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# Organic matter properties of Fennoscandian ecosystems: potential oxidation of northern environments under future change?

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## Abstract

The oxidative ratio (OR) of an ecosystem, which reflects the ratio of $O_2$: $CO_2$ associated with ecosystem gas exchanges, is an important parameter in understanding the sink of $CO_2$ represented by the terrestrial biosphere. There is a growing body of ecosystem-based approaches to understand OR; however, there are still a number of unknowns. This study addressed two gaps in our understanding of the oxidation of the terrestrial biosphere: (1) What is the oxidation state of Arctic ecosystems, and in particular permafrost soils? (2) Will coupled climate and land use change cause the terrestrial organic matter oxidation state to change? The study considered eight locations along a transect from southern Sweden to northern Norway and sampled different organic matter types (soil, litter, trees, and herbaceous vegetation) as well as different soil orders (Inceptisols, Spodosols, Histosols, and Gelisols). The study showed that although there was no difference between soil orders, there was a significant effect due to location with OR increasing from 1.03 at the southernmost location to 1.09 in the

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northernmost location; this increase is independent of soil order or type of organic matter. The pattern of post hoc differences in the OR with latitude suggests that the increase in OR is correlated with the northern limit of arable agriculture. The study suggests that the combined effects of climate and land use change could lead to a decrease in terrestrial organic matter OR and an increase in its oxidation state.

**Keywords**

Terrestrial carbon cycle; permafrost-affected soil; Norway; Sweden; Finland

## 1. Introduction

To apportion anthropogenic $CO_2$ emissions between the atmosphere, biosphere, and oceans, estimates can be made through measurements of relative changes in atmospheric gases, such as $O_2$ and $CO_2$ (Keeling et al., 1996). These approaches require an understanding of the global biosphere's oxidative ratio (OR), which is the molar ratio of $O_2$ and $CO_2$ fluxes associated with net ecosystem exchange. OR has a natural range of values from 0 ($CO_2$) to 2 ($CH_4$) (Masiello et al., 2008) and can be used as a tracer of processes associated with organic matter synthesis and destruction, and can be associated with carbon both pools (e.g. soils, biomass) and carbon fluxes (e.g. $CO_2$ exchange) (for examples, see Table 1 in Gallagher et al., 2014). In this way, it can be thought of as analogous to other tracers such as $\delta^{13}C$ which can also be calculated through gas exchange measurements, or though sampling of organic matter pools.

Battle et al. (2000) proposed partitioning equations for the terrestrial and oceanic carbon sinks of fossil fuel emissions, which included an OR term, to calculate fluxes of $CO_2$ to the land and oceans (see equations 10 and 11 in "Global terrestrial biosphere OR calculation"). Many studies use a value of 1.1 for the OR of the terrestrial biosphere (e.g. Battle et al., 2000;

Steinbach et al., 2011), though 1.05 is also sometimes used (Keeling & Shertz, 1992). The source of this value dates to the origins of the methodology, where the value of 1.1 was based on a single study within the ‘Biosphere 2’ experiment (Severinghaus, 1995).

Worrall et al. (2013) compiled elemental analysis from the literature for whole soil and vegetation data from across the globe to provide a flux-weighted estimate of global OR, and found a value of 1.03 ± 0.03 would be more appropriate and argued that the commonly used in the literature (i.e. 1.1) represents the 97th percentile of observed values. Whilst the changes in OR may appear small (i.e. changes within the 1st or even 2nd decimal place), in using this updated value, Worrall et al. (2013) were able to show, when used within global partitioning equations (e.g. Battle et al., 2000), current estimates are potentially underestimating $CO_2$ uptake by the terrestrial biosphere by up to 14%.

Worrall et al. (2013) identified a number of gaps in the global database, specifically the lack of OR data for certain USDA soil orders (e.g. Gelisols, Ultisols) as well as global biomes (e.g. savannas, shrublands). Subsequent studies have started to fill some of these gaps (Clay & Worrall, 2015a; Clay & Worrall, 2015b), whilst other studies have explored the role of disturbances on ecosystem-level OR including: fertiliser management (Worrall et al., 2016a); land use and crop distributions (Gallagher et al., 2014); fire (Hockaday et al., 2009); and elevated $CO_2$ concentrations (Hockaday et al., 2015). Randerson et al. (2006) showed that changes in the organic matter pools as an environment undergoes change will lead to an additional carbon sink effect as the organic matter changes oxidation state in response to disturbance.

Therefore, this study addresses two aspects of global OR that are not presently understood. Firstly, the only soil order for which no information is currently available is permafrost affected soils i.e. Gelisols. Permafrost soils store large quantities of carbon (Schuur et al., 2015; Tarnocai et al., 2009) and understanding carbon cycling processes in these environments is important when considering the potential impact on these stores from ongoing climate change (e.g. Schuur et al., 2015)). Secondly, future climate change will likely result in the northward retreat of biomes, land use, and soil types typical of southern latitudes, which will encroach on boreal and tundra environments (though local variations, as well as other factors, may lead to complex patterns of response, Skre et al., 2002).

Peatland environments are sensitive to changes in climate (i.e. temperature and precipitation) and modelling studies have suggested that under future climate scenarios the climatic envelopes supporting peatland development may be substantially altered (e.g. Gallego-Sala & Prentice, 2013). Approximately 25% of Fennoscandia is covered by peat formations (Parviainen & Luoto, 2007), with raised bogs in the more southerly regions, to aapa and palsa mires as the most northerly complex in the permafrost regions in the Arctic Circle (Seppä, 2002; Seppälä, 1988). Many studies have examined the relationship between climatological gradients and mire complexes in Fennoscandia (e.g. Luoto et al., 2004), and modelling suggests that under future climate change scenarios the area suitable for palsa mire development will be reduced dramatically (Aalto et al., 2014).

This study, therefore, targets the organic-rich soils of Fennoscandia to test changes in OR in ecosystems across a climatic and land-use gradient. We would hypothesise that OR will vary in a statistically significant manner along the transect and that terrestrial organic matter will be more reduced with increasing latitude meaning that climate change and land use will drive oxidation of these soils.

## 2. Methods

This study sampled organic matter pools at sites in eight locations along a transect from southern Sweden into Arctic Norway (Table 1, Figure 1). The transect covered the transition from mineral to organic soils, and from organic soils into permafrost (firstly discontinuous and then continuous permafrost). The Varanger Peninsula (location 8 – Table 1, Fig 1) is the only place in Scandinavia with lowland continuous permafrost. The study could also consider the transition from arable to pasture; the limit of settled agriculture is at location 6 and where location 7 is beyond the limit of settled agriculture at all altitudes (although grazing at sea-level is possible at location 8). For all locations, it was possible to sample Histosols, and for all but the most northerly location it was possible to sample birch trees (Betula pendula R.). The transect could also include Gelisols in both discontinuous and continuous permafrost from location 5 through 8.

This study therefore utilises a space-for-time substitution to explore future trajectories of these ecosystems. Although there are benefits and shortcomings of such approaches (Pickett, 1989), it has been suggested that careful use of space-for-time substitutions are appropriate in modelling responses to climate change (Blois et al., 2013).

