AMBIENT AQUATIC LIFE WATER QUALITY CRITERIA FOR

ACROLEIN

(CAS Registry Number 107-02-8)

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U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF WATER
OFFICE OF SCIENCE AND TECHNOLOGY
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NOTICES

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FOREWORD

Section 304(a) (l) of the Clean Water Act of 1977 (P.L. 95-217) requires the Administrator of the Environmental Protection Agency to publish water quality criteria that accurately reflect the latest scientific knowledge on the kind and extent of all identifiable effects on health and welfare that might be expected from the presence of pollutants in any body of water, including ground water. Criteria contained in this document replace any previously published EPA aquatic life criteria for the same pollutant(s).

The term "water quality criteria" is used in two sections of the Clean Water Act, section 304(a)(l) and section 303(c)(2). The term has a different program impact in each section. In section 304, the term represents a non-regulatory, scientific assessment of ecological effects. Criteria presented in this document are such scientific assessments. If water quality criteria associated with specific stream uses are adopted by a state as water quality standards under section 303, they become enforceable maximum acceptable pollutant concentrations in ambient waters within that state. Water quality criteria adopted in state water quality standards could have the same numerical values as criteria developed under section 304. However, in many situations states might want to adjust water quality criteria developed under section 304 to reflect local environmental conditions and human exposure patterns. Alternatively, states may use different data and assumptions than EPA in deriving numeric criteria that are scientifically defensible and protective of designated uses. It is not until their adoption as part of state water quality standards that criteria become regulatory. Guidelines to assist the states and Indian tribes in modifying the criteria presented in this document are contained in the Water Quality Standards Handbook (U.S. EPA 1994). This handbook and additional guidance on the development of water quality standards and other water-related programs of this agency have been developed by the Office of Water.

This final document is guidance only. It does not establish or affect legal rights or obligations. It does not establish a binding norm and cannot be finally determinative of the issues addressed. Agency decisions in any particular situation will be made by applying the Clean Water Act and EPA regulations on the basis of specific facts presented and scientific information then available.

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CONTENTS

TABLES

FIGURES

Introduction[1]

Acrolein, also known as acrylaldehyde, allyl aldehyde and 2-propenal, has a wide-variety of applications. It is used directly as a biocide for aquatic weed control, and is currently registered under the trade name MAGNACIDE® H primarily for use in irrigation canals. This product is commonly applied to surface waters at a rate of 1-15 mg/L, which is much higher than the acutely toxic levels for most aquatic animals tested (Fritz-Sheridan 1982; U.S. EPA 2007). Acrolein is also used for algae, weed and mollusk control in recirculating process water systems; for slime control in the paper industry; to protect liquid fuels against microorganisms; and to control sulfate reducing bacteria that produce corrosive hydrogen sulfide in oilfield water systems (IARC 1985; U.S. EPA 2007). It is also used for cross-linking protein collagen in leather tanning and for tissue fixation in histological samples.

Different forms of acrolein are widely used as an intermediate in the chemical industry (ATSDR 1989). The dimmer, which is prepared by a thermal, uncatalyzed reaction, has several applications including use as an intermediate for cross-linking agents, humectants, plasticizers, polyurethane intermediates, copolymers, and homopolymers and creaseproofing cotton. The monomer is utilized in synthesis via the Diels-Alder reaction as a dienophile or a diene. Acrolein is widely used in copolymerization, but its homopolymers do not appear commercially important. The copolymers of acrolein are used in photography, for textile treatment, in the paper industry, as builders in laundry and dishwasher detergents, and as coatings for aluminum and steel panels, as well as other applications.

Isolated acrolein is produced in a closed system by heterogeneously catalyzed gas-phase oxidation of propene. Acrolein is also produced as a non-isolated intermediate during the manufacture of acrylic acid. In the 1990's, worldwide production was about 120,000 tons. Worldwide capacity was estimated at 125,000 tons/year, of which U.S. capacity was 35,000 tons/year (WHO 2002).

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[1]A comprehension of the "Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and their Uses" (Stephan et al. 1985), hereafter referred to as the Guidelines, is necessary to understand the following text, tables and calculations.

Acrolein is a colorless liquid at room temperature with a structural formula of CH_2=CHCHO and a molecular weight of 56.06 g/mol. It melts at -86.95°C, boils at 52.5 to 53.5°C and has a density of 0.8410 at 20°C (Weast 1975). The vapor pressure at 20°C is 29.3 to 36.5 KPa, and its water solubility is 206 to 270 g/L at 20°C (Standen 1967; WHO 2002). It has an octanol/water partition coefficient (Log K_{ow}) range of -0.01 to 0.90 (-0.01 is recommended by Karickhoff and Long 1995), and an organic carbon/water partition coefficient (Log K_{oc}) of -2.19 to 2.43 (WHO 2002).

A flammable liquid with a pungent odor, acrolein is an unstable compound that undergoes polymerization to the plastic solid disacryl, especially under light or in the presence of alkali or strong acid (Windholz 1976). It is the simplest member of the class of unsaturated aldehydes, and the extreme reactivity of acrolein is due to the presence of a vinyl group (H_2C=H^-) and an aldehyde group on such a small molecule (Standen 1967). Additions to the carbon-carbon double bond of acrolein are catalyzed by acids and bases. The addition of halogens to this carbon-carbon double bond proceeds readily (Standen 1967).

Acrolein is released into the environment as a product of natural fermentation (WHO 2002), as a volatile component of essential oils extracted from the wood of oak trees (Slooff et al. 1994), as a product of the incomplete combustion of organic matter (Lipari et al. 1984), and by photochemical oxidation of hydrocarbons in the atmosphere (Ghilarducci and Tjeerdema, 1995). As a product of the incomplete combustion of organic matter, acrolein is released by waste incinerators, furnaces, fireplaces, power plants, burning vegetation (e.g., forest fires), combustion of polyethylene plastics, and the cooking of food (WHO 2002).

Potential routes of acrolein degradation are via volatilization, microbial metabolism, and absorption into plants by cross-linking of protein. Degradation products include 3-hydroxypropanol, acrylic acid, allyl alcohol, propanol, propionic acid and oxalic acid. A unique feature of 3-hydroxypropanol is that it is in equilibrium with acrolein, and thus does not fully degrade via hydrolysis. Data are not available to characterize the rate of acrolein photolysis in water (U.S. EPA 2007).

Bowmer et al. (1974) described the loss of acrolein by volatilization and degradation in sealed bottles and tanks of freshwater. The amounts of acrolein dissipated after eight days were 34 percent from the tank and 16 percent from the bottles. The lack of turbulence in the tank

reduced acrolein loss by volatilization to 1/20 of what would be expected if volatilization were controlled only by resistance in the gas phase and any discrete surface layers. The primary degradation reaction is reversible hydrolysis to β-hydroxypropionaldehyde, which is less volatile than acrolein (Geyer 1962).

Acrolein can enter the aquatic environment by its use as an aquatic herbicide, from industrial discharge, and from the chlorination of organic compounds in wastewater and drinking water treatment. It is often present in trace amounts in foods and is a component of smog, fuel combustion, wood, and possibly other fire and cigarette smoke.

