ACUTE TOXICITY OF FIRE-RETARDANT AND FOAM-SUPPRESSANT CHEMICALS TO HYALELLA AZTECA (SAUSSURE)

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Abstract—Acute toxicity tests were conducted with Hyalella azteca Saussure (an amphipod) exposed in soft and hard waters to three fire retardants (Fire-Trol GTS-R, Fire-Trol LCG-R, and Phos-Chek D75-F) and two foam suppressants (Phos-Chek WD-881 and Silv-Ex). The chemicals were slightly to moderately toxic to amphipods. The most toxic chemical to amphipods in soft and hard water was Phos-Chek WD-881 (96-h mean lethal concentration [LC50] equal to 10 mg/L and 22 mg/L, respectively), and the least toxic chemical to amphipods in soft water was Fire-Trol GTS-R (96-h LC50 equal to 127 mg/L) and in hard water was Fire-Trol LCG-R (96-h LM50 equal to 535 mg/L). Concentrations of ammonia in tests with the three fire retardants and both water types were greater than reported LC50 values and probably were the major toxic component. Estimated un-ionized ammonia concentrations near the LC50 were frequently less than the reported LC50 ammonia concentrations for amphipods. The three fire retardants were more toxic in soft water than in hard water even though ammonia and un-ionized ammonia concentrations were higher in hard water than in soft water tests. The accidental entry of fire-fighting chemicals into aquatic environments could adversely affect aquatic invertebrates, thereby disrupting ecosystem function.

Keywords—Ammonia   Amphipods   Fire retardants   Foam suppressants   Hyalella azteca

INTRODUCTION

Yearly, millions of liters of fire-retardant chemicals are used on a wide array of ecosystems for suppression and control of range and forest fires [1]. These chemicals are often applied in environmentally sensitive areas, which may contain endangered, threatened, or economically significant plant and animal species. Relatively little information is available on the acute toxicity of these chemicals to aquatic life or on their effect on the environment as a whole.

Long-term fire-retardant chemicals and short-term fire-suppressant foams are two general categories of chemicals typically used in fire fighting. Long-term fire-retardant chemicals are typically composed of ammonium sulfate, ammonium phosphate, or polyphosphate with an attapulgite clay thickener such as hydrated magnesium silicate, or di-ammonium phosphate with a guar gum derivative. Long-term retardants result in the formation of a combustion inhibiting agent on the fuel following evaporation of the carrier. The effectiveness of these salt formulations in retarding combustion depends greatly on the amount of salt deposited per unit of surface area. Salt content is often increased by using highly concentrated solutions that are highly corrosive [2]. Products are formulated with inhibitors such as sodium ferrocyanide and tolyltriazole to control corrosion. They also contain small amounts of ferric oxide or other coloring agents to mark the location of retardant drops (C. Johnson and C. George, personal communication).

Although the extensively used ammonium compounds are essentially fertilizer formulations and are thought to have minimal toxicological or ecological impact, fish kills have occurred in streams accidentally contaminated by fire-retardant chemicals [2]. Studies have reported the toxicity of the active ammonium salts found in most fire-retardant chemicals [3–6], but there are few reports of studies exposing aquatic animals to actual fire-retardant chemicals [7].

Short-term fire-suppressant foams are typically composed of surfactants and a variety of solvents. Fire-suppressant foams enhance the extinguishing power of water by increased water retention on fuel sources or by reduced evaporation or both. The surfactant portion of foam suppressants has been studied and was determined to be detrimental to aquatic life because it decreases water tension, thereby decreasing the aquatic organism’s ability to obtain life-sustaining oxygen [8,9]. Few studies exposing aquatic animals to actual fire-suppressant chemicals have been reported [10].

Based upon the paucity of reported studies concerning fire-retardant chemicals and formulations, it is impossible to ascertain their effect on organisms without additional research. Moreover, the effects of repeated applications of fire-fighting chemicals on aquatic and terrestrial ecosystems are unknown. Fire managers and policy developers need information on the biological effects of fire-control chemicals to ensure that sound decisions are made concerning fire-fighting activities on private, state, and federal lands.

