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Compartmentalisation and groundwater–surface water interactions in a prospective shale gas basin: Assessment using variance analysis and multivariate statistics on water quality data

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Abstract

An environmental concern with hydraulic fracturing for shale gas is the risk of groundwater and surface water contamination. Assessing this risk partly involves the identification and understanding of groundwater–surface water interactions because potentially contaminating fluids could move from one water body to the other along hydraulic pathways. In this study, we use water quality data from a prospective shale gas basin to determine: if surface water sampling could identify groundwater compartmentalisation by low-permeability faults; and if surface waters interact with groundwater in underlying bedrock formations, thereby indicating hydraulic pathways. Variance analysis showed that bedrock geology was a significant factor influencing surface water quality, indicating regional-scale groundwater–surface water interactions despite the presence of an overlying region-wide layer of superficial deposits averaging 30–40 m thickness. We propose that surface waters interact with a weathered bedrock layer through the complex distribution of glaciofluvial sands and gravels. Principal component analysis showed that surface water compositions were constrained within groundwater end-member compositions. Surface water quality data showed no relationship with groundwater compartmentalisation known to be caused by a major basin fault. Therefore, there was no chemical evidence to suggest that deeper groundwater in this particular area of the prospective basin was reaching the surface in response to compartmentalisation. Consequently, in this case compartmentalisation does not appear to increase the risk of fracking-related contaminants reaching surface waters, although this may differ under different hydrogeological scenarios.

KEYWORDS

compartmentalisation, groundwater, hydraulic fracturing, shale gas, surface water, water quality
1 INTRODUCTION

The rapid expansion of hydraulic fracturing (fracking) to exploit unconventional shale gas reservoirs in the United States has led to a range of environmental concerns: induced seismicity (Davies, Foulger, Bindley, & Styles, 2013); water usage and contamination (Kondash, Lauer, & Vengosh, 2018; Vengosh, Jackson, Warner, Darrah, & Kondash, 2014; Vengosh, Warner, Jackson, & Darrah, 2013); fugitive methane (CH4) emissions (Boothroyd, Almond, Qassim, Worrall, & Davies, 2016; Boothroyd, Almond, Worrall, Davies, & Davies, 2018); human health effects (Currie, Greenstone, & Meckel, 2017); air quality and noise (Goodman et al., 2016); and surface footprint (Clancy, Worrall, Davies, & Gluyas, 2018). Potential contamination of surface waters and groundwater from spills or subsurface contaminant migration has been a particularly common concern (Vidic, Brantley, Van denbosche, Yoxtheimer, & Abad, 2013). As surface waters and groundwater can be hydraulically connected by pathways, contamination of either water body could result from surface activities, for example, spills and surface water discharge (Gross et al., 2013; Olmstead, Muehlenbachs, Shih, Chu, & Krupnick, 2013), or from the potential subsurface upward migration of formation fluids, stray gas or injected fluids (usually predominantly water but chemicals can be added to: reduce friction; help carry proppants; prevent biological growth and metal corrosion; and remove drilling mud damage) (Myers, 2012; Osborn, Vengosh, Warner, & Jackson, 2011; Warner et al., 2012). Consequently, the vulnerability of surface waters and shallow groundwater resources (<400 m deep as defined by UKTAG, 2011) must now also be considered from a bottom–up perspective (e.g. Loveless et al., 2019) in addition to the classic top–down approach for groundwater vulnerability from surface sources (e.g. Palmer & Lewis, 1998; Worrall & Kolpin, 2004). In both cases an essential part of understanding the vulnerability of surface waters or groundwater is identifying groundwater–surface water interactions, which are indicative of potential pathways contaminants may follow.

Literature reports of proposed water contamination from fracking operations are relatively rare compared to the number of stimulated boreholes and are often disputed. In Weld County, CO, Gross et al. (2013) reported 77 surface spills (0.5% of active wells) between July 2010 and July 2011 contaminated groundwater with benzene, toluene, ethylbenzene and xylene (BTEX) components of crude oil. In northeastern Pennsylvania and southeastern New York, Darrah, Vengosh, Jackson, Warner, and Poreda (2014) reported seven discrete clusters of fugitive gas contamination from 114 groundwater samples, and in central Texas one discrete cluster from 20 groundwater samples. Well integrity failure was hypothesized as the most likely contamination pathway (Darrah et al., 2014) and has also been proposed by others (e.g. Llewellyn et al., 2015). In Susquehanna County, PA, Jackson et al. (2013) and Osborn et al. (2011) found that shallow groundwater CH4 concentrations increased with proximity to the nearest shale gas well. Conversely, it was argued that CH4 is naturally ubiquitous in groundwater and elevated CH4 concentrations relate to topography and groundwater geochemistry (Molofsky, Connor, Farhat, Wylie, & Wagner, 2011; Molofsky, Connor, Wylie, Wagner, & Farhat, 2013; Molofsky et al., 2016). For other nations considering or in the early stages of shale exploitation, it is therefore important that the risk of water contamination is assessed, particularly where surface waters and groundwater form important natural resources.

Surface waters and groundwater in England provide on average ~70% and 30% of public water supply, respectively (BGS, 2019a). Water resources in England are managed under the Water Resources Act 1991 (UKPGA, 1991a) and the Water Industry Act 1991 (UKPGA, 1991b), as well as their subsequent revisions. Furthermore, the European Union Water Framework Directive requires EU member states to achieve good chemical and quantitative status of all water bodies (EU, 2000). Site based environmental regulation in England, including at shale gas sites, is carried out by the Environment Agency (EA). Activities related to the onshore oil and gas industry require a range of environmental permits, for example mining waste permits, and authorisations under the Environmental Permitting Regulations 2016 (UKSI, 2016). These permits control discharges and any other relevant risks to the water environment. The EA also determine and publish water protection zones (e.g. Groundwater Source Protection Zones and Drinking Water Protected Areas Safeguard Zones) to protect water resources, as well as publishing River Basin Management Plans every 6 years which consider the water environment in each river basin. To date, two fracking operations (Preese Hall and Preston New Road), both located in the Bowland Basin,1 northwest England, have taken place (Figure 1). These operations targeted the Bowland Shale, which is considered to be England’s largest prospective shale gas resource (Andrews, 2013).

The slow development of shale gas resources compared to that in the United States has provided the opportunity to undertake environmental baseline assessments of surface waters and groundwater (e.g. Ward et al., 2018), and further understand the water contamination risk posed by any fluids moving from the deep to shallow subsurface. Historic water quality monitoring, along with focused sampling, can be used for determining baseline conditions and understanding controls on risks to water quality. For example, the influence of underlying bedrock geology on surface water quality, and therefore groundwater interaction and the presence of hydraulic pathways in specific river catchments (Jarvie, Oguchi, & Neal, 2002; Neal et al., 2011; Oguchi, Jarvie, & Neal, 2000) or geographic regions (Rothwell et al., 2010a, 2010b; Thornton & Dise, 1998). Statistical analyses of groundwater and surface water quality data are often employed to infer interaction (similarities indicating hydraulic pathways and vice versa) (e.g. Guggenmos, Daughney, Jackson, & Morgenstern, 2011). However, geological information is not always included as an objective parameter. Likewise, groundwater–surface water interactions can be interpreted and quantified using the baseflow index method, but the inclusion of geological parameters is also subjective because it requires an initial ‘expert judgement’ (Bloomfield, Allen, & Griffiths, 2009). Additionally, the baseflow index method requires hydrograph data. In the United Kingdom, hydrograph data are generally only available on major rivers and tributaries, and are therefore not usually available in the same spatial density as water quality monitoring datasets.
This study includes geological bedrock formations in the statistical analysis of surface water and groundwater quality data from a prospective shale gas basin to investigate groundwater-surface water interactions, and thus potential contaminant pathways. Furthermore, Wilson, Worrall, Davies, and Hart (2017) showed that groundwater compartmentalisation by low-permeability faults can restrict regional horizontal groundwater flow and encourage upward flow, thereby increasing the vulnerability of shallow groundwater to contamination from the upward migration of fracking-related fluids. However, as yet no study has demonstrated if compartmentalisation increases the risk to surface waters with respect to contamination from below or whether compartmentalisation can be identified from surface water...
quality data alone. Although compartmentalisation can be effectively identified using subsurface data, for example, water levels, chemistry and pressure (Hamaker & Harris, 2007; Hortle, Xu, & Dance, 2009; Mohamed & Worden, 2006), the drilling of new groundwater monitoring boreholes can be expensive and time-consuming. For example, when monitoring for groundwater contamination at Pavillon, WY, the expense of drilling boreholes was the main limiting factor in the number of monitoring boreholes installed by the Environmental Protection Agency (DiGiulio, Wilkin, Miller, & Oberley, 2011). In some prospective basins surface water quality data may provide an alternative cost-effective and higher spatial resolution method for identifying compartmentalisation and assessing groundwater-surface water interactions as a means of evaluating the vulnerability of water resources to contamination from shale gas operations. Therefore, the aims of this study were to determine: if groundwater in underlying bedrock formations influences surface water quality, thereby indicating potential contaminant pathways; if groundwater compartmentalisation could be identified from surface water quality data; and if groundwater compartmentalisation increases the risk to surface waters?

