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.

Lignins

Crops

Identification of Petitioned Substance

Chemical Names:
Soda lignin; Sodium lignin; Sodium carbonate lignin; Kraft lignin; Lignin sulfonate

Other Names:
Alkali lignin; Alkaline lignin; Sulfur-free lignin; Sulfur-free anionic sodium carbonate lignin

Trade Names:
Polybind 300

CAS Numbers:
8068-05-1 Alkali lignin, alkali soluble lignin, kraft lignin, soda lignin
9005-53-2 Lignin
8062-15-5 Lignin sulfonate
8061-51-6 Sodium lignin sulfonate
8061-54-9 Magnesium lignin sulfonate
8061-53-8 Ammonium lignin sulfonate
8061-52-7 Calcium lignin sulfonate

Other Codes:
N/A

Summary of Petitioned Use

Sodium carbonate lignin has been petitioned for use in organic crop production through addition to the National List at 205.601(j)(4) of “lignins” as a dust suppressant. Lignin sulfonate, another type of lignin, is currently listed at 205.601(j)(4) for use as a chelating agent and dust suppressant.

Characterization of Petitioned Substance

This report focuses primarily on alkali lignins, including sodium carbonate lignin. Supplemental information on other lignin derivatives from the kraft (sulfonated), sulfite, and organosolv processes is also included but is not the primary focus of this report. Lignins that are chemically modified subsequent to or beyond the pulping and its associated extraction steps are outside of the scope of this report. Table 1 provides a summary of the lignin derivatives covered in this report.

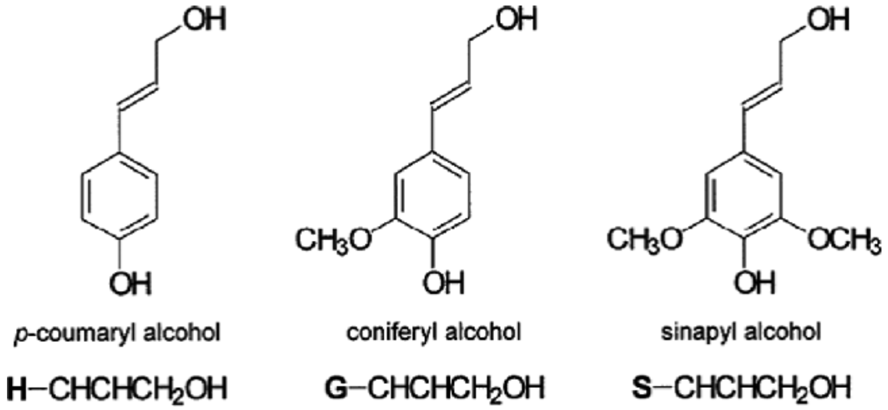
Table 1. Lignin derivatives addressed in this report

	Lignin type			
	Soda lignin	**Organosolv lignin**	**Kraft lignin**	**Lignin sulfonate**
Alternate or additional name(s)	Alkali lignin; Alkaline lignin; Sodium lignin; Sodium carbonate lignin	Acetosolv lignin; Organocell lignin	Alkali lignin; Alkaline lignin; Alkaline sulfite lignin; Lignin sulfonate	Lignin sulfonate; Salts of lignosulfonic acid
Source process	Soda pulping	Organosolv pulping	Kraft pulping	Sulfite pulping
Sulfonated end product	No	No	Extent of sulfonation depends on process	Yes

Composition of the Substance:
Native lignins found in plant cell walls are amorphous, complex biopolymers (Peretti, Barton and Teixeira Mendonca 2016). They are made up of phenylpropane units (C6–C3), known as monolignols. These monolignols are *p*-coumaryl, coniferyl, and sinapyl alcohols. The main difference between these different phenylpropane

derivatives is the number of methoxyl groups attached to the phenolic unit (Peretti, Barton and Teixeira Mendonca 2016) (see Figure 1). There are other, less abundant lignin monomers of different phenylpropane units and some carbohydrate moieties. In native lignin biosynthesis, all of these components combine in various ways to form three-dimensional, cross-linked polymers that do not have one regular, ordered macromolecule. Thus, lignins are physically and chemically heterogeneous, lacking a defined primary structure (Calvo-Flores, et al. 2015; Košíková and Gregorová 2005; Karak 2016; Du, et al. 2013; Peretti, Barton and Teixeira Mendonca 2016; Garcia-Valls and Hatton 2003).

Figure 1. Building blocks of lignin. (Du, et al. 2013). The subindices H, G, and S indicate the alcohol moiety of each monolignol: *p*-hydroxyphenyl, guaiacyl, and syringyl, respectively.



Industrial processes such as paper pulping and bioethanol production separate different components of plant biomass and produce lignins as a byproduct, which may then be commercialized. These lignin byproducts differ from native lignin in size and structure (Ahvazi and Ngo 2018) depending on the method of extraction used (Agrawal, Kaushik and Biswas 2014). The chemical structure of these lignin polymers includes significant quantities of three important functional groups: phenolic hydroxyl groups, aliphatic hydroxyl groups, and carboxylic acid groups (Ahvazi and Ngo 2018). The types and quantities of these functional groups in any lignin byproduct depend largely on the pulping process used to extract the byproduct. These extracted lignins also differ in size of polymeric fragments depending on the methods used to recover them from the pulping black liquor (i.e., the extraction liquid resulting from the pulping process) (Ahvazi and Ngo 2018).

The petitioned material results from a paper pulping process that uses sodium carbonate and sodium hydroxide to extract lignin. In contrast, lignin sulfonates are produced using a sulfite chemical pulping process, where sulfur dioxide is used to extract lignin under pressure. A 2011 technical report on lignin sulfonate includes detailed information on this particular type of lignin (USDA NOP 2011). The petitioner of the present substance states that its composition is made up of lignin fragments, carbohydrates from the breakdown of hemicellulose, and residual sodium carbonate. The lignin in this mixture is in varying states of degradation and complexation with cellulose and hemicellulose (Legnochem 2019). Soda lignin has little to no sulfur and a low quantity of hemicellulose but can contain high amounts of silicate and nitrogen depending on the extraction procedure used (Espinoza-Acosta et. al. 2016). Lignins from soda ash pulping have also been observed to have higher sodium ion content than other lignins (Vivekanandhan, Misra and Mohanty 2015). One report on sulfur-free lignin suggested that these lignin derivatives contain more lignin with macromolecular size (about 50–75 percent) and structure akin to native lignin than those in lignin sulfonates (Liu, et al. 2020). The sulfur-free lignin used in the study was a byproduct of ethanol production and contained 91.2 percent lignin, 0.12 percent residual cellulose/hemicellulose, and 0.67 percent ash (Liu, et al. 2020). The sodium content of an alkali kraft lignin precipitated from the pulping black liquor using carbon dioxide was reported to be 10 kg, or 1 percent, of sodium per ton of lignin (Stigsson and Lindstrom 2007).