The toxicity of five fire-retardant and foam-suppressant chemicals was determined for Hyalella azteca. The chemicals tested were selected because they are the most common chemicals used to fight forest and rangeland fires and are currently applied to a wide variety of habitats. Tests were conducted with three fire retardants, Fire-Trol GTS-R, Fire-Trol LCG-R, and Phos-Chek D75-F, and two fire-suppressant foams, Phos-Chek WD-881 and Silv-Ex.
MATERIALS AND METHODS

Culture

This study was conducted at the Yankton Field Research Station (YFRS) of the Midwest Science Center, Columbia, Missouri, USA. *Hyalella azteca* were intensively cultured based on established methods [11,12]. The culture media (hardness 725 mg/L as CaCO₃, alkalinity 518 mg/L as CaCO₃, pH 8.72) were replenished with YFRS well water to replace evaporation losses. The culture aquaria were placed in a temperature-controlled water bath with the temperature maintained at 20 ± 1°C. An artificial substrate of nylon coiled-base web material (3M, St. Paul, MN, USA) was placed in the bottom of each aquarium. A layer of hard maple leaves was scattered over the artificial substrate. Maple leaves were soaked in well water for at least 30 d to soften them, to remove tannins, and to initiate periphyton growth. Once weekly, a handful of *Tetra-Min®,* flake food was crushed and scattered over the water surface for the amphipods to feed on ad libitum. The culture was provided with a 16:8-h light:dark photoperiod.

Dilution water

Standardized soft (hardness 41 mg/L as CaCO₃, alkalinity 32 mg/L as CaCO₃, pH 7.45) and hard (hardness 162 mg/L as CaCO₃, alkalinity 111 mg/L as CaCO₃, pH 8.36) waters were used in tests with amphipods [13]. The water was reconstituted in blending tanks by adding the appropriate amounts of reagent grade salts to deionized water. All dilution water was analyzed for general chemical characteristics according to standard methods [14] prior to use to verify adherence to established methods [13].

Test chemicals

The fire-retardant chemicals tested were Fire-Trol LCG-R (FT LCG-R), Fire-Trol GTS-R (FT GTS-R), and Phos-Chek D75-F (PC D75-F), and the foam-suppressant chemicals were Phos-Chek WD-881 (PC WD-881) and Silv-Ex.

All are proprietary products; therefore, proportional compositional analyses were not available. Consequently, all test concentrations and subsequent mean lethal concentrations (LC50s) were based on a 100% active formulation. A general listing of the components of the chemicals is given in Appendix 1. Test chemicals were obtained from the U.S. Forest Service, Intermountain Fire Sciences Laboratory, Missoula, Montana, USA.

Acute toxicity testing

Acute toxicity tests conducted with *H. azteca* were based on established methods [13]. Mature *H. azteca* (0.677 ± 0.239 mg dry weight) were tested in 96-h static acute toxicity tests with separate waterborne test chemicals. In each test, 10 animals were exposed to each of eight or nine toxicant concentrations with a 60% dilution factor between each concentration, in addition to exposure to a control treatment. One control exposure was used for each chemical and each water quality tested.

Three days prior to testing, the appropriate number of mature amphipods were transferred by pipetting them into an acclimation vessel containing approximately 4 L of culture water. At the time of transfer, the amphipods were fed crushed *Tetra-Min®* flake food ad libitum. The amphipods were provided with gentle aeration during acclimation. Acclimation began 48 h prior to testing and was accomplished by removing 50% of the culture water and replacing it with an equal quantity of dilution water twice daily.

During preliminary testing in our lab and in reports by others [15], *H. azteca* exhibited cannibalism when 10 animals were placed in a single test vessel. To prevent cannibalistic behavior, amphipods were tested in a single-animal per exposure-vessel system. Test apparatuses were constructed from a 20-× 26-cm plexiglass sheet with 20 holes, 3.8 cm in diameter, to hold 30-ml disposable plastic cups. The plexiglass was supported by four 75-cm long brass screws and covered with a 20-× 26-cm plexiglass sheet to prevent evaporation of the test solution. The test concentration was prepared in 2-L beakers containing 1 L of dilution water. Glass volumetric pipettes were used to transfer 20 ml of test solution into each cup. Each test concentration was randomly assigned to either half of five stands and a control was included for each chemical tested. One animal was placed in each cup with 10 cups per test concentration. Transfer of the animals was accomplished by holding a pipette with an animal below the surface and allowing the animal to swim out of the pipette.

The number of affected amphipods in each test vessel was monitored at 24-h intervals. The effect criterion for *H. azteca* was death as defined by the American Society for Testing and Materials (ASTM) [13].

