

Humic Acids

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Identification of Petitioned Substance

Chemical Names:	14	Trade Names:
NA	15	NA
Other Name:		CAS Numbers:
Humic acid		1415-93-6
Humic acid, sodium salt		68131-04-4
Humic acid, potassium salt		68514-28-3
Humates		(EPA, 2004)
		Other Codes:
		NA

Characterization of Petitioned Substance

Composition of the Substance:

Humic substances are a group of complex organic compounds consisting of humic acids, fulvic acids, natural salts of these acids (e.g., calcium humates), and sponge-like substances called humin (Weber, undated). Humic substances (which includes humic acids) naturally constitutes a large fraction of the organic matter in soil, and is formed through the process known as "humification." Humification is the natural conversion of organic matter into humic substances by microorganisms in the soil (Mayhew, 2004). This process begins with microorganisms separating out sugars, starches, proteins, cellulose, and other carbon compounds from the organic matter. The microorganisms use these components in their own metabolic processes. Subsequently, the microorganisms transform the majority of the organically bound nutrients into a mineral form that are used by plants and other organisms. The portions of the organic matter that are not digested by the microorganisms accumulate as humic substances (Sachs, undated). Humification does not occur in one step, but involves an intermediate substance called compost, which consists of a mixture of humic substances and partially decomposed organic matter. As the humification process proceeds, various chemicals dominate at different times until conversion to humic substances is complete (Mayhew, 2004).

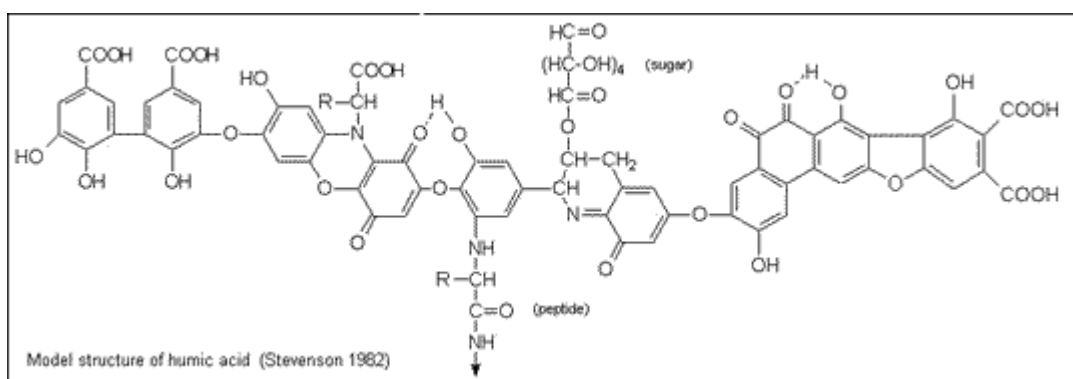
The decomposition of organic matter in soil is dependent on several factors, including the amount of available free oxygen, the amount of moisture present in the soil, and the temperature of the soil. The amount of free oxygen determines whether aerobic or anaerobic microorganisms will conduct the decomposition process. Aerobic microorganisms decompose organic material at a faster rate than do anaerobic organisms. However, greater amounts of humic substances are found in soils produced by anaerobic organisms because in these conditions accumulation is favored over destruction of humic substances. Although microorganisms need moisture to function, too much or too little water can decrease the rate of decomposition. Increasing soil temperature leads to greater microbial activity and decreased humic substance content because decomposition is occurring at a faster rate than accumulation (Sachs, undated).

In addition to humic substances originating from soil, commercially available humic substances are derived from coal. Leonardite is a highly oxidized low-rank coal originating from plant matter that serves as a key mined source for the production of humic acids. The humification process that yields leonardite may take 70 million years. In comparison, peat can be formed in about a few thousand years. Leonardite possesses a high humic substance content as a result of being highly decomposed by microorganisms. At 40 to 85 percent humic and fulvic acids, leonardite-sourced humic substances have a

53 much higher humic/fulvic acid content than other sources (such as black peat at 10 to 40 percent,
 54 sapropel peat at 10 to 20 percent, manure at 5 to 15 percent, and compost at 2 to 5 percent). Natural soil
 55 typically has 1 to 5 percent humic and fulvic acids. Additionally, in contrast to compost, leonardite-
 56 sourced humic acids do not compete with plants for nutrients, because leonardite-sourced humic acids
 57 are completely decomposed (Humintech, undated).

