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Relationships between reservoir water quality and catchment habitat type

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Abstract

Numerous catchment characteristics including topography, geology, soil and vegetation are reported to exert a strong influence on mean surface water properties. The present study employs a geographical information system (GIS) approach to examine, for the first time, the relationship between reservoir water quality (dissolved organic carbon (DOC) concentration, colour, nitrate concentration and pH) and catchment Phase 1 Habitat coverage. Analysis was conducted on 2 occasions and at 2 different spatial scales. Numerous statistically significant correlations were identified, suggesting the use of Phase 1 Habitat data could help improve predictive models of surface water quality. The occurrence and strength of correlations varied seasonally in response, we argue, to temporal variations in hydrological regime and anthropogenic activity. The data also suggest that the proximity of habitat types to the reservoir is significant in affecting reservoir water quality. The findings are used to recommend suitable measures for drinking water companies to mitigate against water quality issues.

Key words: dissolved organic carbon; drinking water; catchment; Phase 1 Habitat; soil; geographical information system.

1. Introduction

The biogeochemical properties of surface waters are acquired, to a large extent, during the passage of water through the catchment due to the interaction of water with vegetation, soils and mineral layers. Various organic and inorganic compounds will be solubilised and transported downstream during runoff, influencing solute concentrations, pH and ionic strength (Stutter et al., 2006). Although surface water quality exhibits temporal variations in response to weather events and seasonal drivers (Gergel et al., 1999; Scott et al., 1998; Soulsby et al., 2006), physical catchment characteristics including topography, geology, soil and vegetation type will, to a large extent, determine mean biogeochemical characteristics (Billett and Cresser, 1992; Clair et al., 1994; Holden et al., 2007; Hope et al., 1994; Sobek et al., 2007). Amongst these variables, soil type is widely considered to represent a dominant control on surface water composition and quality (Aitkenhead et al., 1999; Billett and Cresser, 1992; Hope et al., 1997; Soulsby et al., 2006; Stutter et al., 2006). Though its development is strongly influenced by other catchment features including soil characteristics, habitat type may also be an important factor affecting surface water quality. Vegetation type influences catchment hydrology, primary production and organic matter inputs (Ordóñez et al., 2008; Zhang et al., 2011), which affect soil composition and chemistry and in turn, drainage water quality. Forested catchments for example, have been associated with the production of dissolved organic carbon (DOC)-rich drainage waters (Grayson et al., 2012; Hope et al., 1994) with differences in DOC concentration and flux also reported between different tree species (Chow et al., 2009; Fröberg et al., 2011; Gough et al., 2012). Wetland habitat coverage is also reported to be a strong predictor of surface water DOC concentration (Gergel et al., 1999; Hope et al., 1994).

Surface water characteristics can also be strongly affected by anthropogenic activity. For example, the application of agricultural fertilisers has been associated with significant leaching of nutrients (nitrates and phosphates) into surface waters (Badruzzaman et al., 2012). Elevated nutrient concentrations may in turn result in eutrophication and algal blooms (Correll, 1998; Freeman et al., 2009; Hecky and Kilham, 1988; Vollenweider, 1968), which are particularly problematic in drinking water supplies (Smith, 1998). Liming of agricultural land has been associated with increased surface water pH (Hindar et al., 2003). Drainage of wetland habitats in an attempt to improve their economic value has also been linked to elevated colour and DOC concentrations in surface waters (Holden et al., 2004; Wallage et al., 2006).

The Phase 1 Habitat Survey of Wales, completed by the Countryside Council of Wales (CCW) in 1997, provides a record of habitat coverage and land use (Howe et al., 2005). In its digitised form, using geographical information system (GIS) software, the data offers a useful means of measuring the spatial extent of different habitat types within catchments. Since the classification scheme includes both natural habitats and anthropogenic features (e.g. arable land and improved grassland), the data holds significant potential for researchers concerned with investigating catchment influences on surface water quality. The characteristics of surface waters supplying drinking water treatment works (WTWs) is important for water companies which have a responsibility to provide a safe and reliable drinking water supply for their customers. The concentration of DOC in surface waters is particularly important, with the removal of DOC from drinking water supplies representing the single biggest treatment cost for the water treatment industry (Watts et al., 2001). Elevated DOC concentrations in raw water can inflate treatment costs by increasing the coagulant and disinfectant doses required (Chow et al., 2005; Edzwald, 1993) and the frequency of filter backwashes (Eikebrokk et al., 2004). DOC in finished water is problematic since it can cause undesirable colour, odour and taste (Davies et al., 2004; WHO, 2011), transports organic and inorganic micro-pollutants (Gao et al., 1998; Rothwell et al., 2007) and leads to bacterial regrowth in distribution systems (Prévost et al., 1998). Crucially, DOC also acts as a precursor to potentially harmful disinfection by-products (DBPs) including trihalomethanes (THMs). These are formed during chlorination, a treatment necessary to ensure that finished water meets microbiological safety standards (WHO, 2011).

