1. Project Summary or Abstract

Sport fish in the San Francisco Bay are exposed to pollution derived from the surrounding urban landscape, and are consumed by people, particularly in low-income and immigrant communities, as well as by apex predators like cormorants and harbor seals. Routine sport fish contaminant monitoring and human health fishing advisories focus on just eight contaminants; investigations of wildlife collected from highly urbanized coastal southern California sites indicate that these regularly monitored contaminants make up a small fraction of the total number of bioaccumulative contaminants present in tissue. The proposed study will employ a novel non-targeted analytical approach to examine samples of Bay sport fish to identify a broad array of persistent and bioaccumulative contaminants of emerging concern (CECs). Analysis of cormorant eggs and harbor seals will be used to assess the potential for biomagnification of these CECs within the foodweb. Comparison of the contaminant profiles of fish species with different behavior and feeding habits and collected from different sites in the Bay will be used to identify pollution hotspots. Information about the potential sources and pathways of these CECs will be obtained through comparison with findings from the PIs' ongoing study of near-shore sediment samples collected from San Francisco Bay. Results will be presented to established committees of international experts and local stakeholders with expertise in CECs, ecotoxicology, and sport fish monitoring and consumption risks. Potential outcomes may include the development of fish consumption advisory tissue levels for newly identified contaminants, follow-up research from the scientific community to fill targeted data gaps, and/or pollution prevention activities. A successful demonstration for the San Francisco Bay could lead to later use of this general approach across the state.

2. Background

As the largest estuary on the western coast of the Americas, San Francisco Bay provides habitat for numerous populations of fish and wildlife living in the midst of an urban area supporting seven million people. The Bay receives continuous inputs of pollutants including CECs from the surrounding urban environment, trapping persistent chemicals and potentially exposing inhabitants to increased risks. Some Bay Area residents, particularly from low-income and immigrant communities, regularly consume sport fish caught from the Bay; this important protein source can expose them to contaminants. State and local entities take steps to reduce human health risks relating to eight contaminants in sport fish, including posting of fish advisories at popular fishing sites. Regular Bay sport fish monitoring for these advisories is conducted by the Regional Monitoring Program for Water Quality in San Francisco Bay (RMP), a collaboration among the Regional Water Quality Control Board, the regulated discharger community, and independent scientists of San Francisco Estuary Institute. The RMP also monitors the Bay for CECs; studies of Bay sport fish have detected persistent and bioaccumulative halogenated organic compounds (HOCs), including polybrominated diphenyl ethers [1], perfluoroalkyl substances [2], and polyhalogenated carbazoles [3]. People who regularly eat Bay sport fish are likely exposed to these, as are apex predators such as cormorants and harbor seals. Are other, as yet unidentified HOCs accumulating in Bay sport fish consumed by humans and wildlife? Which of these HOCs might pose the greatest risk to human and non-human populations? Are there hotspots of contamination within the Bay? Our recent study of bottlenose dolphin blubber from coastal Southern California, habitat with a similarly

strong urban influence, identified more than 300 HOCs, excluding regularly monitored legacy contaminants like DDTs and PCBs [4]. Eighty-six percent of the HOCs, including 133 anthropogenic chemicals and 41 natural products, are not regularly monitored [4]. We expect that there are many similarly unmonitored HOCs in San Francisco Bay. Because regularly monitored contaminants represent a small subset of full contaminant exposure, many unknown or unrecognized contaminants with the potential to cause physiological harm fall outside routine ecosystem monitoring efforts.

3. Project Goals and Objectives

The goal of this study is to use an innovative non-targeted analytical approach to identify the presence of unexpected HOCs typically not monitored in San Francisco Bay sport fish, cormorants and harbor seals and to assess the potential for human and wildlife exposures.
Objective 1: Identify typically unmonitored HOCs in sport fish in San Francisco Bay.
Objective 2: Evaluate their biomagnification potential through food chains in San Francisco Bay.
Objective 3: Test if there are distinguishable differences in the HOC profiles among sport fish with different diets and habits (feeding in benthic vs. pelagic zones; species with high site fidelity vs. those with wide-ranging, ocean-migrating habits).
Objective 4: Determine spatial difference of HOC profiles (South, Central, and North San Francisco Bay, as well as Tomales Bay) to identify hotspots of pollution.
Objective 5: Determine potential sources and pathways of HOCs by comparison with those identified in ongoing collaboration among the PIs to analyze sediment from San Francisco Bay.

