Lignin compound composition of post-glacial sediments in Glacier Bay, Alaska

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Abstract

Lignin derived phenols detected and quantified by CuO digestion and Gas Chromatograph with Flame Ionization Detector (GC-FID) can be compared in proportions and concentrations to determine the vegetative source of those compounds. Syringyl to vanillin and cinnamyl to vanillin ratios indicate that sediment samples primarily contain lignin compounds derived from gymnosperm woods (soft woods) with a component of non-woody material such as grasses mixed with some samples. The Lignin Phenol Vegetative Index (LPVI) provides a convenient way to display changes in vegetative type down a core which is variable, ranging from 12 to 250, at the location discussed in this paper. Acid to aldehyde ratios indicate lignin phenols range from a degradation ratio of 0.53 to 16, which are all high compared to literature values, and samples which contain more angiosperm tissue tend to be more degraded than samples that do not as shown plotted against LPVI values. It is concluded that sediment deposition mechanisms have varied over the past due to the observed change in lignin derived vegetation source type.

Introduction

The UW senior Oceanography class of 2008; 22 undergraduate students including myself, 1 graduate teaching assistant and 5 faculty members; embarked with the crew on the *R/V Thomas G. Thompson* from Seattle, Washington to Glacier Bay, Alaska on 14 March 2008. The science party and crew spent approximately 5 days in Glacier Bay collecting data and samples for the various projects being conducted to return to Seattle on 26 March 2008.

Many years prior to our trip, in 1879, preserved tree stumps and trunks were discovered around the shores of Glacier Bay, Alaska by John Muir. These trees, including others that were discovered later, were non-mineralized, and identified as having been covered and preserved by the glaciers since the last interglacial period (Cooper, 1923).

It is broadly understood that the terrestrial and marine environments are coupled in many ways. Understanding the intricacies in this biologically important region could reveal how climate and changing regional dynamics affect the tree and vegetation distribution of the region which then impacts water and nutrients that are deposited into the water.

I collected sediment samples using a Kasten core at locations throughout Glacier Bay (Fig. 1, Table 1). Samples of leaves, needles, branches and wood were also collected from land for comparison which is also indicated in Table 1.

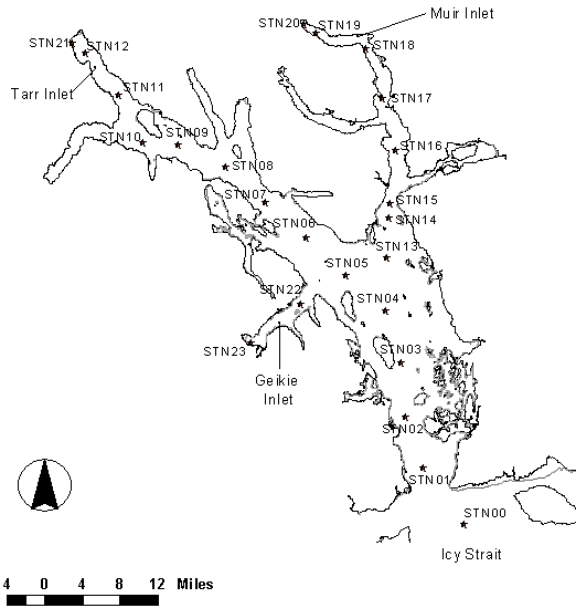

Figure 1: Map of Glacier Bay and previously monitored CTD locations. Locations marked with STN## are referred to as KC-## throughout this paper (i.e. STN16 is KC-16) (Hooge et al. 2000).

Sediment and land samples were processed for lignin signatures to determine possible sources of those lignin compounds including source type (gymnosperm, angiosperm and non-tree plants) and tree tissue type (wood, leaves and needles). This analysis is made possible due to knowledge of ratio compositions of lignin phenols and tree/plant tissue types as in Fig. 2 (Tareq et al. 2004).

Methods

Field

Sediment cores were collected astern the *Thompson* by using the onboard a-frame to deploy a ∼3 meter long Kasten core at the stations indicated in Table 1. Sampling stations were selected based on the collective needs of all onboard students, time constraints for vessel use as well as previous observations (Cooper, 1923).

