DRAFT Articles November 29, 2010
Pulse of the Delta

Draft Articles

1. Introduction: Introduction | Overview | Opening Article
2. Management Update: Delta RMP: Re-thinking Water Quality Monitoring in the Delta
3. Feature Articles:
    a. Ammonia in the Delta: State of the Science, Implications for Management
    b. Not What We Had Hoped For: How Delta Studies Have Reshaped our Understanding of Pyrethroid Insecticides
    c. Contaminants of Emerging Concern (CECs): Adapting to a Moving Target

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Introduction | Overview

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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). The *Pulse of the Delta* is intended to make important information on water quality in the Delta available to managers, decision-makers, and the public. Publication of 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. Delta water supports diverse beneficial uses, including irrigation and drinking water supply, wildlife habitat, and recreation. Yet at the same time, water quality problems are ever-present and serious. Key water quality problems such as pollutants in runoff from cities and farms, mercury from historic mining, and salts entering from the ocean and in irrigation tailwater are inseparable from other problems such as the fragile levee system and the decline of native species. The intense search for solutions to the Delta's problems has highlighted the importance of comprehensive information on its condition. The Delta RMP will address this need by better defining water quality problems of regional concern. The *Pulse of the Delta* is designed to help the Delta RMP fulfill this goal by communicating the most relevant information to advance public debate about the issues and to support informed decisions that lead to a healthy, sustainable, and productive Delta ecosystem.

This first edition introduces the basic structure of the *Pulse of the Delta*. Each Pulse will be organized around a general theme that represents a regional water quality management priority for the Delta. It is widely recognized that managing the Delta's resources in a sustainable manner will depend on reliable information about the Delta ecosystem and possible consequences of human activity. The Delta RMP will help - in collaboration with existing programs - by identifying and trying to remedy specific problems that currently prevent such comprehensive regional assessments. As an initial step toward this goal, the theme of this first edition is "Re-thinking Monitoring in the Delta".

Re-Thinking Monitoring

The opening article of this issue (**page XX**) 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 provided a first attempt at comprehensively assessing a Delta water quality issue by synthesizing data from various sources. And second, it illustrates many of the problems the Delta RMP will need to solve to fulfill its role in 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, 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. The major goal of the U.C. Davis study was to determine whether contaminants could be implicated in the cause of 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 data owners, 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 monitoring practices. These changes include regularly compiling, assessing, and reporting data, and better coordination of 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.

Working Together for Better Monitoring Information

The Management Update section of this edition is entirely devoted to the approach taken by the Delta RMP for "re-thinking the monitoring system" (**page XX**). Coordination and collaboration are of central importance in changing the monitoring system, and the Delta RMP will need to build strategic partnerships with existing programs to foster realistic solutions. The Delta RMP will focus initially on contaminants-related issues under the direct control of the State and Central Valley Water Boards (Water Boards). Program development will proceed gradually, based on funding availability and feasibility. The Water Boards are investing resources in developing and establishing the Delta RMP in order to build additional interest and involvement in the region. But the Water Boards cannot develop a successful RMP on their own: a truly successful and sustainable program will require support from stakeholders. The Water Boards are fully committed to the success of a Delta RMP and are willing to negotiate changes to regulatory requirements in order to achieve more comprehensive and integrated monitoring. Stakeholders with an interest in the Delta region will need to actively contribute time and resources to continue developing the major aspects of the program: governance, monitoring objectives, funding, data integration, and coordination with other programs. Initial work will concentrate on improving the current system of data management and on developing efficiencies through improved coordination of existing monitoring.

Regional Monitoring in the Delta: Past, Present, and Future

The three Feature Articles in this issue cover Delta water quality topics that are 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 XX**). Ammonia levels in Delta water have increased significantly over the past decade. However, only recently have enough data accumulated 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. However, ammonia may be having a significant impact on fish through its influence on the productivity of the food web. An emerging hypothesis links higher ambient ammonia levels to low algal production in Suisun Bay and the Delta - one of the factors that may contribute to the POD by reducing the food supply for fish. There is a growing consensus about these effects on the foodweb in Suisun Bay. The evidence is building that ammonia inhibits the spring bloom of diatoms, algae that are an important component of the Bay-Delta foodweb. 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, 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 they cause widespread toxicity to sediment-dwelling invertebrates in suburban creeks in the Sacramento area (**page xx)**. Pyrethroids were introduced as an alternative to organophosphorus insecticides, when the latter were phased out from uses in home products and by professional pest control firms. The organophosphates were widely known to cause toxicity in aquatic systems after heavy 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, environmental monitoring, much of it in the Delta, has 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 XX**). Over the past 30 years more than 100,000 chemicals have been registered or approved for commercial use in the U.S. For most of these chemicals, major information gaps limit our ability to assess their potential risks and monitoring of these chemicals does not routinely occur. 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. 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 XX**) 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 XX**). Several types of high volume use chemicals have gained the attention of researchers and regulators, including pharmaceuticals and personal care products (PPCPs), 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 deficiency of information 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 California, a number of efforts are underway to develop strategies for CEC identification and prioritization, as well as processes for determining thresholds of concern. 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.

In this first edition, the *Pulse of the Delta* presents an overview of selected topics that water quality regulators have identified as current priorities. As the Delta RMP evolves, it will continue to develop high-quality information on water quality parameters critical to the health of the Delta. Gradually, a more comprehensive picture of water quality will emerge, and, incrementally, our understanding will advance. The experience with the POD underscores the tremendous need for such comprehensive water quality information, especially in a resource that faces as many and intertwined challenges as the Delta.

Did Contaminants Play a Role in the Pelagic Organism Decline?

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The Pelagic Organism Decline (POD) involves four 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 (**Figure 1**). Identifying the cause of their decline has become the focus of a large effort by numerous state and federal agencies. As part of this effort, the State Water Resources Control Board and the Central Valley Regional Water Quality Control Board sponsored a review 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 this review:

- Are available water chemistry 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 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?

The Water Boards’ review, “Evaluation of Chemical, Toxicological, and Histopathological Data to Determine Their Role in the Pelagic Organism Decline”

(Johnson et al. 2010), was published in April 2010 and is available on the Delta RMP homepage. It concluded that a step decline did occur between 2000 and 2002 for at least three species (Delta smelt, threadfin shad, striped bass) and that the longfin smelt experienced a more gradual decline. 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 (**Figure 2**).

The conclusion that contaminants are unlikely to be a major cause 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.

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). Similarly, it is not possible to determine if lesions in POD fish were more or less common or severe prior to the POD years, primarily because of the lack or histopathology data from the pre-POD and early POD years. Even in the later POD years, when more data are available, there is little evidence of lesions in either POD or non-POD species.

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 Water Boards review raised a number of questions that are being addressed in follow-on studies. Unfortunately, while future research can better assess the relative sensitivity of POD species to contaminants in the Delta, it cannot recreate history and fill the key data gaps in the historical record. In order to help ensure that future Delta-wide synthesis efforts related to contaminants have data adequate to address questions at the regional scale, the Johnson et al. (2010) report makes a number of specific recommendations, 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;
- 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.

Lessons Learned: Why the POD and Contaminants Story Can't Be Told

One of the main messages of the Water Boards' Contaminants Synthesis Report is that data are insufficient in both quantity and quality to determine the role of contaminants in the POD. Future research may improve our general understanding of how contaminants impact POD species but the main question "Did contaminants play a larger role in the POD?" will likely remain open to debate. The investigations of the role of contaminants in the POD were hindered because data were either missing, unavailable, scattered among various data owners, or not in a format that would allow the types of analyses needed for such an assessment.

Several types of problems were encountered, some of which have been corrected over time but several of which continue to hamper current studies. Inadequate documentation was a severe problem with historical data and made the majority of historical data unusable. Inadequate detection limits, poor preservation, and missing or incomplete quality assurance data reduced the utility of a large percentage of aquatic chemistry and toxicity data. Even where individual data points met the data quality requirements, spatial and temporal gaps in coverage limited the ability to draw conclusions about trends over the Delta as a whole. In addition, data from many sources were not publicly available or were available in hard copy or electronic formats that did not support data integration and analysis.

While many of these technical issues have been corrected, current monitoring designs and data management approaches are not sufficient to enable integrated assessments at the scale of the Delta. Comprehensive conceptual models, large-scale assessment designs, and improved data management procedures and systems are critical prerequisites to such assessments.

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

SIDEBAR

Pelagic Organism Decline (POD)

Serious declines of several important fish species in the Estuary are continuing. Summer and fall abundance indices calculated by the Interagency Ecological Program (IEP) suggest recent marked declines in numerous pelagic fishes in the Delta and Suisun Bay, known as the "pelagic organism decline (POD)". The fall indices have been collected for all but two of the last 30 years. The indices for the last three years continue to hover at record low levels for Delta smelt, striped bass, longfin smelt, and threadfin shad.

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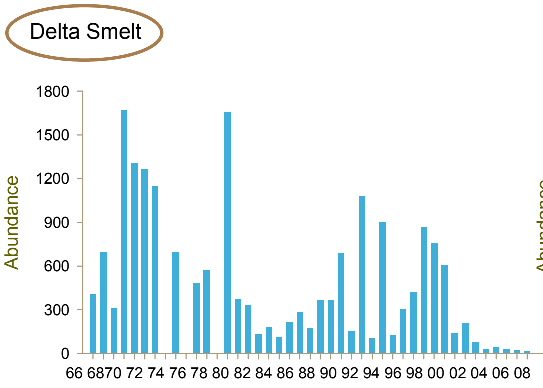

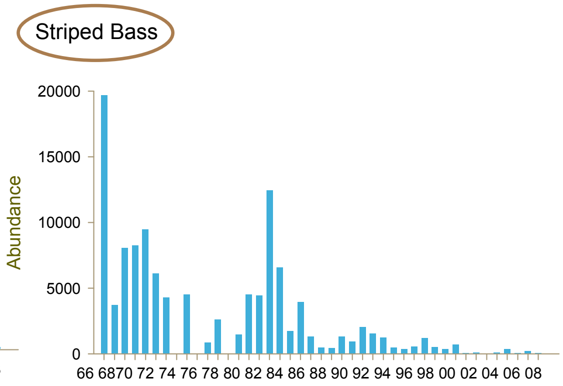

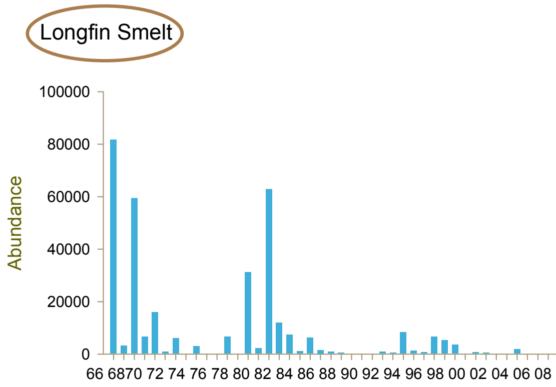

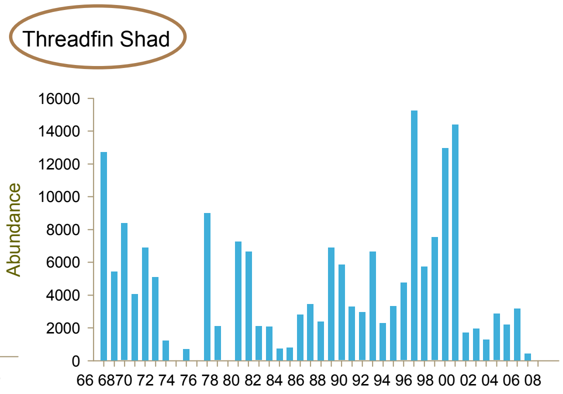

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Delta RMP stakeholders.