## 2.1. Field sampling

Field sampling was carried out during July 2014 along a transect from southern Sweden to northern Norway (Figure 1) and in total 52 sites were visited across the eight locations (Table 1). At each site soil, litter, and herbaceous vegetation were sampled whenever present, and were chosen to reflect the dominant vegetation groups at each site. Additionally, samples of silver birch (Betula pendula R.) and Scots pine (Pinus sylvestris L.) were collected wherever possible. However, for some sites, it was not always possible to obtain all four pools (e.g. limited tree samples at high latitude sites).

Whilst the chemical composition of vegetation may vary throughout the year, if we consider that carbon is fixed over a limited period of time (e.g. growing period), then they can effectively be thought of as closed systems, and measurements of OR will reflect the OR of the flux of formation (Gallagher et al., 2014). Furthermore, there is evidence to suggest that at least on an annual timescale, OR is relatively stable, with variation within vegetation types often smaller than between vegetation types (e.g. Clay & Worrall, 2015a; Gallagher et al., 2014). The compartmentalising of the C pools has shown to be a suitable first approximation of ecosystem level OR (e.g. Clay & Worrall, 2015a).

Soils were sampled from the upper 5 - 10 cm using a trowel, which was in part due to difficulties in sampling frozen ground in many of the permafrost-affected soils. To be consistent and balance the sampling design, we decided to stick to this depth range across the transect. Herbaceous vegetation was carefully removed using secateurs, whilst tree samples were extracted using a tree corer from a living tree trunk. All samples were bagged in the field and air dried in the evenings to reduce the moisture content and the possibility of oxidation prior to international shipping. Sites were classified into one of 15 biomes, based on the International Geosphere-Biosphere Programme (IGBP) land cover classes, and into one of 12 soil orders of the United States Department of Agriculture (USDA) soil taxonomy. Furthermore, peatland sites were sub-divided depending on their form: blanket peat; aapa mire; and palsa mire – the latter being classified as Gelisols.

Two further locations were considered as opportunistic sampling opportunities to add data to the global OR database (sensu Worrall et al., 2013), but were not part of the main experimental design. These two locations were not included in the ANOVA in this study (see “Statistical Analysis”), but were included as part of the re-calculation of global OR (see “Global terrestrial biosphere OR calculation”). The first additional location was an Entisol under evergreen forest on an abandoned braid bar in northern Finland. The second was a palsa mire in northern Finland and samples were considered under Gelisols.

## 2.2. CHNO analysis

All samples were dried at 60°C until a constant weight was achieved prior to further analysis. Soil samples (mineral and organic) were ground using a rotary ball mill, whilst herbaceous vegetation, tree, and litter samples were ground using a Spex 6770 Cyromill.

All samples were analysed for their carbon, hydrogen, nitrogen, and oxygen (CHNO) concentrations. For CHN concentrations, samples were analysed on a Thermo EA1110 elemental combustion system with pneumatic autosampler set up for CHN analysis. For O concentrations, a Costech ECS 4010 Elemental combustion system with pneumatic autosampler was used and set up for O analysis. For both CHN and O setups calibration curves with $r^2 > 0.999$ were created using cyclohexanone and acetanilide, respectively. Each sample (litter, soil, herbaceous vegetation or tree) was analysed in triplicate i.e. three times on the CHN setup and a further three times on O set up, and a mean calculated for C, H, N, and O.

## 2.3. Carbon oxidation state ($C_{ox}$) and oxidative ratio (OR) calculation

OR can be calculated from an organic matter pool's carbon oxidation state ($C_{ox}$). $C_{ox}$ describes the bonding arrangements of C atoms in a sample and can range from -4 at the most reduced end (i.e. methane, $CH_4$) to +4 at the most oxidised end (i.e. carbon dioxide, $CO_2$) (Masiello et al., 2008). $C_{ox}$ can be readily measured using elemental analysis (Masiello et al., 2008):

$$C_{OX} = \frac{2[O]-[H]+3[N]}{[C]} \qquad \text{Equation 1}$$

Where: [X] = molar concentration of C, H, N, or O, and assuming the majority of organic nitrogen exists as amine groups in amino acids.

As $C_{ox}$ and OR are related through the balancing of organic matter synthesis, the OR value is calculated as the ratio of $O_2$ and $CO_2$ coefficients (for further details see Masiello et al., 2008). Simplified it is then calculated as:

$$OR = 1 - \frac{C_{ox}}{4} + \frac{3[N]}{4[C]} \qquad \text{Equation 2}$$

Equation 2 assumes that there is no contribution to the $C_{ox}$ from S or P, and it has been shown that the error in the OR of making such an assumption would be only ± 0.002 (Hockaday et al., 2009). This equation also assumes that the nitrogen source in carbon fixation is $N_2$; this assumption is robust against small variations of the source of N. For example, if ecosystems receive 20% of their N as $NO_3^-$ instead of $N_2$, then the error associated with such input would only be 0.01 OR units (Masiello et al., 2008).

In addition to the above parameters, the degree of unsaturation (the number of rings and p-bonds within a molecule) was calculated, where for molecules without any halogens the degree of unsaturation is:

$$\Omega = \mathrm{C} - \frac{\mathrm{H}}{2} - \frac{\mathrm{N}}{2} + 1 \qquad \text{Equation 3}$$

Where: X = the number of atoms with X = C, H and N. Pure alkane would have $\Omega = 0$ and for benzene $\Omega = 4$.

## 2.4. Calorimetry

Gross heat values ($\Delta H_c$) were measured for all organic soils, herbaceous vegetation, tree, and litter samples; mineral soils could not be analysed and limited sample volumes prevented some organic samples from being analysed. Masiello et al. (2008) have shown that it is possible to derive $C_{ox}$ values (and therefore OR values) from calorimetry data. Analysis was performed on a 6200 Isoperibol Calorimeter (0.1% Precision Classification, Parr Instrument Company, Illinois, USA) with 1108(P) Oxygen Bomb. Calibration was performed as a rolling average of 10 measurements using benzoic acid standards. For comparative purposes, three standard, naturally-occurring organic compounds were analysed: lignin (Aldrich, CAS 8068-05-1), humic acid (Alfa-Aesar, CAS 1415-93-6),, and cellulose (Whatman, CAS 9004-36-4).

Previous studies have compared $\Delta H_c$ to OR and have shown that it is reasonable to describe OR patterns in terms of $\Delta H_c$ and to identify unusual observations (e.g. Clay & Worrall, 2015b). Therefore, $\Delta H_c$ values were plotted against OR values for the different organic matter types along with the standard materials.

### 2.5. Statistical Analysis

The experiment was designed to answer two questions. Firstly, are Gelisols different from other soil orders? Secondly, is there a change in OR with latitude and therefore climatic zones? The design of the study allowed several factors to be considered. Firstly, a location factor which had 8 levels (detailed in Table 1) and within each location there were multiple sampling sites. We would hypothesize that if climatic zones have a significant effect on OR then there would be a significant difference between locations in line with their climatic zones. The second factor considered was the type of organic matter sample (henceforward referred to as material type) which had four levels – soil, litter, herbaceous vegetation, and tree. The third factor considered were the soils (henceforward referred to as soil order) which could be divided into four soil orders – Inceptisols, Spodosols, Histosols, and Gelisols. All these soil orders were deliberately sampled at more than one location and so were not collinear with location. As an alternative to considering the soil order factor having four levels, the nature of the soils were classed simply as either mineral (Inceptisols and Spodosols) or organic (Histosols and Gelisols). The nature of the environment means that it is not always possible to be perfectly cross-classified with respect to all factors levels, but the design was carefully chosen to ensure maximum cross-classification.

