RMP October 2006 Update

REGIONAL MONITORING PROGRAM
FOR WATER QUALITY IN THE SAN FRANCISCO ESTUARY
A Cooperative Program Managed by the San Francisco Estuary Institute

INSIDE THIS UPDATE

Double-crested Cormorants as Sentinels of Bay Contamination

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Many contaminants of concern in the Bay, including mercury, PCBs, polybrominated diphenyl ethers (PBDEs), and others, reach their highest concentrations at the top of the food web. Consequently, fish-eating wildlife such as seals and seabirds face the greatest health risks from these chemicals. The high concentrations that accumulate in these species also make them valuable sentinels of the ecosystem, both for assessing trends in pollutants that are persistent in the environment and for early detection of pollutants of emerging concern.

Avian egg monitoring has proven to be a highly effective tool for assessment of long-term trends in persistent, bioaccumulative contaminants in aquatic ecosystems around the globe. The RMP has recently completed a pilot study examining the value of Double-crested Cormorant eggs as an indicator of long-term trends and regional spatial patterns in contamination in the Bay. Cormorant eggs have been chosen as a potential RMP contaminant exposure indicator for several reasons: cormorants are year-round residents in the Bay; they eat Bay fish almost exclusively; they have been the subject of many contaminant studies in the Bay and elsewhere; their eggs are easy to collect at several Bay locations; the colonies and eggs are reliably present; and they are known to accumulate a variety of contaminants.

Figure 1. Cormorant egg sampling locations (brown triangles) in San Francisco Bay, 2002 and 2004.

Double-crested Cormorants are a native bird species in San Francisco Bay commonly seen on pier pilings, utility towers, and other structures around the Bay. When not foraging, cormorants are often seen with their black wings spread out, drying their feathers in the sun and wind. Cormorants primarily consume Bay fish and therefore are highly exposed to contaminants that accumulate in these fish. Cormorants also forage over ranges of several miles and therefore integrate contamination on a regional scale.

Sampling of a broad suite of persistent, bioaccumulative contaminants in eggs of the Double-crested Cormorant was completed in 2002 and 2004. Eggs were collected from three locations in the Bay (Wheeler Island, Richmond Bridge, and the Don Edwards National Wildlife Refuge) and analyzed for mercury, selenium, PCBs, PBDEs, dioxins, legacy pesticides, and several other contaminants of emerging concern (**Figure 1**). This pilot study builds on previous cormorant contaminant monitoring completed by the CISNET study. With the CISNET study, there are now five years of data for certain contaminants for the Richmond Bridge site.

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Steps Towards Improved Monitoring of Pyrethroid Insecticides

By Sarah Lowe, (sarahl@sfei.org)

SFEI/PRISM Workshop on Pyrethroids

In May, the RMP and PRISM (Pesticide Research and Identification of Source and Mitigation) sponsored the first of a series of special topic workshops: "Pyrethroid Insecticides – Facing Up to the Challenges in Pyrethroids Methods Development and Field Monitoring". The goal was to provide a forum for toxicologists and chemists who are investigating pyrethroid detection and effects in the environment to meet and discuss findings, methods, and processes. Prominent researchers from the San Francisco Bay Area, other parts of California, and Canada presented their latest work on chemical and toxicological laboratory and field monitoring studies. The meeting was well attended and discussions ensued on detailed topics including: how best to measure pyrethroids; developing laboratory tests that

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Cormorants

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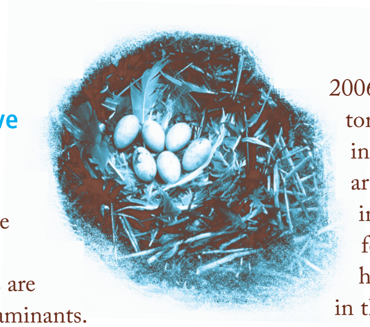

Early Life Stages Sensitive to Many Contaminants

Egg monitoring also provides a tool for evaluating the potential for toxic effects in water birds. Early life stages are most sensitive to many contaminants. For example, mercury, a neurotoxin, has been linked with mental impairment, impaired coordination, and other developmental abnormalities in human children (US EPA, 1997). As in humans, earlier, developmental avian life stages are at greater risk to effects from contaminants. Contaminants are passed from female birds into eggs. By measuring contaminant levels in bird eggs we can determine both exposure (in order to measure differences across space and through time) and potential for effects (both at the individual and potentially the population level). Laboratory and field studies have yielded 'effects thresholds' for some contaminants and species. Effects thresholds are the lowest contaminant level at which effects have been observed. Bird eggs collected from the Bay can be compared to effects thresholds to determine if environmental contaminant concentrations are at levels that are potentially detrimental.