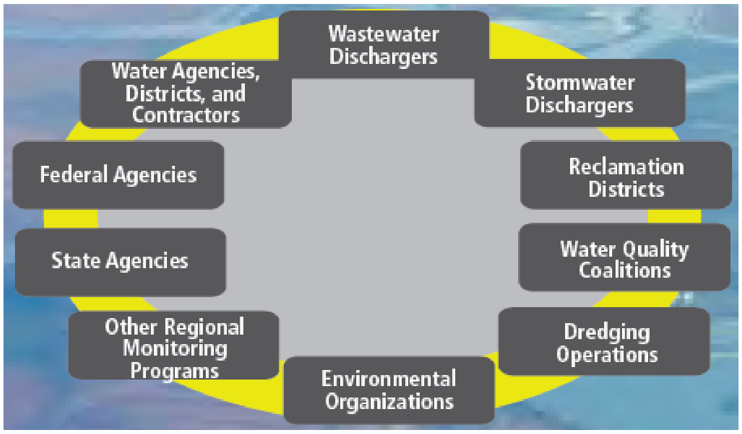
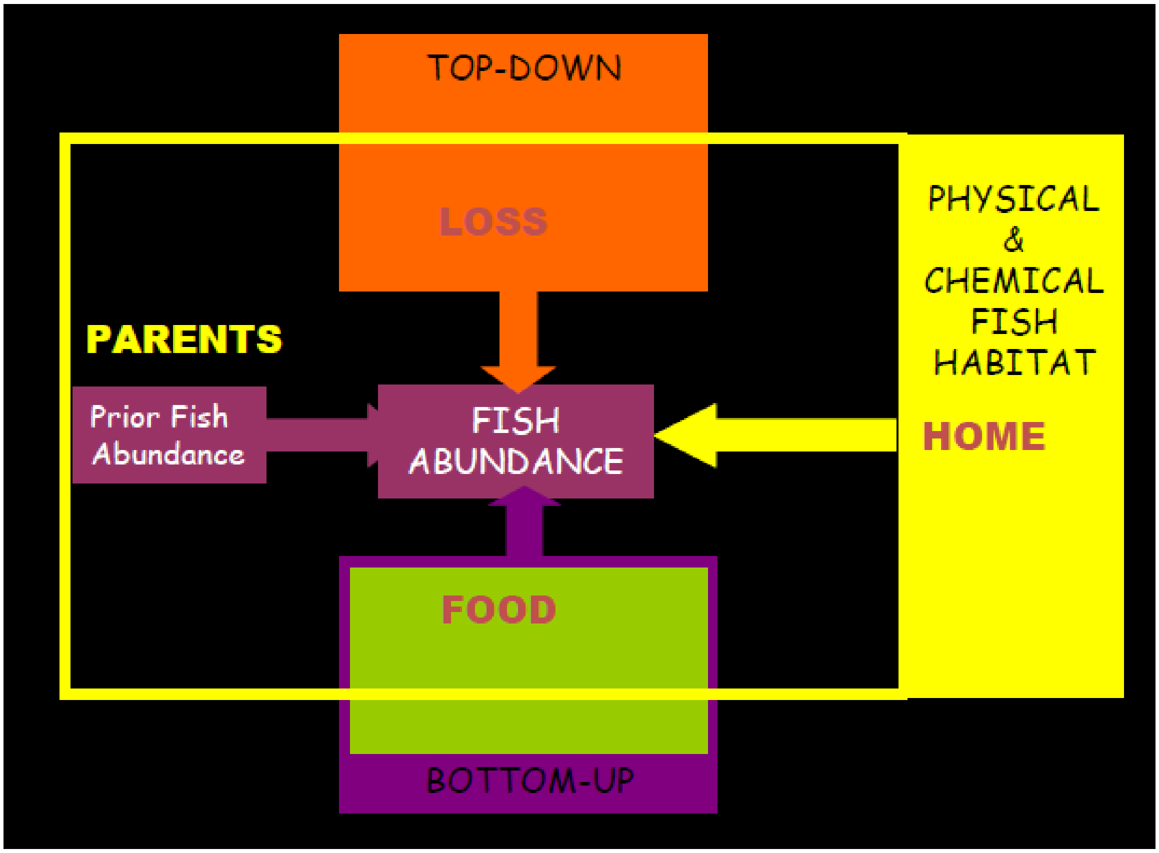


Figure 1.

The four POD species: Delta smelt, longfin smelt, striped bass, and threadfin shad. Delta smelt is a finger-sized fish that is native to the San Francisco Estuary and listed as threatened under the federal Endangered Species Act. Longfin smelt is found in several estuaries and lakes along the northern Pacific coast and is listed as a threatened species under the California Endangered Species Act. Striped bass were introduced from the East Coast in the late 1800s by the California Fish and Game Commission and are popular with anglers. Threadfin shad are a favorite food for striped bass and other sport fish.

Figure 2.

Conceptual model of the POD. This conceptual model is rooted in food web and fisheries ecology and identifies four possible causes for the POD: prior low fish abundance (1), degraded water quality (2), increased mortality (3), and reduced food availability (4). (**1**) Prior fish abundance: decimated fish population produce less young, exacerbating the effect of stressors. (**2**) Degraded water quality: 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 of fishes' habitat. (**3**) Increased mortality: predators and the pumps of the water projects decimate fish populations. (**4**) Reduced food availability: 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. Adapted from Sommer et al 2007.



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Management Update

Delta RMP: Re-thinking Water Quality Monitoring in the Delta

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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

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.

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**), 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 condition. 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).

The workplan includes several actions that 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 a regional monitoring program that is developed through a comprehensive stakeholder process. 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 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. The 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 the public. Researchers will also be able to use data generated through the RMP to augment data they collect themselves.

The RMP can play a large role in informing the public of the challenges and opportunities that exist within the Delta. Publications like the *Delta Pulse*, 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 the 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 will need to actively contribute time and resources to continue developing the major aspects of the program: governance, monitoring objectives, funding, data integration, and coordination with other programs. To date, the Delta RMP has developed under strong control and guidance from the Water Boards and Aquatic Science Center. 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. 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’s 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. Widely understood is 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 different 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. Through coordination and collaboration with other programs, the Delta RMP can foster integrated water quality monitoring and assessments. The envisioned outcome is sustainable, better protected uses of Delta water.