As well as the multiple factors that could be considered in the design it was possible also to include two further analyses. First, degrees latitude was included in the ANOVA as a covariate. The degrees latitude is by design collinear with the location factor and so when latitude was included the location factor was not also considered. Second, the data were considered relative to the local birch tree sample. It was hypothesized that by ratio to a common organic matter pool site to site variation in the sampling would be minimised and the difference between organic matter pools and reservoirs enhanced. All samples from a location were ratioed to the value for the birch tree at that location and the relative values were then tested with ANOVA as above.

Before any analysis of variance (ANOVA) was performed the data were Box-Cox transformed to remove outliers and tested for normality using the Anderson-Darling test – it did not prove necessary to transform the data for any of the metrics in this study. The magnitude of the effects of each significant factor and interaction was calculated using the generalised $\omega^2$, and values were presented as least square means (otherwise as marginal means).

Power analysis was performed to estimate the effect size of the design used for each factor and given its particular number of levels. The power analysis was performed using the G*Power 3.1 software (Faul et al., 2007; http://gpower.hhu.de/) - a priori the acceptable power was set at 0.8 (a false negative probability $\beta$ = 0.2). The G*Power software measures effect size as f, where f is defined as:

$$f = \sqrt{\frac{\omega^2}{1-\omega^2}} \qquad \text{Equation 4}$$

Thus, the effect size at a power of 0.8 could be calculated and compared to measured value of $\omega^2$.

## 2.6. Global terrestrial biosphere OR

A revised estimate of global terrestrial OR ($OR_{terra}^{global}$) could be made by updating the meta-analysis of Worrall et al. (2013) with the new data on Gelisols from this study. The data from this study were also combined with data from other recent studies (Clay & Worrall, 2015a; Clay & Worrall, 2015b; Worrall et al., 2016a; Worrall et al., 2016b).

Worrall et al. (2013), as well as subsequent studies (e.g. Clay and Worrall, 2015b), have calculated the $OR_{terra}^{global}$ by using a weighted sum of the OR of global soils ($OR_{soil}^{global}$) and global vegetation ($OR_{veg}^{global}$). The weighting factor for soils and vegetation OR is the proportion of the annual $CO_2$ flux from the soil and vegetation, respectively.

$$OR_{terra}^{global} = \varphi_{soil}^{global} OR_{soil}^{global} + \varphi_{veg}^{global} OR_{veg}^{global} \qquad \text{Equation 5}$$

$$\varphi_{soil}^{global} + \varphi_{veg}^{global} = 1 \qquad \text{Equation 6}$$

Where: $\varphi_{x}^{global}$ = the proportion of the annual terrestrial biosphere C annual flux that is due to x (x = soil or vegetation); and $OR_{x}^{global}$= the global OR of x (x = soil or vegetation).

The comparative sizes of the soil and vegetation reservoirs were estimated from Eswaran et al. (1993), Tarnocai et al. (2009) and Olson et al. (2001). The proportion of carbon in the soil reservoir was taken as 0.72 and in the vegetation reservoir as 0.28. The average carbon residence time for soils was taken as between 20 and 40 years based upon a study by Jenkinson and Rayner (1977). The average carbon residence time for vegetation was taken as between 2 and 5 years (e.g. Gaudinski et al., 2000). Given the above approach, the values of $\varphi_{soil}^{terra}$= 0.27 and $\varphi_{\mathrm{veg}}^{\mathrm{terra}}$ = 0.73.

Using the method of Worrall et al. (2013), as updated by Worrall et al. (2016b), we are able to allow for the form of organic matter release from soil types. Organic matter can be released from the soil and vegetation organic matter pools as dissolved organic matter (DOM), particulate organic matter (POM), and methane ($CH_4$), and not just $CO_2$ as previously assumed by Worrall et al. (2013). For many environments, the proportion of the carbon flux that is due to DOM, POM or $CH_4$ is very low or negligible (e.g. $\varphi_{DOM}^{n} = 0$), and it is perhaps only in environments with organic-rich soils where all such exchanges are relevant. Histosols, Mollisols and Gelisols were taken as exporting carbon as DOM, POM and $CH_4$ in proportion to that predicted by the stoichiometric equation of Worrall et al. (2009). For all other soil orders export via $CH_4$ or DOM was negligible, i.e. zero.

We assumed that all soils exported some carbon as POM. In Histosols, such as peat, where the soil is approximately 100% organic matter then the erosion will be 100% organic carbon. However, in mineral soils the organic carbon content of the particulate flux will be lower, and so will be the fraction of the carbon pool turned over via this mechanism. In the absence of further information, the value of $\varphi_{POM}^{terra}$ was allowed to vary between 0 and 12% (based upon the POM fluxes reported for the UK – Worrall et al., 2014) for all soil orders other than Histosols, Mollisols and Gelisols.

The value of $OR_{CH4}^{n}$ is by definition 2 and the value of $OR_{DOM}^{n}$ OR was taken as 0.92 with an inter-quartile range of 0.91 to 0.94 based on the review of Worrall et al. (2013) and the measurements of Worrall et al. (2016b). The value of $OR_{POM}^{n}$ was taken as the same as the soil from which it eroded. The values of $OR_{veg}^{n}$ and $OR_{CO2}^{n}$ were based on the available vegetation and soil measurements and were considered as the median and 5th to 95th percentile range.

The $\mathrm{OR}_{\mathrm{soil}}^{\mathrm{global}}$ was estimated as:

$$\mathrm{OR}_{\mathrm{soil}}^{\mathrm{global}} = \sum_{\mathrm{i}}^{\mathrm{n}} \delta_{\mathrm{n}} [\varphi_{\mathrm{CO2}}^{\mathrm{n}} \mathrm{OR}_{\mathrm{CO2}}^{\mathrm{n}} + \varphi_{\mathrm{DOM}}^{\mathrm{n}} \mathrm{OR}_{\mathrm{DOM}}^{\mathrm{n}} + \varphi_{\mathrm{POM}}^{\mathrm{n}} \mathrm{OR}_{\mathrm{POM}}^{\mathrm{n}} + \varphi_{\mathrm{CH4}}^{\mathrm{n}} \mathrm{OR}_{\mathrm{CH4}}^{\mathrm{n}}]$$

Equation 7

$$\varphi^{n}_{CO2} + \varphi^{n}_{DOM} + \varphi^{terra}_{POM} + \varphi^{terra}_{CH4} = 1 \qquad \text{Equation 8}$$

Where: $\delta_n$= the proportion of the global soil carbon store that is in soil order n; $\varphi^{n}_{x}$ = the proportion of the flux from soil order n that is due to x (x = $CO_2$, DOM, POM or $CH_4$); and $OR^{n}_{x}$ = the OR for soil order n for component x (x = $CO_2$, DOM, POM or $CH_4$).

