

Carbon Sequestration Enhancing Agrochemical Products

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Abstract

The present technology provides materials and methods to increase the quantity of carbon stored in decaying terrestrial plant biomass. Incorporating modified macromolecule precursors into key plant structures during growth increases the ability of the subsequent decaying plant biomass to withstand environmental degradation and the catabolic activities of degradative microorganisms. Modified lignin precursors incorporated into plant-produced lignin macromolecules reduce the rate of degradation of that modified lignin polymer material containing biomass. Additionally, the increased potency of the anti-microbial properties associated with modified lignin breakdown products retards the degradation of plant biomass by microorganisms. This technology has the potential to reduce the rate at which carbon dioxide is released into the atmosphere from decaying biomass when living plant materials are pre-treated with modified lignin precursor molecules. The present technology comprises a new product category within the agrochemical industry and may be deployed with existing application methods and equipment to increase the amount of carbon that is sequestered in a terrestrial ecosystem.

Introduction

The marketplace requires products that are capable of effectively decreasing the quantity of carbon dioxide present in the atmosphere. These products must be cost-effective, safe, environmentally sound and potentially reversible. Terrestrial soils are widely recognized as natural carbon storage sinks and agrochemical products that act to increase the amount of carbon maintained and stored in soils could offset a significant portion of the carbon dioxide gas present in the atmosphere. Such agrochemical products may act by decreasing the natural rate of degradation of plant-sourced soil organic matter. Carbon dioxide in the atmosphere could be reduced by inhibiting the rate of release of this gas into the atmosphere by reducing the rate of respiration of soil-dwelling microorganisms that naturally degrade soil organic material. For example, the application of long-lived, systemic fungicidal agents to living plants protects the subsequent plant-sourced soil organic matter from microbial degradation.

An increase in the potency of lignin degradation related anti-microbial compounds could substantially inhibit the metabolic activities of microbial species that degrade lignin. This would result in extended periods required for degradation of soil-sequestered carbon and retard release of gaseous carbon dioxide. It would also result in increased amounts of sequestered carbon contained in terrestrial ecosystems. Such carbon sequestration enhancing agrochemical products could be delivered with existing application equipment. They would comprise a new category of products within the agrochemical industry. These products would be applied to living and metabolizing plant materials. They would be designed to be incorporated into plant materials and to protect the resulting dead plant residues from degradative microbial attack thereby decreasing the rate of microbial respiration of soil carbon and the release of gaseous carbon dioxide.

Lignin precursors that are not naturally produced by plants can be applied to plants, utilized as substrates for monolignol biosynthesis and subsequently incorporated into lignin polymers. Essentially, by incorporating unnatural monolignols, the lignin polymer has become a "prodrug." The desired "drug" which is a potent anti-microbial agent based on the unnatural lignin precursor

is released only when and where lignin biodegradation is actively occurring. As an early-stage example, application of chemically modified cinnamyl- and benzyl- based lignin precursor materials demonstrates that the technology is capable of becoming both cost and quantity effective in sequestering significant amounts of carbon. Preliminary calculations based on non-optimized materials and methods yield estimates that: i) an increase in tons of soil sequestered carbon can be achieved via the application of hundreds of grams of lignin precursor materials to plants, and ii) the resulting increases in soil sequestered carbon can be potentially sustained over multi-decade timeframes.

Using this technology, the anti-microbial properties and the rates of biodegradation of the different prodrug components can be determined and manipulated. Manipulation of these anti-microbial properties will impact the rates of lignin and lignocellulose biodegradation and determine the levels of soil-sequestered carbon. Specific chemical agents can be easily screened for their applicability and potential use in this technology by determining: i) if the chemical displays significant phytotoxicity, and ii) if treated plant material subsequently displays an increased resistance to degradation by lignin degrading microbial species.

Carbon Sequestration in Terrestrial Ecosystems

Carbon sequestration in terrestrial ecosystems is the net removal and storage of carbon dioxide from the atmosphere into stable and long-term non-gaseous terrestrial carbon pools. Carbon capture or removal from the atmosphere, when combined with increased levels of sequestration of this carbon and its long term storage in terrestrial soil ecosystems constitutes one approach for uncoupling of the current linkage between fossil fuel use with resulting atmospheric increases in the levels of greenhouse gas.