SIDE BAR

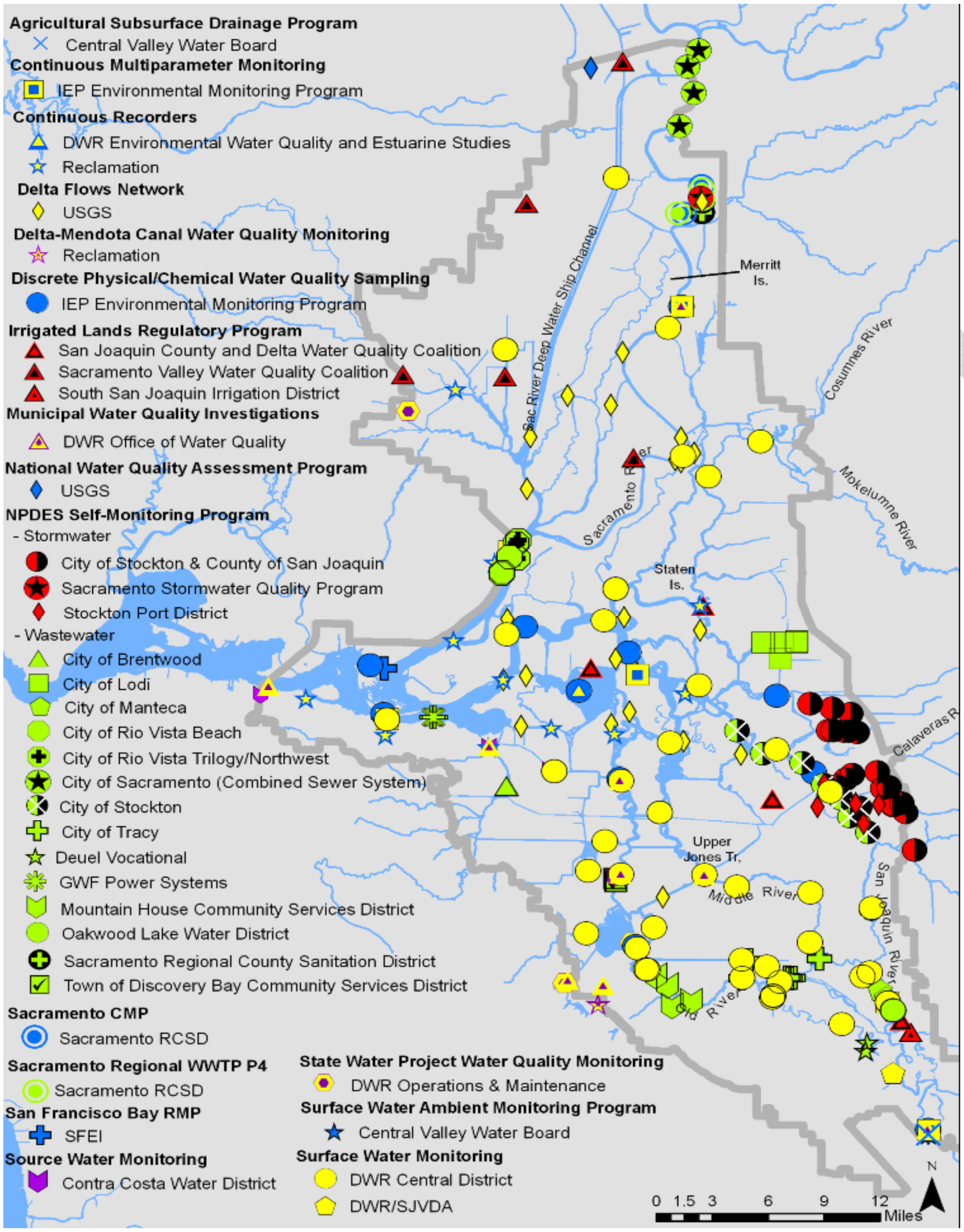
1. Delta Vision

In February 2007, the governor appointed the independent Delta Vision Blue Ribbon Task Force to find a durable vision for sustainable management of the Delta. Delta Vision was based on a growing consensus among scientists and decision makers that current conditions in the Delta are not sustainable and a new approach is needed to secure California's water supply and protect this unique ecosystem. Perhaps *the* core Task Force recommendation is the one to “create a California Delta Ecosystem and Water Council to govern the co-equal values of healthy estuarine ecosystem function and a reliable water supply, and to approve policies for enhancing the Delta as a place.” The recommendation resulted in the formation of the Delta Stewardship Council, which is charged with developing a comprehensive Delta Plan for achieving the co-equal goals of water supply and ecosystem. The Delta Stewardship Council must adopt and implement the Delta Plan by January 1, 2012.

More information: http://deltacouncil.ca.gov/.

2. Water Quality Monitoring in the Delta

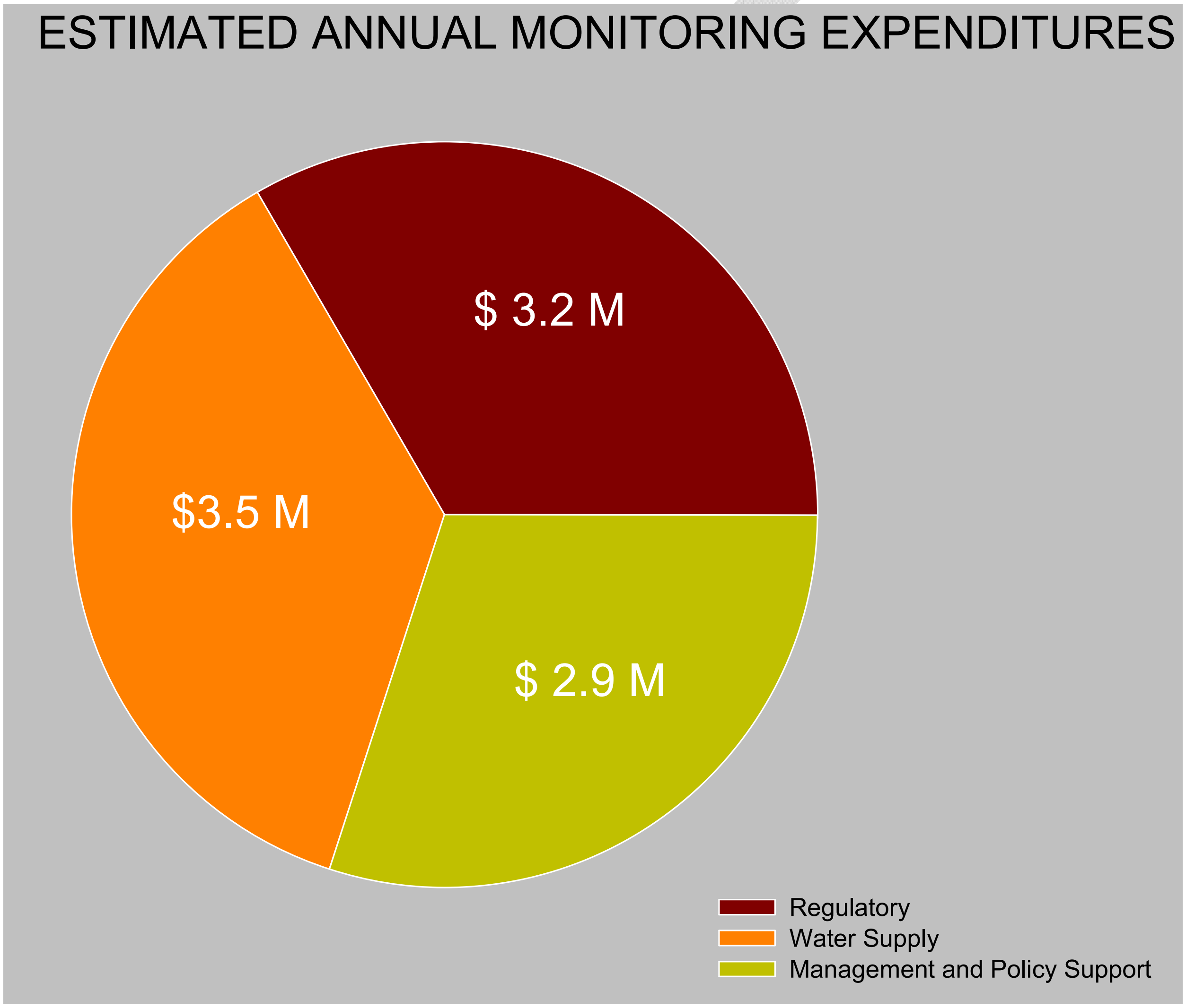
Seventeen long-term water quality monitoring programs are underway in the Delta, collecting data at more than 200 different sampling locations. At least 22 different entities are involved in collecting the data, at an estimated annual cost of $9 to $12M.



ILLUSTRATIONS

FIGURE 1.

Total annual cost of surface water monitoring in the Delta is estimated to be in the range of $9 to $12M. Based on available data, monitoring expenditures in the Delta exceed $9M. Cost estimates were not available for all monitoring programs.



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Ammonia in the Delta: State of the Science, Implications for Management

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Highlights

- ⇨ A significant increase in total ammonia levels in waters of the Delta has occurred over the past 10 years
- ⇨ Total ammonia is the sum of free ammonia (also known as unionized ammonia, chemical symbol NH_3) and ammonium (or ionized ammonia, chemical symbol NH_4^+)
- ⇨ Elevated concentrations of free ammonia can be toxic to fish and other aquatic life
- ⇨ One of the key findings of recent monitoring is that ambient levels of free ammonia are unlikely to be toxic to fish in the Delta
- ⇨ An emerging hypothesis links elevated ammonium levels to low primary production in Suisun Bay and 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

Rising Concerns Over Ammonia

A significant increase in ammonia levels in Delta waterways over the past 10 years has triggered concerns about their impact 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 an emerging hypothesis for how current ammonia levels may be significantly 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. 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. There are also other sources of ammonia to the Bay-Delta system, particularly in the vicinity and downstream of Suisun Bay. These include other wastewater treatment plants, agricultural runoff, atmospheric deposition, internal cycling, and possibly discharges from wetlands.

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 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 (**Figure 4**).

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 (**Figure 5**). 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. Other reported results indicate that toxic effects to freshwater mussels are possible, if sensitive mussels are present immediately below the SRWTP outfall. The State Water Contractors (SWC) compared ambient ammonia levels immediately downstream of the SRWTP mixing zone with the draft USEPA. ammonia criterion for freshwater mussels. The SWC report that the draft USEPA. ammonia criterion was exceeded 21 percent of the time between 2007 and 2008 and 41 percent of the time in 2009. 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 below the SRWTP outfall.

The research group of Dr. Swee Teh from the U.C. Davis School of Veterinary Medicine reported that ambient ammonia levels could affect the reproduction and survival of larvae of the copepod *Pseudodiaptomu*s *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

An emerging hypothesis links increased ambient levels of ammonium to low algal growth rates and chlorophyll levels in Suisun Bay and the Delta – this is considered to be one of the factors possibly contributing to the POD (see **Opening Article** on page **XX**). Studies inside the Delta so far have not been entirely conclusive, but there is a growing consensus about downstream effects on the food web in Suisun Bay. 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 algae blooms from developing when conditions are otherwise favorable. (An algal bloom is a rapid increase in the number of algal cells such that the blooming algae dominate the algal community.) They observed that spring blooms only occur in years when ambient ammonium is below levels reported to inhibit nitrate uptake and algal production (**Figure 6**). 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. At all other times, ammonium levels in Suisun Bay were above this threshold and no blooms were observed. Suppression of algal blooms in Suisun Bay is presently the most compelling evidence for beneficial use impairment by ammonia and ammonium originating in the Delta’s watershed.

There are also growing concerns that current ammonium levels may suppress algal growth in the Delta upstream from Suisun Bay. Ammonium levels in the river downstream of the SRWTP are high enough to shut down nitrate uptake in algae (Parker et al. 2010). This is an important observation, since it points to a possible mechanism for the observed shift in the Delta algae community from ecologically important diatoms to smaller, less desirable flagellates and blue-green algae (Brown, 2010; Lehman, 2010, Glibert 2010). Support for this possible link comes from statistical correlations between long-term changes in ammonium loadings to the Delta from the SRWTP and the observed system-wide changes in the algae community (Glibert 2010). 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). For zooplankton, an important link in the food web of fish, diatoms are considered to be more nutritious as prey than smaller algae such as flagellates and blue-green algae. As experiments in large experimental enclosures show (**Figure 7)**, small flagellates and blue-greens dominate phytoplankton communities with high ammonium uptake, whereas diatoms prevail in communities with high nitrate uptake. This implies that the smaller flagellates and blue-green algae have an edge competing for nutrients and grow faster than diatoms when the ambient nitrate-ammonium balance shifts from nitrate to ammonium. A higher growth rate of flagellates and blue-green algae would cause these "bad food" smaller-sized cells to gradually replace the "good food" diatom-dominated community. A recently published study suggests that not only changes in the ammonium-nitrate balance, but also changes in the nitrogen-phosphorus balance over the past decade are now favoring blue-greens and flagellates over diatoms (Glibert 2010). It has been documented that the algal community of the Delta has changed from a community dominated by diatoms to a community dominated by flagellates and blue-green algae (Brown, 2010; Lehman, 2010), consistent with these predictions. Whether this is in fact the result of the observed changes in nutrient levels or some other factor is not known, because some critical monitoring data are still missing. 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.