2 | APPROACH AND METHODOLOGY

The main approach taken was a factorially designed survey of a newly collected EA surface water quality dataset. It was not possible to use existing EA surface water quality data because of the sparser sampling density and the complexity in inconsistent sampling frequency since the establishment of the publically available EA dataset in the year 2000. However, publically available EA groundwater quality data since the year 2000, compiled by Wilson, Worrall, Davies, and Hart (2019), were analysed with the new surface water quality data to further the interpretation.

2.1 | Study region

This study considered the rivers and aquifers that cross the Bowland Basin in northwest England. The basin contains the Bowland Shales, which may be the United Kingdom’s largest prospective shale gas resource (Andrews, 2013). Bedrock geology across the study region ranges in age from Carboniferous to Triassic. In the low-lying west of the basin (the Fylde) bedrock consists of the Triassic Mercia Mudstone and Sherwood Sandstone Groups (Figure 2). In the northern Fylde the boundary between the two groups is conformable, whereas in the central and southern Fylde the boundary is faulted by the Woodsfold fault (Figure 2). The Mercia Mudstone and Sherwood Sandstone Groups do not outcrop in the Fylde and are instead overlain by a complex distribution of superficial deposits, which consist of glacial sands, gravels and tills (clay dominated in this region), tidal flats, peat, alluvium and blown sands (BGS, 2019a,b; Cripps, Burker, Lee, & Housh, 2016). The superficial deposits are on average 30–40 m thick across the Fylde (Cripps et al., 2016). Cripps et al. (2016) postulated that the glacifluvial deposits could provide laterally extensive and unpredictable flow pathways which may connect surface waters to the underlying bedrock. In the east of the basin, where the Forest of Bowland Area of Outstanding National Beauty is located, bedrock geology is composed of the Carboniferous Millstone Grit and the Bowland High and Craven Groups (Figure 2). These formations are mostly overlain by superficial deposits (consisting of till, peat and alluvium) but outcrops do exist across the Forest of Bowland. The boundary between the Carboniferous and Triassic sediments is faulted or unconformable (Mott MacDonald, 1997). A limited band of Permian sediments (Manchester Marl) also occurs along this boundary (Figure 2). The southeastern edge of the study region is marked by the Lower Coal Measures (Figure 2).

Precipitation over the study region can be split into two zones which correspond to both elevation and bedrock geology. The low-lying Fylde, which is predominantly arable land, has average precipitation <1,000 mm/year. Across the higher elevations of the Forest of Bowland, which is made up of moorland and rough pastures, average precipitation is ~1800 mm/year (Mott MacDonald, 1997, 2010). The study region is also split in two by the two major river catchments present: the River Wyre and the River Ribble catchments. The River Wyre, located in the north of the basin, originates in the Forest of Bowland and flows onto the Fylde, through Garstang, and eventually into the south of Morecambe Bay (Figure 1). The River Ribble in the south of the basin originates further inland than the River Wyre, beginning in the Yorkshire Dales. From the Yorkshire Dales the River Ribble runs south then southwestwards, skirting the southern edge of the Forest of Bowland before running through Preston and into the Irish Sea (Figure 1). A major tributary of the River Ribble is the River Hodder which originates in the Forest of Bowland. The watershed divide between the Wyre and Ribble catchments in the Fylde approximately follows the east–west M55 motorway between Preston and Blackpool.

The Sherwood Sandstone Group forms the principal aquifer in the eastern Fylde and is the focus of groundwater abstractions in the study region. Recharge of the Sherwood Sandstone Group is considered to occur by two mechanisms. In the northern Fylde most recharge is considered to occur as vertical leakage through the overlying superficial deposits where low-permeability glacial till is absent (Mott MacDonald, 1997; Sage & Lloyd, 1978). In the southern Fylde it is thought that lateral inflow from the adjacent Carboniferous strata, driven by the topographic difference, helps recharge the Sherwood Sandstone Group (Mott MacDonald, 1997, 2010). The Millstone Grit forms the aquifer unit across the Forest of Bowland and recharge occurs from direct precipitation and infiltration through the superficial deposits. Across the Fylde low-permeability faults are considered to compartmentalise groundwater and influence flow directions (Wilson et al., 2019). The main groundwater flow paths are towards Morecambe Bay in the north and the Ribble Estuary in the south. No groundwater abstractions from the Sherwood Sandstone Group occur in the western Fylde where the Sherwood Sandstone Group is confined by the Mercia Mudstone Group. The confined Sherwood Sandstone Group is considered isolated from the eastern Fylde by the Woodsfold fault, based on the presence of brine at depths of 360–500 m (BGS, 2019c). Minor private water abstractions occur.
from the superficial deposits across the Bowland Basin, including west of the Woodfold fault. The superficial deposits are predominantly classified as secondary (undifferentiated) aquifers by the EA, meaning that they have been considered both minor aquifers and non-aquifer because of their complex characteristics (DEFRA, 2020).

2.2 | Surface water sampling

Surface water samples were collected in two fieldwork campaigns during the 2018 United Kingdom summer, which was one of the hottest and driest summers on record in the United Kingdom (NOAA, 2019a,b). The Wyre and Ribble rivers, and their major tributaries, generally have a baseflow index of ∼0.3 (NRFA, 2020), but during the 2018 summer surface waters were consistently at baseflow conditions with therefore an increased chance of identifying any bedrock groundwater signatures in the surface water quality data. Sampling locations were planned in advance and were located on publically accessible land with nearby road access (Figure 1). Sampling locations included both surface waters running over multiple bedrock formations and those originating and running across a single formation. The first campaign (20–23 July 2018) collected samples from 128 locations in the River Wyre catchment and surrounding area. Unfiltered water samples (25.0 mL) were acidified in the field (1.0 mL of ∼30% nitric acid) to fix metal ions prior to laboratory analysis. Water temperature, electrical conductivity, pH and redox potential were measured in the field using electrode methods. Samples were refrigerated on the same day as returning from the field. A further
111 locations, including 5 locations common to the first campaign, were sampled from 10 to 14 September 2018 in the River Ribble and Hodder catchments. In total 239 surface water samples were collected from 234 unique locations (Figure 1).

2.3 Temperature correction for electrical conductivity

To compare electrical conductivity between sampling locations it was necessary to normalize field conductivity measurements to a standard temperature. In line with environmental water quality monitoring undertaken by the EA, field conductivity was normalized to 25°C (specific conductance) using the linear equation of Sorensen and Glass (1987):

$$EC_{25} = \frac{EC_t}{1 + a(t - 25)},$$

where $EC_t$ is electrical conductivity measured in the field at temperature $t$ (°C), $EC_{25}$ is electrical conductivity at 25°C, and $a$ is a temperature compensation factor. A standard value of $a = 0.02$ was used (Hem, 1985; Matthey, 1982).

2.4 Tidally influenced sampling locations

Due to the low-lying nature of the Fylde and proximity to the Irish Sea, some sampling locations were tidally influenced. Surface water samples from these locations could be some mixture of sea and fresh water, depending on the tidal direction and river discharge. This study focussed on fresh water and so samples considered to be dominated or strongly influenced by sea water were removed from the dataset (Figure 1). Locations to be removed were identified by abnormally elevated conductivity measurements, and in some cases elevated pH and reduced redox potential compared to non-tidal water samples.