The fate of acrolein in freshwater was observed in buffered solutions and in natural channel waters (Bowmer and Higgins 1976). Equilibrium between acrolein and its degradation products was reached in the buffered solution following dissipation of 92 percent of parent compound, but in the natural channel waters there was no indication of equilibrium, with the dissipating reaction apparently continuing on to completion. Also, in the natural channel waters, the accumulation of a reaction (degradation) product was greater at higher initial acrolein concentration, and decay was rapid when acrolein concentrations fell below 2 to 3 mg/L. The initial period of slow decline preceding the rapid dissipation period was thought to be the result of microbiological processes. Unlike earlier works (Bowmer et al. 1974), there was an 8- to 10-fold increase in the observed dissipation rate as compared to the expected rate in two of four flowing water channels, suggesting major losses in volatilization and absorption. A half-life of approximately seven hours was observed for acrolein in freshwater by Nordone et al. (1998), but the authors noted that the dissipation rate was both concentration and temperature dependent. The presence of viable microbial populations also heavily influences the acrolein degradation rates in freshwater systems (Smith et al. 1995).

In the marine environment, acrolein undergoes hydrolysis and oxidation to form β-hydroxypropanol and β-hydroxy propionic acid (Smith 1962). A half-life of less then 20 hours was reported by Rustenbil (1981).

Limited studies are available reporting the concentrations of acrolein in freshwater, and saltwater occurrence data are lacking. Analysis of Dayton, Ohio municipal effluents showed the

presence of acrolein in 6 of 11 samples, with concentrations ranging from 20 to 200 μg/L (U.S. EPA 1977). During the 1980s, acrolein was not detected in raw or treated Canadian water supplies, with the limit of detection ranging from 0.1-2.5 μg/L (Environment Canada 1989a,b,c,d; Otson 1987). For 798 well or surface water samples collected from unspecified locations in the United States, acrolein was detected (detection limit not reported) in only 2 samples, and the median concentration of acrolein in these samples was <14 μg/L (Staples et al. 1985).

Monitoring studies conducted after field application show that acrolein can be transported up to 61 miles from the point of application. Reported half-lives ranged from 2 to 20 hours based on concentrations measured downstream of application. Field studies also determined that acrolein volatilizes from treated waters and represents a source of exposure to non-target animals through inhalation (U.S. EPA 2007).

The mechanism of toxic action of acrolein, observed in mammalian and other systems, includes cell wall degradation and disrupting the cell's ability to inactivate toxic chemicals (Siemering et al. 2008). Other effects on cell energetics include reduction in intracellular ATP levels in tissue culture (Monteil et al. 1999), and reduced beating activity of myocytes (Toraason et al. 1989).

A comprehension of the "Guidelines" for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses" (Stephan et al. 1985), hereinafter referred to as the "Guidelines," and the response to public comments concerning that document (U.S. EPA 1985) is necessary to understand the following text, tables and calculations. Results of such intermediate calculations as recalculated LC50s and Species Mean Acute Values (Table 1) and chronic values (Table 2) are given to four significant figures to prevent roundoff error in subsequent calculations, not to reflect the precision of the value. The criteria presented herein are the agency's best estimate of maximum concentrations of the chemical of concern to protect most aquatic organisms, or their uses, from any unacceptable short- or long-term effects. Whenever adequately justified, a national criterion may be replaced by a site-specific criterion (U.S. EPA 1983a), which may include not only site-specific criterion concentrations (U.S. EPA

1983a), but also site-specific durations of averaging periods and site-specific frequencies of allowed excursions (U.S. EPA 1991). The latest comprehensive literature search for this document was conducted in June, 2009, with some new information also included.

Acute Toxicity to Aquatic Animals

Data that are suitable, according to the "Guidelines," for the derivation of a freshwater Final Acute Value (FAV) are included in Table 1. Fifteen species representing fourteen genera were tested with acrolein to determine its acute toxicity to these species (Table 3). Species Mean Acute Values (SMAV) ranged from 7 μg/L for the African clawed frog (*Xenopus laevis*) to 5,920 μg/L for an insect (*Peltoperia maria*). The white sucker (*Catostomus commersoni*) was the second most sensitive species tested, with a SMAV of 14 μg/L. Rainbow trout (*Oncorhynchus mykiss*) and the bluegill sunfish (*Lepomis macrochirus*) were the third and fourth most sensitive species tested, with SMAVs of 16 and 27.19 μg/L, respectively.

The least sensitive group of freshwater species to acrolein toxicity was invertebrates. The insect (*Peltoperia maria*) was the most tolerant to acrolein with a SMAV of 5,920 μg/L, followed by the midge (*Chironomus riparius*) with a SMAV of 510 μg/L, the snail (*Physa heterostropha*) with a SMAV of 368 μg/L, and the scud (*Gammarus minus*) with a SMAV of 180 μg/L. The snail *(Aplexa hypnorum*) and midge (*Tanytarsus dissimilis*) had SMAVs of >151 μg/L acrolein each. The planktonic crustacean, *Daphnia magna*, was the most acutely sensitive invertebrate to acrolein with an SMAV of <39.76.

Freshwater SMAVs and Genus Mean Acute Values (GMAV) were derived from available acute values (Tables 1 and 3). GMAVs were available for 14 genera; the most sensitive was the amphibian, *Xenopus*, which was 846 times more sensitive than the least sensitive species, an insect, *Peltoperia* (Figure 1). The four most sensitive genera were within a factor of 4.1 of one another. The freshwater FAV for acrolein is 5.920 μg/L and was calculated using the procedure described in the "Guidelines" and the GMAVs in Table 3. The FAV is slightly lower than the lowest freshwater SMAV of 7 μg/L for the African clawed frog, *X. laevis*.

The acute toxicity of acrolein to saltwater animals has been tested with only four species (Table 1). The most sensitive was the brown shrimp (*Penaeus aztecus*) with a SMAV of 100 μg/L, followed by the eastern oyster (*Crassostrea virginica*), with a SMAV of 106 μg/L. The two most tolerant species were the mysid (*Americamysis bahia*) and the sheepshead minnow (*Cyprinodon variegatus*), with SMAV values of 500 and 428 μg/L acrolein, respectively (Figure 2).

Since SMAVs are available for only three of the eight required families as specified in the Guidelines (Stephan et al. 1985), a saltwater FAV cannot be calculated for acrolein at this time.

Chronic Toxicity to Aquatic Animals

The available data that are usable according to the "Guidelines" concerning the chronic toxicity of acrolein are presented in Table 2a. All tests were conducted with measured concentrations of acrolein. Macek et al. (1976) conducted the only freshwater invertebrate chronic test. Based on the cumulatively reduced survival of *D. magna* through three generations, a chronic value of 23.83 μg/L was obtained from chronic limits of 16.9 and 33.6 μg/L (Table 2a). The acute value for this species by the same investigators was 57 μg/L, and this results in an acute-chronic ratio (ACR) of 2.392 (Table 2b).

Macek et al. (1976) also conducted a life cycle toxicity test with acrolein and the fathead minnow, *P. promelas*, that resulted in a chronic value of 11.4 μg/L based on an EC20 analysis of the data (Table 2a). Survival of newly-hatched second generation fathead minnow fry was significantly reduced at 41.7 μg/L. A dilutor malfunction killed or severely stressed the fish at an intermediate concentration (20.8 μg/L), so no second generation fish were produced. A 6-day incipient LC50 value of 84 μg/L was the only acute value reported for this species by the same authors using a flow-through test with unmeasured concentrations (Table 6).

Two additional chronic tests have been conducted with acrolein and the fathead minnow. Sabourin (1986, 1987) conducted a flow-through measured early life-stage (ELS) toxicity test

with acrolein and *P. promelas* in a reverse osmosis-treated and well water blended mixture. Embryos and larvae were exposed in a continuous-flow diluter for a total of 32 days to five concentrations of acrolein that ranged from 3.8 to 66.8 μg/L. The no-observed-effects-concentration (NOEC) and lowest-no-observed-effects-concentration (LOEC) for survival were recorded at 9.1 and 30.8 μg/L, respectively, with a resultant chronic value of 16.74 μg/L (Table 2a). The ACR of 1.774 was calculated using the acute value of 29.7 μg/L from a companion study and dividing by the chronic value of 16.74 μg/L (Table 2b).

