United States Department of Agriculture Agricultural Marketing Service | National Organic Program Document Cover Sheet https://www.ams.usda.gov/rules-regulations/organic/national-list/petitioned

Document Type:

□ National List Petition or Petition Update

A petition is a request to amend the USDA National Organic Program's National List of Allowed and Prohibited Substances (National List).

Any person may submit a petition to have a substance evaluated by the National Organic Standards Board (7 CFR 205.607(a)).

Guidelines for submitting a petition are available in the NOP Handbook as NOP 3011, National List Petition Guidelines.

Petitions are posted for the public on the NOP website for Petitioned Substances.

⊠ Technical Report

A technical report is developed in response to a petition to amend the National List. Reports are also developed to assist in the review of substances that are already on the National List.

Technical reports are completed by third-party contractors and are available to the public on the NOP website for Petitioned Substances.

Contractor names and dates completed are available in the report.

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alfur is a nonmetallic element of group 16 in			
rins, which dossess different in chemical of			
	roperties (e	e.g., solubility, relative density, crystalline form, etc.	
teudel 1982).			
ourses on Origin of the Substances			
Source or Origin of the Substance:			
Sulfur is one of few elements found in its elemental form in nature, typically in limestone/gypsum formations, limestone/anhydrite formations associated with salt domes, or in volcanic rock (d'Aquin 2007)			
Elemental sulfur – in nearly pure form, extracted from salt domes – has been obsolete since the late 20th century. Current sulfur production is as a side product of other industrial processes, such as oil refining. In			
5 1	1	1 0	
these processes, sulfur often occurs as undesired or detrimental compounds, mainly hydrogen sulfide. Hydrogen sulfide is recovered into elemental sulfur by the Claus process (Eow 2002).			
yurogen suinde is recovered into elementa	ii suitur by	the Claus process (Eow 2002).	
roperties of the Substance:			
nysical and chemical properties of the subs	tance are su	ummarized in Table 1.	
Table 1. Physical and (Themical Pr	roperties of Sulfur (Lide 2003).	
	chemical I I	contract of Sumar (Line 2000).	
Property Chemical formula	1	Value	

32.06 g/mol

insoluble

120 °C

Light yellow flakes, crystals, or powder

Molar mass

Appearance Solubility, water

Melting point

Property	Value
Density	2.1 g/cm^3

47

- 48 Sulfur forms polyatomic molecules with different chemical formulas, the best-known allotrope
- being octasulfur, cyclo- S_8 (Rettig 1987). Octasulfur is a soft, bright-yellow solid that is odorless and
- 50 sublimes easily (Earnshaw 1997). At elevated temperatures below its melting temperature, cyclo-octasulfur
- 51 changes from α -octasulfur to the β -polymorph. The structure of the S₈ ring is virtually unchanged by this 52 phase change, which affects the intermolecular interactions. Between its melting and boiling temperatures,
- 53 octasulfur changes its allotrope again, turning from β -octasulfur to γ -sulfur, again accompanied by a lower
- 54 density but increased viscosity due to the formation of polymers. At higher temperatures, the viscosity
- 55 decreases as depolymerization occurs. Molten sulfur assumes a dark red color above 200 C. All stable
- 56 allotropes of sulfur are excellent electrical insulators.
- 57 Sulfur burns with a blue flame with formation of sulfur dioxide, which has a suffocating and irritating
- odor. Sulfur is insoluble in water but soluble in nonpolar organic solvents, such as carbon
- 59 disulfide and benzene. Sulfur reacts with nearly all other elements except gold, platinum, iridium,
- 60 nitrogen, tellurium, iodine, and the noble gases. Some of those reactions need elevated temperatures
- 61 (Earnshaw 1997).

62 Specific Uses of the Substance:

- 63 Elemental sulfur is a commonly used pesticide on many American and European farms. It is approved for
- 64 use on both conventional and organic crops to help control fungus and other pests. It is also used as a soil
- 65 amendment by using the strong acidifying effect to replace sodium with calcium on high pH alkali spots.

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

Elemental sulfur is currently listed on the National List of Allowed and Prohibited Substances as a synthetic
 substance allowed for use in organic crop production for the following categories:

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74

- For uses as an insecticide, including acaricides or mite control (7 Code of Federal Regulations (CFR) 205.601 (e)(5)).
- For plant disease control (7 CFR 205.601(i)(10)).
- As plant or soil amendments (7 CFR 205.601(j)(2)).
- Sulfur is listed as a stabilizer when used in a pesticide formulation applied to animals (40 CFR 180.930).
- 75 76

577 Sulfur is currently registered for use under the U.S. Environmental Protection Agency (EPA)'s Federal

- Insecticide, Fungicide, and Rodenticide Act (FIFRA) Section 3 as an insecticide and fungicide on a wide range of field and greenhouse-grown food and feed crops, livestock (and livestock quarters), and indoor
- and outdoor residential sites. Use sites include tree fruit, berries, vegetables, root crops, field crops, pets
- and outdoor residential sites. Use sites include tree truit, berries, vegetables, root crops, field crops, pe
 (dogs), ornamentals, and turf (including residential lawns and golf courses). Sulfur is also one of the
- active ingredients in four fumigant (gas-producing) cartridge products which are used for rodent control
- 83 on lawns, golf courses, and in gardens.