Rising surface water DOC concentrations have been observed in many areas of central and northern Europe and North America in the past couple of decades (Freeman et al., 2001; Hejzlar et al., 2003; Monteith et al., 2007; Skjelkvåle et al., 2005; Stoddard et al., 2003; Worrall et al., 2003). In the UK, measurements undertaken at 22 upland sites showed a mean increase in DOC concentration of 91% between 1988 and 2003 (Evans et al., 2005). DOC concentrations tend to be highest, and rising most rapidly in peat-dominated, upland catchments (Freeman et al., 2001), which in the UK, supply over 70% of drinking water (Watts et al., 2001). In this context of declining surface water quality, developing a better understanding of catchment influences is crucial for the drinking water industry. The importance of catchment characteristics in affecting the quality of drinking water supplies is recognised by the UK drinking water regulator, the drinking water inspectorate (DWI) who recommend that *"catchment and raw water source protection"* is included in the drinking water safety plans of drinking water providers (DWI, 2005).

A GIS approach, which can offer an effective means of visualising and measuring landscape features is increasingly being used in the study of catchment influences on hydrochemistry. GIS software has become an important tool in the modelling of hydrological processes and its use in developing predictive models for various water quality parameters within catchments based on land use and other catchment characteristics is particularly relevant for water treatment companies. For example Foster and McDonald (2000) used GIS and spatially referenced data on pastoral farming intensity to model and display sources of cryptosporidium risk in drinking water catchments. Lake et al. (2003) developed a nitrate leaching model using GIS and information on a number of physical catchment characteristics. This was used to identify areas of groundwater vulnerable to nitrate pollution. Recently, Grayson et al. (2012) used a GIS approach, and ITE land cover data (similar to Phase 1 Habitat data) to identify correlations between drinking water reservoir colour and the spatial extent of different land cover classes. A multicriteria evaluation approach was then used to develop a predictive model for water colour production potential in the catchments and create a colorimetric, risk-based map from the data. However, as yet, the use of Phase 1 Habitat data for predicting catchment water quality has not been explored.

This study investigates potential relationships between Phase 1 Habitat classes and reservoir water quality (DOC concentration, colour, nitrate concentration and pH). GIS mapping was used to measure the spatial extent of Phase 1 Habitat types in 16 drinking water reservoir catchments in north Wales. Correlation analysis was then used to identify statistically significant relationships between these land cover classes and reservoir water quality in spring and autumn. Analyses were carried out both at a whole-catchment scale, and in a 250 m buffer zone surrounding the reservoirs in order to assess the importance of proximity in the occurrence and strength of the correlations. Such research is important for informing future catchment management practices. Identifying problematic land cover will also help water treatment companies target monitoring programmes and mitigation strategies, and improved understanding of seasonality in raw water quality will also enable better optimization of treatment processes.

2. Methods

2.1. Study sites and sampling regime

Water samples were collected on 2 occasions (in September 2007 and March 2008) from the raw water (i.e. pre-treatment) supply of 16 WTWs in north Wales. Where the raw water supply was derived from more than 1 reservoir, composite samples were collected, and Phase 1 Habitat data was also combined. The timing of sampling was chosen to correspond with the seasonal maximum (autumn) and minimum (spring) in reservoir DOC concentration. 14 of the WTWs included in this study are located in upland catchments, with the remaining 2 situated in lowland, agricultural areas. Uplands are defined as areas more than 250 m above sea level (Mitchell, 1991). These areas are typically characterised by high rainfall, low mean temperatures and acidic soils (Foster and McDonald, 2000).

2.2. Hydrochemical analysis

pH was measured on un-filtered samples using a Mettler Toledo S20 pH meter (Mettler Toledo, Leicester, UK), calibrated daily with pH 4 and pH 7 reference standards (Sigma-Aldrich, Dorset, UK).

Colour measurements (Hazen) were obtained from WTW data at the time of sample collection. One degree Hazen (1 mg L^{-1} Pt/Co) is defined as the colour produced by 1 mg L^{-1} Pt (as K_2PtCl_6) in the presence of 2 mg L^{-1} cobalt (II) chloride hexahydrate (Mitchell and McDonald, 1992).

Before DOC measurement, samples were passed through a 0.45 µm cellulose acetate filter to remove particulate organic carbon, as per the operational definition of DOC (Thurman, 1985). DOC concentrations were determined using a Shimadzu Total Organic Carbon 5000 analyser (Shimadzu, Milton Keynes, UK), with a carrier gas of high purity air at a flow rate of 150 mL min^{-1} and a 33 µL injection volume. Calibration was performed with a one point calibration, using a 100 mg L^{-1} $KO_4H_5C_8$ solution (total organic carbon – TOC) and a 100 mg L^{-1} Na_2CO_3/100 mg L^{-1} $NaHCO_3$ solution (inorganic carbon – IC). DOC concentrations were calculated by subtracting IC values from TOC values. Analysis of TOC and IC standard solutions at 10 mg L^{-1} intervals demonstrated that the analyser performed linearly from 0 to 200 mg L^{-1}, with r^2 values > 0.9. All reagents were supplied by Sigma-Aldrich, Dorset, UK.

Nitrate concentration was determined using a Dionex DX-120 ion chromatograph equipped with an IonPac AS14A anion analytical column (both Thermo Scientific, Hertfordshire, UK). The eluent was a 1.0 mM Na_2HCO_3/8.0 mM $NaCO_3$ solution (reagents supplied by Sigma-Aldrich, Dorset, UK) made with Milli Q water and the flow rate, 1 mL min^{-1}. Concentrations were determined using a five point calibration with standard Dionex solutions.

