

Assessing the biodegradability of terrestrially-derived organic matter in Scottish sea loch sediments

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Abstract. Lignin oxidation products, oxygen uptake rates, molar organic carbon to nitrogen (OC/N) ratio (from bulk elemental analysis) and R_p values (from loss on ignition experiments, the ratio of the refractory to total organic matter, OM) were determined for sediments along transects of Loch Creran and Loch Etive. Lignin data indicated the importance of riverine inputs contributing to land-derived carbon in the lochs as total lignin (Λ , mg/100 mg organic carbon, OC) decreased from 0.69 to 0.45 and 0.70 to 0.29 from the head to outside of Loch Creran and Loch Etive, respectively. In addition, significant correlations of lignin content against total OM and OC ($p < 0.05$) also suggested a distinct contribution of terrestrial OM to carbon pools in the lochs. The general trend of decreasing oxygen uptake rates from the head ($20.8 \text{ mmole m}^{-2} \text{ day}^{-1}$) to mouth ($9.4 \text{ mmole m}^{-2} \text{ day}^{-1}$) of Loch Creran indicates decomposition of OM. Biodegradability of the sedimentary OM was also characterized by the increase of R_p values from the head to mouth of the lochs: 0.40 to 0.80 in Loch Etive and 0.43 to 0.63 in Loch Creran. Furthermore, the molar OC/N ratio decreased from 11.2 to 6.4 in Loch Creran, and from 17.5 to 8.2 in Loch Etive. Derived rate constants for OM degradation were found to decrease from LC0 to LC1, and increase from RE5 to RE6. This work demonstrates that oxygen uptake rates, R_p values and molar OC/N ratio are able to serve as useful proxies to indicate the biodegradability of sedimentary OM.

1 Introduction

The meaning of biodegradation is the biologically catalysed reduction in the complexity of chemicals and usually results in conversion of organic carbon (OC), nitrogen (ON), phosphorus and sulphur to inorganic products (Alexander, 1999). Hence, “biodegradability” refers to the susceptibility of the organic matter (OM) to degradation; or to the “freshness” or “quality” or “diagenetic state” of OM. Early attempts to determine biodegradability were carried out by Westrich and Berner (1984), who studied oxygen uptake rates in laboratory incubated sediments. Studies have since used the oxygen uptake rate in intact incubated sediment cores, as this represents the amount of OM directly oxidised during aerobic degradation (Parsons et al., 1977; Henrichs, 1992; Overnell et al., 1995). Others have used oxygen uptake rate as a measure of OM mineralization through an aerobic pathway, the oxygen being supplied by the activity of burrowing organisms (Wassman, 1984; Grant and Hargrave, 1987; Glud et al., 1994). However, there are some shortcomings of this approach. The oxygen uptake could also be due to the oxidation of reduced species formed during anaerobic OM degradation (Elsgaard and Jorgensen, 1992; Overnell et al., 1995).

Because of its resistance to microbial degradation, the use of lignin as a tracer to study land-derived OM has been well documented (Hedges and Parker, 1976; Hedges and Ertel, 1982; and references therein). Numerous studies have used lignin to study the distribution of marine and land-derived OM (Hedges and Parker, 1976; Wilson et al., 1985; Mitra et al., 2000). The importance of riverine inputs contributing terrestrial debris into near shore sediments is also well documented (Liss et al., 1991; Milliman, 1991; Ward et al., 1994), as is an offshore decrease of lignin-derived phenols (Hedges



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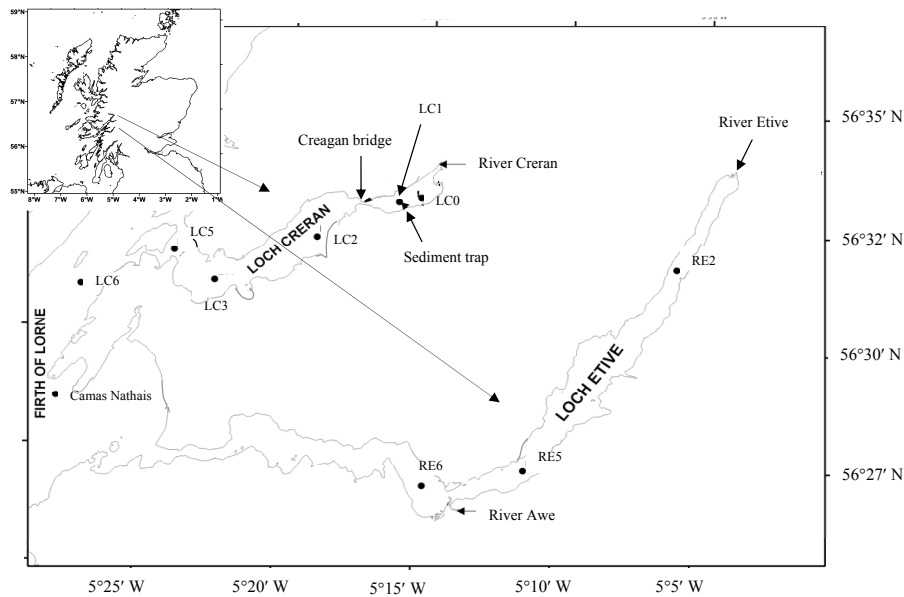


Fig. 1. Map of study area showing the sampling locations (inset, map of Scotland).

Table 1. Sampling locations and water depths in Lochs Creran and Etive (surface sediments and sediment trap).

Lochs	Sampling locations	Water depth (m)	Latitude (N)	Longitude (W)
Loch Creran	LC0	15.42	56°33'	05°15'
	LC1	37	56°33'	05°16'
	LC2	17	56°32'	05°19'
	LC3	49	56°31'	05°23'
	LC5	13	56°32'	05°24'
	LC6	48.94	56°31'	05°27'
	Sediment trap	10	56°33'	05°16'
Loch Etive	RE2	37	56°32'	05°06'
	RE5	123	56°27'	05°11'
	RE6	57	56°27'	05°15'
	Camas Nathais	20	56°29'	05°28'

and Parker, 1976; Miltner and Emeis, 2001; Bianchi et al., 2002). Studies conducted at the Lower St. Lawrence Estuary and Saguenay Fjord further reported lignin, together with OC, total nitrogen and organic phosphate to indicate OM diagenesis (Louchouart et al., 1997).