Carbon dioxide is naturally and continually removed from the atmosphere by photosynthesis that results in plant growth with the carbon being sequestered in plant organic materials or plant biomass. Over time, plant organic materials or litter are deposited in their substrate soils and these materials contribute the primary organic fraction present in all soils. World wide, soil organic materials represent an enormous quantity of stored carbon. Over time, quantities of these soil organic materials are continually increased in amount by addition of newly-formed plant litter and decreased in amount by soil organic material degradation and microbial metabolic respiration processes that release this carbon, as gaseous carbon dioxide, into the atmosphere. The primary cause of the release of gaseous carbon dioxide from soil organic materials is the degradation of these materials and the metabolic activities of soil microorganisms on the largest sources or pools of plant-sourced, soil organic materials that are cellulose and lignin.

Most plant biomass enters the soil organic material pools where its carbon is subsequently respired as carbon dioxide at a rate that depends on the biochemical composition of the organic material, on the degrading microbes and on the environmental conditions. The inherent microbial decomposability of soil organic matter is a property that primarily depends on the chemical nature of the organic residues. Lignin is significantly more refractory to microbial degradation than other organic residues. As the lignin content of plant organic material increases the ability of soil microorganisms to decompose that material decreases. Additionally, lignin is incorporated, integrated and chemically associated with the other plant organic materials such as cellulose so that further protects and sequesters these complexes such as lignocellulose from degradation and decomposition.

The capacity to catabolically attack lignin as a substrate is not widespread among microorganisms. Additionally, the first products of lignin degradation yield several compounds with significant anti-microbial properties that further slow the degradation of lignin. It is now

generally accepted that the underlying basis for the slowly decomposing components of soil organic materials is primarily lignin and lignin associated biomass that determine the rate and the timing of the long-term decay of soil organic materials. Consequently, in seeking to increase the sequestration of carbon in terrestrial ecosystems a focus should be placed on the quantitative amount and the qualitative chemical characteristics of lignin.

An increase in the potency of the lignin degradation related anti-microbial compounds would more effectively inhibit or delay the catabolic and related respiratory activities of microbial species capable of degrading lignin. An extension in the effective life of the lignin degradation related anti-microbial compounds would increase their presence and result in higher levels of these microbe-inhibiting compounds. The presence of more potent and higher concentrations of anti-microbial compounds will result in longer timeframes necessary for lignin and lignocellulose degradation. For a given time frame, the amount of microbe-refractory, carbon sequestering soil materials degraded by these microbes would decrease. Microbial inhibition thus results in increased amounts of sequestered carbon present and contained in terrestrial ecosystems and in extended periods of time required for the microbial degradation and respiration of that sequestered carbon into the atmosphere as gaseous carbon dioxide.

This publication describes a novel, early stage and broadly applicable technology that both increases the anti-microbial potency and extends the active life of the anti-microbial products associated with lignin biodegradation. This publication describes an inexpensive, potentially quantifiable and reversible technology requiring deliberate human-induced and human-based activity with minimal environmental impact. This publication describes a technology that can contribute to the goal of reducing atmospheric carbon dioxide levels and can potentially contribute to avoiding the anticipated excessive climate change.

The technology described in this publication can also be useful for improving the quality of soils by increasing their content of carbon containing organic matter and of humus. Soil incorporation of treated plant biomass that is more resilient to microbial catabolism will decrease the metabolic activity of lignin and lignocellulose degrading soil microorganisms resulting in enhanced soil organic material and soil characteristics. The broad technology described in this publication can also be useful in protecting treated plants from certain diseases since some plant pathogens attack lignin and lignocellulose during the disease infection process.

