A REPORT OF THE DELTA REGIONAL MONITORING PROGRAM

2011

THE PULSE OF THE DELTA

MONITORING AND MANAGING WATER QUALITY IN THE SACRAMENTO – SAN JOAQUIN DELTA

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Re-thinking Water Quality Monitoring

March 2011
Contribution No. 630

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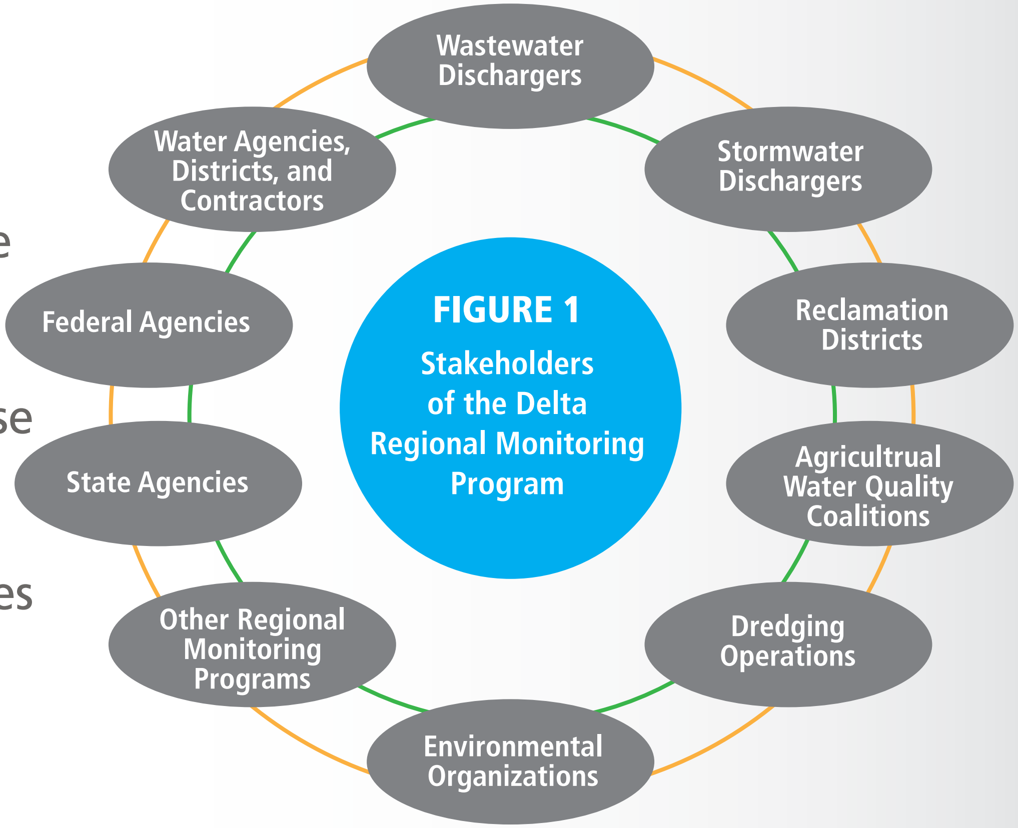
INTRODUCTION

Georgiana Slough, Central Delta. Photograph by Thomas Jabusch. →

OVERVIEW

WELCOME TO THE PULSE OF THE DELTA!

Welcome to the first issue of the *Pulse of the Delta: Monitoring and Managing Water Quality in the Sacramento – San Joaquin Delta*, the new publication of the emerging Delta Regional Monitoring Program (RMP). This report is a direct response to Delta RMP stakeholders' desire for an accessible water quality summary for the Delta that addresses important regional questions.



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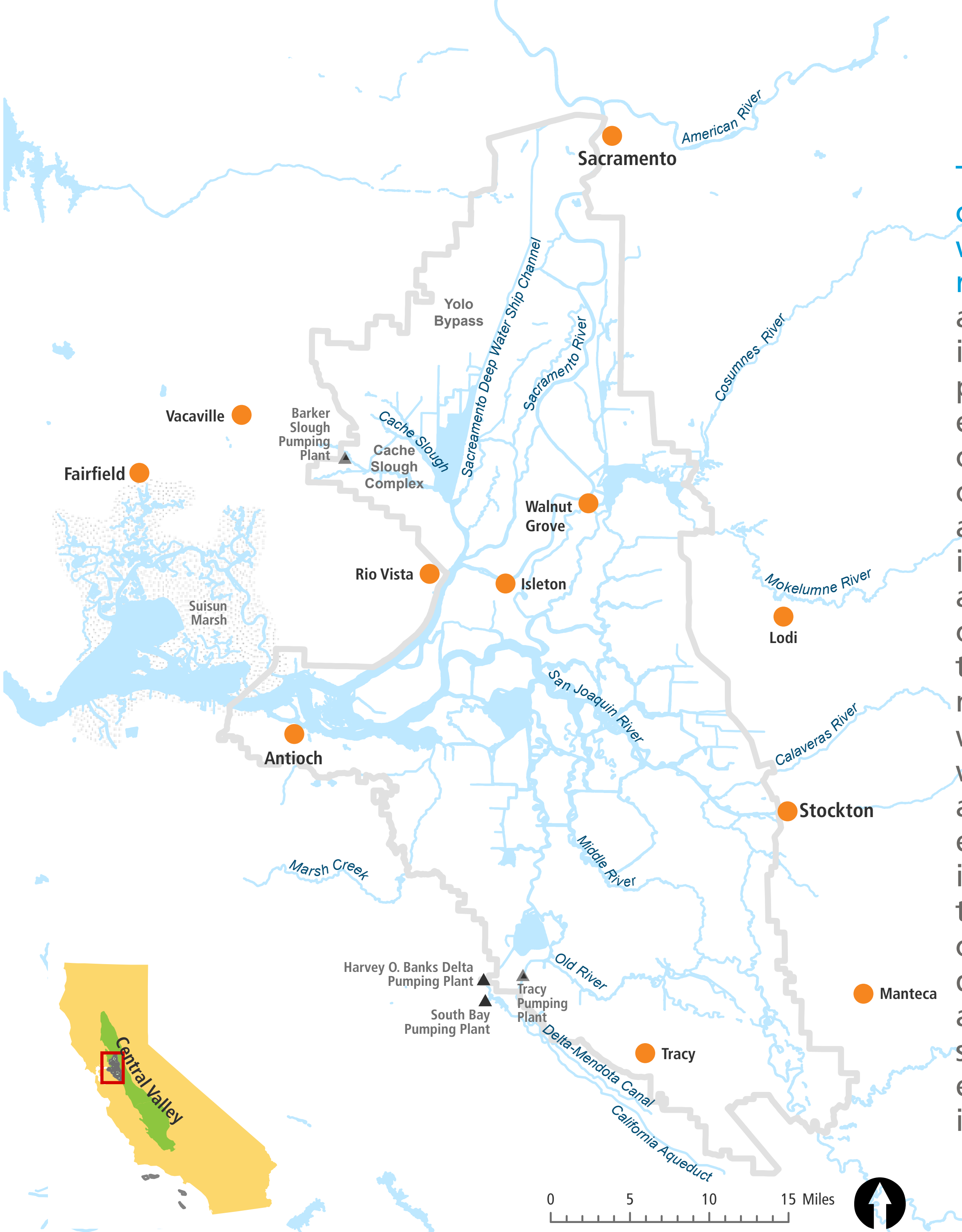

THE SACRAMENTO – SAN JOAQUIN DELTA

The Delta's water supports diverse beneficial uses, including irrigation and drinking water supply, wildlife habitat, fishing, and recreation. Yet at the same time, concerns about degraded water quality and its impact on these beneficial uses are ever-present and serious. For example, degraded water quality has been implicated as one of the possible causes for the decline of native species, along with various other and seemingly interconnected issues facing the Delta, such as water diversions and the loss of habitat. The complexity of the Delta's challenges has highlighted the importance of comprehensive information on its condition. The Delta RMP will address this need by better defining water quality issues of regional concern and working to improve the quality and efficiency of water quality monitoring information. The *Pulse of the Delta* intends to help the Delta RMP fulfill this goal by communicating current, relevant water quality information to advance awareness and consideration of the issues and to support informed decisions that lead to an effectively managed Delta ecosystem that is healthy, sustainable, and productive.

ABOUT THIS REPORT

The vision for the *Pulse of the Delta* is to make the wealth of available information on water quality in the Delta accessible to water quality managers, decision-makers, scientists, and the public. By targeting such a diverse audience and focusing on water quality, this report fills a previously unoccupied niche and will complement existing reporting products published by other programs.

To reach its diverse audience most effectively, the *Pulse* is written in language that is accessible to an educated but non-technical reader. The report format and design are modeled after its successful sister publication, the San Francisco Bay RMP's *Pulse of the Estuary*. For example, detailed figure captions are written to convey the basic take-home messages of each article. Readers that are pressed for time can glean many of the important findings from the *Pulse of the Delta* by reviewing the figures and captions and browsing the key points highlighted at the beginning of each article.

Current plans are to publish the *Pulse of the Delta* annually. This first edition introduces the basic structure of the report, consisting of the following sections:

Overview: introduces the theme of the edition and provides a short overview of each item in the report so readers can readily find topics of greatest interest.

Management Update: features contributions that summarize successes and future challenges of the Delta RMP and other important developments from a water quality management perspective

Feature Articles: provides broad overviews of topics of current interest in water quality management and science.

Future editions are planned to include a Status and Trends section that presents a graphical summary of the latest water quality monitoring results generated each year by the Delta RMP and other programs.

Each edition of the *Pulse of the Delta* will be organized around a general theme that represents a regional water quality management priority for the Delta, and the theme of this first edition is "Re-thinking Water Quality Monitoring in the Delta". This topic was selected to support the Delta RMP's initial efforts to improve the coordination and efficiency of permit-mandated water quality monitoring, as a first step toward enhancing the ability to conduct comprehensive assessments. As the Delta RMP's efforts evolve to address a range of concerns, future editions of the *Pulse of the Delta* will focus in concert on water quality topics and activities relevant to the management agencies involved.

AQUATIC SCIENCE CENTER

This first edition was produced and published by Aquatic Science Center as a pilot product with funding and assistance from the State Water Resources Control Board (State Water Board) and Central Valley Regional Water Quality Control Board (Central Valley Water Board). The theme and topics featured in this first edition represent current water quality management priorities of the Central Valley Water Board and were discussed with stakeholders at the May 12, 2010 Delta RMP stakeholder meeting. Program stakeholders were also invited to review draft articles. ***The publication process will adapt to responses and evolving needs. One possibility is to establish a Technical Review Committee and charge it with decisions on content, authors, and the review process.***

A BRIEF REVIEW OF THE ARTICLES

RE-THINKING WATER QUALITY MONITORING

The opening article of this issue (page 14) summarizes a study by U.C. Davis researchers that evaluated the role of contaminants in the decline of some of the Delta's fish populations (Johnson et al. 2010). This study has special significance for the Delta RMP for two main reasons. First, it attempted to comprehensively assess a potential regional water quality issue affecting the Delta ecosystem by synthesizing water quality data from multiple sources. And second, it illustrates many of the problems the Delta RMP must solve to fulfill its role of gathering, synthesizing, and communicating water quality information to support management decisions.

In the early 2000s, a collapse in the abundance of four Delta fish species, delta smelt, longfin smelt, young of the year striped bass, and threadfin shad (see sidebar **PELAGIC ORGANISM DECLINE**), captured the attention of resource managers, scientists, politicians, and the general public. This fish population crash became known as the POD and many studies have been conducted to find its causes. The major goal of the U.C. Davis study was to determine whether contaminants could be implicated in the POD. Pesticides and other contaminants were suspected as one of the possible causes. Analyses of contaminants' potential role were hindered, however, because data were either missing, unavailable, scattered among various parties, or not in a format suitable for analysis.

The inability of regulators and researchers to respond more adequately to this public concern highlighted the need for changes in water quality monitoring and data reporting practices. These changes include regularly and systematically compiling, assessing, and reporting data, and better coordinating water quality monitoring with other monitoring efforts. The need for these changes provided the impetus for developing the Delta RMP. The new Program intends to be a forum for "re-thinking monitoring" in the Delta, with the ultimate goal of producing more useful and accessible water quality information.

Coordination and collaboration are crucially important tools for changing the monitoring system, and the Delta RMP will need to build long-term strategic partnerships with other programs to foster improvements in these areas.

WORKING TOGETHER FOR BETTER WATER QUALITY INFORMATION

The Management Update section of this edition is devoted to the Delta RMP's initiative for "re-thinking the water quality monitoring system" (page 22) to improve its capacity for supporting comprehensive regional assessments.

The desire to rethink the monitoring system is shared by many involved in monitoring the Delta, and, naturally, the Delta RMP cannot and should not be doing the re-thinking alone. Coordination and collaboration are crucially important tools for changing the monitoring system, and the Delta RMP will need to build long-term strategic partnerships with other programs to foster improvements in these areas. The Delta RMP will focus initially on contaminants-related monitoring that is under the direct control of the State and Central Valley Water Boards (Water Boards). For such programs, the Water Boards can more readily implement changes to regulatory requirements (for example, station locations, sampling frequencies, data management protocols) to improve monitoring coordination and efficiency, key ingredients for more comprehensive and integrated monitoring.

From this starting point, development of the Delta RMP will proceed gradually, based on funding availability and feasibility. While the Water Boards are investing resources in developing and establishing the Delta RMP, success will require support from stakeholders and cooperation with other monitoring programs such as those coordinated by the Interagency Ecological Program (IEP). A key role for the Water Boards is therefore to build interest and active participation by potential partners, in order to continue developing the major aspects of the program: governance, monitoring objectives, funding, data integration, and coordination with other programs. While such decisions will depend on input from stakeholders and partners, one model for improving collaboration and coordination is described in the California Water Quality Monitoring Council's recently released *Comprehensive Water Quality Monitoring Program Strategy for California.* This model focuses efforts on improving access to user-oriented water quality information.

The pyrethroids story demonstrates that monitoring programs must adapt to the array of constantly changing threats or risk monitoring for the problems of yesterday.

REGIONAL MONITORING IN THE DELTA: PAST, PRESENT, AND FUTURE

The three Feature Articles in this issue cover Delta water quality topics that have been identified by regulators as top priorities and are currently receiving a great deal of attention: ammonia, pyrethroids, and contaminants of emerging concern (CECs). They represent an old (ammonia), a new (pyrethroids), and a possible future management concern (CECs).

AMMONIA has been a concern in the Delta for more than 10 years (page 30). Only recently have data been collected and analyzed to address the question of whether current ammonia levels are causing impairments to the Bay-Delta ecosystem. One of the key findings of recent monitoring is that ambient ammonia levels are unlikely to be toxic to fish in the Delta (Foe et al. 2010). However, ammonia may be having a significant impact on fish through its influence on the productivity of the food web. Multiple, interactive stressors are believed to be involved in the POD, including limited food availability, reduced and highly modified flows, habitat degradation, and introduced species. Based on the recent studies, ammonia is suspected as one of the causes, by inhibiting the spring bloom of diatoms, algae that are an important component of the Bay-Delta foodweb (Dugdale et al. 2007; Foe 2010; Jassby 2008; Marchi et al. 2010; Wolfe 2010). The ammonia issue provides a prime example of the challenges involved in identifying cause and effect in a complex ecosystem affected by multiple, interactive stressors. The fact that most of the ammonia of concern originates from a source in the Delta (Jassby 2005), while at least one of the apparent impacts extends into the San Francisco Bay region, complicates scientific investigations and regulation. The Delta RMP can play a coordinating role and ensure Central Valley stakeholder input and representation on this type of issue.

PYRETHROIDS have demanded the attention of regulators since the mid-2000s. Concern was heightened in 2005, when U.C. Berkeley researchers found pyrethroids to be the most likely cause for widespread toxicity to sediment-dwelling invertebrates in suburban creeks in the Sacramento area (page 40). Pyrethroids were introduced as an alternative to organophosphorus insecticides (which were originally introduced to replace organochlorine pesticides such as DDT), when the latter were phased out from uses in home products and by professional pest control firms. The phase-out occurred after organophosphates were identified as the most likely cause of toxicity in aquatic systems when rains washed residues into creeks and rivers. Many had hoped the shift to pyrethroids would eliminate these unintended effects on aquatic life. But in recent years, toxicity tests on samples collected by environmental monitoring programs, many of them in the Delta, have shown we have largely just traded one toxicant for another. Before these studies, the widespread toxicity caused by pyrethroids went unnoticed in California for many years, and is probably still going unnoticed elsewhere, because monitoring programs have not been looking for it or haven't been able to detect it. The pyrethroids story illustrates how the mixture of toxicants in Delta waters changes over time as pesticides and other chemicals fall in and out of favor. It also demonstrates that monitoring programs must adapt to the array of constantly changing threats or risk monitoring for the problems of yesterday.

CONTAMINANTS OF EMERGING CONCERN (CECS) are the potential water quality challenges of tomorrow (**page 48**). Over the past 30 years more than 100,000 chemicals have been registered or approved for commercial use in the U.S. Many of these chemicals are not routinely monitored and have not been adequately tested for their potential impacts to humans and wildlife, yet are continuously released to the environment. Analytical methods have progressed to the point that it is possible to measure trace quantities (below parts per trillion) of many contaminants in water, which has led to frequent detection of a variety of previously unmonitored chemicals in the environment. Determining whether or not some of these chemicals may be a problem is a formidable challenge. Observations of endocrine disruption in fish and other organisms at low contaminant concentrations in aquatic environments (**page 52**) have raised concerns regarding the potential for impacts of other CECs that have been detected at similar concentrations. Water bodies that continuously receive wastewater effluent and runoff from highly urbanized areas are of particular concern (**page 56**). Several types of high volume use chemicals have gained the attention of researchers and regulators, including pharmaceuticals and personal care products (PPCPs), steroid hormones used in animal feed, surfactants, stain repellents, flame retardants, antimicrobials, and nanomaterials. The considerable challenge of managing CECs is largely due to limitations in the regulatory system at the state, national, and international level. The information deficiency for current-use chemicals poses an obstacle to regulators and scientists in their endeavors to focus on the highest risk chemicals and avoid repeating past mistakes that resulted in extensive global contamination by toxic chemicals (as happened, for example, with polychlorinated biphenyls and organochlorine pesticides). In particular, state-of-the-art analytical facilities are needed to measure the extremely low concentrations of CECs that are biologically active. In California, a number of efforts are underway to develop strategies for CEC identification and prioritization, as well as processes for determining thresholds of effect on aquatic life and other beneficial uses. An effective strategy for the Delta RMP will be to partner with other programs and to stay apprised of the lessons to be learned from them. Collaborating with other programs on chemical prioritization approaches and projects of mutual interest will reduce costs, maximize program effectiveness, and increase the collective understanding of CEC occurrence and risks.

The information deficiency for current-use chemicals poses an obstacle to regulators and scientists in their endeavors to focus on the highest risk chemicals and avoid repeating past mistakes.

DID CONTAMINANTS PLAY A ROLE IN THE PELAGIC ORGANISM DECLINE?

The four POD series, clockwise from top: striped bass, Delta smelt, longfin smelt, threadfin shad. Fish photographs by René Reyes.

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The Pelagic Organism Decline (POD) involves four open water (pelagic) fish species (Delta smelt, longfin smelt, threadfin shad, and striped bass) that spend a portion of their life in the Delta and are considered indicators of the overall health of the Delta ecosystem. These fishes have each decreased to precariously low levels in the past decade (Baxter et al. 2010). Since three of these fishes have also experienced more gradual long-term declines, and since nearly all fish populations have naturally occurring peaks and valleys in abundance, identifying the cause or causes of the POD is a particularly daunting challenge and has become the focus of a large effort by nine state and federal agencies working together in the IEP (see Pelagic Organism Decline on page 19). As part of this effort, the State Water Resources Control Board and the Central Valley Regional Water Quality Control Board sponsored a review by U.C. Davis researchers of the available data on contaminants, water and sediment toxicity, and histopathology to evaluate the role of contaminants in the POD.