Lignin compounds are found only in vascular land plants (Sarkanen and Ludwig, 1971). These lignin phenols can be used to characterize different vegetation sources: for example, elevated S/V ratios are indicative of angiosperm tissues, whilst elevated C/V ratios indicate the presence of non-woody tissues (Hedges and Mann, 1979b; Bianchi and Argyrou, 1997; Goni et al., 1998). The vanillic acid to vanillin ratio, (Ad/Al)_v is indicative of the diagenetic state, as relatively high (Ad/Al)_v indicates more degraded material (Hedges et al., 1982; Miltner and Emeis, 2001). Lignin parameters such

as C/V, S/V and (Ad/Al)_v ratios, along with molar OC/N ratios, have been used to study lignin diagenesis (Ishiwatari and Uzaki, 1987).

A valuable tool for linking OM source to sediment biodegradability is the *R_p* index (Kristensen, 1990). Calculated as the ratio of the refractory to total OM, the author showed that the more easily degradable environmental samples have lower *R_p* values, and vice versa. *R_p* values, in conjunction with molar OC/N ratio, provide a strong tool to measure the OM biodegradability. During the initial stages of OM degradation the OC/N ratio increases due to preferential nitrogen utilization; later decreasing due to nitrogen immobilization (Benner et al., 1991). Increase in the OC/N ratio also implies the presence of plant materials which have a higher proportion of C to N than marine OM (Pocklington,

1976), whilst a decrease in the OC/N ratio, with an associated increase in $(Ad/Al)_v$, indicates diagenesis (Pocklington and MacGregor, 1973). The hypothesis of this study was that oxygen uptake rates, molar OC/N ratio and R_p values could be used as proxies to indicate biodegradability of sedimentary OM in sea loch systems.

2 Materials and methods

2.1 Study areas

Loch Creran and Loch Etive are neighbouring sea lochs located on the west coast of Scotland (Fig. 1). Over the lower ground surrounding the lochs and rivers, deciduous plants such as oak, beech and birch dominate. Gymnosperms such as spruce cover the higher ground.

2.1.1 Loch Creran

Loch Creran is 12.8 km long with a surface area of 13.5 km². This loch has a relatively small catchment area of 164 km². The mean freshwater input is $286 \times 10^6 \text{ m}^3 \text{ yr}^{-1}$ and the flushing time is three days (Edwards and Sharples, 1986). Since Loch Creran is relatively small and shallow, the seasonal hydrography follows the pattern of the Firth of Lorne and tidal flushing is sufficient to ensure mixing throughout the water column (Gage, 1972). There are four sills which separate the loch into distinct basins. There are five sampling locations situated along the length of the loch: LC0, LC1, LC2, LC3 and LC5; LC6 is located outside the loch in the Firth of Lorne. LC0 and LC1 are situated in the upper basin of the loch, after the sill at Creagan Bridge; LC2, LC3 and LC5 are situated in the second basin, between the sill at Creagan Bridge and the sill separating the entrance to the loch from the Firth of Lorne. River Creran, at the head, is the major source of freshwater input to the loch (Table 1, Fig. 1).

2.1.2 Loch Etive

The larger of the two lochs, Loch Etive, is 29.5 km long with surface area of 28.3 km² and catchment of 1400 km² (Gage, 1972; Wood et al., 1973; Edwards and Edelstens, 1977). The mean freshwater input is $3037.5 \times 10^6 \text{ m}^3 \text{ yr}^{-1}$ (Edwards and Sharples, 1986). Loch Etive is characterized by prolonged periods of water stratification. The residence time of isolated bottom waters may extend up to 30 months, with a mean of 16 months (Edwards and Trusdale, 1997). Periodic intense freshwater inflow, following prolonged periods of low freshwater runoff, controls an occasional ventilation and replenishment of the deep basins (Gage, 1972; Edwards and Grantham, 1986; Edwards and Trusdale, 1997). Loch Etive has a sill at the seaward entrance to the lower loch (Falls of Lora), and a shallow narrow at the opening to the upper loch (Bonawe). Sampling sites RE2 and RE5 are located in the upper loch, RE6 in the lower loch and Camas Nathais in the

Firth of Lorne (Table 1, Fig. 1). The major freshwater inputs are River Etive at the head of the loch, and River Awe at Bonawe (Gage, 1972; Edwards and Sharples, 1986).

2.2 Sampling and sample pre-treatment

Three undisturbed sediment cores were obtained from each location using a Craib corer (Craib, 1965) lined with an acrylic core tube of 24 cm long \times 5.9 cm i.d. Site LC1 was visited at monthly intervals. All other locations were visited every four months. Loch Etive was visited for three consecutive months. A sediment trap was deployed in Loch Creran (see Table 1 for location) 10 m below the surface (m.b.s.) of water. The trap consisted of four collecting tubes (dimensions: 11 cm internal diameter and 100 cm in length) and was serviced once a month. In the laboratory, sediments in the collecting tubes were allowed to settle, and the overlying water was siphoned off. The sediment slurry was then centrifuged at $600 \times g$ for 10 min and, after pouring off the supernatant, was subjected to freeze-drying.

In the laboratory, oxygen uptake rates were measured on whole sediment cores. Upon completion, the top 1 cm slice was removed from each core, frozen overnight and freeze-dried the following day. Dried sediments were then ground to fineness using a pestle and mortar for the lignin, loss on ignition and bulk elemental determinations.

2.3 Analytical methods

2.3.1 Oxygen uptake rate analysis

Oxygen uptake rates were determined by measuring the decrease in dissolved oxygen concentration in the overlying water from incubated intact sediment cores (Parkes and Buckingham, 1986; Glud et al., 1994; Overnell et al., 1995). After collection, the core tubes were sealed with rubber bungs and transported back to the laboratory (Overnell et al., 1995). Here the cores were transferred to a container of seawater collected from 10 m.b.s. at the sampling site (i.e. below the mixed layer). The cores were kept overnight in the dark at in situ temperature, with the upper bungs removed. The overlying water column was gently aerated to maintain a saturated dissolved oxygen concentration. On the following day, submersible stirrers were fitted onto the core tubes, thus isolating the core and its overlying water. The stirring rate was adjusted to prevent stagnation of the overlying water without causing sediment resuspension and in order to maintain uniform oxygen concentrations (Overnell et al., 1995). At time zero, replicate water samples were collected from the container using 10 ml glass syringes. The samples were fixed immediately following collection. Every 10 ml water sample was fixed with 0.1 ml alkaline iodide and 0.1 ml of MnSO_4 . The cores were incubated for twenty four hours, after which three samples were collected from the overlying water of each core and fixed. The dissolved oxygen concentration was

measured by Winkler titration with potentiometric detection of the end point (Hansen, 1999). The oxygen uptake rate was calculated from the difference in oxygen concentration of the overlying water between the start and end of the incubation. Method validation was based on repeated analyses of samples: 15 replicates of a single sample, plus routine triplicate analyses of all samples for environmental interpretation. The precision determined was over the range 0.10–7.90% coefficient of variation. Oxygen uptake rates were calculated after Skoog et al. (1996) and Hansen (1999).