Dissolved oxygen, pH, and ammonia were measured in the control and low, medium, and high test chemical solutions at 0, 48, and 96 h. Because there was not enough chemical solution in the exposure vessels, dissolved oxygen and pH were measured directly in the test solution remaining in the 2-L beakers, which were covered with plastic wrap to simulate the covered exposure vessels. Ammonia concentrations were analyzed in 100 ml of the solution remaining in the 2-L beakers. When the tests were terminated, the exposure water was pooled and a sample was taken for ammonia analysis. Temperature was measured daily in the waterbath.

The size of *H. azteca* was determined gravimetrically. After test termination, control animals were placed in predried and preweighed 43-mm aluminum weigh boats and placed in a 60°C oven for 24 h until a constant weight was attained.

Ammonia analysis

Total ammonia concentrations, measured as nitrogen (NH₃-N) concentrations, were taken with an Orion 95-12 electrode (ATI Orion, Boston, MA, USA) using a Fisher Accumet model 610 pH meter and were adjusted for temperature and pH to determine the concentrations of un-ionized ammonia. A regression equation was determined for each test to allow the prediction of the NH₃-N concentration that would be present at the time the test was initiated for the 96-h LC50 concentration. This equation was determined by regressing the NH₃-N values in the low, medium, and high test concentrations at the time the test was initiated against the corresponding 96-h LC50 for the test chemical. The un-ionized ammonia concentration in the 96-h LC50 cannot be predicted because the pH of the solution is unknown.

Statistical analysis

The moving-average angle method was used to calculate the 96-h LC50 and 95% confidence intervals [16]. Regression analyses for the ammonia data were calculated using Lotus 1-2-3 and Statistical Analysis System programs [17]. The standard error of the difference was calculated to determine significant differences (p ≤ 0.05) and rank order between the LC50 for each set of tests [18]. All LC50 values are expressed as nominal concentrations of the fire-control chemical.
Table 1. Acute toxicity (expressed as the mean lethal concentration [LC50]; mg/L; 95% confidence interval in parentheses) of five fire-retardant chemicals to adult *Hyalella azteca* exposed in American Society for Testing and Materials soft and hard waters.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Water type</th>
<th>Exposure period</th>
<th>24 h</th>
<th>96 h</th>
<th>24-h LC50 (95% CI)</th>
<th>96-h LC50 (95% CI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fire-Trol GTS-R</td>
<td>Soft</td>
<td>24 h</td>
<td>363W</td>
<td>24D</td>
<td>813 (627±992)</td>
<td>385 (312±482)</td>
</tr>
<tr>
<td></td>
<td>Hard</td>
<td>24 h</td>
<td>394W</td>
<td>22Y</td>
<td>46 (38±58)</td>
<td>45 (34±57)</td>
</tr>
<tr>
<td>Fire-Trol LCG-R</td>
<td>Soft</td>
<td>24 h</td>
<td>73*B</td>
<td>27Y</td>
<td>417 (329±560)</td>
<td>961 (771±1,183)</td>
</tr>
<tr>
<td></td>
<td>Hard</td>
<td>24 h</td>
<td>10*C</td>
<td>35</td>
<td>974 (752±1,244)</td>
<td>535X (424±654)</td>
</tr>
<tr>
<td>Phos-Chek D75-F</td>
<td>Soft</td>
<td>24 h</td>
<td>53*B</td>
<td>22Y</td>
<td>421 (317±610)</td>
<td>974 (752±1,244)</td>
</tr>
<tr>
<td></td>
<td>Hard</td>
<td>24 h</td>
<td>6-17</td>
<td>46</td>
<td>35 (29±45)</td>
<td>22Y (17±28)</td>
</tr>
<tr>
<td>Phos-Chek WD-881</td>
<td>Soft</td>
<td>24 h</td>
<td>10*C</td>
<td>46</td>
<td>45 (34±57)</td>
<td>22Y (17±28)</td>
</tr>
<tr>
<td></td>
<td>Hard</td>
<td>24 h</td>
<td>6-17</td>
<td>46</td>
<td>35 (29±45)</td>
<td>27Y (22±35)</td>
</tr>
<tr>
<td></td>
<td>Hard</td>
<td>24 h</td>
<td>6-17</td>
<td>46</td>
<td>35 (29±45)</td>
<td>27Y (22±35)</td>
</tr>
</tbody>
</table>

* Values with different letters (A–D for comparison in soft water; W–Y for comparison in hard water) or an asterisk (for comparison between soft and hard waters for each test chemical) are significantly different (p = 0.05); that is, LC50s with the same letter are not statistically different.