4. Methods

Sample Collection

Samples include sport fish, cormorant eggs, harbor seal blubber, and sediment (Table 1). Sport fish samples will be obtained by leveraging the RMP's 2019 sport fish sample collection effort. Three species will be targeted: Shiner surfperch (*Cymatogaster aggregata*), an abundant and popular benthic-feeding sport fish that exhibits high site fidelity, useful for assessing regional differences; striped bass (*Morone saxatilis*), a popular sport fish that provides an integrated signal for higher trophic predators due to its wide-foraging behavior and opportunistic consumption of prey fish; and northern anchovy (*Engraulis mordax*), an abundant sport fish that is prey for larger fish and predators. Samples will be collected at up to three popular fishing sites within the Bay (Figure 1). Additional samples will be collected at a reference site with relatively low urban influence, Tomales Bay (Figure 1).

Cormorant (*Phalacrocorax auritus*) egg samples will be obtained by leveraging the RMP's 2018 sample collection effort. Samples will be obtained from three regularly monitored sites (Figure 1): Richmond Bridge (Central Bay), Wheeler Island (Suisun Bay/Delta), and Don Edwards Wildlife Refuge (South Bay). Harbor seal (*Phoca vitulina*) blubber samples will be collected during capture events in two locations (Figure 1), a seal colony in the South Bay (Corkscrew Slough), and a reference site (Tomales Bay). Finally, an ongoing study funded by the RMP, to identify CECs in sediment collected from near-shore sites in the southern Bay, will be supplemented through analysis of samples collected at the reference site, Tomales Bay (Figure 1).

Chemical Analysis

Analysis of HOCs will be performed using previously developed and successfully implemented extraction, cleanup, and non-targeted instrumental methods [4-9]. Final extracts will be analyzed using a LECO Pegasus 4D comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GC×GC/TOF-MS) system. The non-targeted analysis generates large datasets with thousands of mass spectra per sample. Therefore, we recently developed and optimized a filtering algorithm to isolate HOCs from the thousands of other chromatographic peaks and associated mass spectra (Figure 2). The filtration reduces the dataset size to approximately 5% of the original (Figure 3) and substantially reduces the time required for manual validation of the mass spectra identities. Contaminant loads and profiles will be analyzed via statistical comparisons (hierarchical clustering, K-means clustering, and principal components analysis).

5. Project Outcomes (to science, specific communities, regulators or the general public)

HOCs identified will be prioritized based on the level of confidence in the identification as well as the frequency and intensity of contaminant signals, and will be reviewed by three RMP advisory panels including leading international experts. The RMP's Emerging Contaminants Workgroup uses a risk-based framework to classify CECs in the Bay and recommend monitoring and management actions [10]. The RMP's Exposure and Effects Workgroup focuses on the biological impacts observed in the Bay, and is informed by top ecotoxicologists. The RMP's Sport Fish Strategy Team guides targeted contaminant monitoring in fish in coordination with the California Office of Environmental Health Hazard Assessment (OEHHA), the agency charged with developing risk-based fish consumption guidance and advisories. By bringing the diverse, independent expertise of these established RMP groups to bear, a risk-based review of the newly identified Bay contaminants would allow for prioritization of those suspected of the greatest potential for harm to people or wildlife. Should a contaminant identified in the proposed study be a human health risk with an established oral reference dose, OEHHA could establish an advisory tissue level that would be used in advisories about the safety of consuming different species of fish. For HOCs with major data gaps, significant detections in San Francisco Bay would be likely to spur additional, independent research within the scientific community.

A successful demonstration for the San Francisco Bay could lead to later use of this general approach across the state. By focusing on sport fish, we target a matrix with direct impacts to both people and wildlife who consume Bay fish. In the Bay Area, residents who regularly eat these fish include members of low income and immigrant communities; assuring the safety of these fish is important for the health of these vulnerable populations, and is essential to protecting fishing as a beneficial use of the Bay. Findings from this study will be disseminated to: 1) state agencies and programs involved in pollution prevention, including California's unique Safer Consumer Products Program; 2) the RMP stakeholder community of over 1,000 local decision-makers, including water quality managers within the regulatory and regulated communities; and 3) the general public. Where detected CECs can be linked to potential sources or uses, pollution prevention efforts may be possible, with consumer education or regulatory activities undertaken by informed entities.

References

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Table 1. Proposed samples: species, tissue type, sampling location, number of samples, and composite or not for contaminant analysis. *Tail, head, and viscera removed.

