# **Calcium Chloride**

#### Crops

**Identification of Petitioned Substance** 

#### 2 **Chemical Names:**

- 3 Calcium chloride; Calcium dichloride
- 4

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#### 5 **Other Names:**

- 6 CaCl2; CalChlor, Caliac, Dichlorocalcium,
- 7 Huppert's reagent, ice melt, Isocal liquical,
- 8 Marley cement accelerator
- 9

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- 10 Trade Names: Briner's Choice, Calcimax, Cor-
- 11 Clear, DowFlake, Hi-Cal, Liquical, Jarcal, Tetra
- 80, Unichem CalClor 12

#### CAS Number:

10043-52-4 (anhydrous) 22691-02-7 (monohydrate) 10035-04-8 (dihydrate) 25094-02-4 (tetrahydrate) 7774-34-7 (hexahydrate)

# **Other Codes:**

CHEBI: 3312 EINECS: 233-140-8 ICSC: 1184 InChi: 1S/Ca.2ClH/h;2\*1H/q+2;;/p-2 InChi Key: UXVMQQNJUSDDNG-UHFFFAOYSA-L INS: 509 RTECS: EV9800000 UNII: M410D6VV5M

# **Summary of Petitioned Use**

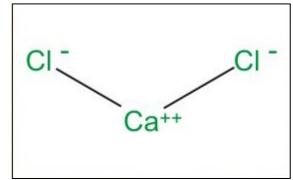
15 16 17 Calcium chloride appears on the National List of nonsynthetic substances prohibited for use in organic crop production. The brine process is natural and prohibited for use except as a foliar spray to treat a physiological 18 19 disorder associated with calcium uptake [7 CFR 205.602(c)]. This Technical Report was requested by the National 20 Organic Standards Board (NOSB) Crops Committee in support of its sunset review of this listing. 21 22 Removal of the substance from the National List would remove the prohibition, render the annotation moot, and 23 effectively allow all uses of nonsynthetic calcium chloride in organic crop production without any limitations. 24 Thus, evaluation of applications of calcium chloride that go beyond the current annotation are included for 25 consideration. Removal of the annotation would prohibit all uses in the crops scope without exception. 26 Reclassification of calcium chloride obtained by the brine process as "synthetic" would also prohibit all uses 27 without exception unless added to the list of allowed synthetics. 28 29 **Characterization of Petitioned Substance** 30

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

32 Calcium chloride is an inorganic salt with the molecular formula CaCl<sub>2</sub>. It can form mono-, di-, tetra-, and

33 hexahydrates (O'Neil, 2013).

# 35 Figure 1. Chemical Structure Depiction of Calcium Chloride



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34

36

Source: (US NLM, 2020)

#### 39

#### 40 **Source or Origin of the Substance:**

41 Commercial calcium chloride is produced by one of three methods: from natural brine deposits that have a

42 high level of calcium chloride, by the Solvay process, and by the hydrochloric acid method. These three

difference sources are explained in greater detail under *Evaluation Question* #2.

44

45 There are also natural terrestrial deposits in some locations in the world, but these are relatively rare, and

the calcium chloride is difficult to recover and refine. Among the ores that contain natural calcium chloride

47 are antarcticite (a hexahydrate form discovered in Antarctica), ghiaraite (a volcanic tetrahydrate form),

48 chlorocalcite (a potassium-calcium chloride salt that is also volcanic), sinjarite (a dihydrate form found in

49 Iraq and Turkmenistan), and tachyhydrite (a magnesium-calcium chloride salt) (Hudson Institute of

50 Mineralogy, 2020). Sea water contains approximately 0.15% calcium chloride (Patnaik, 2003).

51

## 52 **Properties of the Substance:**

#### 53 54

### Table 1. Physical and Chemical Properties of Calcium Chloride<sup>†</sup>

55

| Property                   | Characteristic / Value               | Source                           |
|----------------------------|--------------------------------------|----------------------------------|
| Molecular Formula          | CaCl <sub>2</sub>                    | (O'Neil, 2013)                   |
| Molecular Weight           | 110.98 g/mol                         | (O'Neil, 2013)                   |
| Percent Composition        | Ca: 36.11 percent, Cl: 63.89 percent | (O'Neil, 2013; Patnaik, 2003)    |
| Color                      | Colorless or white to off-white      | (Inchem, 2012; US NLM, 2020)     |
| Physical state at 25°C / 1 | Cubic crystals, flakes, granules,    | (O'Neil, 2013; Vrana, 2014)      |
| Atm.                       | powder, or fused masses              |                                  |
| Melting point              | 772–782°C                            | (Inchem, 2012; O'Neil, 2013; US  |
|                            |                                      | NLM, 2020; Vrana, 2014)          |
| Boiling point              | 1,670-1,935°C                        | (Inchem, 2012; Patnaik, 2003; US |
|                            |                                      | NLM, 2020)                       |
| Solubility in water        | 0.745 g / mL @ 20°C                  | (US NLM, 2020)                   |
| Solubility in ethanol      | 0.258 g / mL @ 20°C                  | (Kiper, 2020)                    |
| Heat of solution           | -81.85 kJ / mol                      | (Vrana, 2014)                    |
| Density at 25°C            | 2.2 g / cm <sup>3</sup>              | (Inchem, 2012)                   |
| Specific gravity at 25°C   | 2.16                                 | (Vrana, 2014)                    |
| and 4°C                    |                                      |                                  |
| Electrical conductivity    | 0.39-4.06 M                          | (Sun & Newman, 1970)             |
| Viscosity at 787°C         | 3.34 mPa s                           | (Kiper, 2020)                    |

56 57 <sup>†</sup>*Data are for the anhydrous form.* 

- Minor impurities, particularly sodium chloride, will cause the physical properties to vary. Calcium 58 59 chloride is freely soluble in water, with liberation of much heat (O'Neil, 2013). Additional ecological
- 60 toxicity information is provided in Table 3 under Evaluation Question #9.
- 61

#### 62 **Specific Uses of the Substance:**

- In the United States, the main use of calcium chloride is on roads for de-icing and dust control (Kemp & 63
- 64 Keegan, 2012). De-icing accounts for about 30 percent of the calcium chloride used in the United States, and
- 65 dust control and road stabilization account for another 25 percent (Vrana, 2014). The anhydrous form is
- 66 hygroscopic, and is used as a drying, dehydrating, or desiccating agent (O'Neil, 2013).
- 67

68 The only permitted use of calcium chloride in organic crop production is as a source of soluble, available

- 69 calcium that is applied to foliage to correct calcium deficiencies (Swezey et al., 2000). Apples (Malus
- 70 domestica) are the primary crop on which it is used, for the purpose of preventing the physiological
- 71 disorder known as bitter pit. Pears (Pyrus spp.) deficient in calcium also respond favorably to calcium
- 72 chloride treatments (Prasad et al., 2015). Calcium chloride is sometimes used to prevent or treat the
- 73 physiological disorder known as blossom end rot in tomatoes (Lycopersicum esculaentum), pepper (Capsicum 74
- anuum), eggplant (Solanum melongena), and watermelon (Citrullus lanatus) (Taylor & Locascio, 2004).
- 75 However, excess chlorine is correlated with increased incidences of blossom end rot and black spotting on 76
- fruit (Geilfus, 2018). Various subtropical and tropical fruit such as lychee (Litchi chinensis) and papaya 77 (Carica papaya) – may also be treated. Other diseases linked to calcium deficiencies are tip burn in lettuce
- 78 (Lactuca sativa) and black heart in celery (Apium graveolens) (De Freitas et al., 2016; Simon, 1978). Calcium
- 79 chloride solution completely suppressed tip burn induced in lettuce grown in growth chambers (Misaghi &
- 80 Grogan, 1978). A University of Hawaii extension publication recommended spraying calcium chloride as
- 81 one effective treatment for black heart control in celery (Nakagawa, 1957).
- 82

