## National Organic Standards Board Crops Subcommittee Petitioned Material Proposal Aluminum Sulfate July 19, 2016

## **Summary of Petition:**

Chemtrade Chemical US LLC has petitioned for the inclusion of aluminum sulfate on the National List at §205.601 (Synthetic substances allowed for use in organic crop production) and §205.603 (Synthetic substances allowed for use in organic livestock production). The petition for inclusion on §205.603 was addressed by the Livestock Subcommittee. This proposal will address the petition for listing aluminum sulfate at §205.601. A <u>technical review</u> of aluminum sulfate was received in May, 2015.

Aluminum sulfate, commonly referred to as alum, is used in conventional livestock production as a litter amendment to reduce volatilized ammonia in livestock facilities. Ammonia is naturally produced in litter as manure decomposes: bacteria hydrolyze uric acid to urea, and then to ammonia. Ammonia is a gas, which is detrimental to animal health and performance, and to the health of workers in livestock production facilities.

Aluminum sulfate hydrolyzes water contained in the litter, producing aluminum hydroxide (precipitate) and sulfuric acid. The sulfuric acid supplies acid ions ( $H^+$ ) which react with ammonia ( $NH_3$ ) to form ammonium cations ( $NH_4^+$ ).

Ammonium cations combine with nitrate, sulfate and phosphate anions in the litter to form non-volatile salts that remain in the litter. This reduces ammonia volatilization, improving the atmosphere in livestock facilities, and also helps retain the nitrogen in the manure/litter, making the litter a higher nitrogen-containing soil amendment.

Aluminum also binds with phosphorus, producing an aluminum-phosphate complex, reducing the presence of soluble phosphorus. The petitioner presents this as an important feature of adding aluminum sulfate to livestock litter—as an environmental aid—to reduce the amount of soluble phosphorus in the litter in order to reduce phosphorus loss to water resources when the litter is applied to soils.

## **Summary of Review:**

The Livestock Subcommittee, in its consideration of the petition to add aluminum sulfate at §205.603, did not think aluminum sulfate was necessary as a litter amendment in organic livestock production because other nonsynthetic materials that perform the same function of reducing ammonia volatilization from livestock litter are currently available and in use. The Livestock Subcommittee voted unanimously to not add ammonium sulfate at §205.603.

The rationale presented in the petition to add aluminum sulfate to §205.601, stated that aluminum sulfate could be considered an environmental aid, because aluminum will adsorb and bind phosphorus, potentially reducing phosphorus loss to water resources when litter is applied to soils. Excess phosphorus in the environment is a problem today, and when too much phosphorus gets into water bodies it causes algal growth and eutrophication.

In regions with many Concentrated Animal Feeding Operations (CAFOs) manure is sometimes applied to fields surrounding the CAFOs frequently, and at high rates, in order to dispose of excess manure. Also, for high nutrient-demanding crops (like corn), when manure is applied at rates needed to supply the nitrogen needs of the crop, the amount of phosphorus also added in the manure is often much higher than crop needs, resulting in the buildup of soil phosphorus in those fields over time.

Soluble phosphorus is naturally adsorbed and complexed with calcium, iron, aluminum and organic matter in soils, limiting soluble phosphorus levels and thereby reducing leaching losses to water resources. However, as phosphorus levels in soils increase beyond sufficiency levels for optimum crop yields, the solubility of phosphorus begins to increase exponentially. Under those conditions, a material to bind phosphorus to reduce its solubility can reduce leaching of phosphorus to water resources.

Organic crop producers are often challenged to be able to procure enough plant nutrients to meet their crop production needs, and are generally not motivated to build soil phosphorus up to levels that would result in excessive levels of soluble phosphorus. The National Organic Standards, Section 205.203(c), requires that "The producer must manage plant and animal materials to maintain or improve soil organic matter content in a manner that **does not contribute to contamination of crops, soil, or water by plant nutrients,** pathogenic organisms, heavy metal, or residues of prohibited substances." [Emphasis added.] Therefore, organic farmers are already required to manage their farming systems to prevent phosphorus contamination of water resources.

