

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 Citrate

## Crops

### Identification of Petitioned Substance

<b>Chemical Names:</b>	19	<b>Trade Names:</b>
Ammonium Citrate	20	N/A
Citric Acid Triammonium Salt	21	
Ammonium Citrate Tribasic		<b>CAS Numbers:</b>
Ammonium Citrate Dibasic		3458-72-8
Ammonium Citrate Monobasic		3012-65-5
Citric Acid Triamine		7632-50-0
1,2,3-Propanetricarboxylic acid, 2-hydroxy-, ammonium salt		<b>Other Codes:</b>
Ammonium Hydrogencitrate		EC No. 222-394-5
		EC No. 221-146-3
<b>Other Name:</b>		EC No. 231-560-6
Citro Triamine		UN No. 3077
Ammonium Salt of Citric Acid		

### Summary of Petitioned Use

The petitioners are requesting to add ammonium citrate, the salt resulting from the neutralization of citric acid with ammonia, as a chelating agent to 7 CFR 205.601 as a “synthetic substance allowed for use in organic crop production.”

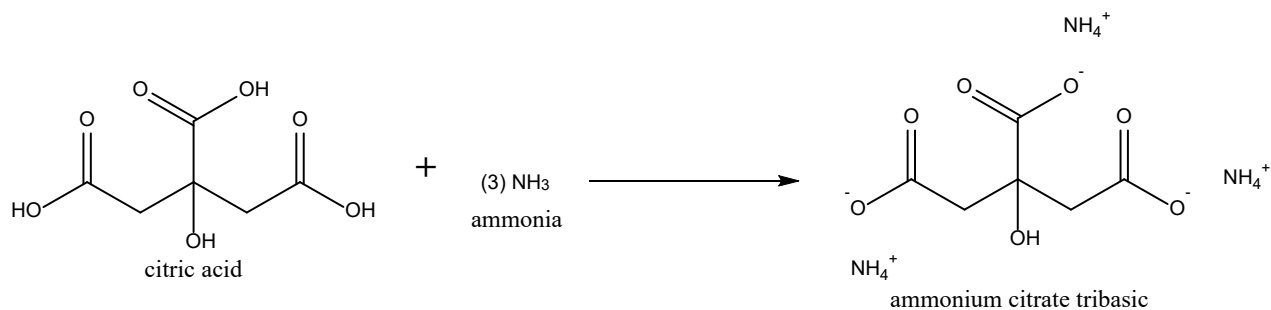
Ammonium citrate acts as a chelating agent for inorganic metal micronutrients ( $Mn^{2+}$ ,  $Zn^{2+}$ ,  $Fe^{2+/3+}$ ,  $Cu^{2+}$ ) to increase their bioavailability and enhance their water solubility, specifically in alkaline (high pH) soils. The petitioned use of the substance is as a micronutrient chelate rather than as the ammonium citrate salt. In this instance the final compound will be a salt composed of a cationic (positively charged) micronutrient and the anionic (negatively charged) citrate ion. The chelated form of the micronutrient (the micronutrient salt described above) increases the solubility and bioavailability of the nutrients, which are essential for the proper growth and functioning of plant systems.

### Characterization of Petitioned Substance

#### **Composition of the Substance:**

Ammonium citrate is a salt that is produced by neutralizing citric acid with ammonia. This produces a salt with a range of possible ammonium ( $NH_4^+$ ) cations. The range depends on the triacidic (containing three acidic coordination sites) citric acid’s degree of neutralization since the citric acid provides the corresponding citrate anion (Kirk-Othmer 1992). There are three forms for ammonium citrate: completely neutralized ammonium citrate tribasic (CAS 3458-72-8), partially neutralized ammonium citrate dibasic (CAS 3012-65-5), and monobasic (7632-50-0). Both the completely neutralized tribasic and the partially neutralized dibasic can be used as chelating agents. The monobasic form is unable to act as a chelating agent due to the presence of only a single coordination site ( $COO^-$  from the neutralized acid). Therefore, the monobasic form of ammonium citrate will not be discussed further in this petition.

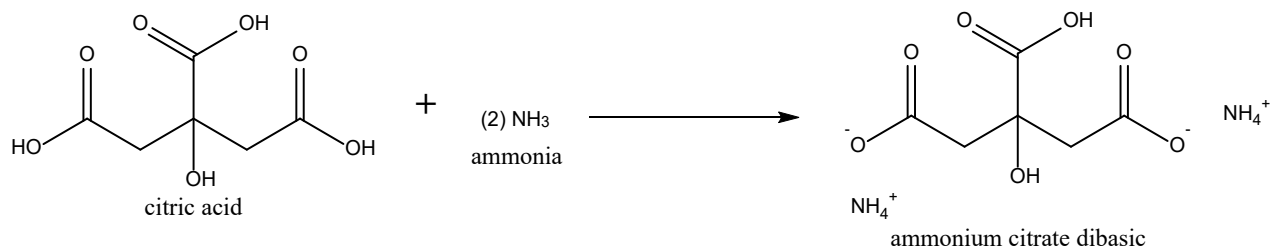
The tribasic form of ammonium citrate is commercially available as white or colorless crystals in 95–99% purity (Sigma-Aldrich 2016). The substance is produced from the complete neutralization reaction shown below in Equation 1 (Kirk-Othmer 1992).



**Equation 1**

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The dibasic form of ammonium citrate is commercially available as white or colorless crystals in 95–99% purity (Sigma-Aldrich 2018). The substance is produced from the incomplete neutralization reaction shown below in Equation 2 (Kirk-Othmer 1992).



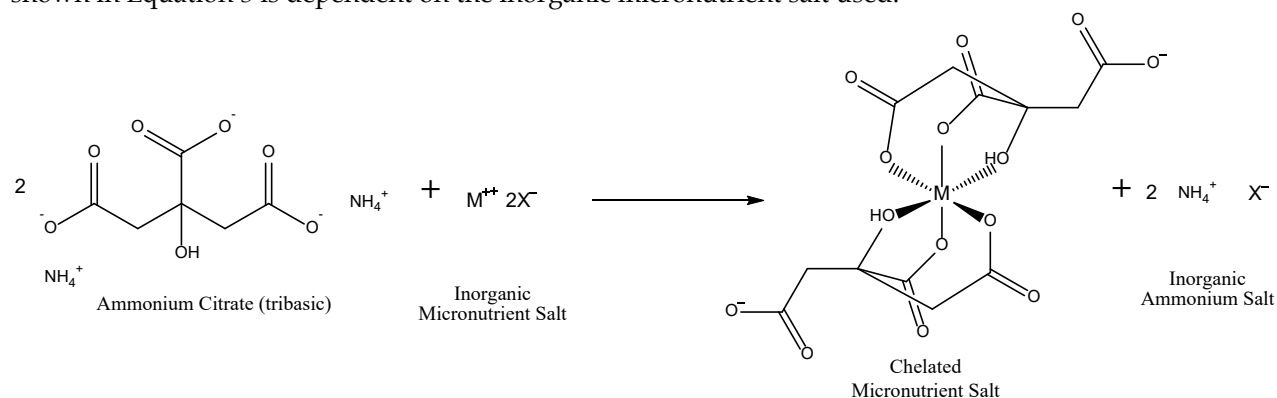
**Equation 2**

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**Source or Origin of the Substance:**

Ammonium citrate (both tribasic and dibasic forms) is produced by the neutralization of citric acid with ammonia (shown above in Equations 1 and 2) (Kirk-Othmer 1992). This is a synthetic process, as ammonium citrate is not known to occur naturally.

