

RESIDUE REVIEWS

Residues of Pesticides and Other
Contaminants in the Total Environment

VOLUME 80

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Contaminants in the Total Environment

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Foreword

Worldwide concern in scientific, industrial, and governmental communities over traces of toxic chemicals in foodstuffs and in both abiotic and biotic environments has justified the present triumvirate of specialized publications in this field: comprehensive reviews, rapidly published progress reports, and archival documentations. These three publications are integrated and scheduled to provide in international communication the coherency essential for nonduplicative and current progress in a field as dynamic and complex as environmental contamination and toxicology. Until now there has been no journal or other publication series reserved exclusively for the diversified literature on "toxic" chemicals in our foods, our feeds, our geographical surroundings, our domestic animals, our wildlife, and ourselves. Around the world immense efforts and many talents have been mobilized to technical and other evaluations of natures, locales, magnitudes, fates, and toxicology of the persisting residues of these chemicals loosed upon the world. Among the sequelae of this broad new emphasis has been an inescapable need for an articulated set of authoritative publications where one could expect to find the latest important world literature produced by this emerging area of science together with documentation of pertinent ancillary legislation.

The research director and the legislative or administrative advisor do not have the time even to scan the large number of technical publications that might contain articles important to current responsibility; these individuals need the background provided by detailed reviews plus an assured awareness of newly developing information, all with minimum time for literature searching. Similarly, the scientist assigned or attracted to a new problem has the requirements of gleaning all literature pertinent to his task, publishing quickly new developments or important new experimental details to inform others of findings that might alter their own efforts, and eventually publishing all his supporting data and conclusions for archival purposes.

The end result of this concern over these chores and responsibilities and with uniform, encompassing, and timely publication outlets in the field of environmental contamination and toxicology is the Springer-Verlag (Heidelberg and New York) triumvirate:

Residue Reviews (vol. 1 in 1962) for basically detailed review articles concerned with any aspects of residues of pesticides and other chemical contaminants in the total environment, including toxicological considerations and consequences.

Bulletin of Environmental Contamination and Toxicology (vol. 1 in 1966) for rapid publication of short reports of significant advances and discoveries in the fields of air, soil, water, and food contamination and pollution as well as methodology and other disciplines concerned with the introduction, presence, and effects of toxicants in the total environment.

Archives of Environmental Contamination and Toxicology (vol. 1 in 1973) for important complete articles emphasizing and describing original experimental or theoretical research work pertaining to the scientific aspects of chemical contaminants in the environment.

Manuscripts for *Residue Reviews* and the *Archives* are in identical formats and are subject to review, by workers in the field, for adequacy and value; manuscripts for the *Bulletin* are not reviewed and are published by photo-offset to provide the latest results without delay. The individual editors of these three publications comprise the Joint Coordinating Board of Editors with referral within the Board of manuscripts submitted to one publication but deemed by major emphasis or length more suitable for one of the others.

Coordinating Board of Editors

Preface

That residues of pesticide and other contaminants in the total environment are of concern to everyone everywhere is attested by the reception accorded previous volumes of "Residue Reviews" and by the gratifying enthusiasm, sincerity, and efforts shown by all the individuals from whom manuscripts have been solicited. Despite much propaganda to the contrary, there can never be any serious question that pest-control chemicals and food-additive chemicals are essential to adequate food production, manufacture, marketing, and storage, yet without continuing surveillance and intelligent control some of those that persist in our foodstuffs could at times conceivably endanger the public health. Ensuring safety-in-use of these many chemicals is a dynamic challenge, for established ones are continually being displaced by newly developed ones more acceptable to food technologists, pharmacologists, toxicologists, and changing pest-control requirements in progressive food-producing economies.

These matters are of genuine concern to increasing numbers of governmental agencies and legislative bodies around the world, for some of these chemicals have resulted in a few mishaps from improper use. Adequate safety-in-use evaluations of any of these chemicals persisting into our foodstuffs are not simple matters, and they incorporate the considered judgments of many individuals highly trained in a variety of complex biological, chemical, food technological, medical, pharmacological, and toxicological disciplines.