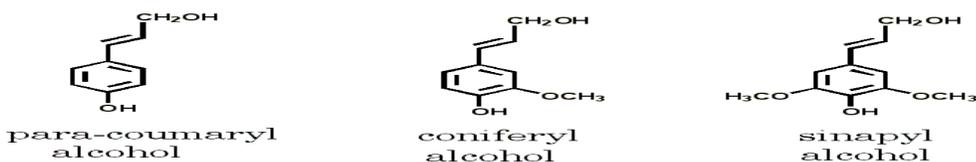
Lignin

Lignin is the generic name for the very common yet very complex aromatic polymers that are major components of terrestrial vascular plants. Lignin is an extraordinarily abundant material; in terms of weight it is probably second only to cellulose among renewable organic materials, and in terms of actual carbon content it might well be the single most abundant organic material. This unique biopolymer occupies a central and pivotal position in the earth's carbon cycle. The enormous tonnage of lignin that accumulates in terrestrial ecosystems via plant photosynthetic processes is largely balanced by the subsequent degradation and decomposition of that lignin by the catabolic action of soil microorganisms that occurs in approximately equal quantities.

Chemically, lignin are complex, heterogeneous, high molecular weight and variable polymeric materials present throughout the plant kingdom that are composed largely of phenylpropanoid (C6-C3) units derived from three cinnamyl alcohols (monolignols): *p*-coumaryl, coniferyl, and sinapyl alcohols. The chemical structures of these three monolignols are depicted in Figure 1. In addition to these monolignols, other phenolic and aromatic compounds can be incorporated into lignin polymers. Lignin imparts strength to plant cell walls, facilitates water transport in plants, impedes biodegradation of plant cell wall polysaccharides, and protects plants against attack by

microbial pathogens, insects and herbivores. The monolignols are produced from the amino acids phenylalanine and tyrosine as precursors via ammonia lyase enzymatic activities that convert these precursors into cinnamic acid (from phenylalanine via phenylalanine ammonia lyase, PAL) and into *p*-coumaric acid (from tyrosine via tyrosine ammonia lyase, TAL) respectively.

Figure 1. Naturally occurring monolignol lignin precursors



PAL and TAL represent the first dedicated and largely irreversible enzymatic steps in phenylpropanoid biosynthesis. The resulting C6-C3 cinnamic acid and *p*-coumaric acid substrate-based chemical intermediates are further modified and then incorporated into numerous plant secondary materials such as pigments and polymeric materials such as lignin. Lignin represents the major endpoint for the products of phenylpropanoid biosynthesis. It is generally accepted that C6-C3-based materials are long-lived in the plants where they are initially synthesized and that plants do not subsequently catabolize the products of phenylpropanoid biosynthesis.

The enzymes leading to the biosynthesis of the lignin-precursor monolignols are unusually “promiscuous” in their catalytic activities and capabilities since they will accept and will act upon several similar yet chemically different C6-C3 substrates. Additionally, numerous monolignol precursors and related C6-C3 compounds can be deliberately supplied to plants via injection, via external applications or sprays or via drench application to roots. These C6-C3 precursors then become covalently incorporated into the then assembling lignin aromatic polymers.

The lignification process encompasses the biosynthesis of monolignols, the transport of monolignols to the cell wall assembly site, and the polymerization of the monolignols and other phenolic and aromatic compounds into the final high molecular weight lignin molecule. The actual formation of lignin is thought to result from oxidative (radical-mediated) coupling between individual C6-C3 monolignol precursors and the growing oligomer/polymer. The process appears to involve the action of peroxidase enzymes and to proceed via dehydrogenative polymerization of monolignol precursors.

Oxidative coupling between monolignols can result in extensive heterogeneity in the final lignin polymer with the oxidative formation of several different inter-monolignol unit linkages. Although lignification is an orchestrated process, it is contemplated that the final coupling of the monolignol units is largely random and that the final composition of the lignin polymer is largely determined by the amounts of the individual monolignol and related precursors that are available at the assembly site during the lignification process. The essential phytochemical variations in lignin composition between divergent plant species (e.g., gymnosperms vs. angiosperms vs.

grasses) appear due to the relative rates of biosynthesis and amounts of specific monolignol or other precursors present during lignification.

The relatively narrow range of microorganisms that have the ability to degrade lignin include the wood-rotting fungi and to a lesser extent some bacteria and actinomycetes. Our understanding of the enzymology and chemistry of lignin degradation has been largely developed with the white-rot fungi that have been widely studied (primarily *Phanerochaete chrysosporium*) and appear to be the most efficient lignin-degraders present in terrestrial ecosystems.