2.3. Geographical information systems (GIS) analysis

Version 9.2 of the ArcGIS package (ESRI, Buckinghamshire, UK) was used to display and quantify the spatial extent of habitat types within each reservoir catchment. First, the watersheds associated with each reservoir were mapped. This was achieved using the *Hydrology* functions in the *Spatial Analyst* extension and a digital elevation model downloaded from Digimap (EDINA, 2014) (10 m resolution). Defined watersheds were then clipped to other GIS layers displaying habitat type. Habitat information was displayed using digitised version of the Phase 1 Habitat Survey of Wales (Howe et al., 2005). In addition to this whole-catchment analysis, habitat coverage was also measured in a 250 m-wide zone around the perimeter of each reservoir.

2.4. Statistical analysis

For statistical analysis, Phase 1 Habitat categories were organized into more generalised groupings (Table 1). Statistical analysis was performed using version 20 of the SPSS statistical package (IBM, New York, USA). Depending on the conditions satisfied by the data, Pearson's correlation and Spearman's correlation analyses was employed to test for significant correlations between Phase 1 habitat type coverage and reservoir water quality. This analysis was also performed using the subset of Phase 1 Habitat data covering a zone of 250 m directly adjacent to the reservoir.

3. Results and discussion

3.1. DOC and colour

The absence of any statistically significant correlations between catchment woodland and scrub coverage and reservoir DOC concentration and colour (Table 2 and 3) is surprising given that previous research indicates a strong positive relationship between forest coverage and DOC concentration (Grayson et al., 2012; Hope et al., 1994). High DOC flux from forested catchments is partly due to high DOC loading as rainwater passes through above ground biomass (Kawasaki et al., 2005; Stevens et al., 1989) as well as the large source of leachable carbon in the litter layer (Hongve, 1999). However, DOC concentrations are also reported to vary significantly between different tree species (Gough et al., 2012). Our habitat categories did not account for this potential variation, which may explain the absence of any statistically significant correlations in this study.

A moderate negative correlation was observed between unimproved grassland and spring DOC concentration at the whole catchment scale ($p < 0.05$; Table 2) and no correlations between unimproved grassland and DOC or colour in the 250 m buffer zone analysis (Table 3). The negative correlation corroborates the findings of previous studies. For example, Grayson et al. (2012) report a significant negative correlation between water colour and moorland grass coverage across 18 drinking water catchments in Yorkshire. In a UK-wide study, Armstrong et al. (2007) found that heather dominated, drained catchments produced the highest water colour followed by mixed vegetation and grass dominated catchments. Van den Berg et al. (2012) also reported lowest mean pore water DOC concentration in grassland sites compared with other vegetation categories (woodlands, heathlands and moorlands) in their survey of 41 UK sites. This association may relate to solubility controls since colour release in temperate grasslands is reported to be suppressed by acidic conditions (Hopkins et al., 1990; Miller, 2008). However, our unimproved grassland category included neutral and calcareous grassland and no correlations were identified in the present study between pH and unimproved grassland coverage.

Negative correlations were identified between tall herb and fern habitat coverage and autumn DOC concentration and colour at the whole catchment scale (both $p < 0.05$; Table 2) and between tall herb and fern coverage and autumn colour in the 250 m buffer zone analysis ($p < 0.05$; Table 3). At first this result seems unexpected since bracken coverage, which was dominant in this habitat class, has been associated with high primary productivity and the accumulation of large amounts of litter, forming a large pool of organic matter (Marrs et al., 2000). However, Potthast et al. (2012) observed that, compared with pasture land (Setaria grass) the litter present in bracken habitat showed a significantly lower rate of decay. In addition, they found a significant decrease in microbial biomass and activity when pasture land was invaded by bracken. Therefore, if bracken coverage tends to replace improved grassland habitats in drinking water catchments, its presence may reduce DOC production. The occurrence of these correlations in autumn may relate to this being the litter fall period, when the leaching of DOC from decomposing litter would normally contribute significantly to DOC export (Kalbitz et al., 2000).

Negative correlations between heathland coverage and DOC concentration and colour occurred at both spatial scales. In the whole catchment analysis, heathland coverage displayed a moderate negative correlation with autumn DOC concentration and colour (both $p < 0.05$) and a strong negative correlation with spring colour ($p < 0.01$; Table 2). In the 250 m buffer analysis a moderate negative correlation was identified with autumn DOC concentration and colour (both $p < 0.05$), a moderate negative correlation with spring DOC concentration ($p < 0.05$) and a strong negative correlation with spring colour ($p < 0.01$; Table 3). These negative relationships were surprising given that *Calluna*, a common species in heath habitats, has been reported to produce highly-coloured drainage water (Grayson et al., 2012). This has been attributed to their relatively dry soil conditions which confer high rates of aerobic microbial decomposition (Clutterbuck and Yallop, 2010). Many heath habitats were also formed as a result of peatland drainage. This former status is likely to further enhance DOC and colour release due to the large carbon stocks associated with peat substrate (Fenner et al., 2009). Conversely however, moisture constraints in heath habitats are reported to inhibit phenol oxidase activity (Toberman et al., 2008). According to the enzymic latch theory, this can suppress DOC production by causing an accumulation of phenolic compounds which inhibit the activity of hydrolase enzymes (Freeman et al., 2001). This may explain the negative correlations between heathland coverage and reservoir DOC concentration and colour observed in the present study. Overall, the relationship appeared stronger at the 250 m buffer scale, suggesting that proximity to the reservoir affected the degree to which this habitat influenced reservoir water quality.

At the whole catchment scale a moderate positive correlation was identified between fen/ mire habitat and autumn DOC concentration ($p < 0.05$; Table 2). This habitat also correlated positively with autumn and spring DOC concentration in the 250 m buffer analysis (both $p < 0.05$; Table 3).