**RESULTS**

**Water quality**

Throughout the tests, dissolved oxygen concentrations were maintained at or above 76.7% saturation. For tests conducted in soft water, the pH measured in pooled exposure water from the control treatments at 96 h ranged from 7.08 to 7.89 and in chemical treatments from 7.20 to 7.91. For hard water tests, the pH measured in pooled exposure water from the control treatments at 96 h ranged from 7.99 to 8.28 and in chemical treatments from 7.75 to 8.26.

**Acute toxicity**

Control mortality occurred in a few tests, but only tests with ≤20% of the control mortality were accepted; this follows guidelines in ASTM [11]. Control mortality of 20% only occurred during the test with PC D75-F in soft water; three tests had 10% and one had 0% mortality. Control mortality of 10% occurred only once, during the hard water test with PC D75-F; all other tests had 0% mortality.

The 96-h LC50s for *H. azteca* tested in soft water with fire retardants ranged from 53 mg/L for PC D75-F to 127 mg/L for FT GTS-R to 353 mg/L for FT LCG-R (Table 1). The foam suppressants yielded LC50s in soft water of 10 mg/L for PC WD-881 and 24 mg/L for Silv-Ex and in hard water, 22 mg/L for PC WD-881 and 27 mg/L for Silv-Ex.

The toxicity of four of the chemicals increased from the 24-h LC50 to the 96-h LC50 although not as substantially for Silv-Ex where the increase was less than two-fold for both hard and soft water. The PC D75-F tested in soft water produced the largest increase, eight-fold, from the 24-h LC50 to the 96-h LC50. Increases in toxicity between 24 and 96 h were less substantial in hard water than in soft water.

The toxicity of four of the chemicals to *H. azteca* was increased significantly in soft water. Only Silv-Ex was equally toxic in both water qualities.

The rank order of toxicity of the chemicals to *H. azteca* from most toxic to least toxic in soft water was: PC WD-881 > Silv-Ex > FT D75-F = FT LCG-R > FT GTS-R. In hard water the rank order from most toxic to least toxic was: PC WD-881 = Silv-Ex > FT GTS-R = PC D75-F = FT LCG-R.

**Ammonia**

Ammonia analysis indicated that the three fire retardants contained more total ammonia, as nitrogen and un-ionized ammonia, than did the fire-suppressant foams (Table 2). Because ammonia was analyzed only in control, and low, medium, and high concentrations and the pH of a solution at an LC50 would be difficult to predict, only a range of un-ionized ammonia concentrations bracketing the LC50s can be reported. Total ammonia, as nitrogen at test initiation, was estimated by regression analysis from the 96-h LC50 concentration in the fire-retardant tests. Total ammonia, as nitrogen, in soft water tests ranged from 7.44 mg/L in FT LCG-R to 24.63 mg/L in FT GTS-R and, in hard water tests, from 56.49 mg/L in FT LCG-R to 80.90 mg/L in PC D75-F. Un-ionized ammonia is reported for the two concentrations bracketing the 96-h LC50 concentration. In soft water, the concentration of un-ionized ammonia ranged from 0.02 to 0.08 mg/L in FT LCG-R to 0.13 to 0.79 mg/L in FT GTS-R and, in hard water tests, from 0.24 to 1.09 mg/L in FT LCG-R to 0.53 to 2.40 mg/L in FT GTS-R. Total ammonia, as nitrogen, at the 96-h LC50 concentration in fire-suppressant foams in soft and hard water tests was 0.22 mg/L or less, and consequently, un-ionized ammonia was ≤ 0.02 mg/L.

**DISCUSSION**

**Water quality**

The pH variations observed in the tests probably did not produce biased results because amphipods are tolerant of pHs as low as 5.7 [19]. Similarly, dissolved oxygen concentrations in the amphipod test treatments exceeded the lower limit set by the ASTM [13].