8485 <u>Action of the Substance:</u>

- 86 Sulfur kills fungi on contact (Turner 2015). The way sulfur works is not completely understood. Some
- 87 researchers believe sulfur may react with plants or fungi to produce a toxic agent (McCallan 1949).
- However, the main theory is that sulfur enters fungi cells and affects cell respiration (Williams 2004). Sulfur
- can kill insects if they touch it or eat it (Turner 2015). It disrupts their normal body function, altering their
- 90 ability to produce energy (Sparks 1996).
- 91
- As a fertilizer, sulfur is readily converted to sulfate (SO_4^{2-}) by autotrophic bacteria for plant uptake.
- As a soil amendment, sulfur's natural conversion to sulfate in the form of sulfuric acid can be used to lower
- the pH of alkaline soil to a range of 5.5 to 7.0 that is more suitable for plant growth.

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

- 97 Elemental sulfur is not effective as a soil amendment unless finely ground sulfur is formed into granules or
- 98 flakes using additives that bind the small particles together and disintegrate rapidly after soil application.

Binding agents include sodium bentonite, sodium sulfate, calcium sulfate (gypsum), and calcium
 lignosulfate or combinations of these. These flaked materials will contain about 90% sulfur. Finely ground

- lignosulfate or combinations of these. These flaked materials will contain about 90% sulfur. Finely ground
 or molten sulfur can be added to anhydrous ammonia or to dry fertilizer during manufacturing. Also,
- 102 finely ground sulfur can be added to suspension fertilizers.
- 103

104 The common dry fertilizers of this type are ammonium sulfate, gypsum, single superphosphate, and

105 potassium sulfate; the liquid fertilizers are ammonium thiosulfate, ammonium bisulfate, and ammonium

106 polysulfate (Nehb and Vydra 2005). Sulfur can also be added to some non-sulfur fertilizers (in combination

- 107 with phosphate rock, sulfur-coated urea, and potassium chloride). Sulfur-bentonite is a new type of 108 fertilizer, typically 10% bentonite and 90% sulfur. The bentonite swells in contact with water and the sulfur
- 108 fertilizer, typically 10% bentonite and 90% sulfur. The bentonite swells in contact with water and the sulfur 109 particles disintegrate to particles of varying size, which secures the availability of sulfur to the plant over a
- 110 long time period (Nehb and Vydra 2005).
- 111
 112

113

Status

- 114 Historic Use:
- 115 According to the EPA, "sulfur has been known and used as a pesticide since very early times and has been
- registered for pesticidal use in the United States since the 1920s" (US EPA 1991). Sulfur plays an important
- role in agriculture production, both as a fertilizer for supporting plant nutrition and as a natural pesticide.
- 118 The crop yield in sulfur-deficient areas can be improved by application of sulfur-containing fertilizers.
- 119 Sulfur is after nitrogen, phosphorus, and potassium the fourth major plant nutrient and is essential for
- 120 crop growth. Its vital role is to form the amino acids methionine, cystine, and cysteine, which are crucial to
- the formation of proteins. Sulfur reduces the quantity of nonprotein nitrogen and nitrate; it is also
- necessary for the formation of chlorophyll, enzymes, and vitamins (Nehb and Vydra 2005).
- 123

124 Fine elemental sulfur has been used traditionally as a fungicide. Because of the development of highly

- effective organic fungicides, this use of elemental sulfur is declining. Sulfur, generally applied by spraying,
- has the advantage of not being consumed by the plant; residues are washed off by rain and act as a nutrient
- 127 in the soil.128

129 Organic Foods Production Act, USDA Final Rule:

- 130 Under the Organic Foods Production Act, elemental sulfur falls under the category of "copper and sulfur
- 131 compounds." Exemption for sulfur in organic production and handling operations is due to sulfur's
- 132 classification by the EPA as a minimal risk inert ingredient on their List of Inert Pesticide Ingredients (List
- 133 4A) and an exemption from a requirement of a tolerance per 40 CFR 180.1236.
- 134
- Additionally, as stated in the summary of petitioned use, elemental sulfur is currently listed on the National List
- of Allowed and Prohibited Substances as a synthetic substance allowed for use in organic crop production for the following categories:
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143

- For uses as an insecticide, including acaricides or mite control (7 Code of Federal Regulations (CFR) 205.601 (e)(5)).
 - For plant disease control (7 CFR 205.601(i)(10)).
 - As plant or soil amendments (7 CFR 205.601(j)(2)).

