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Regional variation in the biogeochemical and physical characteristics of natural peatland pools

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Abstract

Natural open-water pools are a common feature of northern peatlands and are known to be an important source of atmospheric methane (CH_4). Pool environmental variables, particularly water chemistry, vegetation community and physical characteristics, have the potential to exert strong controls on carbon cycling in pools. A total of 66 peatland pools were studied across three regions of the UK (northern Scotland, south-west Scotland, and Northern Ireland). We found that within-region variability of pool water chemistry was low; however, for many pool variables measured there were significant differences between regions. PCA analysis showed that pools in SW Scotland were strongly associated with greater vegetative cover and shallower water depth which is likely to increase dissolved organic carbon (DOC) mineralisation rates, whereas pools in N Scotland were more open and deeper. Pool water DOC, particulate organic carbon and dissolved CH_4 concentrations were significantly different between regions. Pools in Northern Ireland had the highest concentrations of DOC (mean = 14.5 mg L^{-1}) and CH_4 (mean = $20.6 \mu\text{g C L}^{-1}$). Chloride and sulphate concentrations were significantly higher in the pools in N Scotland (mean values 26.3 and 2.40 mg L^{-1} , respectively) than elsewhere, due to a stronger marine influence. The ratio of UV absorbance at 465 nm to absorbance at 665 nm for pools in Northern Ireland indicated that DOC was sourced from poorly humified peat, potentially increasing the bioavailability and mineralisation of organic carbon in pools compared to the pools elsewhere. This study, which specifically aims to address a lack of basic biogeochemical knowledge about pool water chemistry, clearly shows that peatland pools are highly regionally variable. This is likely to be a reflection of significant regional-scale differences in peatland C cycling.

Key words: peatlands, pools, carbon, DOC, water chemistry, biogeochemistry, spatial distribution.

1. Introduction

Peatlands play a major role in moderating atmospheric CO₂ concentrations through their ability to sequester carbon, with northern peatlands alone storing an estimated 500-600 gigatonnes of carbon (Yu, 2012). Open-water pools are a common feature of many peatlands and have been reported on every continent except Antarctica (Glaser, 1998). They are prevalent in temperate and boreal peatlands of the northern hemisphere, often forming extensive complexes where their area may equal or exceed that of the intervening terrestrial area (Bragg and Tallis, 2001; Connolly et al., 2014). Pool areas are also rapidly expanding in a warming Arctic (Jorgenson et al., 2001; Vonk et al., in press; Walter et al., 2007), and they are becoming a more commonplace feature in peatlands undergoing restoration as drains are blocked (Parry et al., 2014). Pools have previously been shown to be sources of CO₂ to the atmosphere and, particularly, hotspots of methane (CH₄) emission, a highly potent greenhouse gas (GHG) (Hamilton et al., 1994; Pelletier et al., 2014; Waddington and Roulet, 1996). Thus, they play an important role in global radiative forcing (Abnizova et al., 2012). The degree to which pools are hotspots of CH₄ may be affected by their physical and chemical properties, but little is known about how such properties vary within and between peatlands.

There are a number of theories on peatland pool formation, but their presence is highly dependent on a combination of factors, including geology, topography, hydrology and climate (Belyea, 2007; Belyea and Lancaster, 2002; Comas et al., 2011; Couwenberg and Joosten, 2005). Pools in bogs (ombrotrophic peatlands) are characterised by low pH, low primary productivity and generally low macrophyte diversity (Lindsay, 1995). Bog water and nutrient sources are dominated by atmospheric deposition, being isolated from mineral groundwater sources. Therefore, bog pool water chemistry may not vary much spatially, except when driven by regional variation in precipitation chemistry. For example, remote bog pool systems located within the range of sea spray-derived deposition (e.g. Coastal British Columbia, western UK, Falkland Islands) have anion concentrations close to that of sea water (Gorham and Cragg, 1960; Proctor, 1992; Vitt et al., 1990), whereas sulphate

concentrations in bog pools within the atmospheric influence of heavy industry have been reported as being many times higher than those in more remote areas (Gorham, 1956; Proctor, 1992).

However, it is not clear whether peatland pool water chemistry may also be related to variability in other factors such as pool size or vegetation cover. Belyea and Lancaster (2002) have shown that although pools vary in size (< 10 m² to > 1000 m²) they have consistent size-shape relationships, with an increase in size over time associated with more elongate and convoluted pool shapes. This suggests that pool size could be used as a proxy for pool age or maturity, which may be an important factor in pool biochemical processes such as productivity.

Previous data on pool water chemistry have usually been reported within the context of another research focus, primarily during studies of peatland vegetation and associated physical and chemical gradients, for example in Japan (Haraguchi and Matsui, 1990), Canada (Vitt and Bayley, 1984, Vitt et al., 1990) and the UK (Pearsall, 1956). Other studies have focussed on chemical variability within the same site or region (e.g. Gorham, 1956; Hannigan and Kelly-Quinn, 2014; Kilroy et al., 2008). Some of the older studies may be outdated due to changing trends in atmospheric deposition over recent decades (Waldner et al., 2014). The widest study to date, in geographical terms, reports water chemistry from 39, mainly ombrogenous, sites across Britain and Ireland (Proctor, 1992). Although the author explored spatial variability and the study covered a relatively large geographical spread, no within-site replication was conducted, and carbon concentrations were not analysed. Therefore, it is unclear how variable bog pool water chemistry is and whether any variation could have implications for carbon cycling in ombrotrophic peatlands.

Pools may act as recipients for dissolved and particulate organic carbon (DOC and POC) in water which flows either through or over the surrounding peat into the pools. The source and, therefore, the composition of these compounds affect how they are mineralised both microbially and photochemically, with rates of mineralisation, in turn, affecting rates of CO₂ and CH₄ emissions from bog pools (Cory et al., 2007; Cory et al., 2014; Köhler et al., 2002). Although a limited number of

studies have reported the DOC concentrations and DOC composition in peatland/wetland pools (e.g. Bendell-Young, 2003; Billett and Moore, 2008; Hamilton et al., 1994; Hannigan and Kelly-Quinn, 2014; Pelletier et al., 2014), how these factors vary spatially has not been reported.

