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Extinguishment Agents

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Synonyms

Extinguisher agents; Fire extinguishers; Fire–
fighting additives; Fire-fighting chemicals; Fire
retardants; Fire suppressants; Flame retardants

Definition

Natural and synthetic substances used as chemical additives to improve water effectiveness for extinguishing wildfires.

Introduction

The use of extinguishment agents in direct and indirect fire-fighting operations started in the early 1930s because these substances delay the ignition, reduce fire intensity (from flaming to smouldering combustion) and spread, decrease fuel consumption, and delay combustion recovery (Kalabokidis 2000; Giménez et al. 2004). The extinguishment agents help to control wood pyrolysis and combustion through several mechanisms (Liodakis et al. 2008): (a) acting as fire-fuel barriers; (b) cooling fuels by the endothermic decomposition of the added chemicals; (c) diluting with noncombustible gases the combustible gases evolved from burning fuels; (d) trapping free radicals; (e) increasing char formation; and (f) reducing volatiles and their heat content. Besides their efficacy in retarding combustion, other characteristics are important in determining how, when, where, and what extinguishment agent should be used: toxicity, active content, optimum mixing, viscosity, density, pH, stability, corrosion, pumpability, abrasion, air drop characteristics, field visibility, and operation field evaluation (Giménez et al. 2004).

Although ground application allows a better control of fuel covering by the extinguishment agents, they must usually be applied from aircrafts in remote regions inaccessible by land. During aerial application, frequently hazardous due to the smoke and erratic winds, many parameters influence retardant droplet size and final ground distribution: flight conditions (altitude, speed), wind direction and speed, tank characteristics, and type and rheological properties (viscosity, elasticity) of the fire retardant (Boulton et al. 2003). Because of their effectiveness, extinguishment agents are frequently used for fighting wildfires in natural areas, sometimes with high wilderness or landscape values, and consequently attention should be paid to their ecological effects (Kalabokidis 2000; Fernández-Fernández et al. 2015).

Types of Extinguishment Agents

Two broad categories of fire-fighting chemicals are usually considered depending on if their effectiveness persists or not (long- or short-term extinguishment agents, respectively) once the carrying water is evaporated.

Long-Term Extinguishment Agents (LTEA)

Classical LTEAs are fertilizer salts (diammonium sulfate; diammonium phosphate; monoammonium phosphate) mixed with thickeners (agar gum, carboxylmethyl cellulose, attapulgite clay), coloring agents (iron oxide) to mark drop sites, corrosion inhibitors (sodium dichromate, sodium ferrocyanide, tolyltriazole), and bactericides (Gaikowski et al. 1996; Boulton et al. 2003).

Fire retardancy of ammonium salts is due to their chemical reaction with fuels' cellulose and evaporative fuel cooling (Adams and Simmons 1999; Liodakis et al. 2008), without affecting lignin decomposition (Liodakis et al. 2008). Thermal decomposition of ammonium sulfates and phosphates liberates ammonia and sulfuric or phosphoric acid (and phosphorous pentoxide), respectively, which modify the thermal decomposition pathway of cellulose, increasing char production and decreasing that of volatile compounds (Liodakis et al. 2008). Effectiveness of phosphate-based LTEAs depends directly on their phosphorous content. Smoke production increases with ammonium phosphate retardants while slightly decreases with ammonium sulfate retardants. Due to incomplete combustion, the amount of smoke and airborne particulates increases.

Aiming to reduce the ecological impacts of LTEAs, Liodakis et al. (2008) proposed formulations based on magnesium carbonate minerals which decompose endothermically at 200–400 °C with three fire retardant effects: (a) flame quenching due to cooling; (b) dilution of combustible gases from fuels with noncombustible $H_2O(g)$ and $CO_2(g)$ from LTEA; and (c) fuel protection from flames and heat by a ceramic barrier. Unlike ammonium-LTEAs which alter cellulose decomposition – and are more efficient

in reducing fire spread – these new LTEAs modify lignin decomposition (Liodakis et al. 2008).

Short-Term Extinguishment Agents (STEA)

As water fire extinguisher effectiveness is limited by its high surface tension, STEAs with foaming agents, wetting agents (anionic surfactants alone or mixed with nonionic synthetic surfactants), foam stabilizers, dispersants, and corrosion inhibitors were developed for improving water extinguishing capacity. STEAs slow water evaporation and increase water adherence to the fuels, thanks to the foaming agents, and enhance water penetration into the fuels, thanks to the wetting agents (Mizuki et al. 2007; Rakowska et al. 2014). As a result, STEAs insulate fuels from the ignition (heat) and oxygen (air) sources until the carrying water is evaporated or drained. Another type of STEA is made of synthetic acrylic acid-acrylamide polymers and fatty acid ester which – like polyacrylamide additives for improving soil water retention capacity – absorbs many times its own weight in water, forming an adhesive aqueous gel (air bubbles-free, unlike foams), that cuts-off the oxygen supply to the burning material, smothering the flames and cooling the fuel.

