United States Department of Agriculture
Agricultural Marketing Service | National Organic Program
Document Cover Sheet
https://www.ams.usda.gov/rules-regulations/organic/national-list/petitioned

Document Type:

☐ **National List Petition or Petition Update**

A petition is a request to amend the USDA National Organic Program's National List of Allowed and Prohibited Substances (National List).

Any person may submit a petition to have a substance evaluated by the National Organic Standards Board (7 CFR 205.607(a)).

Guidelines for submitting a petition are available in the NOP Handbook as NOP 3011, National List Petition Guidelines.

Petitions are posted for the public on the NOP website for Petitioned Substances.

☒ **Technical Report**

A technical report is developed in response to a petition to amend the National List. Reports are also developed to assist in the review of substances that are already on the National List.

Technical reports are completed by third-party contractors and are available to the public on the NOP website for Petitioned Substances.

Contractor names and dates completed are available in the report.

Ammonium Soaps

Crops

Identification of Petitioned Substance

Chemical Names:
Anhydrous Ammonium Soaps

Other Name:
Ammonium Soaps
Ammonium Salt of Fatty Acids
Perlargonic Acid, Ammonium Salt

Trade Names:
Hinder®

CAS Numbers:
84776-33-0 (Ammonium soaps of fatty acids C8 – C18)
63718-65-0 (Ammonium nonanoate)

Other Codes:
EPA Registration No.: 66702-7-39609 (Ammonium soaps of fatty acids)
EPA PC Code: 031801 (Ammonium salts of fatty acids (C8 – C18)

Summary of Petitioned Use

Ammonium soaps have been approved by the United States Department of Agriculture's (USDA) National Organic Program (NOP) for a range of uses pertaining to crop production. These uses are listed in 7 CFR 205.601, and include applications as synthetic substances to act as algicides/demossers ((a)(7)), herbicides ((b)(1)), insecticides ((e)(8)), and animal repellents (d). The application of ammonium soaps as an herbicide was covered by a 2011 technical report on ammonium nonanoate (USDA 2011); algicide/demossing applications were included as a component of a technical report on soap-based algicides/demossers (USDA 2015a); and herbicide applications were included as a component of a technical report on soap-based herbicides (USDA 2015b).

The purpose of this report is to provide information about the use of ammonium soaps as animal repellents to protect organically produced crops from unwanted browsing.

Characterization of Petitioned Substance

Composition of the Substance:
Ammonium soaps are produced from the hydrolysis of ester linkages in fatty acids. When hydrolysis is performed under basic conditions, a process known as saponification, the result is a carboxylate salt of the original fatty acid, commonly referred to as soap. Natural fatty acids are composed of a mixture of both saturated fats (all single carbon–carbon bonds) and unsaturated fats (containing multiple carbon–carbon bonds). Therefore, the soap product consists of a variety of carbon chains (Anneken et al. 2012, AMVAC 2015, Schultz Company 2016). Most commercially relevant fatty acids consist of linear carbon chains with a length of six to twenty-two carbons, with soaps frequently containing chains of eight to eighteen carbon chains, with ammonium nonanoate (9 carbons) being among the most prevalent (EPA 2000, USDA 2011, Anneken et al. 2012, EPA 2013, USDA 2015a, USDA 2015b). The base that is used determines which cation is associated with the soap, and ammonium soaps are formed from treatment of fatty acids with ammonium hydroxide (NH_4OH) or ammonia (NH_3, which forms NH_4OH when dissolved in water) (Anneken et al. 2012, AMVAC 2015, USDA 2015a, USDA 2015b).

Source or Origin of the Substance:
Ammonium soaps are manufactured by subjecting natural fatty acids (from both animal and plant sources) to the process of saponification. The saponification hydrolyzes the ester linkages in the natural fatty acid (derived from animal fats or plant oils) in the presence of a base, specifically ammonium hydroxide (NH_4OH) or aqueous ammonia ($NH_{3(aq)}$), which reacts with water to form ammonium hydroxide *in situ* (Reiling and Robert 1962, Nora and Koenen 2010, USDA 2011, Anneken et al. 2012, Jianu 2012, USDA 2015a, USDA 2015b).

Ammonia is a naturally occurring inorganic gas that is a product of many metabolic reactions (MeSH D000641). Ammonia is a commodity chemical, and most commercially available ammonia is produced through the iron catalyzed reduction of atmospheric nitrogen (N_2) with a hydrogen source in the Haber-Bosch process (Clayton and Clayton 1994). Ammonium hydroxide (NH_4OH) is produced by an acid-base reaction in which ammonia (base) removes a proton (H^+) from water (acid) (Czuppon et al. 1992, Silberberg 2003).

Properties of the Substance:

The chemical and physical properties of ammonium soaps are dependent on the length of the carbon chain. Longer carbon chains produce a more nonpolar molecule, which increases the hydrophobicity of the soap product (Anneken et al. 2012, EPA 2013, USDA 2015a, USDA 2015b). As a result, long chain ammonium soaps have reduced water solubility compared to soaps with shorter carbon chains, which bear a larger ratio of negative charge per molecular weight. Since commercial ammonium soaps consist of a range of possible chain lengths (8–18), their water solubility varies, although they trend toward low water solubility (Anneken et al. 2012, USDA 2015a, USDA 2015b).

