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Sampling and Analysis Plan for a Screening Study of Bioaccumulation on the California Coast

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SAMPLING AND ANALYSIS PLAN FOR A SCREENING STUDY OF BIOACCUMULATION ON THE CALIFORNIA COAST

The Bioaccumulation Oversight Group (BOG)

Surface Water Ambient Monitoring Program

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THE BIOACCUMULATION OVERSIGHT GROUP

TERRY FLEMING
BOB BRODBERG
MICHAEL LYONS
CHRIS FOE
MARY ADAMS
MARK STEPHENSON
GARY ICHIKAWA
JAY DAVIS
DAVE CRANE
CASSANDRA LAMERDIN
JENNIFER DOHERTY
MARCO SIGALA
BILLY JAKL
AUTUMN BONNEMA
DYLAN SERVICE
KEN SCHIFF
AROON MELWANI

I. INTRODUCTION

This document presents a plan for sampling and analysis of sport fish in a two-year screening survey of bioaccumulation on the California coast. This work will be performed as part of the State Water Resources Control Board's Surface Water Ambient Monitoring Program (SWAMP). This effort is part of a new long-term Bioaccumulation Monitoring Project that is providing comprehensive monitoring of bioaccumulation in California water bodies.

Oversight for this Project is being provided by the SWAMP Roundtable. The Roundtable is composed of State and Regional Board staff and representatives from other agencies and organizations including USEPA, the Department of Fish and Game, the Office of Environmental Health Hazard Assessment, and the University of California. Interested parties, including members of other agencies, consultants, or other stakeholders are also welcome to participate.

The Roundtable has formed a subcommittee, the Bioaccumulation Oversight Group (BOG) that focuses on the Bioaccumulation Monitoring Project. The BOG is composed of State and Regional Board staff and representatives from other agencies and organizations including USEPA, the Department of Fish and Game, the Office of Environmental Health Hazard Assessment, and the San Francisco Estuary Institute. The members of the BOG individually and collectively possess extensive experience with bioaccumulation monitoring.

The BOG has also convened a Bioaccumulation Peer Review Panel that is providing programmatic evaluation and review of specific deliverables emanating from the Project, including this Sampling Plan. The members of the Panel are internationally-recognized authorities on bioaccumulation monitoring.

The BOG was formed and began developing a strategy for designing and implementing a statewide bioaccumulation monitoring program in September 2006. To date the efforts of the BOG have been focused on a two-year screening survey of bioaccumulation in sport fish of California lakes and reservoirs (Davis et al. 2008). Under this effort, fish were collected in the summers of 2007 and 2008. A draft report on results from the first year is currently in review. A final report covering both years of the survey will be prepared in the fall of 2009.

II. GENERAL ASPECTS OF THE SWAMP BIOACCUMULATION MONITORING PROJECT

A. Addressing Multiple Beneficial Uses

Bioaccumulation in California water bodies has an adverse impact on both the fishing and aquatic life beneficial uses (Davis et al. 2007). The fishing beneficial use is affected by human exposure to bioaccumulative contaminants through consumption of sport fish. The aquatic life beneficial use is affected by exposure of wildlife to bioaccumulative contaminants, primarily piscivorous species exposed through consumption of small fish. Different indicators are used to monitor these different types of exposure. Monitoring of status and trends in human exposure is accomplished through sampling and analyzing sport fish. On the other hand, monitoring of status and trends in wildlife exposure can accomplished through sampling and analysis of wildlife prey (small fish, other prey species) or tissues of the species of concern (e.g., bird eggs or other tissues of juvenile or adults of the species at risk).

Over the long-term, a SWAMP bioaccumulation monitoring program is envisioned that assesses progress in reducing impacts on both the fishing and aquatic life beneficial uses for all water bodies in California. In the near-term, however, funds are limited, and there is a need to demonstrate the value of a comprehensive statewide bioaccumulation monitoring program through successful execution of specific components of a comprehensive program. Consequently, the BOG has decided to focus on sampling that addresses the issue of bioaccumulation in sport fish and impacts on the fishing beneficial use. This approach is intended to provide the information that the state government and the public would consider to be of highest priority. Monitoring focused on evaluating the aquatic life beneficial use will be included in the Project when expanded funding allows a broader scope.

B. Addressing Multiple Monitoring Objectives and Assessment Questions for the Fishing Beneficial Use

The BOG has developed a set of monitoring objectives and assessment questions for a statewide program evaluating the impacts of bioaccumulation on the fishing beneficial use (Table 1). This assessment framework is consistent with frameworks developed for other components of SWAMP, and is intended to guide the bioaccumulation monitoring program over the long-term. The four objectives can be summarized as 1) status; 2) trends; 3) sources and pathways; and 4) effectiveness of management actions.

