Lignin biogeochemistry: from modern processes to Quaternary archives

Catherine N. Jex [a,b,c], Gary H. Pate [d], Alison J. Blyth [e], Robert G.M. Spencer [f], Peter J. Hernes [g], Stuart J. Khan [b], Andy Baker [a,c,*]

[a] Connected Waters Initiative Research Centre, University of New South Wales, Sydney, New South Wales 2052, Australia
[b] Water Research Centre, School of Civil and Environmental Engineering, University of New South Wales, Sydney, New South Wales 2052, Australia
[c] National Centre for Groundwater Research and Training (NCGRT), Australia
[d] School of Biological, Earth and Environmental Science, University of New South Wales, Sydney, New South Wales 2052, Australia
[e] WA-OIGC, Department of Chemistry, Chemistry and Resources Precinct, Curtin University, GPO Box U 1987, Perth, WA 6845, Australia
[f] Woods Hole Research Center, Falmouth, MA 02540, USA
[g] Land, Air and Water Resources, University of California, Davis, CA 95616, USA

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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.

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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;

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 $\sum_{11}$ $\sum_8$ $\sum_6$	Sum of LOPs vanillyl, syringyl, cinnamyl and *p*-hydroxybenzoic groups. Sum of LOPs vanillyl, syringyl, and cinnamyl groups. Sum of LOPs vanillyl and syringyl 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.
λ_8 or Λ_6 Λ_6 or Λ_6	Sum of LOPs vanillyl, syringyl, and cinnamyl groups, normalised to TOC. Sum of LOPs vanillyl and syringyl 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.
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 C/V	Ratio of $\sum_3 S$ to $\sum_3 V$ Ratio of $\sum_3 C$ to $\sum_3 V$	No units No units	Source of OM. Classification of plant tissues according to a plot of S/V vs. C/V (Fig. 1).
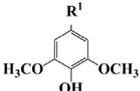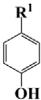
Ratios of S/V and C/V were first classified for environmental research by Hedges and Mann (1979), in their study of fresh plant material from twenty-three vascular and non-vascular plants in which four interpretive categories were defined: gymnosperm woods, non-woody gymnosperm tissues, angiosperm woods and non-woody angiosperm tissues (Fig. 1). Each of these was assigned a characteristic range of lignin parameters: S/V, C/V, V, S and C. Since then this has been expanded by many others (Goñi et al., 1997, 1998) to produce the classification plot as shown in Fig. 1. The V group includes vanillin, acetovanillone and vanillic acid. These phenols are ubiquitous to vascular plants and are found in both woody and non-woody tissues (i.e. leaves, needles, bark and stems) of both angiosperms (flowering, enclosed seed bearing plants, such as hardwood trees, herbs and grasses) and gymnosperms (enclosed seed bearing plants such as ferns and conifers) (Hedges and Mann, 1979). In environmental studies, the absolute concentrations of the V group phenols provides an end-member for the DOM in rivers, lakes and marine waters, sourced from terrigenous vascular plants (Hernes et al., 2007; Spencer et al., 2009b). The syringyl (S) group includes syringaldehyde, acetostringone and syringic acid, and are found exclusively in angiosperms (for example, alder (*Alnus*), oak (*Quercus*), Birch (*Betula*), palm (Arecaceae)) whilst quantitatively insignificant in gymnosperms (e.g. Redwoods (Cupressaceae), Pine (*Pinus*), cedar (*Cedrus*), spruce (*Picea*), Fir (*Abies*)). The cinnamyl (C) group, which includes p-coumaric and ferulic acids are only found in non-woody plant tissues (Hedges and Mann, 1979). Thus, the relative concentrations of S and C to V can illicit further details, distinguishing between angiosperm (S/V > 0) and gymnosperm (S/V = 0) production, and their relative composition of woody (C/V = 0) to non-woody (C/V > 0) tissues (Hedges and Mann, 1979). As such, the S/V and C/V ratios can provide information on the type of vegetation as shown in Fig. 1, whilst total down core changes in LOPs are used as indicators of changes in terrestrial biomass production through time (Hedges et al., 1982; Leopold et al., 1982; Visser et al., 2004).
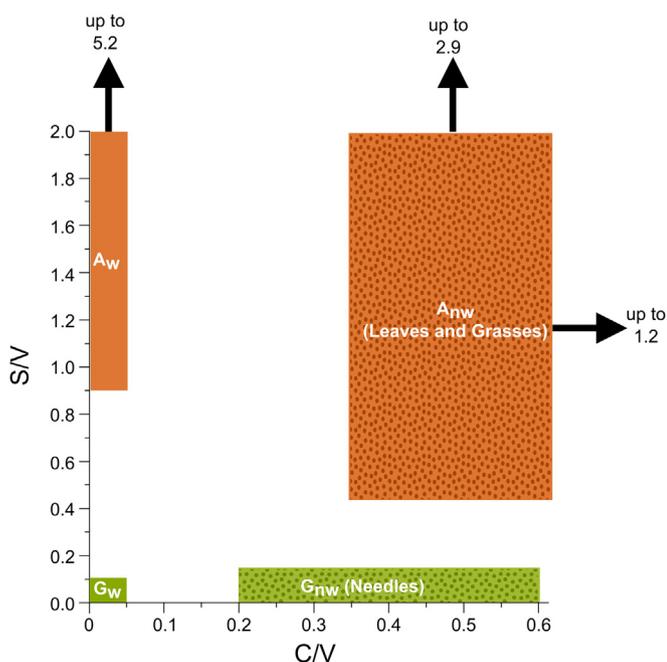
Fig. 1. S/V vs. C/V scatter plot with boundaries according to Hedges and Mann (1979) and Goñi et al. (1998) (and references therein). A_w: woody angiosperms; G_w: woody gymnosperms; A_{nw}: non-woody angiosperms and G_{nw}: non-woody gymnosperms.

3. Analytical methods

Prior to analysis, environmental samples are chemically degraded to release the phenolic units, which are typically reported as raw concentrations (total terrigenous OM flux) and as carbon normalised yields (relative contribution of terrigenous OM to total organic carbon (TOC)) (Hedges et al., 1982) as summarised in Table 1. A detailed review of analytical approaches to characterise soil organic matter (SOM) at the molecular level was published by Kögel-Knabner (2000) and Spencer et al. (2010a), in which many applicable techniques were described. Here we focus on the most commonly utilised methods in modern environmental and Quaternary studies of recent years.

3.1. CuO oxidation

Oxidation with alkaline cupric oxide is the most widely reported method of determining lignin phenol concentrations. In short, a freeze dried, homogenised solid sample or an extracted DOM sample is reacted with sodium hydroxide (NaOH) along with a stoichiometric excess of CuO at elevated temperature and pressure, either by use of reaction vessels capable of withstanding high temperature and pressure (Hedges and Parker, 1976) or a laboratory microwave reaction system with purged vessels (Goñi and Montgomery, 2000). In either method, additional reagents may include ferrous ammonium sulphate as an oxygen scavenger, and lignin-free glucose in low OM samples (less than 2 mg of organic carbon) to prevent superoxidation of lignin during the reaction (Louchouarn et al., 2000; Spencer et al., 2010a). Upon oxidation the contents of the reaction vessels are centrifuged to separate the solids from the eluent. The latter is subsequently acidified to pH 2 and either extracted with either ethyl acetate or diethyl ether or by SPE columns (Kaiser and Benner, 2011) to isolate the lignin oxidation products (LOPs). Analysis is frequently carried out by GC—MS, which requires derivitisation to silylate the lignin phenols for optimal detection, though GC-FID is also reported by many laboratories. A detailed review of the mass-spectrometric techniques was provided by Louchouarn et al. (2000) and will not be covered here.

