Developing Water Quality Monitoring Programs Associated with the Use of Herbicides in the Control of Aquatic Weeds

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The California Statewide General NPDES Permit for Discharges of Aquatic Pesticides to Waters of the United States requires that the agency that is conducting an aquatic weed control program monitor the impacts of this program on the water-quality-related beneficial uses of the waterbodies that could be impacted by the control program. Of particular concern is the impact of the herbicides used for weed control on aquatic life toxicity, bioaccumulation of the herbicide chemical that represents a threat to higher trophic level organisms, as well as the impacts of the chemicals released from the decay of the killed vegetation such as oxygen demand and ammonia. Presented herein is guidance on the characteristics of the monitoring program that should be conducted as part of an aquatic weed control program.

Overall Approach

The overall approach that should guide the development of a water quality monitoring program has been presented by Lee and Jones-Lee (2002). They discuss a number of components of a technically valid water quality monitoring program. Each of the components of the monitoring program should be critically examined, including

- Clearly establish the objectives of the monitoring program.
- Understand the nature of "water quality," water quality concerns, beneficial uses, and their assessment for the waterbodies of concern.
- Select the parameters to be measured and justify potential significance of each parameter selected.
- Examine previous studies to understand variability in each area of the waterbody to be monitored.
- List factors that can influence results of the monitoring program and how they may influence the results.
- Determine the level of confidence at which the objective is to be achieved.
- For each area of each waterbody to be monitored, determine the number and location of samples to be collected.
- If no data are available from previous studies or if existing data are inadequate to define variability and other characteristics needed to establish a reliable monitoring program, conduct a pilot study of representative areas to define the characteristics of the area that are needed to develop a reliable water quality monitoring program.

- Select sampling techniques and methods of analysis to meet the objectives and level of confidence desired.
- Verify that analytical methods are appropriate for each area of the waterbody, with particular reference to the time of aquatic weed control program implementation.
- Conduct studies to evaluate precision of sampling and analytical procedures and technique, reliability of preservation, and variability of the system.
- Critically examine the relationship between present and past studies.
- Determine how the data will be analyzed, with respect to compliance with water quality standards, using existing data or synthetic data that are expected to be representative of the site.
- Screen/evaluate data as they are collected.
- Analyze, interpret and store data, and report on the results of the analysis and interpretation.

Aquatic Life Toxicity

One of the issues of primary concern in the use of herbicides for aquatic weed control is the toxicity of the herbicide and its associated chemicals to non-target organisms. A common error made by those who conduct aquatic weed control programs is the assumption that the application of a US EPA Office of Pesticide Programs (OPP) registered herbicide for aquatic weed control in accordance with the label restrictions will not cause adverse impacts to other aquatic life. US EPA OPP registration of a herbicide and its use in accordance with the label does not mean that there will be no adverse impacts to other forms of aquatic life. The US EPA OPP allows a significantly different degree of protection of non-target aquatic life than the Clean Water Act. The Clean Water Act dictates that there shall be no toxicity, while the US EPA OPP allows toxicity if it is not “significant,” and the evaluation of significance can include economic considerations and other factors.

Further, the US EPA OPP does not necessarily include the interaction of other chemicals used with the herbicide such as surfactants, colorants as well as other chemicals that may be in the water being treated. The interaction of the herbicide with other chemicals can cause additive and synergistic effects which can enhance toxicity to non-target organisms. While it is impossible to predict or even measure all potential problems of this type, a reasonable effort should be made to screen for these types of problems, through conducting a comprehensive water quality monitoring program associated with the aquatic weed control program.

Further, the weed control program should be conducted in phases, so that an evaluation can be made of potential impacts discerned by the monitoring program during the early phases, and appropriate adjustments can be made in further control efforts. Since mechanical and other means of controlling aquatic weeds also will have adverse impacts on water quality/beneficial uses, it will be important to monitor their impacts, as well.

In addition to testing the water column for aquatic life toxicity, there is also need to conduct toxicity tests on the sediments, especially for those herbicides that tend to become strongly attached to sediment particles. Pesticides that have been characterized as being strongly adsorbed to particles are being found to be absorbed by benthic organisms into their tissues through their intestinal tract (see Weston, 2002). The toxicological effects of this absorption are not understood at this time.