2.3.2 Lignin analysis

The alkaline CuO oxidation method used to extract lignin-derived phenols from environmental samples follows the methods detailed in previous studies (Hedges and Ertel, 1982; Readman et al., 1986; Goni and Hedges, 1992). The CuO oxidation method used in this study has been described by Loh et al. (2002, 2008); it consists of a series of steps involving oxidation, extraction, silylation and finally detection of a suite of eight simple lignin phenols, as their trimethylsilylated forms, by gas chromatography (Hedges et al., 1982; Miltner and Emeis, 2000).

Approximately 0.5 g dry sediment was oxidized at 155°C for three hours with 1.0 g CuO and 7 ml of 8% w/v NaOH solution in an oxygen free atmosphere, in a PTFE-lined stainless-steel reaction vessel. Products which had been extracted three times with diethyl ether were spiked with the internal standard ethyl vanillin. The combined extracts and standards were treated with anhydrous Na₂SO₄, filtered and rotary evaporated to near dryness.

The dried extract was subjected to a silylation process, to convert lignin phenols to their more thermodynamically stable trimethylsilylated forms. The oxidation product was dissolved in 100 µl dried toluene. An equal volume of bis(trimethylsilyl)trifluoroacetamide with 10% trimethylchlorosilane (BSTFA:TMCS=10:1; Sigma Aldrich) was added as a catalyst (Poole, 1979). Samples were heated at 90°C (Wilson et al., 1995) for 10 min and then analysed using a GC-FID (Perkin-Elmer 8410) fitted with a 0.25 mm i.d. × 30 m of 100% dimethylpolysiloxane (ZB-1, Phenomenex, Zebron) column and a split ratio of 100:1. The initial temperature was 100°C, increased at 5°C per minute to 200°C, and held for 10 min. For the second ramp, the temperature increased at 20°C per minute to 300°C and this was held for 5 min. Both injector and detector temperatures were 300°C. The equilibration time was 2 min.

Total lignin is the sum of vanillyl (V; vanillin, acetovanillone and vanillic acid) syringyl (S; syringaldehyde, acetosyringone and syringic acid) and cinnamyl (C; p-coumaric and ferulic acids) phenols, reported as Λ (mg/100 mg organic carbon, OC; Hedges and Mann, 1979a). Based on replicate analyses the range of sample reproducibilities for total lignin concentrations was 7.8–37.4% (coefficient of variation).

Gas chromatography with mass spectrometry (GC-MS) analysis was used to confirm the chemical nature of the lignin phenol compounds (Hedges and Parker, 1976; Onstad et al., 2000): a TRACE MS Thermo Quest, Finnigan instrument was used, fitted with a 0.25 mm i.d. × 30 m of 5% phenylmethylpolysiloxane capillary column (RTX-5MS, RESTEK CORP.), employing a split ratio 100:1. The initial temperature was 100°C, increasing at 5°C per minute to 200°C, and held for 10 min. For the second ramp, temperature was increased at 20°C per minute to 300°C. The inlet temperature was 300°C, the oven maximum temperature was 350°C and the equilibration time was 0.5 min.

2.3.3 Loss on ignition

Significant losses of mass between 250°C and 300°C have been observed (Mook and Hoskin, 1982); hence 250°C was used in this work as the initial combustion temperature. Although it is difficult to determine the exact nature of the material burned off at 500°C, it is likely that most refractory terrestrial and aquatic OM will be included. Most inorganic carbon has been shown to oxidize above 500°C (Hirota and Szyper, 1975; Kristensen and Andersen, 1987); hence 500°C was used as the higher temperature.

Method validation was carried out by subjecting a single sample to repeated analyses. Approximately 0.5 g aliquots of dried sediment were weighed precisely into crucibles. These were ashed (250°C for 16 h) in a muffle furnace, cooled and reweighed. Sediments were then heated to 500°C (Kristensen and Andersen, 1987) for 16 h (Sutherland, 1998), cooled and reweighed. The percentage weight losses after combustion at these two temperatures were defined as the % labile and % refractory OM respectively. The sum of % labile and % refractory OM was taken to be the % total OM. The *R_p* value, which is defined as the ratio of the refractory to total OM, is used to determine the stage of decomposition of biogenic materials (Kristensen, 1990). Percentage reproducibility obtained from validation experiments and sample analyses were within the range 10–20% coefficient of variation.

2.3.4 Bulk elemental and isotope analyses

For organic carbon (%OC) and total nitrogen (%TN) determinations, approximately 10 mg sediment samples were acidified with 1 ml of 5% w/v sulphurous acid in vials. These were allowed to stand overnight in a fume cupboard and were subsequently freeze-dried. The product was quantitatively transferred into tin capsules and CHN analyses were performed in triplicate using a LECO CHN-900 analyzer. For total carbon (TC) determination, 10 mg dry sediment was transferred into 8 × 5 mm tin capsules and analysed similarly. Sample reproducibilities for the %TC and %TN ranged from 0–20.6% and 0–19.2%, respectively.

Table 2. Lignin parameters for Lochs Creran and Etive (surface sediments and sediment traps).