Equally, the $OR^{global}_{veg}$ was calculated as:

$$OR^{global}_{veg} = \sum_{i}^{n}\left[\alpha_n OR^{n}_{veg}\right] \qquad \text{Equation 9}$$

Where: $\alpha_n$ = the proportion of global area that is in biome n; and $OR^{n}_{veg}$ = the OR for vegetation for biome n.

Given the ranges for each input into Equations 5 to 9 the calculation of $OR^{global}_{terra}$ was based upon 100 calculations with values drawn randomly from the available ranges.

By using equations from Battle et al. (2000) (as re-formulated by Worrall et al., 2016b) it is possible to calculate the size of the terrestrial and oceanic sinks (equations 10 and 11 respectively):

$$f_{land} = -\frac{CS}{OR^{global}_{terra}} f_{fuel} + \frac{1}{k_1 k_2 OR^{global}_{terra}} \frac{d\left(\frac{O_2}{N_2}\right)}{dt} \qquad \text{Equation 10}$$

$$f_{ocean} = -\frac{1}{k_1}\frac{d(CO_2)}{dt} - \frac{1}{k_1 k_2 OR^{global}_{terra}} \frac{d\left(\frac{O_2}{N_2}\right)}{dt} - \frac{OR^{global}_{terra} - CS}{OR^{global}_{terra}} f_{fuel} - f_{cement} \qquad \text{Equation 11}$$

Where: $f_x$ = the annual flux of $CO_2$ (Gt $CO_2$ $yr^{-1}$) with x = land, ocean, fuel or cement; positive values represent a sink i.e. positive $f_{land}$ and $f_{ocean}$ represent sequestration. ($O_2/N_2$) = the molar ratio of atmospheric $O_2$ and $N_2$; CS = the combustion stoichiometry (1.43 - Battle et al., 2000); $OR_{terra}^{global}$ = the oxidative ratio of the global terrestrial biosphere; constants $K_1$ and $K_2$ convert from Gt C to ppm $CO_2$, and from ppm to per meg (which is ppm on a molecular basis for oxygen alone), respectively, and where the values are 0.471 and 4.8 respectively.

## 3. Results

In total 163 samples were analysed for their CHNO concentrations and $\Delta H_c$ values across the main material groups: litter, organic (peat) soils, mineral soils, above-ground herbaceous vegetation, and trees; after Box-Cox transformation and the opportunistic sampling sites were excluded, 145 samples remained. Summary statistics are shown Table 2.

### 3.1. ANOVA

With respect to OR (and $C_{ox}$), the general linear model showed significant effects for both location and material type factors, but no significant effect due to the differences between soil order. This model explained 26% of the variance in the original dataset but no interaction terms could be assessed. As an alternative, the soil order factor was re-classified only as either organic or mineral soils. When this classification of samples was used then the model explained 37% of the original variance and interaction terms could be assessed. Henceforward, the soil factor was considered with only two levels – mineral and organic (Table 3).

With respect to the OR (and $C_{ox}$) values, the most important factor was the material type (explained 35% of the variance explained, where the critical effect size at a power of 0.8 was 27%). Post hoc testing showed that there was no significant difference between the tree and herbaceous vegetation samples (least square mean values of 1.079 ± 0.01 and 1.071 ± 0.007

respectively), whereas the soil and litter samples were both significantly different from all other organic matter types and from each other (least squares mean values of 1.031 ± 0.007 and 1.056 ± 0.01 respectively).

The second most important factor was the location factor which explained 34% of the variance explained (critical value of $\omega^2$ at a power of 0.8 was 32%). The main effects plot of the location factor shows that, apart from location 3 (Figure 2), there is a clear trend to increased OR across the locations. Locations 1 and 2 are significantly different from locations 5 through 8; location 3 is not significantly different to other locations. The least squares means shows that OR rose from 1.03 at location 1 at the very southern tip of Sweden to 1.09 for location 8 in Arctic Norway. The location factor is also significant factor for $C_{ox}$ where the least squares means showed a variation from -0.12 and -0.39 between locations 1 and 8.

There was no significant difference between soil types when re-classified into just organic and mineral soils; however, there was a significant interaction between the material type and soil order factor which explained 6% of the original variance explained (critical value of $\omega^2$ at a power of 0.8 was 26%). The post hoc analysis showed that the only significant difference was between soils organic matter between the organic and the mineral soil orders (and not the other material types such as litter);no other interactions were found to be significant.

When degree of unsaturation was considered there were significant differences due to the material type and order factors with the most important being the former (Table 3). The highest $\Omega$ values were for the litter samples whilst the lowest were found in the soil samples. Within the soils the Gelisols had the highest $\Omega$ and Inceptisols the lowest $\Omega$. The location factor was not significant for $\Omega$ (Table 3). For the elemental ratios the location factor was not found to be significant in any case (Table 3). In each case material type was significant with trees having the highest C/N and soil having both the highest O/C and H/C ratios. The soil order was significant for the H/C ratio with both Inceptisols and Spodosols significantly higher than Histosols and Gelisols – there was no need in this latter case to degrade the classification of soil order to organic vs. mineral.

When latitude was included as a covariate then the location factor became insignificant but latitude as a covariate was only significant at $p = 0.08$. Using a partial regression analysis, the OR is most closely related to the variation in the O/C ratio followed by H/C ratio the least important, although still significant was the C/N ratio.

When samples from birch trees alone were considered there was no significant trend with location or latitude, i.e. despite sampling birch across the transect, it is statistically possible to say that birch has a uniform OR = 1.077 ± 0.004. When all the data were assessed relative to its local birch tree sample there was no increase in the proportion of the variance explained for OR (37% of original variance). Upon consideration of the relative OR data then there is no longer a significant effect due to the soil order or the interaction between location and soil order factors; however, there were significant effects due to location and material type factors as well as the interaction between the material type and soil order factors (Table 3). The most important factor was the difference between locations and the post hoc analysis showed again the change occurred between locations 1 & 2 and locations 5 – 8 (Figure 3). With respect to the material type factor the post hoc analysis shows that both tree and herbaceous vegetation samples are not significantly different from 1.00 which means they are statistically the same as the birch samples. The samples of litter are significantly lower than 1 (relative OR = 0.984 ± 0.008) as are soils (relative OR = 0.962 ± 0.006) implying that there is an oxidation of organic matter from primary productivity to litter and into soil. The significant interaction between soil order and material type is between the mineral (relative OR = 0.985 ± 0.009) and organic soils (relative OR = 0.939 ± 0.009).

### 3.2. Variation in organic matter composition

The comparison between OR and $\Delta H_c$ for the different organic matter reveals some interesting patterns (Figure 4). As might be expected from the relationship in Masiello et al. (2008), the standard materials show a linear relationship where higher OR values are accompanied by higher $\Delta H_c$ values, although with the low samples size amongst the standards the relationship is not significant ($r^2 = 0.96$, $p = 0.124$, $OR = 0.012\ \Delta H_c + 0.807$),. The majority of the litter, herbaceous vegetation, and tree samples plot on or above the line bounded by the lignin and cellulose standards, whilst the majority of the organic soils plot below this line. As a group, the tree samples plot closest to the lignin standard, whilst the litter and herbaceous vegetation samples represent a more diverse range of compositions spread between the lignin and cellulose standards (Figure 4). The organic soils generally plot lower than the standard line indicating that these samples have higher than expected $\Delta H_c$ values relative to the organic matter standards (Figure 4).