It is hoped that "Residue Reviews" will continue to serve as an integrating factor both in focusing attention upon those many residue matters requiring further attention and in collating for variously trained readers present knowledge in specific important areas of residue and related endeavors involved with other chemical contaminants in the total environment. The contents of this and previous volumes of "Residue Reviews" illustrate these objectives. Since manuscripts are published in the order in which they are received in final form, it may seem that some important aspects of residue analytical chemistry, biochemistry, human and animal medicine, legislation, pharmacology, physiology, regulation, and toxicology are being neglected; to the contrary, these apparent omissions are recognized, and some pertinent manuscripts are in preparation. However, the field is so large and the interests in it are so varied that the editors and the Advisory Board earnestly solicit suggestions of topics and authors to help make this international book-series even more useful and informative.

"Residue Reviews" attempts to provide concise, critical reviews of timely advances, philosophy, and significant areas of accomplished or needed endeavor in the total field of residues of these and other foreign chemicals in any segment of the environment. These reviews are either general or specific, but properly they may lie in the domains of analytical chemistry and its methodology, biochemistry, human and animal medicine, legislation, pharmacology, physiology, regulation, and toxicology; certain affairs in the realm of food technology concerned specifically with pesticide and other food-additive problems are also appropriate subject matter. The justification for the preparation of any review for this book-series is that it deals with some aspect of the many real problems arising from the presence of any "foreign" chemicals in our surroundings. Thus, manuscripts may encompass those matters, in any country, which are involved in allowing pesticide and other plant-protecting chemicals to be used safely in producing, storing, and shipping crops. Added plant or animal pest-control chemicals or their metabolites that may persist into meat and other edible animal products (milk and milk products, eggs, etc.) are also residues and are within this scope. The so-called food additives (substances deliberately added to foods for flavor, odor, appearance, etc., as well as those inadvertently added during manufacture, packaging, distribution, storage, etc.) are also considered suitable review material. In addition, contaminant chemicals added in any manner to air, water, soil or plant or animal life are within this purview and these objectives.

Manuscripts are normally contributed by invitation but suggested topics are welcome. Preliminary communication with the editors is necessary before volunteered reviews are submitted in manuscript form.

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April 15, 1981

F.A.G.
J.D.G.

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Carbaryl: A literature review

By

MICHAEL E. MOUNT* and FREDERICK W. OEHME**

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I. Introduction

Carbaryl (1-naphthyl-*N*-methylcarbamate; Sevin),¹ a reversible inhibitor of cholinesterase, is an agricultural pesticide used in the control of over 150 major pests (BACK 1965). It belongs to the major class of insecticidal compounds, the carbamates.

In 1947, the Geigy Company in Switzerland developed *N*-dimethylcarbamates for herbicidal action. Concurrent with the Geigy developments, Metcalf and his co-workers were studying the mechanisms of action of organophosphate insecticides (METCALF and MARCH 1950). During this time, the quaternary ammonium substituent of the carbamic acid esters, physostigmine (CHADWICK and HILL 1947) and neostigmine (KOLBEZEN

¹ Chemical designations of pesticides mentioned in text are listed in Table IV; Table V lists the scientific names of organisms mentioned in text.

et al. 1954), were found to inhibit insecticidal cholinesterase but they did not show any insecticidal action because of hindered penetration into the insects due to the substituent charge. METCALF's group developed uncharged substituted-phenyl methylcarbamates that not only inhibited the activity of fly-head cholinesterase, but also showed insecticidal activity. As a result, the aryl methylcarbamates introduced a new insecticide era (WEIDEN 1971). Interestingly, the Geigy scientists rejected the dimethylcarbamate aryl analogues since they showed only slight herbicidal activity.

Union Carbide Company of the United States synthesized the *N*-methylcarbamate, carbaryl, in 1953 (LAMBRECH 1959). It was introduced in 1958 as a commercial insecticide under the name of "Sevin" and has become the best known of the present carbamate insecticides (O'BRIEN 1967, SPENCER 1968, BACK 1965). It has been used extensively as a broad-spectrum insecticide which possesses both contact and systemic toxicity to a variety of insects.

The susceptibility of insects to carbaryl toxicity varies considerably. The bee, for example, is highly susceptible while the housefly is somewhat resistant (O'BRIEN 1967, METCALF *et al.* 1967). However, carbaryl has wide-spectrum, low-hazard, and short-term residual properties making it one of the most widely used carbamate insecticides. In 1974, carbaryl was ranked as the most used insecticide on U.S. forests (DEWEESE *et al.* 1979).

