper & Sedlak, 2013; Jasper et al., 2014; Bear et al., 2017; Jones et al., 2014).

This report section provides the water quality results from monitoring of the pilot-scale treatment system. Details are provided on the effectiveness of ozone and open-water treatment cells for removing monitored contaminants. In addition, the effectiveness of combined ozone/wetland treatment, and implications for full-scale treatment systems are discussed.

## **2. Methods**

### **2.1 Target Analytes**

The target analytes for this study included indicator compounds, contaminants of emerging concern (CECs), nutrients, metals, and general water quality parameters.

Indicator compounds are trace organic contaminants that were selected to represent the wide array of contaminants present in wastewater. Six pharmaceuticals were used as indicator compounds. These pharmaceuticals occur frequently in wastewater effluent and exhibit a range of susceptibility to ozone and open-water wetland treatment. Further, previous studies with these compounds provide benchmarks against which to compare the removal efficiency observed in the pilot-scale treatment system (Jasper et al., 2014, Lee et al., 2013).

The CECs evaluated in this study included two pyrethroid pesticides (bifenthrin and permethrin), the phenylpyrazole pesticide fipronil and three commonly-detected degradates (fipronil sulfide, fipronil desulfinyl, and fipronil sulfone), the neonicotinoid pesticide imidacloprid, and two perfluorinated compounds (perfluorooctane sulfonate, PFOS, and perfluorooctanoic acid, PFOA). These compounds were selected based on their anticipated contributions to aquatic toxicity. Further details on their selection are provided in the ROCMP SAP. Notably, the pyrethroid pesticides were present below the limit of detection in all samples collected through August 2018 (i.e., <20 ng/L permethrin and <5 ng/L bifenthrin), after which monitoring of these compounds was discontinued. Implications of CECs for Bay toxicity concerns are discussed in Chapter 3.

Analysis of nutrients and metals was focused on contaminants that are currently regulated in the South Bay receiving waters or are under consideration for regulation. The monitored nutrients included ammonia, nitrate, nitrite, total nitrogen, phosphate, and total phosphorus. Copper and nickel were monitored due to the site-specific water quality objectives in South San Francisco Bay (SFBRWQCB, 2015). Mercury, lead, and zinc were monitored as priority metals from the California Toxics Rule. Selenium is under consideration for regulation in the South Bay and was also included in the pilot-scale study.

General water quality parameters, such as dissolved oxygen, pH, alkalinity, and dissolved organic carbon (among others, full details provided in ROCMP SAP, Chapter 5), were monitored to evaluate biomat activity and provide a basic characterization of the RO concentrate.

## **2.2 Pilot-Scale System Design**

The pilot-scale treatment system comprised two open-water treatment cells receiving ROC from the Silicon Valley Advanced Water Purification Center. This facility receives secondary nitrified municipal wastewater, which is then treated by microfiltration, reverse osmosis, and UV disinfection. The concentrate from the RO process (ROC) was fed directly to one open-water engineered treatment cell, while the other cell received ROC pre-treated by an on-site ozone unit. Each cell was approximately 190 m<sup>2</sup> in area and received a flow rate of 19000 L/day, resulting in a hydraulic residence time of approximately 3 days.

A pilot-scale ozone generator (MiPRO™ Advanced Oxidation Pilot System, Xylem, Inc., USA) was used to apply ozone to 13.2 L/min of ROC. The ozone dose was calculated based upon the flowrates of the gas from the ozone generator and the ROC, and the difference between continuous measurements of the gas-phase ozone concentrations prior to and after the ozone mixing chamber. A separate liquid-phase ozone sensor verified that there was no measurable ozone residual after the first ozone contact chamber, which had a residence time of five minutes. The ozone dose was set to approximately 20 ppm and was adjusted to 40 ppm for three sampling events during the summer of 2018 to investigate the effect of ozone dose on treatment effectiveness. Since the DOC of the ROC was ~40 mg/L, these doses correspond to ~0.5 or ~1.0 mg O<sub>3</sub>/mg DOC.

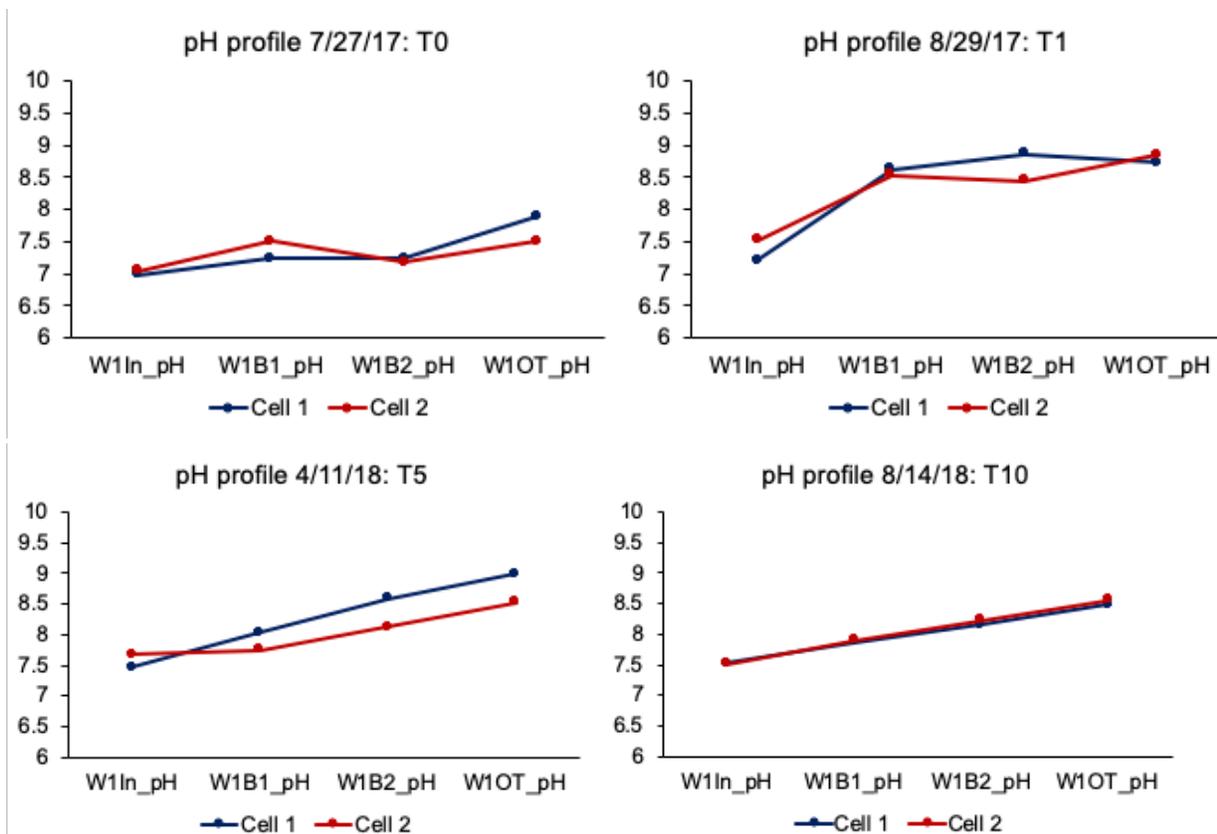
The pilot-scale treatment system was operated from July 2017 - September 2019. Samples for water quality analyses were collected every 2-4 weeks during the summer months and approximately bimonthly during the winter. Complete sampling and QA/QC schedules and procedures, as well as details of water quality analyses, are designated in the ROCMP Sampling and Analysis Plan.

## **3. Results**

### **3.1 System startup and establishment of treatment performance**

The open-water treatment cells were operated beginning in July 2017 but required an initial period of biomat growth before performance reached a point at which biotransformation of trace organics and removal of nitrate was observed. Within one month of the start of operation, pH and dissolved oxygen increases within the cells indicated photosynthetic activity, implying the growth of a diatomaceous biomat (Figure 1), which was consistent with the performance of previous open-water treatment cells (Jasper et al., 2014; Bear et al., 2017; Jones et al., 2014). However, significant biomat growth was not observed until the spring of 2018, when biomat covered the bottoms of both cells. Contaminants susceptible to biological treatment were more effectively removed after the biomat was well established, with greater removal starting in the summer of 2018.

Floating and suspended algae also limited the initial performance of the open-water cells. During the fall of 2017, floating algae grew in the treatment system due to shutdowns at the advanced treatment facility coupled with holding tank limitations. Stagnant water sitting in the cells coincided with floating algae growth. This issue was alleviated when larger holding tanks were installed in 2018 to preclude cessation of flow to the open-water cells.



**Figure 1. pH profiles in the open-water treatment cells. W1IN = inlet locations, W1B1 = first baffle locations (1/3 of the flow path of the cells), W1B2 = second baffle locations (2/3 of the flow path of the cells), W1OT = outlet locations (see diagram of open-water treatment cell in Chapter 5).**

To assess the treatment effectiveness of the open-water cells, we considered contaminant removal observed after consistent flow and the biomat were well-established because these conditions represent levels of treatment that would be expected during long-term operation of open-water treatment cells. We therefore focus here on the results from the final winter (November 2018 to March 2019) and summer (June to August 2019) of operation.

Startup issues also occurred with the on-site ozone treatment unit. For several sampling rounds during the fall of 2017, the ozone generator was not operational due to various system failures; Xylem indicated that the particular pilot unit provided was not designed for the continuous long-term operation needed to supply the open-water treatment cells. Results of ozone treatment effectiveness are presented for the final winter and summer of operation, as for the open-water cells, as well as the three summer sampling events in 2018 when a 40-ppm ozone dose was applied.

## 3.2 Contaminant Removal by Ozone Pre-Treatment alone

### Nutrients

Neither nitrate nor phosphate concentrations were affected by ozone treatment, as both are already present as the most oxidized forms of the compounds encountered in the aquatic environment.

### Trace organics

Ozone treatment of 20-ppm removed significant (> 80%) quantities of indicator compounds propranolol, sulfamethoxazole, carbamazepine and trimethoprim. Increasing the ozone dose from 20-ppm to 40-ppm increased removals of atenolol and metoprolol from 43% to 79% and from 57% to 86%, respectively. Trace organics removal with ozone did not significantly change between winter and summer or from 2018 to 2019. Fipronil (50%) was removed more efficiently than imidacloprid (20%) by 20-ppm ozone; 40-ppm ozone increased these removals to 70% and 28%, respectively. Fipronil transformation products were not significantly impacted by ozone, although slightly higher concentrations of fipronil sulfone were measured following ozone treatment, indicating that fipronil removal did not result in formation of the monitored transformation products or that oxidation products, such as fipronil sulfone, were further transformed within the ozone treatment unit. Total fiproles (the sum of fipronil and its transformation products) concentrations decreased by 30% and 60% due to treatment with 20-ppm or 40-ppm ozone, respectively. PFOS and PFOA were not removed by ozone. Other organic contaminants monitored due to Bay toxicity concerns are discussed further in Chapter 3.

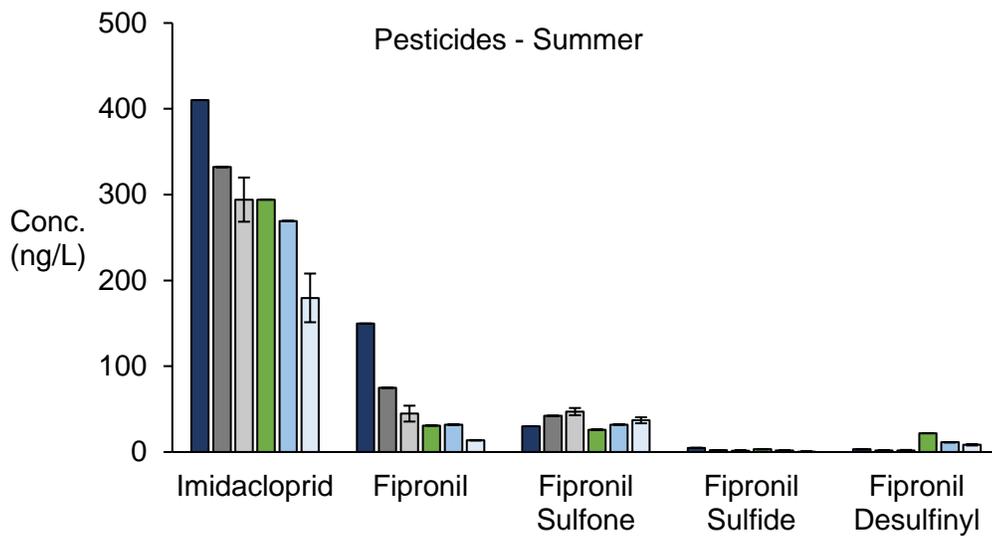
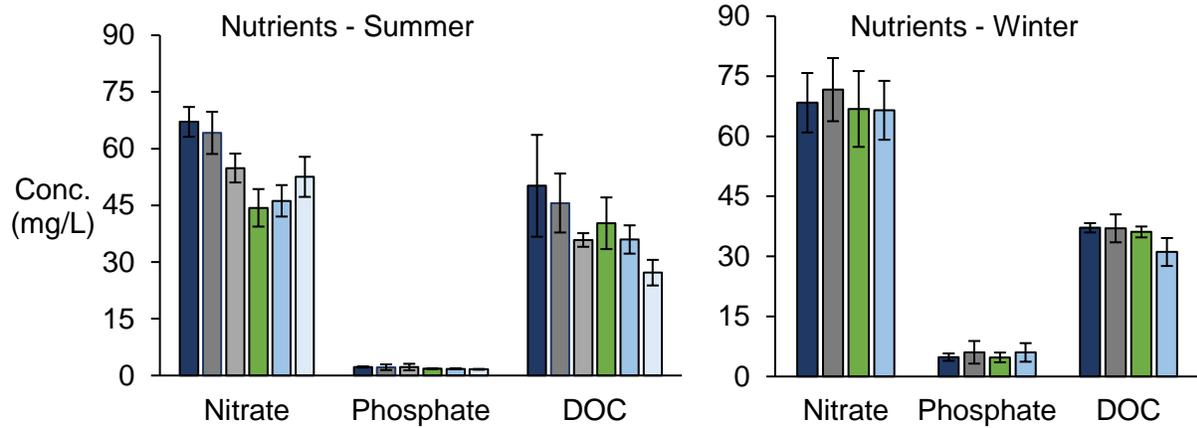
### Metals

Ozone did not change metals concentrations. In previous studies, it was shown that ozone had some ability to release metals from the chelated form, but a second treatment process, such as high pH precipitation, was needed to remove the freed metals.

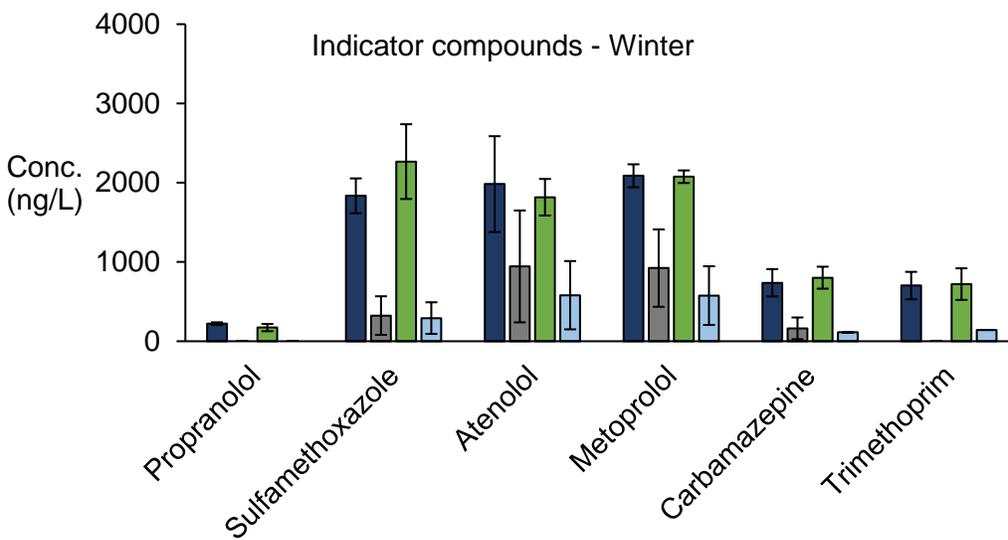
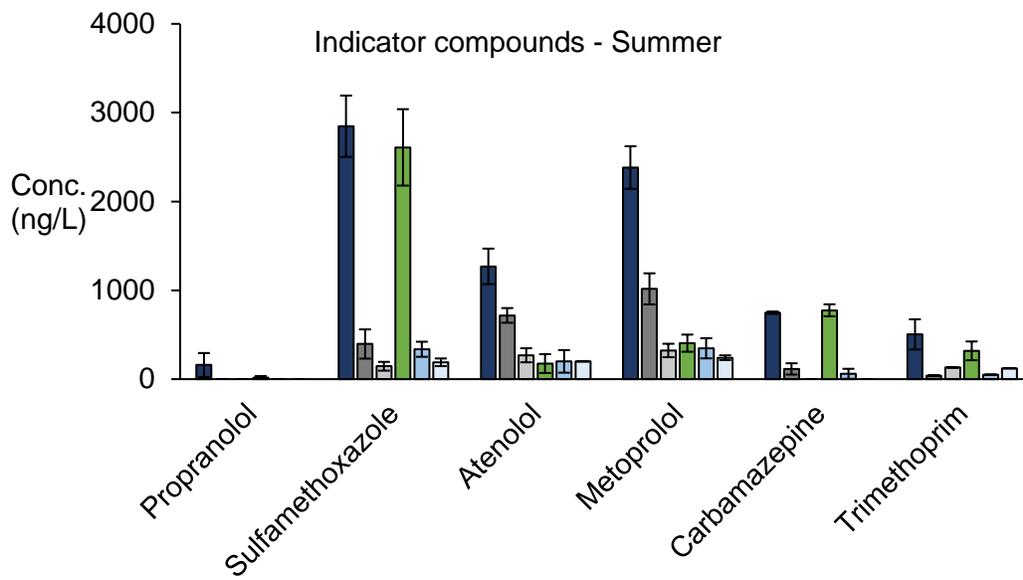
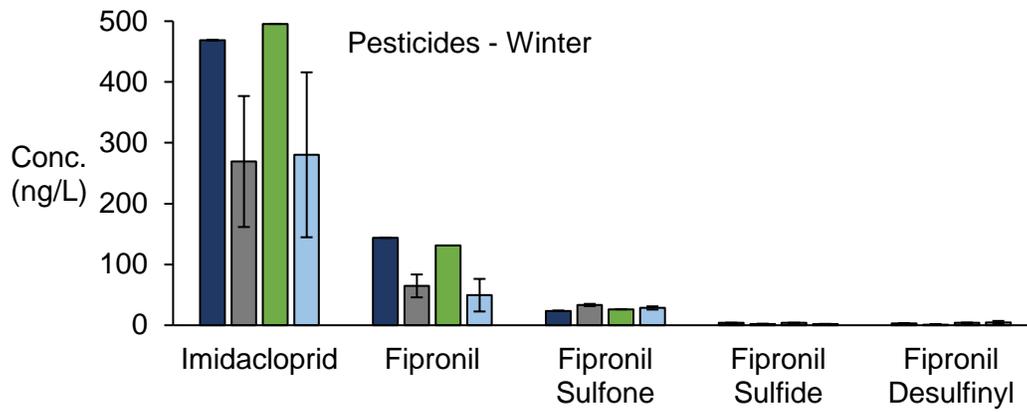
### **Byproducts (i.e., bromate)**

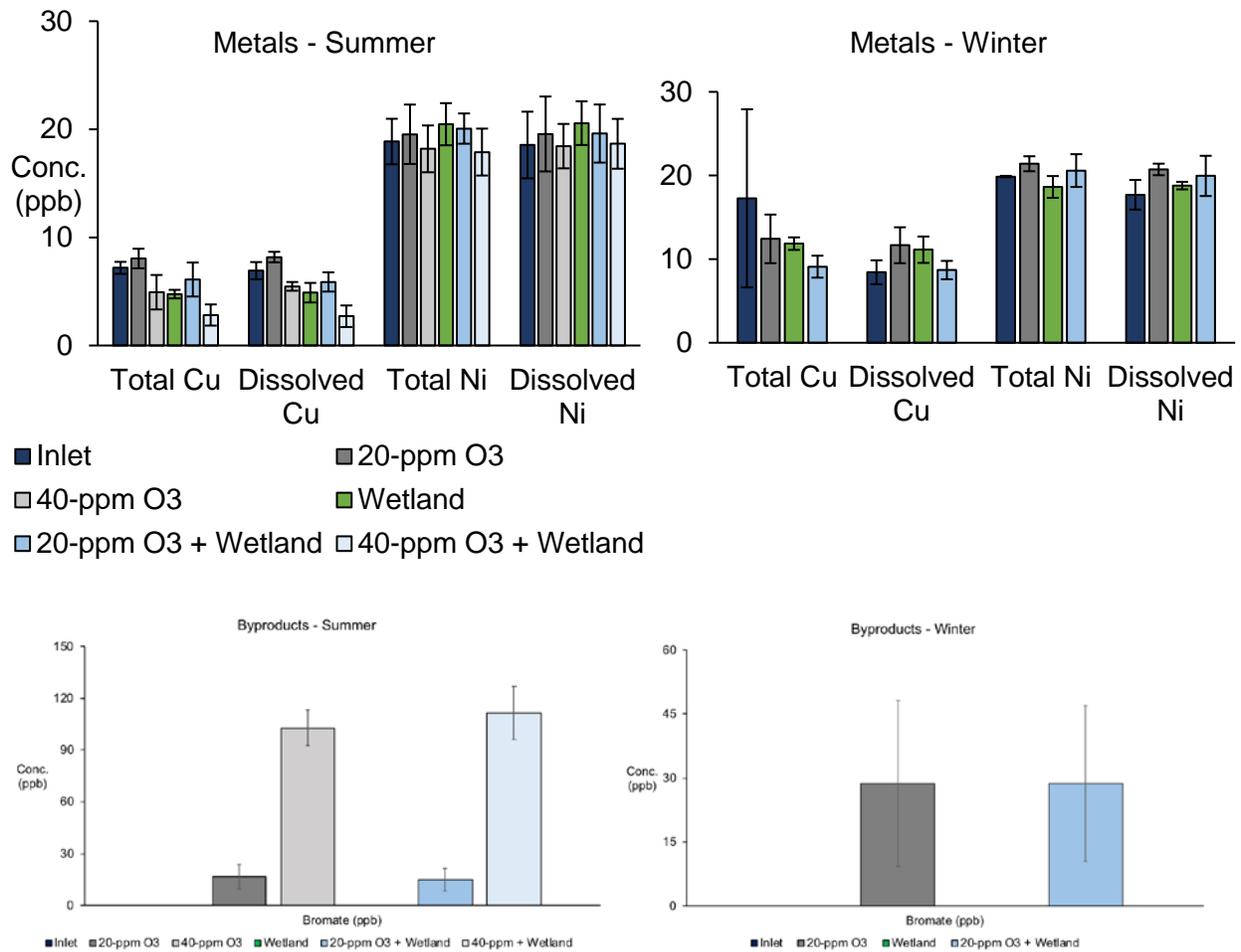
Ozone reactions with bromide form bromate, a compound that could pose risks to aquatic life at elevated concentrations. Treatment with 20-ppm ozone generated 6-57 ppb bromate, with an average of 21 ppb. Doubling ozone dose to 40 ppm increased bromate ~ 5-fold to 91-110 ppb. The sharp increase in bromate formation when doubling ozone dose could be due to the longer contact time of RO concentrate with molecular ozone; molecular ozone reacts more quickly than •OH to form bromate, and increasing ozone dose decreases the relative effect of ozone-scavenging compounds

(e.g., nitrite), thus more molecular ozone is present to react with bromide. Bromate concentration does not appear to have seasonal variations; variance is likely due to shifts in DOC and bromide concentration because the ozone/DOC ratio is the predominant predictor of removal of contaminants during ozonation, and bromide is a precursor of bromate.



■ Inlet ■ 20-ppm O3 □ 40-ppm O3 ■ Wetland ■ 20-ppm O3 + Wetland □ 40-ppm O3 + Wetland





**Figure 2. Contaminant concentrations in untreated (inlet), and treated (with ozone, wetland, or both) ROC. Bars represent average (+/- standard deviation) concentrations observed across three sampling events per season.**

### 3.3 Contaminant Removal in Open-Water Treatment Cells alone

#### Nutrients

Nitrate was the primary form of inorganic nitrogen in the ROC and was partially removed in the open-water treatment cells. During initial sampling rounds in 2017, prior to biomat establishment, no nitrate removal was observed. Following the development of a biomat, nitrate removal increased. In the summer, 5-29% of inlet nitrate was removed in 2018, and 28-47% was removed in 2019 on a mass basis. Inlet concentrations of nitrate varied from 49-74 mg-N/L throughout the study, and seasonal average concentrations used to calculate removals exhibited relative standard deviations of 5-11%. Nitrate removal in the open-water cells was seasonal due to changes in temperature affecting biomat activity. In the winter months, outlet water

temperatures were 14-15° C, versus 22-23° C in the summer. During the cooler winter months in 2018 and 2019, <15% of the inlet nitrate was removed. Coincident with nitrate removal, nitrite concentrations increased somewhat during the summer months. Inlet nitrite concentrations increased on average from 1.7 to 4.8 mg-N/L and from 0.4 to 0.8 mg-N/L in the summers of 2018 and 2019, respectively. Finally, up to 9 mg-N/L entered the open-water cells as ammonia. Concentrations of ammonia decreased in the open-water cells during the summer of 2018 and 2019, typically to below the reporting limit of 1.3 mg-N/L. Anammox accounted for a small fraction of nitrogen removal in open-water wetlands treating municipal wastewater effluent (Jones et al., 2014) and may have contributed to ammonia removal in the pilot-scale ROC treatment cells.

The possibility of enhancing nitrate removal by providing additional organic carbon sources was evaluated both in the laboratory and in the pilot-scale system. Laboratory microcosms with biomat sampled from the pilot-scale open-water treatment cells exhibited enhanced nitrate removal when a supplemental source of carbon (i.e., acetate or wood chips) was added. These results indicated that supplying an additional carbon source for heterotrophic denitrification could enhance nitrate removal in open-water treatment cells. To test this approach, permeable, mesh bags containing wood chips and gravel (to weight down the bags) were added to the final section (i.e., the last 33%) of each treatment cell in October 2018. Observations over the subsequent 11 months did not provide evidence for enhanced nitrate removal. It is possible that the location of the carbon source relative to biomat organisms (i.e., the wood chip amendment was placed on top of the existing biomat) was not suitable for delivering labile carbon to the biomat. To enhance nitrate removal at the pilot- or full-scale, a system for adding carbon to the biomat could be included in the initial installation (e.g., wood chips could be added prior to biomat development). Alternatively, a labile carbon source, such as acetate, could be dosed into the wetland to enhance nitrate removal.

Phosphate was present in the ROC and was partially, but not consistently, removed in the open-water wetland cells. Average phosphate concentrations in summer decreased by 37% in 2018 and by 24% in 2019. Dissolved organic carbon concentrations decreased 20% on average, from 50 mg-C/L to 40 mg-C/L, during open-water treatment in the summer, and were unaffected by the open-water cells in the winter.

### **Trace organic contaminants**

$\beta$ -adrenergic blockers were well-removed in the open-water cells in the summer, with less removal in the winter. In the summer of 2019, 92% and 82% of inlet atenolol and metoprolol were removed, respectively. Atenolol was slightly removed (8%) in the winter, whereas metoprolol was not removed in the winter. The decreased removal of

atenolol and metoprolol in the winter was attributable to slower biological activity, since these compounds are primarily removed via biological processes in open-water treatment cells (Jasper et al., 2014). Propranolol concentrations decreased by 88% during open-water treatment in the summer and 22% in the winter. Propranolol is primarily removed via phototransformation in open-water treatment cells. The slower removal of propranolol observed in the winter was therefore likely due to decreased sunlight irradiance (both intensity and duration of sunlight) in the winter months (Jasper & Sedlak, 2013).

Sulfamethoxazole, trimethoprim, and imidacloprid were partially removed from ROC in the summer and not removed to an appreciable extent in the winter. Sulfamethoxazole removal was 8% during the summer, whereas 37% and 28% of trimethoprim and imidacloprid were removed, respectively. No removal was observed for carbamazepine in summer or winter, consistent with observations in previous open-water cells treating municipal wastewater effluent (Jasper *et al.*, 2014; Bear *et al.*, 2017).

Fipronil was partially removed in the open-water wetlands and formation of a phototransformation product, fipronil desulfinyl, was observed. In the summer, 79% of inlet fipronil was removed, whereas in the winter 9% was removed. Concentrations of fipronil sulfone, an oxidation product of fipronil, remained constant during open-water cell treatment, while fipronil sulfide concentrations decreased slightly. Fipronil desulfinyl concentrations increased from 3.2 ng/L to 21.9 ng/L in the summer and stayed approximately constant in the winter. Total fiprole concentrations decreased by 56% and 5% in the open-water wetlands in the summer and winter, respectively. PFOS and PFOA were not removed by open-water wetlands and are discussed further in Chapter 3.

### **Trace metals**

Copper was partially removed in the open-water treatment cells, whereas nickel was not removed. Total copper concentrations decreased 34% in the summer and on average decreased 31% in the winter, although inlet concentrations in the winter exhibited high variability. Due to differences in inlet concentration, the average total copper concentration in ROC after treatment in the open-water cells was 4.8 ppb in summer and 11.9 ppb in winter. Nickel was not removed in the open-water cells and total nickel concentrations were similar in the summer (18.9 ppb on average) and winter (19.9 ppb on average).

## **Byproducts**

Bromate was only measurable in the open-water treatment cell with ozone pre-treatment because bromate is a byproduct of ozone reactions with bromide and would not be in the water otherwise. All non-ozonated water samples were below detection (< 5 ppb).

## **3.4 Combined Treatment by Ozone and Open-Water Treatment Cells**

### **Nutrients**

Nitrate and phosphate were not removed by ozone treatment, and their removal was similar in open-water cells with and without ozone pre-treatment. Inlet and outlet concentrations of nitrate were similar for both cells when operating with a 20-ppm ozone dose in the final year of operation. During the summer of 2018, when 40-ppm ozone was applied in pre-treatment, the biomat was less active in both treatment cells, resulting in relatively slower nitrate removal compared to sampling dates in 2019. Phosphate concentrations were similar before and after combined treatment. These results indicate that ozone pre-treatment did not provide a benefit for removal of nitrate and phosphate.

Combined treatment resulted in greater DOC removal than either treatment step alone. Combined treatment resulted in 28% and 16% removal of DOC in the summer and winter, respectively. With a dose of 40-ppm ozone, the combined treatment resulted in 32% removal of DOC.

### **Trace organics**

Combined treatment resulted in greater removal of  $\beta$ -blockers than ozone or open-water treatment cells alone. Atenolol and metoprolol were similarly removed by open-water cells and combined treatment in the summer but were better removed by combined treatment in the winter. Propranolol was removed to below the limit of quantification during ozone treatment and therefore did not benefit from combined treatment.

Sulfamethoxazole, carbamazepine, and trimethoprim were well removed by the combined treatment, with ozone pre-treatment providing most of the removal. Concentrations of all three compounds were similar after ozone and combined treatment in summer and winter.

Pesticides were most effectively removed by the combined treatment system. Imidacloprid was best removed by combined treatment in the summer, and removal was similar for combined or ozone treatment in the winter. In the summer, combined treatment resulted in removal of 34% of inlet imidacloprid using 20-ppm ozone, and 73% using 40-ppm ozone. In the winter, ozone removed on average 43% of the imidacloprid in the ROC, and imidacloprid concentrations did not change in the open-water treatment cells. Fipronil concentrations decreased by 79% during combined treatment with 20-ppm ozone in the summer, which was similar to removal in the open-water cells alone. In the winter, fipronil was primarily removed by ozone pre-treatment, and concentrations were similar with and without the open-water treatment cells. Fipronil sulfone concentrations were slightly higher following combined treatment compared to open-water cells alone (32 ng/L vs. 26 ng/L in the summer), whereas fipronil desulfinyl concentrations were lower following combined treatment (11.3 ng/L vs. 29.0 ng/L for open-water cells alone). Total fiprole concentrations decreased by 59% and 68% due to hybrid treatment with 20-ppm and 40-ppm ozone in the summer, respectively.

## **Metals**

Combined treatment did not enhance metals removal compared to open-water treatment cells in the summer, but ozone pre-treatment slightly increased copper removal in the winter. Concentrations of total copper in treated ROC in the summer were slightly higher following combined treatment with 20-ppm ozone (6.1 ppb on average) compared to open-water treatment (4.8 ppb on average). During the period in the summer of 2018 when a 40-ppm ozone dose was applied, the inlet concentrations of copper were lower, and greater removal was observed during combined treatment (22% with 20-ppm ozone vs. 47% with 40-ppm ozone). Nickel removal was not observed for any treatment scenario.

## **Byproducts**

Wetland treatment did not significantly change the concentration of bromate concentration produced during ozonation; the average wetland outlet concentration with 20-ppm ozone pre-treatment was 19 ppb, similar to the 21-ppb inlet concentration. When the ozone dose was 40-ppm, bromate was 103 ppb in the inlet and 112 ppb in the outlet. Biological processes in the wetland therefore do not remove bromate.

# **4. Summary and Recommendations**

Overall, the combination of ozone and open-water treatment cells for ROC partially removed nutrients and organic contaminants, with enhanced removal of many

contaminants using the combined treatment system. Nitrate was partially removed by open-water wetlands during the summer, whereas nitrate was generally not removed in the winter. The seasonality of nitrate removal in open-water cells may be acceptable because higher concentrations of nitrate released in the winter would coincide with greater dilution by environmental flows in the winter.

Removal of some trace organics was enhanced by the combined system, whereas others were primarily removed either by ozone or open-water cells, and some compounds were not removed by the hybrid system. For the  $\beta$ -blockers, which were well removed in the wetland during the summer, using higher ozone doses in the winter could mitigate the lower removal observed in open-water cells during the winter months. For several compounds with high ozone reaction rate constants, such as sulfamethoxazole and carbamazepine, ozone treatment provided most of the removal year-round. Open-water cells alone are not sufficient to reduce concentrations of these contaminants. Fipronil and imidacloprid were best removed by the combined system. Though these compounds were not fully removed at the pilot-scale system, the use of higher ozone doses or longer wetland hydraulic retention times could enhance removal of these compounds. Perfluorinated compounds (PFOS and PFOA) were not removed by the hybrid system. Alternative approaches would be required to reduce inputs of these contaminants to the Bay.

Nickel and copper were not well removed by the combined treatment system. Although some copper removal was observed in the open-water treatment cells, the removal mechanism and the longevity of this treatment function is unknown. Alternative treatment technologies, such as ozone followed by pH-induced precipitation, would likely be required to remove trace metals.

Bromate is formed as a byproduct of ozone reactions and is not removed by wetland treatment. However, the aquatic toxicity of bromate is relatively low and ozonation strategies to mitigate bromate can be implemented if necessitated (e.g., chlorine addition pre-ozone). Bromate is not present when ROC is only subjected to open-water treatment. The implications of bromate formation for toxicity to the Bay are discussed further in Chapter 3.

## 5. References

Bear, S. E., Nguyen, M. T., Jasper, J. T., Nygren, S., Nelson, K. L., Sedlak, D. L., 2017. Removal of Nutrients, Trace Organic Contaminants, and Bacterial Indicator Organisms

in a Demonstration-Scale Unit Process Open-Water Treatment Wetland. *Ecol. Eng.* 109, 76–83. <https://doi.org/10.1016/j.ecoleng.2017.09.017>.

Benner, J., Salhi, E., Ternes, T., Von Gunten, U., 2008. Ozonation of Reverse Osmosis Concentrate: Kinetics and Efficiency of Beta Blocker Oxidation. *Water Res.* 42, 3003–3012. <https://doi.org/10.1016/j.watres.2008.04.002>.

Jasper, J. T., Nguyen, M. T., Jones, Z. L., Ismail, N. S., Sedlak, D. L., Sharp, J. O., Luthy, R. G., Horne, A. J., Nelson, K. L., 2013. Unit Process Wetlands for Removal of Trace Organic Contaminants and Pathogens from Municipal Wastewater Effluents. *Environ. Eng. Sci.* 30 (8), 421–436. <https://doi.org/10.1089/ees.2012.0239>.

Jasper, J., Sedlak, D., 2013. Phototransformation of Wastewater-Derived Trace Organic Contaminants in Open-Water Unit Process Treatment Wetlands. *Environ. Sci. Technol.* 47, 10781–10790. <https://doi.org/10.1021/es304334w>.

Jasper, J. T., Jones, Z. L., Sharp, J. O., Sedlak, D. L., 2014. Nitrate Removal in Shallow, Open-Water Treatment Wetlands. *Environ. Sci. Technol.* 48 (19), 11512–11520. <https://doi.org/10.1021/es502785t>.

Jasper, J. T., Jones, Z. L., Sharp, J. O., Sedlak, D. L., 2014. Biotransformation of Trace Organic Contaminants in Open-Water Unit Process Treatment Wetlands. *Environ. Sci. Technol.* 48 (9), 5136–5144. <https://doi.org/10.1021/es500351e>.

Jones, Z. L., Jasper, J. T., Sedlak, D. L., Sharp, J. O., 2014. Sulfide-Induced Dissimilatory Nitrate Reduction to Ammonium Supports Anaerobic Ammonium Oxidation (Anammox) in an Openwater Unit Process Wetland. *Appl. Environ. Microbiol.* 83 (15), 1–14. <https://doi.org/10.1128/AEM.00782-17>.

Lee, Y., Gerrity, D., Lee, M., Bogeat, A. E., Salhi, E., Gamage, S., Trenholm, R. A., Wert, E. C., Snyder, S. A., von Gunten, C., 2013. Prediction of micropollutant elimination during ozonation of municipal wastewater effluents: Use of kinetic and water specific information. *Environ. Sci. Technol.* 47, 5872-5881. <https://doi.org/10.1021/es400781r>.

SFBRWQCB. 2012. San Francisco Bay Nutrient Management Strategy. Francisco Bay Regional Water Quality Control Board, Oakland, CA. Published online: [http://sfbaynutrients.sfei.org/sites/default/files/Nutrient\\_Strategy%20November%202012.pdf](http://sfbaynutrients.sfei.org/sites/default/files/Nutrient_Strategy%20November%202012.pdf).

# **Chapter 2: Laboratory-Scale Evaluation of Ozone and Wetland Microcosm Treatment for Reverse Osmosis Concentrate from Water Reuse Facilities Throughout California**

Summary of research performed in support of a novel treatment system for reverse osmosis concentrate at the Silicon Valley Advanced Water Purification Center

Jack King, Rachel Scholes, William Mitch and David Sedlak

National Science Foundation Engineering Research Center for Reinventing the Nation's Urban Water Infrastructure (ReNUWIt)

Submitted by Galen O'Toole on behalf of Santa Clara Valley Water District

December 31, 2019

# 1. Introduction

The Reverse Osmosis Concentrate (ROC) Management Project includes the evaluation of ozone and open-water engineered treatment cells as a treatment technology to remove contaminants of concern in reverse osmosis concentrate produced during potable reuse operations. Concerns over discharges of ROC to coastal waters center around the potential for these discharges to exert toxicity to organisms in receiving waters. However, the drivers of this potential toxicity have not been characterized. This study focused on the removal of inorganic nitrogen (i.e., nitrate and ammonia) as a potential driver for eutrophication, and specific contaminants hypothesized to contribute to toxicity. These contaminants include the pesticides imidacloprid, fipronil and fipronil degradates, and nickel and copper, which likely occur as chelates; the concentrations of these contaminants in ROC typically exceed thresholds associated with aquatic toxicity (see Section II). This study also evaluated several other contaminants which exhibit a range of reactivity with ozone to serve as indicators of the performance of ozone and wetland treatment for different contaminants. Finally, bromate is a toxic byproduct formed during ozone treatment that could be harmful to aquatic life. Ozone reactions with bromide form bromate, a potential human carcinogen with a 10 µg/L Maximum Contaminant Level (MCL) in drinking water. Although aquatic toxicity thresholds are not well-established, they are likely much higher, with a lowest observed effects concentration for inhibition of cell division in marine phytoplankton of 13.6 mg/L (Hutchinson et al., 1997).

Evaluation of the treatment technology has been undertaken at both laboratory-scale and pilot-scale, with a pilot system installed at the Silicon Valley Advanced Water Purification Center in July 2017. The pilot-study incorporated a pilot-scale ozone system followed by two pilot-scale wetland systems in parallel, each with. One wetland received ROC, while the other received ozone-treated ROC. In addition to long-term performance at pilot-scale, the pilot study evaluated the effects of different ozone doses, and seasonal temperature variations on the efficacy of the combined ozone/wetland treatment system. Data collection at the pilot-scale system was completed in October 2019, and a final report on the pilot study is being compiled.

This report provides the results from a set of laboratory experiments conducted by researchers at the University of California at Berkeley and Stanford University to assess the transferability of findings from the pilot-scale treatment system to RO concentrate treatment sampled from five facilities throughout the state of California including the Silicon Valley Advanced Water Purification Center (item 2.3.3 in the overall ROC Management Project work plan). Data from this facility is labeled ROC 1 in the following report. The other four facilities were facilities (ROC 2 through ROC 5) that incorporate reverse osmosis process units for the reuse of municipal wastewater

effluent from the State of California, but were provided on condition that the results were anonymized. Section II provides background water quality results that indicate the similarities and differences between the facilities.

The first section describes results from testing conducted to assess the use of ozone in terms of 1) removal of organic contaminants and as a pre-treatment for removal of metals, 2) precipitation of metals liberated by ozone treatment, and 3) bromate formation and mitigation. The second section describes research conducted in microcosms designed to simulate conditions occurring in the open water unit process wetlands.

## 2. Background Water Quality

Background water quality data are critical to understand the degree to which the ROC samples are similar, and thus whether the more detailed results obtained during the pilot study at facility 1 are applicable to other facilities. Moreover, these parameters may affect treatment by ozone and wetlands. For example, DOC and nitrite reduce the efficacy of ozone treatment by competing with target contaminants for reaction with ozone. Table 1 provides water quality results from the samples (ROC1 through ROC5) collected from the five facilities. The DOC ranged from 22.5-63.2 mg/L in ROC1, ROC2, ROC3 and ROC5; the ROC 4 featured 86.7 mg/L DOC. The TDS concentrations ranged from 3442-5742 mg/L, consistent with a ~7-fold concentration factor from secondary effluents for RO systems operated at 85% recovery (i.e., 500-900 mg/L TDS in secondary effluents). The high calcium content and alkalinities suggest that alkaline precipitation could facilitate co-precipitation of nickel and copper with calcium carbonate.

The high ammonia concentrations and low nitrate concentrations in Facilities 3 and 4 suggest that these facilities do not practice nitrification. However, note that the highest nitrite concentration was observed at facility 4; nitrite serves as an efficient scavenger of ozone, which can thereby hinder the efficacy of the ozone treatment process. It also absorbs sunlight and can produce a unique suite of transformation products of organic compounds during wetland treatment. The other three facilities practice nitrification and partial denitrification.

