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.

Calcium Acetate

Crops

Identification of Petitioned Substance

Chemical Names:
Calcium Acetate
Calcium Diacetate
Acetic Acid, Calcium Salt
Calcium (II) Acetate
Calcium Ethanoate
Calcium Acetate Monohydrate
Calcium Diacetate Hydrate
Calcium Diacetate Monohydrate
Acetic Acid, Calcium Salt, Monohydrate

Other Names:
Lime Acetate
Acetate of Lime
Lime Pyrolignite
Vinegar Salts

Trade Names:
PhosLo®
ProcalAmine®
Full Measure Cal™ 30
Reflections™

CAS Numbers:
62-54-4 (Calcium Acetate)
5743-26-0 (Calcium Acetate Monohydrate)
114460-21-8 (Calcium Acetate Hydrate)

Other Codes:
EC No. 200-540-9 (Calcium Acetate)
EC No. 611-528-1 (Calcium Acetate Monohydrate)
FEMA No. 2228
ICSC No. 1092
RTECS No. AF7525000
UNII No. Y882YXF34X (Calcium Acetate)
UNII No. 7ZA48GIM5H (Calcium Acetate Monohydrate)

Summary of Petitioned Use

The petitioners are requesting to add calcium acetate, the salt resulting from the neutralization of acetic acid with calcium hydroxide or calcium carbonate, to Title 7 of the Code of Federal Regulations section 205.601 (7 CFR 205.601) as a "synthetic substance allowed for use in organic crop production."

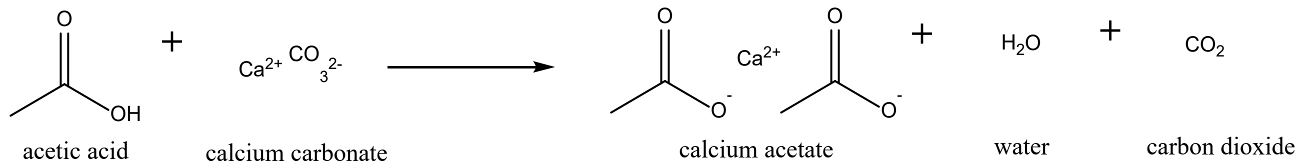
Calcium acetate acts as a soil amendment, plant micronutrient, pH adjuster, and preventative of sunscald. Calcium acetate provides a water-soluble and bioavailable source of the essential micronutrient calcium for plant absorption. When used as petitioned, calcium acetate is applied as an aqueous mixture with calcium carbonate (limestone) and a surfactant. The combination of calcium acetate and calcium carbonate serves to increase soil alkalinity (pH adjustment). The petitioned mixture also prevents sunscald by blocking direct sun exposure and lowering soil temperature.

Characterization of Petitioned Substance

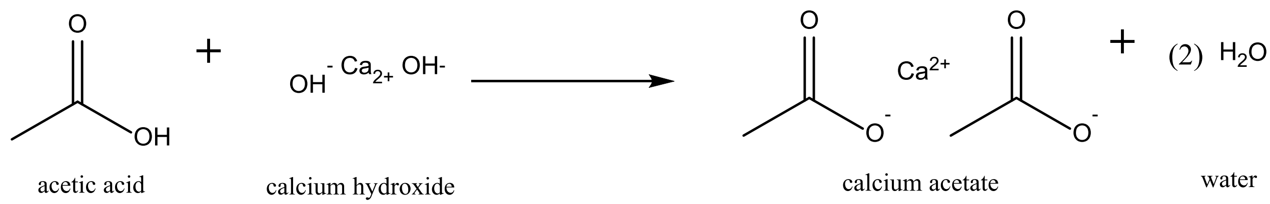
<u>Composition of the Substance:</u>
Calcium acetate is an organic salt that is found as a component in the metabolic pathways of a variety of animals, including humans (EFSA 2009, EFSA 2012). Commercial forms of calcium acetate are manufactured by the neutralization of acetic acid with either calcium carbonate or calcium hydroxide salts (EPA 2010a, Hawley 2016). The petitioned substance is hygroscopic (absorbs water) making most commercial sources calcium acetate hydrates (including water molecules), although anhydrous calcium acetate (calcium acetate without water incorporation) is also available (Capot 2013, ILO 2002, Merck 1996, EU 2012, Perry 2011, PubChem 6116, PubChem 82163, Sigma-Aldrich 2016, Sigma-Aldrich 2018).

<u>Source or Origin of the Substance:</u>
Calcium acetate is a naturally occurring substance, which is produced and broken down in the metabolic cycles of a range of humans and animals; however, it is most commonly manufactured by the

neutralization of acetic acid with calcium carbonate (limestone, Equation 1) or calcium hydroxide (hydrated lime, Equation 2) (EFSA 2009, EFSA 2012, EPA 2010a, Hawley 2016).



Equation 1



Equation 2

<u>Properties of the Substance:</u>

Calcium acetate is commercially available as a solid in >98% purity in anhydrous, monohydrate, and hydrate forms. However, the anhydrous form (calcium acetate) is hygroscopic (absorbs water/moisture), and since the substance is used in an aqueous mixture, the monohydrate or hydrate forms are more likely to be used for the petitioned application (Merck 1996). The properties of the commercially-available forms of calcium acetate are summarized in Table 1.

