

Oxidized Lignite / Humic Acid Derivatives

Crops

Identification of Petitioned Substance

Chemical Names:

Oxidized Lignite

CAS Numbers:

129521-66-0 (lignite coal)

1415-93-6 (humic acids)

68131-04-4 (humic acid, sodium salt)

68514-28-3 (humic acid, potassium salt)

94948-59-1 (humic acid, ammonium salt)

154730-80-0 (humic acid, ammonium salts)

No separate CAS number for the petitioned form of liquefied oxidized lignite

Other Name:

Humate, Humic Acid, Fulvic Acid, Leonardite, Lignite, Liquefied Oxidized Lignite, Potassium Humate, Sodium Humate, Ammonium Humate.

Trade Names:

Revitagro (petitioned form), Actagro, Actasol, AgroLig, BioHume, Borregro, Enhance THA, Ful-Humix, Growmate, Huma K, HumiGain, HumiSolve, Humax, Jenner 8, Liqhumus, Liquid Hume, Powhumus, Trihumic, many others.

Other Codes:

EINACS: 215-809-6; 208-608-0

RTECS: MT6544000; MT6550000

Characterization of Petitioned Substance

Composition of the Substance:

Humic substances are comprised of a complex, amorphous mixture of heterogeneous compounds characterized as chemically reactive yet refractive produced from the decomposition of organic matter (McCarthy, 2001). Organic matter in the soil, particularly from dead plants, will decompose into allomelanins, amino acids, carbohydrates, lipids and various other complex organic compounds (Allard, 2006). When the dead plants fossilize, they form peat then low-rank coal, then higher rank coal. Humic substances obtained from fossil sources are chemically distinct from soil organic matter or humus formed from the decomposition of plants, animals and microorganisms in the following ways.

The first stages of humification are distinguished by higher molecular weight compounds that are readily digested by microorganisms. Lipids in lignite humic acids were found to be almost entirely aliphatic (Allard, 2006). Soil organic matter is characterized by abundant amino acid complexes, along with a mix of hydrophobic and hydrophilic structures (Sutton and Sposito, 2005). Coal and other fossil sources of humic substances are characterized by a higher percentage of simple aromatic structures that are resistant to attack by decomposing microorganisms as opposed to more complex biochemical structures (Schnitzer and Khan, 1972).

Synthetic transformations of fossilized humic substances can be accomplished with alkali extraction with sodium, potassium or ammonium hydroxide; acid extraction with nitric or hydrochloric acid; strong oxidizing agents like hydrogen peroxide, ozone and potassium permanganate; and strong reducing agents such as zinc and palladium (Schnitzer and Khan, 1972; Griffith and Schnitzer, 1989; Lawson and Stewart, 1989). The specific form petitioned is obtained from lignite coal that has been oxidized using hydrogen peroxide (SHAC, 2011). Alkali extracted forms will also be considered to provide supplemental information to a previous evaluation (ICF, 2006).

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Properties of the Substance:

Humic acids consist of a mixture of complex macromolecules having polymeric phenolic structures with the ability to chelate with metals, especially iron (O'Neill, 2006). Leonardite and other lignite deposits can be highly variable in their humic acid content and molecular weights (Lawson and Stewart, 1989; Simandl, et al., 2001). Humic substances in soil are highly variable in their structure and properties. Nuclear magnetic resonance (NMR) has been used to show that most humic substances in soil are from recently decomposed microbes and plants; recalcitrant non-living macromolecular lignins forming a relatively small fraction (Kelleher and Simpson, 2006). Soil organic matter can have ¹⁴C ages of humic acid fractions that are many hundreds of years (Simonson, 1959; Scharpenseel and Schiffmann, 1977; Paul et al., 1997).

Humic substances are also reported to have growth regulator properties active on a variety of different plants (Lee and Bartlett, 1976; Albuzio, et al., 1989; Piccolo, et al., 1992). The studies cited were based on humic substances extracted from composted plant and animal sources as well as fossil source extracts. The direct and indirect properties of humic substances remain a source of debate and research in soil science and plant nutrition (Varanini and Pinton, 2001). Plant pathologists have also hypothesized that humic substances play a role in inducing resistance to various parasitic attacks, mainly in the form of soil organic matter (Cook, 1988). However, humic substances have not been screened for efficacy or safety in their use as fungicides.

Table 1
Physical and chemical Properties of Oxidized Lignite

Physical or Chemical Property:	Value:
Physical State	Liquid
Appearance	Blackish-Brown
Odor	Clean Coal
Carbon Content	55.1% ±5.0%
Oxygen Content	35.6% ±5.8%
Hydrogen Content	5.0% ±1.1%
Nitrogen Content	3.5%±1.5%
Molecular Weight	Highly variable
Solubility	Slightly soluble in water; soluble in alkali solution and carbonates; soluble in nitric acid.
Relative Density at 20°C [68°F].	1.1 kg/l [10.7 lb/gal]
pH	2.5-3.4

Sources: McCarthy, 2001; O'Neill, 2006; SHAC, 2011.