Loch Creran	Sediment trap	LC0	LC1	LC2	LC3	LC5	LC6
V (mg/g)	0.13	0.15	0.09	0.08	0.03	0.05	0.02
S (mg/g)	0.09	0.09	0.06	0.05	0.02	0.02	0.01
C (mg/g)	0.08	0.09	0.07	0.05	0.02	0.03	0.02
Total lignin (mg/g)	0.30	0.33	0.22	0.18	0.07	0.10	0.05
Total lignin, Λ (mg/100 mg OC)	0.50	0.69	0.55	0.58	0.39	0.43	0.45
S/V	0.69	0.60	0.67	0.63	0.67	0.40	0.50
C/V	0.62	0.60	0.78	0.63	0.67	0.60	1.00
(Ad/Al) _v	2.69	1.07	0.83	0.96	1.19	0.52	0.90
Loch Etive	RE2	RE5	RE6	Camas Nathais			
V (mg/g)	0.16	0.14	0.14	0.03			
S (mg/g)	0.17	0.14	0.14	0.02			
C (mg/g)	0.09	0.07	0.07	0.01			
Total lignin (mg/g)	0.42	0.35	0.35	0.06			
Total lignin, Λ (mg/100 mg OC)	0.70	0.71	0.71	0.29			
S/V	1.06	1.00	1.00	0.67			
C/V	0.56	0.50	0.50	0.33			
(Ad/Al) _v	0.74	0.72	0.71	0.52			

Abbreviations: V = vanillyl phenols (sum of vanillin, acetovanillone and vanillic acid); S = syringyl phenols (sum of syringaldehyde, acetosyringone and syringic acid); C = cinamyl phenols (sum of p-coumaric and ferulic acids); Λ = sum of V+S+C (mg/100 mg OC); S/V = ratio of syringyl:vanillyl phenols; C/V = ratio of cinamyl:vanillyl phenols; (Ad/Al)_v = ratio of the vanillic acid to vanillin (Loh et al., 2008¹).

¹ The lignin data was previously used as the biomarker for terrestrial OM in our studies to determine the fate of terrestrial OM in the lochs (Loh et al., 2008).

For the carbon isotope determination, approximately 0.1 mg dried sediment was weighed into a 8×5 mm tin capsule and analysed using a 20-20 Stable Isotope Analyzer (PD2 Europa Scientific Instruments). Percentage reproducibilities ranged from 0.0–16.9%. The standard used was L-isoleucine, which was pre-calibrated against a Pee Dee Belemnite (PDB; Bashkin, 2002) standard. The $\delta^{13}\text{C}$ value was calculated from the measured carbon isotope ratios of the sample and standard gases (Degens, 1969; Boutton, 1991):

$$\delta^{13}\text{C} (\text{‰}) = \times 10^3 \quad (1)$$

where $R_{\text{sample}} = {}^{13}\text{C}/{}^{12}\text{C}$ ratio in the sample, and $R_{\text{standard}} = {}^{13}\text{C}/{}^{12}\text{C}$ ratio in the standard.

2.3.5 Statistical analyses

Single factor ANOVA was used to determine whether there is any significant difference of results between sampling times. Regression analyses were used to determine whether there are significant correlations among these parameters: lignin, oxygen uptake rates, labile, refractory and total OM, OC, R_p values and OC/N ratios.

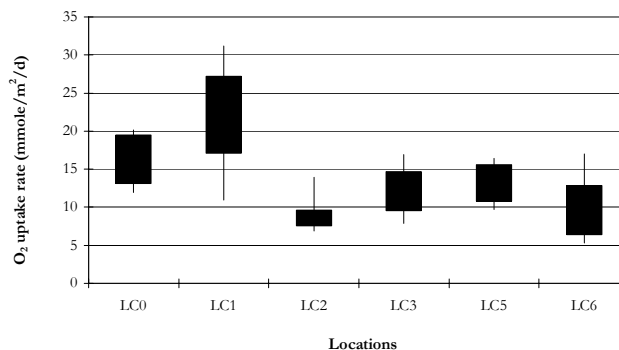


Fig. 2. Mean oxygen uptake rates for sediment cores from locations in Loch Creran. Each bar represents the highest and lowest values, and the first and third quartiles of the data.

3 Results

3.1 Yields of land-derived organic matter

Overall, lignin parameters at individual locations exhibited no distinct change with time hence these have been averaged for presentation in Table 2. There was no temporal variation in either sediment trap or sedimentary organic matter. The range of Λ values in Loch Creran and Loch Etive (0.29 to 0.71; Table 2) are within limits reported for riverine, estuarine and marine sediments (Hedges and Mann, 1979b;

Table 3. Average oxygen uptake rates in Loch Creran.

Locations	Oxygen uptake rate (mmole/m ² /day) for 2002										
	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Mean
LC0		18.7>	16.7						15.9		17.1
LC1		14.5<	21.2	18.7<	26.4	27.8>	23.5>	18.9	24.3>	11.8	20.8
LC2			9.2					9.6			9.4
LC3	9.0<	13.6						14.8			12.5
LC5	12.3				14.4<					18.7	15.1
LC6	6.6					14.2>		7.5			9.4

The oxygen uptake rates were measured every month at LC1, but for the other locations, they were visited in successive orders. The symbols “>” and “<” indicate significantly more and less than the value in the following month (ANOVA: $p < 0.05$).

Readman et al., 1986; Requejo et al., 1986; Ishiwatari and Uzaki, 1987; Prahl et al., 1994; Goni et al., 1997 and 1998; Goni et al., 2000; Miltner and Emeis, 2001; Bianchi et al., 2002). It was found that vanillyl phenols are the major lignin oxidation products, followed by the syringyl and cinnamyl phenols.

In Loch Creran, the highest Λ values (0.69) were found in LC0 surface sediments. Further down the loch, Λ decreased to 0.55 at LC1, and increased slightly to 0.58 at LC2, decreased to 0.39 at LC3, and increased slightly again to 0.43 (LC5) and 0.45 (LC6). Similarly to Loch Creran, Loch Etive also displays lower lignin content away from the freshwater input (ANOVA: $p < 0.05$ between RE2, RE5 and RE6 with Camas Nathais). Compared to Loch Creran, however, all three stations (RE2, RE5 and RE6) in Loch Etive displayed a higher yield of total lignin, with Λ ranging from 0.70 to 0.71. Camas Nathais in the Lynn of Lorn had by far the lowest Λ of 0.29 (ANOVA: $p < 0.05$). Sediments from LC0 surface sediments show the most depleted $\delta^{13}\text{C}$ values of -24.7% , respectively. Sediments from LC6 have the most enriched values (-14.6%). Similarly, in Loch Etive, the $\delta^{13}\text{C}$ values increased seawards; RE2, RE5 and RE6 had an average $\delta^{13}\text{C}$ value of approximately -25.8% , while Camas Nathais had the highest $\delta^{13}\text{C}$ values of -13.5% .