### 3.3. Global OR

The updated distributions of the OR for the global soil types and biomes are given in Tables A.1 and A.2 (see Supplementary Material) and in total 866 samples of organic matter are now considered in the analysis. The updated values are $OR_{veg}^{global}$ = 1.06 (1.04 to 1.07) and $OR_{soil}^{global}$ = 1.06 (1.03 to 1.10) and thus $OR_{terra}^{global}$ = 1.06 (1.05 to 1.08), where values in parentheses are 5th to 95th percentiles. Given that the new values of $OR_{veg}^{global} = OR_{soil}^{global}$ then the value of $OR_{terra}^{global}$ is not sensitive to assumptions of the residence time ($\varphi_{soil}^{terra}$ and $\varphi_{\mathrm{veg}}^{\mathrm{terra}}$ ). Therefore, given Equations 10 and 11, and leaving all other terms from Table 1 of Battle et al. (2000) in Equations 10 and 11 the same, based on the period 1991 - 1997, then $f_{land}$ = 1.45 Gt C yr$^{-1}$ (1.29 to 2.28 Gt C yr$^{-1}$) and $f_{ocean}$ = 2.06 Gt C yr$^{-1}$ (1.48 to 2.64 Gt C yr$^{-1}$) – again values in parentheses are 5th to 95th percentiles.

Using the previously used value of OR ($OR_{global}^{terra}$ = 1.1), then $f_{land}$ = 1.40 Gt C yr$^{-1}$ and $f_{ocean}$ = 2.11 Gt C yr$^{-1}$ (Battle et al., 2000).

## 4. Discussion

The study has shown that there was a significant change in OR with latitude with higher OR and lower $C_{ox}$ at higher latitudes. It should be emphasized that this change of OR with location is independent of the change in vegetation or soil type as these were accounted for within the design. Therefore, the observed change with location, and therefore latitude, is not due to an increase in the area of organic soils or the loss of trees, but rather it shows that all organic matter reservoirs are more reduced at higher latitudes. How can this be explained?

We hypothesised that OR might vary between climate zones so the study design deliberately included the locations with the greatest range of average temperature in Scandinavia, and indeed we found that the OR at location 2 (the warmest average location) is significantly different from the OR of location 7 (the coldest point). This difference may, however, be due to land use differences at the various locations rather than climate per se. If location 3 is not considered, then the post hoc comparisons in Figure 2 show that the greatest difference lies between location 4 and location 5. Location 4 was chosen because it was the northern limit of arable production implying that cultivation could be a possible reason for the more oxidised state of more southerly locations. However, location 3 does not fit either a pattern based upon climate or land use. There was no under-sampling at location 3 with four sites sampled and all organic matter types considered (i.e. herbaceous vegetation, litter, trees, and soil from both mineral and organic soils). Examination of the data from location 3 shows that its high OR value does not come from one specific site at location 3; all four sites at location 3 have some sample type with an OR value above 1.1 and the sample types above 1.1 include soils, herbaceous vegetation, tree, and litter. Therefore, we unfortunately cannot offer a substantive explanation for the high OR values of location 3.The post hoc analysis of the location did not show location 3 to be different, rather the significant post hoc difference lay between locations 1 and 2, and locations 5 and 8. However, the overall pattern of OR increases with latitude remains a novel finding. There are a number of changes that occur with latitude that may influence organic matter compositions, and therefore OR; for example, average temperatures, snow days or sunshine hours. Although the effect of changing sunlight and insolation would be expected to be greatest for litter samples rather than soil samples and the latitudinal effect was significant independent of the organic matter type.

Randerson et al. (2006) proposed that increased levels of disturbance to biomes (mainly from anthropogenic activities) would favour plant functional types with lower OR values (e.g. favouring herbaceous plants over woody vegetation). The shift from lignin-rich to cellulose-rich organic matter would cause the terrestrial biosphere to become more oxidised (i.e. lower OR values) with time. The transect in this study was chosen to cover a climate and land use gradient across Fennoscandia, but this transect could also be thought of as an organic matter gradient. The study has made an ergodic assumption that by studying a transect from southern to northern Scandinavia the study is also considering the potential shifts with time, i.e. the northward retreat of permafrost. The results suggest that such ongoing change will result in an oxidation of the terrestrial biosphere (i.e. from high OR values to low OR values); whether this is due to changes in climate itself, or related expansion of certain land uses, is unknown.

Carter & Kankaanpää (2003) have estimated that cropping zones in Finland would retreat between 120 and 150 km northward for every 1K average temperature rise. There is strong evidence to show that the Arctic region has been warming substantially over the recent decades (IPCC, 2013) and in some regions these temperatures are potentially higher than in the past 44,000 years (Miller et al., 2013). The change in oxidation state predicted in this study with climatic change must always be viewed in the light of the impact on the carbon stores itself. The northward expansion of croplands at the extent of pasture will lead to a decrease in soil carbon stocks (e.g. Guo & Gifford, 2002), and loss of permafrost has been associated with long term changes to greenhouse gas emissions (Schuur et al., 2015). However, this study suggests that once at equilibrium the northward expansion of cropland and concomitant retreat of permafrost will leave more oxidised environments.

The study has modified and further enhanced the estimate of $OR_{terra}^{global}$. While other values of OR have been used in the literature other than 1.1 (e.g. 1.05, Keeling & Shertz, 1992), it is increasingly clear that a single global value of 1.1 is not the most suitable. Adopting the approach of Battle et al. (2000), it has been possible to estimate the global fluxes of carbon to the land ($f_{land}$ = 1.45 Gt C yr$^{-1}$ (1.29 to 2.28 Gt C yr$^{-1}$)) and oceans ($f_{ocean}$ = 2.06 Gt C yr$^{-1}$ (1.48 to 2.64 Gt C yr$^{-1}$)). By way of comparison, Battle et al. (2000) report $f_{land}$ = 1.4 ± 0.8 Gt C yr$^{-1}$ and $f_{ocean}$ = 2.0 ± 0.6 Gt C yr$^{-1}$ for the period 1991 – 1997, whilst Le Quere et al. (2016) report fluxes for the 1990 – 1999 period as $f_{land}$ = 2.6 ± 0.8 Gt C yr$^{-1}$ and $f_{ocean}$ = 2.2 ± 0.5 Gt C yr$^{-1}$. The $f_{land}$ estimate from this study, using an updated global OR value, is slightly larger than, but similar to Battle et al. (2000); however, they are both lower than the Le Quere et al. (2016) estimate, though lie within published errors. Values for $f_{ocean}$ are consistent between all three studies. Whilst the values do not dramatically alter our estimates of global carbon cycling, they do better constrain carbon flux partitioning between the atmosphere, oceans and biosphere.