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Specific Uses of the Substance:

The primary specific use of the substance is as an adjuvant to enhance plant uptake of nutrients, particularly trace elements. Humates are applied as a soil conditioner to increase cation exchange capacity, enhance mineral availability, improve soil structure, stimulate soil microorganisms, and provide broad-spectrum trace elements. Efficacy for such purposes is not clearly established in the scientific literature. Granular humates are used when compost availability is limited such as in broad-scale crop production and in large-scale reclamation (Karr, 2001).

Other agricultural uses include as a fertilizer carrier, as growth hormones for plants, and as a manure treatment (SHAC, 2011). Humates are used as a feed additive for livestock (Zimmer, 1996; Islam, et al., 2005; SHAC, 2011). Humates derived from lignite deposits have been sold as a dietary supplement (Lown,

84 1997) and used as folk medicine (Cromarty, 2004). Humic acid derivatives are also used in mud baths,
85 drilling muds, and pigments for printing inks (O'Neill, 2006).

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

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90 Humic acids are used in blended fertilizers and sometimes by themselves to enhance plant growth. Used as
91 a manure treatment. Use as a feed additive has not been approved in the US (SHAC, 2011).

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94 **Action of the Substance:**

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96 Humic acids have been observed to increase uptake of certain specific nutrients under a number of
97 conditions. The effect of commercial humic acid products is not consistent or predictable and efforts to
98 determine which humic acid products are most effective and why have yielded mixed results. Humic acid
99 can serve as a reducing agent for iron under some circumstances (Szilágyi, 1971). Increased uptake of iron
100 observed in tomato roots was proposed to be the result of humic acid reducing ferric iron (Fe^{3+}) to the more
101 plant-available ferrous form (Fe^{2+}) (Adani, et al., 1996).

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104 **Combinations of the Substance:**

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106 Humic acid derivatives are rarely applied alone and are usually combined with various plant nutrients and
107 plant growth regulators to increase plant uptake of substances designed to enhance plant growth. Research
108 has shown that humic acids derived from lignite coal by themselves do not significantly increase
109 production, yield or quality even in cases where they enhance the uptake of various nutrients and increase
110 yield in combination with other fertilizers (Bauder, 1976; Kirn et al., 2010). The coal industry world-wide
111 has explored various combinations of plant nutrients with lignite coal. Most efforts have focused on nitric
112 acid oxidation and ammonium hydroxide extraction (Coca, et al., 1984).

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114 Many formulated humic acid products are prohibited under the current NOP rule. The status of certain
115 formulations under the NOP is ambiguous given the current annotation: "Humic acids - naturally
116 occurring deposits, water and alkali extracts only." [7 CFR 205.601(j)]. Most humic acid derivatives
117 currently used in organic production include potash, a plant macronutrient, from the potassium hydroxide
118 used for extraction. However, the NOP rule does not provide clear guidance on the level of potash that
119 would exceed the amount needed for extraction and result in a prohibited fortified product. Ammonium
120 hydroxide is not expressly prohibited under the current annotation, and products that contain significant
121 levels of nitrate ammoniacal nitrogen from nitric acid oxidation and ammonium hydroxide extraction are
122 marketed in some places as organic fertilizers. Humic acid derivatives may be combined with calcium in
123 the form of calcium lignite, as well as cation micronutrients including copper, iron, manganese, and zinc.
124 Commercial preparations may also have their pH adjusted using hydrochloric acid or sodium sulfite
125 (Schwartz, 1963).

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Status

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131 **Historic Use:**

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133 The primary use of lignite, a mineral classified as low-rank brown coal, has been as a fuel source. However,
134 it usually is not competitive with higher rank coals with greater BTU capacity without cheap extraction
135 methods (McMurtrie and Oppelt, 1956). Lignite was first recognized to have chemical and structural
136 similarities to soil humus as early as the 1920s (Marcusson, 1925). The humic acid fraction of soils, peat, and
137 organic materials with sodium hydroxide was elucidated in the 1920s and 30s (Beckley, 1921; Waksman,
1926; Thiessen and Engelder, 1930). The agricultural application of humic acids derived from fossil sources

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139 goes back to at least the 1930s (Ludmila, 1936; Waksman, 1936; Lawson and Stewart, 1989). Synthetically
140 derived lignite products have been referred to as 'organic fertilizers' at least since the early 1960s (Young
141 and Frost, 1963). Humic acid derivatives have been allowed in organic production in the United States
142 since the first private standards were developed in the early 1970s (Steffan, et al., 1972).

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145 **OFPA, USDA Final Rule:**

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147 Humic acid derivatives are on the National List with the following annotation: naturally occurring
148 deposits, water and alkali extracts only." [7 CFR 205.601(j)(3)]. Lignite reacted with hydrogen peroxide
149 does not fall within the existing annotation. According to a Materials Review Organization recognized by
150 the USDA, lignite oxidized with hydrogen peroxide is prohibited for all uses in organic production
151 (Schulze, 2011).