83 Other agricultural uses include the stabilization of ammonia nitrogen. Natural sources of ammonia, such as 84 manure, can retain nitrogen more effectively if combined with calcium chloride when applied to soil (Heck, 85 1931; Witter & Kirchmann, 1989). The calcium precipitates as calcium carbonate in manure and the

- 86 ammonia forms ammonium chloride (Witter & Kirchmann, 1989):
- 87
- 88 89

# $(NH_4)_2CO_3 \cdot H_2O + CaCl_2 \rightarrow CaCO_3 \downarrow + 2NH_4Cl + H_2O$

90 Synthetic ammonia-based fertilizers, including ammonium thiosulfate and urea, can also be combined with

91 calcium chloride to reduce volatilization and increase the amount of plant-available nitrogen (Sloan &

- 92 Anderson, 1995). The reactions depend on the nitrogen source being conserved, soil type, temperature, 93 moisture, and soil biological activity.
- 94
- 95 Chlorine is an essential element for plant growth taken up by plants in the chloride form (Brady, 1984; 96 Broyer et al., 1954; Tisdale & Nelson, 1966). Crops observed to have symptoms of chlorine deficiencies 97 include barley (Hordeum vulgare), beets (Beta vulgaris), carrots (Daucus carota), clover, corn (Zea mays), cotton 98 (Gossypium hirsutum), kiwifruit (Actinida deliciosa), lettuce (Lactuca sativa), oil palms (Elaeis spp.), spinach 99
- (Spinacia oleacea), and wheat (Triticum aestivum) (Broyer et al., 1954; Geilfus, 2018; Ozanne, 1958; Tisdale &

100 Nelson, 1966). Chlorine deficiencies are rare and occur only in heavily leached soils without any chlorine 101 inputs (Marschner, 2011). More common are toxic excesses of chlorine in soils, which reduces yields and

- 102 degrades soil quality (Geilfus, 2018).
- 103
- 104 Seed priming is a technique where seeds are treated with water or a solution that initiates germination and 105 reduces plant stress. Halopriming involves soaking seeds in an aerated saline solution to prepare them for
- 106 planting in saline soils. Calcium chloride is one of the salts commonly used for halopriming (Sher et al.,
- 107 2019; Singh et al., 2015). Wheat, millet, and sorghum were all documented to have improved performance
- 108 under saline conditions when the seed was primed with a calcium chloride solution prior to planting (Sher
- 109 et al., 2019).
- 110
- 111 Calcium chloride is a food and feed additive. In food, it is used as a humectant and curing agent (Klaassen,
- 112 2001). It is also used to coagulate cheese and extract alginates from seaweed (Saltmarsh, 2000). Calcium

- chloride is used as an alternative to sodium chloride as a salt in low-sodium foods. In brewing, calcium
- chloride is used to reduce the hardness of water (Saltmarsh, 2000). As a feed additive, it is used as an
- available source of nutrient calcium and chloride, as an electrolyte and as a sequestrant [21 CFR 582.6193].
- 116

#### 117 Approved Legal Uses of the Substance:

- 118 Calcium chloride and its hydrated forms appear in the Association of American Plant Food Control
- 119 Officials (AAPFCO) Official Publication as a recognized calcium source with the chemical formula of CaCl<sub>2</sub>
- 120 (AAPFCO, 2020). It is also Generally Recognized As Safe (GRAS) by the U.S. Food and Drug
- 121 Administration (FDA) as a direct food substance [7 CFR 184.1193] and as a general use feed additive [21
- 122 CFR 582.1193]. The Food Safety Inspection Service (FSIS) approves calcium chloride as a tenderizing agent
- in meat products [9 CFR 424.21]. Calcium chloride is exempt from tolerance as an active or inert ingredient
- 124 in pesticidal products by the U.S. Environmental Protection Agency (EPA) [40 CFR 180.940] and was
- 125 previously classified as List 4B on the obsolete list of inert ingredients (US EPA, 2004). The EPA has also 126 registered antimicrobial pesticides for indoor use where calcium chloride is labeled as an active ingredient
- registered antimicrobial pesticid(US EPA, 2020a).
- 128

### 129 Action of the Substance:

- 130 In solution, calcium chloride disassociates into ionic divalent calcium (Ca<sup>2+</sup>) and monovalent chloride (Cl<sup>+</sup>)
- in a 2:1 ratio of chloride to calcium. When the aqueous solution is fed to plants by foliar application, the
- disassociated ions penetrate the plant cuticles via aqueous pores (Schönherr, 2000). The rate of diffusion
- depends on several factors, including the waxiness of the plant cuticles, temperature, humidity, and
- 134 whether a surfactant is used. The role of calcium in plant nutrition is complex.
- 135

136 Calcium is responsible for cell wall development and accounts for firmness in fruit (P.K. Hepler & Wayne,

- 137 1985; Shear & Faust, 1970; Simon, 1978). How calcium is taken up by plants and is transported to the cell
- walls has been studied extensively. The movement of calcium ions ( $Ca^{2+}$ ) are thought to be taken up by the
- 139 roots and move through the xylem in aqueous solution to be metabolized in plant tissue (Demarty et al.,
- 140 1984). Experiments showed that  $Ca^{2+}$  rapidly responds to light and serves as a second messenger for cell
- growth in light-stimulated responses (P.K. Hepler & Wayne, 1985). Ca<sup>2+</sup> binds to cross-linked negative
- regions in pectin, creating a rigid structure in plant cell walls (Hepler & Winship, 2010). Boron plays a key
   role in calcium metabolism through interaction with plant polysaccharides (Matoh & Kobayashi, 1998).
- 143

145 Calcium's relation to fruit formation indicates that it plays a reproductive role (Hepler & Wayne, 1985).

146 Pollen tubes are particularly dependent on Ca<sup>2+</sup> for structural support at pollination (Hepler & Winship,

147 2010). Uptake and transport varies by species, growth stage, soils, temperature, moisture, plant hormones,

and the availability of other nutrients (Albrecht & Smith, 1952; Shear & Faust, 1970; Simon, 1978; P.K.

- 149 Hepler & Wayne, 1985; Hocking et al., 2016).
- 150

151 Calcium chloride is relatively soluble compared with most other sources of calcium – such as calcium

- acetate, calcium carbonate, calcium sulfate, and calcium phosphate and can be taken up by both the roots
- and leaves (Albrecht & Jenny, 1931; Kadir, 2005; Kazemi, 2014; Poesch, 1937; Reid & Padfield, 1975). See
- 154 Evaluation Question #11 for more information on other calcium sources. In certain crops most significantly
- apples calcium is mobile through the plant's xylem for only a short period early in the growing season,
- 156 making it less available to the fruit (Marschner, 1974; Simon, 1978). Only a few sources of calcium are
- available through the leaves, and then only under certain limited conditions (Shear & Faust, 1970). Calcium
- 158 chloride is one of the few soluble sources of calcium that can be translocated from leaves to fruit during the
- 159 growth and maturation stage when soil calcium is relatively unavailable (Chittenden et al., 1969).
- 160
- 161 Foliar applications of calcium are often more effective in highly leached tropical and sub-tropical soils.
- 162 Lychee fruit in Pakistan treated with calcium chloride and borax had less fruit cracking than a no-treatment
- 162 control (Haq et al., 2013). Papaya fruit quality was also improved by foliar applications of calcium (Madani
   164 et al., 2016).
- 165
- 166 Looking at the nutrients individually, an excess of calcium can cause poor germination and slower growth.
- 167 Excess calcium may also manifest itself as a deficiency of other nutrients, particularly iron and

- phosphorous (White & Broadley, 2003). In general, plants are less sensitive to excess calcium than to
   excesses of other nutrients, so an excess of calcium rarely presents a problem (Parnes, 1990).
- 170171 The chloride moiety's mode of action in plant physiology is even more complicated than that of calcium.
- As mentioned above, chlorine is an essential element for plant growth (Brady, 1984; Broyer et al., 1954).
- 173 Excess chlorine can induce abiotic plant stress that adversely affect yield and quality (Geilfus, 2018). The
- 174 symptoms of excess chlorine can result in toxicity that, in most crops and soils, can only be corrected by a
- reduction of plant-available chloride. While plants can grow and thrive over a broad range of calcium
- 176 levels, even a small difference in soil and plant levels of chlorine could mean the difference between a
- limiting deficiency and a toxic excess. Chlorine deficiencies are relatively rare; toxic excesses are morecommon.
- 179

180 When applied to fruits and vegetables post-harvest, calcium chloride reacts with natural pectin. The result 181 of the reaction is firmer fruit and less decay. In algae, calcium chloride is used to cross-link alginate gels, 182 making their structure more stable (Saltmarsh, 2000). Calcium chloride's mode of action as a foliar feed is 183 by transport through the aqueous pores of the leaves. Waxier cuticles permit less diffusion of calcium 184 chloride into leaves when applied as a foliar spray than do leaves of less waxy plants (Schönherr, 2000).

