The biological consequences of selenium in aquatic ecosystems

Elizabeth A. Davis ❑ Kurt J. Maier ❑ Allen W. Knight

Trace amounts of the element selenium are essential to many forms of life. It has long been recognized, however, that too much selenium may be harmful.

Selenium occurs naturally in rocks and soils, at least in minute amounts (table 1). The worldwide average for soils is about 400 parts per billion (ppb), but in some locations the amount greatly exceeds the average. Portions of the west side of the San Joaquin Valley are among the high-selenium locations and may contain up to 2,000 ppb of the element. Selenium stored in rocks and soils is released to the environment through weathering and erosion. Human activities such as subsurface drainage water collection, coal combustion, and mining speed the liberation of selenium.

Natural weathering processes are estimated to release 100,000 to 200,000 metric tons of selenium per year worldwide from rocks and soils. Runoff from high-selenium watersheds may reach harmful levels of selenium without human input. This problem has necessitated dryland farming in some areas of Wyoming and South Dakota so as not to speed up the process by irrigation.

California's selenium troubles have their roots in the solution to another problem—excess salt in soil. The productivity of one-half million acres of farmland in the Central Valley is threatened by waterlogging and soil salt buildup. To reduce the salt concentration and the water level, 8,000 acres were drained on a trial basis beginning in 1978. The drainage water was conveyed by the San Luis Drain into ponds at Kesterson Reservoir, near Los Banos. But the 8,000 acres, located mainly in the Panoche Fan area, are composed of marine sediments naturally high in selenium as well as salt. The drainage water contained an average of 350 ppb selenium and occasionally as much as 1,350 ppb.

By 1982, mosquitofish in the reservoir had reportedly accumulated selenium in their tissues at concentrations 36 to 72 times higher than the national average. In 1983, birds nesting at the reservoir apparently suffered a decrease in fertility and high incidence of deformed hatchlings. Although it seemed clear after an initial investigation that selenium was a major cause of the deformities, the mechanisms of selenium cycling in the environment, its toxicity and interaction with other factors, and its possible movement through the food chain were not immediately apparent. This report summarizes some of what scientists have learned in subsequent research and what remains to be discovered.

Chemistry and toxicity

An undersupply of selenium for aquatic creatures (less than about 0.1 ppb, depending on the organism) leads to nutritional deficiency and disease. Deficiency has been more common than selenium poisoning. The toxic threshold for aquatic organisms studied so far ranges from 3 ppb in some protozoa to 5,000 ppb in some fish. A conservative water quality goal for the protection of aquatic organisms, a level where no adverse effects should occur, appears to be between 1.0 and 1.5 ppb.

Selenium may be taken up by organisms directly or through the food they eat. Some plants take up selenium from the soil, concentrating large amounts in their tissues. Eating such plants, or ordinary forages and feeds grown on seleniferous soils, can be harmful to livestock. This type of selenium poisoning has been recognized for nearly a century and is actually quite rare.

Selenium may have a greater impact in aquatic ecosystems where human activities have made it more available. Selenium in solution is more available to a variety of organisms directly. In aquatic systems, selenium is cycled predominantly through biological pathways—food chains and metabolic processes. Aquatic food chains are often relatively simple, making them suitable for tracing the pathway of a toxin (fig. 1).

TABLE 1. Distribution of selenium in natural and anthropogenic materials

Material	Se concentration
Terrestrial:	*ppm*
Earth's crust	0.09
Limestone	0.1 - 14.0
Shales and phosphate rocks	<1 - 55
Crude oil	0.06 - 0.39
Coal	0.5 - 11.0
Soils:	
Nonseleniferous	<0.1 - 2.0
Seleniferous	2 - 200
Aquatic:	
Ocean water	10^{-4} - 4×10^{-3}
River water	10^{-4} - 4×10^{-4}
Aquatic plants	0.02 - 0.14
Plankton	1.1 - 2.4
Fish	0.5 - 6.2
Anthropogenic:	
Petroleum products	0.15 - 1.65
Fly ash	1.2 - 16.5
Sewage sludge	1.8 - 4.8
Paper products	1.6 - 19.0

Selenium exists in water in four oxidation states, each with different physical and biological properties: selenate (Se^{+6}), selenite (Se^{+4}), elemental selenium (Se^{0}), and selenide (Se^{-2}). Selenium is also found in several organic forms; measurements have revealed that up to 60 percent of the selenium in some fresh and marine waters is organic. In most water systems, however, the inorganic forms selenate and selenite dominate. The various forms of selenium are not always available to organisms in direct proportion to the amount found in water. In many cases, organic forms are taken up by organisms (bioaccumulated) faster and to higher concentrations and are retained longer in their systems.