Recent work has explored the spatial and temporal variations in ecosystem OR (e.g. Gallagher et al., 2014; Hockaday et al., 2015). However, the measurements of OR of this study, and previous ones that have questioned the global values of OR, have been based upon the organic matter left behind in the environment, or at best, material that is in slow transition in its interaction with the atmosphere and not based upon the component directly interacting with the atmosphere. Baldock et al. (2004) conducted litter bag experiments and showed that the fraction of terrestrial organic matter remaining after decomposition is more reduced than the initial biomass, i.e. the component of the terrestrial organic matter that was interacting with the atmosphere was more oxidised than which was left behind. Indeed, estimates of ecosystem OR based on atmospheric measurements have found even lower values of ecosystem OR than suggested in this study with Ishidoya et al. (2015) giving a value of 0.86 and van der Laan et al. (2014) a value of 0.89.

## 5. Conclusions

The study has shown that there is a significant difference in the oxidation state of organic matter, independent of soil or vegetation type, across a transect from minerals soils under arable through to areas of continuous permafrost. The terrestrial organic matter oxidative ratio (OR) rose from 1.03 for southern Swedish locations to 1.09 in northern Norway and this corresponded with a decrease in average carbon oxidation state ($C_{ox}$) from -0.12 to -0.39. The change could be related to climatic differences, but post hoc tests show that the differences are coincident with the limit of arable agriculture.

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Figure 1. Sampling locations in Norway, Sweden, and Finland. Note, within each location multiple sites were visited.

Figure 2. The least mean squares of the location factor with respect to OR. Location numbers are as in Table1 and error bars are given as the standard error in the least squares mean.

Figure 3. The least mean squares of the location factor with respect to OR when judged relative to a local birch sample. Location numbers are as in Table 1 and error bars are given as the standard error in the least squares mean.

Figure 4. Plot of OR and $\Delta H_c$ values for herbaceous vegetation, trees, litter and soils . Standard materials (cellulose, lignin, and humic acid) are included for comparative purposes.

Table 1. Latitude and longitude, USDA soil taxonomic group, and land-use for each location.

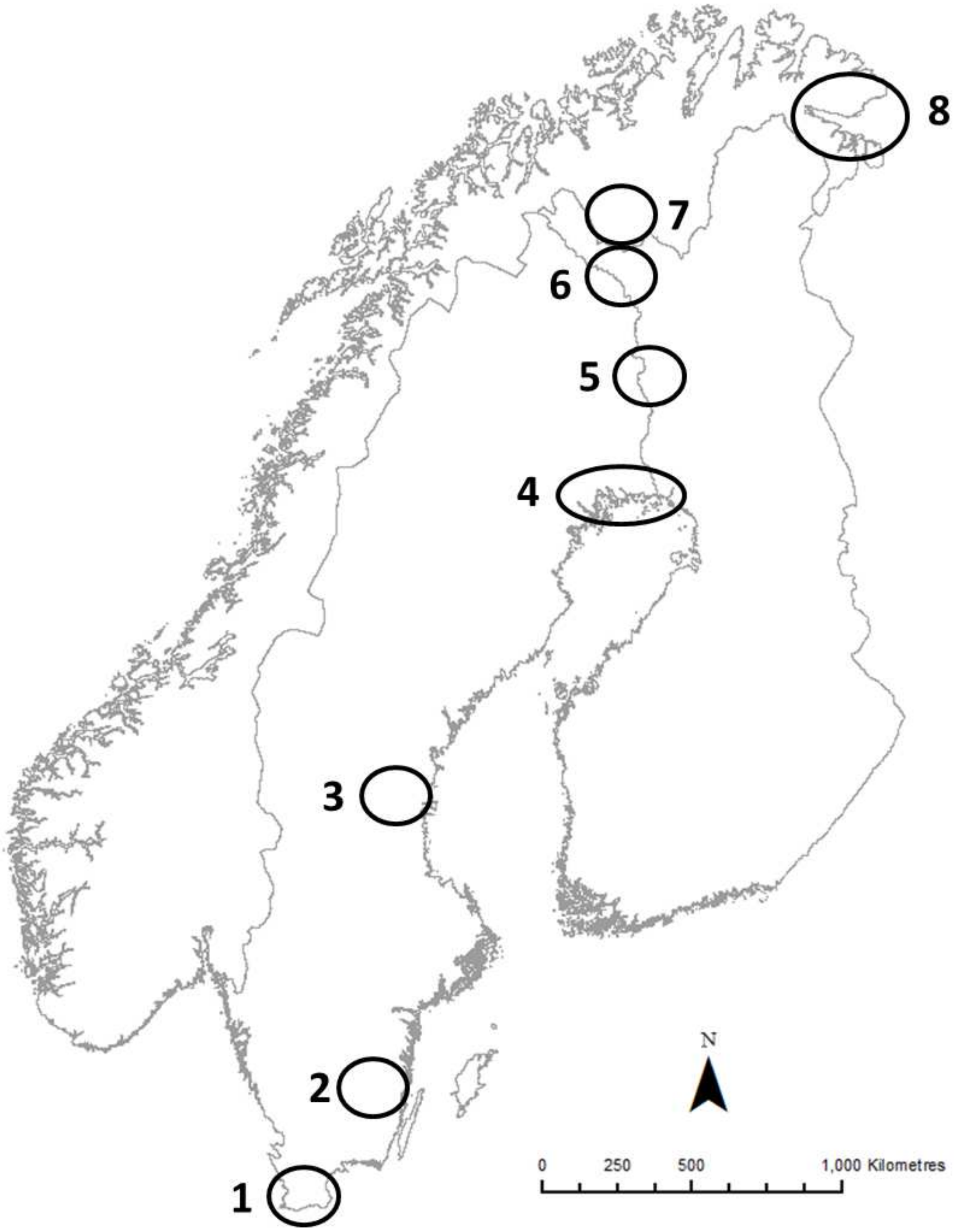
| | | | | | Number of samples per location | | | |
|---|---|---|---|---|---|---|---|---|
| Location | Approximate Lat/Long | Rationale for site selection | Soil types | Vegetation/Land-use | Litter | Soil | Tree | Herbaceous vegetation |
| 1.Smygeham (Sweden) | 55.34<br>13.35 | Southernmost point in Sweden | Inceptisols, Spodosols & Histosols | Grass, Arable & Forest | 4 | 8 | 5 | 7 |
| 2.Mälilla (Sweden) | 57.38<br>15.81 | Highest average temperature in Scandinavia | Inceptisols, Spodosols & Histosols | Grass, Arable & Forest | 3 | 3 | 3 | 5 |
| 3.Ljusdals (Sweden) | 61.83<br>16.04 | Northern limit of winter wheat (e.g. Triticum aestivum L.) | Inceptisols, Spodosols & Histosols | Grass, Arable & Forest | 2 | 3 | 1 | 4 |
| 4.Lulea/Boden (Sweden) | 65.58<br>22.15 | Northern limit of rye (Secale cereal L.) | Inceptisols, Spodosols & Histosols | Grass, Arable & Forest | 4 | 5 | 5 | 6 |
| 5.Yliäsjokisuu (Finland) | 67.34<br>23.82 | Southern limit of discontinuous permafrost | Histosols, Entisols & Gelisols | Grass & Forest | 6 | 8 | 5 | 10 |
| 6.Vuontisjärvi (Finland) | 68.43<br>23.98 | Northern limit of settled agricultural (grass production) | Histosols, Entisols & Gelisols | Grass & Forest | 0 | 5 | 1 | 5 |
| 7.Kautokeino (Norway) | 69.01<br>23.04 | Coldest average temperature in Scandinavia | Histosols, Entisols & Gelisols | Boreal forest | 4 | 5 | 3 | 5 |
| 8.Vardǿ (Norway) | 70.37<br>31.10 | Southern limit of continuous permafrost | Histosols, Entisols & Gelisols | Grass | 3 | 9 | 1 | 7 |