2.5 Duplicate sampling locations

To combine the datasets from the two fieldwork campaigns, five locations sampled during the second campaign were common to both campaigns. The five duplicate locations were chosen to cover the geographical extent and varying elevation of the study area. The two sets of results for specific conductance, pH and redox potential from these five locations were compared using one-way analysis of variance (ANOVA). The one factor considered (‘Campaign’) had two levels (‘First’ or ‘Second’ campaign) and the ANOVA was run with and without elevation as a covariate (‘Elevation’). Sample location elevations were extracted from Ordnance Survey (OS) Terrain 50 data (OS, 2019) using Esri ArcGIS 10.3. Statistical significance was judged at the 95% probability of the factor not having zero effect. Prior to ANOVA, measurements were tested for normality using the Anderson–Darling test (Anderson & Darling, 1952) and were transformed if necessary.

2.6 Ion concentration analysis

Of the 239 surface water samples 170 non-tidal samples were analysed for ion concentrations using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). Samples were analysed using Thermo Scientific ICAP 6000 Series ICP-AES. Calibration standards were made following serial dilution of Romil (Cambridge) 1,000 mg/L reference solutions. All samples, blanks and standards had a 1.0 mg/L Yttrium (Y) spike used as an internal standard to correct for any minor ionization or other matrix effects during the analysis. The 170 samples included all sampling locations overlying the Mercia Mudstone Group (40 samples) and Sherwood Sandstone Group (69 samples), as well as 29 samples overlying the Millstone Grit, two samples overlying the Lower Coal Measures and 30 samples overlying the Bowland High and Craven Groups. Ions measured were: calcium (Ca), iron (Fe), potassium (K), magnesium (Mg), manganese (Mn), sodium (Na) and sulphur (S). Concentrations were corrected for the dilution due to acidification. Sulphur concentrations were used to estimate sulphate (SO$_4^{2-}$) concentrations under the assumption that all S was present as SO$_4^{2-}$.

2.7 Factorial survey design

The study was designed to answer two questions using ANOVA: does bedrock geology influence surface water quality and can groundwater compartmentalisation affect surface water quality data?

To assess the former question three ANOVAs were run. Firstly, a one-way ANOVA was run on the surface water field measurements and ion concentrations (collectively referred to as ‘determinands’), with and without elevation included as a covariate (‘Elevation’). Underlying bedrock geology at sampling locations, determined using British Geological Survey (BGS) 1:625000 Bedrock Geology data, was included as the one factor (‘Geology’) with five levels: Mercia Mudstone Group, Sherwood Sandstone Group, Lower Coal Measures, Millstone Grit and Bowland High and Craven Groups. The second ANOVA was run on the same determinands but from mean-averaged (at each borehole location) groundwater quality data compiled by Wilson et al. (2019). The groundwater data consisted of 21 samples with specific conductance and 31 samples with pH and ion concentrations. Redox potential data were not available. The inferred aquifer sampled (as defined by Wilson et al., 2019 using BGS borehole information) was included as the one factor (‘Aquifer’) with four levels: Mercia Mudstone Group, Sherwood Sandstone Group, Coal Measures and Carboniferous. The Millstone Grit and Bowland High and Craven Group samples were combined in one level (Carboniferous) because the groundwater data did not allow distinction between the two. Groundwater samples from coal measures were classed as Coal Measures because no distinction was possible between the Upper, Middle
or Lower Coal Measures. The third ANOVA combined both the surface water and groundwater quality data. The two factors considered were ‘Water body’ and ‘Geology’. The Water body factor had two levels: Surface water and Groundwater. The Geology factor had four levels: Mercia Mudstone Group, Sherwood Sandstone Group, Coal Measures and Carboniferous.

To assess the potential effect of groundwater compartmentalisation on surface water quality data a three-way ANOVA was conducted on the samples overlying the Mercia Mudstone and Sherwood Sandstone Groups. Wilson et al. (2019) interpreted the Woodsfold fault (Figure 2) to compartmentalise the central and southern Fylde but not the north. This contrast meant it was possible to test whether compartmentalisation could impact surface water quality. The ANOVA considered three factors, each with two levels: ‘Catchment’ (Wyre or Ribble, i.e. north or south in the basin, respectively), ‘Fault’ (East or West of the Woodsfold fault) and ‘Geology’ (Mercia Mudstone or Sherwood Sandstone Group). It was necessary to investigate interactions between all three factors because the contact between the Mercia Mudstone and Sherwood Sandstone Groups in the central and southern Fylde is the Woodsfold fault. The test of our question was whether there was a significant interaction between the Catchment and Fault factors, that is, was there a significant difference between east and west of the fault in the south and central Fylde compared to the north of the Fylde? If yes, then it could not be ruled out that compartmentalisation was affecting surface water quality.

Prior to any ANOVA, data were tested for normality using the Anderson–Darling test (Anderson & Darling, 1952) and transformed if necessary. Statistical significance was judged at the 95% probability of the factor or interaction not having zero effect. Results are presented as least squares means (otherwise known as marginal means). The proportion of the variance explained by significant factors, interactions and covariates was calculated using the generalized $\omega^2$ method (Olejnik & Algina, 2003). Where factors had more than two levels, post hoc Tukey tests were carried out to assess where significance lay within factors.

Power analysis was also performed post hoc to estimate what effect size could have been detected given the sampling design used to investigate the impact of compartmentalisation, that is, the effective detection limit for differences between bedrock formations and across the Woodsfold fault. Power analysis was performed using G*Power 3.1 software (Faul, Erdfelder, Lang, & Buchner, 2007)—a priori the acceptable power was set at 0.95 (a false negative probability $\beta = .05$). The G*Power software measures effect size ($f$) using the measured value of $\omega^2$ as derived above from the method of Olejnik and Algina (2003):

$$f = \sqrt{\frac{\omega^2}{1-\omega^2}}$$ (2)

### 2.8 Principal component analysis

Principal component analysis (PCA) is a multivariate statistical technique used to reduce large numbers of observations while still maintaining the majority of information. Wilson et al. (2019) previously used PCA to analyse groundwater quality data from the study region. In this study, PCA was firstly used to identify surface water quality trends and end-members. A priori measurements for specific conductance, Ca, Fe, K, Mg, Mn, Na and SO4 were normalized using $z$-transformation to allow for comparison of determinands with different units. Principal components (PCs) were chosen based on eigenvalues >1, which represent components that explain more of the underlying variation than any of the original variables (Chatfield & Collins, 1980). Scatter plots of PC values for each location were used to interpret trends and end-members. No trends or end-members were assumed prior to this interpretation. A second PCA was carried out on the surface water data combined with the groundwater data used by Wilson et al. (2019). The aim of this PCA was to investigate how groundwater trends and end-members identified by Wilson et al. (2019) related to those identified for surface waters. A total of 57 groundwater locations with measurements for specific conductance and concentrations for Ca, Fe, K, Mg, Mn, Na and SO4 were extracted from the dataset of Wilson et al. (2019).

### 3 RESULTS

Four surface water samples were identified as being dominated or strongly influenced by sea water. These samples were removed prior to further analysis, leaving a total of 235 surface water samples from 231 unique sampling locations. All field measurements (235 samples) and ion concentrations (170 samples) are provided in Tables S1 and S2, respectively.

#### 3.1 Duplicate sampling locations

For field measurements at the duplicate sampling locations (Table S3), the Anderson–Darling test indicated no transformations were required prior to ANOVA. ANOVA showed that differences in specific conductance, pH and redox potential between the fieldwork campaigns were not significant (Table 1). Elevation was not a significant covariate for pH and redox potential but was significant for specific conductance, however the Campaign factor remained insignificant. The inclusion of a covariate increases the sensitivity of the analysis.

| Response          | Covariate | $R^2$ (%) | p-value |
|-------------------|-----------|-----------|---------|
| Specific conductance | None      | 6.47      | .478    | —       |
|                   | Elevation | 89.36     | .078    | <.0005  |
| pH                | None      | 29.84     | .102    | —       |
|                   | Elevation | 39.74     | .105    | .319    |
| Redox potential   | None      | 17.66     | .227    | —       |
|                   | Elevation | 42.25     | .187    | .128    |
with respect to the difference between the campaigns, further assuring that the two campaigns could be directly compared. Given these results the data from the two campaigns were combined for further analysis without any corrections required.