Elemental selenium is stable, insoluble in water, and poorly assimilated by aquatic organisms. It is deposited in sediments lacking oxygen. It is not completely inert in this form, and is slowly converted to selenite when oxygen is present.

Inorganic selenide joins with hydrogen or various metals in oxygen-free environments. Hydrogen selenide, while 100 times more toxic than hydrogen cyanide, is readily oxidized to insoluble elemental selenium upon contact with oxygen. The metal selenides are also insoluble and are not considered to be environmentally hazardous.

Selenate and selenite are both water soluble and are the most common inorganic oxidation states in oxygenated waters. Of the two, selenite is frequently the more toxic. Selenate or selenite ions diffuse or are actively absorbed from water in contact with cell surfaces into the cells of aquatic organisms. Gills or other thin membranous tissues may be sites of particularly high uptake. Higher aquatic plants may also acquire selenium through their roots. The absorbed selenium is reduced within the cell to either elemental selenium or selenide.

Thereafter, when at low concentrations, selenium acts as a micronutrient for many aquatic organisms and is synthesized into a variety of essential compounds. At higher concentrations within the cell, the extra selenium undergoes different reactions. Inorganic selenium poisoning occurs when selenide in the cell forms temporary bonds with available sulfur groups in amino acids. These amino acids then become incorporated into various enzymes and other proteins. Because the selenide bonds alter the