58
 59 Humic acids are not a substance with a single molecular formula. Figure 1 shows one example of a humic
 60 acids molecule. Humic acids may be described as “complex colloidal supermixtures” (Mayhew, 2004)
 61 that are characterized by their functional groups (Heise and Brendler., undated). The composition and
 62 structure of humic acids can vary from one soil to another (Sachs, undated). Generally, humic acids are
 63 considered to be aromatic in structure with amino acids, amino sugars, peptides, and aliphatic
 64 compounds linking the aromatic groups. The hypothetical structure of humic acid, as shown by the
 65 example in Figure 1, is believed to consist of free and bound phenolic hydroxyl groups, quinines, oxygen
 66 and nitrogen bridges, and carboxy groups (Weber undated). Adding to their complexity, the structure of
 67 humic acids is continuously influenced by their surroundings. For example, changes in pH can result in
 68 broken hydrogen bonds. (Heise and Brendler, undated).

69
 70 **Figure 1. An Example of the Chemical Structure of Humic Acids**



73 Source: Weber, Jerzy. Undated. Definition of soil organic matter. Available online at:
 74 http://www.humintech.com/001/articles/article_definition_of_soil_organic_matter.html. Last Accessed:
 75 January 10, 2006.

76
 77 The surface of humic substance particles consists of compounds that contain hydrogen ions
 78 capable of being replaced by cations (positively charged ions) like calcium, magnesium, potassium
 79 or sodium. In soil with high hydrogen ion activity (low pH), humic substances are saturated with
 80 hydrogen ions forming humic acid. Humic acid, in turn, reacts with mineral particles in the soil
 81 causing these particles to release basic cations (e.g., calcium, potassium, and magnesium). Humic
 82 acid then replaces its hydrogen ions with the basic cations and is converted into a salt called
 83 humate (Sachs, undated).

84
 85 **Properties of the Substance:**

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 87 As previously stated, humic substances consist of humic acid, fulvic acid, and a sponge-like
 88 substance called humin. Humic substances are divided into three fractions on the basis of their
 89 solubility characteristics. These fractions are soluble over a wide pH range. The first fraction,
 90 humic acid, is not soluble in water under acidic conditions (pH < 2), but is soluble at higher pH
 91 values. Humic acid is the major extractable fraction of humic substances and ranges from dark
 92 brown to black in color. It can be extracted from soil by various reagents. The second fraction,
 93 fulvic acid, is soluble in water under all pH conditions. Fulvic acid, which stays in solution after
 94 the extraction of humic acid, ranges from light yellow to yellow-brown in color. After the first two
 95 fractions have been extracted, the third fraction, called humin, remains. This fraction, which is
 96 black in color, is not soluble in water at any pH, nor in any alkali solution (Weber, undated).

97

98 Generally, the humin fraction of humic substances is the dominant organic material in soils and
99 sediments. However, little information exists regarding the properties of this fraction (Kohl and
100 Rice, 1996). Variations between humic and fulvic acids include differences in molecular weight,
101 number of functional groups, and extent of polymerization. Humic acid has a higher molecular
102 weight, fewer functional groups that are acidic in nature (e.g. COOH and OH), greater carbon
103 content, and lower oxygen content than fulvic acid. Finally, the majority of oxygen in humic acid
104 is located as a structural constituent of its nucleus, while the oxygen in fulvic acid is found
105 predominantly in the functional groups (Weber, undated).

106

107 **Specific Uses of the Substance:**

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109 Humic acids (naturally occurring deposits, water and alkali extracts only) are currently on the National
110 List for use as a plant or soil amendment. Specifically, humic acids are used by organic growers as a
111 component of traditional fertilizers.

