Soluble Boron Products

Crops

l		•	
2	Identification o	of Peti	tioned Substance
3	Chaminal Namon	21	Ashahas
+	Chemical Names:	31	Annybor
)	(PLLO, how are a side harden over how to)	32	Optibor
) 7	(DH3O3, DOFACIC acid, hydrogen borate)	33	Etibor
,	(Na R Q)	34	Etidot
	(Na2D4U7)		CAC Numberry
	(Na P.O. 511 O)		CAS Numbers: 10042 25 2 (horis acid)
	(Na2D4O7 · SH2O)		10045-55-5 (DOFIC ACIC) 1220, 42, 4 (diag diagent totagh or state)
	$(N_{12} = P_{12} = 10 H_{12})$		12170 04 2: 12045 88 4 (diso divers totrahorets
	$(1Na_2D_4O_7, 10\Pi_2O)$		12179-04-3; 12043-88-4 (disodium tetraborate
	$(N_{12} P O + 4H O)$		1202 06 4 (diag dium tatuaharata dagahudrata)
	$(1Na_2D_8U_{13} \cdot 4\Pi_2U)$		12080-02.4 (disoulum tetraborate decanydrate)
	Other Name		12280-05-4 (disodium octaborate tetranyurate)
	barata galta haria avida haray (tingal hudratad		Other Codeci
	sodium horata Na B O (10H O) kornita		DET THURSDA (ED A LINII) horis acid)
	(budrated adjum barate Na $B \cap (OH)$, within (01MPZ9H200 (EDA UNII, diogdium totuchorato
	(invurated sourium borate, $Na_2D_4O_6(OH)_2 \times SH_2O_3$),		91MDZ8H3QO (FDA UNII; disodium tetraborate
	borate Co P O (1511 O) vilovite (codium coloium		LIZEE CO170C (EDA LINILI, disa dium astabarata
	borate, Ca ₂ D ₆ O ₁₁ · SH ₂ O), ulexite (sodium calcium		UZEECOT/OG (FDA UNII; disodium octaborate
	borate NaCaR O (OH) , 5H O) probartito		48214/67CDE4 (EDA LINIL boron triouido)
	borate, $NaCab_5O_6(OH)_6$ (SH_2O), probertite		465W67CFF4 (FDA UNII; boron thoxide)
	(Solutin calcium botate hydroxide, NaCaB O (OH), 2H O)		215 540 4 (EC number, disadium tatraharata)
	$NaCaD_5O_7(OII)_4^{+}SII_2O)$		602 411 0 (EC number, disodium tetraborate)
	Trada Namos		docebudrato)
	Solubor		decanyurate
	Granubor		
	Fertibor		
	Summary	of Pe	titioned Use
	Summary	0110	
	Soluble boron products appear on the National Lis	st of A	Allowed and Prohibited Substances (hereafter referre
	as the National List) under the Micronutrients	listii	ig at / CFR 205.601(j)(/). Also included under
	ivitoronutrients are suitates, carbonates, oxides a	ind SL	licates of zinc, copper, iron, manganese, molybdenur
	selenium, and cobait. Synthetic micronutrients on	the N	ational List are restricted for use as described in the
	annotation for Micronutrients, which currently	states	, that micronutrients may not be used as defoliants,
	nerbicides, or desiccants, that nitrate and chloride	iorms	s are prohibited, and that deficiencies must be
	accumented by soil or tissue testing or another ve	rinab	ie method as determined by a certifying agent.

- 46 The majority of synthetic boron compounds used in agriculture, including USDA organic agriculture, are at least
- 47 moderately soluble, including boric acid and the sodium borate salts. Insoluble or barely soluble boron
- 48 compounds are typically used in other industrial or commercial applications (Smith, 2000) and are not widely
- 49 useful as fertilizers due to their limited release of boron to plants.
- 50

Technical Evaluation Report

51 52	Several and bo	l naturally occurring boron minerals are commercially important, including ulexite, colemanite, kernite, rax (tincal, crude borax) ¹ (USGS, 2021b). These minerals are the most prevalent starting materials for
53	borates	s used across all industries. As nonsynthetic minerals, these boron sources are permitted in organic crop
54	produc	ction as long as they do not contribute to contamination of crops, soil, or water by plant nutrients,
55	pathog	renic organisms, heavy metals, or residues of prohibited substances (7 CFR 205.203). This technical report
56	will for	cus on the widely used processed boron sources with medium to high solubility. The most common
57	agricul	turally applied boron sources are nonsynthetic crushed ores, and processed disodium tetraborate,
58	disodiu	um tetraborate pentahydrate, disodium tetraborate decahydrate, disodium octaborate tetrahydrate, and
59	boric a	cid (Martens & Westermann, 1991; Shorrocks, 1997). In contrast to these forms exhibiting moderate to high
50	solubil	ity, borosilicate glass frits ² are sometimes used due to their extremely low solubility, allowing for a very
51	slow re	elease of boron in soils that are prone to leaching (Martens & Westermann, 1991).
52		
53	Natura	ally occurring, nonsynthetic borate mineral sources are available and marketed for use in organic
54	agricul	ture (OMRI, 2021). Due to lower solubility than refined borate salts and boric acid, ulexite and
55	colema	nite minerals are marketed as slow release boron fertilizers (Broschat, 2008; ETIMADEN ETIMINE
56	USA Ir	nc., 2018b). Since naturally occurring borate minerals are permitted in organic crop production (as
57	describ	bed above), this report concentrates on synthetically produced soluble boron compounds appearing
58	on the	National List.
59		
70	This te	chnical report is intended to support the NOSB's sunset review of "Soluble boron products." As boron was
71	not dis	cussed at length in the 2010 Micronutrients Technical Evaluation Report (USDA, 2010), the NOSB has
72	reques	ted this report include information that was absent in the previous technical report. The focus questions
73	are:	
74		
75 76	1)	Is there a toxic or other adverse action of the petitioned substance or its breakdown products? (7 U.S.C. §6518(m)(2).)
77	- `	
78	2)	Describe any environmental contamination that could result from the petitioned substance's
79		manufacture, use, misuse, or disposal (7 U.S.C. §6518 (m)(3)).
30	2)	
31	3)	Describe and summarize any reported effects upon human health from use of the petitioned substance (7
82		U.S.C. $(56517(c)(1)(A)(1), 7 U.S.C. (56517(c)(2)(A)(1) and 7 U.S.C. (56518(m)(4)).$
33		
54	As phr	ased, Focus Question #1 nearly duplicates the first part of Evaluation Question #5, so the relevant
35 36	inform	ation will be addressed there in this report.
37		Characterization of Petitioned Substance
88 89	Compo	osition of the Substance:
90	Due to	its reactivity, elemental boron does not occur naturally in the environment (Kot, 2015). Boron readily loses

91 electrons to non-metals like oxygen (oxidation) and can form three or four bonds with other atoms. These bonds

are typically covalent or coordinate-covalent³ (dative) bonds, and result in a variety of boron compounds
 (including the soluble borate salts), much like occurs with silicon and carbon (Bhat et al., 2005; Kochkodan et al.,

(including the soluble borate salts), much like occurs with silicon and carbon (Bhat et al., 2005; Kochkodan et al.,
 2015; Kot, 2015). Typically, salts of boron are at least partially water soluble (Kochkodan et al., 2015).

⁹⁵

¹ Ulexite, colemanite, kernite, and tincal are mineralogically classified as sodium calcium borate hydroxide, calcium borate hydroxide, sodium borate hydroxide minerals, respectively (USGS, 2021b; Woods, 1994).

 $^{^{2}}$ Frits are small particles of silica (SiO₂) glass, often containing other chemical substances incorporated into the structure. In many cases, the reason for incorporating another material is to reduce that material's mobility (Plodinec, 2000).

³ Covalent bonds occur when a pair of electrons are shared between two atoms. Coordinate-covalent (dative) bonds occur when one of the atoms donates *both* of the electrons that are shared, as opposed to each atom donating one electron each (Mingos, 2016).

96 Out of 200 naturally occurring boron minerals known, just 12 are commercially important in a wide range of 97 applications (Adair, 2007; Kochkodan et al., 2015). Four of these comprise 90% of all boron material production: 98 ulexite, colemanite, kernite, and borax (tincal) (Adair, 2007). Other commercial borate minerals include invoite,

99 priceite, szaibelyite, inderite, pinnoite, hydroboracite, datolite, and ludwigite (Garrett, 1998).