185

### 186 **Combinations of the Substance:**

- 187 Commercial grade anhydrous calcium chloride is 94–97 percent CaCl<sub>2</sub>, the chief impurity being calcium
- 188 hydroxide (Ca(OH<sub>2</sub>)) (O'Neil, 2013). It forms mono-, di-, tetra-, and hexahydrates (O'Neil, 2013; Vrana,
- 189 2014). Food grade anhydrous calcium chloride is between 93.0 percent and 100.5 percent CaCl<sub>2</sub> and food
- 190 grade calcium chloride dihydrate is between 99.0 percent and 107.0 percent CaCl<sub>2</sub> 2H<sub>2</sub>O (Food Chemicals
- 191 Codex Committee, 2018). Naturally occurring impurities of concern are acid-insoluble matter, arsenic,
- 192 fluoride, lead, and magnesium and alkali salts.
- 193
- 194 Storage is crucial to retain the form and consistency of calcium chloride. Because calcium chloride is 195 hygroscopic, it absorbs moisture from the air, depending on relative humidity and temperature (Patnaik, 196 2003). The lump and granular products are subject to agglomeration, and even the flaked form – produced 197 with a superficial anhydrous coating to prevent caking – can clump under moist conditions or with high 198 humidity (Vrana, 2014). Commercial- and industrial-grade sources of calcium chloride will use anti-caking 199 agents, such as Prussian blue (ferric ferrocyanide), Prussian yellow (sodium ferrocyanate), and various 200 chromates and phosphates (Ramakrishna & Viraraghavan, 2005). Formulations for de-icing will also 201 include anti-freeze agents (including some made from glycol ethers) and corrosion inhibitors to impede 202 rust on de-icing equipment and vehicles (Fay & Shi, 2012).
- 203

Wetting agents and surfactants may increase the uptake of foliar applied calcium chloride (Schönherr,
 2000). For that reason, some brand name products recommend blending calcium with adjuvants, including

- 206 various glycol ethers, non-ionic surfactants, pinene polymers, and silicone-based wetting agents.
- 207 Commercial products containing calcium chloride are often formulated with micronutrients, such as boron.
- 208 Boron is particularly important for the transport of calcium in apples (Faust & Shear, 1968). Similar
- 209 synergistic responses are found between calcium chloride and boron for other fruits and fruit vegetables as
- well, including lychee (Haq et al., 2013) and tomatoes (Haleema et al., 2018; Rab & Haq, 2012). Some
- calcium chloride products are also formulated with magnesium sulfate or Epsom salts (OMRI, 2020).
- 212
- Humic acids are sometimes added to improve nutrient uptake, and has been shown to be effective in improving tomato quality (Kazemi, 2014). Ammonium sulfate and urea also have been used as additives to calcium chloride foliar feeds, but at least one study showed them to be ineffective in improving calcium transport in apples (Shear & Faust, 1970). Various pesticides are sometimes added in tank mixes to reduce the number of orchard passes. Thus, commercial foliar feed products may be formulated with various wetting agents, spreaders, and other adjuvants.
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- 221 222

#### 223 Historic Use:

Calcium chloride was first discovered in the 15<sup>th</sup> century, but industrial applications were not explored
until the late 18<sup>th</sup> century (Vrana, 2014). The invention of the Solvay process to produce sodium carbonate
resulted in calcium chloride as a by-product (Solvay, 1887). When the Solvay process was first introduced
to the United States, calcium chloride had little commercial value. Most early uses were non-agricultural,
including use in fire suppression, refrigeration systems, anti-freeze, cement curing, and dust suppression.
It has a long history of use as a desiccant and preservative in the post-harvest handling of dried fruits and
vegetables (Stone, 1919).

231

232 Calcium chloride has been used to conserve ammonia nitrogen in manure since the 1920s (Heck, 1931;

233 Witter & Kirchmann, 1989). Confined Animal Feeding Operations (CAFOs) may use calcium chloride to 234 stabilize ammonia in poultry litter, swine slurry, or dairy lagoons (Buchanan et al., 2003; Shi et al., 2001; 235 Ullman, 2005). Calcium chloride may be mixed with manure at the time of spreading or application or top-236 dressed on the soil following application. Researchers found calcium chloride to be relatively effective in 237 retaining ammonia in poultry litter (Kithome et al., 1999; Nahm, 2005) but less effective with cattle (Husted 238 et al., 1991) and swine manure (Nahm, 2005). Conserving ammonia reduces greenhouse gas emissions and 239 improves the fertilizer value of the manure by retaining a higher nitrogen content. Evidence suggests that 240 calcium chloride may be effective in the sorption of soluble phosphorous from manure to precipitate as 241 calcium phosphate, but differences were seen based on manure and soil type (Bolster & Sistani, 2009).

242

Greenhouses have used calcium chloride as a way to treat calcium deficiencies in potted plants since at
least the 1930s (Poesch, 1937). Calcium chloride's solubility makes it a preferred choice for supplying

calcium to plants grown in hydroponic systems, compared to calcium nitrate (Goble, 2018).

246

The use of calcium chloride as a foliar treatment for bitter pit in organic apple production is relatively recent compared with its uses in non-organic production. In the 1950s, the link between bitter pit and cation imbalances was first put forward as a working hypothesis (Garman & Mathis, 1956). Prior to 1969, calcium deficiencies in apple orchards were primarily addressed through the application of pulverized limestone in both organic (Rodale, 1970) and conventional (Childers, 1975) systems. Experimental foliar

treatments of calcium as bitter pit treatment began in New Zealand in the 1960s. The preferred foliar

treatment was with calcium nitrate (Kidson et al., 1963) Early attempts to correct the deficiency with soil
 applications of calcium met with little success (Chittenden et al., 1969).

255

After almost twenty years of research from that initial observation, researchers were able to predict the correlation between the levels of available calcium and other cationic nutrients and the incidence of bitter pit (Wills et al., 1976). The conclusion was that the condition was treatable by application of calcium chloride as a post-harvest dip (Reid & Padfield, 1975; Sharples et al., 1979). Apple producers were using calcium chloride as a foliar treatment of apples before peer-reviewed science supported its efficacy.

261 Calcium chloride was allowed for foliar treatment of apples by most, but not all certification agents

- operating in the U.S. prior to implementation of the National Organic Program (USDA, 2001). A 2001
- 263 review of the literature found most of the peer-reviewed articles supporting pre-harvest foliar application
- of calcium chloride were published in the late 1990s (Conway et al., 2001).
- 265

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

As noted above, calcium chloride appears on the National List of nonsynthetic substances prohibited for use in organic crop production with the following annotation: "brine process is natural and prohibited for use except as a foliar spray to treat a physiological disorder associated with calcium uptake" [7 CFR 205.602(c)]. Calcium chloride appears on the National List of nonagricultural (nonorganic) substances allowed as ingredients in or on processed products labeled as "organic" or "made with organic (specified

ingredients or food groups) without a restrictive use annotation" [7 CFR 205.605(a)]. Nonsynthetic calcium

chloride is implicitly allowed in organic livestock production because it is not included on the National List

of nonsynthetic substances prohibited for use in organic livestock production [7 CFR 205.604].