**Table 1: Water Quality Results for RO Concentrate Samples**

Facility Number	Unit	1	2	3	4	5
pH		7.7	7.4	6.7	6.9	7.3
DOC	mg/L	36.0	42.9	63.2	86.7	22.5
Alkalinity	mg/L as CaCO <sub>3</sub>	640	808	664	848	385

TDS	mg/L	4217	5742	4863	3934	3442
Chloride	mg/L	1263	1593	1151	978	1063
Bromide	mg/L	2.6	2.4	1.8	1.6	2.1
Bromate	µg/L	<10	<10	15.4	15.2	108
Ammonia	mg-N/L	4.6	3.1	290	317	<0.2
Nitrite	mg-N/L	0.4	1.1	<0.2	5.9	<0.2
Nitrate	mg-N/L	66	65	<0.2	<0.2	59
Calcium	mg/L	257	499	357	233	278
Atenolol	ng/L	1530	1290	910	1010	<200
Metoprolol	ng/L	2070	2370	710	2290	<100
Propranolol	ng/L	150	180	20	<20	<20
Trimethoprim	ng/L	310	1180	<10	960	<10
Sulfamethoxazole	ng/L	2910	3620	650	1840	210
Carbamazepine	ng/L	540	980	<10	300	<10
Imidacloprid	ng/L	534	800	408	1080	53
Fipronil	ng/L	151	212	95	280	12
Fipronil Sulfone	ng/L	32.7	49.1	27.5	41.1	14.5
Fipronil Sulfide	ng/L	4.1	5.8	9.4	13.2	<1.0
Fipronil Desulfinyl	ng/L	5.5	5.8	3.7	4.5	1.1
Total Cu	µg/L	7.4	8.8	30	38	23
Total Ni	µg/L	19	27	19	72	18

Bromide concentrations ranged from 1.6-2.6 mg/L, high enough to promote bromate formation during ozonation. Untreated ROC 5 had a significant bromate concentration (108 µg/L) (Fig. 5), likely because the potable reuse treatment train applies ozone prior to RO. Lower levels of background bromate (~15 µg/L) were detected in ROC 3 and 4, for similar reasons.

The samples contained nickel (18-72 µg/L), copper (7.4-38 µg/L), fipronil (12-280 ng/L) and imidacloprid (53-1077 ng/L) at concentrations that exceeded their benchmark chronic concentrations for aquatic toxicity (3.1 µg/L, 8.2 µg/L, 11 ng/L and 110 ng/L, respectively) in all five RO concentrate samples, with the exception of imidacloprid in ROC from facility 5 (United States Environmental Protection Agency, 2018 and 2019).

### 3. Ozone Experiments

The objectives of the ozone experiments were to: 1) determine whether degradation of contaminants could be predicted across different ROC samples as a function of ozone dose on a mg O<sub>3</sub>/mg DOC basis, 2) evaluate whether metals could be removed by precipitation after liberation of metals from chelates by ozone oxidation, and

3) evaluate the potential for bromate formation and the application of chlorine and ammonia to mitigate this formation.

### 3.1. Experimental Design

Ozone can oxidize contaminants by either direct reactions with contaminants or by producing hydroxyl radicals, which can then oxidize the contaminants. Previous research on ozonation of secondary municipal wastewater effluent indicated that organic contaminants could be sorted into five Groups based upon their reaction rate constants with ozone and hydroxyl radical (Lee et al., 2013). Group I contaminants featured the highest reaction rate constants with both ozone and hydroxyl radical, while Group V contaminants featured the lowest rate constants. Their research demonstrated that when ozone doses were normalized by DOC concentrations (i.e., mg O<sub>3</sub>/mg DOC), the degradation of contaminants at these ozone doses was similar across different secondary wastewater effluents for compounds within the same group. While the drivers of toxicity in ROC samples are unclear, when specific toxicity drivers are identified by future research, it would be advantageous if their degradation during ozonation in ROC could be predicted as a function of ozone dose (mg O<sub>3</sub>/mg DOC) based solely on their reaction rate constants with ozone and hydroxyl radical. Whether the contaminant grouping scheme of Lee et al. (2013) applies to the more concentrated matrix of ROC is unclear. Testing this predictive capability was the primary objective of this ozone research.

We identified five organic contaminants within each of the Groups identified by Lee et al. (2013): sulfamethoxazole (Group I, spiked as 106 nM in lab experiments), atenolol (Group II, 100 nM), DEET (Group III, 125 nM), atrazine (Group IV, 125 nM), and TCEP (Group V, 236 nM). Low concentrations of each of these organic contaminants were spiked as a mixture into ROC samples prior to ozonation. Spiking was pursued to ensure that concentrations were sufficient to permit the detection of significant degradation following ozonation. Samples were treated with a range of ozone doses (0, 0.30 mg O<sub>3</sub>/mg DOC, 0.59 mg O<sub>3</sub>/mg DOC, 0.89 mg O<sub>3</sub>/mg DOC, and 1.18 mg O<sub>3</sub>/mg DOC), then analyzed to evaluate the ozone doses required for removal of the spiked contaminants. We also spiked in fipronil, imidacloprid, Ni-EDTA and Cu-EDTA as contaminants of likely toxicological concern in ROC. Based upon their ozone and hydroxyl radical reaction rate constants, which we measured, we categorized fipronil as Group II/III, imidacloprid as Group III, Ni-EDTA as Group III/IV and Cu-EDTA as Group IV. We spiked in fipronil and imidacloprid within the same concentration range as the other contaminants. Ni-EDTA and Cu-EDTA were spiked at 4 μM to be above their detection limit.

Note that tests were conducted separately for ozone treatment and open water mesocosm treatment of the RO concentrate samples. We dosed ozone from

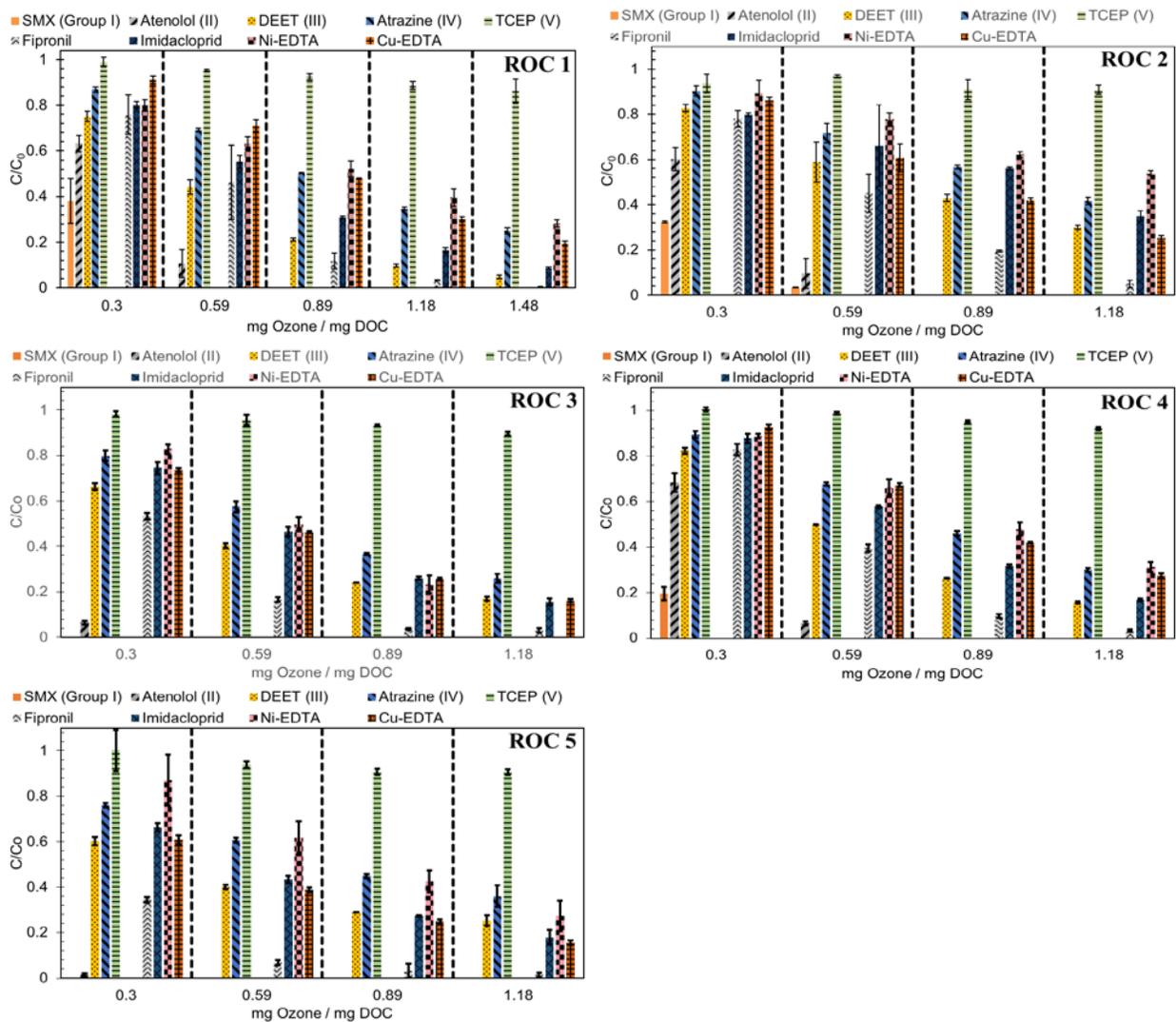
concentrated aqueous stock solutions. Significant sample dilution resulted when the ozone was applied to achieve the desired mg O<sub>3</sub>/mg DOC concentrations. This dilution could affect the performance of the mesocosm (e.g., the ozonated RO concentrate matrix would be less concentrated than the non-ozonated control, potentially enhancing the efficacy of open water mesocosm treatment).

### 3.2 Results for Degradation of Spiked Contaminants vs. Ozone Dose

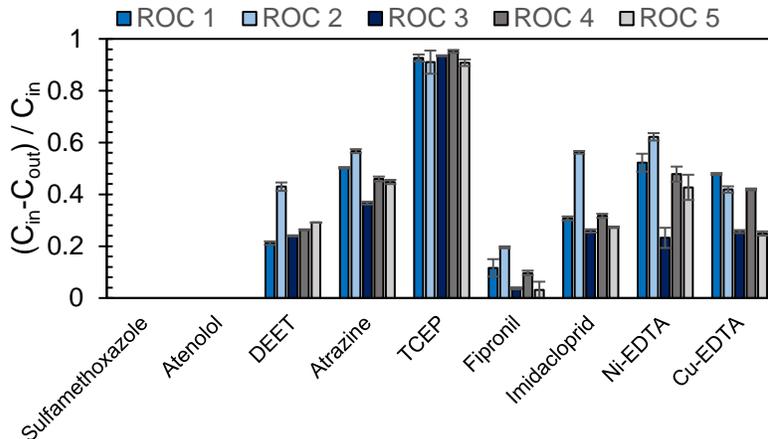
When the spiked RO concentrate samples from each facility were treated with 0.29-1.18 mg O<sub>3</sub>/mg DOC, degradation of contaminants decreased with increasing Group number (i.e., decreasing ozone and hydroxyl radical reaction rate constants) (Fig. 1). Sulfamethoxazole (Group I) was completely removed at 0.59 mg O<sub>3</sub>/mg DOC, while only ~10% degradation of TCEP (Group V) was observed at 1.18 mg O<sub>3</sub>/mg DOC. Some differences were observed between RO concentrate samples that correlated with the presence of nitrite. During application of 0.3 mg O<sub>3</sub>/mg DOC to ROC 5, which lacked nitrite, sulfamethoxazole (Group I) was completely removed, and the removal of atenolol (Group II) was 98% (Fig. 1). For the same dose applied to ROC 4 (5.9 mg-N/L NO<sub>2</sub><sup>-</sup>), sulfamethoxazole removal was 80% and atenolol removal was 32%. Nitrite most likely scavenged O<sub>3</sub> in ROC 4, ROC 1, and ROC 2. Scavenging of O<sub>3</sub> by nitrite also caused higher removal of DEET (40%) and atrazine (24%) in ROC 5 than in ROC 4 (18% DEET and 11% atrazine) when treated with 0.30 mg O<sub>3</sub>/mg DOC. However, at higher ozone doses (e.g., 0.89 mg O<sub>3</sub>/mg DOC), nitrite scavenging was less important and contaminant removal was similar across all concentrates (Fig. 2). The removal of each compound in these RO concentrates was within the range observed in secondary effluent samples in previous studies for the same range of O<sub>3</sub> doses on a mg O<sub>3</sub>/mg DOC basis (Lee et al., 2013).

The degradation of fipronil, imidacloprid, Cu-EDTA and Ni-EDTA as a function of ozone dose had not been evaluated previously in studies of secondary wastewater effluent (Lee et al., 2013). The degradation of these contaminants was similar to that observed for the representative compounds in their Groups (i.e., atenolol, DEET and atrazine), assigned based on their ozone and hydroxyl radical reaction rate constants. Application of 0.89 mg O<sub>3</sub>/mg DOC is similar to the doses being considered for treatment of secondary wastewater effluents in Europe and treatment of wastewater in potable reuse trains based on ozone and biological activated carbon in the U.S. This dose removed 80-97% and 44-75% of emerging contaminants fipronil and imidacloprid, respectively (Fig. 2). These results provide additional confirmation that this categorization scheme can serve as a useful tool to predict removal of newly identified contaminants in ROC if their ozone and hydroxyl radical reaction rate constants are known.

Overall, these results suggest that the pattern of contaminant degradation by ozone observed in secondary effluents applies to RO concentrates. A dose of 0.89 mg O<sub>3</sub>/mg DOC would provide significant removal of Groups I-IV contaminants, including pesticides and metal-EDTA complexes, but would not provide significant (i.e., >50%) removal of Group V contaminants (e.g., TCEP). For the range of DOC in these ROC samples, this dose would be equivalent to absolute ozone doses of 20-77 mg/L.



**Figure 1.** Removal of a set of spiked contaminants in RO concentrate from five facilities after treatment with a range of ozone doses. Experiments were done in triplicate. Figures adapted from the Supporting Information of King et al., 2019 (submitted).



**Figure 2.** Removal of a set of spiked contaminants in RO concentrates after treatment with 0.89 mg O<sub>3</sub>/mg DOC. Experiments were done in triplicate. Sulfamethoxazole and atenolol (no bars) were removed completely in each ROC.

### 3.3 Metal Removal by Precipitation

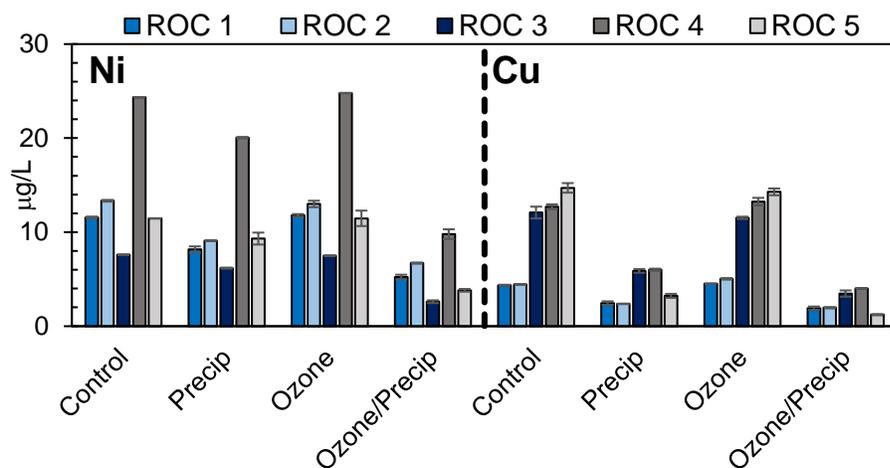
Chelated metals are difficult to remove by techniques such as precipitation, a process that may occur within engineered treatment wetlands. Ozone can degrade the chelate portion of metal-chelates (e.g., EDTA in Ni-EDTA), but does not degrade the metals. Accordingly, we evaluated the extent to which ozone pre-treatment could facilitate precipitation of metals, by liberating them from chelates. The identities of the Cu and Ni chelates in the un-spiked ROC samples was unclear. Initial experiments involved treatment of ROC samples with 1 mg O<sub>3</sub>/mg DOC and then alkaline precipitation. Alkaline treatment consisted of adjusting pH to 11 with sodium hydroxide and adding 300 mg/L calcium oxide, letting precipitates settle overnight, and analyzing the supernatant for metals. These extreme conditions were expected to maximize precipitation of metal carbonates liberated from chelates in combination with the native carbonates (see the high alkalinities in Table 1).

Although ozone partially degrades Ni-EDTA and Cu-EDTA (Fig. 2), no difference in total nickel or copper concentrations was observed without addition of sodium hydroxide or calcium oxide (Fig. 3). When the RO concentrate samples were treated with 300 mg/L calcium oxide at pH 11 without ozone pretreatment, total copper concentrations decreased by 51-53% for facilities 1-4, but 78% for facility 5 (Fig. 3). Total nickel concentrations decreased by 18-31% across all 5 facilities. Thus, a portion of the total native metals in each RO concentrate was labile to precipitation, with copper more labile than nickel, especially at facility 5. When these samples were ozonated and then subjected to alkaline conditions, the total copper concentrations declined by 59-71% for facilities 1-4 and 92% for facility 5. Total nickel concentrations declined by 60-

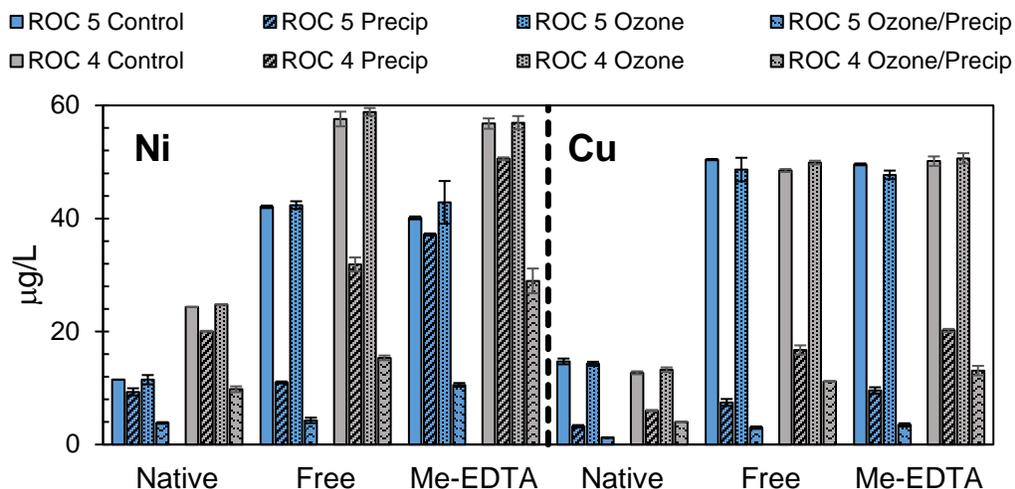
67% across all 5 facilities. Ozone pretreatment therefore further enhanced precipitative removal of nickel (~3-fold increase versus no ozone) than copper (~25%).

We also evaluated the effect of ozonation and precipitation on free nickel (spiked as NiCl<sub>2</sub> salt) and copper (CuCl<sub>2</sub>) or Ni-EDTA and Cu-EDTA spiked into ROC 4 and ROC 5 at ~4 times higher than the total concentrations of the native metals (Fig. 4). For nickel, the behavior between the native metals (i.e., originally in the ROC) and after spiking with Ni-EDTA was most similar (versus free metal spiking), suggesting that the native metals occurred in strongly-bound chelates. For native, free or EDTA-bound copper, removal of different metal species was similar; precipitation alone removed ~50% of the total copper and ozone further promoted copper removal, particularly at facility 5. It is likely that the native copper was bound to similar chelating agents as nickel, but that the copper chelates were more labile to precipitation.

In summary, ozone pre-treatment was necessary to facilitate nickel precipitation, but precipitation alone was able to remove a large fraction of copper. However, the precipitation treatment used would produce significant amounts of sludge (e.g., ~10 tons/day for a 4 million L/day facility), necessitating that technologies other than precipitation are pursued in conjunction with ozone pre-treatment to remove metals partially liberated from chelates.



**Figure 3.** Removal of nickel and copper in ROC with and without applying 1 mg O<sub>3</sub>/mg DOC ozone and alkaline treatment (300 mg/L CaO at pH 11). Experiments were done in duplicate.



**Figure 4.** Removal of native, and spiked free and EDTA-complexed nickel and copper in RO concentrate from two facilities with and without after applying 1 mg O<sub>3</sub>/mg DOC ozone and alkaline treatment (300 mg/L CaO at pH 11). Experiments were done in duplicate.

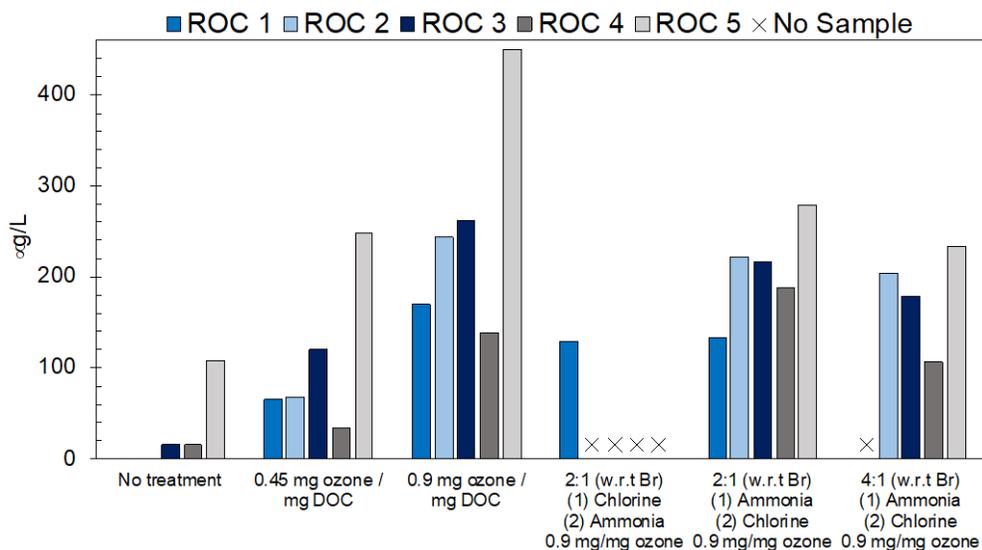
### 3.4 Bromate

Bromate formation during ozone treatment was measured and bromate mitigation strategies using chlorine and ammonia were tested for each concentrate. Chlorine and ammonia were added sequentially prior to ozonation in 2-4-fold molar excess of Br<sup>-</sup> for each concentrate. Reagents were added five minutes apart, followed by ozone addition five minutes later. Chlorine was added as HOCl, and ammonia was added as NH<sub>4</sub>Cl.

Bromate formation among the five concentrates ranged from 34-247 µg/L at 0.45 mg O<sub>3</sub>/mg DOC and 139-451 µg/L at 0.9 mg O<sub>3</sub>/mg DOC (Fig. 5). The highest bromate formation was in ROC 5, which had the lowest DOC and no detectable nitrite; the lowest formation was in ROC 4, which had the highest DOC and nitrite concentrations.

As a bromate mitigation measure, we added chlorine and ammonia prior to ozonation to convert bromide to HOBr and then bromamines; sequestering bromide within bromamines inhibits bromate formation since bromamines are less reactive with ozone. Chlorine (sodium hypochlorite) and ammonia (ammonium chloride) were added sequentially prior to ozonation in 2 or 4-fold molar excess relative to bromide for each sample. Reagents were added five minutes apart, followed by ozone addition five minutes later. Adding chlorine and ammonia at a 2:1 molar ratio relative to Br<sup>-</sup> for ROC 1 decreased bromate formation by ~23% irrespective of which reagent was added first (Fig. 5). Addition of ammonia and then chlorine to the other four ROC samples at a 2:1 molar ratio relative to Br<sup>-</sup> reduced bromate formation by 9-38%, and at a 4:1 ratio by 16-48%. Preformed monochloramine (not shown) had no effect on bromate formation,

highlighting the slow reaction between chloramines and bromide, relative to free chlorine. Note that chloramines occur in RO concentrate since chloramines are applied upstream of RO to inhibit biofouling, and chloramines can pass through RO membranes. These results indicate that the native chloramines would be unable to significantly inhibit bromate formation.



**Figure 5.** Bromate formation during ozone treatment of RO concentrate with and without applying mitigation strategies with chlorine and ammonia. Experiments are single samples.

## 4. Open Water Unit Process (OWUP) Wetland Microcosms

### 4.1 Experimental Design and Methods

RO concentrate was treated in laboratory microcosms which simulated the conditions of open-water wetland treatment. The microcosm experiments were conducted in triplicate for each facility, in 600-mL black-painted beakers containing biomat sampled from the pilot-scale system, illuminated with a solar simulator. Microcosm experiments were conducted as follows:

- 1) Fresh biomat was sampled from the pilot system prior to each set of microcosm experiments.
- 2) 500 mL of RO concentrate was added to beakers containing 50 mL biomat, and the biomat microorganisms were allowed to acclimate to the composition of the RO concentrate sample for 3 days. Microcosms were maintained under a solar simulator, irradiated for 8 hours per day, in a water bath at 25°C, and were

continuously mixed by stir bars suspended from above to avoid suspension of biomat solids.

- 3) After acclimation, the RO concentrate was decanted from the microcosm, and replaced with 500 mL of concentrate from the same initial sample. The addition of the second batch of 500-mL concentrate marked the start of the microcosm evaluation ('t<sub>0</sub>').
- 4) Subsamples for nitrate and trace organics were taken daily for 3 days following the introduction of RO concentrate.
- 5) After 3 days, microcosms were subsampled for nitrate, trace metals, and trace organics analyses. The remainder of the treated RO concentrate was used for solid phase extraction followed by analysis of pesticides (fipronil, imidacloprid, and transformation products).

A 3-day experimental length was selected to align with the hydraulic residence time of RO concentrate in the pilot open-water treatment cells.

All microcosm experiments were run in triplicate (i.e., three parallel beakers each containing 500-mL concentrate from the same facility).

## 4.2 Results

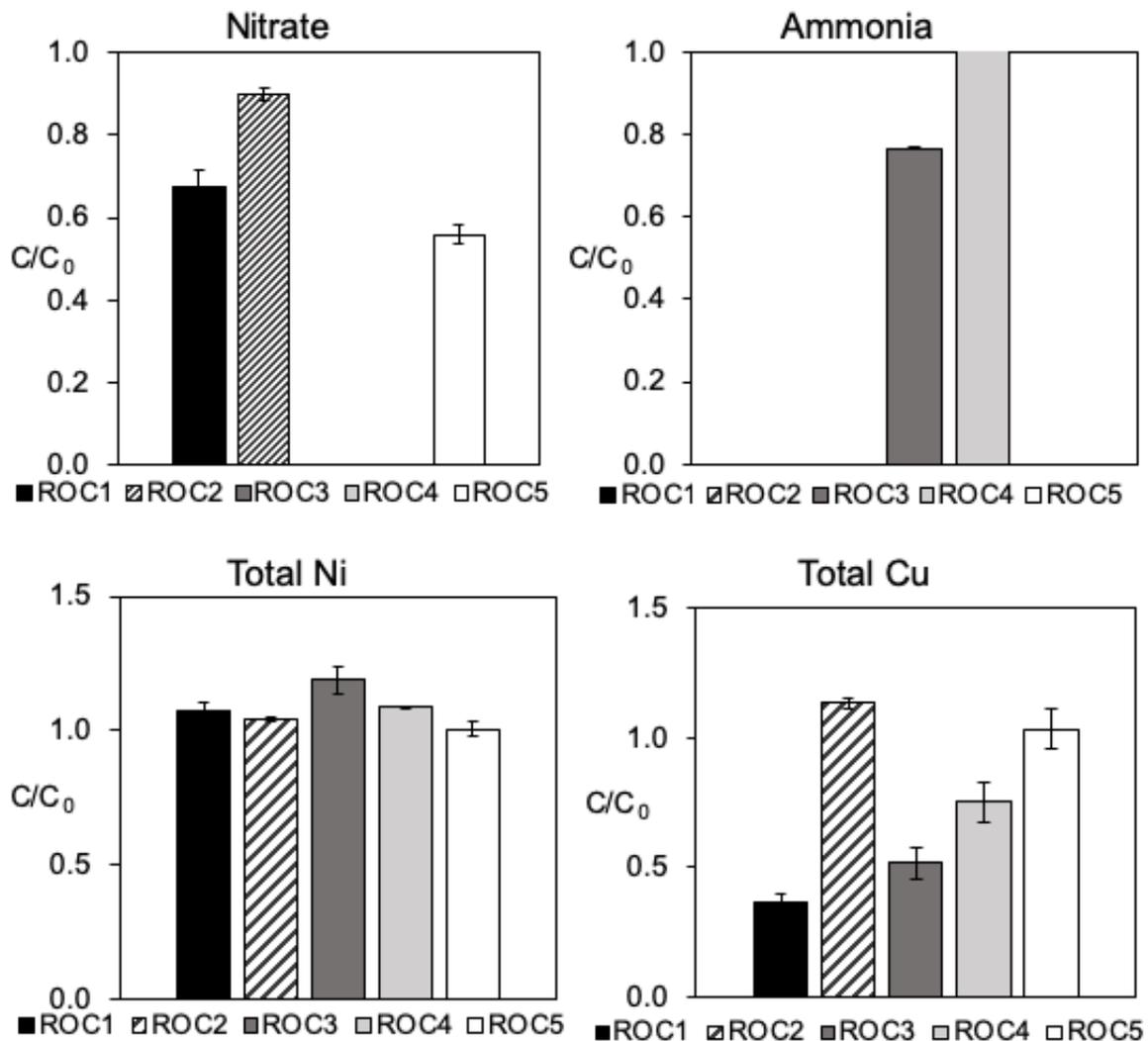
### Nutrients & Metals

Nitrate was the predominant inorganic nitrogen species in ROC samples 1, 2, and 5, accounting for 80 to 100% of the total dissolved nitrogen species (the sum of nitrate, nitrite, and ammonia). Nitrate concentrations decreased by 10-44% in the microcosms, with the greatest removal observed in ROC5 and the least removal in ROC2 (Figure 6a). Although the percentage removal varied among the three nitrate-rich RO concentrate samples, the absolute decrease in concentration was similar for ROC1, sampled from the Silicon Valley Advanced Water Purification Center (19.5 mg-N/L removed) and ROC5 (21.8 mg-N/L removed). Less removal of nitrate (i.e., 5.1 mg-N/L) was observed in ROC2, indicating that biological denitrification occurred more slowly in concentrate from this facility.

Ammonia was the predominant form of dissolved nitrogen in ROC samples 3 and 4, accounting for 100 and 98% of the total dissolved nitrogen species, respectively (Figure 6b). In ROC3, the ammonia concentration decreased by approximately 20% whereas the concentration of ammonia increased by approximately 25% in ROC4. Neither the biomat used in microcosms nor the microbes in the RO concentrate were expected to oxidize ammonia under the conditions used in this study because ammonia-oxidizing bacteria (i.e., nitrifiers) would not have been selected for in the open-water wetlands in which the biomat was grown (i.e., in a biomat treating RO concentrate with negligible ammonia and with high nitrate concentrations) and the duration of the experiments (i.e.,

3 days) was relatively short. The increase in ammonia concentrations in ROC4 could have been due to release of the compound from the biomat or microbial reductive processes occurring in the anaerobic sediments. Further research would be necessary to assess whether open water unit process wetlands could be used for ammonia removal.

Copper and nickel were also analyzed before and after wetland microcosm treatment. Nickel concentrations increased slightly in all microcosms due to evaporation. Copper concentrations were stable or decreased following microcosm treatment.



**Figure 6.** Fraction of inorganic nitrogen and metals removed in wetland microcosms. ROC3 and ROC4 contained negligible concentrations of ammonia. ROC1, ROC2, and ROC5 contained negligible concentrations of nitrate.

## **Organic Contaminants**

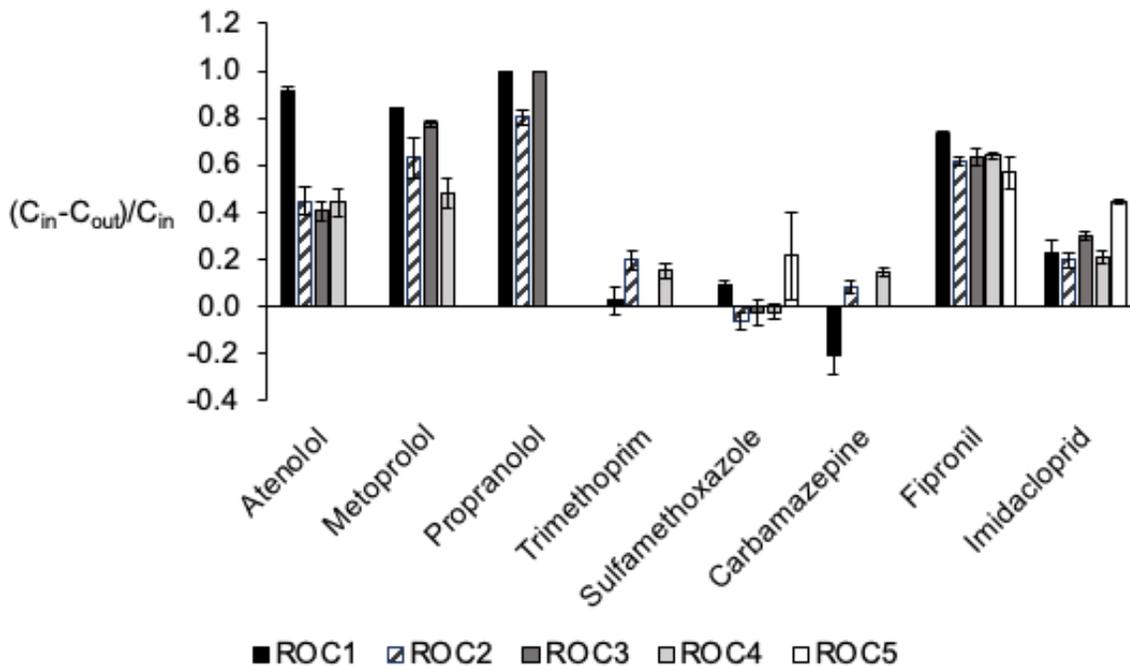
In general, the removal of organic contaminants from the RO concentrate was similar among samples collected from different locations (Figure 7). With a few exceptions, the percent of the compounds removed varied by less than 20% among samples from the five facilities.

Atenolol removal was greater in ROC1 (i.e., 92%) than in the other four samples (i.e., 40-45%). This could have been related to the fact that ROC1 was collected from the location where the biofilm was grown. It is noteworthy that removal of the other beta-blockers (i.e., metoprolol, propranolol) and fipronil were also higher for ROC1. These results indicate that the other compounds that were amenable to biotransformation in the biomat are also transformed in other RO concentrates. Additional pilot- or full-scale research would be needed to determine if biomats grown in other RO concentrates could obtain better removal of these compounds.

Trimethoprim, sulfamethoxazole, and carbamazepine removal was relatively low in all of the RO concentrate samples. These compounds are primarily removed during ozone pre-treatment in the combined treatment system.

Fipronil was present in all five concentrate samples and was removed to a similar extent in all of the wetland microcosms. Between 19 and 30% of the imidacloprid was removed in ROC1-4, and was 55% removed in ROC5. However, the starting concentration was much lower in ROC5 than in other samples.

Overall, the consistent trends of removal of trace organics across RO concentrate samples indicate that open-water wetlands may be similarly effective for bio- and phototransformation of trace organics in concentrates from a variety of water reuse facilities.



**Figure 7.** Fraction of trace organic contaminants removed in wetland microcosms. Contaminants present below the limit of quantification in an RO concentrate sample (e.g., atenolol, metoprolol, and propranolol in ROC5) are excluded.

## 5. Summary and Recommendations

This study evaluated the ability of ozone and open water wetland treatment to degrade chemical contaminants in RO concentrates to address concerns regarding their discharge to marine waters. Primary contaminants of concern included 1) organic contaminants (e.g. pesticides), 2) metals (in the form of EDTA chelates), and 3) nutrients. Ozone and open water wetlands were complementary for the removal of a set of organic contaminants (e.g. sulfamethoxazole was not removed by wetlands but completely removed by ozone), including emerging pesticides fipronil and imidacloprid. The presence of nitrite caused some differences in removal of organics at lower ozone doses (e.g. 0.30 mg O<sub>3</sub>/mg DOC) but those differences became smaller at higher ozone doses more typical of wastewater treatment (e.g. 0.89 mg O<sub>3</sub>/mg DOC). Additionally, ozone pre-treatment facilitated metal removal by alkaline precipitation by partially degrading EDTA chelates with nickel and copper, although excessive sludge was generated during precipitation treatment. Bromate formed during ozonation but could be reduced up to ~50% by adding chlorine and ammonia. Open water wetland microcosms

partially removed nitrate and organic contaminants. Nitrate removal rates were similar in two concentrate samples, and slower in a third. The remaining two concentrate samples contained ammonia, rather than nitrate, which was approximately 20% removed in one sample and was not removed in the other. Trace organic contaminant removal was consistent across concentrate samples, indicating that bio- and phototransformation processes in open-water wetlands may be similarly effective across a range of RO concentrates.

These studies indicated that the water qualities were similar between RO concentrate samples, and that the behavior of the RO concentrate samples with respect to ozone and open water wetland treatment were also similar. While these treatment systems were capable of removing organic contaminants, they achieved only partial removal of nutrients and metals liberated from chelates by ozonation; additional treatment would likely be needed to meet future regulatory limits. Additional studies are recommended to identify technologies capable of removing liberated metals and nutrients.

## 6. References

Hutchinson, T.H., Hutchings, M.J., Moore, K.W., 1997. A Review of the Effects of Bromate on Aquatic Organisms and Toxicity of Bromate to Oyster (*Crassostrea gigas*) Embryos. *Ecotoxicol. Environ. Saf.* 38, 238–243. <https://doi.org/10.1006/eesa.1997.1584>

King, J.F., Szczuka, A., Zhang, Z., Mitch, W.A. Efficacy of Ozone for Removal of Pesticides, Metals and Indicator Virus from Reverse Osmosis Concentrates Generated During Potable Reuse of Municipal Wastewaters. Submitted to *Water Research*, November 2019.

Lee, Y., Gerrity, D., Lee, M., Bogeat, A.E., Salhi, E., Gamage, S., Trenholm, R.A., Wert, E.C., Snyder, S.A., von Gunten, U., 2013. Prediction of micropollutant elimination during ozonation of municipal wastewater effluents: Use of kinetic and water specific information. *Environ. Sci. Technol.* 47, 5872–5881. <https://doi.org/10.1021/es400781r>

United States Environmental Protection Agency, 2019. National Recommended Water Quality Criteria - Aquatic Life Criteria Table [WWW Document]. URL <https://www.epa.gov/wqc/national-recommended-water-quality-criteria-aquatic-life-criteria-table> (accessed 5.8.18).

United States Environmental Protection Agency, 2018. Aquatic Life Benchmarks and Ecological Risk Assessments for Registered Pesticides [WWW Document]. URL <https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-and-ecological-risk> (accessed 5.8.18).

# **Chapter 3: Toxicological Evaluation of ROC Contaminants and Application of Open-water Treatment Cell System**

Diana Lin, Miguel Mendez, Ezra Miller, Rebecca Sutton  
San Francisco Estuary Institute

## **1. Introduction**

The beneficial uses of surface waters receiving wastewater effluent and ROC discharges can be impacted by excessive levels of anthropogenic contaminants. While discharge of ROC would not generally be expected to change the overall contaminant loads from wastewater to receiving waters, the concentrations of chemicals at the point of discharge are likely to increase, potentially leading to more impacts on aquatic organisms in these locations. On the other hand, effective treatment of ROC to reduce contaminants may provide the opportunity to improve overall water quality of receiving waters by efficiently decreasing contaminant loads derived from wastewater. Treating and removing contaminants in ROC may be more effective compared to treating wastewater because contaminants are concentrated in the ROC waste stream.

To assess these issues, the State Water Board recently funded a project to develop Reverse Osmosis Concentrate Management Plans for the expansion of the Silicon Valley Advanced Water Purification Center (SVAWPC), and additional Advanced Water Purification Facilities (AWPFs) that could be located in South San Jose, Palo Alto, Sunnyvale, or Morgan Hill. A primary component of this project was pilot-scale testing of ozone treatment followed by engineered open-water treatment cells to evaluate the removal of contaminants in ROC, including nutrients, metals, and several trace organics with potential ecotoxicity concerns in receiving waters. The treatment train explored by this pilot study represents a relatively low-cost and sustainable means of treating ROC. However, its performance must be evaluated to provide adequate data for decision-making that will impact ROC management statewide.

The purpose of this chapter is to assess the toxicological impacts of discharging ROC to the Bay by evaluating contaminant concentrations measured in the pilot study. A risk assessment and evaluation of different management options to reduce risks are beyond the scope of this report. The pilot study comprised two open-water treatment cells receiving ROC from the Silicon Valley Advanced Purification Center (Chapter 1); ROC entering one of the open-water treatment cells was pre-treated with ozone, while

ROC entering the other was not. We evaluated the concentrations in ROC in the inlets and outlets of the open-water treatment cells to determine their capacity to manage ROC contaminants, and also assessed potential impacts to the San Francisco Bay ecosystem, particularly near the discharge location. Chemical analytes that were monitored in the pilot-scale treatment system were compared to available regulatory limits and protective toxicity thresholds to prioritize contaminants that are of potential concern to the Bay.

## **2. Evaluation of Toxicological Impacts**

To evaluate toxicological impacts of contaminants in ROC, chemical concentrations in ROC were compared to available toxicity information and NPDES permit thresholds. Monitored chemicals were grouped into three categories: nutrients, contaminants of emerging concern (CECs), and metals.

### **2.1 Toxicity Thresholds**

Nutrient discharges are an important consideration in the Bay due to concerns of potential impacts to beneficial uses and ecological health. Currently, the Nutrient Management Strategy, which is a collaborative effort among the San Francisco Bay Regional Water Quality Control Board and municipal wastewater treatment agencies, is in the information gathering phase, and no numeric targets have been set for nutrient discharge limits (Senn and Novick, 2014). To evaluate the impacts of ROC treatment, we compared the changes in concentrations for different nutrients due to the pilot treatment.