Amphipods were significantly more sensitive to four of the five chemicals when exposed to them in soft water than when the amphipods were exposed to the chemicals in hard water. The increased sensitivity of amphipods in soft water may be related, in part, to the physiological state of the test animals. The ASTM [13] recommends culturing test animals in the dilution water that will later be used for the test solutions. Amphipods used in these tests were cultured in hard water. Animals used in these tests were allowed to acclimate to dilution waters over a period of 48 h and were fed as recommended by the ASTM [13]. This acclimation period may not have been long enough to alleviate some of the stress placed on the animals during testing. However, mortality was not problematic during acclimation, and control mortality averaged 10% in soft water tests, whereas control mortality never exceeded 10% in hard water tests. This control mortality did not exceed the criterion for an acceptable test with the amphipod, which is ≥80% control survival [20].

**Acute toxicity**

The toxicity of fire-retardant chemicals to the amphipod *Gammarus pseudolimnaeus* reported by Johnson and Sanders [7] did not increase over time, in contrast to what was observed in the present tests. They reported that toxic effects of fire-retardant chemicals were observed within the first 24 h of their tests and did not change significantly throughout the test duration. In the present study, toxicity of FT GTS-R, FT LCG-R, and PC D75-F doubled between the 24-h and 96-h observations, thus indicating a possible delayed effect.

The 96-h LC50s for *G. pseudolimnaeus* in their tests con-
ducted in hard water (hardness 272 mg/L as CaCO₃) was 62 mg/L for Fire-Trol 100 (FT 100), which was about six-fold lower than our value for FT GTS-R, a similar chemical. Both FT 100 and FT GTS-R contain ammonium sulfate, but FT 100 contains 35% clay and dichromate as a corrosion inhibitor, whereas FT GTS-R contains no dichromate and uses 3 to 4% guar gum in place of clay to control viscosity. The dichromate may have been an important toxicant in the FT 100 tested by Johnson and Sanders [7]. Similarly, the 96-h LC₅₀ for Fire-Trol 931 (FT 931) to G. pseudolimnaeus in hard water was 55 mg/L, whereas our value for FT LCG-R, which differs from FT 931 primarily in the manufacturer of the polyphosphates (C. Johnson, personal communication), was 10 times higher.

The two Phos-Chek compounds, PC 202 and PC 259, tested by Johnson and Sanders [7] with G. pseudolimnaeus had 96-h LC₅₀s of 52 and 40 mg/L, respectively. Phos-Chek D75-F, a combination of monoammonium phosphate and diammonium phosphate with guar gum thickener, is similar to these compounds, except that PC 202 contained only diammonium phosphate with carboxymethyl cellulose as the thickener and PC 259 contained only diammonium phosphate with guar gum as the thickener. However, our LC₅₀ value was eight to 10 times higher for PC D75-F. Interlaboratory comparison of these results produces a ratio of 10.3 for Fire-Trol chemicals and 9.8 for Phos-Chek chemicals. These ratios are more than two times higher than the four-fold variation typically found between laboratories [21]. This substantial difference in toxicity suggests that G. pseudolimnaeus is more sensitive than H. azteca, or that the compounds tested in the present study are substantially less toxic than the compounds tested by Johnson and Sanders [7], or a combination of these two possibilities.

In general, foam-suppressant chemicals were more toxic to amphipods than fire retardants. Foam-suppressant chemicals are typically composed of approximately 30 to 40% surfactant, which is the most likely toxic constituent. These surfactants lower the surface tension of water thereby interfering with the animals’ ability to obtain oxygen from water [10].

The actual toxic threshold of surfactants is dependent, in part, on their carbon-chain length [22]. Both PC WD-881 and Silv-Ex contain anionic surfactants of unknown carbon-chain length. Sanchez Leal et al. [8] reported a linear increase in toxicity to Daphnia magna with increasing surfactant molecular weight. No information was found on the toxicity of surfactants to amphipods. Daphnia magna has been reported to be more sensitive to surfactants than other invertebrates [9,22].