The properties of mixed-chain ammonium soaps and ammonium nonanoate, the most common chain length, are summarized below in Table 1 (EPA 2000, EPA 2013, USDA 2015a, USDA 2015b).

Table 1. Properties of Ammonium Nonanoate and Ammonium Soaps

Compound	Ammonium Soaps C8 – C18	Ammonium Nonanoate
CAS No.	84776-33-0	63718-65-0
Molecular Weight	N/A	175.27 g/mol
General Appearance	Brown to white/clear liquid, ammonia and/or soapy odor	Clear/pale liquid, slight ammonia odor
Solubility	Water Insoluble	Water Soluble
Melting Point	-1 ^{o}C	N/A
Boiling Point	101 ^{o}C	104.4 ^{o}C
Specific Gravity	0.80 – 0.988	1.0
pH	7 – 10	8 – 9

Sources: AMVAC 2015, Biosafe Systems 2017, Schultz Company 2016, PubChem 21902950

Specific Uses of the Substance:

Ammonium soaps have a wide range of uses for organic agricultural crop production. These applications include the use of ammonium soaps as a herbicide for the control of mosses, algae, and weeds (USDA 2015a, USDA 2015b). Herbicidal applications of ammonium soaps are present in a range of agricultural settings, including sidewalks, roadways, ditches, and building perimeters (USDA 2015a, USDA 2015b). Applications of ammonium nonanoate and other ammonium soaps have also been used as insecticides for the control of aphids and other sucking insects and pests (Sarwar and Salman 2015).

Ammonium soaps are also used as animal repellents, primarily for protection against deer and rabbit browsing (Boggess 1981, Andelt et al. 1991, Pierce and Wiggers 1997, Craven et al. 2001, Wagner and Nolte 2001). Within organic agriculture, the application of ammonium soap repellents is limited to "no contact with soil or edible portion of crop," as stipulated in 7 CFR 205.601. However, in non-organic agriculture the application of soap is allowed as a contact repellent on edible crops (Swihart and Conover 1991, Pierce and Wiggers 1997, Ward and Williams 2010) .

Approved Legal Uses of the Substance:

The United States Food and Drug Administration (FDA) has approved the use of "salts of volatile fatty acids," specifically "ammonium salts of mixed 5-carbon acids," and the "ammonium salt of isobutyric acid" for use "as a source of energy in dairy cattle feed" at 21 CFR 573.914. The FDA has also approved the use of "salts of fatty acids" for use "in food and in the manufacture of food components" at 21 CFR 172.863, however, this usage has not been extended to fatty acid salts with ammonium cations.

The United States Environmental Protection Agency (EPA) has described the manufacture of soap at 40 CFR 417.30 as the “neutralizing refined fatty acids with an alkaline material in approximately stochiometric amounts.” The EPA has designated “soap” as an “inert ingredient permitted in minimum risk pesticide products,” and have been granted “exemptions for pesticides of a character not requiring [Federal Insecticide, Fungicide, and Rodenticide Act] FIFRA regulation” at 40 CFR 152.25. However, this exemption is specified for “the water-soluble sodium or potassium salts of fatty acids produced by either the saponification of fats and oils, or the neutralization of a fatty acid,” and therefore has not been extended to soaps with ammonium cations (40 CFR 152.25).

The USDA organic regulations allow ammonium soaps as a “synthetic substance allowed for use in organic crop production” at 7 CFR 205.601. These ammonium soaps have been approved for several organic crop applications, including as an algicide/demosser or herbicide “for use in farmstead maintenance (roadways, ditches, right of ways, building perimeters) and ornamental crops” (7 CFR 205.601(b)(1)). However, the approved use pertaining to this technical report is that of an animal repellent “for use as a large animal repellent only, no contact with soil or edible portion of crop” (7 CFR 205.601(d)).

Action of the Substance:

When ammonium soaps are used as repellents, they fall under both broad categories of area and contact repellents (Boggess 1981, Osko et al. 1993, Craven and Hyngstrom 1994). When used as area repellents, ammonium soaps include residual ammonia from the saponification manufacturing process (AMVAC 2015). Additionally, ammonia can be liberated by a reaction of the ammonium soap with bases found in the agro-ecosystem, as seen in Equation 1 (Boggess 1981). Such bases are prevalent within the environment, with many soils being basic or alkaline (high pH) in nature (Al Omari et al. 2016).

$$\underset{\text{base}}{\ddot{B}^{\ominus}} + \underset{\text{ammonium}}{{}^{\oplus}NH_4} \longrightarrow \underset{\text{conjugate acid}}{\ddot{B}H} + \underset{\text{ammonia}}{NH_3}$$

Equation 1

Ammonium soaps are also included as contact repellents. Within this context the substance is classified as an aversion repellent (Conover 1995, Ward and Williams 2010, Williams and Short 2014). Aversion repellents work by producing a negative physiological effect (e.g. nausea) when consumed by the target animal, most commonly deer and rabbits (Osko et al. 1993, Conover 1995, Pierce and Wiggers 1997, Wagner and Nolte 2001). Over time the target animal begins to associate the mild illness with the treated plant, and this negative association builds a natural aversion to the treated plant, providing eventual protection (Conover 1995, Ward and Williams 2010, Williams and Short 2014).