Table 1: Properties of Calcium Acetate

Compound	Calcium Acetate	Calcium Acetate Hydrate	Calcium Acetate Monohydrate
CAS No.	62-54-4	114460-21-8	5743-26-0
Molecular Weight	158.17 g/mol	158.17 g/mol	176.18 g/mol
Appearance	Colorless-white crystalline solid	Solid	Brown, gray, or white solid powder
General Properties	Very Hygroscopic, Slight odor of acetic acid	Hygroscopic, Slight odor of acetic acid	Hygroscopic, Slight odor of acetic acid
Solubility	Soluble in water, slightly soluble in alcohols	N/A	Soluble in water, slightly soluble in alcohols
Melting Point	160 °C (decomposes)	N/A	N/A (decomposes)
Density	1.5 g/cm^3	N/A	N/A

Sources: (Capot 2013, ILO 2002, Merck 1996, EU 2012, Perry 2011, PubChem 6116, PubChem 82163, Sigma-Aldrich 2016, Sigma-Aldrich 2018)

<u>Specific Uses of the Substance:</u>

Calcium acetate is petitioned for use as a soil amendment. Calcium acetate is a water-soluble salt for use as a bioavailable source of the essential micronutrient calcium (Ca^{2+}) (Merck 1996, EU 2012, Peacock 2005, Perry 2011, PubChem 6116, PubChem 82163, Sigma-Aldrich 2016, Sigma-Aldrich 2018). Calcium is an important micronutrient for plant growth, providing important structural rigidity to cell walls and membranes, protection from microbial diseases, and proper regulation of cellular transport and enzyme function (Bennett 1993, Frizzel and Loosemore 2010, Helper 2005, Hirschi 2004, Marschner 1995). The petitioned substance improves the delivery of calcium compared to other calcium treatments (e.g., lime) due to its increased water solubility (Frizzel and Loosemore 2010, Peacock 2005). When the petitioned substance is combined with insoluble calcium carbonate, the mixture acts to further improve the fertilization method by delivering immediate calcium nutrition with calcium acetate and prolonged nutrition from calcium carbonate (Frizzel and Loosemore 2010). Furthermore, calcium acetate has been reported to increase plant absorption of calcium ions (Ca^{2+}) compared to salts with other organic and inorganic anions (e.g., lactate, citrate, oxalate, chloride, nitrate) (Borchert 1986).

Calcium acetate is also petitioned for adjustment of soil pH. Acetate is the conjugate base of the weak organic acid acetic acid (Equations 1 and 2); therefore, the application of acetate will act to establish a buffer and increase the alkalinity (and raise the pH) of the soil by reacting with both strong and weak acids. However, the applied mixture will consist of ~5% calcium acetate, with the remaining calcium content in the form of calcium carbonate. Calcium carbonate is naturally produced and exists in many forms, including mineral deposits (e.g., limestone, calcite, and marble) and as a structural component of bones and shells (e.g., eggshells, seashells) (USDA 2018, USGS 2008). Calcium carbonate will also react as a base, neutralizing strong and weak acids and resulting in the formation of a new calcium salt, water, and carbon dioxide (CO_2) gas (as seen with the neutralization of acetic acid in Equation 1) (Al Omari et al. 2016, EFSA 2011, Holman and Stone 2001, Oates 1998). Although calcium carbonate has very low water solubility, the ionic compound is broken up by acids, greatly increasing the solubility of the calcium cation and providing access to the basic properties of the carbonate anion (EFSA 2011, Oates 1998).

Calcium acetate is petitioned for use as an aqueous mixture that also includes calcium carbonate, xanthan gum (as a stabilizer), and in some cases humic acid. This mixture of substances is not completely soluble, and its suspended solid particles shield plants from ultraviolet radiation and regulate plant temperature. Sunscald occurs when exposure to sunlight overheats crops and results in scar formation (Piskolczi et al. 2004). These scars are visible on the surface of the crop, and persist into sub-surface layers, affecting the color, taste, and properties of the crop before and after harvest (Lurie and Watkins 2012, Piskolczi et al. 2004, Schrader et al. 2001). The aqueous mixture — which includes the petitioned calcium acetate, calcium carbonate, and the surfactant xanthan gum — is petitioned for protection of crops from sunscald. This protective property is due to the opaque nature of the mixture, largely due to the presence of insoluble calcium carbonate in the final formulation, which protects plants from ultraviolet radiation while simultaneously regulating plant temperature (Frizzel and Loosemore 2010).

Calcium acetate has been used in animal feeds for nutritional purposes as well as a preservative and veterinary medicine due to its mild anti-microbial effects (EFSA 2012). Calcium acetate has also been established for a range of other non-agricultural applications, including cosmetics and various household products (EFSA 2012).

Calcium acetate has been approved by the United States Food and Drug Administration (FDA) as an "inert ingredient permitted in minimum risk pesticide products," at 40 CFR 152.25. Calcium acetate is employed in a contained trap and is used to attract yellow jackets through scent recognition, after which the yellow jackets are trapped in the container (EPA 2010a, EPA 2010b).

<u>Approved Legal Uses of the Substance:</u>

Calcium acetate has been given GRAS (Generally Recognized as Safe) status by the FDA as a "sequestrant," at 21 CFR 582.6185 and a "direct food substance," at §184.1185. The FDA has approved calcium acetate as a "firming agent, pH control, processing aid, sequestrant, stabilizer, thickener, and texturizer," at §184.1185. This section further specifies that calcium acetate is approved as an "ingredient used in food with a maximum level as served of 0.2 percent for baked goods; 0.02 percent for cheese; 0.2 percent for gelatins, puddings, and fillings; 0.15 percent for sweet sauces, toppings, and syrups; and 0.0001 percent for all other food categories."

The FDA has approved calcium acetate for use in food processing as a "substance classified as a stabilizer when migrating from food-packaging material," at 21 CFR 181.29. Calcium acetate has also been classified by the FDA as a "miscellaneous material" for use as a "resinous and polymeric coating [that] may be safely used as the food-contact surface of articles intended for use in producing, manufacturing, packing, processing, preparing, treating, packaging, transporting, or holding food," at §175.300.