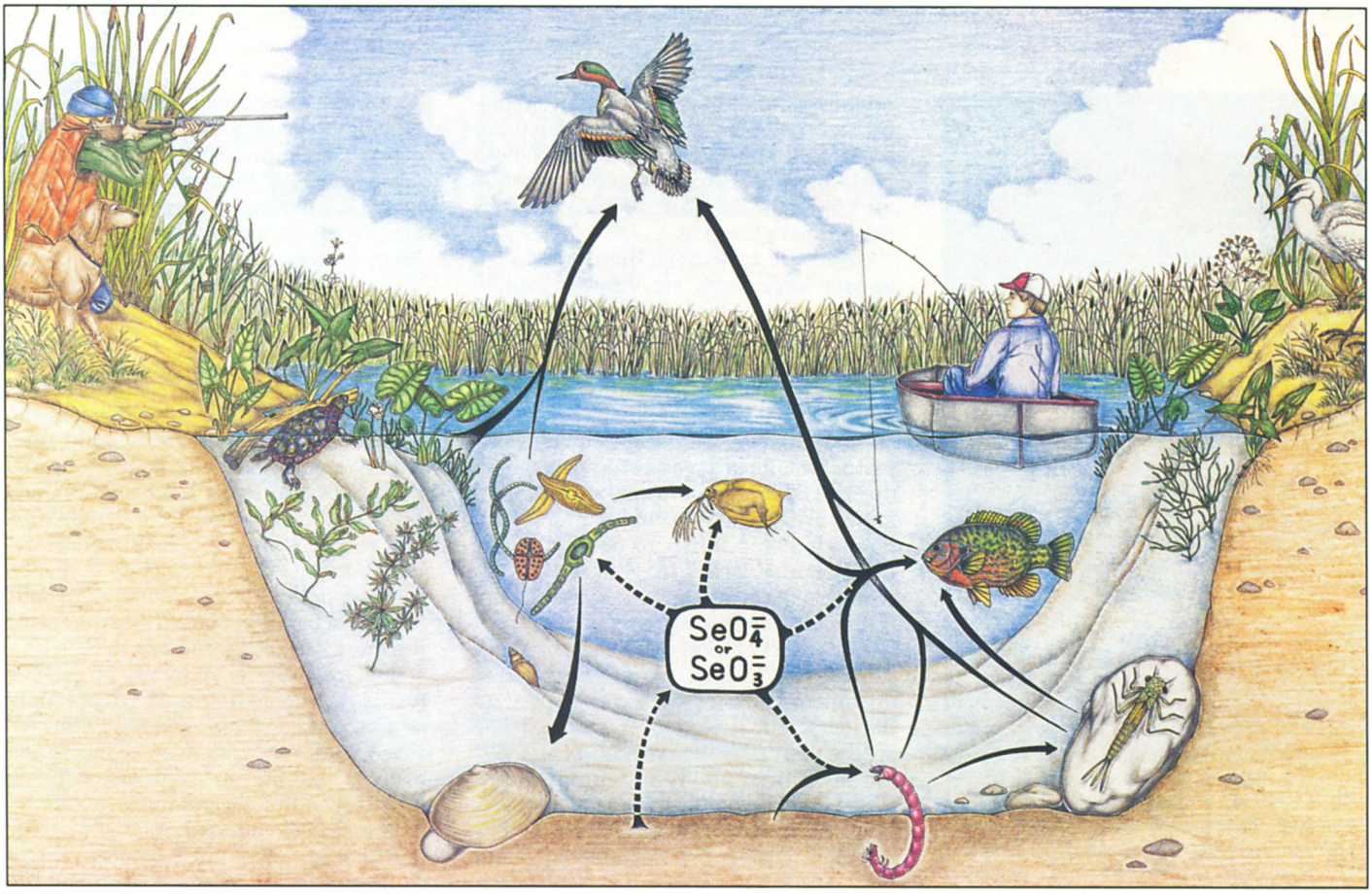


Fig. 1. Uptake and transfer of selenium in a model aquatic food chain.

three-dimensional structure of the proteins, they are unable to function normally. This toxicological mechanism resembles that of many heavy metals.

While more is known about inorganic selenium toxicity, organic selenium appears to be more toxic and ecologically important. "More toxic" implies that a lower concentration can achieve the same effect as a greater amount of a less toxic substance. The process resulting in organic selenium toxicity begins in a manner similar to inorganic toxicity. Selenium is absorbed and reduced by plants, algae, and bacteria. Instead of forming temporary bonds with amino acids, however, the plants and bacteria use selenium as a sulfur analog, such as in the synthesis of the amino acids cysteine and methionine.

Bacteria and photosynthesizing organisms serve as the bases of aquatic food chains (fig. 1). They synthesize organic selenium compounds, which consumer organisms then acquire in their diets. When used in the formation of proteins, the seleno-amino acids can alter the three-dimensional structure of the proteins and affect their function.

Selenium cycling

Organisms complete the selenium cycle by returning organic selenium to the environment through methylation (gasification) and mineralization. While considerable evidence has established the presence of each of these segments of the selenium cycle, little information exists on the rates at which they take place or on the relative importance of the organisms involved.

Selenium is also returned to the environment through decomposition of selenium-laden bodies, as indicated by the selenium content in crude oil and coal as well as in cretaceous marine shales. Fossilization allows the selenium to remain in organic form. Methylation and mineralization return organic selenium to an inorganic state.

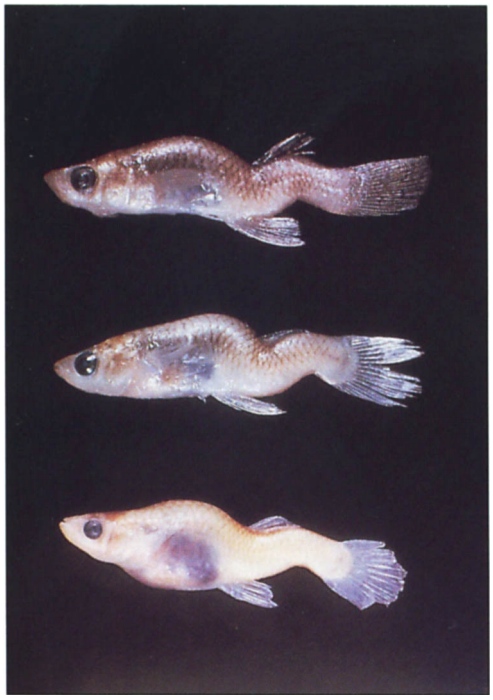
Vascular plants, some aquatic animals, microorganisms, and algae are capable of methylation of selenium—the attachment of one or more methyl groups to selenium. Methylation is part of the mechanism of incorporating selenium into several biologically important organic selenium compounds and a way that organisms may rid themselves of excess selenium.