275

#### 276 International

277 Canadian General Standards Board (CGSB) Permitted Substance List

- Calcium chloride appears on the Canadian Organic Regime's Permitted Substances List, Table 4.2, under
   the listing for "Calcium" with the following annotation for origin and usage: "Calcium chloride derived
   from network with the following annotation for origin and usage: "Calcium chloride derived
- from naturally occurring brines and not chemically treated" (CAN/CGSB, 2020).
- Regarding the interpretation of what is "derived from naturally occurring brines and not chemically
- treated," the Organic Federation of Canada's Standards Interpretation Committee (SIC) published the
- following Question and Answer (OFC-SIC, 2020):
- 286 "Is calcium chloride made from the purification of naturally occurring brine allowed
  287 under the listing of 'Calcium' in Table 4.2?" (384)
- "Yes and No. Yes. Calcium chloride that is purified from naturally occurring brine via
  evaporation is allowed. Such calcium chloride may be used to address nutrient
  deficiencies and physiological disorders. No. Other purification processes of naturally
  occurring brine that involve additional processing steps (e.g., bromine removal, sulphur
  oxide addition, use of strong acid precipitation agents or lime, etc.) render the calcium
  chloride synthetic according to the COS (see 'Mined Minerals, unprocessed' in Table
  4.2)."
  - Version 2020
  - "Yes. Calcium chloride that is purified from naturally occurring brine via evaporation is allowed. Such calcium chloride may be used to address nutrient deficiencies and physiological disorders."
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- 301 CODEX Alimentarius Commission, Guidelines for the Production, Processing, Labelling and Marketing of
   302 Organically Produced Foods (GL 32-1999)
- 303 Calcium chloride does not explicitly appear on Table 1: "Substances for use in soil fertilizing and
- conditioning." It does appear in Table 4: "Processing aids which may be used for the preparation of
- products of agricultural origin referred to in section 3 of these guidelines" with the annotation that it can be
   used as a coagulation agent for plant products, and as a firming and coagulation agent in cheese making
   (FAO/WHO Joint Standards Programme, 2007).
- 308
- 309 European Economic Community (EEC) Council Regulation, EC No. 834/2007 and 889/2008
- 310 Calcium chloride solution is permitted as a fertilizer and soil conditioner on Annex I with the condition of
- 311 use for foliar treatment of apple trees after identification of deficit of calcium (Organic Production and
- Labelling of Organic Products with Regard to Organic Production, Labelling and Control, 2008). The
- 313 regulation does not specify compositional or source requirements.314
- 315 Japan Agricultural Standard (JAS) for Organic Production
- Calcium chloride appears on Table 1 of the Japanese Agricultural Standard for Organic Plants (Japanese Agricultural Standard for Organic Plants, 2017). The listing does not have criteria to limit source or use.
- 318
- 319 *IFOAM Organics International*
- 320 http://www.ifoam.bio/en/ifoam-norms
- 321 Appendix 2 (Fertilizers and Soil Conditioners) of the IFOAM Standards includes calcium chloride with no 322 conditions for use (IFOAM, 2014).
- 323
- 324 325

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328

- 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
- compounds, toxins derived from bacteria; pheromones, soaps, horticultural oils, fish emulsions, treat
   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?
- 336

Calcium chloride is being reviewed for crop use as a fertilizer and soil amendment [7 USC 6508(b)]. It may
 also be used as a pesticide inert or active ingredient. Depending on the source and manufacturing process,

- it may be synthetic or nonsynthetic. Only calcium chloride from the brine process is considered
- 340 nonsynthetic (NOSB, 1996). Other naturally occurring sources exist, such as antarcticite, chlorocalcite,
- 341 ghiaraite, sinjarite, and tachyhydrite as well as sea water, but these sources are not commercially available
- in the United States. Synthetic sources, such as those from the Solvay or hydrochloric acid processes, do not
- appear on the National List and are prohibited for use in organic crop production [7 CFR 205.105(a)]. The
- reasons for considering them synthetic are reviewed in *Evaluation Question* #2. Synthetic calcium chloride is allowed under 7 CFR 205.601(m) as an EPA 2004 List 4 inert ingredient. It is exempt from the
- requirement of a tolerance when used as an inert ingredient pre- and post-harvest [40 CFR 180.910].
- 347
- 348 <u>Evaluation Question #2:</u> Describe the most prevalent processes used to manufacture or formulate the
- 349 petitioned substance. Further, describe any chemical change that may occur during manufacture or
- 350 formulation of the petitioned substance when this substance is extracted from naturally occurring plant,
- 351 animal, or mineral sources (7 U.S.C. § 6502 (21)).
- 352

The most prevalent process used to manufacture calcium chloride is by brine extraction. Calcium chloride from natural brine sources accounted for approximately 70–75 percent of the supply in 1983, with synthetic sources declining in importance since that time (Kemp & Keegan, 2012). The Solvay process accounts for about 15–20 percent of commercial supply of calcium chloride. The basic processes have been unchanged for more than 40 years. These methods were described in detail in the 2001 TAP Review considered by the NOSB (USDA, 2001) and are briefly summarized here.

- 359
- 360 Brine Extraction

361 Brine deposits in Michigan are the primary source of calcium chloride sold in the United States. The brine process is considered an extraction process under NOP Guidance 5033 §4.6. The brine in the Michigan 362 363 Basin contains bromine, magnesium, sodium, and other impurities in addition to calcium and chlorine. The 364 basinal brine from Michigan has an unusually low pH and high calcium content found in only a few sub-365 surface deposits in the world (Warren, 2017). Chlorine, bromine, and iodine are in the brine as 366 disassociated chloride (Cl<sup>-</sup>), bromide (Br<sup>-</sup>), and iodide (I<sup>-</sup>) ions (i.e., halide ions). One early method used to 367 remove impurities was to superheat and supersaturate the solution to 190°C, then cool it to below 175°C under pressure. The solution was then crystallized and reduced to fine particles. The original method was 368 369 able to achieve above 75 percent purity of CaCl<sub>2</sub> (Smith, 1928).

370

Iodine is the heaviest stable halide in the brine and can be concentrated by centrifugation (Lauterbach &
Ober, 2011). Iodide in an acidified solution is removed first in liquid phase by ion exchange. The first ion
exchange media used was activated charcoal (Chamberlain & Boundy, 1935). Later methods used
quaternary ammonium type anion resins (Glenn, 1960). Activated charcoal is still used, particularly where
iodine concentrations are relatively low (Lauterbach & Ober, 2011).

376

Bromine is also removed from the brine. The superheated and supersaturated solution treated with sulfur
dioxide (SO<sub>2</sub>) gas yields hydrogen bromide, and sulfuric acid:

379 380 381

 $Br_2 + SO_2 + 2H_2O \rightarrow 2 HBr + H_2SO_4$ 

382 Once the halides heavier than chlorine are removed, the free chlorine gas can be used to liberate the free

ionic bromide as bromine gas. The bromine gas is then blown out of the solution with air (Hooker, 1939).

Calcium chloride purity was subsequently increased in a similar way by the removal of the other halogens.