As with nutrients, CECs do not have regulatory thresholds. In this case, ROC concentrations were evaluated relative to toxicity thresholds that were obtained by querying multiple toxicity databases. When possible, thresholds based on chronic toxicity to multiple species were used. For example, predicted no effect concentrations (PNECs) for aquatic ecosystems have been calculated for several CECs based on the lowest concentrations observed to cause chronic toxicity in species sensitivity distributions (SSDs). For pesticides, the US Environmental Protection Agency's (EPA) Office of Pesticide Programs (OPP) publishes aquatic life benchmarks, which are extracted from the most recent publicly available OPP risk assessment for an individual pesticide, and are typically based on the most sensitive taxa of the available aquatic toxicity data (US EPA, 2019). Aquatic life benchmarks are estimates of the concentrations below which pesticides are not expected to represent a risk of concern for aquatic life. The OPP aquatic life benchmarks are intended for comparison with freshwater concentrations; there is generally a lack of saltwater ecotoxicity data, and estuarine and marine species tend to be more sensitive to pesticides, but may be equally or less sensitive to other contaminants (Wheeler et al., 2002). Therefore, using the OPP aquatic life benchmarks is appropriate because it is the best available data.

In the absence of an aquatic life benchmark, PNEC, or SSD for a given compound, available no observed effect concentration (NOEC), lowest observed effect concentration (LOEC), or half maximal effective concentration (EC50) data were used as an estimated protective threshold. Chronic test values were preferentially chosen over acute values as a more protective estimate; chronic values were available for all compounds with available experimental toxicity testing data. For compounds that had no toxicity testing data available, US EPA's Ecological Structure Activity Relationships (ECOSAR) Predictive Model was used to predict chronic aquatic toxicity estimates for algae, daphnids, and fish. These estimates are expressed as ChV, or Chronic Value, and defined as the geometric mean of the predicted NOEC and LOEC. Following US EPA guidance for interpreting ECOSAR results, we calculated a Concentration of Concern (COC) as the lowest ChV divided by an uncertainty factor of 10 (US EPA, 2012). For PFOS and PFOA, we compared ROC concentrations to the US EPA drinking water health advisory of 70 parts per trillion (ppt; ng/L) combined as a screening threshold for purposes of prioritization only, due to the absence of clear and consistent ecotoxicity thresholds (discussed below). Toxicity thresholds based on available toxicity information are summarized in **Table 1**.

**Table 1:** Toxicity thresholds for CECs monitored in open-water treatment cells.

Analyte	Subgroup	Toxicity Threshold	Reference
4-Nonylphenol	Industrial compound	721 ng/L	freshwater and marine aquatic PNEC (Wang et al., 2018)
Acetaminophen	Pharmaceutical	1000 ng/L	freshwater aquatic PNEC (Verlicchi et al., 2012)
Atenolol	Pharmaceutical	10 µg/L	marine aquatic PNEC (Minguez et al., 2016)
Bifenthrin	Pesticide	0.095 ng/L <sup>1</sup>	freshwater aquatic PNEC (European Chemicals Agency, 2010a)
Caffeine	Pharmaceutical	9 µg/L	marine aquatic PNEC (European Chemicals Agency, 2010b)
Carbamazepine	Pharmaceutical	500 ng/L	freshwater and marine aquatic PNEC (Ferrari et al., 2004; Moermond and Smit, 2016)
Cotinine	Pharmaceutical	1000 ng/L	freshwater aquatic PNEC (Gosset et al., 2017)

Analyte	Subgroup	Toxicity Threshold	Reference
Diethyltoluamide (DEET)	Pesticide	10.4 µg/L	freshwater aquatic PNEC (Aronson et al., 2012)
Dilantin	Pharmaceutical	8.7 mg/L	immobilization of <i>D. magna</i> EC50 (Calleja et al., 1994)
Fipronil	Pesticide	11 ng/L	OPP Aquatic Life Benchmark <sup>3</sup>
Fipronil Desulfinyl	Pesticide Degradate	540 ng/L	OPP Aquatic Life Benchmark <sup>3</sup>
Fipronil Sulfide	Pesticide Degradate	9 ng/L	immobilization of <i>C. dilutus</i> EC50 (Weston and Lydy, 2013)
Fipronil Sulfone	Pesticide Degradate	7 ng/L	immobilization of <i>C. dilutus</i> EC50 (Weston and Lydy, 2013)
Gemfibrozil	Pharmaceutical	300 ng/L	freshwater aquatic PNEC (Orias and Perrodin, 2013)
Imidacloprid	Pesticide	10 ng/L	OPP Aquatic Life Benchmark <sup>3</sup>
Meprobamate	Pharmaceutical	1 mg/L	ECOSAR COC for fish <sup>4</sup>
Metoprolol	Pharmaceutical	100 ng/L	freshwater aquatic PNEC (Orias and Perrodin, 2013)
Perfluorooctane-sulfonic acid (PFOS)	PFAS	70 ng/L <sup>2</sup>	Drinking Water Health Advisory (US EPA, 2016)
Perfluorooctanoic acid (PFOA)	PFAS	70 ng/L <sup>2</sup>	Drinking Water Health Advisory (US EPA, 2016)
Permethrin	Pesticide	1.4 ng/L	OPP Aquatic Life Benchmark <sup>3</sup>
Primidone	Pharmaceutical	50 µg/L	ECOSAR COC for fish <sup>4</sup>
Propranolol	Pharmaceutical	20 ng/L	freshwater aquatic PNEC (Vestel et al., 2016)

Analyte	Subgroup	Toxicity Threshold	Reference
Sucralose	WWTP tracer	18000 mg/L	<i>S. capricornutum</i> growth EC50 (European Chemicals Agency, 2018)
Sulfamethoxazole	Pharmaceutical	1790 ng/L	freshwater aquatic PNEC (Straub, 2016)
Triclosan	Antimicrobial	168 ng/L	marine aquatic PNEC (European Chemicals Agency, 2011)
Trimethoprim	Pharmaceutical	319 ng/L	marine aquatic PNEC (Minguez et al., 2016)
Tris (2-chloroethyl) Phosphate (TCEP)	Organophosphate Ester Flame Retardant	65 µg/L	freshwater aquatic PNEC (European Chemicals Agency, 2009)

<sup>1</sup>OPP Aquatic Benchmark is less protective at 1.3 ng/L.

<sup>2</sup>Indicates toxicity threshold is based on a drinking water health advisory for combined PFOA a and PFOS concentrations. Currently, available ecotoxicity thresholds are wide-ranging and rapidly evolving, as discussed below.

<sup>3</sup><https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-and-ecological-risk>

<sup>4</sup><https://www.epa.gov/tsca-screening-tools/ecological-structure-activity-relationships-ecosar-predictive-model>

In contrast to CECs and nutrients, current NPDES discharge permits from San Jose/Santa Clara Water Pollution Control Plant, Palo Alto Water Quality Control Plant, and Sunnyvale Water Pollution Control Plant have specified discharge limits for metals based on water quality objectives for the Bay defined in the Water Quality Control Plan for the San Francisco Bay (SFRWQCB, 2017a). Concentrations of metals in ROC were compared to these permit thresholds as well as water quality objectives (**Table 2**). Note that the water quality objectives are expressed as the dissolved fraction and the permit thresholds are expressed as totals. NPDES discharge permits specify metals translators that are used to translate water quality objectives expressed as dissolved fraction to permit thresholds expressed as totals.

## 2.2 Evaluating ROC to Thresholds

To evaluate contaminants in ROC, measured average contaminant concentrations in ROC were divided by the relevant ecotoxicological threshold to get a ratio; contaminants with ratios of one or greater were prioritized for further evaluation (**Table 3**). Average ROC concentrations are based on monitoring results from the pilot study, which was more frequently monitored during the summer.

**Table 2:** Toxicity and permit thresholds for metals monitored in open-water treatment cells.

Analyte	Toxicity Threshold <sup>1</sup> (µg/L)	Permit Threshold <sup>2</sup> (µg/L)	Reference
Lead	8.1 (dissolved)	135 (total)	Marine Water Quality Objective (SFRWQCB, 2017a, 2017b) All WWTP Discharge Permits
Mercury	2.1 <sup>3</sup> (dissolved)	0.027 (total)	Marine Water Quality Objective (SFRWQCB, 2017a, 2017b) San Francisco Bay Mercury and PCBs Municipal and Industrial Discharges Permit
Selenium	0.2 (dissolved)	5 (total)	Proposed water-column Se concentrations in SF Bay criterion (US EPA, 2018) All WWTP Discharge Permits
Copper	6.9 (dissolved)	10 (total)	Water Quality Objective (SFRWQCB, 2017d, 2017a) Sunnyvale Discharge Permit
Nickel	11.9 (dissolved)	24 (total)	Water Quality Objective for San Francisco Bay (SFRWQCB, 2017d, 2017a) Sunnyvale Discharge Permit
Zinc	81 (dissolved)	161 (total)	Marine Water Quality Objective (SFRWQCB, 2017a, 2017b) All WWTP Discharge Permits

<sup>1</sup>Water Quality Objectives are expressed as a 4-day average, except for mercury, which is expressed as a 1-hour average. Metal objectives are expressed as dissolved fraction.

<sup>2</sup>Permit limits expressed as total recoverable fraction. This is the lowest permit threshold from available WWTP discharge permits for the Lower South Bay comprising Palo Alto, Sunnyvale, and San Jose/Santa Clara. Monitoring for metals is based on 24-hour composites collected once per month, except for mercury, which is collected as a grab sample once per month.

<sup>3</sup>Mercury value is expressed as a 1-hour average. Chronic water quality objective is 0.2 mg/kg wet weight mercury in fish tissue (SFRWQCB, 2017c).

Prioritized compounds with average ROC concentrations similar to or higher than toxicity thresholds include metals (i.e., selenium, copper, nickel, and zinc) and CECs including pesticides (i.e., imidacloprid, fipronil and degradates), per- and polyfluorinated alkyl substances (PFAS; i.e., PFOA and PFOS), pharmaceuticals (i.e., carbamazepine, sulfamethoxazole, metoprolol, propranolol, and trimethoprim), and an antimicrobial used in personal care products (i.e., triclosan). The ecotoxicological impacts of these contaminants are described below, along with a brief summary of whether these contaminants were effectively removed by the open-water treatment cell pilot study; the effects of treatment are described in more depth in Chapter 1.

**Table 3:** Contaminants in ROC that exceeded toxicity thresholds.

<b>Analyte</b>	<b>Average ROC Concentration<sup>1</sup> (ng/L)</b>	<b>Toxicity Threshold (ng/L)</b>	<b>Ratio: ROC Concentration: Toxicity Threshold</b>
Carbamazepine	760	500	1.5
Copper, Total	8,550	6,900	1.2
Fipronil	166	11	15
Fipronil Sulfone	34	7	5
Imidacloprid	583	10	58
Metoprolol	2,100	100	21
Nickel, Total	18,700	11,900	1.6
Propranolol	194	20	10
Perfluorooctanesulfonic acid	41	70 <sup>2</sup>	1.1
Perfluorooctanoic acid	34	70 <sup>2</sup>	1.1
Selenium, Total	2,850	200	14
Sulfamethoxazole	2,410	1,790	1.4
Triclosan	130	168	0.8
Trimethoprim	530	319	1.7
Zinc, Total	74,000	81,000	0.9

<sup>1</sup>Average concentrations are based on monitoring results from the pilot study collected from June 2016—September 2019

<sup>2</sup>Indicates toxicity threshold is based on a drinking water health advisory for combined PFOA and PFOS concentrations. Currently, available ecotoxicity thresholds are wide-ranging and rapidly evolving, as discussed below.

The open-water treatment cell pilot study demonstrated better contaminant treatment efficiencies for nutrients and CECs during the summer when solar intensity is highest and warmer temperatures generally support more biological activity, compared to more limited performance during the winter months (Chapter 1). The monitoring data also indicated improved performance during the second and third years of monitoring after the biomat had formed a sufficiently thick layer. Therefore, the concentrations used to evaluate treatment efficiency from the pilot study are based on summer concentrations measured during the third year of study (June—August 2019), unless otherwise stated. Winter concentrations reported are based on winter concentrations measured during the second year of study (November 2018—March 2019). For some contaminants, we also modeled removal efficiency expected from an open-water system with twice the size and hydraulic residence time, assuming first order kinetics, to

evaluate whether reductions below toxicity thresholds could be achieved with a scaled-up open-water treatment system.

### **3. Evaluation of Ecological Impacts of Contaminants Monitored in ROC**

Currently, the health of the Bay ecosystem is impacted by various point and non-point discharges, tidal conditions, turbidity, freshwater outflows and climatic conditions. While discharge of ROC would not generally be expected to change the overall contaminant loads from wastewater to receiving waters, the concentrations of chemicals at the point of discharge will increase, potentially leading to more localized impacts on aquatic organisms. Furthermore, many water quality regulations have been crafted around concentration limits, while a more flexible, loads-based approach may be appropriate for some contaminants, such as nutrients. At present, both concentrations and loads of contaminants must be evaluated when examining issues around ROC discharge. This study seeks to evaluate potential impacts to the Bay from contaminants monitored in ROC from the pilot study.

Provided below are descriptions of the potential impacts, including toxicological concerns, associated with nutrients, CECs, and metals; the ecological thresholds or regulatory limits for each contaminant, where available; and the impact of the pilot treatment train on ROC contaminant concentrations, as well as expectations for the removal function of a larger open-water treatment cell. A risk assessment is beyond the scope of this study.

#### **3.1 Nutrients**

While San Francisco Bay receives high nutrient loads from wastewater effluent and other sources (agricultural runoff, stormwater drainage), the Bay has historically exhibited resistance to the classical impacts from nutrient over-enrichment, due in large part to a combination of high turbidity, strong tidal mixing, and abundant filter-feeding clam populations (Senn and Novick, 2014). While dissolved inorganic nitrogen and phosphorus are essential nutrients for primary production that supports estuarine food webs, nutrient over-enrichment can cause high phytoplankton biomass, which in turn can cause low dissolved oxygen as phytoplankton-derived organic matter is digested by oxygen-consuming microorganisms. Low dissolved oxygen can lead to fish kills, die-off of benthic organisms, and loss of critical habitat that results in reduced survival, reproductive success, or recruitment success of fish and benthic organisms. Elevated nutrient concentrations can also increase the frequency and severity of harmful algal blooms (HABs) and the levels of HAB-related toxins that bioaccumulate and can cause toxicity to consumers at all levels of the food web, including humans.

In 2012, the San Francisco Bay Regional Water Quality Control Board launched the San Francisco Bay Nutrient Management Strategy (NMS), a regional science program focused on investigating nutrient-related water quality impacts and informing management decisions related to protective nutrient loads to the Bay. The NMS launch was catalyzed by observations of increasing phytoplankton biomass in the Bay, which suggested the system's resistance to nutrient over-enrichment has the potential to weaken or vary substantially over time (Cloern, 2007; Cloern and Jassby, 2010; SFEI, 2017, 2015). Recent NMS studies have focused on HABs in deep subtidal habitats (Sutula et al., 2017; Peacock et al., 2018) and dissolved oxygen in shallow margin habitats (Lower South Bay sloughs; MacVean et al., 2018), and point to other potential nutrient-related adverse responses that until recently had not received much attention (Senn and Novick, 2014).

Because ROC discharge, as well as treatment of ROC through engineered systems, may affect concentrations and loads of the nutrients nitrogen (N) and phosphorus (P) discharged to the Bay, ROC concentrations and removal efficiency through the pilot treatment train are summarized here. N concentrations are discussed in terms of dissolved inorganic N, which includes three N-containing compounds (nitrate, ammonium, and nitrite).

The open-water treatment cell removed ~30% of dissolved inorganic nitrogen (DIN) from ROC. During summer months, DIN was reduced from an average of 69 mg-N/L to 46 mg-N/L in the open-water cells without ozonation (**Table 4**). In all three waste streams, nitrate was the predominant form of DIN (>92%; **Table 5**). Minimal DIN or nitrate removal was observed during the winter months. No DIN or nitrate was removed by ozone treatment as well. Phosphorus, in the form of phosphate, was present in the ROC and was modestly, though not consistently, removed in the open-water wetland cells. Average phosphate concentrations in summer decreased from 2.3 to 1.8 mg-P/L in 2019 (**Table 6**). Ozone treatment did not affect phosphate concentrations.

Nitrogen and phosphorus are not currently regulated in wastewater discharges, though permit limits may be introduced as early as 2024. Informed by the scientific understanding developed through the San Francisco Bay Nutrient Management Strategy (NMS), these permit limits are expected to be based on mass loads, not concentrations. ROC discharges would not change nutrient loads compared to current conditions based on effluent discharges, and the performance of the pilot treatment train suggests significant reductions in nitrate concentrations and loads would be anticipated for a full-scale open-water treatment cell in the summer months. If a nutrient cap is implemented in 2024, treatment of ROC to offset overall nutrient load may be necessary.

**Table 4:** Average ( $\pm$  SD) total dissolved inorganic nitrogen (DIN) concentration (mg-N/L) in the open-water treatment cell pilot study during summer and winter.

ROC Treatment Level	Summer <sup>1</sup>	Winter <sup>2</sup>
Untreated ROC <sup>3</sup>	69 $\pm$ 9	80 $\pm$ 3
ROC Treated through Open-Water Cell <sup>4</sup>	46 $\pm$ 5	78 $\pm$ 1
ROC Treated with Ozone <sup>6</sup>	68 $\pm$ 9	82 $\pm$ 3
ROC Treated with Ozone and Passed through Open-Water Cell <sup>7</sup>	48 $\pm$ 4	77 $\pm$ 3

<sup>1</sup>Summer concentrations based on average concentrations monitored during summer of 2019.

<sup>2</sup>Winter concentration based on average concentration measured monitored winter of 2018-2019.

<sup>3</sup>**Untreated ROC** represents concentrations measured in untreated ROC that was sampled from the inlet of the pilot open-water treatment cell #1.

<sup>4</sup>**ROC Treated through Open-Water Cell** represents concentrations measured in the outlet of the same cell.

<sup>6</sup>**ROC Treated with Ozone** represents measured concentration of ROC treated with 20 mg-O<sub>3</sub> per L of ROC that was measured in the inlet of the open-water treatment cell #2.

<sup>7</sup>**ROC Treated with Ozone and Passed through Open-Water Cell** represents measured ROC concentration measured at the outlet of the same cell.

**Table 5:** Average ( $\pm$  SD) nitrate concentration (mg-N/L) in the open-water treatment cell pilot study during summer and winter.

ROC Treatment Level	Summer <sup>1</sup>	Winter <sup>2</sup>
Untreated ROC <sup>3</sup>	67 $\pm$ 4	68 $\pm$ 7
ROC Treated through Open-Water Cell <sup>4</sup>	44 $\pm$ 5	67 $\pm$ 10
ROC Treated with Ozone <sup>6</sup>	67 $\pm$ 4	68 $\pm$ 7
ROC Treated with Ozone and Passed through Open-Water Cell <sup>7</sup>	44 $\pm$ 5	67 $\pm$ 10

<sup>1</sup>Summer concentrations based on average concentrations monitored during summer of 2019.

<sup>2</sup>Winter concentration based on average concentration measured monitored winter of 2018-2019.

<sup>3</sup>**Untreated ROC** represents concentrations measured in untreated ROC that was sampled from the inlet of the pilot open-water treatment cell #1.

<sup>4</sup>**ROC Treated through Open-Water Cell** represents concentrations measured in the outlet of the same cell.

<sup>6</sup>**ROC Treated with Ozone** represents measured concentration of ROC treated with 20 mg-O<sub>3</sub> per L of ROC that was measured in the inlet of the open-water treatment cell #2.

<sup>7</sup>**ROC Treated with Ozone and Passed through Open-Water Cell** represents measured ROC concentration measured at the outlet of the same cell.

**Table 6:** Average phosphate concentration in the open-water treatment cell pilot study.

ROC Treatment Level	Phosphate Concentration <sup>1</sup> (mg-P/L)
Untreated ROC <sup>2</sup>	2.3
ROC Treated through Open-Water Cell <sup>3</sup>	1.8
ROC Treated with Ozone <sup>4</sup>	2.2
ROC Treated with Ozone and Passed through Open-Water Cell <sup>5</sup>	1.8

<sup>1</sup>Concentrations based on average concentrations monitored during summer of 2019.

<sup>2</sup>**Untreated ROC** represents concentrations measured in untreated ROC that was sampled from the inlet of the pilot open-water treatment cell #1.

<sup>3</sup>**ROC Treated through Open-Water Cell** represents concentrations measured in the outlet of the same cell.

<sup>4</sup>**ROC Treated with Ozone** represents measured concentration of ROC treated with 20 mg-O<sub>3</sub> per L of ROC that was measured in the inlet of the open-water treatment cell #2.

<sup>5</sup>**ROC Treated with Ozone and Passed through Open-Water Cell** represents measured ROC concentration measured at the outlet of the same cell.

### 3.2 Contaminants of Emerging Concern

Contaminants of emerging concern (CECs) are defined as synthetic or naturally occurring chemicals that are unregulated or inadequately regulated, not commonly monitored in the environment (e.g., as part of permit compliance), and have the potential to enter the environment and cause adverse ecological or human health impacts. As a group, CECs encompass thousands of chemicals, and for the majority, very little is known about them.

The Regional Monitoring Program for Water Quality in San Francisco Bay (RMP) has established a tiered risk-based framework for evaluating emerging contaminants in the Bay (Lin et al., 2018a; Sutton et al., 2017). This framework is an adaptation of one first proposed by California's Ambient Ecosystems CEC Advisory Panel as part of a broader strategy for monitoring CECs in the waters of California (Anderson et al., 2012). Several classes of emerging contaminants have been prioritized for additional attention in the Bay (i.e., classified as Moderate Concern within the tiered risk-based framework); a number of these were monitored as part of this study. In addition, pharmaceuticals and personal care product ingredients were included as analytes; several of these have been recommended for further evaluation in the Bay based on an analysis of influent and effluent samples collected voluntarily in 2016 and 2017 by seven wastewater treatment facilities located throughout the Bay Area (Lin et al., 2018b). The array of CECs selected for monitoring represents a diverse set of contaminants with different

physical and chemical properties and potential toxicity concerns, allowing evaluation of removal efficiencies as well as potential concerns for receiving waters. While discharge of ROC would not generally be expected to change the overall contaminant loads from wastewater to receiving waters, the concentrations of chemicals at the point of discharge will increase, potentially leading to more localized impacts on aquatic organisms. Therefore, CEC concentrations in ROC monitored before and after treatment through the pilot treatment system were compared to available ecotoxicological thresholds to assess potential impacts near the points of discharge.

As described previously in Methods, the subset of CECs discussed below were identified as those for which the measured average concentrations in ROC was similar to or greater than the relevant ecotoxicological threshold (**Table 3**). Three additional monitored CECs that were not detected in ROC may still be of ecological concern because reporting limits were above the ecotoxicological thresholds (**Table 7**).

**Table 7:** CECs with reporting limits above toxicity thresholds.

Analyte	Subgroup	Reporting Limit (ng/L)	Toxicity Threshold (ng/L)	Reference
4-Nonylphenol	Industrial Compound	1200	721	Wang et al., 2018
Bifenthrin	Pesticide	5	0.095	European Chemicals Agency, 2010a
Permethrin	Pesticide	40	1.4	OPP Aquatic Life Benchmark

### 3.2.1 Pharmaceuticals

This class of contaminants is highly variable in terms of chemical properties, and therefore treatment removal efficacy and possible impacts on biota. Furthermore, because pharmaceuticals are designed to be biologically active, many may have effects on aquatic organisms or ecological communities. While acute effects are unlikely, chronic effects that could lead to ecosystem-level changes are possible.

#### ***Metoprolol and Propranolol***

Metoprolol and propranolol are beta-blockers used to reduce blood pressure by blocking the effects of the hormone epinephrine, also known as adrenaline. Data for these compounds' effects on aquatic life are scarce; however, PNECs have been estimated from available acute toxicity data for freshwater and saltwater ecosystems by several different methods (Godoy et al., 2015; Orias and Perrodin, 2013; Vestel et al., 2016).

Average metoprolol and propranolol concentrations in untreated ROC were 2,100 and 190 ng/L, respectively. These values exceeded the PNEC values for metoprolol (100 ng/L) and propranolol (20 ng/L) by a factor 21 and 10, respectively (**Table 3**).

Metoprolol and propranolol ROC concentrations were reduced by over 80% after treatment through the open-water treatment cell, down to summer averages of 410 and 20 ng/L (**Table 8**), respectively, which are in the range of PNEC values. Treatment with ozone alone reduced propranolol concentrations below the 10 ng/L detection limit. The combination of ozone and open-water treatment was most effective overall, reducing concentrations of metoprolol and propranolol to 350 and <10 ng/L, respectively, in summer months.

Doubling the dose of ozone treatment and increasing the hydraulic residence time in the open-water treatment cell is expected to increase removal efficiencies and reduce metoprolol down to 9 ng/L, which is well below the toxicity threshold, and represents a removal efficiency of 99.6%. While the benefits of the open-water treatment cell are significantly reduced in the winter months, stormwater flows during these months may reduce concentrations of pharmaceuticals in receiving waters.

Other classes of antihypertensives (e.g., angiotensin receptor blockers, calcium channel blockers) were not monitored and have received little to no ecotoxicity study, but are commonly detected in treated wastewater effluent and environmental surface waters at similar concentrations, and could also have adverse effects on aquatic life (Godoy et al., 2015).

**Table 8:** Average metoprolol and propranolol concentrations (ng/L) in the open-water treatment cell pilot study during summer and winter seasons.

ROC Treatment Level	Metoprolol	Metoprolol	Propranolol	Propranolol
Season	Summer	Winter	Summer	Winter
Untreated ROC <sup>1</sup>	2,400	2,100	160	220
ROC Treated through Open-Water Cell <sup>2</sup>	410	2,100	20	170
Predicted ROC Treated through Open-Water Cell with Double Residence Time <sup>3</sup> (modeled)	70	2,100	2	130
ROC Treated with Ozone <sup>4</sup>	1,000	920	<10	<10
ROC Treated with Ozone and Treated through Open-Water Cell <sup>5</sup>	350	580	<10	<10
Predicted ROC treated with double-dose of ozone and open-water cell with double residence time <sup>6</sup> (modeled)	9	350	<10	<10

<sup>1</sup>**Untreated ROC** represents concentrations measured in untreated ROC that was sampled from the inlet of the pilot open-water treatment cell #1.

<sup>2</sup>**ROC Treated through Open-Water Cell** represents concentrations measured in the outlet of the same cell.

<sup>3</sup>**Predicted ROC Treated through Open-water Cell with Double Residence Time** represents predicted concentration that would be measured after an open-water treatment cell that had double the hydraulic residence time of that in the pilot study.

<sup>4</sup>**ROC Treated with Ozone** represents measured concentration of ROC treated with 20 mg-O<sub>3</sub> per L of ROC that was measured in the inlet of the open-water treatment cell #2.

<sup>5</sup>**ROC Treated with Ozone and Treated through Open-Water Cell** represents measured ROC concentration measured at the outlet of the same cell.

<sup>6</sup>**Predicted ROC Treated with Double-dose of Ozone and Open-Water Cell with Double Residence time** represents predicted concentration that would be measured after treated ROC 40 mg-O<sub>3</sub> per L ROC and after treatment through an open-water treatment cell that had double the hydraulic residence time of that in the pilot study.

### ***Sulfamethoxazole, Trimethoprim, and Triclosan***

Antimicrobials, including antibiotics, are explicitly designed to affect microorganisms, and can therefore affect natural microbial communities, which play a key role in many fundamental ecological processes (Grenni et al., 2018). Short-term effects include bactericide and bacteriostatic actions, which exert a selective effect on microbial communities and can result in disappearance of some microbial populations and their ecological functioning. Longer-term indirect impacts include the development of antibiotic resistant bacteria, and changes in biodegradation, and therefore subsequent impacts, of organic contaminants. Antibiotic resistance genes from the

environment may also be transmitted to human pathogens (Bengtsson-Palme et al., 2018).

Antibiotics may also have effects on non-target organisms. For example, sulfamethoxazole and trimethoprim sequentially inhibit enzyme systems involved in bacterial folate synthesis, but can inhibit the same biosynthesis pathway in algae and plants, decreasing growth (Miazek and Brozek-Pluska, 2019). Decreased primary productivity could result in reduced food abundance to support higher trophic levels. The available PNEC values are 1,790 ng/L for sulfamethoxazole and 319 ng/L for trimethoprim (**Table 1**). The antimicrobial triclosan (a common ingredient in many personal care products) can also be toxic to algae due to shared biosynthesis pathways with bacteria. Triclosan is also weakly estrogenic, and has been implicated in changes in hormone synthesis, fin length, sperm counts, and sex ratios in fish (Brausch and Rand, 2011). Triclosan use is expected to decrease due to new regulations that prohibit the use of triclosan in rinse-off products. The marine PNEC available for triclosan is 168 ng/L (**Table 1**).

Average concentrations of the antibiotics sulfamethoxazole and trimethoprim in untreated ROC were 2,400 and 530 ng/L, respectively, near or above the PNECs (**Table 3**). The average triclosan concentration was 130 ng/L, which is also in the range of the PNEC.

Sulfamethoxazole and trimethoprim were well removed by the combined treatment of ozone and the open-water cell, with ozone pre-treatment providing most of the removal. An ozone dose of 20 mg O<sub>3</sub> per L effectively reduced sulfamethoxazole concentrations to 400 ng/L and trimethoprim concentrations below detection limits (<10 ng/L; **Table 9**). Doubling the dose of ozone treatment showed further reduction of sulfamethoxazole to 150 ng/L, which is below the toxicity threshold.

Triclosan monitoring was limited in the treatment cell (n=3 between June 2018 and September 2019). The results suggest that triclosan is effectively reduced by both the open-water treatment cell as well as with ozone treatment; concentrations measured after treatment by either method were 21 ng/L or below, which is below the toxicity threshold (**Table 9**).

**Table 9:** Average sulfamethoxazole, trimethoprim, and triclosan concentrations in the open-water treatment cell pilot study.

Treatment Level	Sulfamethoxazole <sup>1</sup> (ng/L)	Trimethoprim <sup>1</sup> (ng/L)	Triclosan <sup>2</sup> (ng/L)
Untreated ROC <sup>3</sup>	2,800	500	148
ROC Treated through Open-Water Cell <sup>4</sup>	2,600	320	13
ROC Treated with Ozone <sup>5</sup>	400	<10	21
ROC Treated with Double-dose of Ozone <sup>6</sup> (modeled)	150	<10	Not measured

<sup>1</sup>Average concentrations monitored during summer of 2019.

<sup>2</sup>Average concentrations monitored based on reduced monitoring schedule (n=3 in June 2018, July 2018, September 2019)

<sup>3</sup>**Untreated ROC** represents concentrations measured in untreated ROC that was sampled from the inlet of the pilot open-water treatment cell #1.

<sup>4</sup>**ROC Treated through Open-Water Cell** represents concentrations measured in the outlet of the same cell.

<sup>5</sup>**ROC Treated with Ozone** represents measured concentration of ROC treated with 20 mg-O<sub>3</sub> per L of ROC that was measured in the inlet of the open-water treatment cell #2.

<sup>6</sup>**ROC Treated with Double-dose of Ozone** represents measured concentration of ROC treated with 40 mg-O<sub>3</sub> per L ROC that was measured in the inlet of the open-water treatment cell #2.

### **Carbamazepine**

Carbamazepine belongs in the class of neuroactive pharmaceuticals that have been shown to affect behavior of fish and aquatic invertebrates at environmentally relevant concentrations (Brodin et al., 2014; Melvin, 2017; Santos et al., 2010). However, these effects often exhibit a non-monotonic dose relationship, making predictions difficult. Different pharmaceuticals can induce similar behavioral alterations in different species, but may also have drug- and/or species-specific effects. For example, both activity and feeding rate can be influenced by antidepressants, psychiatric drugs, and antihistamines, but not necessarily in the same direction between, or even within, species. Furthermore, behaviors are more sensitive to pharmaceuticals than more commonly used toxicological endpoints, limiting data availability. Behavioral changes may cause larger ecological effects, as they may influence feeding rate, reproductive success, and predator avoidance, which in turn can influence ecological parameters such as community structure and ecosystem function.

The average carbamazepine concentration in untreated ROC was 760 ng/L (**Table 10**), and exceeded the PNEC value (500 ng/L) by a factor of 1.5 (**Table 3**). Carbamazepine was well removed by the combined treatment train, with ozone providing all of the removal benefits. Ozone treatment reduced carbamazepine

concentrations down to an average of 90 ng/L, which represents a treatment efficiency of 88%, and is well below the PNEC value.

Carbamazepine’s transformation products were not monitored, and the literature indicates carbamazepine’s photolytic degradation products are more toxic than the parent compound (Donner et al., 2013). Other neuroactive pharmaceuticals that were monitored in the pilot study include mepromate, dilantin, and primidone. Dilantin appears to be relatively non-toxic to aquatic life, and there is not enough ecotoxicological data to set a threshold for meprobamate or primidone. Several other neuroactive pharmaceuticals are frequent constituents in treated wastewater effluent at concentrations known to cause behavioral effects, but were not measured. For example, antidepressants such as selective serotonin reuptake inhibitors (SSRIs), benzodiazepines, antihistamines, and illicit drugs can all significantly alter aquatic organism behavior at low concentrations (Brodin et al., 2014; Fabbri and Franzellitti, 2016; Santos et al., 2010).

**Table 10:** Average carbamazepine in the open-water treatment cell pilot study.

ROC Treatment Level	Carbamazepine (ng/L) <sup>1</sup>
Untreated ROC <sup>2</sup>	750
ROC Treated through Open-Water Cell <sup>3</sup>	780
ROC Treated with Ozone <sup>4</sup>	90
ROC Treated with Ozone and Treated through Open-Water Cell <sup>5</sup>	90

<sup>1</sup>Average concentrations monitored during summer of 2019.

<sup>2</sup>**Untreated ROC** represents concentrations measured in untreated ROC that was sampled from the inlet of the pilot open-water treatment cell #1.

<sup>3</sup>**ROC Treated through Open-Water Cell** represents concentrations measured in the outlet of the same cell.

<sup>4</sup>**ROC Treated with Ozone** represents measured concentration of ROC treated with 20 mg-O<sub>3</sub> per L of ROC that was measured in the inlet of the open-water treatment cell #2.

<sup>5</sup>**ROC Treated with Ozone and Passed through Open-Water Cell** represents measured ROC concentration measured at the outlet of the same cell.

<sup>6</sup>Calculated by dividing untreated ROC concentration by a factor of five.

### 3.2.2 Urban Pesticides

Imidacloprid, fipronil, and fipronil degradates are moderately persistent in the environment, and can be dispersed widely in aquatic ecosystems (Chandler et al., 2004; Hladik et al., 2018). Ecological toxicity thresholds are based on the US EPA OPP’s published aquatic life benchmarks unless otherwise described. While the OPP aquatic life benchmarks are intended for comparison with freshwater concentrations, there is

generally a lack of saltwater ecotoxicity data, and estuarine and marine species tend to be more sensitive to pesticides (Wheeler et al., 2002).

### ***Imidacloprid***

Imidacloprid is a neonicotinoid insecticide, which selectively affects the central nervous system of insects by binding to their nicotinic acetylcholine receptors. It is highly toxic to non-target invertebrates, especially aquatic insects. Ephemeroptera (mayflies), Trichoptera (caddisflies), and Diptera (flies and midges), species that are critical for supporting aquatic and terrestrial food webs, are particularly sensitive (Morrissey et al., 2015; Wood and Goulson, 2017; Hladik et al., 2018). More environmentally relevant multi-species community effects are often observed at neonicotinoid concentrations well below single species toxicity thresholds observed in the laboratory. Low concentrations of neonicotinoids have been observed to alter predator-prey interactions and invertebrate community structure in experimental aquatic communities (Morrissey et al., 2015). Imidacloprid has also been shown to cause altered feeding behavior in aquatic invertebrates, which can cause broader ecosystem effects such as changing the rates of plant litter breakdown, downstream drift, and altered sensitivity to other stressors such as food quality and increased temperature (Hoyle and Code, 2016).

Imidacloprid concentrations in ROC exceeded the aquatic life benchmark of 10 ng/L by a factor of ~60, and may be a major ecological risk factor for CECs monitored in this study of ROC. Of note, imidacloprid concentrations in final effluent measured from eight Bay Area wastewater treatment facilities, including San Jose-Santa Clara, ranged between 58-306 ng/L (Sadaria et al., 2017).

Average imidacloprid concentrations measured after treatment through the open-water treatment cell were reduced to 290 ng/L (**Table 11**). Pre-treatment with ozone provided additional benefits, with 20 mg-O<sub>3</sub> per L alone reducing concentrations by 20% (down to 330 ng/L). The average concentration measured after combined treatment of ROC with ozone and the open-water cell was 270 ng/L, which represents a reduction of 34% during summer months. While treated ROC concentrations are above the aquatic life benchmark, treatment would be expected to provide an overall water quality benefit because the overall pesticide load is reduced. Significant changes in localized impacts would not be expected relative to current effluent discharges.

While there was no removal from the open-water cell during the winter season, removal via ozone was effective regardless of the season. Stormwater flows during winter months are unlikely to reduce treated ROC concentrations below the imidacloprid aquatic life benchmark, as imidacloprid is widely observed in concentrations above the aquatic life benchmark in small tributaries that drain to the Bay during both wet and dry seasons (Ensminger et al., 2013; Weston et al., 2015). As a result, ecological impacts

due to imidacloprid exposure could be a concern, especially near discharge locations. Treatment combined with source control efforts may be an effective means of reducing imidacloprid risks to receiving waters.

**Table 11:** Average imidacloprid ROC concentration (ng/L) after treatment through open-water treatment cell study in summer and winter.

ROC Treatment Level	Summer <sup>1</sup>	Winter <sup>2</sup>
Untreated ROC <sup>3</sup>	410	470
ROC Treated through Open-Water Cell <sup>4</sup>	290	470
Predicted ROC Treated through Open-Water Cell with Double Residence Time <sup>5</sup> (modeled)	210	470
ROC Treated with Ozone <sup>6</sup>	330	270
ROC Treated with Ozone and Treated through Open-Water Cell <sup>7</sup>	270	280
Predicted ROC Treated with Double-dose of Ozone and Open-Water Cell with Double Residence Time <sup>8</sup> (modeled)	150	230

<sup>1</sup>Summer concentrations based on average concentrations monitored during summer of 2019.

<sup>2</sup>Winter concentration based on average concentration measured monitored winter of 2018-2019.

<sup>3</sup>**Untreated ROC** represents concentrations measured in untreated ROC that was sampled from the inlet of the pilot open-water treatment cell #1.

<sup>4</sup>**ROC Treated through Open-Water Cell** represents concentrations measured in the outlet of the same cell.

<sup>5</sup>**Predicted ROC Treated through Open-water Cell with Double Residence Time** represents predicted concentration that would be measured after an open-water treatment cell that had double the hydraulic residence time of that in the pilot study.

<sup>6</sup>**ROC Treated with Ozone** represents measured concentration of ROC treated with 20 mg-O<sub>3</sub> per L of ROC that was measured in the inlet of the open-water treatment cell #2.

<sup>7</sup>**ROC Treated with Ozone and Treated through Open-Water Cell** represents measured ROC concentration measured at the outlet of the same cell.

<sup>8</sup>**Predicted ROC Treated with Double-dose of Ozone and Open-Water Cell with Double Residence time** represents predicted concentration that would be measured after treated ROC 40 mg-O<sub>3</sub> per L ROC and after treatment through an open-water treatment cell that had double the hydraulic residence time of that in the pilot study.

A larger open-water treatment cell and higher dose of ozone pretreatment could improve treatment efficiencies. A larger open-water treatment cell with double the residence time and a doubling of the dose of ozone to 40 mg O<sub>3</sub> per L of ROC treated is predicted to have a removal efficiency of 63%. However, the predicted concentration from this treatment (150 ng/L) would still exceed toxicity thresholds, suggesting the potential for localized effects at the point of discharge.

Imidacloprid transformation products were not monitored and are under-studied, but may also be of concern. Photolytic degradation products may have greater or equal toxicity to the parent compound, and are likely to be persistent (Diamond, 2017; Todey et al., 2018). Other degradation pathways produce products with equal or slightly reduced toxicity (Todey et al., 2018). Photolysis of imidacloprid also produces a potent greenhouse gas, nitrous oxide (Diamond, 2017).

### ***Fipronil and Degradates***

Fipronil is a phenylpyrazole insecticide used to control ants, cockroaches, termites, and fleas (such as in topical pet flea control products). Fipronil causes neurotoxicity in insects by selectively inhibiting gamma-aminobutyric acid (GABA) regulated chloride channels. Fipronil is highly toxic to many non-target terrestrial and aquatic invertebrates, especially mysids and daphnids, and can also bioaccumulate.

In the abiotic environment, fipronil may be transformed into a number of degradates depending on the reaction mechanism. Commonly observed degradates examined in this study include fipronil desulfinyl, produced through photolysis; fipronil sulfone, produced primarily through oxidation; and fipronil sulfide, produced primarily through reduction. Although the OPP aquatic life benchmarks for fipronil sulfone (37 ng/L), fipronil sulfide (100 ng/L) and fipronil desulfinyl (540 ng/L) are higher than the fipronil parent product (11 ng/L), their ecotoxicity has not been well studied. Recent studies indicate these degradation products, especially fipronil sulfone and sulfide, appear to be just as toxic as the parent compound (Gunasekara et al., 2007; Weston and Lydy, 2014). Therefore, the toxicity thresholds used in this evaluation for fipronil sulfone (7 ng/L) and sulfide (9 ng/L) are based on a study reflecting similar toxicity levels to the parent compound (Weston and Lydy, 2013). Of note, the wastewater effluent concentration of fipronil from San Jose/Santa Clara wastewater facility collected from a single sampling event in September 2015 was measured to be 42.9 ng/L (Sadaria et al., 2017), which exceeds the aquatic life benchmark for fipronil.

Average fipronil and summed fiprole (sum of fipronil and degradates) ROC concentrations were 150 and 190 ng/L, respectively. The average fipronil concentration exceeded the aquatic life benchmark (11 ng/L) by a factor of 15.

The concentration of the fipronil parent compound was reduced to 31 ng/L through the open-water treatment cell, which represents a reduction of 79%. Summed fiproles only decreased by 56% due to the formation of fipronil desulfinyl in the open-water treatment cell (**Table 12**). Lower reductions were observed in other single degradates, such as fipronil sulfone, which was reduced by 14%. Ozone treatment alone at a dose of 20 mg-O<sub>3</sub> per L also achieved fipronil reduction of 50% and summed fiprole reduction of 36%. While the parent compound concentrations measured from ozone and open-water cell treatment were above the aquatic life benchmark (11 ng/L),

these concentrations are in the range of wastewater effluent concentrations previously measured at the facility (42.9 ng/L; Sadaria et al., 2017).

Based on these observations, the pilot treatment effectively reduced the relative loads of fipronil and summed fiproles discharged to the Bay, particularly during summer months. A higher dose of 40 mg-O<sub>3</sub> per L increased removal of fipronil to 70%, illustrating that ozone treatment could be used to compensate for lower removal from the open-water treatment cell during the winter. This is an important finding because, similar to imidacloprid, fipronil is present in Bay Area stormwater at levels exceeding the aquatic life benchmark (Ensminger et al., 2013; Weston and Lydy, 2013), indicating that seasonal rainfall patterns alone may not adequately reduce potential risks to Bay wildlife near ROC discharge sites. Nevertheless, the overall reduction in loads suggests that ROC treatment would result in an improvement to Bay water quality relative to the current situation.