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153 Humic acid salts resulting from the extraction of fossil sources by alkali extraction are also used in organic
154 production under the National Organic Program (NOP) Standards [7 CFR 205.601(j)(3)]. These may include
155 potassium salts of humic acids provided that the amount of potassium hydroxide used is limited to the
156 amount necessary for extraction and is not used to fortify the potassium analysis (OMRI, 2010). Humic
157 acids fortified with excessive potassium or ammonia nitrogen are prohibited as synthetic macronutrient
158 fertilizers [7 USC 6508(b)(2); 7 CFR 205.105(a); 7 CFR 205.203(e)(1)], but the National List does not provide a
159 clear limit on what is extraction and what is fortification [7 CFR 205.601(j)(3)].

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161 **International**

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163 **Canada** - Canadian General Standards Board - Organic Production Systems Permitted Substances List
164 (June 2011):

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166 Humates, humic acids and fulvic acids are permitted if they are extracted by microbial fermentation or
167 potassium hydroxide. The annotation further reads: "Shall not exceed the limits (category C1) for
168 acceptable levels (mg/kg) of arsenic, cadmium, chromium, copper, lead and mercury specified in the
169 Guidelines for the Beneficial Use of Fertilizing Residuals, published by the Quebec Ministère du
170 Développement durable, de l'Environnement et des Parcs, Direction du milieu rural. Potassium hydroxide
171 levels used in the extraction process may not exceed the amount required for extraction." (CGSB, 2011).

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173 **CODEX Alimentarius Commission**

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175 Neither oxidized lignite nor humic acid derivatives appear on the Codex Alimentarius Commission's
176 Guidelines for the Production, Processing, Marketing and Labelling of Organically Produced Foods Table
177 1, Substances for use in Soil Fertilizing and Conditioning (Codex, 2001). The Codex lists of substances are
178 not inclusive or exclusive. Exceptions are subject to bilateral agreements between trading partners. Among
179 major trading partners with the US, Canada and the EU do not prohibit synthetic humic acid derivatives in
180 their equivalency agreements, but Japan does not consider the allowance of humic acid derivatives to be
181 equivalent to the Japanese Agricultural Standard.

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

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186 Humic acid derivatives and oxidized lignite do not appear on Annex I, Fertilizers, soil conditioners and
187 nutrients referred to in Article 3(1) and Article 6d(2) (EC, 2008). The EU requires all substances used as a
188 fertilizer, soil conditioner or nutrient in organic production in the EU appear on that Annex (EC, 2007).
189 However, humic acids do appear on Annex VII, Products for Cleaning and Disinfection (EC, 2008).

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191 Humic acid products have historically been used in organic farming in a number of the member states,
192 particularly Spain (Gonzalves, 2004). Commercial humic acid products were claimed to be used by organic
193 farms in several of the Eastern European countries prior to accession to the European Union, and use on

194 certified organic farms may have been grandfathered by derogation after EU membership. Humic acids are
195 among the substances considered biostimulants and plant strengtheners, a term found in the organic
196 legislation of some EU member states. Humic acids are among the unclassified materials that are under
197 consideration for harmonization of EU fertilizer regulations (Spaey, 2012).

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200 **International Federation of Organic Agriculture Movements (IFOAM) –**

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202 Humic acid derivatives do not appear on Appendix 2: Fertilizers and Soil Conditioners. However, the use
203 of humic acids are covered under a derogation found in §4.4.6, which reads:

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205 “Mineral fertilizers shall be applied in the form in which they are naturally composed and
206 extracted and shall not be rendered more soluble by chemical treatment, other than addition
207 of water and mixing with other naturally occurring, permitted inputs.

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209 *“Under exceptional circumstances, and after consideration of all relevant information, and having
210 regard to Appendix 1, the standard-setting organizations may grant exception to this requirement.
211 These exceptions shall not apply to mineral fertilizers containing nitrogen.”* (IFOAM, 2005.

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213 Derogation in italics).

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216 **Japan Agricultural Standard (JAS) for Organic Production**

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218 The Japanese Agricultural Standard for Organic Production does not include humic acid derivatives or
219 oxidized lignite on Table 1, Fertilizers and Soil Improvement Substances (JMAFF, 2012). Alkali extracted
220 humic acid is banned for use on products grown for export to Japan under the Equivalency Agreement
221 between the Japanese Ministry of Agriculture, Forestry and Fisheries and the USDA’s National Organic
222 Program, the only such substance currently to have that status (Arai, 2008).

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

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228 **Evaluation Question #1: What category in OFPA does this substance fall under:** (A) Does the substance
229 contain an active ingredient in any of the following categories: copper and sulfur compounds, toxins
230 derived from bacteria; pheromones, soaps, horticultural oils, fish emulsions, treated seed, vitamins and
231 minerals; livestock parasiticides and medicines and production aids including netting, tree wraps and
232 seals, insect traps, sticky barriers, row covers, and equipment cleansers? (B) Is the substance a synthetic
233 inert ingredient that is not classified by the EPA as inerts of toxicological concern (i.e., EPA List 4 inerts)
234 (7 U.S.C. § 6517(c)(1)(B)(ii))? Is the synthetic substance an inert ingredient which is not on EPA List 4,
235 but is exempt from a requirement of a tolerance, per 40 CFR part 180?