The FDA has approved calcium acetate for use in "drug products containing certain active ingredients offered over-the-counter (OTC)" for astringent drug products, "except calcium acetate monohydrate when combined with aluminum sulfate tetradecahydrate to provide an aluminum acetate solution," at 21 CFR 310.545. Furthermore, the FDA has approved calcium acetate as a precursor to aluminum acetate in "astringent products," at §347.52(a). Calcium acetate is also approved for relieving minor skin irritations such as those caused by poison ivy, oak, or sumac as well as rashes from a variety of soaps and detergents. It is approved "for use as a soak," at §347.52(b) and (c), respectively.

The United States Environmental Protection Agency (EPA) has granted calcium acetate an "exemption for pesticides of a character not requiring FIFRA [(the Federal Insecticide, Fungicide, and Rodenticide Act)] regulation," and has classified the substance as an "inert ingredient permitted in minimum risk pesticide products," at 40 CFR 152.25. Calcium acetate has been registered as a pesticide for yellowjackets with the EPA in 2010 (EPA 2010a, EPA 2010b).

Action of the Substance:

Calcium acetate works as a soil amendment in two ways, one of which is for micronutrient delivery. Calcium is an important structural component in plants, providing rigidity to the cell wall and stabilizing lipids within cell membranes (Bennett 1993, Frizzel and Loosemore 2010, Helper 2005, Hirschi 2004, Marschner 1995). Calcium is also important for the regulation of many cellular processes, ranging from transport across cellular membranes to enzymatic function (Bennett 1993, Helper 2005, Hirschi 2004, Marschner 1995). The application of calcium acetate as a micronutrient fertilizer provides superior absorption compared to other fertilization programs (e.g., lime). This increased absorption is due to the increased water solubility, and therefore bioavailability, of the calcium ions (Borchert 1986, Frizzel and Loosemore 2010, Peacock 2005). This increase in bioavailability is more pronounced in alkaline (high pH) soils, where micronutrients (i.e., calcium) are present as insoluble carbonate and hydroxide salts (Frizzel and Loosemore 2010, Peacock 2005). Borchert (1986)reported that calcium absorption from calcium acetate was superior to other soluble organic and inorganic calcium salts and proposed the increased calcium uptake because of the acetate anion. When used as a soil amendment, humic acid may be added to the final aqueous mixture for additional nutrition. Humic acids have been reported to act as chelating agents, which increase the water solubility and bioavailability of micronutrients following their coordination (Merck 2006, USDA 2012).

The petitioned substance also acts as a soil pH adjuster. When used as petitioned, the substance is applied as an aqueous mixture of calcium acetate, calcium carbonate, and a surfactant (xanthan gum). Both calcium sources (acetate and carbonate) are conjugate bases of weak acids (acetic acid and bicarbonate, respectively). As such, they can react with and neutralize weak and strong acids. Both calcium salts enable the creation of a buffering system that raises the pH of the soil, while also providing an increased buffering capacity (alkalinity) to the soil (Frizzel and Loosemore 2010, Peacock 2005). Calcium carbonate has long been applied as a soil amendment to raise pH and is present as a buffering agent in a wide range of environments due to its prevalence in the earth's crust (Al Omari et al. 2016, EFSA 2011, USGS 2008).

When used for sunscald prevention, calcium acetate operates under a different mode of action. Sunscald results from crops overheating, producing discolorations and affecting taste and other post-harvest properties (e.g., storage and marketability) (Lurie and Watkins 2012, Piskolczi et al. 2004). When used as petitioned, the aqueous mixture including calcium acetate prevents sunscald due to the suspension of solid particles in the mixture that yields an opaque liquid when applied (Frizzel and Loosemore 2010). The nature of the mixture physically protects crops from ultraviolet radiation and regulates plant temperature to prevent the overheating that results in sunscald formation.

Combinations of the Substance:

When used as petitioned, calcium acetate is applied as an aqueous mixture that also includes calcium carbonate, xanthan gum as a surfactant, and in some cases, humic acid for additional nutrition. Thirty percent (30%) of the final mixture is made from calcium acetate and carbonate salts, with calcium acetate accounting for ~5% and calcium carbonate accounting for the other ~25% (USDA 2017).

Calcium carbonate contrasts with calcium acetate by being insoluble in water and is present in the petitioned substance as suspended solid particles (Millipore-Sigma 2015, PubChem 10112). Calcium carbonate aids in all three applications of the petitioned substance. Calcium carbonate is a source of calcium ions (Ca^{2+}), which although initially insoluble, become accessible upon reaction with an acid (Equation 1) (EFSA 2011, Oates 1998). Calcium carbonate also acts to raise soil pH by reacting with acids in the environment (Equation 1). The application of calcium carbonate results in increased soil alkalinity, enhancing the buffering capacity of the ecosystem (USGS 2008). The insoluble nature of calcium carbonate in aqueous mixtures results in a slow release soil amendment, both in terms of nutrition and pH adjustment, complementing the immediately available calcium acetate (Frizzel and Loosemore 2010). Moreover, the insolubility of calcium carbonate results in the opaque character of the final mixture, allowing for sunscald prevention (Frizzel and Loosemore 2010, USDA 2017).

Xanthan gum provides important stabilization of calcium carbonate particles by keeping them in suspension (Frizzel and Loosemore 2010). Without the additional characteristics of the xanthan gum surfactant, the insoluble calcium carbonate would settle out of solution, eliminating the opaque character of the mixture and sunscald prevention and resulting in a product that could be difficult to apply as a liquid.

The primary purpose for the inclusion of humic acid is to enhance plant absorption of nutrients, which is facilitated through chelation and facilitated cation exchange (USDA 2012).

Status

Historic Use:

There has been no historic use of calcium acetate in organic agricultural production.

Calcium acetate has been used as a soil amendment in conventional agricultural production as a soil amendment. Calcium acetate provides plant nutrition by delivery of the micronutrient calcium (Ca^{2+}) in a water soluble, bioavailable form, especially important in high pH soils. Calcium acetate also provides a method of pH adjustment. Due to its properties, the acetate anion neutralizes acids and raises pH. Calcium acetate is also used as a mixture with calcium carbonate and the surfactant xanthan gum as an opaque aqueous mixture applied to plants to prevent sunscald and regulate temperature.