144 International

- 145 The Canadian General Standards Board (CGSB) includes non-synthetic elemental sulfur as a permitted
- 146 substance for organic production systems under CAN/CGSB-32.311-2015 for use as a soil amendment
- 147 where more buffered sources of sulfur are not appropriate and as a foliar application. Chemically
- 148 synthesized substances cannot be added, and chemical treatment is prohibited. The CGSB also permits the
- 149 use of sulfur for the control of external parasites and sulfur smoke bombs in conjunction with other
- 150 methods used for rodent control when a full pest control program is maintained but temporarily
- 151 overwhelmed.
- 152

153 154 155 156	The Codex Alimentarius Commission's Guidelines for the Production, Processing, Labelling and Marketing of Organically Produced Foods (GL 32-1999) lists elemental sulfur as an allowed substance for pest and disease control.
150 157 158 159	The European Economic Community (EEC) Council Regulation, authorized under Regulation (EEC) No 2092/91 and carried over by Article 16(3)(c) of Regulation (EC) No 834/2007, permits the use of sulfur as a fungicide, acaricide, and repellent in organic food production.
160	Tungiciue, acariciue, and repenent in organic rood production.
161	The Japan Agricultural Standard (JAS) for Organic Production (Notification No. 1605 of 2005) permits the
162	use of sulfur as a fertilizer or soil improvement substance and as a substance for plant pest and disease
163	control.
164	
165	The International Federation of Organic Agriculture Movement's (IFOAM) Norms for Organic Production
166	and Processing lists sulfur as an approved substance for pest and disease control, for use as fertilizer/soil
167 168	conditioner, and for use as a crop protectant and growth regulator.
168	
170	Evaluation Questions for Substances to be used in Organic Crop or Livestock Production
171	L'unanton Questions for Subsumees to be used in organic crop of Errestoer Frouderion
172	Evaluation Question #1: Indicate which category in OFPA that the substance falls under: (A) Does the
173	substance contain an active ingredient in any of the following categories: copper and sulfur compounds,
174	toxins derived from bacteria; pheromones, soaps, horticultural oils, fish emulsions, treated seed,
175	vitamins and minerals; livestock parasiticides and medicines and production aids including netting,
176	tree wraps and seals, insect traps, sticky barriers, row covers, and equipment cleansers? (B) Is the
177	substance a synthetic inert ingredient that is not classified by the EPA as inerts of toxicological concern
178 179	(i.e., EPA List 4 inerts) (7 U.S.C. § 6517(c)(1)(B)(ii))? Is the synthetic substance an inert ingredient which
179	is not on EPA List 4, but is exempt from a requirement of a tolerance, per 40 CFR part 180?
180	The petitioned substance, elemental sulfur, contains sulfur as an active ingredient that falls under the
182	aforementioned category of "copper and sulfur compounds." Sulfur is classified by the U.S. EPA on their
183	List of Inert Pesticide Ingredients (List 4A), as a minimal risk inert ingredient. Sulfur is also a substance
184	exempt from a requirement of a tolerance per 40 CFR 180.1236.
185	
186	Evaluation Question #2: Describe the most prevalent processes used to manufacture or formulate the
187	petitioned substance. Further, describe any chemical change that may occur during manufacture or
188 189	formulation of the petitioned substance when this substance is extracted from naturally occurring plant, animal, or mineral sources (7 U.S.C. § 6502 (21)).
189	animal, or initieral sources (7 0.5.C. § 0502 (21)).
191	World resources of sulfur have been estimated at 25×10 ⁹ tons: 4.0% as elemental sulfur; 4.1% in sulfide
192	ores; 83.6% in coal; 3.0% in crude oil; 5.3% in natural gas (Nehb and Vydra 2005). Elemental sulfur and
193	sulfur containing ores are found in the upper layers of the earth's crust and are either of sedimentary or
194	volcanic origin, but ore bodies worthy of large-scale exploitation are restricted to only a few regions.
195	Depending on the geology of the deposit, sulfur ore is excavated by traditional open-pit or underground
196	mining operations. Elemental sulfur can be extracted from sulfur ores by various processes (e.g., flotation,
197	autoclaving, filtration, melting out, etc.). The nature of the deposit and economics dictate the applied
198	extraction process. Deposits of elemental sulfur are directly reclaimed by direct infusion with hot water,
199	known as the Frasch process (Nehb and Vydra 2005).
200 201	The only economic method for extraction of elemental sulfur from natural deposits is the Frasch process.
201	However, technical and economic considerations limit its use to the Gulf region of the U.S. and Mexican
202	sulfur fields. The process consists of injecting large quantities of hot water directly into the deposit, and
203	then pumping the molten sulfur to the surface (Nehb and Vydra 2005). By a method akin to that used by
205	the oil industry, a well is drilled through the cap layers and the sulfur-bearing layers at a depth of ca. 50 –
206	800 m. Three coaxial pipes are introduced into the borehole. The outermost pipe, with a typical diameter of
207	ca. 200 mm, reaches to the bottom of the borehole. The middle (sulfur delivery) pipe is somewhat shorter,