Combinations of the Substance:

When used as approved the ammonium soap is the active ingredient in the repellent, providing protection through the low-level emission of ammonia (odor) and by aversion due to nausea after ingesting the soap (Boggess 1981, Osko et al. 1993, Craven and Hyngstrom 1994, Ward and Williams 2010, Williams and Short 2014).

Literature studies suggest that ammonium soaps may be combined commercially with surfactants to enhance adhesion to the plant and increase the effective lifetime of the product, however, when used in organic agriculture these additional substances must also comply with USDA regulations at 7 CFR 205.601(m) (Ries et al. 2001, Rahimov and Asadov 2013).

Status

Historic Use:

Ammonium soaps have several historic applications within organic agricultural production, as detailed at 7 CFR 205.601. These include being used in farmstead maintenance as an herbicide to prevent the growth of algae, moss, and undesirable weeds.

Ammonium soaps are also used to protect both ornamental and edible crops. This protection is offered because ammonium soaps act as both an insecticide and as a large animal repellent (Osko et al. 1993, Conover 1995, Pierce and Wiggers 1997, Wagner and Nolte 2001, Sarwar and Salman 2015). As an insecticide, ammonium soaps penetrate cellular membranes, causing the insect to undergo cell damage and respiratory system disruption (Sarwar and Salman 2015). When applied as an animal repellent, ammonium soaps work through two pathways: area repellents through the slow release of low-level ammonia and contact repellents which induce nausea following ingestion (Boggess 1981, Osko et al. 1993, Craven and Hyngstrom 1994).

Organic Foods Production Act, USDA Final Rule:

Ammonium soaps are not listed in the Organic Foods Production Act of 1990 (OFPA). Ammonium soaps are listed as a "synthetic substance allowed for use in organic crop production" for use as an "algicide/demosser," "herbicide," and a "large animal repellent" in the USDA organic regulations at 7 CFR Part 205.601. Ammonium soaps were first approved as a "large animal repellent" in 2000 (6 FR 80547).

International

Canadian General Standards Board Permitted Substances List —

Ammonium soaps are listed in the CAN/CGSB-32.311-2015 — Organic production systems - permitted substances lists.

Ammonium soaps are listed in Table 4.3 "Crop production aids and materials," as "a large animal repellent," with the requirement that "direct contact with soil or edible portion of crop is prohibited," and in Table 8.2 "Facility pest management substances," with the requirement that "direct contact with organic products is prohibited."

Soap is listed as soaps in Table 4.3 "Crop production aids and materials," with the definition that "soaps (including insecticidal soaps) shall consist of fatty acids derived from animal or vegetable oils."

Soaps are listed as a surfactant in Table 4.2 "Soil amendments and crop nutrition," and Table 4.3 "Crop production aids and materials," with the requirement of being "nonsynthetic." Soap is listed as a surfactant with no restrictions in Table 7.4 "Cleaners, disinfectants, and sanitizers permitted on organic product contact surfaces for which a removal event is mandatory."

Soap is listed as a wetting agent in Table 4.3 "Crop production aids and materials," and Table 7.4 "Cleaners, disinfectants, and sanitizers permitted on organic product contact surfaces for which a removal event is mandatory," with the requirement of being "nonsynthetic."

Soap is listed as a formulant in Table 4.3 "Crop production aids and materials," when "classified in [Pest Management Regulatory Agency] PMRA List 4A or 4B or nonsynthetic."

Soap-based algicides (demossers) are listed in Table 7.4 "Cleaners, disinfectants, and sanitizers permitted on organic product contact surfaces for which a removal event is mandatory."

CODEX Alimentarius Commission, Guidelines for the Production, Processing, Labelling and Marketing of Organically Produced Foods (GL 32-1999) —

Ammonium soaps are not listed in the CODEX.

European Economic Community (EEC) Council Regulation, EC No. 834/2007 and 889/2008 —

Ammonium soaps are not listed in the EEC EC No. 834/2007 or 889/2008.

However, potassium soaps are listed in EC No. 889/2008 as "fatty acid potassium salt," as an insecticide with applications "from traditional use in organic farming." Potassium and sodium soaps are listed in EC No. 889/2008 as "products for cleaning and disinfection of buildings and installations for livestock production."

Japan Agricultural Standard (JAS) for Organic Production —
Soap is listed in the JAS for Organic Production Notification No. 1608 as an "agent for cleaning or disinfecting of housing for livestock."

Potassium soap is also listed in the JAS for Organic Production Notification No. 1606 as a "chemical agent," with the exception of "the purpose of pests control for plants."

International Federation of Organic Agriculture Movements (IFOAM) —
Ammonium soaps are not listed in IFOAM.

