



# Environmental Implications of Fire-Retardant Chemicals

## Project Summary

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## Major Results

- The presence of YPS (sodium ferrocyanide) increased the toxicity of fire retardants
- Ultraviolet radiation increased the toxicity of fire retardants containing YPS.
- Toxic cyanide concentrations were observed during stream tests.
- Toxicity of fire retardants may persist in rainwater runoff from treated areas particularly from sandy or rocky surfaces
- As fire-retardant chemicals aged in the environment toxicity was not consistently associated with the presence of toxic concentrations of cyanide or unionized ammonia.
- High organic soils rapidly decreased chemical persistence
- Combustion eliminated toxicity of the retardant
- Fish are capable of avoiding fire retardant chemical in streams.
- Other fire-related factors such as ash effluents and high temperatures may exceed the chemical toxicity of fire retardant chemicals.

Each year a variety of fire chemicals are used to fight wildland fires. The long-term fire retardants are ammonia-based chemicals considered to be non-toxic to terrestrial organisms and of low to moderate toxicity to aquatic organisms (Finger 1997). Certain fire-retardant chemicals contain sodium ferrocyanide, (yellow prussiate of soda or YPS) as an anticorrosive agent. Concern about YPS arose because this chemical releases cyanide when it is exposed to the ultraviolet radiation (UV) in sunlight and may pose an environmental hazard due to this UV-enhanced toxicity. Human health risk assessments reveal that cyanide exposure from the use of fire retardants is of limited toxicity to humans or other terrestrial organisms (Labat-Anderson 1994). However early literature suggest that YPS causes significant toxicity to fish (Burdick and Lipschuetz 1950). To ensure the environmental safety of fire-retardant chemicals used to fight forest fires, the U.S. Forest Service requested an investigation to determine the potential for UV-enhanced toxicity and environmental persistence of fire-retardant chemicals.

During the course of this project the U.S. Geological Survey Columbia Environmental Research Center (USGS) evaluated UV-enhanced toxicity of fire retardants in the laboratory and field, persistence of toxicity after periods of weathering or combustion, and avoidance of fire retardants by fish.

### **Does UV increase the toxicity of fire-retardant chemicals?**

USGS conducted a series of laboratory tests (Figure 1) during which juvenile rainbow trout and southern leopard frog tadpoles were exposed to fire chemicals alone and in the presence of UV radiation (Little and Calfee 2000). The tests were conducted over 96

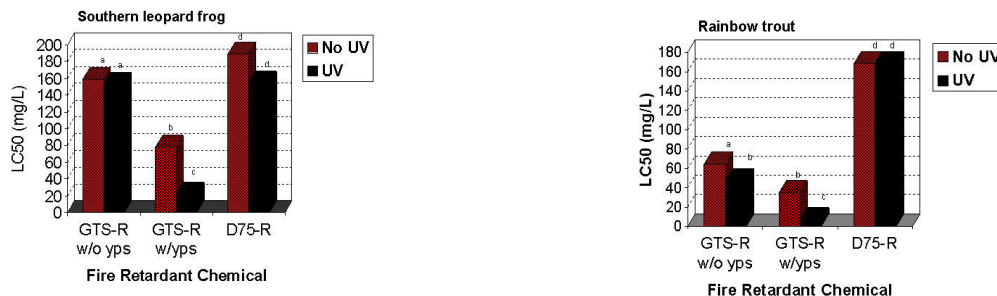
hours using a range of concentrations (ASTM 1993). These studies determined the concentrations of fire-retardant chemicals lethal to 50 % of the test organisms (LC50). The higher the LC50 value, the lower the toxicity of a chemical.



**Figure 1. In laboratory tests juvenile rainbow trout and southern leopard frog tadpoles were exposed to fire-retardant chemicals with and without YPS. Studies were conducted in a solar simulator and various filtering materials were used to control UV exposure similar to that found in natural aquatic habitats (Little and Fabacher 1996).**

We tested Fire-Trol® GTS-R (Fire-Trol Holdings, LLC) and Phos-Chek® D75-R (Astaris, LLC). GTS-R normally contains YPS, and was tested with and without YPS. D75-R does not contain YPS. Comparison of LC50 values of chemicals tested in the presence and absence of UV allowed us to determine the potential effects of UV exposure on the YPS additive.

