Tellus regional stream water geochemistry: environmental and mineral exploration applications

Vincent Gallagher*, Eric C. Grunsky, Mairéad M. Fitzsimons, Margaret A. Browne, Sophie Lilburn and James Symons

Geological Survey Ireland, Haddington Road, Dublin D04K7X4, Ireland

© VG, 0000-0002-5679-0924; ECG, 0000-0003-4521-163X; MMF, 0000-0003-2869-1678; MAB, 0000-0003-2533-2047; SL, 0000-0002-3071-0439
*Correspondence: vincent.gallagher@gsi.ie

Abstract: Regional stream water geochemistry acquired as part of the Tellus programme in Ireland has been analysed to assess its potential for application to environmental assessment and mineral exploration. Interpolated geochemical maps and multivariate statistical analysis, including principal component analysis and random forest classification, demonstrate broad geogenic control of stream water chemistry, with both bedrock and subsoil contributing to the patterns observed. Surface water regulations set Environmental Quality Standard values for individual Priority Substances and Specific Pollutants that may depend on background concentrations and/or water hardness. The high resolution of Tellus stream water data and their location on low-order streams have allowed estimation of background concentrations and water hardness in the survey area, with significant implications for water monitoring programmes. Anthropogenic inputs to stream water in the survey area come mainly from agricultural sources and Tellus data suggest few catchments are unaffected. Comparison of Tellus stream water geochemistry with stream sediment and topsoil geochemistry suggest that stream water geochemistry has strong potential for use in mineral exploration, with the same base metal and gold pathfinder anomalies apparent in all three data sets. Cluster analysis indicates that base metals in stream water are associated with organic matter but statistical analysis may be employed to distinguish mineralization-related signatures.

Keywords: hydrochemistry; geogenic; background concentrations; water hardness; anthropogenic contaminants; mineral deposits

Supplementary material: Comparison of cation/anion associations using Piper plots and principal component analysis is available at https://doi.org/10.6084/m9.figshare.c.5683094

Thematic collection: This article is part of the Hydrochemistry related to exploration and environmental issues collection available at: https://www.lyellcollection.org/cc/hydrochemistry-related-to-exploration-and-environmental-issues

Received 30 July 2021; revised 26 October 2021; accepted 26 October 2021

Regional geochemical mapping has been conducted in parts of Ireland since the 1970s (Webb et al. 1973; O’Connor et al. 1988; O’Connor and Reimann 1993). Plans to cover the whole island began with the Resource and Environmental Survey of Ireland (RESI) (Bullock and Clinch 2001). As the island of Ireland is divided into two jurisdictions, the six counties of Northern Ireland (part of the United Kingdom) in the NE and the remaining 26 counties of Ireland, RESI was intended as a collaboration between the Geological Survey of Northern Ireland (GSNI), the British Geological Survey (BGS) and Geological Survey Ireland (GSI). Its aim was to produce high-quality digital data sets of geochemical and geophysical parameters to support government planning and promote mineral exploration. RESI did not proceed but did lead directly to the original Tellus Project, which was carried out by GSNI and covered Northern Ireland only (Young and Donald 2013). The Tellus Border Project, covering the adjacent six counties in Ireland, was completed between 2011 and 2014 by GSI and GSNI (Gallagher et al. 2016a, b; Young 2016). Since 2014, the Tellus Programme of GSI has continued as a Government of Ireland initiative undertaking geochemical and geophysical surveying over the remainder of the island of Ireland.

Geochemical samples collected for Tellus include topsoil, stream sediment and stream water. By 2021 topsoil had been collected and analysed from the entire northern half of the island (Young and Donald 2013; Gallagher et al. 2016a; Browne and Gallagher 2020; Browne et al. 2021) and this part of the programme is continuing with the aim of completing collection across the island by 2024. Stream sediment and stream water data are available for Northern Ireland (Young and Donald 2013) and parts of Ireland (Geological Survey Ireland 2020a, b, c, d).

The Tellus stream water geochemical data collected to date have received less attention than soil and sediment data, despite their potential to contribute to the understanding of regional geochemical controls. The FOREGS geochemical atlas of Europe (De Vos et al. 2006) demonstrated that regional stream water geochemistry reflects, inter alia, bedrock composition, including mineralization, subsoil composition, climatic factors and anthropogenic influences. Similar controls were manifest in regional stream water geochemical surveys in Northern Ireland (Young and Donald 2013) and the River Clyde catchment in Scotland (Smedley et al. 2017). In recent years, hydrogeochemistry has attracted attention as a potential mineral exploration tool, particularly groundwater (e.g. Wallace et al. 2020) but also surface water (e.g. Simpson et al. 1993; Wang et al. 2005). Advances in analytical techniques, specifically inductively coupled plasma mass spectroscopy (ICP-MS), leading to lower detection limits have facilitated the use of surface water in which element concentrations tend to be lower than in groundwater.