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237 Humic acid derivatives, including oxidized lignite, do not explicitly fall into any of the categories for
238 production found in 7 USC 6517(c)(1)(B)(ii).

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241 **Evaluation Question #2: Describe the most prevalent processes used to manufacture or formulate the**
242 **petitioned substance. Further, describe any chemical change that may occur during manufacture or**
243 **formulation of the petitioned substance when this substance is extracted from naturally occurring plant,**
244 **animal, or mineral sources (7 U.S.C. § 6502 (21)).**

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246 Most lignite is surface mined at a relatively shallow depth (Vorres, 2000). The most prevalent method to
247 produce humic acids from fossil sources is by alkali extraction using potassium or sodium hydroxide
248 (Stewart and Lawson, 1989). Ammonium hydroxide is less effective at extracting humic acids, but may be
used to fortify the nitrogen content of a fertilizer and slow the release of the ammoniacal nitrogen (Lawson

249 and Stewart, 1989). Recovery rates are greatly improved by high temperature and pressure (Dekker and
250 Cronje, 1991). The yield decreases as the rank (maturity) increases, with bituminous coal yielding very little
251 soluble humic acid compared with lignite. Lignite yields less than peat and peat yields less than plant
252 organic matter. As coal rank increases, there are fewer functional groups and higher aromaticity (Lawson
253 and Stewart, 1989).

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255 The petition describes in general the oxidation of lignite by hydrogen peroxide (SHAC, 2011). The specific
256 steps of the manufacturing process are confidential. In general, all oxidative degradation of humic
257 substances produces aliphatic substances, including alkanes, fatty acids, and aliphatic carboxylic acids;
258 phenolic acids, and benzocarboxylic acids (Griffith and Schnitzer, 1989). Specific information regarding the
259 manufacturing process has been redacted as Confidential Business Information (CBI) (SHAC, 2011).
260 Reaction of soil humic substances with hydrogen peroxide yielded phenolic compounds, as well as
261 benzoic, malonic, oxalic and o-phthalic acids (Mehta et al., 1963; Mendez and Stevenson, 1966). Lignite coal
262 can also be oxidized using ozone and superheated water – essentially vaporized hydrogen peroxide under
263 pressure – to ‘crack’ the coal into aliphatic and aromatic fractions (Oyunbold, et al., 2010).

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

269
270 The petitioned substance, liquefied oxidized lignite, is produced by a manufacturing process that involves
271 an oxidation reaction of lignite with hydrogen peroxide (SHAC, 2011). The Organic Materials Review
272 Institute has issued the opinion that the substance is synthetic (Schulze 2011). Low-rank coal that is close to
273 the surface and weathered by a slow, natural oxidation process is also referred to as ‘oxidized lignite’
274 (Fowkes and Frost, 1960; Jackson, 1993).

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

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279 Lignite itself is very persistent, chemically and physically changing slowly into bituminous coal in a period
280 of over millions of years (Lawson and Stewart, 1989; Schweinfurth, 2009). Stability of alkaline extracted
281 humic acid derivatives will depend on a number of factors and is not homogeneous. Factors such as the
282 age of the lignite, the temperature at the time of extraction and the ratio of aliphatic / aromatic in the raw
283 lignite can all be factors in the degradation rate of alkaline humic substances (Pokorná, et al., 2001).

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285 Oxidized lignite can be divided into various fractions (Mae, et al., 1997; Oyunbold, et al., 2010). Some are
286 stable and some are volatile. The cleaved compounds tend to become more labile, but many of the high
287 molecular weight structures remain recalcitrant. The less reactive structures can be expected to behave like
288 lignite. However, there are differences of opinion in the scientific literature about the pathway for their
289 degradation (Peyton et al., 1989). Lignite will turn into bituminous or anthracite coal if the temperature and
290 pressure conditions are favorable (Stewart and Lawson, 1989).

291
292 The peroxy radicals from the extraction process are volatile and assumed to degrade rapidly to the point
293 they are undetected in the final product (SHAC, 2011). These results are consistent with those found in
294 other experiments in hydrogen peroxide (Mae, et al., 1997) and ozone (Oynbold, et al., 2010) extractions of
295 lignites.

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

301
302 Coal and coal derivatives are well-documented to have adverse health effects that are severe and often
303 fatal; widespread, affecting many millions of people; and complex, requiring a multidisciplinary approach

with epidemiology and toxicology (Finkelman, et al., 2006). Most of the literature regarding health effects of coal examines the respiratory illnesses caused by mining and combustion of such as bituminous and anthracite coals for energy production and is beyond the scope of this report. However, there is an extensive literature regarding the toxicity of coal derivatives, including those from lignite.