Positive correlations between swamp coverage and reservoir DOC concentration and colour were also identified and were striking in terms of the strength of the correlations observed and their occurrence at both spatial scales and both sampling times (Table 2 and 3); all were strong positive correlations ($p < 0.01$) except for the swamp/ autumn DOC concentration correlation at the whole catchment scale which was a moderate positive trend ($p < 0.05$). These positive relationships are likely to be linked to the wetland status of these habitats. Percentage wetland coverage has been identified as an important predictor of stream water DOC concentration (Eckhardt and Moore, 1990; Gergel et al., 1999; Hope et al., 1994). A combination of high primary productivity and low decomposition rates causes the accumulation of deep layers of peat in wetland environments (Mitsch and Gosselink, 2000). The considerable depth of organic material in such environments provides a large pool of available carbon (Thurman, 1985) and the inhibitory effect of anaerobic conditions on microbial metabolism promotes the formation of DOC end products (Fenner et al., 2009). In addition, in wetland systems, the depth of the organic horizon limits contact between drainage waters and the adsorption sites within the mineral soil horizon, which also contributes to high DOC loading (Tipping et al., 1999). However, our data also show an absence of statistically significant correlations between DOC concentration/ colour and other habitat categories which are, or include, wetlands (marsh/ marshy grassland, bog, flush and spring). This suggests that the type of wetland present may be an important determinant of drainage water DOC concentration. It may be significant that, of these wetland habitat types, swamp and fen/ mire habitats tend to be more nutrient-rich than the other wetland habitats (Mitsch and Gosselink, 2000) which may support higher rates of primary productivity and thus a larger pool of organic carbon.

Strong positive correlations between arable coverage and DOC concentration were observed at the whole catchment scale in autumn and spring (both $p < 0.01$; Table 2). Moderate positive correlations were also identified with colour at both sampling times (both $p < 0.05$). The 250 m buffer zone could not be included in this analysis since there was only 1 catchment where arable land was present in this zone (Figure 1). The interpretation of these positive correlations is not straightforward since in previous studies arable land use has been associated with lower carbon content than other land use types. For example, soil solution carbon concentrations for soils in northern Saskatchewan, Canada, decreased in the following order: aspen forest > recently cleared forest > wheat/ fallow field (McFee and Kelly, 1995). Similarly, in their review article, Chantigny (2003) reports that dissolved organic matter concentrations vary as follows: forest soils > grassland soils > arable soils. This variation, it is suggested, is partly due to differences in vegetation type (e.g. tree vs. herbaceous plant) (Chantigny, 2003) as well as the lower carbon content associated with arable soils (Zsolnay, 1996). In addition, aerobic conditions, which tend to occur in arable soils encourage the complete mineralisation of organic matter to CO_2, as opposed to DOC and CO_2 end products in anaerobic decomposition (Boddy et al., 2008; Fenner et al., 2009). However, water soluble carbon content in arable soils is also reported to vary depending on crop plants used (Zsolnay, 1996) and temporally, during crop cycles (Campbell et al., 1999) and with successive cultivations (Delprat et al., 1997). In addition, application of organic fertilisers on agricultural soils is reported to substantially increase the concentration of soluble organic carbon (Gregorich et al., 1998). Although it is not possible to isolate the cause of the positive correlations observed here between arable land use and DOC concentration/ colour, it is notable that the correlations occurred despite this land use being virtually absent in the reservoir 250 m buffer zone.

At the whole catchment scale moderate positive correlations were identified between buildings coverage and autumn DOC concentration ($p < 0.05$) and between the “other” category and autumn DOC concentration ($p < 0.05$) and spring colour ($p < 0.05$; Table 2). A moderate positive correlation was also found between buildings coverage and autumn DOC concentration in the 250 m buffer zone analysis ($p < 0.05$; Table 3). Given the rural location of the catchments in the present study it is likely that farm buildings will account for a significant proportion of the buildings category. Indeed, a strong positive correlation between buildings and arable coverage was identified in the whole catchment data ($r_s = 0.803$, $p < 0.01$). This correlation may therefore explain the relationship between buildings and DOC concentration, though the reason for this being confined to the autumn analysis is unclear. The correlations between the “other” category and DOC concentration and colour at the whole catchment scale are also difficult to interpret since this category includes unknown habitat classes (“not accessed” land and “illegible” data inputs). It may be significant however, that bare ground (J.4; Table 1) is included in this category, which may provide a source of readily-leachable organic matter.

3.2. Nitrate and pH

Strong positive correlations were observed between arable coverage and nitrate concentration in the whole catchment analysis in autumn and spring (both $p < 0.01$; Table 2). This is likely to be caused by the leaching of organic or inorganic fertiliser (Neill, 1989). The stronger correlation in the spring analysis may be due to the timing of fertiliser application, which for arable crops tends to occur in late winter/spring (MAFF, 2000; Trudgill et al., 1991). As mentioned earlier, the 250 m buffer zone could not be included in the analysis due to there being only 1 catchment where arable was present in this zone. It is interesting therefore that strong correlations exist at the whole catchment scale despite arable coverage being virtually absent in the 250 m buffer zone. The application of fertiliser may also explain the strong positive correlations between improved grassland coverage and nitrate concentration in both the whole catchment analysis ($p < 0.01$ in autumn and spring; Table 2), and the 250 m buffer zone analysis ($p < 0.05$ and $p < 0.01$ in autumn and spring, respectively; Table 3). Again, stronger correlations in the spring analysis at both spatial scales are likely to be due to the timing of fertiliser application. The strong positive correlations between woodland and scrub coverage and spring nitrate concentrations at both spatial scales (both $p < 0.01$; Table 2 and 3) may be explained by the application of fertiliser prior to tree planting in commercial forestry plantations (Drinan et al., 2013).