This contribution reviews the Tellus stream water geochemistry for samples collected in Ireland between 2011 and 2017, as part of the Tellus Border project and ensuing GSI Tellus Programme.
While stream water data are available for Northern Ireland, they have yet to be merged with the GSI Tellus data and are thus not considered further here. Young and Donald (2013) provide an overview of these data.

**Tellus stream water: sampling and analysis**

Figure 1 shows the location of Tellus stream water sample sites. Locations were planned in advance using a geographical information system to achieve as even a spread of sites as possible consistent with the natural drainage density, while also ensuring locations were distributed across geological parent materials and catchments. The survey area comprises c. 24 000 km² in north and NW Ireland, covering Counties Donegal, Sligo, Leitrim, Cavan, Monaghan, Louth, Mayo and parts of Galway, Roscommon and Clare. Data are available for 6835 sites, giving an overall sampling density of one site per 3.5 km².

Sample sites are typically located on low-order streams, with 99% on first- (40.0%), second- (52.2%) or third-order (6.8%) streams according to the Strahler stream order classification system (1957, 1964). Sampling took place at least 75 m upstream of roads, livestock watering or crossing points and other visible potential sources of contamination. Samples were typically taken from the centre of streams between May and September when baseflow conditions predominated.

At each site, two <0.45 μm filtered stream water samples were collected, one unacidified (F/UA) for analysis of anions and NPOC (non-purgeable organic carbon ≈ dissolved organic carbon), the other acidified (F/A) with super-purity concentrated nitric acid (1% v/v) for multielement analysis by ICP-MS. Each F/A sample was further acidified by addition of 0.5% v/v super-purity hydrochloric acid in the laboratory to improve the solubility of Ag and Sn. Unfiltered water was also collected for field determinations of pH, specific electrical conductance and total alkalinity to determine bicarbonate concentration.

Laboratory analyses were carried out at the Inorganic Geochemistry Laboratory of the BGS, Keyworth, Nottingham, UK. Each F/UA stream water sample was analysed by a total organic carbon (TOC) analyser for NPOC using a Shimadzu TOC-VP CPH total organic carbon analyser. F/UA samples were also analysed for major and trace anions (Cl⁻, SO₄²⁻, NO₃⁻, NO₂⁻, Br⁻, HPO₄²⁻ and F⁻) using a Dionex ICS5000 ion chromatograph (IC) system. The uncertainty associated with the NPOC analyses is in the region of ± 8%, while the IC analyses of Cl⁻ and SO₄²⁻ have an uncertainty on the order of ±10%, and F⁻, NO₃⁻, Br⁻, NO₂⁻, and HPO₄²⁻ have uncertainties on the order of ±20%. Each F/A stream water sample was analysed using an Agilent 7500cx series quadrupole ICP-MS with an octopole reaction system. Generally the uncertainty associated with measurement by ICP-MS away from the detection limit is ±10%. However, the overall analytical uncertainty for Na, Ca, Si, P, S, K, Fe, Zn, Sr and Ba is on the order of ±15% and for Li, B and Al the overall uncertainty is in the region of ±20%.

Table 1 lists the analytes, reporting units and reported lower limits of detection. ANOVA analysis of duplicate and replicate samples indicate that the majority of analytes in the Tellus dataset exhibit a combined analytical and sampling variance of less than 5%, so the uncertainty associated with sampling and laboratory analyses is typically small. The data are thus well suited to regional geochemical mapping.
Table 1. Tellus stream water data: analytes, reporting units and lower limits of detection (LLD)