Because the methods used to delignify plant matter influence the structure and size of the final lignin byproduct, lignins are typically characterized by their extraction process (Serrano, et al. 2012). For example, *soda lignins* are derived from cooking plant matter in sodium hydroxide. *Organosolv lignins* are obtained from the use of organic solvents used in the organosolv process. *Kraft lignins* are derived from the kraft process, and *lignin sulfonates* result principally from the sulfite pulping process. However, there are some areas of discrepancy in how lignins are reported in the literature, with inconsistent use of terms. For example, some reports refer to alkali or alkaline lignins as those resulting from the soda or soda ash process and as being distinct from kraft lignins (Marin, et al. 2017; Calvo-Flores, et al. 2015). Conversely, the kraft process uses the alkaline materials sodium hydroxide and sodium sulfide, and Colins (2019) lists alkali pulping as also being known as kraft pulping. Ahvazi and Ngo (2018) refer to "alkaline kraft extraction." Another report refers to the kraft process as the "alkaline sulfite method" (Khristova, et al. 2002). In some reports the term "alkali lignin" is not defined in terms of specific processing chemicals (Agrawal, Kaushik and Biswas 2014). No studies reviewed for this report expressly referred to lignin sulfonates as alkali lignins, though lignin sulfonates are also produced under strong alkali conditions. See Table 1 for alternate names associated with the various pulping processes and Table 3 for process details.

Inconsistent terminology also appears in the literature when the sulfur content of lignin products is discussed. Numerous reports identify "sulfur-free lignin," which may be derived from wood prehydrolysis (Košíková and Gregorová 2005), bioethanol production (Liu, et al. 2020), organosolv, soda (Collins 2019), or soda ash processes. Calvo-Flores et al. (2015) identify sulfur-free lignin as that obtained from soda, organosolv, and ionic liquid processes. Other lignins are acknowledged to contain sulfur, such as lignin sulfonates. Espinoza-Acosta et al. (2016) group kraft lignins with lignin sulfonates as sulfur-containing. However, Agrawal et al. (2014) note the availability of a commercial sulfur-free kraft lignin.

Ahvazi and Ngo (2018) measured the sulfur content of various lignins, which differs primarily based on extraction method. They found that samples of soda lignin from wheat straw and organosolv lignin from hardwood both had <0.50 percent sulfur, while another soda lignin from wheat straw had a sulfur content of 1.19 percent. Two kraft lignins from hardwood and softwood showed sulfur values of 1.93 percent and 1.32 percent, respectively. These values are in contrast to the 4.16 percent sulfur measured in a low-sulfonated kraft lignin from softwood and the 6.63 percent and 6.59 percent sulfur content found in lignins from sulfite pulping of softwood (Ahvazi and Ngo 2018).

Calvo-Flores et al. (2015) similarly reported a sulfur content of 6.5 percent for lignin sulfonate compared to 1.6 percent for kraft lignin. Thus, kraft lignin may or may not contain significant amounts of sulfur depending on its processing. Other lignins are identified as "sulfur-free lignins" without disclosing their processing chemicals (Sahoo, et al. 2011). Thus, identification of lignins by sulfur content does not directly correspond to the general process-based characterizations in every case.

Although the extraction process is the predominant identifier for a lignin, the source plant material also has bearing on the makeup of the final lignin product. Lignins may be derived from hardwoods, softwoods, or herbaceous plants (Agrawal, Kaushik and Biswas 2014). Softwood lignins contain almost exclusively guaiacyl units, while hardwoods contain guaiacyl and syringyl units in different ratios (Ahvazi and Ngo 2018), and herbaceous plants contain all of the three moieties (Ponnusamy, et al. 2019) with significant amounts of *p*-hydroxyphenyl units (Agrawal, Kaushik and Biswas 2014). Regardless of the plant source, however, all lignins have β-*O*-4 linkages as major interunit bonds (Calvo-Flores, et al. 2015).

Source or Origin of the Substance:

Lignin is a basic, albeit heterogeneous and complex, structural component of plants. It makes up approximately 20–30 percent of plant cell walls (Peretti, Barton and Teixeira Mendonca 2016), 30 percent of the total mass in softwoods, 20–25 percent of the total mass in hardwoods, and smaller percentages of the total mass in herbaceous species (Calvo-Flores, et al. 2015). Commercial lignins are obtained as byproducts of the paper pulping and bioethanol industries.

The particular lignin derivative identified in the petition, sodium carbonate lignin, comes from soda ash pulping of wood chips, in which sodium carbonate and sodium hydroxide are used for extraction (Legnochem 2019). The milder reagents of sodium hydroxide and sodium carbonate—along with others such as aqueous ammonia mixed with potassium hydroxide, and sodium hydroxide with the pulping additive anthraquinone (AQ)—have been reported to be more suitable for pulping straw (Marin, et al. 2017) than stronger chemicals used in other processes.

Based on existing literature, soda ash pulping is not in widespread use. Soda pulping is more common but is not the predominant pulping process. In the United States, soda pulping fell from 420,000 metric tons (MT) in 1960 to 300,000 MT in 1990. By comparison, kraft pulping in the United States produced 14,590 MT in 1960 and 50,000,000 MT in 1990 (Biermann 1996). Global kraft pulp production was approximately 118,000,000 MT in 2015, accounting for 80% of global paper production (Fernández-Rodríguez, et al. 2019). The literature reviewed for this report indicates that sources of sodium carbonate lignin specifically may be limited, though there are numerous kinds of technical lignins that vary based on both their plant source and the method used to extract them.

Properties of the Substance:

Lignin byproducts from plant processing differ from native lignin in terms of size and structure. The properties of these lignins also vary based on the origins of varied molecular and structural composition as well as different methods of extraction and recovery (Košíková and Gregorová 2005; Espinoza-Acosta, et al. 2016). Ahvazi and Ngo (2018) report that the nature of a lignin's hydrophilic functional groups is dependent on the pulping process, and that the size of the polymeric pieces depend on the methods used to recover the lignins from the pulping black liquor. Both of these factors influence a lignin's properties.

Espinoza-Acosta et al. (2016) conducted an assessment of molecular weight and poldispersity of different types of lignins, which is summarized in Table 2 below. Among the different lignins, lignin sulfonates have the highest overall molecular weight. However, determination of any particular lignin's molecular weight may vary depending on the measurment method used. For example, when measured as a solution property, the molecular weight will reflect the portion soluble in the organic solvent, whereas the molecular weight of the whole isolated lignin may be orders of magnitude greater (Calvo-Flores, et al. 2015). A property perhaps more descriptive of the reactive potential of any given lignin is that of polydispersity. The polydispersity index (PDI) is a measure of the breadth of a polymer's molecular weight distribution. It is defined as Mw/Mn, where Mw is the average molecular weight and Mn is the number average molecular weight. A polymer with uniform molecular weight distribution for all of its polymeric components would have a PDI value of 1. Lignins have high polydispersity, meaning their polymeric units are diverse sizes.

Table 2. Physiochemical Properties of Technical Lignins. Adapted from Espinoza-Acosta, et al. 2016 .