However, potassium soaps are listed in IFOAM as "an equipment cleanser and equipment disinfectant," with the requirement that "an intervening event or action must occur to eliminate risks of contamination."

Evaluation Questions for Substances to be used in Organic Crop or Livestock Production

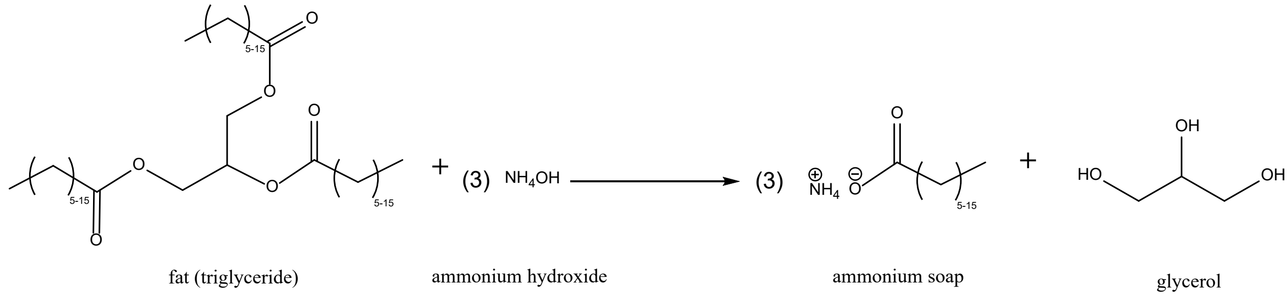
Evaluation Question #1: Indicate which category in OFPA that the substance falls under: (A) Does the substance contain an active ingredient in any of the following categories: copper and sulfur compounds, toxins derived from bacteria; pheromones, soaps, horticultural oils, fish emulsions, treated seed, vitamins and minerals; livestock parasiticides and medicines and production aids including netting, tree wraps and seals, insect traps, sticky barriers, row covers, and equipment cleansers? (B) Is the substance a synthetic inert ingredient that is not classified by the EPA as inerts of toxicological concern (i.e., EPA List 4 inerts) (7 U.S.C. § 6517(c)(1)(B)(ii))? Is the synthetic substance an inert ingredient which is not on EPA List 4, but is exempt from a requirement of a tolerance, per 40 CFR part 180?

A) The substance is categorized as a soap. Ammonium soaps are composed of an ammonium cation (NH_4^+) associated with the carboxylate anion of a neutralized fatty acid (ROO^-) with a chain length eight to eighteen carbons long and are commonly referred to as "soaps."

B) Ammonium soaps are not listed by the EPA as an inert ingredient of toxicological concern. The EPA has designated "soap" as an "inert ingredient permitted in minimum risk pesticide products," and it has been granted "exemptions for pesticides of a character not requiring FIFRA regulation" at 40 CFR 152.25. However, this exemption is specified for "the water soluble sodium or potassium salts of fatty acids produced by either the saponification of fats and oils, or the neutralization of a fatty acid," and therefore has not been extended to soaps with ammonium cations.

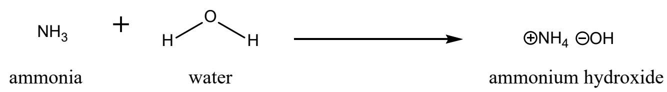
Evaluation Question #2: Describe the most prevalent processes used to manufacture or formulate the petitioned substance. Further, describe any chemical change that may occur during manufacture or formulation of the petitioned substance when this substance is extracted from naturally occurring plant, animal, or mineral sources (7 U.S.C. § 6502 (21)).

Ammonium soaps are manufactured by the hydrolysis of fats (triglycerides) with an alkaline source in a process known as saponification (Anneken et al. 2012). In this process, the base reacts with the fatty ester to break the ester linkages, resulting in the formation of a salt with the cation of the base and the carboxylate anion that remains at the end of the hydrolysis, as illustrated in Equation 2 below (Reiling and Robert 1962, Anneken et al. 2012, Jianu 2012).



Equation 2

In the manufacture of ammonium soaps, ammonium hydroxide is commonly used as the base for the hydrolysis reaction, as shown in Equation 2. However, ammonia may also be used as the basic reagent for the treatment of an aqueous mixture of fats (Reiling and Robert 1962, Anneken et al. 2012). In this instance the ammonia ($NH_{3(g)}$) is dissolved and reacts with water to form the active ammonium hydroxide (NH_4OH) substance *in situ*, as shown in Equation 3.



Equation 3

A wide range of fats may be used in the saponification process, including both plant and animal fats. These fats are commonly sourced by further processing crude by-products (palm oil, sunflower oil, vegetable oil, coconut oil, olive oil, and tallow sources) from human nutritional industries (Kostka and McKay 2002, Anneken et al. 2012, Rahimov and Asadov 2013, Burns-Moguel 2014). Due to the abundance of fat sources, the final soap salt is comprised of a range of carbon chain lengths, rather than a consistent chain length throughout the final product.

Alternative manufacturing processes exist to produce synthetic soaps from long-chain hydrocarbons. However, due to the relative abundance of fats and their low cost, most soaps are produced by the saponification of natural fats isolated from plant and animal sources (Anneken et al. 2012).