The following three specific questions motivated that review:

Do available water quality data indicate the presence of contaminants in the Delta at concentrations necessary to cause sublethal or lethal effects sufficient to cause and/or maintain the POD?

Are available toxicity data sufficient to indicate the presence of contaminants in the Delta at concentrations necessary to cause sublethal or lethal effects sufficient to cause and/or maintain the POD?

Are available histopathology data sufficient to indicate that species of fish in the Delta have been exposed to contaminants at concentrations necessary to cause sublethal or lethal effects sufficient to cause and/or maintain the POD?

Because the larval and juvenile stages of all four species are found in the Delta between January and June, it is possible that toxicity due to contaminants could affect these sensitive life stages, either directly or through impacts on their prey items. However, the review concluded that, while contaminants are unlikely to be a major cause of the POD, they cannot be eliminated as a possible contributor to the decline. The report, "Evaluation of Chemical, Toxicological, and Histopathological Data to Determine Their Role in the Pelagic Organism Decline" (Johnson et al. 2010), was completed in April 2010 and is available on the Delta RMP homepage.

The conclusion that there is no obvious linkage between contaminants and the POD is supported by three findings: First, where data were available to compare, contaminants were not found at higher concentrations during the POD years compared to previous years. Second, there is no evidence that POD species are more sensitive to chemicals present in the Delta than are other fish. And third, there was as much or more toxicity in water collected in the Delta prior to as there was during the POD period.

The ambiguity of the overall conclusion stems in part from gaps in the historical data record, as well as from data quality issues associated with older data, and the difficulty involved in finding, accessing, and integrating data from multiple sources. For example, only a few chemicals had a time series of historical data sufficient to assess their role in the POD. Problems with historical data included detection limits above toxic levels, inadequately preserved samples, and insufficient sampling during the presumed sensitive January to June period (except for diazinon and chlorpyrifos).

Where data were sufficient to make pre- and post-POD comparisons, there does not appear to be a strong signal that distinguishes the two periods. For example, the toxicity data indicate there was as much or more overall toxicity in the Delta in the pre-POD years as in the POD years. Even so, there are unanswered questions about the possible role of sediment toxicity and toxicity from the organophosphorus pesticide chlorpyrifos (the only chemical to exceed water quality objectives in more than 5% of samples) on prey items. While striped bass are more sensitive to chlorpyrifos than are other, non-POD, species, the Water Board study reached the preliminary conclusion that POD species are not on the whole more sensitive than non-POD species to the mixture of chemicals found in the Delta. The U.C. Davis study illustrates the difficulty of conducting comprehensive, Delta-wide assessments. While time and budget constraints prevented the use of all existing datasets known to contain contaminant data, it identified significant problems with those datasets that were acquired for analysis. The review raised a number of questions that are being addressed in follow-on studies and made a number of specific recommendations for ensuring that future Delta-wide synthesis efforts related to contaminants have data adequate to address questions at the regional scale, including:

- develop a long-term water quality monitoring program that includes regionally coordinated water chemistry, toxicity, and histopathology samples and incorporates new and emerging contaminants in a multiple lines-of-evidence assessment approach;
- develop a conceptual model of the Delta that combines critical physical forcing functions and biological elements of the ecosystem and apply this model to inform decision-making and the adaptive management process;
- provide for ongoing data integration and interpretation aimed at both scientists and decision-makers;
- improve data management and integration to provide for more consistent quality control and easier access, perhaps through the California Environmental Data Exchange Network or other data portals; and
- address key research needs such as identification of unknown toxicants, the toxicity of contaminants on invertebrate prey species, improved data mining of historical data, and the role of sediment toxicity, among others.

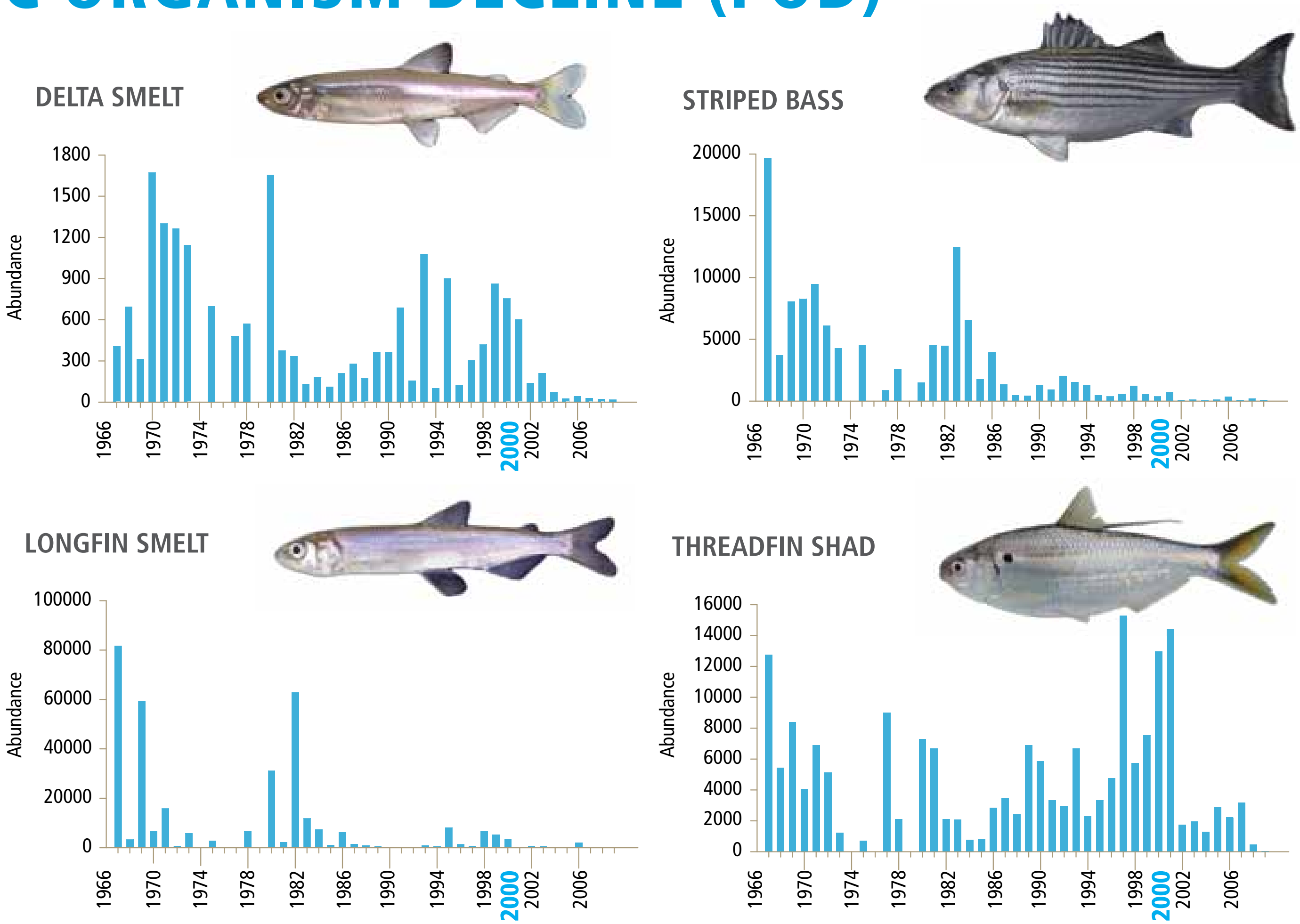
Contact: Mike Johnson, MLJ-LLC, mjohnson@mlj-llc.com.

For more information: http://www.waterboards.ca.gov/centralvalley/water_issues/delta_water_quality/comprehensive_monitoring_program/index.shtml

View of the Sacramento River at Miller Park. Photograph by Thomas Jabusch.

THE PELAGIC ORGANISM DECLINE (POD)

Fall fish abundance indices calculated by the IEP show continued declines in four pelagic fishes in the Delta and Suisun Bay. These fish declines beginning after 2000 became known as the "pelagic organism decline (POD)". The fall indices have been collected for all but three of the last 42 years. The indices for the last nine years have hovered at or near record low levels for delta smelt, age-0 striped bass, longfin smelt, and threadfin shad. For more information about the Pelagic Organism Declines and studies to investigate its causes, see http://www.water.ca.gov/iep/.



Graphic and fish data: Randy Baxter, California Department of Fish and Game, rbaxter@dfg.ca.gov

Contact: Anke Mueller-Solger, Delta Stewardship Council, anke.mueller-solger@deltacouncil.ca.gov

More information: http://www.water.ca.gov/iep/

WHAT CAUSED THE POD?

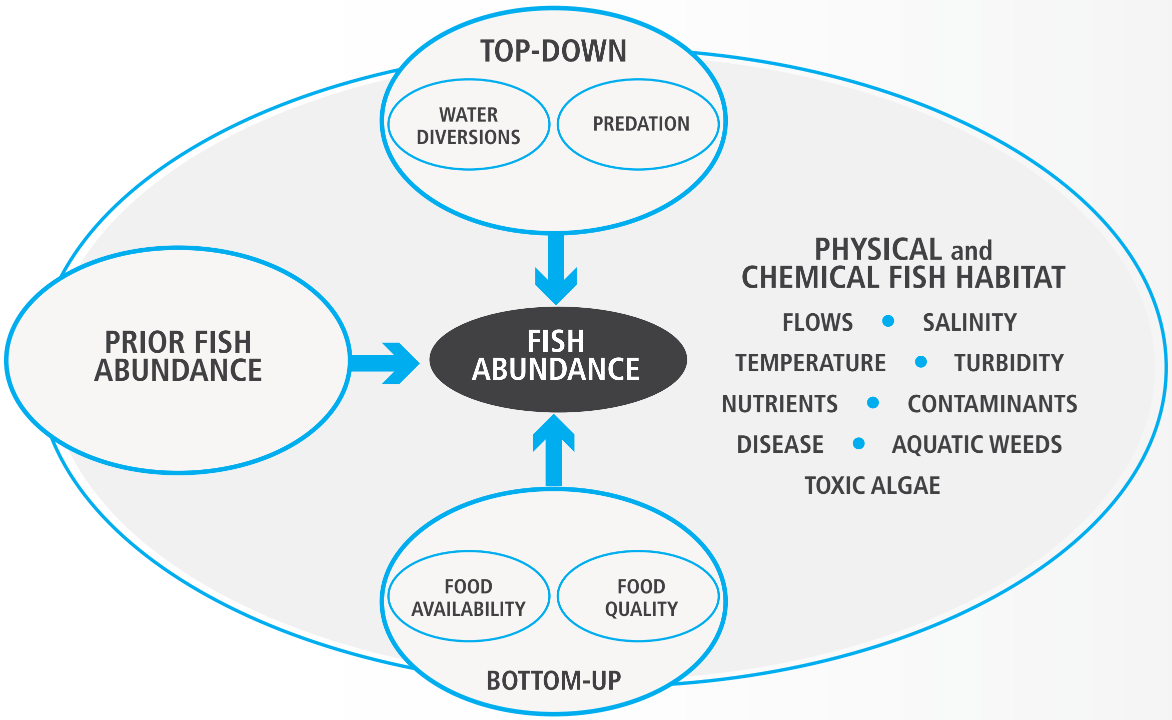
In 2005, the IEP formed a Pelagic Organism Decline Management Team (POD-MT) to evaluate the potential causes of the declines.

The POD-MT has developed several conceptual models to guide POD work plan development and synthesize results. These conceptual models try to explain the "POD story" from different perspectives. The 2010 POD report contains three conceptual models.

1 The "basic POD conceptual model" (**FIGURE 2**) was introduced in 2006 and groups the effects of potential drivers of the POD into four categories (previous abundance, habitat, top-down effects, and bottom-up effects). The emerging conclusion is that the POD was caused by multiple and often interacting drivers.

2 "Species-specific conceptual models" were introduced in 2008. They show how the major drivers differ for each of the four POD fish species, and how they differ in relative importance during different life history stages or seasons. The results can inform management actions for individual POD species.

3 A new conceptual model posits that the POD represents a rapid ecological "regime shift" that followed a longer-term erosion of ecological resilience. This conceptual model represents a working hypothesis for future investigations. The POD regime shift story may inform management strategies aimed at shifting the ecosystem into a more desirable state and improving long-term ecosystem resilience.



Footnote: Conceptual model from Baxter et al 2010. Adapted from Sommer et al. 2007.

FIGURE 2

FOUR POSSIBLE CAUSES OF THE POD.
This conceptual model is rooted in food web and fisheries ecology and identifies four possible causes for the POD: **(1)** Prior low fish abundance: decimated fish populations produce less young, exacerbating the effect of stressors. **(2)** Physical and chemical stressors: the presence of contaminants and other detrimental changes - at least partially due to and in tandem with extremely modified flows - have resulted in a severe decline in fish habitat quality. **(3)** Top-down (high loss of individuals): predators and the pumps of the water projects decimate fish populations. **(4)** Bottom-up (food issues): invasive species, flow modifications, and changes in nutrient levels have drastically altered the food web and impair the survival and reproduction of the POD species through reduced food availability and quality.

MANAGEMENT UPDATE

Sacramento River near Freeport Bend. Photograph by Thomas Jabusch. →

DELTA RMP: RE-THINKING WATER QUALITY MONITORING IN THE DELTA

HIGHLIGHTS

- There are numerous active water quality monitoring programs in the Delta
- A majority of the existing programs are narrowly focused, designed to comply with regulations and satisfy individual permit requirements
- Due to different program mandates, different permit requirements, different procedures for proving compliance, and difficulties in combining existing data, there is no method for utilizing the information comprehensively
- The proposed remedy for the lack of integrated, comprehensive monitoring and analysis is a Delta Regional Monitoring Program (Delta RMP)
- The Water Boards are committed to the success of a Delta RMP and are willing to negotiate regulatory requirements in order to achieve more integrated monitoring.
- Stakeholders with an interest in Delta water quality will need to contribute time and resources to continue developing the major aspects of the program: governance, monitoring objectives, funding, data integration, and coordination with other programs

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MONITORING AND MANAGING WATER QUALITY IN THE DELTA

The Delta is California's water crossroads. It provides two-thirds of Californians - an estimated 25 million people - with water. The Delta also supports more than 80% of the state's commercial salmon fishery, and is home to more than 750 plant and animal species - including 31 species that are threatened or endangered – that, in some cases, are found nowhere else.

The Delta is the heart of California's water system. And it is in crisis.

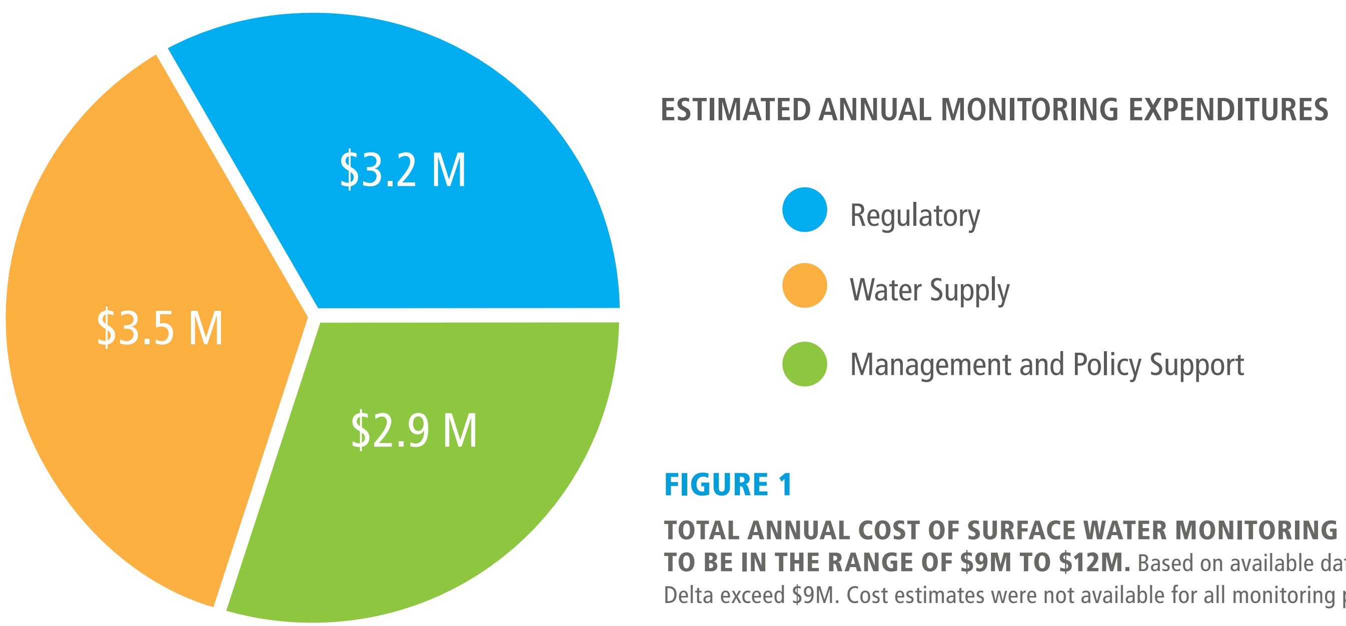


FIGURE 1

TOTAL ANNUAL COST OF SURFACE WATER MONITORING IN THE DELTA IS ESTIMATED TO BE IN THE RANGE OF $9M TO $12M. Based on available data, monitoring expenditures in the Delta exceed $9M. Cost estimates were not available for all monitoring programs.

Preserving the Delta's resources requires decision-makers to carefully evaluate and balance how its waters are used. Recently, but especially in the past decade, the challenges associated with this balancing have escalated. The drastic, simultaneous decline of several key fish species, known as the Pelagic Organism Decline (POD), left water quality managers wondering "What happened?" Immediately following this decline, numerous studies tried to find a cause. Despite millions of dollars of effort (**FIGURE 1** on **page 23**), no simple answer was found. In addition, it was clear that the data collected was not comprehensive and easy to use.

A majority of the existing monitoring programs are designed to comply with regulations and satisfy individual permit requirements. These efforts are extremely useful to ensure that discharges do not exceed established limits and impair the health of receiving waters. However, due to different program mandates, different permit requirements, different procedures for proving compliance, and no established method to combine collected data, there is no way to reach a comprehensive understanding of Delta conditions. It's time to rethink the existing monitoring scheme.

By coordinating efforts and making data available, regulatory compliance monitoring will become more efficient, consistent, and cost-effective while developing a more comprehensive view of the Delta. Improvements in the way water quality monitoring is managed will lead to improvements in the way the Delta is managed.

THE WATER BOARDS ARE COMMITTED TO DEVELOPING THE DELTA RMP

The recognition that data from existing monitoring could not be combined easily, let alone combined to identify a definitive reason for the POD, was a wake-up call to regulatory agencies, including the State Water Resources Control Board and the Central Valley Regional Water Quality Control Board (collectively, the Water Boards). Despite being tasked with protecting the beneficial uses of state waters, the researchers and the Water Boards could not definitively conclude whether or not contaminants were a factor in the decline of the pelagic species. This lack of understanding sparked a renewed effort from the Water Boards to determine factors important to the health of the Delta. As a result, the State Water Board, the San Francisco Bay Regional Water Board, and the Central Valley Regional Water Board jointly developed a Bay-Delta Team and a strategic workplan to "improve coordination of Water Board activities affecting the Delta and moderate impacts to the beneficial uses of water in the Bay-Delta."

The workplan includes several actions that:

1. implement the Water Boards' core water quality responsibilities;
2. continue to meet prior Water Board commitments;
3. are responsive to priorities identified by the Governor and the Delta Vision Blue Ribbon Task Force; and
4. build on existing initiatives, such as the Bay Delta Conservation Plan (BDCP).

These actions require coordination with other efforts and entities. The development of a comprehensive water quality monitoring program is included as a priority action. The Water Boards have repeatedly demonstrated their commitment to an RMP that is developed through a comprehensive stakeholder process including all other agencies and organizations involved and interested in monitoring in the Delta. The Water Boards have dedicated staff and funding to assist in coordinating the development of a successful, sustainable program.