112

113 Although humic acids are most commonly used as a soil amendment, they are also used as a foliar spray
114 (Jackson, undated). In general, plants are capable of absorbing small amounts of nutrients from the use of
115 foliar sprays on leaves. However, it is not possible to supply significant amounts of nutrients this way;
116 root uptake is more efficient (Witney, 1996). Application of humic acid as a foliar spray is believed to
117 promote the photosynthesis of leaves; increase yield and quality of plants; promote root development;
118 and improve nutrient uptake through the root system (HumaTech, Inc, undated).

119

120 Commercially available humic substances do not provide additional nutrients to plants, but rather affect
121 soil fertility by making micronutrients (e.g., iron) more readily available to plants. By chelating (or
122 binding) nutrients (especially iron), humic substances cause insoluble and unstable, and therefore
123 unavailable, compounds in the soil to remain available for plant uptake (Obreza et al, 1989).

124

125 The use of humic acids for agricultural purpose continues to grow, and as result, the number of products
126 and vendors continues to grow. However, there is currently a lack of standardized analysis for
127 substances marketed as humic substances, resulting in the marketing of some products that produce
128 minimal to no results. However, the benefits of using humic acid substances in agriculture have been
129 researched and documented by scientists (Mayhew, 2004).

130

131 **Approved Legal Uses of the Substance:**

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133 As stated above, humic acids (naturally occurring deposits, water and alkali extracts only) are currently
134 on the National List for use as a plant or soil amendment.

135

136 The US Environmental Protection Agency (EPA) granted an exemption from the requirement for a
137 tolerance for residues of humic acids, sodium salts, used as an inert ingredient (adjuvant, UV protectant)
138 in pesticide formulations applied to growing crops and raw agricultural commodities after harvest (EPA,
139 2000).

140

141 In 2003, the EPA proposed to amend the existing tolerance exemption for humic acid, sodium salt to
142 include humic acid, potassium salt and humic acid. The EPA stated that such humate materials would be
143 used as inert ingredients in pesticide formulations applied to growing crops under the Federal Food,
144 Drug, and Cosmetic Act (FFDCA), as amended by the Food Quality Protection Act of 1996 (FQPA) (EPA,
145 2003). In 2004, the existing tolerance exemption was amended eliminating the need to establish a
146 maximum permissible level for residues of humic acid; humic acid, sodium salt; and humic acid,
147 potassium salt (EPA, 2004).

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Action of the Substance:

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According to Mayhew (2004), humic substances have demonstrated the ability to:

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- Chelate (bind) soil nutrients;
- Improve nutrient uptake;
- Reduce the need for nitrogen fertilizer;
- Remove toxins from soils;
- Stimulate soil biological activity;
- Solubilize minerals;
- Improve soil structure; and
- Improve water holding capacity.

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In general, commercially-available humic substances do not promote plant growth by providing substantial amounts of nutrients to plants. Instead, humic substances affect soil fertility by making nutrients (e.g., iron) more readily available to plants. In order for plants to take up nutrients, the nutrients need to be in solution, or dissolved in water. However, nutrients predominantly exist in soil as the insoluble forms of soil minerals and organic matter. Humic substances, which are negatively charged, make nutrients more available by attracting the positively charged nutrients and holding them in reserve. These readily available nutrients are subsequently released into solution to replace nutrients taken up by the plant roots (Cogger, 2000; Obreza et al., 1989; Senn and Kingman, undated).

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Humic acids also promote plant growth by enabling root penetration in soils with high clay content. These types of soil can become extremely dense and compact due to salts located on their surface. The salts cause the negatively-charged clay particles to become neutral and move together. This compaction can create resistance to plant rooting. The addition of humic acids results in the removal of the salts, which causes the clay soil to loosen up for greater root penetration (Bio Ag, 1999). Seed germination and top growth also are stimulated (Obreza et al 1989). In the presence of humic acid, both a larger percentage of seeds germinate and germination occurs at a faster rate. This increased rate and occurrence of germination is related to the greater efficiency of binding of nutrients and water that takes place in the presence of humic substances (Bio Ag, 1999).