This review does not extend into the year 1980. Although not all citations on carbaryl are referenced, the review is extensive. The organization of data according to the outline sections was useful in categorizing the numerous reports, but various references could have been reviewed in more than one section.

II. Chemistry

a) Chemical properties

Carbaryl is a naphthyl carbamate. It is the 1-naphthyl ester of *N*-methyl carbamic acid, a white crystalline powder. It is almost insoluble in water, but is soluble in corn oil and cottonseed oil, which are solvents suitable for oral administration to animals (BOYD 1972).

Carbaryl has a 64.5 olive oil/water partition coefficient, indicating it to be lipophilic (O'BRIEN and DANNELLY 1965). The formula for carbaryl is $C_{12}H_{11}NO_2$ with C (71.62%), H (5.51%), N (6.96%), and O (15.90%) and a molecular weight of 201.22. The crystals melt at 145° C; density is 1.232. It is moderately soluble in *N,N*-dimethylformamide, acetone, isophorone, and cyclohexanone. Solubility in water is less than 1% (ANONYMOUS 1976). The structure of carbaryl is given in Figure 1.

b) Mode of action

The basic carbamate structure given in Figure 2 is responsible for the chemical's mode of action in a biological system. Inhibition of acetyl-

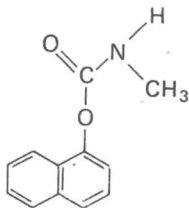


Fig. 1. Chemical structure of carbaryl.

cholinesterase is the basic biochemical lesion leading to the cholinergic effects. Carbaryl is referred to as a reversible acetylcholinesterase inhibitor, as depicted in Figure 3.

K_a , the affinity constant, which may be defined as k_{-1}/k_1 , governs the initial reaction shown in Figure 3 (KUHR and DOROUGH 1976). The larger the k_1 is, the smaller the affinity constant would be. With carbamates, K_a (the affinity constant) is very low, favoring the reversible complex formation. Then, k_2 quickly removes this complex to the carbamylated acetylcholinesterase, keeping the reversible complex at a minimum. However, k_3 is the key to understanding the term "reversible inhibitor". k_3 is much slower than k_2 resulting in a build up of the carbamylated complex. The k_3 for carbamates is approximately 5 times faster than the k_3 of organophosphates (0.04 vs. 0.008, see below). Aging is also associated with organophosphate insecticides. The k_3 results in the hy-

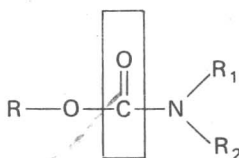


Fig. 2. Basic carbamate chemical structure. The portion enclosed within the rectangle forms the ester linkage with the cholinesterase enzyme.

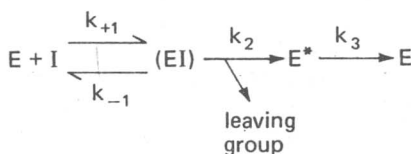


Fig. 3. Reaction of anticholinesterase insecticide (I) with the cholinesterase enzyme (E). EI represents the reversible complex while E^* is the carbamylated or phosphorylated enzyme. The last step involving the k_3 yields reactivated cholinesterase (E) and a metabolic by-product (not shown).

drolysis of the carbamate-enzyme complex and the release and re-activation of the acetylcholinesterase enzyme. Carbamates are therefore thought of as being reversible (release of acetylcholinesterase enzyme) in comparison to the slower release by organophosphates.

An illustration of this is seen by comparing the number of molecules that are hydrolyzed per minute by one molecule of acetylcholinesterase. For acetylcholine, k_2 and k_3 are very rapid and 300,000 molecules of acetylcholine are hydrolyzed per minute compared to 0.04 for methyl carbamates and 0.008 for dimethylphosphates (MURPHY 1975). The slowness of the k_3 of carbamates compared to the k_3 of acetylcholine is responsible for the toxicity of these compounds. The reversible action of carbamates is due to the higher k_3 when compared to organophosphates and the aging process associated with organophosphate insecticides. Other aspects of the kinetic model of cholinesterase inhibition and reversal have been studied by WATTS and WILKINSON (1977).