3.2 Proxies for sediment biodegradability

3.2.1 Oxygen uptake rates

Results of the oxygen uptake rate analyses for Loch Creran are presented in Table 3. At LC0, these were highest during April ($18.7 \text{ mmole m}^{-2} \text{ day}^{-1}$) and decreased significantly during the following months (ANOVA: $p < 0.05$). For other locations, it seems that higher oxygen uptake rates occurred later in the year. The mean oxygen uptake rate at LC1 was $20.8 \text{ mmole m}^{-2} \text{ day}^{-1}$, whilst the observed trend for LC1 was an increase from July to November 2002. The significant differences (ANOVA: $p < 0.05$) of the rates between some of the months are given in Table 3. There are no significant differences (ANOVA: $p > 0.05$) in the measured

rates at LC2, whilst at LC3 the rate increased significantly (ANOVA: $p < 0.05$) from March to April, and was highest in October. At LC5 and LC6 the highest oxygen uptake rates occurred during December and August respectively. The mean rate within the upper most basin ranged from 17.1 to $20.8 \text{ mmole m}^{-2} \text{ day}^{-1}$ (from LC0 to LC1) and in the middle basin from 9.4 to $15.1 \text{ mmole m}^{-2} \text{ day}^{-1}$ (from LC2 to LC5). Oxygen uptake rates decreased significantly from the head to mouth of the loch (ANOVA: $p < 0.05$; Fig. 2).

3.2.2 Loss on ignition and bulk elemental composition

As there was also no significant seasonal trend for the loss on ignition and bulk elemental results at individual locations, mean data are presented in Table 4. The sediment trap material had the highest contents of labile (14.8%), refractory (8.7%) and total OM (23.4%) compared to all surface sediments. However, during transport to the sediments, the OM and OC contents decreased significantly (ANOVA: $p < 0.05$). Comparison between surface sediments shows that the location nearest the river input (LC0) had the highest labile (9.8%), refractory (7.3%) and total OM (17.1%). Overall the R_p values increased significantly (ANOVA: $p < 0.05$) from 0.43 at LC0 to 0.63 outside the loch at LC6, whilst the percentage labile, refractory and total OM decreased from the head to mouth of the loch. The surface sediment molar OC/N ratios in Loch Creran also decreased further down the loch: the highest was found at LC0 (11.2) and the lowest at LC 6 (6.4). R_p values show negative correlation with total lignin (Loch Etive, $r^2=0.98$; Loch Creran $r^2=0.90$), %TC ($r^2=0.91$, $p < 0.05$, $n=7$) and %TN ($r^2=0.80$, $p < 0.05$, $n=7$) along the length of the lochs.

Similarly, the %TC, %TN, and %TOC of surface sediments decreased significantly from the head to mouth of Loch Creran (ANOVA: $p < 0.05$). Of the surface sediments, LC0 had the highest %TC (5.1), %TN (0.5) and %TOC (4.8) whilst LC6 had the lowest contents of %TC (1.9), %TN (0.2) and %TOC (1.1) respectively. Sediment trap material contained the highest %TC (6.4) and %TN (0.8).

Table 4. Loss on ignition and bulk elemental results for Lochs Creran and Etive (surface sediments and sediment traps).

Site	$\delta^{13}\text{C}$ (‰)	Loss on ignition				Bulk elemental results			
		% labile OM	% refract OM	% TOM	<i>Rp</i>	%TC	%TN	%TOC	Molar OC/N
Loch Creran									
LC0	−24.7	9.8	7.3	17.1	0.43	5.1	0.5	4.8	11.2
Sediment trap	−21.3	14.8	8.7	23.5	0.37	6.4	0.8	6.0	8.8
LC1	−23.8	9.1	6.8	15.9	0.43	4.6	0.5	4.0	9.3
LC2	−23.8	6.8	6.1	12.9	0.47	3.6	0.4	3.1	9.0
LC3	−17.3	3.5	4.9	8.4	0.58	2.7	0.3	1.8	7.0
LC5	−21.0	1.3	3.2	4.5	0.71	3.3	0.3	2.3	8.9
LC6	−14.6	3.6	6.0	9.6	0.63	1.9	0.2	1.1	6.4
Loch Etive									
RE2	−25.8	10.6	7.1	17.7	0.40	6.3	0.4	6.0	17.5
RE5	−25.8	10.9	9.4	20.3	0.46	5.6	0.5	4.9	11.4
RE6	−25.7	11.7	11.1	22.8	0.49	5.8	0.5	4.9	11.4
Camas Nathais	−13.5	3.0	12.1	15.1	0.80	3.5	0.3	2.1	8.2

Abbreviations: OM = organic matter; TOM = total organic matter; *Rp* = % refractory/%TOM (Loh et al., 2008²).

² The loss on ignition and bulk elemental results were previously used in Loh et al (2008) to determine the fate of terrestrial OM in the water column, during transportation down the lochs, and upon burial in the sediment.

In Loch Etive the % labile OM was relatively constant from RE2 to RE6, whilst % refractory OM increased by ~56%. RE2, situated nearest the river input, had the highest %TC and %TOC and molar OC/N ratio. RE5 and RE6 had almost the same values for these variables and %TN.

At Camas Nathais there was a dramatic decrease in % labile OM (74% lower than RE6), whilst % refractory OM remained of a similar order to the other stations: the lowest %TC, %TN, %TOC and molar OC/N ratio were also observed here. Seemingly, during transportation the OM undergoes decomposition; hence the OM at Camas Nathais was relatively highly degraded.

4 Discussion

4.1 Sources of terrestrial organic matter

The distribution of total OM and OC in both lochs is largely influenced by the terrestrial inputs from River Creran to Loch Creran, and Rivers Etive and Awe to Loch Etive. Vanillyl phenols were present in greater amounts than syringyl and cinnamyl phenols (Table 2), most probably because vanillyl phenols are produced by both angiosperms and gymnosperms; while syringyl phenols are produced only by angiosperms (Sarkanen and Ludwig, 1971; Hedges and Mann, 1979b; Hedges et al., 1982). Total lignin (Λ , mg/100 mg OC) in the upper Loch Creran surface sediments ranged from 0.54 to 0.69, and in the lower loch from 0.39 to 0.45. The Λ values in the upper Loch Etive surface sediments ranged from 0.70 to 0.71, falling to 0.29 at Camas Nathais. River Awe,

which drains into the loch between RE5 and RE6, most probably contributes to the high lignin and OM contents at both sites. These results demonstrate the importance of Rivers Creran, Etive and Awe, contributing terrestrial materials to the respective lochs. This is also supported by the gradual increased of $\delta^{13}\text{C}$ values from the head to mouth of the lochs. $\delta^{13}\text{C}$ values from −22‰ to −35‰ indicate the dominance of terrestrial OM (Cerling et al., 1995; Goni and Thomas, 2000), $\delta^{13}\text{C}$ values from −12‰ to −23‰ indicate marine OM (Gearing et al., 1984; Ruttenberg and Goni, 1997; Gordon and Goni, 2003), and $\delta^{13}\text{C}$ values from −11‰ to −16‰ indicate contribution of C4 plants (Boom et al., 2001).