Aluminum can be phytotoxic in low pH soils. It is well documented that in low pH soils aluminum becomes more soluble and toxic to plants. Aluminum toxicity to plants results in reduced root systems, a variety of nutrient-deficiency symptoms, and reduced yields. Caution should be used in applying materials containing aluminum to soils with low pH. The acidic conditions of low-pH soils will solubilize aluminum hydroxide to  $Al_3^+$ .

In summary, the Crops Subcommittee does not think that aluminum sulfate is needed in organic crop production because: 1) Nonsynthetic alternatives to aluminum sulfate are available to control ammonia volatilization in livestock facilities. 2) Organic crop producers normally do not apply phosphorus at levels beyond sufficiency levels for optimum crop production, so excessive soluble phosphorus should not be a problem, 3) Adding aluminum to low-pH soils could contribute to phytotoxicity.

#### Category 1: Classification

1. For CROP use: Is the substance Non-synthetic or Synthetic? Substance is synthetic. Is the substance formulated or manufactured by a process that chemically changes a substance extracted from naturally occurring plant, animal, or mineral sources? [OFPA §6502(21)] If so, describe, using NOP 5033-1 as a guide.

The manufacturing process for all the forms of aluminum sulfate included in the petition involves reacting liquid sulfuric acid with either bauxite ore containing aluminum hydroxide (Al(OH) 3) and hydrated aluminum (Al2O3·3H2O), or synthetic hydrated aluminum previously refined from bauxite. Bauxite ore is the main source of aluminum for the world and contains various aluminum minerals and two iron minerals (Amethyst Galleries 2014). The process creates hydrated aluminum sulfate per the following reactions:

From bauxite:  $3 \text{ H2SO4} + 2 \text{ Al}(OH)3 + 12 \text{ H2O} \rightarrow \text{Al2}(SO4)3 \cdot 18 \text{ H2O} 52$ From hydrated aluminum:  $3 \text{ H2SO4} + \text{Al2O3} \cdot 3 \text{H2O} + 12 \text{ H2O} \rightarrow \text{Al2}(SO4)3 \cdot 18 \text{ H2O} 53$ 

The acidified formulation also contains synthetically produced sulfuric acid.

## 2. Reference to appropriate OFPA category:

Is the substance used in production, and does it contain an active synthetic ingredient in the following categories: [§6517(c)(1)(B)(i)]; 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; or (ii) is used in production and contains synthetic inert ingredients that are not classified by the Administrator of the Environmental Protection Agency as inerts of toxicological concern?

The substance contains sulfur. The substance is not an inert ingredient. The substance aluminum sulfate is **not** classified by the EPA as an inert of toxicological concern (it is on EPA List 4 (2004)). The substance is, however, approved as an adjuvant, used pre-harvest, and is exempted from the requirement of a tolerance (40 CFR 180.920).

## **Category 2: Adverse Impacts**

 What is the potential for the substance to have detrimental chemical interactions with other materials used in organic farming systems? [§6518(m)(1)]

#### TR LINES 435-478:

Aluminum sulfate is being petitioned as an amendment to poultry litter for consideration in organic livestock application. Aluminum sulfate undergoes various chemical interactions with the poultry litter, altering several key chemical characteristics of the litter:

- The pH of the litter is reduced; however it is unlikely to fall below pH 7.0 in litter collected after the final grow out flock. Initially the treated litter pH does fall to about 5.7 and that pH is maintained for about 3-4 weeks (Moore et al. 2000) (Table 2).
- Aluminum sulfate reacts with water and naturally-occurring NH3 in the litter to form NH4+,
  thus stabilizing nitrogen and reducing NH3 gas volatilization to the atmosphere. In the soil
  environment, NH4+ is transient and is either rapidly taken up by plants, microbially
  transformed to NO3- which can be taken up by plants or lost to leaching, or anaerobically
  transformed by microorganisms to N2 and N2O which are lost to the atmosphere (Halvin et
  al. 2005).
- Poultry litter is a significant source of NH3 in the atmosphere, which causes formation of aerosol particles. It is also a source of nitric acid deposition to land or water bodies where it causes land and water acidification and nitrate pollution (NOAA 2000). Aluminum sulfate decreases atmospheric pollution of NH3 by reducing litter pH, which converts NH3 to water-soluble NH4+ (Shah et al. 2006). Incubation studies estimate approximately 14 g N / kg litter is lost from non-treated litter as NH3, while ammonia loss from litter treated with aluminum sulfate ranges between 0.7 to 4.07 g N / kg litter between the high and low application rates (Moore et al. 2000. Assuming 40,000 lbs. of litter for a 16,000 square foot poultry house containing 20,000 broilers (Moore and Watkins 2012), this represents a reduction of about 400 lbs. of NH3-N lost to the atmosphere over a 42-day period with low rates of aluminum sulfate, and about 560 lbs. of NH3-N at high rates of aluminum sulfate.