Carbamates inhibit true and pseudocholinesterase and aliesterasés, but not arylesterases (CASIDA 1963). Aliesterases appear to be less reversibly inhibited by carbaryl than are the cholinesterases (PLAPP and BIGLEY 1961).

III. Acute toxicity

a) *Arthropod pests*

Carbaryl is employed in a dose of ¼ to 2 lb/A of vegetables, cotton, and other crops with little or no evidence of phytotoxicity (SPENCER 1968), but with effectiveness against many pests.

Individual species' biological response to carbaryl should not be construed as indicative of the degree of response expected from other members of the same taxonomic category. For example, carbaryl is toxic to ticks, parasitic mites, rust mites, and predaceous mites but is inactive against tetranychid mites which are members of the same class *Acarina* (WEIDEN and MOOREFIELD 1965). BRATTSTEN and METCALF (1970) studied taxonomic variations by comparing LD₅₀ values following topical application of carbaryl with and without piperonyl butoxide, an insecticidal synergist inhibiting mixed function oxidative enzymes. The susceptibility of insects varied greatly between members of the same taxonomic group. Resistant and susceptible species occurred in different taxonomic groups as exemplified by the resistant housefly whose LD₅₀ value following topical application of carbaryl was 900 µg/g vs. 2.3 µg/g for the honeybee (METCALF *et al.* 1967). The housefly was studied by METCALF *et al.* (1967) and it rapidly detoxified carbaryl primarily by ring hydroxylation.

Insect control of numerous pests has been used on fruit and nut trees;

forage, field, and vegetable crops; small fruits (e.g., grapes, blueberries, and strawberries); lawn areas; shade trees and ornamentals; and non-agricultural areas for mosquito control. The expanded list of insects associated with these usages is available from the manufacturer, *Union Carbide Corporation*. Carbaryl has been effective against the gypsy moth caterpillar (GYRISCO 1960), army cutworm (MANGLITZ *et al.* 1973), European corn borer (KUHR and DAVIS 1975, BRATTSTEIN and METCALF 1970), western corn rootworm (BALL 1969), lygus bug (LEIGH and JACKSON 1968), elm leaf beetle (BREWER 1973), aster leafhopper (ECKENRODE 1973), western budworm (DEWEESE *et al.* 1972), and the grasshopper (MC EWEN *et al.* 1972), as well as numerous other insects.

Livestock and animal uses for carbaryl have been extensive due to its low toxicity. Carbaryl has been shown effective for the control of ticks (DRUMMOND 1959), horn flies (JOHNSON and LONFORD 1960), and lice (MOORE 1959) in livestock. The minimum effective time for carbaryl was 4 days for horn flies (ROBERTS *et al.* 1960). It has been extensively used for the control of ectoparasites on poultry (ZIV *et al.* 1977) including its use to control chicken mites and lice, as well as bedbugs, northern fowl mites, and fleas (*Union Carbide Corporation*). It has also been used to control the pests and predators of oysters, such as oyster drills, ghost or mud shrimp, and pea crabs (ANDREWS 1968, KARINEN *et al.* 1967, HAVEN *et al.* 1966, HAYDOCK 1964, SNOW and STEWART 1963, LINDSAY 1961). Carbaryl formulations (chiefly Sevin dusts) are applied to dogs and cats and their premises to control ticks, fleas, and lice (*Union Carbide Corporation*). Carbaryl-impregnated flea collars used in dogs and cats have effective control of the cat flea (MILLER *et al.* 1977).

Poisoning by carbamates in insects has been described by WEIDEN (1971). Regurgitation, defecation, nervous excitation, body jerks and wing fanning, loss of coordination, and flaccid paralysis have been observed. Recovery can occur even following flaccid paralysis depending on the detoxification capabilities of the insects. MILLER (1976) used clinical signs to distinguish carbamate poisoning from organophosphate poisoning in the housefly, and carbaryl matched the proposed scheme for classifying carbamate effects.