The mechanisms of CH₄ release to the atmosphere from water bodies are diffusion, ebullition, and plant-mediated transport, and pool vegetation is likely to play a significant role in pool C cycling. Plants containing aerenchymous tissue (e.g. *Eriophorum angustifolium*, *Menyanthes trifoliata*) are common in pools and transport CH₄ directly to the atmosphere (Bridgham et al., 2013), bypassing the zone of potential oxidation. Conversely, bryophytes such as the Sphagna, which can occur as floating mats on peatlands pools, have a mutualistic relationship with CH₄-oxidising bacteria (Putkinen et al., 2014) and may inhibit CH₄ emissions. Surface vegetation also alters the physical characteristics of the air-water interface, changing surface turbulence and open water area and hence influencing the net gas exchange rate. The influence of vegetation on emissions is likely to be strongly seasonal, and related to water depth, with deeper pools less able to support rooting plants. Bog pools are commonly quite shallow (< 1 m deep) (e.g. Abnizova et al., 2012; Belyea and Lancaster, 2002; McEnroe et al., 2009) but have been reported at up to 2 m depth (Pelletier et al., 2014). Belyea and Lancaster (2002) also found that pools often have asymmetric depth profiles, with over-deepening, or 'trench development' on the down-slope margin. The presence of alternative electron acceptors (e.g. nitrate, sulphate) in pool waters may also have a strong influence on the production and oxidation of CO₂ and CH₄ (Bridgham et al., 2013; Deutzmann and Schink, 2011; Smemo and Yavitt, 2011,).

While it is evident there has been some biogeochemical research on peatland bog pools, this has not been conducted systematically over large regions, and thus spatial variability of pool chemistry is poorly understood. Our study is a first step in addressing this research gap. We analysed a range of chemical variables, including dissolved carbon and GHG concentrations, pool depth and vegetation cover from 66 natural bog pools at six sites across north and southwest Scotland, and Northern

Ireland (latitudinal range 55° 00' – 58° 23' N). This represents the first analysis of both inter- and intra-site spatial heterogeneity in peatland pool systems of this magnitude. We hypothesize that the chemical composition of bog pools varies spatially, and that relationships exist between pool chemistry, physical parameters, and vegetation cover.

2. Methods

2.1 Study Sites

Natural pools ($n = 66$) were sampled at six peatland sites under the same temperate maritime climatic influence (Fig. 1, Table 1). The sites were selected to cover a wide geographical area within the distribution range of natural bog pools in the UK. All the pool complexes occupy a similar topographical setting within the surrounding peatland landscape: the pools are located on ombrotrophic plateaux with minimal slope ($< 1.75^\circ$ across the pool complex at all sites) and thus low hydraulic gradients (site maps created using Digimap [<http://digimap.edina.ac.uk/>] or Northern Ireland Environment Agency online maps [<http://maps.ehsni.gov.uk/MapView>] are available in Supplementary Material 1) Although all of the pools surveyed were contained within the peat matrix and did not contact the underlying geology, geological classifications are given to enhance site characterisation (Table 1) and were taken from the British Geological Survey (NERC, 2014). The sites were visited over a four week period (September - October 2013) so that comparisons reflect the same general conditions and were not confounded by seasonal factors. The UK climate is classified as temperate maritime, and ice cover of pools is generally limited to surface freezing for brief periods during the winter (i.e., days or weeks rather than the duration of the season). Climatic characteristics presented in Table 1 for each site are long-term averages (30 year: 1981 – 2010) taken from the weather station nearest the study site and sourced from the UK Met Office (www.metoffice.gov.uk). Regional antecedent precipitation over seven days prior to sampling ranged from 11 – 51 mm (UK Met Office).

Three pool complexes (Table 1) on near-natural peatlands were visited within the 'Flow Country' of northern Scotland, the largest blanket peatland in Europe (c. 4000 km²). The Cross Lochs and Loch Leir pool complexes are within the Forsinard nature reserve owned by the Royal Society for the Protection of Birds (RSPB). Pool vegetation is broadly limited to aquatic Sphagna (*Sphagnum cuspidatum* and *S. denticulatum*), *Eriophorum angustifolium*, and bog bean (*Menyanthes trifoliata*). Local terrestrial vegetation comprises a mosaic of typical blanket bog species, including *Sphagnum* mosses, (*S. papillosum*, *S. tenellum* *S. capillifolium*) sedges (*Eriophorum angustifolium*, *E. vaginatum*, *Trichophorum cespitosum*), ericaceous shrubs (*Calluna vulgaris*, *Erica tetralix*), sundews (*Drosera rotundifolia*, *D. intermedia* and *D. anglica*), bog asphodel (*Narthecium ossifragum*) and the locally common liverwort (*Pluerozia purpurea*). Distinct hummocks are commonly dominated by woolly fringe-moss (*Racomitrium lanuginosum*). The third Flow Country pool complex, Munsary, lies to the eastern side of Cross Lochs and Loch Leir. Whilst typical vegetation coverage is comparable to the two other Flow Country site, Munsary is notable for its population of marsh saxifrage (*Saxifraga hirculus*), a species in decline in the UK.

Two pool complexes were visited within the Silver Flowe (Table 1), a blanket peatland located in a glacial valley in Galloway, southwest Scotland. The site has a variable microtopography, with discrete areas of ridge-pool-hummock amongst non-patterned blanket bog. Pools are generally aligned along contours amid *S. capillifolium* hummocks and *S. papillosum* lawns. Pools and hollows are populated by *S. cuspidatum*, *E. angustifolium* and *M. trifoliata*. More detailed vegetation descriptions may be found in Boatman (1983). The pool complexes are located on near-natural peatland; however, shallow drains on areas without pools (the nearest being c.200 m from our study sites) were blocked in 2012 as part of peatland restoration work (Andrew Jarrott, pers. comm).

Two pool complexes were visited in County Antrim, Northern Ireland (Table 1). Slieveanorra, an upland raised bog forming part of the Slieveanorra and Croaghan Area of Special Scientific Interest (ASSI), is bordered by coniferous plantation but remains near-natural. Typical vegetation at the site

is a mix of dwarf shrubs *C. vulgaris* and *E. tetralix*, *Sphagna* characteristic of hummock and lawn microtopography including *S. capillifolium* and *S. magellanicum*, and frequent *E. vaginatum*, *T. cespitosum* and *N. ossifragum*. The Garron Plateau is one of the largest areas of near-natural upland blanket bog in northern Ireland, and forms the greater part of the Dungonnell Reservoir catchment area. Vegetation types are broadly similar to those found at Slieveanorra, though surrounding slopes are dominated by *Molinia caerulea*.