When used as petitioned, the substance will react with an inorganic micronutrient salt (MX<sub>2</sub>), as shown in Equation 3 (Glusker 1980). This reaction will result in a chelated form of the micronutrient that has increased water solubility, especially in alkaline (high pH) soils. The identity of the inorganic ammonium salt product shown in Equation 3 is dependent on the inorganic micronutrient salt used.



**Equation 3**

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74 **Properties of the Substance:**

75 The properties of the tribasic and dibasic forms of ammonium citrate are summarized in Table 1.

76

77

**Table 1. Properties of Ammonium Citrate**

Properties	Ammonium Citrate Tribasic	Ammonium Citrate Dibasic
CAS No.	3458-72-8	3012-65-5
Molecular Formula	C <sub>6</sub> H <sub>17</sub> N <sub>3</sub> O <sub>7</sub>	C <sub>6</sub> H <sub>14</sub> N <sub>2</sub> O <sub>7</sub>
Molecular Weight	243.22 g/mol	226.18 g/mol
Appearance	White or colorless crystalline solid, white granules	White or colorless crystalline solid, white granules
Melting Point	185 °C (365 °F)	n/a
Density	1 g/cm <sup>3</sup> at 25 °C (77 °F)	0.4 - 0.6 g/l (bulk density)
pH	n/a	5.12 at 50g/l at 20 °C (68 °F)
Solubility	Soluble in water and slightly soluble in alcohol	Soluble in water and alcohol

78 Sources: (PubChem 13725959, PubChem 18171, Sigma-Aldrich 2016, Sigma-Aldrich 2018, Hall 1915).

79

80 **Specific Uses of the Substance:**

81 Ammonium citrate is petitioned to be used as a chelating agent for the delivery of micronutrients (e.g.,  
 82 Mg<sup>2+</sup>, Zn<sup>2+</sup>, Fe<sup>2+/3+</sup>, Cu<sup>2+</sup>) to crops. Chelating agents, also known as chelators, are defined as having  
 83 multiple coordination sites to the same metal center, meaning that one molecule makes attachments  
 84 through two or more single bonds to a central atom (usually a metal center; in this report, a micronutrient  
 85 cation (Mn<sup>2+</sup>, Zn<sup>2+</sup>, Fe<sup>2+/3+</sup>, Cu<sup>2+</sup>)) (IUPAC 1997). Once the chelating agent has formed its multiple bond  
 86 attachment to a central atom, the resulting complex is known as a chelate. If both the central atom and  
 87 chelating agent are charged (ionic species), the resulting chelate is a metal salt, as all salts consist of  
 88 positively charged (cation) and negatively charged (anion) species. Chelates are differentiated from the  
 89 generic term “salt,” as they result in an enveloped central atom, changing its reactivity and chemical  
 90 properties. Micronutrient chelates take advantage of the change in chemical properties, specifically the  
 91 increased water solubility because of ammonium citrate, to increase the bioavailability and plant uptake of  
 92 the micronutrients.

93

94 Chelating agents are also referred to as “sequestration agents” or “sequestrants.” However, this  
 95 nomenclature is only appropriate when the resulting chelation removes a substance either physically or  
 96 chemically. This sequestration can occur when strong interactions between the central atom and chelating  
 97 agent result in an unreactive chelate (chemical) or when the chelate produces a change in physical  
 98 properties of the central atom, reducing its solubility and effectively removing the undesired substance  
 99 (physical). The use of ammonium citrate as petitioned is not intended to act as a sequestrant; however,  
 100 studies have indicated increased resistance to aluminum toxicity in relation to ammonium citrate through  
 101 sequestration, as discussed in more detail in Evaluation Question #8.

102

103 Micronutrients are chelated by attachment of a single metal center to a chelating agent (citrate anion) at  
 104 multiple coordination sites (IUPAC 1997). The resulting chelate becomes more water soluble, and therefore  
 105 more bioavailable, than the naturally occurring metal salts in most soils (Blancquaert et al. 2017, Datir et al.  
 106 2010, Grusak et al. 1999, Janmohammadi et al. 2016). The effect of chelation becomes more dramatic in  
 107 alkaline and water deficient settings, where the inorganic micronutrient metal cations tend to form low  
 108 solubility hydroxide salts (Durrett et al. 2007, Janmohammadi et al. 2016). After chelation happens, the  
 109 increased bioavailability of micronutrients provides an efficient system of delivering essential agricultural  
 110 nutrition, and is especially powerful for applications in alkaline (high pH), and water deficient soils.

111

112 Non-synthetic forms of citric acid are allowed as “chelating agents” for organic production (§205.105 and  
 113 NOP 5034-1). However, citric acid itself is not a chelating agent. Citric acid (reactant in Equations 1 and 2)  
 114 provides the bulk of the structure for the anion that is able to act as a chelating agent. However, in its  
 115 natural state (the state approved for use as a chelating agent), citric acid is unable to bond to metal centers.  
 116 This inability is due to the lack of carboxylate groups (-COO<sup>-</sup>), which are required for the coordination of  
 117 organic acids (citrate). Upon neutralization with a base (ammonia (NH<sub>3</sub>)), citric acid becomes the anion

118 citrate (-COOH converted to -COO<sup>-</sup>, as shown in Equations 1 and 2), and the negatively charged species  
119 becomes capable of chelation.

120  
121 Ammonium citrate has been approved for use in livestock production, at 21 CFR 582.80, as a “trace mineral  
122 added to animal feeds” in the form of iron ammonium citrate.

123  
124 **Approved Legal Uses of the Substance:**

125 Ammonium citrate has been approved by the Food and Drug Administration (FDA) as a stabilizer  
126 “prior-sanctioned food ingredient,” at 21 CFR 181.29. The FDA has also approved the incorporation of  
127 ammonium citrate as an “indirect food additive: adhesive and component of coatings,” for adhesives at  
128 §175.105(c), and resinous and polymeric coatings at §175.300(b).

129  
130 An iron chelate resulting from the coordination of an iron cation (Fe<sup>2+/3+</sup>) by the tribasic form of  
131 ammonium citrate (iron ammonium citrate) has been approved by the FDA for use as a “trace mineral  
132 added to animal feeds,” at §582.80, and is also listed as a “food additive permitted in feed and drinking  
133 water of animals,” at §573.560. Iron ammonium citrate has also been approved by the FDA as a component  
134 of “weight control drug products,” at §310.545(b) and as “an anticaking agent in salt for human  
135 consumption,” at §172.430.

136  
137 The Environmental Protection Agency (EPA) has listed ammonium citrate dibasic as a hazardous  
138 substance at 40 CFR 116.4. This citation is pursuant to the identification of the substance that “when  
139 discharged in any quantity into or upon the navigable waters of the United States or adjoining shorelines  
140 or the waters of the contiguous zone or in connection with activities under the Outer Continental Shelf  
141 Lands Act or the Deepwater Port Act of 1974, or which may affect natural resources belonging to,  
142 appertaining to, or under the exclusive management authority of the United States (including resources  
143 under the Magnuson Fishery Conservation and Management Act of 1976), present an imminent and  
144 substantial danger to the public health or welfare, including, but not limited to, fish, shellfish, wildlife,  
145 shorelines, and beaches,” as stated in §311(b)(2)(A) of the Federal Water Pollution Control Act.

