Wood Chemistry

Wood Chemistry

PSE 406 / Chem E 470

Lecture 22: Decay

(Part 2)

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Enzyme Function

- There are a large number of fungal enzymes responsible for the breakdown of each wood component. Each enzyme plays specific roles (cellulase example from reading*):
  - » **Cellobiohydrolase** (CBH), acts on the end of the molecule successively cleaving off the disaccharide cellobiose.
  - » **Endo-beta-1,4-glucanase** acts within the chain, breaking it into smaller units and providing more "ends" for CBH.
  - » **Beta-glucosidase** (or cellobiase) which cleaves cellobiose to two glucose units.
- These enzymes working together produce glucose which is consumed by the fungi.

* http://helios.bto.ed.ac.uk/bto/microbes/armill.htm

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How do Enzymes Function?

- Enzymes react with cellular components through free radical* processes.
- Free radicals (as earlier discussed and covered in notes section) are very reactive species.
  - » Enzymes in the form of free radicals will oxidize wood components directly (abstracting an electron thus turning the wood chemical into a reactive free radical).
  - » Lignin peroxidases are able to oxidize a wide variety of compounds through this process.
  - » Other enzymes are not able to do this.

Notes

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Other Oxidizing Techniques

- Because the enzymes are so large, it is most often necessary to use small reactive free radicals (or other reactive species) to do the dirty work.
- A good example of this are the manganese peroxidases. In this system, the enzyme oxidizes Mn^{2+} to the powerful oxidant Mn^{3+} which can penetrate the cell wall to react with cell wall components.
- Many of the small radicals are produced through reaction of the enzymes with cellular components (like lignin).

Free Radical Candidates

- Compounds present in the plant material
  - » Metals (Mn, Fe, Cu)
  - » Oxygen (see next slide)
- Compounds produced by enzyme
  - » H_2O_2, veratryl alcohol, oxalates
- Degradation products from wood
  - » Phenolic compounds (example: RO•)
  - » Other aromatic compounds (example: RCO_2•)
  - » Quinones

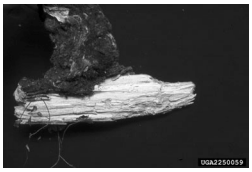
Reactive Oxygen Species

$$O_2 \xrightarrow{e^-, H^+} HO_2\bullet \xrightarrow{e^-, H^+} H_2O_2 \xrightarrow{e^-, H^+} HO\bullet \xrightarrow{e^-, H^+} H_2O$$

- HO_2• : hydroperoxy radical, pKa ~ 4.8
  - » Ionized form (- O_2•) : Superoxide radical = weak oxidant.
- H_2O_2: hydrogen peroxide, pKa ~ 11.6
  - » ionized form (-HO_2): hydroperoxy anion = weak oxidant
- HO˙ : Hydroxide radical (strong oxidizer), pKa ~ 11.9
  - » Ionized form (-O•): oxyl anion radical
- Many of these species are formed through the interaction with metals: Fenton's chemistry

Summary (to date)

- So here is what we have learned to date:
- Decay by fungi is caused through enzymatic free radical reactions.
  - » The reactions can either be the enzymes themselves or smaller free radical species produced through reaction with the enzymes.
  - » These free radicals react with the cellular components breaking them into fragments many of which are useable by the fungi.



What Happens to the Chemicals Unloved by the Fungi?

- Basically the question is what happens to all of the organic material that is not consumed by the organisms?
- In this picture, the log is rotting leaving a pile of organic material on top of the soil.
- Does this organic material simply disappear?

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Soil Organics

- The answer to the question on the last slide is of course not, the organic material doesn't disappear it is simple changed into the soil organics: Fulvic Acids, Humic acids, and Humins. These materials are classified by their solubility.
  - » Fulvic Acids (Acid soluble fraction)
  - » Humic acids (Alkali soluble fraction/ acid insoluble)
  - » Humin (Insoluble organics)

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Soil Organics II

- These materials are very important to the soil (As lignin is to everything else)
- The amounts of these compounds is very soil type dependent.
  - » 60-70% of soils organics are humin, humic acids and fulvic acids
  - » Soil organic matter ranges from 0.5 to 20 % of the soil material

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Structure of Soil Organics

- These soils organics are large polymers and thus like lignin structural determination is somewhat difficult.
  - » Fulvic acid Mw~2000+, humic acids higher, humins as high as 300,000?
- These materials are more difficult than lignin for structural studies because they are produced from so many different materials (unlike lignin: 3 possible precursors)

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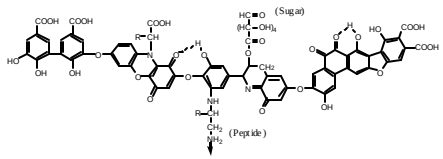
Proposed Humic Acid Structure

- This is a proposed segment of humic acid by Stevenson*
  - » Notice the phenolics, the sugars, and the peptides
  - » It is obvious that this molecule does not arise directly from any component but is built from pieces of other components.



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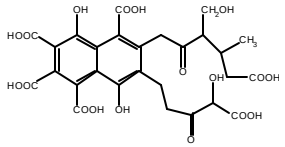
Proposed Fulvic Acid Structure

- This is a proposed structure for a fulvic acid fragment by Buffle



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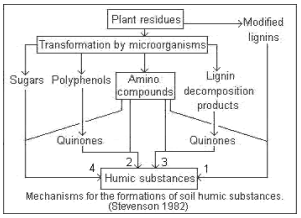
Formation of Soil Organics

- There is a tremendous amount not known about this process.
- This figure (borrowed from a website) shows 4 proposed routes to humic substances



Mechanisms for the formations of soil humic substances. (Stevenson 1982)

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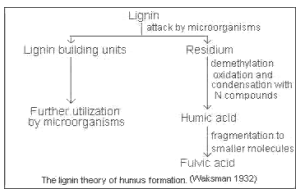
Formation of Humus Directly from Lignin

- This is an old theory (1932) that was accepted for a very long time but is now in disfavor.
- In this route, lignin is modified by enzymatic reactions forming humic substances.



The lignin theory of humus formation. (Waksman 1932)

Once again this is a borrowed image

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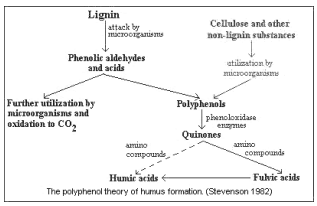
Formation of Humus from Degradation Products

- In these 2 pathways, lignin and carbohydrates are broken into fragments which are modified and then linked together to form the polymers.
- These routes are more highly accepted.



The polyphenol theory of humus formation. (Stevenson 1982)

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Formation of Humus from Sugar-Amine Condensation

- In this final route, the organic material is formed through reactions between sugar degradation chemicals and organic nitrogen materials.