208 ending about halfway down the perforated part of the outer pipe. A collar on the end of the middle pipe closes off the annular space between the two pipes. Water at ca. 165 C, under sufficient pressure to keep it 209 from boiling (2.5 – 3 MPa), is forced down the annular space between the outer and middle tubes and into 210 211 the deposit. The water penetrates into the cracks, pores, and larger voids of the sulfur-bearing limestone, and heats and melts the sulfur around the end of the pipe. After a reservoir of molten sulfur has been 212 213 established (which requires heating for 24 h or longer), the hot water is turned off and the sulfur can flow 214 through the delivery pipe. Hot compressed air at about 3 MPa is injected, and the resulting foam of sulfur 215 and air is very light and easily rises to the surface. Injection of hot water is continued to maintain the 216 melting process. At the surface, the sulfur froth is deaerated and transferred to a heated storage tank, or to 217 a sulfur-forming device, to be solidified as slates, prills, pellets, or pastilles. The extracted sulfur is quite pure (99.7 - 99.8%) and light yellow in color. 218

219

220 The most prevalent source of sulfur today is fossil resources (d'Aquin 2007). Most fossil fuels – natural gas, petroleum, and coal – contain some chemically combined sulfur. In natural gas, it is present mainly as 221 222 hydrogen sulfide, with only minor proportions of organic sulfur compounds. Petroleum contains a variety 223 of organic compounds such as thiols, alkyl and aryl sulfides and disulfides, thiophenes, and more complex condensed aromatic heterocyclic sulfur compounds. These are also present in coal, which usually contains 224 225 a high proportion of inorganic sulfur as the iron sulfides pyrite and marcasite. In both the desulfurization 226 of fuel oil and the conversion of heavy distillate fractions into light products, organic sulfur compounds are 227 converted mainly into hydrogen sulfide.

228

Because hydrogen sulfide has few industrial uses and is inherently dangerous, once it has been separated from other useful constituents of the gas mixture, it is normally converted into a more useful form of sulfur (e.g., sulfuric acid or elemental sulfur). The product of choice is typically elemental sulfur, which is cheap and easy to transport. The conversion of hydrogen sulfide to elemental sulfur is accomplished via the Claus process, which converts hydrogen sulfide to elemental sulfur in two steps:

- 234 $H_2S + 3/2 O_2 \rightarrow SO_2 + H_2O$ (1)
- 235 $2 H_2S + SO_2 \rightarrow 3/x S_x + 2 H_2O(2)$

236 The multi-step Claus process produces elemental sulfur from recovered gaseous hydrogen sulfide from 237 natural gas or derived from refining crude oil (Nehb and Vydra 2005). In the initial thermal step, hydrogen 238 sulfide is heated to temperatures in excess of 850 °C in the presence of dioxygen, which promotes the 239 flame-free total oxidation of hydrogen sulfide to sulfur dioxide. The generated sulfur dioxide then further 240 reacts with hydrogen sulfide to yield gaseous elemental sulfur and water. Approximately 60-70% of the 241 elemental sulfur is collected in this step. The gas stream is transferred to an additional reactor where the 242 Claus reaction continues in a catalytic step using activated aluminum or titanium oxides as catalysts to 243 boost the sulfur yield. More hydrogen sulfide reacts with the sulfur dioxide formed during combustion in the thermal step. The gas is then cooled in a condenser in which sulfur solidifies for collection. Thus, the 244 245 catalytic recovery of sulfur consists of three sub steps: heating, catalytic reaction, and cooling plus 246 condensation. These three steps are normally repeated a maximum of three times. Depending on the 247 composition of the petroleum or natural gas feedstock, additional processes such as the scrubbing of ammonia or carbon dioxide are required. 248

249

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

252

The most prevalent source of elemental sulfur is fossil resources. Elemental sulfur is manufactured from a chemical process (i.e., the Claus Process), by which hydrogen sulfide from natural gas or petroleum refining is converted to elemental sulfur. Elemental sulfur can be directly harvested from natural deposits

256 (e.g., the Frasch process) (Nehb and Vydra 2005).