### 3.2 | Surface water quality and bedrock geology

Figure 3 shows the numerical distributions of all surface water determinands in relation to underlying bedrock geology. Specific conductance and ion concentrations appear to vary with underlying bedrock geology; samples underlain by the Mercia Mudstone and Sherwood Sandstone Groups generally have higher specific conductance and concentrations than those underlain by the Lower Coal Measures, Millstone Grit and Bowland High and Craven Groups (Figures 3 and 4). However, this pattern was also true for elevation (Figure 3d), suggesting that elevation could be the dominant control or, more likely, that elevation is influenced by the different bedrock formations and their weathering rates.

Anderson–Darling tests indicated that field measurements required no transformation prior to ANOVA. ANOVA showed that Geology was a significant factor controlling the specific conductance, pH and redox potential of surface water samples across the basin (Table 2). The Geology factor explained 49.2% of the variation in specific conductance, which increased to 55.4% with the inclusion of the Elevation covariate. However, the Geology factor remained significant even after inclusion of the Elevation covariate. Elevation was a significant covariate for specific conductance and pH, explaining 6.0 and 7.3%, respectively, of the variance as calculated using the generalized $\alpha^2$ method. For pH the inclusion of the Elevation covariate resulted in the Geology factor becoming insignificant. For redox potential the Elevation covariate was insignificant and the Geology factor remained significant. The best-fit model for the field measurements had an $R^2$ value of 55.4% (Table 2) which means that a minimum of 44.6% of the original variance was not explained by any of the ANOVA. Unexplained variance in ANOVA includes the measurement error and any factors, covariates and their interactions that were not considered in the original experimental design, for example, changing land use. The magnitude of the unexplained variance does not negate the significance, or not, of the factors that were included.

Post hoc Tukey tests showed that for specific conductance, significant differences lay between the Mercia Mudstone Group, the Sherwood Sandstone Group and the Millstone Grit and Bowland High and Craven Groups (Figure 5 and Table 2). Differences between the Lower Coal Measures and other bedrock formations were insignificant, which might result from the small sample size (two samples) obtained from surface waters overlying the Lower Coal Measures.

Prior to ANOVA, Fe, Mg, Mn, Na and $SO_4$ concentration data were log-transformed. The Anderson–Darling test suggested that no transformation was necessary for either Ca or K. The ANOVA showed that Geology was a significant factor controlling the concentrations of all seven ions (Table 2). The Geology factor explained from 12.0% of the variation in Fe concentrations to 51.2% of the variation in Na concentrations (Table 2). Elevation was a significant covariate for all ions, except Fe, and increased the overall fit of the models (i.e. $R^2$ values increased), but in all cases did not alter the significance of the Geology factor, that is, there was a geological control on surface water quality over and above that due to elevation. The proportion of variance explained by the Geology factor was greater than that explained by the Elevation covariate for all ions except Mg (Table 2).

Post hoc Tukey tests showed that significant differences lay between the Mercia Mudstone Group, the Sherwood Sandstone Group, and the Millstone Grit and Bowland High and Craven Groups for Ca, Mg, Na and $SO_4$ (Figure 5 and Table 2). For Fe and Mn, the Mercia Mudstone Group was the only bedrock formation that was significantly different from all other formations, excluding the Lower Coal Measures (Figure 5 and Table 2). For K, the Mercia Mudstone and Sherwood Sandstone Groups were grouped together and were significantly different from the Millstone Grit and Bowland High and Craven Groups (Figure 5 and Table 2). The Lower Coal Measures were only significantly different to the Mercia Mudstone Group for Ca and Mg.

### 3.3 | Groundwater quality and aquifers

All groundwater determinands except pH were log-transformed prior to ANOVA because of improved Anderson–Darling test values compared to the raw data. ANOVA showed that Aquifer was a significant factor in explaining differences in all determinands, bar pH, across the aquifer formations (Table 3). The Aquifer factor explained from 27.1% of the variation in Mn concentrations to 71.8% of the variation in $SO_4$ concentrations (Table 3). Post hoc Tukey tests showed that groundwater in the Mercia Mudstone Group was significantly different to all other aquifer formations for specific conductance, Ca, Na and $SO_4$, and different to the Sherwood Sandstone Group and Carboniferous for all determinands except Fe and Mn (Figure 5 and Table 3). No significant differences existed between the Sherwood Sandstone Group, Coal Measures and Carboniferous strata for any determinands (Figure 5 and Table 3).

### 3.4 | Combined surface water and groundwater quality ANOVA

Prior to ANOVA all determinands, except pH, were log-transformed. ANOVA results showed that Geology was a significant factor for all determinands (Table 4). Within the Geology factor all determinands from the Mercia Mudstone Group, expect pH, were significantly different from the other geological formations, which was confirmed by groupings from the post hoc Tukey tests (Table 4). Post hoc Tukey tests also showed that the Sherwood Sandstone Group and Carboniferous were significantly different from each other for all determinands except Fe and Mn (Table 4). The Coal Measures were not significantly different from any of the other geological formations as shown by the shared Tukey Test groups. The Water body factor, with levels of
FIGURE 3  Box plots showing the maximum, minimum, mean, and first SD values of field measurements, elevation and ion concentrations, split by underlying bedrock geology. (a) Specific conductance, (b) redox potential, (c) pH, (d) elevation, (e) Ca concentration, (f) Fe concentration, (g) K concentration, (h) Mg concentration, (i) Mn concentration, (j) Na concentration, and (k) SO$_4$ concentration. Where lower whiskers are not shown, the SD is greater than the minimum value and so the base of the box represents the minimum value. BHCG, Bowland High and Craven Groups; LCM, Lower Coal Measures; MG, Millstone Grit, MMG, Mercia Mudstone Group; SSG, Sherwood Sandstone Group.
surface water and groundwater, was significant for specific conductance, Ca, Mg and Na, but not for Fe, K, Mn, SO₄ and pH (Table 4). In other words, whereas significant differences in Fe, K, Mn, SO₄ and pH occurred between the different geological formations, no differences were observed between surface waters and groundwater. The generalized ω² method showed that the Geology factor always explained more of the variance in determinands than the Water body factor or the interaction between the two factors, ranging from 2.1% of the variance in pH to 44.8% of the variance in specific conductance (Table 4).

The interaction between the Geology and Water body factors was significant for Ca, Fe, K, Na and SO₄. Post hoc Tukey tests showed that for Ca, Na and SO₄, groundwater in the Mercia Mudstone Group was significantly different to all other waters, including surface waters overlying the Mercia Mudstone Group (as shown by lines in Figure 6). No significant differences were observed for any determinands between groundwater and surface waters of the Coal Measures, and only K showed a significant difference between groundwater and surface waters of the Sherwood Sandstone Group (Figure 6). For the Carboniferous, significant differences between groundwater and surface waters occurred for Ca and Na, but not for Fe, K or SO₄. Considering interactions between groundwaters of the different geological formations, no significant differences between the Sherwood Sandstone Group, Coal Measures and Carboniferous strata were observed for any determinands (as shown by the absence of lines in Figure 6). For surface waters, all determinands were significantly different between the Carboniferous and Mercia Mudstone Group. Surface waters overlying the Carboniferous were also significantly different to those overlying the Sherwood Sandstone Group for Ca, K, Na and SO₄, but not for Fe. Lastly, surface waters overlying the Sherwood Sandstone Group were significantly different to those overlying the Mercia Mudstone Group for Fe, Na and SO₄.
The power analysis performed for the experimental design was irrelevant for the Geology factor because all determinands proved to be significant at the 95% probability. For the Water body factor the detectable difference was greater for each determinand than for the Geology factor (Table 4), i.e. it was easier to detect differences between the different geological formations than the difference between the water bodies. For example, for specific conductance the detectable difference between surface waters and groundwater was 142 μS/cm whereas the detectable difference between the different geological formations was lower at 125 μS/cm. However, it should be noted that while the detectable difference for Na concentration was 1850 mg/L, the detectable difference for pH was only 0.15 pH units which may not be meaningfully physical given the typical accuracy of field measurements for this determinand.

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### 3.5 Water quality trends and end-members

The PCA reduced the eight surface water determinands from the 170 surface water samples to two PCs, which explained 79.5% of the variance in the data (Table 5). All determinands had positive loadings in PC1, suggesting that PC1 was a general concentration component. In PC2 the strongest positive loadings were for Fe and Mn, and the strongest negative loading was for SO₄ (Table 5).