The presence of YPS consistently increased the toxicity of fire retardants. In the absence of UV, formulations with YPS were more than twice as toxic as formulations without YPS. However, in the presence of UV, the toxicity of products with YPS more than doubled. Mortality commonly occurred within a few hours of exposure. For example, the UV-enhanced toxicity of GTS-R to frog tadpoles was clearly apparent as an increase of almost 300 % when tested in the presence of UV (Figure 2). In contrast, GTS-R without YPS was not significantly affected by UV exposure. The toxicity of D75-R that never contained YPS was slightly increased in the presence of UV.

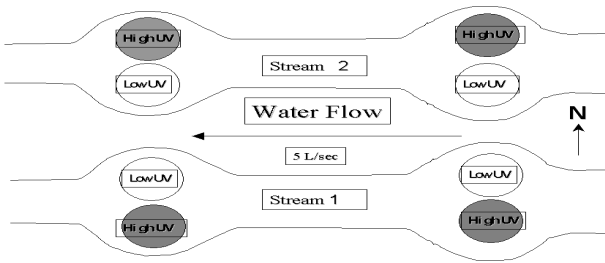


**Figure 2. 96 hour lethal concentrations of GTS-R with and without YPS, and D75-R in the presence and absence of UV determined in tests with southern leopard frog tadpoles and juvenile rainbow trout. Bars with different letters are statistically different.**

Similar responses were observed when rainbow trout were exposed. These initial studies confirm the UV-enhanced toxicity of products containing YPS under controlled laboratory conditions.

### Does UV-enhanced toxicity occur under field conditions?

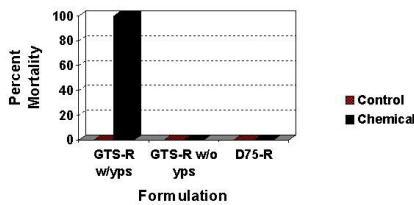
Stream tests were conducted to determine the toxicity of a pulse of exposure as fire retardant chemical is rinsed into a stream from treated watersheds by rainfall (Little and Calfee 2002a). Two artificial 150-meter experimental streams were dosed with different concentrations of GTS-R, D-75-R, or uncontaminated water. Replicate groups of fathead minnows were added to screened containers (10 fish per container) and exposed to retardant chemicals in the recirculating flow of the stream for up to 6 hours.



**Figure 3. Experimental streams were dosed with different concentrations of GTS-R, D-75-R, or uncontaminated water. Replicate groups of fathead minnows were added to screened containers (10 fish per container) and exposed to retardant chemicals in the recirculating flow of the stream**

Total mortality occurred in chemicals containing YPS in the presence of UV. However no mortality occurred in the controls or in treatments without UV (Figure 4).

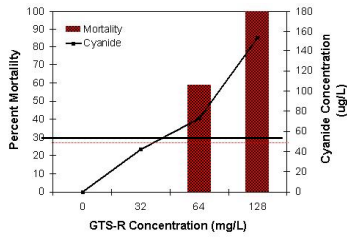
#### Retardant with YPS was toxic during stream tests



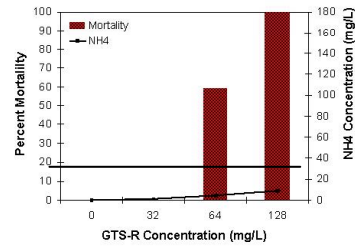
**Figure 4. Average mortality observed after a 6-hour exposure to uncontaminated water or GTS-R with YPS, GTS-R without YPS, and D75-R**

Free cyanide is the most likely form of cyanide to result from the breakdown of YPS by UV (Burdick and Lipschuetz 1950). Lethal concentrations of cyanide (greater than 50 µg/liter; Smith et al. 1978;1979) were observed during the stream tests of GTS-R, however ammonia concentrations (Thurston et al. 1983, Fairchild et al. 2000) were below lethal concentrations for fathead minnows (Figure 5).