146  
147 **Action of the Substance:**

148 Ammonium citrate acts as a chelating agent that, through multiple bonds to a metallic micronutrient cation  
149 (e.g., Mn<sup>2+</sup>, Zn<sup>2+</sup>, Fe<sup>2+/3+</sup>, Cu<sup>2+</sup>), increases the water solubility of the species. These micronutrients are  
150 important for both proper plant function, and the subsequent nutritional value of the crop  
151 (Alvarez-Fernandez et al. 2014, Datir et al. 2017, Durrett et al. 2007, Grusak et al. 1999, Wu et al. 2018).  
152 While all of these cationic micronutrients are required for proper plant function, iron’s importance within  
153 the photosynthetic pathway has made it the most widely studied. Moreover, daily diet iron deficiency  
154 affects billions of people around the globe in what has come to be known as “hidden hunger” (Blancquaert  
155 et al. 2017, Tulchinsky 2010).

156  
157 Due to iron’s (Fe<sup>2+/3+</sup>) importance for both plants and the human population, and the implications for  
158 similar divalent cation micronutrients (Mn<sup>2+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup>), iron’s bioavailability is a relevant concern. While  
159 iron is abundant in most types of soils, it is present primarily in the form of iron (III) hydroxides (Fe(OH)<sub>3</sub>),  
160 which have low water solubility (Durrett et al. 2007). This low water solubility translates to iron’s low  
161 bioavailability for plant uptake, which becomes a much more dramatic problem in the context of soils with  
162 high alkalinity or water deficiency (Boiteau et al. 2018, Grusak et al. 1999, Janmohammadi et al. 2016).

163  
164 Plants have natural responses to increase the uptake of the essential micronutrients, known commonly as  
165 Strategy I and Strategy II, both of which include excreting a chelating agent (Grusak et al. 1999). This  
166 chelating agent sequesters the iron present in the soil and increases the water solubility of the  
167 micronutrient, which can then be transported to the root and absorbed by the plant. In Strategy I, the  
168 chelating agent efflux occurs in concert with the release of organic acids, decreasing the pH of the soil  
169 around the root and making the iron more soluble still (Grusak et al. 1999). While the iron uptake process  
170 has been intensely studied, it is also thought to be a general mechanism for other essential micronutrients,  
171 such as Cu<sup>2+</sup>, Mn<sup>2+</sup>, and Zn<sup>2+</sup> (Grusak et al. 1999).

172

173 Recent studies have also shown how important chelating agents are for translocating micronutrients upon  
174 plant uptake. Among these, citrate is thought to be the major chelating agent, and it is responsible for  
175 nearly all iron translocation within a plant through the xylem (Durrett et al. 2007, Grusak et al. 1999, Wu et  
176 al. 2018). In fact, studies have shown that high citrate concentrations in plant cells leads to increased plant  
177 function in iron deficient soils as compared to plants in iron rich environments with low levels of citrate  
178 (Durrett et al. 2007, Wu et al. 2018).

179  
180 The action of the petitioned substance is to provide a similar mechanism for increasing micronutrient  
181 bioavailability. In these applications, the micronutrient is chelated by ammonium citrate, increasing its  
182 water solubility and enhancing uptake by crops. Chelation enhances the delivery of these species, catering  
183 to the micronutrient needs of crops and soil. Moreover, due to the multiple attachment points of the  
184 chelating species (citrate), it is not easily displaced by competing, low solubility anions such as OH<sup>-</sup> and  
185 CO<sub>3</sub><sup>2-</sup> (Grusak et al. 1999). This strategy has shown promise in several studies, where chelated  
186 micronutrients significantly increased crop growth, yield, and quality (Datir et al. 2010, Wu et al. 2018).  
187 This result is particularly important in areas with limited irrigation, where the chelated micronutrients  
188 outperformed conventional fertilization programs (Janmohammadi et al. 2016). Because citrate is important  
189 for translocating micronutrients following plant uptake, the application of citrate-chelated nutrients may  
190 result in improved plant function as well.

191  
192 **Combinations of the Substance:**  
193 As stated in the section titled “Composition of the Substance,” ammonium citrate can take monobasic,  
194 dibasic, and tribasic forms, depending on the degree of neutralization of the original citric acid; however,  
195 only the dibasic and tribasic forms are capable of chelation. The degree of neutralization is controlled by  
196 the titration process with ammonia (NH<sub>3</sub>) reacting with the citric acid to produce the resultant ammonium  
197 citrate salt (Hall 1915). Both the dibasic and tribasic varieties are commercially available in purity >95%,  
198 with the major impurities being excess ammonia (NH<sub>3</sub>) or water that has been incorporated into the crystal  
199 structure (Hall 1915).

200  
201 However, ammonium citrate as petitioned is not meant to be applied to crops as a chelating agent alone,  
202 but rather in the chelate form (coordinated to a metal cation). In this instance, the coordinated cation would  
203 be determined based on the particular crop and soil conditions. The most likely candidates are Mn<sup>2+</sup>, Zn<sup>2+</sup>,  
204 Fe<sup>2+/3+</sup>, and Cu<sup>2+</sup>, all of which are natural minerals and essential micronutrients. Moreover, salts of these  
205 cations have been approved for use by the National Organic Program for organic crop production, at 7 CFR  
206 205.601.

207  
208 **Supplemental Information:**  
209 NOP requested technical clarification of the terms “ligand,” “chelating agent,” and “chelate.” It is beneficial  
210 to begin with the differences between the related terms “ligand” and “chelating agent.” The petitioner  
211 claims that NOP has used “chelating agent” incorrectly (discussed in more detail below) and suggests  
212 replacing the term “chelating agent” with “ligand.” Therefore, it seems that, prior to the analysis of NOP’s  
213 usage of the term “chelating agent,” a discussion of the two terms may be helpful. A ligand has been  
214 defined as an ion or molecule that is covalently bonded to a metal atom that can also have an independent  
215 existence (Silberberg 2003, Shriver and Atkins 2008). A chelating agent is a specific type of ligand and is  
216 characterized by its ability to form multiple bonds to the metal center from multiple attachment points (i.e.,  
217 a polydentate ligand) (Silberberg 2003, Shriver and Atkins 2008). Based on these definitions, it is technically  
218 correct to classify all chelating agents as ligands. However, in the United States it is far more common to  
219 refer to these polydentate ligands as “chelating agents,” rather than the more general, “ligand.” Moreover,  
220 the term chelating agent is typically reserved for ligands that not only have the capacity to form multiple  
221 attachment points, but also ligands that tend towards forming these attachment points as a rule – a  
222 tendency that results in a specific set of properties and applications. In conclusion, the term ligand is *not*  
223 synonymous with chelating agent, with chelating agents comprising a specific mode of coordination while  
224 ligand refers to anything molecule or ion that coordinates to a metal atom.

225  
226 With the differences between ligands and chelating agents established, the terms “chelating agent” and  
227 “chelate” will be discussed. As stated, these terms are related. Chelates are defined as “a complex

228 [molecule consisting of a metal atom(s) that are bonded to a set of ligands] in which a ligand forms a ring  
229 that includes the metal atom" (Shriver and Atkins 2008). More simply, a chelate is the result of the  
230 chelating agent forming multiple attachment points to a metal atom. This principle is illustrated in  
231 Equation 3, in which the ammonium citrate tribasic salt is the chelating agent (left), and the final product  
232 consisting of the citrate ion having former multiple bonds to the metal center (M) is the chelate (right).  
233 Therefore, the difference between a chelating agent and a chelate can be simplified as the chelating agent  
234 has the capacity to form multiple bonds to a metal atom, while a chelate no longer has the capacity to form  
235 bonds with multiple attachment points. Rather, a chelate includes a metal atom to which bonds from  
236 multiple attachment points have been made.