Spehar (1989) conducted a 32-day flow-through measured ELS toxicity test with acrolein and *P. promelas* in filtered Lake Superior water. Survival, the most sensitive endpoint, was significantly reduced at 35 μg/L compared to controls, but not at acrolein concentrations of 14 μg/L and lower. Based upon survival, the chronic value was 22.14 μg/L. Spehar (1989) also determined an acute value of 27 μg/L for this species, and when divided by the chronic value of 22.14 μg/L, yields an ACR of 1.220 (Table 2b).

A 32-day ELS test was also conducted with embryos and fry of the flagfish, *Jordanella floridae* in filtered Lake Superior water (Spehar 1989). Five acrolein exposure concentrations were tested which ranged from 1.4 to 42 μg/L in the flow-through measured test. Percent hatch was not affected by any of the acrolein concentrations. At the end of the test, survival was not significantly reduced in any of the exposure concentrations; however, growth (weight) was significantly reduced in the highest exposure concentration (42 μg/L) relative to the controls. Based upon growth, the chronic limits were 16 and 42 μg/L, and the resultant chronic value for flagfish was 25.92 μg/L. A companion acute test was conducted in the study, and division of the acute value (51 μg/L) by the chronic value (25.92 μg/L) yields an ACR of 1.968 for flagfish (Table 2b).

Three valid freshwater ACRs are available for acrolein using the fourth, sixth and seventh most acutely sensitive tested species of freshwater animals (Table 3). Two ACRs were available for the fathead minnow, *P. promelas*, which differed by a factor of approximately 1.5 times. The geometric mean of these two values is 1.471. Since the three valid ACRs (1.471, 1.968 and 2.392) differed by only a factor of 1.6 (Table 3), the Final Acute to Chronic Ratio (FACR) is

calculated as the geometric mean of the three values, or 1.906. These data show that there is little difference in concentrations between the acute and chronic effects of acrolein on *D. magna* and the tested fish species. As stipulated in the Guidelines (Stephan et al. 1985), if the most appropriate species mean ACRs are less than 2.0, acclimation has probably occurred during the chronic test, and the FACR should be assumed to be 2.0. Thus the FACR for acrolein is 2.0. It appears from available data (Figure 3) that all tested freshwater species will be protected from adverse effects due to chronic acrolein exposure by the freshwater Chronic Value (3.0 μg/L).

Toxicity to Aquatic Plants

Four acceptable tests are available with freshwater plant species exposed to acrolein in tests lasting from 5 to 14 days (Table 4). Even though the exposures were measured in the studies conducted by Hughes and Alexander (1992a,b,c,d,e), the authors reported nominal effect concentrations because the acrolein concentrations at test termination was less than the detection limit. Based on this approach, the adverse effect concentrations from these freshwater tests ranged from 36 μg/L for *Anabaena flos-aquae* to 72 μg/L for the duckweed, *Lemna gibba*.

Toxicity tests with acrolein have been conducted using a single saltwater plant species (Table 4). The diatom, *Skeletonema costatum*, had a five-day EC_{50} value of 28 μg/L acrolein based on cell density.

Additional fresh- and saltwater plant information is included with "Other Data." These published studies describe the use of acrolein to control aquatic macrophytes and algae (see Table 6); no appropriate plant effect data are available. In some cases, test methods were insufficiently described to evaluate reported results. In others, because of the methods used, no actual exposure concentration under field conditions could be calculated. In a few instances, results were reported where acrolein was used in the control of the weeds, but no quantitative measurements were made (Ferguson et al. 1965, Unrau et al. 1965, van Overbeek et al. 1959).

A Final Plant Value, as defined in the Guidelines, cannot be obtained because no test in which the endpoint was biologically important and the concentrations of acrolein were

sufficiently measured has been conducted with an important aquatic plant species.

Bioaccumulation

One study was conducted to measure the bioconcentration of acrolein in freshwater animals that, according to the "Guidelines," meet the requirements for inclusion in this section of the document (Table 5). Barrows et al. (1978) measured the whole body burden in juvenile bluegill (*Lepomis macrochirus*) exposed to 13.1 μg/L acrolein for 28 days. The half-life in tissue was greater than seven days, and thin-layer chromatography was used to verify concentrations. Lipid concentrations were measured (Johnson 1980) for the test fish and the bioconcentration results were lipid normalized, which increased the bioconcentration factor from 344 to 7,167.

No bioconcentration factors are available for saltwater species based on the literature search conducted.

No U.S. FDA action level or other maximum acceptable concentration in tissue, as defined in the "Guidelines," is available for acrolein. Therefore, a Final Residue Value cannot be calculated.

Other Data

Additional data on the lethal and sublethal effects of acrolein on freshwater species that do not comply with the data requirements described in the "Guidelines" for inclusion in other tables are presented in Table 6. Reduced DNA synthesis of the green alga, *Dunaliella bioculata*, was observed at 100 μg/L (Marano and Puiseux-Dao 1982), and various species of aquatic weeds were damaged or destroyed following treatment with 500 to 25,000 μg/L of acrolein (Ferguson et al. 1965; Fritz-Sheridan 1982; Unrau et al. 1965; van Overbeek et al. 1959). Bringmann and Kuhn (1978) determined that the 72-hour toxic concentration to the protozoan, *Entosiphon sulcatum*, was 850 μg/L of acrolein.

Ninety-eight percent of *Australorbis glabratus* adult snails and 100 percent of snail embryos died after a 24-hour exposure to 10,000 μg/L (Ferguson et al. 1961), and the 24-hour EC50 of acrolein exposed Asiatic clams (*Corbicula fluminea*) was 300 μg/L (Foster 1981). Acutely fed and chronic unmeasured toxicity values were determined for the cladoceran, *Ceriodaphnia dubia* (Union Carbide Corporation 1997), yielding a ACR value of 2.857 (400÷140 μg/L), which is very similar to the ACR value of 2.392 determined for *Daphnia magna* (Macek et al. 1976). Mayfly nymphs (*Ephemerella walkeri*) were observed to avoid acrolein concentrations greater than 100 μg/L (Folmar 1978).

Ten short-term exposures (either 24 or 48 hours) with seven fish species yielded acute toxicity values in the range of 46 to 140 μg/L. Static tests with unmeasured concentrations were run by Bond et al. (1960), Folmar (1976), Louder and McCoy (1962) and Bridie et a1. (1979). The studies of Burdick et al. (1964) and Macek et al. (1976) were performed under flow-through conditions with unmeasured concentrations. The value from Bartley and Hattrup (1975), who reported 32 percent mortality of rainbow trout in 48 hours at 48 μg/L, was the only value based on a flow-through exposure with measured acrolein concentrations. Because of differences in test methods and the volatility of acrolein, no meaningful comparison of relative sensitivity among the fish species is possible.

The avoidance response of rainbow trout at 100 μg/L is above reported acute levels (Folmar 1976). Folmar (1980) reported flavor impairment of rainbow trout flesh for up to four days after a four-hour exposure to 90 μg/L.