A plot of PC2 versus PC1, colour-coded by underlying bedrock geology, indicated at least three end-members exist for surface waters (Figure 7a). Surface water end-member A (SW-A) comprised of two sampling locations (location numbers 132 and 139) in the Forest of Bowland, underlain by the Millstone Grit (Figure 7). These locations had low ion concentrations and specific conductance (~74 μS/cm) (Table S2) when compared to the entire dataset. The trend from SW-A to SW-B (location number 104) showed increasing PC1, signifying increased ion concentrations and specific conductance, and increasing PC2 as a result of SW-B having the highest Fe concentration in the dataset (214 mg/L) (Table S2). SW-B was located in the northwest Fylde and was underlain by the Mercia Mudstone Group (Figure 8). The trend from SW-A to SW-D (location number 232) showed increasing PC1 and decreasing PC2, resulting from SW-D having the highest SO₄ concentration in the dataset (458 mg/L) (Table S2). SW-D was located in the southwest Fylde and was underlain by the Mercia Mudstone Group (Figure 8). A fourth end-member, SW-C (location number 97) was interpreted to lie between SW-B and SW-D (Figure 7a). SW-C had elevated Na concentrations (185 mg/L) and was 1.4 km from SW-B, and was also underlain by the Mercia Mudstone Group (Figure 8).

### Table 2: ANOVA and post hoc Tukey test results for the field measurements and ion concentrations

| Determinand | Covariate | p-value | Geology | Elevation | R² (%) | p-value | Geology | Elevation | ω² (%) | Groupings from Tukey tests |
|-------------|-----------|---------|---------|-----------|--------|---------|---------|-----------|--------|--------------------------|
| Specific conductance | None | <.0005 | - | 49.2 | | | | | 48.3 | MMG, SSG, BHCG |
| Elevation | <.0005 | <.0005 | 55.4 | 11.5 | 6.0 | MMG, SSG, BHCG |
| pH | None | <.0005 | - | 8.8 | | | | | 7.2 | MMG, SSG, BHCG |
| Elevation | .241 | <.0005 | 16.5 | - | 7.3 | MMG, SSG, BHCG |
| Redox potential | None | <.0005 | - | 14.6 | | | | | 13.1 | MMG, SSG, BHCG |
| Elevation | <.0005 | .208 | 15.2 | - | 12.2 | MMG, SSG, BHCG |
| Ca | None | <.0005 | - | 48.3 | | | | | 46.9 | MMG, SSG, BHCG |
| Elevation | <.0005 | <.0005 | 54.6 | 13.1 | 6.0 | MMG, SSG, BHCG |
| Log Fe | None | <.0005 | - | 12.0 | | | | | 9.8 | MMG, SSG, BHCG |
| Elevation | .003 | .689 | 12.1 | - | 6.7 | MMG, SSG, BHCG |
| K | None | <.0005 | - | 34.0 | | | | | 32.3 | MMG, SSG, BHCG |
| Elevation | .002 | .003 | 37.5 | 5.2 | 3.1 | MMG, SSG, BHCG |
| Log Mg | None | <.0005 | - | 49.3 | | | | | 47.9 | MMG, SSG, BHCG |
| Elevation | <.0005 | <.0005 | 57.7 | 7.4 | 8.1 | MMG, SSG, BHCG |
| Log Mn | None | <.0005 | - | 22.8 | | | | | 20.8 | MMG, SSG, BHCG |
| Elevation | <.0005 | .034 | 24.9 | 12.8 | 1.6 | MMG, SSG, BHCG |
| Log Na | None | <.0005 | - | 51.2 | | | | | 49.9 | MMG, SSG, BHCG |
| Elevation | <.0005 | <.0005 | 59.5 | 9.1 | 8.0 | MMG, SSG, BHCG |
| Log SO₄ | None | <.0005 | - | 35.9 | | | | | 34.3 | MMG, SSG, BHCG |
| Elevation | <.0005 | .002 | 39.6 | 9.5 | 3.3 | MMG, SSG, BHCG |

Note: Groups from the Tukey tests that do not share a letter are significantly different.
Abbreviations: BHCG, Bowland High and Craven Groups; LCM, Lower Coal Measures; MG, Millstone Grit; MMG, Mercia Mudstone Group; SSG, Sherwood Sandstone Group.
of the data variance (Table 5). In PC1 all determinands had positive loadings, again suggesting PC1 was a general concentration component. In PC2 the strongest loadings were for Fe and Mn, but with reversed polarity to the PCA on just the surface water data (Table 5). This polarity reversal occurred because a number of groundwater samples had very high values for specific conductance and Na.

A plot of PC2 versus PC1 for the combined surface water and groundwater PCA showed that the surface water data lay inside the groundwater end-members and SW-A coincided with the fresh water groundwater end-member (GW-A) identified by Wilson et al. (2019) (Figure 7b). GW-A comprised of two sampling locations in the Forest of Bowland; New Drop Inn borehole and Saddleside Springs, which sampled the Millstone Grit and an unknown aquifer, respectively (Figure 8). SW-B and GW-B (Blackpool Promenade Borehole no. 9) plotted towards an Fe-rich groundwater end-member at Withnell Quarry (Fe concentration 330 mg/L) (Figures 7b and 8), which was not identified as an end-member by Wilson et al. (2019).

### FIGURE 5

Diagram of post hoc Tukey test results for each determinand from the variance analysis on surface water (top surface) and groundwater (front surface) quality data. Double-ended arrows represent significant difference. For example, for surface water SC the Mercia Mudstone Group, Sherwood Sandstone Group, and Carboniferous samples were all significantly different to each other. Surface water samples overlying the Lower Coal Measures and groundwater samples from the Coal Measures are not shown. CARB, Carboniferous (comprising of MG—Millstone Grit and BHCG—Bowland High and Craven Groups); MMG, Mercia Mudstone Group, RP, Redox Potential; SC, specific conductance; SSG, Sherwood Sandstone Group

### TABLE 3

ANOVA and post hoc Tukey test results for the groundwater determinands with inferred aquifer as the factor

| Determinand          | p-value | \( R^2 (%) \) | MMG | SSG | CM  | CARB |
|----------------------|---------|---------------|-----|-----|-----|------|
| Log specific conductance | <.0005  | 63.0          | A   | B   | —   | B    |
| pH                   | .563    | 7.2           | —   | —   | —   | —    |
| Log Ca               | <.0005  | 47.7          | A   | B   | B   | B    |
| Log Fe               | .003    | 40.5          | A   | AB  | B   | B    |
| Log K                | .001    | 44.4          | A   | AB  | AB  | B    |
| Log Mg               | .001    | 45.8          | A   | B   | AB  | B    |
| Log Mn               | .034    | 27.1          | A   | B   | AB  | AB   |
| Log Na               | <.0005  | 52.9          | A   | B   | B   | B    |
| Log SO\(_4\)        | <.0005  | 71.8          | A   | B   | B   | B    |

Note: Groups from the Tukey tests that do not share a letter are significantly different. Abbreviations: CARB, Carboniferous strata (including Millstone Grit and Bowland High and Craven Groups); CM, Coal Measures; MMG, Mercia Mudstone Group; SSG, Sherwood Sandstone Group.
## Table 4
ANOVA, post hoc Tukey test, and power analysis results for the combined surface water and groundwater dataset

| Determinand                | $R^2$ (%) | Factor and interaction p-values | Level p-values | Groupings from Tukey tests |
|----------------------------|-----------|---------------------------------|---------------|---------------------------|
|                            | Water body| Geology | Water body × Geology | Groundwater | Surface water | MMG | SSG | CM | CARB | MMG | SSG | CM | CARB |
| Log specific conductance   | 49.52     | <.0005 | <.0005 | – | <.0005 | <.0005 | <.0005 | .036 | .311 | <.0005 | A | B | ABC | C |
| pH                         | 8.51      | .920   | .034   | .984 | .920   | .920   | .837   | .245 | .564 | .028   | AB | A | AB | B |
| Log Ca                     | 47.59     | <.0005 | <.0005 | .042 | <.0005 | <.0005 | <.0005 | .300 | .887 | .033   | A | B | AB | B |
| Log Fe                     | 19.25     | .786   | <.0005 | .016 | .786   | .786   | <.0005 | .936 | .602 | .008   | A | B | B | B |
| Log K                      | 44.69     | .148   | <.0005 | <.0005 | .148   | .148   | <.0005 | .187 | .800 | <.0005 | A | B | ABC | C |
| Log Mg                     | 56.11     | <.0005 | <.0005 | .056 | <.0005 | <.0005 | <.0005 | .021 | <.0005 | .005   | A | B | ABC | C |
| Log Mn                     | 23.39     | .320   | <.0005 | .130 | .320   | .320   | <.0005 | .001 | .887 | .033   | A | B | AB | B |
| Log Na                     | 55.90     | <.0005 | <.0005 | <.0005 | <.0005 | <.0005 | <.0005 | .005 | .184 | <.0005 | A | B | BC | C |
| Log SO$_4$                 | 50.09     | .072   | <.0005 | <.0005 | .072   | .072   | <.0005 | .272 | .004 | <.0005 | A | B | BC | C |