Moderate positive correlations were identified between fen/ mire coverage and reservoir nitrate concentration in spring sampling at the whole catchment scale ($p < 0.05$; Table 2) and in both autumn and spring in the 250 m buffer analysis (both $p < 0.05$; Table 3). These correlations are likely to relate to the nutrient status of this habitat; fen systems are typically associated with relatively high nutrient concentrations due to their being supplied by drainage water from surrounding mineral soil (Mitsch and Gosselink, 2000).

The positive correlation between buildings and nitrate concentration at the whole catchment scale in spring ($p < 0.05$; Table 2) may be due to the positive correlation mentioned earlier between buildings and arable coverage. In addition, the urine and droppings of mammals and birds has been identified as an important non-agricultural source of ammonia (DEFRA, 2002). Nitrifying bacteria in the soil may then convert ammonia to nitrate. Therefore, assuming that a significant proportion of the buildings in this category are farms, then the leaching of ammonia from domestic animals may also account for this correlation. The leaching of nitrates from septic tanks and fertiliser stores may also explain this association.

A moderate positive correlation was observed between marsh/ marshy grassland coverage and reservoir nitrate concentration but only in the 250 m buffer analysis in spring ($p < 0.05$; Table 3). The reason for this is not clear but may be an artefact of the positive association between marsh/ marshy grassland and other habitat types displaying a positive correlation with nitrate. For example, in the 250 m buffer zone analysis, marsh/ marshy grassland coverage correlates positively with woodland and scrub ($r_s = 0.646$, $p < 0.01$), improved grassland ($r_s = 0.771$, $p < 0.01$) and fen/ mire habitat ($r_s = 0.560$, $p < 0.05$), all of which show a positive correlation with spring nitrate concentration at this spatial scale.

The supply of nitrate and phosphate is critical in determining the growth rates of phytoplankton in freshwater systems with elevated concentrations resulting in eutrophication in some cases (Hecky and Kilham, 1988). In drinking water sources algal blooms can lead to a number of treatment issues including taste and odour problems, elevated TOC levels, increased coagulant and chlorine demand, membrane fouling and an increase in DBPs (Bernhardt et al., 1991; Li et al., 2012; Nguyen et al., 2005). Elevated reservoir nitrate concentrations may also increase the formation of nitrogenous

DBPs (NDBPs), produced during the disinfection stage of water treatment either directly, or indirectly *via* increased algal biomass and consequently increased concentrations of dissolved organic nitrogen in the raw water (Ritson et al., 2014).

The negative correlation between heathland coverage and reservoir pH in the 250 m buffer analysis ($p < 0.05$; Table 3) is likely to be related to the preference of heath vegetation for acidic soils (Holden et al., 2007) which has a corresponding effect on drainage water pH (Cresser and Edwards, 1987). A positive relationship has been reported between DOC solubility and pH (Lumsdon et al., 2005). Thus solubility controls may also help to explain the negative correlations between heathland coverage and reservoir DOC concentration and colour.

The absence of correlations between pH and some of the other habitat types which tend to be associated with peat substrates (bare peat, bog, fen/ mire, flush and spring and swamp) is surprising given that peatlands tend to produce acidic drainage waters. This is reported to result from the accumulation of organic acids, the enhanced activity of sulphur-metabolising bacteria under waterlogged conditions and high cation exchange capacity (Clymo, 1964; Urban et al., 1995). Coniferous forest stands, which represent a large proportion of forest coverage in north Wales, are also associated with acidic drainage waters (Eisalou et al., 2013; Gough et al., 2012). A significant decrease in pH has been reported as rainwater passes through coniferous canopies and litter (Eisalou et al., 2013), due to the high exchangeable acidity of coniferous foliage and litter and the fact that coniferous litter is readily leached of organic acids (Alfredsson et al., 1998; Nykvist, 1963).

3.3. Temporal and spatial variations in correlations

At the whole catchment scale, more associations between Phase 1 Habitat categories and DOC concentration were identified in autumn than in spring. A difference in hydrological regime due to higher rainfall in September than March may explain this contrast. Higher rainfall will result in a larger contribution of surface runoff to discharge water (Horton, 1933) which is likely to enhance the influence of surface characteristics such as vegetation/ litter characteristics. The influence of habitat may also be enhanced by higher above ground biomass following the growing season.

Overall there were fewer statistically significant correlations identified between habitat types and reservoir nitrate concentration in autumn compared with spring (Table 2 and 3). We have already suggested that fertiliser application may be significant in explaining a number of correlations between habitat type and reservoir nitrate concentration (Neill, 1989), and that its timing may explain the greater number and strength of correlations in spring (MAFF, 2000; Trudgill et al., 1991). However, the drivers of seasonal variations in surface water nitrate concentration are known to be complex, comprising numerous biogeochemical and hydrological processes (Martin et al., 2004). Stream nitrate concentrations tend to exhibit a summer minima and a winter maxima (Neill, 1989; Reynolds et al., 1992). This is explained in part by variations in the supply of nitrogen. For example, in the summer, the availability of leachable nitrate in the soil is limited by lower atmospheric inputs and plant uptake and in streams by macrophyte uptake (Cooke and Cooper, 1988) and denitrification (Hill, 1979). In winter on the other hand, plant uptake decreases, atmospheric inputs increase and in-stream losses decrease due to lower primary productivity (Reynolds et al., 1992). Surface water nitrate levels may also be transport-limited, with a strong association reported with precipitation and discharge (Neill, 1989; Trudgill et al., 1991). However, given that lower rainfall totals were recorded in March than in September, it is more likely that reservoir nitrate levels in spring (which were higher than in autumn), were supply-limited.