PCBs and Mercury in Cormorant Eggs

Two contaminants of particular concern in Bay wildlife are PCBs and mercury. These legacy contaminants are persistent in the sediments and waters of the Bay, accumulate in the food web, and pose risks to sensitive life stages of Bay wildlife.

There were geographic differences in egg concentrations of PCBs and mercury. Egg PCB concentrations were statistically significantly higher at the Richmond Bridge site than at the Don Edwards site. Higher PCB concentrations at the Richmond Bridge site might be expected due to its proximity to urban and industrial land uses, especially the Richmond Harbor area, a known PCB hotspot (SFBRWQCB, 2004). Urban runoff and in-Bay PCB hotspots are two of the main pathways for entry of PCBs into the Bay food web (SFBRWQCB, 2004; Davis et al. 2006). PCBs historically deposited in Bay sediments are also a continuing source to the food web, and historic deposits in the Richmond Bridge area may be contributing to the PCBs found in cormorant eggs.

Egg mercury concentrations also showed some geographic differences across the Bay. Mercury concentrations at the Don Edwards site were statistically significantly higher than egg concentrations at the Richmond Bridge site. Mercury concentrations may be higher at the Don Edwards site due to the proximity to a known mercury source – the historic New Almaden mercury mine is located in the watershed of the Guadalupe River. The Guadalupe River drains into Alviso Slough, which is adjacent to the Don Edwards salt ponds. Birds foraging in the lower South Bay appear to be exposed to higher mercury levels in their prey and are passing this mercury into their eggs. Other studies have also found relatively high concentrations of mercury in the South Bay food web. Schwarzbach and Adelsbach (2003) documented high mercury concentrations in eggs of other fish eating birds (Forster's and Caspian Terns) in this region.

Trends in egg PCB and mercury concentrations over time have not yet been established. Additional sampling in the future will be required to discern temporal trends. However, the sampling performed in 2002 and 2004 has established an excellent foundation for future comparison.

The concentrations of PCBs and mercury observed in this study may be high enough to have adverse impacts on cormorant embryos. PCB concentrations of some samples exceeded the lowest observed effects level. Forty percent of the Richmond Bridge samples exceeded the lower range of the effects threshold (**Figure 2**). This indicates that PCB concentrations in cormorant eggs are at levels that could be having effects on embryos such as mortality and beak deformity. Mercury concentrations in the South Bay are also at levels of potential concern for effects on cormorant reproduction. Three out of the four Don Edwards samples exceeded the lowest observed effects threshold (**Figure 3**). All other samples were below the effects threshold. Cormorants are relatively insensitive to mercury in their eggs, so whether or not these concentrations would elicit effects in this species is unclear.

PBDEs: Are Concentrations Increasing?

Emerging contaminants of concern were also found in cormorant eggs. PBDEs are a class of contaminants of growing concern to Bay managers due to increasing concentrations in Bay wildlife and humans. PBDEs are chemicals that are used as flame retardants in a number of commercial products such as electronic equipment and furniture. Forster's Tern eggs collected from south San Francisco Bay in 2002 and 2003 had the highest PBDE concentrations ever reported for any species worldwide, suggesting that the Bay and its watershed may have large reservoirs of this contaminant (She et al., 2004). A ban on the use of two of the commercial flame retardant mixes (the more bioaccumulative mixtures of chemicals) took effect in California in June 2006. Food web monitoring will be essential to tracking the effectiveness of the ban in reducing environmental concentrations of PBDEs. The RMP is gathering data on the occurrence of PBDEs in the water, sediment, and food web of the Bay.

Unexpectedly, PBDE concentrations at the Wheeler Island site were higher than both the Richmond Bridge and Don Edwards site for 2002 samples (**Figure 4**). The Wheeler Island colony is in the least urbanized of the three regions sampled, far from the primary suspected sources of PBDEs (wastewater effluent and urban runoff). Mean concentrations in 2002 at Wheeler Island were more than two times higher than the Richmond Bridge mean and almost five times higher than the Don Edwards mean. This suggests a PBDE source near Suisun Bay, either a local source such as a landfill or wastewater effluent, or transport from Central Valley sources into Suisun Bay via Delta outflow.