The core was lowered and stopped a few meters above the sediment, subsequently lowered into the sediment at 20 meters per minute and recovered once the technician determined it had penetrated to a maximum depth. During recovery, the nose cone of the core was placed on deck and the core's top was tilted to an approximate 45 degree angle using an air tugger and line attached to the top of the core. The highest panel on the core above the surface of the collected sediment was removed and foam pads were inserted at the top of the sediment to fix the vertical profile when the core was lowered further to a horizontal orientation.

Metal dividers and spatulas were used to sample all sediment in each core at 2 cm intervals and each 2 cm interval was split between two bags. These bags were stored in a refrigerator at approximately 2°for the remainder of the cruise.

A large chunk of wood was also collected and tentatively identified by Lewis Sharman, ecologist in Glacier Bay who accompanied the class on the *Thompson* while it was in the bay, as being from a pre-glacial advance tree. He made this identification based on two things: the chunk of wood is larger than can be provided by any currently living trees and it has a very old appearance (L. Sharman, verbal communication, 2008).

Laboratory

Sediment samples were transferred into glass vials and desalted by adding distilled water, centrifuging the vials at 3000 rpm for 10 minutes and then pipetting the water off the sediment. Kimwipes and flat-bottom vials were used in a centrifuge with rounded bottoms which caused some of the vials to break. Sediment which was still contained in the vial was recovered from and the centrifuge was thoroughly cleaned after each of these cases. Desalting was done to prevent copious amounts of salt in the sediment from interfering with laboratory analyses. Terrestrial samples (leaves, twigs, needles and wood) were positively identified upon visual inspection by Lewis Sharman (personal communication). All samples were then freeze dried and broken up

Station Name	Latitude	Longitude	Penetration Depth (m)	Water Depth (m)
KC-10	58.8996°	-136.838°	2.07	398
KC-16	58.8962°	-136.092°	.68	294
KC-21	59.0481°	-137.056°	.57	217
KC-23	58.5985°	-136.505°	.93	99
Interglacial Wood	58.7989°	-136.152°	N/A	N/A
Terrestrial Samples	58.4623°	-135.854°	N/A	N/A

Table 1: Displays the names and approximate lat./long. locations of cores and other samples taken in Glacier Bay as well as the penetration depth and water depth of each core. Only samples from station KC-16 are discussed.

