Developing a Reliable Program to Monitor Water Quality Impacts of Aquatic Pesticides

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July 13, 2004

In June 2004 the California State Water Resources Control Board (SWRCB) adopted a National Pollutant Discharge and Elimination System (NPDES) statewide general permit for application of aquatic pesticides, without specific details on the required water quality monitoring that should be conducted to evaluate whether the pesticide/herbicide used, either alone or in combination with other chemicals in the water, is adverse to non-target organisms outside the zone of application. Justification for a comprehensive water quality monitoring program associated with pesticide/herbicide applications for aquatic weed control arises from the fact that the US EPA Office of Pesticide Programs (OPP) and the California Department of Pesticide Regulation (DPR) registration of pesticides **does not** ensure the prevention of significant adverse impacts to non-target aquatic life. This situation means that it is necessary for the water quality regulatory agencies, such as the SWRCB and the Regional Water Quality Control Boards (RWQCBs) to establish the requirements for comprehensive water quality monitoring to ascertain the near-term and long-term impacts associated with the application of aquatic pesticides/herbicides to waterbodies.

For years chemicals have been added to waterbodies to control excessive growths of aquatic weeds, algae and other pests, without properly evaluating the impacts of these chemicals on the aquatic-life-related beneficial uses of the waterbody. The development of a comprehensive, credible water quality monitoring program is long overdue. While those responsible for aquatic weed control assert that comprehensive monitoring of the potential adverse impacts of the pesticide/herbicide application is costly compared to the funds that have been used in the past for such evaluations, the cost of such a program should be part of the cost associated with aquatic weed control.

As part of commenting on the preliminary draft, draft and revised draft NPDES permit associated with the application of pesticides/herbicides to waterbodies for aquatic weed and other pest control, Dr. Jones-Lee and I (Lee, 2003, 2004a,b; Lee and Jones-Lee, 2003, 2004) have provided detailed comments on the need for comprehensive water quality monitoring/evaluation. In our comments we have discussed the components of such a program that should be developed. A reliable program to properly evaluate the water quality impacts of pesticides/herbicides used for aquatic weed control requires chemical monitoring, aquatic life toxicity assessment and bioassessment, and for persistent chemicals, bioaccumulation monitoring. A summary of these monitoring/evaluation program components is presented below. For further information on monitoring associated with aquatic pesticide/herbicide impact evaluation, review Lee and Jones-Lee (2002a, 2003a).

Chemical Monitoring

The monitoring program should include comprehensive monitoring of the fate (transport) and persistence of the pesticide and any chemicals that are added with it that have the potential to be adverse to aquatic life. The purpose of this monitoring is to establish a concentration-duration of potential exposure relationship for the added pesticide and its associated chemicals within and near the area of application of the pesticide/herbicide. Data obtained from such a chemical monitoring program are compared to known critical concentrations (water quality standards) for the chemicals monitored. For most of the pesticides/herbicides used there are no water quality criteria against which the chemical concentration data obtained in monitoring can be compared, to determine if the application of the chemical and its associated chemicals violates a water quality standard (objective).

A potential approach that could be used to evaluate possible problems of aquatic life toxicity is to use the US EPA OPP pesticide registration database, which contains aquatic life toxicity data that were submitted by the registrant for several types of organisms (fish, zooplankton, algae, etc.). This database typically contains LC50 data for various periods of exposure. Since LC50 data results in the death of half of the organisms in the test system, there is need to interpret these data in light of concentrations that are not toxic to aquatic life. Typically, concentrations that are 10 to as much as 100 times less than the LC50 are indicative of chronic "safe" concentrations of chemicals. It is suggested that 0.05 times the LC50 for fish and zooplankton be used as a screening guideline for potential water quality problems.

As discussed in my comments on the preliminary draft, draft, and revised draft statewide general NPDES permit for application of aquatic pesticides/herbicides (Lee 2003; 2004a,b), concentrations of potentially toxic chemicals below the water quality standard (objective) or less than 0.05 times the LC50 for the most sensitive organisms tested in registering the pesticide can still, through additive or synergistic effects of the added pesticides with each other or with other chemicals in the water, cause adverse impacts to aquatic life. In order to begin to address these types of problems, it is necessary to conduct toxicity testing.