Implications for Nutrient Management

There is a growing consensus that ambient ammonia levels in the Delta may be causing beneficial use impairments. 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) confirmed the Delta as a source of ammonia to Suisun Bay. Recent monitoring by the San Francisco Bay Water Board found elevated ammonia levels at both ends of Suisun Bay, indicating that not all of the ammonia originates from the Delta and thus the SRWTP. 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 ammonia levels in the Delta will require more stringent nutrient load controls on wastewater treatment plants that discharge significant loads of ammonia to Suisun Bay and the Delta.

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. There is growing evidence that current ammonia levels in the Delta are impairing beneficial uses, but it is not clear if they are a prime factor responsible for the observed demise of the Delta food web. 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 growing 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 with 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. The emerging Delta RMP can play a valuable role in developing the needed long-term monitoring, coordinating resources and sampling activities, 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, complicating 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.

SIDEBARS

1. The Different Forms of Ammonia

Two forms of ammonia are commonly reported and considered in a water quality management context: 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 the more toxic form to fish. Total ammonia is easy to measure and can be converted into a value for free ammonia, based on the pH and water temperature, which are the two major factors that determine the balance between free ammonia (NH_3) and ammonium (NH_4^+) in water - a pH or temperature increase, the proportion of free ammonia, the more toxic form, increases. Ammonium, or ionized ammonia, is the form of ammonia nitrogen taken up by algae as a nutrient.

2. 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 California Data Exchange Center (CDEC) 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**). Intensive sampling was conducted on three occasions at Rio Vista and Antioch by collecting water every two hours for two days from each site. This was done to determine whether there were diel (day/night) or tidally induced changes in nutrient concentrations, but no consistent pattern was observed. Comparison of ancillary data with those from the remotely operated CDEC meters suggests good agreement in pH but significant differences in some other parameters (turbidity and chlorophyll). This result reaffirms the importance of collecting quality-assured ancillary parameters as part of each ambient monitoring study.

ILLUSTRATIONS

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 discharges to the Delta between Garcia Bend and Hood.

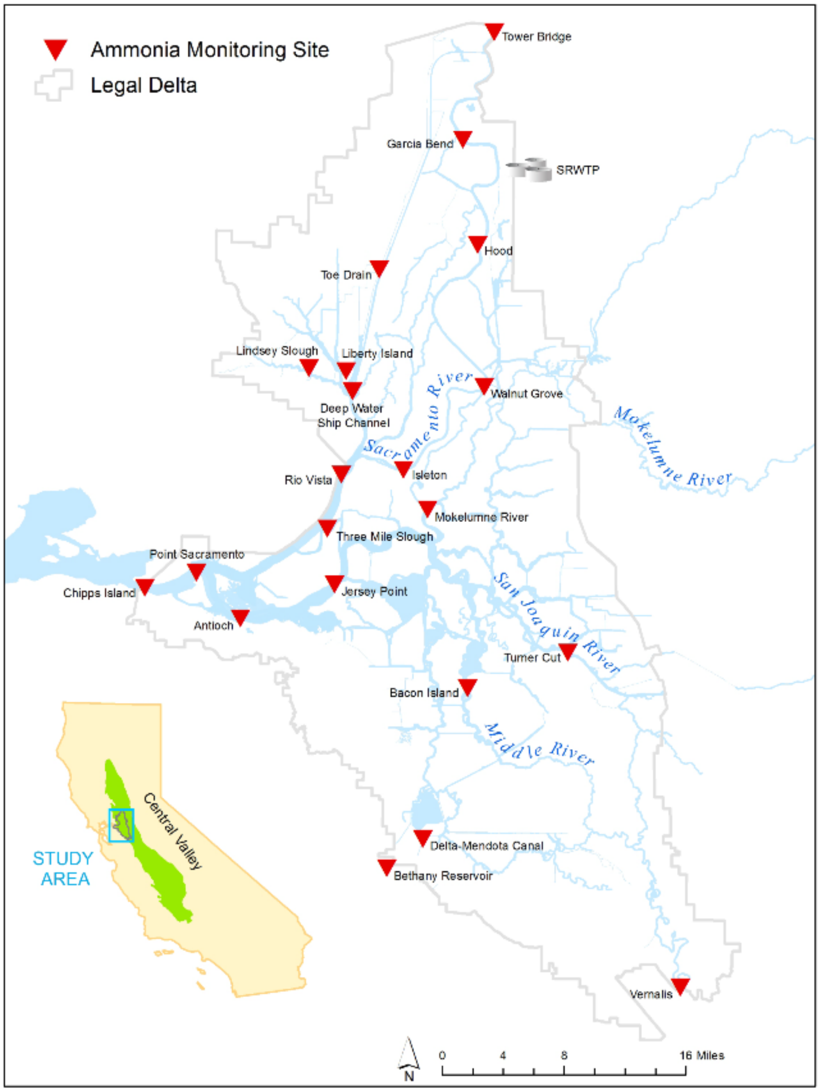


Figure 2.

Ammonia concentrations increased below the SRWTP outfall and gradually declined downstream. Total dissolved nitrogen (TDN) is the sum of all forms of dissolved forms of 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.

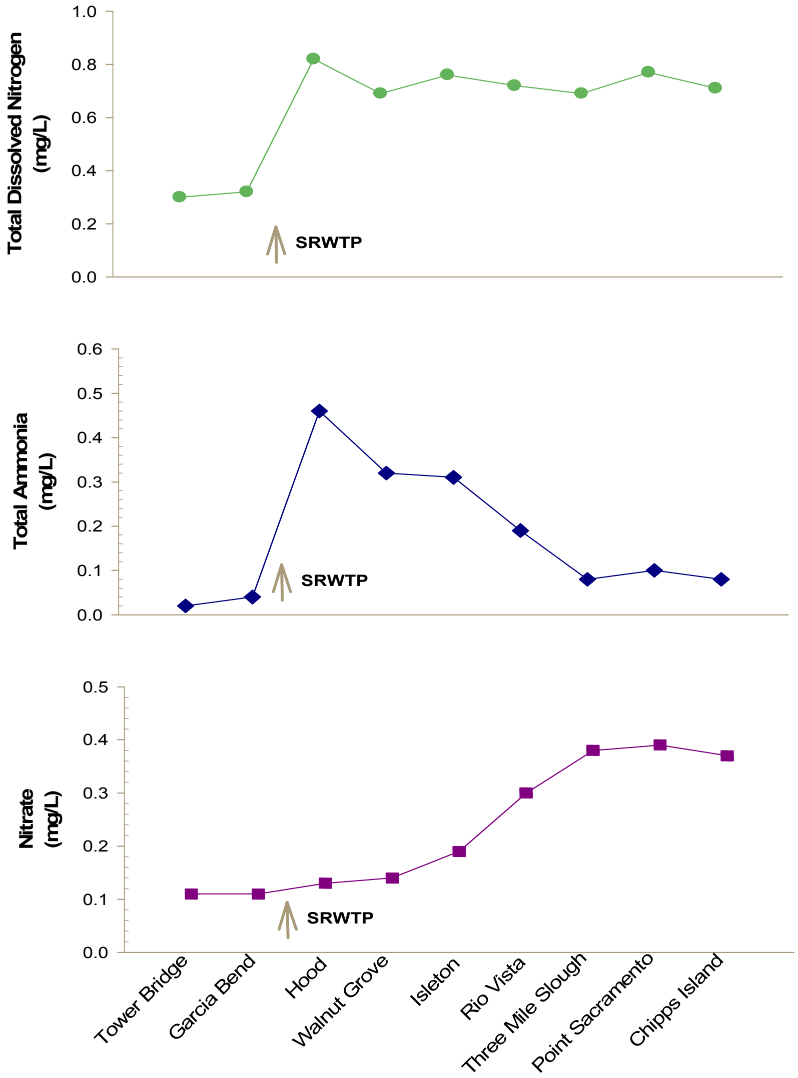


Figure 3.

Measured free ammonia concentrations at Delta sampling sites are below the estimated no effect threshold for 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.

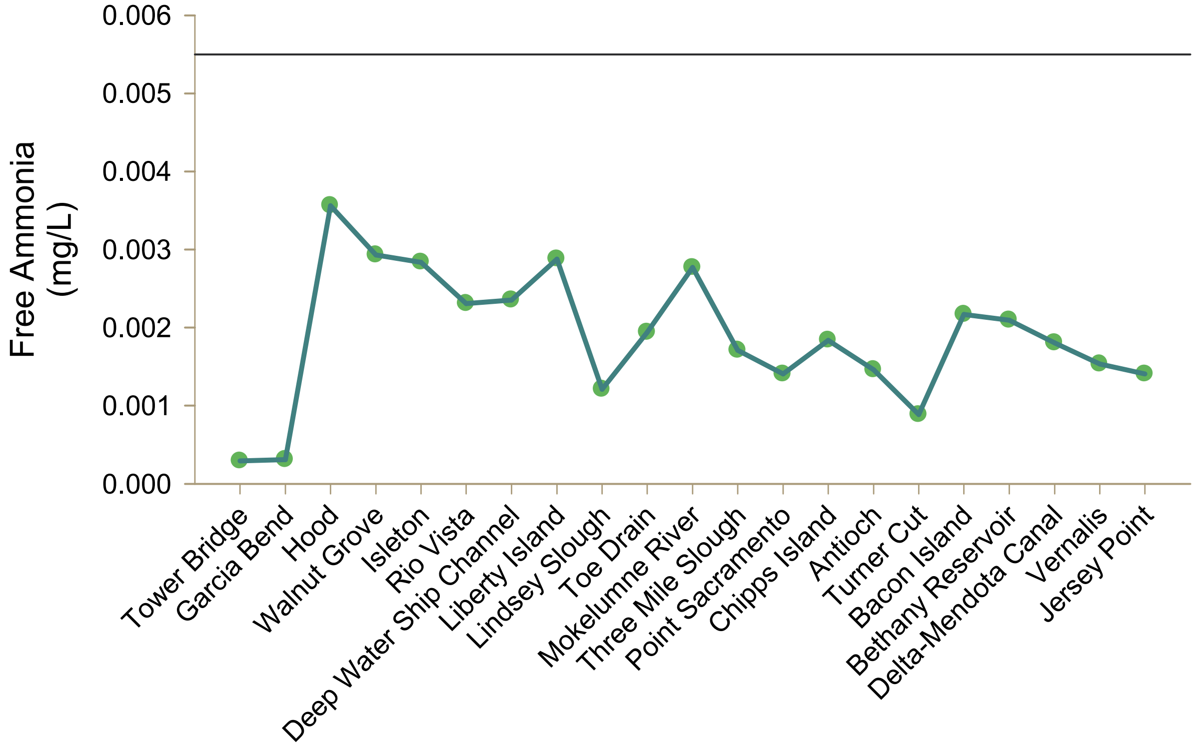


Figure 4.