2.2 Water chemistry

A 500 mL water sample was collected from each pool approximately 10 cm below the water surface and 1 m from the pool edge for analysis of DOC, POC and DIC (dissolved inorganic carbon), total nitrogen (TN) and phosphorus (TP), and chloride, nitrate and sulphate. In the field a 2 mL subsample was passed through a 0.45 µm syringe filter (Avonchem SF-3020) for DOC analysis to minimise post-sampling mineralisation of DOC. All water samples were stored in the dark at ~4°C. Water temperature, pH (corrected to 20°C), dissolved oxygen, and electrical conductivity (EC) were recorded *in situ* using a handheld Hach-Lange HQ40D multi meter.

Dissolved CO₂ and CH₄ concentrations were calculated using the headspace technique (Dinsmore et al., 2013; Kling et al., 1991). A 40 mL water sample was equilibrated with 20 mL ambient air at pool temperature by shaking underwater for 1 minute. The equilibrated headspace was then transferred to a pre-evacuated 12 mL Exetainer® vial (Labco, Lampeter, UK). Headspace samples were analysed on a Hewlett Packard HP5890 Series II gas chromatograph (detection limits: CO₂ 7 ppmv; CH₄ 4 ppbv) with electron capture (ECD) and flame ionization detectors (with attached methaniser).

Concentrations of gases dissolved in the pool water were calculated from the headspace and ambient concentrations using Henry's Law (e.g. Hope et al., 1995).

DOC and DIC concentrations were determined using an Analytik Jena Multi N/C 2100S combustion Total Organic Carbon analyser (detection limit: 1.06 mg L⁻¹). To evaluate the composition of DOC, UV

absorption was measured on the 0.45 μm filtered samples using a Jasco V-630 UV-Vis spectrophotometer. Absorbance at 254 nm (A_{254} , units: m^{-1}), specific UV absorbance (SUVA_{254}) and the ratio of absorbance at 465 nm to absorbance at 665 nm (E_4/E_6) are reported. SUVA_{254} is defined as the ratio of A_{254} to DOC concentration (units: $\text{L mg C}^{-1} \text{m}^{-1}$) and has been reported as strongly positively correlated ($r^2 = 0.97$) with DOC aromaticity % (Weisshaar et al., 2003). Humic and fulvic acids are the two dominant components of DOC, and absorb light in different quantities at different wavelengths dependent on DOC composition (Grayson and Holden, 2012). Humic acids are more dominant in well-humified peats; therefore the E_4/E_6 ratio is commonly used as an indicator of the condition of the source peatland area from which the pool water is derived.

Subsamples of the main 500 mL pool water sample were filtered through 0.45 μm syringe filters for further chemical analyses. Chloride (Cl^-), nitrate (NO_3^-) and sulphate (SO_4^{2-}) concentrations were determined using a Dionex ICS-3000 Ion Chromatography System (detection limits: Cl^- 0.38 mg L^{-1} ; NO_3^- 0.24 mg L^{-1} ; SO_4^{2-} 0.11 mg L^{-1}). Non-marine SO_4^{2-} ($x\text{SO}_4^{2-}$) was determined using the following equation (Evans et al 2001):

$$xA = A - (R \times \text{Cl}) \quad (1),$$

where xA is the non-marine fraction of the total concentration of ion A in $\mu\text{eq L}^{-1}$, and R is the ratio of that ion to Cl^- in seawater (which is 0.104 for SO_4^{2-}). An assumption is made that all Cl^- is from a marine source. TN and TP were analysed by colorimetry using a Skalar San⁺⁺ Continuous Flow Analyzer (detection limits: TN 0.17 mg L^{-1} ; TP 0.02 mg L^{-1} , respectively). The remaining pool water samples (~450 mL) were filtered through pre-ashed, pre-weighed Whatman GF/F 0.7 μm filter papers for particulate organic carbon (POC) analysis, which was calculated using loss-on-ignition (Ball, 1964).

2.3 Physical characteristics and vegetation

The area and perimeter of each pool was calculated using Google Earth Pro where imagery was of sufficient quality, which was the case for all pools except seven from the Silver Flowe (SF9, SF15-SF18, SF20, and SF21). The dates of satellite imagery acquisition varied (2004 for CL and MU; 2005 for LL and SF; 2011 for SL and GP) and no account has been made for potential regional differences in water level (and thus, potentially, pool area) due to different imagery dates being associated with different antecedent hydrological conditions. A Shape Index (SI) (Moser et al., 2002) was used to explore pool shape complexity:

$$SI = \frac{P}{2\sqrt{\pi a}} \quad (2),$$

where P is the pool perimeter (m) and a is the pool area (m²). SI has no units and has the range ≥ 1 ; a circle has an SI value of 1, which increases with shape complexity.

Manual depth measurement can be problematic in peatland pools because basal sediments tend to be very soft; thus, identifying the ‘true’ base can be subjective. To standardise the measurements, a lightly weighted perforated disc was attached to the end of a 1 metre rule, which was suspended from an extendable pole able to reach the centre of all pools (cf. Belyea and Lancaster, 2002). The apparatus was lowered until it came to rest on the surface of the soft sediment without applying further pressure: any sediment penetration was thus consistent between measurements. Pool depth is presented as an average of ~15 depth measurements evenly spaced across the pool.

Vegetation cover included both submerged and emergent vegetation, and is limited to broad classifications: *Sphagnum*, *Eriophorum*, *Menyanthes*, and algae (which include algae and cyanobacteria). Cover was estimated using a modified version of the Braun-Blanquet cover-abundance scale, where: r = few individuals; + = sparsely present, cover <5%; 1 = plentiful, but cover <5%; 2 = very numerous, cover 5-25%; 3 = cover 25-50%; 4 = cover 50-75%; 5 = cover >75%.

Modifications amount to the removal of the ‘r’ class, and ‘+’ being assigned a value of 0.1 to enable

ordination analysis. The amount of open water on the pool surface (i.e. free of emergent or floating vegetation) was estimated visually in the field as a percentage.

2.4 Statistical analysis

Site data were grouped by region and Kruskal-Wallis tests used to detect significant differences between regional water chemistry because not all data were normally distributed. Mann-Whitney 'post-hoc' pairwise comparisons (sequential Bonferroni corrected p values) were used to identify which regions were significantly different from each other ($p < 0.05$). Hierarchical cluster analysis was performed on the full dataset minus the incomplete area, perimeter and SI data, using the `pvcust` (correlation matrix) package in R (R Core Team, 2013). The package assesses uncertainty for each cluster by calculating two types of p -value: Approximately Unbiased using multiscale bootstrap resampling, and Bootstrap Probability using normal bootstrapping. The AU p -value is considered a better approximation of the unbiased p -value (Suzuki and Shimodaira, 2006). Ordination of the full dataset was carried out in R using principal components analysis (PCA) with a correlation matrix. Correlation analysis combined with significance tests were performed using the `corrplot` package (Wei, 2013) in R (R Core team, 2013).