385 The calcium chloride from the natural brine is crystallized as a double salt with magnesium chloride

| 386<br>387<br>388<br>389<br>390<br>391<br>392<br>393<br>394<br>395<br>396<br>397<br>398<br>399<br>400<br>401<br>402 | <ul> <li>(CaCl<sub>2</sub> 2MgCl<sub>2</sub> 6H<sub>2</sub>O), with magnesium chloride having the greater concentration. To separate the double salt, calcium oxide (CaO), otherwise known as lime, is introduced to the solution prior to evaporation and crystallization (Collings, 1932). The lime disassociates in aqueous solution to form calcium hydroxide (Ca(OH)<sub>2</sub>), otherwise known as slaked lime, hydrated lime, or milk of lime (Speight, 2002). The magnesium chloride is also converted to magnesium hydroxide, facilitating its removal from the natural brine (Faith et al., 1975). The magnesium hydroxide is precipitated and filtered. Less than 1 percent of the added lime remains in the brine (USDA, 2001). Sodium chloride solubility decreases next and is precipitated when the calcium chloride concentration reaches approximately 35 percent (Mavity, 1976). The remaining calcium chloride liquor is then evaporated through a double- or triple-effect vacuum evaporator. Settlers and centrifuges are used to remove unwanted alkali chlorides, particularly sodium chloride (Miller, 1991). Calcium sulfate (CaSO<sub>4</sub>), precipitated as scale, is removed by high-pressure water jets and chemical solvents (Mavity, 1976). A final high-temperature evaporation results in a final product that will be between 78–94 percent calcium chloride (Vrana, 2014).</li> <li>In evaluating the brine process using NOP Guidance 5033, §4.6, the following criteria are considered:</li> <li>Calcium chloride has not been transformed into a different substance via chemical change. While</li> </ul> |
|---|---|
| 403<br>404  | calcium and chloride in solution undergoes structural change into crystalline form, this is not considered a chemical change.   |
| 405   | <ul> <li>Calcium chloride occurs in nature.</li> </ul>  |
| 406   | <ul> <li>The synthetic materials used to extract, separate, and isolate the calcium and chlorine in the brine</li> </ul>  |
| 407   | go through a removal step and ultimately have no technical or functional effect on the final calcium  |
| 408   | chloride product.   |
| 409   | 1   |
| 410   | The answer in NOP Guidance 5033-1 step 2b is "Yes," at the end of brine extraction calcium chloride meets   |
| 411   | all criteria described at §4.6 of NOP 5033.   |
| 412   |   |
| 413   | The final calcium chloride has not undergone a chemical change in that it is not chemically different from  |
| 414   | how it naturally occurs in the source material. Although calcium chloride is structurally different in that   |
| 415   | the water and impurities have been removed (i.e., it is crystalline calcium chloride rather than calcium and  |
| 416   | chloride ions in solution), other products of crystallization have been considered non-synthetic by the   |
| 417   | NOSB. Examples include sea salt (sodium chloride), nigari (magnesium chloride and magnesium sulfate),   |
| 418<br>419  | and potassium sulfate from saltwater evaporation and crystallization.   |
| 419   | Solvay Process  |
| 421   | The second most prevalent method for making calcium chloride is by the Solvay process (Solvay, 1887). As  |
| 422   | with the brine process, calcium chloride is considered a byproduct, in this case of the manufacture of  |
| 423   | sodium bicarbonate (Speight, 2002). The Solvay process involves five reaction steps that use ammonia as a   |
| 424   | catalyst and sodium chloride, calcium carbonate, and water as initial reactants (ESAPA, 2004; Speight,  |
| 425   | 2002). While the process is intricate and involves multiple steps, it can be represented as (Kemp & Keegan,   |
| 426   | 2012):  |
| 427   |   |
| 428   | $2 \operatorname{NaCl} + \operatorname{CaCO}_3 \rightarrow \operatorname{Na_2CO}_3 + \operatorname{CaCl}_2$   |
| 429   |   |
| 430   | Evaluating the Solvay process using NOP Guidance 5033-1, sodium chloride and calcium carbonate are  |
| 431   | transformed into sodium carbonate and calcium chloride via a chemical change, rendering products of the   |
| 432   | chemical reaction synthetic.  |
| 433   | Understation Arid Matter A  |
| 434<br>435  | Hydrochloric Acid Method<br>A third method currently used to produce industrial quantities of calcium chloride involves adding  |
| 435<br>436  | A third method currently used to produce industrial quantities of calcium chloride involves adding hydrochloric acid to calcium carbonate, producing calcium chloride and carbonic acid (Krohn et al., 1987):   |
| 430   | ny chormone actuate carciant carbonate, producing carciant chorne and carbonic actu (Kronin et al., 1907).  |
| 438   | $CaCO_3 + 2HCl \rightarrow CaCl_2 + H2CO_3$   |
| 439   |   |
|   |   |

440 Evaluating the hydrochloric acid method using NOP Guidance 5033-1, calcium carbonate has been 441 transformed into a different substance via acidulation with hydrochloric acid. The chemical change makes calcium chloride derived from this process synthetic. 442 443 444 Evaluation Question #3: Discuss whether the petitioned substance is formulated or manufactured by a 445 chemical process, or created by naturally occurring biological processes (7 U.S.C. § 6502 (21)). 446 447 Calcium chloride may be manufactured by one of two chemical processes, which were described above, or 448 extracted from natural brine. It is not created by naturally occurring biological processes. The NOSB 449 determined that calcium chloride extracted from brine is nonsynthetic and that non-brine processes were 450 synthetic (NOSB, 1996). 451 452 Evaluation Question #4: Describe the persistence or concentration of the petitioned substance and/or its 453 by-products in the environment (7 U.S.C. § 6518 (m) (2)). 454 As an ionic salt, calcium chloride readily dissolves in water and is not persistent or concentrated. The 455 calcium and chloride moieties are elemental, persist in the environment, and are regarded as dissolved 456 457 solid pollutants reportable under the Clean Water Act (US EPA, 1995). Although persistent, calcium and 458 chlorine are also ubiquitous in the environment, are constituents of living organisms, and pose little risk to 459 the environment (Housenger, 2016; OECD, 2002). 460 461 Calcium and chlorine cannot be considered biodegradable (OECD, 2002). However, they are nutrient elements that are consumed and sometimes accumulated or concentrated by various organisms. For 462 example, calcium chloride is readily metabolized by Bacillus species and other soil microorganisms, 463 sometimes sequestering carbon dioxide to make calcium carbonate (Anbu et al., 2016). Earthworms 464 465 forming calcium carbonate while metabolizing available calcium was demonstrated in the 1930s, and was 466 first documented by Charles Darwin in the 1880s, when he observed that earthworms of various species 467 converted vegetable matter into calcite (CaCO<sub>3</sub>) (Robertson, 1936). 468 Evaluation Question #5: Describe the toxicity and mode of action of the substance and of its 469 470 breakdown products and any contaminants. Describe the persistence and areas of concentration in the 471 environment of the substance and its breakdown products (7 U.S.C. § 6518 (m) (2)). 472 473 The EPA did not require a quantitative risk assessment for human health effects of calcium chloride used 474 as an antimicrobial pesticide in enclosed spaces as a moisture absorber. The reasons given were the lack of 475 exposure and hazard concerns. The EPA concluded that there were no risks of concern for human health or 476 non-target organisms (Chen & Parsons, 2016). As a direct food additive that is Generally Recognized As 477 Safe (GRAS), calcium chloride is regarded by experts as posing reasonable certainty of no harm under 478 conditions of intended use in food (Klaassen, 2001). The acute and chronic toxicity of calcium chloride is 479 summarized in Table 2. 480 481 Table 2. Toxicity of Calcium Chloride Study Reculto Source

| Sludy               | Kesuits                                   | Source          |
|---------------------|---|-----------------|
| Acute oral toxicity | LD <sub>50</sub> Rat: 10 g/kg             | (US NLM, 2020)  |
|                     | LD <sub>50</sub> Mouse: 1,940 mg/kg       |                 |
|                     | $LD_{50}$ Rabbit: 1,384 mg/kg             |                 |
| Acute subcutaneous  | LPLD Cat: 249 mg / kg                     | (US NLM, 2020)  |
| toxicity            | LPLD Dog: 274 mg / kg                     |                 |
| Acute intravenous   | $LD_{50}$ Mouse: 42.4 mg/kg               | (Syed & Hosain, |
| toxicity            |   | 1972)           |
| Subchronic toxicity | NOAEL Rat: > 2,000 mg / kg over 12 months | (OECD, 2002)    |
| Developmental       | NOEL Maternal Rat: 176 mg / kg            | (OECD, 2002)    |
| toxicity /          | NOEL Maternal Mouse: 189 mg / kg          |                 |
| Teratogenicity      | NOEL Maternal Rabbit: 169 mg / kg         |                 |
| Genetic toxicity    | Negative (Salmonella typhimurium)         | (OECD, 2002)    |
|                     |   |                 |

482

- When heated to decomposition, hydrated calcium chloride emits toxic fumes of hydrogen chloride or hydrochloric acid (HCl) (Lewis & Sax, 1996). The mono-, di-, tetra-, and hexa-hydrate forms decompose at 260°, 175°, 45.5°, and 30°C, respectively (Patnaik, 2003).
- 486

# 487Evaluation Question #6:Describe any environmental contamination that could result from the488petitioned substance's manufacture, use, misuse, or disposal (7 U.S.C. § 6518 (m) (3)).