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Additionally, the same action described in the previous paragraph allows for greater water penetration in clay soils. Humic acid also acts in decreasing water evaporation from soils. This is essential in arid areas with sandy soils that retain little to no water. With water present, the compounds that were previously bound by humic acid are partially ionized (or given a charge). As a result, the bonded compound's positive attractive force is partly restored. Subsequently, the negatively-charged oxygen atom of the water molecule loosely bonds to the positively charged compound, while the hydrogen end of the water molecule becomes more positive. This leads to another negatively charged oxygen from a water molecule binding to the positively charged hydrogen ion of the original water molecules. This continues until the attractive forces of the water molecules are stabilized (Bio Ag, 1999)

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Status

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International

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Canada - Canadian General Standards Board -

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http://www.pwgsc.gc.ca/cgsb/032_310/32.310epat.pdf

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No information was identified at the listed site.

198

199

The Certified Organic Associations of British Columbia (undated) allows:

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201

- Humates (if not fortified with synthetic nutrients); and

- 202 • Humic acid derivatives (non-synthetic or using potassium hydroxide as an extractant but not to
203 fortify the product – no other sources are allowed)

204

205 They prohibit humic acids extracted by ammonium or sodium hydroxide or synthetic bases other than
206 potassium hydroxide.

207

208 **CODEX Alimentarius Commission –**

209 <ftp://ftp.fao.org/docrep/fao/005/Y2772e/Y2772e.pdf>

210 No information was identified at the listed site.

211

212 **European Economic Community (EEC) Council Regulation 2092/91 –**

213 http://europa.eu.int/eur-lex/en/consleg/pdf/1991/en_1991R2092_do_001.pdf

214 No information was identified at the listed site.

215

216 Humic acids are not allowed in the EU. However, some certifiers/authorities may consider the extracts
217 from certain fossilized organic matter to be 'peat' products, which are covered under Annex IIA. This is
218 more common in recognized third countries like Hungary than in the EU (Organic Trade Association
219 2002).

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221 **Japan Agricultural Standard for Organic Production –**

222 <http://www.ams.usda.gov/nop/NOP/TradeIssues/JAS.html>

223 No information was identified at the listed site.

224

225 **California Certified Organic Growers International (CCOF) –**

226 <http://www.ccof.org/pdf/GlobalMarketAccessDraftForReview.pdf>

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228 According to the 2005 CCOF's Draft Manual III: Global Market Access Program, alkali-extracted humic
229 acids are prohibited and/or restricted on crops for the USDA/Export, European Union Export, and
230 International Federation of Organic Agriculture Movements (IFOAM) export programs.

231

232 **Washington State Department of Agriculture: European Organic Verification Program (EOVP) –**

233 <http://agr.wa.gov/FoodAnimal/Organic/default.htm>.

234

235 According to this program, alkali-extracted humic acid may not be used on raw or processed organic food
236 exported to Japan.

237

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

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240 **Evaluation Question #1: Is the petitioned substance formulated or manufactured by a chemical**
241 **process? (From 7 U.S.C. § 6502 (21))**

242

243 Extraction of humic substances from terrestrial sources, such as soil, peat, compost, oxidized lignites, and
244 other coals (Karr, 2001), is commonly conducted using potassium hydroxide, water, or (rarely) ammonia
245 (Original TAP Database Form, 1995). Various extraction processes are described in the following
246 paragraphs:

247

248 **Alkali Extraction of Humic Substances:**

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250 The process begins with the separation of organic matter from the inorganic matrix of sand, silt,
251 and clay. The terrestrial source is leached with hydrochloric acid (HCL) to remove calcium and
252 other positively-charged ions and to increase the efficiency of extraction of organic matter with
253 alkaline reagents. Next, a stronger sodium hydroxide solution is used to create a liquid solution
254 (Weber, undated). The extracted liquid solution is incompatible with acids because it is very
255 alkaline, in the range of 8 to 12 pH, and can be treated with an acid to precipitate out the humic
256 acid portion (Mayhew, 2004).