The benefits of a local, stakeholder-developed RMP will be numerous. An RMP that engages all the different interests involved with Delta water quality can help the Water Boards reassess their policies, permits, and regulations and focus actions on the most pressing concerns, many of which require region-wide cooperation for long-term solutions. A well-developed RMP can effectively guide management decisions and establish priorities that benefit multiple parties.

An RMP can help transform existing piecemeal monitoring into a more efficient, whole-scale system. Focusing on the Delta system as a whole may reveal opportunities to combine, change, or reduce existing regulatory monitoring requirements. Not only can this save money, it can help develop a broader picture of the condition of the Delta ecosystem.

In addition to coordinating monitoring, an RMP can improve the management of the resulting data. An RMP will help standardize data formats and protocols, increasing the ease with which data can be combined and extracted from various databases. One of the biggest benefits of an RMP will be improved access to the wealth of collected data. Improved data management systems will help ensure monitoring serves a broad purpose. The information will be used to inform not just Water Board decisions, but also other agencies and the public. Researchers will also be able to use data generated through an RMP to augment data they collect themselves.

An RMP can play a large role in informing the public of the challenges and opportunities that exist within the Delta. Publications like the *Pulse of the Delta*, newsletters, and related writings can disseminate information in non-technical formats. An RMP can reduce misinformation and help attract additional focus on specific problems. With an RMP, regulators can gain a better idea of specific impacts and attract funding for research, restoration, additional studies, and more.

The Water Boards have focused efforts on developing and establishing a Delta RMP in order to build additional interest and involvement in the region. The Water Boards cannot develop a successful RMP on their own. The Water Boards are fully committed to the success of the Delta RMP and are willing to negotiate regulatory requirements in order to achieve more integrated monitoring.

MOVING FORWARD WITH THE DELTA RMP

While the Water Boards have contributed time and funding to the early development of the Delta RMP, a truly successful and sustainable program will require partnership with stakeholders. Stakeholders with an interest in the Delta region (see Figure 1 of the Introduction, **page 6**) will need to actively contribute time and resources to continue developing the major aspects of a combined, sustainable program which is useful to all involved: governance, monitoring objectives, funding, data integration, and coordination with other programs. The ultimate goal is a win-win-win for the community, regulators, and the environment, achieved through more efficient monitoring, more comprehensive information, and more effective water quality protection. To date, the Delta RMP has developed under strong control and guidance from the Water Boards. Staff have produced the existing documents and coordinated all stakeholder meetings and workgroups. As we continue to move forward in developing a strong, independent Delta RMP, the voluntary, ad-hoc workgroups will need to become more formalized and develop a structure to run with less direction from the Water Boards. This structure has not been pre-determined and is likely to evolve as further coordination develops through programs like the Interagency Ecological Program and the Delta Science Program, among others. Regardless, an RMP with active support and involvement from parties directly affected by its findings will be more likely to succeed over the long term. And it is clear from events like the POD that we desperately need to establish an understanding of baseline status and be able to track trends in water quality over time.

BETTER INFORMATION FOR BETTER MANAGEMENT

The Delta RMP has been a long time in coming. There are formidable challenges to overcome, as is apparent from previous attempts at developing a comprehensive monitoring program for the Delta. It is widely thought that these previous attempts failed mainly because they were too ambitious. Lessons learned from these previous efforts and from the successful implementation of RMPs in other regions (San Francisco Bay, Southern California Bight) are expected to help avoid these and other potential pitfalls in the future. The following principles will be followed to develop a Delta RMP that is feasible, sustainable, and widely supported:

- start small and focused
- strive for cost neutrality
- approach planning and implementation in several consecutive phases that build on each other
- institutionalize periodic external program review and provide mechanisms for the continuous adaptation of the Delta RMP based on information generated, and
- pursue an inclusive, tiered stakeholder approach (not just government agencies) and develop a manageable governance structure for obtaining stakeholder input.

Initially, the Delta RMP will focus on contaminants-related issues and the program development will proceed gradually, based on funding availability and feasibility. With stakeholder support, the Delta RMP will be able to make strides in creating efficiencies in the current monitoring system and improving access to important water quality information. Early success of the Delta RMP could then attract additional funding sources. The ultimate goal is to directly address key questions about Delta water quality from a managers' perspective. Through coordination and collaboration with other programs, including biological and physical monitoring programs, the Delta RMP can foster integrated monitoring and assessments that can generate and deliver this information while reducing duplicative monitoring efforts. The envisioned outcome is sustainable, better protected uses of Delta water.

Comments or questions regarding the Delta Regional Monitoring Program can be addressed to Meghan Sullivan, Central Valley Regional Water Board, (916) 464-4858, msullivan@waterboards.ca.gov.

To join the Delta Water Quality mailing list, please go http://www.swrcb.ca.gov/rwqcb5/water_issues/delta_water_quality/index.shtml.

WATER QUALITY MONITORING IN THE DELTA

Seventeen long-term water quality monitoring programs are underway in the Delta, collecting data at more than 200 different sampling locations. At least 22 different entities are involved in collecting the data, at an estimated annual cost of $9 to $12M.

AGRICULTURAL SUBSURFACE DRAINAGE PROGRAM

1 Central Valley Water Board

CONTINUOUS MULTIPARAMETER MONITORING

2 IEP Environmental Monitoring Program

CONTINUOUS RECORDERS

3 Department of Water Resources (DWR) Environmental Water Quality and Estuarine Studies

4 Bureau of Reclamation

DELTA FLOWS NETWORK

5 U.S. Geological Survey

DELTA-MENDOTA CANAL WATER QUALITY MONITORING

6 Bureau of Reclamation

DISCRETE PHYSICAL/CHEMICAL WATER QUALITY SAMPLING

7 IEP Environmental Monitoring Program

IRRIGATED LANDS REGULATORY PROGRAM

8 San Joaquin County and Delta Water Quality Coalition

9 Sacramento Valley Water Quality Coalition

10 South San Joaquin Irrigation District

MUNICIPAL WATER QUALITY INVESTIGATIONS

11 DWR Office of Water Quality

NATIONAL WATER QUALITY ASSESSMENT PROGRAM

12 U.S. Geological Survey

NPDES SELF-MONITORING PROGRAM

Stormwater

13 City of Stockton & County of San Joaquin

14 Sacramento Stormwater Quality Program

15 Stockton Port District

Wastewater

16 City of Brentwood

17 City of Lodi

18 City of Manteca

19 City of Rio Vista Beach

20 City of Rio Vista–Trilogy/Northwest

21 City of Sacramento (Combined Sewer System)

22 City of Stockton

23 City of Tracy

24 Deuel Vocational

25 GWF Power Systems

26 Mountain House Community Services District

27 Oakwood Lake Water District

28 Sacramento Regional County Sanitation District

29 Town of Discovery Bay Community Services District

SACRAMENTO COORDINATING MONITORING PROGRAM

30 Sacramento Regional County Sanitation District

SACRAMENTO REGIONAL WASTEWATER TREATMENT PLANT PRIORITY POLLUTANT PREMIUM PROGRAM

31 Sacramento Regional County Sanitation District

SAN FRANCISCO BAY RMP

32 San Francisco Estuary Institute

SOURCE WATER MONITORING

33 Contra Costa Water District

STATE WATER PROJECT WATER QUALITY MONITORING

34 DWR Operations & Maintenance

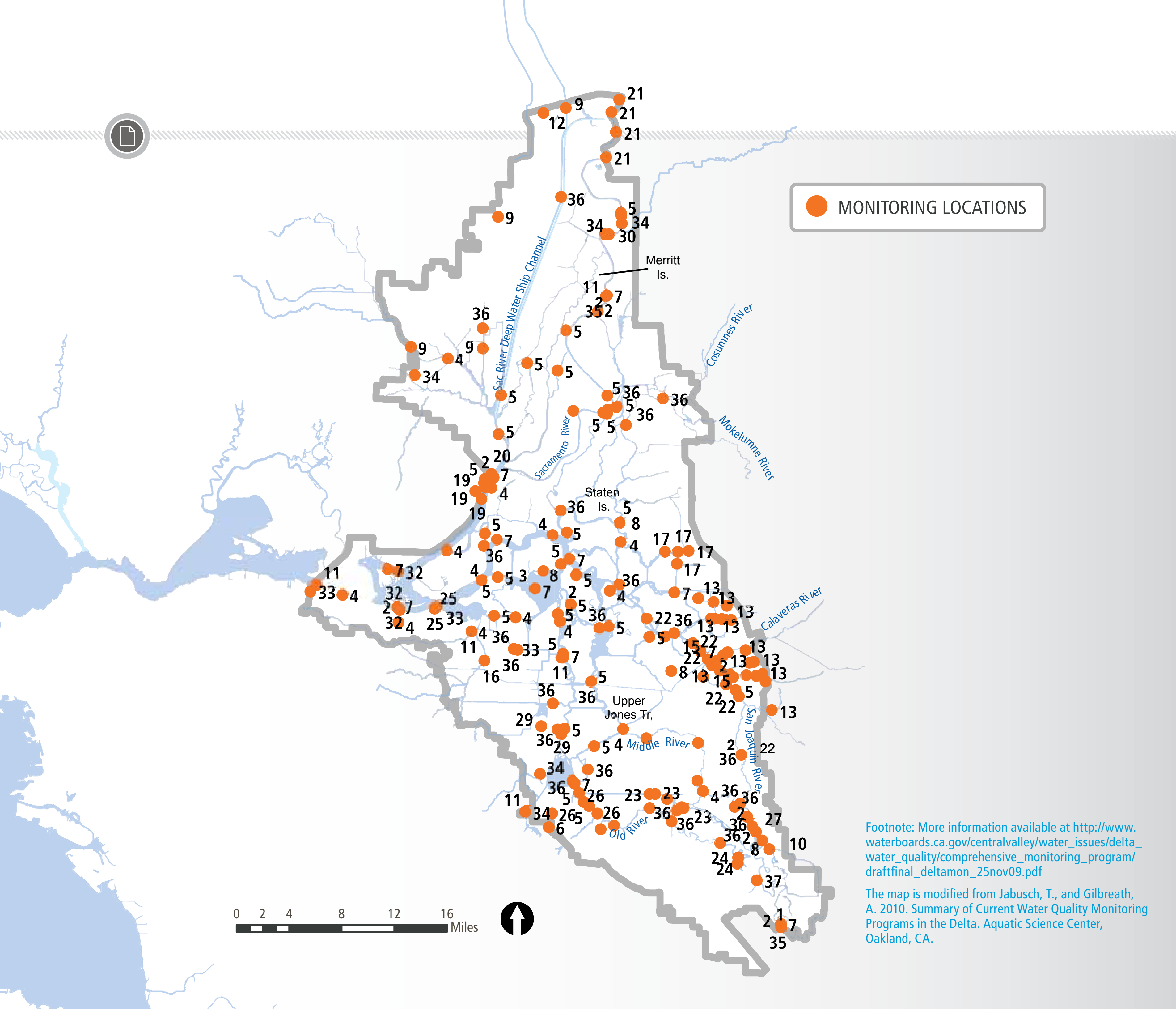
SURFACE WATER AMBIENT MONITORING PROGRAM

35 Central Valley Water Board

SURFACE WATER MONITORING

36 DWR Central District

37 DWR/San Joaquin Valley Drainage Authority



Footnote: More information available at http://www.waterboards.ca.gov/centralvalley/water_issues/delta_water_quality/comprehensive_monitoring_program/draftfinal_deltamon_25nov09.pdf

The map is modified from Jabusch, T., and Gilbreath, A. 2010. Summary of Current Water Quality Monitoring Programs in the Delta. Aquatic Science Center, Oakland, CA.

FEATURE ARTICLES

Georgiana Slough near Walnut Grove. Photograph by Thomas Jabusch. →

AMMONIA IN THE DELTA: STATE OF THE SCIENCE, IMPLICATIONS FOR MANAGEMENT

HIGHLIGHTS

- Total ammonia levels have doubled in portions of the Delta over the past 20 to 25 years
- One of the key findings of recent monitoring is that ambient levels of ammonia are unlikely to be toxic to fish in the Delta
- Another key conclusion from recent monitoring is that elevated ammonium levels may be linked to low primary production in Suisun Bay and the Delta
- Wastewater discharges to the Delta portion of the Sacramento River are the single largest source of ammonium to the Bay-Delta ecosystem
- Recent monitoring found elevated ammonium levels at both ends of Suisun Bay, indicating that not all of the ammonium in Suisun Bay originates from wastewater discharges in the Delta
- Further monitoring and modeling will be essential to evaluate how altered ammonium levels and nutrient balances are affecting the Delta's phytoplankton community and what types of nutrient management strategies might help the Delta-Suisun Bay food web recover

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RISING CONCERNS OVER AMMONIA

A significant increase in ammonia levels in Delta waterways over the past 20 to 25 years (Jassby 2008) has triggered concerns about impacts on the Bay-Delta ecosystem. Ammonia can be toxic to fish and other aquatic life and, as ammonium (see Sidebar: The Different Forms of Ammonia), may also be a factor controlling algal growth. This article summarizes recent studies evaluating the role of ammonia and presents a hypothesis for how current ammonia levels may be impacting the Delta and San Francisco Bay.

As part of an integrated series of workshops sponsored by the IEP, the Central Valley Regional Water Board organized the 2009 Ammonia Summit to discuss current knowledge about the role of ammonia in the Bay-Delta ecosystem. In this article, we report on the status of ammonia research and assessment since the Summit. Ammonia is one of a number of non-listed contaminants that are implicated in the Delta's ecological crisis, along with insufficient flows and a variety of contaminants for which the Delta has been listed under section 303(d) of the Federal Clean Water Act (Crader et al. 2010). Only recently have enough data accumulated through focused monitoring and experimental studies to begin to address the question of whether current ammonia levels are causing beneficial use impairments to the Bay-Delta ecosystem.

Estimates based on available nutrient monitoring data and river flow information identify the Sacramento Regional Wastewater Treatment Plant (SRWTP) as the source of 90% of the total ammonia in the Delta portion of the Sacramento River and as the single largest source of ammonia in the Bay-Delta system (Jassby 2008). Other sources of ammonia to the Bay-Delta system include other wastewater treatment plants, agricultural runoff, atmospheric deposition, and possibly discharges from wetlands (Ballard et al. 2009).

AMMONIA TOXICITY IN THE DELTA: SEARCHING FOR THE SMOKING GUN

One of the key findings of recent monitoring is that ambient free ammonia concentrations (SEE SIDEBAR: THE DIFFERENT FORMS OF AMMONIA) found at Delta sampling sites during a two-year monitoring study (SEE SIDEBAR: AMMONIA MONITORING IN THE DELTA) never exceeded known toxicity thresholds for sensitive local fish species like Delta smelt (FIGURE 3). Free ammonia concentrations were highest at Hood, the first monitoring station downstream of the SRWTP, and lowest at the two upstream stations. Compared to the U.S. Environmental Protection Agency (USEPA) chronic ammonia criterion for juvenile fish present in the Delta, ambient ammonia levels at all Delta sites were considered safe.

THE DIFFERENT FORMS OF AMMONIA

Two forms of ammonia are commonly reported and considered in water quality management: total ammonia and free ammonia. Total ammonia is the sum of both free ammonia (also known as unionized ammonia, chemical symbol NH_3) and ammonium (or ionized ammonia, chemical symbol NH_4^+). This distinction is important because free ammonia is more toxic to fish and most invertebrates, and ammonium is the form taken up by algae and plants as a nutrient. Total ammonia is easy to measure and can be converted into values for free ammonia and ammonium, based on the pH and water temperature. As pH or temperature increase, the ratio of free ammonia (NH_3) to ammonium (NH_4^+) increases.

AMMONIA MONITORING IN THE DELTA

To evaluate impacts of ammonia levels downstream of the Sacramento Regional Wastewater Treatment Plant (SRWTP), staff from the Central Valley Regional Water Board measured nutrient patterns at 21 sites between March 2009 and February 2010 (Foe et al. 2010). The study was designed to fill in critical information for assessing possible beneficial use impairments caused by ammonia that could not be gleaned from existing long-term monitoring datasets. The purpose of this study was threefold. First, collect nutrient data, including ammonia, at key locations in the Delta throughout an annual hydrologic cycle to characterize concentrations and compare with reported toxicity endpoints for sensitive local aquatic organisms. Second, determine biologically and tidally induced short-term variability in nutrient concentrations at key locations. Third, compare ancillary water quality measurements collected in this study with real-time remote sensing values reported by the IEP Environmental Monitoring Program (EMP) for the same time and place to determine the comparability of the two data sets. The sampling sites include nine stations along the Sacramento River from the City of Sacramento to Chipps Island (**FIGURE 1**). Each station was visited monthly and samples were analyzed for different forms of nitrogen (including ammonia), phosphorus, chlorophyll, and additional water quality parameters. Of particular importance was the measurement of ammonia concentrations together with the associated pH values to estimate ambient levels of free ammonia.

The data were used to characterize ammonia levels and compare them with USEPA chronic and acute toxicity criteria and other toxicity thresholds for sensitive local species. The measured ammonia concentrations never exceeded any of these values. The transect sampling resolved clear spatial trends downstream of the SRWTP that point to the microbial transformation of ammonia to nitrite and nitrate as the environmental process with the largest effect on nutrient patterns downstream of the SRWTP (**FIGURE 2**).

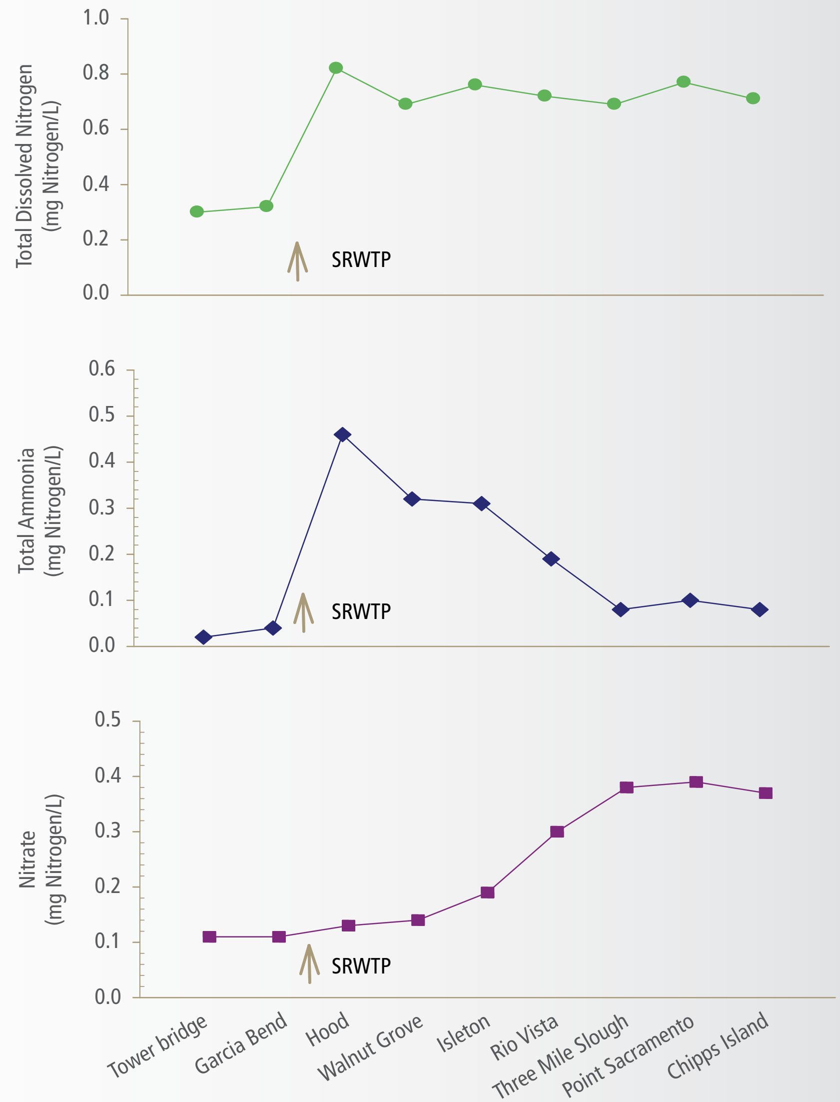
Footnote: From Foe et al. 2010

← FIGURE 1

CENTRAL VALLEY REGIONAL BOARD STAFF MONITORED NUTRIENTS, INCLUDING AMMONIA, AT 21 SITES in the Delta between March 2009 and February 2010. The SRWTP, currently the largest identified source of ammonia to the Delta, discharges between Garcia Bend and Hood.