Chemical measurements should be made of the persistence of the pesticide/herbicide in the sediments in and near the zone of application. However, the evaluation of the water quality significance of such measurements must be done cautiously. Lee and Jones-Lee (2002b, 2003b) have discussed the unreliability of trying to interpret water quality impacts of sediment-associated constituents based on chemical concentrations of potential pollutants in the sediments. Of particular concern is the unreliability of trying to use co-occurrence-based so-called "sediment quality guidelines" to predict the toxicity of sediments. As discussed by Lee and Jones-Lee (2002b, 2003b), such an approach can, depending on the situation, overestimate or underestimate the water quality significance of a chemical constituent in sediments. A reliable approach for assessing whether a chemical measured in sediments is adverse to aquatic-life-related beneficial uses of the waterbody is to determine first whether the sediments are toxic, and then, through toxicity investigation evaluations (TIEs), the cause of this toxicity.

Since TIE procedures may not be available for all types of pesticides/herbicides, a standard additions approach, as described below, can be used to determine whether a measured concentration of a chemical in sediments is responsible for toxicity. An example of the need to use the standard addition approach to assess whether a pesticide is responsible for sediment toxicity occurs with the pyrethroid-based pesticides. At this time there are no reliable TIE procedures for this group of pesticides because of the strong sorption tendencies of this group of pesticides for aquatic sediment particles.

Using the standard additions approach, a sediment which has been found to contain pyrethroid-based pesticides or other chemicals for which there are no TIE procedures and which has also been found to be toxic to standard test organisms such as *Hyalella*, is subjected to a series of toxicity tests using increasing small amounts of the chemical of concern to determine if the toxicity increases proportional to the addition. Several small, incremental increases in the chemical should be used. From the relationship found, it is possible to extrapolate to zero-addition conditions, and thereby gain inference on whether the toxicity in the untreated sediments is likely due to the chemical of concern. Consideration should be given to the need to use similar times of equilibration between the added chemical and the sediments to properly simulate the conditions that occurred with the pesticide application to a particular waterbody.

Toxicity Testing

A fundamental component of a program to evaluate aquatic pesticide/herbicide impacts to non-target organisms is aquatic life toxicity testing using water column and sediment organisms. The US EPA (2000, 2002a,b,c) has developed several standardized toxicity tests that can be used for this purpose. The finding of toxicity outside of the zone of application using the standardized tests is a strong indication that there are potential adverse impacts to non-target organisms. However, as discussed below, there is need to provide an evaluation of the water quality significance of aquatic life toxicity testing results to evaluate whether the laboratory-based toxicity testing results are applicable to the conditions that exist in the receiving waters for pesticide application.

Water Quality Significance of Aquatic Life Toxicity. One of the issues that should be addressed is the water quality/beneficial use significance of aquatic life toxicity found in the water column or sediments following a pesticide application. From a regulatory/legal point of view, the finding of toxicity is a violation of the Central Valley Regional Water Quality Control Board's Basin Plan requirements of no toxics in toxic amounts. Therefore, such toxicity must be controlled. It is possible, however, that toxicity can occur to a restricted type of organism, such as some forms of zooplankton, that would not be significantly adverse to the beneficial uses of the waterbody as a result of the fact that the zooplankton that is particularly susceptible to a pesticide's toxicity may not be the only source of food for larval fish or other aquatic life.

Another issue of concern is the duration of toxicity testing compared to the concentration duration of exposure relationship that exists in the waterbody at or near the zone of application of the pesticide. The toxicity found within the zone of application could be sufficiently rapidly dissipated so that laboratory toxicity tests involving several days of exposure are not relevant to the field conditions. In order to demonstrate that the toxicity found (or projected, through chemical concentration data) is not significantly adverse to the beneficial uses of the waterbody, those who wish to use the chemical will need to conduct comprehensive studies in cooperation with the regulatory agencies.

The US EPA (1994), in its Water Quality Standards Handbook, provides guidance on how to adjust chemically based criteria for site-specific conditions. It is possible that regulatory agencies at the state and federal level would accept the site-specific adjustment of toxicity criteria for particular situations, although to my knowledge, this has never been done. It is certainly appropriate, however, since there will be situations where laboratory toxicity tests will yield toxic responses that are not reliable assessments of aquatic life toxicity under field conditions.