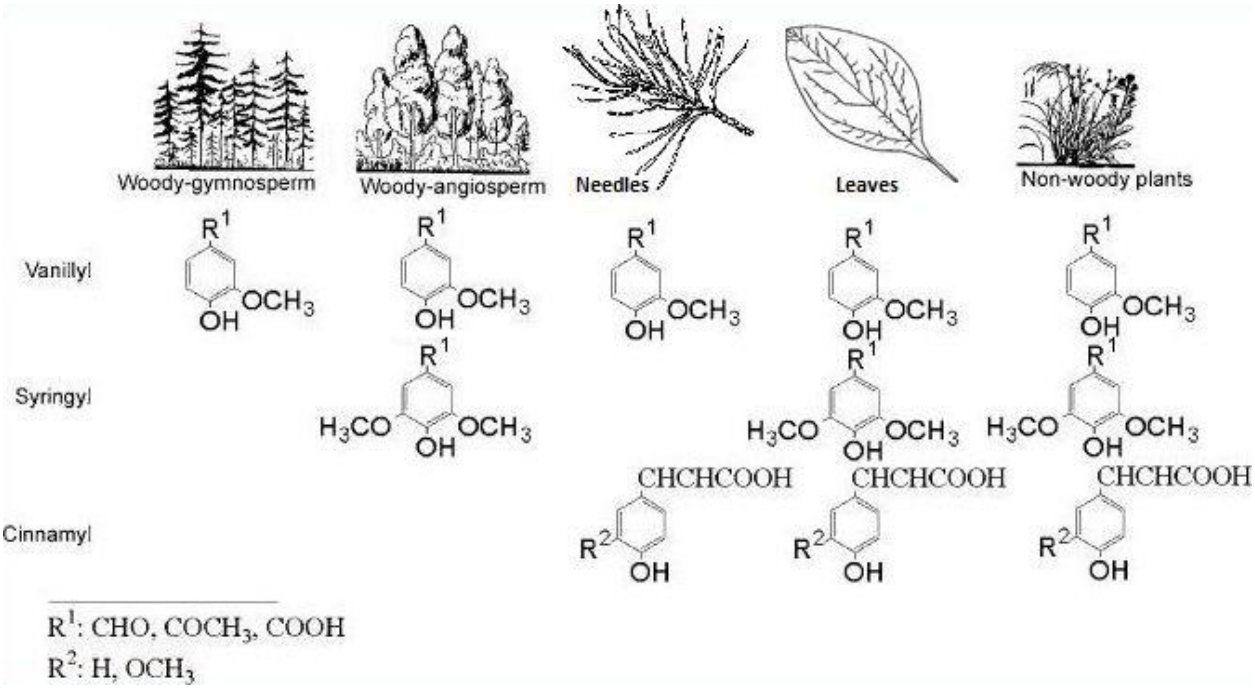

Figure 2: Lignin monomer composition of plant materials (Modified from Tareq et al. 2004).

using a glass mortar and pestle or ground with an electric grinder when appropriate.

These samples were analyzed for lignin compounds using a standard microwave digestion and gas chromatograph method (Goni 2000). Organic compounds were removed from the sediment sample after microwave digestion with ethyl acetate, dried down, suspended in pyridine and derivatized with N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) and Trimethylchlorosilane (TCMS) before they were finally analyzed with a GC-FID. Lignin phenols were identified by comparing retention times of each compound in the gas chromatograph to laboratory standards with known column retention times for each.

Compounds were then quantified with ratios to other compounds and multiplying the molecular weight of each compound by the concentration of the compound to get a total mass of

each compound. Quantifications were corrected by scaling raw quantities to detected quantities of 1 mM ethyl vanillin and trans-cinnamic acid solutions which were added immediately after the microwave digestion stage.

Results

Concentrations and proportions of all eight vanillin, syringyl and cinnamyl phenols are presented in Table 2. Samples from KC-16 were split between two different digestions on two different days which may account for some of the variability in data presented throughout this paper.

Syringyl to vanillyl, cinnamyl to vanillyl ratios as well as acid to aldehyde ratios for both vanillin and syringyl phenols are presented in Table 3.

The Lignin Phenol Vegetative Index (LPVI) identifies the wood and/or tissue type source of lignin containing samples based on the ratios of the major lignin phenols in the samples. The LPVI values, calculated using the equation given by Tareq, of each sample in KC-16 are presented with the average depth of the sample in Table 4 (Tareq et al. 2004).

Discussion

The source of vegetative lignin phenols can be reasonably determined by plotting the ratio of syringyl to vanillin compounds against cinnamyl to vanillin compounds which can be seen in Fig. 3 (Ertel 1984). The linear trend, supported by an R^2 value of 0.51, indicates that samples at KC-16 are primarily comprised of lignin compounds from gymnosperm woods with a mixture of non-woody angiosperm tissue. The samples do not indicate a significant presence of angiosperm woods, so the non-woody angiosperm tissue is likely from grasses and other non-tree derived sources. Because the linear trend line has a slope of less than one, it may also indicate a mixing of lignin phenols from non-woody gymnosperm tissue (i.e. needles). The possible angiosperm wood tissue contribution to the signature at 8-10 cm, which falls farthest from the trend line, could be indicative of a temporary change in sediment deposition processes that brought more angiosperm wood tissue the KC-16 sampling location.

The LPVI values of samples at KC-16, presented in Table 4 earlier, plotted by depth (Fig. 4) visualizes changes in vegetation material type down the core. This can be used as a proxy for change in vegetation type or change in deposition mechanism over time. The changing LPVI values down core likely represents a change in the deposition process for KC-16 because the values range from low to high and back to low several times rather than representing a single change in vegetative type. LPVI values at average depths of 9, 25, 49 cm respectively fall within the angiosperm wood range, but because Fig. 3 indicates that no angiosperm wood was present in the samples, this must be representative of a mixture of non-woody angiosperm tissue and gymnosperm tissue to yield an average LPVI value which is lower than the non-woody angiosperm tissue range, but higher than the gymnosperm tissue ranges.