b) Nontarget arthropods and annelids

The honeybee, which is highly susceptible to carbaryl exposure, is the main concern. Serious losses in honeybees have coincided with the change from DDT-toxaphene to carbaryl agricultural applications (BARKER 1970). JOHANSEN (1961) studied the toxicities of numerous insecticides on the honeybee. SHAW and FISCHANG (1962) reported carbaryl was less toxic than the organophosphates tested, but not appreciably so. Carbaryl had a moderate toxic effect, with this relationship of toxicity to honeybees; parathion > dieldrin > carbaryl > DDT > ethion at the LD₉₅ concentration of the insecticide. ANDERSON and ATKINS (1958) de-

terminated the percent mortality in the honeybee following application of 2% carbaryl dust along with 22 other compounds. Carbaryl was rated highly toxic although several organophosphate insecticides produced faster kills than carbaryl. A field study of aerial application of carbaryl stimulating spraying for the gypsy moth by STRANG *et al.* (1968) had heavy losses in young bees following the initial kill of foragers. They concluded that death was not only due to pollen collected the day of collection by foragers but also due to the younger bees which consumed contaminated pollen collected earlier and stored in the colony. However, 5 to 7 days after spraying, little carbaryl residue remained; therefore, the removal of bees prior to spraying and returning them 7 days following carbaryl application was recommended to commercial raisers. MORSE (1961) found that aerial application of 1.25 lb of carbaryl/A resulted in a loss of 19,917 bees compared to control losses of 2,936 bees. The mortalities of bees were above normal for 3 weeks following the insecticide application.

Susceptibility of alfalfa leafcutting bees to carbaryl was related to metabolism differences in age and sex of the bees (GUIRGUIS and BRINDLEY 1975). Older male bees, which are more susceptible, had longer carbaryl persistence than younger bees and females of the same age. Penetration of carbaryl into the bees was one factor related to toxicity, but oxidative metabolism and conjugation mechanisms which deteriorated with age were also thought responsible for the persistence of carbaryl in the adult bee. WALLER (1969) also studied susceptibility of these bees to insecticide residues in foliage.

BARRETT (1968) determined that both biomass and numbers of arthropods were reduced more than 95% in a field treated with 2 lb of carbaryl/A. Seven weeks following spraying, the total biomass had returned to normal. Phytophagous insects were more severely affected than predaceous insects and spiders. Spiders were back to normal density 3 weeks following carbaryl application. SUTTMAN and BARRETT (1979) compared the effect of carbaryl applied at 227 g/0.1 ha (2 lb/A) on arthropods in agricultural monoculture fields and inactive field communities. The functioning taxa of monocultural communities were more affected than those of the inactive community. Plant-feeding insects were most severely reduced in number and biomass in the monoculture plots. However, the effect of biomass and numbers was delayed and lasted longer in the inactive field community.

The effect of carbaryl on earthworms has been studied. Application of 0.1% suspension of carbaryl caused paralysis and irreversible histopathologic changes to earthworms (AN DER LAN and ASPOCK 1962). Field studies by THOMPSON (1971) demonstrated a 59.8% reduction in numbers of earthworms and a 68.3% reduction in total biomass of worms in plots treated with 2 lb of carbaryl/A. In comparison to the organophosphates tested and to carbofuran, carbaryl had moderate effects upon the earthworm population.

c) Aquatic animals

LC₅₀ is the lethal concentration of insecticide where 50% of test animals died following exposure for a designated period of time. TL_m and ED₅₀ values listed in various references meant the same thing, therefore, the terms were changed here to LC₅₀ for consistency.

Carbaryl is not as toxic to fish as are various organophosphate insecticides (MACEK and McALLISTER 1970). Fish are also not as sensitive to carbaryl as they are to the highly toxic organochlorine insecticides, endrin and toxaphene, whose 96-hr LC₅₀ to bluegills are 0.6 and 3.5 ppb, respectively (JOHNSON 1968), while the LC₅₀ value of carbaryl was 2,500 ppb for 48-hr exposure to bluegills (COPE 1966). COPE (1966) also gave 48-hr LC₅₀ carbaryl values for channel catfish as 19,000 ppb and for rainbow trout as 2,000 ppb. The 96-hr LC₅₀ for juvenile striped bass was greater than 1 ppm (KORN and EARNEST 1974). Studies of the acute toxicity for various marine fish are reviewed by KATZ (1961) and BUTLER (1962 and 1963). An indirect effect upon fish involves the aquatic food chain. BURDICK *et al.* (1960) reported that 1.25 lb of carbaryl/A was not toxic to fish directly, but food items were reduced 97.2%. Table I gives the LC₅₀ values of carbaryl for various fish (PIMENTEL 1971).