No specific enzymes capable of degrading lignin, of hydrolyzing the interconnecting linkages in lignin, or of disrupting the lignin-carbohydrate association in lignocellulose have been characterized. Instead of enzyme specific degradation of the variable, high molecular weight, lignin polymers, it is currently thought that these heterogeneous materials initially undergo, at least in part, a non-enzymatic and more random degradation or “ambient temperature combustion-like” process mediated by the direct attack of oxygen radicals. Such direct chemical mediated degradation involves activated oxygen species such as OH*, H₂O₂, and O₂* and these radicals produce an initial depolymerization of polymeric lignin.

Lignases, the non-specific, extracellular enzymes produced by white-rot fungi that are associated with generalized lignin biodegradation, comprise a family of heme-containing peroxidases. This family of lignase enzymes, now generally called lignin peroxidases, are low molecular weight enzymes that require a metal cofactor (Mn⁺⁺) to produce the oxygen radicals involved in lignin biodegradation. Lignin depolymerization is contemplated to begin at the side chain carbons and not with the aromatic rings.

Biodegradation of the lignin polymer results in an initial depolymerization that generates heterogeneous and diverse products that are compounds containing one, two, or three of the hydroxy- or hydroxymethyl- substituted aromatic ring moieties. These products of depolymerization that are diverse and low molecular weight aromatic compounds are more soluble and accessible to a wide range of soil and litter dwelling fungi and bacteria. Soil microorganisms are able to take-up and incorporate these low molecular weight aromatic compounds and are able to further degrade and catabolize these compounds and utilize them as carbon sources for respiration and growth.

Products of lignin depolymerization include numerous compounds directly resulting from the oxygen radical and enzyme catalyzed modifications of the original lignin-contained, monolignol-sourced aromatic moieties. These products comprise significant levels of phenol-related aromatic moiety containing compounds that are continually produced during the degradation process. These phenolic compounds constitute the major contributors to the anti-microbial properties naturally associated with lignin degradation and are the primary cause of the reduced metabolic capabilities of adjacent microorganisms. The presence of these aromatic phenolic compounds retards lignin biodegradation. The rate of lignin biodegradation, and hence the amount of carbon sequestered in soils, is a consequence of the potency or effectiveness of these anti-microbial compounds.

It is one goal of the technology described in this publication to increase the anti-microbial properties of the phenolic, poly-phenolic and related compounds released during lignin biodegradation thereby increasing their potency and their biological effectiveness. It is another goal of the technology described in this publication to increase the recalcitrance of the phenolic and related compounds to enzymatic catalyzed breakdown thereby increasing their concentration levels and their biological effectiveness as anti-microbial agents. Both of these goals will result

in a decrease in the rate and in the amount of lignin and lignocellulose degraded by soil microorganisms. These decreases in lignin degradation will result in an increase in amount of the carbon retained in and sequestered by the soil.

The Technology and an Hypothesis to Describe its Mode of Action

We have developed an early stage technology that decreases the rate and the extent of the biodegradation of lignin materials. It is our hypothesis that the observed reduction in lignin biodegradation is due at least in part to the increases the effectiveness of the lignin degradation associated anti-microbial compounds. One application of the technology involves treating plants with C6-C3 phenylpropanoid acid, aldehyde and alcohol lignin precursors that are not naturally produced by plants. Another application of the technology could involve treating plants with C6-C2 (phenylacetic/phenylacetyl) or C6-C1 (benzoic/benzyl) acid, aldehyde and alcohol compounds that are not naturally produced by plants. These precursors can be produced synthetically and contain substitutions in the C6 aromatic portion or in the aliphatic portion or in both portions of the C6-C3, C6-C2 or C6-C1 molecule. The substitutions to the lignin precursors can be of any sort and are well known in organic chemistry.

The synthetic lignin precursors can often be taken up by treated plants, may be employed as substrates by the enzymes of monolignol biosynthesis, and may be transformed into the corresponding unnatural monolignol lignin precursors within the plant. The unnatural monolignol may then be incorporated into lignin polymers. These events result in lignin materials that are chemically distinct yet functionally similar to natural lignin. Once these chemically distinct lignin polymers are present in plant litter they then are subject to the biodegradative actions of soil microorganisms. Specific chemicals selected from these classes of agents can be easily screened for their applicability and potential use in this invention by determining: i) if the chemical displays significantly phytotoxicity, and ii) if treated plant material displays increased resistance to degradation by lignin degrading microorganisms.