Safety factor values for all Delta sites were greater than one when compared against the USEPA chronic ammonia criterion for protection of juvenile fish. A safety factor greater than one is considered safe.

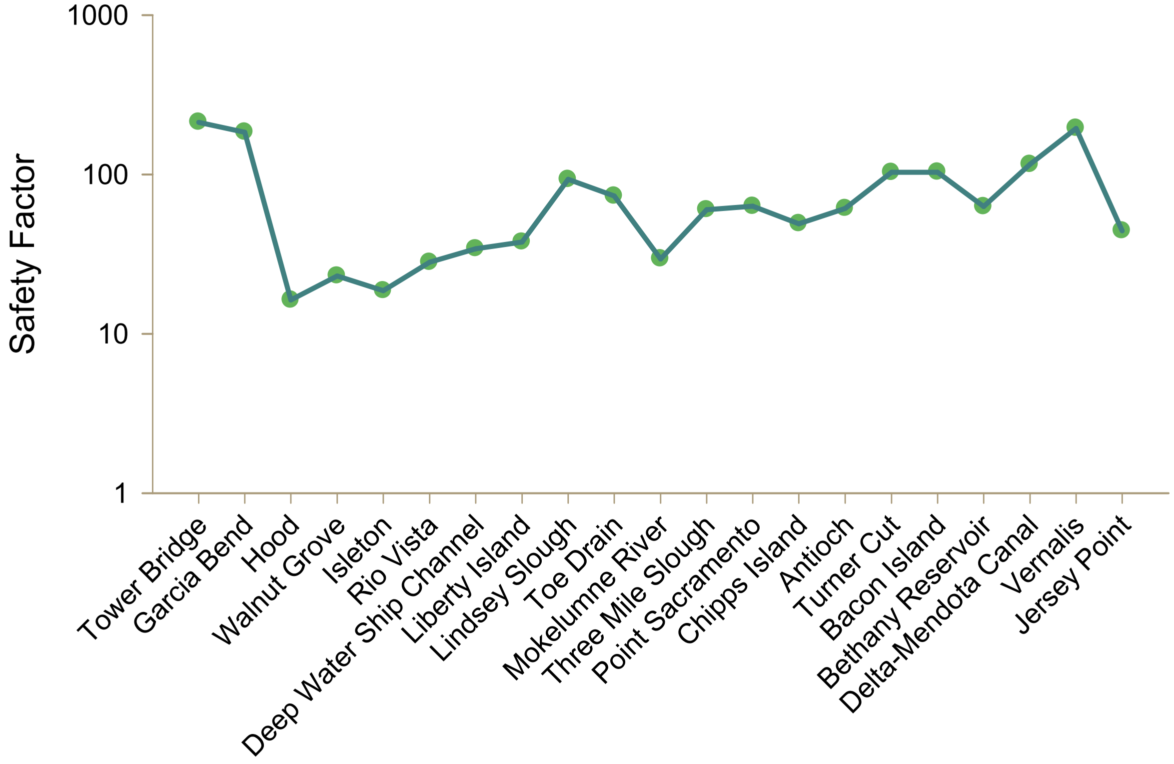


Figure 5.

Ammonia levels in Delta water never exceeded USEPA's new draft criterion for freshwater mussels. Mussels are more sensitive to ammonia than larval fish, and the safety factor of four at Hood indicates a relatively small safety margin.

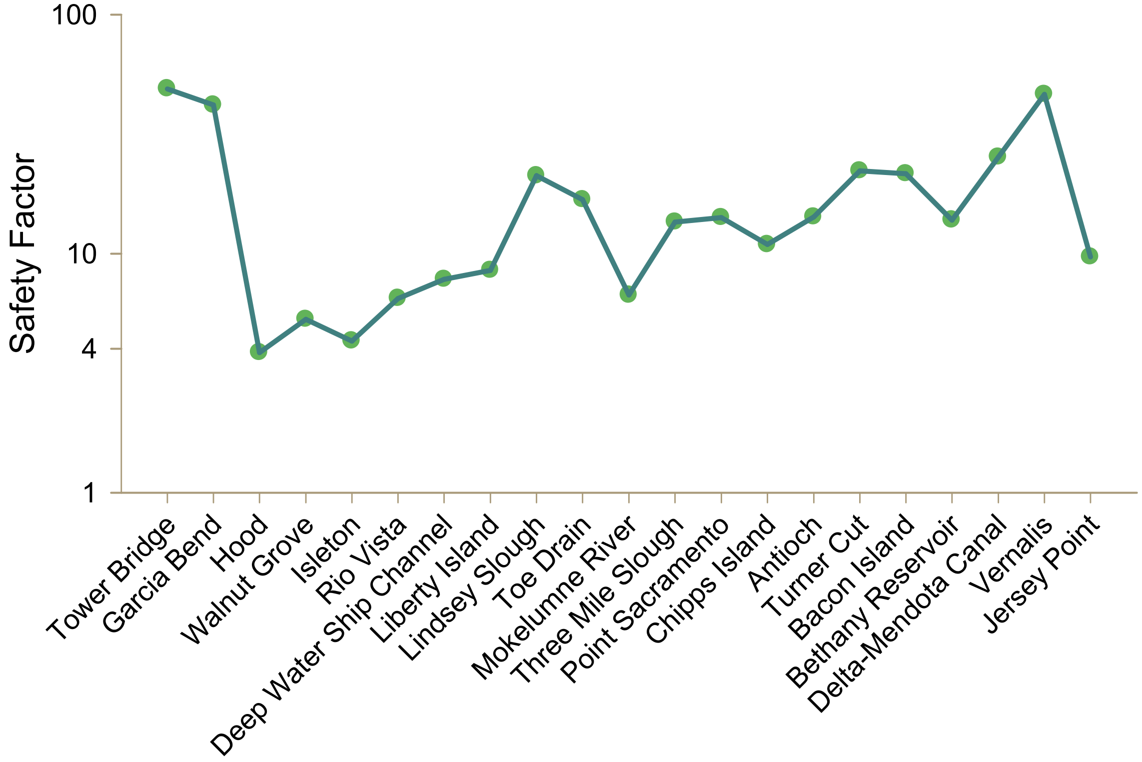


Figure 6.

Spring blooms in San Francisco Bay coincide with low ammonium concentrations. Four spring peaks in chlorophyll (blooms) occurred in San Pablo and Central Bays (Fig. 6a) and coincided with reduced ammonium concentrations, often near zero (Fig. 6b). 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 (Fig. 6c) 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 (Fig. 6b), except during the spring bloom periods.

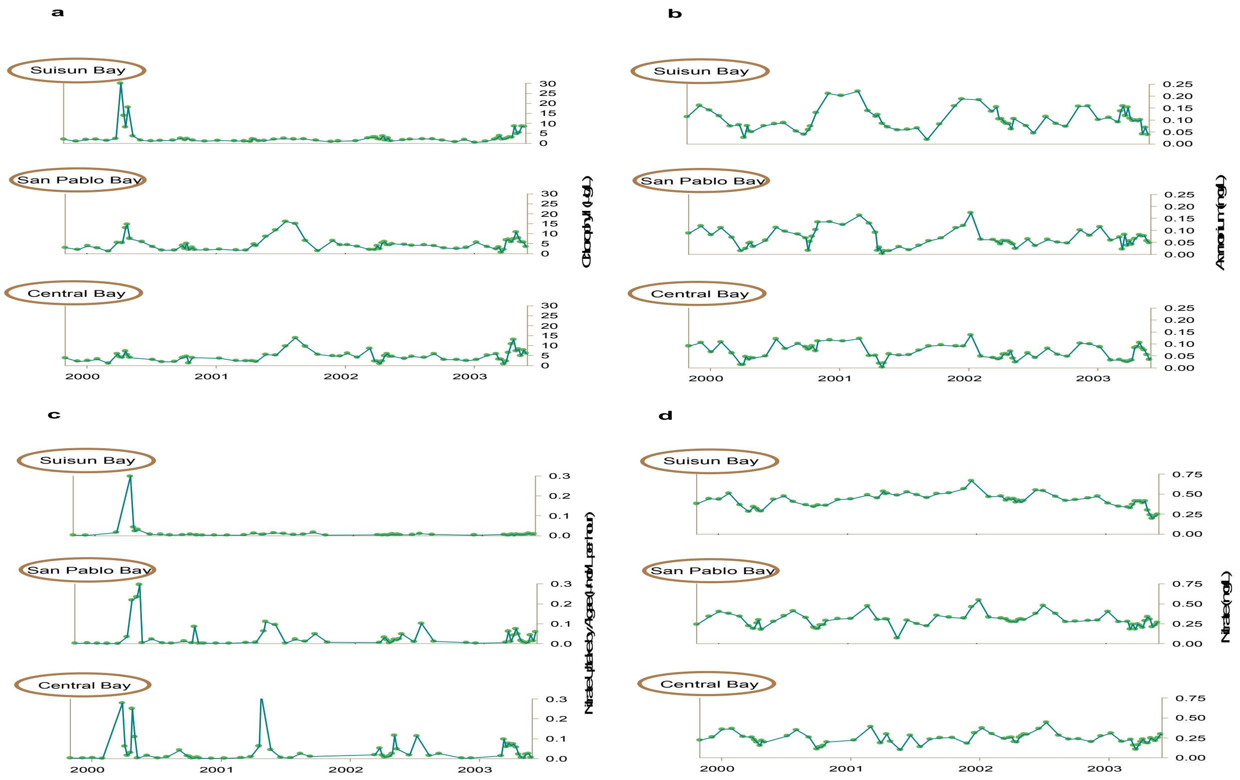
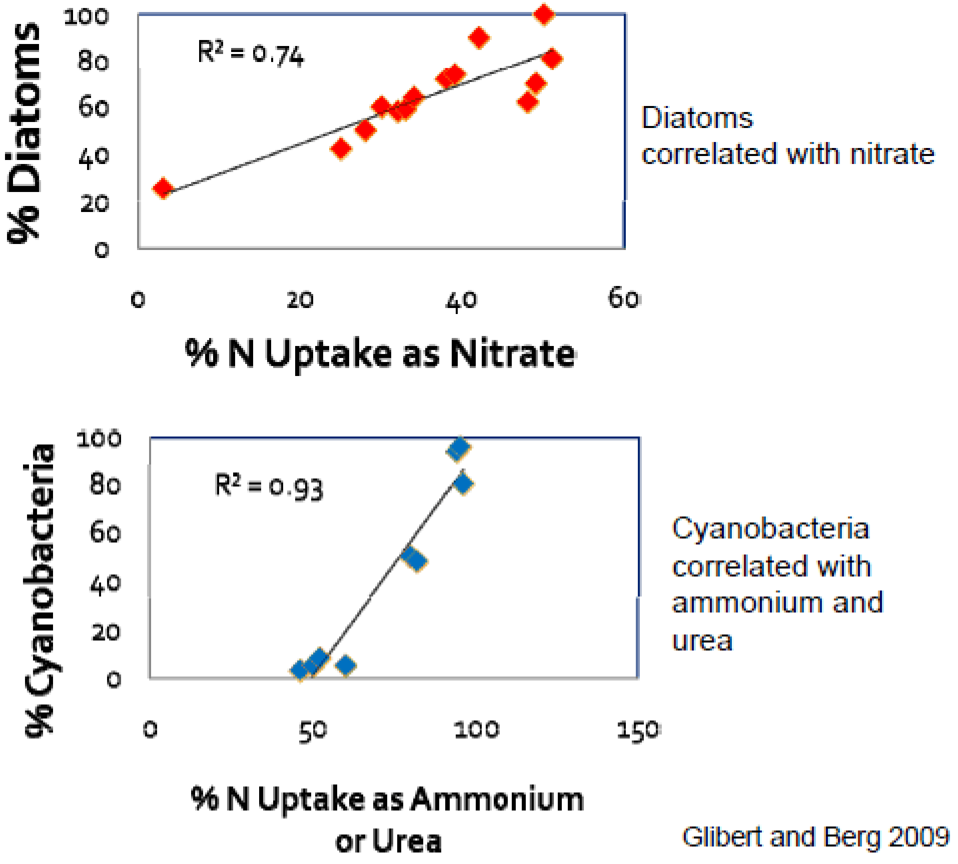