In reviewing the potential for aquatic life toxicity of the herbicide(s), it is appropriate to review the US EPA OPP Ecotoxicity Database for information on toxicity to various types of aquatic organisms. The information in this Database is derived from registrants as part of conducting the required testing for registration of the pesticide. It has been reviewed by an expert in the field. For example, the Database contains about 90 entries for the herbicide glyphosate. It shows that there are zooplankton and some fish that have 48-hour or 96-hour LC_{50}s on the order of a few milligrams per liter. However, no information is provided in the US EPA OPP Ecotoxicity Database on the toxicity of glyphosate in combination with other chemicals.

One of the issues that should be addressed in developing the monitoring program is a plausible worst-case scenario evaluation of the concentration of the herbicide(s) that could occur when applied in accordance with label instructions, and when the applied chemical is assumed to be dispersed evenly in the water column at the time of application. The monitoring program should be developed around measuring the worst-case conditions, where there is the greatest potential for aquatic life toxicity to non-target organisms to occur.

Selection of Monitoring Parameters

All constituents that are used in the chemical treatment for control of aquatic weeds should be monitored, independent of whether their monitoring is required by the Statewide General Permit. It is possible that in combination with other chemicals they could be adverse to the beneficial uses of the waters in the area of treatment. Table 1 presents the parameters that should be monitored as part of the aquatic weed control program.

The toxicity testing should include sensitive fish larvae and zooplankton. For San Francisco Bay marine systems, Ogle (2003) recommends that the zooplankton *Americamysis bahia* (Opossum shrimp, formerly *Mysidopsis bahia*) and the fish larvae *Atherinops affinis* (topsmelt) or *Menidia beryllina* (Inland Silversides) should be used. Standard US EPA (1994a) testing procedures using these organisms should be used. For freshwater systems, the zooplankton *Ceriodaphnia dubia* (water flea) and the fish larvae *Pimephales promelas* (fathead minnow) should be used following the procedures described by Lewis, *et al*. (1994).

There is need to test the sediments for toxicity to sensitive species. For San Francisco Bay marine systems, it is recommended by Ogle (2003) that the amphipods *Eohaustorius estuarius* and *Ampelisca abdita* be tested using US EPA (1994b) testing procedures. *Eohaustorius estuarius* is less sensitive to sediment grain size. Freshwater sediment toxicity should be evaluated to *Hyalella azteca* (amphipod) using procedures described in US EPA (2000). Other organisms may be used than those recommended above. They should, however, be considered “sensitive” organisms.

Table 1
Monitoring Parameters

Visual
- Site description (channel/marsh depth or width, estimate of percent cover by vegetation, etc.)
- Appearance of waterway (sheen, color, clarity, etc.)
- Weather conditions (fog, rain, wind, etc.) just prior to the time of application, at the time of application and for the next few days

Physical
- Temperature
- Turbidity
- Electrical conductivity/salinity
- Total suspended solids (TSS)

Chemical
- pH
- Dissolved oxygen (DO)
- Herbicides and associated chemicals such as surfactants, colorants, and transformation products etc.
- Total Kjeldahl nitrogen (TKN) and ammonia
- Nitrate
- Total and dissolved phosphorus
- Biochemical oxygen demand (BOD)
- Total organic carbon (TOC) in the water column and sediments

Toxicity
- Fish larvae and zooplankton
- Algae (?)
- Sediment organisms

Bioaccumulation
- Benthic organism uptake

The total concentration of the herbicide in the sediments should be measured, and the DO concentrations should be monitored in the waters in the treated area over several weeks to determine if the DO is decreased to critical levels due to the decay of aquatic vegetation.

The transport/fate of the killed aquatic weeds should be determined. If the killed species are carried by the tide/current to an area where they are deposited on the sediments, monitoring should also be conducted in this area for all the parameters to be certain that the dead aquatic weeds do not transport the hazardous chemicals from the point of application to another location where the chemicals and vegetation decay products (including elevated ammonia and low DO) are adverse to aquatic-life-related beneficial uses in the water column or sediments.

Another test that should be done is to examine whether the treatment chemicals in the sediments cause problems for germination of non-target species. Ogle (2003) has recommended the use of *Typha latifolia* (cattail) seed germination tests.

