Studies Relating Pesticide Concentrations to Potential Effects on Aquatic Organisms in the San Francisco Bay-Estuary, California

by Kathryn M. Kuivila

Published in U.S. Geological Survey Toxic Substances Hydrology Program--Proceedings of the Technical Meeting, Charleston, South Carolina, March 8-12, 1999, v. 2. Contamination of hydrologic Systems and Related Ecosystems, 1999, U.S. Geological Survey Water-Resources Investigations Report 99-4018 B.

ABSTRACT

A variety of pesticides are applied in large quantities to agricultural and urban areas in the Central Valley of California and are transported into the San Francisco Bay-Estuary dissolved in water and associated with suspended sediments. These pesticides can have deleterious effects on aquatic organisms. Three studies that relate pesticide concentrations to potential effects on aquatic organisms are currently underway by the U.S. Geological Survey's San Francisco Bay-Estuary Toxic Substances Hydrology Project. These studies are (1) measuring the impacts of herbicides on phytoplankton primary production, (2) determining the exposure of Delta smelt to dissolved pesticides, and (3) assessing the effects of pesticides on the Asian clam, *Potamocorbula amurensis*.

INTRODUCTION

Large quantities of various pesticides are applied to agricultural and urban areas in the Central Valley of California that drain into the Sacramento-San Joaquin Delta (Delta) and then San Francisco Bay. Together, the Delta and San Francisco Bay are known as the San Francisco Bay-Estuary (Estuary). Several monitoring studies have measured elevated concentrations of dissolved pesticides in the Sacramento and San Joaquin Rivers, upstream of the Estuary (fig. 1) (MacCoy and others, 1995; Domagalski, 1996; Panshin and others, 1998). Fewer measurements of dissolved pesticides have been made in the Sacramento-San Joaquin Delta or farther downstream in the Estuary (fig. 1) (Kuivila and Foe, 1995; Kuivila and others, 1999). Pesticides also are transported into the rivers and Estuary associated with suspended sediments, but little is known about the concentrations and residence times of these pesticides (Domagalski and Kuivila, 1993; Bergamaschi and others, 1999; Bergamaschi and others, in press).

Once in the aquatic environment, pesticides can have deleterious effects on aquatic organisms; controlling factors include the concentration, exposure time, and bioavailability of the pesticide of concern. When assessing a biological effect, it is important to use the appropriate endpoint or indicator. Endpoints reflect responses at various levels—physiological, whole organism, population, and community. Field and laboratory studies can be used to assess effects of pesticides on aquatic organisms. Field studies take into account the complexity of the ecosystem, but that complexity makes it difficult to assign a single cause to an observed effect. In contrast, direct cause and effect are more easily shown in laboratory studies, but at the expense of oversimplifying the interrelations in the ecosystem. A combination of field and laboratory studies usually provides the most powerful approach.

The purpose of this report is to summarize continuing studies by the U.S. Geological Survey's (USGS) San Francisco Bay-Estuary Toxic Substances Hydrology Project (S.F. Bay Toxics Project) that relate measured pesticide concentrations to observed biological effects in the Estuary. These studies are (1) measuring the effect of herbicides on primary productivity and species composition of phytoplankton in the Sacramento-San Joaquin Delta; (2) determining the exposure of Delta smelt to dissolved pesticides during spawning and larval stages; and (3) assessing the effect of pesticides on the Asian clam, *Potamocorbula amurensis* (*P. amurensis*), in field and laboratory studies.

HERBICIDES AND PHYTOPLANKTON

Half a million pounds of more than 30 different herbicides are applied on agricultural lands each year in the Delta and an additional 5 million pounds are applied upstream in other watersheds (California Department of Pesticide Regulation, 1996). Some of these herbicides are designed to kill plants by inhibiting photosynthesis. However, little is actually known about the effects of herbicides on primary productivity and species composition of phytoplankton in aquatic environments (Schneider and others, 1995).

A USGS study is evaluating the impairment of phytoplankton primary productivity in the Delta due to herbicides. The project is part of the S.F. Bay Toxics Project and is cooperatively funded by the Interagency Ecological Program for the Sacramento-San Joaquin Estuary (IEP). Herbicide concentrations and phytoplankton primary production rates (P_{max}) were measured concurrently in 53 Delta water samples from May through November 1997. The concentrations and possible sources of the herbicides are summarized in Kuivila and others (1999) and the results of the primary productivity measurements are discussed in Edmunds and others (1999). It is known that the concentration of an herbicide must exceed some minimum level before there is an "observable effect" on the phytoplankton's rate of photosynthesis. Although the herbicide concentrations in the Delta usually were less than a lowest observable effect concentration (LOEC), the lowest P_{max} measured during the study was observed in the one sample with an herbicide concentration that exceeded a LOEC (Edmunds and others, 1999). This sample from French Camp Slough on November 11 had a diuron concentration of 2,141 nanograms per liter. No correlation was found between measured values of P_{max} and herbicide concentrations in the other 52 samples. In these instances, measured herbicide concentrations were less than published LOECs.