489 490 Because this review is only of the nonsynthetic brine-derived source, the environmental impacts of the 491 manufacturing processes for the Solvay process and hydrochloric acid method are not under consideration 492 here. In the Michigan Basin, the brine is found in sandstone formations formed in the middle Paleozoic era 493 (Schaetzl, 2020). The first producing brine well was drilled in 1841 (Cook, 1914; Kieta, 2018). The basin contains about a trillion tons of brine (Schaetzl, 2020). It has been referred to as an inexhaustible supply 494 495 (Cook, 1914). At 1983 extraction rates, the Michigan Basin deposits would take more than 1,000 years to be 496 depleted (Kemp & Keegan, 2012; Schaetzl, 2020). The U.S. Geological Survey has not published brine 497 extraction rates since then because the data was withheld to avoid disclosing proprietary company data. 498 There is no indication that extraction has increased to a significant degree.

499

500 The brine used to make calcium chloride contains several other halogens and alkali elements. The bromine, chlorine, iodine, lithium, magnesium, sodium, and potassium are recovered and used for industrial and 501 502 commercial purposes. A certain amount of the spent brine is unusable. Environmental concerns with the 503 manufacturing process were not considered until the last quarter of the 20<sup>th</sup> century (Kieta, 2018). Waste 504 disposal from brine-extraction of calcium chloride is a growing concern, as spent brine is injected 505 underground into deep wells for solution mining (US EPA, 1999). These injection wells are categorized by the US EPA as Class II and are currently unregulated at the Federal level (US EPA, 2020b). Class II injection 506 507 wells are intended for oil- and gas-related brines. Michigan has approximately 1,250 active Class II 508 injection wells, with over half used for brine disposal (MEGLE, 2020). With these wells, brine disposal may 509 be combined with the waste brines created by hydraulic fracturing (fracking) for oil and gas. Deep-well 510 injection will often have a mix of hazardous substances, including radioactive material (US EPA, 2020b). 511 Concerns with deep well injection include groundwater contamination and increased seismic activity (Folger & Tiemann, 2016). Intensive pumping and cracked casings in aging brine wells were linked to 512 contamination of fresh groundwater (Dumouchelle et al., 1987). Dow Chemical, the largest producer of 513 514 calcium chloride from brine in the U.S., was linked to soil damage and groundwater contamination caused 515 by at least three historic brine spills (Michigan DEQ, 2015).

516

517 Agricultural use of calcium chloride poses relatively little risk of environmental contamination in comparison with its use as a de-icer. Environmental incidents involving the agricultural use and misuse of 518 519 calcium chloride were not found in a thorough search of the literature. However, careless loading and mixing of foliar spray rigs near open water pose risks of runoff and potential chloride accumulation and 520 saline pollution of fresh water. The adverse impact of such misuse is localized in nature. Calcium is already 521 522 the most common cation found in fresh surface water on a global scale and is widely distributed (OECD, 523 2002). On the other hand, chloride is more variable in its occurrence in fresh surface water, with local 524 geological factors determining background levels, and human use factors from pollution having greater 525 influence on sensitive ecological systems. For that reason, chloride is used as an indicator of water 526 pollution from human activity (Hawkins & Judd, 1972; Sonzogni et al., 1983). The Great Lakes in North 527 America are seen as being at risk from growing chloride pollution (Chapra et al., 2009, 2012; Sonzogni et 528 al., 1983). Calcium chloride as a de-icer was identified as one of the top sources of chloride pollution 529 (Chapra et al., 2012). Smaller bodies of water – ponds, lakes, brooks, and streams – have less buffering 530 capacity than major bodies of water and often have sensitive species adapted to a relatively pristine 531 ecosystem. Many small lakes and ponds have seen even the most salt-tolerant native freshwater species not 532 survive heavy salt run-off incidents (Hawkins & Judd, 1972).

533

#### 534 Evaluation Question #7: Describe any known chemical interactions between the petitioned substance

and other substances used in organic crop or livestock production or handling. Describe any

536 environmental or human health effects from these chemical interactions (7 U.S.C. § 6518 (m) (1)).

| 537        |  |
|------------|--|
| 538<br>539 | Calcium chloride has ionic bonds and dissolves easily into Ca <sup>2+</sup> and 2 Cl <sup>-</sup> . These ions in solution can then form ionic bonds with other available cations and anions. Calcium is a secondary plant nutrient, and |
| 540        | soluble calcium in the soil is readily taken up by plants. Chlorine is a halogen that is highly reactive.  |
| 541        | Sodium chloride is a significant contaminant of the natural brine source of calcium chloride. Addition of  |
| 542        | sodium chloride to the soil can have adverse effects on plants, soil structure, and cation balance (Awada et   |
| 543        | al., 1995).  |
| 544        |  |
| 545        | Calcium chloride solution introduced to smectite clay soils under laboratory conditions inhibited  |
| 546        | adsorption of four pesticides not used in organic production (Li et al., 2006). While it is not possible to infer  |
| 547        | how calcium chloride will interact with any specific substances used in organic production based on the  |
| 548        | study, the authors noted that calcium chloride's strong hydration impedes the direct contact of aromatic   |
| 549        | rings with opposing clay siloxane surfaces.  |
| 550        |  |
| 551        | The application of calcium chloride as a foliar feed is a response to a deficiency in calcium uptake by  |
| 552        | plants. Such deficiency results from a complex set of factors including soil nutrient levels, pH, cation   |
| 553        | exchange capacity, and others.   |
| 554<br>555 | In addition income and shooth enous in the soil mean he immediated has the addition of colorism (107hite f   |
| 555<br>550 | In addition, iron and phosphorous in the soil may be immobilized by the addition of calcium (White &   |
| 556<br>557 | Broadley, 2003).   |
| 558        | Evaluation Question #8: Describe any effects of the petitioned substance on biological or chemical   |
| 559        | interactions in the agro-ecosystem, including physiological effects on soil organisms (including the salt  |
| 560        | index and solubility of the soil), crops, and livestock (7 U.S.C. § 6518 (m) (5)).   |
| 561        |  |
| 562        | Calcium chloride's impact on microorganisms and soil biology is complex and depends on various factors.  |
| 563        | Some microorganisms are inhibited while others thrive after calcium chloride is introduced under   |
| 564        | experimental conditions (Greaves, 1922; Greaves & Carter, 1922; Winslow & Dolloff, 1928; Albrecht &  |
| 565        | Jenny, 1931; Sindhu & Cornfield, 1967; Anbu et al., 2016). Calcium chloride was found to be more toxic to  |
| 566        | coliform bacteria than potassium chloride or sodium chloride, and less toxic than magnesium chloride   |
| 567        | (Winslow & Dolloff, 1928). The researchers found that mixtures of the different salts in different   |
| 568        | proportions could have either beneficial or antagonistic effects on microbial growth as measured by carbon   |
| 569        | dioxide production.  |
| 570        |  |
| 571        | Another study found that nitrification – the bacterial conversion of ammonia nitrogen to nitrite and nitrate   |
| 572        | forms by oxidation – was suppressed by calcium chloride, while mineralization – the release of nitrogen  |
| 573        | from organic matter by biodegradation – was increased by a small but statistically significant amount  |
| 574        | (Sindhu & Cornfield, 1967).  |
| 575        |  |
| 576        | Various <i>Bacillus</i> species in soil form calcium carbonate as a form of mineral calcite in a process known as  |
| 577        | Minerally Induced Calcium Carbonate Precipitation (MICCP). Calcium chloride was found to be more   |
| 578        | efficient than calcium oxide, calcium acetate, and calcium nitrate to carry out MICCP under laboratory   |
| 579        | conditions (Achal & Pan, 2014). There is increased interest in MICCP as a possible way to sequester soil   |
| 580        | carbon (Anbu et al., 2016).  |
| 581        |  |
| 582        | Calcium chloride was not included in the original study that established the salt index (Rader et al., 1943).  |
| 583        | No peer-reviewed source that replicated the Rader method was found that compared the osmotic pressure  |
| 584        | caused by calcium chloride in plant leaves with that of sodium nitrate (NaNO <sub>3</sub> ). An alternative method to  |
| 585        | estimate the salt index is to compare the electrical conductivity of a fertilizer with sodium nitrate (Jackson,  |
| 586<br>587 | 1958):   |
| 587<br>588 | Estimated Salt Index (ESI) = (μmhos Fertilizer solution / μmhos 0:1 percent NaNO <sub>3</sub> ) x 100  |
| 588<br>589 | Estimated balt index (EST) = ( $\mu$ minos retrinzer solution / $\mu$ minos 0.1 percent indivo <sub>3</sub> ) x 100  |
| 590        | Calcium chloride has a higher electrical conductivity and thus a higher salt index than sodium nitrate using   |
| 591        | the Jackson method (Isono, 1984; Haynes, 2010). At 20°C, the electrical conductivity of a 1 percent solution   |