Toxicity testing using algae, while sometimes conducted, generally does not lead to information of value. Some herbicides that are used for higher plants are also toxic to algae. This toxicity would be expected to be temporary/short-term, and not be adverse to the overall beneficial uses of the waterbody. At times the destruction of higher-trophic-level plants will lead to an algal bloom associated with the increased light penetration and the release of nutrients from the decaying vegetation.

The analytical methods that will be used should be specified, as well as their detection/quantitation limits. Further, the QA/QC program that is used should be defined and should be at least equivalent to the US EPA water quality monitoring QA/QC program. Lee and Jones-Lee (2002) have presented a QA/QC program for water quality monitoring that would be appropriate.

Characteristics of the Monitoring Program

The first sampling should be done in an attempt to collect what would likely be worst-case conditions – i.e., the highest concentration of the herbicide(s) in the water column. If screening for worst-case conditions shows that there is no obvious problem, then the likelihood of other problems occurring will be small.

If potentially toxic concentrations of the herbicide and/or toxicity is found under worst-case conditions, then studies should be conducted to track the movement/fate of the waters that first leave the treated area, using drogues (such as oranges), where measurements are made along the drogue path. This information will give an indication of the potential duration of exposure experienced by planktonic organisms associated with the worst-case waters. Also, samples should be collected just downstream of the treatment area for marine systems on the next tidal cycle at the same stage of the tidal cycle as occurred during and immediately following treatment. For freshwater systems, samples should also be collected just downstream of the treatment area on the day after treatment.

One or more untreated reference areas should be included for similar measurements.

Data Review and Management

The data should be reviewed as soon as possible after collection. This review should occur in the shortest possible timeframe in order to be used to guide monitoring at other treatment sites. The approach that will be used to determine whether there is a potential adverse impact should be specified.

The method of data storage and retrieval should be specified, as well as the timeframe for availability of a draft report for public review.

Provisions and funding for follow-up and/or special studies should be included in the monitoring plan, in the event that the data indicate that there is need for such studies.

Acknowledgment
We wish to acknowledge the assistance of Dr. Scott Ogle of Pacific EcoRisk, Martinez, California, for help in selecting test organisms.

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Experience of
G. Fred Lee, PhD, PE, DEE and Anne Jones-Lee, PhD
in
Aquatic Plant Management

Dr. G. Fred Lee became involved in the control of excessive growths of aquatic plants in 1960, while he held a university professorship in water chemistry at the University of Wisconsin, Madison. In this position he developed, and then directed for a period of 13 years, a graduate-level degree program which focused on investigating and managing water quality problems in surface and ground waters. One of his primary areas of research was on the excessive fertilization of waterbodies, focusing on factors influencing and management of algae and other aquatic plants.

In the 1960s Dr. Lee was involved in a number of projects on the control of excessive growths of aquatic plants, including a project sponsored by the Wisconsin Department of Conservation (equivalent to the California Department of Fish and Game) devoted to evaluating the potential impacts of various types of herbicides for control of aquatic plants. The project included adding herbicides to fish hatchery ponds and examining the effects of the herbicides on fish, including their reproduction, growth, etc.

Dr. Lee's work on excessive fertilization management included mechanical harvesting of aquatic plants, where he served as an advisor to the predecessor of the US EPA (Federal Water Pollution Control Association) National Eutrophication Research Program on the benefits of mechanical harvesting of aquatic plants on water quality in Lake Sallie in Minnesota. Dr. Lee has been a long-term member of the Aquatic Plant Management Society, and continues to follow closely work that is done on aquatic plant management in various parts of the US.

Dr. Lee received a bachelors degree in environmental health sciences from San Jose State College in 1955, a Master of Science in Public Health degree focusing on water quality issues from University of North Carolina, Chapel Hill, in 1957, and a PhD degree from Harvard, University, Cambridge, Massachusetts, in 1960, in environmental engineering.

During the 30 years that he held university graduate-level teaching and research positions, Dr. Lee conducted over $5 million in research and published over 500 papers and reports on this work. In addition to holding professorial positions at the University of Wisconsin, Madison, he also held similar positions in the University of Texas system and at Colorado State University.