During degradation by fungus and some bacteria, the aldehyde and ketone types of lignin phenols degrade to their corresponding acids (Hedges et al. 1988). Thus the ratio of lignin acids to aldehydes provides a good picture of how degraded the woody remains are in samples. High acid to aldehyde ratios are indicative of highly degraded samples. Plotting Ad/Al for the vanillyl phenols (because they are present in both gymnosperm trees and grasses) against LPVI will also display which types of lignin containing organic matter are most and least degraded. Materials with low LPVI values (gymnosperm woods) contain both the most and least degraded sources of lignin compounds (Fig. 5). The angiosperm grass remains are of intermediate degradation compared to gymnosperm wood remains. Compared to literature values,

Sample	Concentration (mg/L)	Concentration (µg/gdw)	$\sum$8 (mg/10g sed)	Λ (mg/100mg OC)
KC-16, 0-2 cm	88	70	0.70	3.8
KC-16, 8-10 cm	71	57	0.57	2.8
KC-16, 16-18 cm	53	42	0.42	1.5
KC-16, 24-26 cm	53	42	0.42	1.5
KC-16, 32-34 cm	50	40	0.40	1.8
KC-16, 40-42 cm	64	51	0.51	3.6
KC-16, 48-50 cm	120	94	0.94	4.3
KC-16, 60-62 cm	21	17	0.17	1.1
KC-16, 66-68 cm	79	63	0.63	4.4

Table 2: Total concentration of all vanillyl, syringyl and cinnamyl lignin phenols by milligrams per liter of solution and micrograms per gram of dry sample weight. Also '$\sum$8' (Sum 8) and 'Λ' (Lambda) values, or total mass of vanillyl, syringyl and cinnamyl lignin compounds in milligrams per ten grams of sediment and per 100 milligrams of organic carbon per sample respectively.

Sample	S/V	C/V	Ad/Al (v)	Ad/Al (s)
KC-16, 0-2 cm	0.38	0.07	1.70	0.39
KC-16, 8-10 cm	0.73	0.27	1.80	0.35
KC-16, 16-18 cm	0.43	0.19	1.30	0.44
KC-16, 24-26 cm	0.52	0.35	2.10	0.24
KC-16, 32-34 cm	0.46	0.21	1.40	0.36
KC-16, 40-42 cm	0.44	0.21	1.60	0.40
KC-16, 48-50 cm	0.62	0.50	3.40	0.34
KC-16, 60-62 cm	0.27	0.10	0.53	0.45
KC-16, 66-68 cm	0.37	0.20	15.00	0.75

Table 3: Ratios of syringyl to vanillyl (S/V), cinnamyl to vanillyl (C/V) as well as acid to aldehyde ratios of vanillyl (Ad/Al (v)) and syringyl (Ad/Al (s)) lignin phenols.

however, angiosperm grass remains are highly degraded (Hedges 1988). The reason for the outlying and very highly degraded sample at 66-68 cm is unknown, but it is the 'oldest' or farthest down core compared to other samples which may contribute to its degradation state.

Conclusion

At three times in the past, lignin phenol sediment composition entering the bay and settling at KC-16 contained gymnosperm wood tissue as well as angiosperm grass tissue compared to other points in the past where sediment was dominated by gymnosperm wood. These angiosperm grasses must have been more degraded than the gymnosperm wood tissues. These variable deposition processes were likely caused by

Sample	Avg. Depth of Sample	LPVI Value
KC-16, 0-2 cm	-1	16
KC-16, 8-10 cm	-9	130
KC-16, 16-18 cm	-17	42
KC-16, 24-26 cm	-25	120
KC-16, 32-34 cm	-33	51
KC-16, 40-42 cm	-41	50
KC-16, 48-50 cm	-49	250
KC-16, 60-62 cm	-61	12
KC-16, 66-68 cm	-67	36

Table 4: Average depth of each sediment sample and the LPVI value of each.

varying deposition processes because the LPVI values alternate between high and low rather than making a single shift from low to high which would indicate a change in vegetative regime.

Without deposition rates for the site or region, it is not possible to estimate the time in which these changes may have occurred. Further research should focus on determining the sediment deposition rates of the bay as well as a comparison to other locations within the bay.