3. Results

3.1 Physical characteristics and vegetation

The pool complexes at all sites are located on flat ombrotrophic peatlands with < 2 m height variability across the sampling area. They are thus not subject to steep hydrological gradients. All sites contained permanent pools of varied sizes and shapes, including near-circular (e.g. Fig. 2B; SI = 1.18), highly convoluted (e.g. Fig. 2E; SI = 3.75), and linear (e.g. Fig. 2F; SI = 1.87). Figure 2 illustrates examples of typical pools within each site. Pool areas ranged from 4.1 – 1757 m² and perimeters from 8.19 – 725 m. Pool areas and perimeters were not significantly different between Flow Country and Silver Flowe pools; however, shape complexity (see Supplementary Material 2) was significantly

higher at Silver Flowe ($p < 0.05$) compared to the other two regions, though it should be noted that no shape data were available for 7 of the 22 pools at Silver Flowe (see above). Pools within the Northern Ireland sites were significantly smaller ($p < 0.05$) than the other two regions. Mean pool depths ranged between 10 and 60 cm (Table 2), with Silver Flowe pools significantly ($p < 0.05$) shallower than those of the other two regions.

Pool edges varied from near-vertical to gently-sloping which clearly influenced the vegetation present: gently sloping boundaries tended to support *Sphagnum* spp. and *Eriophorum angustifolium*. Gently sloping pool edges were more common in the linear and convoluted pools of Silver Flowe, although they were present in some pools at all sites. In general, there was a low diversity of vegetation in all pools. The only truly-emergent plant species was *Menyanthes trifoliata*, which was (based on Braun-Blanquet cover-abundance scale results; Supplementary Material 3) abundant in Flow Country pools, frequent at Silver Flowe, and absent from the pools surveyed in Northern Ireland. Although submerged algal matter was more frequent at pools in Northern Ireland and Silver Flowe, it was present throughout. Aquatic *Sphagnum* species were more common in Silver Flowe pools, and were often submerged rather than present as a floating mat. Sphagna at the sites in the Flow Country only tended to occur as small floating mats or at pool edges. Silver Flowe pools had a significantly ($p < 0.05$) lower proportion of open water than elsewhere (Table 2).

Sedimentary material was extremely loose in all pools, consisting of algae and algal debris, together with decomposed material from vegetation where present. Pool bases at Silver Flowe were notable for the abundance of allochthonous *Molinia caerulea* litter, blown into the pools from adjacent areas.

3.2 Water chemistry

The full range of DOC concentrations across all regions was 3.10 – 20.44 mg L⁻¹. DOC concentrations were comparable between the Flow Country and Northern Ireland sites, but significantly lower ($p <$

0.05) at Silver Flowe (Table 2). POC was generally $< 6 \text{ mg L}^{-1}$ at all sites, with the exception of three pools at Silver Flowe (SF8, SF19 and SF22), and significantly lower ($p < 0.05$) at pools in Northern Ireland than in the other two regions. A_{254} values reflect the pattern of DOC concentration between regions, with Silver Flowe pools having a significantly lower median value; however, $SUVA_{254}$ values were not significantly different. E_4/E_6 values for pools in Northern Ireland were significantly higher than for other regions, with five pools (SL7-SL10, and GP6) having values > 10 . All the pools were supersaturated in dissolved CO_2 and CH_4 relative to the atmosphere. The full ranges of $\text{CO}_2\text{-C}$ and $\text{CH}_4\text{-C}$ were $0.15 - 2.01 \text{ mg L}^{-1}$ and $0.19 - 93.0 \text{ } \mu\text{g L}^{-1}$, respectively. Dissolved CO_2 concentrations were not significantly different between regions, but there was a significant difference in CH_4 concentrations between the Silver Flowe and Northern Ireland pools (Table 2).

Concentrations of TN were generally $< 1 \text{ mg L}^{-1}$ with no significant differences between the regions (Table 2). TP concentrations were very low in all pools ($< 0.08 \text{ mg L}^{-1}$) and NO_3^- was below detection limits in nearly all the samples (hence data not presented). Both Cl^- and SO_4^{2-} concentrations were significantly ($p < 0.05$) higher in the Flow Country pools, which was also reflected in the EC values. Cl^- and SO_4^{2-} concentrations and EC were lowest at Silver Flowe. Non-marine derived sulphate ($x\text{SO}_4^{2-}$) values were consistently slightly negative for all regions. All pools were acidic, with median pH values of $4.30 - 4.44$ across the three regions.

The hierarchical cluster analysis of measured pool variables revealed that pools clustered into meaningful groups based on geographical region (Fig. 3). The Flow Country pools form one group (Group 1) that is distinct from all the pools from the other two regions. The majority of pools at Silver Flowe form two distinct groups (Groups 2 and 4), and these groups are more similar to the Northern Ireland pools than those in the Flow Country. There is a single outlier from the Silver Flowe (SF19) that shows no similarities to any other pool. The Northern Ireland pools also form two distinct groups (Groups 3 and 5), with only a single pool from Silver Flowe (SF1) grouping with the pools in

Group 3; however, Group 5 pools from Northern Ireland (containing pools from both Slieveanorra and Garron Plateau) cluster separately from Groups 2, 3 and 4.

PCA analysis (Fig.4) shows some distinct site and regional associations with water chemistry, physical characteristics and vegetation type. The first PCA axis is strongly associated with pool physical characteristics (open water and depth), vegetation type and Cl^- and SO_4^{2-} concentrations, and explains 27.3% of the variance. Pools from the Flow Country (pool codes CL, MU and LL) appear associated with greater pool depth, more open water and higher concentrations of SO_4^{2-} and Cl^- . These characteristics also appear to be associated with the presence of *Menyanthes trifoliata*. Conversely, some pools from Silver Flowe are associated with shallower water depths, and increased vegetative cover (SF1, SF7, SF9, SF10, SF16). PCA axis 2 accounted for a further 17.3% of the variance, and appears primarily to be a carbon compound related axis. Pools from Northern Ireland (codes SL and GP) are associated with higher values of A_{254} , SUVA_{254} , E_4/E_6 , CO_2 and CH_4 , whereas many of the Silver Flowe pools are associated with higher values of POC.