It is our hypothesis that the initial microbial biodegradation of these chemically distinct lignin polymers will result in chemically different phenolic compounds that may display increased anti-microbial activities and/or retarded rates of decomposition when compared with the anti-microbial phenolic degradation products from natural lignin polymers. These chemically different phenolic compounds will be directly related to the parent C6-C3 phenylpropanoid acid, aldehyde and alcohol lignin precursor molecules or other phenolic compounds that were introduced into treated plants and incorporated into their lignin polymers. Essentially, by incorporating unnatural monolignols the lignin polymer has become a “prodrug.” The desired “drug” which is the anti-microbial agent is released only when and where lignin biodegradation is actively occurring.

Using this technology, the anti-microbial properties and the rates of biodegradation of the different phenolic compounds can be determined and manipulated. This control can be accomplished by selecting the types of chemical substitutions introduced into unnatural phenylpropanoid lignin precursors and by selecting the rates and timings of the applications of these synthetic phenylpropanoid agents. Manipulation of these anti-microbial properties will impact the rates of lignin and lignocellulose biodegradation and determine the levels of sequestered carbon. Using this technology, the amounts of carbon sequestration in terrestrial ecosystems can be predictably manipulated.

Plants are fully capable of biosynthesizing and elaborating all of the monolignol and related aromatic compounds required for lignin production. Consequently, chemical agents that inhibit, modulate or effect the enzymatic steps that underlie or are related to the elaboration or the

modification of lignin precursors can be employed to further control lignin production. These chemical agents may effect both the production of lignin precursors and the characteristics of lignin polymers. These agents can act to enhance the quantity, composition, or anti-microbial properties of lignin polymers in plants treated with synthetically produced lignin precursors. For example, some of these chemical agents that are aromatic hydrocarbon biosynthesis modulating or inhibiting chemical agents includes several commercial herbicides (e.g., glyphosate) and plant growth regulators (e.g., glyphosine) as well as chemical agents that inhibit or effect the expression of the ammonia-lyase enzymes, PAL and TAL.

An Example: Halogen-Substituted Precursors

One possible application of the technology would be to use halogen-substituted cinnamic acids as the synthetically produced and unnatural C6-C3 phenylpropanoid lignin precursors. There is a wide-range of halogenated cinnamic acids that are both commercially available and are relatively inexpensive. Most of these substituted cinnamic acids are not phytotoxic, many of them are taken up by plant tissues when applied as a spray, a drench or an injection and a number of the halogen substituted cinnamic acids can be incorporated by plants into lignin polymers. Additionally, they can be employed either individually or in combination as required. Although halogen-substituted cinnamic acids may be enzymatically converted into the corresponding monolignol lignin precursor they do appear to be incorporated into lignin and they do not appear to be catabolized or degraded by the plants that have acquired and incorporated these synthetic chemical precursors.

Another possible application of the technology described in this patent would be to use halogen-substituted benzaldehyde compounds as the synthetically produced and unnatural C6-C1 compounds. Again, there is a wide-range of halogenated benzaldehydes that are both commercially available and inexpensive. Some of these substituted benzaldehydes are not phytotoxic while others are phytotoxic (and potentially herbicidal), and many of them are taken up by plant tissues when applied as a spray, a drench or an injection. Additionally, they can be employed either individually or in combination as required. A rapid screening of these compounds can determine which of these compounds are phytotoxic and hence are not appropriate for use in this technology.