FIGURE 2 →

AMMONIA CONCENTRATIONS INCREASED BELOW THE SRWTP OUTFALL AND GRADUALLY DECLINED DOWNSTREAM. Total dissolved nitrogen (TDN) is the sum of all forms of dissolved nitrogen. TDN concentrations remain constant between Hood and Chipps Island while ammonia and nitrite/nitrate concentrations are the mirror image of each other. The data suggest that there are no other large nitrogen sources or sinks and that the microbial transformation of ammonia to nitrite and nitrate is a key process in determining nitrogen patterns along the water flow path. In the presence of oxygen, bacteria in the water column convert ammonia to nitrite and nitrate in a two-step process called nitrification. First, ammonia is oxidized to nitrite (NO2), and then nitrite is oxidized to nitrate (NO3),



Footnote: From Foe et al. 2010. See Figure 1 for station locations.

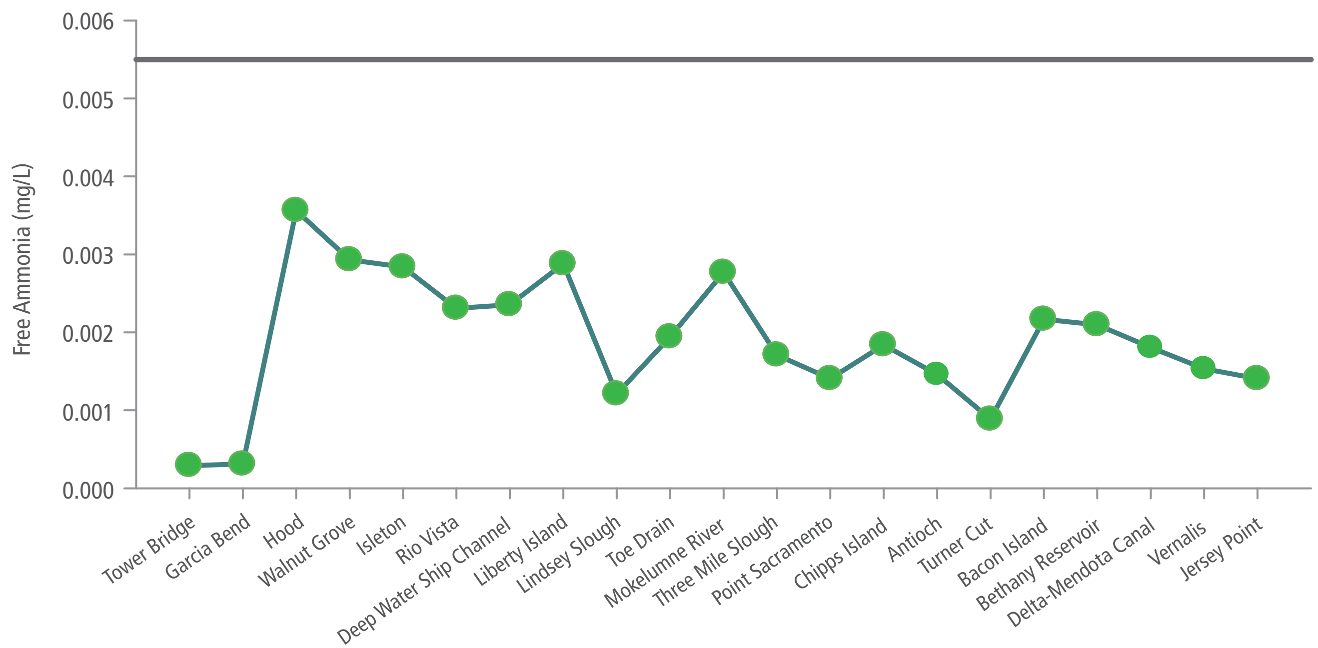


FIGURE 3

MEASURED FREE AMMONIA CONCENTRATIONS AT DELTA SAMPLING SITES ARE CONSIDERED TOO LOW TO AFFECT DELTA SMELT. The black line represents a conservative estimate of the chronic no effect concentration for Delta smelt. Symbols represent mean of free ammonia levels in the Delta between March 2009 and February 2010.

Footnote: From Foe et al. 2010.

Free ammonia levels from the ambient monitoring study also never exceeded USEPA's new and more stringent draft criteria for freshwater mussels, but the safety margin was much smaller than for juvenile fish. Because freshwater mussels are more sensitive to free ammonia than fish, the proposed chronic ammonia criterion to protect freshwater mussels is about five to ten times lower than the existing chronic criterion for juvenile fish. The new criterion is intended to protect highly sensitive Unionid freshwater mussels, which have been reported in the Sacramento watershed (personal communication, Jeanette Howard of The Nature Conservancy) but have not been confirmed at the SRWTP outfall.

The research group of Dr. Swee Teh from the U.C. Davis School of Veterinary Medicine reported that ambient ammonia levels in the Sacramento River below the outfall could affect the reproduction and survival of larvae of the copepod *Pseudodiaptomus forbesi*, a zooplankton species that is an important forage organism for larval fish in the Delta (Teh et al. 2009). They also observed more toxicity at lower pH values, suggesting that ammonium ions may be more toxic to these invertebrates than free ammonia, a finding that is at odds with our current understanding of ammonia toxicity. Additional experiments are now being performed to confirm these findings.

IMPACTS ON THE DELTA-SUISUN BAY FOODWEB

A second key conclusion from recent monitoring is that elevated ammonium levels may be linked to an altered, diminished Delta-Suisun foodweb. A dwindling algal food supply of inferior quality is one of the "bottom up" factors suspected to contribute to the POD (Sommer et al. 2007, Baxter et al. 2010). There has been a downward trend in the abundance and productivity of algae over the last few decades combined with a "demographic" change in the algal community from ecologically important diatoms to smaller, less desirable species (Brown 2009; Jassby 2008; Lehman 2000). For many species of zooplankton, an important food for fish larvae, diatoms are considered to be more nutritious than smaller algae such as some species of flagellates and most blue-green algae. Several drivers are thought to play a role in these changes to the algal community. Among them are invasive species, water diversions, and changes in upstream nutrient loadings (Baxter et al. 2010, Nieuwenhuyse 2007). Researchers and regulators are now considering whether increased ambient levels of ammonium are linked to observed changes in the algal community and lowered algal growth rates and chlorophyll levels.

Drs. Richard Dugdale and Frances Wilkerson and their colleagues at San Francisco State University have studied the role of ammonium in controlling phytoplankton productivity in the San Francisco Estuary since 1999 (Dugdale et al. 2007). Their studies provide evidence that ammonium-induced shutdown of nitrate (another form of nitrogen that is an important nutrient for algal growth) uptake prevents spring diatom blooms from developing when conditions are otherwise favorable. (A "bloom" is a rapid increase in the number of algal cells such that the blooming algae dominate the algal community.) They observed that spring diatom blooms only occur in years when ambient ammonium is below levels reported to inhibit nitrate uptake and algal production (**FIGURE 4**). Focused monitoring in spring 2010 detected two diatom blooms in Suisun Bay. Both occurred when ammonium was below the nitrate uptake shutdown level of 0.056 mg/L (**FIGURE 5A**). At all other times, ammonium levels in Suisun Bay were above this threshold and no blooms were observed (**FIGURE 5B**). Suppression of diatom blooms in Suisun Bay is presently the most compelling evidence for beneficial use impairment by ammonia and ammonium originating in the Delta's watershed. High filtration rates by the introduced clam *Corbula* and high turbidity (cloudiness) caused by suspended sediments are additional factors that may be responsible for reducing diatom production and standing algal biomass in Suisun Bay. A combination of the above three factors - increased ammonium, grazing by *Corbula*, and high turbidity - could explain the low diatom abundance now present in Suisun Bay.

There are also concerns that current ammonium levels may suppress diatom growth in the Delta upstream from Suisun Bay, but results are not entirely conclusive. Dr. Alex Parker from San Francisco State University led two studies to determine the effect of ammonium on algal production in the Sacramento River and Delta (Parker et al. 2010 a and b). The first study evaluated the impact of elevated ammonia levels on nitrogen uptake and primary production rates in the Sacramento River immediately above and below the SRWTP. The second study measured nitrogen uptake and primary production rates along a much longer transect (about 100 miles) from above the SRWTP to San Pablo Bay. Results from both studies indicate that ammonium levels in the river downstream of the SRWTP are high enough to shut down nitrate uptake in algae. This is an important observation, since as noted above it points to a possible mechanism for the observed shift in the Delta algae community from important diatoms to smaller species. In the longer transect study, a U-shaped pattern of primary production and chlorophyll was observed on both of two cruises with a maximum in the river above the SRWTP and again to the west in San Pablo Bay, essentially a mirror image of the distribution of ammonia concentrations. These results are consistent with the earlier observations for Suisun Bay that ammonia concentrations suppress algal primary production and standing chlorophyll levels and appear to extend these findings to the freshwater Delta.

IMPLICATIONS FOR NUTRIENT MANAGEMENT

There is evidence that ambient ammonia levels may have detrimental effects on biological productivity and algal community composition in the Delta-Suisun Bay system. This has significant implications for water quality control, ecosystem restoration, and future monitoring and research.

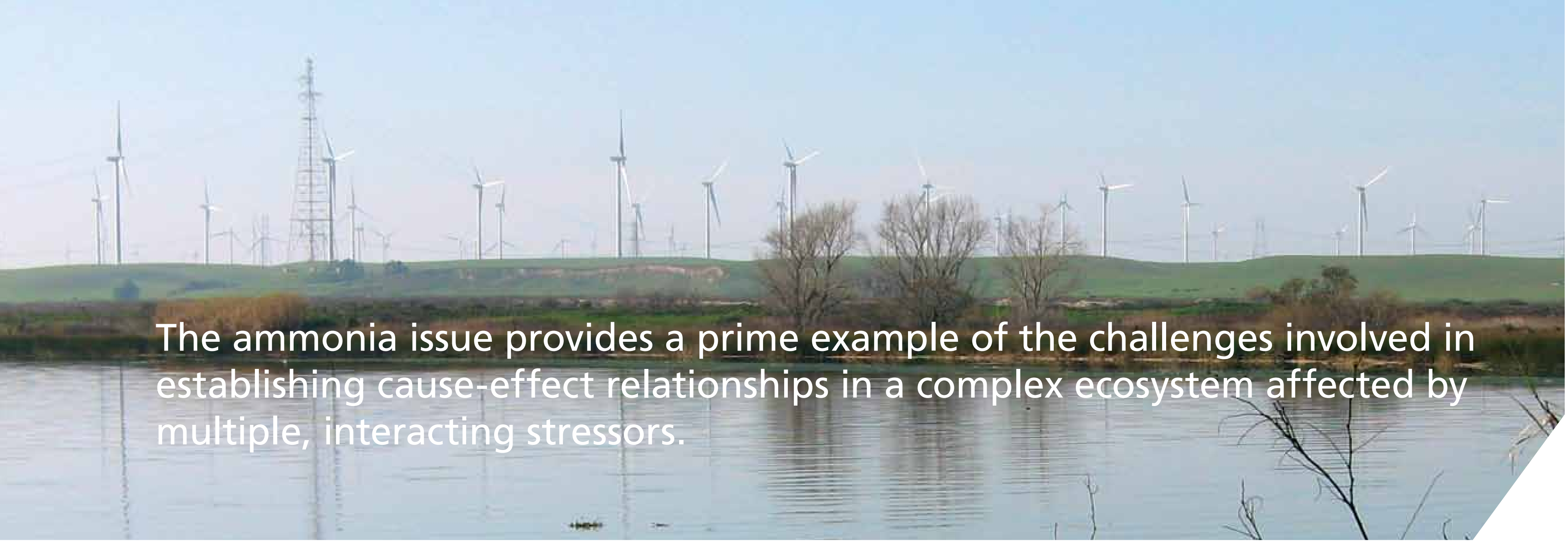
The Central Valley Water Board's monitoring study (see sidebar, **page 32**) confirmed the Delta as a major source of ammonium to Suisun Bay. Recent monitoring by the San Francisco Bay Water Board found elevated ammonium levels at both ends of Suisun Bay, indicating that not all of the ammonium originates from the Delta and thus the SRWTP (**FIGURE 5**). Preliminary calculations suggest that combined ammonia loads may need to be reduced by 50 to 85 percent to eliminate ammonium-induced suppression of diatom production in Suisun Bay. Reducing ammonium levels in the Delta will require more stringent nutrient load controls on all wastewater treatment plants that discharge significant loads of ammonia to Suisun Bay and the Delta (Jassby 2008).

In December 2010, the Central Valley Regional Water Board adopted a new NPDES permit for the SRWTP with more stringent effluent limits for ammonia. The new permit requires a 20-fold ammonia reduction in the daily maximum concentration (from 45 to 2 parts per million) and a 13-fold reduction in the average monthly concentration (24 to 1.8 parts per million). When implemented, the new limits are expected to reduce ammonium concentrations below values thought to inhibit nitrate uptake by diatoms at all locations in the Delta and Suisun Bay. The SRWTP is appealing the new permit to the State Water Board, on the grounds that the Regional Board did not adequately demonstrate that ammonia releases were causing beneficial use impairments in the Delta.

FIGURE 4

SPRING BLOOMS IN SAN FRANCISCO BAY ARE OBSERVED ONLY WHEN AMMONIUM CONCENTRATIONS ARE LOW AND NITRATE UPTAKE IS HIGH. Algae can utilize ammonium, but this nutrient only supports slow growth rates and suppresses the uptake of nitrate. This ammonia-induced suppression of nitrate uptake is thought to prevent spring algal blooms from developing when conditions are otherwise favorable, since fast algal growth depends on the algae's ability to use nitrate. Therefore, the onset of spring blooms requires ammonium "draw-down" (through algal uptake or dilution by runoff) below a threshold level where it no longer limits the algae's access to nitrate. Once ammonium has dropped below the threshold, algae can access nitrate and a bloom can unfold (Wilkerson et al. 2006; Dugdale et al. 2007). Between 1999 and 2003, four spring peaks in chlorophyll (blooms) occurred in San Pablo and Central Bays (**FIGURE 4A**) and coincided with reduced ammonium concentrations, often near zero (**FIGURE 4B**). In Suisun Bay, only one bloom was observed, in 2000, that occurred when ammonium concentrations were low in the spring. The chlorophyll peaks in all bays were coincident with peaks in nitrate uptake (**FIGURE 4C**) that was otherwise very low (almost zero) the rest of the time. In all three bays sampled, concentrations of ammonium were above 0.056 mg/L most of the year (**FIGURE 4B**), except during the spring bloom periods.

Footnote: Adapted from Dugdale et al. 2007.



Sacramento River near Montezuma Hills. Photograph by Thomas Jabusch.

OUTLOOK FOR MONITORING AND RESEARCH

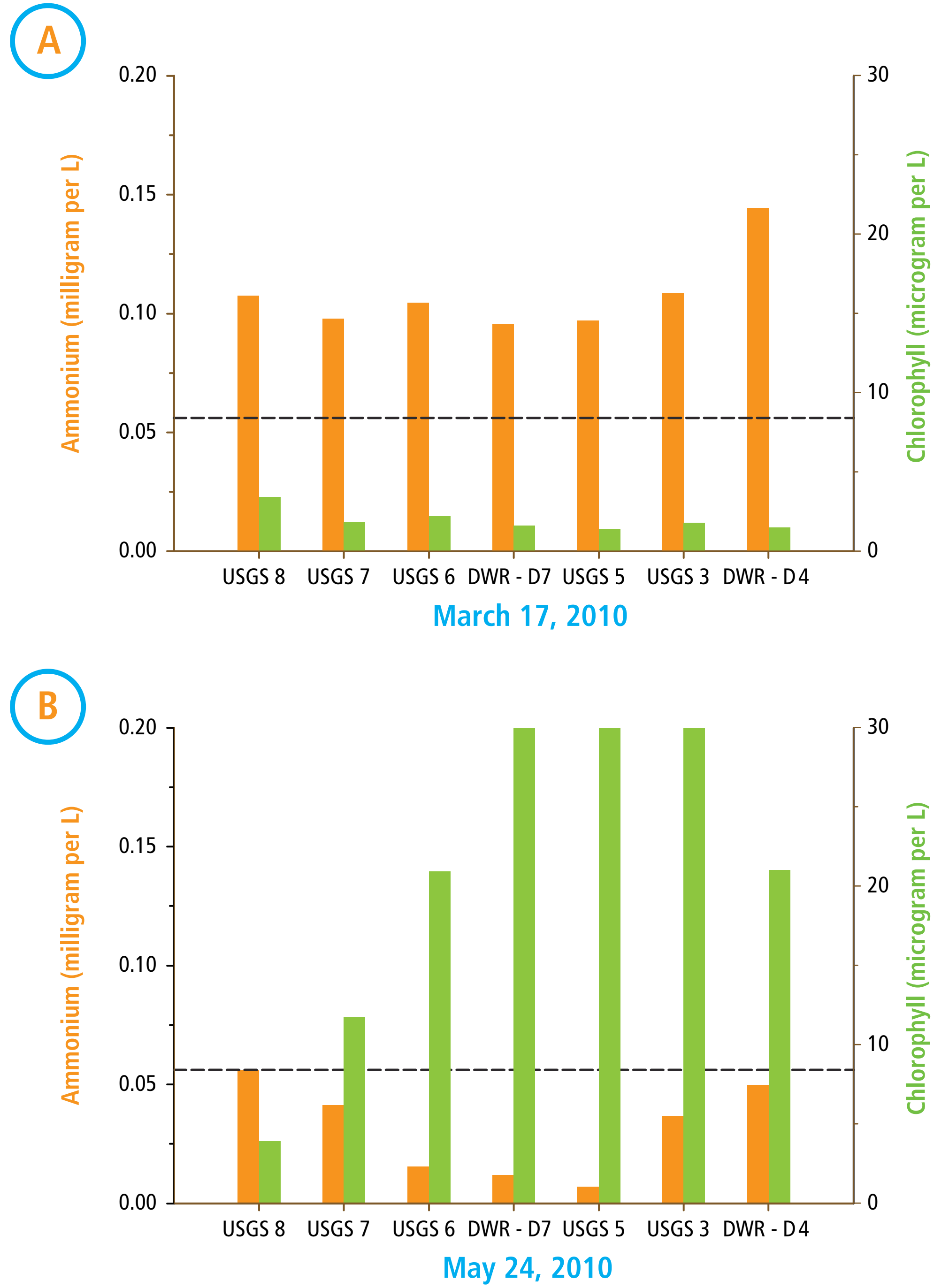
The ammonia issue provides a prime example of the challenges involved in establishing cause-effect relationships in a complex ecosystem affected by multiple, interacting stressors (Meyer et al. 2009). There is compelling evidence that current ammonia levels are impacting the diatoms of Suisun Bay, but it is not clear if they are a prime factor responsible for the observed demise of the Delta-Suisun Bay foodweb. By itself, the ammonia issue is but one of the many facets of an extremely complex and highly modified system. The issue is significant as an indicator of altered hydrology and nutrient supply, which arguably represent the main concerns of managers. There is a consensus that current research and monitoring programs are too narrowly focused to provide answers to these big questions. New holistic approaches are needed to study the Estuary and to compare it to past conditions and to other estuaries of similar size. Holistic approaches will require multidisciplinary collaborations that integrate water quality studies with hydrologic modeling, landscape ecology, and historical and comparative system analyses.