257

258 Alkali extraction can also be conducted using potassium hydroxide, which is a typical alkali used by
259 manufacturers to extract humic acid from leonardite. The extracted liquid solution is also incompatible
260 with acids because it is very alkaline, in the range of 8 to 12 pH, and can be treated with an acid to
261 precipitate out the humic acid portion (Mayhew, 2004).

262

263 **Processes Inconsistent with the Current Listing**

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265 Continued experimentation has led to development of a recently patented process that solubilizes the
266 "humin" fraction of leonardite and mixes it with liquid phosphate fertilizer. This solution is used as an
267 early-season soil treatment or as a foliar spray, and enhances the efficiency of the phosphate in the
268 fertilizer. (Kline and Wilson, 1994)

269

270 Lignite and other coals serve as a natural source that can now be synthetically oxidized to produce
271 biochemically active humic substances. The coal is converted to humic substances through either "dry or
272 wet oxidative depolymerization" or "nitric acid oxidation and ammonation."

273

274 A recent innovation in extraction of humic acid uses microbial digestion of lignite to form a humic
275 substance with the trade name Actosol (Kline and Wilson, 1994).

276

277 **Evaluation Question #2: Is the petitioned substance formulated or manufactured by a process that**
278 **chemically changes the substance extracted from naturally occurring plant, animal, or mineral sources?**
279 **(From 7 U.S.C. § 6502 (21).)**

280

281 Humates and humic acids are extremely complex and varied in chemical structure. Some chemical
282 reactions do occur during the processes by which humic materials are obtained from terrestrial sources,
283 such as soil, peat, compost, oxidized lignites, and other coals (Karr, 2001). However, it may not be
284 possible to characterize the reactions and the extent to which there is a chemical change beyond the
285 simple effects of shifting pH on hydrogen ion availability for displacement.

286

287 **Evaluation Question #3: Is the petitioned substance created by naturally occurring biological**
288 **processes? (From 7 U.S.C. § 6502 (21).)**

289

290 In nature, organic matter is converted into humic substances by microorganisms. This natural
291 humification process, however, does not occur as a result of the specific process (i.e., application of
292 NaOH) used for commercial manufacturing.

293

294 **Evaluation Question #4: Is there environmental contamination during the petitioned substance's**
295 **manufacture, use, misuse, or disposal? (From 7 U.S.C. § 6518 (m) (3).)**

296

297 Humic acids are a natural substance that can also be manufactured from natural sources (e.g., coals).
298 There is no information available from EPA to suggest that environmental contamination results from the
299 manufacture, use, misuse, or disposal. Improper disposal of acids or bases used in the extraction process
300 could be a source of environmental contamination, and the mining of lignite/leonardite or other source
301 materials has environmental impacts.

302

303 **Evaluation Question #5: Is the petitioned substance harmful to the environment? (From 7 U.S.C. §**
304 **6517 (c) (1) (A) (i) and 7 U.S.C. § 6517 (c) (2) (A) (i).)**

305

306 No. Humic acids are a primary component of soil. Humic acids are nearly completely broken down by
307 soil organisms, and are not known to produce toxicity to plants, soil organisms, or higher animals (Original
308 TAP Database Form, 1995). According to Humintech (undated), humic acids will not harm soil or
309 contaminate groundwater or soil. As discussed above (see "Action of the Substance"), humic acids have a
310 number of beneficial properties in soil.