100

101 Boric acid

- 102 Boric acid (sometimes called boracic acid or hydrogen borate) is a weak acid with the formula $B(OH)_3$. Boric acid
- 103 typically occurs as a solid, and its water solubility increases with temperature (Kochkodan et al., 2015; Smith,
- 104 2000). When dissolved, boric acid does not carry a charge. It acts as a Lewis acid (an acceptor of electrons), so it
- 105 can accept a hydroxyl group (OH^{-}) and form the borate anion $B(OH)_{4}^{-}$. These substances occur in equilibrium: at
- 106 high pH (greater than approximately 8.5-9) the borate anion is dominant; at lower pH the boric acid molecule is 107 dominant (Kochkodan et al., 2015; Parks & Edwards, 2005). The equilibrium equation follows:
- 108
- 109
- 110

$B(OH)_3 + H_2O \leftrightarrow B(OH)_4^- + H^+$ boric acid + water ↔ borate anion + hydrogen ion

111 112 Sodium borate salts

This group of substances are simply sodium salts of boric acid. They are a framework of boron and oxygen atoms 113

114 attached to sodium metal ions. They tend to be sparingly soluble to soluble in water (Kochkodan et al., 2015) (see

115 Properties of the Substance, below).

116

117 Sodium tetraborate salts incorporate varying amounts of water molecules into their molecular structures

118 (hydration states) (Smith, 2000). The number of water molecules incorporated determines the identity of the

119 substance. Disodium tetraborate decahydrate is commonly referred to as "borax." Disodium tetraborate

120 *pentahydrate* and disodium tetraborate *anhydrous* are sometimes identified as borax pentahydrate and anhydrous

121 borax, respectively. The hydration states of disodium tetraborate can be changed by adding heat or water. The

122 most common commercial forms are decahydrate and pentahydrate (Smith, 2000).

123

124 Disodium octaborate tetrahydrate has a higher boron content compared to the compounds listed above (Smith,

125 2000). It is composed of a boron and oxygen framework connected to sodium ions.



Disodium Tetraborate



Disodium Tetraborate Pentahydrate

Borate Anion

-H

0-

-н



Disodium Tetraborate Decahydrate









Figure 1: Structures of Soluble Boron Compounds

129 Source or Origin of the Substance:

Boron occurs in the Earth's crust at an average concentration of 10 parts per million (ppm) (Smith, 2000).

- 131 This level can be significantly elevated in certain volcanic environments and sedimentary deposits (Kot,
- 132 2015; Smith, 2000; Wisniak, 2005). It is thought that clay-rich sediments become enriched in boron by
- adsorbing the dissolved solids from seawater (Chao et al., 2011). These sediments are transported to
- 134 continental margins by plate tectonics, leading to boron enriched zones (Chao et al., 2011). As more
- 135 common minerals crystallize from magma, rare elements become concentrated in the left-over fluids,
- 136 eventually crystallizing into uncommon mineral deposits (Garrett, 1998).
- 137

Borax results from the solar evaporation of saline brines in arid playas, typically appearing as dried crusts

- 139 on the shores of shallow lakes or associated with the drying of mineral spring waters (Garrett, 1998). Large
- bedded deposits occur in Boron, California, Argentina, and Turkey. Though not extensive, native borax
- 141 deposits are also found near dry lake shores throughout California, Nevada, and the Tibetan plateau
- 142 (Garrett, 1998).

- 143 Kernite (sodium borate) is often associated with the same environments as borax deposits; borax 144 dehydrates to kernite in hot conditions adjacent to volcanic activity at depth (Garrett, 1998). 145 146 Colemanite (calcium borate) is thought to result from hot geothermal springs containing abundant boron 147 mixing with calcium derived from sedimentary deposits (Garrett, 1998). Colemanite also occurs in 148 evaporated lake environments in California, Argentina, Turkey, Russia, and the Himalayan plateau 149 (Garrett, 1998). 150 151 Ulexite (sodium calcium borate) is often associated with colemanite deposits and the two minerals (along 152 with borax) form in different beds depending on the calcium and sodium content of the geothermal springs (Garrett, 1998). Springs containing elevated sodium levels may form ulexite and borax in alternating 153 154 geological units (Garrett, 1998). Ulexite/colemanite suites may be found in California, Argentina, Bolivia, 155 Chile, Peru, and Turkey. 156 157 The United States and Turkey are the largest boron mineral producers by far (each producing millions of 158 metric tons per year), followed by Chile, China, Bolivia, Peru, Russia, and Argentina (producing between 159 70 - 400 thousand metric tons each per year) (Garrett, 1998; USGS, 2021a). The majority of boron products used in the United States are produced domestically in one California pit mine, derived from solid ores of 160 161 kernite, borax, and ulexite, and to a lesser extent from brine solution mining, also in California (USGS, 162 2021b; Woods, 1994). 163 164 The processing of soluble boron products involves crushing ores, mixing with various clarifiers or other 165 mineral reactants to remove waste minerals, crystallization, and temperature control to achieve different 166 hydration states. The resulting sodium borates can be further processed into boric acid (Smith, 2000). See 167 *Evaluation Question #2* for more information on the manufacture of soluble boron products. 168 169 **Properties of the Substance:** Despite the many naturally occurring borate minerals and various refined borate compounds, they all 170 171 inevitably become boric acid or borate anion when dissolved in water (Brown et al., 2002; Kochkodan et al., 172 2015). Heating tends to decompose the boric acid/borate system into boron oxide (Smith, 2000). The 173 solubility of boric acid and borate salts also increases with increasing temperature and pressure 174 (Kochkodan et al., 2015). Boric acid is a very weak acid⁴ containing three protons capable of dissociating 175 (Brown et al., 2002). 176 177 Unlike the other micronutrients that are absorbed by plants as dissociated ions, plants uptake boric acid 178 directly in its undissociated form, indicating a unique uptake mechanism (Brown et al., 2002). The 179 observation that boric acid is absorbed directly as the entire molecule rather than as charged ions has not 180 been fully explained in the literature and disagreements remain about whether boron enters plant cells 181 passively (by diffusion that does not require metabolic energy) or actively (through a transport mechanism 182 requiring energy input) (Brown et al., 2002). 183 184 Sodium borate salts hydrate or dehydrate depending on humidity, temperature, and pressure, and these 185 conversions are usually reversible by altering atmospheric conditions (Smith, 2000). See Table 1 for further 186 details regarding the physical and chemical properties of common boron compounds. 187 188 189
 - 190

⁴ The dissociation constant for the first proton in boric acid is 5.8×10^{-10} mol/L and 1.8×10^{-13} and 3×10^{-14} for the second and third, respectively, at 25°C (Kochkodan et al., 2015), and the acid strength increases with increasing temperature. These values indicate extremely limited potential to dissociate into acidic hydrogen ions.

Property	Boric acid	Disodium tetraborate	Disodium tetraborate pentahydrate	Disodium tetraborate decahydrate	Disodium octaborate tetrahydrate
Physical State and Appearance	Solid, crystalline	Solid, crystalline	Solid, powder	Solid, crystalline	Solid, powder
Odor	Odorless	Odorless	Odorless	Odorless	Odorless
Color	White	White/gray	White	White	White
Molecular Weight (g/mol)	61.84	201.2	291.3	381.4	412.5
Density (g/cm ³)	1.5	2.37	1.82	1.73	1.87
pН	3.8-4.8	9.3 (20°C)	9.3 (20°C)	9.3 (20°C)	8.5 (23°C)
Solubility in Water (g/100 ml)	5.6	2.56	3.8	5.1	n/aª
Stability	Stable	Hydrates in damp air	Stable	Stable	Stable
Reactivity	Decomposes upon heating	Decomposes upon heating	Low reactivity, incompatible	Decomposes upon heating	Stable

Table 1: Chemical and Physical Properties of Soluble Boron Compounds

^a Precise solubility cannot be determined because the compound converts to boric acid when dissolved and tends to

193 supersaturate.

194 Source: American Elements, 2021; Chemical Book, n.d.; European Chemicals Agency, 2009; National Center for

Biotechnology Information, n.d.-d, n.d.-a, n.d.-c, n.d.-b; United States Department of Labor, 2021; US EPA, 1993

196

191

197 Specific Uses of the Substance:

- 198
- 199 *Crop micronutrient*

200 Approximately four percent of boron extracted globally is used in the correction of trace element

201 deficiencies in crops (Kot, 2015; Woods, 1994). Shorrocks (1997) states that boron deficiency was reported in

202 over 80 countries in 132 crops over the second half of the twentieth century, and that approximately 15

203 million hectares of land are treated with boron compounds yearly. More recent figures could not be located

at the time of this report. Of these numerous crop varieties, the most susceptible to boron deficiency are

205 celery, groundnuts, beets, brassicas, rutabaga, coffee, carrots, palms, eucalyptus, cotton, sunflower, apple,

206 alfalfa, olives, pine, and grapes⁵ (Shorrocks, 1997; Woods, 1994).

207

208 Several growing regions worldwide are particularly susceptible to boron deficiency. Notably, the eastern

and northwestern United States, northern Europe, eastern China, and certain nations in west and central

210 Africa have reported common boron deficiencies (Shorrocks, 1997). These deficiencies are linked to soil

211 types including ultisols, alfisols, oxisols, and spodosols⁶ (Shorrocks, 1997). Soils become deficient in boron

through leaching, which is common in sandy or silty soils (Blevins & Lukaszewski, 1998).

