

Nitrate Poisoning, Fire Retardants, and Fertilizers—Any Connection?¹

MARVIN DODGE

*State Forest Ranger, California Division of Forestry,
assigned to the Pacific Southwest Forest and
Range Experiment Station, Forest Service,
U.S. Department of Agriculture,
Berkeley, Calif.²*

Highlight

Fire retardants used in combating forest and range fires have been accused of killing livestock by nitrate poisoning. Ammonia-based retardants cannot cause nitrate poisoning directly. They must first enter the soil, be converted to nitrates, then be absorbed and accumulated by plants. This process occurs only under special climatic conditions and requires two to three weeks. The possibility of injury to livestock from fire retardant materials is very slight—much less than that from a range or pasture fertilization program.

No phase of forest fire control has developed as rapidly, or changed so drastically, as the use of fire retardant chemicals. Retardants dropped by air tankers have brought about a complete revolution in firefighting methods. Properly used, they can be valuable tools in the constant fight against loss of natural resources by fire.

Since the introduction of the ammonium-base retardants, a few isolated cases of damage to crops and animals have been reported. Some of these cases have been injury or physical damage to crops ready for market. For example, one air tanker jettisoned a load of retardant over a pear orchard in northern California. The retardant caused skin blemish on the ripening fruit, resulting in a de-grade of the crop.³ A similar incident occurred when a load was jettisoned over an apple orchard in Washington. None of these incidents resulted in any permanent damage to the trees. In fact, they probably had an over-all fertilizing effect on the orchards, although the growers involved suffered a one-time crop loss in the area covered by the drop pattern. There have also been several reports of fish killed when retardants were dropped directly into streams. In one case, the fire retardant increased the salt content of the water for several hundred feet downstream, killing a number of trout.⁴ However, this condition was only temporary, and the stream soon returned to normal con-

dition as the salt concentration was diluted down to a tolerable level. In a potentially more serious case, ammonium sulphate salt was washed into a pasture. Shortly thereafter, several animals died with symptoms of nitrate toxicity.⁵

This paper reviews the possible toxic effect of ammonium phosphate and sulphate fire retardants to domestic animals and wildlife. It describes the chemical change of ammonium phosphate and sulphate into nitrate and the probability of this occurring under natural conditions. And it discusses the probability of animals getting nitrate and nitrate poisoning from other sources.

Nitrate Poisoning

Most fertilizers and fire retardants are ammonium-based. The ammonium salts must be changed to nitrates in the soil, absorbed by plants, and eaten by animals before nitrate poisoning can occur. And at each stage of this three-step process—from soil to plant to animal—the excess accumulation of nitrates can be halted.

Nitrification in the Soil

Nitrification, the first stage, is the oxidation of ammonium salts to nitrate. Nitrification is almost entirely a bacterial activity and only takes place in soil. It is a two-step process, accomplished by two separate micro-organisms: *Nitrosomonas* oxidizes ammonia to nitrite, $\text{NH}_3 \rightarrow \text{NO}_2^-$; and *Nitrobacter* oxidizes the nitrite to nitrate, $\text{NO}_2^- \rightarrow \text{NO}_3^-$ (Thimann, 1963). Both nitrate (NO_3^-) and ammonia (NH_3) are relatively nontoxic to animals and humans.

Both *Nitrosomonas* and *Nitrobacter* are strictly aerobic—they function only in a well-aerated environment (Fry, 1955). The amount of nitrate produced from the ammonium-based fertilizers depends on the amount of oxygen present in the soil.

Amer and Bartholomew (1951) treated soil samples with ammonium sulphate and exposed them to air streams of varying oxygen content. After 21 days, the level of nitrate was highest in the highest concentration of oxygen tested (20%). At low oxygen levels there was very little nitrate. As the oxygen level approached zero, the nitrate level was zero, indicating reduction or denitrification of nitrate originally present in this soil.

Denitrification by micro-organisms is especially common when soil remains saturated with standing water for any considerable period of time. Thimann (1963) reported that in waterlogged soils, such as flooded rice fields, nitrate often disappears completely and ammonia may accumulate. When the soil dries out again, and aerobic conditions prevail, nitrate may reappear.

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²Author stationed at Riverside, California.

³Correspondence on file, State Forester's Office, California Division of Forestry, Sacramento, California, August–October, 1964.