Edmunds and others (1999) conclude that the study results do not indicate system-level impairment of primary production in the Delta, but caution that there are localized events when production is impaired. Of the herbicides that inhibit photosynthesis, diuron and hexazinone had the highest concentrations and most frequent detections; more sampling is needed to determine if these two herbicides frequently occur at concentrations high enough to impair primary production. The limited number of samples in this study made it difficult to determine the sources of diuron and hexazinone, and to predict herbicide concentrations.

Species composition also was measured in the study but the data analysis has not been completed. The sensitivity of different species of phytoplankton to herbicides can vary by as much as one or two orders of magnitude (Hollister and Walsh, 1973; Rand, 1995; Sabater and Carrasco, 1996, 1998; Peterson and others, 1997). This variability of response could influence species composition, allowing less sensitive species to dominate in locations and times of high herbicide concentrations. This shift in species composition could have an effect up the food chain because the phytoplankton species vary in their caloric value to higher trophic levels (Peterson and others, 1997).

EXPOSURE OF DELTA SMELT TO DISSOLVED PESTICIDES

Delta smelt are a threatened species in the Estuary. While the decline of some fish species have been attributed to factors such as low Delta outflow or number of spawners, the decline of Delta smelt cannot be explained by these factors (Bennett and Moyle, 1996; Kimmerer, 1998; Nobriga, 1998). Therefore, various other explanations for the decline of the Delta smelt are being explored, including chronic effects from exposure to dissolved pesticides.

A 2-year study (October 1998 – September 1999) in collaboration with California Department of Fish and Game (CDFG) is measuring the exposure of Delta smelt to dissolved pesticides during vulnerable egg and larval stages. The project was funded by the IEP and the USGS as part of the S.F. Bay Toxics Project. Sampling for dissolved pesticides was coordinated with

CDFG's Delta-smelt surveys to concurrently determine pesticide concentrations and Delta smelt larval abundance.

Delta smelt spawn in early spring and one primary spawning ground is the northwestern part of the Delta (Cache, Lindsey, and Prospect Sloughs) (fig. 1). During some years, the Delta smelt also spawn closer to the central Delta. Very little data are available on concentrations of pesticides in the Delta during this time of year, but rice pesticides (molinate, thiobencarb, and carbofuran) have been detected in the Delta and at upstream sites (Domagalski and Kuivila, 1991; Crepeau and others, 1994; K.M. Kuivila, U.S. Geological Survey, unpublished data, 1997). During the spawning period (typically April-June), water samples for dissolved pesticide analyses are collected weekly at sites in the northwestern Delta and less frequently at central Delta sites concurrently sampled by CDFG.

About 1 month after spawning, Delta smelt larvae become motile and move into Suisun Bay. Larval fish sampling in Suisun Bay shows a distinct peak of larval Delta smelt at 2 parts per thousand (ppt) salinity, with considerably fewer larvae at higher and lower salinities. Water samples are being collected every 1-2 days at a site in Suisun Bay at approximately 2 ppt salinity during the ebb tide in the summer.

Related studies are being conducted by the University of California at Davis (U.C. Davis) to look at different indicators of contaminant effects on Delta smelt, including growth rates, histopathology, and DNA strand breaks (William Bennett, Swee Teh, and Susan Anderson, University of California at Davis, written commun., 1998). Recently, Delta smelt have been cultured in the laboratory which will allow for future laboratory studies of the direct effects of dissolved pesticides on Delta smelt.

BIOACCUMULATION AND STRESSES ON THE ASIAN CLAM

Contaminant effects on the Asian clam, *P. amurensis*, are being assessed in continuing studies by the USGS (Brown and others, 1999). The long-term field study measures bioaccumulation of trace elements, concurrent population biology, and physiological indicators of stress. Enzymatic, histopathologic, and biochemical biomarkers in these populations of *P. amurensis* are being studied by U.C. Davis to compare the biomarkers with the trends in contaminants (S.L. Clark, University of California at Davis, and C.L. Brown, U.S. Geological Survey, oral commun., 1998).