⁵ Martens & Westermann (1991) report the following optimum sodium borate fertilization rates for the following crops, when deficient, in kg/hectare: alfalfa (2.24), brassicas (0.45), grapes (0.76), pine (5.7), soybeans (1.12), beets (2.2-3.4).

⁶ Generically, ultisols are soils occurring in warm, humid areas that tend to be enriched in clay and have low base saturation (a term describing a soil's ability to exchange ions). Alfisols tend to occur in colder climates than ultisols and are characterized by moderate base saturation and occurrence of clays. Oxisols, commonly occurring in the tropics, are highly degraded soils which are easily depleted when cultivated. Spodosols tend to occur in cool, humid areas and are characterized as sandy, coarse, rich in aluminum and organic matter, but largely infertile (USDA Soil Survey Staff, 1999).

- 213 Crop farmers apply boron directly to soils before seeding, or apply it as part of a foliar spray, typically 214 mixed with other nutrients (Martens & Westermann, 1991). After crops are established, boron is sometimes 215 216 applied again, particularly in coarse soils subject to boron leaching (Martens & Westermann, 1991). 217 Disodium tetraborate decahydrate (borax) is popular in soil applications due to its increased solubility but 218 is subject to leaching for the same reason. The other disodium tetraborate hydrates, with lower solubility, 219 are also used in soils, as well as the more soluble boric acid to a lesser extent. Disodium octaborate 220 tetrahydrate is used in soil and dissolved foliar applications and dissolves easily (Martens & Westermann, 221 1991). 222 223 Excessive boron in soils can be phytotoxic (Rámila et al., 2015). Symptoms include leaf burn, leaf chlorosis, 224 reduced elongation of roots and shoots, and reduced crop yields. Arid and semi-arid regions are naturally 225 prone to this problem, but human activity (industrial glass and detergent production) has also increased 226 boron concentrations in surface waters, contributing to the problem. Excess boron in soil and water can be 227 difficult to remove (Rámila et al., 2015). 228 229 Pesticide 230 Boric acid and borate salts (particularly disodium octaborate tetrahydrate) are commonly used in wood 231 treatments to protect against fungi and termites (Woods, 1994). As insecticides, borates and boric acid can 232 be effective stomach poisons against cockroaches, wood-boring beetles, fleas, and ants (Krieger, 2010; 233 Woods, 1994). 234 235 236 Other uses 237 The majority of boron compounds produced are used in the manufacture of fiberglass insulation, glass, 238 enamels, bleach, and other non-agriculturally related chemicals (Woods, 1994). Due to boron's exceptional 239 ability to absorb neutrons, boron compounds are used in several capacities in nuclear energy reactors and 240 in nuclear waste management. Boric acid, boron carbide, boron-containing polymers and metal-boride 241 compounds are used in sensors, radiation shielding, nuclear material storage, reactor control rods, and in 242 vitrifying nuclear waste (Subramanian et al., 2010; Woods, 1994). 243 244 Boric acid is also used in eyewashes, contact lens solutions, oral gargles, cosmetics, and topical medicines 245 (Locatelli et al., 1987). 246 247 Approved Legal Uses of the Substance: The USDA National Organic Program (NOP) currently permits soluble boron products for use as a crop 248 249 micronutrient at 7 CFR 205.601(j), and boric acid for structural pest control at 7 CFR 205.601(e). Borax (disodium 250 tetraborate decahydrate), disodium tetraborate, boric acid, disodium tetraborate pentahydrate, disodium 251 octaborate, and disodium octaborate tetrahydrate all appear on 2004 EPA List 3, Inerts of Unknown Toxicity (US 252 EPA, OCSPP, 2015). These substances are permitted on the National List as inert ingredients in passive 253 pheromone dispensers at 7 CFR 205.601(m). 254 255 The United States Environmental Protection Agency (EPA) requires boric acid and its sodium salts to be 256 registered when used as insecticides, fungicides, and herbicides (US EPA, 1994). Residues of boric acid and 257 its salts, borax (sodium borate decahydrate), disodium octaborate tetrahydrate, boric oxide (boric 258 anhydride), sodium borate and sodium metaborate are exempted from the requirement of a tolerance in or 259 on raw agricultural commodities when used as active ingredients in insecticides, herbicides, or fungicides
- 260 preharvest or postharvest in accordance with good agricultural practices (40 CFR 180.1121).
- 261
- The FDA permits borax and boric acid to be used in adhesives and coatings in the manufacture of paper and paperboard products used in food packaging (21 CFR 181.30).
- 264

265 Action of the Substance:

When compared to the other recognized plant micronutrients, deficiency in boron is the most common (Blevins & Lukaszewski, 1998; Kot, 2015). Boron deficiency is responsible for significant crop losses, whether in volume or quality, every year (Goldbach & Wimmer, 2007; Shorrocks, 1997). Despite extensive study, the role boron plays in plants is not completely understood (Bolaños et al., 2004; Kot, 2015; Woods,

- 270 1994). It appears that boron plays a role in cell walls, cell membranes, plant development, and plant
- 271 metabolism (Blevins & Lukaszewski, 1998; Bolaños et al., 2004; Brown et al., 2002; Goldbach & Wimmer,
- 272 2007; Kot, 2015; Teasdale & Richards, 1990).
- 273274 *Cell walls*

275 Boron-deficient plants exhibit a characteristic tissue brittleness, while plants exposed to toxic levels of

- boron are more flexible (Loomis & Durst, 1992). Boron acts as a chemical bridge, forming bonds between
- 277 molecules of the cell wall sugar rhamnogalacturonan II⁷ (RG-II) (Chormova & Fry, 2016; Goldbach &
- Wimmer, 2007; Matoh et al., 1996; Power & Woods, 1997). A deficiency of boron leads to a reduction in
- bonds cross-linking RG-II in cell walls, causing the leaf brittleness observed in boron-deficient plants
- 280 (Blevins & Lukaszewski, 1998; Chormova & Fry, 2016). Goldbach & Wimmer (2007) have postulated that
- 281 RG-II may have contributed to the evolution of terrestrial vascular plants by allowing upright growth of
- aquatic plant ancestors through boron cross-linking.
- 283
- 284 *Cell membranes*
- In cell membranes, boron is thought to have a structural stabilizing effect (Blevins & Lukaszewski, 1998;
- 286 Goldbach & Wimmer, 2007). Deficiencies in boron lead to "leakage" of nutrients (notably potassium),
- 287 amino acids, and sugars from plant cells (Blevins & Lukaszewski, 1998; Cakmak et al., 1995; Goldbach &
- 288 Wimmer, 2007).
- 289
- 290 Plant development
- 291 Deficiency in boron has a striking effect on plant reproduction, inhibiting budding, pollination, flowering,
- and fruit-setting, as well as leading to prematurely dropped fruit (Brown et al., 2002; de Wet et al., 1989).
- Boron is important for cell elongation in plants but does not appear to affect cell division (Song et al., 2021).
- 294 The application of boron to soil dramatically increases seed and pollen tube production but has relatively
- little effect on vegetative growth (Blevins & Lukaszewski, 1998; Brown et al., 2002; Shireen et al., 2018).
- 296
- 297 Plant metabolism
- Boron deficiency can effect plant metabolism, though the complexity of cellular systems have made it
- 299 extremely difficult for researchers to reach solid conclusions (Brown et al., 2002). Deficiencies in this
- 300 micronutrient have been linked to disruptions in the ascorbate-glutathione cycle⁸ (Lukaszewski & Blevins,

301 1996), phenol metabolism⁹ (Ruiz et al., 1998), nitrogen metabolism, and nitrogen fixation by rhizobial

- 302 bacteria (Bolaños et al., 1994; Camacho-Cristóbal & González-Fontes, 2007; Shireen et al., 2018).
- 303
- Boron can enhance the uptake of other nutrients in the soil, and affects the nitrate content within plant
 tissues (Ahmed et al., 2011; Camacho-Cristóbal & González-Fontes, 2007; Shireen et al., 2018).
- On cotton crops, Ahmed et al. (2011) showed that the application of boron resulted in a significant increase in the uptake of nitrogen, phosphorus, potassium, copper, iron, and zinc, but simultaneously reduced calcium, magnesium, and manganese levels. The study demonstrated an increased crop yield.
- On greenhouse tomatoes, the application of boron caused increased uptake of calcium,
 magnesium, sodium, and zinc, while reducing uptake of manganese (Smit & Combrink, 2004). The
- 312 reduced manganese did not appear to affect the quality of fruit.
- On boron-deficient hydroponic tobacco, Camacho-Cristóbal & González-Fontes (2007)
 demonstrated that plants did not assimilate nitrate through their roots as they normally would.
 Instead, the deficiency promoted ammonia uptake.

⁷ Rhamnogalacturonan II is a type of pectin (Chormova & Fry, 2016).

⁸ The ascorbate-glutathione cycle is critical in the control of oxygen free radicals in a cell. Reactive oxygen is produced as a byproduct of many metabolic processes, and the ascorbate-glutathione system helps to regulate the levels of reactive oxygen species (Drążkiewicz et al., 2003).