Coal derivatives were among the first cancer-causing agents (carcinogens) discovered (Pitot and Dragan, 2001). Among the aromatic compounds isolated from oxidized humus are benzenecarboxylic and phenolic acids (Griffith and Schnitzer, 1989). Quinones may also be isolated from coal (Khan and Schnitzer, 1972). While these are not carcinogens by themselves, they may form carcinogens under certain conditions (Pitot and Dragan, 2001). Coal tar derivatives are classified as known carcinogens (IARC, 2011; NTP, 2011). However, based on existing evidence, coal dust by itself cannot be classified as a carcinogen (IARC, 1997). Phenols are highly variable in their toxicity, depending on the biological response to the chemical (Stewart and Stewart, 2001). Given the complex nature of humic acids from oxidized lignite, the toxicity is difficult to estimate but cannot be assumed non-toxic as previous reviews have asserted (TAP, 1996; ICF, 2006).

The correlation of lignite-derived compound with damage to kidney tissue is a relatively recent discovery. Lignite coal is believed to be the cause of Balkan endemic nephropathy, a kidney damage syndrome that leads ultimately to renal failure (Bunnell, et al., 2007). High incidents of renal pelvic cancer are noted in areas where drinking water is contaminated with organic compounds from lignite, including Louisiana's Gulf Coast (Bunnell, et al., 2006) and the Powder River Basin of Wyoming (Orem, et al., 2007).

Lignite is known to have higher than average concentrations of uranium and other radioactive isotopes. The greatest risk is with ash from combustion of lignite for fuel (Vorres, 2000).

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

Fossil sources of humic acids are obtained from coal. Most of the coal deposits are of the lower rank, being in the form of lignite. Major deposits in North America are found in the Badlands and Black Hills of North Dakota, the Ravenscrag formation in Saskatchewan, and New Mexico. The primary form of recovery is simple surface mining (Schobert, 1995; Vorres, 2000). Surface mining poses lower risks for safety than does underground mining, but disturbs a significantly greater amount of soil and habitat than underground shaft mining in most cases. The exception is where an underground mine has a persistent fire, such as in Centralia, Pennsylvania. Surface mining is less likely to result in explosions and groundwater contamination than underground mining. However, surface mines are more likely than underground mines to result in surface water pollution through sedimentation from erosion and acid runoff (EPA, 2008).

Oxidation of lignite results in the fractionation of the coal into aliphatic and aromatic structures (Oyunbold, et al., 2010). Treatment with hydrogen peroxide results in the release of carbon dioxide (CO₂) into the atmosphere (Mae, et al., 1997). While it may be feasible to recover the CO₂, such a process is not described in the public petition. The product also produces a solid waste of indeterminate nature and its disposal is not described in the public petition.

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

Humic acids are functionally interactive with many substances used in organic crop and livestock production as well as with handling. Humic acid derivatives are used in organic farming because of this functionality. Humic acids make cation nutrients more biologically available, but also increase the uptake of various toxic metals. However, because of their widely varying structures and functions, it is difficult to predict with certainty the effects of humic substances in the soil. Impacts on model cations and non-polar substances such as herbicides yield various results depending on cation exchange capacity (CEC) and soil

359 pH (Haberhauer, et al., 2001). Humic acid is amphoteric, with its net surface charge changing from positive
360 to negative at lower pH. This effect can be significant in soils that already have a high CEC (Kretzchmar, et
361 al., 1997).

362
363 Humic acid released into the aquatic environment becomes a form of dissolved organic matter (DOM).
364 Various hydrophobic organic molecules will be bound with the DOM and taken up by various aquatic
365 organisms (McCarthy, 1989). Given the diverse nature of compounds contained in humic substances, their
366 biological and chemical effects in the aquatic environment are inconsistent and difficult to characterize
367 (Petersen, 1989). While humic substances may be correlated with increased biological activity in the soil,
368 contamination of the aquatic environment by humic substances is considered to be adverse because of the
369 stress that organic matter places on the aquatic ecosystem and its organisms (Steinberg, et al., 2008).

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371 Humic acid derivatives have been documented to increase soil nutrient availability and facilitate nutrient
372 transport of certain specific nutrients under certain specific laboratory and greenhouse controlled
373 conditions. The element with the most consistent result has been iron. Canola showed a positive growth
374 response due to increased uptake of sulfur (Akinremi, et al., 2000). Nitrogen uptake in the ammoniacal
375 form has been increased in some studies. However, the increased carbon may reduce nitrogen availability
376 and may result in nitrogen deficiencies, particularly at high loading rates required to achieve responses for
377 other limiting nutrients. When compared with compost, lignite extracted by sodium hydroxide and sodium
378 phosphate appeared to slow the microbial decomposition of organic matter and maintain carbon
379 sequestration (Spaccini, et al., 2002).