Greater hydraulic residence time is expected to remove fipronil at greater rates, and modeled removal efficiency assuming first order kinetics estimates that an open-cell water treatment of twice the size and double the hydraulic residence time would reduce fipronil parent compound concentrations to 6 ng/L, a removal efficiency of 96%, which is in the range of toxicity thresholds. However, other degradates may increase, such as fipronil desulfinyl.

**Table 12:** Average fipronil (parent) and degradate (sulfone, sulfide, desulfinyl) concentrations (ng/L) in ROC during the summer 2019 after treatment through the open-water treatment cell study.

ROC Treatment Level	Parent	Sulfone	Sulfide	Desulfinyl
Untreated ROC <sup>1</sup>	150	30	4.8	3.2
ROC Treated through Open-Water Cell <sup>2</sup>	31	26	3.2	21.9
ROC Treated with Ozone <sup>3</sup>	75	42	2.2	2
ROC Treated with Ozone and Treated through Open-Water Cell <sup>4</sup>	32	32	2	11.3

<sup>1</sup>**Untreated ROC** represents concentrations measured in untreated ROC that was sampled from the inlet of the pilot open-water treatment cell #1.

<sup>2</sup>**ROC Treated through Open-Water Cell** represents concentrations measured in the outlet of the same cell.

<sup>3</sup>**ROC Treated with Ozone** represents measured concentration of ROC treated with 20 mg-O<sub>3</sub> per L of ROC that was measured in the inlet of the open-water treatment cell #2.

<sup>4</sup>**ROC Treated with Ozone and Passed through Open-Water Cell** represents measured ROC concentration measured at the outlet of the same cell.

### 3.2.3 Per- and Polyfluorinated Alkyl Substances (PFAS)

Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) were monitored in ROC and are only two compounds within a very broad class of perfluorinated and polyfluorinated alkyl substances (PFAS), with more than 3,000 PFAS used in commercial and industrial applications. The carbon-fluorine bonds in PFAS are some of the strongest known to science, which means PFAS (or, in the case of polyfluorinated precursors, their perfluoroalkyl degradates) show extremely high persistence in the environment. PFOS and PFOA are two of the most studied members of the perfluoroalkyl family, and have been shown to be highly toxic. Studies based on laboratory animals and human populations exposed to higher concentrations provide evidence that PFOS and PFOA are multi-system toxicants and developmental toxicants; they can cause liver damage, adverse developmental effects, cancer, and suppression of the immune system (Sedlak et al., 2018).

Top predators, including humans, aquatic mammals, and piscivorous birds are most at risk, as PFAS can be bioaccumulative. For example, PFOS, the most studied PFAS in wildlife, can affect predatory birds consuming aquatic organisms at levels higher than a proposed protection threshold of 50 ng/L (Rostkowski et al., 2006). In San Francisco Bay, monitoring of harbor seals and cormorant eggs has suggested current exposures of PFAS are a concern for these higher trophic organisms, especially in the South Bay (Sedlak et al., 2018, 2017). PFAS have also been detected in sport fish in the South Bay at concentrations approaching thresholds for protection of human health

(Sun et al., 2017). However, lower trophic level aquatic organisms appear to be relatively insensitive; the most sensitive species, midges, only show effects at ~90 µg/L, which is several orders of magnitude lower than for other aquatic invertebrates such as cladocerans (Ding and Peijnenburg, 2013). Fish also appear relatively insensitive, with no effects observed at mg/L concentrations (Ding and Peijnenburg, 2013).

Available ecotoxicity thresholds for PFAS range widely, and reflect the rapidly evolving understanding of these contaminants. For example, Canada's 2013 draft Federal Environmental Water Quality Guidelines for PFOS is 6,000 ng/L (Canada and Environment Canada, 2013) while the more recent EU Water Framework Directive lists a much lower Environmental Quality Standard limit value for PFOS of 0.65 ng/L in inland surface waters and 0.13 ng/L in seawater ("Emerging chemical risks in Europe — 'PFAS,'" 2019). The US EPA has not established ecotoxicity thresholds for PFOS or PFOA.

In the absence of clear and consistent ecotoxicity thresholds, we compare ROC concentrations to the US EPA drinking water health advisory as a screening threshold for initial comparison to study data for purposes of prioritization only. The agency has established a drinking water health advisory for PFOS and PFOA combined of 70 parts per trillion (ppt; ng/L) based on adverse human health effects such as developmental effects to fetuses, cancer (e.g., testicular and kidney), liver damage, immune effects, and other adverse outcomes. This human health advisory specific to drinking water is not meant to serve as an ecotoxicity threshold, which would be intended to protect a broader range of species and account for diverse exposure pathways. However, given the disagreement concerning ecotoxicity evident in the range of thresholds calculated internationally, a single intermediate value is useful to determine whether PFOS and PFOA should be prioritized for assessment within ROC.

Average concentrations of PFOS and PFOA in untreated ROC were 34 and 41 ng/L, which is within or above the range of the drinking water health advisory (**Table 3**), and therefore suggests this contaminant to be a priority in evaluating the impacts of ROC discharges. Of note, wastewater effluent concentrations of PFOA (44 ng/L) and PFOS (18 ng/L) from San Jose/Santa Clara wastewater facility collected from a single sampling event in the Fall of 2014 were in a similar range (Houtz et al., 2016).

Pilot study of the open-water cell indicated no removal of either compound. Ozone treatment also did not show any removal. These results are not unexpected, given the persistence of these compounds and their resistance to typical environmental degradation processes. While ROC treatment would not be expected to change the loads of PFAS discharged to the Bay, higher concentrations at discharge points have the potential to lead to more localized risk of impacts in these areas.

Many other PFAS are likely to be present in ROC based on previous detections in Bay wastewater effluent (Houtz et al., 2016). Other PFAS have received little to no testing; however, structural similarities suggest that they are likely to trigger similar concerns for human and ecological health.

### **3.3 Metals**

#### **3.3.1 Selenium**

Selenium (Se) is an essential micronutrient for living organisms, but it is also a reproductive toxicant at higher concentrations, affecting subcellular, cellular, organ, and system level processes. Developing young are the most at risk from these effects, which can lead to craniofacial, fin, and spinal deformities in fish larvae, and high rates of embryo mortality and multiple deformities in aquatic birds (Ohlendorf, 2003). Invertebrates are not particularly sensitive to Se, although information concerning adverse effects to invertebrates under field conditions is limited. Higher trophic level organisms are especially at risk because Se biomagnifies up food chains. Managing Se inputs to aquatic systems is complicated because of the narrow margin between concentrations that are required as micronutrients and those that are potentially harmful.

The deformities and mortality associated with excess Se occur in developing organisms, which can have significant effects on populations, resulting in a lack of recruitment and subsequent declines or disappearances of affected species. When Se inputs are reduced, populations may recover, but contaminated sediments can serve as a continuing source for Se cycling (Lemly, 1987).

San Francisco Bay is known to contain Se levels that may cause toxicity to aquatic organisms. The US EPA is proposing to revise the current federal Clean Water Act Se water quality criteria applicable to the Bay to ensure the criteria are set at levels that protect aquatic life and aquatic-dependent wildlife, including federally listed threatened and endangered species. This prompted concern over whether the proposed criteria were appropriate for the South Bay because data specific to the North Bay and Delta had been used to develop the proposed criteria. In response, US EPA and the United States Geological Survey (USGS) predicted Se bioaccumulation using site-specific data for South Bay, and specifically Lower South Bay (LSB). The range of aqueous Se concentrations that would be protective for LSB depends upon the species chosen for protection and the diet of those species, but the range for the most likely scenarios is relatively small (0.3–0.5 µg/L for fish; 0.2–0.4 µg/L for birds) (Luoma and Presser, 2018).

These values are significantly below the average concentration measured in ROC, which was 2.9 µg/L. Using the lower bound value of 0.2 µg/L as the ecological

threshold, the measured Se concentration in ROC was a factor of 14 greater than the ecological threshold. This suggests that ROC discharge might have the potential to pose risks to wildlife living or foraging in the area near the discharge. However, the levels in ROC are below the current 5 µg/L water quality objective for South Bay.

No removal was observed from open-water treatment train for selenium. Therefore, other measures would be needed to manage the potential ecological impacts of selenium.

### **3.3.2 Nickel**

Nickel may exert toxicity on aquatic organisms via disruption of calcium, magnesium, or iron homeostasis, oxidative damage from the formation of reactive oxygen species, or an allergic-type response of respiratory epithelia (Brix et al., 2017). These cellular-level impacts can lead to reductions in growth, reproduction, and/or alterations in energy metabolism. The tolerance of species varies widely, depending on species, pH, and water hardness, although invertebrates appear to be particularly sensitive (Gissi et al., 2016). The Basin Plan specifies a chronic water quality objective of 11.9 µg/L (dissolved fraction) for the relevant region of the Lower San Francisco Bay (SFRWQCB, 2017a, 2017d). This value is used as the toxicity threshold. Wastewater NPDES permit thresholds are based on total recoverable fraction of the metal, and are based on the Water Board's water quality objectives (**Table 2**) while taking into account estimated ratio of dissolved and total metal concentration, and in some cases account for dilution at the discharge location. The lowest wastewater permit threshold, which is designed to meet the water quality objectives, is 24 µg/L (total recoverable fraction) for Sunnyvale discharges (SV Tentative Permit, 2020).

Average measured dissolved Ni and total Ni concentrations in ROC were 18 and 19 µg/L, respectively, with maximum concentrations of 23 and 25 µg/L. These values are in the range of NPDES discharge permit thresholds of 24 µg/L (SV Tentative Permit, 2020). These concentrations are above the ecological thresholds (11.9 µg/L dissolved fraction) based on the Water Quality Objective for the San Francisco Bay (SFRWQCB, 2017a).

No removal was observed from open-water treatment cells or from ozone treatment. Therefore, other management options are needed to manage the ecological impacts of nickel.

### **3.3.3 Copper**

Like Se, copper (Cu) is an essential micronutrient, but can be highly toxic to aquatic organisms at higher concentrations. However, unlike Se, Cu is not bioaccumulative. The most bioavailable form of Cu, and therefore the most toxic, is the cupric ion (Cu<sup>2+</sup>) present in the dissolved fraction. Cu toxicity can vary significantly due

to various water quality characteristics, including temperature, dissolved organic compounds, suspended particles, pH, and various inorganic cations and anions, including those composing hardness and alkalinity. These factors alter Cu<sup>2+</sup> bioavailability, and therefore toxicity. Cu in ROC likely occur as chelates, which can also affect Cu bioavailability and toxicity to different species.

In addition to varying with water chemistry, Cu toxicity also varies significantly between taxa. The most sensitive species are algae, especially blue-green algae, which can be 1,000 times more sensitive to toxic effects than mammals (Nor, 1987; Solomon, 2009). Cu negatively affects photosynthesis and growth, and is frequently used as an algicide. Aquatic invertebrates, especially molluscs, can also be sensitive to Cu. Sensitivity varies by species, and adverse effects could result in reduced prey abundance and quality for higher trophic organisms. In addition to potentially impacting food sources, Cu also exerts a wide range of physiological effects on fishes, including decreasing resistance to disease and altering behavior, metabolism, and growth (Eisler, 1997). Of particular concern is the impairment of salmonid olfactory response, which can occur at concentrations as low as 5 µg/L (Sommers et al., 2016). The Water Quality Control Plan for the San Francisco Bay (Basin Plan) specifies a chronic continuous concentration water quality objective (4-day average) of 6.9 µg/L (dissolved fraction) for the relevant region of the Lower San Francisco Bay (SFRWQCB, 2017a, 2017d). This value is used as the toxicity threshold. Wastewater NPDES permit thresholds are based on total recoverable fraction of the metal, and are based on the Water Board's water quality objectives while taking into account estimated ratio of dissolved and total metal concentration, and in some cases account for dilution at the discharge location (PA Permit, 2019; SJ-SC Tentative Permit, 2020; SV Tentative Permit, 2020). The lowest permit threshold for Cu among the three facilities is 10 µg/L (total recoverable fraction) for Sunnyvale discharges (SV Tentative Permit, 2020).

Average measured dissolved Cu and total Cu concentrations in ROC were 5.9 and 8.6 µg/L, respectively, with maximum concentrations of 9.4 and 24.8 µg/L. These concentrations are in the range or exceed NPDES discharge permit thresholds of 10 µg/L (total) for Sunnyvale (SV New Permit). These concentrations are also in the range or above the ecological thresholds based on the water quality objective (6.9 µg/L dissolved fraction).

Dissolved and total Cu concentrations in ROC were partially removed after passing through the open-water treatment cell. The average concentration after treatment was 5 µg/L of Cu, which is in the range of permit discharge limits and ecological thresholds. Total Cu removal through the open-water treatment cell without ozone treatment calculated from concentrations measured during the summer months of 2019 was 34% (**Table 13**). Ozone treatment alone had no effect on copper concentration. While open-water treatment cells showed partial benefits of Cu removal

from ROC, concentrations treated through the open-water treatment cells were still in the range of ecotoxicity thresholds and permit thresholds, and therefore may still be of ecological concern.

**Table 13:** Average concentration ( $\mu\text{g/L}$ ) of dissolved and total copper in ROC in the open-water treatment cell pilot study, calculated from measured concentration during the summer of the third year (2019) of monitoring.

ROC Treatment Level	Dissolved	Total
Untreated ROC <sup>1</sup>	6.9	7.2
ROC Treated through Open-Water Cell <sup>2</sup>	4.9	4.8
ROC Treated with Ozone <sup>3</sup>	8.2	8.1
ROC Treated with Ozone and Treated through Passed through Open-Water Cell <sup>4</sup>	5.9	6.1

<sup>1</sup>**Untreated ROC** represents concentrations measured in untreated ROC that was sampled from the inlet of the pilot open-water treatment cell #1.

<sup>2</sup>**ROC Treated through Open-Water Cell** represents concentrations measured in the outlet of the same cell.

<sup>3</sup>**ROC Treated with Ozone** represents measured concentration of ROC treated with 20 mg-O<sub>3</sub> per L of ROC that was measured in the inlet of the open-water treatment cell #2.

<sup>4</sup>**ROC Treated with Ozone and Passed through Open-Water Cell** represents measured ROC concentration measured at the outlet of the same cell.

### 3.3.4 Zinc

Zinc (Zn), like Se and Cu, is also an essential micronutrient, but can be toxic to aquatic organisms at higher concentrations. Zinc is one of the most widely used metals in the world, and is widely distributed in the environment. Most Zn introduced into the aquatic environment is sorbed to clay minerals and organic carbon, which increases its solubility. Aquatic toxicity can vary significantly due to various water quality characteristics that affect sorption, and therefore bioavailability, particularly water hardness, pH, and temperature. Precipitation can also reduce the mobility of Zn in reducing environments. Tolerant of Zn will vary by species based on the form of Zn most readily bioavailable and the organism's ability to regulate internal concentrations (US EPA, 1987). Insects are generally fairly tolerant, whereas cladocerans (e.g., water fleas) are sensitive. Zinc is not bioaccumulative. The Basin Plan specifies a marine water quality objective of 81  $\mu\text{g/L}$  (dissolved fraction) expressed as a 4-day average, which is used as the toxicity threshold. All three wastewater facilities have specified discharge limits of 161  $\mu\text{g/L}$  total fraction, which is designed to meet the governing water quality objective corrected for hardness of the receiving water and estimated ratio of dissolved and total metal concentration, and in some cases account for dilution at the discharge location.

Average untreated ROC concentration was 74 µg/L (total) and below the permit threshold of 161 µg/L (total fraction). This value is in the range of the toxicity threshold before correcting for receiving water hardness and fraction of metals in the dissolved fraction.

No removal was observed from open-water treatment cells or from ozone treatment. Therefore, other management options are needed to manage the ecological impacts of Zn.

### **3.4 Byproducts Formation**

Bromate was formed as a byproduct of ozone treatment, and is produced when ozone reacts with bromide. Bromate is a known carcinogen and is listed on California's Proposition 65. OEHHA has a Public Health Goal of 100 ng/L in drinking water. The EU has a less conservative maximum threshold in drinking water of 10 µg/L. Environmental thresholds are not available for bromate, although available data suggest aquatic organisms are less sensitive than humans (Hutchinson et al., 1997). Bromate concentrations in untreated ROC were below detection levels (10 µg/L). Bromate concentrations in ROC that had been treated with 20 mg-O<sub>3</sub> per L ROC ranged between 6—57 µg/L, with an average of 21 µg/L. Doubling the dose of ozone increased the bromate concentration by a factor of 5 (Chapter 1). Open-water treatment did not significantly change bromate concentrations in ROC.

### **3.5 Implications for Using Open-water Treatment Cells to Manage Contaminants in ROC**

The open-water treatment pilot study provided promising removal of nutrients. The treatment cell effectively removed approximately one-third of the DIN, mostly in the form of nitrate, in ROC during the summer months. This removal efficiency is particularly notable given the relatively low-cost and sustainable nature of a treatment train including open-water cells. While the nutrient removal benefits were limited to the summer months, overall nutrient concentrations in the Bay in winter are expected to be diluted naturally from influxes of stormwater during California's wet season. Thus, the pilot study suggests this technological solution to ROC disposal is likely to yield water quality benefits for the Bay.

The combination of ozone pre-treatment and open-water treatment provided an additional benefit in terms of removal of some unregulated organic contaminants from ROC. Ozone pretreatment effectively removed the pharmaceuticals carbamazepine, sulfamethoxazole, and trimethoprim in ROC to below ecotoxicological thresholds. In addition, the open-water treatment led to significant removal (>60%) of the pesticide fipronil, the pharmaceuticals metoprolol and propranolol, and the antimicrobial triclosan. Imidacloprid concentrations were reduced by 34% in the open-water treatment cell pilot

study through combined ozone and open-water cell treatment. The removal efficiency for the contaminants that were effectively removed by the open-water treatment cell is a function of the hydraulic residence time, and the size of the treatment cell could be scaled-up to obtain greater contaminant removal rates.

While there are no regulatory limits associated with discharge of these CECs, their full or partial removal via the pilot treatment train represents a valuable co-benefit to protect the beneficial uses of receiving waters. However, it is important to note that treatment should generally not be considered a replacement for source control, where possible, as a means of reducing contaminant concentrations and loads to the environment.

In fact, source control will be an important approach for those CECs that are known to be difficult to remove via this pilot treatment train, as well as other technologies under consideration. For example, PFAS are persistent compounds that resist environmental degradation processes; increased use of RO and discharge of ROC would not be expected to change the loads to the Bay, but could result in higher exposures and related ecotoxicity concerns near outfalls.

The open-water treatment cell pilot study showed low to no removal rates of metals. Therefore, other management options are needed to manage the ecological impacts of these contaminants.

Many of the contaminants in this evaluation exceeded ecotoxicological thresholds by more than a factor of ten (**Table 3**). This is the case for imidacloprid, fipronil, metoprolol, propranolol, and selenium. Therefore, dilution of ROC with wastewater effluent at the level being considered is unlikely to be sufficient to reduce discharge concentrations below ecotoxicological thresholds. The effectiveness of diluting ROC with wastewater effluent is discussed and evaluated further for specific Valley Water portfolio scenarios further below.

### **3.6 Study Limitations**

In reviewing the findings from this study, there are a number of caveats to consider: i) the representativeness of the ROC evaluated may be limited, ii) there are gaps in our understanding of adverse ecological impacts of the contaminants monitored, and iii) there are additional unknown and potentially concerning contaminants whose occurrence and possible adverse impacts were not evaluated as part of this study.

First, ROC from Valley Water's Advanced Water Purification Facility (AWPF) in San Jose was evaluated for this study, but ROC from other facilities may have varying levels of contaminant concentrations. Reverse osmosis treatment uses membranes that concentrate nearly all contaminants except low molecular weight non-polar organic

compounds usually weighing less than 100 daltons. This means differences in contaminant concentrations in the original wastewater effluent will affect contaminant concentrations in ROC. Several characteristics of the wastewater effluent may affect contaminant concentrations including: geographic location; residential, commercial, and industrial populations served; type of wastewater treatment; source water; and infiltration from stormwater, groundwater, or ocean water. However, laboratory tests of ROC from San Jose and four additional facilities in California indicated that ROC water quality was similar across facilities. Behavior of ROC samples with respect to ozone oxidation and open-water treatment cells was also similar. This suggests that removal efficiencies evaluated in the pilot study could be broadly applicable to facilities throughout the state.

Secondly, it is important to acknowledge that our understanding of potential impacts of the monitored contaminants to the Bay continues to evolve based on new information, including Bay monitoring data and new toxicity information. For example, while currently there are no discharge limits for nutrients to the Bay, there is a significant effort underway to rigorously update our understanding of what nutrient loads and concentrations are protective of ecosystem health in the Bay. This effort is being led by NMS, which is a collaborative effort among the San Francisco Bay Regional Water Quality Control Board and municipal wastewater treatment agencies.

Finally, there may be other compounds that are of toxicological concern in ROC that were not monitored in this study, including transformation products. The contaminants monitored in ROC and ROC treated through the pilot study open-water treatment systems were carefully selected to include: a) six indicator compounds consisting of pharmaceuticals that have previously been used to efficiently track chemical and biological processes active in treatment systems (Chapter 1); b) an additional eight compounds that includes pesticides and long-chain perfluorinated alkyl substances (PFAS), which represent a subset of prioritized CECs in the Bay; and c) select nutrients and metals that are regulated or being evaluated for regulation (*Sampling and Analysis Plan*, 2017). Additional CECs prioritized as concerns for the Bay were added after the development of the Sampling and Analysis Plan, including imidacloprid, tris (2-chloroethyl) phosphate (TCEP; an organophosphate ester flame retardant), and 4-nonylphenol (an alkylphenol) (SFEI, 2019). Seventeen additional pharmaceuticals, the insect repellent DEET, and the antimicrobial triclosan, were also added to the analyses.

However, the compounds selected for monitoring were not meant to be an exhaustive list of all contaminants that may be of concern in ROC, but a diverse set of contaminants to evaluate the removal efficiency of contaminants with different physical and chemical properties and potential toxicity concerns in the Bay. There are other regulated contaminants in ROC that were not examined as part of this study and that

may exceed current discharge limitations without blending or dilution. A list of these contaminants is summarized in Table 2.1 of the report, “Task 4 - Evaluation of ROC Management Options” (GHD, 2019).

In addition, the handful of monitored and unmonitored contaminants described above are a small subset of the more than 100,000 chemicals that have been registered or approved for commercial use in the U.S. Only a very small fraction have been regulated or targeted for routine monitoring in any environmental matrix. Several classes of emerging contaminants have been prioritized by the RMP for additional attention in the Bay; while a number of these were monitored via this study, notable exceptions include bisphenols, organophosphate esters (other than TCEP), alkylphenols and alkylphenol ethoxylates (other than 4-nonylphenol), long-chain perfluorocarboxylates (other than PFOA), and microplastics (Lin et al., 2018a; Sutton et al., 2017).

The State of California is planning to reconvene the Ambient Ecosystems CEC Advisory Panel, and the State Water Board has contracted with the Aquatic Science Center to synthesize and evaluate available data on CECs to inform this panel and a statewide CEC initiative monitoring and management strategy. Findings from these efforts may provide an indication as to the representativeness and relevance of the contaminants analyzed in this study for investigations of ROC.

### **3.7 Evaluation of ROC Dilution for Valley Water Portfolios and Scenarios**

Dilution of ROC at the discharge point is another ROC management option being considered by Valley Water, and various dilution management alternatives have been evaluated (GHD, 2019). One of these alternatives is blending ROC with available wastewater effluent at facilities’ existing shallow outfall locations. Another alternative is construction of enhanced mixing outfall locations near current locations with greater dilution characteristics and smaller mixing zones compared to current conditions. Discharge to a deep water outfall is also proposed. Dilution management options have been developed for each of the four portfolios representing potential construction of AWPFS for potable reuse (PR) in South San Jose, Palo Alto, Sunnyvale, or Morgan Hill. The purpose of this section is to evaluate whether dilution with available wastewater effluent can be used to manage specific contaminants in ROC to address toxicity concerns at current outfall locations. All portfolios evaluated here have only included flows from AWPFS for potable reuse (PR) and have not taken into account those for non-potable reuse (NPR+). Flows within these portfolios are predicted values to model future water management scenarios and consistent with GHD and the Countywide Reuse Master Plan.

Here, an analysis of site-specific scenarios is conducted to better understand the potential ecological implications of contaminant concentrations from ROC blending with wastewater at each site. The evaluation of contaminant concentrations in previous sections compared undiluted ROC to available ecotoxicological thresholds. In order to evaluate the worst-case ecotoxicological impacts of ROC diluted with effluent in each portfolio, the blended discharge scenario for each portfolio is based on the monthly discharge that is the most concentrated with ROC and produces the largest discharge flow (Minimum Flow scenario in **Table 13**). Future monthly discharges, obtained from the Countywide Reuse Master Plan, are the most detailed projected flows available. While minimum daily flows would be more conservative for evaluating permit compliance and toxicity impacts, this data was not available for evaluations. Under the minimum flow conditions, contaminants in the ROC discharge would be highest. Since these conditions may overestimate ROC-diluted discharge concentrations in more typical scenarios, we also evaluated ROC-diluted discharge concentrations using average flows for comparison (Mean Flow scenario in **Table 14**).

Portfolio 1, comprising scenarios A and B, provides for an expanded AWWPF at the San Jose-Santa Clara Regional Wastewater Facility (SJ-SC RWF) for PR. Since this facility has high wastewater flows, the expanded AWWPF would continually operate at full capacity to produce 24 MGD of permeate (potable water) and 4.24 MGD of ROC. Additional wastewater flows of 22.3 MGD are blended with ROC, which give a total discharge of 26.5 MGD with 16% ROC for the minimum flow month (or worst case scenario) for this portfolio. A monthly flow average of available wastewater for blending is 47.2 MGD with a total average discharge of 51.4 MGD (8% ROC). For portfolio 1, discharges would occur at new outfall "outside the fence line" of the SJ-SC WRF.

Portfolio 2 considers an AWWPF in either Palo Alto (Scenario A) or Sunnyvale (Scenario B) with combined influent flows from the WWTPs in both cities. The flows for these two scenarios are the same, with the AWWPF having a target permeate capacity of 24 MGD and up to 4.24 MGD of ROC by 2035. Wastewater flows in the worst case scenario from Palo Alto and Sunnyvale would equal 1.5 MGD, which combined with 2.9 MGD ROC in the minimum flow month would produce a discharge of 4.4 MGD composed of 67% ROC. The monthly average flows include 3.7 MGD of ROC blended with 3.3 MGD of wastewater effluent with a total discharge of 7 MGD (53% ROC). For Portfolio 2A, where the AWWPF is located in Palo Alto, the blended effluent is planned to be discharged at the current shallow outfall in San Francisco Bay under their existing NPDES permit. In Portfolio 2B, the AWWPF is located in Sunnyvale, where a new outfall will be required to meet dilution standards.

**Table 14:** Monthly minimum and mean flows identified in Portfolios 1 (Scenario A + B) and Portfolio 2 (Scenario A + B).

		Portfolio 1	Portfolio 1	Portfolio 2	Portfolio 2
Flow Type	Source of Flow	Minimum Flow <sup>1</sup> (MGD)	Mean Flow (MGD)	Minimum Flow (MGD)	Mean Flow (MGD)
AWPF Influent	Total Wastewater Effluent Available for Potable Reuse	50.5	75.4	20.8	27.8
	Actual Flow (Feed)	28.2		19.3	24.4
AWPF Effluent	Potable Water	24		16.4	20.8
	ROC	4.24		2.9	3.7
WWTP <sup>2</sup> Effluent	Wastewater Effluent Available for Blending	22.3	47.2	1.5	3.3
	Total Discharge	26.5	51.4	4.4	7
	Ratio = ROC:Total Discharge	0.16	0.08	0.67	0.53

<sup>1</sup>Minimum flows were identified for a particular month in each scenario

<sup>2</sup>WWTP = wastewater treatment plant

Portfolio 4 incorporates two regional AWWPs in Palo Alto and Sunnyvale with respective PR production capacities at 14 and 10 MGD, along with 2.47 MGD and 1.76 MGD of ROC, respectively. There would be no transfer of final effluent between WWTPs, and it would be discharged at the same outfall locations in Portfolio 2. Within the scope of this report, flows specifically from Portfolio 4 will not be considered. Instead more relevant flows from Portfolio 2, nearly identical to Portfolio 4 with greater ROC flows and blended discharges, will be used to model worst case scenarios in Palo Alto and Sunnyvale.

GHD conducted analyses to estimate the concentrations of contaminants within the ROC and blended effluent discharge flows (GHD, 2019). The evaluation assumed an 85% RO recovery, 100% rejection of contaminants, and concentration of contaminants by a factor of roughly 6.7. Currently, SVAWPC operates at a slightly lower RO recovery of 80%. Within each portfolio, several regulated contaminants within unblended ROC and blended effluent already exceed current thresholds, particularly for metals (i.e., copper and selenium). In particular, dilution will not work for ROC contaminants with concentrations that exceed toxicity thresholds by a factor greater than 6.7.

For our analysis, we used the same assumptions (including both 80 and 85% recovery rates) to determine the potential for dilution of contaminants based on the

predicted effluent and ROC flows. Diluted ROC discharge concentrations were estimated by using dilution ratios in Table 13, average untreated ROC concentrations from the AWPf at San Jose used in the pilot study, and calculated wastewater concentrations derived from the ROC concentration (ROC concentration divided by 5 or 6.7). Note that concentrations at Palo Alto and Sunnyvale are assumed to be the same as those measured at SVAWPC using effluent from SJ-SC RWF because ROC from Palo Alto and Sunnyvale were not measured as part of this study. When compared to toxicity thresholds, our evaluation found dilution may be sufficient for certain contaminants with ratios <10.

Sulfamethoxazole, for example, is sufficiently managed through dilution. The ROC concentration of sulfamethoxazole is 2,410 ng/L with a calculated effluent concentration of 360 ng/L (based on an effluent to ROC concentration ratio of 6.7). The latter effluent concentration is a reasonable value as it is in the range of effluent concentrations previously measured from seven Bay area wastewater facilities (Lin et al., 2018). In the worst case for Portfolio 1, the calculated ROC-diluted discharge concentration is 688 ng/L, and is less than half of the toxicity threshold of 1,790 ng/L. Even if we use current SVAWPC operating conditions of 80% recovery, and back-calculate an effluent concentration of 482 (based on an effluent to ROC concentration ratio of 5), the calculated discharge concentration is similar, with a value of 790 ng/L. ROC-diluted discharge concentrations based on average flows are predicted to be even lower. In Portfolio 2, the calculated ROC-diluted concentrations for the minimum flows scenario (1,733 ng/L) and average flows scenario (1,446 ng/L) are within the range of the toxicity threshold. Using ROC treated through a treatment train similar to the pilot study would reduce total loads entering the Bay as well as further reduce discharged concentrations below these values.

For copper, the average ROC concentration was 8.55 µg/L and the corresponding calculated effluent concentration is 1.28 µg/L (based on an effluent to ROC concentration ratio of 6.7). The effluent concentration is reasonable, as the maximum effluent concentration (MEC) detected from September 2014 through September 2019 was 4.08 µg/L (SJ-SC Tentative Permit, 2020). For Portfolio 1 minimum and average flow, ROC-diluted Cu concentrations were calculated to have a concentration of 2.4 and 2.1 µg/L, respectively. Both are in the range of the toxicity threshold of 6.9 µg/L. Under current SVAWPC conditions with 80% RO Recovery, Cu concentrations would be increased in effluent and discharge (1.71 and 2.80 µg/L, respectively), though below current toxicity thresholds. In Portfolio 2, calculated ROC-diluted Cu concentrations in the discharge were calculated to be 6.15 and 5.13 using minimum and average flow, which are above the toxicity threshold. Further, water quality modeling on future discharges also indicates Cu will not meet permit standards during summer months after dilution for both scenarios A and B in Portfolio 2, because of the higher proportion of ROC to effluent for these scenarios (RMA, 2019). In their most recent permit, Palo Alto has been granted dilution credits for copper that will help it meet its discharge requirement. Overall, dilution of ROC with wastewater effluent are in the range of water quality criteria.

As described in the previous section, other prioritized contaminants in ROC that exceed ecotoxicological thresholds by greater than a factor of ten cannot be managed by dilution with wastewater alone because contaminant concentrations in effluent are likely to already exceed ecotoxicological thresholds. For example, selenium in ROC had an average concentration of 2.9 µg/L and a predicted concentration of 0.43 µg/L in wastewater effluent (based on an effluent to ROC concentration ratio of 6.7). The latter value is reasonable because the MEC for Se from September 2014 through September 2019 was 1.2 µg/L. The effluent concentration already exceeds the ecotoxicological threshold of 0.2 µg/L, meaning dilution will do little to lower Se concentrations. In previous evaluations, GHD found Se in ROC would not be diluted sufficiently during dry weather months to meet current permit requirements in Portfolios 2 and 4 (GHD, 2019).

### **3.8 Other Management Options**

While the open-water treatment cell pilot study showed benefits for partial contaminant removal, application has some limitations due to reduced treatment efficiency in the winter and partial or limited removal of some contaminants in ROC. This treatment technology can complement other management options that are being considered for specific contaminants of concern.

Source control is expected to be an appropriate means to address some contaminants, such as the pesticides fipronil and imidacloprid. A previous study of Bay Area wastewater influents and effluents suggested topical (“spot-on”) flea control products are a major source of these pesticides to the wastewater pathway (Sadaria et al., 2017). A follow-up investigation of fipronil flea control products led by the California Department of Pesticide Regulation (DPR) confirmed that significant amounts of the active ingredient could be washed off treated dogs weeks after treatment (Teerlink et al., 2017). Based on these findings, local wastewater agencies have already begun educating veterinarians and pet owners about the water quality concerns relating to spot-on flea control products and the availability of effective oral medications for pets as safer alternatives. While DPR has not taken regulatory action concerning these flea control products, the agency recently led implementation of a labeling change for fipronil products sprayed around buildings to control ants, which is expected to significantly reduce levels of discharge to the stormwater pathway. Reduced use of harmful chemicals, whether through consumer education or regulatory action, can be expected to lead to lower levels of these contaminants in ROC and receiving waters.

Additionally, other nature-based solutions that wastewater treatment plants are evaluating for potential nutrient load reductions and shoreline resilience may provide additional benefits of contaminant removal (Wren et al., 2019). The horizontal levees system in Oro Loma is currently being evaluated for ROC contaminant removal. Also, discharge to baylands marshes (Chapter 3) may remove additional contaminants before reaching the Bay. For example, the City of Palo Alto discharges wastewater effluent to

Renzel Marsh along the Palo Alto baylands, which provides additional nitrogen removal (SFEP, 2018).

Valley Water is currently evaluating other management options, including other treatment technologies and potential changes to discharge locations through infrastructure development to enhance mixing of discharges with Bay waters. While enhancing dilution may reduce contaminant concentrations near the vicinity of the outfall, this management option will not reduce total loads of contaminants entering the Bay.

## 4. Conclusions

The pilot study indicated that treatment of ROC through combined use of ozone and the open-water treatment cell can be a relatively low-cost and sustainable approach to reduce contaminant discharges and improve water quality. The open-water treatment cell performed best during the summer, while ozone pre-treatment provided additional contaminant removal benefits year-round.

The overall reduction of nutrient loads to the Bay from this treatment train could be an important piece of the nature-based solutions needed to reduce nutrient input and related impacts to the Bay. The treatment train removed approximately one-third of the DIN, mostly in the form of nitrate, in ROC during the summer months. While nutrient removal was limited during the winter, this may be acceptable because nutrient concentrations may be diluted naturally during the winter from stormwater flows.

Additionally, the treatment train removed significant amounts of several unregulated organic contaminants in ROC, which would reduce potential impacts to wildlife near the point of discharge. In particular, pharmaceuticals, such as beta-blockers (e.g., metoprolol and propranolol), antibiotics (i.e., sulfamethoxazole, trimethoprim, and triclosan), and carbamazepine were significantly reduced in the pilot study. The urban pesticides fipronil and imidacloprid were also partially removed by ozone and the open-water treatment cell. Treatment of ROC may therefore be an efficient way of reducing loads of these contaminants to the Bay. While removal from the open-water treatment cell may be reduced in the winter, removal by ozone would occur year-round and, in some cases, ozone dose could be increased during the winter to compensate for seasonal reduced removal from the open-water cell.

ROC treatment can complement management actions for specific contaminants, including source control measures designed to reduce environmental contamination and limit risks to Bay wildlife. Some contaminants, specifically metals and PFAS, showed limited removal from the treatment train; additional management options for these contaminants should be considered.

Development of a monitoring strategy to assess water quality changes and potential toxicity concerns associated with ROC discharge is recommended. Monitoring should include chemical analysis as well as toxicity testing to account for potential unknown contaminants. Care should also be taken to choose Bay-appropriate species for toxicity testing, as salinity differences can interfere with results for many classic test species. Effect monitoring in bayland ecosystems receiving ROC discharge may also be appropriate.

## 5. References

Anderson, P.D., Denslow, N.D., Drewes, J.E., Olivieri, A.W., Schlenk, D., Scott, G.I., Snyder, S.A., 2012. Monitoring Strategies for Contaminants of Emerging Concern (CECs) in California's Aquatic Ecosystems: Recommendations of a Science Advisory Panel (No. Technical Report 692). Southern California Coastal Water Research Project, Costa Mesa, CA.

Aronson, D., Weeks, J., Meylan, B., Guiney, P.D., Howard, P.H., 2012. Environmental release, environmental concentrations, and ecological risk of N,N-Diethyl-m-toluamide (DEET). *Integrated Environmental Assessment and Management* 8, 135–166. <https://doi.org/10.1002/ieam.271>

Bengtsson-Palme, J., Kristiansson, E., Larsson, D.G.J., 2018. Environmental factors influencing the development and spread of antibiotic resistance. *FEMS Microbiol Rev* 42. <https://doi.org/10.1093/femsre/fux053>

Brausch, J.M., Rand, G.M., 2011. A review of personal care products in the aquatic environment: Environmental concentrations and toxicity. *Chemosphere* 82, 1518–1532. <https://doi.org/10.1016/j.chemosphere.2010.11.018>

Brix, K.V., Schlekot, C.E., Garman, E.R., 2017. The mechanisms of nickel toxicity in aquatic environments: An adverse outcome pathway analysis. *Environmental Toxicology and Chemistry* 36, 1128–1137. <https://doi.org/10.1002/etc.3706>

Brodin, T., Piovano, S., Fick, J., Klaminder, J., Heynen, M., Jonsson, M., 2014. Ecological effects of pharmaceuticals in aquatic systems—impacts through behavioural alterations. *Phil. Trans. R. Soc. B* 369, 20130580. <https://doi.org/10.1098/rstb.2013.0580>

Calleja, M.C., Persoone, G., Geladi, P., 1994. Comparative acute toxicity of the first 50 Multicentre Evaluation of In Vitro Cytotoxicity chemicals to aquatic non-vertebrates. *Arch. Environ. Contam. Toxicol.* 26, 69–78. <https://doi.org/10.1007/BF00212796>

Canada, Environment Canada, 2013. Perfluorooctane sulfonate in the Canadian environment: environmental monitoring and surveillance in support of the chemical management plan.

Chandler, G.T., Cary, T.L., Volz, D.C., Walse, S.S., Ferry, J.L., Klosterhaus, S.L., 2004. Fipronil Effects on Estuarine Copepod (*amphiascus Tenuiremis*) Development, Fertility, and Reproduction: A Rapid Life-Cycle Assay in 96-Well Microplate Format. *Environ*

Toxicol Chem 23, 117. <https://doi.org/10.1897/03-124>

Cloern, J.E., 2007. Habitat Connectivity and Ecosystem Productivity: Implications from a Simple Model. *The American Naturalist* 169, E21–E33. <https://doi.org/10.1086/510258>

Cloern, J.E., Jassby, A.D., 2010. Patterns and Scales of Phytoplankton Variability in Estuarine–Coastal Ecosystems. *Estuaries and Coasts* 33, 230–241. <https://doi.org/10.1007/s12237-009-9195-3>

Diamond, M.L., 2017. Surprising Degradation Products from an Under-Fire Insecticide. *ACS Cent. Sci.* 3, 97–98. <https://doi.org/10.1021/acscentsci.7b00033>

Ding, G., Peijnenburg, W.J.G.M., 2013. Physicochemical Properties and Aquatic Toxicity of Poly- and Perfluorinated Compounds. *Critical Reviews in Environmental Science and Technology* 43, 598–678. <https://doi.org/10.1080/10643389.2011.627016>

Donner, E., Kosjek, T., Qualmann, S., Kusk, K.O., Heath, E., Revitt, D.M., Ledin, A., Andersen, H.R., 2013. Ecotoxicity of carbamazepine and its UV photolysis transformation products. *Science of The Total Environment* 443, 870–876. <https://doi.org/10.1016/j.scitotenv.2012.11.059>

Eisler, R., 1997. Copper Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review (Biological Science Report No. USGS/BRD/BSR-1997-0002). U.S. Geological Survey, Biological Resources Division.

Emerging chemical risks in Europe — ‘PFAS’ [WWW Document], 2019. . European Environment Agency. URL <https://www.eea.europa.eu/themes/human/chemicals/emerging-chemical-risks-in-europe> (accessed 3.3.20).

Ensminger, M.P., Budd, R., Kelley, K.C., Goh, K.S., 2013. Pesticide occurrence and aquatic benchmark exceedances in urban surface waters and sediments in three urban areas of California, USA, 2008–2011. *Environ Monit Assess* 185, 3697–3710. <https://doi.org/10.1007/s10661-012-2821-8>

European Chemicals Agency, 2018. 1,6-dichloro-1,6-dideoxy- $\beta$ -D-fructofuranosyl... - Registration Dossier [WWW Document]. URL <https://echa.europa.eu/registration-dossier/-/registered-dossier/25256> (accessed 3.13.20).

European Chemicals Agency, 2011. Triclosan - Registration Dossier [WWW Document].

URL <https://echa.europa.eu/registration-dossier/-/registered-dossier/12675> (accessed 3.13.20).

European Chemicals Agency, 2010a. Directive 98/8/EC concerning the placing biocidal products on the market: Bifenthrin Product-type PT8 (Wood preservatives) Assessment Report.

European Chemicals Agency, 2010b. Caffeine - Registration Dossier [WWW Document]. URL <https://echa.europa.eu/registration-dossier/-/registered-dossier/10085> (accessed 3.13.20).

European Chemicals Agency, 2009. European Union Risk Assessment Report: Tris (2-Chloroethyl) Phosphate, TCEP.

Fabbri, E., Franzellitti, S., 2016. Human pharmaceuticals in the marine environment: Focus on exposure and biological effects in animal species. *Environmental Toxicology and Chemistry* 35, 799–812. <https://doi.org/10.1002/etc.3131>.