Carbaryl has been shown to be more toxic to invertebrates than to vertebrates (HENDERSON *et al.* 1960, LOOSANOFF 1960). The effects of carbaryl on aquatic varieties have been studied and reviewed by STEWART *et al.* (1967) and TAGATZ *et al.* (1979). STEWART *et al.* (1967) concluded

Table I. The LC₅₀ values of carbaryl for various fish.^a

Species	Exposure time (hr)	LC ₅₀ (ppm)
Longnose killifish	24	1.75
Harlequin fish	24	3.4
Shiner perch	24	3.9
English sole	24	4.1
White mullet	24	4.25
Three-spine stickleback	24	6.7
Brown trout	48	1.5
Yellow perch	96	0.745
Coho salmon	96	0.764
Brown trout	96	1.95
Rainbow trout	96	4.38
Carp	96	5.28
Largemouth bass	96	6.4
Bluegill	96	6.76
Redear sunfish	96	11.2
Fathead minnow	96	13.0
Goldfish	96	13.2
Channel catfish	96	15.8
Black bullhead	96	20.0

^a Data from PIMENTEL (1971), p. 10.

marine arthropods were more sensitive to carbaryl and that the mollusks and fish they studied were more sensitive to 1-naphthol, a hydrolytic product of carbaryl. The 48-hr LC_{50} carbaryl values for brown shrimp were 27 ppb but only 13 ppb for white shrimp (BUTLER 1962). TAGATZ *et al.* (1979) stated the 96-hr LC_{50} for the estuarine mysid, *Mysidopsis bahia*, was 7.7 ppb. Adult Dungeness crabs demonstrated secondary poisoning within 6 hr when they developed paralysis following ingestion of cockle clams which had been exposed to 1 ppm of carbaryl or higher concentration for 24 hr (BUCHANAN *et al.* 1970). This supported the description of SNOW and STEWART (1963) of a Dungeness crab kill following carbaryl usage in an oyster bed. MUNCY and OLIVER (1963) studied the toxicity of insecticides on freshwater crayfish, *Procambarus clarki*, and concluded carbaryl was very toxic but of a magnitude less than DDT, endrin, and methyl parathion. Table II lists the LC_{50} values of carbaryl for various aquatic arthropods (PIMENTEL 1971).

The LC_{50} carbaryl values for mollusks were 2.3 ppm for bay mussel larvae at 48 hr, and 2.2 ppm for Pacific oyster larvae and 7.3 ppm for adult cockle clams at 24 hr (STEWART *et al.* 1967). DAVIS (1961) found inhibition of the development and growth of embryos and larvae of clams at 2.5 ppm and of embryos of oysters at 1.0 ppm. BUTLER *et al.* (1968) determined the LC_{50} in juvenile cockle clams at 96 hr to be 3.75 ppm. The 96-hr LC_{50} was 2.7 ppm for 1-naphthol. Growth of the clams was more inhibited by this metabolite than by carbaryl itself. A concentration of 1.6 ppm of carbaryl markedly reduced food consumption and food conversion efficiency.

Marine phytoplankton were studied following exposure to carbaryl by UKELES (1962) and BUTLER (1962 and 1963). UKELES found 1.0 ppm

Table II. The LC_{50} values of carbaryl for various aquatic arthropods.^a

Species	Exposure time (hr)	LC_{50} (ppm)
Stonefly (<i>Pteronarcella badia</i>)	24	0.005
Stonefly (<i>Claassenia sabulosa</i>)	24	0.012
Stonefly (<i>Pteronarcys californica</i>)	24	0.030
Amphipod (<i>Gammarus lacustris</i>)	24	0.040
Mud shrimp	24	0.04–0.13
Ghost shrimp	24	0.13
Shore carb	24	0.27–0.71
Dungeness carb	24	0.60–0.63
Stonefly (<i>P. californica</i>)	48	0.0013
Waterflea (<i>Daphnia pulex</i>)	48	0.006
Waterflea (<i>Simocephalus serrulatus</i>)	48	0.008
Amphipod (<i>G. lacustris</i>)	48	0.022
Ghost shrimp	48	0.03–0.08
Red crawfish	48	3.0

^a Data from PIMENTEL (1971), p. 11.