380
381 Humic substances treated with hydrogen peroxide and ultraviolet light degraded pollutants more rapidly
382 than humic substances treated with ozone and ultraviolet light in a photochemical reactor under
383 controlled laboratory conditions (Peyton et al., 1989). No direct comparisons of humic substances treated
384 with hydrogen peroxide and various alkali solvents were found in the literature.

385
386 When reacted with free chlorine similar to what is used to treat drinking water and wash water, humic
387 substances will form trihalomethanes and other chlorinated organic compounds (Rice and Gomez-Taylor,
388 1986). Many of these compounds indicate a strong mutagenesis with the Ames test (Loper, et al., 1978). A
389 number of reaction products of humic substances with chlorinated water are linked to induced mutation or
390 mutagenesis (Meier, et al., 1978; Holmbom, 1989). The most significant mutagen isolated was the
391 compound 3-chloro-4-(dichloromethyl)-5-hydroxy-2-(5H)-furanone, also known as "MX" (Holmbom,
392 1989).

393
394 Humic substances appear to depress some organisms in the environment while stimulating others
395 (Peterson, 1989). Humic substances can be toxic to various organisms, including humans as noted above,
396 and poses a particular problem when found in drinking water (Wetzel, 2001). Phenols in drinking water
397 can combine with halogens used to disinfect the water and lead to toxic by-products (Stewart and Stewart,
398 2001).

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

403
404 The impact of oxidized lignite on soil organisms is inconclusive, with some studies showing benefits, some
405 showing a negative effect, and some showing no significant difference. An exhaustive review of the
406 literature regarding all forms of humic acid from all sources is beyond the scope of this report. Most studies
407 are based on either naturally occurring soil humic acids or alkali extracted humates, with few studies done
408 on hydrogen peroxide liquefied oxidized lignite. Some field experiments use commercial humic acid
409 preparations made by alkali extraction. Some are cited in the petition or the previous technical reviews
410 (TAP, 1996; ICF, 2006). Relatively few studies specifically examine the impacts of lignite oxidized by
411 hydrogen peroxide in the agroecosystem. The petition does not include any peer-reviewed scientific
412 studies to substantiate some of their statements (SHAC, 2011).

413

414 A few significant relationships found in the literature that were not discussed in the previous reports are
415 worth mentioning. Chlorination of humic substances causes the production of trihalomethanes and high
416 molecular weight organohalides (Kruithof, et al., 1989). Many such halogenated organic compounds are
417 suspected to be carcinogens, but evidence has been inconsistent and inconclusive (Periera, et al., 1982;
418 WHO, 2005).

419
420 In addition to increasing the storage capacity, mobility and uptake of nutrients, soil humic acids can also
421 adsorb toxic substances. This property can have both positive and negative consequences for interactions in
422 the environment. Also, the relatively small amounts of humic acids derived from lignite coal may have an
423 insignificant effect. Under some circumstances, humic acids can adsorb toxic substances and immobilize
424 them in a way that prevents uptake by plants. Microbial degradation can also be enhanced by elevated
425 levels of humic acids. For example, lignite treated with sodium hydroxide and combined with zeolite
426 increased the degradation of pentachlorophenol (PCP) (Derková, et al., 2007).

427
428 Humic acids can have both beneficial and detrimental effects with the same contaminant. For example,
429 humic acids may increase the adsorption of arsenic (Thanabalasingam and Pickering, 1986). The effect is
430 particularly pronounced in soils where iron is low (Warwick, et al., 2005). The ability of humic acid to
431 enhance uptake of arsenic is noted with its use as an excipient of arsenical chemotherapy treatments, where
432 that property could be considered beneficial (Ting, et al., 2010).

433
434 Mercury uptake was decreased by increased levels of humic acid in the soil (Wang, et al., 1995). On the
435 other hand, mercury may be complexed by humic acid under certain circumstances, increasing its
436 solubility and transport to surface water where it is correlated to increased levels in fish (Melamed, et al.,
437 2000). Cadmium, copper and lead all are capable of being complexed by humic acids in conditions
438 comparable to seawater (Plavšić, et al., 1991). Such complexing can be detrimental or beneficial. For
439 example, one study found the presence of humic acids reduced toxicity of cadmium and zinc to a model
440 algal species (Koukal, et al., 2003). Arsenic and lead are non-synthetic substances prohibited for organic
441 production [7 CFR 205.602]. Cadmium is considered a priority heavy metal by the Organic Materials
442 Review Institute (OMRI, 2010). These elements are naturally present in the environment even when not
443 used as a direct crop input.

444
445 The petitioned process using hydrogen peroxide has the advantage over alkali extraction in that it does not
446 create additional metal salts from the reaction (Lawson and Stewart, 1989).