Over the long-term, the primary emphasis of the statewide bioaccumulation monitoring program will be on evaluating status and trends. Bioaccumulation monitoring is a very effective and essential tool for evaluating status, and is often the most cost-effective tool for evaluating trends. Monitoring status and trends in bioaccumulation will provide some information on sources and pathways and effectiveness of management actions at a broader geographic scale. However, other types of monitoring (i.e., water and sediment monitoring) and other programs (regional TMDL programs) are more appropriate for addressing sources and pathways and effectiveness of management actions.

In the near-term, the primary emphasis of the statewide bioaccumulation monitoring program will be on evaluating Objective 1 (status). The reasons for this are:

1. a systematic statewide assessment of status has never been performed and is urgently needed;

2. we are starting a new program and establishing a foundation for future assessments of trends;
3. past monitoring of sport fish established very few time series that are useful in trend analysis that this program could have built upon.

C. Addressing Multiple Habitat Types

SWAMP has defined the following categories of water bodies:

- lakes and reservoirs;
- bays and estuaries;
- coastal waters;
- large rivers;
- wadeable streams; and
- wetlands.

Due to their vast number, high fishing pressure, and a relative lack of information on bioaccumulation (Davis et al. 2007), lakes and reservoirs were identified as the first priority for monitoring. Coastal waters have been selected as the next priority, due to their importance for fishing and a relative lack of past monitoring. A Coastal Fish Contamination Monitoring Program was in initiated in 1998 (Gassel et al. 2002). This program was developed to assess the health risks of consumption of sport fish and shellfish from nearshore waters along the entire California coast. The CFCP was considered to be a critical component of a comprehensive coastal water quality protection program, and an important opportunity to build a long-term coastal monitoring database for water quality and contaminants in fish. However, the CFCP, along with the other two major state bioaccumulation monitoring programs (the Toxic Substances Monitoring Program and the State Mussel Watch Program) were discontinued in 2003 as plans for SWAMP began to take shape. Systematic monitoring of bioaccumulation in fish on the coast was therefore only in place for a few years. Given the extensive area, multiple habitats (coastline, bays and estuaries), diversity of species to be covered, and the amount of funding available ($500,000 of SWAMP funds for sampling and analysis), the coastal waters survey is also going to be a two-year effort spanning 2009 and 2010. In 2011, SWAMP will monitor bioaccumulation in California rivers and streams. In 2012, the long-term plan calls for beginning another five-year cycle of monitoring, with another two-year lake survey.

In summary, focusing on two closely associated habitat types (the coast and bays and estuaries), one objective (status), and one beneficial use (fishing) will allow us to provide reasonable coverage and a thorough assessment of bioaccumulation in California's coastal waters over a two-year period.

III. DESIGN OF THE COASTAL WATERS SURVEY

A. Management Questions for this Survey

Three management questions have been articulated to guide the 2009-2010 survey of the status of bioaccumulation in sport fish on the California coast. These management questions are specific to this initial screening effort.

One major difference between this set of questions and the questions for the lakes survey is that the question regarding 303(d) listing is not included here. The 303(d) question was a major driver of the design of the lakes survey. On the coast, however, 303(d) listing is not a high priority for the Water Boards.

Management Question 1 (MQ1)
Status of the Fishing Beneficial Use
For popular fish species, what percentage of popular fishing areas have low enough concentrations of contaminants that fish can be safely consumed?

Answering this question is critical to determining the degree of impairment of the fishing beneficial use across the state due to bioaccumulation. This question places emphasis on characterizing the status of the fishing beneficial use through monitoring of the predominant pathways of exposure – the popular fish species and fish areas. This focus is also anticipated to enhance public and political support of the program by assessing the resources that people care most about. The determination of percentages captures the need to perform a statewide assessment of the entire California coast. The emphasis on safe consumption calls for: a positive message on the status of the fishing beneficial use; evaluation of the data using thresholds for safe consumption; and performing a risk-based assessment of the data.

The data needed to answer this question are average concentrations in popular fish species from popular fishing locations. Inclusion of as many popular species as possible is important to understanding the nature of impairment in any areas with concentrations above thresholds. In some areas, some fish may be safe for consumption while others are not, and this is valuable information for anglers. Monitoring species that accumulate high concentrations of contaminants ("indicator species") is valuable in answering this question: if concentrations in these species are below thresholds, this is a strong indication that an area has low concentrations.

Management Question 2 (MQ2)
Regional Distribution
What is the distribution of contaminant concentrations in fish within regions?