237  
238 The petitioner has questioned the use and technical accuracy of the terms "chelate" and "chelating agent,"  
239 within NOP documents, including the National List. A review of the National List shows a singular usage  
240 of "chelating agent," which is used to describe the approved usage of lignin sulfonate at 9 CFR 205.601. In  
241 this context, the use of the term "chelating agent" is used correctly to describe the ability of the lignin  
242 sulfonate to form multiple bonds to a metal atom.

243  
244 Further investigation of NOP documents shows the use of the term "chelating agent" in NOP 5034-1,  
245 "Guidance Materials for Organic Crop Production." In this document, a section on chelating agents states:  
246 "Natural chelating agents are allowed. Allowed sources of chelating agents include, but are not limited to,  
247 non-synthetic amino acids, citric acid (to form citrate in solution), tartaric acid made from grape wine, and  
248 gluconic acid. Synthetic chelating agents are only permitted if included on the National List for that  
249 purpose" (NOP 5034-1). The technical accuracy of this usage is difficult to gauge given the lack of context  
250 in the application and formulation of the chelating agent. However, within this usage, the term is applied  
251 in a contradictory manner. This is highlighted with "citric acid (to form citrate in solution)," which uses the  
252 term correctly, but implies that in the other natural acids listed, this change would not occur when used as  
253 a chelating agent (which is incorrect) (NOP 5034-1). All the listed compounds (citric, tartaric, gluconic, and  
254 non-synthetic amino acids) share the same carboxylic acid functional group (shown in the neutralization  
255 reactions in Equations 1 and 2). Like the formation of citrate from citric acid, all the listed acids would be  
256 required to undergo a similar neutralization reaction *before* they could function as chelating agents.  
257 Therefore, NOP should alter document 5034-1 in order to reflect the technically correct usage of the term  
258 (e.g. "Organic acids such as non-synthetic amino acids and citric acid may be used a precursors to chelating  
259 agents, with the chelating agents being the neutralized carboxylate salt of the approved acid.").

260  
261 NOP requested clarification on the ability of neutral acids to act as chelating agents. While the neutral  
262 forms of the chelating agents listed in NOP 5034-1 (citric, tartaric, gluconic, and amino acids) technically  
263 could form bonds due to the availability of lone pairs of the carboxylic acid groups (-COOH), these neutral  
264 forms will include only weak interactions. Therefore, the neutral acids are not considered to be chelating  
265 agents until they have undergone neutralization of the carboxylic acid group (-COOH) to yield the  
266 carboxylate anion (-COO-) (illustrated in Equations 1 and 2). This allows for the formation of strong,  
267 covalent interactions with the metal atom to form a chelate.

268  
269 This leads us to the question posed by NOP as to if citric acid is neutralized to citrate, can it still be  
270 considered citric acid? The short answer here is no. Once a neutralization reaction occurs, the citric acid is  
271 transformed to a citrate salt, which will have entirely different chemical and physical properties, and is  
272 further accentuated by the assignment of a new CAS number (citric acid = 77-92-9, while the citrate CAS  
273 number is dependent on its corresponding cation). This does not mean that the citrate is no longer acidic.  
274 Because neutral citric acid has three carboxylic acid groups, it is capable of continued acidity even after the  
275 neutralization of a single functional group (as is true for any acid with multiple carboxylic acid groups).  
276 However, the acid strength of the compound is dramatically reduced with each subsequent neutralization  
277 as illustrated by the increasing pKa values for the first, second, and third neutralizations (3.13, 4.76, and  
278 6.40, respectively) (Merck 1983).

279  
280 There are a wide range of possible cations that will act to counter the negative charge of the carboxylate  
281 anion following the dissociation of the carboxylic acid proton (H<sup>+</sup>). These cations include, but are not  
282 limited to, lithium (Li<sup>+</sup>), sodium (Na<sup>+</sup>), potassium (K<sup>+</sup>), and ammonium (NH<sub>4</sub><sup>+</sup>). However, due to the

283 characterization of the neutral acids as chelating agents by the NOP, a list of cations found in approved  
284 substances does not exist (NOP 5034-1). If the use of ammonium ( $\text{NH}_4^+$ ) including or producing bases (e.g.,  
285 ammonium hydroxide ( $\text{NaOH}$ ), ammonia ( $\text{NH}_3$ )) are permitted for treatment of approved acids to produce  
286 chelating agents, the petitioned substance then appears to fall under this approval.

287  
288 The strength of chelation (a chelating agent bonding to a metal atom to form a chelate) is dependent upon  
289 many factors. These include the identity of both the chelating agent and metal atom, as well as the  
290 environment that the chelate is subjected to (e.g., pH, temperature, etc.). Therefore, it is impossible to  
291 predict the widespread utility of any single chelating agent. However, it is also likely that several  
292 applications will be better served by a greater diversity of approved chelating agents to choose from,  
293 allowing the consumer to choose the chelating agent that is best suited for the application of a specific  
294 micronutrient (metal atom) within the given environmental constraints. Chelating agents have been shown  
295 to increase the solubility and bioavailability of micronutrients applied as soil amendments. However, the  
296 efficacy of the delivery by the chelating agent is dependent on the identity of the chelating agent and  
297 micronutrient, as well as the environmental conditions of the agroecosystem. With this in mind, increasing  
298 the diversity of approved chelating agents allows for the most effective pairing for a given micronutrient  
299 and environmental system. For this reason, the presence of other approved chelating agents on the  
300 National List (e.g., humates and lignin sulfonate) does not make the petitioned substance unnecessary.

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### Status

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#### **Historic Use:**

305 No historic use of ammonium citrate in organic agricultural production has been recorded. As a  
306 non-synthetic substance, the parent compound citric acid is permitted in organic production USDA organic  
307 regulations (7 CFR 205.105) when used in a non-synthetic form. Ammonium citrate has seen limited use in  
308 agricultural production, mostly as a component of indirect food additives such as adhesives and resinous  
309 and polymeric coatings, as described in 21 CFR 175.300 and §175.105.

310

311 Iron ammonium citrate and iron-citrate chelate have been used in agricultural production in the form of  
312 added trace minerals for animal feed and drinking water as described in 21 CFR 582.80 and §573.560. Iron  
313 ammonium citrate is also used as an anticaking agent in "salt for human consumption," at §172.430.

314

#### **Organic Foods Production Act, USDA Final Rule:**

316 Ammonium citrate is not listed in the Organic Foods Production Act of 1990 (OFPA) or the U.S.  
317 Department of Agriculture (USDA) organic regulations, at 7 CFR 205. However, a variety of synthetic  
318 micronutrients have been approved for use at 7 CFR 205.601(j), and minerals have also been approved as  
319 synthetic substances at §6517.

320

#### **International**

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##### **Canadian General Standards Board Permitted Substances List**

324 Ammonium citrate is not listed in the CAN/CGSB-32.311-2015 – Organic production systems –  
325 Permitted substances lists. However, several other citrate salts are listed. Iron citrate is listed in Table 4.2 –  
326 *Soil amendments and crop nutrition*, as a method "to correct documented iron deficiencies." Calcium,  
327 potassium, and sodium citrate salts are listed in Table 6.3 – *Ingredients classified as food additives*, with  
328 sodium citrate having a restriction of "non-synthetic sources." Sodium citrate is also listed in Table 7.3 –  
329 *Food-grade cleaners, disinfectants and sanitizers permitted without a mandatory removal event*, with the added  
330 restriction of "non-synthetic sources," and in Table 7.4 – *Cleaners, disinfectants and sanitizers permitted on*  
331 *organic product contact surfaces for which a removal event is mandatory*.