Methylation is known to take place in both the presence and the absence of oxygen. Since the methylated compounds are volatile and relatively insoluble, they are easily lost to the atmosphere from aquatic systems. It is thought that they may be returned to earth later in rainwater as inorganic selenium after photooxidation in the atmosphere. Methylation is therefore a potential method of removing (and distributing) selenium from contaminated waters.

Mineralization is the conversion of organic forms of an element or compound to less complex inorganic forms. In the case of selenium, this involves the oxidation of seleno-organic compounds like selenocysteine and selenomethionine to elemental and inorganic selenium salts by microorganisms. In preliminary experiments in our laboratory, we have added selenomethionine to aerobic and anaerobic Sacramento-San Joaquin Delta sediments and water and recovered small amounts of selenite after 15 to 21 days. However, little is known of the actual organisms, rates, or pathways involved.

Toxic effects

The most common means of characterizing the toxicity of selenium to aquatic invertebrates and vertebrates is the LC_{50} value, which is the concentration of the test chemical that causes death in 50 percent of the test population in a given period of time. Such tests determine the acute, or lethal, toxicity level of selenium. Chronic, or sublethal, effects are those responses of an organism to long-term concentrations of the toxicant that do not lead directly to death but may render the



U.S. Fish & Wildlife Service

Certain forms of selenium have sublethal effects on some aquatic species, such as the spinal deformities in these mosquitofish.

organism more susceptible to physiological and ecological stresses. Acute studies are usually conducted in a 48- to 96-hour period, while chronic studies continue for a time greater than 10 percent of the test animal's lifespan.

Results of toxicity studies for selected aquatic organisms are summarized in table 2. Only a few studies have tested organic selenium and aquatic organisms. Most of these have been acute toxicity comparisons of organic and inorganic selenium and in general have demonstrated that organic selenium is more toxic. Results of several studies have indicated that organic forms of selenium are approximately 10 times more toxic than inorganic forms to aquatic algae, invertebrates, and fish. Studies on the chronic effects of organic selenium are conspicuously lacking.

The effects of inorganic selenium, both acute and chronic, are slightly better documented. More research is needed on the long-term, sublethal effects since they are the most prevalent in nature.

The reduced ability to reproduce is a toxic effect of selenium found at all levels of the food chain. The classic example is the high number of nonviable eggs and severe developmental deformities (teratogenic effects) of birds at Kesterson Reservoir. Selenium toxicity in algae is usually determined by measuring alterations in cell division rates. Green algae are generally less tolerant of selenium than blue-green species. Green algae show signs of toxicity at approximately 0.01 ppm selenate; blue-green algae are affected at about 5 ppm selenate.

Reduced reproductive success has also been demonstrated as a sublethal effect of selenium in aquatic invertebrates and vertebrates. The most thoroughly studied invertebrates, several species of water flea (*Daphnia*), suffer decreased growth rates and longer time to first reproduction when exposed to selenite concentrations between 200 and 800 ppb. Other effects reported for invertebrates include abnormal osmoregulation and decreased feeding rates among filter feeders.

Sublethal effects reported in fish are typically decreased growth, edema, and/or abnormal development of various tissues including bone, liver, kidneys, and ovaries. Significant decreases in blood iron concentrations and red cell volumes have also been reported.

Although selenium tolerance varies from species to species, younger life stages are generally less tolerant than older organisms. The longer the selenium exposure, the less toxicant needed to produce the effects. It also appears that, as a group, invertebrates are more acutely sensitive to selenium than vertebrates.

The water in systems where selenium is a problem usually contains other chemicals, which may act synergistically or antagonistically with selenium. Most of the other substances are toxic in their own right in sufficient quantities. Boron, arsenic, cadmium, chromium, and molybdenum in particular are receiving attention from researchers. Boron, for example, is thought to enhance the toxicity of selenium when the two occur together; arsenic is believed to lessen selenium toxicity to some extent.

Other physical and chemical factors are suspected of altering selenium's toxicity or the rate at which it is taken into living systems. These include water hardness, salinity, pH, temperature, and dissolved oxygen content.