Ferrari, B., Mons, R., Vollat, B., Fraysse, B., Paxéus, N., Lo Giudice, R., Pollio, A., Garric, J., 2004. Environmental risk assessment of six human pharmaceuticals: are the current environmental risk assessment procedures sufficient for the protection of the aquatic environment? *Environ. Toxicol. Chem.* 23, 1344–1354.

GHD, 2020. Task 4 -Evaluation of ROC Management Options (No. GHD Project Number 11110722). Valley Water.

Gissi, F., Stauber, J.L., Binet, M.T., Golding, L.A., Adams, M.S., Schlekat, C.E., Garman, E.R., Jolley, D.F., 2016. A review of nickel toxicity to marine and estuarine tropical biota with particular reference to the South East Asian and Melanesian region. *Environmental Pollution* 218, 1308–1323. <https://doi.org/10.1016/j.envpol.2016.08.089>

Godoy, A.A., Kummrow, F., Pamplin, P.A.Z., 2015. Occurrence, ecotoxicological effects and risk assessment of antihypertensive pharmaceutical residues in the aquatic environment - A review. *Chemosphere* 138, 281–291. <https://doi.org/10.1016/j.chemosphere.2015.06.024>

Gosset, A., Durrieu, C., Orias, F., Bayard, R., Perrodin, Y., 2017. Identification and assessment of ecotoxicological hazards attributable to pollutants in urban wet weather discharges. *Environmental Science: Processes & Impacts* 19, 1150–1168.

Grenni, P., Ancona, V., Barra Caracciolo, A., 2018. Ecological effects of antibiotics on natural ecosystems: A review. *Microchemical Journal* 136, 25–39.  
<https://doi.org/10.1016/j.microc.2017.02.006>

Gunasekara, A.S., Truong, T., Goh, K.S., Spurlock, F., Tjeerdema, R.S., 2007. Environmental fate and toxicology of fipronil. *J. Pestic. Sci.* 32, 189–199.  
<https://doi.org/10.1584/jpestics.R07-02>

Hladik, M.L., Main, A.R., Goulson, D., 2018. Environmental Risks and Challenges Associated with Neonicotinoid Insecticides. *Environ. Sci. Technol.* 52, 3329–3335.  
<https://doi.org/10.1021/acs.est.7b06388>

Houtz, E.F., Sutton, R., Park, J.-S., Sedlak, M., 2016. Poly- and perfluoroalkyl substances in wastewater: Significance of unknown precursors, manufacturing shifts, and likely AFFF impacts. *Water Research* 95, 142–149.  
<https://doi.org/10.1016/j.watres.2016.02.055>

Hoyle, S., Code, A., 2016. Neonicotinoids in California's Surface Waters 17.  
Hutchinson, T.H., Hutchings, M.J., Moore, K.W., 1997. A Review of the Effects of Bromate on Aquatic Organisms and Toxicity of Bromate to Oyster (*Crassostrea gigas*) Embryos. *Ecotoxicology and Environmental Safety* 38, 238–243.  
<https://doi.org/10.1006/eesa.1997.1584>

Lemly, A.D., 1987. Aquatic Cycling of Selenium: Implications for Fish and Wildlife. U.S. Department of the Interior, Fish and Wildlife Service.

Lin, D., Sutton, R., Shimabuku, I., Sedlak, M., Wu, J., Holleman, R., 2018a. Contaminants of Emerging Concern in San Francisco Bay: A Strategy for Future Investigations 2018 Update. SFEI Contribution No. 873. San Francisco Estuary Institute, Richmond, CA.

Lin, D., Sutton, R., Sun, J., Ross, J., 2018b. Screening of Pharmaceuticals in San Francisco Bay Wastewater (No. Contribution No. 910). San Francisco Estuary Institute, Richmond, California.

Luoma, S.N., Presser, T.S., 2018. Status of Selenium in South San Francisco Bay—A Basis for Modeling Potential Guidelines to Meet National Tissue Criteria for Fish and a Proposed Wildlife Criterion for Birds (Open-File Report No. 2018–1105).

MacVean, L.J., Thompson, S., Hutton, P., Sivapalan, M., 2018. Reconstructing Early

Hydrologic Change in the California Delta and its Watersheds. *Water Resources Research* 54, 7767–7790. <https://doi.org/10.1029/2017WR021426>

Melvin, S.D., 2017. Effect of antidepressants on circadian rhythms in fish: Insights and implications regarding the design of behavioural toxicity tests. *Aquatic Toxicology* 182, 20–30. <https://doi.org/10.1016/j.aquatox.2016.11.007>

Miazek, K., Brozek-Pluska, B., 2019. Effect of PHRs and PCPs on Microalgal Growth, Metabolism and Microalgae-Based Bioremediation Processes: A Review. *Int J Mol Sci* 20. <https://doi.org/10.3390/ijms20102492>

Minguez, L., Pedelucq, J., Farcy, E., Ballandonne, C., Budzinski, H., Halm-Lemeille, M.-P., 2016. Toxicities of 48 pharmaceuticals and their freshwater and marine environmental assessment in northwestern France. *Environmental Science and Pollution Research* 23, 4992–5001. <https://doi.org/10.1007/s11356-014-3662-5>

Moermond, C.T.A., Smit, C.E., 2016. Derivation of water quality standards for carbamazepine, metoprolol, and metformin and comparison with monitoring data. *Environmental Toxicology and Chemistry* 35, 882–888. <https://doi.org/10.1002/etc.3178>

Morrissey, C.A., Mineau, P., Devries, J.H., Sanchez-Bayo, F., Liess, M., Cavallaro, M.C., Liber, K., 2015. Neonicotinoid contamination of global surface waters and associated risk to aquatic invertebrates: A review. *Environment International* 74, 291–303. <https://doi.org/10.1016/j.envint.2014.10.024>

Nor, Y.M., 1987. Ecotoxicity of copper to aquatic biota: A review. *Environmental Research* 43, 274–282. [https://doi.org/10.1016/S0013-9351\(87\)80078-6](https://doi.org/10.1016/S0013-9351(87)80078-6)

Ohlendorf, H.M., 2003. Ecotoxicology of Selenium, in: *Handbook of Ecotoxicology*. Lewis Publishers, Boca Raton, pp. 465–500.

Orias, F., Perrodin, Y., 2013. Characterisation of the ecotoxicity of hospital effluents: A review. *Science of The Total Environment* 454–455, 250–276. <https://doi.org/10.1016/j.scitotenv.2013.02.064>

PA Permit, 2019. Palo Alto Regional Water Quality Control Plant and wastewater collection system NPDES discharge permit (ORDER No. R2-2019-0015; NPDES No. CA0037834). San Francisco Bay Regional Water Quality Control Board.

Peacock, M.B., Gible, C.M., Senn, D.B., Cloern, J.E., Kudela, R.M., 2018. Blurred

lines: Multiple freshwater and marine algal toxins at the land-sea interface of San Francisco Bay, California. *Harmful Algae* 73, 138–147.  
<https://doi.org/10.1016/j.hal.2018.02.005>

RMA, 2019. Hydrodynamic Modeling and Analysis of ROC Discharge Options: Outfall Location and Dilution Modeling Analysis. Resource Management Associates.

Rostkowski, P., Yamashita, N., Ka So, I.M., Taniyasu, S., Lam, P.K.S., Falandysz, J., Lee, K.T., Kim, S.K., Khim, J.S., Im, S.H., Newsted, J.L., Jones, P.D., Kannan, K., Giesy, J.P., 2006. Perfluorinated compounds in streams of the shihwa industrial zone and lake shihwa, south korea. *Environ Toxicol Chem* 25, 2374.  
<https://doi.org/10.1897/05-627R.1>

Sadaria, A.M., Sutton, R., Moran, K.D., Teerlink, J., Brown, J.V., Halden, R.U., 2017. Passage of fiproles and imidacloprid from urban pest control uses through wastewater treatment plants in northern California, USA. *Environmental Toxicology and Chemistry* 36, 1473–1482. <https://doi.org/10.1002/etc.3673>

Santos, L.H.M.L.M., Araújo, A.N., Fachini, A., Pena, A., Delerue-Matos, C., Montenegro, M.C.B.S.M., 2010. Ecotoxicological aspects related to the presence of pharmaceuticals in the aquatic environment. *Journal of Hazardous Materials* 175, 45–95. <https://doi.org/10.1016/j.jhazmat.2009.10.100>

Sedlak, M., Sutton, R., Wong, A., Lin, D., 2018. Per and Polyfluoroalkyl Substances (PFASs) in San Francisco Bay: Synthesis and Strategy (No. 867). San Francisco Estuary Institute, Richmond, CA.

Sedlak, M.D., Benskin, J.P., Wong, A., Grace, R., Greig, D.J., 2017. Per- and polyfluoroalkyl substances (PFASs) in San Francisco Bay wildlife: Temporal trends, exposure pathways, and notable presence of precursor compounds. *Chemosphere* 185, 1217–1226. <https://doi.org/10.1016/j.chemosphere.2017.04.096>

Senn, D.B., Novick, E., 2014. Scientific Foundation for the San Francisco Bay Nutrient Management Strategy (No. SFEI Contribution 979). San Francisco Estuary Institute. SF Bay Permit, 2017. Waste discharge requirements for mercury and PCBS from municipal and industrial wastewater discharges to San Francisco Bay (Order No. R2-2017-0041; NPDES No. CA0038849). San Francisco Bay Regional Water Quality Control Board.

SFEI, 2019. The Pulse of the Bay 2019: Pollutant Pathways. SFEI Contribution No. 954.

San Francisco Estuary Institute, Richmond, CA.

SFEI, 2017. The Pulse of the Bay: The 25th Anniversary of the RMP. San Francisco Estuary Institute, Richmond, CA.

SFEI, 2015. 2015 Pulse of the Bay: The State of Bay Water Quality - 2015 and 2065. San Francisco Estuary Institute, Richmond, CA.

SFEP, 2018. Treatment Wetlands and Sea Level Rise: Ensuring the San Francisco Bay Water Board's Wetland Protection Policies are Climate Change Ready (White Paper). California Regional Water Quality Control Board, San Francisco Bay Region & The San Francisco Estuary Partnership.

SFRWQCB, 2017a. Water Quality Control Plan (Basin Plan) for the San Francisco Bay Basin [WWW Document]. Basin Planning. URL [https://www.waterboards.ca.gov/sanfranciscobay/basin\\_planning.html](https://www.waterboards.ca.gov/sanfranciscobay/basin_planning.html) (accessed 4.11.20).

SFRWQCB, 2017b. Table 3-3: Marine Water Quality Objectives for Toxic Pollutants for Surface Waters [WWW Document]. URL [https://www.waterboards.ca.gov/sanfranciscobay/water\\_issues/programs/planningtmdls/basinplan/web/tab/tab\\_3-03.pdf](https://www.waterboards.ca.gov/sanfranciscobay/water_issues/programs/planningtmdls/basinplan/web/tab/tab_3-03.pdf) (accessed 3.30.20).

SFRWQCB, 2017c. Table 3-3B: Marine Water Quality Objectives for Mercury in San Francisco Bay [WWW Document]. URL [https://www.waterboards.ca.gov/sanfranciscobay/water\\_issues/programs/planningtmdls/basinplan/web/tab/tab\\_3-03b.pdf](https://www.waterboards.ca.gov/sanfranciscobay/water_issues/programs/planningtmdls/basinplan/web/tab/tab_3-03b.pdf) (accessed 4.11.20).

SFRWQCB, 2017d. Table 3-3A: Water Quality Objectives for Copper and Nickel in San Francisco Bay Segments (ug/L) [WWW Document]. URL [https://www.waterboards.ca.gov/sanfranciscobay/water\\_issues/programs/planningtmdls/basinplan/web/tab/tab\\_3-03a.pdf](https://www.waterboards.ca.gov/sanfranciscobay/water_issues/programs/planningtmdls/basinplan/web/tab/tab_3-03a.pdf) (accessed 3.30.20).

SJ-SC Tentative Permit, 2020. San Jose/Santa Clara Water Pollution Control Plant, City of San Jose wastewater collection system, City of Santa CLara wastewater collection system (TENTATIVE ORDER No. R2-2020-XXXX; NPDES No. CA0037842). San Francisco Bay Regional Water Quality Control Board.

Solomon, F., 2009. Impacts of Copper on Aquatic Ecosystems and Human Health 4. Sommers, F., Mudrock, E., Labenia, J., Baldwin, D., 2016. Effects of salinity on olfactory

toxicity and behavioral responses of juvenile salmonids from copper. *Aquatic Toxicology* 175, 260–268. <https://doi.org/10.1016/j.aquatox.2016.04.001>

Straub, J.O., 2016. Aquatic environmental risk assessment for human use of the old antibiotic sulfamethoxazole in Europe. *Environmental Toxicology and Chemistry* 35, 767–779. <https://doi.org/10.1002/etc.2945>

Sun, J., Davis, J., Shira, B., Ross, J., Wong, A., Yee, D., Fairey, R., Bonnema, A., Crane, D., Grace, R., Mayfield, R., Hobbs, J., 2017. Contaminant Concentrations in Sport Fish from San Francisco Bay: 2014 (No. 806). San Francisco Estuary Institute, Richmond, CA.

Sutton, R., Sedlak, M., Sun, J., Lin, D., 2017. Contaminants of Emerging Concern in San Francisco Bay: A Strategy for Future Investigations. 2017 Revision. San Francisco Estuary Institute, Richmond, CA.

Sutula, M., Kudela, R., Hagy, J.D., Harding, L.W., Senn, D., Cloern, J.E., Bricker, S., Berg, G.M., Beck, M., 2017. Novel analyses of long-term data provide a scientific basis for chlorophyll-a thresholds in San Francisco Bay. *Estuarine, Coastal and Shelf Science* 197, 107–118. <https://doi.org/10.1016/j.ecss.2017.07.009>

SV Tentative Permit, 2020. Sunnyvale Water Pollution Control Plant and wastewater collection system NPDES Discharge Permit (TENTATIVE ORDER No. R2-2020-XXXX NPDES No. CA0037621). San Francisco Bay Regional Water Quality Control Board.

Teerlink, J., Hernandez, J., Budd, R., 2017. Fipronil washoff to municipal wastewater from dogs treated with spot-on products. *Science of The Total Environment* 599–600, 960–966. <https://doi.org/10.1016/j.scitotenv.2017.04.219>

Todey, S.A., Fallon, A.M., Arnold, W.A., 2018. Neonicotinoid insecticide hydrolysis and photolysis: Rates and residual toxicity. *Environmental Toxicology and Chemistry* 37, 2797–2809. <https://doi.org/10.1002/etc.4256>

US EPA, 2016. Drinking Water Health Advisory for Perfluorooctanoic Acid (PFOA) (No. EPA 822-R-16-005).

US EPA, 2012. Sustainable Futures / P2 Framework Manual 2012 EPA-748-B12-001 6. Estimating Aquatic Toxicity Using ECOSAR.

US EPA, 1987. Ambient Water Quality Criteria for Zinc - 1987 (No. EPA-40/5-87-003).

U.S. Environmental Protection Agency, Washington, DC.

US EPA, 2019. Aquatic Life Benchmarks and Ecological Risk Assessments for Registered Pesticides [WWW Document]. US EPA. URL <https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-and-ecological-risk> (accessed 3.16.20).

US EPA, 2018. Water Quality Standards: Establishment of Revised Numeric Criteria for Selenium for the San Francisco Bay and Delta, State of California [WWW Document].

US EPA. URL <https://www.epa.gov/wqs-tech/water-quality-standards-establishment-revised-numeric-criteria-selenium-san-francisco-bay> (accessed 3.16.20).

Verlicchi, P., Al Aukidy, M., Zambello, E., 2012. Occurrence of pharmaceutical compounds in urban wastewater: Removal, mass load and environmental risk after a secondary treatment—A review. *Science of The Total Environment, Special Section - Arsenic in Latin America, An Unrevealed Continent: Occurrence, Health Effects and Mitigation* 429, 123–155. <https://doi.org/10.1016/j.scitotenv.2012.04.028>

Vestel, J., Caldwell, D.J., Constantine, L., D'Aco, V.J., Davidson, T., Dolan, D.G., Millard, S.P., Murray-Smith, R., Parke, N.J., Ryan, J.J., Straub, J.O., Wilson, P., 2016. Use of acute and chronic ecotoxicity data in environmental risk assessment of pharmaceuticals. *Environmental Toxicology and Chemistry* 35, 1201–1212. <https://doi.org/10.1002/etc.3260>

Wang, Y., Na, G., Zong, H., Ma, X., Yang, X., Mu, J., Wang, L., Lin, Z., Zhang, Z., Wang, J., Zhao, J., 2018. Applying adverse outcome pathways and species sensitivity-weighted distribution to predicted-no-effect concentration derivation and quantitative ecological risk assessment for bisphenol A and 4-nonylphenol in aquatic environments: A case study on Tianjin City, China. *Environmental Toxicology and Chemistry* 37, 551–562. <https://doi.org/10.1002/etc.3994>

Weston, D.P., Chen, D., Lydy, M.J., 2015. Stormwater-related transport of the insecticides bifenthrin, fipronil, imidacloprid, and chlorpyrifos into a tidal wetland, San Francisco Bay, California. *Science of The Total Environment* 527–528, 18–25. <https://doi.org/10.1016/j.scitotenv.2015.04.095>

Weston, D.P., Lydy, M.J., 2014. Toxicity of the insecticide fipronil and its degradates to benthic macroinvertebrates of urban streams. *Environ. Sci. Technol.* 48, 1290–1297. <https://doi.org/10.1021/es4045874>

Weston, D.P., Lydy, M.J., 2013. Toxicity of the Insecticide Fipronil and Its Degradates to Benthic Macroinvertebrates of Urban Streams. *Environ. Sci. Technol.* 48, 1290–1297. <https://doi.org/10.1021/es4045874>

Wheeler, J.R., Leung, K.M.Y., Morritt, D., Sorokin, N., Rogers, H., Toy, R., Holt, M., Whitehouse, P., Crane, M., 2002. Freshwater to saltwater toxicity extrapolation using species sensitivity distributions. *Environ. Toxicol. Chem.* 21, 2459–2467.

Wood, T.J., Goulson, D., 2017. The environmental risks of neonicotinoid pesticides: a review of the evidence post 2013. *Environ Sci Pollut Res Int* 24, 17285–17325. <https://doi.org/10.1007/s11356-017-9240-x>

Wren, I., 2019. Nature Based Solutions for Nutrient Load Reductions from Wastewater: Scoping and Evaluation Plan. Bay Area Clean Water Agencies.

## 6. Appendix

**Table A. Average Concentration of CECs in ROC Compared to Toxicity Thresholds.**

Analyte	Average ROC Concentration (ng/L)	Toxicity Threshold (ng/L)	Ratio ROC Concentration: Toxicity Threshold
4-Nonylphenol	ND	721	ND
Acetaminophen	ND	1000	ND
Atenolol	1549	10000	0.15
Bifenthrin	ND	0.095	ND
Caffeine	103	9000	0.01
Carbamazepine	760	500	1.5
Cotinine	67.2	1000	0.07
Diethyltoluamide (DEET)	402	10400	0.04
Dilantin	474	8700000	0.00
Fipronil	166	11	15.1
Fipronil Desulfinyl	5.65	540	0.01
Fipronil Sulfide	5.23	9	0.58
Fipronil Sulfone	33.7	7	4.81
Gemfibrozil	86.7	300	0.29
Imidacloprid	583	10	58.3
Meprobamate	418	1100000	0.00
Metoprolol	2102	100	21
Perfluorooctanesulfonic Acid	41.4	70 <sup>1</sup>	1.08
Perfluorooctanoic Acid	34.3	70 <sup>1</sup>	1.08
Permethrin	ND	1.4	ND
Primidone	578	45000	0.01
Propranolol	194	20	9.70
Sucralose	146	18000000000	0.00
Sulfamethoxazole	2410	1790	1.35
Triclosan	130	168	0.77
Trimethoprim	530	319	1.66
Tris(2-chloroethyl) phosphate (TCEP)	1144	65000	0.02

ND indicates no data were collected.

<sup>1</sup>Indicates toxicity threshold is based on a drinking water health advisory for combined PFOA and PFOS concentrations. Currently, available ecotoxicity thresholds are wide-ranging and rapidly

evolving, as discussed previously.

**Table B. Average Concentration of Metals in ROC Compared to Toxicity Thresholds**

<b>Analyte</b>	<b>Average ROC Concentration (µg/L)</b>	<b>Toxicity Threshold (µg/L)</b>	<b>Ratio ROC Concentration: Toxicity Threshold</b>
Copper, Dissolved	5.92	6.9	0.86
Copper, Total	8.55	6.9	1.24
Lead, Total	0.175	8.1	0.02
Mercury, Total	0.007	2.1	0.003
Nickel, Dissolved	18.2	11.9	1.54
Nickel, Total	18.7	11.9	1.57
Selenium, Total	2.9	0.2	14.5
Zinc, Total	73.5	81	0.91

# **Chapter 4: Effects of ROC Discharge on Bayland Habitats**

Jeremy Lowe, Ellen Plane, Ezra Miller, Lydia Vaughn, Donna Ball, Melissa Foley  
San Francisco Estuary Institute

## **1. Introduction**

Historically, a range of habitats were supported by salinity gradients in South Bay marshes. These gradients have been lost due to urban development and the consequent rerouting of freshwater into pipes and channels. There may be opportunities to enhance existing marsh habitat and increase marsh resilience to climate change by mimicking historical freshwater inputs using treated reverse osmosis concentrate (ROC). However, there are constraints to consider prior to implementing these new types of discharges. ROC has a higher concentration of contaminants than treated wastewater effluent that is currently discharged to the Bay. Appropriate pretreatment and dilution will be necessary to reduce localized impacts at outfall locations, even though overall contaminant loadings to the Bay will be unchanged. Ecosystem impacts of discharging treated wastewater directly to bayland habitats are not well-studied but important to consider when planning new types and locations of outfalls.

In this chapter, the opportunities and constraints associated with local discharge of treated ROC into bayland marshes are explored. This preliminary review sets the stage for future research investigating the impacts of ROC discharge to bayland habitats through mesocosm studies, pilot projects, and monitoring.

## **2. Opportunities associated with discharge to baylands**

Prior to extensive salt pond creation in the Lower South Bay in the first half of the 20th century, freshwater entered the baylands directly from streams and diffusely from groundwater and surface runoff. Some of these inputs contributed freshwater to the baylands year-round (e.g., at the mouth of Coyote Creek or at willow groves and springs) while other freshwater inputs were intermittent, with seasonal flows from streams and areas adjacent to seasonal wetlands (Collins and Grossinger, 2004). These freshwater inputs created salinity gradients that were an important component of the baylands ecosystem, increasing physical and ecological diversity of the landscape

(Goals Project, 1999; Collins and Grossinger, 2004). Sediment inputs to tidal marshes from fluvial sources were also a key component of tidal marsh formation and maintenance, allowing for rapid vertical marsh growth. This was particularly true during high flows, when streams transported material from watersheds to marshes, allowing for sediment accretion.

Today, the volume, timing, and type of freshwater inputs have been greatly altered. In the Lower South Bay, freshwater input to the tidal marshes and circulation have been affected by urban development, stormwater drainage channels, and creation of salt evaporation ponds that channelized inputs. These changes have interrupted the gradual historical topographical and salinity gradients — terrestrial to wetland to estuarine and fresh to brackish to salt — of the landscape. In general, current practices have created highly centralized systems of wastewater and stormwater discharge rather than diffuse inputs that occurred naturally. Instead of streams discharging into freshwater wetlands near the baylands or tidal marsh, freshwater sources have been paved over for development or re-routed to stormwater channel networks, which carry freshwater discharges past the baylands to the open waters of the Bay. As stream flow now almost exclusively bypasses the baylands, the historical extent of the fresh-brackish-saline mixing zone and sediment delivery from the streams to baylands have been greatly reduced. Seasonality of freshwater flows has also shifted, from streams with summer-dry or low base flow conditions historically to discharges now dominated by more consistent year-round flow. Dry season base flows have generally increased due to additional water contributions from urban water uses. Peak flows have also increased due to urban development of the landscape, and upstream water storage alters seasonal timing.

Much of the freshwater entering the Bay today is from wastewater treatment plants, with treatment plants discharging an average of 446 million gallons per day into the Bay from 2012-2018 (BACWA, 2018). These discharges vary geographically and seasonally. For instance, over the period 1999-2011, EBDA's treated effluent flow rates varied seasonally between 60-120 MGD, with highest and lowest flows in winter and summer, respectively, and the majority of estimates falling in the range of 60-80 MGD (EBDA, 2015).

The 2015 report prepared for the East Bay Dischargers Association (EBDA) summarized the potential benefits of using decentralized wastewater discharges to emulate the historical diffuse flow of freshwater to achieve multiple benefits in the context of sea level rise (EBDA, 2015). The report described in detail the habitat and resiliency benefits associated with reestablishing historical freshwater flows to the baylands through reconnecting creek mouths and shifting wastewater outfalls to more

diffuse discharges. In this chapter, many of the benefits associated with discharging ROC to the baylands are drawn directly from the 2015 EBDA report. However, much more detail on ecotoxicology and designs for specific locations is included here.

Below is Table 1 from the 2015 EBDA report, which summarizes landscape changes associated with freshwater inputs to the baylands. The changes to Bay inflows and tidal marshes are summarized in the first two columns. The third column illustrates possible future changes that would benefit the baylands. These are discussed more fully in the following opportunities and constraints sections.

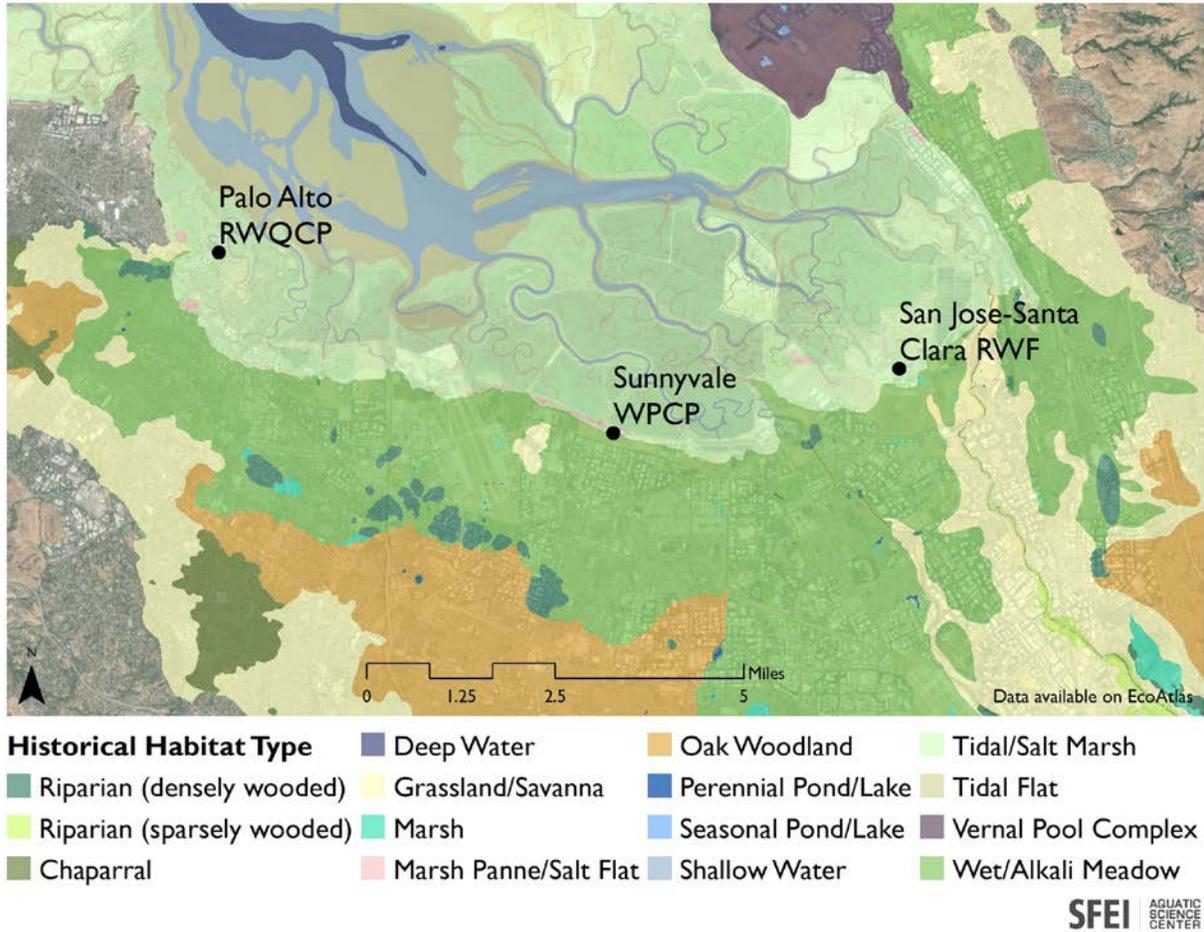
**Table 1.** Description of landscape influences associated with freshwater discharge to the baylands

	<b>Historical</b>	<b>Contemporary</b>	<b>Future Opportunities</b>
<b>Freshwater Influence</b>	<ul style="list-style-type: none"> <li>• Flows highly seasonal/intermittent</li> <li>• A few large freshwater influence zones from large watersheds which disperse at the landward margin of the baylands</li> <li>• Smaller freshwater influence zones from small watersheds and groundwater discharge through springs or former alluvial fan channels</li> <li>• More diffuse inputs from overland flows</li> </ul>	<ul style="list-style-type: none"> <li>• Timing of flows more perennial</li> <li>• Highly connected systems which bring freshwater outputs directly to the Bay due to wastewater outfalls/development/levee channels</li> <li>• Less diffuse surface runoff as water is re-routed to storm drain networks, wastewater treatment plants, or constrained behind dams</li> <li>• Peak flows have increased with urbanization (impermeable surface)</li> </ul>	<ul style="list-style-type: none"> <li>• Disperse freshwater flows at landward margin of baylands</li> <li>• Find opportunities to mimic diffuse flow at freshwater wetland-tidal marsh interface</li> </ul>
<b>Salinity Gradients</b>	<ul style="list-style-type: none"> <li>• Salinity gradients contributed to a complex interface between tidal and terrestrial habitat types creating physical heterogeneity and ecological diversity to the landscape</li> </ul>	<ul style="list-style-type: none"> <li>• Fresh-brackish marsh zone reduced or eliminated except locally near wastewater treatment plants</li> </ul>	<ul style="list-style-type: none"> <li>• Strategically re-introduce freshwater to tidal baylands to create larger fresh-brackish zones</li> <li>• Fresh and brackish marshes can accumulate organic matter faster than salt marsh and thus grow vertically with less inorganic sediment</li> </ul>
<b>Habitat Types</b>	<ul style="list-style-type: none"> <li>• Dominant large connected salt marsh</li> <li>• Intermixed pattern of brackish marsh zones, and natural salt pond/salinas, and wet and alkali meadow transition zones associated with soil types</li> </ul>	<ul style="list-style-type: none"> <li>• Tidal marshland extent greatly reduced from conversion to other land uses</li> <li>• Remnant disconnected marshes constricted by salt pond levees</li> <li>• Salinas are gone, some diked former marsh managed for salt production</li> </ul>	<ul style="list-style-type: none"> <li>• Increased resilience with available natural areas and constructed horizontal levees</li> <li>• Wider marsh potential between alluvial fans</li> </ul>

## 2.1 Marsh habitat and transition zones

Historically, the extensive tidal marsh in the South Bay provided abundant habitat for endemic wildlife species such as Ridgway's rail (*Rallus obsoletus*), black rail (*Laterallus jamaicensis*), common yellowthroats (*Geothlypis trichas*), Alameda song sparrow (*Melospiza melodia pusillula*), and salt marsh harvest mouse (*Reithrodontomys raviventris*). Large numbers of waterfowl passed through seasonally, resting and foraging in the salinas/natural salt ponds, pools and channels. The broad mudflats provided foraging habitat for shorebirds and haul out areas for harbor seals (*Phoca vitulina*). The adjacent tidal marsh-terrestrial transition zone supported Pacific chorus frogs (*Pseudacris regilla*), red-legged frogs (*Rana draytonii*), and grassland/wet meadow birds including savannah sparrows (*Passerculus sandwichensis*) and meadowlarks (*Sturnella neglecta*). The complex channel network within the baylands supported resident fish, including longjawed mudsuckers (*Gillichthys mirabilis*), provided rearing habitat for steelhead, and provided additional habitat for Bay fish, such as leopard sharks (*Triakis semifasciata*). The conversion of large amounts of tidal marsh to managed salt ponds and developed land over the past 150 years has limited the habitat available to marsh wildlife, despite some remaining tidal marsh patches along Coyote Creek, the east side of the Lower South Bay, the Palo Alto Baylands, and north of San Francisquito Creek (SFEI-ASC, 2016).

Estuarine-terrestrial transition zones are ecotones that provide a link between terrestrial areas and tidal marsh habitats. They were historically common in the South Bay and were an integral part of the marsh ecosystem (Nur et al., 2018). These transition zones included low-gradient, seasonally flooded fresh and brackish wetlands, alkali meadows, and seeps (Figure 1) that are now limited or absent throughout the South Bay. Depending on local geographic variations, they would have supported dense stands of clonal perennial species, such as saltgrass (*Distichlis spicata*), creeping wild rye (*Elymus triticoides*), alkali-heath (*Frankenia salina*), field sedge (*Carex praegracilis*), basket sedge (*Carex barbarae*), and Western goldenrod (*Euthamia occidentalis*) (Baye et al., 2000; Baye, 2000; Beller et al., 2013; SFEI and SPUR, 2019). These species provide strong, stabilizing root structures that are resilient to extreme flooding from storm events and to wave erosion.



**Figure 1.** Historical habitats of the Lower South Bay overlaid on modern aerial imagery, with wastewater treatment plants of interest labeled. Wet/alkali meadows (bright green) were extensive in this region and provided transition zone habitat and diffuse freshwater inputs to the back of the tidal marsh complex.

The historical diffuse freshwater flows supported ecological functions and services of both fresh and brackish zones, creating habitat for feeding, breeding, refuge, and dispersal or migration for both aquatic and terrestrial wildlife, including a number of threatened and endangered species (Goals Project, 2015; Beller, 2013). Diking for salt pond production and development at the back edges of the remaining fringing marshes has disconnected the historic freshwater inputs to the baylands and drastically reduced the extent of wet meadows and seeps that comprise this valuable transition zone habitat. Most of the transition zones in the South Bay are now developed for industry or other land uses (Beller et al., 2013). Along the urban edges of Alviso, Palo Alto, East Palo Alto, and Mountain View, tidal marsh habitat combined with suitable upland refugia for marsh wildlife species is very limited. Estuarine-terrestrial transition zones that support a variety of amphibians and upland bird species have been largely lost and now comprise a patchwork of low-quality narrow fragments.

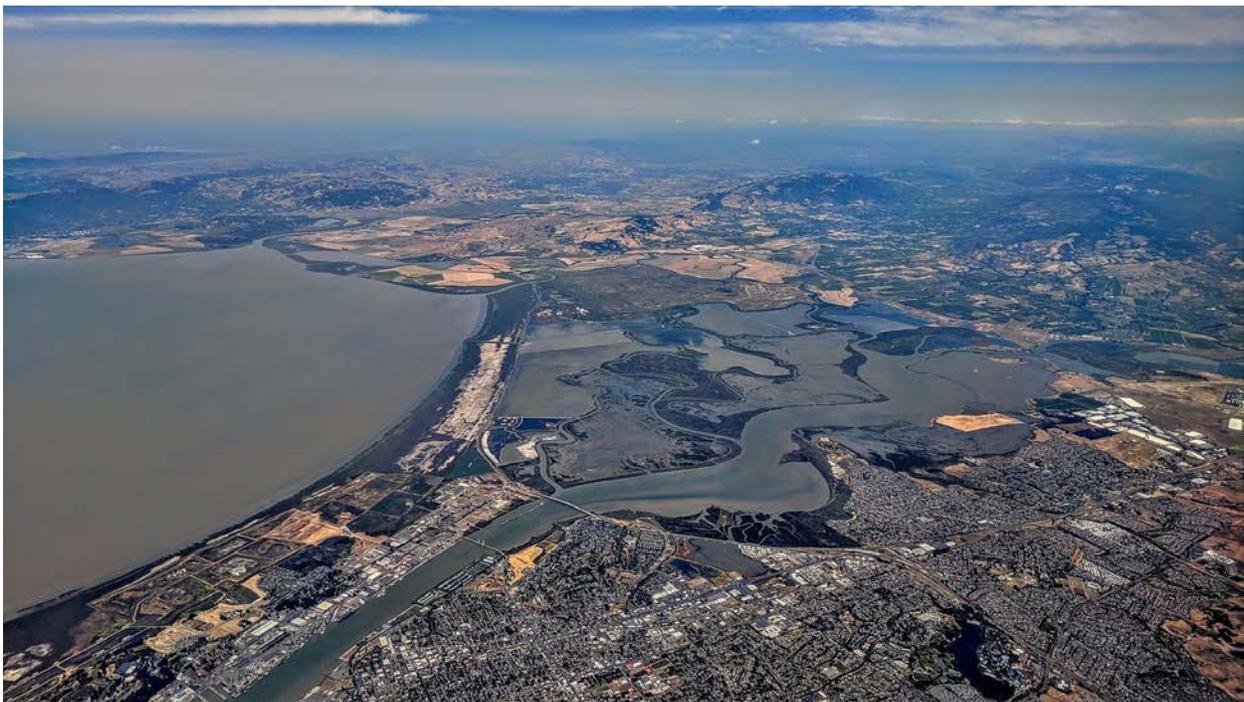
This loss of available refugia combined with anticipated sea-level rise poses a threat to wildlife in the area, and current opportunities for upland refuge from high-tide events are very limited, if not completely absent (AECOM, 2017). Wildlife are more resilient to changing climatic conditions when landscape processes, including transition zone connections, are functional (Goals Update, 2015). Urbanization has decreased this resilience by interrupting connections between tidal marshes and terrestrial habitat. Given this context, and a rapidly changing climate, there is a need to focus on reconnection of landscape processes, including freshwater connections to the baylands, which were historically a key element of the transition zone.

## **2.2 Using treated wastewater effluent to recreate marsh salinity gradients**

In areas where transition zone habitats are limited, wastewater may be a way to recover some ecological functions and services associated with historical transition zones. Transition zones historically bridged the salinity gradient between freshwater inputs and tidal salt marshes along a complete marsh continuum of fresh-to-brackish-to-saline conditions. Discharging treated wastewater effluent to the back of tidal marshes may re-establish aspects of these natural fresh to saline gradients and mimic the seepages and wet meadow habitat that were historically found along the edges of the Bay, including the South Bay (SFEI and SPUR, 2019). However, not all aspects of this historical habitat can be recreated with wastewater, as there are some key differences between wastewater effluent discharge and the freshwater flows that historically entered marshes, including chemistry and seasonality (wastewater flows are year-round while much of the historical flow was intermittent). Design and management of discharges using both outfalls and flows to marshes may allow flows to be adjusted to more closely recreate historical conditions.

Due to its slightly higher salinity than other types of wastewater effluent, a wider range of design options for discharge to marshes may be available with ROC, which can be mixed with other effluent to manage discharge salinities to meet specific habitat goals. The lower volume of effluent associated with RO treatment may also allow for a greater proportion of overall effluent to be discharged to bayland habitats in the future, with associated co-benefits for habitat. However, there are also multiple constraints to consider when planning for and designing ROC discharge to bayland habitats, which are discussed in depth in Section 3 below.

The Baylands Goals Update (2015) recommended the use of carefully monitored pilot projects to understand how alternative freshwater sources like treated wastewater effluent and stormwater could be used to safely reconnect baylands function. The investigation of ROC treatment at the Oro Loma horizontal levee and the exploration of possible ROC discharges at the three treatment plants in this study is in line with that goal. In planning for potential discharges of treated wastewater to the baylands in the Lower South Bay, there are likely to be synergies and opportunities to collaborate with other ongoing shoreline projects, including the South Bay Salt Pond Restoration Project, monitoring and maintenance goals for the Don Edwards National Wildlife Refuge (USFWS), the SAFER Bay Project, the USACE's South San Francisco Bay Shoreline Project, and other ongoing efforts. The following section outlines two concepts for ROC discharge to the baylands (creek mouth and horizontal levee) and considerations for the three treatment plants in this study.



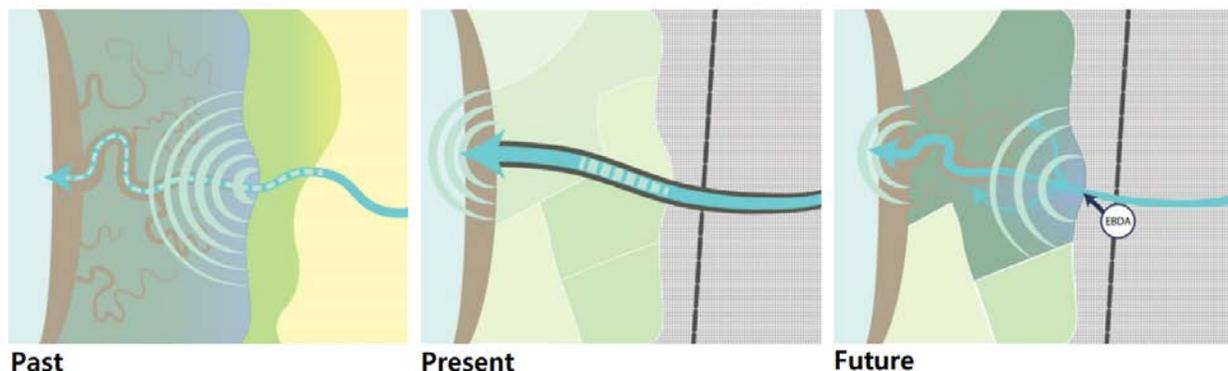
**Figure 2.** Example of a creek mouth flowing into the baylands: reconnection of the Napa River to the Napa-Sonoma Marshes (photo courtesy of Wikimedia Commons).

### 2.2.1 Creek mouth concept

One design concept for incorporating discharges into the baylands is to mimic flow from a creek mouth into the back of a marsh. Freshwater would spread over the tidal marsh plain and flow through the tidal marsh channel network to the Bay, gradually mixing with saltwater and creating a salinity gradient from the discharge point to the Bay (Figure 2). Establishing new freshwater flow through this tidal marsh floodplain would

allow for diverse vegetative communities to establish and create a range of habitat types for wildlife.

Though using treated wastewater effluent would allow creation of diverse habitat along a salinity gradient, it would not mimic all the functions of a natural creek mouth. For instance, treated wastewater does not bring sediment from the watershed to promote marsh accretion, nor does it necessarily mimic the timing, volumes, or seasonality of natural flows. Adding wastewater flow through a “creek mouth” discharge may provide many environmental benefits, but without additional seepage slope treatment on a horizontal levee before the ROC enters the marsh, there may be concerns about the impact of nutrients and contaminants on habitat (see “Constraints” section 3 below). Yet to be explored are the addition of other freshwater inputs from fluvial channels and stormwater drainage channels which could further dilute inputs and increase gradients. However, these other flows are more seasonal, while wastewater discharges tend to be year-round. Figure 3 (Figure 9 from the EBDA 2015 report) visually describes the “Creek Mouth” strategy and how it could emulate historical conditions.