Fluorinated STEAs containing a solvent (glycol ether), anionic and amphoteric fluorocarbon surfactants, hydrocarbon surfactants, and corrosion inhibitors (tolyltriazole) are used to extinguish hydrocarbon-fuel fires (Moody and Field 2000). Therefore, fluorinated STEAs are not employed in forest fires but could eventually be used in WUI-Fires. Compared to hydrocarbon surfactants (hydrophobic and more or less biodegradable), fluorinated surfactants are both hydrophobic and oleophobic, thermally and chemically more stable and long-lasting in the environment (Moody and Field 2000; Wang 2015).

As for LTEAs, there is an emerging research line for developing eco-friendly STEA foams based on natural soaps with surfactant properties (Mizuki et al. 2007; Kawano et al. 2014). Rakowska et al. (2014) proposed a biodegradable STEA based on sodium alkylobenzenesulfonate and nonionic surfactant poly(oxypropylenediol)–propylene glycol while, for replacing fluorinated-LTEAs, Wang (2015) developed a foam based on

alkyl glucose amide and organosilicone surfactant.

Environmental Effects

Besides humans, the extinguishment agents may strike all ecosystem components (air, water, soil, flora, and fauna) during fire-fighting operations, with negative effects when applied at the wrong place or dose. LTEAs formulations have included phosphorus, sulfur, antimony, chlorine, bromine, boron and nitrogen. Borate salts are not longer in use because of their negative side effects (soil sterilization; high toxicity) and presently the ammonium, phosphate, and sulfate radicals are the chemicals most likely to have environmental adverse effects (Kalabokidis 2000). In STEAs, surfactants are the most detrimental constituents (Boulton et al. 2003). The environmental effects of LTEAs and STEAs may be influenced by: (a) site-specific characteristics, such as topography, soil type, and cation exchange capacity, or stream size and flow (Kalabokidis 2000; Giménez et al. 2004); (b) postapplication weather (Cruz et al. 2005; Angeler et al. 2006); (c) water quality and hardness (Gaikowski et al. 1996; Mizuki et al. 2007); and (d) species/communities considered (Boulton et al. 2003).

Aquatic Ecosystems
Although LTEAs can be moderately toxic to algae (McDonald et al. 1996), nitrogen- and phosphorous-rich LTEAs can increase algae biomass (Adams and Simmons 1999) and cause eutrophication of aquatic ecosystems (Kalabokidis 2000; Couto-Vázquez and González-Prieto 2006). The accumulation of guar gum (thickener/flocculent) from LTEAs on the substrate of aquatic ecosystems can physically damage bottom-dwelling invertebrates, by clogging their respiratory systems (McDonald et al. 1997). Toxicity of LTEAs for aquatic animals is due to unionized ammonia from the dissociation of ammonium salts, which increases with water pH and temperature, and to hydrogen cyanide from the dissociation of corrosion inhibitors (sodium ferrocyanide), which increases

in water and with UV-B (Gaikowski et al. 1996; McDonald et al. 1997). The concentration of unionized ammonia in LTEAs is two orders of magnitude higher than the US EPA threshold for aquatic life protection (McDonald et al. 1996) and the main cause of massive fish mortality after accidental spills. Because of a joint effect of ammonium and unionized ammonia, LTEAs toxicity increases with water hardness (McDonald et al. 1997). In temporary vernal pools or salt marshes, either after winter or spring flooding, abundance, taxonomic richness, and biodiversity of aquatic invertebrates decrease with increasing dose of phosphate-LTEA and, despite their resilience to perturbations by these chemicals, the impact may be disproportionately higher on isolated wetlands (Angeler et al. 2006).

STEAs can also be moderately toxic to algae (McDonald et al. 1996) and surfactants from STEAs lessen the aquatic fauna ability to obtain oxygen and impair their mobility, decimating or eliminating the populations of some taxa (McDonald et al. 1996; Boulton et al. 2003), and alter the permeability of biological membranes, allowing an increased uptake of inorganic and organic pollutants (Giménez et al. 2004). Toxicity of surfactants is probably due to their anionic portion (Gaikowski et al. 1996), and they need a dilution factor of 3–6 orders of magnitude to approach safe concentrations for aquatic organisms (McDonald et al. 1997; Boulton et al. 2003). Compared to LTEAs, toxicity of STEA foams is 10–100-fold higher for crustacean zooplancton, fry, and later fish life stages, and can increase over time (Gaikowski et al. 1996; McDonald et al. 1997). Nevertheless, in streams with harsh abiotic conditions, no effects of STEA foams on macroinvertebrate assemblage composition or taxon richness have been reported (Boulton et al. 2003). The few available information about the environmental effects of perfluorinated surfactants suggests a moderate-to-high toxicity for marine and freshwater organisms, bioaccumulation in fish, potential harmfulness for aquatic birds, and unknown effects on microbial ecology and activity (Moody and Field 2000).