257

258 259 260	<u>Evaluation Question #4:</u> Describe the persistence or concentration of the petitioned substance and/or its byproducts in the environment (7 U.S.C. § 6518 (m) (2)).
261	According to the EPA's Sulfur-Reregistration Eligibility Decision, sulfur is a pervasive element to which
262	all humans are exposed, though its impact to the environment causes little or no harm. This component
262	along with its variants comprise nearly 1.9% of the earth's weight, and high volumes of sulfur are found in
264	the majority of land and sea environments (US EPA 1991).
265	
266	EPA's Reregistration Eligibility document also states that all environmental fate data requirements were
267	waived for sulfur in the EPA 1982 Registration Standard due to its organic nature within the environment;
268	furthermore, no environmental concerns are raised by its use as a pesticide or a soil amendment due to its
269	incorporation into the natural sulfur cycle (US EPA 1991). Elemental sulfur is slowly converted to sulfate
270	in soil by the action of autotrophic bacteria. Thus, elemental sulfur leaches into soil as sulfate at a slow
271	rate. About 3–6% of the sulfur (formulation and purity unspecified) applied at 56 kilograms/hectare
272	(kg/ha) leached through lysimeters of loam soil (soil depth unspecified) as a result of 40 inches of rain
273	over a six-month period. After two years, 23–29% of the applied sulfur had leached (US EPA 1982).
274	over a six monar period. There is o years, 25 25 % of the appread suntai had reached (00 Er H 1502).
275	A 2004 study summarized risk assessments and findings for sulfur in the environment when used as plant
276	protection agent (Paulsen 2005). Elemental sulfur has low toxicity for mammals, birds, and fish and high
277	no-observed-effect-concentration (NOEC) values for plants. Soil application of 10 and 100 kg/ha of sulfur
278	lowered N- and C-mineralization. The legislative limit of a level of 75% of the N- and C-mineralization in
279	sulfur-treated soil in comparison to untreated soil after 100 days was reached after 14 and 66 days,
280	respectively. Sulfur is relatively immobile in soils and is leached as sulfate (SO ₄ ²⁻) after incorporation and
281	oxidation in the soil sulfur cycle. Sulfur is hydrophobic and not water soluble. When reaching surface
282	water it is incorporated in the soil after sedimentation. Additional SO ₄ -loads to water sources from
283	oxidation under aerobic conditions are irrelevant under consideration of natural water contents.
284	
285	In fact, there is undoubted evidence of sulfur deficiency in soil in some areas of the world (Lucheta and
286	Lambais 2012). A slight deficiency affects crop yield and quality, while the symptoms of severe deficiency
287	are yellowing of the leaves and dwarfing of the plant. The main reasons for the sulfur deficiency are:
288	
289	• Increasing levels of specific agricultural production, with proportional increase of sulfur uptake.
290	• Shift in fertilizer practices, from ammonium sulfate and single superphosphate, to multi-nutrient
291	(compound) fertilizers with little or no sulfur.
292	Decrease in the atmospheric sulfur supply, owing to increasing environmental controls on sulfur
293	dioxide emissions.
294	 Decline in the usage of sulfur-based herbicides and pesticides.
295	
296	Evaluation Question #5: Describe the toxicity and mode of action of the substance and of its
297	breakdown products and any contaminants. Describe the persistence and areas of concentration in the
298	environment of the substance and its breakdown products (7 U.S.C. § 6518 (m) (2)).
299	
300	Elemental sulfur has low toxicity for mammals, birds, and fish and high NOEC values for plants. Elemental
301	sulfur, applied as pesticide or soil amendment, will become incorporated into the natural sulfur cycle. The
302	fate of sulfur is dependent on environmental redox conditions. Under aerobic conditions, elemental sulfur
303	is oxidized to sulfate (SO_4^2) via microbial metabolism. The dissipation of sulfate is dependent on leaching
304	and soil organic matter immobilization. Therefore, elemental sulfur should not pose an environmental
305	problem because it dissipates rapidly into the natural environment (Paulsen 2005).
306	
307	The major environmental concern with elemental sulfur is that upon oxidation it forms sulfuric acid, which
308	can acidify soil or water ecosystems. In soil management systems, elemental sulfur is a common soil
309	amendment used to acidify calcareous soil and increase the sulfur fertility; it is expected to have a similar

- effect when used as a pesticide. In soil and water management systems, the application of lime (i.e.,
- 311 CaCO₃) is recommended to neutralize the acidity generated via sulfur oxidation.