⁹ Phenolic compounds (a class of chemicals that all share an aromatic hydrocarbon ring bonded to hydroxyl groups) play many roles in plant biochemistry, including enzymatic processes, growth regulation, and cell-wall formation (Ruiz et al., 1998).

317 <u>Combinations of the Substance:</u>

- 318 Uniformity of application is important when using boron fertilizers since there is a narrow range between
- deficiency and toxicity for many crops (Brdar-Jokanović, 2020; Garrett, 1998; Goldberg, 1997). Borates are
- 320 sometimes mixed with sand or soil before applying (Shireen et al., 2018; Shorrocks, 1997). Uniform
- application is often achieved by mixing boron sources with blended fertilizer mixes, sometimes through
- 322 irrigation lines (Martens & Westermann, 1991; Shorrocks, 1997).323
- 324 Many boron products on the market are formulated with macronutrient fertilizers, other plant
- 325 micronutrients, growth regulators, or chelating agents (OMRI, 2021). Some products without additional
- formulants contain label instructions to mix with fertilizer products or wetting agents before application (OMRI, 2021).
- 327 328
- 329

316

Status

- 330
 331 <u>Historic Use:</u>
- 332 Researchers believe that natural borax (or tincal) was first exported from the Far East to Babylon during the
- Bronze Age (around 3,300 to 1,200 BCE), possibly from the dry lakes on the Tibetan plateau (Garrett, 1998;
- Wisniak, 2005; Woods, 1994). It was used in metallurgy and medicine (Wisniak, 2005). Evidence indicates
- that natural borax was later traded in the Middle East (beginning in the eighth century A.D.) for use in
- precious metal refining, building materials (as a component of wall plaster), and ceramics, and later used in goldsmithing in medieval Europe (Garrett, 1998; Ozturk et al., 2010; Woods, 1994).
- 338

339 During the late 19th and early 20th centuries, large borate deposits were found in Turkey and the United

- 340 States, and it was discovered that these minerals could be converted into borax through a reaction with
- 341 sodium sesquicarbonate¹⁰ (Woods, 1994). At that time, a significant amount of borax was used in soap and
- 342 detergent (Travis & Cocks, 1984).
- 343

Boron was recognized as an essential plant nutrient in the early 20th century, specifically in legumes

345 (Loomis & Durst, 1992; Shorrocks, 1997). Later, boron essentiality was identified in a great diversity of

346 plants (Loomis & Durst, 1992). Boron fertilizer application became commonplace for many crops after this

discovery, and it became apparent that each species has a different boron requirement (Blevins &
Lukaszewski, 1998).

348 349

During World War I, the import of potash fertilizers from Germany ceased and new potash sources in the
 United States were used for crop fertility (Shorrocks, 1997). Brine-derived potash from California contained

- 352 elevated levels of boron, sometimes leading to toxicity from over-application (Breckenridge, 1921;
- 353 Shorrocks, 1997). At the same time, small amounts of boron were found to be beneficial to plant growth,
- indicating a small window between a plant's boron requirement and an injurious dose (Blevins &
- 355 Lukaszewski, 1998; Breckenridge, 1921).
- 356

357 Organic Foods Production Act, USDA Final Rule:

- Boron products are not specifically identified by name in the Organic Foods Production Act of 1990
- (OFPA). However, since soluble boron products appear on the National List, Section 2118 (c)(1)(A) [7
 U.S.C. 6517] is applicable.
- 361

Soluble boron products have appeared on the National List for use as micronutrients since it was first
published in the year 2000 (*National Organic Program, 65 Fed. Reg. 80547, 2000*).

365 <u>International</u>

366

367 Canadian General Standards Board Permitted Substances List

¹⁰ Sodium sesquicarbonate is derived from naturally occurring trona ore. It is a combination of sodium carbonate and sodium bicarbonate (Kent, 2012).

368	
369 370	Soluble boron products are permitted by the Canadian Organic Standards at CAN/CGSB 32.311-2020 Table 4.2, column 1, entry for <i>Boron</i> . Borate (boric acid), sodium tetraborate (borax and anhydrous), and
371	sodium octaborate are permitted only when one of the following has been established:
372	 soil and plant deficiencies are documented by visual symptoms
373	 testing of soil or plant tissue demonstrates the need
374	• the need for a preventative application can be documented (CGSB, 2020)
375	
376 377	The <i>Boron</i> entry further references the <i>Micronutrients</i> annotation at CAN/CGSB 32.311 Table 4.2, column 1. This entry permits using chelating agents also appearing on CAN/CGSB 32.311 Table 4.2 with
378 379	micronutrients. The <i>Micronutrients</i> annotation also specifically prohibits ammonium and nitrate forms and those chelated ¹¹ with:
380	• ethylenediaminetetraacetic acid (EDTA)
381	diethylenetriaminenentaacetic acid (DTPA)
382	• ethylenediamine_N N'-bis((2-bydrovynhenyl)acetic acid) (EDDHA) (CCSB 2020)
382	• Entylenedianune-N,N -Dis((2-nydroxyphenyl)acene acid) (EDD11A) (CG3D, 2020).
384	CODEX Alimentarius Commission Guidelines for the Production Processing Labelling and Marketing of
385	Organically Produced Foods (GL 32-1999)
200	The Codey guidelines includes "Trace elements (e.g. heren conner iron mengeness meluhdenum rine)"
201	in Table 1, substances for use in soil fortilizing and conditioning (EAO, 2007). The need must be "recognized by
280	In Table 1, substances for use in soil fertilizing and conditioning (FAO, 2007). The need must be recognized by
389	the certification body or authority (FAO, 2007).
390	European Economic Committee (EEC) Council Boostation EC No. 824/2007 and 880/2008
391	European Economic Community (EEC) Council Regulation, EC No. 854/2007 and 889/2008
392 202	Convert house substances are allowed for soil more convert and fortilization by the European Union encourie
393 204	Several boron substances are allowed for soil management and refinization by the European Union organic
394 205	regulations. EC Regulation No. 889/2008 Article's permits the use of substances appearing in Annex I
395	Provide the nutritional needs of plants cannot be met by certain preventative measures (European
396	Parliament, Council of the European Union, 2008). Annex I permits the use of boric acid, sodium borate,
397	calcium borate, and boron ethanolamine (European Parliament, Council of the European Union, 2003).
398	
399	Japan Agricultural Standard (JAS) for Organic Production
400	
401 402	Trace elements (manganese, boron, iron, copper, zinc, molybdenum, and chlorine) are permitted by the Japanese Agricultural Standard for Organic Plants as fertilizers and soil improvement substances if a crop
403	is unable to grow normally because of a micronutrient shortage (MAFF, 2017).
404	
405	IFOAM – Organics International
406	
407	Boric acid, sodium borate, calcium borate, and "borethanolamin" (presumably referring to boron
408	ethanolamine) of mineral origin are permitted as fertilizers and soil conditioners in the IFOAM NORMS,
409	where soil or plant nutrient deficiency can be documented by soil or tissue testing or diagnosed by an
410	independent expert. Chloride and nitrate forms are prohibited, as are micronutrients used as defoliants,
411	herbicides, or desiccants (IFOAM Organics International, 2019).
412	
413	Evaluation Questions for Substances to be used in Organic Crop or Livestock Production
414	
415	Evaluation Question #1: Indicate which category in OFPA that the substance falls under: (A) Does the
416 417	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,
	¹¹ Chelating agents are molecules that can bind to metals (using coordinate-covalent bonds) with at least two separate

¹¹ Chelating agents are molecules that can bind to metals (using coordinate-covalent bonds) with at least two separate chemical groups (Lehman, 1963; Schubert, 1981). When a chelating agent and metal are in the bonded state, one or more rings is formed as a result. All else being equal, this formation is more stable than non-chelated chemical arrangements (Lehman, 1963; Schubert, 1981).