In 1989, he completed his university teaching and research career as a Distinguished Professor at the New Jersey Institute of Technology. At that time Dr. Anne Jones-Lee, with whom he has worked since the 1970s, and he expanded the part-time consulting that Dr. Lee had been doing while a university professor into a full-time activity, under the name of G. Fred Lee & Associates. Drs. Lee and Jones-Lee are the two principals in the firm.

Dr. Anne Jones-Lee has a bachelors degree in biology from Southern Methodist University, and masters and PhD degrees in environmental sciences, focusing on water quality, from the University of Texas at Dallas. She held university professorial positions for 11 years.

Drs. Lee and Jones-Lee worked on excessive fertilization problems as consultants to a number of countries, including South Africa, Israel, Jordan, Norway, the Netherlands, France, Spain, Japan, Canada, the USSR, Tunisia, Egypt and several of the US states. Their work included completion of a contract for the US EPA devoted to the US part of the Organization for Economic Cooperation and Development (OECD) eutrophication studies that were conducted in the 1970s. In that activity they developed a synthesis report on nutrient load eutrophication response relationships for about 100 waterbodies located throughout the US. The OECD eutrophication study was a five-year, $50-million, 22-country nutrient load eutrophication response investigation which involved the study of 200 waterbodies located in western Europe, North America, Japan and Australia. Subsequent to the completion of this work, Drs. Anne Jones-Lee and G. Fred Lee have expanded the database to over 750 waterbodies located throughout the world.

In 1989, when Dr. Lee completed his teaching and research career, he and Dr. Anne Jones-Lee moved to the Sacramento area to service new clients that had developed in California. This work involved examining eutrophication-related water quality issues in the Sacramento-San Joaquin River Delta, as a consultant to Delta Wetlands, Inc. Drs. Lee and Jones-Lee have been active in Central Valley water quality issues since 1989, including most recently serving as the coordinating PI for a $2-million, one-year CALFED project devoted to the low-DO problem in the San Joaquin River Deep Water Ship Channel located near Stockton, California. They have recently completed a 280-page Synthesis Report covering three years of work that has been done on the low-DO problem in the Deep Water Ship Channel. This problem is related to excessive growths of algae in the San Joaquin River watershed. This report is available on their website, as

> Lee, G. F. and Jones-Lee, A., "Synthesis and Discussion of Findings on the Causes and Factors Influencing Low DO in the San Joaquin River Deep Water Ship Channel Near Stockton, CA: Including 2002 Data," Report Submitted to SJR DO TMDL Steering Committee and CALFED Bay-Delta Program, G. Fred Lee & Associates, El Macero, CA, March (2003). http://www.gfredlee.com/SynthesisRpt3-21-03.pdf

During the mid- to late 1990s, Dr. Lee was responsible for conducting about $500,000 of 205(j) and 319(h) research on behalf of Orange County, California, and the Santa Ana Regional Water Quality Control Board, concerned with water quality problems (pesticide-caused toxicity) in the Upper Newport Bay watershed. As part of this effort he became familiar with the excessive fertilization problems of Upper Newport Bay and the approaches that need to be taken to control these problems.

During 2002 Drs. Lee and Jones-Lee completed reports for the Central Valley Regional Water Quality Control Board concerned primarily with nonpoint source water quality management issues in the Central Valley. These reports,

Lee, G. F. and Jones-Lee, A., “Review of Management Practices for Controlling the Water Quality Impacts of Potential Pollutants in Irrigated Agriculture Stormwater Runoff and Tailwater Discharges,” California Water Institute Report TP 02-05 to California Water Resources Control Board/Central Valley Regional Water Quality Control Board, 128 pp, California State University Fresno, Fresno, CA, December (2002).
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were funded in part by the US EPA through the State Water Resources Control Board on behalf of the Central Valley Regional Water Quality Control Board. Drs. Lee and Jones-Lee developed these reports as employees of the California Water Institute at California State University, Fresno. One of the key issues that is emphasized in these reports is the development of appropriate nutrient monitoring and management programs to control excessive fertilization of Central Valley waterbodies.

Additional information on Drs. Lee and Jones-Lee’s expertise and experience pertinent to conducting studies on the control of aquatic weeds is available on their website, www.gfredlee.com, or from Dr. Lee at gfredlee@aol.com.