Answering this question will provide information that is valuable in formulating management strategies for observed contamination problems. This information will allow managers to prioritize their efforts and focus attention on the areas with the most severe problems. Information on regional distribution will also provide information on sources and fate that will be useful to managers.

This question can be answered with different levels of certainty. For a higher and quantified level of certainty, a statistical approach with replicate observations in the spatial units to be compared is needed. In some cases, managers can attain an adequate level of understanding for their needs with a non-statistical, non-replicated approach. With either approach, good estimates of average concentrations within each spatial unit are needed.

Management Question 3 (MQ3)

Need for Further Sampling

Should additional sampling of bioaccumulation in sport fish (e.g., more species or larger sample size) in an area be conducted for the purpose of developing comprehensive consumption guidelines?

This screening survey of the entire California coast will provide a preliminary indication as to whether many areas that have not been sampled thoroughly to date may require consumption guidelines. Consumption guidelines provide a mechanism for reducing human exposure in the short-term. The California Office of Environmental Health Hazard Assessment (OEHHA), the agency responsible for issuing consumption guidelines, needs samples representing 9 or more fish from a variety of species abundant in a water body in order to issue guidance. It is valuable to have information not only on the species with high concentrations, but also the species with low concentrations so anglers can be encouraged to target the low species. The diversity of species on the coast demands a relatively large effort to characterize interspecific variation. Answering this question is essential as a first step in determining the need for more thorough sampling in support of developing consumption guidelines.

Overall Approach

The overall approach to be taken to answer these three questions is to perform a statewide screening study of bioaccumulation in sport fish on the California coast. Answering these questions will provide a basis for decision-makers to understand the scope of the bioaccumulation problem and will provide regulators with information needed to establish priorities for both cleanup actions and development of consumption guidelines.

It is anticipated that the screening study may lead to more detailed followup investigations of areas where consumption guidelines and cleanup actions are needed. Funding for these followup studies will come from other local or regional programs rather than the statewide monitoring budget.

B. Coordination

Through coordination with other programs, SWAMP funds for this survey are going to be highly leveraged to achieve a much more thorough statewide assessment than could be achieved by SWAMP alone.

First, this effort will be closely coordinated with bioaccumulation monitoring for Bight ’08, a comprehensive regional monitoring program for the Southern California Bight (SCB). Every five years, dischargers in the SCB collaborate to perform this regional monitoring. Bioaccumulation monitoring is one element of the Bight Program. Most of the work for this most recent round of Bight monitoring was performed in 2008. The bioaccumulation element, however, was delayed to 2009 in order to allow coordination with the SWAMP survey. The Bight group wanted to conduct sport fish sampling, but lacks the infrastructure to perform sample collection. The Bight group is therefore contributing approximately $240,000 worth of analytical work (analysis of PCBs and organochlorine pesticides in 225 samples) to the joint effort. This is allowing more intensive sampling of the Bight region than either program could achieve independently.

The SWAMP survey will also be coordinated with intensive sampling in San Francisco Bay by the Regional Monitoring Program for Water Quality in the San Francisco Estuary (RMP). The RMP conducts thorough sampling of contaminants in sport fish in the Bay on a triennial basis (see Hunt et al. [2008] for the latest results). This sampling has been conducted since 1994. The RMP will provide complete and thorough coverage of the Bay, with no additional effort by SWAMP needed. In addition, to coordinate with the SWAMP effort, the RMP will analyze additional species to allow for more extensive comparisons of the Bay with coastal areas and bays in other parts of the state. The RMP will benefit from this collaboration by SWAMP contributing: 1) a statewide dataset that will help in interpretation of RMP data and 2) a statewide report that will include an assessment and reporting of Bay data that will make production of a separate report by the RMP unnecessary. The RMP effort represents $215,000 of sampling and analysis.

In addition, the Region 4 Water Board is going to supplement the statewide survey with another $110,000 to provide for more thorough coverage of the SCB.

In all, these collaborations are more than doubling the total amount of SWAMP funding available for sampling and analysis in year 1 of the coastal waters survey. Each of the collaborating programs will benefit from the consistent statewide assessment, increased information due to sharing of resources, and efforts to ensure consistency in the data generated by the programs (e.g., analytical intercalibration).

The Bight group and the RMP each have committees that provide oversight of these long-term monitoring programs and a history of monitoring in their regions. Consequently, the sampling design in each of these regions will vary in minor ways from the design for the rest of the state. More information on these programs and the specific designs for these regions is provided in Section L.

C. Phased Approach

The survey is being conducted over two years to allow thorough coverage of the entire coast with available funds. The study is being phased to facilitate coordination and continuing demonstration of successful monitoring by placing a priority on generating information that is of maximum value to regulators and the public.