Additional data on the lethal and sublethal effects of acrolein on saltwater species that do not comply with data requirements described in the "Guidelines" for inclusion in other tables are presented in Table 6. The 48-hour LC50 values for three saltwater species are in the range from 240 to 2,100 μg/L, with the juvenile longnose killifish, *Fundulus similis*, being the most sensitive. Rustenbil (1981) observed detachment of the mussel, *Mytilus edulis*, at a concentration of 600 μg/L acrolein.

Unused Data

Based on the requirements set forth in the guidelines (Stephan et al. 1985), the following studies are not acceptable for the following reasons and are classified as unused data. Some data concerning the effects of acrolein on aquatic organisms and their uses were not used because the tests were conducted in mixtures of chemicals (i.e., Albarino et al. 2007; Blondeau 1959; Bowmer and Smith 1984; Corbus 1982; Donohue et al. 1966; Hayworth and Melwani 2004; McLarty 1960; Power 1982; Snyder-Conn 1997) or a control was not included with the study (i.e., Bowmer and Sainty 1977; Bowmer et al. 1979).

Results were not used when the test organism or the test material were not adequately described (i.e., Baker Performance Chemical 1991; Hopf and Muller 1962; Juhnke and Luedemann 1978; Mayer 1974; Tchan and Chiou 1977), the organism tested is not resident to North America (i.e., Alabaster 1969), the site was previously contaminated (i.e., Underwood and Paterson 1993), or the test material was just sprayed on the plants (i.e., Blackburn 1963; Siemering et al. 2008).

Baker Performance Chemical (1991), Beauchamp et al. (1985), Butler (1965a,b), Eisler (1994), Epstein and Legator (1971), Folmar (1977), Freidig et al. (1999), Grahl (1983), McKim (1977), Russom (1997), Seward et al. (2001), Siemering et al. (2003) and Yarbrough and Schultz (2007) compiled data from other sources, and non-English studies were not translated (i.e., Baran-Marano and Izard 1968; Bringmann and Kuhn 1980, 1981; Bringmann et al. 1980). Data were not used if there were no interpretable concentration, time, or response data, or if the toxicity test evaluated only a limited number of test organisms (<six) or less than three exposure concentrations (i.e., Applegate et al. 1957; Bentivegna and Fernandez 2005; Bentivegna et al. 2004; Frank et al. 1961; Jordan et al. 1962; Kobbia 1982; MacPhee and Ruelle 1969; Nordone et al. 1998; Peterson et al. 1994; St. Amant et al. 1964).

Data were not used when organisms were dosed by injection (i.e., McKim et al. 1987) or gavage (i.e., Loeb and Kelly 1963), or if no useable data on acrolein toxicity or bioconcentration was presented (i.e., Anderson 1946; Coello and Khan 1998; Dean et al. 2004; Geiger et al. 1990;

Johnson and Epel 1983; Rebhun and Ben-Amotz 1986; Union Carbide Chemical and Plastics Co. 1991; Woodiwiss and Fretwell 1974; Yarzhombek et al. 1991). Dypbukt et al. (1989), Horton et al. (1997), Minko et al. (2008), Seiner et al. (2007), Szadkowski and Myers (2008) and Thompson and Burcham (2008) only exposed enzymes, excised or homogenized tissue, or cell cultures.

Summary

Sufficient data are available to derive freshwater criteria for acrolein, but the lack of data precludes the estimation of saltwater criteria, a final plant value and a residue value. Additional studies are needed to provide the necessary data to satisfy the criteria derivation requirement as currently specified in the Guidelines.

Acute toxicity of acrolein was tested in fifteen species representing fourteen genera of freshwater organisms. Toxicity values ranged from 7 μg/L for the African clawed frog *Xenopus laevis* to 5,920 μg/L for the insect *Peltoperia maria*. Of the four most sensitive freshwater species tested, one was an amphibian and three were fish species (Table 3 and Figure 1). No relationships have been demonstrated between water quality characteristics (such as hardness and pH) and toxicity. The least sensitive group of freshwater species to acrolein toxicity was invertebrates. The freshwater Final Acute Value (FAV) is 5.920 μg/L, which is slightly lower than the LC50 for the most sensitive tested species, *X. laevis*. Acute toxicity has been tested with only four species of saltwater organisms (Table 1 and Figure 2). Species Mean Acute Values ranged from 100 μg/L for the brown shrimp (*Penaeus aztecus*) to 500 μg/L for the mysid (*Americamysis bahia*). Since SMAVs are available for only three of the eight required families as specified in the Guidelines (Stephan et al. 1985), a saltwater FAV cannot be calculated for acrolein at this time.

Chronic toxicity of acrolein was tested in three freshwater species, but no saltwater species (Table 2a and Figure 3). More studies are needed for marine animals in order to estimate acute and chronic saltwater criteria for acrolein. The most chronically sensitive freshwater

species tested was the fathead minnow, *Pimephales promelas*, with a Chronic Value (CV) of 11.4 μg/L based on reduced survival (Macek et al. 1976). Two additional studies with this species had measured CVs of 16.74 μg/L (Sabourin 1986) and 22.14 μg/L (Spehar 1989), also based upon a survival endpoint. The remaining freshwater fish tested, the flagfish *Jordanella floridae*, had a CV of 25.92 μg/L based on growth (Spehar 1989). The only freshwater invertebrate tested chronically was the cladoceran *Daphnia magna*, with a CV of 23.83 μg/L based on survival (Macek et al. 1976). Data were available to calculate a Final Acute-Chronic Ratio (FACR) using three freshwater species: *D. magna*, the fathead minnow and the flagfish. Since the three valid ACRs (2.392, 1.471 and 1.968) differed by only a factor of 1.6, the FACR is calculated as the geometric mean of the three values, or 1.906. These data show that there is little difference in concentrations between the acute and chronic effects of acrolein on *D. magna* and the tested fish species. As stipulated in the Guidelines (Stephan et al. 1985), if the most appropriate species mean ACRs are less than 2.0, acclimation has probably occurred during the chronic test, and the FACR should be assumed to be 2.0. Thus the FACR for acrolein is 2.0. It appears from available data that all tested freshwater species will be protected from adverse effects due to acrolein by the freshwater Chronic Value (Figure 3).

Acceptable data on the toxicity of acrolein to freshwater and saltwater plants are available for five species. Freshwater algae are affected by concentrations of acrolein as low as 36 μg/L, based on data for three species. The duckweed, *Lemna gibba*, was similarly affected at 72 μg/L acrolein, as was the marine diatom, *Skeletonema costatum*, with a EC_{50} value of 28 μg/L.

One study estimated the bioconcentration of acrolein in bluegill, with a lipid normalized freshwater bioconcentration factor of 7,167 (Barrows et al. 1978). Bioconcentration factors are not available for saltwater species based on the literature search conducted. No U.S. FDA action level or other maximum acceptable concentration in tissue, as defined in the "Guidelines," is available for acrolein. Therefore, a Final Residue Value cannot be calculated.

National Criteria

The procedures described in the "Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses" (Stephan et al. 1985) indicate that, except possibly where a locally important species is very sensitive, freshwater aquatic organisms and their uses should not be affected unacceptably if the one-hour average concentration of acrolein does not exceed 3.0 μg/L more than once every three years on the average, and if the four-day average concentration of acrolein does not exceed 3.0 μg/L more than once every three years on the average.

Since SMAVs are available for only three of the eight required families as specified in the Guidelines (Stephan et al. 1985), a saltwater FAV cannot be calculated at this time for acrolein. Likewise, the lack of chronic data precludes the development of a saltwater chronic criterion at this time.