447
448 **Evaluation Question #9: Discuss and summarize findings on whether the petitioned substance may be**
449 **harmful to the environment (7 U.S.C. § 6517 (c) (1) (A) (i) and 7 U.S.C. § 6517 (c) (2) (A) (ii)).**

450
451 The oxidation of lignite with hydrogen peroxide (H_2O_2) releases carbon dioxide (CO_2), a greenhouse gas.
452 Hydrogen peroxide pre-treatment of various lignite samples resulted in between 2% and 20% losses to CO_2 .
453 Losses were a function of molecular weight of the lignite, H_2O_2 concentration, temperature of the extraction
454 solution, and other co-solvents used (Mae, et al., 1997). Carbon dioxide emissions from the application of
455 soil amendments are linked directly and indirectly to global warming and climate change (Reikosky, et al.,
456 2000). Other methods of production of humic acids would release lower levels of carbon dioxide and
457 would have less of an impact on climate change and air pollution. Practices such as cover crops and
458 composting sequester carbon and reduce carbon dioxide content in the atmosphere. However, composting
459 will also release significant amounts carbon dioxide and ammonia to the atmosphere in the process of
460 preparing humic acids.

461
462 Coal-derived humic acids have greater levels of aromatic structures than humic acids derived from plant
463 and animal sources. Aromatic substances such as benzene have been linked to carcinogenicity (Pitot and
464 Dragan, 2001). Potential increased emission of CO_2 through production might be offset to an unknown
465 extent through enhanced plant growth, leading to larger amounts of plant biomass being returned to the
466 soil and possibly sequestered.

467
468

469 **Evaluation Question #10: Describe and summarize any reported effects upon human health from use of**
470 **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**
471 **(m) (4)).**

472
473 As mentioned above, coal and coal-derivatives can be carcinogenic (Pitot and Dragan, 2001). Oxidation of
474 organic matter through the use of hydrogen peroxide may activate some of the carcinogenic substances
475 (Rice and Gomez-Taylor, 1986). While there are no reported direct adverse effects on human health by the
476 agricultural application of oxidized lignite, there is also no evidence that toxicology of the petitioned
477 substances have been performed under field conditions and use of the petitioned substance has been
478 limited relative to alkali extracted humic acid derivatives.

479
480 Coal mining is linked to the respiratory disease known as coal worker's pneumoconiosis, also known as
481 'black lung' and other respiratory problems (Finkelman, et al., 2002). Balkan endemic nephropathy (BEN),
482 an irreversible kidney disease of unknown origin, has been related to the proximity of lignite deposits and
483 contamination of drinking water with organic compounds from lignite coal (Tatu et al., 2000; Bunnell et al.,
484 2007). Drinking water from lignite aquifers in the US have been linked to renal cancer and microorganisms
485 believed to use lignite as a food source (Bunnell et al., 2006).

486
487 **Evaluation Question #11: Describe all natural (non-synthetic) substances or products which may be**
488 **used in place of a petitioned substance (7 U.S.C. § 6517 (c) (1) (A) (ii)). Provide a list of allowed**
489 **substances that may be used in place of the petitioned substance (7 U.S.C. § 6518 (m) (6)).**

490
491 Humic acid is formed by the decomposition of organic matter. Compost, cover crops, manure, mulch, and
492 other natural sources of organic matter can all increase humic acid content of the soil (Magdoff and Weil,
493 2004). Humic acids from decaying organic matter have been empirically shown to have the same benefits
494 as those from fossil sources, such as lignite (Weil and Magdoff, 2004). These include nutrient storage and
495 release; cation exchange capacity; sorption of organic compounds; anion sorption; metal mobility; soil pH
496 buffering and amelioration; and growth regulating substances (literature review contained in Weil and
497 Magdoff). In addition, actively managed organic matter in the soil increases soil biological activity and
498 serves to sequester carbon.

499
500 Fossil sources of humic acids are relatively difficult to extract compared with humic acids from
501 decomposing organic matter that has not fossilized (Lawson and Stewart, 1989). Even low-rank coal, such
502 as lignite, only has a small percentage of its humic acids in a biologically active form. Non-synthetic lignite
503 may be used in place of the liquefied oxidized or alkali treated lignite. As mentioned above, lignite is
504 highly variable. Improved analytical and quality control methods may be used to evaluate natural lignite
505 deposits for the suitability for agricultural application (Chassapis and Roulia, 2008).

506
507 Commercial humic acid derivatives are distinctly different from humic substances that naturally occur in
508 soil and water (Malcolm and MacCarthy, 1986; MacCarthy and Malcolm, 1989). Commercial preparations
509 are generally in a salt form complexed with the metal moiety with which it was extracted – usually either
510 potassium or sodium – and has a pH sufficient high that they cannot be considered truly 'acid' (MacCarthy
511 and Malcolm, 1989). While synthetic, alkali-extracted humic acids are commercially available and
512 permitted for organic production. There are over 50 brand name products on the OMRI List in that
513 category (OMRI, 2012).

514
515 Carbon obtained from the roasting of plant-derived organic matter – a substance known as 'biochar' –
516 could be considered non-synthetic when produced under certain conditions. Biochar is beyond the scope of
517 this report, and the status of biochar under the NOP rule remains unresolved as of this date. Unlike humic
518 acids derived from fossilized sources, biochar is considered biogenic and may be considered closer to wood
519 ash than to a coal. Soil amended with biochar showed significant fertility improvements consistent with the
520 presence of stable humic acids (Novak, et al., 2009).