TABLE 2. Selected toxicological responses of aquatic organisms to selenium

Species	Common name	Concentration of Se compound	Effect
		ppm	
Algae:			
Ankistrodesmus falcatus		0.01 selenate	decrease in cell divisions
Selenastrum capricornutum		0.1 selenite	20% decrease in cell divisions
Scenedesmus dimorphus		40.0 selenate	100% "
"		40.0 selenite	100% "
Anabaena nidulans		50.0 selenate	24% "
"		50.0 selenite	21% "
Anabaena flos-aquae		5.0 selenate	decrease in cell divisions
"		4.0 selenite	"
"		0.3 selenomethionine	"
Invertebrates:			
Daphnia magna	water flea	2.4 selenate	96 hr. LC_{50}
"	"	0.6 selenite	"
"	"	0.04 selenomethionine	"
"	"	0.03-0.28 selenite	survival and reproduction unaffected
"	"	1.1 selenite	48 hr LC_{50}
"	"	1.0 selenite	decreased reproduction
Daphnia pulex	water flea	0.2-0.8 selenite	insignificant rise in O_2 consumption
"	"	"	decrease in filtration rate
"	"	3.87 selenite	48 hr LC_{50}
"	"	0.13 selenite	96 hr LC_{50} cellular damage
Daphnia pulicaria	water flea	0.006 selenite	96 hr LC_{50}
Chironomus decorus	midge	25.0 selenate	48 hr. LC_{50}
"	"	50.0 selenite	"
"	"	<200 selenomethionine	"
Orconectes immunis	crayfish	0.1-1.0-	osmoregulatory changes
Hyallela azteca	amphipod	1.0 selenite	96 hr LC_{50}
"	"	1.0 selenate	"
Entosiphion sulcatum	protozoan	0.003 selenite	decreased reproduction
Vertebrates:			
Lepomis machrochirus	bluegill	40.0 selenite	96 hr LC_{50}
Ictalurus punctatus	catfish	18.2 selenite	"
Carassius auratus	goldfish	36.6 selenite	"
Pimephales promelas	fathead minnow	1.1-7.3 selenite	"
Gambusia affinis	mosquitofish	76.0 selenite	"
Salmo gairdneri	rainbow trout	8.1 selenite	"
"	"	0.044 selenite	increased mortality

Bioaccumulation

Bioaccumulation, the uptake of an element or chemical by an aquatic organism from the surrounding environment, can be accomplished by either bioconcentration or biomagnification.

Bioconcentration is the result of the direct uptake of a chemical from water or

Continued on page 29

with nut clusters. Among these 14, OBLR larvae had webbed together several nuts in the cluster and then fed on the stem and hull tissue. Stems were consumed at the point of nut attachment to the extent that larvae entered the mature pistachio shell cavity and fed on the nut meats. Additional random counts of nuts in July and August 1984 showed 19 of 1,053 clusters (1.8 percent) infested to some degree. Most nuts in infested clusters were not extensively damaged, however, leading to an estimate that less than 0.1 percent of all nuts sampled were lost.

Conclusions

At present, it is unclear what the potential of obliquebanded leafroller may be as a pest on pistachios. Earlier work has indicated that this leafroller is not common in the arid southwestern states, but the area in Madera County known to be infested is generally hot and dry during most of the year, with an annual rainfall of 10.7 inches and maximum temperatures routinely over 100°F from June through September. Cultural practices in the infested Madera orchards, primarily low-angle sprinkler irrigation and permanent clover ground cover, which would tend to cool the orchard, may have contributed to the development of obliquebanded leafroller in this location. Economic populations of OBLR are reported relatively slow to develop on filberts in Oregon. Thus, a decision on the potential of OBLR as a pest on pistachios should be deferred until additional observations can be made.

Examination of OBLR nests in pistachios during this study revealed the presence of two parasitic wasps. These parasites were identified as *Macrocentrus iridescens* French (Hymenoptera: Braconidae) and *Pteromalus* (*Habrocytus*) sp. (Hymenoptera: Pteromalidae). The effect of these and perhaps other parasites and predators, such as *Brochymena sulcata* and *Phytocoris* spp., on OBLR is undetermined.

Richard E. Rice is Lecturer and Entomologist, Department of Entomology, University of California, Davis, stationed at the UC Kearney Agricultural Center, Parlier; Donald L. Flaherty is Farm Advisor, Cooperative Extension, Tulare County; and Richard A. Jones is Staff Research Associate IV, Department of Entomology, UC Davis, stationed at Parlier. *The authors thank Dr. E. E. Grisell and Dr. P. M. Marsh, USNM, for identification of the* Pteromalus *and* Macrocentrus *parasites, respectively, and to Dr. T. D. Eichlin, California Department of Food and Agriculture, for identifications of* Commophila *and* Macrotheca *spp.*

Selenium *continued from page 20*

associated sediments. Many algae and bacteria can accumulate many times their dry weight in selenium, and the resulting concentration in their cells may be over a hundred times greater than background water levels.