Organic Foods Production Act, USDA Final Rule:

Calcium acetate is not listed in the Organic Foods Production Act of 1990 (OFPA) or the U.S. Department of Agriculture (USDA) organic regulations, 7 CFR Part 205.

International:

Canadian General Standards Board Permitted Substances List

Calcium acetate is not listed in the CAN/CGSB-32.311-2015 — Organic production systems - permitted substances lists.

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

Calcium acetate is not listed in the CODEX.

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

Calcium acetate is not listed in the EEC EC No. 834/2007 or 889/2008.

Japan Agricultural Standard (JAS) for Organic Production

Calcium acetate is not listed in the JAS.

International Federation of Organic Agriculture Movements (IFOAM)
Calcium acetate is not listed in IFOAM.

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

<u>Evaluation Question #1: Indicate which category in OFPA that the substance falls under:</u> (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?

Calcium acetate falls under category A and is petitioned for use as a mineral for the delivery of calcium ions (Ca^{2+}). Calcium acetate provides a water-soluble, bioavailable form of the micronutrient essential for plant structure and regulation (Bennett 1993, Frizzel and Loosemore 2010, Helper 2005, Hirschi 2004, Marschner 1995).

<u>Evaluation Question #2:</u> 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)).

Calcium acetate is most commonly manufactured by the neutralization of acetic acid with calcium carbonate (limestone) or calcium hydroxide (hydrated lime) (EPA 2010a, Hawley 2016).

Acetic acid is a naturally occurring substance, although most acetic acid is commercially synthesized. Most acetic acid is produced through methanol carbonylation such as the Cativa™ process, where methanol and carbon dioxide are reacted in the presence of an iridium catalyst (EFSA 2012, Jones 2000, Sunley and Watson 2000). Acetic acid is separated from other byproducts of the reaction by distillation, affording the substance as glacial acetic acid in >99% purity (EFSA 2009, EFSA 2012, Jones 2000, Sunley and Watson 2000).

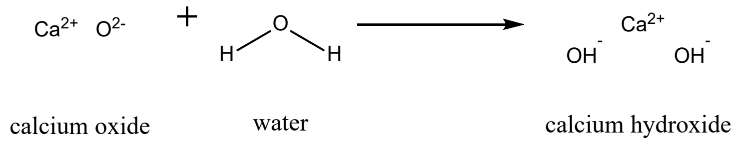
Calcium carbonate is a naturally occurring mineral that is prevalent in the earth's crust in forms such as limestone, chalk, and marble, and is isolated through mining operations (USDA 2018). It is also found in shells (USDA 2018). Calcium carbonate ($CaCO_3$) is isolated from its ground mineral sources through the process of calcination (heating to high temperatures in air), resulting in the loss of CO_2 gas to produce quicklime (calcium oxide (CaO)) as seen in Equation 3 (Domingo et al. 2004).

$$Ca^{2+}\,CO_3^{2-} \xrightarrow{\text{heat}} Ca^{2+}\,O^{2-} + CO_2$$

calcium carbonate (impure, from mineral deposits) — calcium oxide — carbon dioxide

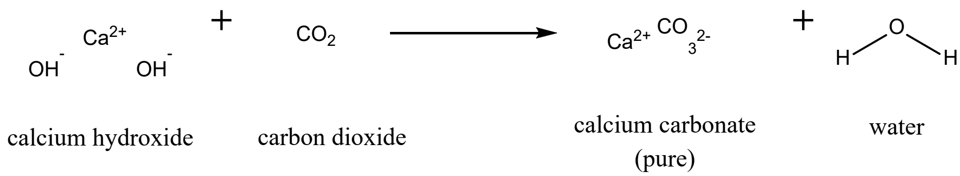
Equation 3

The resulting quicklime undergoes the slaking process (hydration of the resulting calcium oxide (CaO) by the controlled addition of water) to produce slaked lime (calcium hydroxide ($Ca(OH)_2$)) as shown in Equation 4 (Domingo et al. 2004, Hassibi 1999, IUPAC 2014).



Equation 4

Finally, pure calcium carbonate ($CaCO_3$) is generated via the carbonation (the addition of CO_2) of slaked lime, reforming purified calcium carbonate ($CaCO_3$) as shown in Equation 5 (Domingo et al. 2004, EFSA 2011).



Equation 5

Calcium hydroxide (hydrated lime) is obtained from the same naturally occurring mineral deposits as calcium carbonate (limestone, chalk, marble, oyster shells), and is isolated by calcination of the mineral (Equation 3) followed by slaking (hydrating) (Equation 4) to yield calcium hydroxide ($Ca(OH)_2$) (Al Omari et al. 2016, Domingo et al. 2004).

The petitioned substance is manufactured by the neutralization of acetic acid with calcium carbonate (Equation 1) or calcium hydroxide (Equation 2). In both reactions, the calcium acetate product is obtained by filtration (removal of residual insoluble calcium carbonate or calcium hydroxide) and the filtrate is spray dried to yield crystals or power (EFSA 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)).**

Commercially available calcium acetate is manufactured through chemical processes (EFSA 2009, EFSA 2012, EPA 2010a, Hawley 2016). Calcium acetate is synthesized by the neutralization of acetic acid with calcium carbonate (Equation 1) or calcium hydroxide (Equation 2) (EFSA 2009, EFSA 2012, EPA 2010a, Hawley 2016).