418 vitamins and minerals; livestock parasiticides and medicines and production aids including netting, 419 tree wraps and seals, insect traps, sticky barriers, row covers, and equipment cleansers? (B) Is the 420 substance a synthetic inert ingredient that is not classified by the EPA as inerts of toxicological concern 421 (i.e., EPA List 4 inerts) (7 U.S.C. § 6517(c)(1)(B)(ii))? Is the synthetic substance an inert ingredient which 422 is not on EPA List 4, but is exempt from a requirement of a tolerance, per 40 CFR part 180? 423 Boron is not specifically addressed in the Organic Foods Productions Act, nor are micronutrients. Synthetic 424 425 soluble boron products are not active ingredients in the above listed categories, or synthetic inert 426 ingredients when used as micronutrients in organic crop production. 427 428 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 429 430 formulation of the petitioned substance when this substance is extracted from naturally occurring plant, 431 animal, or mineral sources (7 U.S.C. § 6502 (21)). 432 433 All soluble boron products are derived from mined borate mineral deposits. Borate minerals can be 434 extracted by surface mining or solution mining (Garrett, 1998). 435 Surface mining involves stripping the surface of vegetation, topsoil and waste rock or blasting 436 open pits with explosives (Garrett, 1998). Deeper ores are reached by cutting benches (ledges) in the pits for access and transport to the surface (Office of Energy Efficiency and Renewable Energy, 437 438 2002). 439 • Solution mining involves the injection of water into subterranean spaces in order to dissolve 440 borates, which can be pumped back as a brine to the surface for processing (Office of Energy 441 Efficiency and Renewable Energy, 2002). 442 443 *Borax/borate salts* 444 Refined sodium borate salts are typically produced by crushing solid borate ores and dissolving in water 445 alongside trona (a double salt of sodium carbonate and sodium bicarbonate), or supersaturating brine with 446 carbon dioxide in the case of solution mining (Office of Energy Efficiency and Renewable Energy, 2002; 447 Smith, 2000). Insoluble waste materials are filtered out of the liquor and disodium tetraborate pentahydrate 448 and decahydrate are selectively crystallized by temperature control and vacuum crystallization, followed 449 by centrifugation and drying (Smith, 2000). To prevent crystallization water loss and caking, disodium 450 tetraborate decahydrate crystals are sometimes washed with a boric acid solution that coats the crystals 451 with a thin layer of the pentahydrate variety (Smith, 2000). 452 453 High purity borax can also be produced in a reaction between boric acid and hot sodium hydroxide (Smith, 454 2000). Various dehydration and rehydration methods can be utilized to selectively produce the different 455 hydration states of disodium tetraborate (Smith, 2000). Boric acid reactions with sodium hydroxide can also 456 be used to produce disodium octaborate tetrahydrate (Kutcel, 2001). 457 Boric acid 458 459 In the United States, boric acid is typically prepared by reacting naturally occurring solid sodium borate minerals with strong mineral acids like sulfuric acid (Smith, 2000). This results in a concentrated solution of 460 461 boric acid and sodium sulfates, after which the boric acid is crystallized by evaporation. In Europe, the 462 source minerals are often calcium or magnesium borate, but the process is similar; sulfuric acid is added, 463 boric acid is crystallized, and calcium and magnesium sulfates are filtered out (Smith, 2000). 464 465 At Searles Lake, California, borax derived from solution mining is chemically bound to an organic¹² chemical in order to facilitate extraction (Garrett, 1998; Smith, 2000). The organic phase (containing the 466 467 borax) is then reacted with sulfuric acid, forming boric acid, sodium sulfate, and impurities. Sodium sulfate is removed through precipitation, and boric acid is crystallized by evaporation (Garrett, 1998; Smith, 2000). 468 469

¹² Containing the element carbon.

470 471 472 473	Some relatively new research has attempted to supplant the use of sulfuric acid with carbon dioxide in a high pressure reactor in order to simultaneously sequester the greenhouse gas and produce purified boric acid from the mineral colemanite (Bingöl & Çopur, 2019). Their proposed reaction follows:
474 475 476	$Ca_2B_6O_{11} \cdot 5H_2O + 2CO_2 + 4H_2O \leftrightarrow 2CaCO_3 + 6H_3BO_3$ Colemanite + carbon dioxide + water \leftrightarrow calcium carbonate + boric acid
477 478 479 480 481 482	The authors propose that the method could be used on an industrial scale and have advantages over the sulfuric acid method; calcium sulfate (gypsum) waste would be eliminated, high-purity boric acid with fewer impurities would be produced, and atmospheric greenhouse gases could be transformed into insoluble mineral constituents for use in building materials and industrial applications (Bingöl & Çopur, 2019).
483 484 485	<u>Evaluation Question #3:</u> Discuss whether the petitioned substance is formulated or manufactured by a chemical process, or created by naturally occurring biological processes (7 U.S.C. 6502(21)).
486 487 488 489	"Soluble boron products" appear on the National List of Allowed and Prohibited Substances at 7 CFR 205.601(j)(7)(i). Soluble boron products are derived from naturally occurring minerals, so are not created by a naturally occurring biological process.
490	Borax/borate salts
491	Two production methods are summarized below.
492	Production method 1:
493 494 495 496	The largest volume of refined sodium tetraborate salts globally is produced at the Rio Tinto Boron Mine, (formerly known as the U.S. Borax Boron Mine) in Boron, California, currently operated by the Rio Tinto Group (Grube, 1970; Smith, 2000). See <i>Evaluation Question</i> #2 for the process of refining sodium borate minerals into purified borax and borax pentahydrate that is used at this refinery (Smith, 2000).
497 498 499 500 501 502 503	Guidance NOP 5033-1 <i>Decision Tree for Classification of Materials as Synthetic or Nonsynthetic</i> states that if a substance has undergone a chemical change (question 2), and the change is not the result of a naturally occurring biological process or by heating or burning biological matter (question 3), then the substance is synthetic (NOP, 2016). Dissolution of borax (tincal), followed by removal of insoluble wastes and selective crystallization, are physical processes. Coating the crystals with disodium tetraborate pentahydrate derived from boric acid that is produced using a chemical process, however, renders the final product synthetic.
504 505 506	Dehydration and rehydration processes used to convert decahydrate to pentahydrate or anhydrous borax are physical processes involving heat and drying.
508 507 508	Production method 2:
509 510 511 512	Sodium tetraborate pentahydrate can also be produced from the mineral colemanite in a complex chemical reaction with sodium carbonate, sodium hydroxide, and boric acid (Mazzinghi, 1989), though a review of the literature is inconclusive regarding the commercial importance of this production method:
512 513 514 515 516	$\begin{aligned} & 2Ca_2B_6O_{11}\cdot 5H_2O + 4Na_2CO_3 + H_2O ~\leftrightarrow 3Na_2B_4O_7\cdot 5H_2O + 4CaCO_3 + 2NaOH\\ & \text{Colemanite + sodium carbonate + water} \leftrightarrow \text{disodium tetraborate pentahydrate + calcium carbonate + }\\ & \text{sodium hydroxide} \end{aligned}$
517 518 519 520 521 522	$2NaOH + 4H_3BO_3 \leftrightarrow Na_2B_4O_7 \cdot 5H_2O + 2H_2O$ Sodium hydroxide + boric acid \leftrightarrow disodium tetraborate pentahydrate + water
523	Boric acid

Industrial production of boric acid relies on the chemical process described in Evaluation Question #2. 524 Mined borate salts of sodium, calcium, or magnesium¹³ are reacted with strong acids to produce boric acid 525 and mineral salts (Kuskay & Bulutcu, 2011; Smith, 2000). Based on Guidance NOP 5033-1, this chemical 526 527 process is synthetic (NOP, 2016). Depending on the source mineral and acid used, the waste salts may be sulfates, chlorides, nitrates, and phosphates of sodium, calcium, and magnesium. 528 529 530 Evaluation Question #4: Describe the persistence or concentration of the petitioned substance and/or its 531 by-products in the environment (7 U.S.C. 6518(m)(2)). 532 533 According to the EPA (2008b), data is limited related to the volume of environmental releases of boron 534 resulting from fertilizer or pesticidal applications, as well as residence times in air, soil, and water. 535 536 As described in Composition of the Substance above, elemental boron does not naturally occur in the 537 environment due to its reactivity (Goldberg, 1997). Boron exists as borate salts, boric acid, or in nearly 538 insoluble silicate minerals (Goldberg, 1997). The by-products resulting from the weathering and 539 breakdown of boron-containing minerals are boric acid or borate anion, depending on the pH of the 540 medium (Woods, 1994). 541 542 The persistence of boron in the environment is dependent on soil type and texture, and climatic region (Goldberg, 1997; Shorrocks, 1997). Boron adsorbs to soil minerals as pH increases, leading to soil boron 543 544 accumulation, but then decreases at pH levels above 10, (Goldberg, 1997). In coarser-grained soils, boron becomes mobile, simultaneously allowing for easier plant uptake and leaching to the water system, while 545 546 finer-grained soils rich in clay minerals (montmorillonite, kaolinite, and chlorite) may hold onto boron 547 (Goldberg, 1997). 548 549 Environmental humidity, soil moisture, and precipitation rates greatly affect boron accumulation in soils 550 (Brdar-Jokanović, 2020; Goldberg, 1997). The mobility of boron in the soil tends to increase in wet or humid 551 zones due to the solubility of borates, and boron concentrations can increase with soil depth as borate leaches downwards (Brdar-Jokanović, 2020). This behavior can lead to deficiency of boron in the soil as 552 553 well as a remobilization into the water system; heavy rain or heavy irrigation can contribute to boron 554 deficiency in plants (Shorrocks, 1997). 555 556 Just as boron concentrations decrease in wet climates, boron accumulates in soils in dry or semi-arid 557 environments (Goldberg, 1997; Shorrocks, 1997). These conditions are exacerbated by further addition of 558 boron from irrigation water derived from desalinated seawater or watersheds associated with boron 559 mining activity (Ozturk et al., 2010; Vera et al., 2019; Yuce & Yasin, 2012). 560 561 Arslan (2013) observed extremely elevated boron levels in streams near boron mining operations in 562 Turkey, reporting a maximum of 16.73 mg/L in stream water and 36.7 mg/L in riverbed sediments. The author determined that the river, sediment, and irrigated land represents a significant sink of boron, with 563 564 the potential for injury to the ecosystem. Rivers draining heavily cultivated farmland in England have been 565 measured to contain up to 0.387 mg/L boron (Kochkodan et al., 2015), a level approximately 40 times lower 566 than the maximum water concentration found in the study in Turkey. Compared to the riverbed sediment 567 values, the compared value is even lower, but sediment values were not explored in the England study. 568 The following evaluation question provides additional information on potential harm to the ecosystem and 569 biological toxicity resulting from elevated boron in the environment. 570 571 Evaluation Question #5: Describe the toxicity and mode of action of the substance and of its breakdown 572 products and any contaminants. Describe the persistence and areas of concentration in the environment 573 of the substance and its breakdown products (7 U.S.C. 6518(m)(2)). 574 575 576 Plants

¹³ Most often, sodium borates are used in the United States (Smith, 2000). Calcium borates are used in European countries and the near East. Magnesium borates are used in Russia (Smith, 2000).