	Kraft lignins	**Lignosulfonates**	**Soda lignins**	**Organosolv lignins**
Molecular weight (*Mw*)	100 to 3000	20,000 to 50,000	800 to 3,000	500 to 4000
Polydispersity (Mw/Mn)	2.5 to 3.5	6 to 8	2.5 to 3.5	1.3 to 4.0
Impurities	Sulfur	Sulfur	Carbohydrates and ash	Carbohydrates and ash

Vishtal and Kraslawski (2011) also summarized properties of different lignins and suggested wider ranges for the molecular weight and polydispersity of lignin sulfonates and higher molecular weight for kraft lignin than the values reported by Espinoza-Acosta, et al. (2016).

The molecular mass of lignins varies based on nature of the raw material and the extraction method (Serrano, et al. 2012) and can also vary based on the pH and temperature applied during recovery (Peretti, Barton and Teixeira Mendonca 2016). Native lignin has high molecular weight and a condensed structure, which make it resistant to chemical and biological processing. Organosolv lignin has a lower molecular weight than soda lignin (Peretti, Barton and Teixeira Mendonca 2016) (Serrano, et al. 2012) because lignins in the soda process are so highly fractionated under the alkaline conditions that they repolymerize into larger fragments (Serrano, et al. 2012).

Lignins can form many bonds. In paper pulp, lignin impedes the formation of bonding between the cellulose fibers (Marin, et al. 2017), which is why pulping processes aim to remove lignin. As aromatic polymers, lignins have many aromatic rings with hydroxyl and methoxyl functional groups that can act as hydrogen acceptors. They also have antioxidant properties (Espinoza-Acosta, et al. 2016). Lignins are readily oxidized, and readily condensed with phenols or thiols (Calvo-Flores, et al. 2015). Organosolv lignins are reported to contain more oxidized functionalities than alkali lignins (Peretti, Barton and Teixeira Mendonca 2016). The colloidal nature of lignins also makes it difficult to separate lignin precipitate from the extracting liquor (Hellstén, et al. 2013). Lignins are also not optically active (Calvo-Flores, et al. 2015).

Lignin's chemical network of strong intra- and inter-molecular hydrogen bonds enable it to display thermoplastic behavior; however, upon initial application of high temperature (approximately 100 °C), lignin will behave as a thermoset material, hardening due to extensive cross-linking reactions (Collins 2019). This would occur at much higher temperatures than would be naturally found in soils and thus would not be a concern for the health of the soil. One study comparing organosolv and soda lignins observed that soda lignins were the most thermally stable of the two (Serrano, et al. 2012).

Soda lignin displays properties similar to those of kraft lignin, with the notable difference that it contains little to no sulfur (Košíková and Gregorová 2005; Wörmeyer et al. 2011; Laurichesse and Averous 2014).

Specific Uses of the Substance:

Lignins have a wide range of agricultural and non-agricultural uses. They are abundant, variable, and naturally reactive due to their many different functional groups (Serrano, et al. 2012). In particular, the use of lignin sulfonates as binders, dust suppressants, and dispersing agents is well documented (Strassberger, Tanase and Rothenberg 2014).

Lignins used for binding

Lignins are added in fertilizer formulations to improve granule formation by binding extrusion granules. This also improves the suspension of granules and the dispersion and suspension of concentrates and particles in fertilizer solutions. The addition of lignins also reduces fertilizer caking during storage and protects fertilizer components from UV photodegradation (Calvo-Flores, et al. 2015). Lignin polymers are employed in controlled-release fertilizer and pesticide formulations (Peretti, Barton and Teixeira Mendonca 2016). Sodium carbonate lignin is referenced in several patents as one option for a binder in fertilizer chemical carrier substrates, along with lignin sulfonates, cane molasses, beet syrup, starch and starch derivatives, or any number of other potential binders (Welshimer, Dunn and Birthisel 2003; Ginn and Gray 2018). In livestock production, lignins are used as pelletizing binders for animal feed to facilitate handling and preservation (Calvo-Flores, et al. 2015).

Lignins used for dust suppression

Lignins are useful as binders in fertilizer and feed formulations because improving the quality of the pelletizing or granulation of these materials is a well-known measure for dust suppression (Kucera and Sawyer 2015). Fertilizers often contain an undesirable level of fine particles that can become airborne dust during the manufacture, storage, and transportation of the fertilizer. Dust can become airborne when the fertilizer materials undergo mechanical abrasion, when chemical reactions or curing processes continue after initial particle formation, when materials lose moisture during storage, or are otherwise affected by temperature and humidity conditions during handling and storage. Adding binders such as lignin increases fertilizer granule strength, thereby reducing the formation of dust during these activities (Kucera and Sawyer 2015).

Lignin sulfonate is used for dust control on roads and for this application would be sprayed on the soil surface or mixed into the top three to six inches of soil (Sanders and Addo 1993). Suggested rates of application are reported as 0.75 pounds of lignin sulfonate per square yard of surface per inch of depth treated, or more than 10,000 pounds of lignin sulfonate per acre (Harmon 1957). Alternatively, lignin sulfonate solution containing 25 percent solids are applied at a rate of 7,260 gallons per acre (Parametrix, Inc. 2003). The use of the petitioned substance is for dust control in the context of a plant or soil amendment, such as in a blended or specialty fertilizer applied to organic crops. Use rates in a fertilizer would be much lower, with the lignin component typically comprising 10 percent or less of a fertilizer formulation and applied at rates of approximately 50–200 pounds of lignin sulfonate per acre (OMRI 2020).

Lignins used for chelation

Lignins, particularly lignin sulfonates, are used to chelate micronutrients in fertilizer formulations (Agrawal, Kaushik and Biswas 2014) and form more stable, yet still soluble, complexes that improve plant micronutrient availability. Forms of lignin sulfonates used as chelating agents include ammonium lignin sulfonate (Wallace and Ashcroft 1956) and other salts of lignin sulfonic acid (Keenportz 1995) resulting from the sulfite pulping process, such calcium, magnesium, and sodium lignin sulfonate (Bennett 1955). These four forms of lignin sulfonates are the most commonly used in organic fertilizer applications (OMRI 2020). There are many other salts of lignin sulfonic acid, including ammonium calcium lignin sulfonate, potassium lignin sulfonate, and zinc lignin sulfonate. Lignins can also chelate heavy metal ions, and as such are used in soil remediation (Garcia-Valls and Hatton 2003). Most literature on the use of lignins as chelating agents covers only lignin sulfonates; one report does describe the complexation (i.e., chelation) of iron cations by lignin anions in soda black liquor (Ghatak 2013). Because the lignins in this report share common properties—such as being large phenolic polymers of complex structure with a diversity of polymeric unit sizes and an abundance of functional groups—it is expected that other lignin products function in a chelating capacity similar to what is seen with lignin sulfonates. The mechanism for lignin chelation is discussed below under *Action of the Substance*.