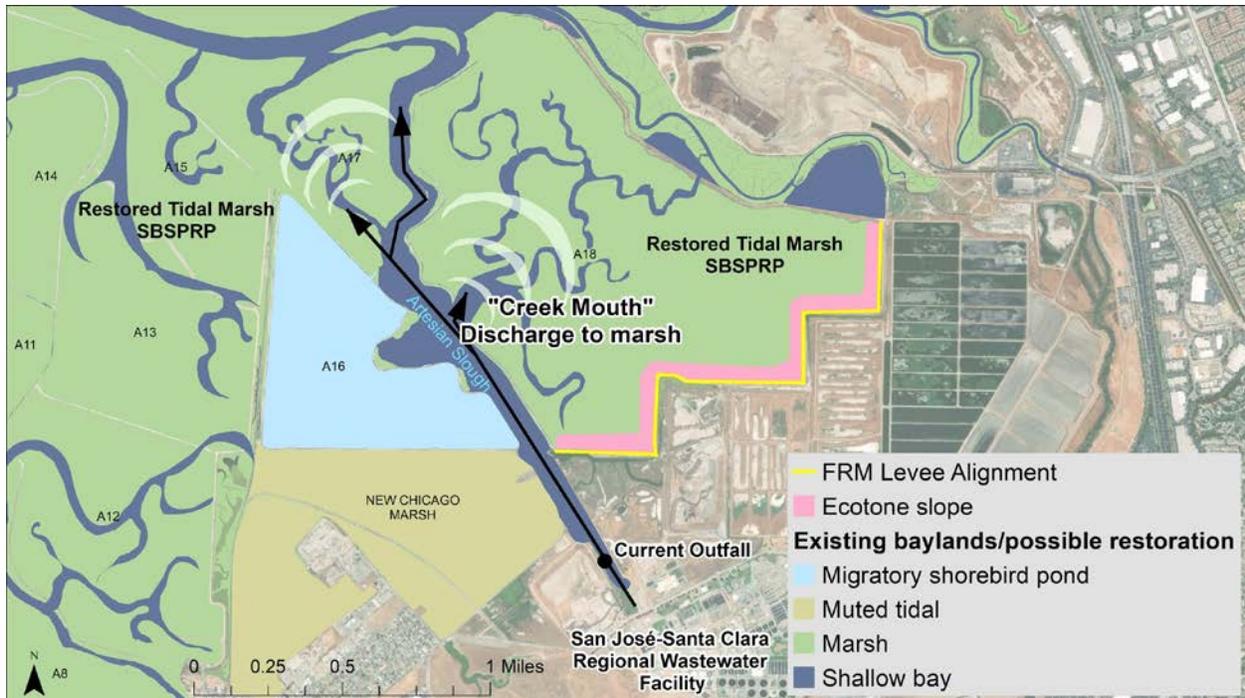


**Figure 3.** Historical condition with freshwater flow from a creek spreading over the baylands (left), today's channelized creek with water discharging past the baylands (center), and a reconnected system with creek levees lowered (right). Figure 9 from the EBDA 2015 report.

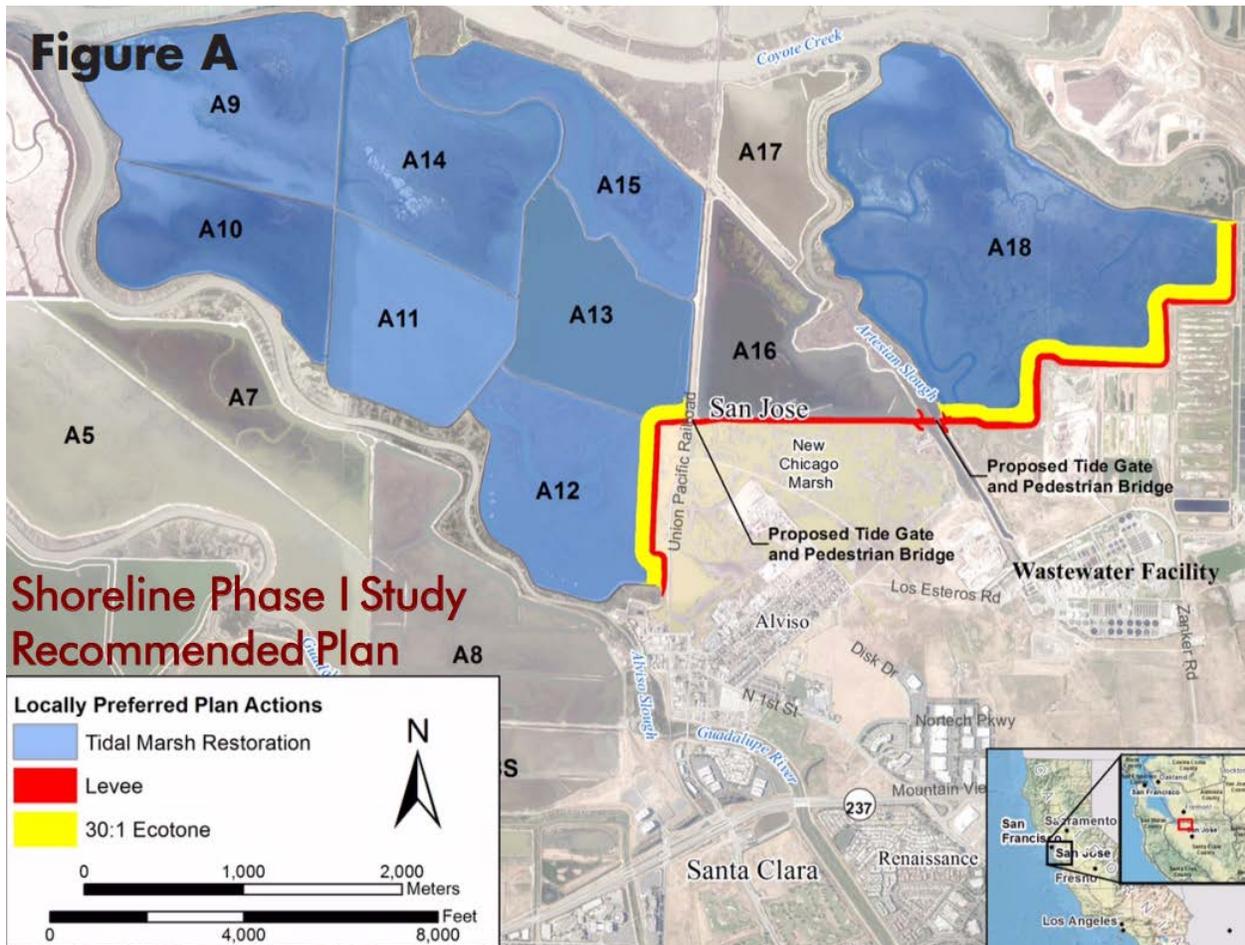
### **Application of creek mouth concept in San Jose**

At the San Jose-Santa Clara Regional Wastewater Treatment Facility, ROC discharge could mimic a creek mouth system if treated wastewater is routed to the back of a restored marsh in Pond A18 (Figure 4). Some of the ROC could flow into Pond A18 through a water control structure from Artesian Slough, some could flow into Pond A17, and the rest would continue to discharge to the Bay through Artesian Slough, as under the current system. Close coordination with partners, including the South Bay Salt Pond Restoration Project, would be required to implement a combined restoration and discharge project. Pond A18 is slated to be restored by the USACE South San Francisco Bay Shoreline Project in partnership with the State Coastal Conservancy, and

Valley Water. As part of that project an ecotone slope will be constructed adjacent to the flood risk management levee to provide valuable estuarine-terrestrial transition zone habitat and refuge for wildlife during high tides and storm events (Figure 5). There may be opportunity to introduce wastewater irrigation on these slopes, though they are not currently being specifically designed for this purpose, so implementation could be challenging. These slopes could be integrated with the adjacent creek mouth discharge design to create transition zone habitat across a broader area.



**Figure 4.** Concept of how ROC may be discharged to the baylands through a “creek mouth” design from Artesian Slough to restored tidal marsh in Ponds A17 and A18 at the San Jose-Santa Clara Regional Wastewater Facility. The ecotone slope along FRM levee is not being designed for wastewater discharge (and this may not be the final levee alignment).

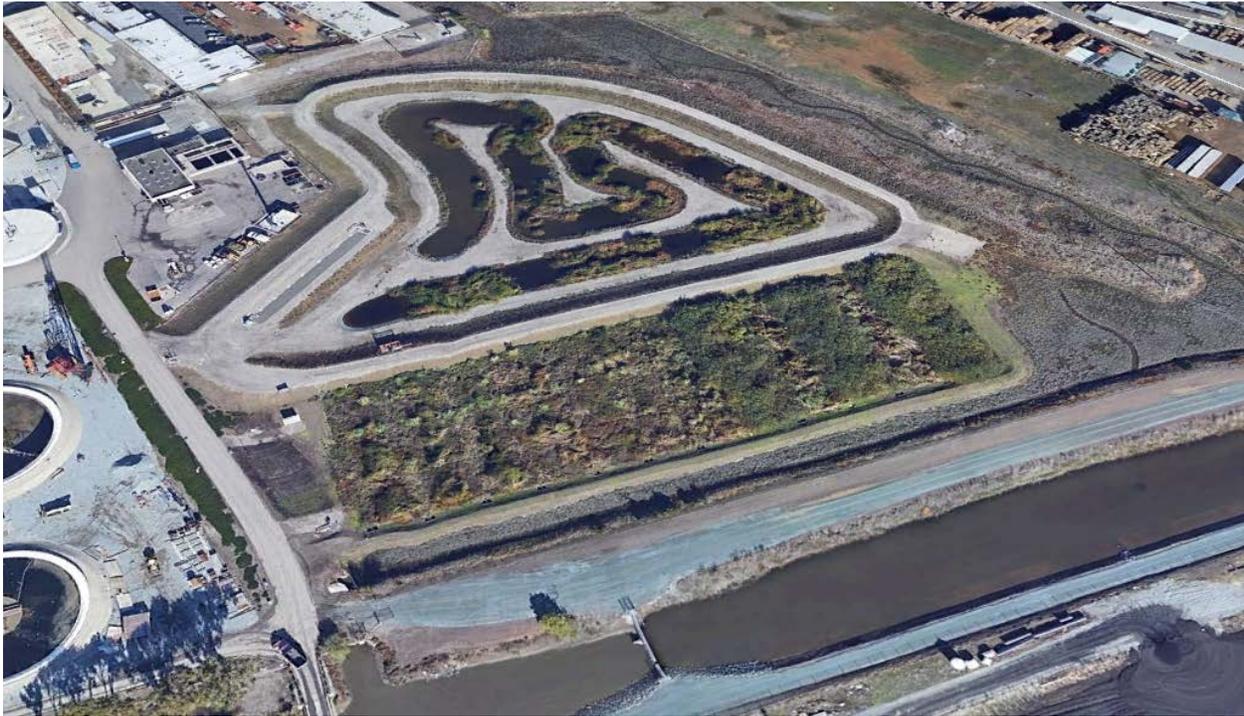


**Figure 5.** Planned Shoreline Study levee alignment for the north San Jose area, including 30:1 ecotone slope at the back of pond A18. Figure from Alviso EIA 11 Fact Sheet (USACE, 2015).

### 2.2.2 Horizontal levee concept

Horizontal levees (Figure 6) incorporating freshwater discharges to the back of marshes could also increase the range of habitat types available. Many existing areas around the back sides of South Bay marshes have steep levees with narrow, fringing habitats that are either fully fresh or fully brackish monocultures, depending on the location of freshwater inputs. Treated wastewater effluent could be used to irrigate horizontal levees to help establish salinity gradients and therefore more dense and diverse native plant communities. Compared to traditional flood risk management levees, which are often characterized by bare levee tops, or monocultures of native or non-native species, including a horizontal levee component provides the opportunity to create an assemblage of species that more closely resemble historical freshwater conditions on the back edges of marshes. Depending on the location, planning

horizontal levees to include medium to tall, dense vegetation associated with fresh and brackish marsh can provide refuge for marsh wildlife that are facing increasing threats from extreme water level events (Overton et al., 2015; Smith et al., 2018). This salinity gradient of marsh habitat types will also benefit a larger suite of non-saltmarsh-obligate birds and mammals by providing areas for refuge, breeding, and food resources.



**Figure 6.** Experimental horizontal levee project at the Oro Loma Sanitary District (image courtesy of Google Earth).

In considering landscape modifications that mimic historical habitat mosaics, it is important to consider existing conditions and wildlife needs. Many existing salt and brackish marshes are inhabited by endangered species, such as the Ridgway's rail and the salt marsh harvest mouse. These existing marshes are smaller and more isolated than they were historically. The planning for the addition of freshwater to these areas must carefully consider potential impacts to existing wildlife and plants. Specifically, conversion of salt marsh to brackish or fresh marsh could potentially impact Ridgway's rail, which is most commonly found in and has its densest populations in salt marsh. Thus, horizontal levees—and the brackish-to-freshwater marsh gradient they bring—should be designed in areas that avoid impacts to high-quality salt marsh habitats and listed species.

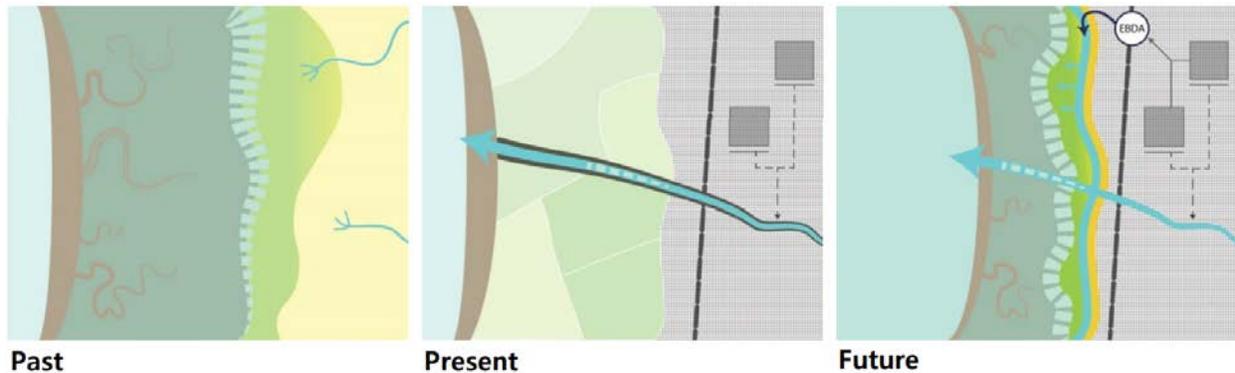
In addition to creating a wider range of habitat conditions, horizontal levees can add capacity for adaptation as environmental conditions shift. If sufficient in size, transition zones can provide important migration space for estuarine transgression as sea level rises (Beller et al., 2013). Horizontal levees may also add capacity for

resilience to changing rainfall conditions if wastewater is used to irrigate the slope. Horizontal levees could provide drought refuge for species, as freshwater inputs from wastewater are likely to be more consistent than creek inputs during droughts. Horizontal levees also provide other environmental benefits, including nutrient transformation and sequestration and shoreline protection. In areas that previously had narrow fringing marsh between the uplands and the tidal salt marsh or shallow open water, horizontal levees can provide shoreline protection by attenuating the tidal flooding and wave runup that contribute to erosion along the landward edge of marshes. Brackish marshes accrete organic material faster than saline marshes, which can help marshes maintain elevation as sea levels rise and help sequester carbon from the atmosphere. Marshes with high primary productivity may be able to accrete more organic matter and be more resilient under increased sea level rise conditions (Schile et al., 2014).

### **Opportunities to Improve Water Quality**

ROC could be discharged to the baylands through a seepage slope on a horizontal levee. The slope would be connected to tidal waters at the toe of the slope, where groundwater mixes with saltwater (brackish marsh area). The ROC would flow through the upper portion of the slope to create fresher conditions. Seepage flow through the horizontal levee has been proposed as an effective way to decrease nutrient loadings and contaminants of concern from discharging to receiving waters.

The Oro Loma Horizontal Levee Project has successfully demonstrated that with subsurface flow, the slope is effective at removing nutrients and some contaminants of concern from treatment plant effluent. Experiments at Oro Loma have shown high removal efficiencies for nitrate (>97% removed), phosphate (>83% removed), trace organic contaminants (>97% removed), and pathogens like F+ coliphage (up to 99% removed) (Cecchetti et al., in review). These results indicate that horizontal levees may have the potential to treat wastewater streams with higher contaminant loads than existing effluent. ROC is now being tested in one of the cells of the Oro Loma to investigate if the higher contaminant concentrations will change the rates of removal. The volume of flow that can be treated is dependent on the size and design of the slope, so the opportunity to realize water quality benefits will depend on those factors. Figure 7 visually describes the horizontal levee strategy and how it emulates historical conditions.



**Figure 7.** Historical diffuse flows to wet meadows (left), elimination of diffuse flows with channelization (center), and routing treated wastewater effluent through a seepage slope to re-establish a salinity gradient to the baylands (right). Figure 10 from the EBDA 2015 report.

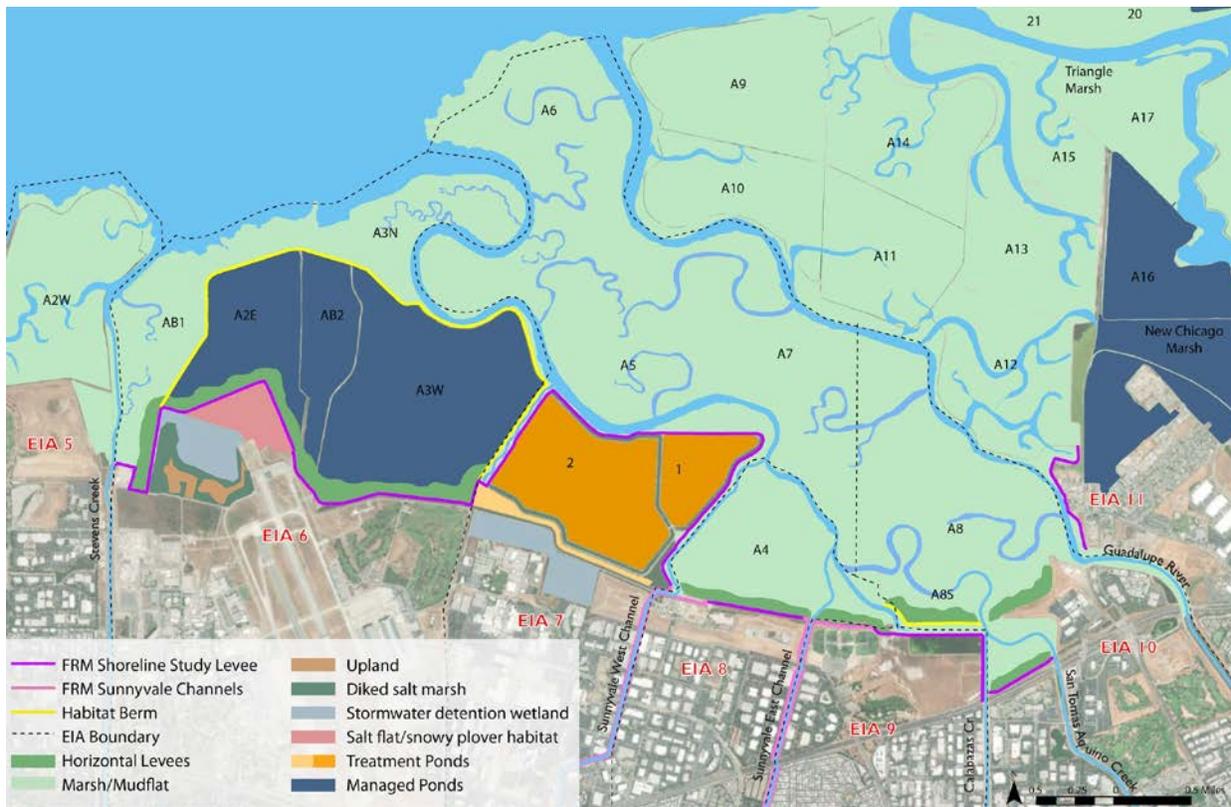
In the context of the Lower South Bay, most opportunities for horizontal levees exist on the bayward side of engineered flood risk management levees. At the Sunnyvale and Palo Alto wastewater treatment plants, there are opportunities to construct horizontal levees on the bayward side of these levees and potentially incorporate ROC discharges on the slopes.

### **Application of horizontal levee concept in Sunnyvale**

The City of Sunnyvale Water Pollution Control Plant (WPCP) is well-suited for a horizontal levee discharge because of its treatment system. Horizontal levees are limited in the volume of flow they can accommodate, because subsurface drainage must be maintained for the treatment process (overland flow does not achieve the same treatment benefits (Cecchetti et al., in review)). Therefore, the Sunnyvale WPCP, with its relatively low volume of flow and high proportion of ROC, may be well-suited for a horizontal levee system. It is possible that local discharge with additional treatment on a seepage slope could eliminate the need to construct a long pipe to a new outfall with better mixing potential. Coordination with ongoing South Bay Salt Pond Restoration project efforts would be required to discharge ROC from a horizontal levee to newly restored marsh.

Multiple opportunity sites for horizontal levee discharge exist near the Sunnyvale WPCP, depending on future levee alignments. A group of stakeholders (including the City of Sunnyvale, Valley Water, Google, Lockheed Martin, NASA, USFWS, and the South Bay Salt Pond Restoration Project) met for multiple workshops in 2019 to discuss the future of the complex Sunnyvale shoreline area. These project partners need to achieve consensus of coastal flood risk management needs and provide levee alignments and marsh restoration options to the U.S. Army Corps of Engineers (USACE). The resulting vision document does not replace any of the stakeholders'

existing planning efforts but rather helps coordinate and identify opportunities for benefits across the different efforts. Three alternative visions for the shoreline were identified; an example of one of these alternatives (Alternative 2, Figure 8) is shown below.



**Figure 8.** Alternative 2 from the Sunnyvale Shoreline Resilience Vision. Ponds A2E, AB2 and the treatment ponds are maintained as today. Pond A4 is restored to tidal marsh and the mouths of Sunnyvale East and West channels are straightened. The mouth of San Tomas Aquino Creek is restored to tidal marsh.

Building upon the Shoreline Resilience Vision, there are multiple possible locations for a horizontal levee where ROC from the Sunnyvale WPCP could be discharged (Figure 9). Option A, outboard of the levee protecting NASA property at Moffett Field, would create a salinity gradient to ponds A2E and AB2, which are slated to be restored to tidal marsh. However, this would require a long pipe from the Sunnyvale WPCP, and similar opportunities exist closer to the plant. Option B, at the back of Pond A3W, could potentially provide better connection from the horizontal levee to upland habitat. However, Pond A3W is deeply subsided and unlikely to be restored to marsh. Therefore, there is little opportunity to create a marsh connection and salinity gradient on the Bayward side of the levee, making this a less attractive option. Option C, at the back of Pond A4, is the closest to the WPCP. If Pond A4 is restored, this could

be a natural choice for a horizontal levee location with connections to the treatment plant, upland habitat on the nearby landfill, and tidal marsh habitat bayward of the levee.



**Figure 9.** There are several potential locations (labeled A - G) in the immediate area of the Sunnyvale treatment plant where ROC could be discharged to a horizontal levee.

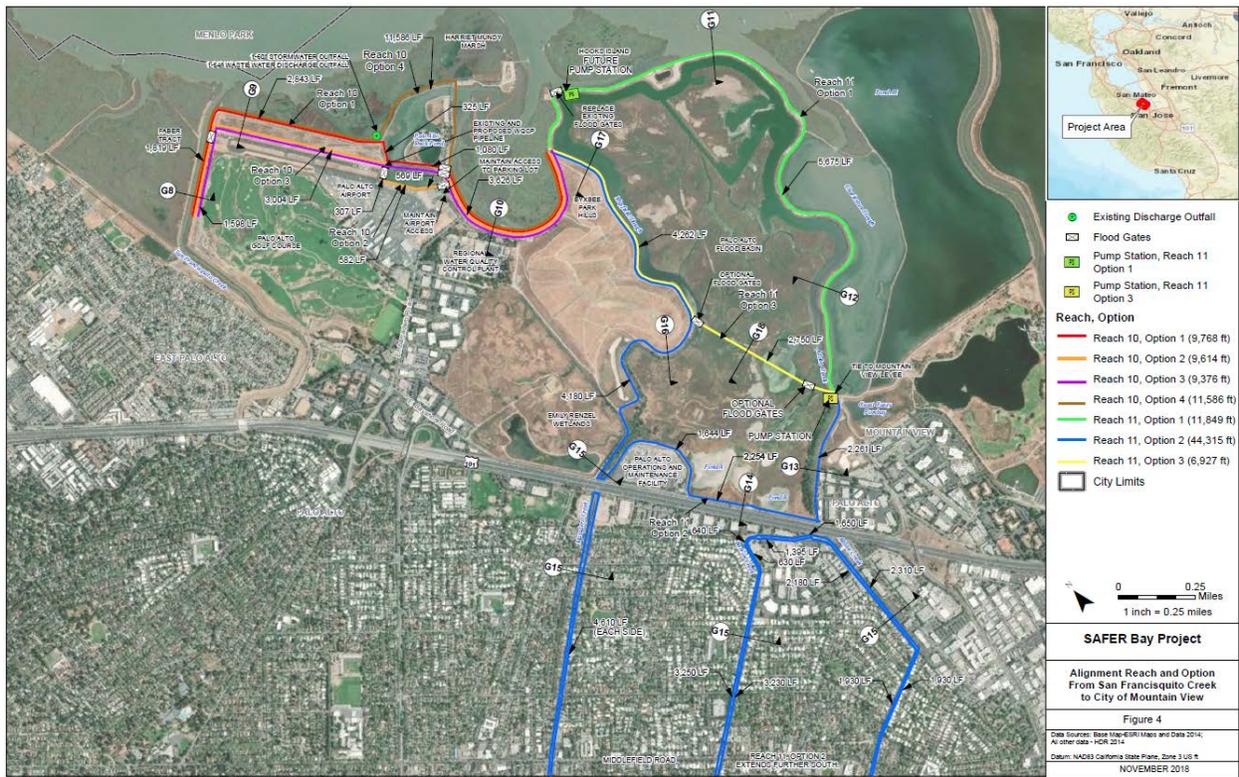
Options D, E, F, and G all connect to Pond A8S. The SBSP Restoration Project/USFWS is currently building ecotone slopes at sites E and G at the back of Pond A8S as sediment becomes available through Valley Water's Stream Maintenance Program. The fact that some of these ecotone slopes are already under construction could present both opportunities (fill material already placed) and challenges (slopes not specifically designed for wastewater discharge). Valley Water is developing a Feasibility Study to explore the benefits of reestablishing creek connections into Pond A8S (San Tomas Aquino Creek is shown reconnected to Pond A8S in Figure 9). The *Resilient Landscape Vision for the Calabazas Creek, San Tomas Aquino Creek, and Pond A8 Area* includes opportunities for wastewater discharge to horizontal levees in conjunction with reestablishing creek connections in this area (SFEI-ASC, 2018).

### **Application of horizontal levee concept in Palo Alto**

Palo Alto is another opportunity site for the horizontal levee discharge concept. Tidal brackish marsh dominated by bulrush (*Bolboschoenus* spp.) currently exists in the vicinity of the existing outfall, with tidal salt marsh extending both north and south of existing brackish marsh (AECOM, 2017). Diverting some ROC away from the new

outfall to the back of the marsh through a horizontal levee could provide a wider range of habitats (for example, wet meadow) than discharging freshwater at the outfall alone. Development of the shoreline has dramatically decreased estuarine-terrestrial transition zone habitat between the Palo Alto Baylands and the Ravenswood Open Space Preserve (SFEI-ASC, 2016). Adding horizontal levees in this area could provide important transition zone habitat in an area where it is lacking.

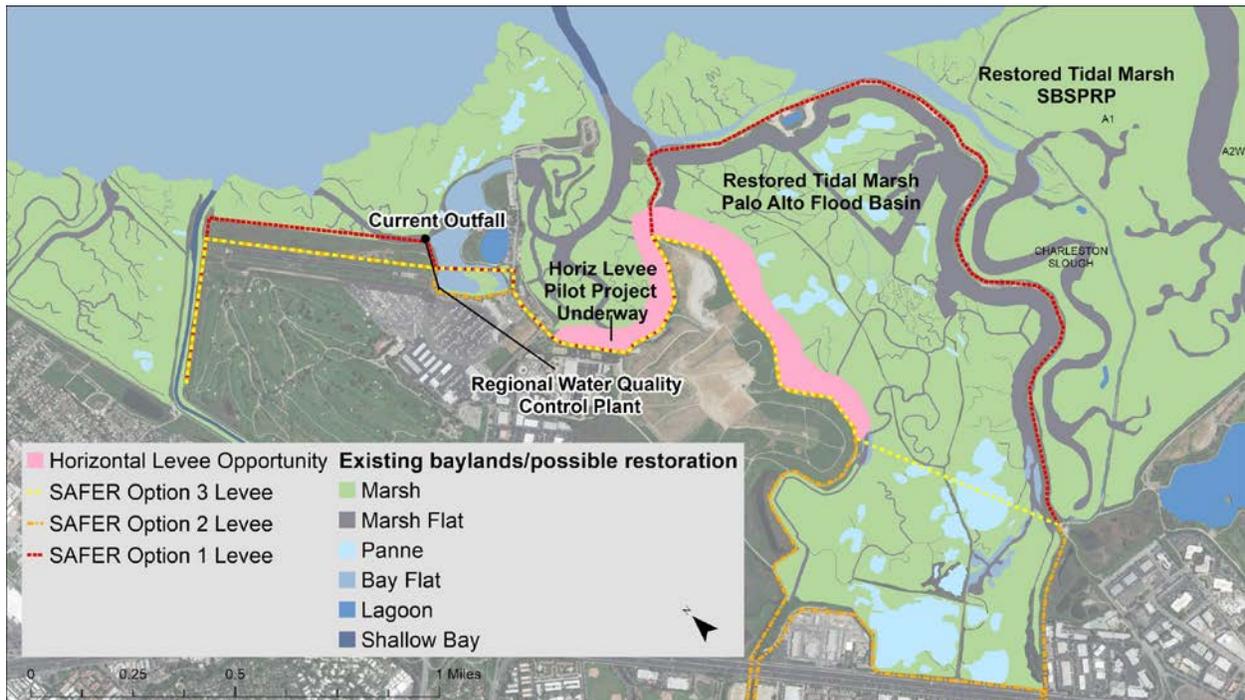
The SAFER Bay project has proposed multiple levee alignments in the vicinity of the Palo Alto Regional Water Quality Control Plant (Figure 10).



**Figure 10.** Possible SAFER levee alignments for Palo Alto. Copy of Figure 4 from the SAFER Bay Project Palo Alto Draft Feasibility Report (June 2019)

A small horizontal levee pilot project in Harbor Marsh (the U-shaped embayment bayward of Palo Alto RWQCP) began in 2017 and is anticipated to be completed in 2023. Wastewater effluent (already treated to a level that meets NPDES permit conditions) will be discharged at the pilot project horizontal levee. The purpose of the project is to demonstrate habitat and sea level rise adaptation benefits rather than test contaminant and nutrient removal. Assuming good results, this pilot could eventually be expanded to ring the rest of the Harbor Marsh levee horseshoe and could be incorporated as part of the ROC treatment process (Figure 11). However, there are additional constraints in the area near the Palo Alto Airport, which would apply to

wetland restorations in general. Another opportunity site for a horizontal levee is on the back edge of the Palo Alto Flood Basin marsh, in front of the levee proposed in SAFER alignment options 2 and 3. A horizontal levee at the back of the marsh could provide a salinity gradient and transition zone, helping restore this tidal basin to a more complete and connected marsh system.



**Figure 11.** Horizontal levee opportunity sites near the Palo Alto RWQCP exist in Harbor Marsh (pilot project underway) and along SAFER levee alignments 2 and 3 at the back of the Palo Alto Flood Basin, bayward of the landfill.

### 3. Constraints associated with discharge to the baylands and Bay

Municipal wastewater treatment facilities successfully remove many pollutants prior to discharging wastewater to San Francisco Bay. However, wastewater discharged to the Bay still contains nutrients, metals, and contaminants of emerging concern (CECs) that could impact ecosystems and species. Discharge of ROC would not change the overall mass loading of these constituents entering the Bay; rather, it would increase the local concentrations. The nature-based treatments explored in previous chapters have the potential to reduce concentrations of contaminants in ROC prior to

discharge. However, treatments do not fully remove nutrients or contaminants. The following section outlines some areas of particular concern to consider regarding impacts of ROC discharge on bayland habitats. Future experimentation and monitoring will be needed to develop informed and specific recommendations for discharge designs to reduce detrimental impacts on species and ecosystems.

### **3.1 Contaminants**

As discussed in the previous chapter, there are several concerns associated with contaminants present in ROC being discharged to the Bay. Current loadings for some contaminants in wastewater effluent are of concern (e.g., PFAS, fipronil), so there could be higher risks for ecological impacts when discharging ROC into retentive bayland locations. Though the addition of ROC will not change mass loadings of contaminants being discharged to the Bay, the concentrations of these contaminants are higher in ROC than other effluent, so local impacts at outfalls may be exacerbated without proper dilution. While similar ROC treatment and water quality across facilities indicates that removal efficiencies observed in open-water treatment should be broadly applicable, contaminants in ROC may change over time due to shifts in chemical use patterns. Furthermore, the study described in previous chapters measured only a small subset of contaminants known to be present in treated wastewater, so there may be additional potential risks from contaminants that were not measured. For example, there are hundreds of pharmaceuticals approved for use in the US, with more being developed. Many of these pharmaceuticals are not effectively removed by wastewater treatment and have unknown effects on aquatic life. Others have been shown to be acutely toxic at high levels, but the impacts of chronic exposures at low concentrations remain unknown. As contaminants found in ROC are essentially a more concentrated mix of contaminants found in treated wastewater, assessing the risks from ROC can benefit from what is known about risks associated with current discharge practices, recognizing that toxicant concentrations may be several times higher in regions near the ROC discharge locations.

One way to assess risk from unknown contaminants is effect monitoring, quantifying discharge effects on the local biological community, either by observations of indicator species or by measures of community structure. However, the current usefulness of effect monitoring for identifying chemicals of concern and guiding management actions is limited, because observed effects may be caused or added to by other pressures in the environment, both biotic and abiotic (Sobek et al., 2019). Because contaminants found in ROC are a more concentrated mix of those already present in and being discharged to the Bay in treated wastewater effluent, to detect

effects specifically caused by the discharge of ROC, effect monitoring would need to be implemented prior to implementation of discharge changes.

For monitored contaminants, even those with well understood toxicities, gaps in our understanding of adverse ecological impacts remain. Assessment of toxicological impacts is still primarily carried out one contaminant at a time on only a few representative species. Safety thresholds for contaminants are set using toxicological data from single contaminant exposure experiments, and therefore do not usually account for contaminant mixtures in the environment. They may also miss the sensitivities of untested species. However, there is growing evidence that single substances present below their individual effect thresholds may still contribute to combined mixture effects (Kienzler et al., 2019; Silva et al., 2002). Transformation products formed after release to the environment are also part of the mixture of chemicals, but their contribution to risk is frequently ignored. In general, contaminants with similar modes of action have predictable additive toxicity, but concern remains for the possibility of synergism or antagonism, and whether fractional approaches to toxicity testing can determine what to expect from chemical mixtures in real world circumstances (Rodea-Palomares et al., 2015).

Monitored contaminants in this study fall into three broad classes, each with their own unique fate and toxicity concerns: nutrients, metals, and organic contaminants. While not directly causing elevated toxicity, increased nutrient loading in ecosystems has the potential to influence phytoplankton and non-phototrophic microbial community structure, and indirectly influence biogeochemical transformations (e.g., respiration) related water quality parameters (e.g., dissolved oxygen levels). Metal bioavailability, and therefore toxicity, is highly dependent on water quality characteristics, such as salinity, dissolved organic matter content, and pH. Furthermore, elevated phytoplankton productivity due to high nutrient inputs, or related effects on redox conditions, can have complex and potentially counterbalancing effects on the production, bioavailability, and trophic transfer of some contaminants like methylmercury (Jonsson et al., 2017; Mazrui et al., 2016; Razavi et al., 2015; Schartup et al., 2013). Organic contaminants have a wide range of chemistries, and their fate and bioavailability may also vary depending on environmental characteristics. Degradation of organic contaminants may occur via abiotic processes, such as photolysis and hydrolysis, or be biologically mediated. Degradation reduces toxicity in many cases, but some transformation products may be more harmful than their parent compound.

Bioaccumulation of contaminants and biomagnification up food chains can be an important source of exposure for both metals and organic contaminants. For example, while copper decreases algal growth, some aquatic plants are relatively insensitive and

can sorb dissolved copper at extremely high rates, increasing exposure to aquatic life that feed upon them (Scannell, 2009; Eisler, 1997). Accumulation of copper in aquatic plants and adverse effects on algae could result in reduced food abundance and quality to support higher trophic levels. Per- and polyfluoroalkyl substances (PFAS) are also a concern for top predators, including humans, aquatic mammals, and piscivorous birds, as lower trophic level aquatic organisms appear to be relatively insensitive to these organic contaminants (Sedlak et al. 2018; Ding and Peijnenburg, 2013). PFAS are known to accumulate to levels of concern in piscivorous birds in the South Bay (Sedlak et al., 2017), and to reach relatively high concentrations in sport fish near the outfall of the San Jose-Santa Clara Regional Wastewater Facility that are approaching thresholds for human health concern (Sun et al., 2017). Concentrations of PBDEs, as another example of a bioaccumulative CEC, have also been relatively high at stations near the San Jose outfall. Bioaccumulative contaminants tend to have chemical properties that would cause them to associate with particles and therefore be retained in wetland environments. Retention of bioaccumulative contaminants could lead to especially high concentrations in wetlands that receive either treated effluent or ROC.

Bioaccumulation to acutely toxic levels is not the only concern for contaminants in aquatic systems. Chronic, low-dose exposure to toxicants can have a variety of effects on individuals, which can in turn have larger ecological effects. These effects may be direct, such as causing developmental abnormalities, decreasing resistance to disease, altering metabolism, or altering behaviors that are crucial for survival (e.g., navigation, foraging, courtship, alarm response). Direct effects on individuals can cause a decrease in populations, and may change community structures. There may also be indirect effects, such as altered feeding behavior in aquatic invertebrates causing broader ecosystem-level impacts, such as reducing food abundance for higher trophic organisms, changing the rates of plant litter breakdown, downstream drift, and altered community sensitivity to other stressors such as increased temperature.

Many contaminants in ROC and treated wastewater effluent may also affect ecosystems in ways that can indirectly affect human health. For example, antibiotics are explicitly designed to affect microorganisms, and can therefore impact natural microbial communities, which play a key role in many fundamental ecological processes (Grenni et al., 2018). Short-term effects include bactericidal and bacteriostatic actions, which exert a selective effect on microbial communities and can result in disappearance of some microbial populations and their ecological functioning. Longer-term indirect impacts include the development of antibiotic resistant bacteria and changes in biodegradation, and therefore subsequent impacts, of other organic contaminants. Antibiotic resistance genes from the environment may also be transmitted to human pathogens (Bengtsson-Palme et al., 2018).

Like antibiotics, antiviral drugs are explicitly designed to affect viruses, and their environmental release is of considerable concern, due to their potential to cause ecosystem alterations and the development of drug resistances (Prasse et al., 2010; Singer et al., 2007). There are very few experimental data on the effects of antivirals on aquatic organisms; however, quantitative structure-activity relationship modeling of almost 3000 different compounds predicts that antiviral drugs could be among the most hazardous pharmaceuticals in terms of their toxicity toward algae, daphnids, and fish (Sanderson et al., 2004). In addition, antivirals could cause development of new resistant strains of wildlife viruses, which have the potential to also infect humans (e.g., wild birds carry strains of influenza). Thresholds for ecological concern are not yet available for many of these pharmaceuticals due to a lack of ecotoxicological assessment for these compounds.

Many of these contaminants are already present in the Bay and input of higher concentrations via discharge of ROC is not likely to drastically alter wider Bay concentrations compared to toxicological thresholds, especially for organic contaminants that degrade once released to the environment and are at least partially removed by other nature-based infrastructure that wastewater treatment plants are evaluating for potential nutrient-load reductions and shoreline resilience. However, for sensitive species that are already facing multiple stressors, the more recalcitrant contaminants may pose a significant concern at discharge locales. For example, local steelhead trout populations may be adversely affected by more concentrated metals discharge.

The proposed changes in outfall locations would increase marsh exposure to wastewater-derived contaminants that were previously being released in shallow/open water. This would alter which food webs have the highest exposures, which may change which endangered species are most at risk from exposure, and which contaminants are of highest concern. South Bay marshes have a greater connection to terrestrial food webs than the open waters. Therefore, increased marsh exposure may result in increased contaminant exposure to endangered vertebrates (birds and mammals). This is most concerning for bioaccumulative contaminants, such as selenium, methylmercury, and PFAS. Monitoring of bioaccumulation and effects of contaminants in the marsh food web would be warranted.

### **3.2 Nutrients**

The addition of ROC to the treated wastewater stream has the potential to increase concentrations of reactive nutrients at the site of discharge to the Bay.

Discharge of treated wastewater effluent is already a major source of reactive N and P to the Bay, primarily in the forms of nitrate ( $\text{NO}_3^-$ ), ammonium ( $\text{NH}_4^+$ ), and phosphate ( $\text{o-PO}_4$ ). The effect of ROC on nutrient concentrations entering the Bay depends on the relative concentrations and flow rates of the effluent and ROC. Measured nutrient concentrations in ROC from a coordinated study of open water treatment wetlands range from 110-160  $\mu\text{M}$  for P and from 4,800-4,900  $\mu\text{M}$  for inorganic N. These values are a factor of 5-10 greater than background concentrations in wastewater effluent, roughly 16  $\mu\text{M}$  P and 930  $\mu\text{M}$  inorganic N (SJ-SC, 2019). Such high concentrations in ROC may increase nutrient concentrations at the point of discharge and in nearby Bay or bayland ecosystems, depending on outfall concentrations and effluent mixing dynamics. Appropriate dilution is needed in order to avoid negative ecological effects due to increased nutrient concentrations.