Commercially available acetic acid is produced by methanol carbonylation using the Cravita™ process (Jones 2000, Sunley and Watson 2000). While calcium carbonate and calcium hydroxide are naturally occurring substances, the commercially available forms are predominantly manufactured from processing the same mineral feedstocks (e.g., including limestone, dolomite, calcite, chalk) (Al Omari et al. 2016, Domingo et al. 2004). Both calcium salts are derived from naturally found minerals, primarily limestone and chalk (USDA 2018). Calcium hydroxide is formed through the calcination of these mineral sources, followed by a slaking process (Al Omari et al. 2016, Domingo et al. 2004, EFSA 2011, Hassibi 1999). Calcium carbonate is manufactured by the carbonation (addition of CO_2) of calcium hydroxide (Al Omari et al. 2016, Domingo et al. 2004, EFSA 2011, Hassibi 1999, IUPAC 2014).

__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)).**

There are no published studies on the environmental persistence of calcium acetate. Calcium acetate may be present in the metabolic cycles of animals; therefore, no risk is posed to the environment (EFSA 2012, EPA 2010a, EPA 2010b). The EPA has placed calcium acetate on the Safer Chemical Ingredients List (SCIL) for processing aids and additives as a safer replacement for traditional ingredients (EPA 2018). Moreover, the EPA has designated calcium acetate as "verified to be of low concern based on experimental and modeled data," and has "not identified any toxic endpoints for birds, plants, aquatic, or soil organisms" (EPA 2010b, EPA 2018).

<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)).

There are no published studies on the environmental impacts of calcium acetate; however, the EPA has "not identified any toxic endpoints for birds, plants, aquatic, or soil organisms" (EPA 2010b).

Calcium acetate acts as a water-soluble and bioavailable source of calcium, especially important in soils with high pH (Borchert 1986, Frizzel and Loosemore 2010, Peacock 2005). The petitioned substance also acts to increase the pH of the soil via acid neutralization of the basic acetate anion. When used as petitioned, the substance also provides protection from sunscald as well as acts as a mechanism for regulating plant temperature due to the opaque nature of the applied liquid (Frizzel and Loosemore 2010). Once introduced into agricultural soils, the salt may result in several different outcomes, including absorption by plants, reacting with acidic chemicals in the soil, or dissolving and entering water systems, depending on the environmental conditions of the soil.

<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)).

As discussed for Evaluation Questions #4 and #5, there are no published studies on the environmental impact of calcium acetate. Calcium is an essential mineral for plant function, and in the water-soluble form, calcium acetate will be absorbed by plants. This makes environmental contamination unlikely (Bennett 1993, Frizzel and Loosemore 2010, Helper 2005, Hirschi 2004, Marschner 1995). Furthermore, when used as petitioned, the final aqueous mixture will contain quantities that are lower than those approved for use as a pesticide (~5% vs. ~20%) (EPA 2010b, USDA 2017). However, due to the limited quantities of calcium acetate, and the limited environmental exposure (applied as an insecticide within a closed container that attracts the insects), toxicological studies were not required for pesticide approval (EPA 2010b).

If used improperly (e.g., overapplication, improper disposal) the petitioned substance could result in water pollution due to its high level of water solubility; however, the EPA has "not identified any toxic endpoints for birds, plants, aquatic, or soil organisms" (EPA 2010b). Moreover, overapplication may result in over adjustment of soil pH due to the presence of both calcium acetate and calcium carbonate and could result in increased soil alkalinity.

The greatest potential for environmental impact is likely to occur in the isolation of precursors (calcium carbonate and calcium hydroxide) for calcium acetate production. These calcium salts are derived from minerals generally accessed through mining. The mining of the minerals could result in contamination from natural contaminants and spills, disruption of the existing ground water, surface water, and subterranean ecosystems (USDA 2018, USGS 2001, USGS 2008).

<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)).

The petitioned substance is known to bind phosphates (Nolan et al. 1990). The binding action of phosphates by calcium acetate could result in the inability for plants to access this nutrient source, resulting in the formation of an insoluble, and biologically inaccessible, calcium phosphate salt. The propensity to bind phosphate groups will result in a reaction with the improper use/storage of phosphoric acid, which has been approved as "an equipment cleaner" at 7 CFR 205.603(a). However, this is unlikely to occur, given that phosphoric acid is approved "*provided* that no direct contact with organically managed livestock or land occurs," as stated at §205.603(a).

The petitioned substance is not known to react with other substances approved for use in organic crop or livestock production.

<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 petitioned substance increases the bioavailable concentration of calcium, resulting in increased absorption by plants and microorganisms. This effect is coupled with the pH adjustment and increased soil alkalinity. The ability of calcium acetate to increase soil alkalinity and pH combats acidic soils that are produced from the application of nitrogen-based fertilizers, which have been documented to result in unintentional fertilization through ammonia and ammonium migration (Erisman et al. 2008). The unintentional migration of ammonia-based fertilizers has been linked with soil acidification and negative impacts on soil microorganisms and earthworms, providing an important need for counterbalancing (pH and alkalinity increasing) substances (Geisseler and Scow 2013, Kirchmann et al. 1994, Peacock 2005, USDA 2001a, Yadvinder-Singh and Beauchamp 1988). Calcium acetate has also been documented to sequester aluminum (Al^{3+}), which is toxic to plants and microorganisms as the free ions in acidic soil (Ma et al. 2001, Nolan et al. 1990).

When used as petitioned, the calcium acetate mixture may also include humic acid, which has been shown to increase the bioavailability and plant absorption of micronutrients and fostering growth of soil microorganisms (Albuzio et al. 1989, Cook 1988, Lee and Bartlett 1976, Piccolo et al. 1992, USDA 2012).

<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)).

As discussed in Evaluation Questions #4 and #5, there are no published studies on the environmental impact of calcium acetate. Calcium acetate is a naturally occurring substance that is commonly found in the diet of humans and animals, and is readily metabolized (EFSA 2009, EFSA 2012). The EPA has "not identified any toxic endpoints for birds, plants, aquatic, or soil organisms," and the prevalence of organisms that metabolize calcium acetate makes its environmental accumulation and contamination unlikely (EFSA 2009, EPA 2010b, EFSA 2012). Furthermore, when used a petitioned, the final aqueous mixture will contain quantities that are lower than those approved for use as a pesticide (~5% vs. ~20%) (EPA 2010b, USDA 2017).