Units for mean $\omega^2$ (%) Mean ± SE in mean Detectable difference for water body Detectable difference for geology

| Determinand | Units for mean | $\omega^2$ (%) | Mean ± SE in mean | Detectable difference for water body | Detectable difference for geology |
|-------------|----------------|-----------------|-------------------|--------------------------------------|----------------------------------|
| Log specific conductance | $\mu$S/cm | 5.1 | 44.8 | 780 ± 1 | 444 ± 1 | 1,050 ± 1 | 721 ± 1 | 454 ± 1 | 347 ± 1 | 142 | 125 |
| pH          | pH units       | 2.1             | 7.30 ± 0.08 | 7.31 ± 0.06 | 7.29 ± 0.09 | 7.38 ± 0.06 | 7.38 ± 0.16 | 7.18 ± 0.04 | 0.15 | 0.14 |
| Log Ca      | Mg/L           | 5.5             | 24.3 | 105 ± 1 | 46.7 ± 1.1 | 176 ± 1 | 78.5 ± 1.1 | 46.6 ± 1.3 | 37.1 ± 1.1 | 49.5 | 43.4 |
| Log Fe      | Mg/L           | 12.8            | 3.1 | 0.9 ± 1.3 | 0.8 ± 1.3 | 3.9 ± 1.4 | 0.9 ± 1.2 | 0.3 ± 1.9 | 0.5 ± 1.2 | 8.2 | 7.2 |
| Log K       | Mg/L           | 17.3            | 5.6 | 5.3 ± 1.2 | 4.0 ± 1.1 | 11.4 ± 1.2 | 39 ± 1.1 | 43 ± 1.4 | 23 ± 1.1 | 2.8 | 2.5 |
| Log Mg      | Mg/L           | 12.5            | 24.6 | 31.0 ± 1.2 | 8.0 ± 1.1 | 46.1 ± 1.2 | 18.4 ± 1.1 | 9.2 ± 1.3 | 7.9 ± 1.1 | 19.2 | 16.8 |
| Log Mn      | Mg/L           | 9.8             | 0.2 | 0.2 ± 1.2 | 0.1 ± 1.2 | 0.4 ± 1.4 | 0.1 ± 1.2 | 0.1 ± 1.8 | 0.1 ± 1.2 | 0.3 | 0.2 |
| Log Na      | Mg/L           | 9.9             | 33.2 | 11.2 | 7.2 ± 1.2 | 18.3 ± 1.1 | 184 ± 1 | 23.8 ± 1.1 | 25.7 ± 1.4 | 15.6 ± 1.1 | 1850 | 1630 |
| Log SO$_4$  | Mg/L           | 39.9            | 14.2 | 65.7 ± 1.2 | 44.3 ± 1.1 | 332 ± 1 | 46.3 ± 1 | 23.9 ± 1.4 | 23.1 ± 1.1 | 226 | 198 |

Note: Groups from the Tukey tests that do not share a letter are significantly different. Means and SE are given in original determinand units.

Abbreviations: CARB, Carboniferous strata (including Millstone Grit and Bowland High and Craven Groups); CM, Coal Measures; MMG, Mercia Mudstone Group; SSG, Sherwood Sandstone Group.
et al. (2019) because of the different water quality determinands used. The Na-Cl groundwater end-member, GW-C (Jameson Road Landfill Site—Figure 8), was clearly observed on Figure 7b and SW-C plotted towards it. Likewise, SW-D plotted towards three SO₄-rich groundwater samples classified as outliers by Wilson et al. (2019) (Figure 7b). The other outlier samples classified by Wilson et al. (2019), i.e. those with very high total dissolved solids, were responsible for the reversed polarity.
Identifying compartmentalisation

The compartmentalisation of groundwater in the central and southern Fylde by the Woodsfold fault is readily identifiable from groundwater quality data. However, the potential effect on surface water quality is unknown. Therefore, a three-way ANOVA was conducted on the surface water quality data to investigate if groundwater compartmentalisation affects surface water quality and thereby, if surface water quality data might be used to identify groundwater compartmentalisation.

Prior to the ANOVA all determinands, except Ca, pH and redox potential, were log-transformed because of improved normality. When single factors were considered the only significant differences observed were for SO4 between the Wyre and Ribble catchments and Mn across the Woodsfold fault (Table 6). When two-way and three-way factor interactions were considered no significant differences were observed (Table 6). Critically, the interaction between the Catchment factor (with levels Wyre or Ribble, that is, north or south in the Fylde) and the Fault factor (with levels East or West of the Woodsfold fault) was not significant, indicating that compartmentalisation across the Woodsfold fault did not significantly affect the surface water quality data. This result could have been due to a lack of effect of groundwater compartmentalisation on surface waters, or that the sampling design was not sufficient to detect the difference, that is, the power of the design was not sufficient and a false negative exists. However, the power analysis showed that it would have been possible at 95% significance and 95% power to detect an effect which explained 10.7% of the original variance. For specific conductance this corresponded to a detectable difference of 157 μS/cm across the Woodsfold fault (Table 6), which is smaller than the difference in mean specific conductance observed between the Mercia Mudstone and Sherwood Sandstone Group surface water samples (Figure 9). Therefore, the survey design was capable of detecting a compartmentalising effect with a difference smaller than that observed between the underlying bedrock formations.

4 | DISCUSSION

4.1 | Does groundwater in underlying bedrock formations affect surface water quality?

Statistical analyses of water quality data have been used in various geographical regions to investigate groundwater–surface water interactions. Kumar, Ramanathan, and Keshari (2009) used major ion
chemistry and multivariate statistics to investigate the effect of monsoon rains on groundwater–surface water interactions in an urbanized section of the River Yamuna in Delhi, India. Guggenmos et al. (2011) also used multivariate statistics to indicate some river systems in the Wairarapa Valley, New Zealand, were recharging shallow aquifers whereas in others, groundwater was providing baseflow. Guggenmos et al. (2011) also highlighted that differences in water quality between surface waters and groundwater can indicate disconnection. In the United Kingdom, various studies have considered how bedrock geology relates to surface water quality, thereby indicating groundwater interaction (Neal et al., 2011; Rothwell et al., 2010a, 2010b; Soulsby et al., 2007; Thornton & Dise, 1998). Rothwell et al. (2010a) found significant relationships between bedrock geology and surface water pH, Ca, Mg and SO₄ concentrations across northwest England, although in the study region the Mercia Mudstone and Sherwood Sandstone Groups were classified as one bedrock type. Neal et al. (2011) studied the Wyre and Ribble river catchments, concluding that under baseflow conditions the upland rivers primarily comprise of groundwater inputs enriched in divalent base cations due to weathering of the underlying Carboniferous bedrock. Nevertheless, only 26 sites were chosen for monitoring, most of which were not located in the Fylde.