For ammonia specifically, Central Valley Regional Board staff evaluated the science needs and priorities that came out of the 2009 Ammonia Summit (http://www.swrcb.ca.gov/rwqcb5/water_issues/delta_water_quality/ambient_ammonia_concentrations/index.shtml) and identified future research priorities. Regional Board staff recommended specific experimental field studies to better understand the effect of ammonia and other nutrients on algal growth and species composition in the Delta. But there will also be a need for comprehensive, integrated long-term monitoring of nutrients and phytoplankton to better understand and adaptively manage the long-term relationships among nutrient levels and algae composition and growth. Follow-up monitoring and forecast models are needed to evaluate how the changed nutrient levels and balances are affecting the Delta's phytoplankton community and what types of nutrient management strategies might help the Delta-Suisun Bay foodweb revert to a healthy, diatom-based system. The emerging Delta RMP can play a valuable role in developing the needed long-term monitoring, coordinating resources and sampling, and synthesizing results.

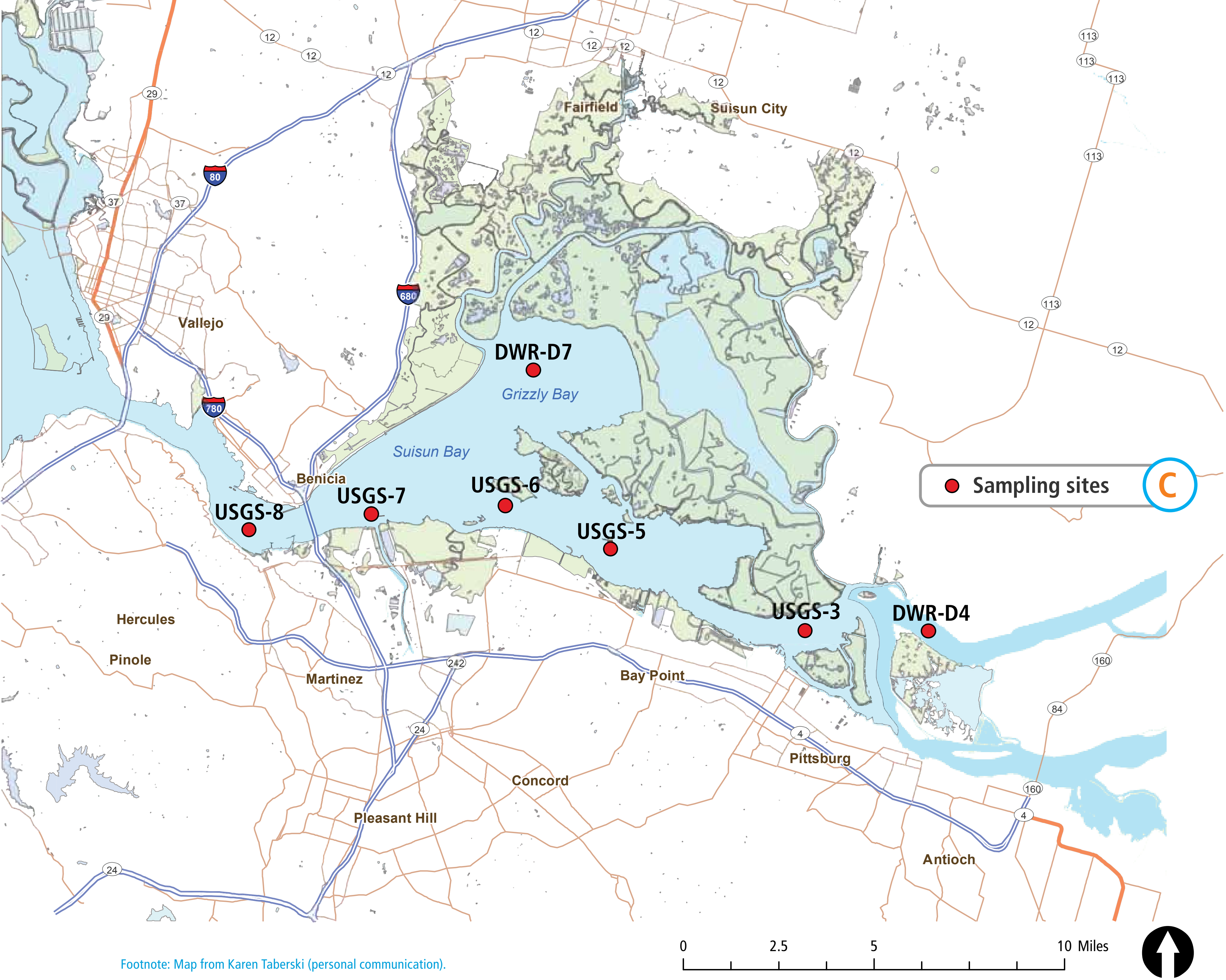
Since most of the ammonia of concern originates in the Central Valley while at least one of the impacts extends into the San Francisco Bay region, two Regional Boards are involved in the issue, requiring coordination of both the scientific investigations and the ultimate regulation. The Delta RMP could also play a role in cross-regional science coordination and ensuring appropriate stakeholder input and representation.

FIGURE 5

FOCUSED MONITORING IN SPRING 2010 DETECTED TWO DIATOM BLOOMS IN SUISUN BAY. Both occurred when ammonium was below the nitrate uptake shutdown level of 0.056 mg/L. **FIGURE 5A** shows representative data from March 17 for ammonium and chlorophyll levels during periods without blooms. Ammonium levels in Suisun Bay were always above this threshold when no blooms were observed. **FIGURE 5B** shows chlorophyll and ammonium data during one of the blooms on May 24. The sampling stations are along an east-west transect in Suisun Bay (**FIGURE 5C**). The San Francisco Bay Water Board found elevated ammonia levels at both ends of Suisun Bay, which would be consistent with ammonium originating from the Sacramento River and from seaward sources



Footnote: Data from Richard Dugdale (personal communication).



Footnote: Map from Karen Taberski (personal communication).

HOW DELTA STUDIES HAVE SHAPED OUR UNDERSTANDING OF PYRETHROID INSECTICIDES

HIGHLIGHTS

- Monitoring studies have shown that actions taken to control organophosphorus pesticides have led to increased use of pyrethroids and new water quality problems
- Pyrethroids are acutely toxic to sensitive species at very low concentrations (around a couple parts per trillion), and current analytical detection limits may be 30 times too high to adequately assess potential effects
- Nearly all urban runoff in northern California contains pyrethroids well above concentrations causing toxicity to sensitive aquatic life
- Pyrethroids in urban runoff originate from pesticide use around homes and commercial establishments
- Toxicity caused by pyrethroids is widespread in California but went unnoticed for many years, because monitoring programs were not looking for it or lacked needed analytical capabilities
- Monitoring programs must adapt to the constantly changing mix of toxic threats or risk monitoring for the problems of yesterday

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PYRETHROIDS "DE-GREENED"

Ten years ago, if you walked the pesticide aisle of the local hardware store, you would have found most insecticide products contained one of the organophosphorus compounds, diazinon or chlorpyrifos. That changed in the early 2000s when the U.S. Environmental Protection Agency (USEPA) and manufacturers agreed to withdraw diazinon and chlorpyrifos products intended for urban or residential usage because of health risks to users and their families. As the products were withdrawn, some of the replacement products were labeled "Looking for Dursban? Try this!" Dursban was a tradename for now-unavailable chlorpyrifos. "This" was any of several insecticides from a class known as pyrethroids.

But in recent years, environmental monitoring, much of it in the Delta, has shown we have largely just traded one toxicant for another.

Starting with the natural plant-produced insecticide pyrethrin, chemists modified the molecule to provide greater potency and longer environmental persistence, and the resulting synthetic compounds became known as pyrethroids. The first pyrethroids were developed in the 1940s, with many more created over the decades that followed. Their use by homeowners had been relatively limited until several of the organophosphates became unavailable in the early 2000s. In agriculture, where organophosphates are still widely used, pyrethroid use remains well behind the organophosphates. But in the urban environment, the withdrawal of the dominant organophosphates led to a dramatic increase in pyrethroid use. In 1999, non-agricultural use of pyrethroids in California was 325,000 pounds. By 2006 it had nearly tripled to 879,000 pounds. More recently (2008), use has declined to 442,000 pounds, possibly due to some extent to the emergence of alternative insecticides (see sidebar **NEW PESTICIDES, page 60**).

It was well documented that winter rains would wash organophosphate residues into creeks and rivers, causing toxicity to the standard freshwater testing species *Ceriodaphnia dubia* (Kuivila and Foe 1995). Many had hoped the shift to pyrethroids would eliminate these unintended aquatic effects. But in recent years, environmental monitoring, much of it in the Delta, has shown we have largely just traded one toxicant for another. For about five years we have known that pyrethroids commonly occur in creek sediments at concentrations toxic to sensitive invertebrates (Weston et al. 2005). In the past two years we have learned that nearly all urban runoff in the Delta contains toxic concentrations of pyrethroids and that municipal wastewater can also be a source (see **FIGURE 1**). We have further learned that pyrethroids also have endocrine disrupting properties (Jin et al. 2010, see sidebar **CEC PROJECTS IN THE DELTA** on **page 54**). Finally, we are just beginning to appreciate that the pyrethroid toxicity initially thought to be limited to sediments also extends into the water column, with water samples from urban creeks and rivers regularly showing toxicity after storms.

PYRETHROID TOXICITY IN URBAN CREEK SEDIMENTS

The first regional reports of pyrethroid-related urban sediment toxicity came from an area of intensive housing development in Roseville, a suburb located northeast of Sacramento (Weston et al. 2005). In laboratory tests, all sediments collected within developed suburban reaches of Pleasant Grove Creek and its tributaries showed toxicity to the crustacean *Hyalella azteca*. *Hyalella* is a standard test organism that is sensitive to pyrethroids and therefore a good indicator of sediment toxicity from this source (see Sidebar: **IDENTIFYING THE CAUSE OF TOXICITY**). Pyrethroid sediment concentrations capable of causing acute toxicity to *Hyalella* vary depending on the specific compound and sediment characteristics, but are often about 5 parts per billion (Amweg et al. 2006). *Hyallela* is common in California freshwater environments. It was present in the Pleasant Grove Creek system as well, though it was absent or present at reduced densities in those reaches of the creek with residential development (Weston et al. 2005; L. Hall, personal communication).

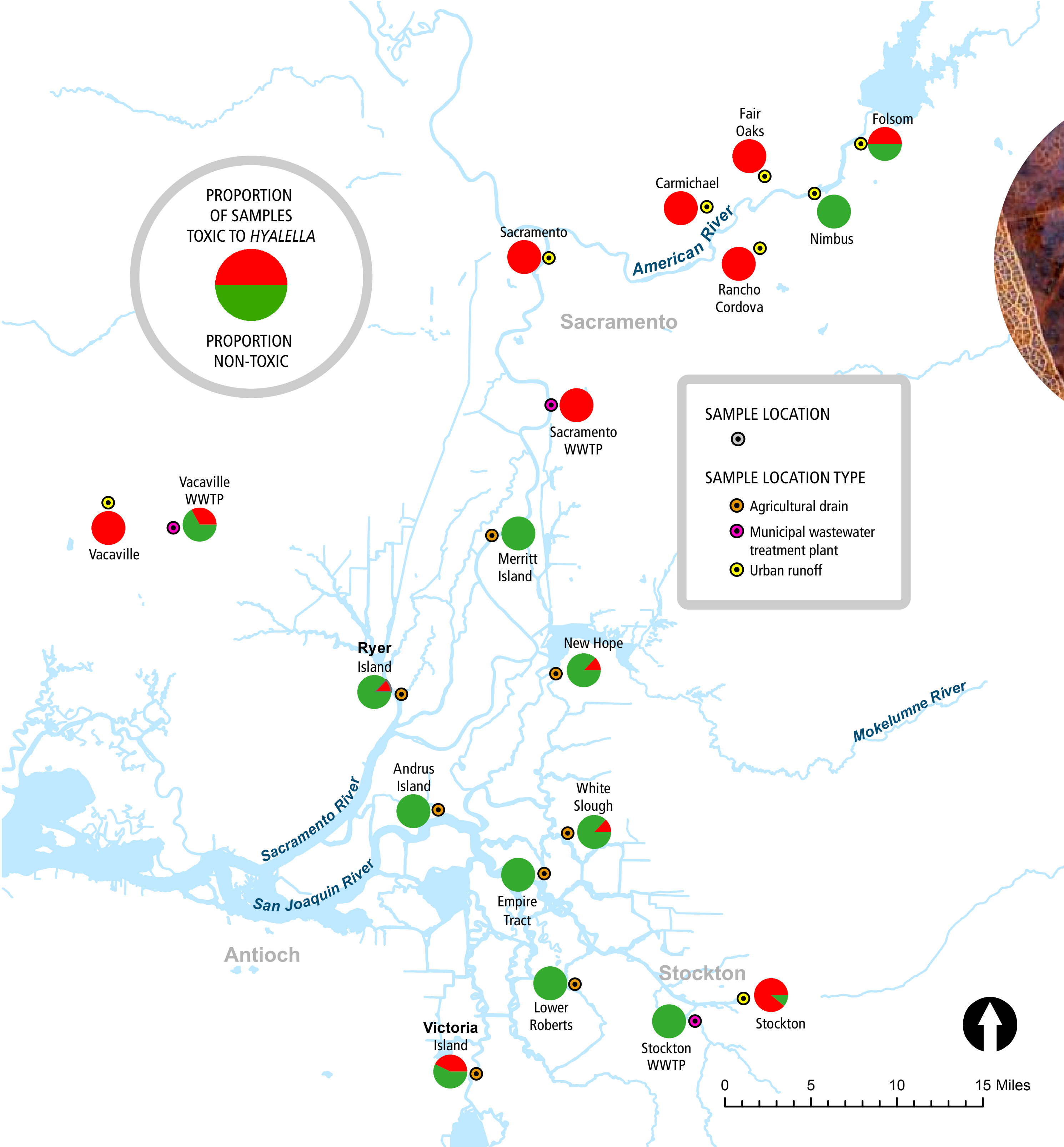
As monitoring efforts expanded, pyrethroid-related toxicity to *Hyalella* was found in about 15% of the agricultural sediment samples collected throughout the Central Valley (Weston et al. 2008). Even more striking was the toxicity in urban sediments, with nearly all sediments tested from Sacramento area creeks showing toxicity (Amweg et al. 2006). Further work by the State Water Board's Surface Water Ambient Monitoring Program demonstrated that urban creek sediment toxicity, much of it likely due to pyrethroids, extended statewide (Holmes et al. 2008). While pyrethroid-related toxicity to *Hyalella* appears widespread in urban creeks, only testing of sediments within the rivers and larger waterways of the Delta have shown little to no toxicity. Only three out of one hundred stations screened in 2007 were significantly toxic, using the 10-day *Hyalella* survival test. None of the 50 stations screened in 2008 were toxic (Lowe et al. 2008).

Despite the fact that pyrethroids are the most widely used insecticide in urban environments nationwide, the vast majority of sediment monitoring data on pyrethroids has come from California, and much of that work has been in the Delta.

Despite the fact that pyrethroids are the most widely used insecticide in urban environments nationwide, the vast majority of sediment monitoring data on pyrethroids has come from California, and much of that work has been in the Delta. But as the data from California have become known and sediment monitoring for pyrethroid toxicity has been initiated elsewhere, similar findings are emerging. Urban creek sediment toxicity to Hyalella, related to pyrethroids, has been documented in Texas and Illinois (Hintzen et al. 2009; Ding et al. 2010). In a nationwide survey by the U.S. Geological Survey (USGS), the pyrethroid bifenthrin, more than any other contaminant measured, best explained the sediment toxicity observed in creeks and rivers throughout the U.S. (C. Ingersoll, personal communication).

PYRETHROIDS ARE ALSO TOXIC IN THE WATER COLUMN

Pyrethroids are strongly associated with the organic matter found in sediments. Pyrethroid concentrations in sediment are typically about 5,000 times higher than concentrations in the overlying water. Therefore, the initial monitoring studies quite logically focused on the sediment, and the toxicity observed was presumed to be a threat only to bottom-dwelling organisms living in or feeding on those sediments. Yet this presumption failed to consider the extraordinarily high toxicity of dissolved pyrethroids. While, as noted above, 5 parts per billion may be a typical threshold of sediment toxicity to *Hyalella*, toxicity testing revealed that thresholds of water toxicity for several pyrethroids are at around 2 *parts per trillion* (Weston and Jackson 2009). Based on a comprehensive review of available toxicity data for all aquatic species, U.C. Davis investigators suggest acute toxicity thresholds for pyrethroids in the range of 1 to 4 parts per trillion and chronic toxicity thresholds in the range of 0.4 to 0.6 parts per trillion (Fojut and Tjeerdema; Fojut et al. 2010; Palumbo et al. 2010).



Hyallela Azteca. Photograph by Scott Brown.

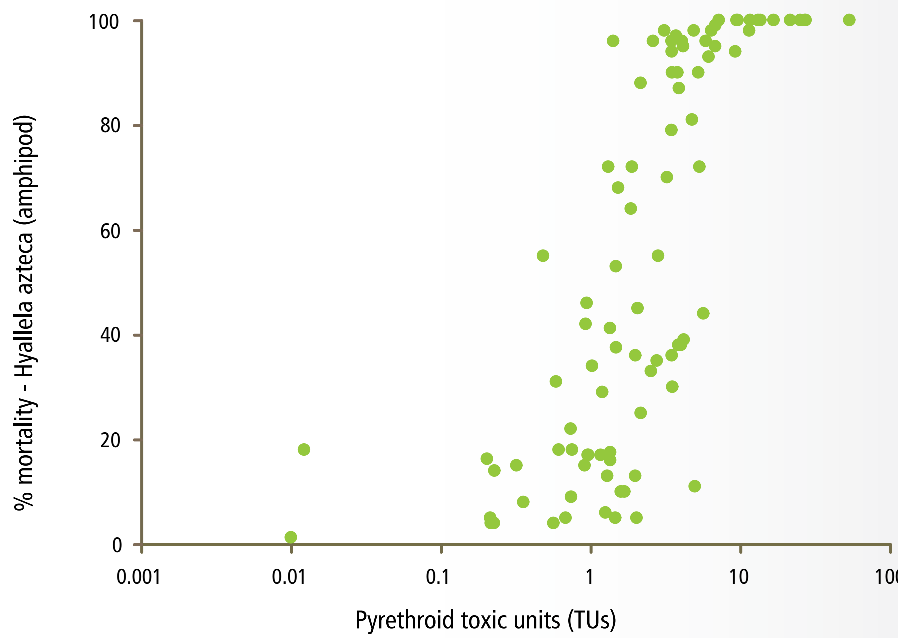
FIGURE 1

THE CRUSTACEAN *HYALELLA AZTECA* HAS RECENTLY BEGUN TO BE USED FOR TESTING OF WATER SAMPLES WHEN PYRETHROIDS ARE OF CONCERN. Most urban runoff causes death or paralysis when tested with *Hyalella*. Agricultural runoff can cause toxicity, but these instances are scattered and infrequent. Wastewater treatment plants vary in the frequency of toxicity in their effluent. Nearly all the *Hyalella* toxicity shown in the figure is believed to be due to pyrethroids, with the organophosphate insecticide chlorpyrifos also playing a role in a few agricultural samples.

Footnote: Data from Weston and Lydy (2010) and subsequent unpublished data from D. Weston. Sampling took place from January 2008 to October 2009. Most locations were visited and tested at least six times.

IDENTIFYING THE CAUSE OF TOXICITY

Urban runoff may contain a wide range of pollutants that are potentially harmful to aquatic organisms. So, if there is toxicity, how can we tell it is from pyrethroids? The answer can be found by comparing the actual toxicity of a water or sediment sample to toxicity estimates based on measured pyrethroid levels. For this purpose, pyrethroid concentrations are translated into toxic units (TUs), where one TU corresponds to a concentration that causes 50% mortality in a 10-day toxicity test with *Hyalella azteca*. So if pyrethroids were the sole cause of toxicity, one would expect about 50% mortality when testing environmental samples containing a pyrethroid concentration of 1 TU, with little or no mortality below that concentration, and complete mortality above it. The graph compares pyrethroid TUs in urban creek sediments from the Bay-Delta region with Hyalella toxicity test results. Overall, pyrethroid TUs are a good predictor of *Hyalella* toxicity, and mortality occurs very near the pyrethroid concentrations one would expect it to occur at if pyrethroids were indeed the cause.