| Analyte | Units | LLD | Analyte | Units | LLD | Analyte | Units | LLD |
|---------|-------|-----|---------|-------|-----|---------|-------|-----|
| pH      | pH unit | 0.01 | Cs      | µg l⁻¹ | 0.001 | Pr      | µg l⁻¹ | 0.002 |
| SEC     | µS cm⁻¹ | 0.001 | Cu      | µg l⁻¹ | 0.1 | Rb      | µg l⁻¹ | 0.01 |
| HCO₃⁻  | mg l⁻¹ | 0.00001 | Dy  | µg l⁻¹ | 0.002 | S       | mg l⁻¹ | 0.5 |
| NPOC    | mg l⁻¹ | 0.5 | Er      | µg l⁻¹ | 0.002 | Sb      | µg l⁻¹ | 0.005 |
| Cl      | mg l⁻¹ | 0.05 | Eu      | µg l⁻¹ | 0.002 | Se      | µg l⁻¹ | 0.04 |
| SO₄²⁻   | mg l⁻¹ | 0.1 | Fe      | µg l⁻¹ | 1 | Si      | µg l⁻¹ | 50 |
| NO₃⁻    | mg l⁻¹ | 0.05 | Ga      | µg l⁻¹ | 0.01 | Sm      | µg l⁻¹ | 0.002 |
| Br      | mg l⁻¹ | 0.02 | Gd      | µg l⁻¹ | 0.002 | Sn      | µg l⁻¹ | 0.02 |
| NO₂⁻    | mg l⁻¹ | 0.01 | Hf      | µg l⁻¹ | 0.01 | Sr      | µg l⁻¹ | 0.01 |
| HPO₄³⁻  | mg l⁻¹ | 0.1 | Ho      | µg l⁻¹ | 0.002 | Ta      | µg l⁻¹ | 0.02 |
| F       | mg l⁻¹ | 0.01 | K       | mg l⁻¹ | 0.02 | Tb      | µg l⁻¹ | 0.002 |
| Ag      | µg l⁻¹ | 0.05 | La      | µg l⁻¹ | 0.002 | Th      | µg l⁻¹ | 0.005 |
| Al      | µg l⁻¹ | 0.02 | Li      | µg l⁻¹ | 0.25 | Ti      | µg l⁻¹ | 0.05 |
| As      | µg l⁻¹ | 5 | Mg      | mg l⁻¹ | 0.01 | Tm      | µg l⁻¹ | 0.002 |
| Ba      | µg l⁻¹ | 0.1 | Mn      | µg l⁻¹ | 0.2 | U       | µg l⁻¹ | 0.002 |
| Be      | µg l⁻¹ | 0.001 | Mo | µg l⁻¹ | 0.03 | V       | µg l⁻¹ | 0.03 |
| Bi      | µg l⁻¹ | 0.01 | Na      | mg l⁻¹ | 0.2 | W       | µg l⁻¹ | 0.02 |
| Ca      | mg l⁻¹ | 0.3 | Nb      | µg l⁻¹ | 0.001 | Y       | µg l⁻¹ | 0.005 |
| Cd      | µg l⁻¹ | 0.001 | Nd      | µg l⁻¹ | 0.01 | Yb      | µg l⁻¹ | 0.002 |
| Ce      | µg l⁻¹ | 0.002 | Ni      | µg l⁻¹ | 0.1 | Zn      | µg l⁻¹ | 0.25 |
| Co      | µg l⁻¹ | 0.01 | P       | mg l⁻¹ | 0.001 | Zr      | µg l⁻¹ | 0.02 |
| Cr      | µg l⁻¹ | 0.05 | Pb      | µg l⁻¹ | 0.02 |

applications. Full details of collection, sample treatment, sample analysis and quality control data, including charge balance, can be found in Geological Survey Ireland (2020e). All data are freely available online from GSI at https://www.gsi.ie/en-ie/programmes-and-projects/tellus.

Survey area: geology, mineralization and land cover

Geology

The bedrock geology of the northern part of Ireland that is covered by the Tellus stream water data is very diverse (Fig. 2). In the NW, the Neoproterozoic (Precambrian) Dalradian Supergroup and Caledonian Donegal granites underlie most of the area. In the west, Dalradian gneiss and schist, Lower Paleozoic clastic sediments and Caledonian igneous intrusions make up the bedrock in the geologically complex Connemara region. Further east, Devonian and Carboniferous rocks, including extensive limestone- and shale-dominated sequences, predominate before giving way in the eastern region to the greywacke–shale units of the Lower Paleozoic (Ordovician–Silurian) Longford-Down Inlier.

The Quaternary geology of the region (Fig. 1, Supplementary Material) is dominated by glacial till and, in upland areas, peat. Glaciofluvialite sand and gravel deposits, and alluvial deposits associated with rivers and lakes, are also common if geographically restricted. The composition of till in the region is typically strongly influenced by bedrock composition, with till derived from metamorphic rocks, Lower Paleozoic sandstone and shale, limestone and granite predominating.

Mineralization

There are numerous occurrences of base metal (Zn, Pb, Cu) mineralization in the region covered by Tellus stream water geochemistry and several of these have been exploited in the past, mostly for Zn and Pb. Other commodities for which deposits have been discovered, if not exploited, include Au, Cr and W.