Measured nutrient concentrations in the Bay show considerable seasonal and spatial variation, due to variation in nutrient loading rates and ecological removal processes (Crauder et al., 2015). Against this variable background, the influence of ROC additions on Bay and bayland nutrient concentrations will thus depend not only on ROC and effluent composition, concentration, and flow rate, but also on local ecological factors that vary in space and time. From USGS data collected at Calaveras Point in 2017 and 2018, dissolved inorganic N (DIN) ranged temporally from a low of  $\sim 40 \mu\text{M}$  in spring to a high of  $\sim 100 \mu\text{M}$  in winter, and  $\text{o-PO}_4$  ranged from  $\sim 5 \mu\text{M}$  in spring to  $\sim 13 \mu\text{M}$  in autumn (<http://sfbay.wr.usgs.gov/access/wqdata/>; Crauder et al., 2015). Spatially, nutrient concentrations in Lower South Bay increase from the Dumbarton Bridge toward the Coyote Creek Artesian Slough confluence, near the current SJSC outfall. Between 2003 and 2012, median DIN and  $\text{o-PO}_4$  concentrations at Artesian Slough were  $\sim 300 \mu\text{M}$  and  $\sim 22 \mu\text{M}$ , respectively, compared with  $\sim 50 \mu\text{M}$  and  $8 \mu\text{M}$ , respectively, at Calaveras Point (Crauder et al., 2015). These patterns in nutrient concentrations in Lower South Bay are caused by effluent mixing over tidal cycles, as well as local biological processes such as atmospheric N-fixation, nitrification, and denitrification (Crauder et al. 2015). Seasonally varying dissolved inorganic N concentrations, for instance, result from multiple process: N loads to the system (+); mobilization of ammonium from the sediment due to mineralization (+); denitrification at the sediment-water interface when water temperatures warm (-); and N uptake by phytoplankton (-) (Crauder et al. 2015). Together, these physical and biological processes control the nutrient concentrations experienced by local ecosystems.

N and P are essential nutrients for the primary producers that support food webs in San Francisco Bay. However, when nutrient loads reach excessive levels they can adversely impact ecosystem health. Individual estuaries vary in their response or sensitivity to nutrient loads, with physical and biological characteristics modulating

estuarine response (Cloern, 2001). Added nutrients interact with local ecosystems through a range of biological processes, including uptake into algae or plant biomass or microbial nitrification or denitrification. The relative importance of these ecological pathways depends on physical and biological factors in the local ecosystem. In some estuaries, longer days and warm summertime temperatures, coupled with abundant nutrients, for instance, can favor algal growth and subsequent periods of low DO (Paerl, 2006). In San Francisco Bay, strong tidal mixing and turbid waters throughout much of the year create light-limited growth conditions for phytoplankton in deep subtidal habitats, and high nutrient inputs appear to have limited impacts on water quality indicators like dissolved oxygen (Crauder et al., 2015). While deep subtidal DO levels exceed the regulatory standard of  $5\text{ mg L}^{-1}$ , DO levels consistently fall below that value in shallow margin habitats, with the effects of those departures currently not well understood (MacVean et al., 2018). Elevated nutrient levels also have the potential to contribute to harmful algal blooms (HABs) (Sutula et al., 2017) or adversely affect plant physiology and community structure, microbial community structure and function, or biogeochemical cycling in sediments (Senn and Novick, 2014).

### 3.2.1 Community-level effects

Additions of N or P can have wide-ranging effects on the composition and structure of local ecological communities. Plant production in coastal wetlands is limited primarily by nitrogen availability as well as by stresses from flooding, salinity, and sulfides (Mendelssohn and Morris 2000). Nutrient enrichment increases flood tolerance in some wetland species like baldcypress (*Taxodium distichum*) (Effler and Goyer, 2006) and bulrush (*Schoenoplectus americanus*) (Langley et al., 2013), and increases salt tolerance in others like *Spartina alterniflora* (Cavalieri and Huang, 1979). While such effects may increase the resilience of certain species and communities, they can also disrupt community structure when they favor algal blooms or invasive species, or when they alter food resources with cascading effects to the aquatic food web. Nitrophilous species like *Phragmites* and *Typha*, for example, may be able to outcompete and replace established species when excess N is present (Rickey and Anderson, 2004).

Excess nutrients can also change the species composition of phytoplankton blooms, including fueling the growth of harmful phytoplankton species. A number of phytoplankton species that have formed harmful algal blooms (HABs) in other systems have been detected throughout San Francisco Bay, and the HAB toxins microcystin and domoic acid have been detected in the Bay (Peacock et al., 2018), the ecological significance of which is not yet known (SFEI, 2014). Although the abundances of HAB-forming organisms in San Francisco Bay have not reached levels that would constitute a major bloom, they do periodically exceed thresholds established for other systems

(Sutula et al., 2017) and thresholds for human exposure via shellfish consumption (Gibble et al., 2016). Moreover, since HAB-forming species are present in San Francisco Bay and nutrients are abundant, HABs could readily develop should appropriate physical conditions create opportunities that HABs can exploit (e.g. the unprecedented large red tide bloom in fall 2004 that followed a rare series of clear calm days, with chl-a levels reaching nearly 100 times their typical values; Cloern et al., 2005).

Another potential impact of algal blooms is their effect on methylmercury (meHg) availability to the aquatic food web. Algal blooms have been shown to have variable effects on meHg, depending on the specific ecological context. In some cases, algal blooms may increase the production of meHg by creating anaerobic conditions that favor the methylation of inorganic mercury (Pickhardt and Fisher, 2007; He et al., 2008). In other cases, increased algae growth has the effect of diluting the Hg in algal biomass, thus lowering Hg concentrations at the base of the food web and reducing Hg uptake by higher consumers (Nam et al., 2011; Pickhardt et al., 2002).

### 3.2.2 Physiological effects

Along with community-level effects, nutrient additions have the potential to alter the physiology of bayland vegetation. Given the limited extent of native wetlands interacting with San Francisco Bay, few local studies have evaluated these effects. More generally, however, studies from other regions have documented consistent trends in wetland-nutrient interactions. With few exceptions, nutrient additions have been documented to increase vegetation biomass in a range of marsh ecosystems (Morris, 1982; Nelson and Zavaleta, 2012; O'Connell, Byrd, and Kelly, 2014). Whereas aboveground biomass generally increases with additional available N, this effect is not consistently seen in roots and rhizomes. Instead, a common effect of N enrichment is an increase in aboveground:belowground growth allocation, presumably to optimize the use of N for photosynthesis in aboveground structures (Morris, 1982; Nelson and Zavaleta, 2012; Vivanco, Irvine, and Martiny, 2015). This effect of changing biomass allocation has been seen in a range of marsh systems, from Atlantic coast and Pacific coast salt marshes dominated by the cordgrass species (*Spartina alterniflora*) (Morris 1982) and pickleweed (*Salicornia pacifica*) (Nelson and Zavaleta, 2012) to freshwater tule (*Schoenoplectus acutus*) marshes in the Sacramento-San Joaquin Delta (O'Connell, Byrd, and Kelly, 2014). In many cases, increased N availability has been seen to have no effect on the growth rate or standing stock of biomass (Morris, 1982; Nelson and Zavaleta, 2012; Vivanco, Irvine, and Martiny, 2015). In other instances, as with tule marshes in the Delta, belowground biomass was actually seen to decrease with N addition (O'Connell, Byrd, and Kelly, 2014). Such reductions in belowground biomass could alter the structural role of marsh vegetation in fringing marsh habitats,

reduce sediment stability, and lower sediment accretion rates (Alldred, Liberti, and Baines, 2017; Nyman et al., 2006).

The capacity for vegetation to utilize and sequester excess nutrients depends not only on the total availability of reactive N and P, but also on the specific forms, concentration, and chemical environment. Marsh vegetation may have nonlinear growth responses to nutrient additions, with strong growth responses at moderate nutrient levels but limited or negative responses when nutrients—particularly ammonium—exceed certain thresholds. In the case of tule, for example, low to moderate ammonium additions have been seen to increase growth, whereas high concentrations (above 60 mg L<sup>-1</sup>) have led to biomass decreases, possibly due to the inhibition of plant respiration (Duguma and Walton, 2014; Hill et al., 1997). Similarly, toxic effects from other wastewater contaminants may limit positive plant growth responses to nutrient enrichment.

### 3.2.3 Biogeochemical effects

In addition to these effects on plant physiology, studies from other sites have reported biogeochemical changes in response to nutrient loading. Nutrient availability is an important factor regulating the rates of microbial processes in sediments and the water column. Where N or P limits microbial respiration or growth, a change in the concentration or form of these nutrients can alter carbon cycling rates and microbial efficiencies (del Giorgio and Cole, 1998; Kuzyakov, Friedel, and Stahr, 2000; López-Urrutia and Morán, 2007; Manzoni et al., 2012). Such changes may have implications for aquatic food webs, by changing food resources for bacteriovores, as well as the abundance of enzyme-mediated decomposition products. These changes may also influence the carbon balance and physical structure of coastal sediments, with implications for climate change and sea level rise resilience. In other ecosystems, N and P fertilization has been seen to increase sediment respiration (CO<sub>2</sub> emissions), leading to measurable decreases in sediment carbon stocks (Morris and Bradley, 1999). By reducing or even reversing organic matter accretion, altered biogeochemical cycling rates could thus limit marsh resilience to rising sea levels (Alldred, Liberti, and Baines, 2017; Nyman et al., 2006).

In addition to CO<sub>2</sub>, emissions of other greenhouse gases—notably nitrous oxide (N<sub>2</sub>O) and methane (CH<sub>4</sub>)—may be affected by nutrient loading to baylands. Additions of inorganic N can stimulate the production of N<sub>2</sub>O, a greenhouse gas nearly 300 times as powerful as CO<sub>2</sub>. For this reason, the effect of inorganic N additions on N<sub>2</sub>O emissions is an important consideration for the design and performance of treatment wetlands and horizontal levees (Stadmark and Leonardson, 2005). In several CA salt marsh ecosystems, N additions have also been shown to stimulate low levels of CH<sub>4</sub>

production and emissions (Irvine et al., 2012; Vivanco, Irvine, and Martiny, 2015). However, even considering its high global warming potential, the CH<sub>4</sub> emitted at these sites had a negligible effect on total greenhouse gas emissions relative to the much higher fluxes of CO<sub>2</sub>.

Ultimately, it is challenging to predict how the addition of ROC discharge points will affect the nutrient balance of Bay and bayland ecosystems. Relationships between outfall nutrient concentrations and the structure, physiology, and biogeochemistry of nearby ecological communities depend on mixing dynamics at outfall locations and complex ecological factors. Given these uncertainties, monitoring is needed to evaluate and mitigate ecological impacts. An effective monitoring program would track nutrient concentrations at a range of locations as well as other indicators of ecological community structure and function.

### **3.3 Mosquitos**

One topic under discussion in horizontal levee design is the idea of including topographic complexity within the slope. This could include small depressions or other topographic features of different habitat types such as willow sausals, depending on the size of the slope and whether they are ecologically appropriate for the location. This increased complexity could allow for a wider range of desired plant and animal species to utilize the slope. However, mosquitoes can occur in poorly drained sites, shallow pools, and willow habitats (Maffei, 2000). While considering these features, it will also be important to consult with local mosquito abatement districts during design phases to limit undesirable mosquito production and minimize potential impacts to public health.

### **3.4 Vegetation Management**

An important question that has emerged from the Oro Loma Horizontal levee project is how to approach the ongoing management of created transition zones. Designing planned species assemblages appropriate to a specific site is important to provide resistance from weed invasions. At the Oro Loma Project, initial weed establishment was successfully minimized by a design that included spreading a native seed mix and planting a diverse plant community of species that formed dense canopy to inhibit the establishment of annual weedy species common to newly restored sites (Save The Bay, 2017). Species were chosen to mimic historic wetland conditions, provide resilience, and to provide rapid colonization. The design was highly successful at establishing a dense native plant community with little to no management over the first several years and continues to exclude most non-native plant species. However, after several years Andean pampas grass (*Cortaderia jubata*) colonized within the site,

likely from seeds blowing into the site. Successful eradication of the pampas grass will require active management. Thus, weed management will likely be a consideration for newly constructed transition zones and it will be important to develop a plan for this to prevent similar occurrences.

### **3.5 Impacts of changes to outfall locations**

To meet permit conditions and habitat goals, ROC discharge designs may take advantage of a wider suite of methods in the future. For example, while the majority of the discharge may go to an open-water outfall for dilution, some portion of treated effluent might be directed to a horizontal levee for seepage slope polishing and creating salinity gradients for ecological benefit. Understanding local hydrology and circulation patterns is important in considering effects on any vegetation in the areas near the outfall locations. For example, locating the outfall further downstream at Artesian Slough (San Jose) to Coyote Creek may alter vegetation communities further downstream shifting them from saline to brackish or brackish to fresh, and this could impact recently restored marshes at Pond A17 or Island Ponds. Similarly, if the outfall is moved further away from the shoreline in Palo Alto, it is important to understand whether the freshwater will distribute over a larger region than it currently occupies and whether that will alter nearby salt marsh communities. A shift to fresher water would alter primary productivity, vegetation structure, and animal communities, which could impact wildlife that are salt marsh obligates. Such a shift from salt marsh to brackish marsh could be a concern for Ridgway's Rails in particular, given their endangered status and dense populations in some salt marshes.

While increased salinity from ROC discharge (rather than other effluent) could lead to decreased overall marsh productivity (Broome et al., 1995; Merino et al., 2010) and favor more salt-tolerant species (Broome et al., 1995), the salinities of ROC are low enough that they would provide negligible impacts. The location of freshwater inputs has more potential to alter saline and brackish marshes in the vicinity of the outfall. Adding outfalls will likely result in decreased salinity in new locations.

Hydrodynamic modeling of dry season conditions showed that the time and area of the Bay required for a 10:1 dilution of effluent varied based on discharge scenario, discharge location, and tidal cycle (RMA, 2019). For all three facilities, the area of Bay water below a 10:1 dilution increased as the volume of effluent increased. The current outfall at Palo Alto (Figure 12) had the most efficient dilution, and ROC quickly moved out of Lower South Bay. The alternate outfall locations for ROC discharge at Sunnyvale and San Jose greatly increased effluent dilution compared to current discharge locations. Effluent concentrations at the new locations did drop below the 10:1 dilution,

however, during neap tidal cycles due to more limited flushing of Lower South Bay.



**Figure 12.** Current outfall for the wastewater treatment plant (WWTP) in Palo Alto, modeled as a part of Portfolio 2 Scenario A and Portfolio 4 (GHD, 2019).

In San Jose, mixing at the existing outfall is limited, but flows from ponds A17 and A16 and tidal action help dilute the discharge. Adding ROC to the current discharge is unlikely to change the salinity conditions in the immediate area. If ROC was discharged at the enhanced mixing outfall (Figure 13), a 10:1 dilution would occur very close to the proposed discharge location for the lowest discharge scenario (7 MGD ROC only). Salinity in Coyote Creek would likely decrease if the new outfall was built. In Artesian Slough, salinity is unlikely to change from current conditions if the enhanced mixing outfall is built because WWTP effluent would continue to be discharged at the current location. However, if water reuse increases, the overall amount of effluent discharged at the current location may decrease. This could result in an increase in salinity at the upper end of Artesian Slough, with the magnitude of change dependent on the ratio of wastewater reused to wastewater discharged.



**Figure 13.** Current and New Enhanced Mixing Outfalls for the Wastewater Treatment Plant (WWTP) in San Jose Santa Clara as a part of Portfolio 1 Scenarios A and B (GHD Draft, 2019). Salinity is likely to decrease at the new outfall.

In Sunnyvale, an enhanced mixing outfall is proposed at the entrance of Guadalupe Slough (Figure 14). Mixing at this location is more efficient than in Moffett Channel, and a 10:1 dilution would occur very close to the proposed discharge location. Adding a new outfall location may impact vegetation communities in Guadalupe Slough (saline to brackish), as well as in Moffett Channel (brackish to saline) if the total volume of effluent is reduced at the current outfall.



**Figure 14.** Current and New Enhanced Mixing Outfalls for the Wastewater Treatment Plant (WWTP) in Sunnyvale as a part of Portfolio 2 Scenario A and Portfolio 4 (GHD, 2019). Moving the current outfall may increase salinity in Moffett Channel.

Competing uses for wastewater (groundwater recharge, recycled water, wetlands) are likely to result in reduced effluent discharge to the Bay in the future. The ratio of ROC:effluent would increase if effluent to the Bay continues to decrease in the future, changing the time and area required for sufficient dilution of ROC, as well as salinity impacts to nearby marsh communities.

#### **4. Effects on wildlife associated with treating ROC in engineered open-water treatment cells**

Treatment of ROC in open-water cells is discussed in detail in Chapter 2 of this report. The pilot studies of open-water cells for ROC treatment have not been designed or located with wildlife in mind, though wildlife use these open-water cells and may be impacted by conditions within them. The open water and vegetation in the cells may attract wildlife while contaminants may be concentrated through the treatment process in the cells, increasing risk of bioaccumulation in wildlife visiting them.

While open-water treatment cells may provide benefits to ecosystems, such as habitat for resident and migratory waterbirds and freshwater for terrestrial species, there could also be a negative impact on individuals if contaminant levels are high, making

the treatment cell an attractive nuisance/habitat sink. In addition to direct effects on wildlife, water quality in the treatment cell may affect the food resources available to wildlife, impacting the value of these cells as foraging habitat. Resident species with longer exposure times are likely to accumulate more contaminants than more transitory species. Treatment cells may also negatively impact native wildlife by providing support for non-native species (e.g., bullfrogs) that harm native species in nearby streams and bayland habitats via predation or competition. Disease is another potential concern, particularly if wildlife are concentrated in the cells and/or the wastewater in the cells facilitates the spread of waterborne pathogens (Fong and Lipp, 2005).

Monitoring wildlife uses of ROC treatment cells will help illuminate which of these factors require further consideration, and may help inform future designs that enhance habitat quality for wildlife without impacting water quality treatment. The design of future treatment cells should include considerations of which species may use them and how. Design goals for wildlife should be created either to encourage or discourage wildlife use. Factors to consider include hydrology, vegetation, and landscape position, including distance from and access to streams and bayland habitats.

## **5. Conclusions**

Opportunities exist to restore historical salinity gradients and their corresponding habitat mosaics to the Lower South Bay using treated wastewater, including treated ROC. As described in Section 2 of this chapter, discharges at the San Jose, Sunnyvale, and Palo Alto WWTPs could be designed to include “creek mouths” or horizontal levees (“wet meadows”) in addition to dilution through outfalls. This could restore diffuse freshwater flows and enhance tidal marsh-terrestrial transition zone habitat in a region where this habitat has been severely degraded.

If these new types of bayland discharges are implemented, a robust monitoring system will be needed to allow managers to track restoration progress and identify unforeseen consequences. Monitoring of salinity, contaminant and nutrient concentrations, vegetation community shifts, algal blooms, wildlife health, and other indicators of ecosystem function will allow for adaptive management of discharges. Some of this monitoring may be undertaken by larger regional monitoring efforts tracking the health of bayland habitats (e.g. Wetlands Regional Monitoring Program; WRMP). Effect monitoring implemented prior to discharge changes can help detect impacts caused by the additional discharge of ROC.

Design of bayland discharges must take into account a range of constraints. Adding ROC discharges will decrease salinity at new outfall locations, and care must be taken not to convert high-quality salt marsh, which provides habitat for the endangered Ridgway's rail (among many other species), to brackish marsh. Contaminants present in ROC are another constraint to consider due to the concentrated mix in ROC and toxicological concerns. Shifting discharges to bayland habitats rather than open water could result in impacts to marsh habitats, and greater connectivity to terrestrial food webs, potentially resulting in bioaccumulation and increased exposure to endangered vertebrates. ROC also has much higher nutrient concentrations than other effluent. Discharge of effluent with higher nutrient concentrations can affect the physiology and community composition of bayland vegetation, increase sediment carbon mineralization rates, and potentially cause harmful algal blooms. Appropriate dilution will be required to mitigate these effects. Other constraints to consider in design of discharges include mosquito abatement and invasive species management. Open-water ROC treatment cells may also provide habitat for wildlife; further research could inform the development of designs for these treatment systems that maximize benefit and minimize harm to species.

## 6. References

- AECOM. 2017. Palo Alto Baylands Existing Conditions. Prepared for the City of Palo Alto Community Services Department and Open Space, Parks, and Golf Administration. <https://www.cityofpaloalto.org/civicax/filebank/documents/62764>
- Allred, M., Liberti, A., Baines, S.B. 2017. Impact of Salinity and Nutrients on Salt Marsh Stability. *Ecosphere* 8 (11): e02010. <https://doi.org/10.1002/ecs2.2010>.
- BACWA. 2018. Group Annual Report: Nutrient Watershed Permit Annual Report. Bay Area Clean Water Agencies, Oakland, CA.
- Baye, P.R., Faber, P.M., Grewell, B. 2000. Tidal marsh plants of the San Francisco Estuary. Baylands Ecosystem Species and Community Profiles: Life Histories and Environmental Requirements of Key Plants, Fish, and Wildlife. San Francisco Bay Regional Water Quality Control Board, Oakland, CA, pp. 9-33.
- Baye, P.R. 2008. Vegetation management in terrestrial edges of tidal marshes, western San Francisco Estuary, California. Prepared for Marin Audubon Society, Mill Valley, CA. <https://www.marinaudubon.org/pdf/MAS%20tidemarsch%20ecotone%20veg%20mgmt%20final%202008-3.pdf>
- Beller, E. E., Salomon, M., Grossinger, R. M. 2013. An Assessment of the South Bay Historical Tidal-Terrestrial Transition Zone. SFEI Contribution No. 693. San Francisco Estuary Institute: Richmond, CA.
- Bengtsson-Palme, J., Kristiansson, E., Larsson, D.G.J. 2018. Environmental factors influencing the development and spread of antibiotic resistance. *FEMS Microbiol Rev* 42. <https://doi.org/10.1093/femsre/fux053>.
- Cavaliere, A.J., Huang, A.H.C. 1979. "Evaluation of Proline Accumulation in the Adaptation of Diverse Species of Marsh Halophytes to the Saline Environment." *American Journal of Botany* 66 (3): 307–12. <https://doi.org/10.1002/j.1537-2197.1979.tb06228.x>.
- Cecchetti, A.R., Stiegler, A.N., Graham, K.E., Sedlak, D.L. 2020 (in review). The horizontal levee: A multi-benefit nature-based treatment system that improves water quality and protects coastal levees from the effects of sea level rise.
- Cloern, J.E. 2001. Our Evolving Conceptual Model of the Coastal Eutrophication Problem. *Marine Ecology Progress Series* 210 (January): 223–53. <https://doi.org/10.3354/meps210223>.
- Cloern, J.E., Schraga, T.S., Lopez, C.B., Knowles, N., Labiosa, R.G., Dugdale, R. 2005. Climate Anomalies Generate an Exceptional Dinoflagellate Bloom in San Francisco Bay. *Geophysical Research Letters* 32 (14). <https://doi.org/10.1029/2005GL023321>.
- Collins, J.N., Grossinger, R.M. 2004. Synthesis of scientific knowledge concerning estuarine landscapes and related habitats of the South Bay Ecosystem. Draft Final Technical Report of the South Bay Salt Pond Restoration Project. SFEI Contribution No 308. San Francisco Estuary Institute, Richmond, CA.
- Crauder, J., Downing-Kunz, M.A., Hobbs, J.A., Manning, A.J., Novick, E., Parchaso, F., Wu, J. et al. 2015. Lower South Bay Nutrient Synthesis. SFEI Contribution No. 732. San Francisco

Estuary Institute, Richmond, CA.

Ding, G., Peijnenburg, W.J.G.M. 2013. Physicochemical Properties and Aquatic Toxicity of Poly- and Perfluorinated Compounds. *Critical Reviews in Environmental Science and Technology* 43, 598–678. <https://doi.org/10.1080/10643389.2011.627016>.

Duguma, D., Walton, W.E. 2014. Effects of Nutrients on Mosquitoes and an Emergent Macrophyte, *Schoenoplectus Maritimus*, for Use in Treatment Wetlands. *Journal of Vector Ecology* 39 (1): 1–13. <https://doi.org/10.1111/j.1948-7134.2014.12063.x>.

East Bay Dischargers Authority (EBDA). 2015. Sea Level Rise Adaptation Planning Project. Prepared by MBA, Molly Mehaffy Design, ESA, SFEI, and EBDA with funding from the California State Coastal Conservancy.

Effler, R.S., Goyer, R.A. 2006. Baldcypress and Water Tupelo Sapling Response to Multiple Stress Agents and Reforestation Implications for Louisiana Swamps. *Forest Ecology and Management* 226 (1): 330–40. <https://doi.org/10.1016/j.foreco.2006.02.011>.

Eisler, R. 1997. Copper Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review (Biological Science Report No. USGS/BRD/BSR-1997-0002). U.S. Geological Survey, Biological Resources Division.

Fong, T., Lipp, E.K. 2005. Enteric viruses of humans and animals in aquatic environments: health risks, detection, and potential water quality assessment tools. *Microbiol. Mol. Biol. Rev.* 69, no. 2: 357-371.

Gibble, C. M., Peacock, M. B., Kudela, R. M. 2016. Evidence of freshwater algal toxins in marine shellfish: Implications for human and aquatic health. *Harmful Algae*, 59, 59-66.

Giorgio, P.A. del, Cole, J.J. 1998. Bacterial Growth Efficiency in Natural Aquatic Systems. *Annual Review of Ecology and Systematics* 29 (1): 503–41. <https://doi.org/10.1146/annurev.ecolsys.29.1.503>.

Goals Project. 1999. Baylands Ecosystem Habitat Goals. A Report of Habitat Recommendations Prepared by the San Francisco Bay Area Wetlands Ecosystem Goals Project. U.S. Environmental Protection Agency and S.F. Bay Regional Water Quality Control Board, San Francisco and Oakland, CA.

Goals Project. 2015. The baylands ecosystem habitat goals update for climate change: What we can do. The 2015 Science Update to the Baylands Ecosystem Habitat Goals, prepared by the San Francisco Bay Area Wetlands Ecosystem Goals Project. California State Coastal Conservancy, Oakland, CA.

Grenni, P., Ancona, V., Barra Caracciolo, A. 2018. Ecological effects of antibiotics on natural ecosystems: A review. *Microchemical Journal* 136, 25–39. <https://doi.org/10.1016/j.microc.2017.02.006>.

He, T., Feng, X., Guo, Y., Qiu, G., Li, Z., Liang, L., Lu, J. 2008. The Impact of Eutrophication on the Biogeochemical Cycling of Mercury Species in a Reservoir: A Case Study from Hongfeng Reservoir, Guizhou, China. *Environmental Pollution, Mercury Cycling and Bioaccumulation in the Environment*, 154 (1): 56–67. <https://doi.org/10.1016/j.envpol.2007.11.013>.

Hill, D.T., Payne, V.W.E., Rogers, J.W., Kown, S.R. 1997. Ammonia Effects on the Biomass

Production of Five Constructed Wetland Plant Species. *Bioresource Technology* 62 (3): 109–13. [https://doi.org/10.1016/S0960-8524\(97\)00085-0](https://doi.org/10.1016/S0960-8524(97)00085-0).

Irvine, I.C., Vivanco, L., Bentley, P.N., Martiny, J.B.H. 2012. The Effect of Nitrogen Enrichment on C1-Cycling Microorganisms and Methane Flux in Salt Marsh Sediments. *Frontiers in Microbiology* 3. <https://doi.org/10.3389/fmicb.2012.00090>.

Jonsson, S., Andersson, A., Nilsson, M.B., Skjellberg, U., Lundberg, E., Schaefer, J.K., Åkerblom, S., Björn, E. 2017. Terrestrial discharges mediate trophic shifts and enhance methylmercury accumulation in estuarine biota. *Science Advances* 3, e1601239. <https://doi.org/10.1126/sciadv.1601239>.

Kienzler, A., Bopp, S., Halder, M., Embry, M., Worth, A. 2019. Application of new statistical distribution approaches for environmental mixture risk assessment: A case study. *Science of The Total Environment* 693, 133510. <https://doi.org/10.1016/j.scitotenv.2019.07.316>

Kuzyakov, Y., Friedel, J. K., Stahr, K. 2000. Review of Mechanisms and Quantification of Priming Effects. *Soil Biology and Biochemistry* 32 (11): 1485–1498.

Langley, J.A., Mozdzer, T.J., Shepard, K.A., Hagerty, S.B., Magonigal, J.P. 2013. Tidal Marsh Plant Responses to Elevated CO<sub>2</sub>, Nitrogen Fertilization, and Sea Level Rise. *Global Change Biology* 19 (5): 1495–1503. <https://doi.org/10.1111/gcb.12147>.

López-Urrutia, Á., Morán, X.A.G. 2007. Resource Limitation of Bacterial Production Distorts the Temperature Dependence of Oceanic Carbon Cycling. *Ecology* 88 (4): 817–22. <https://doi.org/10.1890/06-1641>.

MacVean, L., Trowbridge, P., Lewis, L., Hobbs, J., Sylvester, Z., Winchell, T., Senn, D. 2018. Dissolved Oxygen in South San Francisco Bay: Variability, Important Processes, and Implications for Understanding Fish Habitat. SFEI Contribution No. 911, San Francisco Estuary Institute, Richmond, CA.

Maffei, W. 2000. In *Baylands Ecosystem Species and Community Profiles: Life histories and environmental requirements of key plants, fish, and wildlife*. Prepared by the San Francisco Bay Area Wetlands Ecosystem Goals Project. P.R. Olofson, editor. San Francisco Bay Regional Water Quality Control Board, Oakland, CA.

Manzoni, S., Taylor, P., Richter, A., Porporato, A., Ågren, G.I. 2012. Environmental and Stoichiometric Controls on Microbial Carbon-Use Efficiency in Soils. *New Phytologist* 196 (1): 79–91. <https://doi.org/10.1111/j.1469-8137.2012.04225.x>.

Mazrui, N.M., Jonsson, S., Thota, S., Zhao, J., Mason, R.P., 2016. Enhanced availability of mercury bound to dissolved organic matter for methylation in marine sediments. *Geochimica et cosmochimica acta* 194, 153–162. <https://doi.org/10.1016/j.gca.2016.08.019>.

McKee, L.J., Gilbreath, A.N. 2015. Concentrations and Loads of Suspended Sediment and Trace Element Pollutants in a Small Semi-Arid Urban Tributary, San Francisco Bay, California. *Environmental Monitoring and Assessment* 187 (8): 499. <https://doi.org/10.1007/s10661-015-4710-4>.

Mendelssohn, I.A., Morris, J.T. 2000. Eco-Physiological Controls on the Productivity of *Spartina Alterniflora* Loisel. In *Concepts and Controversies in Tidal Marsh Ecology*, edited by Michael P. Weinstein and Daniel A. Kreeger, 59–80. Dordrecht: Springer Netherlands.

[https://doi.org/10.1007/0-306-47534-0\\_5](https://doi.org/10.1007/0-306-47534-0_5).

Morris, J.T. 1982. A Model of Growth Responses by *Spartina Alterniflora* to Nitrogen Limitation. *The Journal of Ecology*, 25–42.

Morris, J.T., Bradley, P.M. 1999. Effects of Nutrient Loading on the Carbon Balance of Coastal Wetland Sediments. *Limnology and Oceanography* 44 (3): 699–702.  
<https://doi.org/10.4319/lo.1999.44.3.0699>.

Nam, D., Adams, D.H., Reyier, E.A., Basu, N. 2011. Mercury and Selenium Levels in Lemon Sharks (*Negaprion brevirostris*) in Relation to a Harmful Red Tide Event. *Environmental Monitoring and Assessment* 176 (1–4): 549–59. <https://doi.org/10.1007/s10661-010-1603-4>.

Nelson, J.L., Zavaleta, E.S. 2012. Salt Marsh as a Coastal Filter for the Oceans: Changes in Function with Experimental Increases in Nitrogen Loading and Sea-Level Rise. Edited by Just Cebrian. *PLoS ONE* 7 (8): e38558. <https://doi.org/10.1371/journal.pone.0038558>.

Nur, N., Wood, J.K., Elrod, M., Ball, D., Thomson, D. 2018. Guiding Restoration of Upland Transition Zones to Benefit Tidal Marsh Wildlife. *Point Blue Conservation Science*.  
<http://www.pointblue.org/wp-content/uploads/2018/12/Summary-Report-Transition-Zone-and-Tidal-Marsh-Point-Blue.pdf>

Nyman, J.A., Walters, R.J., Delaune, R.D., Patrick, W.H. 2006. Marsh Vertical Accretion via Vegetative Growth. *Estuarine, Coastal and Shelf Science, Salt Marsh Geomorphology: Physical and ecological effects on landform*, 69 (3): 370–80. <https://doi.org/10.1016/j.ecss.2006.05.041>.

O’Connell, J.L., Byrd, K.B., Kelly, M. 2014. Remotely-Sensed Indicators of N-Related Biomass Allocation in *Schoenoplectus Acutus*. *PLoS ONE* 9 (3).  
<https://doi.org/10.1371/journal.pone.0090870>.

Overton, C.T., Takekawa, J. Y., Casazza, M.L., Bui, T.D., Holyoak, M., Strong, D.R. 2015. Sea-level Rise and Refuge Habitat for Tidal Marsh Species: Can Artificial Islands Save The California Ridgway’s Rail. *Ecological Engineering*: (74):337-344.

Paerl, H.W. 2006. Assessing and Managing Nutrient-Enhanced Eutrophication in Estuarine and Coastal Waters: Interactive Effects of Human and Climatic Perturbations. *Ecological Engineering, Advances in coastal habitat restoration in the northern Gulf of Mexico*, 26 (1): 40–54. <https://doi.org/10.1016/j.ecoleng.2005.09.006>.

Peacock, M.B., Gobble, C.M., Senn, D.B., Cloern, J.E., Kudela, R.M. 2018. Blurred Lines: Multiple Freshwater and Marine Algal Toxins at the Land-Sea Interface of San Francisco Bay, California. *Harmful Algae* 73 (March): 138–47. <https://doi.org/10.1016/j.hal.2018.02.005>.

Peterson, D.H., Smith, R.E., Hager, S.W., Harmon, D.D., Herndon, R.E., Schemel, L.E. 1985. Interannual Variability in Dissolved Inorganic Nutrients in Northern San Francisco Bay Estuary. In *Temporal Dynamics of an Estuary: San Francisco Bay*, 37–58. Springer.

Pickhardt, P.C., Folt, C.L., Chen, C.Y., Klaue, B., Blum, J.D. 2002. Algal Blooms Reduce the Uptake of Toxic Methylmercury in Freshwater Food Webs. *Proceedings of the National Academy of Sciences* 99 (7): 4419–23. <https://doi.org/10.1073/pnas.072531099>.

Prasse, C., Schlüsener, M.P., Schulz, R., Ternes, T.A. 2010. Antiviral Drugs in Wastewater and Surface Waters: A New Pharmaceutical Class of Environmental Relevance? *Environ. Sci. Technol.* 44, 1728–1735. <https://doi.org/10.1021/es903216p>

Razavi, N.R., Qu, M., Chen, D., Zhong, Y., Ren, W., Wang, Y., Campbell, L.M., 2015. Effect of eutrophication on mercury (Hg) dynamics in subtropical reservoirs from a high Hg deposition ecoregion. *Limnology and Oceanography* 60, 386–401. <https://doi.org/10.1002/lno.10036>

Resource Management Associates. 2019. Hydrodynamic modeling and analysis of ROC discharge options: outfall location and dilution modeling analysis. Technical Memorandum, 79 pp.

Rickey, M. A., Anderson, R.C. 2004. Effects of Nitrogen Addition on the Invasive Grass *Phragmites Australis* and a Native Competitor *Spartina Pectinata*. *Journal of Applied Ecology* 41 (5): 888–96. <https://doi.org/10.1111/j.0021-8901.2004.00948.x>.

Rodea-Palomares, I., González-Pleiter, M., Martín-Betancor, K., Rosal, R., Fernández-Piñas, F. 2015. Additivity and Interactions in Ecotoxicity of Pollutant Mixtures: Some Patterns, Conclusions, and Open Questions. *Toxics* 3, 342–369. <https://doi.org/10.3390/toxics3040342>

Sanderson, H., Johnson, D.J., Reitsma, T., Brain, R.A., Wilson, C.J., Solomon, K.R. 2004. Ranking and prioritization of environmental risks of pharmaceuticals in surface waters. *Regulatory Toxicology and Pharmacology* 39, 158–183. <https://doi.org/10.1016/j.yrtph.2003.12.006>.

San Francisco Estuary Institute-Aquatic Science Center (SFEI-ASC). 2016. San Francisquito Creek Baylands Landscape Change Metrics Analysis. A Report of SFEI-ASC's Resilient Landscapes Program, Publication #784, San Francisco Estuary Institute-Aquatic Science Center, Richmond, CA.

San Francisco Estuary Institute-Aquatic Science Center (SFEI-ASC). 2018. Resilient Landscape Vision for the Calabazas Creek, San Tomas Aquino Creek, and Pond A8 Area: Bayland-Creek Reconnection Opportunities. A SFEI-ASC Resilient Landscapes report developed in cooperation with the Healthy Watersheds, Resilient Baylands Design Advisory Team, Santa Clara Valley Water District, and South Bay Salt Ponds Restoration Project, Publication #870, San Francisco Estuary Institute-Aquatic Science Center, Richmond, CA.

Save The Bay. 2017. Oro Loma Horizontal Levee Vegetation Report. [https://oroloma.org/wp-content/uploads/STB-Oro-Loma-Report\\_11.13.17.pdf](https://oroloma.org/wp-content/uploads/STB-Oro-Loma-Report_11.13.17.pdf)

Scannell, P.W. 2009. Effects of Copper on Aquatic Species: A review of the literature (No. 09–04). Alaska Department of Fish and Game. [https://www.adfg.alaska.gov/static/home/library/pdfs/habitat/09\\_04.pdf](https://www.adfg.alaska.gov/static/home/library/pdfs/habitat/09_04.pdf)

Schartup, A.T., Mason, R.P., Balcom, P.H., Hollweg, T.A., Chen, C.Y., 2013. Methylmercury Production in Estuarine Sediments: Role of Organic Matter. *Environmental Science & Technology* 47, 695–700. <https://doi.org/10.1021/es302566w>.

Schile, L.M., Callaway, J.C., Morris, J.T., Stralberg, D., Parker, V.T., Kelly, M. Modeling Tidal Marsh Distribution with Sea-Level Rise: Evaluating the Role of Vegetation, Sediment, and Upland Habitat in Marsh Resiliency. *PLOSOne* e88760. February 2014: Volume 9, Issue 2.

- Sedlak, M. D., Benskin, J. P., Wong, A., Grace, R., Greig, D. J. 2017. Per-and polyfluoroalkyl substances (PFASs) in San Francisco Bay wildlife: Temporal trends, exposure pathways, and notable presence of precursor compounds. *Chemosphere*, 185, 1217-1226.
- Sedlak, M., Sutton, R., Wong, A., Lin, D. 2018. Per and Polyfluoroalkyl Substances (PFASs) in San Francisco Bay: Synthesis and Strategy. SFEI Contribution No. 867. San Francisco Estuary Institute, Richmond, CA.
- Senn, D.B., Novick, E. 2014. Scientific Foundation for the San Francisco Bay Nutrient Management Strategy. SFEI Contribution No. 979. San Francisco Estuary Institute, Richmond, CA.
- SFEI and SPUR. 2019. San Francisco Bay Shoreline Adaptation Atlas: Working with Nature to Plan for Sea Level Rise Using Operational Landscape Unites. SFEI Contribution No. 915, San Francisco Estuary Institute, Richmond, CA.
- Silva, E., Rajapakse, N., Kortenkamp, A. 2002. Something from “Nothing” – Eight Weak Estrogenic Chemicals Combined at Concentrations below NOECs Produce Significant Mixture Effects. *Environ. Sci. Technol.* 36, 1751–1756. <https://doi.org/10.1021/es0101227>.
- Singer, A.C., Nunn, M.A., Gould, E.A., Johnson, A.C. 2007. Potential Risks Associated with the Proposed Widespread Use of Tamiflu. *Environmental Health Perspectives* 115, 102–106. <https://doi.org/10.1289/ehp.9574>.
- SJ-SC. 2019. San Jose-Santa Clara Regional Wastewater Facility 2019 Self-Monitoring Annual Report. San Jose-Santa Clara Regional Wastewater Facility.
- Smith, K.R., Riley, M.K., Barthman-Thompson, L., Woo, I., Statham, M., Estrella, S., Kelt, D.A. 2018. Toward Salt Marsh Harvest Mouse Recovery: A Review. *San Francisco Estuary and Watershed Science*. Volume 16, Issue 2.
- Sobek, A., Undeman, E. 2019. Tunnel vision in current chemicals management cannot deal with the unknown risk of synthetic chemicals in aquatic systems. *Acta Limnologica Brasiliensia* 31. <https://doi.org/10.1590/s2179-975x4219>.
- Stadmark, J., Leonardson, L. 2005. Emissions of Greenhouse Gases from Ponds Constructed for Nitrogen Removal. *Ecological Engineering, Constructed wetlands for wastewater treatment*, 25 (5): 542–51. <https://doi.org/10.1016/j.ecoleng.2005.07.004>.
- Sun, J., Davis, J. A., Bezalel, S. N., Ross, J. R., Wong, A., Yee, D., Mayfield, I. R. 2017. Contaminant Concentrations in Fish from San Francisco Bay, 2014. SFEI Contribution No. 806. Regional Monitoring Program for Water Quality in San Francisco Bay, Richmond, CA.
- US Army Corps of Engineers (USACE), Coastal Conservancy, Santa Clara Valley Water District. 2015. The South San Francisco Bay Shoreline Study: Alviso Ponds & Santa Clara County Interim Feasibility Study (EIA 11 Fact Sheet). <http://www.southbayshoreline.org/documents/Alviso%20EIA11%20Sheet%20061515%20BA.pdf>
- Vivanco, L., Irvine, I.C., Martiny, J.B.H. 2015. Nonlinear Responses in Salt Marsh Functioning to Increased Nitrogen Addition. *Ecology* 96 (4): 936–47. <https://doi.org/10.1890/13-1983.1>.

# Chapter 5: Treatment of Reverse Osmosis Concentrate by Advanced Oxidation Processes and Open-Water Engineered Treatment Cells

## Sampling and Analysis Plan

for

Santa Clara Valley Water District  
San Francisco Estuary Institute  
University of California Berkeley  
Stanford University  
GHD, Inc.

Prepared by:

San Francisco Estuary Institute  
University of California Berkeley  
Stanford University

July 10, 2017



Stanford  
University

SFEI

AQUATIC  
SCIENCE  
CENTER

# 1. Introduction

## 1.1 Project Overview

The University of California at Berkeley, Stanford University, and the San Francisco Estuary Institute will help the Santa Clara Valley Water District in evaluating the technical and economic feasibility of treating reverse osmosis (RO) concentrate via engineered open water treatment cells to reduce concentration of priority pollutants, emerging contaminants, metals and nutrients, as follows:

- (1) *Engineered open water treatment of RO concentrate.* Open-water based treatment has the potential to remove organic contaminants, nutrients, metals and pathogens, while increasing the total dissolved solids (through evaporation) and providing brackish water habitat. To assess the efficacy of engineered open-water treatment of RO concentrate, experiments will be conducted under conditions likely to be encountered in a full-scale treatment system.
  