To confirm pyrethroids as the cause of toxicity, a more elaborate laboratory procedure called Toxicity Identification Evaluation (TIE) can be done. A TIE alters the toxicity of only a small subset of all the potential toxicants in a sample through various chemical and physical manipulations. For example, pyrethroids tend to be more toxic at colder temperature, whereas the opposite effect of increased toxicity with higher temperatures is much more common for other toxicants. The appearance of greater toxicity when a sample is tested at reduced temperatures suggests pyrethroids as the potential cause. There are a variety of similar manipulations that may make pyrethroids more or less toxic, and typically a series of such manipulations is done to build a case for causality, based on weight of evidence. UC Berkeley investigators have done TIE tests on 12 river or urban runoff water samples showing toxicity to *Hyalella*, and results from all samples pointed to pyrethroids as the cause of toxicity.

While *Hyalella* has not traditionally been used for testing water column toxicity, it is a common resident in local creeks, sensitive to pyrethroids, and for that reason used by several labs in California when pyrethroids are of potential concern. Pyrethroids in the water column of California waterways have been found to be toxic, though monitoring is still very limited. Water column toxicity due to pyrethroids has been reported in Suisun Bay sloughs (Werner et al. 2010). The creeks draining Vacaville have shown toxicity after rain events, with pyrethroid concentrations in the water about 10 times the acutely toxic threshold (Weston and Lydy 2010).

The recent studies also report pyrethroid toxicity in larger streams and rivers. In the American River, toxicity was documented in the reach between Rancho Cordova and Sacramento, due to pyrethroids in stormwater runoff from the surrounding urban lands (Weston and Lydy 2010). Flows in the American River are dam controlled, and are often at their lowest during the winter months when storm runoff contributes the most pyrethroids. Presumably, the low flows are exacerbating the impact of pyrethroids, since there is less water in the river available to dilute them to below-toxic levels. In still larger river systems, pyrethroid-related water toxicity has been limited to isolated instances (San Joaquin River) or not found (Sacramento River).

PYRETHROID SOURCES

Prior to these recent studies, conventional wisdom probably would have identified agriculture as the primary source for pyrethroids in particular, and pesticides in general. Through focused monitoring, a different picture is emerging. Sampling by U.C. Berkeley investigators has shown that agriculture can indeed be a source of pyrethroids that can lead to contaminated sediments and isolated events of water toxicity, but toxic pyrethroid inputs from agricultural runoff are scattered and infrequent. For example, 27% of samples from agricultural return drains in the Delta contained pyrethroids. Yet only 10% of the samples had sufficient concentrations to expect acute *Hyalella* toxicity (**FIGURE 1**).

More striking are the inputs through urban runoff. Nearly all urban runoff that has been sampled in northern California contains pyrethroids well above concentrations causing toxicity (Weston et al. 2009: Weston and Lydy 2010). Similar findings have emerged from sampling in about a dozen communities extending from the San Francisco Bay area to the Sacramento region (**FIGURE 1**). Runoff from Delta cities typically contains pyrethroids about 10 times higher than acutely toxic threshold concentrations to *Hyalella*, and concentrations in Southern California are higher still (L. Oki, personal communication). The pyrethroid bifenthrin stands out among the group for its elevated concentrations and frequency of detection in urban runoff, though urban runoff can also contain toxicologically significant concentrations of other pyrethroids such as cypermethrin, cyfluthrin, lambda-cyhalothrin, and permethrin.

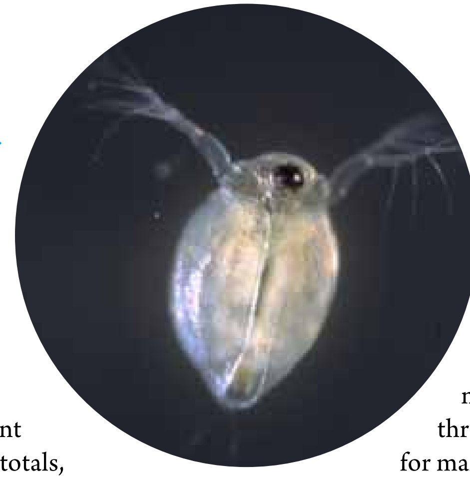
The pyrethroids in urban runoff originate from pesticide use around homes and commercial establishments. However, it is difficult to distinguish the contributions of homeowner-applied pyrethroids from those applied by professional pest control firms, since both groups often use the same compounds. At least for bifenthrin, the pyrethroid of greatest water quality concern, professional applicators in California use four times the quantities applied by homeowners (Weston et al. 2009).

Another surprising source, only recently identified, is municipal wastewater (**FIGURE 1**, Weston and Lydy 2010). Treatment plants receive pyrethroids either through seepage of stormwater runoff into the sanitary sewer systems; drain disposal of products for the treatment of flea and ticks in pets, head lice or bed bugs; or laundering of pyrethroid-treated fabrics. It had generally been presumed that given their strong tendency to bind to organic matter, pyrethroids would be retained in the sludges that treatment plants are designed to remove from the wastestream. While it is likely that most of the pyrethroids entering the wastestream are removed, enough can remain to cause toxicity in the final effluent. Based on limited data currently available, treatment plants appear to vary dramatically in the presence of pyrethroids or toxicity in their effluent. The causes of this variation have not yet been investigated but are likely related to differences in treatment processes and merit further investigation.

PLANNING FOR BETTER ENVIRONMENTAL PROTECTION

The challenge of measuring extremely low concentrations has been one of the biggest obstacles to recognizing the threats posed by pyrethroids, and even now remain an obstacle to quantifying those threats. It may come as a surprise to the general public, but the inability to measure a pesticide at levels of concern in the environment has not typically prevented state and federal authorities from approving its use. With pyrethroids, the challenges are particularly daunting. Acute toxicity to *Hyalella* begins to appear at about 2 parts per trillion for several pyrethroids in water. Effects from long-term (chronic) exposure to pyrethroids are often manifested at about one-tenth the concentration of acute effects (Fojut et al. 2010; Fojut and Tjeerdena 2010; Palumbo et al. 2010), so it is possible that unobserved chronic toxicity occurs at about 0.2 parts per trillion. Moreover, at colder winter temperatures pyrethroids are about three times more toxic, bringing the threshold down to about 0.07 parts per trillion. Finally, as a general rule of thumb, in order to be adequately protective it would be desirable to quantify pyrethroids not at concentrations at which they are already toxic, but at about 10% of that threshold, or in other words 0.007 parts per trillion. Yet no laboratory has been able to detect pyrethroids at less than about 0.2 parts per trillion, and many labs have far higher detection limits. Existing analytical capabilities are about 30-fold too insensitive relative to where they should optimally be. These estimates illustrate that it is quite likely that the compounds could be present at concentrations capable of causing chronic, or even acute, toxicity, yet be undetectable by even the best analytical lab.

Recent work with pyrethroids has exposed another shortcoming hindering our ability to protect environmental quality: the lack of reliable quantification of certain pesticide uses. The California Department of Pesticide Regulation (DPR) maintains a Pesticide Use Reporting database to which all professional applicators have to report their pesticide use. The database is a unique and extremely valuable tool, far more comprehensive than that maintained by any other state. Yet it does not incorporate retail sales. Most insecticide products available at retail outlets are pyrethroids, so their retail sales and use certainly represent a significant contribution to statewide totals, but the amount sold and used remains unquantified. In addition, even for professional applications, the database does not distinguish between subsurface treatments, such as for termites, and surface applications for ants, spiders and similar pests. Only the surface applications of pyrethroids are likely to present a risk for off-site transport, but the amounts used in such applications are not distinguished from subsurface use.



Ceriodaphnia dubia. Photograph by Jack Kelly Clark. Courtesy of the Regents of the University of California.

Following the findings of environmental toxicity due to pyrethroids described earlier, the DPR initiated a process known as "re-evaluation" for the hundreds of products sold in California containing pyrethroids. This process, which began in August 2006 and is on-going, provides a way for DPR to obtain from the pesticide registrants the environmental fate and toxicity data needed to establish the extent of the hazard and to mitigate it. Reevaluation is intended to resolve many of the environmental issues noted above. But the pace of the process (four years and counting) presents a significant challenge for regulatory authorities, since pesticide use is a moving target. While pyrethroids have replaced organophosphates in urban uses, fipronil, a newer pesticide for which there are few environmental monitoring data, is now replacing pyrethroids in some applications.

A ROLE FOR THE DELTA REGIONAL MONITORING PROGRAM

The widespread toxicity in environmental samples caused by pyrethroids went unnoticed in California for many years, and is probably still going unnoticed elsewhere, because monitoring programs were not looking for it. In the rare instances when they did, the analytical methods had detection limits that we now know to be grossly inadequate. Toxicity testing was (and is) usually done with *Ceriodaphnia dubia*, a species extremely sensitive to diazinon and chlorpyrifos, but considerably less sensitive to pyrethroids than is *Hyalella*.

The pyrethroids story illustrates how toxicants in Delta waters change over time as pesticides fall in and out of favor. Monitoring programs must adapt to the constantly changing threats or risk monitoring for the pesticides, and problems, of yesterday. Currently, monitoring of pyrethroids is required by a number of dischargers regulated under the National Pollution Discharge Elimination System program and the Irrigated Lands Regulatory Program. The Delta RMP can play an important role by serving as a forum where analytical methods and monitoring approaches can be assessed, and by encouraging the adoption of comprehensive monitoring programs for emerging pesticides. In addition, the RMP can provide information that will help shape the regulatory framework and control programs for pesticides that are under development by the Regional Board and provide a measure of success.

MEASURING PYRETHROIDS AND THEIR ENVIRONMENTAL EFFECTS

As the pesticides in use change, so must the analytical methods that are used to measure them. Pyrethroid insecticides are more difficult to measure than some other current-use pesticides because of their strong tendency to bind to particles and their toxicity at extremely low concentrations (requiring equally low detection limits). Routine environmental analyses for pyrethroids have typically involved whole-water or bed sediment samples quantified via gas chromatography-electron capture detection (GC-ECD) or gas-chromatography-mass spectrometry (GC-MS). Newer techniques such as tandem mass spectrometry (MS-MS) and negative chemical ionization mass spectrometry have achieved detection levels near 0.1 parts per trillion in water and 0.1 parts per billion in sediment. As newer instrumentation is developed, the detection limits may be lowered further.

Water measurements are being refined with techniques that split a sample into its dissolved and particulate (filterable) fractions (Hladik and Kuivila 2009). The dissolved and particulate fractions can then be analyzed separately to better understand pyrethroid location and movement in the environment. Techniques such as solid-phase microextraction (SPME) are being used to measure the bioavailability of pyrethroids in sediment porewater (Bondarenko et al. 2007), providing a better indication of organism exposure.

Analyses of pyrethroid effects on organisms are shifting from extrapolations based on sediment and water concentrations to analysis of concentrations in tissues of the exposed organisms (Smalling et al 2010). Additionally, work has begun on identifying changes in gene expression that could be indicative of pyrethroid exposure; these techniques can help determine physiological effects of pyrethroids on organisms (see, for example, Beggel et al. 2010 and Connon et al 2009). Progress has also been made in assessing the effects of pyrethroid mixtures (Brander et al. 2009) or examining the nonlethal and sublethal effects of complex chemical mixtures including pyrethroids (see CEC Projects in the Delta, **Page 54**).

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More information available at: http://ca.water.usgs.gov/user_projects/toxics

CONTAMINANTS OF EMERGING CONCERN (CECS): ADAPTING TO A MOVING TARGET

HIGHLIGHTS

- There are potentially thousands of CECs, the number is increasing, and little information is available to assess risks to humans and wildlife
- Few data are available for CECs in the Delta, though studies in San Francisco Bay may provide some insights
- Endocrine disrupting chemicals are a concern but more information is needed
- There are several 'new' CECs for which environmental occurrence, fate, and toxicity information is lacking or not available
- Delta water quality managers can implement strategies used by other state and regional agencies to minimize the impacts of CECs

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KEITH MARUYA, Southern California Coastal Water Research Project

A LACK OF INFORMATION

Over the past 30 years more than 100,000 chemicals have been registered or approved for commercial use in the U.S. These substances include more than 84,000 industrial chemicals, 9,000 food additives, 3,000 cosmetics ingredients, 1,000 different pesticide active ingredients, and 3,000 pharmaceutical drugs (**FIGURE 1**). For industrial chemicals alone, production and import in the U.S. totaled 27 trillion pounds in 2005, an 80% increase from 2002 (Wilson and Schwarzman 2009). Global chemical production is projected to continue growing by about 3% per year, and double every 24 years. The primary challenge for regulators and scientists is managing this ever-growing amount and variety of chemicals to insure they do not adversely impact human and environmental health.

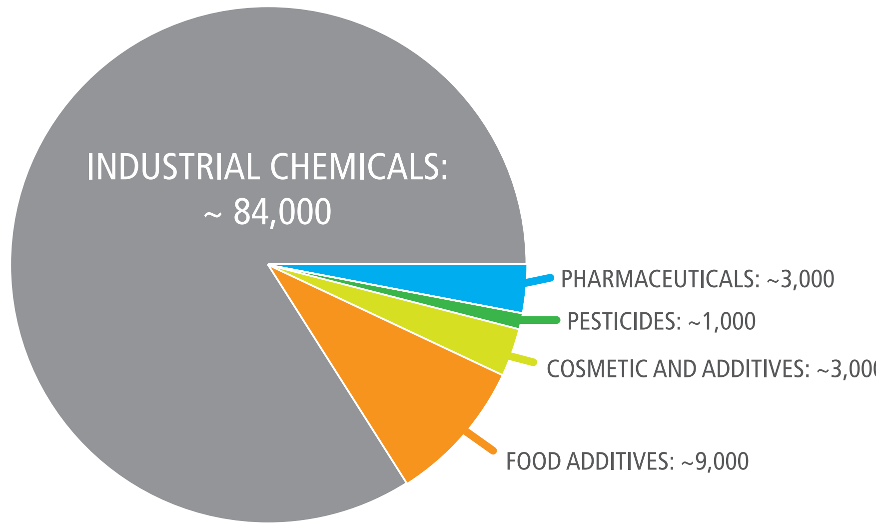

FIGURE 1

APPROXIMATELY 100,000 INDIVIDUAL CHEMICALS HAVE BEEN REGISTERED FOR COMMERCIAL USE IN THE U.S. OVER THE PAST 30 YEARS; WE KNOW LITTLE ABOUT MOST OF THEM. Global chemical production is projected to continue growing by about 3% per year, and double every 24 years. The primary challenge for regulators and scientists is managing this ever-growing amount of chemicals to insure they do not adversely impact human and environmental health. For most of these chemicals currently, major information gaps limit scientists' ability to assess their potential risks and monitoring of these chemicals does not routinely occur. For example, analytical methodologies are currently limited to several hundred of these non-regulated chemicals. As a result, many chemicals that have not been adequately tested for their potential impacts to humans and wildlife are continuously released to the environment. Chemical classes that receive the majority of public attention (pharmaceuticals, cosmetics, food additives, and pesticides) constitute only a small percentage of this inventory.

Footnote: This figure was adapted from Muir and Howard (2006).

Only a very small fraction of the large number of chemicals in use is routinely monitored in the environment. These generally include persistent and bioaccumulative compounds such as polychlorinated biphenyls (PCBs), chlorinated pesticides, heavy metals such as mercury, and other chemicals on the USEPA list of 128 regulated priority pollutants. The risks these conventional contaminants pose to ecosystem and human health are relatively well-established and regulatory compliance monitoring is conducted as part of risk reduction actions. However, for most chemicals currently in use, major information gaps limit scientists' ability to assess their potential risks and monitoring of these chemicals does not routinely occur. As a result, many chemicals that are continuously released to the environment have not been adequately tested for their potential impacts to humans and wildlife.

Despite the information gaps, researchers and some government agencies have begun to collect occurrence, fate, and toxicity data on a variety of unregulated chemicals over the last decade. Analytical methods have progressed to the point that it is possible to measure trace quantities (below parts per trillion) of many contaminants in water, which has led to frequent detection of a variety of previously unmonitored chemicals in the environment. These chemicals have been classified as CECs. They can be broadly defined as any chemicals that are not commonly monitored but have the potential to enter the environment and cause adverse ecological or human health impacts. Pharmaceuticals and personal care products (PPCPs), current use pesticides, and industrial chemicals such as flame retardants and perfluorinated compounds (PFCs) constitute the majority of chemicals that are commonly considered CECs due to their high volume use, potential for toxicity in non-target species, and the increasing number of studies that report their occurrence in the environment.

SCANNING FOR CECs

The Bay RMP has recently partnered with the National Institute of Standards and Technology (NIST) to take a novel approach to identifying CECs. In contrast to the traditional analytical approach, which targets a specific chemical or chemical class in an environmental sample, this 'broadscan' approach takes advantage of recent advancements in analytical instrumentation by screening samples for a wide variety of chemicals. Compared to traditional sample preparation procedures, the sample is carried through fewer 'clean-up' steps, and is analyzed using two-dimensional gas chromatography and time-of-flight mass spectrometry. What makes this approach unique is its ability to separate out individual chemicals in a complex chemical mixture that would otherwise be too difficult to analyze using the traditional 'targeted' approach.

The methods developed by NIST will be applied to mussels and harbor seals from San Francisco Bay and are expected to reveal the presence of several compounds that have not been previously targeted for analysis. Once identified, the Bay RMP will be able to evaluate the detected chemicals for their potential to adversely impact Bay wildlife. The Bay RMP is collaborating with The Marine Mammal Center, SCCWRP, and San Diego State University for the project, which is expected to be completed at the end of 2011.

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RISKS ARE DIFFICULT TO ASSESS

Determining which of the thousands of chemicals in commerce are CECs and whether or not they may be a problem is a formidable challenge. For most chemicals in use, a number of limitations prevent researchers from assessing their potential risks.

- The identities of chemicals used in commercial formulations, their applications, and product-specific uses are characterized as confidential business information or are not readily available.
- Methods to reliably measure most chemicals in use do not exist. Development of new analytical methods for new chemicals is resource-intensive. Researchers tend to focus their method development efforts on chemicals deemed to be the highest priority risk.
- Little to no information exists on chronic toxicity for realistic exposures, toxicity in non-target species (particularly for pharmaceuticals), or sensitive toxicological endpoints, such as endocrine disruption. Knowledge of toxic modes of action for most CECs is minimal and details of toxicity studies conducted by chemical manufacturers are typically not available for public review.

Such large information gaps make it difficult for researchers and regulators to pre-emptively target CECs for monitoring and control. For the vast majority of chemicals in use today, occurrence, persistence, and toxicity data are still needed to establish exposure and risk thresholds to protect the beneficial uses of aquatic ecosystems.

RESULTS FROM SAN FRANCISCO BAY

Currently little information on CECs is available for the Delta, though studies are on-going (for examples, see **CEC PROJECTS IN THE DELTA**). Downstream of the Delta, however, the Regional Monitoring Program for Water Quality in the San Francisco Estuary (Bay RMP) has generated one of the most comprehensive datasets for CECs in aquatic ecosystems. Since 2001 the Bay RMP has conducted pilot studies investigating CECs in water, sediment, and wildlife. CECs investigated to date include PFCs, alkylphenol ethoxylates, more than 100 PPCPs, and a variety of flame retardants including polybrominated diphenyl ethers (PBDEs) and their replacements. Many of these CECs have been detected in the Bay. Sites in the Delta have not been included in these small pilot studies because they are not within the scope of the Bay RMP. However, sediment, water, and resident clams at the western boundaries of the Sacramento and San Joaquin Rivers, and double-crested cormorant eggs from a nesting site on Wheeler Island (Suisun Bay) are routinely monitored for a variety of chemical contaminants. Bay RMP contaminant loadings studies have also been conducted at Mallard Island, where water flows out of the Delta and into the Bay. Data from these sampling sites are also direct or indirect indicators of potential CEC contamination in the Delta. Among the CECs studied to date by the Bay RMP, only PBDEs and pyrethroid pesticides have so far been added to the routine monitoring.