The ANOVA on surface water determinands showed that surface water quality was generally distinct when comparing between the Mercia Mudstone Group, Sherwood Sandstone Group and Carboniferous bedrock (Figure 5). This result indicates that on a regional-scale groundwater in underlying bedrock formations interacts with surface waters despite the widespread presence of superficial deposits which average 30–40 m thickness in the Fylde (Cripps et al., 2016). Although an assessment of the physical and geochemical characteristics of the superficial deposits is beyond this study, it is likely that localized pathways between bedrock and surface waters occur in the absence of glacial till and the presence of glaciofluvial sands and gravels. These glaciofluvial pathways are considered to allow recharge of the Sherwood Sandstone aquifer in the Fylde (Mott MacDonald, 1997, 2010; Sage & Lloyd, 1978). Alternatively, direct hydraulic connections might

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**FIGURE 7** Principal components plots of PC2 versus PC1 for (a) 170 surface water samples analysed for ion concentration, and (b) 170 surface water samples and 57 groundwater samples analysed for ion concentrations. Interpreted SW and GW end-members (from Wilson et al., 2019) are labelled, as are high SO₄ (blue ellipse), total dissolved solids (TDS), and Fe trends. BHCG, Bowland High and Craven Groups; GW, groundwater; LCM, Lower Coal Measures; MG, Millstone Grit; MMG, Mercia Mudstone Group; SSG, Sherwood Sandstone Group; SW, surface water
exist around undiscovered bedrock highs where superficial deposits are thin or absent (Cripps et al., 2016).

Specific areas where there was evidence for interaction were identified through the PCA. SW-C and GW-C were Na-dominated end-members both located in the northwest Fylde (Figure 8), suggesting they could be related. Wilson et al. (2019) suggested that the groundwater Na concentrations could be the result of landfill leachate, sea water intrusion or in situ dissolution of the Preesall Halite found within the Mercia Mudstone Group of the northwest Fylde (Wilson, 1990; Wilson & Evans, 1990). Considering SW-C is ~5.6 km from GW-C (Figure 8), landfill leachate can likely be dismissed as the cause of the Na concentrations at SW-C and the hypotheses of in situ halite dissolution or sea water intrusion are preferred explanations (note that the source of Na and Cl concentrations at GW-C may be different to SW-C and could relate to landfill leachate). Evidence for interaction also occurs in the southwest Fylde (Figure 8). SW-D and surrounding surface water samples were Ca-rich and contained the highest concentrations of SO₄ in the study. The Kirkham Mudstone Formation of the Mercia Mudstone Group, which is the bedrock in this area (BGS, 2019b), is rich in gypsum (CaSO₄.2H₂O) (Wilson, 1990). Therefore, the Ca and SO₄ concentrations in surface waters may relate to gypsum dissolution by groundwater in the underlying Mercia Mudstone Group.

ANOVA on groundwater determinands showed that groundwater in the Sherwood Sandstone Group and Carboniferous could not be distinguished from each other (Figure 5), implying similar bedrock mineralogy and/or well-mixed groundwater. This result contradicts the surface water results which suggested distinct groundwater–surface water interactions across the bedrock types. The contradiction may be explained by surface waters mostly interacting with groundwater in a shallow weathered bedrock layer but not with groundwater deeper in the bedrock formations. Evidence for a weathered bedrock layer in the Fylde comes from borehole data and suggests the weathered layer may be up to 5 m thick (Cripps et al., 2016).

**FIGURE 8** Map of the study region showing surface water and groundwater sampling locations used in the principal component analysis. Source: Contains BGS data © Crown copyright and database right (2019). A BGS/EDINA supplied service
Groundwater within the Mercia Mudstone Group was distinct from other bedrock formations (Figure 5) and the level interactions from ANOVA on surface water and groundwater determinands indicated that groundwater in the Mercia Mudstone Group was distinct from the overlying surface waters (Figure 6). This result contradicts the surface water ANOVA which indicated groundwater–surface water interaction from the significant difference in surface water quality observed between the Sherwood Sandstone and Mercia Mudstone Groups. The contradiction could be explained if groundwater within the Mercia Mudstone Group is stratified; surface waters interact with groundwater in a weathered layer of the upper Mercia Mudstone Group but groundwater in the lower Mercia Mudstone Group does not mix. Evidence for this hypothesis comes from SW-D and surrounding surface water samples. These samples were not dominated by Na like the Na-Cl dominated brine found in the lower Mercia Mudstone Group at the Kirkham Borehole (SD43/20) and in the underlying Sherwood Sandstone Group at Roseacre Wood (BGS, 2019c; Wilson et al., 2019). Shallow groundwater stratification within the low-permeability Mercia Mudstone Group may be a common occurrence; in the nearby Mersey Basin Na and Cl concentrations in the Mercia Mudstone Group rapidly increase from 5,950 and 9,260 mg/L at 120 m depth to 123,000 and 192,000 mg/L at 150 m, respectively (Tellam, 1995).

### 4.2 The origin of the Na-Cl brines

Based on the absence of halite at groundwater sampling depths (240–260 m in the Kirkham Borehole) in the Mercia Mudstone Group, Wilson et al. (2019) proposed the origin of Na-Cl brines in the Mercia Mudstone and Sherwood Sandstone Groups was halite dissolution in the Mercia Mudstone Group in the offshore East Irish Sea Basin, with onshore emplacement driven by basin compaction; this process being analogous to that proposed to account for brines found in the Sellafield region further north (Bath et al., 2006). However, the absence of halite and previously overlooked presence of brecciation and collapse structures in the Kirkham Borehole may be explained by halite dissolution. Consequently, the origin of the Na-Cl brines might be in situ halite dissolution in the Mercia Mudstone Group and migration into the underlying Sherwood Sandstone Group. This process has been proposed to account for saline waters found in the Sherwood Sandstone Group in the Mersey Basin and Market Weighton Block (Bottrell, West, & Yoshida, 2006; Tellam, 1995).

### 4.3 Does compartmentalisation affect surface water quality?

The Woodsfold fault (Figure 2) is considered to form a low-permeability barrier in the central and southern Fylde, compartmentalising groundwater in this part of the study region (Ove Arup and Partners Ltd., 2014a; Wilson et al., 2019). On the west side of the fault groundwater in the Sherwood Sandstone Group is of brine nature (BGS, 2019c) whereas on the east side fresh water abstractions occur (Figure 9; Mott MacDonald, 1997, 2010). Furthermore, groundwater levels either side of the fault are different, decreasing from 5 to 10 m above Ordnance Datum (OD) east of the fault to 16.8 m below OD west of the fault (Ove Arup and Partners Ltd., 2014a,b). The three-way ANOVA on surface water quality data showed no significant evidence of compartmentalisation across the Woodsfold fault, indicating no transfer of compartmentalisation to surface waters. It was not possible to support this interpretation with ANOVA that incorporated groundwater data because there is a paucity of groundwater boreholes and hence data in this area (see Wilson et al., 2019, fig. 1).

The absence of evidence of a significant compartmentalising effect could result from a lack of data, for example, not enough surface water bodies (and hence samples) cross-cut the fault in question, or the determinands measured were not sensitive enough. However, the measurements were sensitive enough to show the impact of underlying bedrock geology on surface water quality (there was a significant

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**TABLE 6** Three-way ANOVA results and power analysis for surface water quality data used to identify compartmentalisation across the Woodsfold fault

| Determinand            | $R^2$ (%) | $p$-value | Geology | Catchment | Fault | Geology × Catchment | Geology × Fault | Catchment × Fault | Geology × Catchment × Fault | Detectable difference |
|------------------------|-----------|-----------|---------|-----------|-------|---------------------|----------------|------------------|------------------------|-----------------------|
| Log specific conductance | 21.45     | .192      | .462    | .329      | .483  | .981                | .303           | .469             | 157 μS/cm              |
| pH                     | 8.04      | .942      | .103    | .176      | .266  | .732                | .729           | .372             | 0.3                    |
| Redox potential        | 25.6      | .237      | .175    | .193      | .928  | .341                | .571           | .944             | 25.5 mV                |
| Ca                     | 20.15     | .213      | .464    | .168      | .997  | .905                | .584           | .484             | 17.3 mg/L              |
| Log Fe                  | 18.9      | .601      | .731    | .061      | .603  | .181                | .131           | 1                | 22.9 mg/L              |
| Log K                   | 11.22     | .472      | .917    | .667      | .35   | .366                | .232           | .421             | 2.0 mg/L               |
| Log Mg                  | 29.03     | .235      | .46     | .241      | .747  | .912                | .407           | .235             | 5.1 mg/L               |
| Log Mn                  | 37.16     | .185      | .527    | .013      | .463  | .337                | .312           | .848             | 0.5 mg/L               |
| Log Na                  | 26.4      | .108      | .141    | .403      | .157  | .944                | .206           | .891             | 21.6 mg/L              |
| Log SO$_4$              | 32.4      | .39       | .004    | .304      | .35   | .948                | .401           | .305             | 48.7 mg/L              |
The difference in surface water quality between the Mercia Mudstone and Sherwood Sandstone Groups, and the power analysis showed that the survey design was capable of detecting a difference smaller than that observed between the bedrock formations. Together, these results indicate that the mineralogical change in geological bedrock formation affected surface water quality but not the groundwater barrier effect of the Woodsfold fault. We propose that although surface waters appear to interact with a weathered bedrock layer via shallow circulation through glaciofluvial sands and gravels of the superficial deposits, there is no chemical evidence to suggest that deeper groundwater from the Mercia Mudstone Group, or below, was rising to the surface in response to the Woodsfold fault acting as a barrier.