In year 1, sampling will focus on the SCB (Water Board regions 4, 8 and 9 – see Figure 1) and San Francisco Bay and adjacent coastal areas (Region 2). This will allow for coordination with Bight ’08 and the RMP, which are scheduled for 2009. This will also provide a basis for a report on year 1 that describes bioaccumulation in the most populated and heavily fished areas in the state near San Francisco and Los Angeles.

Sampling in year 2 will cover the other coastal regions (1 and 3) and any other remaining areas not covered in year 1. The second year report will present the data for these areas and also provide a comprehensive assessment of the entire two-year dataset.

D. Spatial Considerations

California has 1600xx miles of coastline that spans a diversity of habitats and fish populations, and dense human population centers with a multitude of popular fishing locations. Sampling this vast area with a limited budget is a challenge.

The approach being employed to sample this vast area is to divide the coast into 70xx spatial units called “zones” (Figure 2). The use of this zone concept is consistent with the direction that OEHHA will take in the future in development of consumption guidelines for coastal areas. Advice has been issued on a pier-by-pier basis in the past in Southern California, and this approach has proven to be unsatisfactory. All of these zones will be sampled, making a probabilistic sampling design unnecessary.

The sampling will be focused on nearshore areas, including bays and estuaries, in waters not exceeding 200 m in depth, and mostly less than 60 m deep. These are the coastal waters where most of the fishing occurs.

Several criteria were considered in drawing the boundaries of the zones.

1. Fishing pressure. Zones are smaller and more numerous in area with more fishing pressure. The location of fishing piers and other fishing access points was an important factor in zone delineation. On the other hand, the zones are larger in remote areas with little fishing activity.
2. Even distribution. To ensure coverage of the entire coast, the zones are generally spread evenly throughout, with adjustments made for fishing pressure as described above.

3. Homogeneity of contamination. Land use and hydrology were considered in drawing boundaries to reflect known patterns of contamination.
4. Stakeholder interest. The boundaries were reviewed by stakeholders (Water Board representatives, stakeholders in the Bight Group) and modified according to their needs.

Popular fishing locations were identified from Jones (2004) and discussions with stakeholders. Zones were developed in consultation with Water Board staff from each of the nine regions, Bight Group stakeholders, and the BOG.

C. Sampling Design Within Each Zone

1. Species Targeted

Selecting fish species to monitor on the California coast is a complicated task due to the relatively high diversity of species, regional variation over the considerable expanse of the state from north to south, variation in habitat and contamination between coastal waters and enclosed bays and harbors, and the varying ecological attributes of potential indicator species. The list of possibilities was narrowed down by considering the following criteria, listed in order of importance.

1. Popular for consumption
2. Sensitive indicators of problems
3. Widely distributed
4. Cleaner species
5. Represent different exposure pathways (benthic vs pelagic)
6. Continuity with past sampling

Information relating to these criteria is presented below.

The BOG elected not to include shellfish in this survey, due to the limited budget available and the lower consumption, lower risks to human health, and the added expense that would be required to collect shellfish.

Popular for Consumption

As recommended by USEPA (2000) in their document "Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories," the primary factor considered in selecting species to monitor was a high rate of human consumption. Fortunately, good information on recreational fish catch is available from the Recreational Fisheries Information Network (RecFIN), a product of the Pacific States Marine Fisheries Commission (PSMFC). Established in 1992, RecFIN is designed to integrate state and federal marine recreational fishery sampling efforts into a single database to provide important biological, social, and economic data for Pacific coast recreational fishery biologists, managers and anglers. Fish catch data are available at: www.recfin.org/forms/est2004.html. Additional data were obtained from Wade Van Buskirk of the PSMFC. The data were for the period Jan 2005 to Dec 2007.

Many different taxonomic groups of fish are found on the coast (e.g., rockfish, surfperch, or sharks) and some of these groups consist of quite a diversity of species. The sampling design is based primarily on coverage of a representative of selected groups within each zone. RecFIN data were used to identify the groups to target. Table 2 shows these data for the three regions (south, central and north) and specific data for the coast (ocean < 3 mi) and bays and harbors. Data include mass of catch in tonnes and counts in thousands (parentheses). The mass and catch data were ranked for each region, then the ranks for each species were averaged to obtain an average rank. The average rank was used as the index of popularity for fish consumption. For example, in southern California coastal waters, the most popular groups included chub mackerel; perch; flatfish; sharks, skates, and rays; rockfish; and croaker. The popular groups varied among the three regions of the state (south, central, and north) and between coastal waters and bays and harbors.