PBDES: Now considered an established rather than an emerging concern, PBDEs are toxic chemicals that are routinely monitored and pervasive throughout the world. PBDEs have been consistently detected in sediments and clams collected at the Bay RMP river sites and in bird eggs collected from Wheeler Island since the analyses began at these sites in 2002. Concentrations in clams at the river sites may be decreasing (**FIGURE 2**). Concentrations measured in bird eggs in 2006 were lower than those measured in 2002. Concentrations in water at Mallard Island have indicated significant PBDE loading from the Delta to San Francisco Bay. Because PBDEs have been or are in the process of being phased out of use in new products, their replacements are now considered CECs and are being monitored in the Bay to better understand their risks (see discussion of current-use flame retardants below).

PYRETHROIDS (also see **FEATURE ARTICLE**, **page 40**): No longer considered an emerging concern, pyrethroid pesticides were added to routine Bay RMP sediment monitoring in 2008. Most compounds analyzed have not been detected at the river sites, with only sporadic detection of cypermethrin (0.6 parts per billion) and allethrin (0.3 parts per billion). This is in contrast to results for other portions of San Francisco Bay, where different pyrethroids were detected more often in 2009. Continued monitoring will help us understand the contribution of pyrethroids to observed toxicity in the Bay.

PFCS: PFCs, chemicals used in non-stick cookware, stain-resistant fabrics, and food packaging, among other products, have been detected in bird eggs collected from Wheeler Island and from other locations throughout the Bay over the past few years. Bay RMP studies are on-going to better understand sources of PFCs, including runoff from the Delta. Although the use of PFCs has been restricted over the past decade because of concerns with their potential toxicity to humans and wildlife, they are frequently detected in the environment worldwide.

Concentrations of chemical contaminants at the Bay RMP river sites are typically lower than those in other Bay segments. This is likely due to dilution from large river and tidal flows. In the Delta, higher concentrations of CECs and other chemical contaminants would be expected at sites closer to urbanized areas and near point sources located further upstream, such as near wastewater and stormwater outfalls.

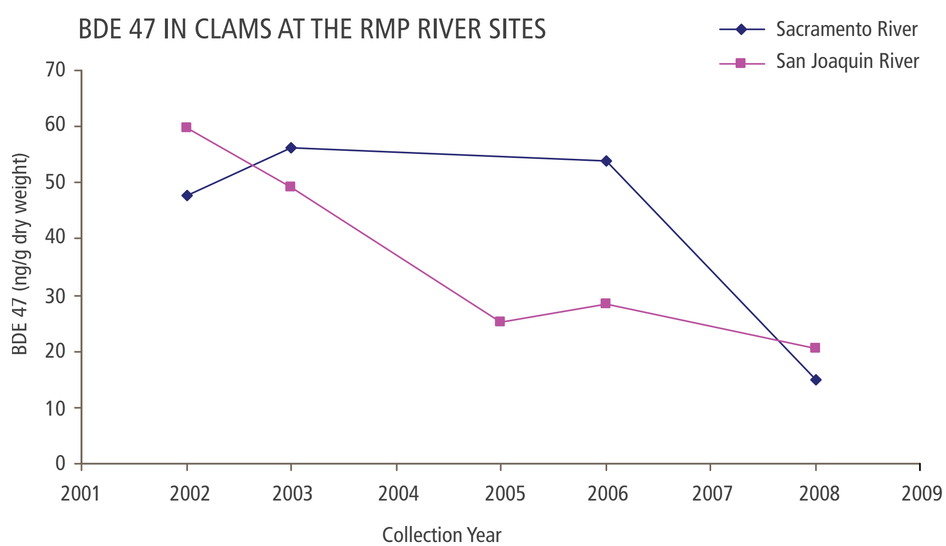

FIGURE 2

CONCENTRATIONS OF PBDES IN DELTA CLAMS MAY BE DECREASING. A partial PBDE phase-out began in 2003. A decreasing trend would be expected in response to the PBDE phase-out.

It has been well-established, particularly in fish, that a variety of chemicals can modulate or mimic steroid hormones, and in some cases interfere with reproduction and development.

ENDOCRINE DISRUPTING CHEMICALS: A FOCAL POINT OF CONCERN?

An area of research that has received considerable attention over the last ten years is the environmental impact of endocrine disrupting chemicals (EDCs). It has been well-established, particularly in fish, that a variety of chemicals can modulate or mimic steroid hormones, and in some cases interfere with reproduction and development. A number of studies have reported feminization of male fish, intersexuality in fish, and induction of the egg precursor protein vitellogenin in male fish at wastewater-impacted sites worldwide (Jobling et al. 1998; Kavanagh et al. 2004). Studies have shown that vitellogenin induction is likely due to exposure to estrogenic chemicals in the effluents, though it is not clear to what extent these substances contribute to intersexuality or the feminization of wild fish (Sumpter et al 2006).

The estrogenic substances suspected to be playing a role in causing these endocrine effects are natural and synthetic steroids, including 17α-ethinylestradiol (EE2), a synthetic estrogen used in birth control pills and management of menopausal symptoms, and alkylphenols such as nonylphenol and its ethoxylate derivatives, which are used as surfactants in a variety of industrial applications and consumer products (Desbrow et al 1998; Sumpter et al 2006). In a landmark study investigating population level impacts of estrogens, Kidd et al. (2007) reported a variety of reproductive effects and near extinction of a fish population exposed to low concentrations of EE2 (5-6 ng/L) over seven years in a whole-lake experiment in the Experimental Lakes Area in Canada. Reported concentrations of EE2 and other estrogenic substances in municipal wastewater effluents and some receiving waters are within range of the concentrations shown to cause effects in fish in the Kidd et al. study and others (Sumpter et al. 2006), suggesting the potential for effects at these locations. While researchers are beginning to understand the potential effects of EDCs and which chemicals may contribute to these effects, further study of potential EDCs is needed to better understand the implications of their occurrence in aquatic environments.

ENDOCRINE DISRUPTORS MAY IMPACT DELTA FISH. This photo shows a largemouth bass, a popular sport fish in the Delta. In some other parts of the country, largemouth bass collected from waterways that contain synthetic organic compounds have been found to show signs of endocrine disruption. In the Potomac River and its tributaries in the Washington D.C. region, some male largemouth bass were even found to grow immature eggs in their reproductive organs.

Photograph by Ben Greenfield.

In the Delta, several studies have investigated estrogenic effects on fish that may be associated with EDCs. Teh (2007) found evidence of intersexuality in 9 of 65 male delta smelt (14%) collected from Delta and Suisun Marsh sites, but did not measure EDCs or their activity in the water (Baxter et al. 2010). Some other studies are highlighted in the sidebar titled **CEC PROJECTS IN THE DELTA** (page 54).

In San Francisco Bay, the Bay RMP is working to address the issue of EDCs through monitoring and effects studies. Alkylphenols were analyzed in Bay water, sediment, and mussels in 2002 and 2010, and a suite of PPCPs, including some potential EDCs, were monitored in water in 2006 and in water, sediment, and mussels in 2010. Many compounds were detected in these studies, though concentrations were at least ten times lower than available toxicity thresholds. Unfortunately the potential for effects due to long-term exposure to these concentrations, a concern not addressed with existing thresholds, is currently unknown. Steroid hormones have not been monitored in the Bay; however, data are expected in

2011 for surface waters at select Bay sites. In 2007, a Bay RMP study observed site-specific alterations in the thyroid endocrine system of Bay fish that were correlated with concentrations of PCBs, PAHs, and chlorinated pesticides in tissues (Brar et al 2010). The Bay RMP is currently planning further monitoring and EDC effects studies on Bay wildlife.

In southern California, the Southern California Coastal Water Research Project (SCCWRP) is collaborating with various partners to characterize the occurrence of CECs and the potential for CEC effects in California coastal waters. In a recently completed study that focused on marine wastewater outfalls, dozens of CECs were detected in effluent, marine waters, marine sediments, and tissue of local flatfish. Although molecular markers provided evidence of CEC exposure in these wild fish, more extreme effects (e.g. intersex, population decline) were not evident. On-going studies are focusing on CEC concentrations and biomarker response for invertebrates and fish in coastal embayments and urban estuaries that receive stormwater runoff. Using this information, SCCWRP and other partners are identifying CECs that should be monitored in recycled and ambient receiving waters throughout the state. As part of these initiatives, SCCWRP is also championing the development and application of molecular tools and screening methodologies to help identify the most toxic CECs and to make monitoring both more efficient and more relevant to protecting beneficial uses of aquatic ecosystems.

NEW CECS

Over the past decade, there has been a substantial increase in the number of studies reporting the occurrence of previously unmonitored chemical contaminants in surface waters and wildlife. These, along with observations of endocrine disruption impacts at low concentrations in aquatic environments, have raised concerns regarding the potential for impacts of other CECs that have been detected at similar concentrations. Water bodies that continuously receive wastewater effluent and runoff from highly urbanized areas are of particular concern. In addition to PPCPs, alkylphenols, and PFCs, several other types of high volume use chemicals have gained the attention of researchers and regulators.

CURRENT-USE FLAME RETARDANTS: Since a partial PBDE phase-out began in 2003, a number of chemicals have taken their place. Many of these have been identified, though their environmental fate and potential toxicity are still largely unknown. Current-use flame retardant chemicals include other brominated chemical mixtures, some of which contain a brominated phthalate, and chlorinated organophosphate compounds (Stapleton et al. 2009).

ANTIMICROBIALS: Triclosan and triclocarban are common components of a wide variety of consumer products, including hand soaps, toothpaste, and other personal care products. They are persistent in the environment and may accumulate in wildlife. Concerns over these compounds include their potential for endocrine disruption in wildlife, the development of widespread antibiotic resistance due to their ubiquitous use, and their potential toxicity to algal and microbial communities (Chalew and Halden 2009).

NANOMATERIALS: The unique properties of nanomaterials make them valuable for commercial applications but their rapidly increasing use in industrial applications and consumer products raises concerns regarding their potential environmental and human impacts, which are currently unknown. Types of nanomaterials currently being studied to investigate their environmental fate and potential toxicity include nanosilver, titanium dioxide, and carbon nanotubes. Scientists are just beginning to understand the behavior of these materials in aquatic environments (Klaine et al. 2008).

CYCLOSILOXANES: These persistent contaminants are used in a wide variety of personal care products, the manufacture of silicones, and as carriers, lubricants, and solvents in a variety of commercial applications. Decamethylcyclopentasiloxane (D5), for example, has been recommended as a safer alternative to the use of perchloroethylene in dry cleaning, despite concerns over its potential toxicity (USEPA 2009). Because of their ubiquitous use and anticipated persistence, cyclosiloxanes like D5 are suspected to be widespread contaminants in aquatic environments; however, information thus far has been limited by the difficulties of measuring these chemicals in environmental matrices (Horii and Kannan 2008).

QUATERNARY AMMONIUM COMPOUNDS (QACS): These cationic surfactants are widely used in a variety of industrial applications and consumer products such as fabric softeners and detergents. Though very few studies have been conducted, QAC concentrations in estuarine sediments have been observed to be comparable to or higher than routinely monitored contaminants such as PAHs and PCBs (Li and Brownawell 2010). Concerns with exposure to these compounds include the development of widespread antibiotic resistance, their potential toxicity to microbial communities, and the lack of environmental fate and toxicity information.

CEC PROJECTS IN THE DELTA

FOR MORE THAN 6 YEARS, THE U.S. FISH AND WILDLIFE SERVICE ENVIRONMENTAL CONTAMINANTS DIVISION HAS PERIODICALLY DEPLOYED WATER SAMPLING DEVICES TO ASSESS POTENTIAL CONTAMINANT EFFECTS ON SPECIAL STATUS SPECIES IN THE BAY-DELTA. The first samplers were deployed quarterly at two sites in Suisun Marsh in 2003. This work was performed in collaboration with researchers from U.C. Davis monitoring Sacramento splittail and another team from the University of Florida who analyzed blood collected from splittail for the presence of vitellogenin (a precursor protein of egg yolk normally found only in females). This study found high levels of vitellogenin in 2 of 12 male splittail indicating the presence of endocrine disrupting chemicals. The sampling devices detected low levels of a number of pesticides in the water including organochlorines, organophosphates, and triazine herbicides. These results led to a much more comprehensive exposure and effects study in 2005. The deployment frequency of the samplers was increased from quarterly to monthly and more sites were added to expand spatial coverage. In laboratory tests, extracts collected from the sampling devices were injected into juvenile striped bass. After the injections, the striped bass were analyzed for vitellogenin and several physiological responses signaling the presence of endocrine disrupting chemicals. Analytical results from the expanded study were consistent with the initial findings: the extracts from the passive sampling devices contained numerous pesticides that were present at low levels in water. The laboratory tests demonstrated that low level mixtures of contaminants found in Delta water can set off responses that signal endocrine disruption in fish. The results indicate a need for a more comprehensive assessment of endocrine disrupting chemicals in the Delta.

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A RESEARCH TEAM FROM U.C. RIVERSIDE AND U.C. BERKELEY FOUND FURTHER EVIDENCE FOR A RELATIONSHIP BETWEEN MIXES OF TOXIC CHEMICALS PRESENT AT LOW LEVELS AND SIGNS OF ENDOCRINE DISRUPTION IN FISH. In their study, the U.C. team tested surface water samples collected throughout the Central Valley for signs of fish feminization and analyzed for more than 100 chemicals, including steroid hormones, pharmaceuticals, current use pesticides, and other emerging contaminants. Water samples from a site in the Delta continually caused feminization of fish in laboratory tests, but steroid hormones and other typical endocrine disruptors were either absent or present at levels below their effect thresholds. In further analyses, the researchers noticed site-specific patterns of endocrine disruption that could not be related to any single compound (Lavado et al. 2009). Subsequent studies at other Delta locations with expanded chemical analyses finally indicated a potential relationship between feminizing activity in fish and a mixture of alkylphenols and alkylphenol ethoxylates (widely used surfactants) and the pyrethroid insecticide bifenthrin. Each individual group of compounds at environmental concentrations failed to elicit fish feminization in the laboratory. But when bifenthrin was combined with the alkylphenol and alkylphenol ethoxylate mixtures, feminization was observed. Studies are now underway to determine whether there are signs of endocrine disruption in local salmon and trout populations of urban Central Valley watersheds, where bifenthrin is commonly observed after storm events (see article on pyrethroids beginning on **page 40**).

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SITES AT WHICH ESTROGENIC AND ANDROGENIC IMPACTS OF ENDOCRINE DISRUPTING CHEMICALS WERE EVALUATED IN MISSISSIPPI SILVERSIDE.

RESEARCHERS FROM THE U.C. DAVIS BODEGA MARINE LABORATORY ARE CURRENTLY EXAMINING THE IMPACT OF ENDOCRINE DISRUPTING COMPOUNDS ON THE MISSISSIPPI SILVERSIDE, AN IMPORTANT FORAGE FISH IN THE DELTA-SUISUN FOODWEB. In 2009 and 2010, the team caught fish monthly from two beaches in Suisun Marsh: Suisun Slough and Denverton Slough. Suisun Slough receives urban runoff and wastewater effluent, and Denverton Slough receives runoff from a local ranch. A bioassay detected estrogenic EDCs at the ranch site and both estrogenic (compounds mimicking female sex hormones) and androgenic EDCs (compounds mimicking male sex hormones) at the urban site.

An assessment of endocrine effects at the molecular, organism, and population levels in silversides found signs of endocrine disruption at both sites. At the ranch site, only estrogenic EDCs were detected. Sex ratios in the ranch population did not appear to be impacted, but males had higher expression of female genes. At the urban site, both estrogens and androgens were detected. The sex ratio was skewed in favor of males in both years, but males had smaller testes here than at the ranch site. Complex interactions of estrogenic and androgenic endocrine disrupting compounds may explain these apparently counterintuitive findings. Overall results suggest that EDCs may negatively affect fish populations and that endocrine impacts should be evaluated at multiple levels in order for impacts to be accurately assessed.

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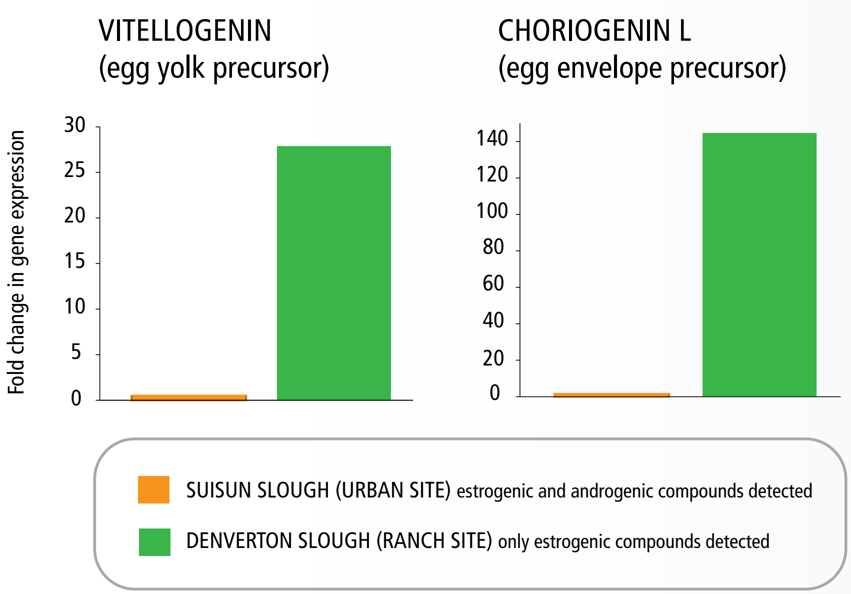
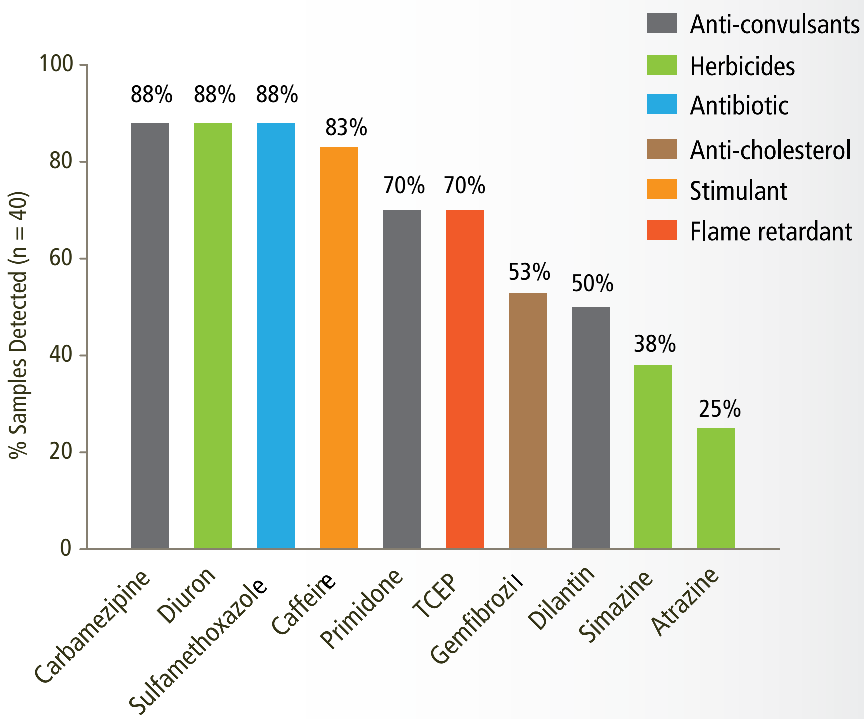


FEMALE GENE EXPRESSION IN MALE FISH AT DENVERTON SLOUGH AND SUISUN SLOUGH. Although males at both sites are exposed to estrogenic EDCs, androgenic EDCs at the urban site appear to be outcompeting estrogenic EDCs. Responses were normalized to reference males from each site that were held in clean laboratory water for at least 4 months.