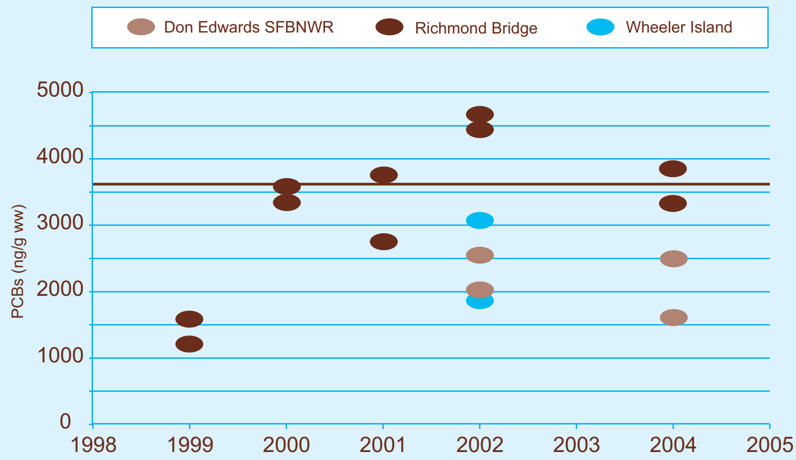

Figure 2. PCB concentrations (ng/g wet weight) in cormorant eggs from San Francisco Bay, 1999-2004. Brown line indicates the lowest effects threshold (3600 ng/g ww).

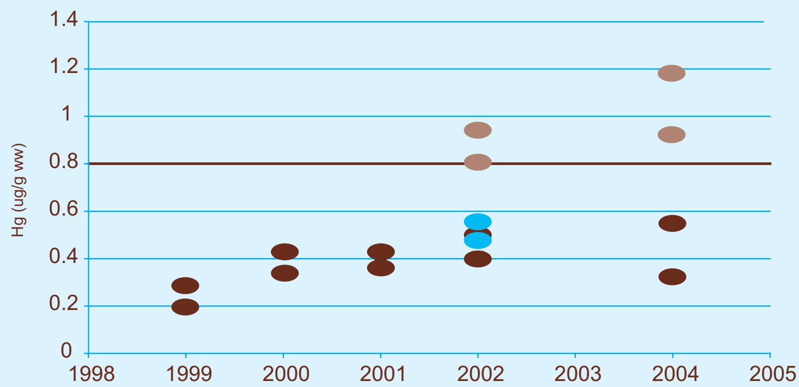

Figure 3. Mercury concentrations (mg/kg wet weight) in cormorant eggs from San Francisco Bay, 1999-2004. Brown line indicates the lowest effects threshold (0.8 mg/kg ww).

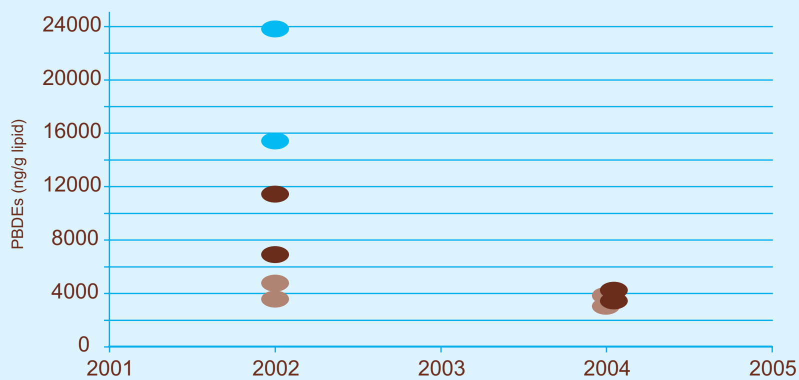

Figure 4. PBDE concentrations (ng/g lipid weight) in cormorant eggs from San Francisco Bay, 2002-2004.

Longer-term trend analysis is not possible since full PBDE analyses were only completed in 2002 and 2004. However, PBDE concentrations at the Richmond Bridge site in 2004 appear to be lower than concentrations measured in 2002. This is an interesting and somewhat surprising finding since PBDE concentrations generally appear to be on the increase worldwide (Hites 2004). A longer time series is needed to place this observation in proper context.

Other Contaminants

Legacy pesticides, selenium, and dioxins were also analyzed in cormorant eggs. DDT concentrations at Wheeler Island appeared to be relatively higher than the other two sites (not enough data to determine statistical significance). The observation of relatively high concentrations in this region is consistent with its proximity to inputs to the Bay from the Central Valley, a vast agricultural area with an historical use of DDT (Connor et al. 2004). One Wheeler Island sample exceeded the low end of the effects threshold range for DDTs. For selenium, statistical spatial differences were not observed between the sites and all samples were below the effects threshold for this contaminant. There were statistically significant spatial differences for dioxins with egg concentrations at Richmond Bridge higher than concentrations at Don Edwards. Dioxins are more associated with urban and industrial environments, therefore higher concentrations at Richmond Bridge might be expected.

Are Cormorants Good Indicators of Bay Contamination?