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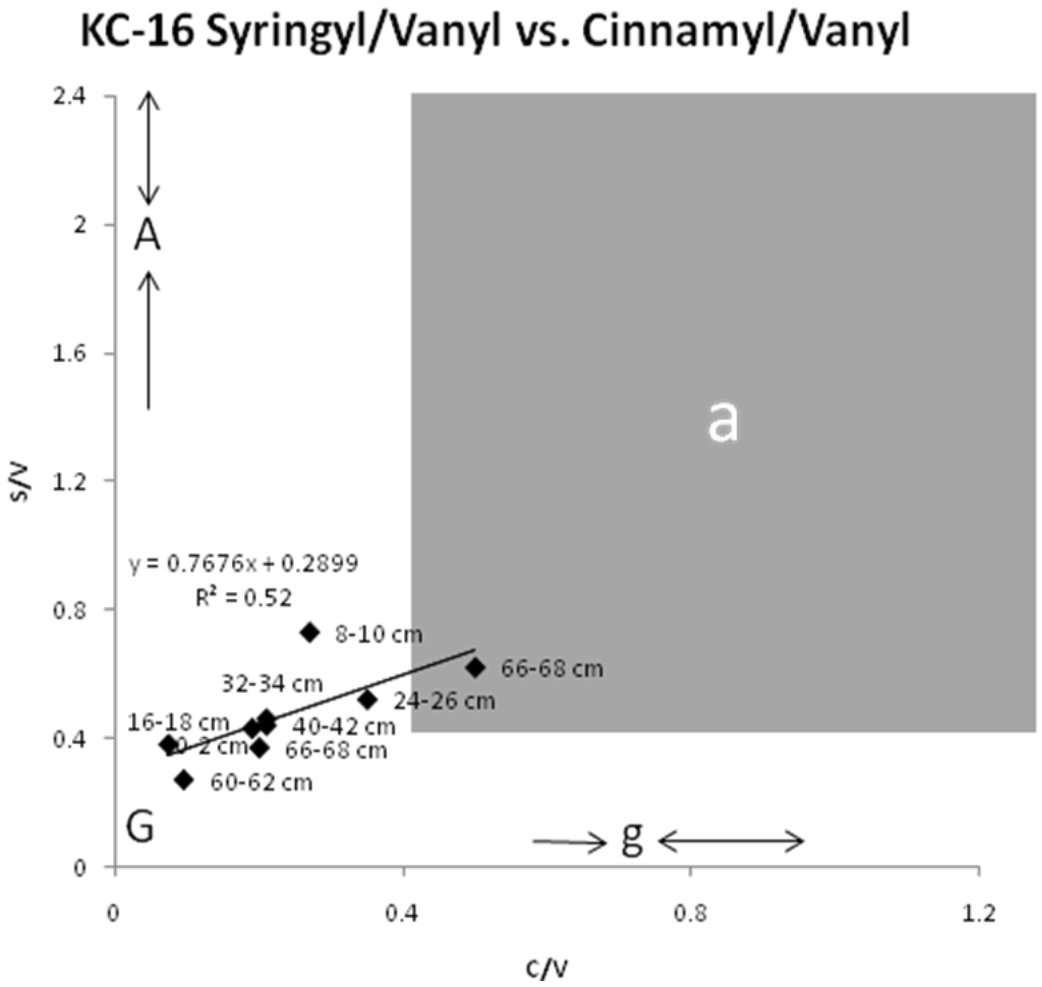

Figure 3: Syringyl to Vanillin and Cinnamyl to Vanillin compounds for all KC-16 samples. Area 'a' represents non-woody angiosperm tissue (leaves and grasses), 'g' along the C/V axis represents non-woody gymnosperm tissue (needles), 'G' at the origin represents gymnosperm woods (hard woods) and 'A' along the S/V axis represents angiosperm woods (soft woods).