**Ammonia**

The toxicity of ammonia is apparently species specific for invertebrates and fish. Macroinvertebrates are reportedly less sensitive to ammonia than fish species [23]. Flow-through tests determined that ammonia was acutely toxic to 19 freshwater macroinvertebrate species at concentrations ranging from 0.53 to 22.8 mg/L, whereas ammonia toxicity to 29 fish species ranges from 0.083 to 4.60 mg/L [23]. Studies conducted by Williams et al. [24] reported 96-h LC₅₀s for ammonia ranging from 0.71 to 2.95 mg/L for 11 macroinvertebrate species. The crustacean species in their study were less sensitive to un-ionized ammonia than non-crustacean species. They reported a 96-h LC₅₀ of 2.05 mg/L for G. pulex exposed to ammonia in moderately hard water (hardness 98–106 mg/L as CaCO₃). In contrast, Monda [25] reported a 96-h LC₅₀ for Chironomus riparius of 9.4 mg/L.

The U.S. Environmental Protection Agency [23] has established an ammonia concentration criterion of 0.02 mg/L of un-ionized ammonia as the concentration below which all aquatic

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**Table 2. Summary of the ammonia characteristics of five fire-retardant chemicals used in tests with adult Hyalella azteca exposed in American Society for Testing and Materials soft and hard waters. A regression equation was fitted for each chemical tested using the total ammonia as nitrogen (NH₄-N) concentrations determined at test initiation (n = 4). Each regression model was used to predict initial NH₄-N (mg/L) in the 96-h mean lethal concentration (LC₅₀).**

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Water type</th>
<th>Regression equation</th>
<th>Predicted total ammonia (NH₄-N, mg/L)</th>
<th>Un-ionized ammonia (mg/L)</th>
<th>96-h LC₅₀ (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fire-Trol GTS-R</td>
<td>Soft</td>
<td>NH₄-N = -0.386 + 0.197LC₅₀</td>
<td>127</td>
<td>24.63</td>
<td>0.13–0.79</td>
</tr>
<tr>
<td></td>
<td>Hard</td>
<td>NH₄-N = -1.834 + 0.215LC₅₀</td>
<td>363</td>
<td>76.21</td>
<td>0.53–2.40</td>
</tr>
<tr>
<td>Fire-Trol LCG-R</td>
<td>Soft</td>
<td>NH₄-N = -0.366 + 0.107LC₅₀</td>
<td>73</td>
<td>7.44</td>
<td>0.02–0.08</td>
</tr>
<tr>
<td></td>
<td>Hard</td>
<td>NH₄-N = -1.291 + 0.108LC₅₀</td>
<td>535</td>
<td>56.49</td>
<td>0.24–1.09</td>
</tr>
<tr>
<td>Phos-Chek D75-F</td>
<td>Soft</td>
<td>NH₄-N = -0.382 + 0.197LC₅₀</td>
<td>53</td>
<td>10.06</td>
<td>0.09–0.25</td>
</tr>
<tr>
<td></td>
<td>Hard</td>
<td>NH₄-N = 5.257 + 0.192LC₅₀</td>
<td>394</td>
<td>80.90</td>
<td>0.38–1.01</td>
</tr>
<tr>
<td>Phos-Chek WD-881</td>
<td>Soft</td>
<td>NH₄-N = 0.0597 + 0.000151LC₅₀</td>
<td>10</td>
<td>0.06</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>Hard</td>
<td>NH₄-N = 0.0418 + 0.000141LC₅₀</td>
<td>22</td>
<td>0.04</td>
<td>0.00</td>
</tr>
<tr>
<td>Silv-Ex</td>
<td>Soft</td>
<td>NH₄-N = 0.0230 + 0.00784LC₅₀</td>
<td>24</td>
<td>0.21</td>
<td>0.00–0.01</td>
</tr>
<tr>
<td></td>
<td>Hard</td>
<td>NH₄-N = 0.0995 + 0.00719LC₅₀</td>
<td>27</td>
<td>0.22</td>
<td>0.00–0.02</td>
</tr>
</tbody>
</table>

*a NH₄-N = total ammonia as nitrogen (mg/L) used as the dependent variable in the regression model; LC₅₀ = 96-h LC₅₀ (mg/L) used as the independent variable in the regression model; adjusted R² = 1 - (1 - R²)(n - 1/d.f. error).