Other uses for lignins

The primary use for lignin byproducts of the pulping industry is onsite at paper mills as boiler fuel (Agrawal, Kaushik and Biswas 2014). Lignins can also be used as a soil additive to reinforce soil structure in engineering projects. One study reported the use of sulfur-free lignin to stabilize soil under different free-thaw cycles and found that it improved frost resistance (Liu et al 2020). Various lignins have been commercialized for use in the formulation of dispersants, adsorbents, adhesives, surfactants, nanomaterials, and as starting material for bulk chemicals (Peretti, Barton and Teixeira Mendonca 2016). Lignin can be used in engineering plastics such as phenolformaldehyde resins, polyolefin films, and polyurethane foams (Košíková and Gregorová 2005). Lignin has also been increasingly employed in composites as a reinforcement agent (Liu, et al. 2020). Lignins can be converted into activated carbon, vanillin, guaiacol, and carbon fiber (Agrawal, Kaushik and Biswas 2014). Organosolv lignins can be used in automotive brakes, biodispersants, and epoxy resins for printed circuit boards (Gallezot 2011). Lignins have also been identified as antioxidants (Espinoza-Acosta, et al. 2016; Serrano, et al. 2012; Sun et al., 2018). It should be noted that, in many applications, lignins are chemically modified beyond what pulping extraction produces; these applications are outside the scope of this report.

Approved Legal Uses of the Substance:

40 CFR 180.910 lists inert ingredients used pre- and post-harvest that are exempt from the requirement of a tolerance. Table 3 below lists the exemptions for lignin and alkali lignin.

Table 3. Exemptions from the requirement of a tolerance (excerpt from 40 CFR 180.910)

Lignin (CAS Reg. No. 9005-53-2)	Surfactant, related adjuvants of surfactants
Lignin, alkali (CAS Reg. No. 8068-05-1)	Do*

*A value of "Do" is the CFR representation of “ditto,” which refers to uses listed immediately preceding that entry in the CFR.

Organosolv lignin (CAS No. 8068-03-9) is subject to reporting at 40 CFR 721.5460, as a significant new use chemical substance, identified as any manufacture, processing, or use of the substance with a number average molecular weight less than 700 daltons.

See the 2011 Lignin Sulfonate Technical Report for approved legal uses of lignin sulfonates (USDA NOP 2011).

Action of the Substance:

In nature, lignin helps reinforce plant structures by binding cellulose fibers in wood, thereby helping to stabilize plants against various stresses (Košíková and Gregorová 2005). The same mechanism is seen with extracted lignins in various binding applications, with the binding being dictated by the structural characteristics of any particular lignin extract (Peretti, Barton and Teixeira Mendonca 2016).

Lignins contain reactive groups that allow for many different types of chemical bonding. As aromatic polymers with complex chemical structures, lignins contain aromatic rings with diverse functional groups including hydroxyl, methoxyl, carboxylic, phenolic, sulfonic, and some terminal aldehyde groups (Agrawal, Kaushik and Biswas 2014; Espinoza-Acosta, et al. 2016). Schreiber et al. (2012) noted that lignin's oxygen-containing radicals facilitate crosslinking reactions.

Liu et al. (2020) applied a sulfur-free lignin derived from corn-based ethanol to soil and observed a redistribution of soil particle sizes, with more particles of larger size after the addition of the lignin. They also recorded increases in the water content needed to turn the soil into a semi-solid state (i.e., its plastic limit) and the water content needed to turn the soil into viscous liquid (i.e., its liquid limit). These results suggested increased soil stabilization, and the authors attributed this action to the physical binding of soil particles with lignin into larger aggregates, which also increases soil aeration. They also believed that the low solubility of the lignin could be contributing to the increased water holding capacity observed (Kucera and Sawyer 2015). These binding characteristics, which result in larger particle sizes and greater water holding capacity, also reduce the formation of air-borne dust particles during fertilizer pelletizing and granulating processes.

Lignin's ability to form chemical bonds is also related to the action of chelation, in which a substance binds at more than one point of connection with the chelating agent. Because lignins are large polymers with many polar binding sites, their ability to chelate metal ions and plant nutrients is well documented (Calvo-Flores, et al. 2015). As noted in *Specific Uses of the Substance*, there is little information on the use of other lignins besides lignin sulfonates chelating metals. However, one group of scientists studied the structure of guaiacol aromatic rings linked by β-O-4 linkages—bonds that are one of the most characteristic linkages in lignins and lignin derivatives—complexed with a series of alkali metal cations (e.g., Li+, Na+, K) using mass spectrometry. Their research found evidence suggesting that the mechanism of complexation was oxygen atoms from multiple β-O-4 linkages involved in chelating the metal (DeBlase, et al. 2016). Additionally, Garcia-Valls and Hatton (2003) report that low molecular weight units in lignin, which contain aromatic rings with certain constituents, complex heavy metal ions. As noted under *Properties of the Substance*, lignins with varying degrees of polydispersity are likely to have some proportion of these low molecular weight units. Thus, it can be expected that other lignin derivatives besides lignin sulfonates would also possess chelating capacities.

Combinations of the Substance:

Different lignins contain different residues of substances used in the various pulping processes herein described. Additionally, anthraquinone (AQ) and soluble anthraquinone (SAQ) are substances that have been cited as pulping additives used in the soda lignin extraction process to reduce the degradation of carbohydrates (Biermann 1996). AQ is a polycyclic aromatic hydrocarbon derived from anthracene or phthalic anhydride (NIH 2020) and is not further considered within the scope of lignins addressed in this technical report.

Garcia-Valls and Hatton (2003) described how lignin obtained as a byproduct from plant biomass conversion can be chemically modified to increase its number of active carboxyl, amine, and hydroxyl sites available for complexation with metal ions. This is accomplished through processes such as oxidation with alkaline nitrobenzene or permanganate, acidolysis, hydrogenolysis, or thioacetolysis. This modification releases low molecular weight units containing aromatic rings. However, lignins that are chemically modified subsequent to or beyond the pulping and its associated extraction steps are not considered within the scope of this report, with the exception of lignin sulfonates produced from kraft lignins, as described below under *Evaluation Question* #2.

Status

Historic Use:

Soda pulping was first invented in England in 1851 using sodium hydroxide as the cooking chemical (Biermann 1996). In the late 1870s, German manufacturers added sodium sulfate to regenerate the sodium hydroxide in the soda pulping process. In doing so, they discovered a much more efficient pulping process with faster delignification, greater selectivity in dissolving the lignin, and less degradation of the cellulose fibers (NC State 2020; Biermann 1996). This led to the development of the kraft process in 1879, which was put into commercial practice in 1890. Most U.S. mills that had used the soda pulping method switched to the kraft process once it was invented (Biermann 1996).

In the 1950s, the U.S. Forest Products Laboratory studied cold soda pulping of hardwoods, where wood chips were soaked in cold sodium hydroxide (5–15 percent); this process was eclipsed by other pulping methods in subsequent decades (Biermann 1996). Currently, soda pulping is reported to have limited use for easily pulped materials such as straw and some hardwoods and is not a predominant process for wood pulping.