- 577 The generally agreed upon value where many crops exhibit toxicity is greater than 5 mg/L in soil (Ozturk 578 et al., 2010). The mechanism by which boron induces toxicity in plants is mostly unknown, but the number 579 of symptoms is extensive and wide-ranging (Landi et al., 2019; Reid et al., 2004). Landi (2019) reports that
- 580 excess boron can cause:
- metabolic imbalances
- 582
 tissue necrosis¹⁴
 fruit malformation
- 583
 6 In the manormation
 584
 6 root growth suppression
- 6 1000 growth suppression
 585 deficiencies of other nutrients
- 586 reduction of photosynthesis
- 587 thinning of leaves
- 588 inhibition of pollen germination
- genotoxic¹⁵ effects
- 590

Responses vary between plants species. Variations in boron tolerance can occur between different cultivarsof the same plant species (Ozturk et al., 2010).

593

Reid et al. (2004) proposed three likely causes for the onset of excess boron toxicity: disruption to cell wall
 creation, binding and disrupting sugar molecules involved with plant metabolism, and binding to RNA or
 sugars leading to suppression of cell division.

- 597
- 598 Animals and Humans

A lethal dose of boron is estimated to be 400-900 mg/kg body weight in animals of all types (Arslan, 2013;

- Emiroğlu et al., 2010). The acute lethal dose in humans is difficult to determine because an individual's
 response to a single dose varies widely depending on age group, weight, or other underlying conditions.
 Researchers (Bakirdere et al., 2010; Locatelli et al., 1987) estimate that the acute lethal single dose (as boric
- 603 acid) is:
- 2,000-3,000 mg in infants
 - 5,000-6,000 mg in children
 - 15,000-20,000 mg in adults
- 606 607

605

Toxicity has been observed at doses as wide-ranging as 100-55,000 mg, however (Bakirdere et al., 2010).

609

610 The biochemical activity of boron in humans also seems to be related to bonding with sugars, particularly

- 611 ribose, a component of adenosine which plays a role in energy metabolism (Khaliq et al., 2018). It has been
- hypothesized that boron interacts with the release of cellular calcium which is related to bone formation,brain activity, liver function, and immune system function, but specific mechanisms remain unknown
- 613 brain activity, liver fr614 (Khaliq et al., 2018).
- 615

Symptoms of acute boron toxicity in humans include dermatitis, kidney inflammation and failure, edema
 (swelling caused by fluid retention), gastrointestinal discomfort, seizure, and delirium (Bakirdere et al.,

617 (swelling caused by fluid retention), gastrointestinal discomfort, seizure, and delirium (Bakirdere et al.,
618 2010; Khaliq et al., 2018; Kingma, 1958). Chronic ongoing exposure has been linked to reproductive effects

such as testicular degeneration, low sperm count, atrophy of seminiferous tissues, and reduction in

- 620 ovulation in animal tests, but these effects have not been conclusively demonstrated in humans (Bakirdere 621 et al., 2010; Khaliq et al., 2018).
- 621 622

623 See *Evaluation Question* #4 for information on the persistence of boron.

624

625 <u>Evaluation Question #6:</u> Describe any environmental contamination that could result from the

- 626 petitioned substance's manufacture, use, misuse, or disposal (7 U.S.C. 6518(m)(3)).
- 627

¹⁴ Necrosis is the process whereby plant tissue dies due to disease or injury (Gowariker et al., 2009).

¹⁵ Genotoxic means that a substance is damaging to genetic material, such as causing DNA mutation or large changes to chromosome structure (Gad, 2016).

- The environmental effects of surface and subterranean boron mining are inherently significant at the local level and contribute to water contamination and reduction of biodiversity.
- 630
- 631 Sulfuric acid is used as a reactant to make boric acid from colemanite, and calcium sulfate is sometimes
- 632 produced as a by-product (see *Evaluation Question* #2). This results in a significant waste stream and can
- have environmental consequences related to the build-up of industrial waste (Bingöl & Çopur, 2019).
- 634 Wastewater discharge is also a source of boron pollution since boron appears in some soaps and washing
- 635 chemicals (Emiroğlu et al., 2010).
- 636

637 Boric acid and borate salts are both soluble and easily adsorbed into soil and sediment (Office of Toxic Substances, 1975). As of 1975, a significant percentage of boron released into the environment resulted from 638 detergents used in washing chemicals, but due to the tendency of boron to adsorb to sediments, contact 639 640 with soil eliminates release to the water system (Emiroğlu et al., 2010; Office of Toxic Substances, 1975). A 1975 estimate by the Office of Toxic Substances department of the EPA (1975) indicated that laundry 641 642 products made up the bulk of anthropogenic boron releases to the environment at 14,000 metric tons, 643 followed by agricultural production (7,000 tons), coal burning (4,000 tons), mining (3,000 tons), and glass and ceramics (1,500 tons), most of which ends up in the water system due to solubility. More recent 644

- 645 estimates could not be located.
- 646
- 647 Borate deposits, being related to volcanic activity, often contain elevated levels of arsenic and heavy metals
- 648 (Drever, 1997). However, data on environmental contamination associated with boron mining in the
- 649 United States was scarce at the time of this writing. The only information found was from a request to the
- 650 California Regional Water Quality Control Board from U.S. Borax to update mine discharge infrastructure
- 651 (California Regional Water Quality Control Board, Lahontan Region, 2018). U.S. Borax, Inc., Rio Tinto
- Minerals reported leakage of processing fluids and arsenic-rich wastewater into the local aquifer and sought to improve containment lining systems.
- 653 sought to improve654
- Borate mining in western Anatolia, Turkey, has led to significant boron, arsenic, and strontium
- contamination in irrigation water, surface water, and groundwater (Gemici et al., 2008; Yuce & Yasin,
- 657 2012). Yuce & Yasin (2012) reported that the level of arsenic in the majority of groundwater samples
- exceeded safe drinking water levels as allowed by the US EPA (10 μ g/liter). This was attributed to improper storage of mine tailings, which also contained elevated levels of strontium. Gemici (2008) found
- 659 improper storage of mine tailings, which also contained elevated levels of strontium. Genici (2008) round 660 arsenic levels as high as 911 µg/liter in groundwater samples taken near boron mines, and all 25 surface
- and groundwater samples taken exceeded the recommended $10 \,\mu g/liter^{16}$. Ozturk et al. (2010) also
- 662 describes significantly elevated boron levels in watersheds near Turkish boron mines, resulting in boron
- toxicity in agricultural lands and a reduction in plant biodiversity in undeveloped areas nearby.
- 664
- Also in western Turkey, biodiversity of aquatic organisms was shown to be reduced in waters and
 sediments associated with elevated boron concentration related to mine leachate, particularly among
 bottom-dwelling (benthic) invertebrates (Arslan, 2013; Emiroğlu et al., 2010).
- 668
- Fish can tolerate boron concentrations of 17 parts per million (ppm) or higher without apparent effect
 (Garrett, 1998). The highest boron concentration recorded in the studies conducted by Emiroğlu et al. (2010)
- was 3.88 ppm in watersheds associated with Turkish borate mine drainage. At 30 ppm, phytoplankton
 experience reduced photosynthesis (Garrett, 1998).
- 673

674 <u>Evaluation Question #7:</u> Describe any known chemical interactions between the petitioned substance

- and other substances used in organic crop or livestock production or handling. Describe any
 environmental or human health effects from these chemical interactions (7 U.S.C. 6518(m)(1)).
- 676 677

¹⁶ Acute arsenic poisoning can result from a single dose as low as 5 mg, resulting in vomiting and diarrhea. A 100-300 mg dose results in death, with the lethal dose calculated to approximately 0.6 mg/kg body weight/day (Ratnaike, 2003). Chronic poisoning resulting from prolonged exposure to small amounts of arsenic over time is more difficult to quantify and can exhibit a wide range of serious symptoms and disease (Ratnaike, 2003).