3.2. Pyrolysis and thermochemolysis

Lignin may alternatively be degraded by rapid heating in the presence of suitable reagents. The most common technique involves either offline or online thermochemolysis of samples with tetramethylammonium hydroxide (TMAH) at elevated temperatures (either pyrolysis or sub-pyrolysis temperatures) resulting in the methylation of the polar hydroxyl and carboxyl functional groups (Hatcher et al., 1995). The products may then be analysed by GC—MS. A larger number of products are obtained than via the CuO method, including analogous monomers to S, V, and C (Syringyl, Guaiacyl, and p-coumaryl respectively) (Hatcher et al., 1995; Wysocki et al., 2008). The main difference from CuO method is that TMAH products include products not only from lignin degradation, but also those from for example, tannins (Filley et al., 2006). This means that a large proportion of the phenolic products which might be ascribed to a lignin source, may in reality derive from other inputs. This issue can be resolved by the use of ^{13}C labelled TMAH, as it then becomes possible to determine which products were methylated during analyte preparation (Filley et al., 1999).

4. Lignin in the environment

Lignin allegedly forms up to one third of all woody material, and is released into soils from plants during decay, where it is

transformed by a range of diagenetic processes (Hedges and Oades, 1997; Heim and Schmidt, 2007). Subsequently, only a fraction of the initial lignin is estimated to remain in the soil, with the rest being remineralized to CO_2 released into the atmosphere or transported via groundwater or fluvial runoff, as such tracing a significant component of the global carbon cycle as illustrated in Fig. 2. From the point of view of Quaternary research, understanding this journey from fresh leaf litter to proxy archive is vital in order to identify the original environmental signal represented by the lignin proxies. In this section we discuss each of the modification processes (as summarised in Fig. 3) encountered from the vascular plant source to soils (Section 4.1), into fluvial and lacustrine systems (Section 4.2) and intertidal and marine environments (Section 4.3). We discuss the impact of these signal modifying processes for paleo-lignin archives during this journey.

4.1. Signal modification in soils and peat

4.1.1. Biological decay of lignin in soils
The main agents of biological decay of lignin in soils and the aerated zone of peat, are fungi and bacteria (Otto and Simpson, 2006; Kuzyakov, 2010; Thevenot et al., 2010). The extracellular oxidative enzymes produced by brown- and white-rot fungi, often initiate breakdown of the lignin polymers (Kuzyakov, 2010). Bacteria on the other hand, are largely secondary consumers of the products of initial fungal breakdown, as they commonly do not produce enzymes capable of directly breaking down lignin (Huang et al., 2013; Klotzbücher et al., 2013). These processes preferentially affect phenols according to the strength of their bonds, and the main identifying parameters are identified in Table 2. The cinnamyl group in particular is observed to be most affected by diagenetic degradation, due to the relative lability of ester-bound cinnamyl phenols, and the non-lignin sources that may (relatively) increase C phenols in the degradation products (Hernes et al., 2007). Syringyl (S) phenols are also more susceptible to biotic decay than the vanillyl (V) group, and

hence the decrease of S:V phenols in combination with over all reduction in LOPs is often used as an indicator for these decay processes in soil incubation experiments (Opsahl and Benner, 1995). The effect of decay on these ratios may be significant when trying to interpret relative inputs from different plant types. The degree of decay can be identified by considering the ratio of aldehyde and their corresponding acid products in both the S and V groups. Acid and aldehyde precursors exist in the parent lignin polymer, which upon CuO oxidation, release acids and aldehydes. Oxidation of lignin during biotic decay has been demonstrated to result in measured elevated acid:aldehyde ratios in the laboratory (Opsahl and Benner, 1995; Otto and Simpson, 2006). Incubation experiments conducted with wood samples inoculated with fungi produced decreasing yields of CuO oxidation products and increases in the acid:aldehyde ratios (Ad:Al) of the vanillyl (Ad:Al(v)) and syringyl (Ad:Al(s)) type monomers with biodegradation (Otto and Simpson, 2006). In a four-year study of litter bag decomposition of five different vascular plant tissues (mangrove leaves and wood, cypress needles and wood, and smooth cordgrass), mass losses of up to 97% of LOPs, increases in C phenols and co-increasing Ad:Al ratios were observed and attributed to microbial degradation (Opsahl and Benner, 1995). However changes in Ad:Al were only obvious, once <25% of the original material remained (Opsahl and Benner, 1995). In some cases, increased Ad:Al ratios may be specifically attributed to biotic degradation by the presence of fungal tissues (Feng and Simpson, 2007). The exact mechanism for such elevated acid and/or aldehyde precursors during decay is debated. It is likely to be due to preferential decay of the aldehyde precursor, or conversion of this to acid precursors, or even both.

4.1.2. Abiotic degradation of lignin in soils
Oxidation of photo-reactive organic matter (including lignin) is of secondary importance to biotic decay in soils (Otto and Simpson, 2006; Feng et al., 2011), but there is some evidence for its occurrence in uppermost levels of exposed soil (Feng et al., 2011). Highly
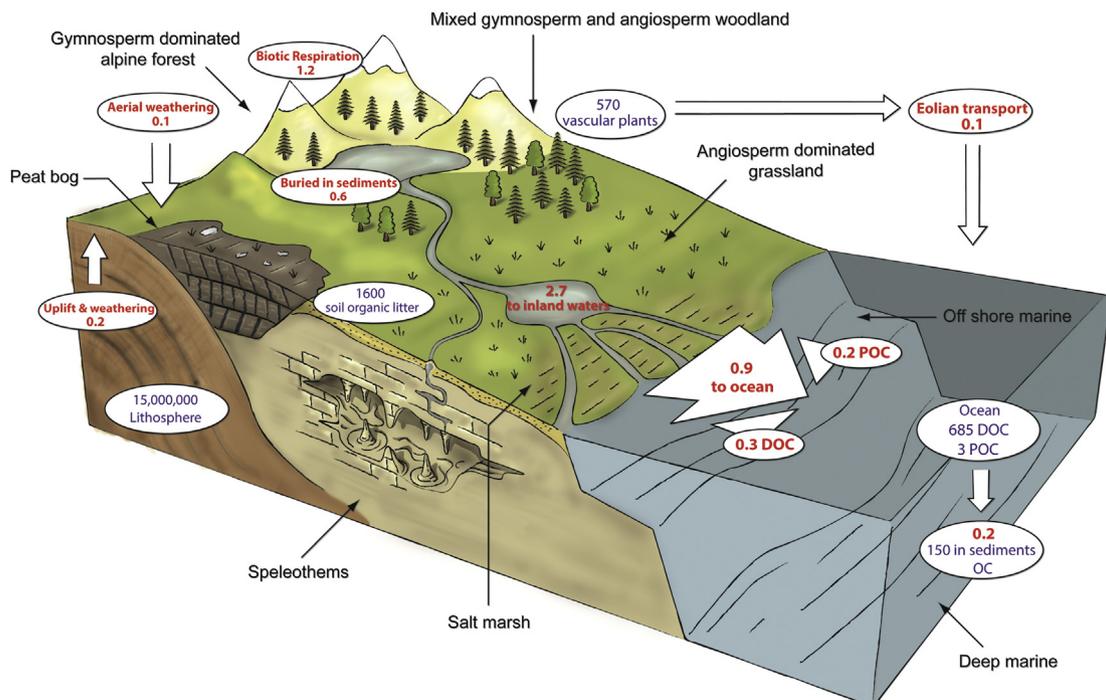
Fig. 2. Terrestrial portion of the carbon cycle with fluxes (red labels, Pg C yr^{-1}) and sinks (blue labels, Pg C) obtained from Denman (2007), Battin et al. (2009) and Bianchi (2011) and references there-in. Key proxy archives are indicated.
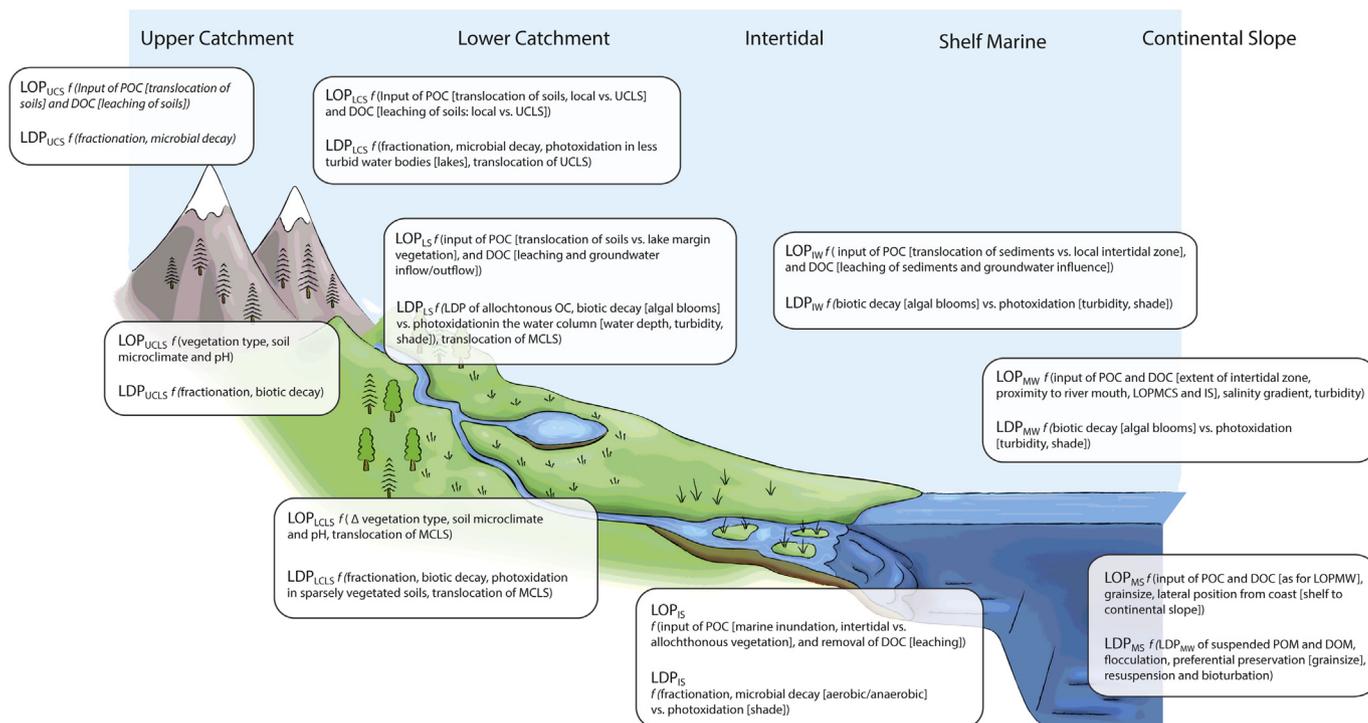
Fig. 3. Lignin oxidation products (LOP) and lignin degradation parameters (LDP) as a function (*f*) of the environmental processes operating en route from its vascular plant source to seafloor sediments. LOPs include Λ and ratios of S/V and C/V, whilst LDPs refer to Ad:Al(v) and (s) and P:(V + S). The diagram is annotated for the Upper Catchment: leaf litter and soils (UCLS) and streams (UCS); Lower catchment: leaf litter and soils (LCLS) and streams (LCS); Lake sediments (LS); Intertidal waters (IW) and sediments (IS); and marine waters (mw) and sediments (ms).