Organosolv pulping was developed in the 1990s as an alternative to conventional chemical delignification; however, it has not become economically viable for large-scale operations (Peretti, Barton and Teixeira Mendonca 2016).

Organic Foods Production Act, USDA Final Rule:

The petitioned substance is related to lignin sulfonate, which is listed at 7 CFR 205.601(j)(4).

International

A survey of regulations and guidelines for organic production from a number of countries and international organizations indicates that the use of sodium carbonate lignin is not generally permitted. The summary below provides international context for the use of sodium carbonate lignin and other lignins in organic crop production.

Canadian General Standards Board Permitted Substances List. CAN/CGSB-32.311

Sodium carbonate lignin is not included on PSL Table 4.2 (Soil amendments and crop nutrition) or 4.3 (Crop production aids and materials). Table 4.3 lists "Lignin sulphonates" as "a chelating agent, as a formulant ingredient and as a dust suppressant." This entry specifically prohibits "ammonium lignosulphonate," suggesting that "lignin sulphonate" is not intended to be read as a broadly inclusive term for any form of lignin sulfonate.

PSL entries for "Chelates" and "Dust suppressants" on both Tables 4.2 and 4.3, and for "Calcium lignin sulphonate" on Table 4.3, refer to the "Lignin sulphonates" entry on Table 4.3.

CODEX Alimentarius Commission, Guidelines for the Production, Processing, Labelling and Marketing of Organically Produced Foods (GL 32-1999)

Sodium carbonate lignin is not included in GL 32-1999 Annex 2 Table 1 (Substances for Use in Soil Fertilizing and Conditioning) or Table 2 (Substances for Plant Pest and Disease Control).

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

Sodium carbonate lignin is not included in EC No. 834/2007 Annex I (Fertilisers and soil conditioners referred to in Article 3(1)) nor in Annex II (Pesticides – plant protection products referred to in Article 5(1)). Any reference to materials of wood- or tree-origin specifies that the material must not be chemically treated after felling.

Japan Agricultural Standard (JAS) for Organic Production

Sodium carbonate lignin does not appear in Notification No. 443 Japanese Agricultural Standard for Organic Plants Partial Revision March 27, 2017. "Lignin sulfonic acid" is allowed in the same Notification as a 'granulating agent and anticaking agent for fertilizer' 'in case of difficulty to manufacture granulating agent and anticaking agent from these substances [natural sources]' on Attached Table 1 Fertilizers and soil improvement substances.

IFOAM-Organic International

Sodium carbonate lignin is not included in the IFOAM Norms Appendix 2: Fertilizers and Soil Conditioners nor in Appendix 3: Crop Protectants and Growth Regulators. "Wood, bark, sawdust, wood shavings, wood ash, wood charcoal" are included, with their Conditions for Use being "only if not chemically treated."

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

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

The processes used to derive commercial lignins from plant matter characterize the different lignin products, since the delignification method influences the final lignin's structure (Serrano, et al. 2012). All of the processes covered in this report have as their primary purpose the delignification of wood or other plant material in order to liberate the plant cellulose for paper fiber production. Other manufacturing processes not covered in this report include biofuel production resulting in lignins as byproducts, as well as other processes aimed at further modification of extracted lignins for added functionality. The four main industrial processes that isolate high-purity lignin are the soda, sulfite, kraft, and organosolv processes (Strassberger, Tanase and Rothenberg 2014); these are discussed below in Table 4 along with other more minor processes.

Soda pulping

The petition describes the process used to manufacture sodium carbonate lignin both as soda ash pulping and soda pulping. While there is some overlap, the scientific literature predominantly reports the singular use of sodium hydroxide as the cooking chemical in soda pulping (Espinoza-Acosta, et al. 2016; Calvo-Flores, et al. 2015; Hellstén, et al. 2013). Hellstén et al. (2013) performed soda extraction on hardwoods and softwoods at cooking temperatures of 165°F and 170°F, respectively, in a liquor-to-wood ratio of 4:1 and an effective alkali of 5.5mol/kg. Another study used an extraction solution of 7.5 percent weight per weight (w/w) sodium hydroxide with a solid-to-liquid ratio of 1:18 at 90°C for 90 minutes on apple wood (Serrano, et al. 2012). Lignin recovery in soda pulping may be done by acid precipitation (sulfuric acid) (Serrano, et al. 2012), maturation and filtration (Strassberger, Tanase and Rothenberg 2014), or centrifugation (Serrano, et al. 2012). The resulting lignins are sulfur-free.

One report described the use of alkaline solutions, typically sodium hydroxide, under conditions similar to kraft pulping (see below) but without the inclusion of hydrogen sulfide anions (Espinoza-Acosta, et al. 2016). In this process, the native lignin network undergoes hydrolytic cleavage, thereby extracting the lignins into the soda black liquor. The authors describe the process of soda lignin recovery from the black liquor using acid precipitation with various mineral acids, heating, and filtration (Espinoza-Acosta, et al. 2016). Precipitation may also be done with carbon dioxide (Hellstén, et al. 2013); however, both methods of precipitation have drawbacks: the formation of colloids which impedes subsequent filtration, the low efficiency of lignin yield with carbon dioxide, and the high cost to incorporate mineral acid precipitation in pulp mills (Hellstén, et al. 2013).

The soda process is commonly employed in the pulping of herbaceous feedstocks such as wheat straw, hemp, and bagasse. Calvo-Flores et al. (2015) noted that the characteristic of the feedstock determines, in part, the ease with which lignin can be obtained by the soda process. Wood lignin requires more aggressive treatment (5 percent NaOH at 130–170°C), while grass lignins can be isolated by mild alkaline treatments even at room temperature (Calvo-Flores, et al. 2015).

Soda ash pulping

Soda ash pulping can be considered a type of soda pulping. Sodium carbonate lignin, as described in the petition, results from a process wherein wood chips are subjected to a solution of either sodium carbonate (6–8 percent solution) or a combination of sodium carbonate (50–85 percent) and sodium hydroxide (15–50 percent) and cooked in steam under 1100 kPa pressure for approximately 14 minutes (Legnochem 2019). The cooked woodchips are then mechanically pressed to separate the spent cooking liquor, also known as the black soda liquor, which is then evaporated to a solution containing 45–55 percent solids, or evaporated until a dry powder is obtained (Legnochem 2019). This process is consistent with the patent referenced in the petition, which also notes an ideal pulping solution of 20 percent sodium hydroxide and 80 percent sodium carbonate, and further specifies a cooking temperature of 375°F (Dillard, Gilmer and Kennedy 1974).

Another study evaluated differing mixtures of sodium carbonate and sodium hydroxide as cooking chemicals for pulping wheat straw (Marin, et al. 2017). Their process was to dissolve analytical grade sodium hydroxide and sodium carbonate in tap water, heat for 30 minutes and cook wheat straw in the liquor at a ratio of 5:1 liquid to solids for 60 minutes at 150°C, 160°C, or 170°C. The alkali charge was also varied by chemical concentrations of 16, 18, or 20 percent sodium hydroxide and mass ratio of sodium carbonate to sodium hydroxide of 1, 5, and 9. The study found that increased sodium hydroxide concentration and increased temperature promoted delignification, but also increased polysaccharide degradation, which was undesirable in terms of pulp yield (Marin, et al. 2017).