- (2) *Advanced Oxidation Process (AOP) treatment of RO concentrate.* AOPs can degrade dissolved organics and inactivate pathogens. When used as a pretreatment for engineered open-water treatment, AOPs may increase the efficiency of engineered open-water treatment by partially breaking down recalcitrant organic compounds, rendering them more susceptible to further biological degradation, and by increasing the UV/visible light transmittance, aiding photodegradation. They also may aid the removal of metals within the treatment system by liberating metals from strong complexes (e.g., EDTA). The project team will study the efficacy of ozone and UV/hydrogen peroxide treatment (and other potential oxidants) of RO concentrates alone and in combination with engineered open-water treatment.

In order to assess the effects of these treatment systems, the research team will measure a wide range of target analytes before and after the treatment cells as well as ancillary information to understand the performance of the cells. The rationale for the selected target analytes is provided in the next subsection. The Details of the sampling locations, methods, frequency, and QA/QC procedures are described in sections 2-8.

### **1.1.1 Rationale for Target Analytes for the Study**

Target contaminants of concern can be grouped into four compound types - indicator compounds, contaminants of emerging concern, nutrients and metals, and general water quality parameters. These contaminants and the rationale for monitoring are described in detail below.

#### ***Indicator Compounds***

Analysis of a subset of readily measurable “indicator compounds” has been developed as a means of efficiently assessing the ability of treatment systems to remove hundreds of different contaminants potentially present in wastewater. Extensive literature on mechanisms of removal supports indicator-based predictions of removal efficiency for those compounds exhibiting similar chemical and physical properties determining behavior during wastewater treatment (e.g., Dickenson et al. 2009, 2011).

Six pharmaceutical compounds have been identified as appropriate indicators to track the chemical and biological processes employed in the treatment system: atenolol, carbamazepine, metoprolol, propranolol, sulfamethoxazole, and trimethoprim. These compounds occur frequently in effluent at concentrations at least five times higher than limits of quantification. They also show a range of reactivities to ozone, as well as to open cell treatment processes including photolysis and biotransformation (Table 1).

These six indicator compounds have been used in previous studies (e.g., Dickenson et al. 2009; Jasper et al. 2014), providing a means of comparing the removal efficiencies of this experimental treatment relative to other treatment trains similarly characterized (Table 1).

#### ***Contaminants of Emerging Concern***

Recent efforts to prioritize CECs for monitoring using risk-based approaches have occurred at state and regional levels. Both processes have identified short lists of contaminants of particular concern based on available monitoring data and established toxicity thresholds (Anderson et al. 2012; Sutton et al. 2017). Among these, eight compounds will be the subject of analysis: two pyrethroid pesticides, bifenthrin and permethrin; the pesticide fipronil and three commonly detected degradates, fipronil sulfone, sulfide, and desulfanyl, and perfluorooctane sulfonate (PFOS), as well as the related perfluorooctanoic acid (PFOA).

The pesticides (and degradates) selected for evaluation have been detected at levels exceeding sediment toxicity thresholds or USEPA benchmarks for aquatic

invertebrates in freshwater ecosystems in California (Holmes et al. 2008; Kuivila et al. 2012; Ensminger et al. 2013; Budd et al. 2015). They are also widely detected in treated wastewater effluent (Markle et al. 2014; Weston and Lydy 2014; Sadaria et al. 2016; Supowit et al. 2016); the potential for additional discharge via RO concentrate subjected to the experimental treatment must be evaluated.

These compounds have not previously been examined in SCVWD RO concentrate. It is likely that the pyrethroid pesticides, bifenthrin and permethrin, may experience efficient removal during microfiltration due to their hydrophobicity and tendency to partition to particles. Should this prove to be the case, no further analysis of these pesticides is required.

In contrast, fipronil is likely to be present in RO concentrate; analysis of fipronil and its degradates can shed light on the dominant chemical and biological processes active in the experimental treatment system. Fipronil sulfone is an oxidation product of the parent compound, while fipronil sulfide is a reduction product, and fipronil desulfinyl is a product of photolysis (Gunasekara and Truong 2007).

PFOS has been identified as a priority for monitoring in the state and the region due to its widespread presence in the California environment, its potential for bioaccumulation in aquatic organisms, and the potential adverse impacts of exposure on wildlife, particularly birds (e.g., Newsted et al. 2005; Custer et al. 2012). PFOS is water soluble, persistent, present in wastewater, and is not amenable to typical wastewater treatment technologies (Schultz et al. 2006; Becker et al. 2008; Houtz et al. 2016). However, it is possible that some adsorption to particles will occur when the RO concentrate is subjected to open cell constructed wetlands treatment.

PFOA, a related compound, is also widely detected in environmental matrices in California, though levels are typically an order of magnitude below PFOS, as bioaccumulation in aquatic species is generally limited (Martin et al. 2003, 2004; Sedlak and Greig 2012; SCCWRP 2015; Sedlak et al. submitted). Like PFOS, PFOA is water soluble, persistent, present in wastewater, and a portion of the contaminant may adsorb to particles during open cell treatment. PFOS and PFOA analyses are complementary.

### ***Nutrients and Metals***

Analysis of selected nutrients and inorganic parameters will focus on compounds that are currently regulated in South Bay receiving waters, or are under consideration for regulation.

Site-specific water quality objectives have been adopted for cyanide, copper and nickel in South San Francisco Bay (SFBRWQCB, 2015), including both chronic (measured as 4-day averages) and acute (measured as a 1 hour average) objectives. Removal of these compounds in treated ROC effluent will be monitored to assess the potential for this concentrated waste stream to cause exceedances of the acute objectives.

Several parameters are also currently under consideration for potential regulation in South Bay. In 2016, the USEPA released draft numeric criteria for selenium in water in San Francisco Bay. Selenium is a naturally occurring element that may be present at elevated levels in source waters.

Nutrient parameters to be monitored will include ammonia, nitrate, nitrite (all measured as N), total nitrogen, phosphate (measured as P), and total phosphorous. Dissolved organic nitrogen will be calculated by difference between total nitrogen and the sum of ammonia and nitrate/nitrite. Management and regulatory decisions related to nutrients are also under consideration by the San Francisco Bay Regional Water Quality Control Board (Water Board), informed by the Nutrient Management Strategy (SFBRWQCB, 2012). Key decisions to be made by the Water Board include developing nutrient objectives for the Bay, revising dissolved oxygen and ammonia objectives, potential 303(d) listings for nutrients or ammonium, establishing nutrient discharge permit requirements, and evaluating specific management actions. Lower South Bay is particularly vulnerable to nutrients and dissolved oxygen impacts due to the large proportion of wastewater discharge and low flushing rates in this embayment. Open water treatment wetlands have previously been shown to facilitate nitrate removal, as well as smaller levels of nitrite, ammonia, and phosphate removal, through denitrification, anammox, and biomat accretion (Jasper et al. 2014a).

Bromate will also be monitored as a surrogate parameter useful for examining the extent of oxidation that has occurred within a sample when measured together with bromide. Bromate formation from bromide has been shown to correlate well with higher removal of target organic indicator compounds in wastewater during advanced oxidation processes (Dickenson et al. 2009). Bromate is also a disinfection byproduct for which USEPA has set the maximum contaminant level (MCL) in drinking water at 10 ppb; it is not currently regulated in wastewater.

**Toxicity**

Water toxicity tests for two species (*Ceriodaphnia dubia*, *Thalassiosira pseudonana*) will be monitored to provide information on potential future NPDES permit compliance issues. Because *Ceriodaphnia* is a freshwater species, salt control tests will be run to control for the effects of toxicity due to elevated salinity in the RO concentrate. Testing with topsmelt (*Atherinops affinis*) should also be considered because of the salinity of the RO concentrate. The project team will decide which species to test in time for the September 2017 quarterly sampling round. The considerations for the decision will be access to suitable laboratories, available budget, and likely regulatory requirements for toxicity testing of treated RO concentrate.

**General Water Quality Parameters**

A suite of general water quality parameters will be measured in order to provide a basic characterization of the RO concentrate, as well as to inform an understanding of the degradation processes occurring. Additionally, water quality objectives for the Bay have also been established in the Basin Plan for dissolved oxygen, pH, salinity, and temperature.

Dissolved oxygen, pH, and temperature will be measured instantaneously in the field, while dissolved organic carbon, dissolved inorganic carbon, alkalinity, and sulfate will be measured in the laboratory. Each of these factors can have a significant influence on transformation rates for various photo- or biodegradation processes, and can be used to understand the types of bacterial communities that are active and the types of degradation processes occurring (Jasper and Sedlak 2013, Jasper et al. 2014).

Conductivity and TDS measurements will provide a measure of the salinity and concentration of salts and related contaminants in each sample. Bromide will be measured together with bromate in order to provide an indication of oxidation levels (see Nutrients and Metals section) Total residual chlorine, which is required to be monitored in any discharged effluent that has been previously chlorinated, will also be measured to ensure the effluent has been fully dechlorinated prior to discharge.

Additional ancillary data will be collected to investigate the effect of system parameters and seasonal variations on contaminant removal. Additional data parameters to collect will include: inflow, outflow, water depth, biomat depth/composition, hydraulic residence time, and weather condition. Biomat depth and composition and hydraulic residence time will be measured as separate experiments 1

or 2 times during the study. The methods for these experiments are not included in this plan.

**Table 1. Indicator Compounds**

Indicator Compound	kO <sub>3</sub> ,app (M-1s-1)*	Ozone-Reactive Moiety*	Removal via Open Cell Treatment**	Dominant Reaction**	Secondary Reaction**
Atenolol	103- 105	Deprotonated amine	Good	Biotransformation	
Carbamazepine	>105	Nonaromatic C=C	Poor	Recalcitrant	
Metoprolol	103- 105	Deprotonated amine	Good	Biotransformation	
Propranolol	>105	Alkoxy Polyaromatic	Good	Photolysis	Biotransformation
Sulfamethoxazole	>105	Amino Aromatic	Good	Photolysis	
Trimethoprim	>105	Deprotonated amine	Good	Biotransformation	Photolysis

\*Dickenson et al. 2009

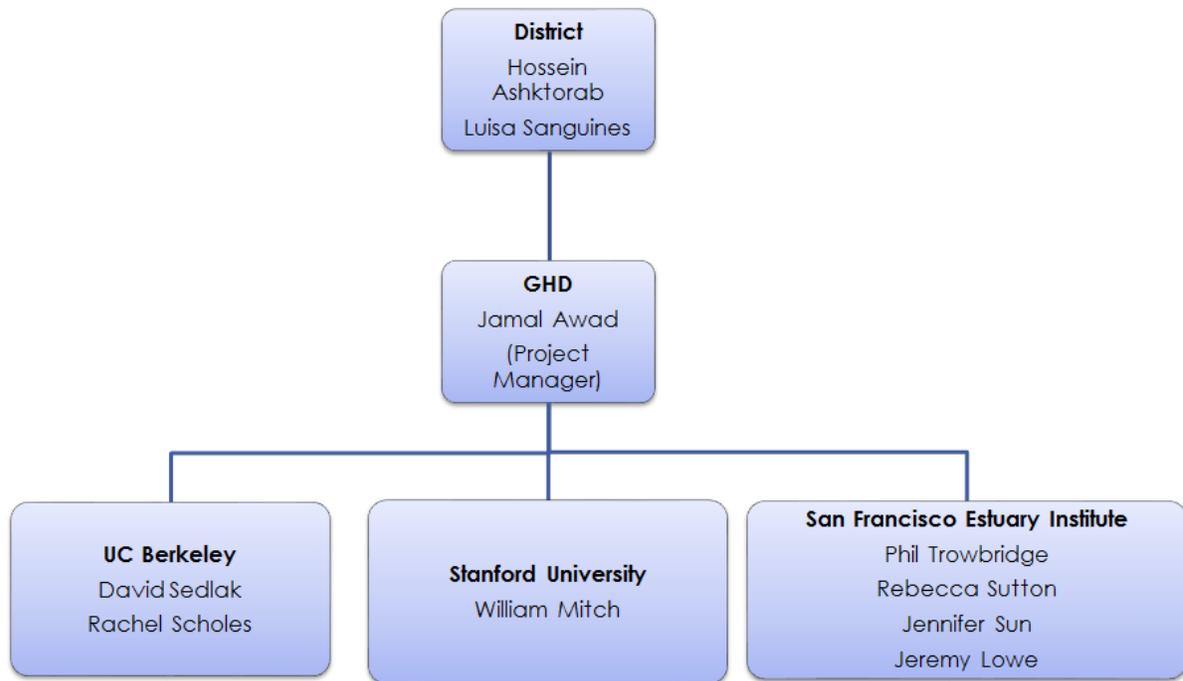
\*\* Jasper et al. 2014

## 2. Key Personnel

**Table 2. Key Personnel**

Name	Agency	Role	Phone	Email
David Sedlak	UC Berkeley	PI - Open Water Treatment Wetland		sedlak@berkeley.edu
Rachel Scholes	UC Berkeley	Sample collection, laboratory analysis		rachel.scholes@berkeley.edu
William Mitch	Stanford	PI - Advanced Oxidation Process		wamitch@stanford.edu
Phil Trowbridge	SFEI	Project Manager	603-340-5220	philt@sfei.org
Rebecca Sutton	SFEI	Study design; data analysis		rebeccas@sfei.org
Jennifer Sun	SFEI	SAP preparation, logistics	949-202-6671	jennifers@sfei.org
Jeremy Lowe	SFEI	Wetland restoration		jeremyl@sfei.org
Hossein Askorab	SCVWD	Program Manager		HAskorab@valleywater.org
Luisa Sangines	SCVWD	Project Manager	408-630-3124	LSangines@valleywater.org
Jamal Awad	GHD	Project Manager		Jamal.Awad@ghd.com
Mike Mitchell	GHD	Main Point of Contact for GHD coordination		Michael.Mitchell@ghd.com
Zachary Helsley	SCVWD	Main Point of Contact for site access and SCVWD laboratory coordination	408-630-2577	ZHelsley@valleywater.org
Triet Trinh	SCVWD	Program Administrator for WQLab	408-630-3211	TTrinh@valleywater.org
Jim Scott	SCVWD	Laboratory Manager		JScott@valleywater.org
Henry Barrientos	SCVWD	Project management	408-630-2078	hbarrientos@valleywater.org

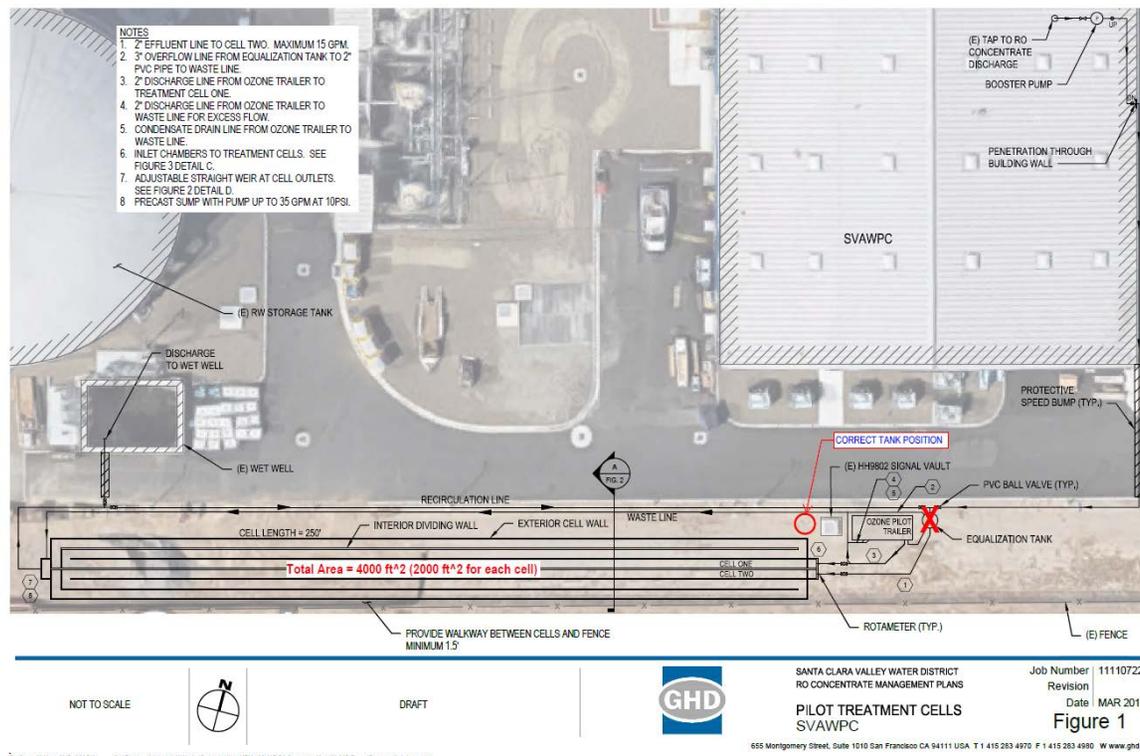
**Figure 1:** Project Organization Chart



### 3. Study Location

The pilot-scale system will consist of two treatment systems: (1) an open water unit process system and (2) a flow-through oxidative treatment system followed by an open water unit process system. The treatment systems will be located adjacent to the Silicon Valley Advanced Water Purification Center in San Jose, CA, and will receive RO concentrate from this facility.

**Figure 2:** Conceptual placement of the ROC pilot treatment cells at the Silicon Valley Advanced Water Purification Center. Note: the actual location of the treatment cells may be different based on site-specific constraints.



## **4. Study Design**

### **4.1 Target Analytes**

Table 3 lists the target compounds that will be measured for the study along with the laboratory responsible for conducting the analysis.

**Table 3.** List of compounds measured as part of the study.

Analyte	Analytical Method	MRL or LOQ*	MRL or LOQ Units	Analytical Laboratory	Sampling Frequency	Rationale for monitoring
<b>Surrogate/Indicator</b>						
Atenolol	LC-MS-MS-ESI	10	ng/L	UCB	monthly	Indicator of treatment process
Carbamazepine	LC-MS-MS-ESI	10	ng/L	UCB	monthly	Indicator of treatment process
Metoprolol	LC-MS-MS-ESI	10	ng/L	UCB	monthly	Indicator of treatment process
Propranolol	LC-MS-MS-ESI	10	ng/L	UCB	monthly	Indicator of treatment process
Sulfamethoxazole	LC-MS-MS-ESI	10	ng/L	UCB	monthly	Indicator of treatment process
Trimethoprim	LC-MS-MS-ESI	10	ng/L	UCB	monthly	Indicator of treatment process
<b>Nutrient &amp; Metal Analytes</b>						
Ammonia-N	SM4500	0.8	mg/L	UCB	monthly	NPDES permitting
Nitrate&nitrite-N	EPA 300	0.2	mg/L	UCB	monthly	NPDES permitting
Total N	Shimadzu TOC/TN-V	5	mg/L	UCB	quarterly	NPDES permitting
Phosphate-P	EPA 300	0.05**	mg/L	UCB	monthly	NPDES permitting
Total P	TP	1	mg/L	UCB	quarterly	NPDES permitting
Cyanide	EPA 335.4		mg/L	SCVWD contract lab	quarterly	NPDES permitting
Copper	EPA 200.8	0.5	ug/L	UCB	monthly	NPDES permitting
Nickel	EPA 200.7	1	ug/L	UCB	monthly	NPDES permitting
Selenium	EPA 200.8	5	ug/L	SCVWD contract lab	quarterly	NPDES permitting
Bromate	EPA 317.1	1	ug/L	SCVWD	quarterly***	NPDES permitting
<b>Emerging Contaminants of State and Regional Concern</b>						

Bifenthrin	USGS method O-2143-09, USGS method code GM011	10	ng/L	Stanford	quarterly	
Fipronil	USGS method O-2143-09, USGS method code GM011	10	ng/L	Stanford	monthly	
Fipronil sulfone	USGS method O-2143-09, USGS method code GM011	10	ng/L	Stanford	monthly	
Fipronil sulfide	USGS method O-2143-09, USGS method code GM011	10	ng/L	Stanford	monthly	
Fipronil desulfinyl	USGS method O-2143-09, USGS method code GM011	10	ng/L	Stanford	monthly	
Permethrin	EPA 525.2	0.5	ug/L	Stanford	quarterly	CCL4
Perfluorooctane sulfonate (PFOS)	EPA 537	5	ng/L	SCVWD contract lab	quarterly	Drinking Water impacts
Perfluorooctanoic acid (PFOA)	EPA 537	5	ng/L	SCVWD contract lab	quarterly	Drinking Water impacts
<b>Toxicity</b>						
<i>Ceriodaphnia dubia</i>				SCVWD	quarterly	NPDES permitting
<i>Thalassiosira pseudonana</i>				SCVWD	quarterly	NPDES permitting
<i>Atherinops affinis</i>				SCVWD	quarterly	Alternative test species that is more tolerant of salinity (SWRCB 1996, ASTM 2000b)
<b>Water Quality Parameters</b>						

DOC	SM5310C	5	mg/L	UCB	monthly	General WQ parameter
DIC	Shimadzu TOC/TN-V	5	mg/L	UCB	monthly	General WQ parameter
Sulfate	EPA 300	0.5	mg/L	SCVWD	monthly	General WQ parameter
Bromide	EPA 300	0.05	mg/L	SCVWD	monthly	General WQ parameter
Conductivity	SM 2510B	na	umhos/cm	SCVWD	monthly	General WQ parameter
Alkalinity (as CaCO3)	SM 2320B	5	mg/L	SCVWD	monthly	General WQ parameter
TSS	SM 2540D		mg/L	SCVWD	monthly	General WQ parameter
TDS	SM 2540C	20	mg/L	SCVWD	monthly	General WQ parameter
Chloride	SM 4500 CL	5	mg/L	SCVWD	quarterly	General WQ parameter
Total Residual Chlorine	DPD method	0.5	mg/L	Stanford	quarterly	General WQ parameter
Temperature	FIELD METER	na	oC	SCVWD	monthly	General WQ parameter
DO	FIELD METER	na	mg/L or %	SCVWD	monthly	General WQ parameter
pH	FIELD METER	na	pH units	SCVWD	monthly	General WQ parameter
Flow	FIELD METER	na		UCB	monthly	

## 4.2 Sampling Locations

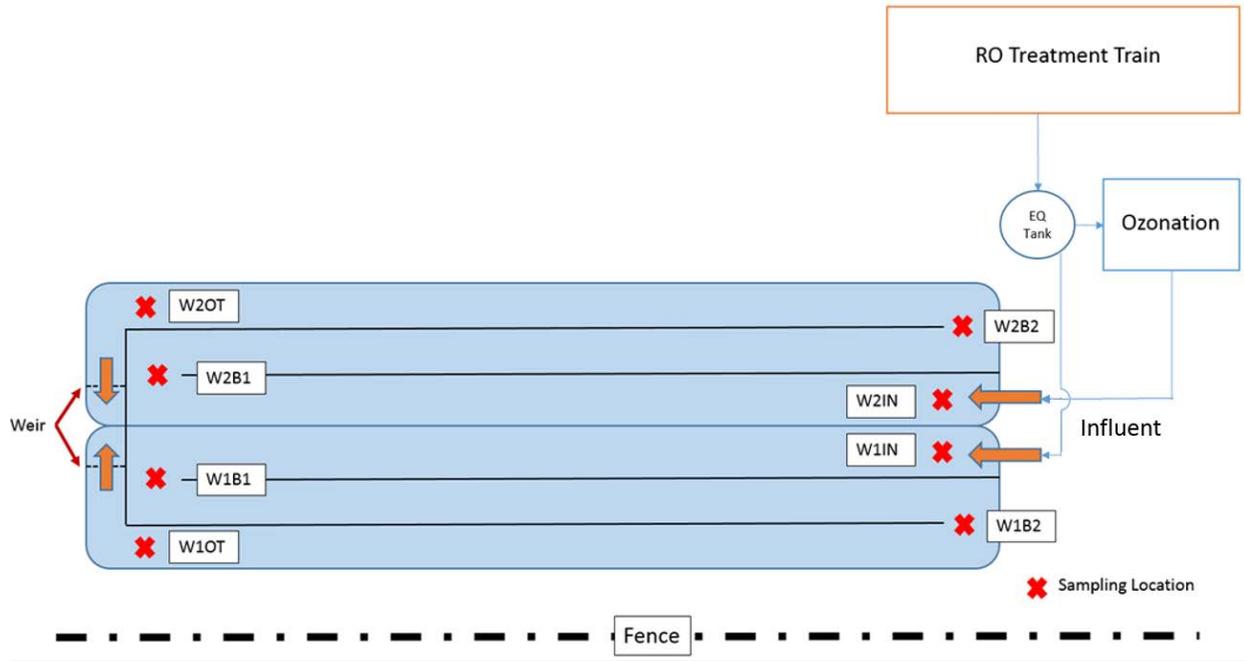
The sampling stations that will be used for this study are shown in Table 4 and Figure 3. These stations represent the minimum locations to be monitored. Stations may be added or subtracted as needed to achieve the study objectives. All stations will be sampled at the same initial frequency, although the frequency of sampling may be altered during the course of the study (i.e. frequency of sampling at baffle sites may be reduced during winter months) as needed to achieve study objectives within project resources.

**Table 4.** Sampling locations

Station Name	Station ID	Grab or Composite Type	Purpose of Station
Wetland 1 Inlet (SVAWPC RO Concentrate)	W1IN	24-hr composite	Monitoring concentrations in ROC being added to the treatment cells
Wetland 1 Baffle 1	W1B1	1-3 grab samples*	Monitoring concentrations in partially-treated ROC in a mixing location
Wetland 1 Baffle 2	W1B2	1-3 grab samples	Monitoring concentrations in partially-treated ROC in a mixing location
Wetland 1 Outlet	W1OT	24-hr composite	Monitoring concentrations in final treated ROC of system with treatment cell only
Wetland 2 Inlet	W2IN	24-hr composite	Monitoring concentrations of ROC treated with AOP only, prior to entering the wetland
Wetland 2 Baffle 1	W2B1	1-3 grab samples	Monitoring concentrations in partially-treated ROC in a mixing location
Wetland 2 Baffle 2	W2B2	1-3 grab samples	Monitoring concentrations in partially-treated ROC in a mixing location
Wetland 2 Outlet	W2OT	24-hr composite	Monitoring concentrations in final treated ROC of system with AOP and treatment cell

\*Grab samples will be collected within the wetland cells (W1B1, W1B2, W2B1, W2B2). Tracer tests will be used to determine whether a single sample from the center of the flow path is representative. If necessary, multiple samples (proposed: 3) will be taken at each station and combined into a composite sample for each site.

**Figure 3:** Schematic of sampling locations in the open-water treatment cell.



### 4.3 Sampling Schedule

Monitoring for the study will consist of three broad phases. There will be an assessment of initial conditions when the treatment cells become operational. Following this time zero (T-0) sample collection, the treatment cells will be monitored for nitrate and pH only for several months until these measurements indicate that a biomat has developed. Once the biomat has developed, all of the target analytes will be measured on a regular schedule for the rest of the study. An approximate sampling schedule is shown in Table 5. This schedule may be altered as needed to achieve the scientific objectives of the study.

**Table 5. Sampling Schedule**

<b>Activity</b>	<b>Date</b>	<b>Sampling Frequency</b>	<b>Stations to be monitored</b>
Engineered treatment cells are operational	July 2017	N/A	N/A
T-0 sample collection (all target analytes)	July 2017 (or within 1 week after flow is introduced)	Single sampling point (T-0)	All sites
Limited water quality sample collection until treatment cells are functioning (Nitrate, nitrite, orthophosphate, and pH monitoring only)	July 2017 - August 2017	Biweekly	Inlet and outlet of the treatment wetlands
Water quality sample collection (all target analytes)	August 2017 - October 2018 (15 months)	See Table 6	All sites, except inlet and outlet sites only for toxicity and CECs of state/regional concern

**Table 6.** Field and quality assurance sample collection schedule.

Event ID	Planned or Actual Sampling Date	Field Sample Collection								QC Sample Collection	
		General WQ	Dissolved Nutrients	Total Nutrients	Monthly Metals	Se, CN	Hg, Zn, Pb	Surrogates & Indicators	CECs	Field Duplicates	Field Blanks
<b>Sampling Schedule for Phase I</b>											
T0	2017-07-27	8	8	8	8	4		8	4	All parameters at W1IN	
T1	2017-08-30	8	8		8			8			
T2	2017-09-27	8	8		8			8		All monthly parameters at W1B1	
T3	2017-10-18	8	8		8			8			
T4	2018-11-17	8	8	8	8	4		8	4	All parameters at W1OT	
T5	2018-04-18	8	8	8	8	4		8	4	All parameters at W2OT	
T6	2018-06-05	8	8	8	8	4		8	4		
T7	2018-06-19	8	8	8	8	4		8	4	All parameters at W2IN	
T8	2018-07-10	8	8	8	8	4		8	4		
T9	2018-07-31	8	8	8	8	4		8	4	All parameters at W1IN	

	<b>Total Samples</b>	<b>80</b>	<b>80</b>	<b>56</b>	<b>80</b>	<b>28</b>	<b>-</b>	<b>80</b>	<b>28</b>		
	Number of Sampling Rounds	10	10	7	10	7	-	10	7		
	# of QC Samples	6	6	4	6	4	-	6	4		
	<b>Sampling Schedule for Phase II</b>										
T10	2018-08-14	8	8	8	8	4	4	8	4		Hg, Zn, Pb
T11	2018-08-29	8	8	8	8	4	4	8	4	All monthly parameters at W1B2 + Hg, Zn, Pb	Hg, Zn, Pb
T12	2018-10-03	8	8		8			8	4	All parameters at W1OT	
T13	2018-11-14	8	8	8	8	4	4	8	4		Hg, Zn, Pb
Cancelled	2018-12										
T14	2019-01	8	8		8			8			
Cancelled	2019-02										
T15	2019-03	8	8	8	8	4	4	8	4	All parameters at W2IN	Hg, Zn, Pb
T16	2019-04	8	8		8			8			
T17	2019-05	8	8	8	8	4	4	8	4	All parameters at W1IN	Hg, Zn, Pb
T18	2019-06	8	8		8			8			
T19	2019-07	8	8		8			8		All monthly parameters at W2B2	

T20	2019-08	8	8	8	8	4		8	4	Hg, Zn, Pb	Hg, Zn, Pb
T21	2019-09	8	8		8			8			
T22	2019-10	8	8		8			8		All monthly parameters at W2B1	
	<b>Total Samples</b>	<b>104</b>	<b>104</b>	<b>48</b>	<b>104</b>	<b>24</b>	<b>20</b>	<b>104</b>	<b>28</b>		
	Number of Sampling Rounds	13	13	6	13	6	5	13	7		
	# of QC Samples	9	9	5	9	5	6	9	5		

## 5. Field Sampling Methods & Field QA/QC

Samples collected at the inlet and outlet of each treatment wetland will be collected using an automatic 24-hour time-weighted compositor provided by UC Berkeley. Samples collected within the compositor will be decanted into a single large container, mixed, and subsequently subsampled on site at the ozone unit trailer bench space. The composite sampler will be stored on site in between sampling periods.

Samples collected within each treatment wetland will be collected manually at a single time point mid-day, as a composite of 1-3 grab samples collected as a cross section perpendicular to the direction of flow (Figure 3). Tracer tests will be used to determine whether a single sample from the center of the flow path is representative. If necessary, multiple samples (proposed: 3) will be taken at each station and combined into a composite sample for each site.

Dissolved oxygen, pH, and temperature will be collected in the field using hand-held multimeters.

Field sampling observations and collection information will be recorded on the Field Data Sheet (see attachment). Weather conditions will be measured and recorded on the Field Data Sheet also. Information on the prior day weather will also be recorded when the compositor is set up 24 hours prior to sample collection.

Field duplicates and field blanks will be collected approximately quarterly at a minimum frequency of 1 QC sample per 20 field samples. Details for how the QA/QC samples will be collected are listed below.

- Field duplicates at inlet and outlet stations will be collected by filling two composite containers within 15 minutes using the autosampler.
- Field duplicates at interior stations will be collected by taking two grab samples within 15 minutes.
- Field duplicates at the inlet and outlet stations are collected as 2 additional samples. Field duplicates at the interior stations are collected as 1 additional grab sample.
- Field blanks at inlet and outlet stations will be collected by pumping DI water through the autosampler (rapidly, not over 24-hours) to fill a composite container.
- Field blanks at interior stations will be collected by taking grab samples of DI water.
- Field duplicates and blanks are not scheduled for toxicity. Internal lab controls serve this function.

- Field duplicates for CECs of state and regional concern will be taken at the inlet and outlet stations only, because these parameters will only be measured at inlets and outlets.
- The schedule and locations for field QA/QC samples is shown in Table 6.

## 5.1 Indirect Measurements

Water quality measurements will also be taken indirectly as part of standard SCVWD sampling of RO concentrate. pH, conductivity, turbidity, and temperature are measured online by SCVWD at the RO reject combined flow location. Conductivity (2510B) and turbidity (2130B) are measured monthly. Manual temperature readings are not currently planned but can be added if necessary.

## 6. Sample Labeling

The sample ID will be used to identify the unique time and location at which a particular sample is taken. A bottle number or analyte ID can be added to this sample ID to uniquely identify each bottle collected in the field, and each subsample created in the laboratory for analyses. The subsample ID (i.e. the sample ID + an analyte ID) can be used to uniquely identify each result value.

### Sample ID

ROC-TX-SiteID-Z, where:

- TX = sampling round number, beginning with T0; samples of nitrate and pH collected during the startup period will be labeled with a letter (TA, TB, TC, TD); samples collected once full sampling begins will be labeled sequentially with a number (T1, T2, T3, T4,...)
- SiteID = specified in Table X
- Z = additional code to specify replicates (1, 2, etc.) or field blanks (B)

### Container Label

ROC-TX-SiteID-Z-ContainerID, where:

- ContainerID = [Lab] + [Bottle #] as specified in Table 3

Each container will also be labeled with the sampling date, time, and initials of sample collector

### Subsample ID

ROC-TX-SiteID-Z-AnalyteID, where:

- Analyte ID = analyte name or an abbreviation specified by the laboratory

## **7. Sample Handling & Custody Protocol**

Samples will be collected in the field by UC Berkeley, Stanford, and SCVWD staff and stored covered and on ice in the field. At least one staff person from each of these three laboratories will be present for each sampling round to collect their samples and transport them to their laboratory (barring exceptions). At least one staff person will be designated to set up the composite samplers the day before sample collection. The District will be notified prior to each sampling or equipment set-up date.

Analytical samples will be aliquoted from field containers on site in the ozone unit trailer, and subsequently filtered, preserved, or otherwise processed as needed and described in Table 3. Field sample handling and hold time requirements, as well as the final laboratory destination, are defined in Table 3.

Sample bottles and any preservative for lab sample processing will be provided by each respective laboratory.

Samples will not be preserved or filtered in the field. Due to the proximity of the laboratories, the samples will be returned to the laboratories immediately after sample collection for subsampling, filtering, and preservation. UCB intends to run some informal checks on nutrient and metals samples to determine if field-filtering samples makes a significant difference in the results compared to lab-filtered samples.

## **8. Analytical Methods and Laboratories**

Analytical methods, method detection limits, and laboratories responsible for each analysis are outlined in Table 3.

## 9. Laboratory QA/QC and Measurement Quality Objectives (MQOs)

A lab blank and lab duplicates will be analyzed with each sample set or lab batch. Recommended sample container volumes should be sufficient to account for duplicate analyses.

Target measurement quality objectives are described below. These MQOs may be altered as needed to achieve the scientific objectives of the study.

Sensitivity: Analytical methods used should have reporting levels equal to or better (lower) than the MRL or LOQ targets listed in Table 3.

Blanks: Target analytes should not be detected at concentrations above the MDL. If analytes are found in blanks and cannot be reduced or removed through method improvements, results may still be reported so long as field sample results are at least 3x higher than the blank result, and field sample results are flagged to indicate possible contribution from blank contamination.

Precision: The Relative Percent Difference (RPD) between field duplicate results should be <50%. Field duplicate samples will be collected at a frequency of at least 1 per 20 samples. The RPD between laboratory duplicate results should be <35%.

Accuracy: The percent recovery for matrix spikes should be between 65-135%. Matrix spikes should be added at concentrations in a range relevant to field samples (ideally between ~2x to 20x maximum field concentrations, once expected concentration ranges are known). The RPD for CRMs or matrix spike duplicates should be <35%. When CRMs are not available, performance testing (PT) standards or other externally cross validated sample types should be considered.

Completeness: Useable data should be available for >80% of the planned field and QC samples.

## 10. 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. Costa Mesa, CA.

Becker, A. M., S. Gerstmann, and H. Frank. 2008. Pefluorooctane surfactants in waste waters, the major source of river pollution. *Chemosphere* 72:115-121.

Budd R, Ensminger M, Wang D, Goh KS. 2015. Monitoring fipronil and degradates in California surface waters, 2008–2013. *J Environ Qual* 44:1233–1240.

Custer CM, Custer TW, Schoenfuss HL, Poganski BH, Solem L. 2012. Exposure and effects of perfluoroalkyl compounds on tree swallows nesting at Lake Johanna in east central Minnesota, USA. *Reprod Toxicol* 33:556-562.

Dickenson ER, Drewes JE, Sedlak DL, Wert EC, Snyder SA. 2009. Applying surrogates and indicators to assess removal efficiency of trace organic chemicals during chemical oxidation of wastewaters. *Environ Sci Technol* 43:6242-6247.

Dickenson ER, Snyder SA, Sedlak DL, Drewes JE. 2011. Indicator compounds for assessment of wastewater effluent contributions to flow and water quality. *Water Res* 45:1199-1212.

Ensminger MP, Budd R, Kelley KC, Goh KS. 2013. Pesticide occurrence and aquatic benchmark exceedances in urban surface waters and sediments in three urban areas of California, USA, 2008–2011. *Environ Monit Assess* 185:3697–3710.

Gunasekara AS, Truong T. 2007. Environmental Fate of Fipronil. Environmental Monitoring Branch Department of Pesticide Regulation. Sacramento, CA.

Holmes RW, Anderson BS, Phillips BM, Hunt JW, Crane DB, Mekebri A, Connor V. 2008. Statewide investigation of the role of pyrethroid pesticides in sediment toxicity in California's urban waterways. *Environ Sci Technol* 42:7003–7009.

Houtz EF, Sutton R, Park JS, Sedlak M. 2016. Poly- and perfluoroalkyl substances in wastewater: Significance of unknown precursors, manufacturing shifts, and likely AFFF impacts. *Water Res* 95: 142-149.

Jasper JT, Jones ZL, Sharp JO, Sedlak DL. 2014. Biotransformation of trace organic contaminants in open-water unit process treatment wetlands. *Environ Sci Technol* 48:5136-5144.

Jasper JT, Jones, ZL, Sharp, JO, Sedlak DL. 2014a. Nitrate Removal in Shallow, Open-Water Treatment Wetlands. *Environ Sci Technol* 48: 11512-11520.

Jasper JT, Sedlak, D.L. 2013. Phototransformation of Wastewater-Derived Trace Organic Contaminants in Open-Water Unit Process Treatment Wetlands. *Environ Sci Technol* 47(19) 10781-10790.

Kuivila KM, Hladik ML, Ingersoll CG, Kemble NE, Moran PW, Calhoun DL, Nowell LH, Gilliom RJ. 2012. Occurrence and potential sources of pyrethroid insecticides in stream sediments from seven U.S. metropolitan areas. *Environ Sci Technol* 46:4297–4303.

Markle JC, van Buuren BH, Moran K, Barefoot AC. 2014. Pyrethroid pesticides in municipal wastewater: A baseline survey of publicly owned treatment works facilities. In *Describing the Behavior and Effects of Pesticides in Urban and Agricultural Settings*, Vol 1168. ACS Symposium Series. American Chemical Society, Washington, DC, pp 177–194.

Martin JW, Mabury SA, Solomon KR, Muir DCG. 2003. Bioconcentration and tissue distribution of perfluorinated acids in rainbow trout (*Oncorhynchus mykiss*). *Environ Toxicol Chem* 22: 196-204.

Martin JW, Whittle DM, Muir DCG, Mabury SA. 2004. Perfluoroalkyl contaminants in a food web from Lake Ontario. *Environ Sci Technol* 38: 5379-5385.

Newsted JL, Jones PD, Coady K, Giesy JP. 2005. Avian toxicity reference values for perfluorooctane sulfonate. *Environ Sci Technol* 39(23): 9357-9361.

Sadaria AM, Sutton R, Moran KD, Teerlink J, Brown JV, Halden RU. 2016. Passage of fiproles and imidacloprid from urban pest control uses through wastewater treatment plants in northern California, USA. *Environ Toxicol Chem* DOI: 10.1002/etc3673.

SCCWRP. 2015. Screening Study for Constituents of Emerging Concern (CECs) in Selected Freshwater Rivers in the Los Angeles Region – Phase 2. Final Report, California State Water Quality Control Board Contract Agreement 12-105-140. Southern California Coastal Water Research Project, Costa Mesa, CA.

Schultz, M. M., C. P. Higgins, C. A. Huset, R. G. Luthy, D. F. Barofsky, and J. A. Field. 2006. Fluorochemical Mass Flows in a Municipal Wastewater Treatment Facility. *Environmental Science & Technology* 40:7350-7357.

Sedlak M, Greig D. 2012. Perfluoroalkyl compounds (PFCs) in wildlife from an urban estuary. *J Environ Monit* 14: 146-154.

Sedlak et al. submitted. Per- and polyfluoroalkyl substances (PFASs) in San Francisco Bay Wildlife: Temporal Trends, Exposure Pathways, and Notable Presence of Precursor Compounds.

SFBRWQCB. 2012. San Francisco Bay Nutrient Management Strategy. Francisco Bay Regional Water Quality Control Board, Oakland, CA. Published online: [http://sfbaynutrients.sfei.org/sites/default/files/Nutrient\\_Strategy%20November%202012.pdf](http://sfbaynutrients.sfei.org/sites/default/files/Nutrient_Strategy%20November%202012.pdf).

SFBRWQCB. 2015. San Francisco Bay Basin (Region 2) Water Quality Control Plan. Incorporating all amendments approved by the Office of Administrative Law as of March 20, 2015. Francisco Bay Regional Water Quality Control Board, Oakland, CA. Published online: [http://www.waterboards.ca.gov/sanfranciscobay/basin\\_planning.shtml](http://www.waterboards.ca.gov/sanfranciscobay/basin_planning.shtml).

Supowit SD, Sadaria AM, Reyes EJ, Halden RU. 2016. Mass balance of fipronil and total toxicity of fipronil-related compounds in process streams during conventional wastewater and wetland treatment. *Environ Sci Technol* 50:1519–1526.

Sutton R, Sedlak M, Sun J, Lin D. 2017. Contaminants of Emerging Concern in San Francisco Bay: A Strategy for Future Investigations. 2017 Revision. Contribution #815. San Francisco Estuary Institute, Richmond, CA.

Weston DP, Lydy MJ. 2014. Toxicity of the insecticide fipronil and its degradates to benthic macroinvertebrates of urban streams. *Environ Sci Technol* 48:1290–1297.