Regional and combined data correlations are shown in Fig.5. Strongly positive, statistically significant correlations were found between CO_2 and CH_4 , DOC and A_{254} in the Flow Country pools; however, these relationships were not observed elsewhere. A strongly inverse, statistically significant, relationship is observed between CO_2 and DO at both the Silver Flowe and Northern Ireland pools, although this relationship is not present at the Flow Country. Statistically significant correlations between CH_4 and proxy indicators of DOC composition are seen at Flow Country pools (A_{254}) and Northern Ireland pools (SUVA_{254}). The only correlative relationship for CH_4 at the Silver Flowe is a strongly inverse one with SO_4^{2-} . The combined data set (Fig.3: All) indicates weak but significant correlations between CO_2 and A_{254} , SUVA_{254} , and CH_4 , and between CH_4 and DOC, A_{254} and SUVA_{254} .

4. Discussion

To our knowledge, this study has provided the first detailed insight into regional variation in physical and chemical properties of bog pools. The 66 pools sampled during this study are all located within active blanket and raised bogs with typical peatland vegetation in a similar cool, wet climate.

Unsurprisingly, there are some clear broad similarities in these systems: all the pools are relatively shallow (in comparison to larger water bodies), they are acidic and oligotrophic. However, there are also some significant specific differences in the water chemistry between regions that have implications for biogeochemical processes and carbon cycling.

The full ranges of $\text{CO}_2\text{-C}$ and $\text{CH}_4\text{-C}$ in this study ($0.15 - 2.01 \text{ mg L}^{-1}$ and $0.19 - 93.0 \text{ } \mu\text{g L}^{-1}$ respectively) were at the lower end of the ranges reported for pools and small lakes in peatlands in Quebec and Ontario, Canada, and Western Siberia: $0.3 - 16 \text{ mg CO}_2\text{-C L}^{-1}$ and $0.4 - 766 \text{ } \mu\text{g CH}_4\text{-C L}^{-1}$ (Hamilton et al., 1994; Pelletier et al., 2014; Repo et al., 2007). Mean pool dissolved CO_2 and CH_4 concentrations in this study (Table 2) were also within the range of those reported from peatland streams in Scotland: $1.05 - 6.83 \text{ mg CO}_2\text{-C L}^{-1}$ and $4.81 - 28.88 \text{ } \mu\text{g CH}_4\text{-C L}^{-1}$ (Dinsmore et al., 2013; Hope et al., 2001). The range of DOC concentration values in this study are comparable to those from pools in other areas of the world: for example, $16.7 - 21.4 \text{ mg L}^{-1}$ at Baie Comeau, Quebec (Pelletier et al., 2014), $\sim 25.0 \text{ mg L}^{-1}$ in open pools at Mer Bleue, Canada (Billett and Moore, 2008), $\sim 2 - 30 \text{ mg L}^{-1}$ at Bealey Spur, New Zealand (Kilroy et al., 2008), and $1.04 - 5.0 \text{ mg L}^{-1}$ in pools at Kinosheo Bog, Hudson Bay Lowlands (Hamilton et al., 1994). DOC concentrations in this study are also within the range of ($\sim 2 - 40 \text{ mg L}^{-1}$) those found in streams draining peatland sites in the UK (Billett et al., 2006; Billett et al., 2007; Clark et al., 2008) and Finland (Dinsmore et al., 2011). Therefore, in terms of carbon concentrations, the pools in this study could be considered broadly similar to other peatland hydrological systems. It should be noted, however, that many of the values quoted from other studies above cover longer time-scales and likely include some seasonal variation.

A major pathway of CH₄ and CO₂ flux from peatland pools is gaseous diffusion and in the case of CH₄, ebullition. Degassing at the water-air interface is primarily driven by the concentration gradient and physical boundary layer conditions. McEnroe et al. (2009) found a link between pool surface area and depth and GHG fluxes in peatland pools in Canada. Average CH₄ and CO₂ fluxes generally decreased with depth, and were up to five times higher in small, shallow pools (<1000 m², <45 cm depth) than larger and deeper pools (>1000 m², >70 cm). This was attributed to possible increased decomposition in shallow pools, as substrate availability, temperature and DO decrease with depth, though the study makes no mention of vegetative cover. This may suggest that older, larger pools approach a biogeochemical equilibrium. Strong positive relationships have been reported between dissolved CO₂ and DOC, with inputs of allochthonous C driving dissolved CO₂ concentrations (Hope et al., 1996). However, inverse relationships between dissolved CO₂ and DO in small lakes and ponds have also been observed (e.g. Kortelainen et al., 2006; Roulet et al., 1997). Strong negative correlations between CO₂ and DO are evident in our study at Silver Flowe and Northern Ireland pools, whereas a positive relationship between CO₂ and DOC is apparent at Flow Country pools (Fig.3), suggesting that different factors are driving CO₂ saturation and in situ organic C processing between regions. Although DOC and CO₂ (and CH₄) plot on the secondary PCA axis (Fig.4), they are weakly related to increasing depth and open water on axis 1. Depth and open water are not significantly different between Flow Country and Northern Ireland pools (Table.2); however, pool area and perimeter are significantly higher at Flow Country pools, suggesting that a greater source area of allochthonous C (in the form of DOC and dissolved CO₂) from the surrounding terrestrial peat pore water may be driving CO₂ concentration in Flow Country pools. Area and perimeter are not significantly different at Silver Flowe pools in comparison to the Flow Country; however, the pools at Silver Flowe are significantly shallower than those of the other regions. In shallow pools a greater proportion of the pool water will be in contact with the sediment layer. As noted in the observations of pool character, the pools at the Silver Flowe contained *Molinia* litter blown into the pools from the surrounding area, which may provide an additional source of allochthonous C. Respiration has

been shown to be an important driver of CO₂ in small lakes and ponds, particularly in shallow waters with abundant organic material present such as leaf litter (Holgerson, 2015), resulting in CO₂ supersaturation and lower O₂ concentrations.

Because the pools at Silver Flowe are significantly shallower than the other two regions, a higher concentration of dissolved CH₄ (often used to derive CH₄ flux using the thin boundary layer technique) may reasonably be expected (McEnroe et al., 2009; Pelletier et al., 2014). However, higher concentrations of dissolved CH₄ were not found at Silver Flowe; these pools were most associated with vegetative cover, particularly *Sphagnum* mosses, some species of which have been shown to have a mutualistic relationship with *Sphagnum*-associated methanotrophs (Basiliko et al., 2004; Putkinen et al., 2014). Thus, it is possible that the *Sphagna* present (which were frequently submerged at the time of sampling) in the Silver Flowe pools are contributing to CH₄ oxidation within the water column. Alternatively, the shallower water depth in these pools may promote better mixing of the water and thus aeration, allowing for greater methanotrophic bacterial activity and thus CH₄ oxidation within the water column.