⁴Correspondence on file, State Forester's Office, Sacramento, California, July–September, 1966.

⁵Letter to Forest Supervisor, Lassen National Forest, November 30, 1966.

Once the ammonium-based fertilizers have been changed to nitrates in the soil, they can be absorbed by plants. But plants vary widely from one species to another in their uptake and use of nitrogen. In general, plants may absorb nitrogen either as nitrate or as ammonium salts. They use ammonium best at a neutral, or alkaline soil reaction and nitrates in an acid medium (McKee, 1962).

Nitrate absorption by plants depends not only on the amount of nitrate in the soil, but also depends upon the kinds and amounts of other ions present (Crawford and Kennedy, 1960; McKee, 1962). A high concentration of phosphate in the soil impedes the absorption of nitrate. There is also an indication that high chloride content may depress the uptake of nitrates by certain plants. Potassium, manganese, and sulphur deficiencies lead to nitrate accumulation (McKee, 1962).

Light intensity and temperatures affect the nitrate content of plants. In New Zealand, Bathurst and Mitchell (1958) found nitrate content highest with low light and high temperatures and lowest with high light intensity and low temperatures. Crawford and Kennedy (1960) also found nitrates increasing in low levels of light. McKee (1962) believed that nitrate use was affected by photosynthesis by the plants, since nitrate accumulates in plants held in the dark.

Drought occurring late in the growth cycle also leads to nitrate accumulation (Crawford and Kennedy, 1960; Whitehead and Moxon, 1952).

Plant treatment by 2,4-D, or related compounds, may cause problems with nitrate. The 2,4-D produces two results: (1) an upset in the plant's nitrogen metabolism may cause an increase in the nitrate level of the plants, and, (2) the treatment increases the palatability of weeds high in nitrates that would not ordinarily be eaten by animals (Kingsbury, 1964; Whitehead and Moxon, 1952).

The growth stages of plants influence nitrate content—nitrates are generally highest in immature plants. Nitrate concentration decreases as plants mature (Crawford and Kennedy, 1960; Kennedy, 1958). Nitrate accumulations are normally found in the vegetative parts of the plant. The nitrate levels of stems are normally highest and next in leaves, whereas grain or seeds have a fairly low nitrate content.

Some plant species are more likely to cause nitrate poisoning than others. Oats seem to be one of the worst offenders—so much so that nitrate poisoning is referred to as "oat-hay poisoning" in many parts of the country (Kennedy, 1958; Kingsbury, 1964; Whitehead and Moxon, 1952). In studies in New York, Kennedy (1958) found that perennials accumulated less nitrate-nitrogen than annual grasses. Most workers have found that weeds are the species most commonly associated with high nitrate levels, though many crop plants

have also been involved. Kingsbury (1964) lists 47 different species of weeds and 21 crop plants that have been responsible for nitrate poisoning or have shown high nitrate levels. Workers in California (Tucker et al., 1961) have compiled a list of 64 species of plants responsible for nitrate poisoning or showing high nitrate levels. Crop plants include oat hay, corn, alfalfa, beets and sudan grass.

Kingsbury (1964) reported that most workers agree that nitrate levels above 1.5% of the plant weight may prove lethal. Lewis (1951) found nitrate levels ranging from 3.2 to 7.2% in oat hay that had caused poisoning. Whitehead and Moxon (1952) report nitrate levels as high as 5.8% in oat hay, 3.1% in wheat hay, but only 0.7% in native grasses. Eight species of weeds had nitrate levels of 4.2 to 7.7%, with an average of 6.0%.

Nitrates in Animals

Most animals, including humans, can get nitrate poisoning. Animals that chew their cud (ruminants) are especially susceptible because they harbor micro-organisms in their rumen (Tucker et al., 1961; Whitehead and Moxon, 1952).