Table 2. Mean (± standard error) values for each parameter for each soil order, soil type, and organic matter type.

| | Parameter | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | n | OR | $C_{ox}$ | O/C | H/C | C/N | Ω | n | $\Delta H_c$ (MJ/kg) |
| Litter | 26 | 1.08 ± 0.01 | -0.23 ± 0.03 | 0.61 ± 0.01 | 1.53 ± 0.03 | 42 ± 4 | 1.93 ± 0.05 | 18 | 19.44 ± 0.54 |
| Soil | 46 | 1.07 ± 0.01 | -0.13 ± 0.04 | 0.71 ± 0.03 | 1.68 ± 0.05 | 29 ± 2 | 1.51 ± 0.06 | 15 | 19.39 ± 1.25 |
| Tree | 24 | 1.08 ± 0.004 | -0.29 ± 0.01 | 0.65 ± 0.01 | 1.62 ± 0.01 | 334 ± 29 | 1.77 ± 0.02 | 17 | 22.70 ± 1.05 |
| Herbaceous | 49 | 1.09 ± 0.004 | -0.29 ± 0.02 | 0.63 ± 0.01 | 1.63 ± 0.01 | 62 ± 15 | 1.75 ± 0.03 | 31 | 21.06 ± 0.42 |
| Mineral Soils | 20 | 1.09 ± 0.02 | -0.21 ± 0.06 | 0.77 ± 0.05 | 1.89 ± 0.09 | 23 ± 2 | 1.22 ± 0.07 | - | - |
| Organic Soils | 26 | 1.05 ± 0.01 | -0.08 ± 0.06 | 0.67 ± 0.03 | 1.52 ± 0.02 | 33 ± 3 | 1.74 ± 0.06 | 15 | 19.39 ± 1.25 |
| Gelisol | 9 | 1.06 ± 0.02 | -0.16 ± 0.10 | 0.63 ± 0.05 | 1.51 ± 0.04 | 35 ± 5 | 1.92 ± 0.10 | 4 | 20.72 ± 2.10 |
| Inceptisol | 7 | 1.10 ± 0.03 | -0.20 ± 0.11 | 0.83 ± 0.10 | 2.05 ± 0.15 | 15 ± 1 | 1.16 ± 0.11 | - | - |
| Histosol | 17 | 1.04 ± 0.02 | -0.03 ± 0.07 | 0.69 ± 0.03 | 1.52 ± 0.03 | 33 ± 4 | 1.64 ± 0.07 | 11 | 18.91 ± 1.55 |
| Spodosol | 13 | 1.09 ± 0.02 | -0.21 ± 0.08 | 0.73 ± 0.06 | 1.80 ± 0.10 | 27 ± 3 | 1.25 ± 0.09 | - | - |

Table 3. The proportion of the variance ($\omega^2$) explained by each factor and interaction. Significant ($p<0.05$) factors or interactions are highlighted in bold. Soil type refers to organic vs. mineral soil.

| Factor or interaction | df | OR | $C_{ox}$ | O/C | H/C | C/N | Ω | OR (relative to birch) |
|---|---|---|---|---|---|---|---|---|
| Location | 7 | **34** | **34** | 7 | 15 | 0 | 8 | **26** |
| Material Type | 3 | **35** | **35** | **49** | **20** | **97** | **62** | **25** |
| Soil Type | 1 | 1 | 1 | 7 | **31** | 0 | **15** | 2 |
| Location × Soil type | 7 | 5 | 5 | 0 | 0 | 0 | 0 | 5 |
| Material type × Soil type | 3 | **6** | **6** | 0 | 0 | 0 | 0 | **11** |
| Error | 123 | 18 | 18 | 38 | 34 | 3 | 15 | 29 |



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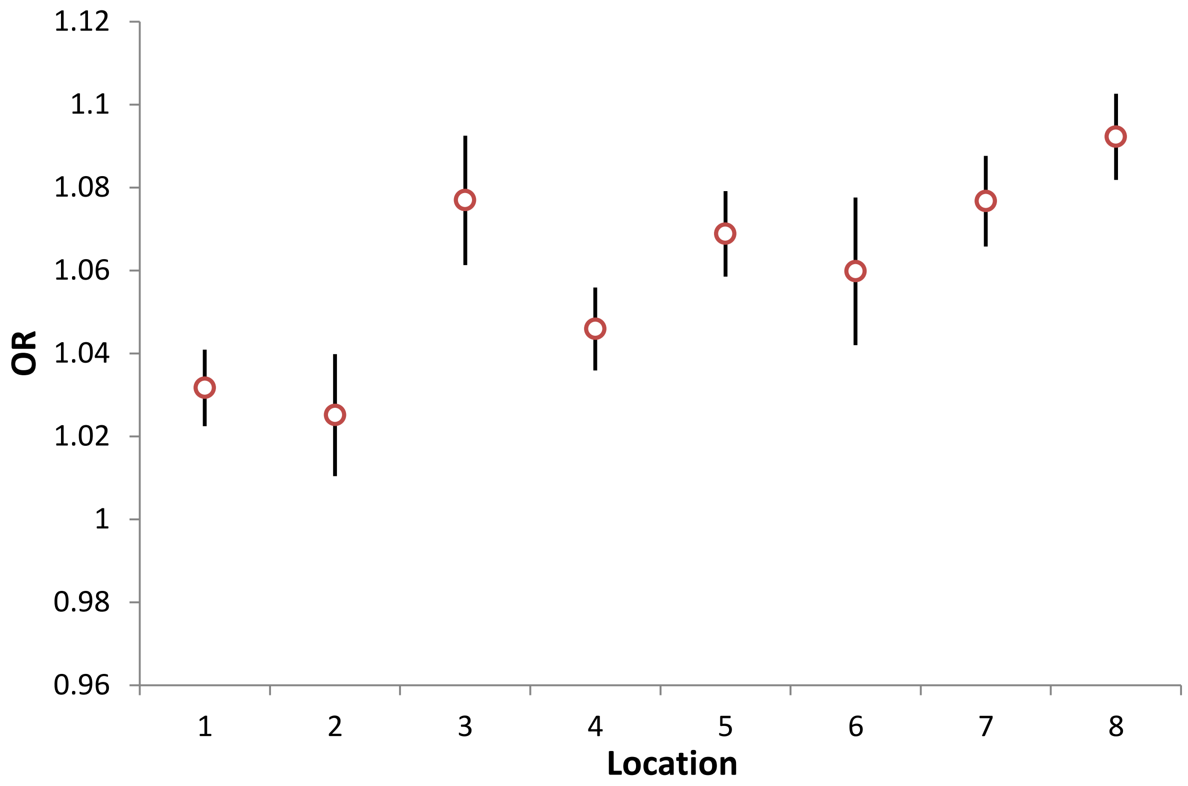

Figure 2. The least mean squares of the location factor with respect to OR. Location numbers are as in Table 1 and error bars are given as the standard error in the least squares mean.