Matrix	Species	Tissue type	Site Locations	Number of Samples/Site	Composite
Fish	Shiner surfperch (popular sportfish)	Whole fish*	South Bay	5	Yes
			San Leandro Bay	5	
			Tomales (reference)	3	
	Striped bass (popular sportfish)	Fillets (skin off)	South Bay	5	Yes
			San Leandro Bay	5	
			Oakland/ SF Waterfront	5	
			Tomales (reference)	3	
	Anchovy (prey fish, also popular sportfish)	Whole fish*	South Bay	5	Yes
			San Leandro Bay	5	
			Tomales	3	
Pinnepeds	Harbor seal	Blubber	South Bay	10	No
			Tomales (reference)	3	
Birds	Cormorant	Egg	South Bay	2	Yes
			Central Bay	2	
			Delta	2	
Sediment		Sediment	South Bay margins	35	No
			Tomales (reference)	3	

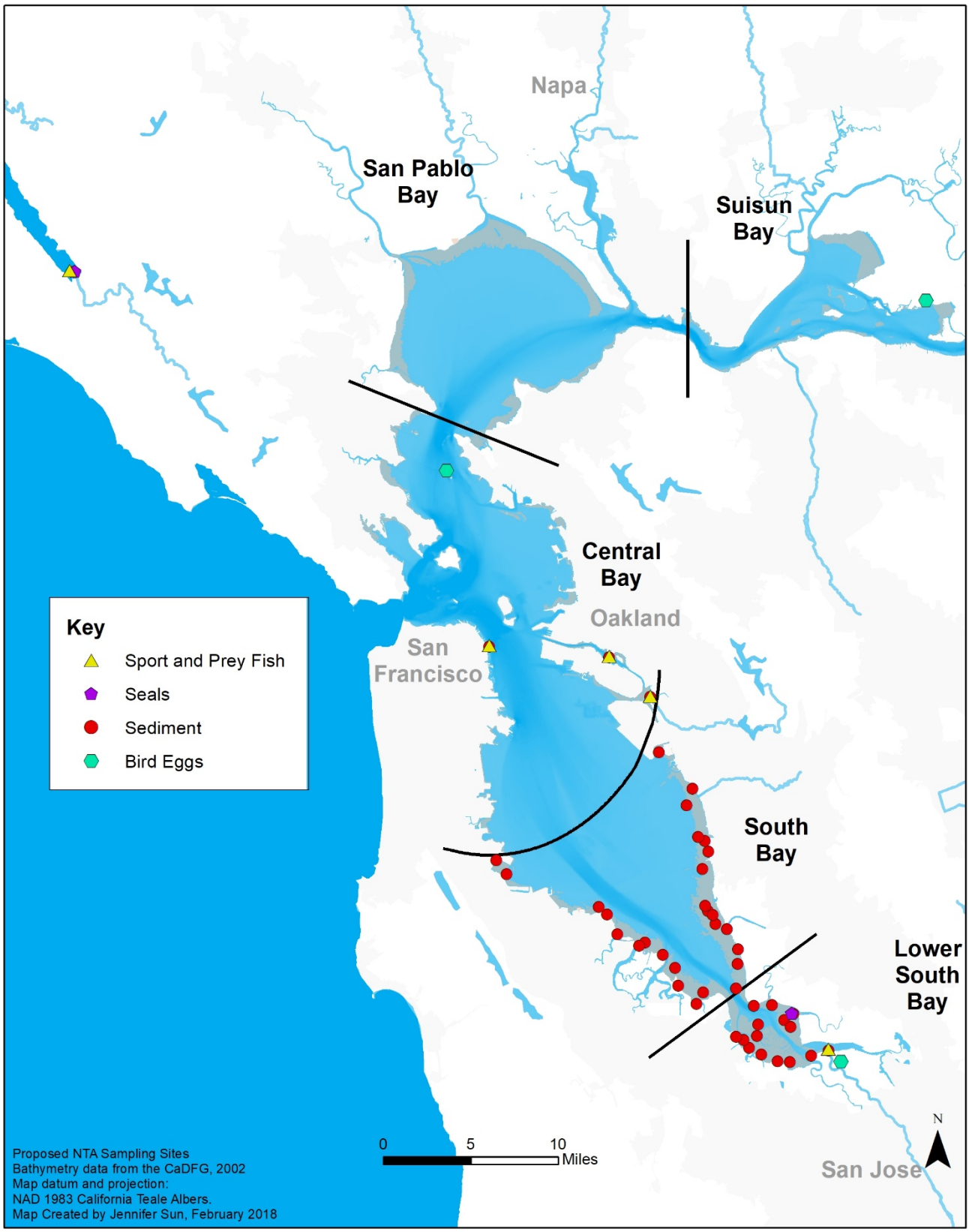

Figure 1. Proposed sampling sites in San Francisco Bay.