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

335 Ammonium citrate is not listed in the CODEX; however, sodium citrate is listed "for the purposes of  
336 processing livestock and bee products only," with the specific conditions of "sausages/pasteurization of  
337 egg whites/milk products."



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

Ammonium citrate is not listed in the EEC EC No. 834/2007 or 889/2008. However, sodium citrates are listed in EC No. 889/2008 under code E 331 for the "preparation of foodstuffs of animal origin." Calcium citrates are also listed in EC No. 889/2008 under code E 333 for the "preparation of foodstuffs of plant origin."

### Japan Agricultural Standard (JAS) for Organic Production

Ammonium citrate is not listed in the JAS; however, sodium citrate is listed in JAS notification No. 1606 as a food additive "limited to be used for dairy products or used for albumen and sausage as low temperature pasteurization."

### International Federation of Organic Agriculture Movements (IFOAM)

Ammonium citrate is not listed in IFOAM. However, a number of other citrate salts are identified. Copper citrate and iron citrate are listed as "fertilizers and soil conditioners... restricted to cases where soil/plant nutrient deficiency is documented by soil or tissue testing or diagnosed by an independent expert." Sodium, calcium, and potassium citrates are also listed as "approved additives and processing/post-harvest handling aids."

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

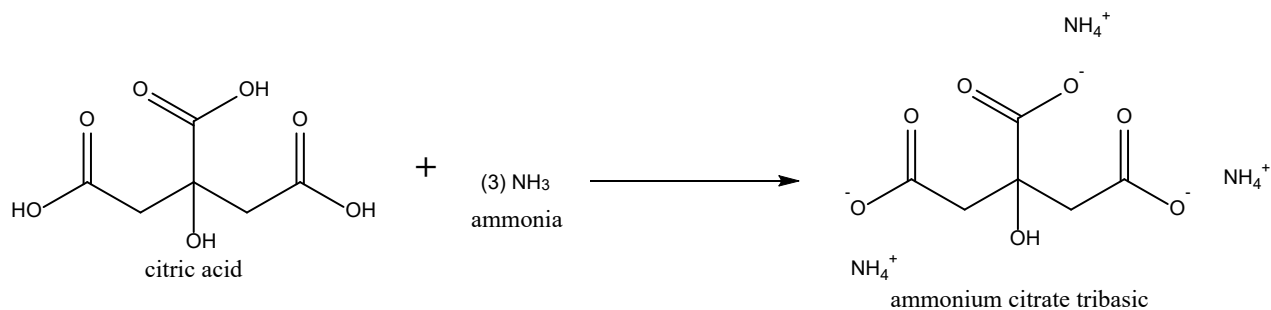
**Evaluation Question #1: Indicate which category in OFPA that the substance falls under: (A) Does the substance contain an active ingredient in any of the following categories: copper and sulfur compounds, toxins derived from bacteria; pheromones, soaps, horticultural oils, fish emulsions, treated seed, 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?**

Ammonium citrate does not contain any of the materials listed in (A). However, as copper is an essential micronutrient for plant development, it may be used in concert with ammonium citrate in the form of a chelate (Equation 3 where M is  $\text{Cu}^{+2}$ ). In this form, the copper is unlikely to be reactive due to the multiple coordination points of the citrate, although the water solubility of the copper (if used) is likely to be increased.

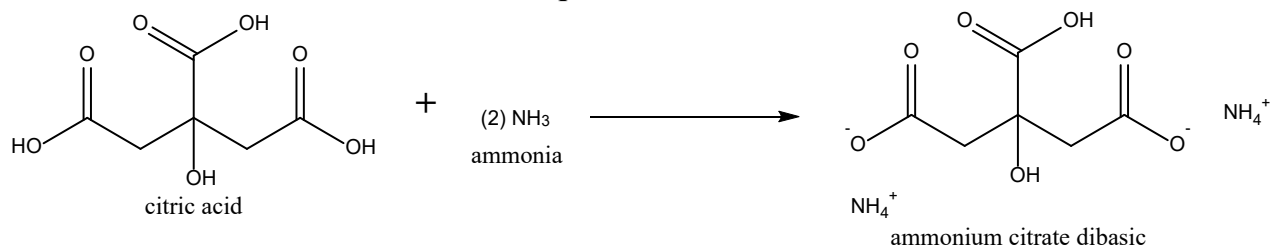
When used as petitioned, ammonium citrate serves as an inert ingredient for the delivery of micronutrients. The citrate chelated micronutrients (product of Equation 3) are inert due to their multiple points of attachment to the micronutrient. The petitioned substance is not listed by the EPA as an inert of toxicological concern and is not listed in 40CFR 180, per (B).

**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)).**

The ammonium citrate product is synthetic and is not known to exist in nature. As stated above in the section titled "Characterization of Petitioned Substance," ammonium citrate (in both its dibasic and tribasic forms) is produced by the neutralization (transfer of  $\text{H}^+$  from acid to base) of citric acid with the base ammonia ( $\text{NH}_3$ ) (Kirk-Othmer 1992, Hall 1915). The quantity of ammonia used in the neutralization process affects what type of ammonium citrate product that is produced (Hall 1915), as shown in Equations 1 and 2. This process forms a salt between ammonium ( $\text{NH}_4^+$ ) cations and citrate anions.



391

**Equation 1****Equation 2**392  
393

394 These neutralization reactions employ anhydrous citric acid and ammonia sources in order to maintain the  
 395 stability of the products and prevent the reformation of citric acid. The reaction is typically carried out in  
 396 an alcohol, due to the solubility of the reactants (citric acid and ammonia), and the relative insolubility of  
 397 the ammonium citrate products. The crystalline products are obtained through the evaporation of the  
 398 solvent (alcohol), leaving ammonium citrate in high purity (Hall 1915).

399

400 Both precursors to ammonium citrate (citric acid and ammonia) are naturally occurring. Citric acid is  
 401 naturally produced in animals, plants, and microorganisms, and is an important molecule in human  
 402 metabolic pathways (Duarte et al. 2012, Lotfy et al. 2007, SCF 1990, Verhoff 2011). Microorganisms  
 403 manufacture the most citric acid by fermenting carbohydrates to citric acid, and the citric acid is typically  
 404 extracted as a liquid or with a lime-sulfuric acid method (Kirk-Othmer 1993, Verhoff 2011).

405

406 Ammonia (NH<sub>3</sub>) is an inorganic gas and is produced biologically in the body as a byproduct of several  
 407 metabolic reactions (MeSH D000641). Ammonia is an industrially important commodity with a range of  
 408 uses from solvents and fuels to agricultural chemicals (PubChem 222). Most ammonia is produced using  
 409 the Haber-Bosch process, in which atmospheric nitrogen gas (N<sub>2</sub>) is reduced with a hydrogen source at  
 410 high temperatures and pressures in the presence of an iron catalyst (Clayton and Clayton 1994).

411

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

414

415 The petitioned substance is manufactured and is not known to exist in nature. Ammonium citrate is a salt  
 416 that is produced by the neutralization reaction that occurs between naturally occurring citric acid and  
 417 ammonia (Equations 1 and 2). Citric acid is prevalent in nature from a variety of sources, including as a  
 418 component of citrus fruits (oranges, lemons, etc.) but is typically produced industrially via a fermentation  
 419 process utilizing microorganisms (discussed in more detail in Evaluation Question #2 (Duarte et al. 2012,  
 420 Lotfy et al. 2007, SCF 1990, Verhoff 2011)). Ammonia is made through natural processes and is an  
 421 industrially important commodity, and as such, it is manufactured through the Haber-Bosch process, as  
 422 described above in Evaluation Question #2 (Clayton and Clayton 1994).