521

522 It is also possible to treat lignite coal by microbial fermentation (Catcheside and Ralph, 1999). The first
523 commercial humic acid fertilizer product made from microbially processed lignite, Actosol, was introduced
524 to the market by Arctech in 1989 (Arctech, 1988; Fakoussa and Hofrichter, 1999).

525
526 Fungi such as *Aspergillus* spp., *Candida* spp., *Paecilomyces* spp., *Penicillium* spp. and *Mucor* spp. are able to
527 grow on raw coal (Bailey, 1985). Fungal degradation can increase the solubility of the humic acids found in
528 lignite. Such products would presumably be currently allowed by the NOP as a non-synthetic that is not
529 listed at 7 CFR 205.602, provided no additional synthetic reactions occur and excluded methods are not
530 used.

531
532 One method involves the use of nitric acid and hydrogen peroxide as oxidizing agents and *Trichoderma* sp.
533 as the fermenting organism (Tao, et al., 2009). The nitric acid and hydrogen peroxide would presumably
534 render the lignite synthetic, with the nitric acid providing a possible non-protein nitrogen source for the
535 *Trichoderma*. At present the only Actosol product that is OMRI® Listed is the alkali extracted Micronutrient
536 Actosol. In addition, Arctech claims that Bio-Activated Granular Actosol is produced by a biological
537 process, but has not disclosed its manufacturing process publicly (Arctech, 2004). Information on the use of
538 these products on organic farms can be obtained from Organic System Plans.

539
540 Research on improving the microbial fermentation of lignite is on-going and several recent breakthroughs
541 are in the scientific literature. At least three different mechanisms are possible for microbial degradation
542 and solubilization of humic substances in lignite: enzymatic attack; basic metabolites; and microbial
543 chelators (Zvodská and Lesný. 2006). Organisms used in the Basidiomycota phylum can depolymerize
544 lignite through enzymatic attack by their manganese peroxidase system. Such humic acid can be stable in
545 solution for days (Hofrichter, et al., 1999). *Trichoderma atroviride* and *Fusarium oxysporum* can also increase
546 the solubility of lignite by action of chelation (Hölker, et al., 1999). While soluble humic acids derivatives
547 by these mechanisms are not known to be commercially available, biologically based alternatives to alkali
548 treated lignite are being actively pursued (Fakoussa and Hofrichter, 1999; Zvodská and Lesný, 2006).
549 However, some of the methods being pursued may involve genetic engineering or other methods excluded
550 under 7 CFR 205.105(e) (Serbolisca, et al., 1999).

551
552 Various naturally occurring carboxylic acids may be used to chelate micronutrients. Citric acid is the most
553 commonly used of these. While effective in complexing nutrients, humic acid derivatives are not as
554 consistent or predictable as other chelating agents (Adani, et al., 1998). Non-synthetic amino acids are also
555 used as chelating and complexing agents in micronutrients

556
557 Synthetic ligninsulfonates are also used as chelating agents for micronutrients [7 CFR 205.601(j)(4)]. Several
558 micronutrient products chelated with lignin sulfonates are commercially available (OMRI, 2012). Winfield
559 Solutions' (St. Paul, MN) Agrisolutions explicitly states that it chelates micronutrients with lignin
560 sulfonates (OMRI, 2012). A list of producers who use these products is not available to the investigators of
561 this report. data may be available through the Organic System Plans submitted to NOP Accredited
562 Certification Agents. Other commercial micronutrient products are also thought to be chelated with lignin
563 sulfonates, but that information may be confidential and is not required to be disclosed on the product
564 label.

565
566 **Evaluation Question #12: Describe any alternative practices that would make the use of the petitioned**
567 **substance unnecessary (7 U.S.C. § 6518 (m) (6)).**

568
569 Humic substances occur in nature in great abundance. Compost, cover crops, mulches, conservation of
570 straw and stubble, and other sources of biological material can provide humic acids to soils and enhance
571 nutrient uptake. In addition, untreated lignite, leonardite, and water-soluble fulvic acids are other non-
572 synthetic sources of humic acids. Applications of freshly mined leonardite not chemically treated were
573 correlated with a positive yield response in canola grown in plastic trays filled with a soil found in Western
574 Canada (Akenremi, 2000).

575

576 A long-term soil building program appears to provide the same benefits as those from oxidized lignite. Soil
577 organic matter provides all the same benefits from humic substances as those claimed in the petitioned
578 substance (see review by Weil and Magdoff, 2004). Various strategies to maintain and increase humic
579 substances in soil include growing green manure cover crops, reduced tillage, application of animal
580 manure, crop rotations that include pasture and perennial crops, incorporation of crop residues into the
581 soil, and conservation practices that reduce erosion (Magdoff and van Es, 2009; Magdoff and Weil, 2004).

582

583

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