Evaluation Question #3: Discuss whether the petitioned substance is formulated or manufactured by a chemical process, or created by naturally occurring biological processes (7 U.S.C. § 6502 (21)).

Soaps do not naturally exist but are manufactured by the treatment of fats with a strong base (e.g. ammonium hydroxide (NH_4OH)) through saponification (Anneken et al. 2012, Jianu 2012). Ammonium cations (NH_4^+) and fatty acid carboxylate anions (ROO^-) both exist in nature; however, they are not typically found associated with one another in salt form (as soaps).

Fatty acids are important molecules in the metabolic cycles of a range of animals and microbes and provide both with key sources of energy (EPA 1992, EPA 2013, Anneken et al. 2012, Rahimov and Asadov 2013). Ammonium is also a natural molecule in the environment and plays an important role in the metabolic pathways of a range of organisms, as well as being a key component of the nitrogen cycle (EFSA 2008).

Due to the relative abundance and low cost of natural fats, they are the primary source of fatty acids to provide the carboxylate anion in commercial soaps (Anneken et al. 2012). When ammonium soaps are desired, ammonium hydroxide (NH_4OH) or ammonia (NH_3) are used as the base for the saponification process (Reiling and Robert 1962, USDA 2011, USDA 2015a, USDA 2015b).

Evaluation Question #4: Describe the persistence or concentration of the petitioned substance and/or its by-products in the environment (7 U.S.C. § 6518 (m) (2)).

Studies conducted by the EPA estimate that ammonium soaps will undergo rapid degradation in the environment, primarily through microbial metabolism, yielding an environmental half-life of less than one day (EPA 1992, EPA 2008, EPA 2013). Both the ammonium cation (NH_4^+) and carboxylate anion (ROO^-) are important molecules for the metabolic cycles for many animals and microorganisms (ESFA 2008, Rahimov and Asadov 2013). Due to the prevalence of both ionic components of ammonium salts in metabolic pathways, they do not persist in the environment (EPA 1992, EPA 2013).

Due to the diversity of metabolic pathways that fatty acids are involved with, their metabolism results in the production of thousands of different products (EPA 1992, EPA 2013, Rahimov and Asadov 2013). The involvement of these products in the metabolic and respiratory cycles microorganisms, animals, and plants makes the persistence and accumulation of ammonium soap by-products is impossible to track (EPA 1992, EPA 2013, Rahimov and Asadov 2013). However, the diversity of systems that these products are involved in, coupled with their natural abundance likely results in a negligible contribution from the application of ammonium soap repellents.

<u>Evaluation Question #5:</u> Describe the toxicity and mode of action of the substance and of its breakdown products and any contaminants. Describe the persistence and areas of concentration in the environment of the substance and its breakdown products (7 U.S.C. § 6518 (m) (2)).

The toxicological profile of the substance differs based on the environment in which it is located. Ammonium soaps are widely regarded as having low toxicity to terrestrial organisms, with little impact to mammals and avian animals (EPA 2013). The EPA has placed the substance in Toxicity Category IV, the lowest available classification (EPA 1992, EPA 2008). Moreover, there have been no long-term studies on the environmental toxicity of ammonium soaps due to their rapid degradation (EPA 2013).

Ammonium soaps are moderately toxic in aquatic environments, although less toxic than potassium soaps (EPA 2008, EPA 2013). The substance has a much larger effect on aquatic invertebrates and has been classified as "highly toxic" to crustaceans (EPA 1992, EPA 2008, Thurston County 2009, EPA 2013). Due to the potential toxicity to aquatic environments, ammonium soap repellent product labels stipulate "This product may be hazardous to aquatic invertebrates. Do not apply to water bodies such as ponds or creeks, areas where surface water is present or to intertidal areas below the mean high-water mark. Do no contaminate water by cleaning of equipment, or disposal of rinse water into such bodies." (EPA 2008).

Ammonium soaps are also used as insecticides (e.g., ammonium nonanoate) (USDA 2011, Sarwar and Salman 2015). The relatively short-chain (C9) fatty acid salt allows increased mobility compared to the longer carbon chains that are also found in ammonium soaps. This increased mobility allows ammonium nonanoate to penetrate cellular membranes in soft-bodied insects (e.g. aphids), disrupting cellular respiration and other processes (Sarwar and Salman 2015). Because ammonium soaps exist as a mixture of carbon chain lengths, the possibility of short-chain ammonium soaps allows for the potential to have unintended insecticidal effects.

As discussed in Question #4, ammonium soaps are not expected to persist in the environment. Fatty acids and their salts are important contributors to the metabolic pathways of a wide range of organisms (REFS). In environmental settings, ammonium soaps are rapidly metabolized, primarily by microorganisms, resulting in an environmental half-life of less than one day for ammonium soaps (EPA 1992, EPA 2008, EPA 2013). Moreover, because these fatty acid salts are incorporated into a diverse array of metabolic pathways across organisms, they form a diverse product pattern (EPA 1992, Rahimov and Asadov 2013). In fact, the breakdown of ammonium soaps throughout these metabolic cycles are predicted to *enhance* the nutritional profile of the environment (Rahimov and Asadov 2013).