The contribution of terrestrially-derived materials to the sedimentary carbon inventory in the lochs was investigated by correlating total lignin with total OM and TC (Table 5). Total lignin was highly correlated with % total OM and TC suggesting that terrestrial materials make a major contribution to total OM and TC in both lochs (regression analysis: $p < 0.05$). %TC shows significant correlation (regression analyses: $p < 0.05$) with total lignin in Loch Creran. Terrestrial material contributes significantly to the total OM and specifically to the labile fraction of OM, as shown by significant relationships for total lignin with % labile OM and with % total OM along the length of Loch Creran, and lignin versus % labile OM in Loch Etive (Table 5). The importance of terrestrial OM fuelling the biogeochemical cycling of carbon in the lochs was explained in better details by Loh et al. (2008).

Degradation of lignin is a slow process owing to its complex nature (Hurst and Burges, 1967; Zeikus, 1980). Some authors found no quantifiable lignin degradation in aerobic

Table 5. Correlation and regression analyses.

	Correlation and regression results
Between oxygen uptake rates and:	
LC1 total lignin	$r=-0.08$
Loch Creran total lignin	$r=0.58, r^2=0.33, p>0.05, n=6$
Loch Creran labile OM	$r=0.51, r^2=0.26, p>0.05, n=6$
Loch Creran OC	$r=0.69, r^2=0.48, p>0.05, n=6$
Between lignin and:	
Loch Creran % labile OM	$r=0.93, r^2=0.87, p<0.05, n=6$
Loch Creran % refractory OM	$r=0.39, r^2=0.15, p>0.05, n=6$
Loch Creran % total OM	$r=0.83, r^2=0.68, p<0.05, n=6$
Loch Creran % <i>Rp</i>	$r=-0.95, r^2=0.90, p<0.05, n=6$
Loch Etive % labile OM	$r=0.97, r^2=0.93, p<0.05, n=4$
Loch Etive % refractory OM	$r=-0.75, r^2=0.56, p>0.05, n=4$
Loch Etive % total OM	$r=0.68, r^2=0.47, p>0.05, n=4$
Loch Etive % <i>Rp</i>	$r=-0.99, r^2=0.84, p<0.05, n=4$
Between lignin and $\delta^{13}\text{C}$:	
Sediment trap	$r=-0.68, r^2=0.47, p<0.05, n=13$
Loch Creran	$r=-0.76, r^2=0.58, p<0.05, n=19$
Loch Etive	$r=-0.96, r^2=0.93, p<0.05, n=4$
Between lignin and %OC:	
Loch Creran	$r=0.85, r^2=0.73, p<0.05, n=6$
Loch Etive	$r=0.95, r^2=0.91, p<0.05, n=4$
Labile OM versus OC	$r=0.96, r^2=0.92, p<0.05, n=7$
Between OC/N ratio and:	
Loch Creran lignin	$r=0.86, r^2=0.72, p<0.05, n=6$
Loch Creran <i>Rp</i> values	$r=-0.60, r^2=0.36, p>0.05, n=6$
Loch Creran OC	$r=0.95, r^2=0.89, p<0.05, n=6$

aquatic environments (Hedges et al., 1986; Ertel et al., 1986; Hamilton and Hedges, 1988) or in anaerobic environments (Eriksson et al., 1990). As a result of these findings, lignin is thought to be found in the refractory OM fraction. This has not been identified in the systems studied here: lignin contents do not have any correlation with the refractory fraction of OM (Table 5). Whilst this may be due to the masking effects of variable inputs/components of the total OM, it may also indicate that refractory material includes lignin that has undergone diagenesis to an undefined “humic” structure (Hurst and Burges, 1967; Christman and Oglesby, 1971; Zeikus, 1980; Hedges and Oades, 1997).

The characteristics, or sources, of plant materials are also determined from the syringyl/vanillyl (S/V) and cinnamyl/vanillyl (C/V) ratios (Bianchi and Argyrou, 1997; Goni et al., 1998). As angiosperms produce more S than V phenols, and gymnosperms produce only V, higher S/V ratios indicate a higher abundance of angiosperms. As only non-woody tissues produce C phenols, higher C/V ratios are indicative of non-woody materials (Leo and Barghoorn, 1970; Sarkanen and Ludwig, 1971; Hedges and Mann, 1979b; Miltner and Emeis, 2001). The S/V ratios in Loch Creran and Loch Etive ranged from 0.40 to 1.06, with a mean value

of 0.59 (from LC0 to LC5 surface sediments) within Loch Creran, and 0.94 (from RE2 to RE6) in Loch Etive. The range of C/V ratios in both lochs is 0.33–1.00, with mean values of 0.66 within Loch Creran and 0.52 within Loch Etive. The S/V and C/V ratios in both lochs are higher than at other locations: for example the Washington continental shelf and slope (Hedges and Mann, 1979a; Prah et al., 1994), Baltic Sea (Miltner and Emeis, 2001), Tamar Estuary (Readman et al., 1986) and Narragansett Bay Estuary (Requejo et al., 1986). Accordingly, these high ratios are indicative of the presence of non-woody angiosperm tissues (Hedges and Parker, 1976; Goni et al., 2000). These non-woody tissues most probably originate from the leaves of plants commonly found around the loch catchments: Hedges and Mann (1979a) considered leaves as the non-woody tissue of a plant.

4.2 Proxies for sediment biodegradability

4.2.1 Oxygen uptake rate

The oxygen uptake rates determined in this study ranged from 6.6 to 27.8 mmole m⁻² day⁻¹. These are within the rates determined previously in other lochs. The range of oxygen uptake rates determined in Loch Etive, Loch Eil and Tay Estuary were 13.6–17.8, 17.8–24.6 and 67.4 mmole m⁻² day⁻¹, respectively (Parkes and Buckingham, 1986). The rates determined for Lochs Linnhe, Goil, Fyne and Etive ranged from 8 to 24 mmole m⁻² day⁻¹ (Overnell et al., 1995). The oxygen uptake rates in the Gulf of Lions ranged from 0.6 to 48 mmole m⁻² day⁻¹ (Accornero et al., 2003). Oxygen uptake rates have previously been seen to increase near riverine discharge, implying the presence of a component of potentially degradable terrestrial material (Rowe et al., 1994; Overnell et al., 1995; Accornero et al., 2003). The various authors did not confirm the presence of terrestrial OM with a biomarker for terrestrial materials.