Table 2
Commonly used lignin derived degradation and fractionation Parameters.

Parameter	Definition	Description	Physical interpretation/limitations
Ad:Al(v)	Ratio of vanillic acid to vanillin.	Proxy for oxidative degradation of aldehydes to corresponding acids via side chain oxidation or aromatic ring cleavage. Varies amongst vegetation species. Also indicative of leaching and sorption processes in submerged plant fragments and soils/sediments.	Proxy for decay by white rot fungi and bacteria. Fresh tissues are typically <0.3; sedimentary plant fragments, lignin in humus and humic and fulvic acids are typically >0.3. Ratios >0.6 are considered highly degraded (Hedges et al., 1998). Fractionation due to leaching and sorption is observed to result in values >>0.6 (as high as 1.21) (Hernes et al., 2007).
Ad:Al(s)	Ratio of syringic acid to syringaldehyde.		Proxy for decay by white rot fungi and bacteria. Less sensitive to white rot decay. Fresh tissues <0.14; highly degraded tissues >0.16 (Hedges et al., 1998) S group phenols are more labile than V, and so more susceptible to leaching and sorption effects. Subsequent fractionation is observed to result in values >>0.6 (as high as 11) (Hernes et al., 2007).
P:(S + V)	Ratio of P to sum of V and S.	No units. Proxy for degradation via demethylation of methoxylated vanillyl and syringyl components due to brown rot fungi.	P (*p*-hydroxyl phenols) are not exclusively produced by vascular plants. They are also found in the oxidation products of protein-rich organisms, such as plankton and bacteria. Caution is needed in using this as sole basis for diagenetic alteration in soils and marine sediments (Goñi and Hedges, 1995; Goñi and Thomas, 2000; Dittmar and Lara, 2001; Otto and Simpson, 2006).
BCAs (Benzene Carboxylic acids).	3,5-dihydroxybenzoic (3,5Bd) and *m*-hydroxybenzoic acids.	Reported either as mg phenols per dry weight of sample, or as a carbon normalised yield (mg (100 mg C)).	Multiple sources: Proxy for charcoal and other forms of black carbon in soils and sediments/oxidation products of tannins and other flavonoids (Otto et al., 2005; Otto and Simpson, 2006; Dickens et al., 2007).

oxidized benzene derivatives e.g. polyhydroxybenzoic or benzenepolycarboxylic acids (BPCAs) however, have been identified in the CuO oxidation products of humic material extracted from a range of soils, peat and paleosols. BPCAs are reported as the chemical oxidation products of black carbon (Opsahl and Benner, 1995; Otto and Simpson, 2006) and whilst not lignin, they may be indicative of fire in paleo archives (Otto and Simpson, 2006). Laboratory experiments have demonstrated increased V total ion counts by GC−MS after 1 min of charring (pine−wood soils), which then decreased rapidly after 4 min of charring representing a complete demethoxylation of the lignin structures (Knicker et al., 2013). Incubation experiments of the charred soils demonstrated that seven weeks later, no V phenols were recovered from the samples charred for 4 min. This has clear ramifications for soils affected by fire, with a complete loss of V phenols (with possible presence of BPCAs) due to biomass burning. For Quaternary records with high temporal-resolution, the effects of fire may be preserved where burning is a functional part of the ecosystem, as the lignin record may be significantly modified or even removed.

4.1.3. Lignin fractionation associated with phase changes in soils

As plant tissues are broken down, mechanically or chemically, lignin becomes present in SOM in a range of size fractions (Heim and Schmidt, 2007; Clemente et al., 2011). These are: coarse particulate OM (CPOM; i.e. plant detritus >63 μm sieve size), fine particulate OM (FPOM; 0.7−0.63 μm) and dissolved OM held in the soil water (DOM; <0.7 μm) (Ertel et al., 1984; Thevenot et al., 2010). DOM in particular is sourced from leaching of soil and litter OM, whilst FPOM may result from the subsequent sorption onto soil minerals. Leaching experiments of modern soil samples suggests that these leaching and sorption processes within soils result in sequentially increased (Ad:Al) of both V and S phenol groups in the resulting DOM (Hernes et al., 2007). This means that these commonly used degradation parameters in soils may be misinterpreted as a degradation signature in environments where phase changes will have occurred. This has important ramifications for paleo-vegetation reconstructions from terrestrial and marine archives, where lignin is more than likely to have participated in one or more phase changes (see Section 4.2.3 with regard to FPOM and DOM in fluvial and lacustrine systems). In a recent experiment, as much as 56% of lignin artificially sorbed to various mineral phases could not be extracted using the CuO method, and had varying compositions according to mineral phases used in the sorption experiments (Hernes et al., 2013).