<u>Evaluation Question #6:</u> Describe any environmental contamination that could result from the petitioned substance's manufacture, use, misuse, or disposal (7 U.S.C. § 6518 (m) (3)).

Environmental contamination from the product is unlikely when used as approved. The rapid metabolism of the substance by microorganisms, coupled with the low toxicologic effect of ammonium soaps on terrestrial animals, makes even the overapplication of repellents unlikely to result in soil contamination (EPA 1992, EPA 2008, EPA 2013, Rahimov and Asadov 2013).

Ammonium soaps have a much higher toxicological impact on aquatic environments, being labeled as "slightly toxic" to freshwater invertebrates and fish, making misuse and application to bodies of water the most likely means of environmental contamination. (EPA 1992, EPA 2008, Thurston County 2009, EPA 2013). Due to the moderate to high toxicity of ammonium soaps to aquatic life, a large-scale contamination could have a dramatic negative impact on the ecological system. Moreover, the use of ammonium soaps as an algicide/demosser could cause widespread disruption of aquatic ecosystems if applied to bodies of water (USDA 2015a). However, longer chain ammonium soaps would have reduced water solubility compared to short-chain soaps (e.g. ammonium nonanoate), which may mitigate the environmental impact of misuse through aquatic application (Anneken et al. 2012, EPA 2013). Furthermore, the reduced solubility of ammonium soaps compared to alkali (potassium (K^+) and sodium (Na^+)) soaps also reduces their environmental impact (EPA 2013). The impact of the substance to nitrogen levels of aquatic ecosystems is not addressed in the published reports on ammonium soaps.

<u>Evaluation Question #7:</u> Describe any known chemical interactions between the petitioned substance and other substances used in organic crop or livestock production or handling. Describe any environmental or human health effects from these chemical interactions (7 U.S.C. § 6518 (m) (1)).

Ammonium soaps are incompatible with a range of multivalent metal ions ($M^{>+1}$) due to the aggregation and precipitation of the resulting salts (EPA 2013). The increased positive charge of multivalent metal ions results in an association to multiple carboxylate anions (fatty acid chains), increasing the hydrophobicity of the salt. The resulting precipitate removes both the metal ion and carboxylate ion from solution. This is a common problem in areas high in minerals (hard water), which leads to the precipitation of soap aggregates (soap scum) (EPA 2013). This would result in undesirable interactions with lime sulfate, hydrate lime, copper sulfate, ferric phosphate, magnesium sulfate, and micronutrient salts that all have been approved for use in organic crop and livestock production at 7 CFR 205.601 and §205.603.

These undesirable interactions are unlikely to result in any effects to the environment or human health as the nature of the soap does not change dramatically upon cation exchange (replacement of positive ammonium (NH_4^+) with another positive metal ion (M^{n+})). Exchange of the ammonium ion for a multivalent metal ion (M^{n+}) reduces the water solubility of the fatty acid soap salt, thereby reducing its concentration in aquatic environments. The diminished water solubility of the soap metallic soap salts may increase the effectiveness of the repellent by extending the application lifetime of the soap (preventing the soap from washing away with rain, dew, etc.).

However, the aggregation would also serve to remove the multivalent metal ions from the agro-ecosystem. This may result in the sequestration of metal ions that have been added as soil amendments (e.g., micronutrients, pH adjusters), which would no longer be bioavailable following their aggregation in a fatty acid salt.

<u>Evaluation Question #8:</u> Describe any effects of the petitioned substance on biological or chemical interactions in the agro-ecosystem, including physiological effects on soil organisms (including the salt index and solubility of the soil), crops, and livestock (7 U.S.C. § 6518 (m) (5)).

The ability of some ammonium soaps (short-chain soaps) to act as insecticides may result in a negative impact on some insects of the agro-ecosystem. Ammonium soaps (ammonium nonanoate) have been registered as pesticides with the EPA and work by disrupting cellular membranes, although these effects are more widely associated with potassium soaps (EPA 2008, EPA 2013). These negative effects are expected to be the most pronounced in soft-bodied insects including aphids, mites, crickets, earwigs, caterpillars, leaf hoppers, scale crawlers, thrips, whiteflies, and beetles, and may also extend to include earthworms and grubs (Davis et al. 1997, USDA 2011, EPA 2013, USDA 2015a, USDA 2015b). Ammonium soaps have been reported to be "practically nontoxic" to honey bees, with an LD_{50} of > 100 μg/bee (EPA 2013). There is no data available on the effects of soaps (ammonium or alkali) on non-target insects (e.g., earthworms (EPA 2008). Ammonium-based substances (e.g., fertilizers) have been reported to cause negative physiological changes in earthworms and microbial communities due to soil acidification (reduced pH) (Edwards et al. 1995, Liu and Greaver 2010, Lu et al. 2011, Geissler and Scow 2013) However, these data are based on the application of ammonia or ammonium fertilizers which are applied in much larger quantity than the applications of ammonium soaps for use as animal repellents.