The highest concentrations of dissolved CH₄ in this study were found in Northern Ireland, where some of the deepest pools were located. A positive correlation between CH₄ efflux and temperature has been previously reported by several authors (e.g. Hope et al., 2001; Olefeldt et al., 2013). There was no significant difference in mean water temperature between Silver Flowe and Northern Ireland pools at the time of sampling, therefore, the higher CH₄ concentrations in the Northern Ireland sites may be simply because they were sampled at different times, albeit within the same four week period (e.g. Billett and Moore, 2008), but without longer-term data we are unable to test this.

CO₂ flux from inland waters to the atmosphere is significant at the global scale, which can be derived directly from the surrounding peat (Garnett et al., 2012), and mineralisation of allochthonous DOC (Koehler et al., 2014). The mineralisation of DOC occurs via two mechanisms – photochemical degradation and microbial respiration – the relative proportions of which are determined by DOC

composition. Photochemical mineralisation rates of DOC are highly dependent on local factors: solar irradiance, depth, water residence time, water absorption, and the concentration and composition of DOC (Vähätalo et al., 2000). Most photochemical breakdown of DOC occurs in the top 10 cm of the water column and decreases exponentially with depth (Vähätalo et al., 2000); however, solar radiation also increases bacterial metabolic mineralisation of organic carbon (Vähätalo et al., 2003). Thus in shallower pools, such as those found at Silver Flowe, it can be expected that a greater proportion of DOC is rapidly mineralised photochemically than in deeper pools, depending on the composition of DOC. On an individual site basis, only Munsary in the Flow Country showed a strong significant relationship between DOC concentration and $\text{CO}_{2\text{diss}}$ (Pearson $r = 0.935$, $p < 0.05$: Fig.5), suggesting a relationship between pool organic carbon concentrations and mineralisation.

SUVA_{254} is strongly correlated with DOC aromaticity, and the values for the pools in this study indicate aromaticity of approximately 20 – 30% (Weishaar et al., 2003). More highly aromatic DOC has also been reported as less bioavailable (Olefeldt et al., 2013). DOC concentrations and A_{254} values in the Silver Flowe pools were significantly lower than the other two regions; however, the SUVA_{254} values were not, which could indicate that a higher proportion of the DOC at Silver Flower is composed of colourless non-humic carbon. Non-humic carbon has been reported as more bioavailable (Wallage et al., 2006), but is potentially mineralised at a slower rate by microbial processes in comparison to photochemical processes (Koehler et al., 2014).

The pools in Northern Ireland have significantly higher E_4/E_6 values than the other two regions. According to Thurman (1985), an E_4/E_6 ratio of 2 to 5 indicates DOC derived from well-humified peat, whereas a ratio of 8 to 10 indicates dominance of less-humified fulvic acid. This convention has been applied to depth-related organic carbon studies where surface peat was found to be higher in fulvic acids and corresponding higher E_4/E_6 values than deeper horizons (Gondar et al., 2005). The higher E_4/E_6 values in the Northern Ireland pools suggested that the DOC was sourced from less-humified peat, which may also indicate depth-wise variation in peat hydraulic conductivity (K) between

regions. High K in deeper peat could potentially lead to old carbon in the form of DOC entering pools via seepage (Beckwith et al., 2003, Holden and Burt, 2003). It is also possible that the pools at the two Scottish study areas have greater connectivity to natural peat pipes (macropores >10 mm) that could potentially supply DOC from deeper peat (Billett et al., 2012). The source of DOC has implications for the mineralisation potential of the DOC (higher aromaticity being more photochemically available) and the long-term carbon cycle (processing of old carbon).

Perhaps the clearest differences in water chemistry between the regions are in the concentrations of anions in the pools in the Flow Country region. There are significant differences in mean concentrations of sulphate and chloride between all three regions. Cl^- concentrations are around three times higher and SO_4^{2-} concentrations an order of magnitude higher in the Flow Country pools, compared to other regions. This likely reflects their location and exposure to prevailing weather systems resulting in greater inputs of sea salt. The negative values for $x\text{SO}_4^{2-}$ (non-marine sulphate) in pool waters from all regions is probably due to an imbalance in the expected ratios of marine-derived Cl^- to SO_4^{2-} , because of the relative higher mobility of Cl^- and retention of S in peat (Evans et al., 2011), coupled with the expected low concentrations of $x\text{SO}_4^{2-}$ at the study sites (Fowler et al., 2005). However, analysis of rainfall SO_4^{2-} and $x\text{SO}_4^{2-}$ from UK Air Quality monitoring sites shows variability of both concentrations and proportions of sulphate; for example, data from the Forsinain weather station (located between the CL and LL sites, Flow Country) show SO_4^{2-} and $x\text{SO}_4^{2-}$ concentrations ranged between 0.54 – 6.0 and 0 – 2.74 mg L^{-1} , respectively, over the period 2009 – 2012. Rain water chemistry is subject to cycles in marine inputs, such as decadal fluctuation of the North Atlantic Oscillation (Evans et al., 2001). Therefore, establishing whether peatland pool anion chemistry reflects atmospheric variability, or if pools act as ‘buffers’ to atmospheric deposition over time, is important and requires further work

Sulphate is a CH_4 electron acceptor that competes with methanogenic archaea for acetate and hydrogen, thus elevated concentrations may stimulate sulphate reduction and suppress

methanogenesis (Artz, 2009; Lovley and Klug, 1983). Concentrations of 5.76 – 28.8 mg L⁻¹ SO₄²⁻ have been found to be sufficient to stimulate SO₄²⁻ reduction (Lovley and Klug, 1983; Wieder et al., 1990). The full range of SO₄²⁻ concentrations at the Flow Country pools was 1.47 – 3.73 mg L⁻¹ which could facilitate increased metabolism of acetate and hydrogen via sulphate reduction over methanogenesis; however, our results show no relationships between dissolved CH₄ and SO₄²⁻ at the Flow Country pools (Figs.4 and 5). In fact, only the Silver Flowe pools show a significant inverse relationship with SO₄²⁻ (Fig.5). This is where some of the lowest anion concentrations were found, suggesting that controls on both CO₂ and CH₄ dynamics are more strongly linked to factors regulating terrestrial organic C content in the pools.