The next task was to select species within each group that was targeted for sampling. For these decisions, RecFIN data for individual species were considered (Table 3). For example, rockfish are a popular group along most of the coast. Data for individual rockfish species were examined to identify the most popular species in each region. In coastal waters (“ocean < 3 mi” in Tables 2 and 3) of southern California, kelp bass (which were included in the “rockfish” group), were the most popular species in this group by far. Therefore, this species was selected as the primary target species for the rockfish group in this region. Since it is not always possible to collect the species that are targeted in every zone, the sampling crew will have a prioritized menu of other potential target species. Primary target species will be given the highest priority. If primary targets are not available in sufficient numbers, secondary targets have been identified. For rockfish, in the southern California ocean region, barred sand bass were the second most abundant species, and are at the top of a list of several possible secondary target species. In this manner, the RecFIN data were used to select primary and secondary targets for all of the sampling strata along the coast.

Sensitive Indicators

While catch data were the primary determinant of the list of target species, some adjustments were made to ensure an appropriate degree of emphasis on sensitive indicators of contamination. USEPA (2000) also recommends consideration of this (expressed as “the potential to bioaccumulate high concentrations of chemical contaminants”) as a criterion of major importance. Including these species is useful in assessing the issue of safe consumption (contained in MQ1) – if the sensitive indicator species in an area are below thresholds of concern then this provides an indication that all species in that area are likely to be below thresholds.

Different contaminants have different mechanisms of accumulation and therefore a combination of species is needed to ensure inclusion of the appropriate sensitive indicators. Mercury biomagnifies primarily through its accumulation in muscle tissue, so predators such as sharks tend to have the highest mercury concentrations. In contrast, the organic contaminants of concern also biomagnify, but primarily through accumulation in lipid. Concentrations of organics are therefore are also influenced by the lipid content of the species, with species that are higher in lipid having higher concentrations. Species such as white croaker tend to have high lipid concentrations in their muscle tissue, and therefore usually have the highest concentrations of organics.

Consequently, target species in this study will include both high lipid species such as croaker and surfperch, and predators that accumulate mercury such as sharks. These considerations had an influence on the target species list. For example, white croaker has a high potential for accumulation of organics and has been sampled extensively in past studies in both southern California and San Francisco Bay. Therefore, even though white croaker did not quite make the list of the top five most popular species in these areas, it was still included as a primary target.

Spatial Distribution

Consideration in selection of target species was also given to their spatial distribution in order to provide better information for answering MQ2 (regional distribution). This is also recommended as an important criterion to consider by USEPA (2000). Due to interspecific variation in bioaccumulation, the availability of consistent species across the spatial units of interest is critical to maximizing information obtained on spatial patterns. The sampling design complies with this criterion as much as possible, given the primary consideration given to the two criteria described previously. As one example, shiner surfperch were selected as a secondary target for the central California coast, even though their catch was a bit lower than walleye surfperch, in order to allow for better comparison with the shiner surfperch data for central California bays and harbors.

Other Factors

Other factors were considered but did not have a major influence on the design due to the limited resources available.

- Cleaner species. Provide information useful in developing safe eating guidelines. More focused effort to obtain information on these species is left to future studies.
- Different exposure pathways (benthic vs pelagic). Not a high priority with the limited budget.
- Continuity with past sampling. This was a consideration in some areas, but past sampling also focused on the popular species, so the actual influence of this was not significant.

The Target Species

Table 4 shows the lists of primary and secondary species for each region and stratum based on the considerations discussed above. The available budget will allow for analysis of five species per zone. Therefore, the Table shows five primary targets for each stratum. One exception is the coast in southern California, where (in accordance with Bight Group preferences) the fifth species to be analyzed will be determined based on what is caught in the sample collection process.

A summary of basic ecological attributes of the primary and secondary target species is presented in Table 5. This information will be useful in performing spatial comparisons in cases where it was not possible to collect the same species in the spatial units to be compared. In these cases, comparisons may be evaluated for species from the same guilds and with similar attributes.

2. Sampling Sites

Within each zone, specific sites will be selected for sample collection. Criteria to be considered in determining the placement of sampling sites will include the existence of discrete centers of fishing activity, road or boat ramp access, known patterns of spatial variation in contamination or other factors influencing bioaccumulation, and possibly other factors. The primary emphasis will be on sampling in areas that are popular for fishing. Popular fishing areas will be identified through published sources (e.g., Jones [2004]) and consultation with agency staff.

3. Replication

There will be no replication of sites within a zone. If the sampling crew is unable to obtain sufficient samples at the first site sampled, they will move to the next site where fishing pressure is high and it is likely to obtain the needed samples.