Calcium Chloride

592 of calcium chloride is 15,700 µmhos and a 1 percent solution of sodium nitrate has an electrical 593 conductivity of 10,600 (Haynes, 2010). Using the formula above, the Jackson salt index for calcium chloride 594 is 148.11. However, the higher salt index from electrical conductivity does not necessarily result in greater 595 osmotic pressure on the leaves. For example, application rates of materials vary widely, and calcium 596 chloride is usually applied at a much lower rate than sodium nitrate or potassium chloride. Additionally, 597 some materials with low salt indices – such as anhydrous ammonia – can be toxic to plants in ways other 598 than exerting osmotic pressure on leaves (Murray & Clapp, 2004). 599 600 Calcium chloride's efficacy as a readily available calcium source has been studied extensively. Some of 601 William Albrecht's early experiments on the role of calcium in base cation saturation ratios and cation 602 balancing used calcium chloride as a calcium source (Albrecht & Davis, 1929; Albrecht & Jenny, 1931; Albrecht & Smith, 1952). While Albrecht's later work focused on limestone and gypsum as preferred 603 604 sources of calcium, particularly in neutral and acidic soils, he recognized that calcium chloride went into 605 solution and was taken up more rapidly as a chloride salt, and also recognized chloride's acidifying role 606 (Albrecht & Smith, 1952). 607 608 When added to biomass made into biochar, calcium chloride shows the potential to increase carbon sequestration. One study using pyrolyzed chicken manure found that calcium chloride prevented carbon 609 610 loss, though less effectively than ferric chloride (FeCl<sub>3</sub> 6H<sub>2</sub>O) (Xiao et al., 2018). 611 612 Plants with calcium deficiencies are often more susceptible to plant pathogens (Simon, 1978). Symptoms of 613 calcium deficiencies include the cracking of fruit, water-soaked tissues, pits and cavities, necrosis of young 614 tissues, and necrosis of leaf tissue (Simon, 1978; White & Broadley, 2003). Blossom end rot of tomatoes has been understood since the 1940s as caused by a cation imbalance and low calcium relative to magnesium, 615 616 potassium, and sodium (Lyon et al., 1942). Calcium chloride has been observed to play a preventive or 617 salutary role in inhibiting some opportunistic plant pathogens. It was observed to reduce damping off 618 caused by various fungal pathogens of soybean (*Glycine max*) seedlings grown in pots, while potassium chloride and magnesium chloride did not (Albrecht & Jenny, 1931). Pre-harvest foliar application of 619 620 calcium chloride improved the calcium content, reduced the incidence of anthracnose and increased the 621 antioxidant activity of papayas grown in Malaysia (Madani et al., 2016). An Egyptian study showed that 622 potatoes (Solanum tuberosum) treated with calcium chloride mixed with commercial baking yeast 623 (Saccharomyces cerevisiae) significantly reduced incidence of early blight (Alternaria solani) compared with a 624 no-treatment control, and outperformed sodium bicarbonate as an alternative treatment (El-Mougy & 625 Abdel-Kader, 2009). 626 627 Calcium chloride is also effective as a blossom thinner on apples (Long, 2002). However, there are no products currently registered with the EPA that are labeled for that purpose (US EPA, 2020a). 628 629 630 Evaluation Question #9: 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) 631 632 (i)). 633 634 Most of the studies that evaluate the environmental impact of calcium chloride are related to its use as a 635 de-icing agent and dust suppressant. Because calcium chloride is composed of a weak base and a strong 636 acid, it has an acidifying effect and will reduce pH (Witter & Kirchmann, 1989). In comparison with sodium 637 chloride, salinization and alkalization were expected to be reduced by substitution of calcium chloride 638 (Brandt, 1973). Calcium chloride can cause damage to vegetation, such as growth inhibition, scorched 639 leaves, and even plant death (Fay & Shi, 2012). Sensitivity of plants to excess chloride is species- and even 640 variety-specific. Some plants are adapted to growing in conditions of high salinity and may suffer from 641 chlorine deficiencies. However, most cultivated plants of economic importance are not adapted to saline 642 conditions. Often, salt damage is caused by excess sodium, though a review of the literature found that salt 643 sensitivity may be more an outcome of excess chlorine than excess sodium in certain species, such as grapes (Vitis spp.) (Greenway & Munns, 1980). 644

645

Calcium chloride can run off into surface water and leach into groundwater (Fay & Shi, 2012; Harless, 2012; 646

647 Ramakrishna & Viraraghavan, 2005). In surface water, calcium chloride can be toxic to freshwater aquatic organisms (Harless et al., 2011; OECD, 2002). Table 3 summarizes the ecological toxicity of calcium

648

649

chloride.

650

#### 651 Table 3. Eco-toxicity of Calcium Chloride

| Study                    | Results  | Source           |
|--------------------------|--|------------------|
| Effective concentration: | EC <sub>50</sub> 72 hr Selenastrum capricornutum: 2,900 mg /           | (OECD, 2002)     |
| algae                    | L  |                  |
| Effective concentration: | EC <sub>50</sub> 48 hr <i>Daphnia magna</i> : 1,062 mg / L             | (OECD, 2002)     |
| invertebrate             |  |                  |
| Lethal concentration:    | LC <sub>50</sub> 48 hr Daphnia magna: 2,770 mg / L*                    | (OECD, 2002)     |
| invertebrate             |  |                  |
| Lethal concentration:    | LC <sub>50</sub> 24 hr Wood frog ( <i>Rana sylvatica</i> ): 4.85 g / L | (Harless et al., |
| amphibian                |  | 2011)            |
| Lethal concentration:    | LC <sub>50</sub> 96 hr Fathead minnow ( <i>Primephales</i>             | (OECD, 2002)     |
| fish                     | <i>promelas</i> ): 4,630 mg / L*                                       |                  |

652 \*EPA test methods

(m) (4)).