In summary, peatland pools remain understudied compared to terrestrial peatland microforms, and their role in peatland ecosystem scale C dynamics is not well understood. Our results are important for the understanding of carbon cycling in peatlands as the area of open water increases in many peatlands due to i) a warming Arctic climate, and ii) the creation of artificial pools during peatland restoration processes. New, shallow, artificial pools may function chemically in a similar way to the shallow pools reported here, processing DOC sourced from surrounding peat and from sediments at a faster rate than older, deeper pools that have reached biogeochemical 'equilibrium'. Although sulphate may act as an alternative methane electron acceptor, our results indicate that concentrations of both CH₄ and CO₂ are more associated with factors regulating allochthonous carbon. Whether this is merely correlation (higher C influx results in higher GHG concentrations), or causation (respiration and photochemical mineralisation processes), is a different question altogether. Regardless, this is evidence that CO₂ and CH₄ concentrations in pools, whether from soil or in situ sources, may not be as strongly regulated by marine salt influences as previously thought. More detailed process based work, particularly focussing on temporal variability is required to fully understand the controls on CH₄ dynamics in pools.

Conclusions

This study has presented a 'snapshot' of the chemical characteristics of peatland pools from three regions of the UK, and has highlighted the complex nature of biogeochemical cycles operating within peatland pools, with variability evident even at a regional scale. We found that some components in the chemical composition of pools vary spatially in relation to proximity to a marine environment, with greater concentrations of chloride and sulphate in pools in geographic proximity to the coast. Pools located in eastern Northern Ireland had the lowest anion concentrations. Pools in the Flow Country of northern Scotland had elevated SO_4^{2-} concentrations compared to other sites. Despite a potential methane suppression effect reported elsewhere in the literature, we found no relationship between CH_4 and SO_4^{2-} concentrations. GHG concentrations were more associated with DOC composition (and potentially respiration). We also found relationships between pool chemistry, physical parameters, and vegetation cover. Shallower pools with greater vegetative cover tended to have lower dissolved CH_4 concentrations, and this is attributed to *Sphagnum*-associated methanotrophy, and greater oxidation in the water column owing to increased mixing. Shallow pools also had a lower concentration of DOC, most likely because a greater proportion of the pool volume is available to photochemically-induced mineralisation processes.

Overall, our work strongly suggests that while inter-site variability of pool water chemistry is high, intra-site variability is low. Thus, while further large-scale pool water chemistry assessments are required, it may be possible to quickly characterise pool water chemistry at individual sites using a relatively small number of pools, particularly if the pools can be characterised and deemed representative of the site based on their physical features. However, the large inter-region variability means that peatland pool water chemistry values that are determined in one region should not be assumed to be representative of other regions. Further work is required to explore variability over longer time scales, and to understand the controls on the variability of peatland pool water chemistry and (most importantly) what role they have in peatland carbon cycling.

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Figures and tables

Fig.1 Location of the study sites.

Fig.2 Example of pools at each site: A) Cross Lochs, N Scotland; B) Loch Leir, N Scotland; C) Munsary, N Scotland; D) Slieveanorra, Northern Ireland; E) Garron Plateau, Northern Ireland; F) Silver Flowe, SW Scotland.

Fig.3 Cluster dendrogram of all measured chemical variables. *P* values (%) for Approximately Unbiased (AU) multiscale bootstrap resampling are shown in red, and *P* values for Bootstrap Probability (BP) normal bootstrapping are shown in green.

Fig.4 PCA analysis showing all measured variables and samples (see Table 1 for explanation of pool codes). DO = dissolved oxygen; EC = electrical conductivity; OW = percent open water.

Fig.5 Correlation matrix with colour-keyed correlation coefficients and significance tests (uncrossed circles indicate significant $p < 0.05$ relationships).

Table 1. Site characteristics

Table 2. Mean values (± 1 standard deviation) of all measured and calculated variables. Superscript letters denote where significant differences were found (Kruskall-Wallis followed by Mann-Whitney posthoc tests). Sites are different where they share no common letters. *Sample size; $n = 15$ for area, perimeter, and shape index

Supplementary files:

SM1 Site maps

SM2 Plots of Shape Index

SM3 Vegetation summary plot

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Table 1: Site characteristics

Region	Meteorological averages (1981-2010)	Site name	Location (Lat, long)	Elevation (m asl)	Geology	Pool codes
Flow Country, N Scotland	Mean daily (MDT) temperatures:	Cross Lochs (CL)	58° 22' N 03° 57' W	211	Migmatitic pelite and semipelite, Moine Supergroup	CL1 to CL6
	Max = 11.7°C	Loch Lier (LL)	58° 23' N 03° 46' W	185	Strath Halladale granite	LL1 to LL6
	Min = 3.6°C	Munsary (MU)	58° 23' N 03°20' W	105	Devonian siltstones, mudstones and sandstone, Lybster Flagstone Formation	MU1 to MU6
SW Scotland	Total annual precipitation = 1196 mm					
	MDT max = 12.8°C	Silver Flowe (SF)	55° 07' N 04° 24' W	280	Granite, Loch Doon pluton	SF1 to SF22
Northern Ireland	MDT min = 5.8°C					
	Precipitation = 1120 mm	Slieveanorra (SL)	55° 05' N 06° 11' W	307	Psammite and pelite, Southern Highland Group (part of the Dalradian Supergroup)	SL1 to SL15
	MDT max = 11.5°C	Garron Plateau (GP)	55° 00' N 06° 04' W	337	Tertiary age mafic lava and mafic tuff	GP1 to GP11
	MDT min = 5.7°C					
	Precipitation = 1313 mm					

Table 2: Mean values (± 1 standard deviation) of all measured and calculated variables. Superscript letters denote where significant differences were found (Kruskall-Wallis followed by Mann-Whitney post hoc tests). Sites are different where they share no common letters. *Sample size; $n = 15$ for area, perimeter, and shape index.

