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Lignin biogeochemistry: from modern processes to Quaternary archives

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ABSTRACT

Lignin has been analysed as a proxy for vegetation change in the Quaternary science literature since the early 1990s in archives such as peat, lakes, and intertidal and marine sediment cores. Historically, it has been regarded as comparatively resistant to various types of degradation in comparison to other plant components. However, studies of modern biogeochemical processes affecting organic carbon have demonstrated significant degradation and alteration of lignin as it is transported through the terrestrial biosphere, including phase changes from particulate to dissolved organic matter, mineral binding and decay due to biotic and abiotic processes. The literature of such topics is vast, however it is not particularly useful to Quaternary research without a comprehensive review to link our understanding of modern processes involving lignin to Quaternary environments. This review will outline the current state of the art in lignin phenol research that is relevant to the Quaternary scientist, and highlight the potential future applications for this important biomarker for vegetation change and terrestrial organic carbon cycling.

1. Introduction

Lignin is a naturally occurring and widely abundant biopolymer found almost exclusively in terrestrial vascular plants, and provides a major contribution to bulk organic matter (OM) preserved in soils, peats and sediments (Hedges and Mann, 1979; Ertel and Hedges, 1984, 1985; Ertel et al., 1984; Hedges and Oades, 1997). In aquatic environments, lignin is present in the water column as both dissolved (DOM) and particulate (POM) organic matter, the latter ultimately preserved in sedimentary deposits as a molecular fossil (Hedges et al., 1982; Ertel and Hedges, 1984). Lignin composition in sediment and peat offers considerable potential value as a proxy in Quaternary research, as analysis of lignin monomers can reveal information about vegetation source, and OM degradation processes.

Lignin has been analysed as a proxy for vegetation change in the Quaternary science literature since the early 1990s in archives such as peat (Bourdon et al., 2000; Tareq et al., 2004; Comont et al., 2006); lakes (Hedges et al., 1982; Ishiwatari and Uzaki, 1987; Meyers and Ishiwatari, 1993; Filley et al., 2001; Pempkowiak et al., 2006; Kuliński et al., 2007; Ishiwatari et al., 2009; Tareq et al., 2011); saltmarsh (Bianchi et al., 2013a), and marine cores (Haberle and Maslin, 1999; Kastner and Goñi, 2003; Pancost and Boot, 2004; Visser et al., 2004; Boot et al., 2006; Maslin et al., 2011, 2012; Sun et al., 2011; Arndt et al., 2013). It has excellent preservation potential and has been extracted from pre-Quaternary fossil archives, from as early as Eocene (Obst et al., 1991; Grimes et al., 2001), and from Pliocene and Pleistocene aquifer sediments (Hartog et al., 2004).

Lignin has largely been regarded as resistant to microbial degradation in comparison to other plant components, for example polysaccharides, rDNA and amino acids. However the use of lignin in studies of the global carbon cycle since the early 1970s, has demonstrated significant degradation potential of lignin as it is transported through the terrestrial biosphere (Pellerin et al., 2010;

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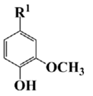
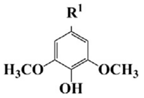
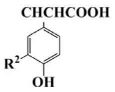
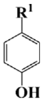
Ward et al., 2013). As lignin and its associated degradation is of importance to a wide range of fields including the paleosciences, soil science, terrestrial and aquatic ecology, water quality and the paper industry, a rich literature exists. Reviews have also been undertaken of its role and fate in the ocean (Hernes and Benner, 2006), and soils (Thevenot et al., 2010), but whilst a 2004 review of terrestrial biomarkers in marine sediments identified lignin as an under-utilised proxy (Pancost and Boot, 2004), there still exists a need for linking our understanding of modern biogeochemical processes to Quaternary environmental research. This review will outline the current state of the art in lignin phenol research that is relevant to the Quaternary scientist. We firstly summarise the biochemistry of lignin (Section 2), the various analytical methods currently available (Section 3), and the environmental controls on lignin transformation pathways and potential for modification of the original lignin signal (Section 4) prior to being incorporated into proxy archives. Finally we conclude by highlighting the current areas of rapid research progress and future research directions for the use of lignin phenols in paleo-environmental research (Section 5).