Known base metal occurrences include the former mines of Tynagh (commodities produced: Zn, Pb, Cu, Ba, Ag), Glengowla (Pb, Ag) and Clements (Pb, Ag) in County Galway; Abbeytown (Zn, Pb) in County Sligo; Twigspark (Pb) in County Leitrim; Keelrum (Pb), Glenaboghill (Pb), Ballyshannon (Pb) and Glentogher (Pb, Ag) in County Donegal; Tassan, Annalough, Coolartragh and Hope mines in County Monaghan (Pb, Ag) (Fig. 2, Supplementary Material).

Gold mineralization occurs in the Dalradian metasediments of north Donegal (Inishowen) (Arkle Resources 2021), the Lower Paleozoic sediments of south Mayo (Lecanvey, Cregganbaun) (Aherne et al. 1992; Thompson et al. 1992), Inishturk island and in the Lower Paleozoic rocks of the Longford-Down Inlier in Monaghan (Clontibret) (Conroy Gold and Natural Resources 2021). Small occurrences of W are widespread throughout the western part of the Connemara Dalradian succession where scheelite is a common component of calc–silicate skarns. Chromium is enriched in mafic rocks of the Connemara Metagabbro and Gneiss Complex, notably in the layered Dawros peridotite (Hunt et al. 2011). It is also sporadically enriched in serpentinite bodies and elastic sequences within both the Dalradian and overlying Lower Paleozoic sequences of Galway and Mayo.

Land cover

Land cover (or land use) in the survey area (Fig. 3, Supplementary Material) comprises mainly agricultural land, chiefly pasture (43% of the area) that varies from good-quality cattle pasture on improved grasslands in the midlands to rough grazing for sheep on higher ground in the west and NW. Peat bogs (26%), chiefly blanket bogs on high ground in the west and NW, comprise the second most important land cover in the survey area. Other agriculture (11.6%), forestry (8.8%), moors and areas of bare rock or sparse vegetation (3.2%), arable land (1.35%), natural grassland (0.9%) and made ground/urban areas (1.2%) account for the bulk of other land uses in the area.

Surface water in Ireland: regulation, monitoring and previous research

In Ireland national monitoring programmes coordinated by the Environmental Protection Agency (EPA) aim to support the
Fig. 2. Bedrock geology (from GSI 1:1 000 000 scale map) of the northern part of Ireland. Basemaps © Ordnance Survey Ireland Licence No. EN 0047221.

Fig. 3. Distribution of Ca concentrations in Tellus topsoil and stream water samples. Basemaps © Ordnance Survey Ireland Licence No. EN 0047221.
Tellus stream water geochemistry

reduction or elimination of contamination of surface water by Priority Substances, Priority Hazardous Substances and Specific Pollutants (SPs) as listed in the Surface Water Regulations 2009 (European Commission 2009). Substances listed that are also part of the Tellus stream water data set are As, Cd, Cr, Cu, F\(^-\), Pb, Ni and Zn. In Irish law, the word ‘pollutant’, as used in the term SP, is defined as follows:

‘Pollutant’ means any substance liable to cause pollution, and, for the purpose of this definition, ‘substance’ includes bacteria and other pathogens, where relevant, and the expression ‘polluting matter’ shall be construed accordingly (p7, European Commission 2009).

In defining the Environmental Quality Standards (EQS) values for SPs the regulations state that the values for all metals, except Cr (VI), are as added values to background concentrations. Background concentrations are not defined in the regulations and presumably refer to local background concentrations.

Nearly half of the surface waters in Ireland are failing to meet the legally binding water quality objectives set by the EU Water Framework Directive because of contamination and other human disturbance (Wall et al. 2020). As stated in the latest EPA water quality report (Trodd and O’Boyle 2020, p2), ‘the main problem damaging [Irish] waters is the presence of too much nutrients such as phosphorus and nitrogen which come primarily from agriculture and waste water’. The most recent survey data for the period from 2017 to 2019 (Trodd and O’Boyle 2020) indicate almost 50% of sites sampled had unsatisfactory nitrate concentrations (>8 mg l\(^{-1}\) NO\(_3\)). Moreover, 44% of sites showed an increasing nitrate trend in the period from 2013 to 2019. The highest concentrations are observed in the south, SE and east of the country where more intensive farming is coupled with freely draining soil and relatively low rainfall (Trodd and O’Boyle 2020). The story for phosphorus (reported as phosphate) is similar. Phosphate in surface and ground waters comes mainly from sewage, industrial discharges and from animal manure and inorganic fertilizers spread on agricultural land.

One third of sites assessed in 2017–2019 had unsatisfactory phosphate levels (>0.035 mg l\(^{-1}\)) while 26% of sites showed a trend of increasing phosphate levels (Trodd and O’Boyle 2020).