4.1.4. Modification of lignin due to soil characteristics

Degradation processes may be further moderated by inherent soil characteristics such as grain size, pH, soil moisture, temperature and mineral content. In the leachate experiments of Hernes et al. (2007) leachates from four plant litters representative of the full range of reported S/V vs. C/V ratios were sorbed onto four geochemically distinct soil types. The resulting lignin compositions of the sorbed soils and DOM varied considerably between the source and end product, indicating that soil characteristics play an important role in degradation and LOP modification. Optimal conditions for fungi growth and bacteria habitation (pH, temperature and moisture) will influence degradation with subsequent changes to LOP yields and their degradation parameters (Otto and Simpson, 2006). Warmer, drier climate typically limits degradation, whilst cooler, wetter conditions may encourage degradation due to greater availability of readily metabolized carbohydrate and/or proteins needed for the co-metabolic degradation of lignin (Otto and Simpson, 2006). Lignin degradation due to microbial decay is also limited in calcareous soils, as alkaline/high salinity soils inhibit enzymatic activity of soil microbial communities (Gelsomino and

Azzellino, 2011). Deep soils tend to yield lowest LOPs, often with the highest state of degradation. There is currently some debate as to whether lignin sorbs to soils and this degradation *in situ* by bacteria and fungi, related to their age and the amount of mechanical breakdown (Thevenot et al., 2010), or whether degraded lignin preferentially sorbs to soils.

Another potentially important process is the short-term development of OC mineralization hotspots, referred to as "priming effects" in the terrestrial carbon cycling literature. Priming effects are defined as short term changes in the turnover of soil organic matter by some temporary factor or process, which substantially elevates mineralization of soil OC above background levels (Blagodatskaya and Kuzyakov, 2008). In terrestrial environments these temporary factors could include input of fertilisers or some mechanical treatment of the soil, such that an input of more labile OM aids and increases the degradation of more recalcitrant or stable OC due to changes in microbial biomass. A few mechanisms have been suggested, and they rely on the interaction between decomposers of freshly input bio-labile OM, which acts as an energy source for the degradation of older, more recalcitrant OM (Guenet et al., 2010).

4.1.5. Modification of lignin due to vegetation cover and land use

Specific trends in lignin phenol distributions and degradation parameters have been observed to vary with vegetation cover and with specific dominant plant species (Otto and Simpson, 2006; Thevenot et al., 2010), land-use practices in agricultural areas (Heim et al., 2010; Mason et al., 2012) and burning (Knicker et al., 2013). Combining lignin phenol with pollen analyses may be a particularly powerful identifier of such biases. Elevated Ad:Al(v) ratios have been observed in fresh spruce (*Picea*) pollen (Hu et al., 1999), whilst a strong relationship between (Ad:Al)(v) vs. C/V in a lake core sediment from Poland were also shown to be coincident with increased abundance of *Pinus* pollen (Kuliński et al., 2007). Conifer lignin is dominated by V group phenols over the less resistant C and S group phenols, and so has a tendency to dominate LOP products and resist degradation, thus further biasing LOP yields (Otto and Simpson, 2006). In such cases, these biases may be dominant drivers of lignin parameters.

Ratios of S/V vs. C/V in soils may distinguish between land use, according to vegetation cover. Arable soils for example, tend to have smaller ratios, whilst grassland and forest are generally higher, and with increased variability due to the variety of plant species and increased degradation potential (Thevenot et al., 2010). Meanwhile degradation parameters based on lignin and non-lignin aromatic derivatives (3,5-dihydroxybenzoic acid and benzenepolycarboylic acids, see Table 2) have further characterised degradation state according to land cover. They observe degradation to be more significant in grassland soils, and lowest in pine forests and attribute this to site specific soil microclimate factors (Otto and Simpson, 2006).

4.1.6. Preservation of lignin in terrestrial paleo-archives

As described so far, there are many opportunities for the original vegetation signal to be modified within soils. Peat, on the other hand, accumulates due to slow degradation rates of organic matter under anoxic conditions of the saturated zone, and as such components of *in situ* plant remains including lignin, are intrinsically protected from fungal and microbial decay which are limited to the zone of oxic exposure according to the height of the water table (Kuder and Kruge, 1998; Zaccone et al., 2008; Schellekens et al., 2012). Within this oxic zone, significant reductions in LOP yields are typically observed (Zaccone et al., 2008; Schellekens et al., 2012) whilst below the water table, anaerobic decay proceeds at a rate considered negligible by comparison (Kuder and Kruge, 1998; Tareq et al., 2004). There are however studies that have identified

long-term demethoxylation of lignin under anaerobic decay in the non-extractable residues from peat (Schellekens et al., 2012), and which could be expected to occur in other anaerobic environments. Past variation in peat hydrology and rates of peat accumulation during the Holocene have nonetheless successfully been inferred using lignin degradation parameters. They assume that lignin degradation is predominantly driven by variable aerobic decay associated with changes in peat hydrology, where increased degradation parameters indicate increased aerobic decay under reduced water table conditions at times of climatic aridity (Bourdon et al., 2000; Tareq et al., 2004; Schellekens et al., 2011).

Characterisation of LOPs in combination with pollen in peat archives has been particularly successful, in identifying local (lignin) vs. regional (pollen) signals and to subsequently track shifting upper Montagne tree lines due to regional climate change (Jansen et al., 2010). It has also resulted in an alternative approach to interpreting the conventional S/V vs. C/V scatter plot, and is referred to as the Lignin Phenol Vegetation Index (LPVI) introduced by Tareq et al. (2004) with modifications by Tareq et al. (2011). The LPVI is defined by equation (1) and is based upon the distributions of S, V and C phenols. Where V, S and C are expressed as a percentage of the Λ_8.

$$\text{LPVI} = \left[\left\{ \frac{S(S+1)}{V+1} + 1 \right\} \times \left\{ \frac{C(C+1)}{V+1} + 1 \right\} \right] \qquad (1)$$

The reported benefits of the LPVI is the non-overlapping boundaries for taxonomic classification (Tareq et al., 2004) observed in the literature for characterising lignin in soils and waters. However, it is questionable whether this offers a significant improvement on the delineation of taxonomic groups over the S/V vs. C/V scatter plot of Hedges and Mann (1979), especially when combined with further classification of soil leachates and consideration of biotic decay processes, as in Hernes et al. (2007). There are overlapping boundaries still, between woody and non-woody angiosperms in the LPVI classification. There is also a band of LPVI values (28–68) which have no assigned taxonomic category (Table 3), and many samples of the peat core analysed by Tareq et al. (2004) plot within this unclassified range of LPVI values. Fundamentally though, it is based upon S, V and C values of fresh plant material, with no leachate end members assigned. In such water-logged environments, dissolved lignin is observed in drainage creek outflows (Krachler et al., 2012) which directly infers that a portion of the original lignin signal is lost via mobilisation and translocation of dissolved lignin into aquatic systems. We suggest therefore, that Ad:Al, S/V and C/V ratios for modern vegetation and leachate end-members should be characterised on a site specific basis to permit a mixing model of these end-members to quantitatively distinguish sources of lignin parameters as in other terrestrial aquatic environmental studies (Spencer et al., 2008).

Table 3
LPVI index boundaries, taken from Tareq et al. (2011). The category ranges first reported by Tareq et al. (2004) were based solely on the data of Hedges and Mann (1979), and have since been updated, based upon data referred to in Tareq et al. (2011).