- Litter treated with aluminum sulfate contains less soluble phosphate (PO43-) than non-treated litter, as Al3+ reacts with PO43- to form insoluble AlPO4 (Table 2). Although the total phosphorous concentration in the litter does not change greatly, phosphorous becomes less plant-available, and likelihood of phosphorous transport to surface water is reduced. Aquatic ecosystems tend to be phosphorous-limited, and phosphorous eutrophication of natural water bodies is reduced when land-applied litter is treated with aluminum sulfate. The insoluble aluminum phosphate is not available to plants as nutrients and instead stays in the soil as a mineral (Moore and Edwards 2005).
- Litter treated with aluminum sulfate contains both higher total aluminum and higher soluble aluminum than non-treated litter (Table 2); however, runoff from fields where aluminum sulfate-treated litter is applied does not contain significantly higher levels of aluminum than fields where non-treated litter is applied (Moore et al. 1998).
- Litter treated with aluminum sulfate contains higher total sulfur and higher soluble sulfur than non-treated litter (Table 2).
- Concentration of soluble arsenic is reduced by aluminum sulfate treatment due to arsenic co-precipitation by aluminum (Violante et al. 2006) (Table 2).
- 2. What is the toxicity and mode of action of the substance and of its breakdown products or any contaminants, and their persistence and areas of concentration in the environment? [§6518(m)(2)]

### TR LINES 356-387:

**Toxicity**: Aluminum sulfate is considered a dry acid, and is an irritant to the skin and eyes (UN-LIO 2012). However, acidity created by the substance is neutralized by the litter, and litter applied to land generally has a near-neutral pH (Sims and Luka-McCafferty 2002).

**Mode of action**: Aluminum sulfate reacts with water to create acid, which reduces ammonia losses from litter in confined poultry operations. Furthermore, aluminum causes precipitation of phosphates, reducing phosphorus solubility in the land-applied litter (Moore and Watkins 2012).

**Breakdown products:** Breakdown products of aluminum sulfate include Al3+, Al(OH)2+, Al(OH)2+, Al(OH)3, SO42-, HSO4-, and H2SO4, and H3O+ (McBride 1996). Aluminum phosphate (Al(PO4)) precipitate is also formed via reaction of Al3+ with phosphates in the litter (Warren et al. 2008).

**Toxicity of breakdown products:** Free Al3+ is a toxic species that increases in concentration as pH decreases, and typically reaches phytotoxic levels when pH falls below 5.0 (Havlin et al. 2005). Poultry litter without aluminum sulfate typically ranges in pH from 8.0 to 8.9 (Sims and Luka-McCafferty 2002). Shortly after aluminum sulfate application, pH of the litter decreases to about 5.7, but becomes neutralized (near pH 7.0) after 3-4 weeks due to reaction with NH3 in the poultry guano (Moore et al. 2000). Thus, although adding aluminum sulfate increases total concentration of aluminum, persistence of the toxic Al3+ species is not enhanced. In contrast, application of litter near pH 7.0 to acidic soils decreases solubility of toxic Al3+ (Moore and Edwards 2005).

**Persistence of the breakdown products:** Aluminum hydroxide and phosphates from aluminum sulfate addition to poultry litter are persistent in the soil after land application due to low solubility (Warren et al. 2008). Sulfates, however, are more soluble, serve as a source of sulfur for crop plants, or are lost to leaching (Havlin et al. 2005).