423 **Evaluation Question #4: Describe the persistence or concentration of the petitioned substance and/or its**  
424 **by-products in the environment (7 U.S.C. § 6518 (m) (2)).**  
425

426 The petitioned substance is not known to accumulate in the environment. Both ammonium ( $\text{NH}_4^+$ ) and  
427 citrate are naturally occurring in a range of plants, animals, and microorganisms. The EPA OPERA (OPEn  
428 (q)saR App) Model on biodegradation predict a half-life of 4.09 days for the citrate anion (EPA).  
429

430 When used as petitioned, ammonium citrate will not be introduced into the environment. The substance  
431 will be reacted with an applicable approved micronutrient (as shown in Equation 3), and a solution of the  
432 chelated micronutrient and inorganic ammonium salt will be employed. Due to the use of the petitioned  
433 substance as a precursor to the desired chelated micronutrient, ammonium citrate itself is not anticipated to  
434 be used for crop applications, and therefore is not expected to be an environmental concern. Moreover, the  
435 need for micronutrients in trace amounts would lead to the introduction of minimal amounts (ppm  
436 applications) of ammonium citrate as a micronutrient chelate when used as petitioned (Boiteau et al. 2018,  
437 Blancquaert et al. 2017, Janmohammadi et al. 2016).  
438

439 Due to the use of the petitioned as a precursor to micronutrient chelates, they will exist in many possible  
440 combinations that are dependent on the micronutrient in question, as well as the inorganic salt that is  
441 chosen as the micronutrient source. Therefore, an analysis of the individual ions in the environment is  
442 important. Both ammonium ( $\text{NH}_4^+$ ) and citrate ions are naturally occurring in a range of plants, animals,  
443 and microorganisms due to their persistence in normal biological environments, and the metabolism of  
444 both ammonium and citrate ions by a variety of organisms (JECFA 1986, EFSA 2008a, EFSA 2008b, SCF  
445 1990). Based on the incorporation of these ions into the metabolic pathway of a variety of organisms, they  
446 are not expected to be long-lived in the environment; therefore, the petitioned substance does not likely  
447 pose a threat to the environment. Moreover, as discussed in the section titled "Action of the Substance,"  
448 citrate is naturally present in the soil because of micronutrient uptake in plants using Strategy I), following  
449 the reaction between the organic acid citric acid and alkaline components in the soil (Grusak et al. 1999).  
450

451 **Evaluation Question #5: Describe the toxicity and mode of action of the substance and of its breakdown**  
452 **products and any contaminants. Describe the persistence and areas of concentration in the environment**  
453 **of the substance and its breakdown products (7 U.S.C. § 6518 (m) (2)).**  
454

455 As discussed above in Evaluation Question #4, the petitioned substance is a salt comprised of ions that are  
456 prevalent in the environment and is predicted to have a half-life of 4.09 days (EPA). When used as  
457 petitioned, ammonium citrate is a precursor to chelated micronutrients (product of Equation 3) for  
458 agricultural applications, and therefore ammonium citrate and its breakdown products are not anticipated  
459 to be an environmental concern. Furthermore, the requirement of micronutrients in trace amounts would  
460 lead to the introduction of minimal amounts (ppm applications) of micronutrient chelates when used as  
461 petitioned (Boiteau et al. 2018, Blancquaert et al. 2017, Janmohammadi et al. 2016).  
462

463 The chelated micronutrient acts to increase the bioavailability of the metal cation to ensure its uptake by  
464 crops. Due to the use of the petitioned as a precursor to micronutrient chelates, they will exist in many  
465 possible combinations that are dependent on the micronutrient in question, as well as the inorganic salt  
466 that is chosen as the micronutrient source. Therefore, an analysis of the individual ions in the environment  
467 is important. Once the water-soluble micronutrient has been absorbed by plant life, the citrate anion and  
468 ammonium salt (product of Equation 3) remain in the soil. However, both ammonium and citrate ions are  
469 prevalent in nature, are readily metabolized by a variety of organisms, and therefore are not anticipated to  
470 have any toxicological impact on the environment (JECFA 1986, EFSA 2008a, EFSA 2008b, EFSA 2008c,  
471 EFSA 2014, SCF 1990). Furthermore, the need for micronutrients in trace amounts would lead to the  
472 introduction of minimal amounts (ppm applications) of ammonium citrate as a micronutrient chelate when  
473 used as petitioned (Boiteau et al. 2018, Blancquaert et al. 2017, Janmohammadi et al. 2016).  
474

475 **Evaluation Question #6: Describe any environmental contamination that could result from the**  
476 **petitioned substance's manufacture, use, misuse, or disposal (7 U.S.C. § 6518 (m) (3)).**  
477

478 As discussed above in Evaluation Questions #4 and #5, ammonium citrate is a salt whose ions are  
479 prevalent in nature and readily metabolized, with a predicted environmental half-life of 4.09 days (EPA).  
480 Ammonium citrate is used a precursor to chelated micronutrients (Equation 3) and will not be applied  
481 directly to crops. Both ammonium and citrate ions are important compounds in the metabolic pathways of  
482 a variety of organisms, and given the small quantities (parts-per-million applications) expected when it is  
483 used as petitioned, they are not anticipated to have an environmental impact.

484  
485 Both of the precursors to ammonium citrate (ammonia and citric acid) are naturally occurring substances.  
486 Ammonia is synthetically produced via the Haber-Bosch process due to its high industrial demand and are  
487 unlikely sources of environmental contamination (Clayton and Clayton 1994).

488  
489 The production of ammonia (NH<sub>3</sub>) and ammonium (NH<sub>4</sub><sup>+</sup>) salts for use in fertilization programs has  
490 dramatically increased the agricultural productivity in regions across the world (Ryan et al. 2012, Tilman et  
491 al. 2002). However, despite the increased productivity, recent studies have shown a decreased efficiency in  
492 uptake of nitrogen nutrients (ammonia and ammonium salts) (Tilman et al. 2002). Much of the “lost”  
493 fertilizer occurs through ecosystem transfer and unintentional fertilization, which can result in reduced  
494 biodiversity (Erisman et al. 2008).

495  
496 Ammonium salts are produced as a byproduct in the synthesis of the chelated micronutrient (Equation 3).  
497 The properties and reactivity of the resultant ammonium salts are dependent on their anion (X<sup>-</sup>), which is  
498 determined based on the inorganic micronutrient salt employed. When used as petitioned, the potential  
499 negative impacts of these ammonium salts (unintentional fertilization, loss of biodiversity as described  
500 above) are expected to be minimal due to the small quantities used in the application processes. However,  
501 the misuse (overapplication) or improper disposal of the chelated micronutrient and ammonium salt  
502 products of Equation 3 may result in negative environmental impacts including unintentional fertilization,  
503 loss of biodiversity, and water pollution given the increased water solubility of the chelated micronutrients.

504

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

508  
509 When used as petitioned, ammonium citrate will be introduced as a micronutrient-chelate compound,  
510 which is not likely to interact with other substances that have been approved for use in organic crop or  
511 livestock production. However, once the chelated micronutrient has been absorbed by plants the citrate  
512 chelating agent may remain in the soil. Since the remaining citrate is a chelating agent, there are several  
513 cations (Ca<sup>2+</sup>, Cu<sup>2+</sup>, Mg<sup>2+</sup>) that may be impacted in salts allowed for use in organic crop and livestock  
514 production, at 7 CFR 205.601 and §205.603, respectively. Due to ammonium citrate having multiple  
515 coordination sites with divalent cations, the metal cations may preferentially form chelates and displace the  
516 original anion. This interaction may result in the increased water solubility of the cation, which may  
517 decrease the effectiveness of the original compound. The effects of this undesired chelation event, resulting  
518 in increased water solubility, could result in the leaching of the other agricultural substances with impacts  
519 to surrounding water sources. However, the chelation of cations is not expected to result in negative  
520 environmental or human health effects, and could in fact increase the effectiveness of some substances via  
521 increases to water solubility. Moreover, due to the metabolism of citrate anions by a variety of organisms,  
522 coupled with the small quantity of micronutrients applied when the substance is used as petitioned, the  
523 anticipated interactions between residual citrate anions and other substances used in organic agricultural  
524 practices are expected to be minimal.