Figure 7.

Relationship of the availability of different forms of nitrogen to phytoplankton composition. Researchers at the University of Maryland conducted algal growth studies in large 10,000 L experimental tanks filled with river water. The abundance of diatoms was correlated with total nitrate uptake by algae and the abundance of blue-green algae (cyanobacteria) was correlated with ammonium and urea uptake (Glibert and Berg 2009).



Glibert and Berg 2009

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Not What We Had Hoped For: How Delta Studies Have Reshaped our Understanding of Pyrethroid Insecticides

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- ⇨ Monitoring studies have shown that actions taken by regulatory agencies and others to control organophosphorus pesticides have led to increased use and water quality problems associated with pyrethroids
- ⇨ 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 the problems of yesterday

Not What We Had Hoped For

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.

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 national economic conditions and the availability of alternative insecticides.

The organophosphates were widely known to cause toxicity in aquatic systems after heavy rains washed residues into creeks and rivers (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. 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**). 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 areas showed toxicity to the crustacean *Hyalella azteca*. Usually widespread and abundant, *Hyalella* were also conspicuously absent from Roseville creeks in all but those stream reaches with the least residential development. *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. 2005).

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.

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 is 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 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*, several pyrethroids are toxic in water at concentrations of 2 *parts per trillion* (Weston and Jackson 2009).

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. But monitoring of pyrethroids in the water column 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 level (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. Flows in the American River are dam controlled, and are maintained 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 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 or by deliberate drain disposal of flea and tick products for pets, products for head lice or bed bug treatment, 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 at the different facilities.

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. Effects from long-term (chronic) exposure are usually manifested at about one-tenth the concentration of acute effects, 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 where 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. 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. Almost all 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 unknown.

Following the findings of environmental toxicity for 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 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.

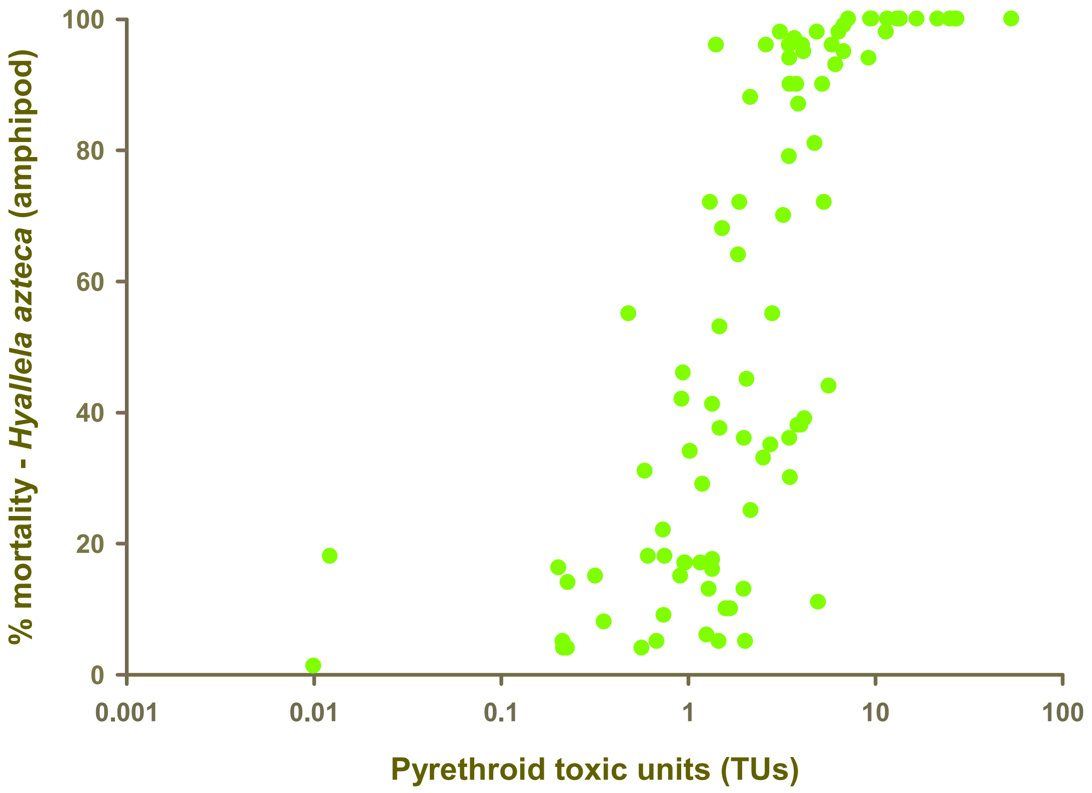
A Role for the Delta Regional Monitoring Program

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 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. The Delta Regional Monitoring Program can play an important role by serving as a forum where limitations in analytical methods and gaps in 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 control programs that are under development by the Regional Board for pesticides and provide a measure of control program success.

SIDEBARS

Identifying the Cause of Toxicity



Urban runoff may contain a whole 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 achieved 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 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 is a good predictor of *Hyalella* toxicity. To confirm pyrethroids as the cause of toxicity, a more elaborate laboratory procedure called Toxicity Identification Evaluation (TIE) was done on 7 runoff samples. A TIE separates the pyrethroids from other toxicants through various chemical and physical manipulations. Toxicity can then be assigned by comparing the toxicity of the manipulated sample with the baseline toxicity of the unaltered sample. The TIE results for all 7 samples pointed to pyrethroids as the cause of toxicity.

Measuring Pyrethroids: The Latest Developments

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. The dissolved and particulate fractions can then be analyzed separately to better understand pyrethroid movement in the environment. Techniques such as solid-phase microextraction (SPME) are being used to measure the bioavailability of pyrethroids in sediment porewater, 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. 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.

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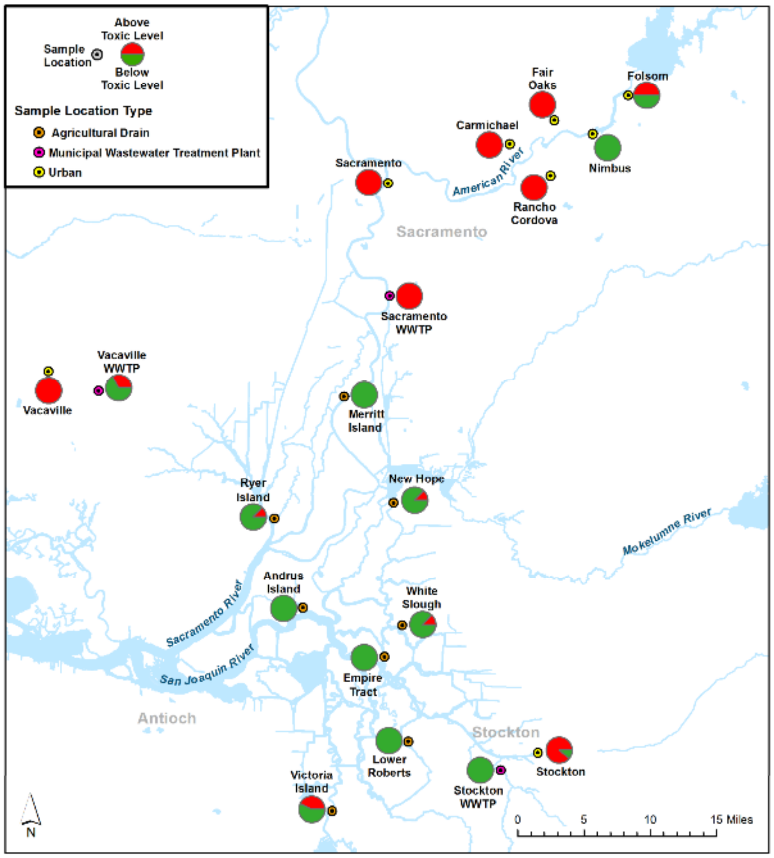
More information available at: http://ca.water.usgs.gov/user_projects/toxics/

ILLUSTRATIONS

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.