*b Un-ionized ammonia = total ammonia, as determined at test initiation and adjusted for temperature and pH.
life may be protected. The un-ionized ammonia concentrations of the fire-retardant chemicals, but not the foam suppressants, exceeded this criterion as much as 120 times (Table 2). Un-ionized ammonia is believed to be more toxic to aquatic organisms than ammonium (ionized ammonia) [23]. The concentration of un-ionized ammonia is greater than ammonium when the pH is high and studies have indicated that ammonia toxicity increases with increasing pH. Ammonium was considered to be nontoxic or at least significantly less toxic [26]. Erickson [27] proposed a joint model in which un-ionized ammonia contributes more to ammonia toxicity at higher pHs and ammonium contributes more at lower pHs. Recent studies support Erickson’s model, citing total ammonia as nitrogen toxicity to *H. azteca* [28–30] rather than the un-ionized form, which is toxic to *Ceriodaphnia dubia* [31]. Borgmann [28] tested the toxicity of ammonia to *H. azteca* and reported a 96-h LC50 of 28 mg/L total ammonia as nitrogen, which he extrapolated from a mortality curve for a chronic toxicity study. Likewise, Ankley et al. [30] reported 96-h LC50s of 20 to 23 mg/L total ammonia as nitrogen for *H. azteca*.

Ammonia toxicity is also dependent on water hardness [28,29]. Ankley et al. [29] reported that in soft water (hardness 42 mg/L as CaCO3), the toxicity of ammonia was similar at pHs 6.5, 7.5, and 8.5. In tests with harder water, toxicity of ammonia increased more pH dependent. In moderately hard water (hardness 100 mg/L as CaCO3), the LC50 doubled between pH 6.5 and 8.5, and in hard water (hardness 240 mg/L as CaCO3) the LC50 increased six-fold between pH 6.5 and 8.5. In addition, the LC50s between hardnesses increased as much as 10-fold at pH 6.5. Their results indicated that as water hardness increased, a joint toxicity between ammonium and un-ionized ammonia occurred, which coincides with the joint model for ammonia toxicity that also considers the contribution of ionized species, as proposed by Erickson [27]. Our results are similar to those of Ankley et al. [29] because in the hard water tests with the three fire retardants, the amphipods were as much as eight times less sensitive to ammonia than in the soft water tests. These values indicate that the toxicity of the ammonia-based fire retardants was probably influenced by the concentration of total ammonia as nitrogen (the sum of ammonium and un-ionized ammonia) rather than un-ionized ammonia.

The ammonia constituent has been determined to be the toxic portion of fire-retardant chemicals to fish [32]. However, toxicity of the ammonia constituent of fire-retardant chemicals may be influenced by other constituents such as spoilage and corrosion inhibitors. Both FT LCG-R and PC D75-F, in soft water, contained less total ammonia as nitrogen than has been shown to be toxic to *H. azteca* (Table 2) [28,29]. Other toxins such as corrosion or spoilage inhibitors may be synergistic with the ammonia constituent thereby increasing the toxicity of ammonia. In contrast, all the fire retardants tested in hard water contained more total ammonia as nitrogen than has been reported to be toxic to *H. azteca*. Other constituents of the compounds may be antagonistic with the ammonia constituent, thereby ameliorating the toxic effect of the total ammonia as nitrogen when it exceeds reported LC50 values. For example, rainbow trout (*Oncorhynchus mykiss*) exposed to a mixture of nitrate and ammonia produced antagonistic results, except when the chemical ratio was low, whereas copper and ammonia were reported to be synergistic [33].

Trophic interactions

Amphipods may be the most abundant year-round macrobenthos [34] inhabiting lotic and lentic systems. They are a major link between top carnivores and the large energy store contained by detritus and its associated microflora and fauna. However, in feeding studies, amphipods have demonstrated a preference for algae over detritus [35].

In tests exposing *Selenastrum capricornutum* to the same fire-retardant and foam-suppressant chemicals as the amphipods of this study, this alga was more sensitive to three of the five chemicals tested [36]. A sublethal response of the alga to four of the five fire-retardant and foam-suppressant chemicals in these tests resulted in a stimulation of growth of 3 to 43% more algal biomass than the controls. An increase in algal biomass at concentrations of fire-retardant chemicals that were sublethal to amphipods would increase the animals’ opportunity to graze and hide [35]. However, the fecundity and growth rate of the amphipods might be impaired when they are fed a poor-quality diet. Algae grown in the presence of fire-retardant and foam-suppressant chemicals may not provide the nutrition required by amphipods because the ideal ratio of phosphorus : nitrogen required for algal growth will be altered by the addition of the chemicals. Sterner et al. [37] reported a decrease in fecundity and growth rate of daphnids when they were fed phosphorus-limited algae. The animals were also sluggish and easily caught, making them easy prey for predators.