525  
526 The potential salts that could be altered by anion exchange (chelation of the cation) via the introduction of  
527 citrate anions are salts containing Ca<sup>2+</sup> (calcium hypochlorite, lime sulfur, and hydrated lime), salts  
528 containing Cu<sup>2+</sup> (copper sulfate, copper hydroxide, copper oxide, and copper oxychloride), and the Mg<sup>2+</sup>  
529 salts (magnesium hydroxide and magnesium sulfate) listed in §205.603. Also, introducing ammonium  
530 citrate would affect other micronutrients that have been added to treat soil deficiency by increasing their  
531 water solubility in the event of a chelation event following delivery of the intended micronutrient.  
532 Although the impact to micronutrients is expected to be negligible since the introduction of the petitioned

533 substance as a micronutrient delivery system is unlikely to be used in concert with other micronutrient  
534 programs, as listed in §205.601 and 205.603.

535  
536 **Evaluation Question #8: Describe any effects of the petitioned substance on biological or chemical**  
537 **interactions in the agro-ecosystem, including physiological effects on soil organisms (including the salt**  
538 **index and solubility of the soil), crops, and livestock (7 U.S.C. § 6518 (m) (5)).**  
539

540 When used as petitioned, ammonium citrate will be introduced into agricultural settings as a chelate with  
541 multiple coordination points to a cationic micronutrient, and in this capacity, it is unlikely to interact with  
542 any other substances or influence any significant change to the biological setting. After delivering the  
543 micronutrient, the ammonium citrate species may coordinate to existing micronutrient sources in the soil  
544 that are of low solubility in their original state, which will increase their water solubility and  
545 bioavailability. The existing micronutrients' movement may eventually change the existing micronutrient  
546 concentration, as they become water soluble and are absorbed and metabolized by plants until the  
547 remaining ammonium citrate is metabolized. However, when the quantity of micronutrients and the ease  
548 of citrate metabolism are considered, the leaching of existing insoluble mineral and nutrient soil deposits is  
549 not anticipated.

550  
551 Additionally, the ammonium citrate's presence may result in increased plant resistance to several toxins,  
552 including aluminum (Ma et al. 2001). Like many of the essential micronutrients discussed in this report,  
553 aluminum is present ecologically. Typically, the presence of aluminum places little threat to plant function  
554 in its prevalent form as unreactive aluminum oxides (Ma et al. 2001). However, in acidic soils these  
555 aluminum oxides are broken down, and aluminum persists as  $Al^{3+}$  ions, with a strong affinity towards  
556 oxygen containing compounds. These interactions with biological, oxygen-containing molecules inhibits  
557 their proper function. Introducing citrate has been shown to increase resistance to aluminum toxicity, as  
558 chelation of the  $Al^{3+}$  ion prevents reactions with other biological compounds (Ma et al. 2001, Wu et al.  
559 2018). It is conceivable that the chelation of other toxic ions ( $Pb^{2+}$ ,  $Cd^{2+}$ ,  $Hg_2^{2+}$ ) may prevent their  
560 toxicological impact on the crops and greater ecosystem.

561  
562 The application of chelated micronutrients and inorganic ammonium salts from the petitioned use of  
563 ammonium citrate may result in physiological changes to the soil. The application of ammonia and  
564 ammonium-based fertilizers has been associated with negative physiological changes to earthworms and  
565 native microbial communities (Edwards et al. 1995, Geisseler and Scow 2013, Liu and Greaver 2010, Lu et  
566 al. 2011, USDA 2001). In both cases, the negative impacts from nitrogen (ammonia and ammonium)  
567 fertilization programs were linked with a reduction of soil pH (acidification) (Geisseler and Scow 2013,  
568 Kirchmann et al. 1994, USDA 2001, Yadvinder-Singh and Beauchamp 1988). However, these negative  
569 impacts were shown to be most damaging in applications to unmanaged ecosystems, due to more dramatic  
570 changes to soil pH (Geisseler and Scow 2013, Treseder 2008). In comparison, studies of nitrogen  
571 fertilization programs on managed ecosystems (e.g., commercial organic farms) resulted in increased  
572 microbial biomass due to the increased productivity of the crops (Geisseler and Scow 2013, Kallenbach and  
573 Grandy 2011). Furthermore, these studies reflect the physiological impacts based on application of nitrogen  
574 fertilizers, which are applied in much greater quantity than the ammonium salts from the portioned  
575 ammonium citrate chelated micronutrients. Therefore, the application of chelated micronutrients and  
576 corresponding inorganic ammonium salts are not anticipated to have physiological impacts on soil  
577 organisms.

578  
579 **Evaluation Question #9: Discuss and summarize findings on whether the use of the petitioned**  
580 **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)**  
581 **(i)).**  
582

583 As discussed in Evaluation Questions #4 and #5, ammonium citrate is a petitioned for use as a precursor to  
584 chelated micronutrients and is not intended to be applied as directly ammonium citrate. Ammonium  
585 citrate is a salt whose ions are prevalent in biological systems. Both ions (ammonium and citrate) are  
586 metabolized by a range of organisms, and when used as petitioned, adding ammonium citrate is not  
587 expected to result in any negative ecological outcomes (EFSA 2008a, EFSA 2008b, JECFA 1973, JECFA 1986,

588 SCF 1990). Moreover, the petitioned substance will be added in minimal amounts, and it is not expected  
589 significantly increase the presence of ammonium or citrate ions. Ammonium citrate has the potential to  
590 change the pH of water systems because the citrate ion is basic, which may result in slightly increased pH;  
591 however, there have not been sufficient studies to determine ecotoxicity. Furthermore, the petitioned  
592 substance is biodegradable in water, and therefore unlikely to result in a significant ecological impact  
593 (JOST 2012).

594  
595 However, as discussed in Evaluation Question #6, ammonia-based fertilization treatments may lead to  
596 ecosystem transfer and unintentional fertilization, which can result in reduced biodiversity (Erisman et al.  
597 2008). The properties of the inorganic ammonium salt produced in Equation 3 is dependent on the anion,  
598 which is determined by the inorganic micronutrient source. Since ammonium salts are prevalent in  
599 nitrogen fertilizers, some of the salts produced in Equation 3 may be sufficiently volatile and result in  
600 unintentional fertilization. However, due to the small quantities of micronutrients required, unintentional  
601 fertilization is unlikely to occur in any significant amount when the substance is used as petitioned.

602  
603 **Evaluation Question #10: Describe and summarize any reported effects upon human health from use of**  
604 **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**  
605 **(m) (4)).**

606  
607 Ammonium citrate is a salt that is composed of ions (ammonium and citrate) that are prevalent in the  
608 body, with citric acid being especially important in human metabolism (the citric acid or Krebs cycle).  
609 Furthermore, both ions have been designated as safe, and are authorized for use in several food additives  
610 (SCF 1990, JECFA 1986).