Organosolv pulping

Organosolv pulping uses organic solvents such as organic acids, alcohols, or ketones to delignify pulp and may or may not include mineral or organic acid catalysts. This manufacturing process involves separating lignin from plant biomass via acid-catalyzed solubilization, in which bonds such as α-aryl ether and aryl glycerol-β-aryl ether bonds in lignin macromolecules are cleaved (Espinoza-Acosta, et al. 2016). One study reported three organosolv processes (Gonçalves and Schuchardt 1999). The first used a methanol/water/NaOH/AQ mixture on spruce wood to produce what was called "Organocell lignin." The second used 93 percent aqueous acetic acid and 0.3 percent hydrochloric acid on bagasse or eucalyptus chips under reflux for 2 hours, followed by 80 percent evaporation of the acetic acid from the pulping liquor and precipitation of the lignin with water, filtering, and drying. The third used an acetone/water/$FeCl_3$ extraction of lignin from bagasse (Gonçalves and Schuchardt 1999). Lignins derived from organosolv methods using acetic acid may be termed "Acetosolv lignin." Another process using acetic acid and phosphinic acid observed up to 88 percent delignification of birch chips cooked at 150°C over 120 minutes, and noted that the rate and structure of delignification followed a function of time (VTT Technical Research Center 2015). Further, an organosolv extraction of apple wood prunings used 60 percent volume per volume (v/v) ethanol-water solution with a solid-to-liquid ratio of 1:10 at 180°C for 90 minutes in a stirred and pressurized reactor, after solids were filtered from the black liquor and the lignin precipitated with acid water and dried (Serrano, et al. 2012).

Kraft pulping

The most predominant process for pulping wood in paper manufacturing and for obtaining lignin from lignocellulosic biomass is the kraft process (Ahmad and Pant 2018). This process uses sodium hydroxide and sodium sulfide to dissolve lignin from wood. Ahmad & Pant (2018) specify the temperature range of 150–180 °C for 2 hours under high pH conditions. This ionizes the phenolic hydroxyl groups, thereby solubilizing the lignin content of the lignocellulosic biomass. Graymont Ltd. (2020) describes loop systems that together generate sodium hydroxide in kraft mills. In one loop, sodium hydroxide is pumped into chambers where it is mixed with wood chips under heat and pressure. The sodium hydroxide attacks the lignin and in the process is converted to sodium carbonate. This sodium carbonate is then pumped into a vessel containing calcium hydroxide (slaked lime). These react to form sodium hydroxide and calcium carbonate. The sodium hydroxide is pumped off for reuse, and the calcium carbonate is transferred to a kiln, heated, and thereby converted to calcium oxide (lime). The calcium oxide is mixed with water and again forms calcium hydroxide (slaked lime). The sodium carbonate returning from the pulping process is then added to the mixture to form sodium hydroxide, and the whole process begins again (Graymont Ltd. 2020).

Ahmad & Pant (2018) describe the lignin and hemicellulose that is collected in the black liquor being sent to evaporators and concentrated. They also note that the sulfur and caustic content is recycled, and that lignins destined for polymer production are precipitated by lowering the pH with carbon after which the lignins are filtered and washed. This filtering removes sulfur compounds from the final lignin product. Lignosulfonates can also be produced from the precipitated kraft lignin by sulfonation with bisulfate or a sulfite compound.

Sulfite chemical pulping

Sulfite chemical pulping is the most predominant lignin-producing process, generating lignin sulfonate (Strassberger, Tanase and Rothenberg 2014). In this process, wood is cooked in an aqueous solution of sulfur dioxide (SO_2) and a base (calcium, sodium, magnesium, or ammonium) (Espinoza-Acosta, et al. 2016). The lignin sulfonates that are extracted into the black liquor are further purified to remove excess sugars through fermentation of the liquor followed by heating to remove generated alcohol (USDA NOP 2011), ultrafiltration, chemical removal, or selective precipitation of carbohydrates (Strassberger, Tanase and Rothenberg 2014). Acid sulfite pulping, alternatively, uses sulfurous acid and sodium, magnesium, calcium, or ammonium bisulfite (USDA NOP 2011).

Neutral sulfite semichemical (NSSC) pulping

The soda process is sometimes referred to as a “semi-chemical pulping” process that does not involve the use of any sulfur compounds or bleaching chemicals (Legnochem 2019). Another process is referred to as “neutral sulfite semichemical pulping” (Dillard, Gilmer and Kennedy 1974). This process uses a liquor of sodium sulfite and sodium carbonate in a molar ration of 7:1–3:1, with optional addition of buffers such as sodium bicarbonate or sodium hydroxide. Alternatively, this process may involve sodium sulfite and sodium bicarbonate in a ratio 5:1 at 14 percent chemical concentration, cooking wood at 170°C and 690 kPa for 2–3 hours. However, this process results in a liquor containing hydrogen sulfide and sulfur dioxide and is thus less desirable due to the malodor and corrosiveness (Dillard, Gilmer and Kennedy 1974).

Steam explosion delignification

Autohydrolysis and steam-explosion are treatments wherein the plant biomass is separated into a liquid stream composed primarily of hemicelluloses, oligomers, and a small fraction of water-soluble lignin (Peretti, Barton and Teixeira Mendonca 2016). Such process parameters have been reported as 150–220°C (Peretti, Barton and Teixeira Mendonca 2016) and 160 °C for 15–210 minutes in a water-to-wood ratio of 4:1 (Lu, et al. 2012). This is sometimes done as a pre-treatment prior to soda pulping (Liu, et al. 2020; Lu, et al. 2012), but it is not effective for obtaining lignins from wood on its own. One report of a hot-water pre-treatment prior to soda pulping found that less than 6 percent lignin (on total wood mass) from virgin woodchips was dissolved in the extraction liquor with hot water extraction of aspen woodchips. Typical pulping extraction yields are around 80 percent of lignin from wood (Lu, et al. 2012).

Enzymatic hydrolysis

Lignins can also be obtained by successive treatment with selective enzymes that hydrolyze carbohydrates; however, not all carbohydrates can be removed enzymatically to obtain the same level of purity obtained by the other methods typically used for milled wood (Agrawal, Kaushik and Biswas 2014).

Table 4. Summary of reviewed processes for lignin production. See *Evaluation Question* #2 text for references.