Bottom-dwelling invertebrates such as *H. azteca* would be susceptible to physical impairment when flocculent materials such as guar gum thickener from fire-retardant chemicals accumulated on the substrate. Such materials could also clog the respiratory systems of these animals. Hargrave [38] observed that the egestion rate of *H. azteca* decreased as the flocculent sediment material was consumed. Concern for secondary effects on aquatic ecosystems was expressed as early as 1977 by Johnson and Sanders [7].

Relationship to environmental considerations

Because environmental factors differ between and along streams and lakes, it is difficult to predict the impact that an accidental introduction of these chemicals would have on aquatic organisms. The impact of an accidental exposure of aquatic organisms to fire-retardant and foam-suppressant chemicals is dependent on a number of factors such as: the route of entry, behavior of the chemical, magnitude of spill, water velocity, shape of the streambed, and substrate composition [39]. A study was conducted to measure the chemical changes in stream water quality using five streams possessing different characteristics [40]. Norris and Webb [40] reported that the physical characteristics of streams and the characteristics of the chemical drop both affected the impact of the chemical in the stream and that water chemistry changes were detected as far downstream as 2,700 m.

A recent incident was reported on September 17, 1995, when a C-130 retardant bomber dropped a partial load of Fire-Trol LCG-F across about 67 m of Murderers Creek in the South Fork John Day River, Oregon (T. Unterweger, personal communication). An estimated 23,000 fish were killed along 2,740 m of stream, including about 718 rainbow and steelhead trout. Murderers Creek is the most significant steelhead trout production stream in the South Fork John Day River sub-basin, and the fish losses were considered biologically significant. Previous fish kills have been attributed to similar introductions of fire-control chemicals, but have not been well documented [39,40].

The application of fire-fighting chemicals is accomplished using a wide variety of aircraft equipped with different storage tank configurations, door sizes, and sequencing speed, which results in a wide range of drop patterns [1]. Drop patterns and the re-
and the ratio of the mixture concentration to the acute toxicity value (i.e., NOEC). Applying a safety factor of 100 to the NOECs would require a 45,400- to 100,000-fold dilution for PC WD-881 and a 37,000- to 41,700-fold dilution for Silv-Ex to approach safe concentrations.

**CONCLUSIONS**

Adverse effects of fire-fighting chemicals on important aquatic invertebrates such as *H. azteca* in the food web could lead to altered biodiversity and shifts in trophic pathways. Disruption of ecosystem functions at lower trophic levels could, in turn, impair the health and well-being of organisms at higher trophic levels such as fish.

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**REFERENCES**

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dard Methods for the Examination of Water and Wastewater, 17th ed. American Public Health Association, Washington, DC, USA.

APPENDIX

Test chemical composition of the three non-foam fire retardants and two foam fire suppressants

<table>
<thead>
<tr>
<th>Chemical name and manufacturer</th>
<th>Formulation type</th>
<th>Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fire-Trol GTS-R</td>
<td>Powder</td>
<td>Ammonium sulfate, Diammonium phosphate, Guar gum thickener, Spoilage inhibitor, Corrosion inhibitor, Iron oxide (red coloring agent)</td>
</tr>
<tr>
<td>Chemonics Ind., Phoenix, AZ, USA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fire-Trol LCG-R</td>
<td>Liquid</td>
<td>Ammonium polyphosphate, Attapulgite clay liquid thickener, Corrosion inhibitor, Iron oxide (red coloring agent)</td>
</tr>
<tr>
<td>Chemonics Ind., Phoenix, AZ, USA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phos-Chek D75-F</td>
<td>Powder</td>
<td>Ammonium sulfate, Ammonium phosphate, Guar gum thickener, Orange coloring agent, Other additives</td>
</tr>
<tr>
<td>Monsanto Co., Ontario, CA, USA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phos-Chek WD-881</td>
<td>Liquid</td>
<td>Anionic surfactants, Alcohol, Hexylene glycol, Additives</td>
</tr>
<tr>
<td>Monsanto Co., Ontario, CA, USA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silv-Ex</td>
<td>Liquid</td>
<td>Anionic surfactants, Glycol and alcohol liquid solvents</td>
</tr>
<tr>
<td>Ansul Fire Protection, Marinette, WI, USA</td>
<td></td>
<td></td>
</tr>
</tbody>
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