Implementation

As discussed in the Water Quality Standards Regulation (U.S. EPA 1983b) and the Foreword to this document, a water quality criterion for aquatic life has regulatory impact only after it has been adopted in a state or tribal water quality standard. Such a standard specifies a criterion for a pollutant that is consistent with a particular designated use. With the concurrence of the U.S. EPA, states and tribes designate one or more uses for each body of water or segment thereof and adopt criteria that are consistent with the use(s) (U.S. EPA 1987, 1994). In each standard a state or tribe may adopt the national criterion, if one exists, or, if adequately justified, a site-specific criterion (if the site is an entire state, the site-specific criterion is also a state-specific criterion).

Site-specific criteria may include not only site-specific criterion concentrations (U.S. EPA 1994), but also site-specific, and possibly pollutant-specific, durations of averaging periods and frequencies of allowed excursions (U.S. EPA 1991). The averaging periods of "one hour"

and "four days" were selected by the U.S. EPA on the basis of data concerning how rapidly some aquatic species react to increases in the concentrations of some pollutants, and "three years" is the Agency's best scientific judgment of the average amount of time aquatic ecosystems should be provided between excursions (Stephan et al. 1985; U.S. EPA 1991). However, various species and ecosystems react and recover at greatly different rates. Therefore, if adequate justification is provided, site-specific and/or pollutant-specific concentrations, durations, and frequencies may be higher or lower than those given in national water quality criteria for aquatic life.

Use of criteria, which have been adopted into state or tribal water quality standards, for developing water quality-based permit limits requires selection of an appropriate wasteload allocation model. Although dynamic models are preferred for the application of these criteria (U.S. EPA 1991), limited data or other considerations might require the use of a steady-state model (U.S. EPA 1986). Guidance on mixing zones and the design of monitoring programs is also available (U.S. EPA 1987, 1991).

Figure 1. Ranked Summary of Acrolein GMAVs - Freshwater.

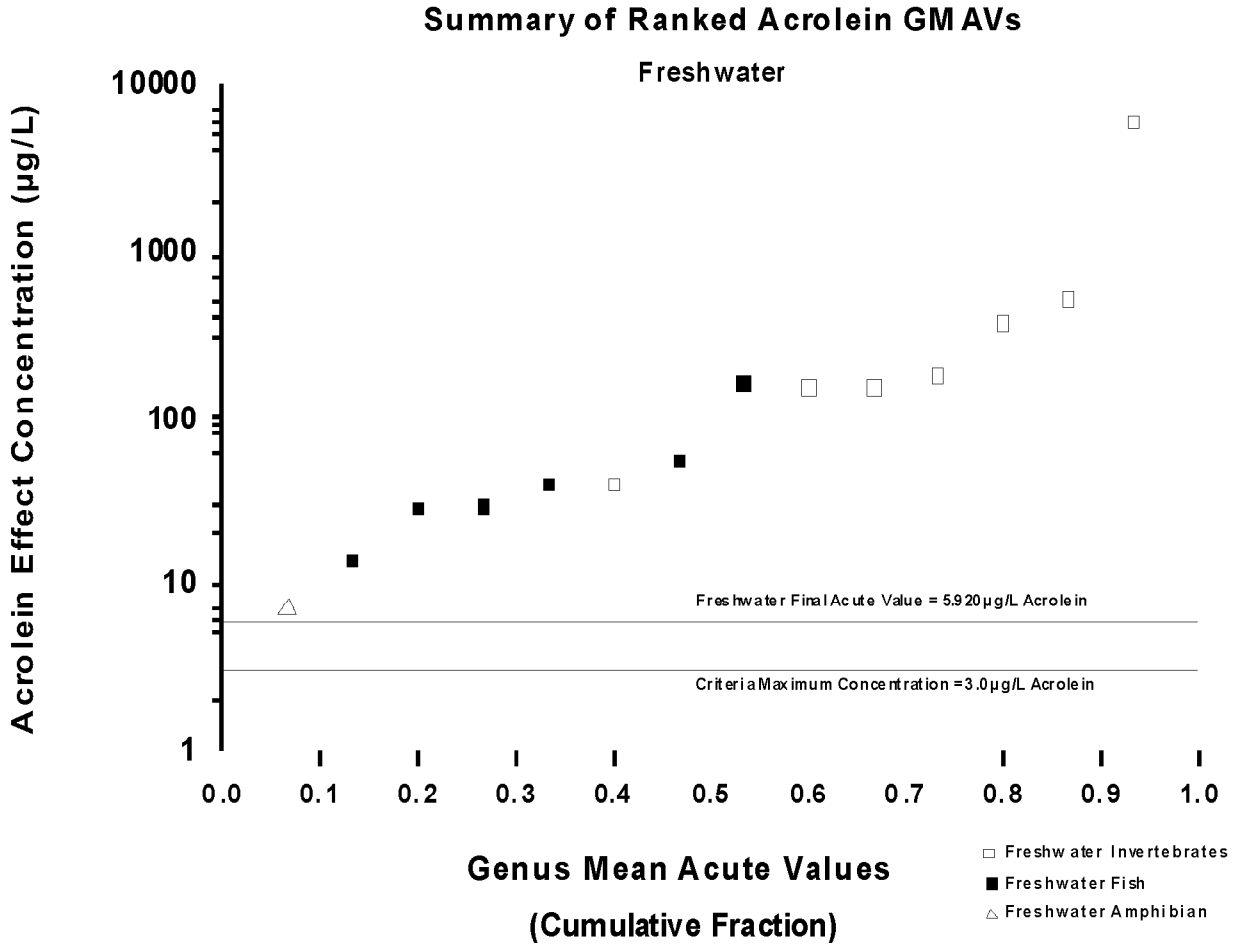

Figure 2. Ranked Summary of Acrolein GMAVs - Saltwater.