It is difficult to interpret the overall effect of spatial scale on relationships between habitat classes and reservoir water quality since at the 250 m buffer scale, a number of habitat classes are present in only a few catchments, or are absent altogether. For example, there was only 1 catchment where arable land was identified in the 250 m buffer zone. However, there was an obvious similarity in the occurrence of significant correlations at the 2 spatial scales. Although there was no clear difference in the strength of the correlations between the 2 spatial scales, this similarity would suggest that

Phase 1 Habitat coverage in the 250 m buffer zone was more important than in the wider catchment in affecting reservoir water quality. Previous studies have reported improved regressions between land use and surface water quality parameters when the riparian area was included, or weighted more heavily than other areas (Levine and Jones, 1990; Osborne and Wiley, 1988).

The relationship between reservoir water quality and catchment characteristics at different spatial scales may also vary temporally. For example, Gergel et al. (1999), in their study of wetland influence on DOC concentrations in Wisconsin lakes and rivers, found that in autumn, wetland coverage in the whole catchment was the best predictor of lake water DOC concentration whereas in summer, wetland coverage within 50 m of lakes was the best predictor. This could relate to seasonal hydrological changes since the timing of sampling in autumn and spring corresponded with base flow and peak flow conditions, respectively (Hurley et al., 1995).

In this study we noted the absence of a number correlations between Phase 1 Habitat classes and surface water parameters that would typically be expected. For example the lack of positive correlations between woodland and scrub habitat and a number of wetland habitats and DOC concentration/ colour was unexpected. This may be due to the influence of various other catchment features not included in the present study, but which previous studies have reported to influence surface water chemistry. For example, slope will mediate the relationship between catchment characteristics and surface water quality due to its influence on surface runoff (Rochelle et al., 1989) as well as being a predictor of soil organic horizon depth (Rasmussen et al., 1989) and wetland abundance (Eckhardt and Moore, 1990). The development of a particular soil type reflects a number of factors including climate, parent material, topography and vegetation and is reported to be a crucial factor in determining surface water composition and quality (Aitkenhead et al., 1999; Billett and Cresser, 1992; Hope et al., 1997). Indeed information on soil chemical characteristics has formed the basis of a number of predictive models for stream water solute concentrations (Billett and Cresser, 1992; Christophersen and Wright, 1981; Cosby et al., 1985). Soil type influences spatial patterns of water flow and storage (Grayson and Western, 2001; Weiler and Naef, 2003). In addition, adsorption processes in mineral soils regulate the transport of organic carbon and the soil organic pool is reported to be the main factor controlling DOC flux in streams (Aitkenhead et al., 1999). It should also be noted that the topographic watershed does not necessarily correspond with groundwater influence, which may also strongly impact on reservoir water quality (Garrison et al., 1987). In addition, the Phase 1 Habitat Survey of Wales was conducted between 1987 and 1997 and it is likely that a number of land use changes have occurred in this time (Stevens et al., 2004). Nonetheless, the present study has demonstrated that the data continues to be relevant to the study of surface water quality and the extent of its coverage represents a significant benefit for drinking water companies.

Various processes occurring in the water body will also affect surface water chemistry. For example, as mentioned earlier, seasonal variations in the uptake of nitrate in surface waters influence nitrate concentrations (Cooke and Cooper, 1988). DOC loss from reservoirs is reported to occur as a result of sedimentation and mineralisation processes (Algesten et al., 2004), with precipitation also affecting DOC concentrations *via* a dilution effect (Engstrom, 1987). Conversely, DOC may be produced within the water body (autochthonous DOC), potentially supressing the relationship between DOC concentration and colour and terrestrial drivers. Nonetheless, a substantial number of correlations were identified between Phase 1 Habitat data and reservoir water characteristics in the present study. This, we suggest, relates both to the direct influence of vegetation/ land cover on runoff and drainage water quality and also to habitat classes being predictors of other physical characteristics such as peat soils or certain management practices.

3.4. Implications for potable water treatment

Though previous research has cited the relationship between catchment wetland coverage and surface water DOC and colour loading (Eckhardt and Moore, 1990; Gergel et al., 1999; Hope et al., 1994), our data suggest that wetland type may significantly affect the magnitude of this relationship.

The identification of positive associations between swamp and, to a lesser extent, fen/ mire habitats and DOC concentration/ colour, possibly the result of their nutrient supply (Mitsch and Gosselink, 2000), may justify monitoring the quality of drainage waters in these areas. Given that these habitat types also occupy very small proportions of the catchments included in this study (Figure 2), it may be that diverting drainage water from these areas would be a cost-effective strategy for improving reservoir water quality. Monitoring of drainage waters and diversion of water courses may also be appropriate for areas of arable land use which arguably exerted the strongest influence on surface water quality. This land use class correlated with DOC, colour and nitrate concentrations at both sampling times despite being virtually absent from the 250 m buffer zone of the reservoirs. The apparent impact of arable land on reservoir water quality highlights the importance of excluding this activity from areas close to the reservoir. In cases where the diversion of problematic drainage waters is not possible, it may be appropriate to blend reservoir water with water from another catchment, as has been employed previously as a strategy to reduce water discolouration from peat (Grayson et al., 2012).