Nitrate poisoning is actually poisoning by nitrite. When forage has a normal nitrate content, nitrate is reduced to ammonia in two steps (Fig. 1):

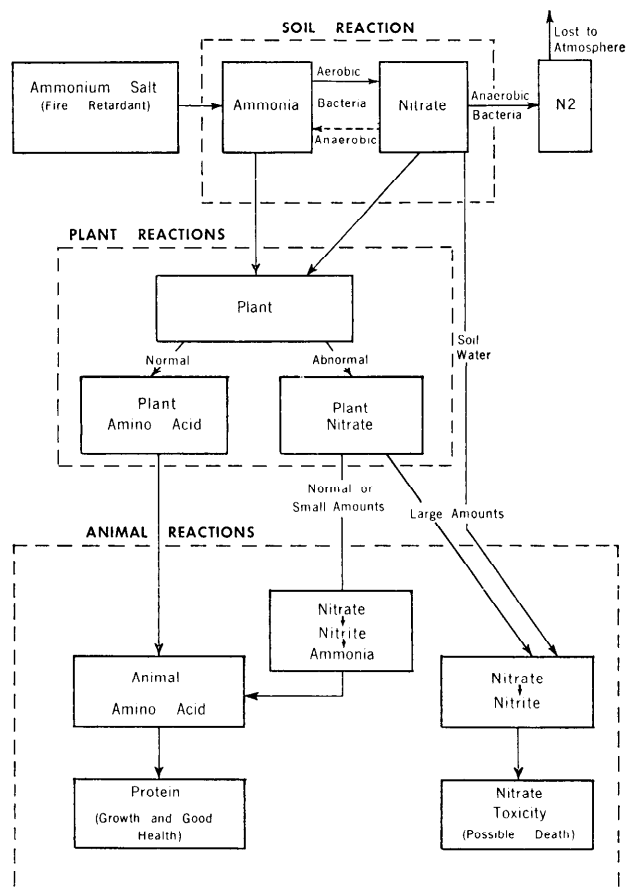


Fig. 1. Flow diagram of nitrate and amino acid conversion.

first, it is reduced to nitrite in the rumen of the animal; second, the nitrite is further reduced to ammonia, which is then absorbed and used to synthesize amino acids and proteins that the animal needs (Lewis, 1951; McDonald, 1948; Pfander et al., 1957). There is no danger of nitrate poisoning as long as this two-step process occurs rapidly and completely.

But what happens when the forage contains excess nitrate? The conversion of nitrate to ammonia slows down, and the intermediate compound (nitrite) accumulates in the bloodstream. There, the nitrite causes a change in the hemoglobin. Normally, ferrous hemoglobin carries the oxygen in the blood. Nitrite oxidizes ferrous hemoglobin to ferric hemoglobin which is termed methemoglobin. Because methemoglobin cannot transport oxygen, the actual cause of death in nitrate poisoning is usually asphyxiation (anoxia).

Lewis (1951) found that 1 gram of potassium nitrate per kilogram of body weight of sheep was a lethal dose. In studies on sheep weighing 60 kilograms, he found 12 grams of sodium nitrate introduced into the rumen gave a rise in ammonia content. But he detected no methemoglobin in the blood. As dosage was increased from 12 to 22 grams, the amount of methemoglobin gradually increased. At 25 grams of sodium nitrate there was a sharp increase.

Workers in Missouri (Pfander et al., 1957) followed the same procedures as Lewis and found that adding glucose helped speed up the reduction of nitrite to ammonia at low levels but became ineffective at higher concentrations of nitrate. They went further and administered potassium nitrate and potassium nitrite intravenously. They found that sheep could tolerate more than 10 times as much intravenous nitrate as nitrite.

Nitrites often accumulate in moist hay. Several investigators, including Crawford and Kennedy (1960), Kingsbury (1964) and Garner (1961), caution about feeding it to livestock. Nitrates in oat hay are converted into nitrites shortly after the hay is moistened by rain, snow or frost. Animals have been observed to graze a mowed forage without harm; but after the forage became wet, the same animals on the same forage became extremely ill or died. After long periods of exposure (up to 10 days), the nitrite disappears, presumably by conversion to ammonia (Garner, 1961).

One simple means of preventing nitrate poisoning is to postpone the harvesting or grazing of plants treated with high amounts of nitrogen fertilizer during, or right after, climatic conditions that lead to nitrate poisoning.

Feeding a high energy supplement, such as glucose or molasses with feed containing moderate amounts of nitrate can also prevent or reduce the danger of poisoning. Another simple prevention

is to mix the high nitrate feed with safe feed or forage to dilute the harmful concentration of nitrate (Kingsbury, 1964; Tucker et al., 1961; Whitehead and Moxon, 1952). And antibiotics may furnish partial protection by reducing the number of bacteria which convert nitrates to nitrite in the rumen (Emerick and Embry, 1961).