Near towns and cities, sewage and industrial discharges can be significant. Drainage from historic mine sites is a source of elevated concentrations of some metals, except Cr, Ni, Pb) and SPs (F\(^-\), As, Cr, Cu and Zn) in the Tellus data set are not generally a cause of EQS failures as a result of EPA monitoring. Sites with elevated concentrations of Cd, Pb and Zn are typically found downstream of historic mine sites and are subjected to repeated surveillance monitoring throughout the year.

Tellus stream water data: mapping and analysis

The objective of the Tellus survey is to collect regional-scale baseline data on major ions, trace elements, pH and TOC by sampling low-order streams, at sites that are located away from known sources of contamination. This study focuses on characterizing the main controls on trace element and major ion geochemistry.

The regional geochemistry of surface water is influenced by numerous factors. Bedrock and subsoil composition typically play a significant role in both major and trace element composition (e.g. Ander et al. 2006; De Vos et al. 2006). The distribution of major ions such as Ca\(^{2+}\), Mg\(^{2+}\), Na\(^+\), HCO\(_3\)\(^-\) and Cl\(^-\) reflects conditions influenced by pH and Eh. Piper plots of the Tellus data (Fig. 4, Supplementary Material) distinguish stream water draining limestone-dominated bedrock, characterized by a relative enrichment in Ca\(^{2+}\)-Mg\(^{2+}\)-HCO\(_3\)\(^-\) from stream water draining other bedrock, such as granite, clastic sediments and mafic rock. In this study we have preferred to employ principal component analysis as a means of characterizing the controls on stream water chemistry, not least because they incorporate trace elements as well as major ions. A comparison of Piper plots and principal component (PC) biplots is documented in the Supplementary Material. Geogenic controls on stream water geochemistry are explored in more detail below using principal component analysis.

The pH of surface water may also influence the distribution of individual elements, depending on their solubility and that of their compounds. The pH of stream water in the study area is predominantly controlled by the distribution of peat and peaty soil (Fig. 5, Supplementary Material). Low pH characterizes the upland areas of Counties Donegal, Mayo, Galway, Leitrim and Roscommon where blanket bog is the predominant subsoil type (Supplementary Material, Figs 1 and 3). Relatively high pH is characteristic of arable land in County Louth and pasture around the midlands where it correlates with high Ca concentrations, reflecting the influence of limestone and agricultural practices, including fertilizer application. In European surface water (Ander et al. 2006) pH appears to exert a strong influence on the distribution of elements such as Al, Cu and Fe. Analysis of the relationship between pH and individual analytes in the Tellus study area shows moderate to weak positive correlations between pH and Ca (r\(^2\) = 0.49), Sr (0.40), Mg (0.28) and U (0.29) (Fig. 6 Supplementary Material). These reflect the coincidence of carbonate bedrock and alkaline stream water. Broad negative correlations can be observed between pH and organic carbon (NPOC), Al and Fe, implying that high concentrations of Al and Fe in stream water at least partly reflect their relatively high solubility under low-pH conditions. Most other analytes in Tellus stream water samples do not correlate well with pH.

Geogenic controls

Univariate maps

Compared to topsoil and stream sediment, the factors controlling the geochemistry of surface water are numerous and complex. They include rainfall, temperature, acidity, organic matter, topography, distance from the ocean and anthropogenic factors, as well as bedrock composition (De Vivo et al. 2006). Nevertheless, interpolated univariate maps of Tellus stream water geochemistry are at least partly consistent with the corresponding maps derived from topsoil and stream sediment geochemistry (Fig. 3) and suggest that stream water chemistry broadly reflects the composition of bedrock and subsoil. Thus, relatively high concentrations of Ca in stream water strongly reflect the distribution of limestone-dominated Lower Carboniferous rocks in the region (Figs 2 and 3). Very low Ca concentrations coincide closely with areas of upland bog. Elevated Cr and Ni concentrations reflect specific known bedrock sources, including the greywacke of the Longford-Down Inlier and the rocks of the South Mayo Trough, which include serpentinite and sediments containing Cr-bearing phases such as chromite and fuchsite. Bedrock units with distinctive topsoil and stream sediment geochemical signatures, such as the Namurian shale of the Leitrim Group (Fig. 2), have similarily distinctive signatures in stream water geochemistry. Known occurrences of gold, base metal and uranium mineralization in the survey area find expression in anomalous concentrations of As, Sb, Zn, Pb, Cd and U in all three sampling media. Interpolated maps for all three media in the survey area can be viewed at https://www.gsi.ie/en-ie/programmes-and-projects/tellus/Pages/Data-and-Maps.aspx.