<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)).

Calcium acetate is a common component of human diet and is readily metabolized (EFSA 2012). Calcium acetate has a long history of use in food products for "physical, nutritional, or other technical effects," and is considered safe at any concentration consistent with achieving these effects (EFSA 2012). Calcium acetate has been authorized for human consumption without limitation by the Joint FAO/WHO Expert Committee on Food Additives (JECFA) and the European Union Scientific Committee on Food (SCF) (JECFA 1974, JECFA 1998, SCF 1990). Furthermore, the FDA has granted calcium acetate GRAS status as a "sequestrant," at 21 CFR 582.6185 and a "direct food substance," at §184.1185. The EPA has placed calcium acetate on the Safer Chemical Ingredients List (SCIL) for processing aids and additives as a safer replacement for traditional ingredients (EPA 2018). Moreover, the EPA has designated calcium acetate as "verified to be of low concern based on experimental and modeled data" (EPA 2018).

<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)).

Calcium carbonate provides an alternative to the petitioned substance, with the ability to act as a soil amendment, pH adjuster, micronutrient source, and for sunscald prevention. Calcium carbonate is included in the final formulation of the calcium acetate mixture and is primarily responsible for sunscald protection due to its low water solubility (Frizzel and Loosemore 2010, Piskolczi et al. 2004). Calcium carbonate is the major and active component of traditional mineral applications (e.g., limestone, marble, calcite) which provide both a source of the micronutrient calcium, and a mechanism for adjusting soil pH (USDA 2018). However, when used alone, calcium carbonate provides limited action as both a micronutrient and pH adjuster due to its low-water solubility. The addition of the petitioned calcium acetate to traditional calcium carbonate-based applications increases the water solubility of the calcium cation (Ca^{2+}) and the effectiveness of the formulation in terms of micronutrient delivery and soil pH adjustment.

There are a range of substances that could be used in place of the petitioned substance for specific applications. For use as a micronutrient (calcium) source, minerals high in calcium (e.g., limestone, marble, calcite) may be applied (USDA 2018). Due to the basic nature of these minerals (calcium carbonate ($CaCO_3$) is the major component), they also provide a mechanism for pH adjustment of soil (USDA 2018). However, the effectiveness of these applications is limited by the low solubility of the calcium salts present.

Another alternative is the application of approved chelating agents to improve the bioavailability of existing calcium sources in the soil. Lignin sulfonate, or lignosulfonate, is a synthetic chelating agent that is approved by the NOP for use in organic agricultural production, at 7 CFR 205.601. Lignosulfonates can form chelates with cationic micronutrients, increasing their water solubility and bioavailability (USDA 2011). Humic acids have also been shown to increase plant absorption of micronutrients, while also promoting the growth of soil microorganisms (Albuzio et al. 1989, Cook 1988, Piccolo et al. 1992, USDA 2012).

Additionally, sodium carbonate (Na_2CO_3) and potassium bicarbonate ($KHCO_3$) are capable of pH adjustments and, due to their water solubility, provide a more suitable alternative to calcium acetate than calcium carbonate mineral sources, calcium hydroxide, and lime sulfur (PubChem 10340, PubChem 516893).

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

An alternative soil amendment to the petitioned substance is the use of a compost program. Organic compost includes micronutrients, natural chelates, and microbes that produce natural chelating agents (Adeleke et al. 2017, Chen et al. 1998, Sorrenti et al. 2012). Furthermore, Sorrenti et al. have reported that compost-based treatments have been shown to enhance yield and quality of pears in calcareous soil (Sorrenti et al. 2012).

As discussed in Evaluation Question #11, the application of calcium carbonate containing minerals including limestone, dolomite, calcite, and ground oyster shells provide an alternative practice for both pH adjustment and a source of calcium. However, these application methods are limited due to the insoluble nature of the applied calcium carbonate sources (USDA 2018).

Alternative practices for sunscald protection are careful pruning to avoid exposure of the harvestable material to direct sunlight (Piskolczi et al. 2004). Additionally, other means of preharvest protection from sunscald include the installation of an artificial shade or an overhead sprinkling canopy (Piskolczi et al. 2004, USDA 2017). Any other means of providing a physical sunblock protection such as the application of kaolin and other clay-based sprays may also provide alternatives for sunscald protection.

Report Authorship

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All individuals are in compliance with Federal Acquisition Regulations (FAR) Subpart 3.11—Preventing Personal Conflicts of Interest for Contractor Employees Performing Acquisition Functions.

References

Adeleke R, Nwangburuka C, Oboirien B. 2017. Origins, roles and fates of organic acids in soils: A review. South African Journal of Botany. 108: 393-406.

Al Omari MMH, Rashid IS, Qinna N, Jaber AM, Badwan AA. 2016. Calcium Carbonate. In Profiles of Drug Substances, Excipients and Related Methodology, edited by H.G. Brittain, 31-132, Elsevier Inc. Cambridge, MA, USA.

Albuzio A, Nardi S, Gulli A. 1989. Plant growth regulator activity of small molecular size humic fractions. Science of the Total Environment. 81-82: 671-674.

Bennett WF. 1993. Nutrient Deficiencies and Toxicities in Crop Plants. St. Paul, MN: APS Press.

Borchert R. 1986. Calcium acetate induces calcium uptake and formation of calcium-oxalate crystals in isolated leaflets of *Gleditsia triacanthos* L. Planta. 168: 571-578.