Lignin type	Reagents	Reagent concentration	Time	Temperature	Recovery Steps
Soda pulping	Sodium hydroxide	Alkali of 5.5mol/kg	Not reported	165°C (hardwood) and 170°C (softwood)	Not reported

	Sodium hydroxide	7.5% (w/w)	90 minutes	90°C	Acid preparation; maturation and filtration; centrifugation
Soda ash pulping	Sodium carbonate and sodium hydroxide	50-85% carbonate and 15–50% hydroxide	14 minutes	Cooked in steam under 1100 kPa pressure	Mechanical pressing and evaporation
	Sodium carbonate and sodium hydroxide	20% hydroxide and 80% carbonate	Not reported	375°F	Not reported
	Sodium hydroxide and sodium carbonate	16, 18, 20%	60 minutes	150–170°C	Not reported
Organosolv pulping	Methanol/ water/ NaOH/ AQ	Not reported	Not reported	Not reported	Not reported
	Aqueous acetic acid; hydrochloric acid	90%; 0.3%	2 hours	Not reported	Evaporation
	Acetic acid and phosphinic acid	Not reported	120 minutes	150°C	Not reported
	Ethanol and water	60% (v/v)	90 minutes	180°C	Filtration and precipitation
Kraft pulping	Sodium hydroxide and sodium sulfide	High pH conditions	2 hours	150–180°C	Precipitation; filtering; washing
Sulfite chemical pulping†	Aqueous solution of sulfur dioxide and a base	Not reported	Not reported	Not reported	Fermentation; ultrafiltration; chemical purification; precipitation
Neutral sulfite semichemical (NSSC) pulping	Sodium sulfite and sodium carbonate	Molar ratio of 7:1–3:1	Not reported	Not reported	Not reported
	Sodium sulfite and sodium bicarbonate	5:1 ratio at 14%	2–3 hours	170°C and 690 kPa	Not reported
Steam explosion delignification	N/A	Water-to-wood ratio of 4:1	15–210 minutes	150–220°C	Not reported

As described above and illustrated in Table 4, the process for obtaining the petitioned substance and the manufacturing process for lignin sulfonate differ principally in the chemicals used to extract the lignins. Sulfite pulping, which produces lignin sulfonates, uses sulfur dioxide and a base, whereas soda ash pulping uses sodium carbonate and sodium hydroxide as the reagents. The literature notes the difference between the resulting lignins primarily in terms of polymer size and sulfur content.

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

Lignins are a naturally occurring component of wood and other plant biomass and are the second largest source of natural organic polymers after cellulose (Ponnusamy, et al. 2019; Liu, et al. 2020). As such, they play an important role in soil carbon cycles, particularly for carbon storage (Thevenot, Dignac and Rumpel 2010). They have historically been considered recalcitrant, or resistant to biodegradation. Only a few organisms are able to degrade lignins' complex structure, including *Streptomyces* sp., *Nocardia* sp., and basidiomycete brown-rot and white-rot fungi. Of these, most can alter lignin structure, but only white-rot basidiomycetes are able to completely mineralize lignin molecules (Thevenot, Dignac and Rumpel 2010; Sierra-Alvarez and Lettinga 1991). There may also be anaerobic organisms and abiotic factors that can contribute to lignin degradation in the soil.

Degradation rates in the field have been found to be extremely variable, but Thevenot et al. (2010) summarized them as being between 48–87 percent over 5 years. These rates may not be slower than those of bulk soil organic carbon and may even be faster (Thevenot, Dignac and Rumpel 2010). Degradation rates are influenced by many factors in the environment, including climate, soil type, pH, moisture level, and management, as well as soil microbial communities. For lignin derivatives, polymer size is also an important factor in degradability. Lignin monomeric model compounds representative of those derived from the soda process are reportedly degradable under anaerobic conditions. Kraft lignins subjected to mixed methanogenic (anaerobic) cultures at moderate to high temperatures showed degradation, but only of low molecular weight material (i.e., less than 600 daltons). Native lignin and higher molecular weight synthetic lignins are highly resistant to anaerobic degradation. Aerobic bacteria are also reported to metabolize low molecular weight lignin fractions (Sierra-Alvarez and Lettinga 1991).

One study applied acid-precipitated kraft lignin to soil samples in order to evaluate soil properties, including the potential for buildup of sodium in the soil (Xiao, Bolton and Pan 2007). The lignin was applied at rates of 1.67 and 3.34 g C kg^{-1} soil and incubated for 8 weeks. The results showed an increase in electrical conductivity with increasing lignin application; however, the authors concluded that the increase was small enough that lignin application at these rates would not pose concerns for soil salinity. Stiggson and Lindstrom (2007) found that washing lignin that had been precipitated from alkali kraft black liquor with carbon dioxide, in a solution containing magnesium or calcium effectively replaced many of the sodium ions with the magnesium or calcium. Beyond these reports, there is little information in the literature regarding the sodium content of sodium carbonate lignin, soda lignin, or other alkali lignins used in dust suppression and their potential to affect the buildup of sodium in the soil.

The study by Xiao, Bolton and Pan (2007) suggested the potential benefit of lignin as a soil amendment, reporting that lignin in the soil acts as an important precursor in the formation of humic substances. Their study found an increase in soil organic carbon and total nitrogen with application of the lignin, as well as increased macroaggregate formation and stability.

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

Paper mill wastewater streams have been identified as a significant environmental challenge (Mandeep and Shulka 2020). These waste streams contain lignocellulosic materials with various organic and inorganic polluting complexes that result not just from pulping but also bleaching processes, e.g., chlorophenols (Mandeep and Shulka 2020). Lignin components in this waste stream have been studied for toxicity; one study attributed pulping effluent toxicity in the form of enzymatic inhibition to hydrophilic, higher-molecular weight lignin fractions using reverse electron transport (Pessala, et al. 2004). The authors of this study found lignins in pulp wastewater to be toxic to the aquatic organisms *D. magna* and *V. fischeri*

(Pessala, et al. 2004). These findings are related to lignins in wood pulping effluents. Removing lignins, including the petitioned substance, from pulping wastewaters to convert them into value-added products (valorization) such as dust suppressants, fertilizer chelating agents, and other products could therefore have some environmental benefits.

In contrast, a summary report on the advantages and disadvantages of lignin valorization concluded, upon review of numerous environmental studies over the last 30 years, that lignin sulfonates are nontoxic at concentrations above those used, and that surrounding vegetation is not affected by the application of lignosulfonates (Strassberger, Tanase and Rothenberg 2014). One study found higher onset of degradation for sulfur-free lignin (trade name Polybind) than for a calcium lignin sulfonate (Sahoo, et al. 2011).

Espinoza-Acosta et al. (2016) investigated lignin-derived polyphenols for their antioxidant capabilities, indicating their advantage over more conventional synthetic antioxidants due to their biodegradability and low toxicity.

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)).