**Contaminants:** The primary contaminants present in the Al2O3 precursor to aluminum sulfate include SiO2, Fe2O3, and Na2O, and could carry though into the final aluminum sulfate product, however do not pose toxicological concerns (Carter and Norton 2007)

# 3. Describe the probability of environmental contamination during manufacture, use, misuse or disposal of such substance? [§6518(m)(3)]

#### TR LINES 392-429:

Aluminum sulfate is a dry acid, and can create zones of high acidity if accidentally spilled. Acid damage severity from a concentrated spill is dependent on the quantity spilled, and also on the moisture available for reacting. If the spilled material does not come into contact with moisture, the majority of the material could be cleaned up before significant acidification occurs. But, surfaces of most soils are typically fissured and loose, and sometimes moist, making complete soil cleanup unlikely. Aluminum sulfate is designated as a hazardous substance under the CERCLA (superfund), and discharges exceeding 5,000 lbs (2,270 kg) require notification to the U.S. Environmental Protection Agency (TABLE 302.4 40 CFR).

Localized environmental acidification has a profound impact on chemical equilibrium regulating biological systems. In the soil, acidic conditions cause enhanced solubility of the Al3+ species, which is toxic to plant roots. Furthermore, both H+ and Al3+ are more strongly adsorbed to soil cation exchange sites than calcium, magnesium, and potassium and cause potential soil depletion of these nutrients via leaching. Soil remediation of large aluminum sulfate spills can be accomplished with a liming agent to neutralize the acidity and reduce solubility of Al3+ (NIH 2014).

Aluminum sulfate is sometimes deliberately added to water bodies impaired by phosphorus eutrophication, but accidental discharge of large quantities could cause excessive water acidification and subsequent solubilization of Al3+ which is toxic to aquatic organisms (UN-ILO 2012).

Personal protective equipment should be used when applying aluminum sulfate in the poultry house, but no specific precautions are needed for handling spent litter treated with aluminum sulfate due to the high level of dilution in the litter. In the poultry house, any aluminum sulfate spills should be incorporated into the litter to prevent ingestion by the birds (Walker and Burns 2000). Applications of liquid ammonium sulfate are typically made by certified applicators due to transport restrictions (Moore and Watkins 2012).

Aluminum sulfate reduces environmental contamination of phosphorus in natural water bodies from surface litter applications, compared to non-treated litter. Moore and Edwards (2005) measured 340% greater cumulative phosphorus load in runoff water from non-treated litter than from treated litter in a paired watershed study.

The process of extracting bauxite ore has a deleterious impact on the environment through habitat degradation and fragmentation by roads, and through carbon emissions (Cooke 1999). After extraction, regulations in some countries require replacement of topsoil and other

remediation measures; however quality of land after remediation is unlikely to be equivalent to before-extraction parameters (Cooke 1999). Most of the bauxite extraction worldwide is for the production of aluminum oxide, and less than 5% of bauxite imported into the U.S. is used for other purposes including aluminum sulfate production (USGS 2014)

4. Discuss the effect of the substance on human health. [§6517(c)(1)(A)(i); §6517(c)(2)(A)(i); §6518(m)(4)].

#### TR LINES 544-563:

Aluminum sulfate reacts with water to form sulfuric acid, which is an irritant. Aluminum sulfate is corrosive to the eyes; skin contact causes a rash and burning feeling, and inhalation causes throat and lung irritation (New Jersey Department of Health 2009). The magnitude of the toxic response to aluminum sulfate is completely dose-dependent, and the substance is permitted as a food additive in small quantities. Minor ingestion of dilute solutions causes stomach upset, while substantial ingestion can rarely cause hemorrhagic gastritis, circulatory collapse and multiorgan failure (United Kingdom National Poisons Information Service 1996).

Aluminum is a subject of medical contention with suspected links to Alzheimer's disease. Implications of a link between Alzheimer's disease and aluminum have been made for approximately 40 years. The current large body of research has not concluded specific roles of aluminum in contributing to Alzheimer's disease, but also has not dismissed aluminum as a non-contributor to the disease (Agency for Toxic Substances and Disease Registry 2008; Exeley 2001). Under FDA regulations, aluminum sulfate is generally recognized as safe (GRAS) as a food additive when used in accordance with good manufacturing or feeding practice (CFR 182.1125(b)).