611  
612 Within the body, ammonium and its precursor ammonia are metabolized in the Krebs cycle to urea, which  
613 is excreted by the kidneys (EFSA 2008a). Citrate is a natural component of many citrus fruits and is a  
614 common food additive that has received an ADI (accepted daily intake) of “not limited” by the JECFA  
615 (JECFA 1973). Citrate is a key component of the Krebs cycle, which is important for human metabolism and  
616 the production of energy and coenzymes (EFSA 2008b).

617  
618 As a solid ammonium citrate has been documented to cause irritation to the nose and throat, as well as to  
619 skin upon contact (NJ Health 2005). These effects can be minimized with the use of proper protective  
620 equipment, including respirators, and the use of exhaust ventilation when possible (NJ Health 2005).  
621 However, as stated previously, ammonium citrate will be applied in minimal quantities when used as  
622 petitioned and is not anticipated to have adverse health impacts when proper application processes are  
623 employed.

624  
625 **Evaluation Question #11: Describe all natural (non-synthetic) substances or products which may be**  
626 **used in place of a petitioned substance (7 U.S.C. § 6517 (c) (1) (A) (ii)). Provide a list of allowed**  
627 **substances that may be used in place of the petitioned substance (7 U.S.C. § 6518 (m) (6)).**

628  
629 There are a range of natural chelating agents excreted by plants and microorganisms, or that are produced  
630 from the decomposition of organic matter, and aid in the delivery of micronutrients in the soil (Adeleke et  
631 al. 2017). These compounds are broadly classified as phytosiderophores or phytometallophores (Adeleke et  
632 al. 2017, Grusak et al. 1999, Welch 1995). These compounds are wide ranging and include organic  
633 (carboxylic) acids and non-synthetic amino acids. However, organic or amino acids must first undergo a  
634 neutralization reaction (similar to Equation 1) with bases in the soil before they are able to act as chelating  
635 agents. In basic (alkaline) soils, the application of these natural organic and amino acids will result in their  
636 neutralization, and the subsequent anions may act as chelating agents for micronutrient sources already  
637 existing in the soil.

638  
639 However, applying these acids in sufficient quantity to change the pH of the soil would result in a more  
640 dramatic ecological change than application of chelated micronutrients. Moreover, the increased acidity of  
641 the soil could result in mineral depletion, and an increase in the toxicity of minerals existing in unreactive  
642 states such as aluminum (Ma et al. 2001, Vitousek et al. 1997). A soil acidification program could also result

643 in leaching of natural mineral deposits and water pollution resulting from the mass migration of mineral  
644 stores from previously insoluble (hydroxide and carbonate) sources (Treseder 2008). Soil acidification is  
645 also associated with the degradation of physiological soil conditions, which has a negative impact on a  
646 range of soil organisms (Geisseler and Scow 2013, Kirchmann et al. 1994, USDA 2001, Yadvinder-Singh and  
647 Beauchamp 1988). Due to the implications of a strategy to increase micronutrient solubility by soil  
648 acidification (loss of mineral content, water pollution, physiological soil degradation, increased mineral  
649 toxicity), this approach does not provide a likely alternative to the petitioned substance.

650  
651 There are a variety of substances in approved in 7 CFR 205.601 that may be used in place of the petitioned  
652 substance as a means of increasing the water solubility of micronutrients. Most of these substances are  
653 acids, which would result in a pH change in the soil, converting insoluble hydroxide salts into more  
654 soluble micronutrient salts. The approved acids are the following: peracetic acid, boric acid, humic acids,  
655 and sulfurous acid. However, like the application of natural organic and amino acids to access natural  
656 chelating agents, the application of approved synthetic acids could result in the negative outcomes  
657 associated with soil acidification.

658  
659 Lignin sulfonate, or lignosulfonate, is a synthetic chelating agent that the National Organic Program has  
660 approved for use in organic agricultural production at §205.601. Like ammonium citrate, lignosulfonates  
661 can form chelates with cationic micronutrients, increasing their water solubility and bioavailability (USDA  
662 2011). Lignosulfonates are derived from the biopolymer lignin via the pulping process (Cieschi et al. 2016,  
663 USDA 2011). Studies have shown that these chelating agents increase the uptake of both zinc and iron  
664 micronutrients in crops (Cieschi et al. 2016). Chelating agents have variable bonding strengths to their  
665 central atoms (micronutrients) that are dependent on the media and pH of that media, as well as the  
666 identity of the micronutrient itself. Based on these differences, it is likely that ammonium citrate may be  
667 more appropriate as a chelating agent for certain micronutrients, and may more efficiently deliver those  
668 micronutrients in certain soil conditions when compared to lignin sulfonate.

669  
670 **Evaluation Question #12: Describe any alternative practices that would make the use of the petitioned**  
671 **substance unnecessary (7 U.S.C. § 6518 (m) (6)).**

672  
673 Trace amounts of micronutrients are essential to ensure proper plant function and the nutritional value of  
674 the crops harvested. However, these cationic species form insoluble hydroxide salts in alkaline soils,  
675 limiting the availability of these nutrients for plant uptake (Grusak et al. 1999, Janmohammadi et al. 2016).  
676 This is exacerbated when water is also deficient in the soil (Janmohammadi et al. 2016). Ammonium citrate  
677 and other chelating agents overcome this problem by increasing the water solubility of the micronutrients,  
678 allowing plants to more efficiently absorb these micronutrients.

679  
680 An alternative to the application of micronutrient chelates is the application of organic matter in the form  
681 of manure or compost. These sources of organic matter include micronutrients, natural chelates such as  
682 organic and amino acids, and microbes that produce natural chelating agents (Adeleke et al. 2017, Chen et  
683 al. 1998, Sorrenti et al. 2012). Sorrenti et al. have reported that compost-based treatments have been shown  
684 to enhance yield and quality of pears in calcareous soil, although these results were less successful than the  
685 application of iron-chelates (Sorrenti et al. 2012).

686  
687 As an alternative to using chelated micronutrients, non-chelated micronutrients may be added to remedy  
688 soil deficiencies, as approved at §205.601. Non-chelated micronutrients exist as inorganic salts and are both  
689 synthetically and minerally derived. They exist in many different combinations of micronutrient cations  
690 and inorganic anions. Since natural forms are found in minerals (solids) they have low water solubility,  
691 limiting their bioavailability for plant absorption. Furthermore, if the soil is alkaline, those micronutrients  
692 with water solubility will likely be converted to the insoluble hydroxide salts discussed above. Moreover,  
693 this approach remains limited in water-deficient soils, which may be unable to sufficiently solubilize the  
694 micronutrients for delivery to the root. In comparison, the application of micronutrients as chelates (such  
695 as citrate chelates) prevents the formation of insoluble salts (such as the hydroxides discussed above) since  
696 the chelated micronutrient is enveloped by the chelating agent, rendering it unreactive.

697

698 Another alternative to chelated micronutrients is acidifying the soil to prevent micronutrient-hydroxide  
699 formation and to liberate the originally insoluble nutrient sources. However, as discussed above in  
700 Evaluation Question #11, this approach may result in significant negative ecological changes, including  
701 depletion of existing nutrient stores, water pollution, physiological degradation of the soil, and increased  
702 mineral toxicity.  
703

### Report Authorship

704  
705  
706 The following individuals were involved in research, data collection, writing, editing, and/or final  
707 approval of this report:

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709 Amherst
- 710 • Samantha Olsen, Technical Writer, Savan Group  
711

712  
713 All individuals are in compliance with Federal Acquisition Regulations (FAR) Subpart 3.11 – Preventing  
714 Personal Conflicts of Interest for Contractor Employees Performing Acquisition Functions.  
715

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