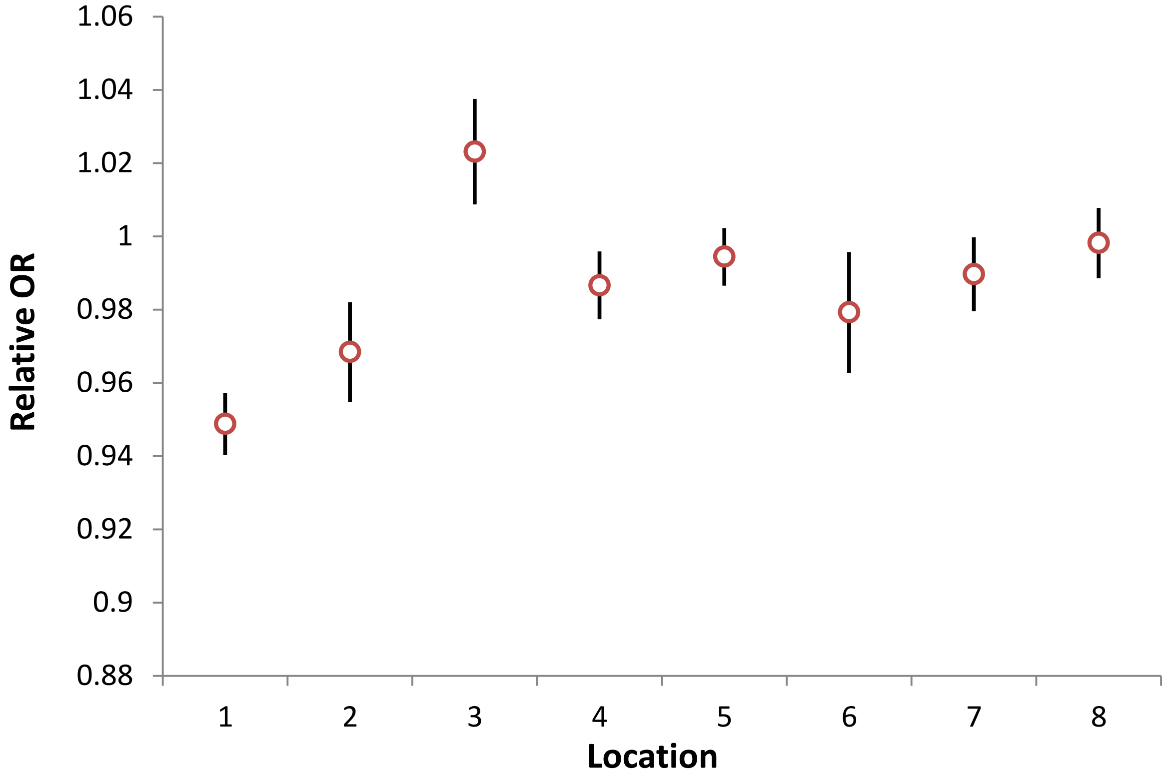

Figure 3. The least mean squares of the location factor with respect to OR when judged relative to a local birch sample. Location numbers are as in Table 1 and error bars are given as the standard error in the least squares mean.

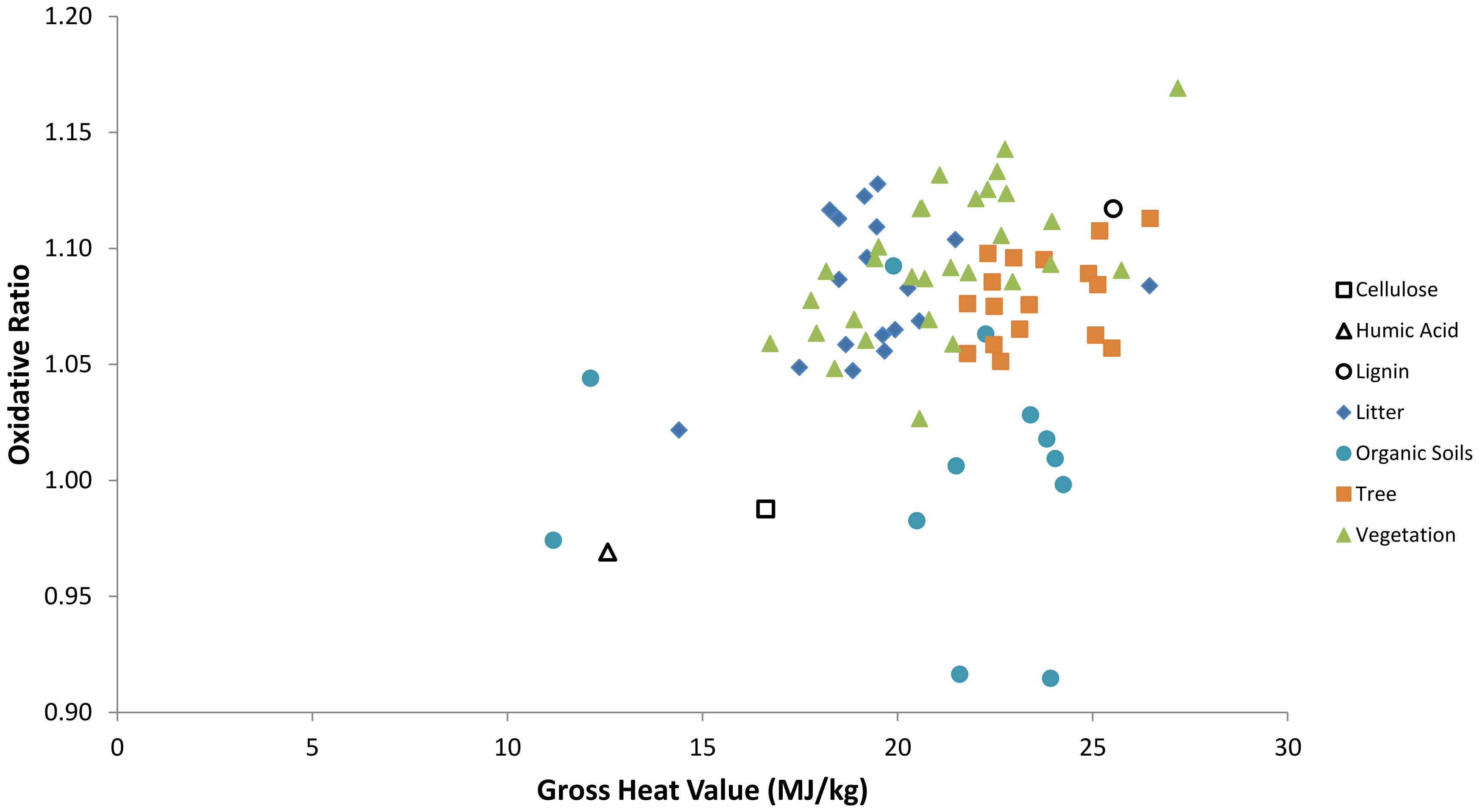

Figure 4. Plot of OR and $\Delta H_c$ values for herbaceous vegetation, trees, litter and soil . Standard materials (cellulose, lignin, and humic acid) are included for comparative purposes.