As discussed in Question #4, fatty acid salts, such as ammonium soaps, are a major component of the metabolic cycles of a range of organisms. The substance is rapidly metabolized by microorganisms in the soil, resulting in an environmental half-life of less than one day (EPA 1992, EPA 2008, EPA 2013). The combination of short environmental lifetime and low toxicity to terrestrial animals makes negative impacts to crop and livestock production unlikely. Moreover, when used as approved, the substance is not applied to the soil, limiting the potential impact to insects within the agro-ecosystem (7 CFR 205.601).

<u>Evaluation Question #9:</u> Discuss and summarize findings on whether the use of the petitioned substance may be harmful to the environment (7 U.S.C. § 6517 (c) (1) (A) (i) and 7 U.S.C. § 6517 (c) (2) (A) (i)).

There is little to suggest that ammonium soaps pose a threat to the environment when used as approved. The substance is readily metabolized by a range of organisms, resulting in short environmental persistence (half-life of less than one day) (EPA 1992, EPA 2008, EPA 2013). Furthermore, the substance has been documented as having low toxicity to terrestrial and avian species, limiting the impact of the substance even when used improperly (EPA 1992, EPA 2008).

Ammonium soaps have moderate to high toxicities in aquatic environments (EPA 1992, EPA 2008, Thurston County 2009). However, the substance has not been approved for aquatic applications, and the low water solubility of ammonium soaps makes environmental contamination of aquatic ecosystems via runoff pollution unlikely (Anneken et al. 2012, EPA 2013). Ammonium soaps can act as an insecticide, and may negatively impact populations of non-target insects, including earthworms and grubs (USDA 2011, USDA 2015a, USDA 2015b)

As discussed in Question #6, environmental studies on ammonium soaps do not address the impact of the substance on nitrogen levels of aquatic ecosystems. Question #6 also addresses the unlikely prospect of soil contamination due to the rapid metabolism of the substance by soil microorganisms (EPA 1992, EPA 2008, EPA 2013, Rahimov and Asadov 2013). However, studies on the application of ammonia and ammonium-based fertilizers have shown reduced efficiency for nitrogen uptake (Tilman et al. 2002). Moreover, the application of ammonium compounds (e.g., fertilizers) may be lost via ecosystem transfer due to the volatility of ammonium ions (Erisman et al. 2008). This unintentional fertilization can result in decreased biodiversity (Erisman et al. 2008). However, these reports are based on the application of ammonia or ammonium fertilizers applied in much larger quantity than the application of ammonium soaps for use as animal repellents.

<u>Evaluation Question #10:</u> Describe and summarize any reported effects upon human health from use of the petitioned substance (7 U.S.C. § 6517 (c) (1) (A) (i), 7 U.S.C. § 6517 (c) (2) (A) (i)) and 7 U.S.C. § 6518 (m) (4)).

The EPA has given ammonium soaps the lowest possible toxicity classification (Toxicity Category IV) (EPA 1992, EPA 2008). Like many other organisms, humans employ fatty acids in their metabolic cycle as a key source of energy and building blocks for other biologically important molecules, contributing to the low toxicity of ammonium soaps in humans (EPA 1992, EPA 2008, EPA 2013, Rahimov and Asadov 2013). Moreover, the EPA has concluded that the oral intake of dangerous levels of the substance is highly unlikely due to the recognizable and undesirable soap taste (EPA 2008).

Despite the low toxicity of ammonium soaps to humans, the substance does pose some health risks. These are primarily irritation-based. Ammonium soaps have been documented to cause occasional skin irritation upon prolonged exposure (BioSafe Systems 2017). Ammonium soaps are also highly corrosive to eyes and may cause severe irritation and possible blindness upon direct exposure (USDA 2011, AMVAC 2015, USDA 2015a, USDA 2015b, Schultz Company 2016, BioSafe Systems 2017).

<u>Evaluation Question #11:</u> Describe all natural (non-synthetic) substances or products which may be used in place of a petitioned substance (7 U.S.C. § 6517 (c) (1) (A) (ii)). Provide a list of allowed substances that may be used in place of the petitioned substance (7 U.S.C. § 6518 (m) (6)).

Animal repellents are broadly classified into two main categories: area and contact repellents (Boggess 1981, Osko et al 1993, Craven and Hyngstrom 1994). Ammonium soaps offer protection through both categories with the emission of ammonia gas ($NH_{3(g)}$) and the negative association with nausea following ingestion of treated plants providing an aversion-based contact protection (Conover 1995, Ward and Williams 2010, Williams and Short 2014). Natural replacements for area repellents include coyote urine, putrid eggs, tankage, and human hair (Craven and Hyngstrom 1994, Pierce and Wiggers 1997, Craven et al. 2001). Natural replacements for contact repellents include capsaicin (from hot peppers), cinnamon, and black pepper oil (Craven and Hyngstrom 1994, Pierce and Wiggers 1997, Craven et al. 2001, Copping and Duke 2007, Ward and Williams 2010).