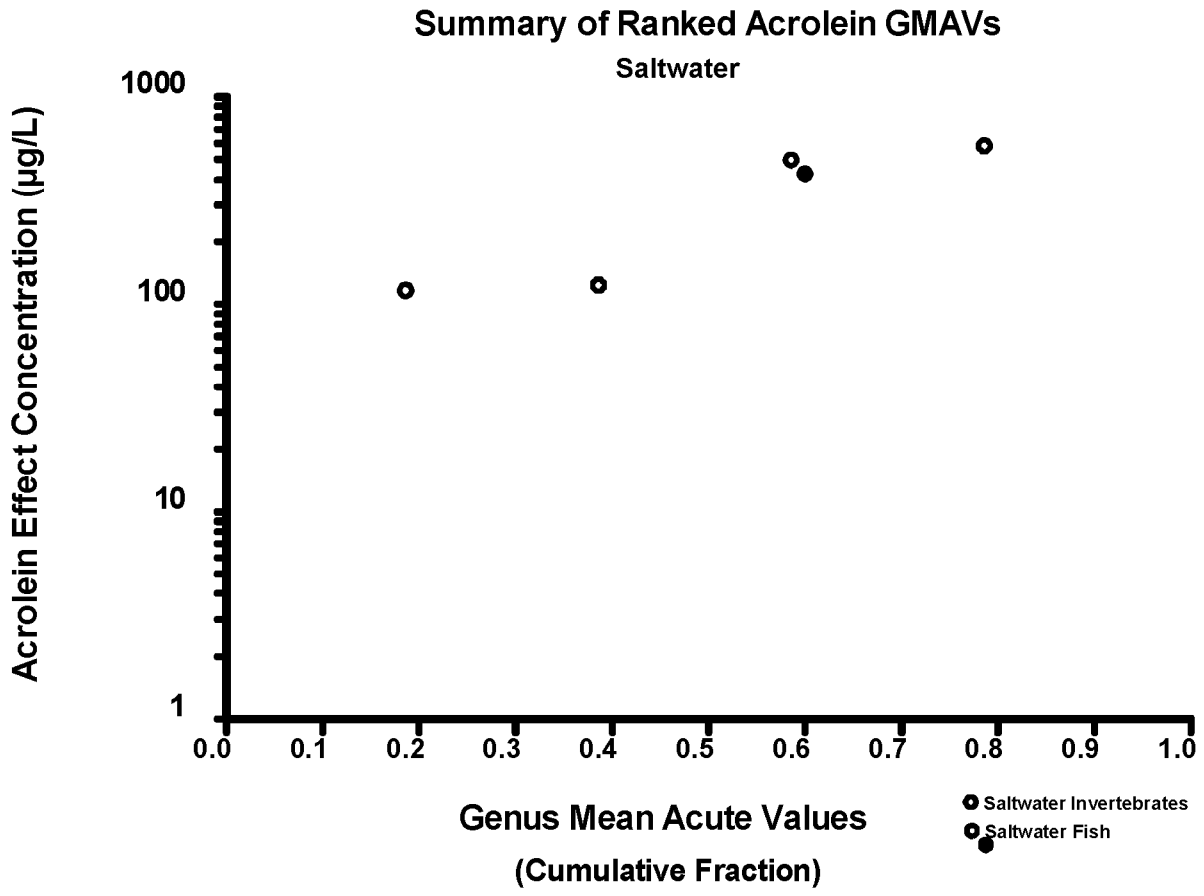

Figure 3. Chronic Toxicity of Acrolein to Aquatic Animals.

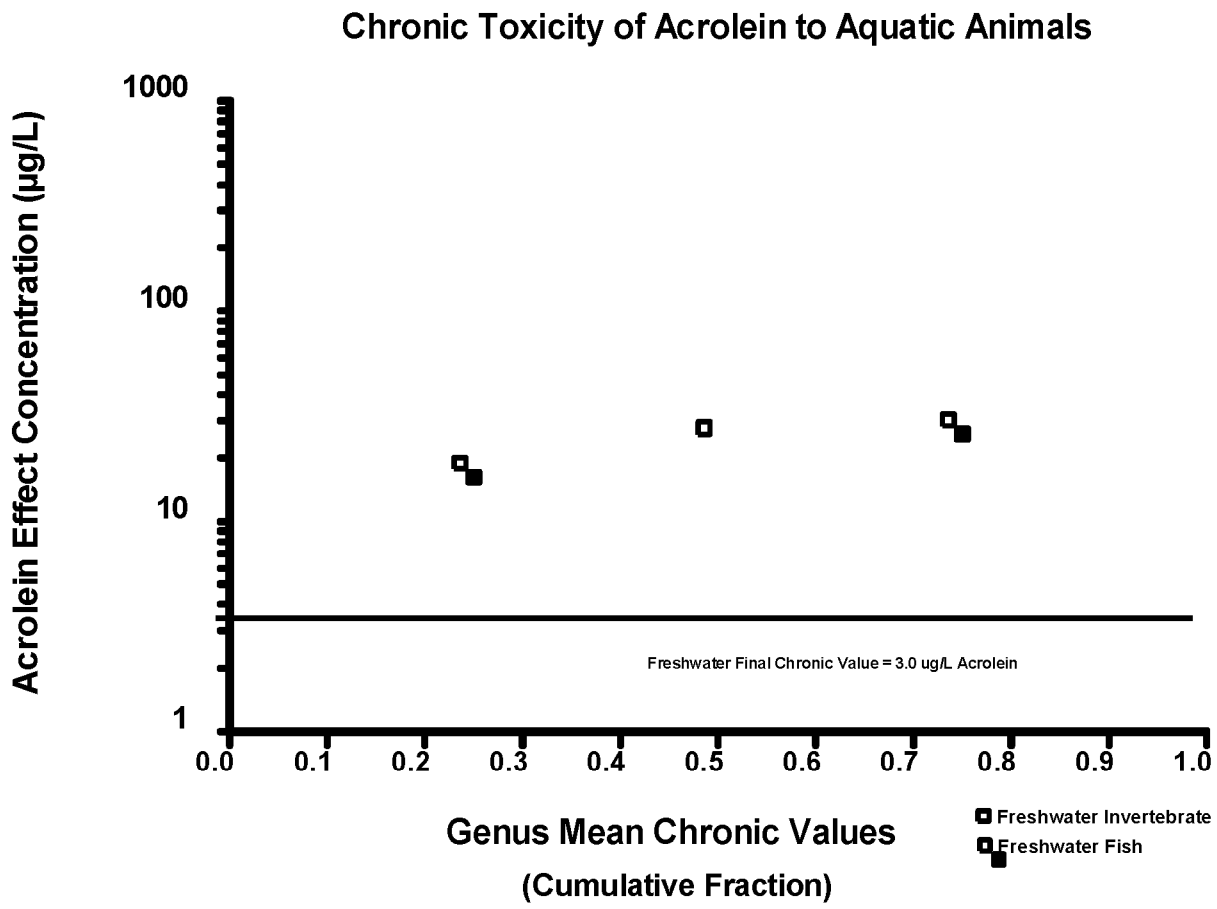

Table 1. Acute Toxicity of Acrolein to Aquatic Animals.

Species	Method[a]	Chemical	LC_{50} or EC_{50} (µg/L)	Species Mean Acute Value[b] (µg/L)	Reference
FRESHWATER SPECIES					
Snail (adult), *Aplexa hypnorum*	F, M	-	>151	>151	Holcomb et al. 1987
Snail (juvenile), *Physa heterostropha*	S, U	-	368	368	Horne and Oblad 1983
Cladoceran, *Daphnia magna*	S, U	99%	57	-	Macek et al. 1976
Cladoceran, *Daphnia magna*	S, U	-	80	-	USEPA 1978
Cladoceran, *Daphnia magna*	S, U	-	93	-	Randall and Knopp 1980
Cladoceran (<24-hr old), *Daphnia magna*	S, U	≥80%	83	-	LeBlanc 1980
Cladoceran (<24-hr old), *Daphnia magna*	F, M	-	51	-	Holcomb et al. 1987
Cladoceran, *Daphnia magna*	F, M	96.4%	<31	<39.76	Blakemore 1990
Scud (juvenile), *Gammarus minus*	S, U	-	180	180	Horne and Oblad 1983
Insect (juvenile), *Peltoperia maria*	S, U	-	5,920	5,920	Horne and Oblad 1983
Midge (juvenile), *Chironomus riparius*	S, U	-	510	510	Horne and Oblad 1983
Midge (3rd and 4th instar), *Tanytarsus dissimilis*	F, M	-	>151	>151	Holcomb et al. 1987
Coho salmon (12-17 months old), *Oncorhynchus kisutch*	S, U	-	68	68	Lorz et al.1979
Rainbow trout (45.7 mm), *Oncorhynchus mykiss*	S, U	-	74	-	Birge et al. 1982
Rainbow trout (juvenile), *Oncorhynchus mykiss*	S, U	-	180	-	Horne and Oblad 1983

Table 1. Acute Toxicity of Acrolein to Aquatic Animals (continued).