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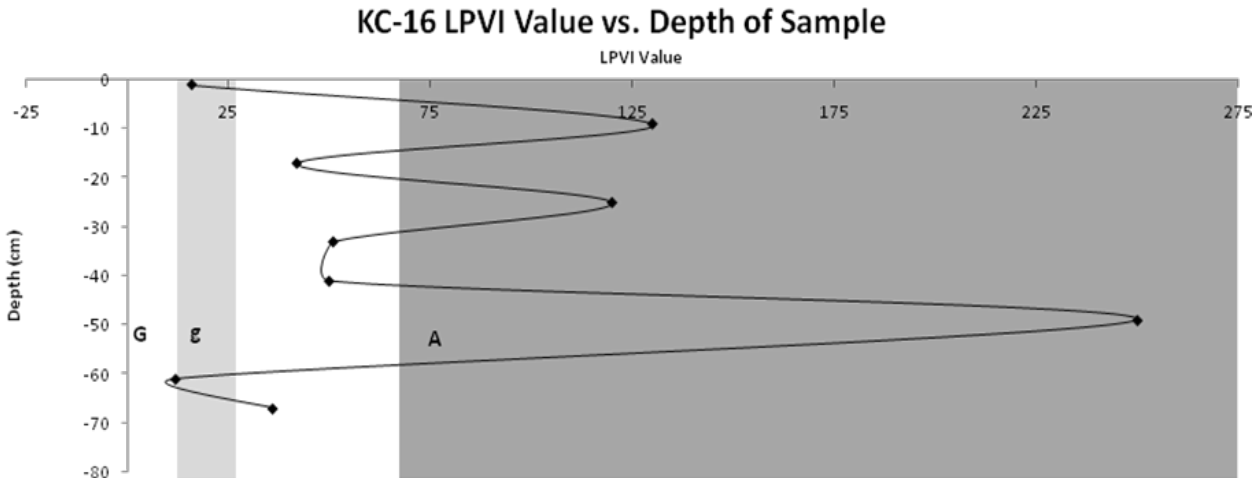

Figure 4: LPVI value for samples at KC-16 to depth sampled in the core retrieved. As in Figure 3, 'G' represents gymnosperm wood, 'g' represents nonwoody gymnosperm tissues, 'A' represents angiosperm woods and nonwoody angiosperm tissues are not represented in this plot, but they cary LPVI values between 378 and 2782 (see Tareq et al., 2004).

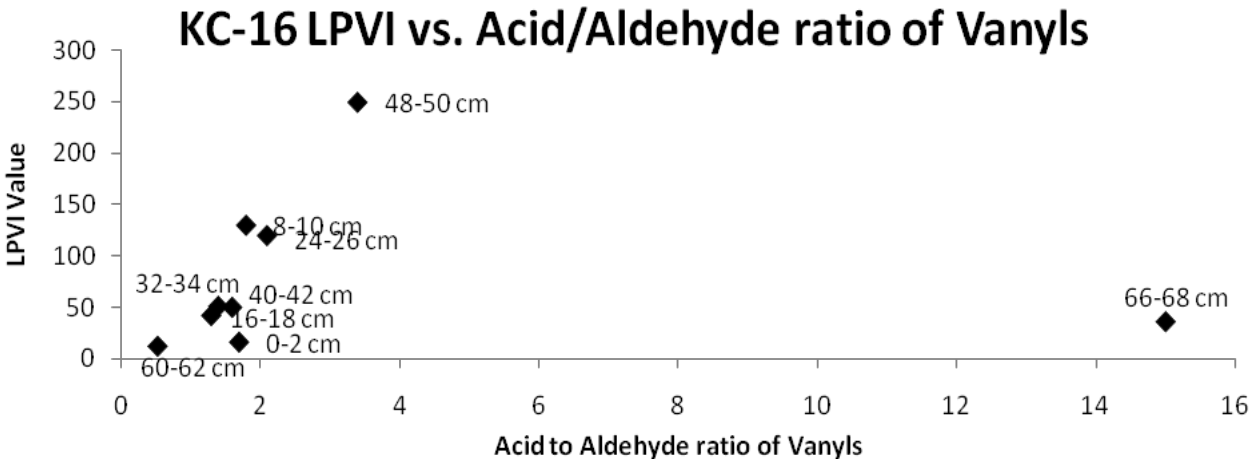

Figure 5: LPVI values of samples at KC-16 against the acid to aldehyde rations of the same samples.

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