Plant types	LPVI value ranges		
	Mean ± SD	Minimum	Maximum
Gymnosperm woods	1 ± 0	1	1
Non-woody Gymnosperm tissues	15 ± 8	3	27
Angiosperm woods	175 ± 101	67	415
Non-woody angiosperm tissues	989 ± 762	176	2782

4.2. Signal modification in fluvial and lacustrine environments

Lignin transported into fluvial and lacustrine systems is likely to be comprised of relatively fresh plant detritus and sorbed soil particulates via erosion or landslides, whilst DOM represents translocated freshly leached leaf litters and soil OM of varying ages, aided by mechanical weathering. Transport of young pools of DOM may occur by surface runoff or by subsurface shallow flow, whereas pools of older, more degraded dissolved lignin could occur by up-welling of groundwater to streams and lakes (Figs. 2 and 3). Very little literature exists on the latter, though it is likely to be an important source of old, degradation resistant lignin (in trace quantities) (Hartog et al., 2004). The controls on lignin in surface waters are very well documented, as rivers are net exporters of C to marine environments, exporting around 0.9 Pg C yr^{-1} (Cole et al., 2007) and as such play a dominant role in global carbon cycling (Fig. 2). However, around twice the amount of C is imported to rivers and lakes (1.9 Pg C yr^{-1}) than is exported to the ocean which suggests that a large part of the lignin containing OC is actively degraded and/or preserved within terrestrial aquatic environments (Cole et al., 2007).

4.2.1. Biological decay of lignin in terrestrial aquatic environments
Microbial activity appears to be the dominant control on lignin degradation in aquatic environments (Hernes and Benner, 2003; Pellerin et al., 2010). Ward et al. (2013) quantify that in the Amazonian terrestrial biosphere, 80 Tg C of lignin is fixed annually, 55% of which is degraded into smaller components within the river continuum and only 5% of intact macromolecules either stored within the river continuum or delivered to the ocean. Following Pellerin et al. (2010), they speculate that biological degradation of lignin is significant, with a complete turnover of lignin possible in the Amazon River over 2–3 weeks. In aquatic systems, input of fresh labile OM in the form of phytoplankton exudates (e.g. carbohydrates and amino acids), labile fractions of plant detritus, leached SOM or the breakdown of soil aggregates following floods or seasonal storm pulses, could in theory, provide fresh labile OM to produce biomineralisaton hotspots (see Section 4.1.4) in rivers and lakes (also in intertidal and marine environments). Only a limited number of studies have so far observed such stimulation of microbial metabolism by introduction of new substrates resulting in an increased loss of OM (Guenet et al., 2010).

4.2.2. Abiotic degradation of lignin in terrestrial aquatic environments
Degradation by photooxidation is also a significant control on LOP yields and degradation parameters in rivers. The relative importance of photo- vs. bio-degradation in a specific environment will depend on the factors that affect light penetration (e.g. turbidity) and microbial degradation (e.g. temperature). Degradation associated with photooxidation was observed to be fivefold higher than that by microbial activity during the course of irradiation experiments on filtered river waters by artificial lighting and solar radiation (Benner and Kaiser, 2011) and by natural sunlight on Mississippi river water samples (Hernes and Benner, 2003). In such experiments, exponential decay of LOP concentrations (both Λ and $\sum$) coincides with elevated lignin degradation parameters with continued UV exposure (Spencer et al., 2009b), and this occurs rapidly. So much so, that often nearly all LOPs are degraded by the end of the experiments e.g. 70% in 10 days (Hernes and Benner, 2003), 75% in 4 weeks (Opsahl and Benner, 1995) and >95% in 2 months (Spencer et al., 2009b). Furthermore the chemical structure of lignin dictates the susceptibility of particular phenols to oxidation by UV-radiation in the following order: S > V > p-hydroxy (P). This results in such observations as negative correlations between

Ad:Al(v) (elevated) vs. S/V (decreased) in DOM degraded by photooxidation (Opsahl and Benner, 1998; Hernes and Benner, 2003; Hernes et al., 2009). This is largely driven by the substitution of methoxy groups on the aryl ring (McNally et al., 2005; Benner and Kaiser, 2011). S phenols have two methoxy substitutions and therefore the largest decay rate constant, V group phenols have 1 and P group phenols don't have any (Benner and Kaiser, 2011).

4.2.3. Lignin fractionation during phase changes in terrestrial aquatic environments

Lignin fractionation during phase changes was introduced in Section 4.1.3, and has particular relevance for considering lignin signal modification in terrestrial aquatic environments where phase changes from the original plant source will have occurred. Until recently it was assumed that DOC in rivers and lakes represented a degraded older pool of OC with typically elevated Ad:Al(v) (Hedges et al., 1997). POC was by comparison considered younger and less degraded, due to observed decrease in the relative yields of carbon normalised LOPs (Λ) in river waters from CPOM > FPOM > DOM (Hernes et al., 2007). Recent studies of how lignin derivatives may be preferentially leached from leaf litters and soils, and subsequent sorption has changed this view. These experiments demonstrate how elevated Ad:Al(v) may be dominated by leaching, sorption processes, and how V yields decrease from litter to leachate, between 17 and 66% depending on plant type (Hernes et al., 2007). These processes in particular impact upon C/V values of leachates, and will result in incorrect source identification according to the S/V vs. C/V plot in Fig. 1 and the LPVI index (Table 3), unless leaching is taken into account. DOM in rivers is now often characterised as relatively young dissolved lignin from freshly leached OM and subsequent partitioning between the dissolved phase and soils and sediments (Hernes et al., 2007). Mixing models have subsequently been applied to disentangle this potential complex picture of leaching and sorption processes and to recalibrate DOM sources in river water (Hernes et al., 2007; Spencer et al., 2008). Carbon normalised sample V yields are compared to mixing lines for corresponding V yields from various soil, leachate, sorbed sediments and fresh vegetation fractions in order to assign a percentage of vascular plant material in any riverine DOM sample (shown in Fig. 4a and b). For example, in Fig. 4b, average carbon normalised V yields from Amazonian HMW DOM, are represented by around 10% vascular
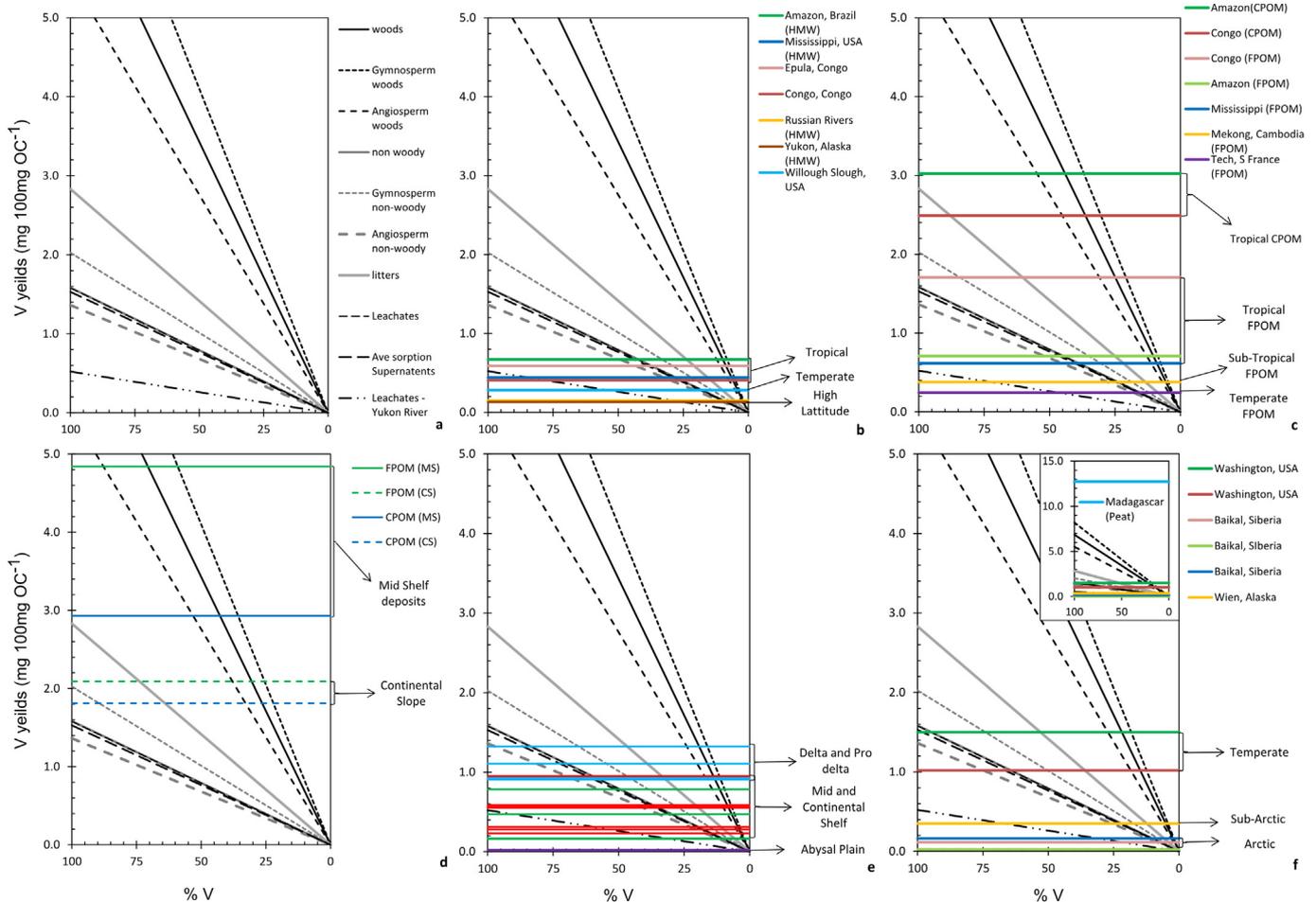
Fig. 4. Published vascular plant mixing lines (diagonal lines in A to F) with mean sample V yields (horizontal lines in B to F) from a variety of environmental settings. Interception of the diagonal and horizontal lines indicates the percent vascular plant material for that sample. The original mixing lines presented by Hernes et al. (2007) along with the addition of high latitude Yukon river leachates by Spencer et al. (2008) are shown in (A). These are overlain with mean V yields of (B) riverine DOM for a range of latitudes in; (C) size fractionated suspended particulate V yields obtained from rivers spanning a latitudinal gradient; (D) size fractionated marine sedimentary POM yields; (E) bulk marine sediments V yields which demonstrates a gradient according to grain size and proximity to the coast; (F) bulk lacustrine sediment V yields spanning a latitudinal gradient. These demonstrate the large range of vascular plant end members according to latitude and the variable preservation potential associated with grain size fraction across all lignin archives. All data are from published sources: A: (Hedges and Mann, 1979; Hernes et al., 2007; Spencer et al., 2008). B: (Hedges et al., 2000; Benner and Opsahl, 2001) (Lobbes et al., 2000; Eckard et al., 2007; Hernes et al., 2008; Spencer et al., 2008; Spencer et al., 2010b; Spencer et al., 2012). C: (Cotrim da Cunha et al., 2001; Ellis et al., 2012); (Hedges et al., 2000; Bianchi et al., 2007) (Keil et al., 1998; Spencer et al., 2012) (Goñi and Thomas, 2000). D: (Keil et al., 1998). E: (Gough et al., 1993; Goñi et al., 1998; Gordon and Goñi, 2004; Tesi et al., 2007; Tesi et al., 2013). F: (Hedges and Ertel, 1982; Orem et al., 1997; Hu et al., 1999; Bourdon et al., 2000).