Principal component analysis

The R statistical environment (R Core Team 2021) was used to process the data for multivariate analysis. Statistical processing
included data transformations to compensate for the compositional nature of the data, exploratory data analysis and multivariate statistical analysis including methods of data exploration and classification that are discussed below.

The stream water geochemistry data were treated as compositional. Unless otherwise noted, in this study a centred logratio transformation was applied to the data (Aitchison 1986) for the application of principal component analysis, cluster analysis and random forest (RF) classification. Details on the treatment of compositional data and methods used to discover and predict geochemical processes can be found in Grunsky (2010) and Grunsky and de Caritat (2019).

Principal component analysis was employed in order to assess the role of bedrock and subsoil composition and other factors in determining stream water geochemistry. Stream water data were classified according to the bedrock and subsoil class underlying each sample site, using GSI’s 1:1 000 000 scale bedrock map (Fig. 2) and the subsoil map published by Teagasc (Fealy et al. 2009; Fig. 1, Supplementary Material). Full details of the principal component analyses and all related outputs can be found in Gallagher et al. (2021).

PC biplots generated from principal component analysis of stream water data (centred logratio) classified by bedrock or subsoil show that for sites underlain by granitic rocks or subsoil derived from them there is relative enrichment in lithophile (Ce, Nd, La, Al, Ti, Sm, Gd, Eu, Yb, Ho, Er, Y, Th), siderophile (Fe) and chalcophile (Pb) elements along the positive portion of the PC1 axis, implying that these elements are strongly associated with this rock type (Fig. 4). For stream water draining Carboniferous limestone or subsoil derived from them, there is a clear association with NO$_3^-$, HCO$_3^-$, Ca, U, F$^-$, Mg, SO$_4^{2-}$, Ba and Mo. The association of U with HCO$_3^-$ likely reflects the stability of hexavalent U carbonates and bicarbonates in solution (De Vivo et al. 2006). The relative enrichment of Ca, Sr, F$^-$, Mg and Ba reflect the underlying Carboniferous limestone-dominated lithologies. These lithologies underlie large areas of pasture and the observed relative enrichment of NO$_3^-$ and SO$_4^{2-}$ may reflect the addition of fertilizer and other agricultural activities. For stream water draining clastic sediments,
such as the greywacke of the Longford-Down Inlier, analysis suggests mixing between the different components, reflecting the diverse range of source material that contributes to clastic sedimentary rocks. There is a significant degree of overlap on the biplots between stream water data classified according to different bedrock/subsoil types but it is clear that the principal component analysis does generally discriminate between the main bedrock/subsoil types, implying that the water geochemistry at least partly reflects geogenic control.

On the PC biplot for stream water classified by subsoil type, there is a clear distinction between water draining raised bogs and blanket bogs, mirroring that between limestone and granite compositions (Fig. 5). Blanket bogs are found within the survey area in upland areas of the west and NW where granitic rocks, gneiss and schist are prominent components of the bedrock. Raised bogs, in contrast, typically occur in the interior lowlands, in areas underlain by limestone bedrock. On the univariate geochemical maps of many elements (e.g. Fig. 3), areas of blanket bog typically coincide with

![PC biplots for stream water data classified by subsoil types, blanket bog (BktPt) and raised or cutover bog (Cut).](image1)

![Fig. 5.](image2)

On the PC biplot for stream water classified by subsoil type, there is a clear distinction between water draining raised bogs and blanket bogs, mirroring that between limestone and granite compositions (Fig. 5). Blanket bogs are found within the survey area in upland areas of the west and NW where granitic rocks, gneiss and schist are prominent components of the bedrock. Raised bogs, in contrast, typically occur in the interior lowlands, in areas underlain by limestone bedrock. On the univariate geochemical maps of many elements (e.g. Fig. 3), areas of blanket bog typically coincide with

![Dendrogram of Tellus stream water data (clr transform) for stream water draining limestone bedrock, based on Ward’s clustering algorithm.](image3)
low element concentrations making interpretation of controls on stream water composition problematic. Principal component analysis suggests that even in areas covered by peat, bedrock signatures can be detected.

Cluster analysis
Hierarchical cluster analysis was applied to the stream water geochemical data (centred logratio transform), using seven different hierarchical clustering methods to create dendrograms for rock types (GSI 1:1 000 000 bedrock geology map) and subsoil (Teagasc subsoils map). Only the results from the application of Ward’s method (Ward 1963) are presented here. The dendrograms have potential use in identifying specific processes but do not provide any geospatial association, which makes it difficult to relate the observed correlations within and between clusters with known or speculative processes. Full details of the hierarchal cluster analyses and all related outputs can be found in Gallagher et al. (2021).