312 313 The dissipation of sulfate is dependent upon leaching and inorganic matter immobilization. In acid and 314 near-neutral soils, sulfate can precipitate as gypsum (CaSO₄ \cdot 2H₂O). Gypsum can be a persistent mineral in 315 soils formed under semiarid to arid climatic conditions; otherwise, it is not expected to persist as a secondary soil mineral. Sulfate can be adsorbed to aluminum oxides and silicate clays by ligand binding 316 317 (replacement of hydroxyl, -OH, groups). These soil retention mechanisms (e.g., precipitation and 318 adsorption) cannot prevent SO_4^{2-} leaching. Since sulfate is a ubiquitous species, it should not pose any 319 environmental risk to ground or surface water pollution. In addition, microbes and plants can assimilate 320 SO_4^{2-} with subsequent immobilization into organic compounds (cysteine, cystine, and methionine). 321 322 No additional ecological effects data are required for sulfur. Sulfur is not soluble in water and the available 323 data indicate low order toxicity to aquatic species (US EPA 1991). In addition to the fact that sulfur is 324 ubiquitous in nature and chronic exposure is common, the available ecotoxicity data on terrestrial 325 organisms indicate that sulfur is practically nontoxic on an acute basis. 326 327 Evaluation Question #6: Describe any environmental contamination that could result from the 328 petitioned substance's manufacture, use, misuse, or disposal (7 U.S.C. § 6518 (m) (3)). 329 330 Since sulfur is a naturally-occurring element that is ubiquitous in the environment, it appears to pose little risk to non-target species. Available acute toxicity studies support this conclusion (US EPA 1991). All 331 332 other ecological toxicity data requirements have been waived. All environmental fate data requirements 333 for sulfur have been waived because sulfur is a naturally occurring element whose behavior in the 334 environment is well-understood and described in published literature. 335 However, too much sulfur (e.g., from a sulfur storage or manufacturing facility) will cause the pH of the 336 soil to drop as low as pH 2.5 or lower. Sulfuric acid (H_2SO_4) in the soil can generally diffuse in the soil as a 337 338 sulfate ion leachate, but the introduction of high levels of sulfur can cause the loss of vegetative ground 339 cover and affect a number of insect species (Cárcamo et al. 1998, Lucheta and Lambais 2012). High sulfur 340 contamination and subsequent acidification has a clear negative effect on earthworms, snails, and several 341 ground beetle species. Among the beetles, ecological specialists are those most vulnerable to acidification, 342 whereas ecological generalists are more resistant (Cárcamo and Parkinson 2001). Earthworms have an 343 important influence on the sulfur turnover in the soil caused by their burrowing, feeding, digestion, and 344 egestion (Grethe et al. 1996). 345 346 The US EPA's Ecological Incident Information System (EIIS) lists three incidents associated with the use of sulfur, all resulting in damage to terrestrial plants. In one incident, there was reported damage to 127 347 acres of citrus treated directly with sulfur. The certainty index for this incident was "probable." A second 348 349 incident report indicated damage to 44 acres of a grape vineyard treated directly with sulfur and trifloxysrobin. The symptoms noted were spotting and speckling. The certainty index for this incident was 350 351 "possible" for sulfur and "probable" for trifloxystrobin. In the third reported incident, a tank mixture of sulfur, fenarimol, and oxyfluorfen applied to a 20-acre plot of grapes may have caused burnt leaves and 352 berries. The certainty index for this incident was "unlikely" for sulfur and fenarimol, and "probable" for 353 oxyfluorfen. No ecological incidents have been reported associated with the use of the rodent control, 354 355 gas-producing cartridge products of sulfur. 356 357 Evaluation Question #7: Describe any known chemical interactions between the petitioned substance 358 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)). 359 360 361 To the best of our knowledge, there are no known reports that suggest any specific chemical interactions between elemental sulfur and other substances used in organic crop or livestock production or handling. 362 Elemental sulfur does react vigorously with chlorates, nitrates, and other oxidizing agents (Nehb and Vydra 363 2005). 364 365