Seasonal studies show a slight increase in oxygen uptake rates at LC1 from July to September 2002; probably the result of enhanced microbial activity (Wassman, 1984; Parkes and Buckingham, 1986; Overnell et al., 1995). The oxygen uptake rates were averaged and showed a significant decrease from the head to mouth of Loch Creran (Fig. 2) in agreement with Overnell et al. (1995) and Loh et al. (2002). Overnell et al. (1995) determined the oxygen uptake rates for several locations along transect of Loch Etive: locations E2, E7 and E9 are represented as RE2, RE5 and RE6 respectively in this study. Oxygen uptake rates decreased from RE2 (22.9 mmole m⁻² day⁻¹) to RE5 (19.2 mmole m⁻² day⁻¹) and it is concluded that the high rate at RE6 (52.3 mmole m⁻² day⁻¹) was most probably due to the influence of terrestrial input from the River Awe. The reoxidation of reduced species produced by, for example, sulphate reduction accounts for only 7–8% of the oxygen uptake rate (Overnell et al., 1995).

Oxygen uptake rates were higher at LC5 in December 2002, and transect wise, higher at LC3 and LC5 than LC2. This fluctuation could be because LC5 is located in a sheltered area which accumulated more terrestrial OM and OC (Tables 2 and 4) which in turn increased the rate of OM degradation. Santos et al. (1994) also recognized small scale sampling heterogeneities on the spatial variability in the sedimentary organic matter quality and quantity in marine sediments. As result there was no significant correlation between oxygen uptake rates with the labile OM and OC (Table 5). There was, however, a significant decrease in oxygen uptake rates (ANOVA: $p < 0.05$) progressing down the loch. Hence, results presented here are proposed to demonstrate a contribution from the degradation of terrestrial OM to the oxygen uptake rate. The highest total lignin (Δ), % labile OM, % refractory OM, % total OM, %TC and %TOC (Table 4) were found in the sediments near the riverine input. Besides, there were significant correlations between lignin and the labile and total OM and OC, and between the OM and OC (regression analysis: $p < 0.05$). This clearly indicates a contribution of terrestrial OM to the carbon in the lochs. Hence, the decrease in oxygen uptake rates from the head to mouth of the lochs strongly implies that terrestrial OM fuels biogeochemical cycling in these systems. This terrestrially-derived OM appears to include much more labile material, with some susceptibility to decomposition in situ.

Our data support the use of the oxygen uptake rate as a proxy to measure sediment biodegradability, as increased rates indicate an increase in mineralization rates of OM. The oxygen uptake rate determination provides a measure of aerobic OM degradation at the sediment-water interface and is closely related to the sedimentary OM and carbon content. The overall significant decrease in the sediment oxygen uptake rates along the length of Loch Creran indicates that it can be used to provide an estimate of biodegradability.

4.2.2 R_p index

The R_p index can be used to provide an indirect measure of sediment biodegradability. As an operational ratio of the refractory to total OM concentrations, relatively high R_p values indicate more refractory OM, or decreased “freshness”, or biodegradability, of the sedimentary OM. The usefulness of R_p values is enhanced by correlating them with other parameters such as lignin and molar OC/N ratios. Lignin decreases down the lochs, indicating a reduction in the contribution of terrestrial materials seawards. R_p values show negative correlation with total lignin (Table 5) implying that lignin material and carbon content decreased through the lochs and the OM became increasingly refractory. Sedimentary OM has higher biodegradability near major riverine inputs.

The reason for decreasing lignin and OM concentrations (Tables 2 and 3) is due to (i) dilution with marine OM; (ii) sedimentation, as supported by the decrease in OM, OC and lignin contents from the head to the mouth of the lochs, as

well as higher OM content in the trap than surface sediment; and (iii) OM decomposition, as indicated by the more highly degraded OM in surface sediments compared to trap materials.

The (Ad/Al)_v values (Table 2) in Loch Creran and Loch Etive do not show a distinctive trend; implying that the lignin materials had not undergone significant degradation in the lochs. Conversely, the R_p values do show a trend: increasing through the lochs seawards, from LC0 (0.43) to LC6 (0.63), and from RE2 (0.40) to Camas Nathais (0.80) respectively. As the content of terrestrial OM decreased from the head to mouth of the lochs, this indicates that there was a fraction of labile terrestrial OM still susceptible to degradation. This labile fraction most probably caused the decreased of the oxygen uptake rates from the head to mouth of the lochs. The gradual increase in the refractory nature of the OM from the head to mouth of the lochs could be supported by the decreased in OC/N ratio. So, whilst it is clear that R_p index can be used as a measure of sediment biodegradability, this should be interpreted in the overall context of terrestrial OM loadings, oxygen uptake, and OC/N ratio.

4.2.3 Molar OC/N ratio

It has long been known that fresh plant material has high nitrogen content and degrades rapidly (Waksman and Tenney, 1927). During the initial stage of OM degradation, molar OC/N ratios increase due to nitrogen utilization (Benner et al., 1991). Care must be taken when interpreting OC/N ratios because sources of OM can also be indicated using these ratios; potentially providing an artefactual indication of degradation. For example, an OC/N of ~ 7 points to a marine source of OM (Goni and Hedges, 1995; Bashkin, 2002) and > 20 for terrestrial OM (Zimmerman and Canuel, 2001; Gordon and Goni, 2003). Bianchi and Argyrou (1997) and Bianchi et al. (2002) also found that terrestrial OM had higher OC/N ratios compared to marine OM. Hence, the molar OC/N ratios in the sediment trap (8.8), and at LC2 (9.0), LC5 (8.9), LC6 (6.4) and Camas Nathais (8.2) have a stronger marine signal than other locations; whilst LC0 (11.2), RE2 (17.5), RE5 (11.4) and RE6 (11.4) show greater terrestrial influence. This is supported by the significant correlations between OC/N ratio with lignin and OC (Table 5).