Species	Method[a]	Chemical	LC_{50} or EC_{50} (µg/L)	Species Mean Acute Value[b] (µg/L)	Reference
FRESHWATER SPECIES					
Rainbow trout (juvenile), *Oncorhynchus mykiss*	R, M	-	38	-	Venturino et al. 2007
Rainbow trout, *Oncorhynchus mykiss*	F, M	96.4%	<31	-	Bowman 1990a
Rainbow trout (2.5 g), *Oncorhynchus mykiss*	F, M	-	16	16	Holcomb et al. 1987
Fathead minnow (adult), *Pimephales promelas*	S, U	-	320	-	Union Carbide Corp. 1974
Fathead minnow (43.2 mm), *Pimephales promelas*	S, M	-	45	-	Birge et al. 1982
Fathead minnow (42-46 day old), *Pimephales promelas*	S, U	99%	14.0	-	Geiger et al. 1986
Fathead minnow (32-day old), *Pimephales promelas*	R, M	99%	19.5	-	Geiger et al. 1986
Fathead minnow (43.2 mm), *Pimephales promelas*	F, M	-	61	-	Birge et al. 1982
Fathead minnow, *Pimephales promelas*	F, M	-	29.7	-	Sabourin 1986
Fathead minnow (1-day old & 30-day old), *Pimephales promelas*	F, M	97%	27	-	Spehar 1989
Fathead minnow (0.4 g), *Pimephales promelas*	F, M	-	14	28.77	Holcomb et al. 1987
White sucker (3.9 g), *Catostomus commersoni*	F, M	-	14	14	Holcomb et al. 1987
Flagfish (1-day old), *Jordanella floridae*	F, M	97%	60	-	Spehar 1989
Flagfish (30-day old), *Jordanella floridae*	F, M	97%	51	55.32	Spehar 1989

Table 1. Acute Toxicity of Acrolein to Aquatic Animals (continued).

Species	Method[a]	Chemical	LC_{50} or EC_{50} (µg/L)	Species Mean Acute Value[b] (µg/L)	Reference
FRESHWATER SPECIES					
Bluegill (1.0 g), *Lepomis macrochirus*	S, U	-	100	-	Louder and McCoy 1962
Bluegill, *Lepomis macrochirus*	S, U		90	-	USEPA 1978
Bluegill (young of year), *Lepomis macrochirus*	S, U	≥80%	90	-	Buccafusco et al. 1981
Bluegill, *Lepomis macrochirus*	F, M	-	33	-	Holcomb et al. 1987
Bluegill, *Lepomis macrochirus*	F, M	96.4%	22.4	27.19	Bowman 1990b
Largemouth bass (1.5 g), *Micropterus salmoides*	S, U	-	160	160	Louder and McCoy 1962
African clawed frog (tadpole), *Xenopus laevis*	F, M	-	7	7	Holcomb et al. 1987
SALTWATER SPECIES					
Eastern oyster, *Crassostrea virginica*	F, M	94.7%	106	106	Bettencourt 1994a
Mysid, *Americamysis bahia*	F, M	94.7%	500	500	Bettencourt 1994b
Brown shrimp (adult), *Penaeus aztecus*	F, U	-	100	100	Butler 1965a
Sheepshead minnow, *Cyprinodon variegatus*	F, M	94.7%	428	428	Bettencourt 1994c

[a] S = static; R = renewal; F = flow-through; M = measured; U = unmeasured.
[b] Each Species Mean Acute Value was calculated from the associated underlined number(s) in the preceding column based on recommendations in the Guidelines (e.g., a flow-through measured test value takes precedence over static tests).

Table 2a. Chronic Toxicity of Acrolein to Aquatic Animals.

Species	Test[a]	Chemical	Chronic Limits (µg/L)[b]	Chronic Value (µg/L)	Reference
FRESHWATER SPECIES					
Cladoceran, *Daphnia magna*	LC	99%	16.9-33.6	23.83	Macek et al. 1976
Fathead minnow, *Pimephales promelas*	LC	99%	-	11.4[c]	Macek et al. 1976
Fathead minnow, *Pimephales promelas*	ELS	-	9.1-30.8	16.74	Sabourin 1986, 1987
Fathead minnow, *Pimephales promelas*	ELS	97%	14-35	22.14	Spehar 1989
Flagfish, *Jordanella floridae*	ELS	97%	16-42	25.92	Spehar 1989
SALTWATER SPECIES					

[a] LC = life-cycle or partial life-cycle; ELS = early life-stage.
[b] Based upon measured concentrations of acrolein.
[c] Based on EC20 analysis of data (see text)

Table 2b. Acute-Chronic Ratios.

Acute-Chronic Ratios				
Species	**Acute Value (µg/L)**	**Chronic Value (µg/L)**	**Ratio**	**Reference**
Cladoceran, *Daphnia magna*	57	23.83	2.392	Macek et al. 1976
Fathead minnow, *Pimephales promelas*	29.7	16.74	1.774	Sabourin 1986, 1987
Fathead minnow, *Pimephales promelas*	27	22.14	1.220	Spehar 1989
Flagfish, *Jordanella floridae*	51	25.92	1.968	Spehar 1989

Table 3. Ranked Genus Mean Acute Values with Species Mean Acute-Chronic Ratios

Rank[a]	Genus Mean Acute Value (µg/L)	Species	Species Mean Acute Value (µg/L)[b]	Species Mean Acute-Chronic Ratio[c]
		FRESHWATER SPECIES		
14	5,920	Insect, *Peltoperia maria*	5,920	-
13	510	Midge, *Chironomus riparius*	510	-
12	368	Snail, *Physa heterostropha*	368	-
11	180	Scud, *Gammarus minus*	180	-
10	>151	Snail, *Aplexa hypnorum*	>151	-
9	>151	Midge, *Tanytarsus dissimilis*	>151	-
8	160	Largemouth bass, *Micropterus salmoides*	160	-
7	55.32	Flagfish, *Jordanella floridae*	55.32	1.968
6	<39.76	Cladoceran, *Daphnia magna*	<39.76	2.392
5	32.98	Coho salmon, *Oncorhynchus kisutch*	68	-
		Rainbow trout, *Oncorhynchus mykiss*	16	-
4	28.77	Fathead minnow, *Pimephales promelas*	28.77	1.471
3	27.19	Bluegill, *Lepomis macrochirus*	27.19	-
2	14	White sucker, *Catostomus commersoni*	14	-
1	7	African clawed frog, *Xenopus laevis*	7	-

[a] Ranked from the most resistant to the most sensitive based on Genus Mean Acute Value.
[b] From Table 1.
[c] From Table 2b.

Table 3. Ranked Genus Mean Acute Values with Species Mean Acute-Chronic Ratios (continued).

SALTWATER SPECIES				
Rank[a]	Genus Mean Acute Value (µg/L)	Species	Species Mean Acute Value (µg/L)[b]	Species Mean Acute-Chronic Ratio[c]
4	500	Mysid, *Americamysis bahia*	500	-
3	428	Sheepshead minnow, *Cyprinodon variegatus*	428	-
2	106	Eastern oyster, *Crassostrea virginica*	106	-
1	100	Brown shrimp, *Penaeus aztecus*	100	-

[a] Ranked from the most resistant to the most sensitive based on Genus Mean Acute Value.
[b] From Table 1.
[c] From Table 2b.

Fresh Water

Final Acute Value = **5.920 µg/L**
Criterion Maximum Concentration = 5.920/2 = **3.0 µg/L**
Final Acute-Chronic Ratio = 2.0 (see text)
Final Chronic Value = (5.920 µg/L)/2.0 = **3.0 µg/L**

Salt Water

Final Acute Value = **cannot be calculated**
Criterion Maximum Concentration = **cannot be calculated**
Final Acute-Chronic Ratio = **NA**
Final Chronic Value =**cannot be calculated**

Table 4. Toxicity of Acrolein to Aquatic Plants.