The interpretation of the dendrograms requires some prior knowledge about how the elements may be linked through processes such as mineralogy, weathering, surface water modification, mass transport and organic complexation/adsorption. Ward’s method (Ward 1963) was chosen as it is based on concepts related to analysis of variance, which is consistent with the methods employed to evaluate multi-element geochemical data in this study.

The dendrogram in Figure 6 shows a cluster analysis of stream water data for sites draining limestone bedrock. The groupings of the elements highlight some general patterns. A multi-element signature related to bedrock is located on the left side of the dendrogram. This grouping contains several lithophile (Al, Fe, Ti) and rare earth elements that are generally associated with silicate and oxide mineral assemblages found in granitoid, metamorphic and clastic rocks. A multi-element cluster in the centre includes NO3−–U–HCO3−–Ca−F−Sr–Mo–Sb–Se−SO4−2–S–Br–K–Mg. Many of these elements are also part of a cluster in dendrograms for other rock types and are associated on PC biplots (Figs 4 and 5). The cluster appears to reflect the composition of limestone bedrock (Ca, Mg, Sr, HCO3−) and subsoil comprising limestone-derived till, as well as agricultural activities that result in nutrient inputs to overlying pastures (NO3−). Elements such as Mo, Se and U may reflect the presence of shale interbedded with limestone. However, U is also commonly associated with HCO3−, owing to the stability in solution of U carbonates and bicarbonates, while Mo and Se are mobile under alkaline conditions (De Vivo et al. 2006) such as those typical of areas of limestone bedrock. The right side of the dendrogram shows at least two groups that likely represent variations on peat and the underlying bedrock. NPOC (organic carbon) is in a cluster with Zn, Cd and other elements such as V and Mn, consistent both with the role of organic matter in complexation of metals and base metal mineralization signatures. The Na–Cl association on the right of the dendrogram is consistent with univariate maps (Gallagher et al. 2021) that show high concentrations of these elements fringing the west and NW coast, reflecting the influence of sea water and marine aerosols on stream water along the coast.

Random forests
RF (Breiman 2001; Harris and Grunsky 2015) is an ensemble, multiple decision-tree classifier. RF classification was applied to Tellus stream water data classified by bedrock type (GSI 1:1 000 000 scale), subsoil and Soil Recovery Facility (SRF) Geochemical Domains. Subsoil and bedrock data were combined to generate a Geochemical Domain map as part of the process of devising waste acceptance criteria for SRFs in Ireland (Glennon et al. 2020). The individual SRF Geochemical Domains comprise areas where bedrock and subsoil have broadly similar geochemical characteristics and are in effect a simplification and combination of the subsoil and bedrock maps. A full description of the RF analysis with accompanying illustrations is contained in Gallagher et al. (2021).

Because of the imbalance of classes in the themes for rock type, Teagasc subsoil and land cover, prior probabilities were included in the RF classification. Imbalance refers to unequal numbers of observations for each class. Classes with large numbers of observations can ‘mask’ and ‘swamp’ classes with a small number of observations. This problem can also result in ‘weak classifiers’, where the prediction of a given class may be no better than a random guess. This is particularly the case for the Teagasc subsoil classes, where numerous classes of very limited geographical extent are intersected by relatively few stream water sites.

A plot of the mean decrease measure of the Gini index (Menze et al. 2009) shows the variable (principal component) significance in discriminating between rock types (Gallagher et al. 2021). A higher Gini index indicates that the variable is better at discriminating between the classes. Based on measures of variance for rock type, PCs 1, 5, 2, 7, 6 are the main variables for classifying the rock types from the water chemistry, with PC1 by far the single most important one.

The overall accuracy of the RF predictions for rock type is 69.7%, which is the average predictive accuracy over all of the classes. The precision of the predicted rock types indicates that amphibolite (57%), greywacke (84%), limestone (93%), sandstone (53%), pelite (57%) and granite (67%) are well predicted (Gallagher et al. 2021). Classes including appinite, felsic volcanic rocks, gabbro, mafic volcanic rocks and orthogynous are not well predicted because (i) they have very low counts in the initial data set and (ii) despite the correction applied by the prior probabilities they overlap with other classes. Sources of error or uncertainty in the predictions may include compositional overlap of the chemistry of the stream water between the rock types, misclassification of the original site and the variability created by the range of influences on stream water chemical composition.

Figure 7 shows two maps, one classifying the stream water data according to mapped bedrock and the other the predicted classes (rock types) based on RF analysis. At the scale of these maps, as presented, the predictions of the rock types appear to be reasonably close to the mapped rock types.