2. Biochemistry and the application of lignin as a paleovegetation proxy

Lignin constitutes up to one third of all wood material of living plants, second only to cellulose as the most abundant plant product (Brown, 1969). As lignin is a large complex molecule, it is analysed as its constituent individual phenols. There are three main phenol groups commonly used in environmental studies (illustrated and defined in Table 1): the vanillyl (V) group, syringyl (S) group and the cinnamyl (C) group, with a 4th, the *p*-hydroxyl (P) group being of lignin and non-lignin origin. The sum ($\sum_8$, or more typically $\sum_6$) of which is used as a tracer for input of terrigenous OM to marine environments (see Table 1).

Table 1
Definition and molecular structures of the most commonly reported lignin and non-lignin parameters in environmental research and their basis for interpretation.

Parameter		Definition	Description	Physical Interpretation/limitations
TLP (Total Lignin Phenols) or $\sum_{11}$		Sum of LOPs vanillyl, syringyl, cinnamyl and *p*-hydroxybenzoic groups.	Reported in metric units (mg, μg or ng) phenols in a known volume of water or sediment (i.e L or g).	Flux in input of vascular plants/ degradation of lignin.
$\sum_8$		Sum of LOPs vanillyl, syringyl, and cinnamyl groups.		
$\sum_6$		Sum of LOPs vanillyl and syringyl groups.		
λ_8 or Λ_6		Sum of LOPs vanillyl, syringyl, and cinnamyl groups, normalised to TOC.	Carbon normalised lignin phenol yield. Reported in metric units (mg, μg or ng) phenols per 100 mg C.	Flux of lignin relative to non-lignin TOC/degradation of lignin.
Λ_6 or Λ_6		Sum of LOPs vanillyl and syringyl groups, normalised to TOC.		
V		Sum of LOPs of the vanillyl group: Aldehyde (Vanillin): $R^1 = CHO$ Ketone (Acetovanillon): $R^1 = COCH_3$ Acid (Vanillic acid): $R^1 = COOH$	Reported in metric units (mg, μg or ng) phenols in a known volume of water or sediment (i.e L or g), or as a carbon normalised yield (i.e. per 100 mg C).	Input of OM from terrestrial vascular plants. Ubiquitous (Gymnosperms, angiosperms and non-woody plants). Less susceptible to early digenesis than S and C and so its value in fresh undegraded biomass is often used as end member for 100% vascular plant component in river tracing and marine sediment studies (Fig. 4).
S		Sum of LOPs of the syringyl group: Aldehyde (syringealdehyde): $R^1 = CHO$ Ketone (Acetosyringone): $R^1 = COCH_3$ Acid (Syringic acid): $R^1 = COOH$		Input of OM from terrestrial vascular plants (angiosperms and non woody plants).
C		Sum of LOPs of the cinnamyl group: *p*-coumaric acid: $R^2 = H$ Ferulic acid: $R^2 = OCH_3$		Input of OM from terrestrial vascular plants (non-woody plants). Most susceptible to degradation than any of the other phenols.
P		Sum of LOPs of the *p*-hydroxyl group: Aldehyde (*p*-hydroxybenzaldehyde): $R^1 = CHO$ Ketone (*p*-hydroxyacetophenone): $R^1 = COCH_3$ Acid (*p*-hydroxybenzoic acid): $R^1 = COOH$		Input of OM from terrestrial vascular plants (gymnosperms and non-woody angiosperms). Also an oxidation product of protein-rich organisms, such as plankton and bacteria.
S/V		Ratio of $\sum_3$S to $\sum_3$V	No units	Source of OM. Classification of plant tissues according to a plot of S/V vs. C/V (Fig. 1).
C/V		Ratio of $\sum_3$C to $\sum_3$V	No units	