Allowing the expansion of habitat types whose coverage correlates negatively with DOC/ colour may be a suitable strategy in some cases. However, the potential benefits to surface water quality may be outweighed by other detrimental impacts. For example, tall herb and fern coverage, which in the present study was dominated by bracken, correlates negatively with DOC and colour but bracken habitat has no economic value and is associated with the leaching of carcinogenic compounds such as ptaquiloside (Rasmussen et al., 2003). Heathland coverage also correlated negatively with DOC concentration and colour in the present study, but this we argue, may relate to site-specific factors such as soil moisture constraints since *Calluna* vegetation is typically associated with highly-coloured waters (Grayson et al., 2012).

Given the number of statistically significant correlations identified in the present study, and the national scale of Phase 1 Habitat data, we suggest that future research should explore integrating

Phase 1 Habitat data into predictive models for reservoir water quality. The present study has also highlights the fact that correlations between catchment characteristics and surface water quality may vary on a seasonal basis; an important consideration as researchers seek to develop more sophisticated predictive models.

4. Conclusions

This study has considered, for the first time, the use of catchment Phase 1 Habitat data for predicting reservoir water quality. Our analysis was conducted at two different spatial and temporal scales, to investigate the effect of season and the proximity of habitat types to the reservoir in affecting potential associations between habitat type and water quality parameters.

Numerous statistically significant correlations were observed between Phase 1 Habitat classes and reservoir water quality. These could be explained either by the direct impact of vegetation on drainage water or its association with other physical catchment characteristics or land management practices. Arable land cover appeared to have the most substantial impact on reservoir water quality, correlating strongly with DOC concentration, colour and nitrate concentration at both sampling times. This was despite arable land being virtually absent from the 250 m buffer zone.

The degree to which habitat classes affected reservoir water quality appeared to vary on a seasonal basis, with more correlations between habitat classes and DOC concentration in autumn, and between habitat classes and nitrate concentration in spring. However, a striking similarity was observed between correlations at the whole catchment scale and within the 250 m buffer zone. We therefore suggest that in general, the influence of habitat coverage on reservoir water quality parameters increases with proximity to the reservoir.

Although previous research has identified a link between wetland abundance and surface water DOC/ colour loading, our findings suggest that the type of wetland habitat present is also important. We found that swamp and fen/ mire habitats were the only wetland types which correlated with reservoir DOC or colour. This specificity, we suggest, may relate to the high nutrient levels in these habitats which may support higher rates of primary production than other wetland types.

Based on the number and strength of correlations observed, we suggest that predictive models for surface water characteristics based on catchment characteristics could be improved by incorporating Phase 1 Habitat data. The findings of this study are important for drinking water companies concerned with maintaining finished water quality and may be of use in targeting monitoring of drainage water in catchments and selecting appropriate mitigation strategies such as diverting or blending water.

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7. Tables and Figures

Table 1. Categorisation of Phase 1 habitat types.

Category used in present study	**Phase 1 Habitat classification**	**Category used in present study**	**Phase 1 Habitat classification**
Woodland and scrub	A.1 A.2	Fen/ mire	E.3
Recently-felled woodland	A.4	Bare peat	E.4
Unimproved grassland	B.1.1 B.3.1	Swamp	F.1 F.2
Improved grassland	B.1.2 B.2.2 B.4	Water	G.1 G.2
Marsh/ marshy grassland	B.5	Rock/ scree/ quarry	I.1 I.2
Tall herb and fern	C.1 C.2 C.3	Arable	J.1.1
Heathland	D.1 D.2 D.3 D.5 D.6	Caravan site	J.3.4
Bog	E.1	Buildings	J.3.6
Flush and spring	E.2	Other	J.1.2 J.4 Not accessed Illegible

Table 2. Correlation coefficients (*r*) for statistically significant correlations between percentage Phase 1 Habitat coverage and reservoir water quality (whole-catchment analysis).

	Autumn [DOC]	Spring [DOC]	Autumn Colour (Hazen)	Spring Colour (Hazen)	Autumn $[NO_3^-]$	Spring $[NO_3^-]$	Autumn pH	Spring pH
Woodland and scrub						0.743**		
Recently-felled woodland								
Improved grassland					0.636**	0.677**		
Unimproved grassland		-0.512*						
Marsh/ marshy grassland								
Tall herb and fern	-0.499*		-0.588*					
Heathland	-0.543*		-0.543*	-0.649**				
Bog								
Flush and spring								
Fen/ mire	0.564*					0.577*		
Bare peat								
Swamp	0.612*	0.690**	0.624**	0.636**				
Water								
Rock/ scree/ quarry								
Arable	0.734**	0.651**	0.508*	0.549*	0.632**	0.721**		
Caravan site								
Buildings	0.596*					0.580*		
Other	0.548*			0.539*				

* indicates $p < 0.05$ and ** indicates $p < 0.01$. All results shown relate to Spearman's correlation analysis.

Table 3. Correlation coefficients (*r*) for statistically significant correlations between percentage Phase 1 Habitat coverage and reservoir water quality (250 m buffer zone analysis).