311

312 **Evaluation Question #6: Is there potential for the petitioned substance to cause detrimental chemical**
313 **interaction with other substances used in organic crop or livestock production? (From 7 U.S.C. § 6518**
314 **(m) (1).)**
315

316 Based on the intended use of the substance, no information was uncovered to suggest that use of humic
317 substances could cause detrimental chemical interaction with other substances used in organic crop
318 production. Humic acids are naturally occurring and are a primary component of soil.
319

320 **Evaluation Question #7: Are there adverse biological or chemical interactions in the**
321 **agro-ecosystem by using the petitioned substance? (From 7 U.S.C. § 6518 (m) (5).)**
322

323 Based on the intended use of humic acids, no evidence of adverse biological or chemical interaction in the
324 agro-ecosystem was identified.
325

326 **Evaluation Question #8: Are there detrimental physiological effects on soil organisms, crops, or**
327 **livestock by using the petitioned substance? (From 7 U.S.C. § 6518 (m) (5).)**
328

329 Soil organisms are affected positively by the addition of humic acids (Original TAP Database file, 1995).
330 Crops generally benefit from, or do not react to, addition of humic acids.
331

332 **Evaluation Question #9: Is there a toxic or other adverse action of the petitioned substance or its**
333 **breakdown products? (From 7 U.S.C. § 6518 (m) (2).)**
334

335 Soil humic acids in nature undergo biochlorination, facilitated by ubiquitous soil enzyme
336 chloroperoxidase. The reaction yields chlorinated humic acid, which in turn is converted to
337 chlorophenols, chloroacetic acids, and chloroform. The chlorophenols have been shown in nature to
338 dimerize to form dioxins. However, this process is natural, and since humic acid is a primary component
339 of soil the intended use would not significantly affect the environment through this process. (Euro Chlor,
340 undated)
341

342 **Evaluation Question #10: Is there undesirable persistence or concentration of the petitioned substance**
343 **or its breakdown products in the environment? (From 7 U.S.C. § 6518 (m) (2).)**
344

345 Humic acids are nearly completely broken down by soil organisms, and are not known to produce
346 toxicity to plants, soil organisms, or higher animals (Original TAP Database Form, 1995).
347

348 **Evaluation Question #11: Is there any harmful effect on human health by using the petitioned**
349 **substance? (From 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).)**
350

351 Based on the intended use, no adverse effects on human health from use of humic acids were identified.
352

353 **Evaluation Question #12: Is there a wholly natural product which could be substituted for the**
354 **petitioned substance? (From 7 U.S.C. § 6517 (c) (1) (A) (ii).)**
355

356 Manures and yard waste compost also contain humic acids and can be applied to soil as alternatives to
357 humic acid as a fertilizer. However, no alternatives are listed for use of humic acids as a soil amendment
358 (Maryland Cooperative Extension, 2003).
359

360 **Evaluation Question #13: Are there other already allowed substances that could be substituted for the**
361 **petitioned substance? (From 7 U.S.C. § 6518 (m) (6).)**
362

363 Other allowed plant or soil amendments on the National List include:
364

- 365 • Aquatic plant extracts (other than hydrolyzed) - Extraction process is limited to the use of
366 potassium hydroxide or sodium hydroxide; solvent amount used is limited to that amount
367 necessary for extraction;

- 368
- Elemental sulfur;
- 369
- Lignin sulfonate - chelating agent, dust suppressant, floatation agent;
- 370
- Magnesium sulfate - allowed with a documented soil deficiency;
- 371
- Micronutrients - not to be used as a defoliant, herbicide, or desiccant. Those made from nitrates or
- 372
- chlorides are not allowed. Soil deficiency must be documented by testing;
- 373
- Soluble boron products;
- 374
- Liquid fish products - can be pH adjusted with sulfuric, citric or phosphoric acid. The amount of
- 375
- acid used shall not exceed the minimum needed to lower the pH to 3.5; and
- 376
- Vitamins, B1, C, and E (USDA 2005).
- 377

378 **Evaluation Question #14: Are there alternative practices that would make the use of the petitioned**

379 **substance unnecessary? (From 7 U.S.C. § 6518 (m) (6).)**

380

381 Potential alternative practices include composting or use of an alternative soil organic soil amendment (see

382 Evaluation Questions #12 and #13). Other soil building practices that could be considered as alternatives

383 to the use of added humic acids (and soil amendments) include tilling, rotating crops, and planting cover

384 crops (Giannangelo Farms Southwest, 2005).

385

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