Biomagnification, the uptake of selenium by way of the diet and food chain, has been questioned by some researchers, at least as far as selenium is concerned. In biomagnification, the chemical is accumulated at lower levels of the food chain and is passed up the chain as higher organisms feed on the lower forms. Due to the constant need for nourishment and the inefficiency of the energy transfer from one level to the next higher level, an organism consumes more food than its own mass. This leads to a greater concentration of the toxicant with each subsequent step in the food chain. Conflicting evidence complicates the picture; some links in the food chain result in higher concentrations in the consumer while others do not. In general, field observations, especially in small ecosystems, support the concept of biomagnification, but it has yet to be substantiated by laboratory experiments.

Seeking solutions

Numerous possibilities for dealing with excess selenium are under investigation, including oceanic or estuarine disposal. An important consideration in any proposal involving transport of selenium from one system to another, however, is whether such a solution would merely spread the problem. Obtaining more concrete knowledge of the selenium cycle is one key to planning the best time, place, and method for removal of excess selenium from a system. Unless it can be shown that selenium is not as harmful as we suspect, dealing with excess selenium will become vital for maintaining the quality of aquatic environments in the Central Valley.

Elizabeth A. Davis is a graduate student in Ecology; Kurt J. Maier is a research assistant and graduate student in Ecology; and Allen W. Knight is Professor of Hydrobiology. All are with the Department of Land, Air, and Water Resources, University of California, Davis.

The authors' research has been supported by grants from the U.S. Geological Survey (#14-08-0001-G1495), the University of California Salinity and Drainage Task Force (#86-9), the Water Resources Center of the University of California (UCAL-WRC-W-669), the Toxic Substances Research and Teaching Program, and the Public Service Research and Dissemination Program.

Synergism *continued from page 22*

More significantly, samples of cotton terminals collected 24 hours after treatment revealed high adult mortality levels associated with combinations of DEF plus pyrethroids in Blythe, and with DEF plus cypermethrin in Brawley (table 2). Overall, DEF plus cypermethrin was the most effective treatment, in which 99.2 percent mortality was recorded in Blythe. Although 94.7 percent mortality was recorded in the DEF-plus-permethrin treatment in Blythe, a distinctly lower mortality level of 77.8 percent was recorded in this same treatment in Brawley. This discrepancy between the two locations for this treatment may be the result of the lower rates used in the Brawley trial. In addition, DEF alone caused relatively high adult mortalities of 77.3 and 81.1 percent in both locations.

The treatment associated with the lowest adult mortality overall was sodium chlorate plus cypermethrin. This was not surprising, since sodium chlorate is not known to have insecticidal or synergistic properties at the dosage used.

In general, the results obtained with the D-vac sampling method were in good agreement with those of the cotton terminal method (table 3). There were significant ($P = 0.01$) differences among all four treatments, with the highest mortality of 91.2 percent occurring in the DEF-plus-cypermethrin treatment.

Conclusion

High toxicity of DEF in combination with cypermethrin or permethrin was demonstrated in both laboratory and field trials. In the field trials, a single application of DEF plus cypermethrin also resulted in superior control of sweetpotato whitefly adults on cotton before harvest. After further evaluation, the use of DEF with pyrethroids, along with other cultural control methods, may prove useful in reducing the threat of SPWF populations to fall plantings of cucurbit and lettuce crops.

A. Rami Horowitz is Postdoctoral Research Associate, Cooperative Extension; Nick C. Toscano is Extension Entomologist and Program Director, Pest Management, Cooperative Extension; Roger R. Youngman is Postdoctoral Research Associate, Department of Entomology; Ken Kido is Staff Research Associate, Pest Management, Cooperative Extension; and George P. Georghiou is Professor, Department of Entomology. All are with the University of California, Riverside. James J. Knabke is Research Biologist, FMC Corporation, Imperial, California. *This work was supported in part by a grant from the California Iceberg Lettuce Board.*