In general, there will be only one composite sample (compositing is discussed further below) collected for each species in each zone. With the limited resources available, it is considered a higher priority to obtain information on different species than to attempt to provide a stronger basis for statistical spatial comparisons among zones. Exceptions to this are the southern California Bight (SCB) and San Francisco Bay. In the SCB, the Bight Group is making funds available for analyzing three replicates of kelp bass, white croaker, and one other species within each zone. These are not site replicates, however – the replicates can be collected from a single site, if that is possible, or from multiple sites if that is necessary. These are simply multiple replicates of the target species from a given zone. This same basic approach will be followed in San Francisco Bay, but the Bay will be divided relatively finely into five zones.

4. Size Ranges and Compositing for Each Species

Size Ranges and Compositing

Chemical analysis of trace organics is relatively expensive ($519 per sample for PCB congeners and $557 per sample for organochlorine pesticides), and the management questions established for this survey can be addressed with good information on average concentrations, so a compositing strategy will be employed for these chemicals.

Chemical analysis of mercury is much less expensive ($66 per sample) and mercury concentrations are known to be closely correlated with fish size in many species. Collecting data on mercury concentrations in individual fish can provide a basis for statistical analysis (ANCOVA) to evaluate spatial or temporal patterns in a manner that filters out the influence of fish size (for example, see Davis et al. [2008]). Consequently, the sampling design for selected mercury indicator species includes analysis of mercury in individual fish. For the mercury indicator species, an analysis of covariance approach will be employed, in which the size:mercury relationship will be established for each location and an ANCOVA will be performed that will allow the evaluation of differences in slope among the locations and the comparison of mean concentrations and confidence intervals at a standard length, following the approach of Tremblay (1998). Experience applying this approach in the Central Valley indicates that to provide robust regressions 10 fish spanning a broad range in size are needed (Davis et al. 2003, Davis et al. 2008).

Specific size ranges to be targeted for each species are listed in Table 6.
XX UNDER CONSTRUCTION
xx are the key mercury indicators. These species have a high trophic position and a strong size:mercury relationship. These species will be analyzed individually for mercury, and composites from these fish will also be prepared for analysis of organics. The numbers and sizes indicated for these species will provide the size range needed to support ANCOVA.

Size ranges for other species are based on a combination of sizes prevalent in past sampling (Melwani et al. 2007) and the 75% rule recommended by USEPA (2000) for composite samples.
XX UNDER CONSTRUCTION

The sampling crew will be reporting their catch back to the BOG on a weekly basis to make sure that the appropriate samples are collected and to address any unanticipated complications.

D. Sample Processing and Analysis

Upon collection each fish collected will be tagged with a unique ID. Several parameters will be measured in the field, including total length (longest length from tip of tail fin to tip of nose/mouth), fork length (longest length from fork to tip of nose/mouth), and weight. Total length changes with freezing and thawing and is best noted in the field for greatest accuracy and because it is the measure fishers and wardens use to determine whether a fish is legal size. Doing fork length at the same time simplifies matters, and might help with IDs later to sort out freezer mishaps.

Whole fish will be wrapped in aluminum foil and frozen on dry ice for transportation to the laboratory, where they will be stored in freezers. Fish will be kept frozen wrapped in foil until the time of dissection. Dissection and compositing of muscle tissue samples will be performed following USEPA guidance (USEPA 2000). At the time of dissection, fish will be placed in a clean lab to thaw. After thawing, fish will cleaned by rinsing with de-ionized (DI) and ASTM Type II water, and handled only by personnel wearing polyethylene or powder-free nitrile gloves (glove type is analyte dependent). All dissection materials will be cleaned by scrubbing with Micro® detergent, rinsing with tap water, DI water, and finally ASTM Type II water.

In general, fish will have the skin dissected off, and only the fillet muscle tissue will be used for analysis. This is inconsistent with the guidance of USEPA (2000) that recommends that fish with scales have the scales removed and be processed with skin on, and skin is only removed from scaleless fish (e.g. catfish). The BOG is aware of this difference, but favors skin removal. Skin removal has been repeatedly used in past California monitoring. All fish (with limited exceptions) in Toxic Substances Monitoring Program, the Coastal Fish Contamination Program, and the Fish Mercury Project have also been analyzed skin-off. Processing fish with the skin on is very tedious and results in lower precision because the skin is virtually impossible to homogenize thoroughly and achieving a homogenous sample is difficult. Also, skin-on preparation actually dilutes the measured concentration of mercury because there is less mercury in skin than in muscle tissue. The most ubiquitous contaminant in fish in California that leads to most of our advisories is mercury. By doing all preparation skin-off we will be getting more homogeneous samples, better precision for all chemicals, and definitely a better measure of mercury concentrations, which are our largest concern. Surfperch samples will be an exception to this rule. Surfperch are too small for skin removal. Procedures used in past monitoring (removing heads, tails, and guts; leaving muscle with skin and skeleton to be included in the composites as in the RMP) will be used.