Although aluminum sulfate has chronic toxicity for human exposure, use of the substance as petitioned should not have negative effects on human health. Use of the substance as petitioned decreases ammonia concentration in the atmosphere of poultry houses, which has a positive impact on both health of the birds and health of workers (Moore et al., 2000).

5. Discuss any effects the substance may have on biological and chemical interactions in the agroecosystem, including the physiological effects of the substance on soil organisms (including the salt index and solubility of the soil), crops and livestock. [§6518(m)(5)]

## TR LINES 485-522:

Aluminum sulfate is not applied while birds are in the poultry house. The substance is not applied before the first flock grow-out; however, it is systematically applied thereafter before every flock is exposed to the litter. Any spills or concentrations of the product should be dispersed into the litter to avoid consumption by young chicks (Walker and Burns 2000). As stated in the petition, aluminum sulfate is not applied to feed. In the event of accidental ingestion, aluminum sulfate is corrosive and irrigating to the digestive system and kidneys of birds (Dumonceaux and Harrison 2013). In one study, Japanese quail fed aluminum sulfate as >0.10% of their diet reduced body weight accumulation, eggshell strength, plasma inorganic phosphorous, feed consumption, and egg production (Hussein et al. 1988). Physiological effects of aluminum sulfate intake by broiler chickens occurs at higher intake levels than quail, with decreases in weight gain when consumed at >0.93% of the diet. Higher concentrations of aluminum sulfate in the diet cause more severe depressions in weight gain, decreased bone strength, and serum phosphorous. At application rates of 100 g / kg litter, birds would need to

ingest 10% of total dietary intake as litter to exceed 0.93% aluminum sulfate in the diet, and the aluminum would need to be in the original non-reacted aluminum sulfate crystalline form which does not persist in the presence of moisture. Typical observed litter ingestion rates are below this threshold, ranging from 2% to 5% of daily dietary intake. Aluminum sulfate is toxic to poultry if directly ingested in large quantities, but not at levels expected from litter consumption (Huff et al. 1996). When aluminum sulfate is used, mortality decreases and poultry weight gain increases, indicating the birds are likely not suffering toxic effects from incidental aluminum sulfate ingestion from the litter (Walker and Burns 2000).

Deleterious effects of aluminum sulfate on the head, skin, feathers, or feet of poultry were not revealed in the literature review, but the material is an irritant (UN-LIO 2012). If aluminum sulfate remains in its original non-reacted dry form, there is potential for foot irritation. Producers can mitigate the potential of bird exposure by rototilling aluminum sulfate into the litter after application, and before birds are placed back in the poultry house. Liquid formulations are less likely to expose birds to concentrations of the chemical due to greater dispersal in the litter compared to dry formulations (Moore and Watkins 2012). Aluminum sulfate tends to dry out the litter, and in turkeys the use of aluminum sulfate decreased the incidence of foot pad dermatitis, which is associated with wet litter (Wu and Hocking 2011).

In addition to the phosphorous-fixing properties of aluminum sulfate, litter treated with aluminum sulfate inhibits microbial phosphorous mineralization from organic matter (Warren et al. 2008). Although the literature review did not reveal problems associated with salinity of litter treated with aluminum sulfate, treated litter contains higher levels of soluble NH4+, and sulfur; thus, the salinity is likely higher than non-treated litter. However, salt damage to crops at normal agronomic application rates is likely low due to dilution factors (Sims and Luka-McCafferty 2002). Effects on bird health are positive, as ammonia accumulation causes lung irrigation to poultry (Walker and Burns 2000). Pathogen loads in the broiler house are reduced with aluminum sulfate, which combined with lower ammonia concentration in the air causes increased bird weight gain (Shah et al. 2006).