In specific early-stage demonstrations of the application of the technology, both sugarcane: (*Saccharum officinarum* L.: cv. B4362) and corn: (*Zea mays* L.: inbred line B73) plants were used as experimental materials. It is important to note that the technology has also been tested and found applicable to both woody and herbaceous plant materials. For these specific demonstrations, plants were cultivated in a sandy loam/peat mixture with standard fertilization in well-drained large containers. Halogenated cinnamyl and benzyl agents were applied as two applications during plant growth via either drench application to the roots or as a foliar spray. The total amount of the two applications of halogenated cinnamyl or benzyl agent applied approximated a final total rate of 100 grams per acre. For sugarcane, mature stalks were harvested, crushed, extracted and washed to remove the sugar and soluble materials resulting in bagasse that was used for an analysis of the time-course of lignin degradation caused by *Phanerochaete chrysosporium*, a lignin degrading fungus. The time-course of the accumulation of fungal biomass was also determined. For corn, treated plants were permitted to naturally mature senesce and dry down. After dry down several sections were taken from nodal and from internodal regions at the base of the stalk for *in situ* soil treatments. For soil treatments, stalk sections were buried in fertile sandy loam topsoil in a cultivated field that had been used for the sequential cultivation of corn for at least the prior two years. The stalk section burial and recovery work was completed in multiple marked plots. The time-course of lignin degradation and the extent of fungal biomass accumulation for the buried stalk sections were established for

the *in situ* soil treatments. The approximate values for lignin degradation and for fungal biomass accumulation were determined by staining intensity and quantified and recorded as 10% step changes. The averaged results of the several replicates of these specific examples are presented in Table 1.

Table 1. Compiled averaged results of the specific examples

Sugarcane

<u>Chemical Agents</u>	<u>Rate of lignin degradation</u>	<u>Fungal biomass accumulation.</u>
	(expressed as % of control after six months of fungal degradation)	
None (control)	100	100
Cinnamic Acid	100	100
2,6-Difluorocinnamic Acid	50	30
3-Cholorcinnamic Acid	50	60
2-Chloro-4-hydroxybenzaldehyde	30	40
3,5-Dibromo-4-hydroxybenzaldehyde	50	60

Corn

<u>Chemical Agents</u>	<u>Rate of lignin degradation</u>	<u>Fungal biomass accumulation.</u>
	(expressed as % of control after nine months of <i>in situ</i> treatment)	
None (control)	100	100
Cinnamic Acid	100	100
2,6-Difluorocinnamic Acid	50	40
3-Cholorcinnamic Acid	40	30
2-Chloro-4-hydroxybenzaldehyde	40	30

For the results presented in Table 1 it is clear that several different classes of synthetic halogenated molecules appear able to significantly retard the subsequent rate of lignin degradation and the associated accumulation of fungal biomass when applied to both sugarcane and to corn. It is also clear that the observed decreases in the rate of lignin degradation and accumulation of fungal biomass are not associated with any specific family of halogenated structure but is a more general property of numerous halogenated structures within broad families of related structures. It is also clear that application of these related chemical agents results in potentially different rates of lignin degradation and fungal biomass accumulation. From results of other early stage examples of this technology not presented here it is also clear that the final quantity or amount of synthetic halogenated lignin precursor applied is also an important variable. For a given synthetic halogenated lignin precursor, application of greater amounts of material result in more significant decreases in the subsequent rate of lignin degradation and fungal biomass accumulation. The initial results based on sugarcane bagasse are repeatable and track the results with corn stalks and stover materials. From results of other initial examples of this technology not presented here confirm that the halogen-substituted lignin materials release more potent anti-microbial agents than do control lignin materials when subject to microbial degradation. These anti-microbial agents have effects on the growth of soil bacteria as well as on lignolytic fungi.

Evidently, the rate and extent of subsequent lignin degradation by white rot fungus is a function of the amount of halogen-substituted lignin precursor incorporated into the lignin polymer. Additionally, that rate and extent can be potentially controlled by the specific halogen-substituted monolignol precursor applied as well as by the dose and timing of the applications. This technology appears to be robust, to be applicable to a wide range of plant species, to perform in *in situ* environmental circumstances and to function as hypothesized.

Degradation of the resulting halogen containing prodrug lignin polymers described in this example would release various compounds including halophenol and bis-phenol type antimicrobial agents. Several commercial fungicides as well as numerous commercial disinfectants and antiseptics are halogen substituted phenolic compounds and bis-phenol agents that are highly active against both bacterial and fungal species. The bis-phenols are hydroxy-halogenated derivatives of two phenolic groups connected by various bridges. A cartoon of the envisioned process employing a synthetic 3-chloro- monolignol precursor is presented in Figure 2.