**FIGURE 9** Diagram of the differences in electrical conductivity of surface waters and groundwater across the Woodsfold fault in the southern Fylde. Electrical conductivities for groundwater from Wilson et al. (2019). Reference geological cross-section (approximate location shown in Figure 4) is based on BGS (1990) and Ove Arup and Partners Ltd. (2014c).
4.4 | Implications for shale gas exploitation

Groundwater–surface water interactions may indicate potential two-way contaminant pathways exist. Identifying and understanding these pathways is therefore essential for assessing the water contamination risks posed by surface spills or subsurface leakage related to shale gas activities, or indeed other anthropogenic activities. Although groundwater monitoring boreholes are undoubtedly useful for this purpose, there may be a lack of existing boreholes or temporal and financial constraints on drilling new boreholes (e.g. DiGiulio et al., 2011). In contrast, surface water sampling (providing a surface water system exists across the prospective basin) can be quicker, cheaper and more spatially comprehensive than groundwater samples. If the underlying bedrock geology is known and an informed conceptual hydrological model exists, surface water samples could be used with or without groundwater samples to infer groundwater–surface water interactions. An additional issue to consider are transient hydraulic effects, for example surface waters may be gaining or losing at different points of the year in response to seasonal precipitation or human-induced effects such as abstraction (Sophocleous, 2002). As a result, the receptors of potential contaminants would also change in response to directional flow changes in the pathway.

For the study region surface water quality data indicated regional-scale groundwater–surface water interaction through the superficial deposits, highlighting the importance of localized investigations to identify specific pathways and receptors in shale gas environmental risk assessments. For sites located west of the Woodsfold fault, the thickness of the Mercia Mudstone Group [~330 m thick in the Kirkham Borehole SD43/20 (UKOGL, 2020)] appears to provide a hydraulic barrier between groundwater in the underlying Sherwood Sandstone Group and groundwater in the overlying superficial formations. Alternatively, differences in surface water quality over the same underlying bedrock geology does not vary across the basin of interest, it may not be possible to detect any chemical signatures from groundwater. Conversely, in basins with no surface water system or one with very limited extent, surface water sampling is not possible or of extremely limited use for understanding the groundwater system and any interaction. Similarly, if bedrock geology does not vary across the basin of interest, it may not be possible to conclude from water quality data that groundwater in bedrock formations interacts with surface waters. On the other hand, differences in surface water quality over the same underlying bedrock geology may indicate localized interactions with groundwater in deeper formations. Alternatively, differences in surface water quality may relate to other environmental factors such as land use or the geochemistry of any superficial deposits (note that the omission of such factors in this study does not negate the significant effect of bedrock geology).

The chemical analyses in this study were limited to field data and ion concentrations due to financial constraints. The additional analysis of other ion concentrations and isotopes (radiogenic and stable) may improve understanding of groundwater–surface water interactions. For example, Radon-222 concentrates in subsurface waters (Dimova, Burnett, Chanton, & Corbett, 2013) and can therefore be used to investigate river/groundwater mixing (Bertin & Bourg, 1994) and groundwater discharge in coastal areas and lakes (Cable, Burnett, Chanton, & Weatherly, 1996; Dimova et al., 2013). Stable strontium isotopes (87Sr/86Sr) have been used effectively as groundwater tracers (Bullen, Krabbenhoft, & Kendall, 1996; Gosselin, Harvey, Frost, Stotler, & Macfarlane, 2004; Gunn, Bottrell, Lowe, & Worthington, 2006), including in the context of unconventional hydrocarbon resources (Chapman et al., 2012; Frost, Pearson, Ogle, Heffern, & Lyman, 2002). The ratios of stable oxygen (18O/16O) and hydrogen (2H/1H) isotopes are also useful because their ratios in rainfall vary with climatic temperature, thereby providing constraints on water body ages and mixing (Abesser, Shand, & Ingram, 2005; Bath et al., 2006; Darling, Bath, & Talbot, 2003). Although it is unlikely that isotopic values would be available in sufficient numbers to enable the type of statistically rigorous and multivariate analyses used in this study, isotopic analyses may provide confirmatory evidence for interpretations drawn from statistical analyses of larger water quality datasets.

4.5 | Study limitations

In the Bowland Basin the Wyre and Ribble rivers, and their major tributaries, generally have a baseflow index of ~0.3 (NRFA, 2020). The hot temperatures and lack of precipitation in the 2018 United Kingdom summer provided an ideal opportunity to sample surface waters across the study region because baseflow conditions increased the probability of detecting chemical groundwater signatures. However, in basins where surface runoff dominates and baseflow is minimal, it may not be possible to detect any chemical signatures from groundwater. Conversely, in basins with no surface water system or one with very limited extent, surface water sampling is not possible or of extremely limited use for understanding the groundwater system and any interaction. Similarly, if bedrock geology does not vary across the basin of interest, it may not be possible to conclude from water quality data that groundwater in bedrock formations interacts with surface waters. On the other hand, differences in surface water quality over the same underlying bedrock geology may indicate localized interactions with groundwater in deeper formations. Alternatively, differences in surface water quality may relate to other environmental factors such as land use or the geochemistry of any superficial deposits (note that the omission of such factors in this study does not negate the significant effect of bedrock geology).

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Additional non-chemical analyses that could be undertaken to investigate groundwater–surface water interactions include the use of hydrograph and temperature data. Hydrograph data can be used to estimate the contribution of groundwater to river flow (or vice versa) through the calculation of baseflow indices (Eckhardt, 2008) and flow accretion values and indices (Grapes, Bradley, & Petts, 2005). However, the use of hydrographs in basins such as the Bowland Basin may be limited by the spatial density of gauging stations, which are often only located on major rivers and tributaries. Conversely, water temperature data can often be collected easily from a greater number of locations. Given that groundwater can be warmer or cooler than surface waters, temperature anomalies in surface waters could be used to infer groundwater–surface water interaction (Briggs, Hare, Boutt, Davenport, & Lane, 2016).

## 5 | CONCLUSIONS

Understanding how groundwater and surface water systems interact is essential for the management and protection of water resources. A variety of data types and methods exist to investigate groundwater–surface water interactions but these can be costly, and thus spatially limited at a basin scale. However, surface water quality data can often be collected and analysed at lower costs, resulting in datasets to which rigorous statistical analyses can be applied rather than subjective interpretations of small datasets. In prospective shale gas basins identifying groundwater compartmentalisation and groundwater–surface water interactions is particularly important for understanding potential contaminant pathways. Using surface water quality data from a prospective basin we showed that bedrock geology was a significant factor influencing surface water quality across the prospective basin, implying regional-scale groundwater–surface water interactions despite the near-ubiquitous presence of superficial deposits with an average thickness of 30–40 m. Principal component analysis supported this conclusion by showing that surface water compositions were constrained within groundwater end-member compositions. Surface water quality data showed no relationship with previously identified groundwater compartmentalisation, even though the statistical analysis was of sufficient power to identify the impact of different aquifer geology on the same surface waters. We propose that although surface waters appear to interact with a weathered bedrock layer via shallow circulation through glaciofluvial sands and gravels of the superficial deposits, there is no chemical evidence to suggest that deeper groundwater in this area of the prospective basin was reaching the surface in response to compartmentalisation-enhanced flow. Consequently, compartmentalisation in this area of the prospective basin does not appear to increase the risk of fracking-related contaminants reaching surface waters.

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## DATA AVAILABILITY STATEMENT

All surface water quality data are available in the Supporting Information. All groundwater quality data are available from Wilson et al. [2019].

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SUPPORTING INFORMATION
Additional supporting information may be found online in the Supporting Information section at the end of this article.

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