**Toxic cyanide occurred during GTS-R stream test**



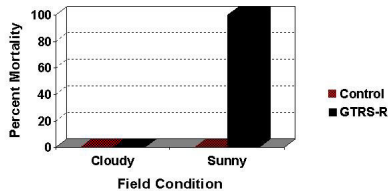
**Ammonia was not toxic during GTS-R stream test**



**Figure 5. Mean percent mortality and cyanide concentrations, or ammonia concentrations observed for different concentrations to GTS-R 6 hours after the onset of exposure in experimental streams. Note: scales for cyanide or ammonia are shown on the right Y-axes. Lines represent lethal concentrations of cyanide and ammonia to fathead minnows.**

Under field conditions toxicity resulted in the presence of sunlight (Figure 6). When GTS-R was tested on sunny days, 100 % mortality occurred. However, when tested during heavily overcast conditions, no mortality occurred. Lethal concentrations of cyanide were measured when GTS-R with YPS exposures were conducted under sunny conditions, but not under cloudy conditions, indicating that a minimum UV level is necessary to induce toxicity as well as the release of cyanide from YPS.

**GTS-R was not toxic under cloudy conditions**

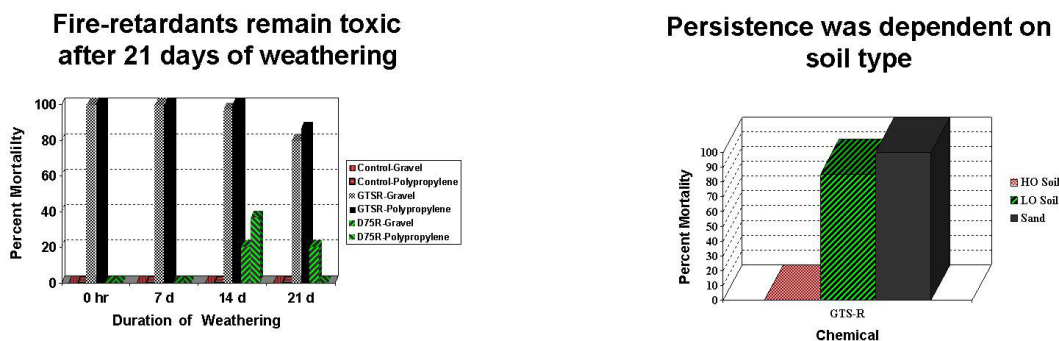


**Figure 6. Mean percent mortality observed during heavy cloud cover and sunny conditions**

**Do fire-retardant chemicals decrease in toxicity over time?**

The environmental risk of a chemical substance is determined by the concentration applied in the environment, its persistence and availability in the environment, and any biotic factors that may mitigate the dose received by the organism. Weathering studies were conducted to determine the persistence of toxicity from chemicals after they have aged in the environment (Little and Calfee 2002b). During these studies different substrates were treated with fire retardant chemicals at mixed retardant concentrations that would normally be used for fire suppression. These treated substrates were placed outside where they were exposed to sunlight, diurnal temperature changes, and humidity. Following intervals of weathering, the aging retardant was dissolved in water, and fish were added to determine toxicity over a 24-hour period.

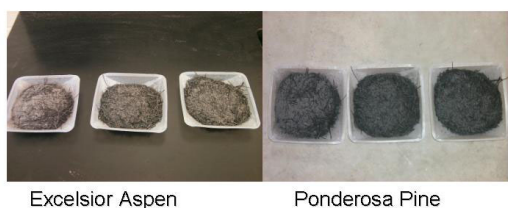
In initial tests with fire chemicals weathered on non-porous surfaces at recommended application concentrations we found that the fire retardants remained toxic for over 21 days (Figure 7). Additional tests with different soil types showed that the persistence of toxicity was dependent on soil quality. Toxicity was often eliminated on soils with high organic content. We also found that mortality was not consistently correlated with cyanide and un-ionized ammonia concentrations. In the overall risk assessment, soil quality is a significant variable to consider.