366 367 368 369	<u>Evaluation Question #8:</u> Describe any effects of the petitioned substance on biological or chemical interactions in the agro-ecosystem, including physiological effects on soil organisms (including the salt index and solubility of the soil), crops, and livestock (7 U.S.C. § 6518 (m) (5)).
370 371 372	Elemental sulfur is generally used for insecticide applications in granular or finely powdered form. Liquids and mixtures are also in use. Small amounts of dusting sulfur or liquids find their way into soils or water, either as part of the manufacturing process, transport and storage or application. None of these
373	applications is recognized as an environmental problem (US EPA 1991). In soils, sulfur is oxidized to
374	sulfuric acid (H_2SO_4) by soil bacteria mostly of the genus <i>Thiobacillus</i> . Important factors for the rate of
375	oxidation include 1) the fineness of the sulfur particles, 2) the resident population of <i>Thiobacillus</i> spp., 3) soil
376	temperature and 4) soil moisture content (Germida and Janzen 1993). Powdered sulfur is readily oxidized.
377	In general, there is very little effect on the vegetation, soil or the invertebrate population of the soil from
378	small amounts of sulfur dust. As mentioned, too much sulfur will cause the pH of the soil to drop to pH ≤
379	2.5. The introduction of high levels of sulfur can cause the loss of vegetative ground cover and affect insect
380	species (Cárcamo et al. 1998, Lucheta and Lambais 2012). High sulfur contamination and subsequent
381	acidification has a clear negative effect on earthworms, snails, and several ground beetle species (Grethe et
382	al. 1996, Cárcamo and Parkinson 2001).
383	
384	<u>Evaluation Question #9:</u> Discuss and summarize findings on whether the use of the petitioned
385 386	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)).
380 387	(1)):
388	According to EPA's Eligibility Decision document, sulfur in its elemental, reduced, or oxidized forms
389	represents approximately 1.9% of the total weight of the earth. The sulfates and sulfides are common in
390	their various mineral forms. Most aquatic and terrestrial environments are high in sulfur (US EPA 1991). In
391	addition, sulfur in microorganisms is considered non-mutagenic (US EPA 1991). There is no evidence that
392	sulfur poses a risk to the environment when used according to good manufacturing practice regulations.
393	
394	Evaluation Question #10: Describe and summarize any reported effects upon human health from use of
395	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
396 397	(m) (4)).
398	According to EPA's Eligibility Decision document, all humans are exposed to sulfur due to its
399	pervasiveness throughout the environment. Representing almost 2 percent of earth's total weight, sulfur
400	may be found in high volumes in the majority of land and sea environments (US EPA 1991). Further, the
401	EPA Eligibility Decision document states that not only have all EPA's data requirements for sulfur
402	toxicology been satisfied for years, but the element maintains a low toxicity, presenting little to no risk to
403	human health. Sulfur has been placed in Toxicity Category IV (i.e., lowest category) for its effect on skin,
404	as short-term studies indicate it causes no skin irritation. Though not a skin sensitizer, sulfur was placed in
405	Toxicity Category III for the effects of eye irritation, dermal toxicity, and inhalation hazards. Exposure to
406	low levels of elemental sulfur has been deemed safe; however, epidemiological studies did indicate that
407	continued exposure to sulfur dust and sulfur dioxide can cause issues such as eye and respiratory
408	disturbances, chronic bronchitis and other effects. With regard to other effects such as those of an
409	oncogenic, teratogenic, or reproductive nature, no known risks are associated with sulfur use (US EPA
410	1991).

411

412 Sulfur may be encountered in food in small measure, though no studies assessing the risks have been

413 conducted to date since no toxic effects have been observed. With regard to diet, sulfur is considered safe

414 per 40 CFR 180.2(a); therefore, residue limits of sulfur in food do not need to be established (US EPA 1991).

Sulfur is listed as an inert ingredient applied to animals with an exemption from the requirement of a

tolerance (40 CFR 180.930). An exemption from the requirement of a tolerance is established for residues of

- 417 sulfur (40 CFR 180.1236).
- 418

- 419 People working with pesticide are among those exposed to sulfur. As indicated by reports of irritation to California field worker's skin and eyes, EPA has deemed that workers' reentry to fields after foliar 420 421 application of sulfur dust poses a hazard; due to this finding, workers must wait at least 24 hours before 422 reentering the area as well as imposing protective clothing requirements on outdoor products containing sulfur (US EPA 1991). 423 424 Over the course of 13 years (1982-1995), California's Pesticide Illness Registry noted 1,698 occupational cases 425 426 related to elemental sulfur exposure, with 155 cases being specifically related to sulfur pesticide handlers. Out of these 155 cases, 44% indicated ocular symptoms, 45% were related to dermatitis, and 32% were 427 428 respiratory or systemic-illness related (Krieger 2001). 429 430 People that live in agricultural communities near applications of elemental sulfur can be adversely affected. Specifically, reports have included nonoccupational cases of contact allergies (Krieger 2001), dyspnea, 431 432 hypoxemia from an individual being exposed to sulfur drifting from a treated field (Calvert 2004), sulfur inhalation leading to a sore throat, chest pain, and acute tracheobronchitis (Ellenhorn 1988). A recent 433 434 report from UC Berkeley studied the correlation between elemental sulfur us and pediatric lung function (Raanan 2017). The study included a data set of 357 children at 7 years of age and evaluated associations 435 436 between residential proximity to elemental sulfur applications and respiratory symptoms. After adjusting for other mitigating factors, the findings suggest that sulfur use in close proximity to residential areas may 437 438 adversely affect the respiratory health of children. Adverse respiratory associations were only found within 439 0.5 and 1 km radii of the agricultural application. A strong correlation between asthma medication usage and respiratory symptoms was observed per every 10-fold increase in the estimated amount of sulfur used 440 441 within 1 km of the child's residence. While the study had several limitations, such as the collection of high quality data from young children or not evaluating the children's personal exposure to elemental sulfur, the 442 findings were consistent with previous reports on adverse respiratory effects associated with elemental 443 444 sulfur in animal models (Krieger 2001), in workers (Sama 1997, Calvert 2004), and in case reports of poisoning (Krieger 2001) This study also lends credibility to reports of drift of elemental sulfur after 445 446 agricultural application (EPA 1991, Calvert 2004). 447 448 Evaluation Question #11: Describe all natural (non-synthetic) substances or products which may be 449 used in place of a petitioned substance (7 U.S.C. § 6517 (c) (1) (A) (ii)). Provide a list of allowed 450 substances that may be used in place of the petitioned substance (7 U.S.C. § 6518 (m) (6)). 451 We were unable to locate any non-synthetic treatment options found on the National List for use as a 452 fungicide, insecticide, or soil amendment. Alternative non-synthetic treatment substances not found on the 453 454 National List that may be used in place of elemental sulfur for use as an insecticide or fungicide: D--Limonene, pyrethrins, diatomaceous earth, garlic powder, soap, oils (canola, soy), and neem oil. 455 456 457 Evaluation Question #12: Describe any alternative practices that would make the use of the petitioned substance unnecessary (7 U.S.C. § 6518 (m) (6)). 458 459 460 There are numerous alternative cultural practices that, in combination, could render the use of elemental 461 sulfur unnecessary (Hill 1989, Katan 2000). Because cultural controls are preventative rather than curative, they are dependent on long-range planning and detailed knowledge of the bio-ecology of the 462 crop-pests-natural controls-environment relationships (Hill 1989). Cultural controls do not afford a solution 463 464 for all disease or pest prevention and control. 465 Cultural controls employ practices that make the environment less attractive to pests and less favorable for their survival, dispersal, growth and reproduction, and that promote the pest's natural controls. The 466 467 objective is to achieve reduction in pest numbers, either below economic injury levels, or sufficiently to
- allow natural or biological controls to take effect. Cultural controls include site selection, planting designand management, site maintenance, and harvesting procedures (Hill 1989, Katan 2000).
 - April 19, 2018