plant material according to its interception with the end-member mixing line for leaf litters. Whereas the interception with the mixing line for the leachates of those leaf litters estimates up to 45% vascular plant material in that same sample. As such, many studies now conclude that leaching along with biological and photochemical degradation is responsible for the vast majority of alteration of lignin parameters in rivers from northern latitudes to tropics (Spencer et al., 2012, 2013; Ward et al., 2013), and that in order to use lignin as a tracer in fluvial environments, site specific V yields of leachates should be used as DOM end-members as opposed to fresh plant detritus (Hernes et al., 2007).

4.2.4. Lignin modification associated with catchment hydrology

In natural river systems, DOC typically relates to the stage of the hydrograph, and hydrologic flow routes, as water moves through the catchment (Spencer et al., 2010b, 2012; Ellis et al., 2012), as well as zones of groundwater upwelling and downwelling along the river continuum. There is evidence for the lignin component of this DOM to likewise follow the hydrograph (Spencer et al., 2010b, 2012). High river discharge coincides with increased lignin phenol concentrations, when the vadose zone becomes saturated, resulting in water moving though the upper, organic rich horizons of the soil column and liberating fresh OM from surface soil and litter layers (Hatten et al., 2012; Ward et al., 2012).

In strongly seasonal climates, when discharge reduces to a base flow during the warm-dry summers, sourced from upper catchment, groundwater flow routes switch to deeper, organic-poor soils and likely older carbon stores with greater tendency to have undergone degradation and/or leaching and sorption processes (Ellis et al., 2012). In the tropical Congo River, such a progression of LOP yields and parameters is observed from post flush/start of the dry period (lowest DOC, $\sum_8$ and Λ_8 and V) to the post dry - start of the flushing period (highest DOC, $\sum_8$ and Λ_8 and V) (Spencer et al., 2010b). Following the wet season, the soils were well leached, had undergone extensive flushing, and experienced increased microbial decay due to the longer residence of water in the system at low (or base) flow (Spencer et al., 2010b). In high latitude rivers, snow melt and spring flush may similarly coincide with elevated DOM, Λ and V group phenols, due to rapid transport and leaching of OM from the upper soil horizons (Spencer et al., 2009a). These may be large, as in the small mountain river system in Oregon (USA) where $\sum_V$ is observed to be more than 370 times higher at high flow than at low flow, yet the composition (S:V) remained constant, suggesting the source of terrestrial OC is consistent within this small catchment (Hatten et al., 2012).

However, carbon normalised LOPs in DOM have also been observed to decrease with increasing discharge, due to contributions from other dissolved organic compounds (carbohydrates, suberin, cellulose etc.) which are generally more easily mobilised than lignin (Ward et al., 2012). Furthermore, irrigation practices (Hernes et al., 2008) or particularly intense storms (Shiller et al., 2012; Bianchi et al., 2013b) will disrupt any natural cycle (Shiller et al., 2012). Such variety in timing and nature of LOP responses to changing discharge, highlights the potential complexity that may arise according to site specific seasonal hydrology, land use and vegetation characteristics as well as major flooding events (Cotrim da Cunha et al., 2001; Hernes et al., 2008; Spencer et al., 2010b; Ellis et al., 2012; Hatten et al., 2012; Shiller et al., 2012; Ward et al., 2012; Goñi et al., 2013; Bianchi et al., 2013b). It also suggests the potential for lignin, to record past changes in flood frequency or mean state in hydroclimate according to LOP yields and degradation parameters.

4.2.5. Preservation of lignin in terrestrial aquatic paleo-archives

The lignin preserved within lake sediments may be a strongly modified signal of source vegetation, according to the dominance or combination of the processes described so far, and this is likely to be specific to any individual catchment. Additionally, it may be modified further by in situ and post depositional processes within the lake water column and sediments (Meyers and Ishiwatari, 1993). For example, groundwater-lake water interactions within pore waters of the sediment (Ziegelgruber et al., 2013), contribution from flora growing alongside lake shorelines (Meyers, 2003), photochemical degradation within the water column, bioturbation of surface sediments and further bacterial degradation are all likely modifying processes (Meyers and Ishiwatari, 1993; Meyers, 2003). However, once buried at anoxic depths in sediments, lignin is relatively stable with minimal microbial or fungal decay (Hedges et al., 1982). In general, shallower lakes, with a shorter settling out distance, may be less susceptible to photooxidation and resuspension. However this may be counterbalanced by potential bioturbation and continued UV exposure once deposited as bottom sediment until fully buried (Meyers and Ishiwatari, 1993). Degradation of lignin containing OM due to bioturbation or microbial activity may conversely be limited in deeper stratified lakes with anoxic bottom waters (Kuliński et al., 2007). In lakes where stratification is seasonal, this results in a seasonal bias in the preservation potential of lignin (Kuliński et al., 2007).