653

#### 654 Evaluation Question #10: 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 655

656

657

658 Calcium chloride is generally considered nontoxic to mammals. As pointed out in Approved Legal Uses of the 659 Substance, it is GRAS as a direct food additive and as such considered not likely to cause harm when intentionally consumed (Chen & Parsons, 2016; Harrison, 2018; Housenger, 2016; Klaassen, 2001; Tran, 660 2016). As a salt, it can have some deleterious effects on human health, with serious local effects by all routes 661 of exposure (Inchem, 2012). Handling precautions are minimal. Open cuts are affected in ways similar to 662

other salts (Mavity, 1976). Prolonged skin contact with calcium chloride can lead to chemical burns (Saeed 663 et al., 1997). 664

665

666 Three cases of calcium chloride necrosis from topical exposure were reported prior to 1957 (Zackheim & Pinkus, 1957). The authors regarded the cases as uncommon. Four patients who had their parathyroids 667

668 removed, and were given intravenous calcium chloride to treat symptomatic hypocalcemia (calcium 669 deficiency), suffered from skin necrosis (Lin et al., 2007). The authors noted that such necrosis was found in 670 only those four patients (out of 96 patients treated), and that renal disease may have been a complicating

671 factor.

672 673 Consumers are widely exposed to calcium chloride as a direct food additive, in medications, and through 674 direct purchase of de-icing agents and condensation traps (OECD, 2002). The greatest risk to human health 675 is as an irritant. Nothing in the literature suggests that agricultural use will pose an additional adverse

- 676 effect beyond these multiple avenues of exposure.
- 677

#### 678 Evaluation Question #11: Describe all natural (nonsynthetic) substances or products which may be 679 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)). 680

681

682 Calcium chloride from brine is considered nonsynthetic, but it is not the only source of nonsynthetic 683 calcium allowed in organic production. Other natural (nonsynthetic) sources of calcium include: calcium 684 carbonate (limestone, dolomite, and oyster shells), calcium sulfate (gypsum), and calcium phosphate (rock phosphate and bone meal) (Parnes, 1990). Calcium deficiencies appear to be correlated with the 685 replacement of organic fertilizers with non-organic fertilizers (Marschner, 1974). 686

687

688 Calcium deficiencies in apple orchards were historically addressed by the application of pulverized limestone in both organic (Rodale, 1970) and non-organic systems (Childers, 1975). With severe cases of 689

- calcium deficiencies, soil application was found to be ineffective (Chittenden et al., 1969). Due to
   differences in solubility which leads to variable rates at which calcium is made available to a crop the
- differences in solubility which leads to variable rates at which calcium is made available to a crop the
   use of another nonsynthetic source of calcium in place of calcium chloride may be unrealistic. Initial
   studies for foliar feeds used calcium acetate (Askew et al., 1960). Calcium nitrate also grew in popularity
- and became the preferred foliar treatment of apple producers (Kidson et al., 1963). Both calcium acetate
- and calcium nitrate, however, are prohibited for use in organic production. Calcium chloride received
   attention because of its relatively low cost and higher calcium content. One of the earliest trials comparing
- 697 calcium nitrate with calcium chloride foliar treatments of apples noted that calcium chloride caused more
- 698 burning of leaves, but had a comparable reduction of bitter pit incidence to calcium nitrate (Chittenden et
- 699 700

al., 1969).

Various other nonsynthetic substances have been used to stabilize ammonia in manure, including peat and
zeolites (McCrory & Hobbs, 2001; Witter & Kirchmann, 1989). Other natural salts used for halopriming
include calcium sulfate and sodium chloride (Sher et al., 2019; Singh et al., 2015).

704

A list of product manufacturers, along with their contact information, that provide USDA Organic

- compliant calcium alternatives is available from the Organic Materials Review Institute (OMRI, 2020).
- 707 OMRI also maintains an approved products list. Products on this list appear within a generic category. The
- table below includes the number of calcium-derived products listed by OMRI at the time of this report. The
- solubility of calcium in these products will likely vary from calcium chloride. Significant variations in
- solubility between calcium sources is the determining factor when identifying true calcium chloride
- 711 alternatives.
- 712

### 713 Table 4. Summary of Calcium Sources Approved by OMRI as of January 2021

| Generic category      | Number of |
|-----------------------|-----------|
|                       | products  |
| Calcium               | 11        |
| Calcium carbonate     | 49        |
| Dolomite, mined       | 18        |
| Limestone             | 32        |
| Gypsum, mined sources | 61        |
| Calcium sulfate       | 10        |
| Phosphate rock        | 28        |
| Bone meal             | 24        |
| Oyster shell lime     | 2         |
| Calcium chloride      | 46        |

714

Natural (nonsynthetic) sources of chloride include compost, manure, potassium chloride, and sodiumchloride.

717

# 718Evaluation Question #12:Describe any alternative practices that would make the use of the petitioned719substance unnecessary (7 U.S.C. § 6518 (m) (6)).

720

The principal alternative practice to foliar application of calcium chloride would be to increase the amount of available calcium in the soil by applying the substances named in *Evaluation Question* #11. Practices that increase plant-available calcium in the soil include conservation and improvement of organic matter, which in turn increases both biological activity and cation exchange capacity. One hypothesis is that a calcium deficiency can be caused by excess hydrogen (Albrecht, 1941; Albrecht & Smith, 1952). Calcium deficiency plants may occur in situations where there is sufficient calcium in the soil, but it is not going into

solution or being taken up by the roots because of insufficient water or soil moisture and oxygen (Olle &

Bender, 2009). Timely watering and mulching to retain soil moisture can help the transport of soil calcium.

- For example, night misting with water was found to reduce the incidence of lettuce tip burn (Cox &
- 730 Dearman, 1981).
- 731

732 Another alternative practice is the use of varieties that are more efficient at producing under conditions of 733 low calcium availability or within a wide range of cation nutrient ratios. Some apple varieties have been 734 observed to be more susceptible to bitter pit than others (Garman & Mathis, 1956). The same principle can 735 be applied to pears, tomatoes, and other crops that are susceptible to calcium deficiencies that are treatable 736 by foliar feeding of calcium chloride. Apple varieties that are more tolerant to low calcium conditions 737 represent a limited portion of available varieties. The development of additional tolerant varieties, for 738 apples and other crops affected by calcium deficiency, requires experimentation and research on the 739 selection of varieties for such conditions. 740 741 In addition to using limestone or gypsum for increasing soil application of calcium, other comparable 742 strategies of calcium foliar treatment to control bitter pit in apples include summer pruning, delayed 743 harvest, and fruit thinning (Van der Boon, 1980). While summer pruning and fruit thinning reduced the 744 incidence of bitter pit and slightly increased marketable yield in one study conducted in the Netherlands, 745 these practices were labor intensive. It is notable that this study used calcium nitrate and not calcium 746 chloride as the foliar treatment for comparison. 747 748 Various calcium deficiencies have been attributed to imbalances in other available nutrients. Bitter pit in 749 apples may be the result of an imbalance caused by excess magnesium and potassium as much as by a 750 shortage of calcium (Garman & Mathis, 1956). Balancing cations in a situation where there is excess may 751 then be accomplished by reducing the amounts of magnesium or potassium applied. However, in soils that 752 are high in magnesium or potassium, this may not be a practical solution. Similar yield- and quality-753 impairing production problems caused by cation imbalances have been observed in a wide range of crops, 754 from alfalfa to tomatoes. The literature on cation balancing with calcium, potassium, magnesium, and 755 sodium with different crops grown on different soils is extensive and beyond the scope of this Technical 756 Report. 757 758 Post-harvest treatment with calcium chloride can be used to treat bitter pit in apples (Reid & Padfield, 1975; 759 Sharples et al., 1979). In a comparison of pre- and post-harvest treatments, pre-harvest foliar feeds were 760 shown to be more effective, but best practice for optimal fruit quality in apples uses both (Conway et al., 761 2001). 762 763 764 **Report Authorship** 765

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