Mercury will be analyzed according to EPA 7473, "Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry" using a Direct Mercury Analyzer. Samples, blanks, and standards will be prepared using clean techniques. ASTM Type II water and analytical grade chemicals will be used for all standard preparations. A continuing calibration verification (CCV) will be performed after every 10 samples. Initial and continuing calibration verification values must be within ±20% of the true value, or the previous 10 samples must be reanalyzed. Three blanks, a standard reference material (DORM-2), as well as a method duplicate and a matrix spike pair will be run with each set of samples.

Organochlorine pesticides will be analyzed according to EPA 8081AM, "Organochlorine Pesticides by Gas Chromatography". PCBs and PBDEs will be analyzed according to EPA 8082M, "Polychlorinated Biphenyls (PCBs) by Gas Chromatography". Samples, blanks, and standards will be prepared using clean techniques. ASTM Type II water and analytical grade chemicals will be used for all standard preparations. A continuing calibration verification (CCV) will be performed after every 10 samples. Initial and continuing calibration verification values must be within ±25% of the true value, or the previous 10 samples must be reanalyzed. One blank, a laboratory control spike (LCS), as well as a method duplicate and a matrix spike pair will be run with each set of samples.

E. Analytes

Table 7 provides a summary of the contaminants included on the list of analytes for the study. Since the study is focused on assessing the impacts of bioaccumulation on the fishing beneficial use, the list is driven by concerns over human exposure. Contaminants were included if they were considered likely to provide information that is needed to answer the three management questions for the study (see pages 6-7).

Additional discussion of the analytes is provided below.

Ancillary Parameters

Ancillary parameters to be measured in the lab include moisture and lipid (Table 8). Fish sex will not be determined as it is not considered critical for this screening study.

Mercury

Mercury is the contaminant of greatest concern with respect to bioaccumulation on a statewide basis. Based on past studies (Davis et al. 2007), mercury is expected to exceed the threshold of concern in many lakes and reservoirs. Mercury will be measured as total mercury. Nearly all of the mercury present in edible fish muscle is methylmercury, and analysis of fish tissue for total mercury provides a valid, cost-effective estimate of methylmercury concentration. Mercury will be analyzed in all samples because a substantial proportion of samples of each are expected to exceed the threshold of concern.

PCBs

PCBs are the contaminant of second greatest concern with respect to bioaccumulation on a statewide basis (Davis et al. 2007). PCBs will be analyzed using a congener specific method. A total of 55 congeners will be analyzed. PCBs will be analyzed in all composite samples.

Legacy pesticides

Based on past studies (Davis et al. 2007), legacy pesticides are generally expected to exceed thresholds of concern in a very small percentage of California lakes and reservoirs. An exception to this would be the portion of the SCB with significant historic contamination. Pesticides will be analyzed in all composite samples.

PBDEs

Few data are currently available on PBDEs in California sport fish, and a threshold of concern has not yet been established. However, a rapid increase in concentrations in the 1990s observed in San Francisco Bay and other parts of the country raised concern about these chemicals, and led to a ban on the production and sale of the penta and octa mixtures in 2006 (Oros et al. 2005). The deca mixture is still produced commercially. A threshold of concern is anticipated to be established soon by USEPA. The most important PBDE congeners with respect to bioaccumulation are PBDEs 47, 99, and 100. These congeners, and a few others, can be measured along with the PCBs at no additional cost as they can be separated using the same column and GC program as the PCBs. Estimated concentrations will be determined for PBDEs 17, 28, 47, 66, 85, 99, and 100. PBDEs will be analyzed in all composite samples.

Dioxins and Dibenzofurans

Few data are available on dioxins and dibenzofurans in California sport fish. Perhaps the best dataset exists for San Francisco Bay, where samples from 1994, 1997, 2000, 2003, and 2006 indicated that concentrations in high lipid species exceeded a published screening value of 0.3 TEQs (for dioxins and furans only) by five fold (Greenfield et al. 2003). However, there are no known major point sources of dioxins in the Bay Area and the concentrations measured in the Bay are comparable to those in rural areas of the U.S. OEHHA did not include dioxins in their recent evaluation of guidance tissue levels for priority contaminants due to the lack of data for dioxins in fish throughout the state (Klasing and Brodberg 2008). Given the relatively high cost of dioxin analysis and these other considerations, OEHHA recommended that dioxins not be included in this screening study (Table 9). Dioxins are considered a higher priority by the RMP, so these analytes will be included for high lipid species (white croaker and shiner surfperch) in San Francisco Bay.