Nonetheless, lignin has been successfully applied as a biomarker for vegetation history over the Quaternary period, based on down core variations of S/V and C/V ratios with Ad:Al ratios to track periods of increased degradation (Hedges et al., 1982; Leopold et al., 1982; Ishiwatari and Uzaki, 1987; Filley et al., 2001). Early examples of the application of lignin to lacustrine sediments include a Holocene vegetation reconstruction of Lake Washington using the scatter-plot approach as shown in Fig. 1 (Hedges et al., 1982; Leopold et al., 1982). In these studies, equal proportions of woody gymnosperms (conifers) and non-woody gymnosperms (ferns) in the early Holocene, are seen to give way to non-woody angiosperms (grasses), before transitioning to a predominance of woody angiosperms and a gradual replacement by conifers towards the present day (Hedges et al., 1982; Leopold et al., 1982). More recently, the LPVI has been applied to two lake core records from China where they differentiated between wetter, angiosperm dominated periods in the early Holocene, vs. drier gymnosperm dominated periods from mid Holocene (7 ka BP) and directly related this to changing precipitation amount associated with the Asian monsoon (Tareq et al., 2006, 2011).

When used in conjunction with pollen, as in peat cores, local vs. regional vegetation trends have been identified (Kuliński et al., 2007). For example, the predominance of grasses originally identified by LOP analyses (Hedges et al., 1982) was later contradicted by pollen analyses which demonstrated a dominance of pinus pollen for this section of the record (Leopold et al., 1982). Such scenarios may be of greater significance where the lake sediments may record localised signals according to catchment size and morphology. Compound specific $\delta^{13}C$ analyses of lignin phenols may elicit further details when combined with a pollen or lipid record when significant lignin degradation and loss of signal is suspected (Huang et al., 1999). Such an approach was adopted for a lake core from Sacred Lake, Mount Kenya, where conventional S/V vs. C/V analyses produced ratios that could not be attributed to any particular plant type. Compound specific $\delta^{13}C$ of lignin phenols and isotopic mass balance modelling however yielded quantitative estimates of percent of C_4 vs. C_3 inputs in excellent agreement with the more qualitative lipid and pollen data (Huang et al., 1999).

The issue of lignin degradation is addressed in part in paleovegetation reconstructions in lake cores, though there is debate as to how best to differentiate between degraded vs. less degraded original source vegetation signals. Indicative ratios of Ad:Al(v) for fresh plants is often quoted to be between 0.10 and 0.30 (Opsahl

and Benner, 1995), and between 0.6 and 2.0 for humic substances extracted from a variety of soils, sediments and natural waters (Ertel and Hedges, 1984; Ertel et al., 1984), with anything in this range suggestive of plant material that is highly degraded. Application of this full range may however be conservative and so comparison of fresh catchment vegetation along with their leachate products at each site is recommended to assign fresh and degradation end-members on a site specific basis. In some instances down-core variability in Ad:Al values may suggest insignificant degradation throughout the period of sediment deposition (Tareq et al., 2004). Where fluctuations are observed however, further analyses may be required. For example, large changes in Ad:Al(v) may equally be driven by site specific factors: the dominance of *pinus* pollen which itself has high Ad:Al(v) values (Hu et al., 1999); or changing sources of OM under fluctuating hydrological regimes as discussed in Section 4.2.4, or changing terrestrial vs. aquatic sourced OM indicated by corresponding changes in Λ and C/N ratios (Hu et al., 1999; Tareq et al., 2006, 2011). Collectively, this highlights the need for modern monitoring using sediment traps and leachate experiments of fresh plant material, leaf litter and soil to accurately classify and quantify vegetation lignin-phenol end-members for POM on a site by site basis.

4.3. Lignin modification in inter-tidal and shallow marine environments

There is an extensive amount of literature on lignin dynamics in marine environments due to its usefulness in characterising terrestrial DOM delivery to the oceans, and in particular intertidal environments (Hedges and Keil, 1995; Hedges et al., 1997). There is a discrepancy between the amount of carbon exported globally from rivers (0.9 Pg C yr^{-1}) and the amount of C that is preserved in marine sediments (0.2 Pg C yr^{-1}) (Fig. 2). In this section, we focus on the literature relevant to tracing temporal change in terrestrial vegetation in the intertidal zone and the fate of this carbon, as it has important implication for sedimentary archives of lignin in intertidal and shallow marine environments.

4.3.1. Biological decay of lignin in intertidal and marine environments

The intertidal zone is a highly dynamic system due to the continuous interaction of marine inundation vs. fluvial inputs with large terrestrially sourced sediment loads at high flows and reduced influence at base flow, making it particularly suitable environment in which to identify terrestrial vs. marine sources of OM over time (Bianchi et al., 2013a). Physical reworking of sediments, bioturbation and degradation by bacteria and salt tolerant fungi may however degrade lignin components of OC (Tesi et al., 2008; Bianchi, 2011). The later may be limited though by flocculation of clay particles and humic substances which physically protect OC from microbial degradation, along with regular occurrence of anoxic conditions (see Section 4.3.3). In addition, priming effects due to mixing of allochthonous and newly-produced autochthonous OM, such as seasonal formation of algal blooms or increased microbial communities may likewise provide an adequate energy source for degradation of more recalcitrant OM (Bianchi, 2011).

In intertidal and marine sediments, several non-lignin sourced CuO oxidation products may further differentiate between OM sources when normalised to carbon. For example, *p*-hydroxybenzene monomers (P group) (see Table 2) derive from the amino acids of marine plankton and bacteria (Tesi et al., 2008), and the B group of benzoic acids (Table 2) may be a product of degraded humic substances and vascular plant tissues in soils (tannins and flavonoids), charcoal or brown macroalgae (Tesi et al., 2008) (and

references therein). Thus the presence of these, and a positive correlation to Λ would likely indicate degraded terrestrial OC from vascular plants. Likewise P:(V + S) ratios have been shown to characterise degradation via brown rot (demethylation of V and S group) (Dittmar and Lara, 2001). These are often clearer indicators of degraded lignin signatures than Ad:Al ratios in water-logged intertidal sediments (Tesi et al., 2008).

4.3.2. Abiotic degradation of lignin in intertidal and marine environments

Photooxidation is an important process for degradation of dissolved lignin in river plumes entering marine environments (Mayer et al., 2009; Spencer et al., 2009b, 2013). As low-salinity river water spreads out in estuarine systems, sediment loads settle out, turbidity reduces, and these optically clearer waters allow for more effective photooxidation. At salinities greater than 6 psu, photooxidation of dissolved lignin appears to increase with increasing salinity, reflecting this process of settling out of terrestrial POM and the competing interaction between photooxidation and microbial degradation, with UV-exposure being the controlling factor (Hernes and Benner, 2003). Furthermore, there appears to be widely reported geochemical barrier at approx. 27–30 psu, above which insignificant quantities of LOPs were recovered due to rapidly increased photochemical oxidation at the boundary between turbid river waters and optically clearer marine waters. Above this boundary, Ad:Al(v) and (s) are observed to increase in both HMW and LMW fractions of DOM (Hernes and Benner, 2003), whilst ratios of S:V in the LMW fraction are also substantially elevated compared to the HMW fraction (Hernes and Benner, 2003). This indicates a zone of maximum photochemical degradation and a transition to marine waters lacking in terrestrially sourced DOM where photooxidation out performs microbial activity as the dominant degradation mechanism of dissolved lignin (Hernes and Benner, 2003; Benner and Kaiser, 2011).

4.3.3. Lignin modification associated with grain size and mineral associations in intertidal and shallow marine environments

Conservative mixing lines based on carbon normalised lignin yields and δ^{13}C of surface sediments, using terrestrial OC and marine phytoplankton end-members are typically used to estimate percentage of TOC that can be assigned to either source (Hedges et al., 1997). However TOC content of marine sediments varies greatly with sediment grain size, which may impede such an approach. The finer grained fraction (clay, <63 μm) of intertidal and marine sediments are typically richer in OC and Λ due to sorption of soil OM to the clay mineral grains, and are often observed to be deposited further out to see than the sand sized, relatively fresh plant debris (Tesi et al., 2008). This often results in significantly different carbon normalised yields according to the nature of sediment grain size of the sample under examination (Hedges et al., 1997). Under flood conditions, this interaction of transport according to grain size could vary, with input of older (more degraded) lignin adsorbed to clay particles deposited nearer shore than usual (Tesi et al., 2008).