Capot (Capot Chemical Company, LTD.) 2013. Calcium Acetate Monohydrate MSDS. [June 2018] Available from https://www.capotchem.com/5743-26-0.html?gclid=CjwKCAjw9-HZBRAwEiwAGw0QcWQvN2_zQM46rjAFReJLkWs-Jued64ejrjw3XdkWjwAkIbYTOtIraRoCvhYQAvD_BwE

Chen L, Dick WA, Streeter JG, Hoitink HAJ. 1998. Fe chelates from compost microorganisms improve Fe nutrition of soybean and oat. Plant and Soil. 200: 139-147.

Cook RJ. 1988. Biological control and holistic plant-health care in agriculture. American Journal of 645 Alternative Agriculture 3: 51-62.

Domingo C, Garcia-Carmona J, Loste E, Fanovich A, Fraile J, Gomez-Morales J. 2004. Control of calcium carbonate morphology by precipitation in compressed and supercritical carbon dioxide media. Journal of Crystal Growth. 271: 268-273.

EFSA (European Food Safety Authority). 2009. Calcium acetate, calcium pyruvate, calcium succinate, magnesium pyruvate magnesium succinate and potassium malate added for nutritional purposes to food supplements. The EFSA Journal. 1088: 1-25.

EFSA (European Food Safety Authority). 2011. Scientific Opinion on re-evaluation of calcium carbonate (E 170) as a food additive. The EFSA Journal. 9: 2318.

EFSA (European Food Safety Authority). 2012. Scientific Opinion on the safety and efficacy of acetic acid, sodium diacetate and calcium acetate as preservatives for feed for all animal species. The EFSA Journal. 10: 2571.

EPA (United States Environmental Protection Agency). 2010a. Calcium Acetate (011470) Fact Sheet. [June 2018] Available from https://www3.epa.gov/pesticides/chem_search/reg_actions/registration/fs_PC-011470_01-Feb-10.pdf

EPA (United States Environmental Protection Agency). 2010b. Biopesticides Registration Action Document Calcium Acetate PC Code 0111470. [June 2018] Available from https://www3.epa.gov/pesticides/chem_search/reg_actions/registration/decision_PC-011470_23-Aug-10.pdf

EPA (United States Environmental Protection Agency). 2018. Safer Chemical Ingredients List. [July 2018] Available from https://www.epa.gov/saferchoice/safer-ingredients#pop62544

Erisman JW, Sutton MA, Galloway J, Klimont Z, Winiwarter W. 2008. How a century of ammonia synthesis changed the world. Nature Geoscience. 1: 636-639.

EU (Commission Regulation of the European Union). 2012. Commission Regulation (EU) No 231/2012 of March 9 2012 laying down specifications for food additives listed in Annexes II and III to Regulation (EC) No 1333/2008 of the European Parliament and of the Council. [June 2018] Available from https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32012R0231&rid=1

Frizzel RB, Loosemore MJ. 2010. Non-Acidic, High Calcium Load Aqueous Fertilizer. U.S. Patent 7,695,541 B1.

Geisseler D, Scow KM. 2013. Long-term effects of mineral fertilizers on soil microorganisms – A review. Soil Biology and Biochemistry. 75: 54-63.

Hassibi M. 1999. An overview of lime slaking and factors that affect the process. From the 3rd International Sorbalit Symposium, New Orleans, LA, USA, November 3-5, 1999. [July 2018] Available from http://www.chemcosystems.net/Files/Admin/Publications/An%20Overview%20of%20Lime%20Slaking.pdf

Hawley's Condensed Chemical Dictionary 16th Ed. 2016. Hoboken, NJ: John Wiley and Sons.

Helper PK. 2005. Calcium: A Central Regulator of Plant Growth and Development. Plant Cell. 17: 2142-2155.

Hirschi KD. 2004. The Calcium Conundrum. Both Versatile Nutrient and Specific Signal. Plant Physiology. 136: 2438-2442.

Holman J, Stone P. 2001. Chemistry, 2nd Edition, Nelson Thornes Ltd. Chemtenham, United Kingdom.

ILO (International Labour Organization). 2002. Calcium Acetate. [June 2018] Available from http://www.ilo.org/dyn/icsc/showcard.display?p_version=2&p_card_id=1092

IUPAC (International Union of Pure and Applied Chemistry) 2014. IUPAC Compendium of Chemical Terminology. [July 2018] Available from https://www.iupac.org/goldbook/C00773.pdf

JECFA (Joint FAO/WHO Expert Committee on Food Additives). 1974. Toxicological evaluation of some food additives including anticaking agents, antimicrobials, antioxidants, emulsifiers and thickening agents. WHO Food Additives Series, No. 05. World Health Organization. Geneva. [July 2018] Available from http://www.inchem.org/documents/jecfa/jecmono/v050je01.htm

JECFA (Joint FAO/WHO Expert Committee on Food Additives). 1998. Safety Evaluation of Certain Food Additives and Contaminants. WHO Food Additives Series, No. 40. World Health Organization. Geneva. [July 2018] Available from http://www.inchem.org/documents/jecfa/jecmono/v040je01.htm

Jones JH. 2000. The Cativa™ Process for the Manufacture of Acetic Acid: Iridium Catalyst Improves Productivity in an Established Industrial Process. Platinum Metals Rev. 44: 94-105.

Kirchmann H, Persson J, Carlgren K. 1994. The Ultuna Long-term Soil Organic Experiment, 1956-1991. Department of Soil Sciences, Swedish University of Agricultural Sciences, Upsala.

Lee YS, Bartlett RJ. 1976. Stimulation of plant growth by humic substances. Soil Science Society of America Journal 40: 876-879.

Lurie S, Watkins CB. 2012. Superficial scald, its etiology and control. Postharvest Biology and Technology. 65: 44-60.

Ma JF, Ryan PR, Delhaize E. 2001. Aluminum tolerance in plants and the complexing role of organic acids. TRENDS in Plant Science. 6: 273-278.