Composition of Fire Retardants

The two most widely used fire retardants—PhosChek and FireTrol—are both ammonium-based compounds.⁶ Both have thickening agents to improve air drop characteristics and adherence to fuels. Both also have corrosion inhibitors to protect mixing and storage equipment and aircraft structures. The composition of each compound is as follows:

*FireTrol*⁷

Ammonium sulfate	fire retardant
Attapulgate clay	thickening agent
Sodium dichromate	corrosion inhibitor
Ferric oxide	coloring agent

*PhosChek*⁸

Diammonium phosphate	fire retardant
Sodium carboxymethylcellulose	thickening agent
"Dowicide A" ⁹ (Sodium orthophenyl phenate)	bactericide
Sodium fluorosilicate	corrosion inhibitor
_____ ¹⁰	corrosion inhibitor
_____ ¹⁰	corrosion inhibitor
_____ ¹⁰	flow conditioning agent
Ferric oxide	coloring agent

Attapulgate clay, the thickening agent used in FireTrol, is a hydrated magnesium silicate. It has a relatively low ion-exchange capacity and slurries made from it show little variation in viscosity and gel strength with large variations in salt content. These same properties lead to wide use as drilling mud in the petroleum industry. The low toxicity of attapulgate clay has led to wide pharmaceutical use for intestinal, absorbent preparations (Grim, 1962).

Sodium carboxymethylcellulose (CMC)—the thickening agent used in PhosChek—is a soluble,

⁶Trade names and commercial products or enterprises are mentioned solely for necessary information. No endorsement by the U.S. Department of Agriculture is implied.

⁷Registered trademark of Arizona Agrochemical Corp.

⁸Registered trademark of Monsanto Co.

⁹Registered trademark of Dow Chemical Co.

¹⁰Ingredients not revealed by Monsanto Co. as they are not yet covered by patents.

relatively stable derivative of wood cellulose (Fettes, 1964). It is subject to decomposition by many microbes, including possibly harmful species. To prevent microbial degradation of the CMC, with a resultant loss in viscosity, the manufacturer adds a bactericide, sodium orthophenyl phenate.

Sodium dichromate, an oxidizing agent, does not oxidize ammonium sulfate to nitrate. The dissociation of ions in the retardant solution may lead to the formation of a slight amount of ammonium dichromate, which is a relatively stable compound. In fact, the commercial preparation of ammonium dichromate is made by mixing sodium dichromate and ammonium sulfate in solution.

All of the corrosion inhibitors are used in retardants in such small quantities that they are harmless, although they may be considered toxic in larger amounts. Toxicity is a relative matter and depends upon the quantity of material. As an example, sodium fluorosilicate is commonly used for fluoridation in toothpastes and drinking water.

Younger Laboratories, St. Louis, Missouri, investigated the formulations of PhosChek. Even though all the ingredients of that retardant are not revealed, we have information from this report on tests of oral toxicity. The compound was fed to rats by stomach tube in increasing doses. "The highest dose of 25,100 milligrams per kilogram was found to be non-lethal by oral ingestion in male and female rats. No larger dose was given in order to avoid seriously overloading the stomach."¹¹

Conclusions

There does not appear to be any toxicity problem with fire retardants. We cannot say positively that ammonium phosphate or sulphate cannot kill livestock, any more than we could say that they could not be killed by an excessive amount of the best hay available, or that they could not drown in their drinking water.

But from this literature review, it appears the danger of nitrate poisoning from fire retardants is very remote. Certainly it is much less than that from a range or pasture fertilization program. Most range and pasture fertilizing projects cover rather large areas at rates of 200 to 800 pounds per acre. The drops of fire retardants at rates of 1,000 to 1,200 pounds per acre normally cover a rather narrow strip, and the total area covered by drops in any given locality would be rather small.

Ammonium-based fire retardants and fertilizers cannot cause trouble until they are cycled through the soil and into plants. Plants rarely accumulate nitrates except under conditions of low light intensity and high temperatures, or when drought occurs late in the growth cycle. Even when these special climatic conditions occur, trouble can still be avoided by deferring grazing for three or four weeks so that plants can convert the extra nitrates into normal, harmless protein.

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¹¹Certificate of analysis, December 6, 1965. Younger Laboratories, 123 Cliff Road, St. Louis, Missouri.