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Contaminants of Emerging Concern (CECs): Adapting to a Moving Target

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Highlights

- There are potentially thousands of CECs, the number is increasing, and little information is available to assess risks to humans and wildlife
- Pest control products (for example flea and ticks shampoos and ant and bug products), drugs (including birth control, menopause management, and psychiatric treatments) and everyday products such as coffee, cars, and furniture are contributing to the problem
- 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

The CEC Challenge

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 of chemicals to insure they do not adversely impact human and environmental health.

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 regulated priority pollutants. The risks these conventional contaminants pose to ecosystem and human health are relatively well-established and 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 have not been adequately tested for their potential impacts to humans and wildlife are continuously released to the environment.

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. CECs can be broadly defined as any synthetic or naturally occurring chemical that is not commonly monitored in the environment but has 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.

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.

Lessons from San Francisco Bay

Currently little information on CECs is available for the Delta, though studies are on-going (for examples, see Sidebars). 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 long-term, 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 phased out of use, 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, p. X): Also 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 ng/g) and allethrin (0.3 ng/g). This is in contrast to results for the other portions of San Francisco Bay, where detection of other compounds was more frequent 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 the 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, such as wastewater and stormwater outfalls, further upstream.

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. 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 ethoxylates, surfactants used 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) for seven years in a whole lake experiment. Reported concentrations of EE2 and other estrogenic substances in 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.

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 identifying next steps regarding 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 on the Horizon

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 is still largely unknown. Current-use flame retardant chemicals include other brominated chemical mixtures, some of which contain a brominated phthalate, and chlorinated organophosphate compounds.

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 with 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.

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.

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 with its potential toxicity. 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.

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. 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.

Responding to the Challenge

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. This includes conducting appropriate risk assessments so that potentially harmful products could be 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 impacts of chemicals in current use.

The deficiency of information 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 of 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 state level biomonitoring program and includes identification and prioritization of CECs. Biomonitoring promises particularly useful results for creating policy and taking other actions that protect the public's health. For example, as more data have become available regarding the general population's exposure to a variety of commercial chemicals, public concerns have been aroused over the health risks posed by exposures to unregulated chemicals, such as flame retardants used in furniture or common pesticides used in and around the home. Biomonitoring California aims 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.
- 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 other recommendations, the participants outlined possible approaches for chemical prioritization and 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 Sidebar).

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.

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 would reduce costs, maximize program effectiveness, and increase the collective understanding of CEC occurrence and fate in the Bay-Delta system.

SIDEBARS

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 sample extracts for a wide variety of chemicals. Following traditional extraction procedures, the sample extract is carried through fewer 'clean-up' steps, and then 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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National Oceanic and Atmospheric Administration (NOAA) Mussel Watch CECs Early Warning Network: California Pilot Project

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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CEC Projects in the Delta

For more than 6 years, the **U.S. Fish and Wildlife Service** (USFWS) 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 (page **XX**).

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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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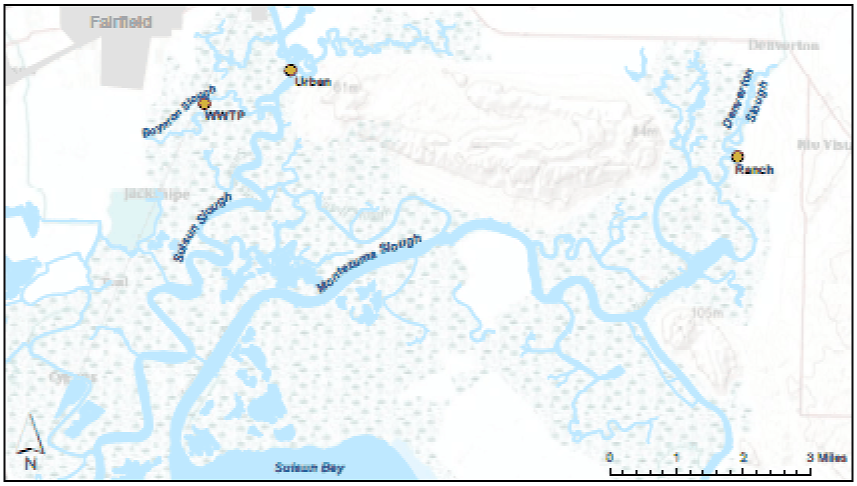
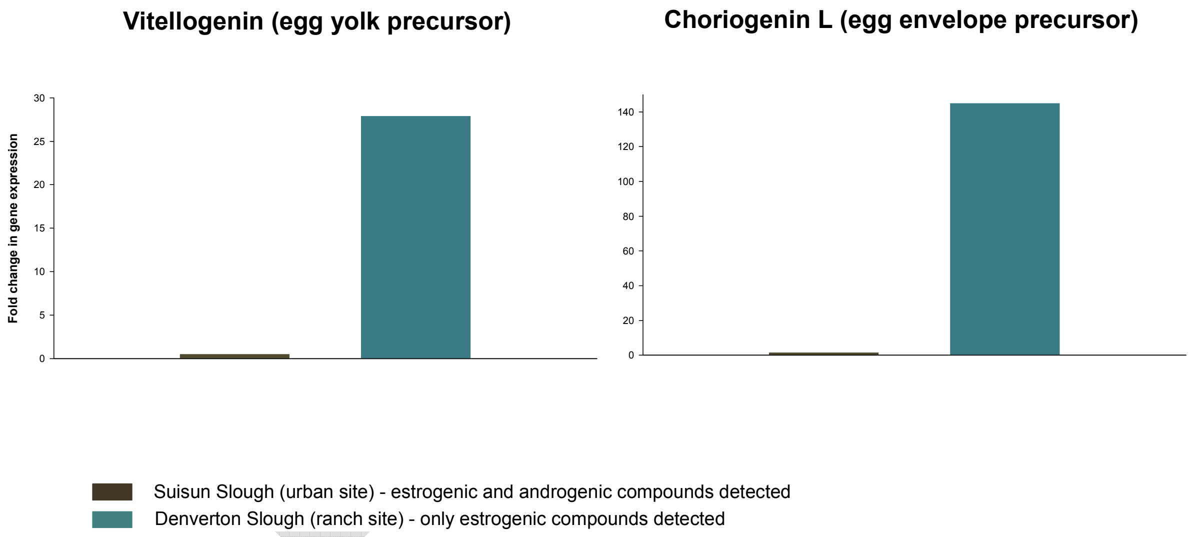


Gene Expression of Egg Precursor Proteins in Male Mississippi Silversides



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 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. The site where no CECs were detected is located at the American River upstream of the Sacramento urban area. At the other ten sites, 21 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.

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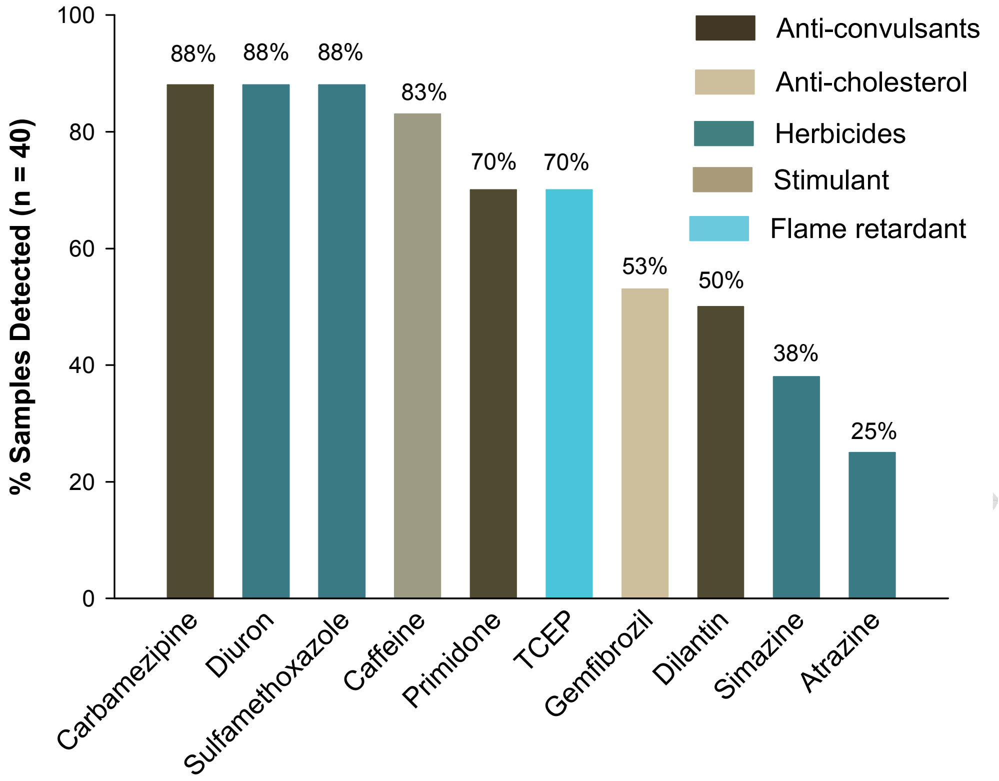
For more information: http://www.nwri-usa.org/CECs.htm

Top 10 CECs Found in Delta Water



New Pesticides

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 (page **XX**).

Fipronil is a pryazole insecticide which has increased in use (almost doubled since 2003) for crop protection, controlling ants and cockroaches, and as the major insecticide used 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.