678 Boron deficiency has been shown to be more prevalent on land that has been treated with lime or calcium 679 carbonate, particularly during times of drought or in soils that drain easily (Shorrocks, 1997). Boron tends 680 to become less available to plants at higher pH, leading to deficiency potential (Abou Seeda et al., 2021). 681 682 The addition of organic matter to soil increases the availability of boron to plants and microorganisms 683 (Vera et al., 2021). Vera hypothesized that this occurs through a possible mechanism involving interaction 684 with easily broken-down carbon and nitrogen compounds, which effectively release boron to plants and 685 microbes as they degrade. 686 687 Boron sometimes appears to have an antagonistic relationship with calcium uptake (Ahmed et al., 2011; Shkolnik, 1984). In field studies, Ahmed et al. (2011) found calcium content decreased in cotton leaves, 688 689 burrs, stems, seeds and lint after increasing applications of borax fertilizer. In contrast, other researchers 690 have noted a synergistic relationship with calcium (in tomatoes), possibly arising from the complex 691 interactions of soil type, plant, and biochemical processes in different environments (Abou Seeda et al., 692 2021). Similarly conflicting reports have been published for nitrogen, phosphorus, potassium, magnesium, 693 zinc, copper, iron, molybdenum, and manganese (Abou Seeda et al., 2021). Interactions may not be related 694 at all. Boron deficiency can exhibit the same effects as boron excess in relation to the uptake of other 695 nutrients, and the full picture of chemical interactions remains unresolved (Abou Seeda et al., 2021). 696 697 Boron addition appears to play a role in blocking the availability of nitrogen to plants (Vera et al., 2019). 698 This may be due to the formation of boron-nitrogen compounds that do not readily break down (Vera et 699 al., 2019). 700 701 Evaluation Question #8: Describe any effects of the petitioned substance on biological or chemical 702 interactions in the agro-ecosystem, including physiological effects on soil organisms (including the salt 703 index and solubility of the soil), crops, and livestock (7 U.S.C. 6518(m)(5)). 704 705 Only recently have researchers begun to address the effect of boron on the soil microbial community, and 706 its effect remains largely unknown. 707 708 In a study of microorganisms and ryegrass in Spain, Vera et al. (2019) treated high carbonate soils with 709 boric acid and borax. At the highest boron doses used (50 mg/L), the authors found a reduction in soil 710 microbial respiration. With boric acid, they observed a reduction of microbial biomass, but an overall 711 increase in total biomass when using borax. Both boric acid and borax treatments led to a reduction in 712 fungal biodiversity. The high levels of boron also negatively affected the ryegrass. Vera et al. (2019) 713 concluded that high boron input interfered with the soil enzyme urease¹⁷, reducing nitrogen uptake by 714 plants and microbes. At lower levels (1 mg/L), no harm was observed to soil or plants. 715 716 Lemon trees are particularly sensitive to boron and show symptoms of toxicity when irrigated with water 717 having a boron concentration of 1 mg/L. Another study by Vera et al. (2021) looked at the effect of boron 718 (ranging from 1 – 15 mg/L) on lemon trees and soil microbiota in a) conventional soils and b) soils 719 amended with composted sheep manure. The authors concluded that soils amended with organic material 720 showed greater mobility of boron, as well as increased boron uptake by plants. The amended soil also 721 resulted in increased tolerance to excess boron by lemon trees. Microbial biomass, particularly bacterial, 722 was also reduced with increasing boron accumulation, but the addition of organic matter helped the 723 microbial community resist boron toxicity. The lemon trees eventually died when the boron content of the 724 water reached 15 mg/L, but the authors propose this may have been a result of fungal infection due to 725 weakened plants, rather than directly resulting from boron poisoning (Vera et al., 2021). 726 727 With increasing demand for freshwater used in irrigation, desalinization of seawater has become more 728 realistic in certain coastal arid regions such as Spain, Israel, and California (Martínez-Alvarez et al., 2016). 729 Desalinated seawater is rich in boron (Vera et al., 2019). Desalinated seawater has a boron content between

¹⁷ It is established in scientific literature that boron can inhibit the soil enzyme, urease (Kumar & Kayastha, 2010). Urease breaks down urea into ammonia.

- 730 0.5 - 1 mg/L, but boron can accumulate to higher levels when regularly applied, particularly in arid and 731 semiarid regions where borate is not sufficiently absorbed by biology, adsorbed to soil minerals, or leached 732 away (Vera et al., 2021). 733 734 Some livestock appear to be less affected by boron compared with plants. For example, cows showed no ill 735 effects when exposed to 120 mg/L boron in drinking water (Garrett, 1998). Sheep are less tolerant, and 736 developed intestinal inflammation after grazing where soil boron ranged between 30-300 mg/L, when their 737 drinking water contained boron between 1-20 mg/L, or when eating food with 40 mg/L boron (Garrett, 738 1998). This still remains above the generally accepted level at which many crops are affected, of 5 mg/L 739 (Ozturk et al., 2010). 740 741 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)(i)). 742 743 744 Natural environmental releases of boron, such as the weathering of rocks, volatilization of seawater, and 745 volcanic processes outweigh anthropogenic releases (US EPA, 2008a). Of the environmental releases caused 746 by humans, agriculture makes up just one source of many, including coal power generation, glass 747 manufacturing, release of wastewater containing borate cleaning agents, borate mining, leaching or 748 burning of treated lumber, and sewage sludge (US EPA, 2008a). The combined human releases of boron are 749 largely insignificant when compared to natural sources arising from the breakdown of rocks, ocean 750 evaporation, and volcanic activity (Landi et al., 2019; Stangoulis & Reid, 2002). 751 752 Ozturk (2010) estimates that boron deficiencies may occur in plants grown in soils with boron 753 concentrations less than 0.5 mg/L, but when boron exceeds 2 mg/L, decreased production may be 754 apparent. Soil boron concentrations greater than 5 mg/L may lead to boron toxicity and a reduction in crop vield, indicating that the addition of large amounts of boron fertilizer should be avoided (Ozturk et al., 755 756 2010). Very small amounts of boron fertilization (1-2 kg/hectare) will correct deficiencies, and rates as low 757 as 100-200 g/hectare may be sufficient in some crops (Shorrocks, 1997). When used as a micronutrient 758 fertilizer, boron carries a low risk of significant environmental contamination when used as directed to 759 remedy a deficiency. Plants absorb soluble boron rapidly (Shorrocks, 1997) and the remainder is either 760 easily leached away or adsorbed to clay minerals in the soil, which does not evoke toxicity in plants 761 (Goldberg, 1997). 762 763 Based upon the information provided in *Evaluation Questions* #4 through #8, the application of boron 764 fertilizers is not likely to contribute to extensive and direct environmental harm. Over-application of boron 765 is more likely to harm the crops themselves than the surrounding environment. However, the effects of 766 boron mining on local environments are significant, including water contamination and biodiversity loss. Large-scale borate mining occurs in a limited number of regions around the world, so associated 767 768 environmental effects are localized. With that said, only a small fraction of mined borates are used for 769 agricultural purposes (Woods, 1994). 770 771 Evaluation Question #10: Describe and summarize any reported effects upon human health from use of 772 the petitioned substance (7 U.S.C. 6517(c)(1)(A)(i), 7 U.S.C. 6517(c)(2)(A)(i)) and 7 U.S.C. 6518(m)(4)). 773 774 Boron is essentially non-toxic to humans at levels found in the environment, even in areas where boron is 775 extremely concentrated such as mines, refineries, and other industrial settings (ATSDR, 2010). The EPA 776 does not currently regulate boron in drinking water, and posits that the boron level in drinking water poses 777 little to no threat to public health (US EPA, 2008a). As a fertilizer, the European Commission (EC, 2008) 778 states that: 779 780 "...it has been assumed that inadvertent ingestion of boron fertilisers (amongst those farmers using such 781 fertilisers) is unlikely to exceed 100 mg/day. Since boron fertilisers may contain around 10% boron, it would 782 appear that the intake of boron could approach the tolerable upper intake level (UL) value of 10 mgB/day [mg of 783 boron] (as recommended by EFSA). However, the UL value is based on consideration of routine daily exposures
- whereas fertilisers would only be applied sporadically during the course of a year.