470 Cultural controls are dependable and are usually specific. Of major importance is the fact that they do not possess some of the detrimental side effects of pesticides, namely the creation of resistance to pesticides, 471 undesirable residues in food, feed crops and the environment, and the killing of non-target organisms. 472 473 Cultural controls are generally the cheapest of all control measures because they usually only require modifications to normal production practices. Sometimes they do not even require extra labor, only careful 474 planning. They are often the only control measures that are profitable for high acreage of low value crops. 475 476 However, cultural controls require long-term planning for greatest effectiveness and they need careful timing. They are often based on the substitution of knowledge and skills for purchased inputs and, as such, 477 478 are more demanding on the farmer's competence. They may be effective for one pest but may be ineffective against a closely related species. The effectiveness of cultural controls is difficult to assess, and they do not 479 480 always provide complete economic control of pests. Also, some cultural controls have adverse effects on 481 fish and wildlife and may cause erosion problems. 482 **Report Authorship** 483 484 The following individuals were involved in research, data collection, writing, editing, and/or final 485 approval of this report: 486 487 Bradley Aaron McKeown, Ph.D. Research Scientist, University of Virginia Audrey Nicoleau, Technical Writer, Savan Group 488 489 490 All individuals are in compliance with Federal Acquisition Regulations (FAR) Subpart 3.11 – Preventing Personal Conflicts of Interest for Contractor Employees Performing Acquisition Functions. 491 492 493 References Calvert GM, Plate DK, Das R, Rosales R, Shafey O, Thomsen C, et al. 2004. Acute occupational pesticide-494 495 related illness in the US, 1998–1999: surveillance findings from the SENSOR-pesticides program. American Journal of Industrial Medicine. 45(1):14-23. 496 Cárcamo HA, Parkinson D, Volney JWA. 1998. Effects of sulphur contamination on macroinvertebrates in 497 Canadian pine forests. Applied Soil Ecology. 9(1): 459-464. 498 499 Cárcamo HA, Parkinson D. 2001. Localized acidification near sour gas processing plants: are forest floor 500 macro-invertebrates affected? Applied Soil Ecology. 17(3): 199-213. 501 d'Aquin GE, Fell RC. 2007. Sulfur and sulfuric acid. In: Kent JA, editor. Kent and Riegel's handbook of 502 industrial chemistry and biotechnology. New York: Springer. 1157-1182. 503 Earnshaw A, Greenwood, N. 1997. Sulfur. Chemistry of the elements. 2nd ed. Oxford: Butterworth-Heinemann. 645-746. 504 505 Ellenhorn MJ, Barceloux DG. 1988. Medical toxicology: diagnosis and treatment of human poisoning. New York: Elsevier Science Publishing Co., Inc. 37. 506 507 Eow JS. 2002. Recovery of sulfur from sour acid gas: a review of the technology. Environmental Progress 508 21(3): 143-162. 509 Germida JJ, Janzen HH. 1993. Factors affecting the oxidation of elemental sulfur in soils. Fertilizer research 35(1): 101-114. 510 Grethe S, Schrader S, Giesemann A, Larink O, Weigel, HJ. 1996. Influence of earthworms on the sulfur 511 512 turnover in the soil. Isotopes in Environmental and Health Studies. 32(2-3): 211-217.

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