In contrast, very little data are available on the concentrations of organic compounds, especially pesticides, in *P. amurensis* in the Estuary. Recent studies in the Estuary (Domagalski and Kuivila, 1993; Pereira and others, 1996; Bergamaschi and others, 1999, in press) have shown elevated concentrations of some pesticides associated with suspended sediments. These results suggest that the potential exists for bioaccumulation in the filter-feeding *P. amurensis*. A 3-year study (October 1998 – September 2001), funded by the USGS Integrated Natural Resource Program, will measure bioaccumulation of a variety of organic compounds in *P. amurensis*. One site in Suisun Bay will be sampled monthly and several synoptic samplings will be done. The wide variety of pesticides used in the Central Valley will be measured in the clam tissues, in addition to typically-analyzed compounds such as polychlorinated biphenyls, polyaromatic hydrocarbons, and organochlorine pesticides.

Laboratory experiments exposing *P. amurensis* to a variety of contaminants under different conditions is another study by the S.F. Bay Toxics Project. For example, clams from populations with different toxicant-exposure histories will be exposed singly and then concurrently to low salinity and various dissolved pesticides to assess direct effects on respiration and glycogen concentration. Studies are continuing to determine the interactive effects between metals and dissolved pesticides on *P. amurensis* (Luoma, 1999). Finally, a related laboratory study is being proposed in collaboration with U.C. Davis to examine the effects of dissolved pesticides on early development of *P. amurensis*.

REFERENCES

Bennett, W.A., and Moyle, P.B., 1996, Where have all the fishes gone? Interactive factors producing fish declines in the Sacramento-San Joaquin estuary, *in* Hollibaugh, J.T., ed., San Francisco Bay—The Ecosystem: San Francisco, American Association for the Advancement of Science, p. 519-542.

Bergamaschi, B.A., Baston, D.S., Crepeau, K.L., and Kuivila, K.M., in press, Determination of pesticides associated with suspended sediments in the San Joaquin River, California, USA, using gas chromatography-ion trap mass spectrometry: Toxicological and Environmental Chemistry.

Bergamaschi, B.A. Kuivila, K.M., and Fram, M.S., 1999, Pesticides associated with suspended sediments in the San Francisco Bay during the first flush, December 1995, *in* Morganwalp, D.W., and Buxton, H.T., eds., U.S. Geological Survey Toxic Substances Hydrology Program—Proceedings of the Technical Meeting, Charleston, South Carolina, March 8-12, 1999—Volume 2—Contamination of Hydrologic Systems and Related Ecosystems: U.S. Geological Survey Water-Resources Investigations Report 99-4018B, this volume.

Brown, C.L., Parchaso, F., Thompson, J.K., and Luoma, S., 1999, Metal trends and effects in *Potamocorbula amurensis* in North San Francisco Bay, *in* Morganwalp, D.W., and Buxton, H.T., eds., U.S. Geological Survey Toxic Substances Hydrology Program—Proceedings of the Technical Meeting, Charleston, South Carolina, March 8-12, 1999—Volume 2—Contamination of Hydrologic Systems and Related Ecosystems: U.S. Geological Survey Water-Resources Investigations Report 99-4018B, this volume.

California Department of Pesticide Regulation, 1996, Pesticide use data for 1995 [digital data]: Sacramento, California Department of Pesticide Regulation.

Crepeau, K.L., Kuivila, K.M., and Domagalski, J.L., 1994, Concentrations of dissolved rice pesticides in the Colusa Basin Drain and Sacramento River, California, *in* Morganwalp, D.W., and Aronson, D.A., eds., U.S. Geological Survey Toxic Substances Hydrology Program–Proceedings of the Technical Meeting, Colorado Springs, Colorado, September 20-24, 1993: U.S. Geological Survey Water-Resources Investigations Report 94-4015, vol. 2, p. 711-718.

Domagalski, J., 1996, Pesticides and pesticide degradation products in stormwater runoff—Sacramento River Basin, California: Journal of the American Water Resources Association, vol. 32, p. 953-964.

Domagalski, J.L. and Kuivila, K.M., 1991, Transport and transformation of dissolved rice pesticides in the Sacramento River Delta, California, *in* Mallard, G.E., and Aronson, D.A., eds., U.S. Geological Survey Toxic Substances Hydrology Program–Proceedings of the Technical Meeting, Monterey, California, March 11-15, 1991: U.S. Geological Survey Water-Resources Investigations Report 91-4034, p. 664-666.

______1993, Distributions of pesticides and organic contaminants between water and suspended sediment, San Francisco Bay, California: Estuaries, v. 16, no. 3A, p. 416-426.