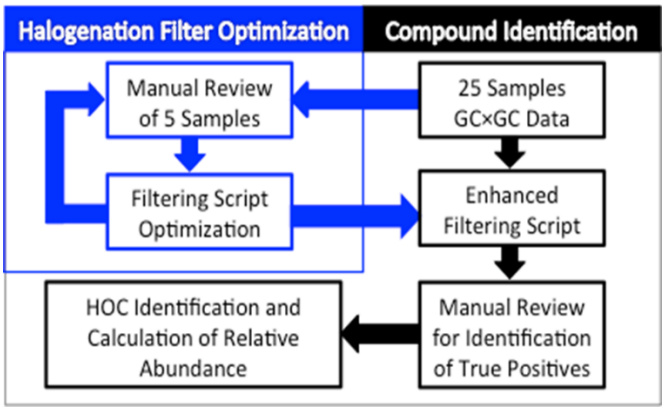

Figure 2. GC×GC/TOF-MS data analysis scheme implemented with the filtering script to automatically select mass spectra of HOCs.

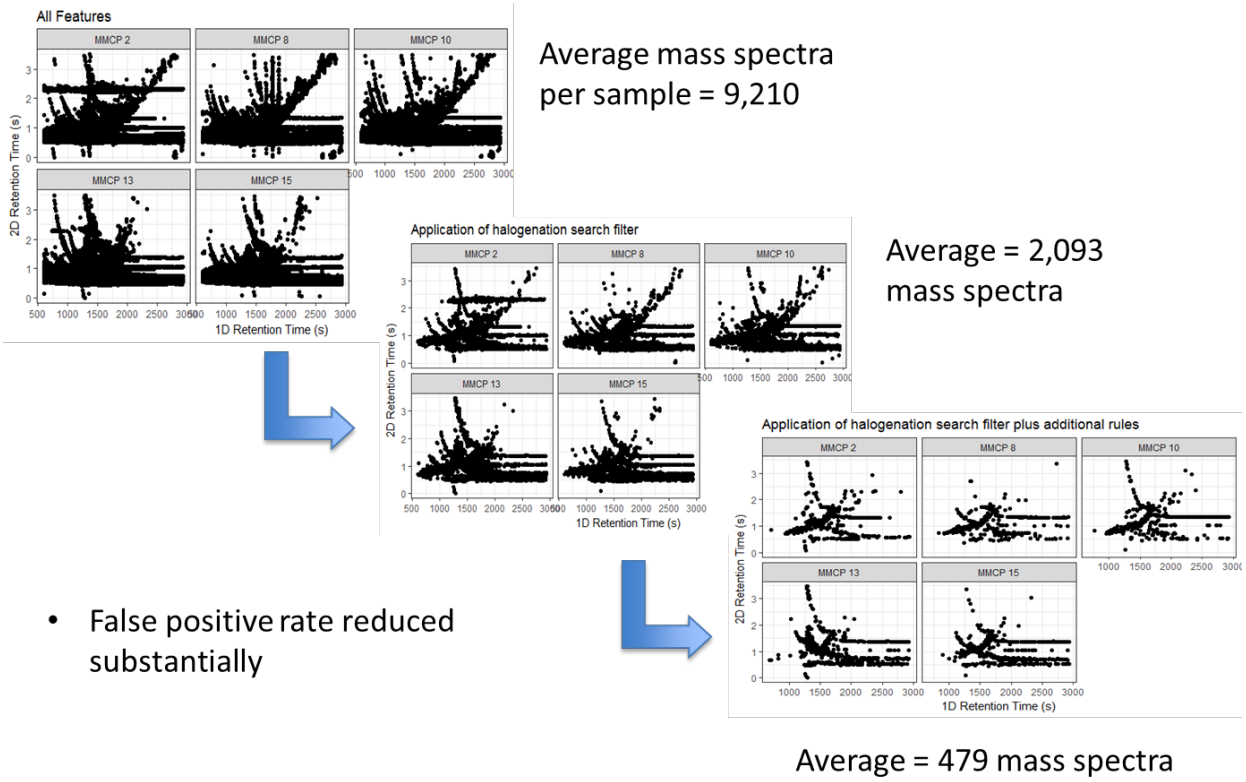

Figure 3. Data reduction of mass spectra by the filtering script. The script isolates compounds containing halogens.