**Figure 7. Average percent mortality of fathead minnows exposed for 24 hours to aqueous solutions of GTS-R or D75-R that had been weathered on gravel or polypropylene for 21 days, or on soils of high organic (HO) low organic (LO) content or sand for 21 days.**

### **Does combustion reduce the toxicity of fire retardant chemicals?**

Another process that might be destructive of the fire chemical is pyrolysis. To examine the toxicity of fire retardants following combustion, pine needles and excelsior were treated with GTS-R and D75-R then subjected to a standardized burn in a combustion chamber (Figure 8). Small amounts (10 grams) of the resulting ash were mixed in a liter of water, filtered, then diluted. Toxicity tests with fish were conducted for 96 hours.



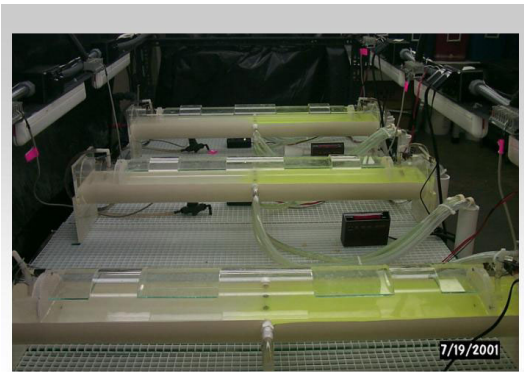
**Figure 8. Ash from Aspen excelsior and Ponderosa pine needles that were treated with fire retardant chemicals prior to standardized combustion tests. Fish were exposed to a 1 percent solution of ash for 96 hours.**

No toxicity occurred when fish were exposed for 96 hours to aqueous leachates of ash prepared from materials that had been treated with fire retardant before combustion. Limited sublethal concentrations of cyanide and iron-bound cyanide were observed, however there was no toxicity. In addition, total ammonia concentrations were

dramatically reduced. Incidental to these studies we also observed that low concentrations of ash readily clog gill surfaces leading to respiratory failure.

### Are fish able to minimize injury from fire-retardant chemicals by avoiding them?

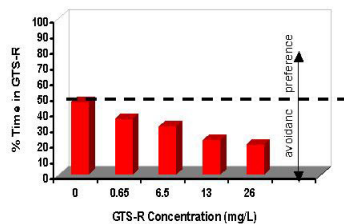
Avoidance of noxious environmental conditions is an adaptive response that enables fish to avoid potentially harmful conditions and injury (Little et al. 1993). Tests were conducted to determine if fish are capable of avoiding fire-retardant chemicals (Little et al. 2002), using a counter-current chamber (Figure 9) that received fire chemical on one side and control water on the other (DeLonay et al. 1996).



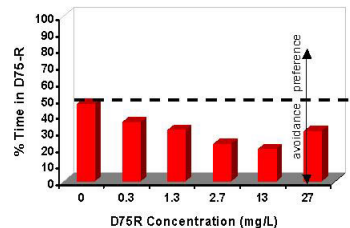
**Figure 9.** Counter-current chambers used to test the avoidance response of fish receive fire retardant chemicals at one end of the chamber and uncontaminated water on the other. A sharp gradient is formed at the center where the apparatus drains. Fish were monitored via overhead camera to measure the amount of time spent in the fire retardant.

Juvenile rainbow trout avoided fire retardant chemicals at concentrations ranging from 1 to 10 % of the LC50 (Figure 10). The presence of colorant and YPS had no influence on the avoidance response. It appears that the salinity of the solution might have been the sensory cue that the fish were responding to when fire chemicals were present. The results indicate that if fish have some avenue of escape, they can limit hazardous exposure by avoiding areas where fire chemicals are present.

**Rainbow trout significantly avoided low concentrations of GTS-R**



**Rainbow trout significantly avoided low concentrations of D75-R**



**Figure 10.** Mean percent of time fish spent in the side of the chamber containing GTS-R or D75-R. Dotted line indicates no-preference response. Response to fire-retardants are statistically less than to controls.

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