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Although the well-documented negative impacts of the extinguishment agents on all aquatic trophic levels may be much lower than those of massive post-fire runoff (Giménez et al. 2004), caution is strongly recommended to prevent direct application of extinguishment agents into aquatic ecosystems and their surroundings.

Terrestrial Ecosystems

Despite their importance as the base of terrestrial ecosystems, the effects of fire-fighting chemicals on soils were scarcely studied until recently (Couto-Vázquez and González-Prieto 2006). After applying LTEA-containing ammonium-sulfate and ammonium-phosphate, soil pH decreases and soil salinity increases transiently (Hopmans et al. 2007) and the added ammonium can promote the weathering of soil silicates (Koufopoulou et al. 2014). Although the fire volatilizes a substantial part of the LTEA-derived ammonium, up to a third of LTEA-nitrogen is lost by leaching as nitrates and, when its amount exceeds the soil retention capacity, as ammonium (Pappa et al. 2008), which can also displace exchangeable sodium, iron, and silicon (but not aluminum, manganese, and copper) to the soil solution and soil leachates (Koufopoulou et al. 2014). Similarly, a variable proportion of LTEA-derived phosphate is leached to the subsoil (Pappa et al. 2006; Hopmans et al. 2007). Diammonium-phosphate LTEAs lower the pH of leachates solubilizing calcium and potentially toxic elements as copper, manganese, lead, and zinc (but not chromium), while magnesium carbonate LTEAs create an alkaline media, reducing the release of calcium, copper, magnesium, and zinc (Liodakis and Tsoukala 2009, 2010). Concerning macronutrient availability, an acrylamide-based STEA reduced soil net nitrogen mineralization leading up to net immobilization (Basanta et al. 2002). Contrarily, ammonium-phosphate LTEAs increased nitrogen and phosphorous available in soil during 1 and 10 years, respectively (Couto-Vázquez and González-Prieto 2006; Fernández-Fernández et al. 2015). Similarly, sulfur availability increases transiently in soils receiving ammonium-sulfate LTEA (Hopmans et al. 2007). The short-lived changes in micronutrient availability due to a prescribed fire (manganese and zinc increase; iron and cobalt decrease) can be enhanced by LTEAs and STEAs, although only the ammonium polyphosphate-LTEA had a medium-term effect on manganese availability and iron/manganese ratio (García-Marco and González-Prieto 2008). Although the impacts of the extinguishment agents on soil microbiota seem lower than those of fire, long-lasting effects of an ammonium phosphate-LTEA and an acrylamide-based STEA on soil microbial communities have been reported (Barreiro et al. 2010; Barreiro et al. 2016). Moreover, the LTEA has lasting influence on β-glucosidase (but not urease) activity, while the acrylamide-based STEA is difficult to biodegrade (Barreiro et al. 2010) and modifies the gram negative to gram positive bacteria ratio (Díaz-Raviña et al. 2006).