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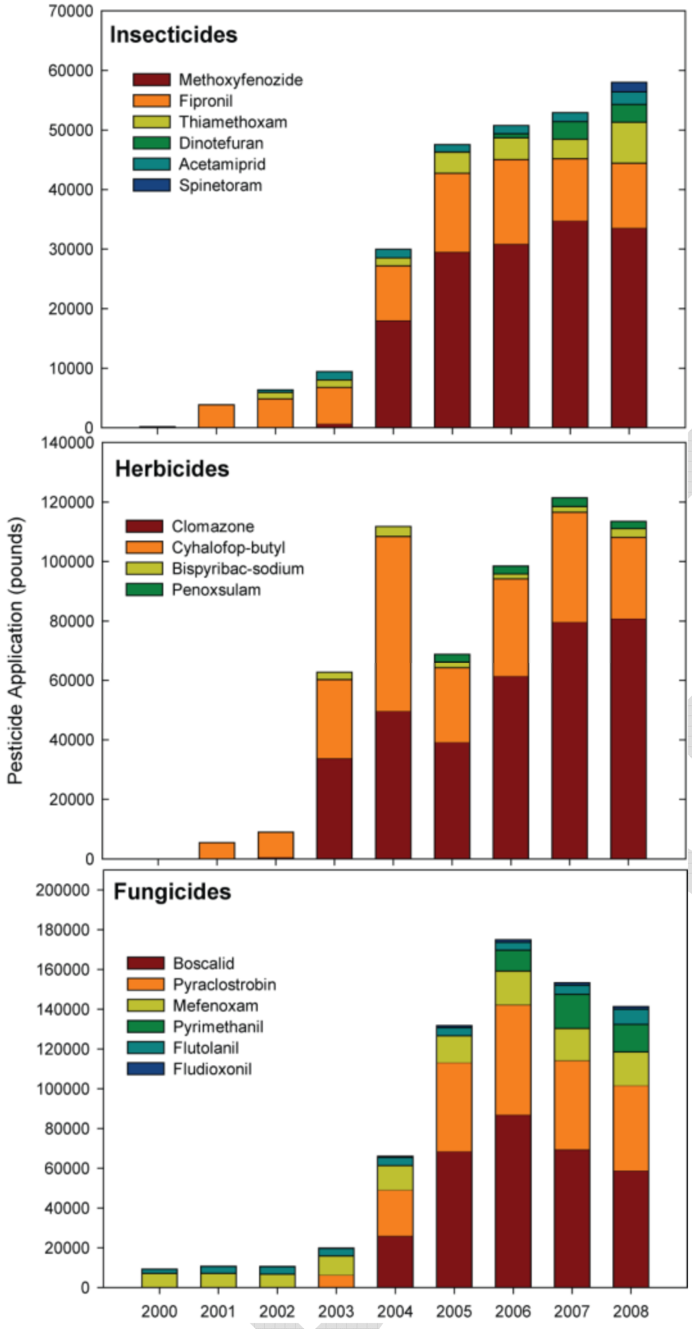
For more information: http://ca.water.usgs.gov/user_projects/toxics/



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2 *Pesticide applications in pounds for the Bay-Delta watershed, based on data contained in the California Department of*

3 *Pesticide Regulation Pesticide Use Database 2000-2008*.

ILLUSTRATIONS

Figure 1.

Approximately 100,000 individual chemicals have been registered for commercial use in the U.S. over the past 30 years. 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.

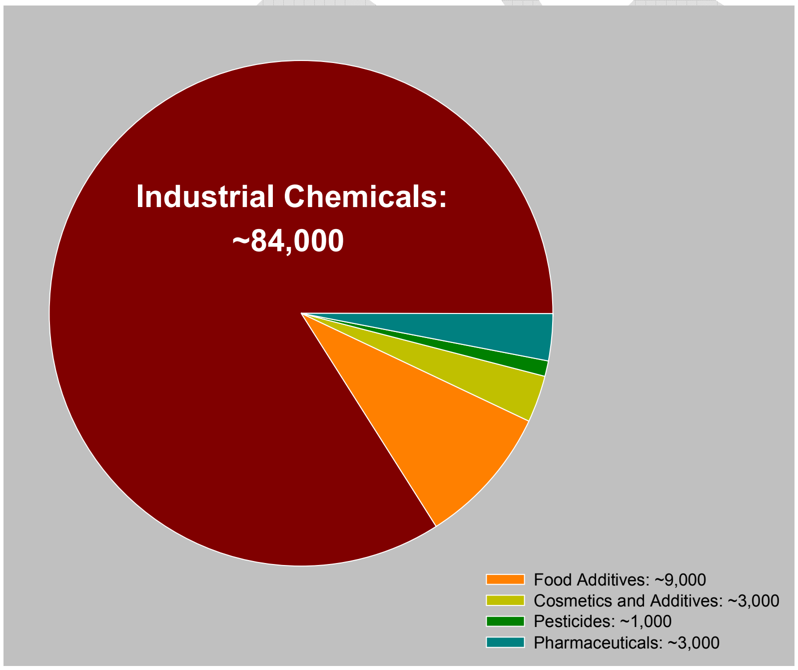

Figure 2.

Samples taken at Delta sites suggest that concentrations of PBDEs in 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.

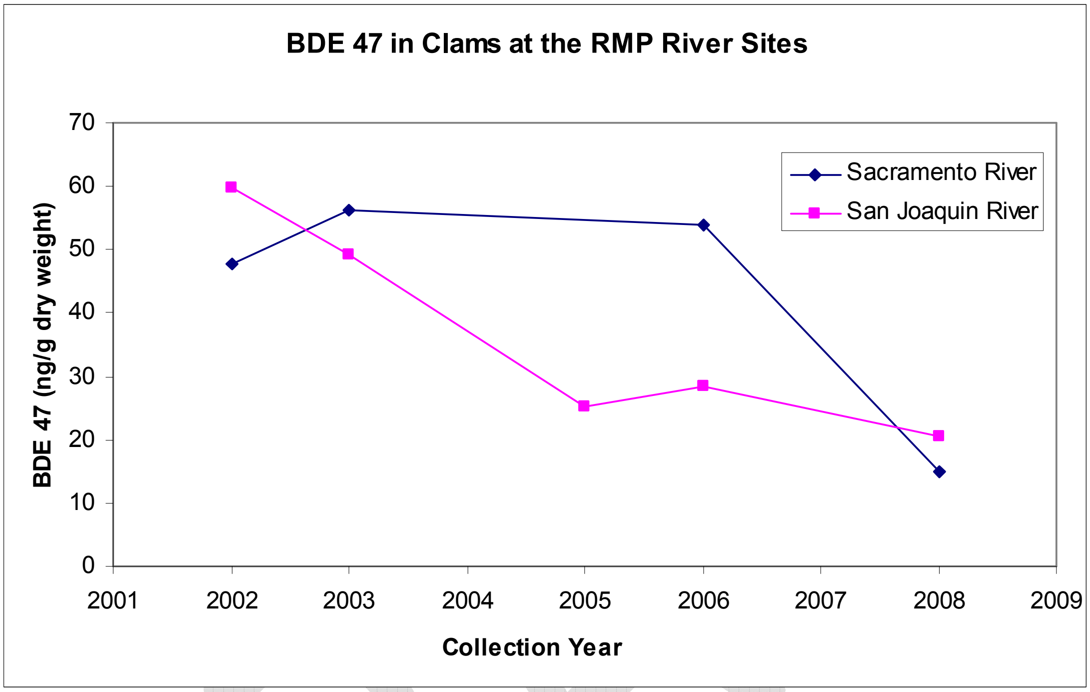

Figure 3.

In 2009, a statewide workgroup developed a tiered system for prioritizing and monitoring CECs. **The prioritization system consists of various levels of risk or effect that are tied to appropriate management actions.** The graph shows the San Francisco Bay Regional Water Quality Control Board's interpretation of the system for various CECs (Tom Mumley, pers. communication).

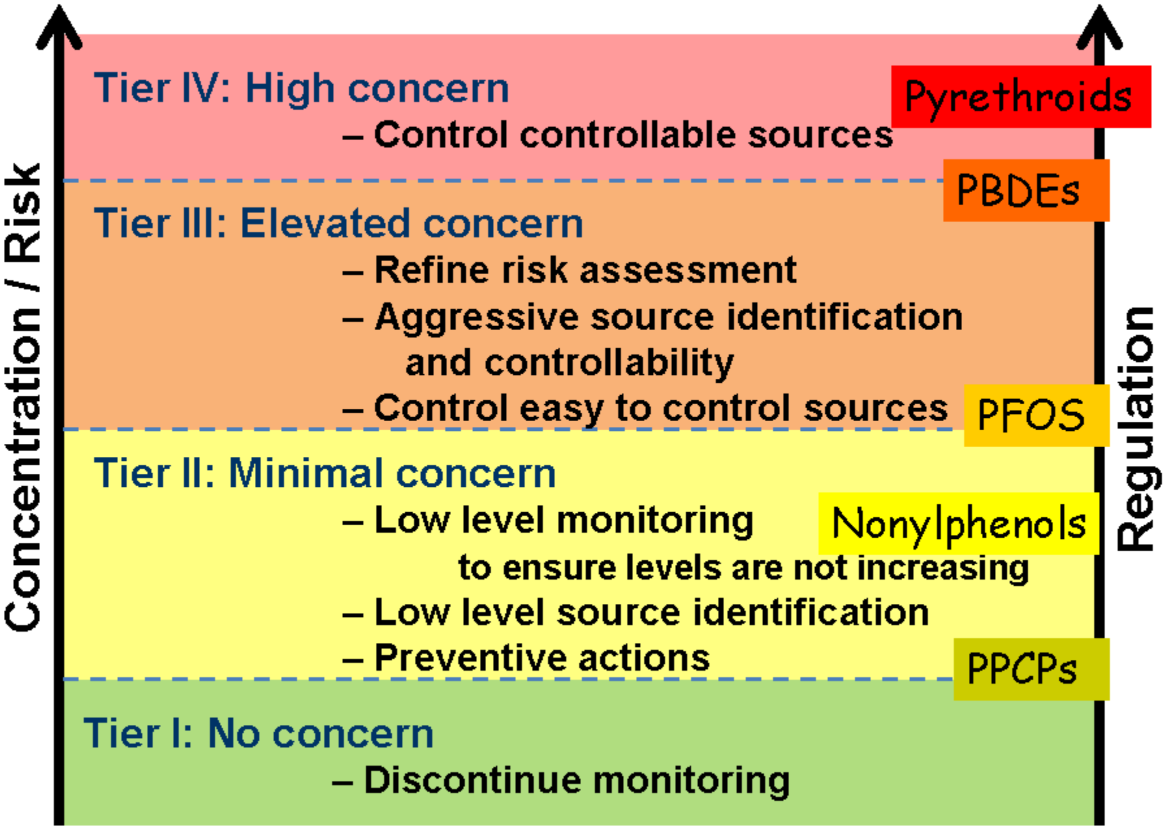

Figure 4.

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.