4.3.4. Lignin modification associated with vegetation cover in intertidal environments

At the intertidal zone, sediments are characterised by a narrow range of S/V and C:V values characteristic of angiosperm grasses, *Spartina* and *Juncas*, with little evidence of a lignin signal originating further up catchment from e.g. forested soils, and so represent a localised vegetation signal (Goñi and Thomas, 2000). Periods of saltmarsh vs. mangrove expansion have been studied in the coastal Gulf of Mexico (North America) in order to understand the potential range in carbon storage associated with these

different types of intertidal zones (Bianchi et al., 2013a). Lignin storage rates (increased LOP yields, and decreased $\delta^{13}C$ from C_4 to C_3 plants) were demonstrated to be substantially higher in mangroves than saltmarshes, and distinct in terms of their lignin composition (Bianchi et al., 2013a). Mangrove derived OM delivered to marine sediments is considered more conservative and degradation-resistant in saline waters compared to terrestrial DOM, and is thus capable of travelling longer distances beyond the 30 psu geochemical barrier referred to in Section 4.3.2 (Dittmar et al., 2001). Three end member mixing models have been used to quantitatively partition between these sources of OM, terrestrial − intertidal (either mangrove or saltmarsh) − marine sources of OM, based on lignin parameters vs. $\delta^{13}C$ (Dittmar et al., 2001). A similar approach could be applied to paleo-archives, assuming that degradation parameters have remained constant over time, and with considerations to limiting factors, such as preservation associated with changing grain size.

4.3.5. Preservation of lignin in intertidal and marine paleosediments

Intertidal zones (i.e. mangroves, deltas and saltmarsh) are increasingly recognised important carbon sinks where the terrestrial signal can be clearly identified from autochthonous or marine sources of OM (Bianchi et al., 2013a), and so offer huge potential for reconstruction of sea-level change and marine inundation over glacial timescales. As described up to now, POM (e.g. pollen, plant debris or charcoal) is evident in shallow and open marine sediments, but there is little evidence for preservation of terrestrially sourced POM beyond coastal sediments due to the degradation pathways described in the previous sections. The small fraction of terrestrial OC that does makes it to the seafloor is described as highly degradation-resistant as this fraction of OM has survived extreme oxic diagenetic pathways it has encountered from soils, to rivers, to intertidal zone to sea, presumably by mineral protection. As such it is likely to be representative of its source vegetation. On this premise, it has proved tremendously useful in paleo-vegetation studies of marine sediments (Hedges and Keil, 1995; Hedges et al., 1997; Arndt et al., 2013). It is worth bearing in mind however that this degradation resistant fraction may or may not be representative of the original vegetation cover as a whole (which would include the degraded fraction) for any particular location.

One of the early applications of lignin analyses to marine research characterised the input of terrestrial OM to marine sediments in the Gulf of Mexico (Hedges and Parker, 1976), identifying reduced lignin input to sediments with distance from the shoreline. Since these early studies the influence of grain size association in particular has been identified as a primary factor influencing lignin preservation with distance from the coast (Gough et al., 1993; Goñi et al., 1997; Loh et al., 2008). For example, C_4 grasslands of the Mississippi River catchment, associated with fine grained (clays) are proposed to be transported further than coarser and denser C_3 plant detritus from coastal swamps and forests, which were deposited closer to shore with silts and sands (Goñi et al., 1997, 1998). This transport bias has huge implications for reconstructing marine vs. terrestrial sourced OM in marine cores using only bulk $\delta^{13}C$ without corresponding lignin and grain size analyses (Goñi et al., 1997, 1998).

Reconstructing the vegetation history of Tropical rainforests during the Quaternary from such sediments is of global interest. The Tropics are centres of global convection that drive extratropical atmospheric circulation, and so constraining past moisture dynamics (rainout and evapotranspiration) in these regions is critical to assign moisture inputs to global climate models and to understand past monsoon dynamics (Haberle and Maslin, 1999; Boot et al., 2006; Maslin et al., 2011). They are also regions of unparallelled biodiversity, and yet the reasons for this have until relatively recently, been unclear (Hoorn et al., 2010). An early hypothesis for how vegetation may have varied over glacial−interglacial cycles, the "Pleistocene tropical rainforest refuge hypothesis", stated that during glaciations, significantly reduced temperatures and precipitation caused widespread replacement of tropical rainforest (C_3) with savannah (C_4) vegetation and that during inter-glacials, this savannah vegetation retreated into isolated pockets at the expense of the dominant tropical forest eventually resulting in the biodiversity of species that we see today (van der Hammen and Hooghiemstra, 2000). However palynological studies of these regions produced in the last few decades do not record any evidence for incursions of C_4 grasses during glacial periods (Colinvaux et al., 2000). Kastner and Goñi (2003) were the first to apply lignin as a proxy, to unequivocally identify the variability in plant taxonomy of the Amazonian region, using deep sea Amazon fan sediments. Their results indicated that these Quaternary sediments were entirely dominated by LOPs with a $\delta^{13}C$ signature that originated from temperate to tropical species, with no indication for C_4 grasses. Their conclusion that the present-day vegetation of the Amazon basin has prevailed for the last 70 ka, and that the vegetation is so diverse precisely because the climate did not change so drastically at the tropics. Subsequent analyses of n-alkane $\delta^{13}C$ in these sediments appeared to confirm the dominance of C_3 vegetation and no evidence for massive incursions of grasslands during the Last Glacial period (Maslin et al., 2012).

5. Future for lignin in Quaternary science

Several proxy archives have yet to take full advantage of lignin as a biomarker. For example, near-estuary corals are known to contain fluorescent organic matter from adjacent major rivers (Matthews et al., 1996), and lignin records from appropriate samples can provide long-term archives of catchment vegetation and organic matter degradation. In contrast, lignin in distal corals could provide an archive of long-term records of the fate of OM in the oceans. In speleothems, lignin-derived phenol distributions have been observed (Blyth and Watson, 2009; Blyth et al., 2010). With their ability to be precisely dated over all timescales using U−Th and U−Pb dating methods, speleothems have the potential for providing well-dated lignin archives. Guaiacyl lignin-derived pyrolysis products have been reported in sedimentary organic matter extracted from Pliocene and Pleistocene aquifer sediments (Hartog et al., 2004), yet this hasn't been replicated with CuO oxidation methods (to eliminate matrix effects common in pyrolysis products) and there is no literature that describes the fate and preservation potential of lignin in groundwater and fractured rock systems that may become preserved in either of these two archives.

Finally, developments in analytical techniques are also important. The ongoing advances in compound specific isotopic analyses by irm-GC/MS (as in Goñi and Eglinton, 1996) should lead to the future application of ^{13}C analysis of lignin. The ^{14}C analysis of lignin (Ingalls et al., 2010) has recently been reported (Feng et al., 2013a, 2013b). The relatively inexpensive lignin extraction procedures available (Goñi and Montgomery, 2000; Kaiser and Benner, 2011) should allow for the method to be adopted by many more laboratories.

The lignin modifying processes in the environment are many and significant. This review has attempted to summarise many of these, as a greater understanding of their influence on proxy records is required for lignin as a biomarker to reach its full potential. In any Quaternary archive, the relative importance of lignin degradation processes needs to be understood. Physical (sorption), chemical (photodegradation) and biological (microbial degradation) processes will all vary in importance. The relative importance

of each process will depend on the specific environmental conditions at that time, such as temperature, sunlight, water turbidity, depth in water column. The extent to which each will act on lignin will depend on the nature and rate of transport of the lignin from its source (vegetation) to its archive. With changing degradation processes and transport rates, the relative importance of the degradation processes should be expected to be non-stationary over time. A thorough understanding of these processes helps interpret any Quaternary lignin archive.

Acknowledgements

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