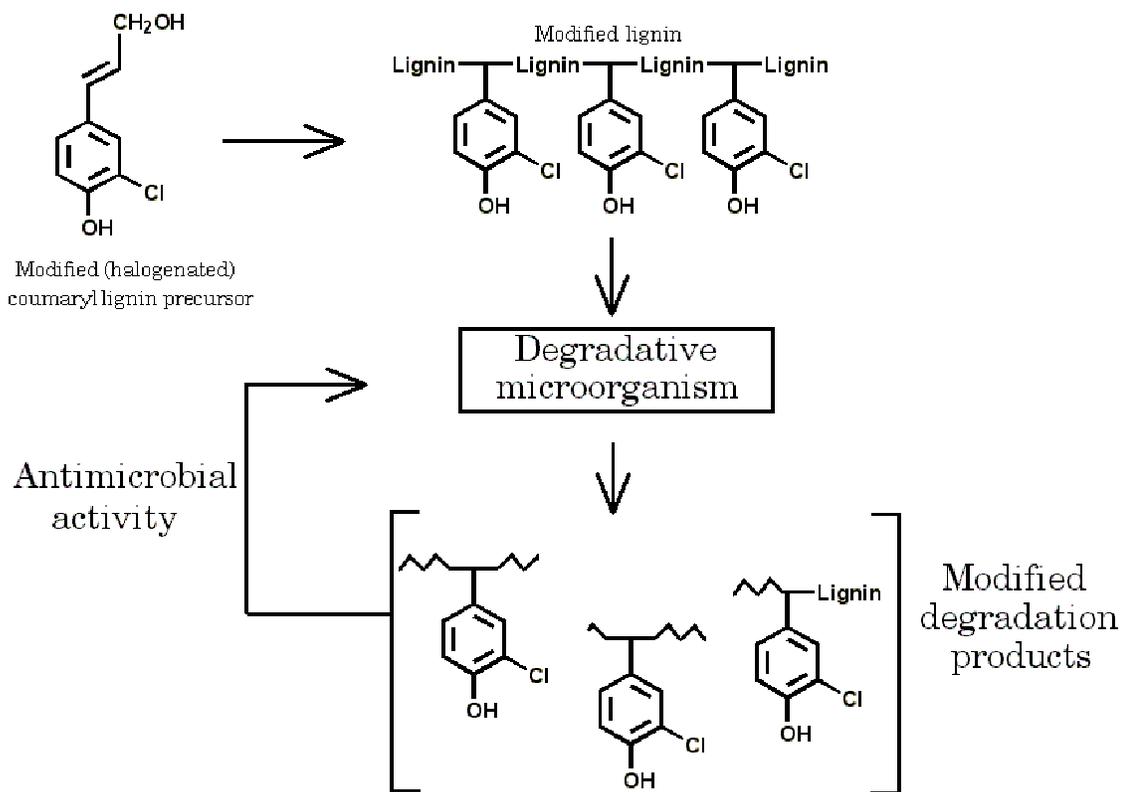


Figure 2: A cartoon representation of the envisioned process employing a 3-chloro-monolignol precursor.

One potential concern for certain regulatory issues may be the halogenated residues that this technology may release into the soil environment. However, lignin degrading fungi (e.g., white-rot fungi) and other soil microorganisms are well known to be able to completely degrade and metabolize a wide range of halogen containing aromatic pesticides and xenobiotic chemicals. This ability includes the halogenated aromatic hydrocarbons that will result from this technology

during the process of lignin biodegradation. As in lignin degradation, lignolytic enzymes should facilitate metabolism of the halogen containing aromatic anti-microbial compounds. Metabolism of xenobiotic compounds generally occurs at a significantly slower rate than does lignin biodegradation. Consequently, any potentially objectionable environmental pollutants that may result from this technology as halogenated aromatic hydrocarbons should be metabolized, degraded and removed.

The underlying process of halogen-modification of plant materials to inhibit rapid biodegradation as described in this specific example appears to happen naturally in the environment during the formation of humic materials in the soil. These humic materials constitute the long-lived carbon sequestering components in terrestrial ecosystems. Surprisingly, long-lived humic materials naturally contain a significant amount of covalently bound chlorine that is added over time to plant-sourced biomass materials resident in the soil. Consequently, the technology as embodied in this halogen-doping example, may be acting by employing, accelerating and accentuating nature's own processes and timetables.