Ammonium-phosphate and ammonium-sulfate LTEAs lead to immediate and widespread shoot and plant death of some species in all vegetation strata (Bell et al. 2005); the recovery can be rapid for overstorey plants, but many understorey species still had a reduced cover after 1 year. As a consequence, changes in species richness and inhibition of (some) leguminous due to the high amounts of LTEA-derived ammonium have been reported and increased competitive advantage of some weeds and invaders is expected (Adams and Simmons 1999; Bell et al. 2005), which may favor some species over others changing community composition (Luna et al. 2007). Ammonium- and phosphate-based LTEAs decrease seed germination and viability because high salts levels reduce the osmotic potential of the solution surrounding seeds (Cruz et al. 2005; Luna et al. 2007). Moreover, although moderate nitrogen concentrations often stimulate seed germination (Cruz et al. 2005), extremely high initial levels of ammonium and available phosphorous are toxic to seeds and seedlings, respectively, and could reduce plant uptake of iron and zinc (Couto-Vázquez and González-Prieto 2006; García-Marco and González-Prieto 2008). The deleterious effect of these nutrient-rich LTEAs may be reversed in the medium term (Luna et al. 2007), thanks to their fertilizing
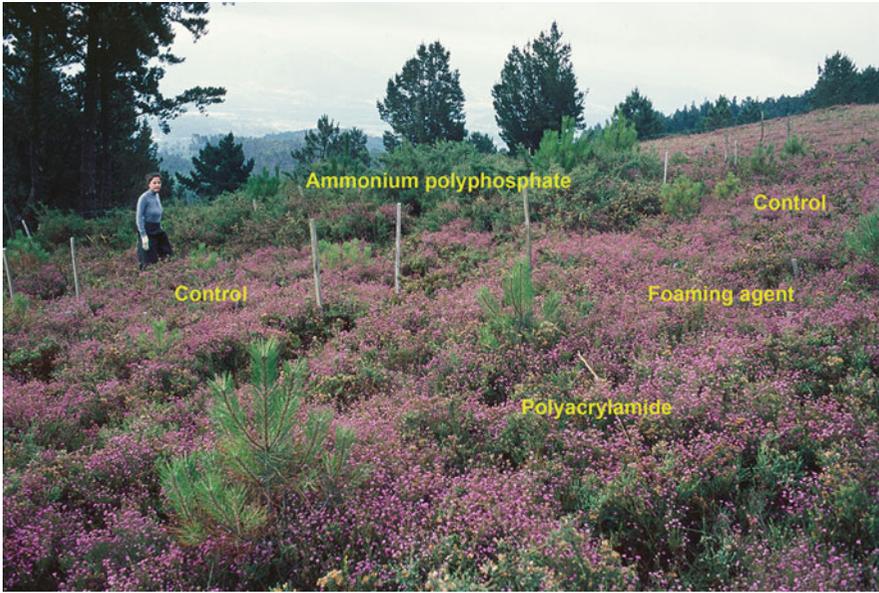
Extinguishment Agents, Fig. 1 Burned plots without (control) or with a long-term (ammonium polyphosphate) and two short-term (foaming agent and polyacrylamide) extinguishment agents after 5 years (experimental site of Couto-Vázquez et al. 2011)

effect that increases plant cover and biomass (Adams and Simmons 1999; Couto-Vázquez et al. 2011) (see Fig. 1). Ammonium-phosphate LTEAs have neither acute toxicity nor effects on species richness, evenness, diversity, and plant density at the short term (Larson et al. 1999), but the "necessary long-term studies of at least 10 years" (Giménez et al. 2004) show that they have important effects on the vegetation (Fernández-Fernández et al. 2015): (a) increased plant phosphorous concentrations by a factor of two; (b) altered sodium and potassium uptake in some shrubs; (c) reduced pine's viability; (d) modified shrub community composition (resprouters favored over obligate seeders); and (e) altered plant N nutrition, likely by decreasing the importance of plant-mycorrhizal associations. The displacement of some species by others favored by the fertilizer effect of nitrogen- and phosphorous-rich LTEAs, even in mesotrophic ecosystems, is a cause of major concern because their impact on sensitive oligotrophic species or ecosystems would probably be stronger (Hopmans et al. 2007; Couto-Vázquez et al. 2011). Although some STEA foams showed

phytotoxicity in laboratory assays, their effects in field conditions are usually subtle and short-lived (Couto-Vázquez et al. 2011; Song et al. 2014). However, shoot damage, suppressed flowering, and foliage death after foam applications can occur (Adams and Simmons 1999), and an STEA hydro-gel is suspicious of decreasing pine viability (Couto-Vázquez et al. 2011; Fernández-Fernández et al. 2015).

Regarding terrestrial fauna, neither LTEAs nor STEAs are harmful for ants or small mammals, but are moderately toxic to lethal for birds and can have adverse effects on bigger mammals (Adams and Simmons 1999; Kalabokidis 2000).

Human Health
Most of the chemicals employed in the extinguishment agents are common ingredients in agricultural fertilizers, domestic products (soaps, cleaners, paints, cosmetics), and even food preservatives. Neither systematic toxicity nor carcinogenic, reproductive, or mutagenic effects have been documented and, therefore, the extinguishment agents are considered innocuous for humans unless prolonged contact – which

can cause skin and eye irritation – or accidental ingestion (Kalabokidis 2000). Nevertheless, as explained before, fire extinction with LTEAs usually increase the production of smoke and airborne particulates – because of the incomplete combustion – and the release of ammonia gas from the thermal decomposition of ammonium-based LTEAs; as a consequence, transitory difficulties to breath, as well as throat and lungs irritation, can occur (Giménez et al. 2004).

Summary

The use of chemical additives to improve water effectivity for fire extinction is a valuable, and sometimes irreplaceable, resource in fire-fighting operations. However, most extinguishment agents are not free of ecological consequences that must be taken into account, particularly in the case of valuable and sensitive habitats or species.

Cross-References

▶ Firefighting Chemical Agents (Retardants) (Wildland Fire Fighting Equipment)
▶ Fuel Retardants (Wildland Fire Mitigation)
▶ Wetting Agents and Foams (WUI Fire Spread Mitigation)

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