	Autumn [DOC]	Spring [DOC]	Autumn Colour (Hazen)	Spring Colour (Hazen)	Autumn $[NO_3^-]$	Spring $[NO_3^-]$	Autumn pH	Spring pH
Woodland and scrub						0.774**		
Recently-felled woodland								
Improved grassland					0.617*	0.655**		
Unimproved grassland								
Marsh/ marshy grassland						0.502*		
Tall herb and fern			-0.559*					
Heathland	-0.560*	-0.517*	-0.499*	-0.652**			-0.558*	
Bog								
Flush and spring								
Fen/ mire	0.600*	0.513*			0.587*	0.578*		
Bare peat								
Swamp	0.647**	0.709**	0.624**	0.636**				
Water								
Rock/ scree/ quarry								
Arable								
Buildings	0.499*							
Other								

* indicates $p < 0.05$ and ** indicates $p < 0.01$. Underlined result relates to Pearson's correlation analysis and the remainder to Spearman's correlation analysis.

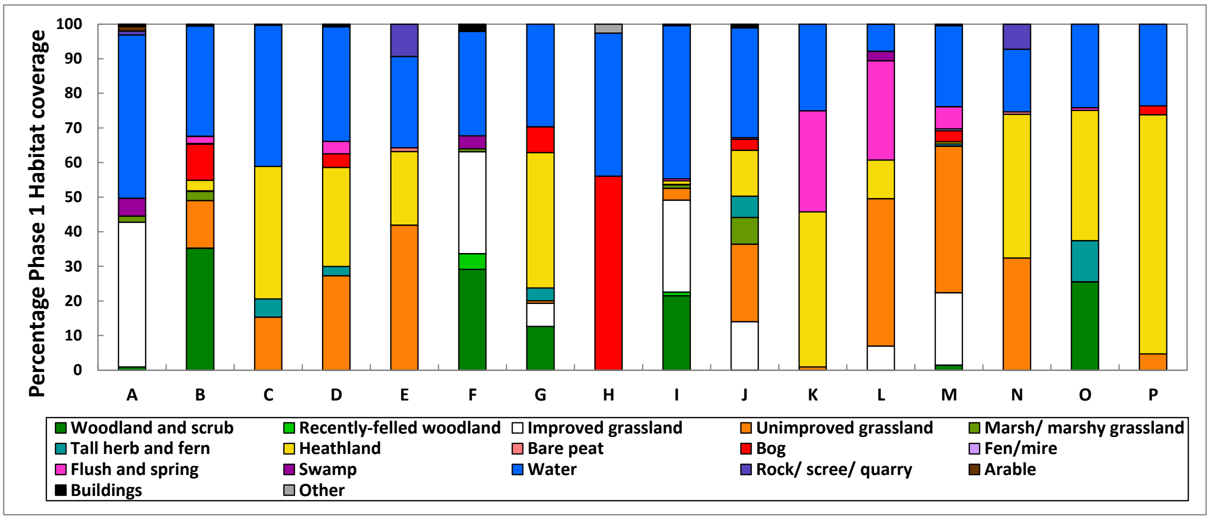

Figure 1. Percentage Phase 1 Habitat coverage in 250 m reservoir buffer zone.

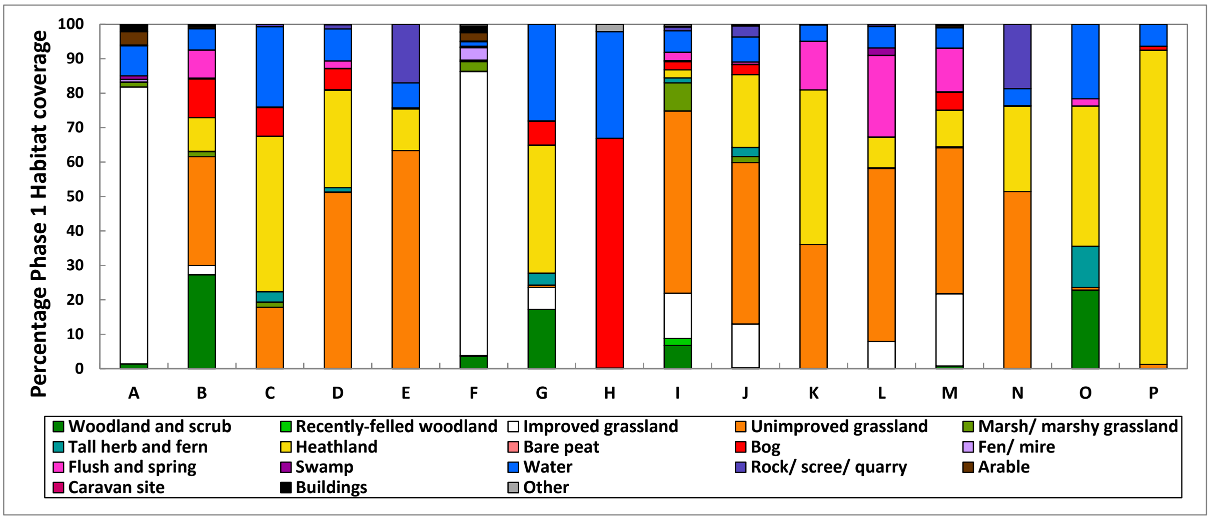

Figure 2. Percentage Phase 1 Habitat coverage in whole reservoir catchments.