	Flow Country	Silver Flowe	Northern Ireland
Sample size (n)	18	22*	26
Pool depth (cm)	36.7 ^a (± 9.8)	28.9 ^b (± 5.2)	39.2 ^a (± 9.7)
Area (m ²)	304 ^a (± 486.6)	98 ^a (± 123.5)	27.4 ^b (± 28.9)
Perimeter (m)	113 ^a (± 173.0)	81 ^a (± 89.9)	32.7 ^b (± 30.5)
Shape Index	1.72 ^a (± 0.89)	2.22 ^b (± 0.93)	1.70 ^a (± 0.64)
Open water (%)	87.61 ^a (± 20.3)	66.32 ^b (± 23.8)	84.96 ^a (± 18.06)
pH	4.43 ^a (± 0.17)	4.32 ^b (± 0.17)	4.36 ^{ab} (± 0.13)
Water temperature °C	13.2 ^a (± 0.89)	9.0 ^b (± 1.85)	9.6 ^b (± 0.64)
EC ($\mu\text{S cm}^{-1}$)	103.4 ^a (± 8.9)	15.1 ^b (± 2.2)	46.9 ^c (± 6.0)
DO (mg L ⁻¹)	9.38 ^a (± 1.27)	11.04 ^b (± 0.73)	10.70 ^b (± 0.51)
DOC (mg L ⁻¹)	13.58 ^a (± 4.58)	6.74 ^b (± 2.02)	14.54 ^a (± 3.12)
POC (mg L ⁻¹)	2.26 ^a (± 1.28)	3.56 ^a (± 4.72)	1.03 ^b (± 0.49)
Abs ₂₅₄ (m ⁻¹)	36.5 ^a (± 20.4)	18.7 ^b (± 5.8)	50.5 ^a (± 14.9)
SUVA ₂₅₄ (L mg C ⁻¹ m ⁻¹)	2.81 (± 1.52)	3.10 (± 1.55)	3.53 (± 1.02)
E ₄ /E ₆ ratio	5.89 ^a (± 1.44)	5.76 ^a (± 1.53)	7.93 ^b (± 1.70)
CO ₂ -C (mg L ⁻¹)	0.67 (± 0.33)	0.56 (± 0.40)	0.73 (± 0.39)
CH ₄ -C ($\mu\text{g L}^{-1}$)	14.29 ^{ab} (± 14.25)	6.71 ^b (± 7.74)	20.61 ^a (± 20.18)
TN (mg L ⁻¹)	0.70 (± 0.18)	0.81 (± 0.44)	0.72 (± 0.17)
Cl ⁻ (mg L ⁻¹)	26.35 ^a (± 4.35)	5.53 ^b (± 0.49)	8.06 ^c (± 0.57)
SO ₄ ²⁻ (mg L ⁻¹)	2.40 ^a (± 0.67)	0.35 ^b (± 0.11)	0.86 ^c (± 0.10)



Flow
Country

2

1

3

Northern
Ireland

6

5

4

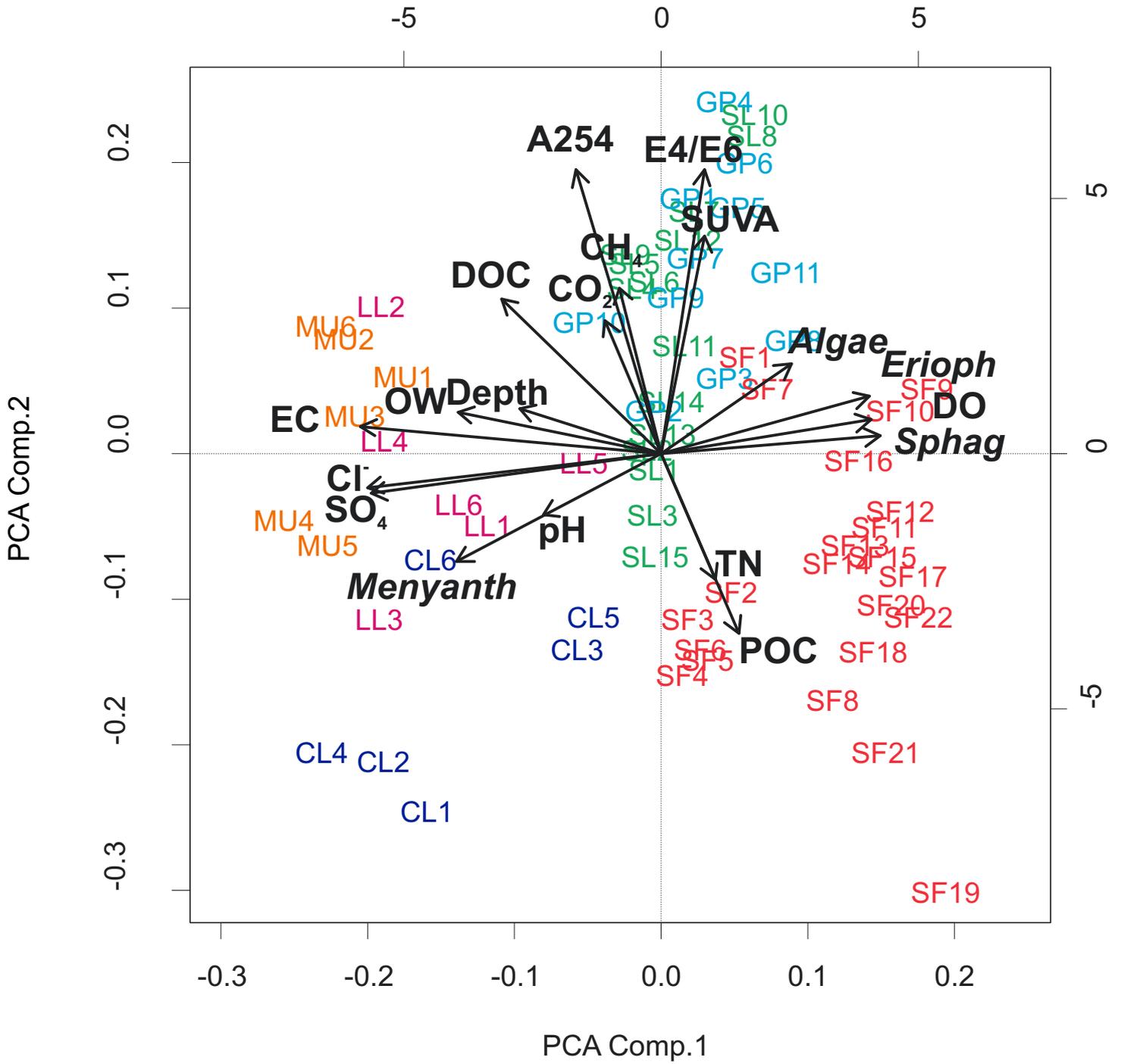
Silver
Flowe

Legend

1. Cross Lochs
2. Loch Leir
3. Munsary
4. Silver Flowe
5. Slieveanorra
6. Garron Plateau









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