785 786 On this basis, it is considered unlikely that the exposure to boron through the use of boron fertilisers would 787 routinely exceed the UL value of 10 mgB/day. This, in turn, suggests that, although borates are likely to be 788 present as free constituents in boron fertilisers and are classified as toxic to reproduction category 2, the 789 associated risks to farmers (and other consumers) using boron fertilisers are unlikely to be of serious concern." 790 791 Reproductive toxicant category 2 under the EC Regulations (European Parliament, Council of the 792 European Union, 2008) refers to substances in which there is some experimental evidence of toxicity to 793 sexual function, fertility, or development, but results are not sufficiently convincing. Categories 1A, and 1B 794 contain those substances known to be reproductive toxicants based on conclusive evidence in human and 795 animal studies, respectively. 796 797 Modern reports of lethal boron poisoning involve accidental or intentional ingestion of boric acid, though 798 88 percent of acute oral exposures were still asymptomatic (ATSDR, 2010). Deaths are largely attributed to 799 infant formula accidentally prepared with boric acid solution in place of water, leading to organ 800 degeneration (ATSDR, 2010; Wong et al., 1964). Thirteen children died in Malaysia following the 801 consumption of noodles contaminated with aflatoxin and boric acid, but the toxicity of the boric acid 802 contamination compared to aflatoxin was not determined (ATSDR, 2010). Symptoms resulting from acute exposure to boric acid by ingestion include vomiting, diarrhea, kidney failure and heart failure, but 803 804 newborn infants appear to be at far higher risk than adults (ATSDR, 2010; Wong et al., 1964). 805 806 The Agency for Toxic Substances and Disease Registry (2010) reports that no clear links between serious illness and chronic occupational exposure to boron have been identified in humans through inhalation or 807 808 skin contact beyond transient irritation of the skin, eyes, nose and throat. Tests have shown that at very 809 high doses ($\geq 100 \text{ mg boron/kg body weight/day}$), animals that are fed boric acid for two weeks to two years become sterile, and significant degeneration of the testicles occurs in mice, rats, and dogs (ATSDR, 810 811 2010; Dieter, 1994; Fukuda et al., 2000; Scialli et al., 2010). Exposure by inhalation did not produce similar 812 effects in rats (ATSDR, 2010). 813 814 Average human consumption of boron in the United States is estimated to be approximately 1 mg/day, but 815 this can vary by diet and region (Meacham & Hunt, 1998; US EPA, 2008a). In Chinese borate mine workers, 816 higher levels of boron may be absorbed by inhalation and ingestion, averaging 11.84 mg boron/day 817 (ATSDR, 2010), but no effects on the male reproductive organs were found, even at levels as high as 41.2 818 mg/day (Scialli et al., 2010). The levels of ingested boron determined to be detrimental in animal tests far 819 exceeds the levels encountered by humans, even with daily occupational contact with boron (Bakirdere et 820 al., 2010). In terms of skin contact, borate ointments and topical medicines are less irritating than soap, and 821 some studies on borate mine workers in California concluded that their lung function was actually 822 healthier than the U.S. average (Garrett, 1998). 823 824 In large-scale borate complexes in Turkey, significant elevation of boron in water, sediments, and wildlife 825 of the region was observed, but no increased incidence of disease was apparent in the residents, whose 826 diets include local plants and fish (Emiroğlu et al., 2010). No reproductive, nervous system, or 827 cardiovascular system abnormalities were reported by the authors, despite many residents working in and 828 living nearby the boron mines. 829 830 One study observed a correlation between elevated boron in the drinking water supply and the incidence 831 of reduced birth weight and birth length among newborn babies in Argentinian Andes communities near 832 boron and lithium mines (Igra et al., 2016). Though the correlation was significant, additional factors may 833 have been causative, including elevated lithium in the drinking water, the low-oxygen high-altitude

- 834 environment of the study area, and that nearly half of the participants chewed coca leaves during
- 835 pregnancy (Bolt et al., 2017; Harari et al., 2015; Igra et al., 2016).
- 836

Some newer research has begun to focus on boron supplementation in the human diet due to its low
dietary availability and a myriad of potential health benefits. Beneficial impacts to bone health, cancer

839 prevention, wound healing, magnesium absorption, cognitive function, chemotherapy recovery, and

hormone utilization have been demonstrated when boron is consumed in excess of the average dietary
intake, particularly in those whose diets do not include substantial fruits, vegetables, and nuts (Bakirdere et al., 2010; Khaliq et al., 2018; Pizzorno, 2015).

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

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848 Since boron is an elemental substance and essential for plant health, there are no absolute substitutes for 849 boron itself. Another element on the periodic table, germanium, has been shown to replace boron in certain metabolic processes (Loomis & Durst, 1992). Ishii et al. (2002) determined, however, that germanium was 850 851 not a viable alternative to boron in the case of cell wall reinforcement because it does not form a stable cross-link of the RG-II polysaccharide (see Action of the Substance above). Additionally, the germanium 852 concentration on the Earth's crust is just 1.5 parts per million (ppm) on average, far lower than the average 853 854 occurrence of boron at 10 ppm, so it is not an economically feasible alternative (USGS Mineral Resources 855 Program, 2015).

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857 Nonsynthetic borate mineral fertilizers may also be used in place of synthetic refined borates or boric acid.

- Boron can be supplied to soil or plants through the application of nonsynthetic, mined colemanite (calcium
 borate), ulexite (sodium calcium borate hydroxide), and probertite (sodium calcium borate hydroxide)
- ores. Typically, these natural borate minerals provide for far slower release of boron due to reduced
- solubilities, and provide less boron per volume of application in comparison with refined borates and boric
- acid (Broschat, 2008). Unrefined borate minerals sometimes contain higher levels of arsenic, strontium,
- aluminum, iron, and sulfates, (ETiMADEN ETIMINE USA Inc., 2018b, 2018a)¹⁸, which might be expected
- for minerals derived from volcanic or hydrothermal processes (as described in *Source or Origin of the Substance* above).
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867 Borate products produced by evaporative rather than reactive mechanisms may be considered

nonsynthetic when following NOP 5033-1, *Guidance, Decision Tree for Classification of Materials as Synthetic or Nonsynthetic* (NOP, 2016). However, it is difficult or impossible to compare production volumes of

- nonsynthetic vs. synthetic products (Garrett, 1998). The limited number of competitive global producers
- (sometimes referred to as an oligopoly) introduces uncertainties in borate production data. High-purity,
- refined (synthetic) products have tended to prevail in the marketplace since the mid-1990s (Garrett, 1998).
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874 OMRI currently lists products in the following categories (OMRI, 2021):

- Borates, nonsynthetic: 6 products
 - Borax (Sodium Tetraborate), nonsynthetic: 2 products
- Boron Products, synthetic: 69 products¹⁹
- 877 878

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

6 Given the prevalence of boron deficiency around the world, the only alternative to direct boron application for plants grown in deficient areas is enhancing the uptake of boron by plants (Shireen et al., 2018). Boron is

- ubiquitous in the Earth's crust, but typically only at very low concentrations (Woods, 1994), so enhancing
- plant uptake in deficient areas could help meet boron needs without requiring the application of boron
 fertilizer (Shireen et al., 2018).
- 886
- Shireen et al. (2018) have proposed several methods to improve boron uptake, including selective breeding,
 grafting of plants onto plant rootstocks known to express enhanced boron uptake or plants with deeper
- root systems, application of growth regulators or mycorrhizal fungi, and through the use of

¹⁸ The ETiMINE USA Inc. website contains composition data for ulexite and colemanite consumer products. Of note, their ulexite product contains 30 ppm arsenic, 0.1% aluminum oxide, 0.6% strontium oxide, 0.02% iron oxide, and 0.2% sulfate. Their colemanite contains 25 ppm arsenic, 0.25% aluminum oxide, 1.15% strontium oxide, 0.04% iron oxide, and 0.3% sulfate.

¹⁹ Many of these are also listed in other categories, indicating that these are blended fertilizer products.

(Shireen et al., 2018).

nanotechnology. As described above, boron may leach down through the soil in wet environments (BrdarJokanović, 2020), so deeper root systems may reach the deeper leached boron. Selective breeding of plants

- with deeper or more extensive root morphology may help alleviate boron deficiency near the surface
- (Shireen et al., 2018). Citrus, stone fruits, grapes, pistachios, and tomatoes have exhibited increased tissue
- boron concentration resulting from grafting onto other varieties known to uptake boron more efficiently
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The addition of humic substances, amino acids, composted sewage sludge, and seaweed extracts to the soil was shown to increase the acquisition of some micronutrients (possibly through complexing mechanisms), but boron uptake specifically was not explored (Shireen et al., 2018).

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Mycorrhizal fungi are essential elements of the soil for many plant nutrient uptake mechanisms. Lavola et
 al. (2011) described significant increases in the boron concentrations of ectomycorrhizal fungi in plots
 fertilized with boron, indicating that these fungi may store soil boron despite little evidence that fungi
 require boron for growth. The authors were not able to conclude whether or not that stored boron would

905 be mobile and available to plants (Lavola et al., 2011).

Some bacterial species have also been shown to absorb high levels of boron in soils, and these might be
utilized to improve available boron mobility to plants as well (Shireen et al., 2018). Novel nanomaterials,
such as nanoparticle chitosan and absorbent polymers, have been shown to improve micronutrient uptake,
reduce fertilizer needs, increase water retention, and reduce leaching, which could help to reduce boron
fertilization requirements (Shireen et al., 2018).

Report Authorship

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All individuals are in compliance with Federal Acquisition Regulations (FAR) Subpart 3.11 – Preventing
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