The slightly higher OC/N ratios for LC0 (mean OC/N=11.2) and LC1 (OC/N=9.3) sediments, compared to the trap samples (OC/N=8.8), could imply greater abundance of terrestrial OM in the surface sediments and more phytoplankton detritus in the trap. This proposition is supported by the higher R_p values for the LC0 ($R_p=0.43$) and LC1 ($R_p=0.43$) surface sediments compared to trap materials ($R_p=0.37$), which indicate more highly degraded plant materials in the surface sediments.

In trying to distinguish between vegetation source and OM degradation stage, R_p index data provide valuable information. In the later stages of degradation the OC/N

Table 6. Rate constants for the degradation of sedimentary OM within the 0–1 cm and 9–10 cm sediment layers.

Location	Rate constant, k ($\times 10^{-5} \text{ d}^{-1}$)				
	Labile OM	Refractory OM	OC	TN	Lignin
LC0	2.2	3.5	1.0	2.3	–
LC1	0.2	2.3	4.1	7.1	4.1
LC3	1.3	1.5	–	–	–
LC5	–	2.3	–	–	4.3
LC6	–	–	–	–	4.6
RE5	1.3	1.7	–	–	–
RE6 (17.1.2001)	3.7	–	–	–	–
RE6 (20.3.2001)	9.3	3.9	–	–	–

The rate constant for the degradation of OM are determined only for the above during the occasions when the OM contents for the subsurface sediments were lower than the surface sediments, indicating OM degradation upon sedimentation. Besides, some of the data are not available for the subsurface 9–10 cm sediment layer.

ratios decrease due to nitrogen immobilization (Benner et al., 1991; Meyers, 1997). The decrease of OC/N ratios seawards through the lochs implies more advanced stages of OM degradation; this is seen by the more pronounced decrease of %TOC compared to %TN further down the lochs. In Loch Creran OC/N decreased from 11.2 to 6.4 and in Loch Etive from 17.5 to 8.2. This is supported by the increase of R_p values from 0.43 to 0.63, and from 0.40 to 0.80 respectively. Published studies have also shown decreasing OC/N ratios with advancing degradation stage for plants and soil materials: Berg et al. (1987) found that the OC/N ratios of plant materials decreased with increased incubation time due to higher decreased in OC and a slight increased in %TN; Xulux-Tolosa et al. (2003) found that the OC/N ratio decreased during the process of degradation of plant materials; Chen et al. (2003) also found that OC/N ratios decreased during OM decomposition of plant and soil residues.

4.3 Rate constant for OM degradation

Quantitative interpretation of the reactivity of OM was provided by the rate constant of OM degradation. Determination of the degradation rate constant (k), has been based on OM contents of surface and subsurface sediments:

$$k = -[\ln(C/C_0)]/t \quad (2)$$

where C = known concentration at the surface sediment, C_0 = concentration at the time of deposition at the subsurface sediment, and t = time for deposition (Canuel and Martens, 1996).

Based on the sediment accumulation rate in the upper and lower Loch Creran of 0.5 and 0.2 cm yr^{-1} (Loh et al., in preparation), and 0.7 cm yr^{-1} in Loch Etive (Howe et al., 2001), the total deposition time beneath the 10 cm sediment layer in Loch Creran are approximately 20 and 50 years, and

for Loch Etive 14.3 years. The degradation rate constant for both lochs ranged from 0.2 to $9.3 \times 10^{-5} \text{ d}^{-1}$ for labile OM, 1.5 to $3.9 \times 10^{-5} \text{ d}^{-1}$ for refractory OM, 1.0 to $4.1 \times 10^{-5} \text{ d}^{-1}$ OC, 2.3 to $7.1 \times 10^{-5} \text{ d}^{-1}$ TN, and 4.1 to $4.6 \times 10^{-5} \text{ d}^{-1}$ lignin (Table 6). For labile OM, k was highest at RE6, followed by LC0, LC3 and RE5; whilst for refractory OM, k was highest at RE6, followed by LC0, LC1, LC5, RE5 and LC3. The higher rate constants at the upper basin of Loch Creran, as well as RE6 compared to RE5, were most probably due to the contribution of relatively fresh terrestrial OM being more susceptible to bacterial action. The “ k ” value for refractory OM was higher at LC5 compared to the locations at the upper Loch Creran. This, as well as the rate constant for lignin which increased further down the loch, is most likely related to the role of bioturbation, introducing oxygen to subsurface sediments. The higher degradation rate constant for OC and TN in LC1 compared to LC0 could also be due to the contribution of terrestrial OM, although more data is needed to enable more detail interpretation.

5 Conclusions

Lignin studies indicate that rivers provide an important source of land-derived carbon to Loch Creran and Loch Etive. Non-woody angiosperm tissues predominate in these two Scottish sea lochs. Although woody plants such as beech, birch and oak are found in abundance around both lochs, these non-woody tissues are indicative of the associated mass of leaf material. The observed decrease in lignin, total OM and OC from the head through the lochs seawards, along with significant correlations among these parameters (regression analyses: $p < 0.05$), indicate that terrestrial material contributes significantly to the sedimentary OM and carbon inventories. The offshore decreases in these parameters further indicate the importance of rivers in contributing terrestrial OM to the lochs and that sedimentation of material occurs during transportation along the lochs.

Lignin is a highly complex compound which is largely refractory to biodegradation. In aquatic environments lignin biodegradation is even more problematic, as water is typically less well oxygenated than surface soils. As a result, published studies have reported no lignin degradation occurring in natural waters. As lignin is closely related to the total OM and OC, however, the overall decrease of oxygen uptake rate through the lochs suggests that terrestrial OM does fuel biogeochemical cycling in these systems.

Oxygen uptake rate and OC/N ratio, combined with R_p index, have been used successfully to indicate the degree of freshness, or biodegradability, of the sedimentary OM. Sediments near to riverine inputs have higher oxygen uptake rates, indicating higher biodegradability of the sediment OM. In these two lochs, terrestrial compounds constitute a significant fraction of the O. Lower R_p values indicate higher fractions of labile OM, which also indicates the presence

of fresher materials, more susceptible to degradation. Sediments near to riverine inputs also have lower R_p values. Finally, we were able to relate the biodegradation of sedimentary OM to molar OC/N ratios. In this work, the study of lignin together with oxygen uptake rate, molar OC/N ratio and R_p index has shown that these parameters can be used as simple proxies to determine the biodegradability of sedimentary OM in sea loch systems; hence the hypothesis of the study is accepted.

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