Edmunds, J., Kuivila, K.M., Cole, B. and Cloern, J.E., 1999, Do herbicides Impair Phytoplankton Primary Production in the Sacramento-San Joaquin River Delta? *in* Morganwalp, D.W., and Buxton, H.T., eds., U.S. Geological Survey Toxic Substances Hydrology Program—Proceedings of the Technical Meeting, Charleston, South Carolina, March 8-12, 1999—Volume 2—Contamination of Hydrologic Systems and Related Ecosystems: U.S. Geological Survey Water-Resources Investigations Report 99-4018B, this volume.

Hollister, T.A. and Walsh, G.E., 1973, Differential response of marine phytoplankton to herbicides—oxygen evolution: Bulletin of Environmental Contamination and Toxicology, vol. 9, no. 5, p. 291-295.

Kimmerer, W., 1998, A summary of the current state of the X2 relationships: Interagency Ecological Program for the Sacramento-San Joaquin Estuary Newsletter, vol. 11, no. 4, p. 14-25.

Kuivila, K.M., Barnett, H.D., and Edmunds, J., 1999, Herbicide concentrations in the Sacramento-San Joaquin River Delta, California, *in* Morganwalp, D.W., and Buxton, H.T., eds., U.S. Geological Survey Toxic Substances Hydrology Program—Proceedings of the Technical Meeting, Charleston, South Carolina, March 8-12, 1999—Volume 2—Contamination of Hydrologic Systems and Related Ecosystems: U.S. Geological Survey Water-Resources Investigations Report 99-4018B, this volume.

Kuivila, K.M. and Foe, C.G., 1995, Concentrations, transport, and biological effects of dormant spray pesticides in the San Francisco Estuary, California: Environmental Toxicology and Chemistry, v. 14, no. 7, p. 1141-1150.

Luoma, S.N., 1999, Emerging contaminant issues from an ecological perspective, *in* Morganwalp, D.W., and Buxton, H.T., eds., U.S. Geological Survey Toxic Substances Hydrology Program—Proceedings of the Technical Meeting, Charleston, South Carolina, March 8-12, 1999—Volume 2—Contamination of Hydrologic Systems and Related Ecosystems: U.S. Geological Survey Water-Resources Investigations Report 99-4018B, this volume.

MacCoy, D., Crepeau, K.L., and Kuivila, K.M., 1995, Dissolved pesticide data for the San Joaquin River at Vernalis and the Sacramento River at Sacramento, California, 1991-1994: U.S. Geological Survey Open-File Report 95-110, 27 p.

Nobriga, M., 1998, Evidence of food limitation in larval Delta smelt: Interagency Ecological Program for the Sacramento-San Joaquin Estuary Newsletter, vol. 11, no. 1, p. 20-24.

Panshin, S.Y., Dubrovsky, N.M., Gronberg, J.M., and Domagalski, J.L., 1998, Occurrence and distribution of dissolved pesticides in the San Joaquin River Basin, California: U.S. Geological Survey Water-Resources Investigations Report 98-4032, 88 p.

Pereira, W.E., Domagalski, J.L., Hostettler, F.D., Brown, L.R., and Rapp, J.B., 1996, Occurrence and accumulation of pesticides and organic contaminants in river sediment, water, and clam tissues from the San Joaquin River and tributaries, California: Environmental Toxicology and Chemistry, vol. 15, p. 172-180.

Peterson, H.G., Boutin, C., Freemark, K.E., and Martine, P.A., 1997, Toxicity of hexazinone and diquat to green algae, diatoms, cyanobacteria, and duckweed: Aquatic Toxicology, vol. 39, p. 111-134.

Rand, G.M., ed., 1995, Fundamentals of aquatic toxicology—Effects, environmental fate, and risk assessment: Washington, D.C., Taylor and Francis Publishers, 1125 p.

Sabater, C., and Carrasco, J.M., 1996, Effects of thiobencarb on the growth of three species of phytoplankton: Bulletin of Environmental Contamination and Toxicology, vol. 56, p. 977-984.

______1998, Effects of molinate on the growth of five freshwater species of phytoplankton: Bulletin of Environmental Contamination and Toxicology, vol. 61, p. 534-540.

Schneider J., Morin, A., and Pick, F.R., 1995, The response of biota in experimental stream channels to a 24-hours exposure to the herbicide Velpar L: Environmental Toxicology and Chemistry, vol. 14, no. 9, p. 1607-1613.

AUTHOR INFORMATION

Kathryn M. Kuivila, U.S. Geological Survey, Sacramento, California