The RMP is presently considering whether to include monitoring of cormorant eggs as a component of long-term monitoring of pollutants in the Bay. Double-crested Cormorant eggs provide a valuable integrative index of contamination over time and space. Continued cormorant egg monitoring would primarily answer questions related to long-term trends and regional spatial patterns in contaminants on both legacy and emerging contaminants. Eggs of fish-eating birds are a powerful trend monitoring tool that would provide a valuable complement to RMP monitoring of bioaccumulative pollutants in bivalves and sport fish. In addition to trend analysis, cormorant egg monitoring would provide information on ecological risks posed by bioaccumulative pollutants.

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What are Pyrethroids?

Pyrethroids are a group of man-made pesticides similar to the natural pesticide pyrethrin, which is derived from dried chrysanthemum flowers. Synthetic pyrethroids were designed to be more toxic and persistent in the environment than their natural derivative. They are often formulated with chemical synergists which increase their potency by compromising an insect's ability to detoxify the pesticide. Pyrethroids are used in agricultural applications, public health (mosquito management), and in residential settings including: termite control in buildings, household insecticides, and pet shampoos.

Are Pyrethroids Toxic?

Pyrethroids can persist in sub-surface soil and in submerged sediments and are extremely toxic to aquatic organisms, including fish, at concentrations at or below the current methods of detection in environmental sediment and water samples. Pyrethroids are neurotoxins acting on the nervous systems of insects and non-target organisms such as fish by interacting with sodium channels (WHO 1990).

Pyrethroid Use in California

While peak tonnage of agricultural application of pyrethroids in California occurred in 1993, newer pyrethroid insecticide formulations contain compounds which may be up to 20 times more toxic than the pyrethroids (i.e., permethrin) used in the early 1990s (Amweg et al. 2006) (Figure 1). When the toxicity of these new pyrethroids are measured in terms of the relative toxicity of permethrin equivalents, agricultural pyrethroid application in California actually increased, between 2001 and 2002 by 58% and is continuing to increase. Statewide use of pyrethroids by professional applicators has increased over the past decade, particularly for non-agricultural uses, such as structural pest control and professional landscaping.

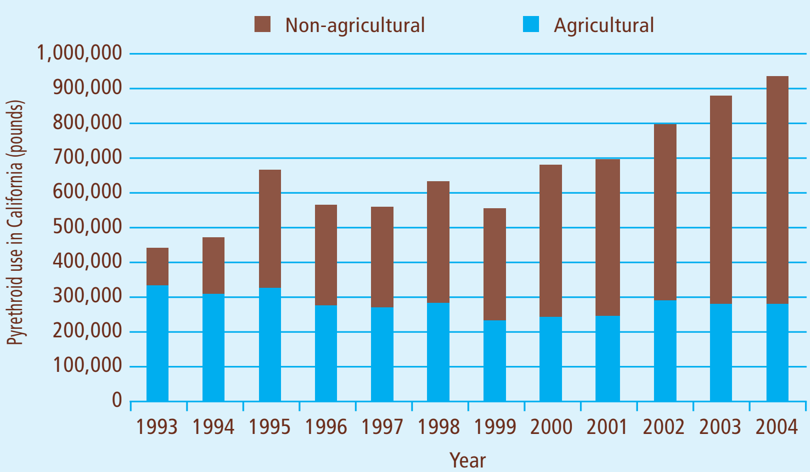

Figure 1. *Statewide use of pyrethroids by professional applicators has increased over the past decade, particularly for non-agricultural uses, such as structural pest control and professional landscaping. (Data are from the Pesticide Use Reporting database of the California Department of Pesticide Regulation and do not include retail sales. Data compiled by Don Weston of UC Berkeley. See http://www.sfei.org/rmp/pulse/2006/ThePulse2006_LowRes-Screen.pdf for complete article on pyrethroids.)*

Pyrethroid Insecticides

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pinpoint toxicity of test organisms to a particular contaminant or type of contaminant including pyrethroids; the need for lower detection limits as toxicologists are finding that many aquatic organisms are extremely sensitive to some pyrethroids; the importance of screening ambient samples for a comprehensive analyte list which includes the 13 pyrethroid pesticides now in use and common synergists; and the importance of investigating sub-lethal, behavioral, and biochemical effects in aquatic organisms.

The group also identified data gaps including: threshold concentrations at which effects are seen in estuarine toxicity test species; the influence of ambient temperatures on the potential for pyrethroid toxicity (as laboratory test protocols use standard temperatures, e.g., 23°C, and some pyrethroids are more toxic at lower temperatures); sources of pyrethroids to the Bay; and sub-lethal effects which are extremely important in evaluating long-term health of the ecosystem.

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For more information on the Workshop and to view the agenda, meeting notes, and PowerPoint presentations please go to: http://www.sfei.org/rmp/presentations/2006_PyrethroidsWorkshop/index.html

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