Bioassessment

Since aquatic life toxicity testing in the water column and in sediments is not sufficiently sensitive to detect chronic toxicity, which kills, impairs reproduction and/or impairs the ability of aquatic life to forage for food, avoid predation, find home stream waters, etc., it is necessary to conduct detailed bioassessments of organism assemblages just before, during, immediately after, and for a period of time after application of the aquatic pesticide/herbicide. As discussed in my comments on the permit, there is no need to find a suitable reference site against which to compare the data. The site itself, through before and after testing in the zone of application and in nearby areas that are not impacted by the pesticide application, provides a suitable reference against which to determine whether the water column organisms, as well as those in the sediments, have been impacted by the pesticide application.

The California Department of Fish and Game (Harrington and Born, 1999; DFG, 2003) and the US EPA (Barbour, et al., 1999) have reported on bioassessment methodology that can be used to assess whether chemical additions to waterbodies are adversely affecting the biological characteristics of the waterbody. Lee and Jones (1982) discussed how the Department of Interior Instream Flow Methodology, which includes bioassessment measurements relative to habitat characteristics, could be used to evaluate point-source discharge impacts on aquatic communities. This same approach can be used to evaluate the impact of chemical additions, such as aquatic pesticides/herbicides.

Secondary Impacts

In addition to the direct impacts of aquatic pesticide applications causing toxicity to non-target organisms, there is also the potential for secondary impacts associated with aquatic weed control. Of concern is the potential for the death and decay of aquatic weeds in waterbodies of limited water circulation (mixing) leading to regions where the dissolved oxygen will be depleted below the water quality objective. The depletion of DO, either alone or in combination with toxicants (such as the pesticide, other chemicals or ammonia released from the decay of aquatic plants) could be adverse to non-target organisms. These types of situations need to be evaluated as part of a reliable evaluation of aquatic pesticide application impacts.

Bioaccumulation

An issue that needs to be considered for chemicals that persist for a significant period of time (more than a few days to a few weeks) is the potential for bioaccumulation of the chemical or its transformation products in aquatic life, which can be adverse to the host organism or higher-trophic-level organisms through food web uptake. Excessive bioaccumulation of formerly used pesticides is one of the most significant problems facing water quality management today. As discussed by Lee and Jones-Lee (2002b), fish taken throughout the

Central Valley of California have excessive concentrations of the legacy organochlorine pesticides. Many fish have sufficient concentrations of these chemicals in their edible tissue so that consumption of the fish can be hazardous to the health of those who eat the fish.

Extrapolation of Monitoring Results

There has been discussion associated with the implementation of the NPDES aquatic pesticide permit about the possibility that the results of monitoring at one site could predict what would happen at other sites. While it is possible that such extrapolation can predict some adverse impacts, it does not necessarily predict all adverse impacts, because of the fact that each site of application will have a different mix of chemicals that can interact with the pesticide and its associated chemicals, which can cause aquatic life toxicity or other adverse impacts. Therefore, there is need for comprehensive monitoring of each of the areas where pesticide/herbicide application takes place in order to properly evaluate potential impacts on non-target organisms.

Adjustment of the Monitoring Program

Ultimately, through comprehensive studies of the type described herein, it will be possible to gain sufficient experience over several years in a variety of situations, so that the amount of monitoring that is necessary for particular chemicals in particular waterbodies can be significantly reduced. However, this point will only come after a substantial database has been obtained which demonstrates the lack of adverse impacts for a particular pesticide formulated in a particular way, applied in a particular manner to a particular waterbody. Ongoing testing is necessary, however, because of the potential for other chemicals to be added to the waterbody which were not there during the original testing and which, in themselves, are not toxic, but in combination with the pesticide, yield toxic conditions.

Need for Comprehensive Monitoring Program

While many of those who have been responsible for application of aquatic pesticides/herbicides claim that there is no need for a comprehensive monitoring program of water quality impacts associated with aquatic pesticide/herbicide application based on the supposition that since problems have not been found in the past, such a position is not technically valid. The basic problem with such claims is that, with few exceptions, the monitoring programs that have been conducted in the past, including those that have been conducted by the San Francisco Estuary Institute (SFEI, 2004) as part of the SWRCB evaluation of the potential impacts of aquatic pesticide/herbicide applications, have not adequately and reliably evaluated the full range of potential water quality beneficial use impacts associated with aquatic pesticide/herbicide application. Monitoring programs that fail to include a detailed analysis of pesticide and associated chemical fate/persistence, aquatic life toxicity testing for water column and sediment organisms, and bioassessment of aquatic organism assemblages within and near the zone of pesticide application, are deficient in properly evaluating the range of impacts that can occur.

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