Selenium, Organophophates, PAHs, TBT, and Cadmium

Past monitoring (e.g., San Francisco Bay work – SFBRWQCB 1995) indicates that concentrations of these chemicals in sport fish are generally far below thresholds of concern for human exposure. Therefore, they will not be included in the present study. One exception is selenium in San Francisco Bay, where a cleanup plan is being developed and the Water Board has requested additional information on concentrations in sport fish.

Other Emerging Contaminants

Other emerging contaminants are likely to be present in California sport fish. Examples include perfluorinated chemicals, other brominated flame retardants in addition to PBDEs, and others. Thresholds do not exist for these chemicals, so advisories or 303(d) listing are not likely in the near future. However, early detection of increasing concentrations of emerging contaminants can be very valuable for managers, as evidenced by the PBDE example. Measuring emerging contaminants would not directly address the management questions guiding this study, so analysis of these chemicals is not included in the design. An exception is San Francisco Bay, where the RMP will be analyzing PFCs.

Omega-3 Fatty Acids

Klasing and Brodberg (2008) concluded that there is a significant body of evidence and general scientific consensus that eating fish at dietary levels that are easily achievable, but well above national average consumption rates, appears to promote significant health benefits, including decreased mortality., and that because of the unique health benefits associated with fish consumption, the advisory process should be expanded beyond a simple risk paradigm in order to best promote the overall health of the fish consumer. Much of the health benefits of fish consumption are derived from their relatively high content of key omega-3 fatty acids, eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA). When these data are available, OEHHA can take them into consideration in developing safe eating guidelines. Few data are available on the omega-3 content of wild fish. The RMP is planning on obtaining these data for San Francisco Bay fish.

F. Quality Assurance

This effort will adhere to quality assurance requirements established for the SWAMP. A QAPP specific to this effort is in preparation.

One of the analytical challenges in this project will be coordinating among different laboratories that will be generating organics data. The Bight Group resource contribution to the study is in the form of analytical chemistry for more than 200 organics samples. Multiple labs from the Bight Group will participate. Discussions are underway to select labs that are capable of generating data of sufficient quality for the study. An intercalibration exercise is planned for the participating labs to identify any comparability problems before analysis of the field samples is initiated (see Appendix 1).

G. Archiving

As described above, aliquots of homogenates of all samples analyzed will be archived on a short-term basis to provide for reanalysis in case of any mishaps or confirmation. In addition, aliquots of selected samples will be archived on a long-term basis.

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This will provide a integrative, representative sample for each zone that can be reanalyzed in later years to confirm earlier analyses, look for new chemicals of concern, provide material for application of new analytical methods, provide material for other ecological research, and other purposes.

H. Ancillary Data

In addition to the primary and secondary target species, other species will also be observed in the process of sample collection. This “bycatch” will not be collected, but the sampling crew will record estimates of the numbers of each species observed. This information may be useful if followup studies are needed in any of the sampled zones.

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OTHERS?

I. Timing

Sampling will be conducted from May 2009 through October 2009. Seasonal variation in body condition and reproductive physiology are recognized as factors that could affect contaminant concentrations. However, sampling as many zones as possible is essential to a statewide assessment, and it will take this many months to sample the zones targeted for 2009.

J. Data Assessment

MQ1 will be assessed by comparing results from each zone to thresholds established by OEHHA in Klasing and Brodberg (2008) (Tables 11 and 12). Maps, histograms, and frequency distributions will be prepared to summarize these comparisons.

MQ2 will be assessed through analysis of variance (or analysis of covariance for the species with mercury in individual fish) for the areas where replicate samples are available (SCB and San Francisco Bay). For the other areas, nonstatistical methods will be used (mapping and graphing). Comparison of concentrations between regions may be performed by treating zones within each region as "replicates".

MQ3 will be assessed in consultation with OEHHA.

K. Products and Timeline

A technical report on the 2009 sampling will be drafted by September 2010 and will include an assessment of data from two of the most heavily fished portions of the coast near the populations centers of Los Angeles and San Francisco. The final report, incorporating revisions in response to reviewer comments, will be completed in January 2011.

A second round of sampling is planned for 2010. This work would follow the same approach described in this document, but focusing on the remaining zones in Regions 1 and 3, and any other zones not yet covered in 2009. This sampling would begin May 2010. Preliminary results from the 2009 sampling will be evaluated to determine whether any adjustments to the design are needed.

L. Regional Enhancements in the Southern California Bight and San Francisco Bay

San Francisco Bay

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The Southern California Bight

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