Fear-Based Area Repellents: Coyote Urine and Putrid Eggs

Coyote urine and putrid eggs are both area repellents that work through fear-based association. In the case of coyote urine, the natural pheromones of the predator are recognized by the target animal (rabbit or deer) (Ward and Williams 2010). Once recognized, the target animal perceives predator activity near the application site, and avoids the area based on a fear response (Ward and Williams 2010). The putrid eggs work through a similar fear-based response. The urine of coyotes and other predators are commercially available as biopesticides (EPA 2004). The sulfurous odors given off by the decomposing egg material mimic natural predator scents, triggering fear in the target animal, with success rates between 85 and 100 percent effective for a 2- to 6-month application lifetime (Craven and Hyngstrom 1994, Pierce and Wiggers 1997, Craven et al. 2001, Ward and Williams 2010). However, these applications have the downside of being foul smelling to humans as well.

Smell-Based Area Repellents: Human Hair, Cinnamon, Tankage

Both tankage and human hair offer area protection through odor. Human hair provides a much subtler odor profile compared to the other area alternatives, however, it also comes with a much more inconsistent success rate (Craven and Hyngstrom 1994, Pierce and Wiggers 1997, Craven et al. 2001). Tankage is a slaughterhouse byproduct that also offers odor-based area protection from the pungent odor of decomposing meat products (Craven and Hyngstrom 1994, Pierce and Wiggers 1997). Much like coyote urine and putrid eggs, the application of tankage repellents produces a strong odor that is also undesirable to humans. Cinnamon has also been reported to have repellent characteristics due to the strong odor it produces (Copping and Duke 2007).

Contact Repellents: Capsaicin, Black Pepper Oil

Contact repellents such as capsaicin and black pepper oil provide protection to plants from the pain-inducing sensation that is produced when ingested (Copping and Duke 2007, Ward and Williams 2010). This pain is felt immediately upon contact of the repellent with the mucous membranes of the mouth and nose and is also felt in the gut. The immediate pain response associated with these repellents offers immediate protection from browsing, unlike the aversion mechanism in play with ammonium soaps, which develops slowly over time (Copping and Duke 2007, Ward and Williams 2010). Capsaicin and black pepper oil also offer advantages over ammonium soaps based on their low toxicity to both terrestrial and aquatic species (Copping and Duke 2007). However, like ammonium soaps, capsaicin has reported insecticidal qualities which are manifested through disruptions to metabolic cycles and the nervous systems of a range of insect species (Copping and Duke 2007).

Evaluation Question #12: Describe any alternative practices that would make the use of the petitioned substance unnecessary (7 U.S.C. § 6518 (m) (6)).

There are a range of alternative practices that would reduce the necessity for application of ammonium soaps and other repellents. These alternatives come in the form of population control of the target animal, alteration of habitat and the installation of physical barriers (fencing).

Population Control

The primary means of population control is through approved hunting practices (Craven and Hyngstrom 1994, Pierce and Wiggers 1997, Craven et al. 2001). Opening orchards and other agricultural lands to hunters during approved hunting seasons provides a means of controlling the size of deer herds, thereby reducing their browsing impact (Pierce and Wiggers 1997). Such population control measures are important due to the elimination of most natural predators, which has resulted in a population explosion among deer herds (Pierce and Wiggers 1997). Other, less common means of population controls include contraceptive programs to limit the reproductive efficiency of the target animal, however, these programs are not widely established (Pierce and Wiggers 1997).

Habitat Alteration

Another alternative to the use of ammonium soaps and other animal repellents is the imposition of modifications to the landscape. This can be achieved in several ways, including the alteration to the type of vegetation and its growth pattern, and the more drastic change imposed by the construction of physical barriers (fencing) (Andelt et al. 1991, Osko et al. 1993, Craven and Hyngstrom 1994, Pierce and Wiggers 1997, Craven et al. 2001, Ward and Williams 2010, Williams and Short 2014). When altering the landscape of the agro-ecosystem to prevent deer browsing, the area should be opened as much as possible, limiting fringes and cover for a browsing herd (Osko et al. 1993, Pierce and Wiggers 1997). When possible, young vegetation, the favored food source of deer, should be removed in favor of more mature and deer-resistant growth (Pierce and Wiggers 1997). When installing new vegetation or landscaping the agro-ecosystem, species should be chosen that are not generally preferred by the target animal to reduce browsing of the new vegetation and crops (Pierce and Wiggers 1997).

Physical Barriers

When alterations to the vegetation are not possible or desirable, the landscape can be altered by the installation of fencing around at-risk crops. Although fencing requires a higher up-front cost and continued maintenance, it also provides improved protection compared to other means of habitat alteration, or the application of repellents (Ward and Williams 2010, Williams and Short 2014). There are a wide range of fencing styles to provide crop protection from a variety of target animals (Pierce and Wiggers 1997, Craven 2001, Williams and Short 2014). Fencing is widely acknowledged as the most effective means of preventing crop damage from unintended browsing (Andelt et al. 1991, Osko et al. 2013, Pierce and Wiggers 1997, Craven et al. 2001, Ward and Williams 2010, Williams and Short 2014).

Report Authorship

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