Species	Chemical	Method[a]	Duration (days)	Effect	Concentration[b] (µg/L)	Reference
FRESHWATER SPECIES						
Blue green alga, *Anabaena flos-aquae*	95%	S, M	5	EC_{50} (cell density)	36	Hughes and Alexander 1992a
Green alga, *Pseudokirchneriella subcapitata*	95%	S, M	5	EC_{50} (cell density)	44	Hughes and Alexander 1992b
Diatom, *Navicula pelliculosa*	95%	S, M	5	EC_{50} (cell density)	47	Hughes and Alexander 1992c
Duckweed, *Lemna gibba*	95%	S, M	14	EC_{50} (frond #)	72	Hughes and Alexander 1992d
SALTWATER SPECIES						
Diatom, *Skeletonema costatum*	95%	S, M	5	EC_{50} (cell density)	28	Hughes and Alexander 1992e

[a] S = static; R = renewal; F = flow-through; M = measured; U = unmeasured.
[b] Effect based on nominal concentration of active ingredient at test initiation. Concentration of test material decreased to non-detectable levels by test termination.

Table 5. Bioaccumulation of Acrolein by Aquatic Organisms.

Species	Chemical	Conc. in Water (µg/L)[a]	Duration (days)	Tissue	Percent Lipid	BCF[b]	Normalized BCF[c]	Reference
FRESHWATER SPECIES								
Bluegill (0.37-0.94 g), *Lepomis macrochirus*	-	13.1	28	Whole body	4.8	344	7,167	Barrows et al. 1978, Veith et al. 1980 Johnson 1980
SALTWATER SPECIES								

[a] Measured concentration of acrolein.
[b] Bioconcentration factor (BCF) is based on the measured concentration of acrolein in water and in tissue.
[c] BCF was normalized to 1% lipid by dividing the BCF by the percent lipid.

Table 6. Other Data on Effects of Acrolein on Aquatic Organisms.

Species	Chemical	Duration	Effect	Concentration (µg/L)	Reference
FRESHWATER SPECIES					
Blue-green alga, *Anabaena* sp.	92%	24 hr	IC50 @ 25°C (photosynthesis)	690	Fritz-Sheridan 1982
Green alga, *Cladophora glomerata*	92%	24 hr	IC50 @ 15°C (photosynthesis)	680	Fritz-Sheridan 1982
Green alga, *Cladophora glomerata*	92%	24 hr	IC50 @ 20°C (photosynthesis)	1,070	Fritz-Sheridan 1982
Green alga, *Cladophora glomerata*	92%	24 hr	IC50 @ 25°C (photosynthesis)	1,000	Fritz-Sheridan 1982
Green alga, *Cladophora glomerata*	92%	24 hr	IC50 @ 30°C (photosynthesis)	760	Fritz-Sheridan 1982
Green alga, *Dunaliella bioculata*	-	48 hr	Reduced DNA synthesis	100	Marano and Puiseux-Dao 1982
Green alga, *Enteromorpha intestinalis*	92%	24 hr	IC50 @ 20°C (photosynthesis)	2,500	Fritz-Sheridan 1982
Green alga, *Enteromorpha intestinalis*	92%	24 hr	IC50 @ 25°C (photosynthesis)	1,800	Fritz-Sheridan 1982
Aquatic macrophytes, *Najas* sp., *Ceratophyllum* sp. and *Ipomea* sp.	-	-	Destroyed or badly scorched one week after application	25,000	Ferguson et al. 1965
Pondweed, *Potamogeton crispus*	-	5 hr	Decayed in 6 days	20,000	Unrau et al. 1965
Aquatic macrophyte, *Elodea densa*	-	24 hr	Cell deterioration	500	van Overbeek et al. 1959
Protozoan, *Entosiphon sulcatum*	-	72 hr	Toxic concentration	850	Bringmann and Kuhn 1978
Snail (adult), *Australorbis glabratus*	-	24 hr	98% mortality	10,000	Ferguson et al. 1961
Snail (embryo), *Australorbis glabratus*	-	24 hr	100% mortality	10,000	Ferguson et al. 1961
Asiatic clam (veliger), *Corbicula fluminea*	-	24 hr	EC50	300	Foster 1981
Cladoceran, *Ceriodaphnia dubia*	-	48 hr	LC50 (fed)	400	Union Carbide Corporation 1997

Table 6. Other Data on Effects of Acrolein on Aquatic Organisms (continued).

Species	Chemical	Duration	Effect	Concentration (µg/L)	Reference
FRESHWATER SPECIES					
Cladoceran, *Ceriodaphnia dubia*	-	7 days	Chronic value (reproduction)	140	Union Carbide Corporation 1997
Mayfly (nymph), *Ephemerella walkeri*	-	1 hr	Avoidance	>100	Folmar 1978
Midge (1st instar), *Chironomus* sp.	-	24 hr	LC50	2,830	Venturino et al. 2007
Black fly (last instar), *Simulium* sp.	-	24 hr	LC50	600	Venturino et al. 2007
Coho salmon (12-17 months old), *Oncorhynchus kisutch*	-	96 hr	Adverse histological effects on gill, kidney and liver	50	Lorz et al.1979
Chinook salmon (fingerling), *Oncorhynchus tshawytscha*	-	24 hr	LC50	80	Bond et al. 1960
Rainbow trout (fingerling), *Oncorhynchus mykiss*	-	24 hr	LC50	65	Bond et al. 1960
Rainbow trout (fry), *Oncorhynchus mykiss*	-	24 hr	LC50	140	Folmar 1976
Rainbow trout (fry), *Oncorhynchus mykiss*	-	1 hr	Avoidance	100	Folmar 1976
Rainbow trout, *Oncorhynchus mykiss*	92%	48 hr	32% mortality	48	Bartley and Hattrup 1975
Rainbow trout, *Oncorhynchus mykiss*	-	4 hr	Tainted flesh at 1 and 4 days post exposure	90	Folmar 1980
Brown trout (fingerling), *Salmo trutta*	-	24 hr	Mean time to death	46	Burdick et al. 1964
Goldfish (6.2 cm), *Carassius auratus*	-	24 hr	LC50 (aerated)	<80	Bridie et al. 1979
Fathead minnow, *Pimephales promelas*	-	6 days	Incipient LC50	84	Macek et al. 1976

Table 6. Other Data on Effects of Acrolein on Aquatic Organisms (continued).

Species	Chemical	Duration	Effect	Concentration (µg/L)	Reference
FRESHWATER SPECIES					
Fathead minnow, *Pimephales promelas*	-	48 hr	LC50	115	Louder and McCoy 1962
Bluegill (fingerling), *Lepomis macrochirus*	-	24 hr	Mean time to death	79	Burdick et al. 1964
Bluegill (92 ± 9mm), *Lepomis macrochirus*	-	1 hr	Adverse effect on cough frequency	70	Carlson 1990
Mosquitofish, *Gambusia affinis*	-	48 hr	LC50	61	Louder and McCoy 1962
SALTWATER SPECIES					
Barnacle (adult), *Balanus eburneus*	92%	48 hr	LC50 (aerated)	2,100	Dahlberg 1971
Barnacle (adult), *Balanus eburneus*	92%	48 hr	LC50 (aerated)	1,600	Dahlberg 1971
Eastern oyster, *Crassostrea virginica*	-	96 hr	55 (shell growth)	55	Butler 1965a
Mussel (1.5 mm), *Mytilus edulis*	-	24 hr	Detachment	600	Rustenbil 1981
Longnose killifish (juvenile), *Fundulus similis*	-	48 hr	LC50	240	Butler 1965b Mayer 1987

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