The paper industry creates a significant environmental burden in the form of emissions (U.S. EPA 2018), effluent, and solid waste (Mandeep and Shulka 2020). Paper mill effluents from processes such as kraft pulping, neutral sulfite semichemical pulping, and bleaching are reported to be poorly degradable (Sierra-Alvarez and Lettinga 1991). Removal of lignins from the effluents is desirable, and alkali lignin is readily separated via acid precipitation and filtration (Sierra-Alvarez and Lettinga 1991). The solid waste lignins recovered from these and other pulping effluents are primarily used as a fuel in the pulping plant. However, this use of the lignin byproduct has been reported to have low efficiency as it is a lower-grade fuel (Strassberger, Tanase and Rothenberg 2014), and the burning of lignins in these fuels adds to atmospheric pollution through the generation of guaiacol (2-methoxyphenol) (Pflieger and Kroflič 2017). Thus, diverting pulp waste away from use as fuel reduces the air pollution generated from the wood pulping process. Mandeep & Shulka (2020) did report on the environmental benefits of diverting pulp wastes, including lignin, from the waste stream and into biorefinery applications, which included low emissions and relatively high efficiency. Garcia-Valls & Hatton (2003) similarly suggested that the environmental burden posed by paper pulping waste lignins can be largely addressed through utilization of the lignin materials in value-added products. One study reported the soda process to have the lowest potential environmental impact of four pulping processes considered, followed by the sulfite, kraft and organosolv processes, as measured by a waste reduction algorithm developed by the EPA's National Risk Management Research Laboratory (Carvajal, Gómez and Cardona 2016). None of the literature reviewed for this report suggested that the use of lignins as petitioned would result in environmental contamination of organic systems.

Evaluation Question #8: 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)).

Liu et at. (2020) investigated soil stabilization with sulfur-free lignin obtained as a byproduct of ethanol production and found a slight decrease in soil pH with application of the lignin, but it was still comparable to the pH of natural soil. They therefore concluded that the sulfur-free lignin did not significantly change the soil pH, despite previous studies finding alkalization of soils treated with lignin sulfonate byproducts of the paper industry. Xiao et al. (2007) found that acid-precipitated kraft lignin significantly decreased soil pH over 8 weeks of incubation and may therefore act as an acidifying agent in the soil. The authors postulated that the acidification observed was likely due to the lignin having been precipitated with acid, as well as nitrification of ammonia nitrogen in the lignin byproduct and mineralization of organic matter in the soil. Liu et al. (2020) also reported a slight increase in the soil cation exchange capacity with addition of the sulfur-free lignin at rates of 3–15 percent lignin applied to soil samples.

Different types of lignin phenols can be inhibitory to some fungal species (Guiraud, et al. 1995); however, they may also stimulate microbial activity depending on the amount of lignin applied (Xiao, Bolton and Pan 2007). In Xiao et al.'s (2007) study, application of a lignin amendment at rates up to 6.12 g kg^{-1} soil appeared to increase soil microbial activity, observed as increased soil nitrification. They also observed an increase in the proportion of larger soil aggregates. While this may be due to the binding nature of the lignins applied, the authors also note the potential contribution of hyphal growth of fungi responsible for lignin degradation (Xiao, Bolton and Pan 2007).

The use of the petitioned substance is for dust control in the context of a plant or soil amendment, and as such is applied to the soil at relatively low rates. This consideration, in combination with the potential effects of lignin to increase soil aggregate size and water retention (Kucera and Sawyer 2015) and enhance microbial activity (Xiao, Bolton and Pan 2007), suggest that its use as petitioned is likely to be benign and may even be ecologically beneficial.

<u>Evaluation Question #9:</u> Discuss and summarize findings on whether the use of the petitioned substance may be harmful to the environment (7 U.S.C. § 6517 (c) (1) (A) (i) and 7 U.S.C. § 6517 (c) (2) (A) (i)).

A review of scientific literature for this technical report did not uncover any reports of environmental harm resulting from the use of lignins, including sodium carbonate lignin, as petitioned.

Some environmental benefits of lignins, in addition to those already mentioned, include dust suppression and slow release of chelated micronutrients. Lignins used in these applications are not applied directly to the soil, but to fertilizers and soil amendments during their manufacture. Fertilizer dust inhalation can pose health concerns, and fertilizer dust can contribute to air pollution and surface water contamination (Kucera and Sawyer 2015). Micronutrients in the soil can be unavailable to plants in certain pH ranges. However, adding these micronutrients in chelated form keeps them bioavailable, as the organic macromolecule of lignin envelops the micronutrient and prevents it binding with other inorganic elements in the soil that would inhibit its uptake by plants (Brady and Weil 2002).

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

The petitioned substance is proposed for use as a dust suppressant. At the time of this report, OMRI has 11 products listed in the category of "Dust Suppressants" and another 29 in the category of "Lignin Sulfonates" (OMRI 2020). Products listed in the "Dust Suppressants" category may contain dust-suppressing agents such as vegetable oils, magnesium or calcium chloride solutions, glycerin, natural fatty acids, or synthetic lignin sulfonates. Wax emulsions or combinations of oil and wax emulsions have also been reported for dust control; however, their effectiveness over time may decrease as oils volatilize or become adsorbed into fertilizer particles (Kucera and Sawyer 2015). Waxes have proven difficult to handle unless at temperatures where they are melted and can absorb into fertilizer particles. Both waxes and oils also have limited binding capacity (Kucera and Sawyer 2015).

Other proposed materials for use in dust control methods include solutions containing molasses, or simple application of water. These methods, however, can increase fertilizer caking and their binding properties are lost with drying, thus rendering them ineffective for longer-term dust control (Kucera and Sawyer 2015).

Other nonsynthetic fibrous materials have been suggested for use as binders to control dust during fertilizer granulation. These include wood flour, peat moss, compost, manure, cotton, straw, brewers condensed solubles, beet syrup, whey starch, soy solubles, corn cob, rice hulls, peanut hulls, ground wheat straw flour, wheat flour, soy flour, cellulose derivates, seed meal, feather meal, soy meal, and humic acid (Kucera and Sawyer 2015). One study reported the use of anaerobic digestate filtrate and limestone used in the granulation of fertilizer. These materials were mixed and dried, yielding granules of acceptable strength (Mangwandi, et al. 2013). Clay additives have also been reported to have consistent and predictable performance in dust suppression applications (Bolander 1997).

Nonsynthetic alternative chelating agents to lignins or lignin sulfonates include amino acids (Hsu 1996) and citric acid (USDA NOP 2011).

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

Agricultural dusts have been reported as a health hazard to farm workers, causing acute and chronic respiratory problems (Kirkorn and Vincent 2000). These effects can be mitigated in some circumstances by engineering controls such as misting and mechanical ventilation systems inside farm equipment. Personal protective equipment in the form of respiratory devices are another option, but their use in practice is limited in part because they are hot and uncomfortable to wear, and because workers may not be aware of the risks of agricultural dusts and therefore not think to use the devices (Kirkorn and Vincent 2000).

More effective, alternative methods of dust suppression are reported in the 2011 Lignin Sulfonate Technical Report, and include management practices such as maintaining vegetative cover in non-traffic areas, mulching, application of stone or gravel to disturbed roads, and air current barriers such as trees. The report notes that the choice of dust control method may be influenced by different costs, available resources, and extent of dust control needed (USDA NOP 2011).

Report Authorship

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All individuals are in compliance with Federal Acquisition Regulations (FAR) Subpart 3.11—Preventing Personal Conflicts of Interest for Contractor Employees Performing Acquisition Functions.

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