## 6. Are there any adverse impacts on biodiversity? (§205.200)

Aluminum sulfate reacts with water and naturally-occurring NH3 in the litter to form NH4+, thus stabilizing nitrogen and reducing NH3 gas volatilization to the atmosphere. In the soil environment, NH4+ is transient and is either rapidly taken up by plants, microbially transformed to NO32- which can be taken up by plants or lost to leaching, or anaerobically transformed by microorganisms to N2 and N2O which are lost to the atmosphere (Halvin et al. 2005). Although nitrogen is more persistent in the litter, there is no effect on cumulative soil nitrogen accumulation compared to non-treated litter, as aluminum sulfate does not alter the organic fraction of the total nitrogen. (TR 443-449)

Litter treated with aluminum sulfate contains less soluble phosphate (PO43-) than non-treated litter, as Al3+ reacts with PO43- to form insoluble AlPO4 (Table 2). Although the total phosphorous concentration in the litter does not change greatly, phosphorous becomes less plant-available, and likelihood of phosphorous transport to surface water is reduced. Aquatic ecosystems tend to be phosphorous-limited, and phosphorous eutrophication of natural water bodies is reduced when land-applied litter is treated with aluminum sulfate. The insoluble aluminum phosphate is not available to plants as nutrients and instead stays in the soil as a mineral (Moore and Edwards 2005). (TR 462-468)

Litter treated with aluminum sulfate contains both higher total aluminum and higher soluble aluminum than non-treated litter (Table 2); however, runoff from fields where aluminum sulfate-treated litter is applied does not contain significantly higher levels of aluminum than fields where non-treated litter is applied (Moore et al. 1998). (TR 469-472)

## Category 3: Alternatives/Compatibility

1. Are there alternatives to using the substance? Evaluate alternative practices as well as non-synthetic and synthetic available materials. [§6518(m)(6)]

Alternatives to litter amendments include management practices such as proper air exchange in barns, removing caked areas and keeping litter areas dry.

#### TR LINES 569-581:

Clinoptilolite is a naturally-occurring aluminosilicate zeolite which can absorb ammonia, reducing volatilization to the atmosphere. The literature contains results of mixed efficacy for this material, with some reports of decreased ammonia in broiler house air, and other reports of increased atmospheric ammonia (Amon et al. 1997; Karamanlis et al. 2008; Shah 2006).

Agricultural lime can be applied to litter between flocks to increase litter pH, chemically inducing volatilization of large quantities of ammonia. The volatized ammonia can then be removed by ventilation before birds are placed back in the poultry house. Removal of ammonia from litter in between flocks reduces ammonia concentration in air for the subsequent grow-out, but does not mitigate ammonia production during the grow-out compared to acidification products. Although lime does not decrease total atmospheric ammonia pollution like aluminum sulfate, phosphorous in the litter is stabilized by complexation with calcium at high pH to reduce eutrophication of natural water bodies after land application of the litter (Shah 2006).

During the Spring 2016 in-person public comment session at the National Organic Standards Board meeting in Washington, DC the board did receive one public comment that stated there are OMRI listed poultry litter amendments currently in use and was provided information from a currently listed OMRI poultry litter amendment product on concerns they had with the TR on all litter amendments being brought forward in 2016. The commenter felt that the board should not approve additional poultry litter amendments when there are already OMRI-certified products being used in the marketplace.

2. In balancing the responses to the criteria above, is the substance compatible with a system of sustainable agriculture? [§6518(m)(7)]

No. This substance requires the use of sulfuric acid in its manufacture. Also, the proposed use of this substance to reduce soluble phosphorus in organic cropping systems assumes the presence of excessive phosphorus levels in soils on organic farms, which is not in keeping with the National Organic Standards or with a system of sustainable agriculture. Further, use of this substance in soils with low pH could result in aluminum toxicity to plants. Also, nonsynthetic alternatives exist to control ammonia volatilization in livestock facilities.

## **Classification Motion:**

Motion to classify aluminum sulfate as synthetic

Motion by: Francis Thicke Seconded by: Harriet Behar

Yes: 6 No: 1 Abstain: 0 Absent: 1 Recuse: 0

## **National List Motion:**

Motion to add aluminum sulfate at §205.601

Motion by: Francis Thicke Seconded by: Harriet Behar

Yes: 0 No: 6 Abstain: 0 Absent: 1 Recuse: 0