CEC PROJECTS IN THE DELTA CONTINUED

SCIENTISTS FROM THE SOUTHERN CALIFORNIA METROPOLITAN WATER DISTRICT (MWD) AND THE ORANGE COUNTY WATER DISTRICT ASSESSED THE OCCURRENCE OF CECS IN DELTA WATER. Sampling took place from April 2008 to April 2009 on a quarterly basis at eleven sites representing source water for the State Water Project. The researchers evaluated the presence of endocrine disrupting compounds together with other pharmaceuticals and personal care products and organic contaminants typically found in wastewater. Detectable amounts of CECs were found at all but one site during one of the four sampling events. The site where no CECs were detected in April 2008 is located at the American River upstream of the Sacramento urban area. Twenty-one out of 49 analyzed CECs were detected, but all at a part per trillion level – millions of times lower than pharmaceutical doses. The general consensus among experts is that the low levels detected do not pose any risk from a drinking water perspective, but more information about their potential environmental impact is needed.

TOP 10 CECS FOUND IN DELTA WATER



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For more information: http://www.nwri-usa.org/CECs.htm

PREVENTING FUTURE PROBLEMS WITH CECS

The considerable challenge of managing CECs is a reflection of limitations in the regulation of chemicals at the state, national, and international level. Ideally, all existing and future high volume use synthetic chemicals, including pharmaceuticals and pesticides, as well as their degradation products, would be produced and used following "Green Chemistry" and "Green Pharmacy" principles. Following these principles includes conducting appropriate risk assessments so that potentially harmful products are screened before large-scale manufacture and subsequent release into the environment. At the federal level, modernization of the Toxic Substances Control Act is underway to improve how chemicals are managed before they are approved for use. Until this is completed, development of CEC prioritization approaches and sophisticated toxicity screening methods are needed to identify potential impacts of chemicals in current use.

INCREASING OUR KNOWLEDGE OF CECS

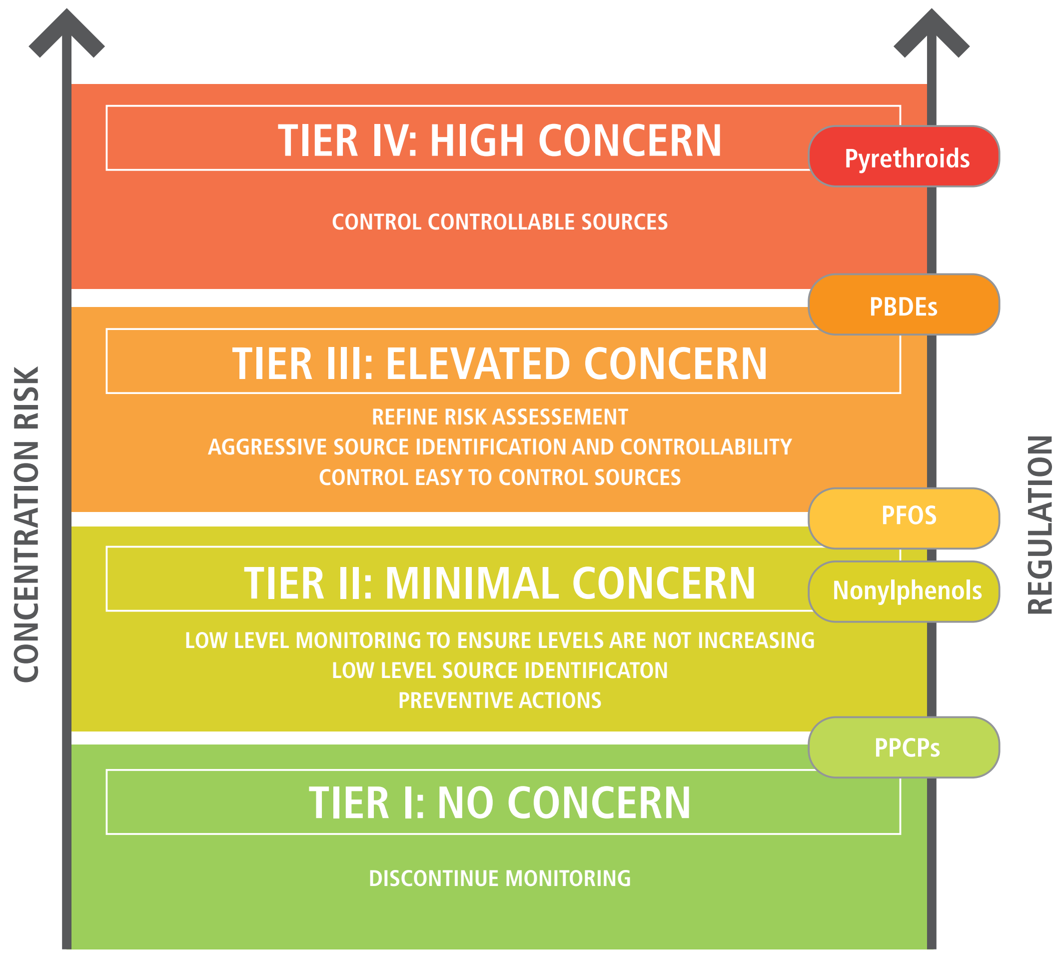
The information deficiency for current-use chemicals challenges regulators and scientists to focus on the highest risk chemicals and avoid past mistakes that resulted in extensive global contamination by toxic chemicals (e.g. PCBs, DDT, and PBDEs). In California, a number of regional, state, and federal efforts have been conducted or are underway to develop strategies for CEC identification and prioritization, as well as processes for determining thresholds of concern.

- The Bay RMP has been monitoring CECs since 2001 and continues to refine approaches for supporting the management of CECs in San Francisco Bay.
- In Southern California, SCCWRP is monitoring CECs in coastal areas, investigating potential wastewater effluent impacts on fish, and developing molecular tools for identification of CECs.
- Biomonitoring California is the first statewide program to determine baseline levels of environmental contaminants in a representative sample of Californians, establish time trends in concentrations, and assess the effectiveness of current regulatory programs aimed at protecting the public's health from chemical risks.
- In 2009, SCCWRP and SFEI, along with other partners, convened a workshop to enhance communication and formulate a path forward for integrating science into an effective CEC management strategy for California. Among their recommendations, the participants outlined possible approaches for chemical prioritization, monitoring, and management of CECs (**FIGURE 3**).
- The State Water Resources Control Board has recently convened expert advisory panels to recommend strategies for the management of CECs in recycled water and waters discharged to coastal and marine ecosystems.
- California's Green Chemistry Initiative aims to reduce or eliminate the use of hazardous chemicals in consumer products and contamination of the environment. This will involve development of regulations that create a process for identifying and prioritizing CECs and creation of methods for assessing alternatives to hazardous chemicals currently in use.
- In 2010 and 2011, various state and federal programs are collaborating to conduct the National Oceanic and Atmospheric Administration (NOAA) Mussel Watch CECs Early Warning Network: California Pilot Project. Project partners developed a list of priority CECs for analysis in mussels collected throughout the state of California (see **NOAA SIDEBAR**, **page 59**).

Although each of these programs has a unique set of goals, they all aspire to reduce the impact of chemical contaminants on human and environmental health. To the extent possible, collaboration among these programs will improve their overall effectiveness in light of the many uncertainties and limited resources. At a minimum, communication of strategies and findings among researchers within these programs would avoid redundancy and therefore benefit efforts to manage CECs.

A ROLE FOR THE DELTA RMP?

Monitoring of CECs is essential for minimizing the impact of chemical contaminants and protecting beneficial uses in the Delta. The Delta RMP can implement a productive strategy by considering 'lessons learned' by the Bay RMP and other CEC monitoring programs, and even more so, by partnering with these programs. Collaboration on chemical prioritization approaches and projects of mutual interest can reduce costs, maximize program effectiveness, and increase the collective understanding of CEC occurrence and fate in the Bay-Delta system.



Footnote: For more information and to view the original proposed framework, please see the workshop final report at http://www.sfei.org/sites/default/files/CA CEC Workshop Final Report Sept 2009.pdf

FIGURE 3

THE CALIFORNIA CEC PRIORITIZATION SYSTEM TIES VARIOUS LEVELS OF RISK OR EFFECT TO APPROPRIATE MANAGEMENT ACTIONS. In 2009, a statewide workgroup proposed a conceptual, multiple threshold system for prioritizing and monitoring CECs. The figure shows the San Francisco Bay Regional Water Quality Control Board's interpretation of the framework for various CECs (Tom Mumley, personal communication).

NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION (NOAA) MUSSEL WATCH CECS EARLY WARNING NETWORK: CALIFORNIA PILOT PROJECT

Photograph from NOAA NATIONAL STATUS & TRENDS: An Assessment of Two Decades of Contaminant Monitoring in the Nation's Coastal Zone report. More information at http://ccma.nos.noaa.gov/stressors/pollution/nsandt/welcome.html

The NOAA National Mussel Watch Program (NMWP) recently teamed up with the Bay RMP, SCCWRP, the State Water Board, U.S. Geological Survey (USGS), and other federal agencies to conduct the NOAA Mussel Watch CECs Early Warning Network: California Pilot Project. Motivated by a desire to increase its focus on CECs, but lacking information on which CECs to monitor, the NMWP suspended its traditional national effort for 2010 and dedicated the entire budget to the California Pilot Project instead. The outcome of the project will be a priority list of CECs to consider in future NMWP efforts nationwide, based on which CECs are detected in mussels throughout California.

Mussels from 75 sites throughout the state will be analyzed for a wide variety of CECs, including over 100 pharmaceuticals and personal care products, polybrominated diphenyl ethers and their replacements, perfluorinated compounds, alkylphenols, and current-use pesticides. Sites were selected to provide information on the relative influence of different land uses, sources, and loading pathways on chemical contamination in coastal waters. The land uses examined include municipal wastewater, agricultural, urban, non-urban, stormwater discharges, and marine protected areas. At sites where resident mussels were not found, caged mussels and passive samplers were deployed. This project will be completed in 2011.

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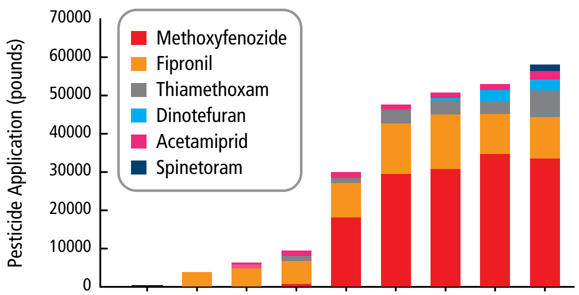
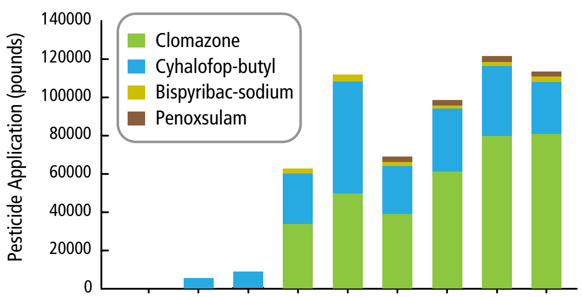
NEW PESTICIDES

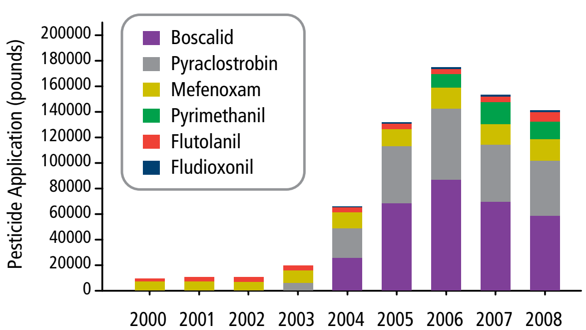
INSECTICIDES



HERBICIDES



FUNGICIDES



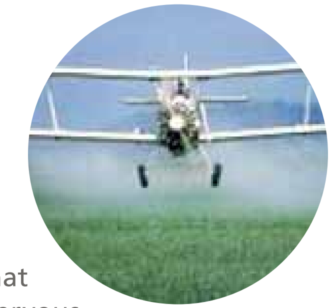
Footnote: Pesticide applications in pounds for the Bay-Delta watershed, based on data contained in the California Department of Pesticide Regulation Pesticide Use Database 2000-2008.

Pesticide use changes with time as older pesticides are withdrawn from use, new pesticides or new uses for pesticides are registered, established pests develop resistance, and new pests become a problem.

Over the past decade, a major change has been the replacement of organophosphorus insecticides with **PYRETHROID INSECTICIDES** for both agricultural and residential use (see article on Pyrethroids on **page 40**).

FIPRONIL is a pryazole insecticide which has increased in use (almost doubled since 2003) for crop protection, controlling ants and cockroaches, and in flea and tick shampoos. As it loses some patent protection in 2010, it is likely that related new products will become available. Fipronil is highly toxic to aquatic organisms and its primary degradates (fipronil disulfinyl, fipronil sulfone, and fipronil sulfide) can exhibit even greater toxicity.

NEONICOTINOIDS are a class of insecticides that have come under scrutiny as a potential factor in the decline of honey bees in the U.S. They are modeled after nicotine, which is a natural insecticide that acts on the central nervous system. Neonicotinoids are particularly effective against sucking insects such as aphids and against chewing pests such as beetles and certain worms. Neonicotinoid compounds are used in crop protection, professional turf management, professional ornamental production, and in the residential indoor, pet, lawn, and garden markets. Use of three of these compounds (acetamiprid, dinotefuran, and thiamethoxam) increased significantly in California, beginning in 2002.



While changes in pesticide use patterns often occur over a period of years, some changes are more immediate and occur in response to new pest threats. The European Grapevine Moth was first reported in California in September 2009 and has sparked a strong effort by state agencies to detect, quarantine, and eradicate this damaging pest. In response to the very recent threat, three insecticides have recently been registered: methoxyfenozide, spinetoram, and spinosad. **METHOXYFENOZIDE** belongs to the diacylhydrazine class of insecticides that cause moth larvae to undergo an incomplete and premature molt resulting in their death. **SPINETORAM** and **SPINOSAD** belong to the spynosyns, a group of chemically modified fermentation products with insecticidal activity that are derived from a soil-dwelling bacterium called *Saccharopolyspora*.

Rice is a major crop in California, with over half a million acres in production. There have been major changes in pesticide use over the past three decades, but the total amount of pesticides applied remains high. Use of the **THIOCARBAMATE HERBICIDES MOLINATE** and **THIOBENCARB** decreased significantly over the past five years. Both have been targets of monitoring programs for almost two decades because of documented problems. In the early 1980s, molinate was identified as the cause of seasonal fish kills in agricultural drains carrying tailwater from rice fields. At the same time, residues of thiobencarb were identified as the cause of taste and smell problems in Sacramento's drinking water. The Central Valley Regional Water Board responded to these problems by establishing regulatory targets and monitoring requirements for these pesticides. As the use of thiocarbamates and some other established rice pesticides declines, several **"NEW GENERATION" RICE HERBICIDES** are phased in. Examples are **BISPYRIC-SODIUM, CYHALOFOP-BUTYL, PENOXSULAM,** and **CLOMAZONE**. In general, these new generation herbicides can suppress weeds at extremely low application rates compared to previously used herbicides and pose low toxicity risk to humans and wildlife. On the downside, they are prone to induce resistance in weed species and have also been found to damage non-target plants at levels that are below the detection limits of standard analytical methods. There is little information on the occurrence of these newer rice herbicides in the environment because they are not being monitored.

As with herbicides, the use of traditional **FUNGICIDES** has decreased, while use of newer fungicides such as **BOSCALID, PYRIMETHANIL, PYRACLOSTROBIN, FLUDIOXONIL, FLUTOLANIL** and **MEFENOXAM** has increased. These compounds are applied to various crops including almonds, tomatoes, and grapes. Environmental fate and toxicity data are limited for these compounds and few are analyzed in monitoring studies.

Herbicide test plots at the Rice Experiment Station in Butte County. Photograph by Thomas Jabusch.

One future change in pesticide use is the expected registration of the fumigant **METHYL IODIDE** in California. Methyl iodide was approved by the USEPA in 2008 as a replacement for methyl bromide. Due to human health concerns, California has set methyl iodide exposure limits at half those allowed by USEPA.

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For more information:http://ca.water.usgs.gov/user_projects/toxics/

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Beaver Slough, Central Delta. Photograph by Thomas Jabusch.

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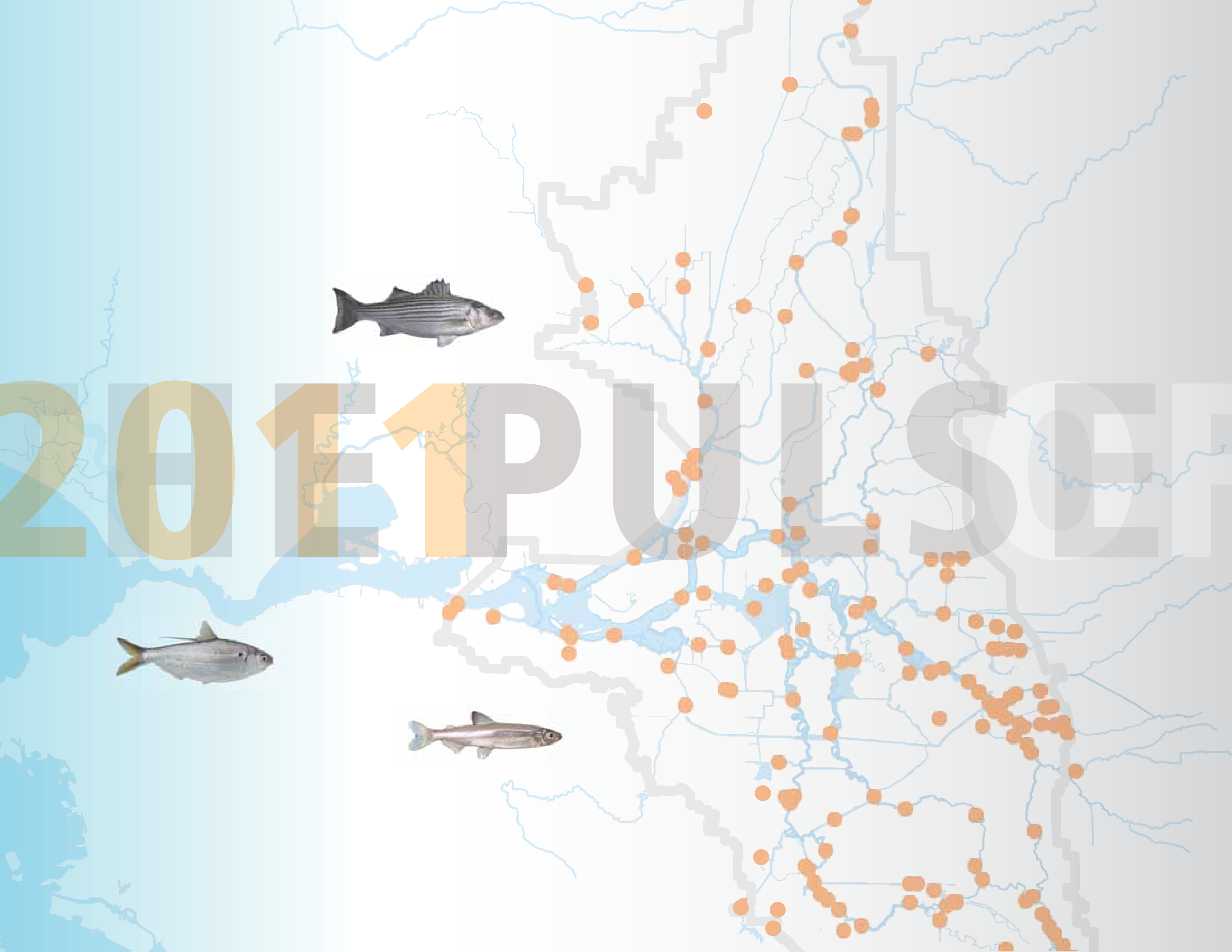
View of Sherman Lake. Photograph by Thomas Jabusch.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