Marschner H. 1995. Mineral Nutrition of Plants 2nd Ed. Boston, MA: Academic Press.

The Merck Index. 1996. 12th Ed. Whitehouse Station, NJ: Merck & Co., Inc.

The Merck Index. 2006. 14th Ed. Whitehouse Station, NJ: Merck & Co., Inc.

Millipore-Sigma. 2015. SDS: Calcium Carbonate CX0110. [July 2018] Available from http://www.emdmillipore.com/Web-US-Site/en_CA/-/USD/ProcessMSDS-Start?PlainSKU=EMD_CHEM-CX0110&Origin=PDP

Nolan CR, Califano JR, Butzin CA. 1990. Influence of calcium acetate or calcium citrate on intestinal aluminum absorption. Kidney International. 38: 937-941.

Oates JAH. 1998. Lime and Limestone: Chemistry and Technology, Production and Uses. Weinheim, Germany: Wiley-VCH.

Peacock W. 2005. Fertigating drip-irrigated vineyards with macro- and micronutrients. Proceedings of the Soil Environment and Vine Mineral Nutrition Symposium. 129-133.

Perry DL. 2011. Handbook of Inorganic Compounds, 2nd Ed. Boca Raton, FL: CRC Press, Taylor & Francis Group, LLC.
Piccolo A, Nardi S, Concheri G. 1992. Structural characteristics of humic substances as related to nitrate uptake and growth regulation in plant systems. Soil Biology and Biochemistry 24: 373-380.

Piskolczi M, Varga C, Racsko J. 2004. A Review of the Meteorological Causes of Sunburn Injury on the Surface of Apple Fruits (*Malus domestica* BORKH). Journal of Fruit and Ornamental Plant Research. 12: 245-252.

PubChem 6116. Calcium Acetate. [June 2018] Available from https://pubchem.ncbi.nlm.nih.gov/compound/6116#section=Top

PubChem 10112. Calcium Carbonate. [July 2018] Available from https://pubchem.ncbi.nlm.nih.gov/compound/10112

PubChem 10340. Sodium Carbonate. [July 2018] Available from https://pubchem.ncbi.nlm.nih.gov/compound/10340

PubChem 516893. potassium Bicarbonate. [July 2018] Available from https://pubchem.ncbi.nlm.nih.gov/compound/516893

PubChem 82163. Calcium Acetate Monohydrate. [June 2018] Available from https://pubchem.ncbi.nlm.nih.gov/compound/82163#section=Top

SCF (Scientific Committee for Food). 1990. Report of the Scientific Committee for Food on a First Series of Food Additives of Various Technological Functions. Twenty-fifth series. [July 2018] Available from http://aei.pitt.edu/40834/1/25th_food.pdf

Schrader LA, Zhang J, Duplaga WK. 2001. Two types of sunburn in apple caused by high fruit surface (peel) temperature. Online. Plant Health Progress. DOIL 10.1094/PHP-2001-1004-01-RS.

Sigma-Aldrich. 2016. Calcium Acetate Hydrate SDS. [June 2018] Available from https://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=US&language=en&productNumber=379964&brand=SIGALD&PageToGoToURL=https%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Fsigald%2F379964%3Flang%3Den

Sigma-Aldrich. 2018. Calcium Acetate SDS. [June 2018] Available from https://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=US&language=en&productNumber=1086334&brand=USP&PageToGoToURL=https%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Fusp%2F1086334%3Flang%3Den

Sorrenti G, Toselli M, Marangoni B. 2012. Use of compost to manage Fe nutrition of pear trees grown in calcareous soil. Scientia Horticulturae. 136: 87-94.

Sunley GJ, Watson DJ. 2000. High productivity methanol carbonylation catalysis using iridium: The Cativa™ process for the manufacture of acetic acid. Catalysis Today. 58: 293-307.

USDA (United States Department of Agriculture). 2001a. Agricultural Management Effects on Earthworm Populations. Soil Quality - Agronomy Technical Note No. 11. [June 2018] Available from https://www.nrcs.usda.gov/Internet/FSE_DOCUMENTS/nrcs142p2_053291.pdf

USDA (United States Department of Agriculture). 2011. Lignin Sulfonate Technical Evaluation Report. [September 2018] Available from https://www.ams.usda.gov/sites/default/files/media/Lignin%20Sulfonate%20Aquatic%20Plants%20TR.pdf

USDA (United States Department of Agriculture). 2012. Oxidize Lignite/Humic Acid Derivatives Technical Evaluation Report. [July 2018] Available from https://www.ams.usda.gov/sites/default/files/media/Ox%20lig%20Technical%20Evaluation%20Report%20%282012%29.pdf

USDA (United States Department of Agriculture). 2017. Calcium Acetate – Agricultural Marketing Service. [June 2018] Available from https://www.ams.usda.gov/sites/default/files/media/PetitionCalciumAcetate.pdf

USDA (United States Department of Agriculture). 2018. Calcium Carbonate Technical Evaluation Report. [June 2018] Available from https://www.ams.usda.gov/sites/default/files/media/CalciumCarbonateTRFinal20180129.pdf

USGS (United States Geological Survey). 2001. Potential Environmental Impacts of Quarrying Stone in Karst—A Literature Review. USGS Open-File Report OF-01-0484. [July 2018] Available from https://pubs.usgs.gov/of/2001/ofr-01-0484/ofr-01-0484po.pdf

USGS (United States Geological Survey). 2008. Limestone—A Crucial and Versatile Industrial Mineral Commodity. USGS Fact Sheet. [July 2018] Available from https://pubs.usgs.gov/fs/2008/3089/fs20083089.pdf

706 Yadvinder-Singh, Beauchamp EG. 1988. Nitrogen transformations near urea in soil with different water potentials. Canadian Journal of Soil Science. 68: 569-576.