Because of the large number (40) of classes represented on the subsoil map there is considerable confusion and uncertainty in the class prediction, reflecting the ‘masking’ and ‘swamping’ referred to above. Despite this, the RF method predicts the subsoil classes in a consistent manner and the distribution of the stream water data, classified by the main mapped subsoil classes, is very similar to that of the predicted subsoil classes (Gallagher et al. 2021). To avoid the complexities posed by the subsoil map, RF classification was carried out using the SRF Geochemical Domain map (Glennon et al. 2020). The main components in descending order of importance are PC2, PC1, PC7, PC5, PC6, PC13, PC4 and PC8 and the overall prediction accuracy is 76.8% (Gallagher et al. 2021). This map contains just seven domains: Namurian clastic rocks (D1 on Fig. 8); limestone (D2); Devonian clastic rocks (D3); Devonian–Carboniferous clastic rocks (D4); Lower Paleozoic sandstone and shale (D5); granitoid rocks (D6) and metamorphic rocks (D7). The accuracies of the predicted domains are 59% (D1), 84% (D2), 23% (D3), 11% (D4), 71% (D5), 46% (D6) and 97% (D7). The measures of precision are better than those reported for the prediction of rock type and subsoil. Figure 8 shows that the geospatial extent of each of the domains on the predicted map is similar to that on the original map. The generally strong agreement between the original domain map and the map predicted by RF analysis validates the Geochemical Domain map itself and provides further support for the observation that the stream water data carry a strong geogenic signal.
As noted above, EQS concentrations for SPs As, Cr (III), Cu and Zn in Surface Water Regulations 2009 (European Commission 2009) should be set as an addition to background concentrations. Estimations of background concentrations in surface water in Ireland have not previously been reported. As surface water chemistry is at least partly controlled by geogenic factors, it follows that natural background concentrations, i.e. net of anthropogenic influences, will vary across the region, based on variation in bedrock and subsoil composition. A further complication is that EQS values for Cu and Zn vary according to water hardness.

Surface water sites monitored by the EPA, local authorities and others for assessing compliance with Surface Water Regulations are typically located on higher-order streams and rivers. Of the sites monitored by the EPA for metal concentrations in the period 2016–2020, 65% are on fourth- or higher-order streams. As the risk of anthropogenic impacts increases down-catchment, such monitoring sites may be unsuitable for assessing natural background concentrations of elements in surface water. Peters et al. (2012) carried out an assessment of ambient background concentrations (ABCs) for metals in freshwater in hydrometric areas and water bodies in the UK, as specified under the EU Water Framework Directive. They defined ABCs as concentrations representing low anthropogenic inputs, rather than natural backgrounds, as the monitoring data used to define them are considered likely to include contributions from natural and anthropogenic (point and diffuse) sources. They recommended that ABCs be based on individual hydrometric areas where sufficient data exist and that they be set at a low, conservative value such as the fifth or 10th percentile (Peters et al. 2012).

In contrast to monitoring sites, over 90% of Tellus stream water sites are located on first- and second-order streams. The Tellus data
are based on sampling in the upper parts of catchments, and sites were selected to minimize the risk of anthropogenic input of metals. In theory, this should allow for an estimate of natural background concentrations.

Figure 9 shows a combination of classical statistical and exploratory data analysis (EDA) plots for SPs As, Cr, Cu and Zn for the entire Tellus data set, which was transformed to log base 10. All elements, except Zn, display log-normal distributions (straight lines in quantile–quantile (Q-Q) plots and symmetrical histograms). Inflection points along the Q-Q curve can be used as ‘breakpoints’ or ‘thresholds’ that define the transition from one process to another (Grunsky 2010). These inflection points can be used as estimations of background concentrations for each element. For As, the estimated breakpoint occurs at 10 μg l⁻¹, for Cr 1.2 μg l⁻¹ and for Cu 10 μg l⁻¹. The Zn Q-Q plot has several inflection points. That observed at the lower end of the range is an artefact related to censoring of values reported below the detection limit (0.25 μg l⁻¹). The Q-Q curve ramps upwards sharply at c. 6.5 μg l⁻¹ and flattens out again at c. 34 μg l⁻¹. These inflection points cover the range of the small peak visible to the right of the main peak on the density plot. This ramp coincides with the 95–99th percentile range for Zn in stream water (Fig. 7, Supplementary Material). Samples in this range are widely dispersed in the study area and, while some can be related to known mineral deposits, most have no clear association with mineralization. Some show a spatial association with peat bogs, e.g. in County Donegal, suggesting complexation by organic matter, whereas others may be linked to bedrock sources, such as Namurian shales (Figs 2 and 7, Supplementary Material). A final inflection point at c. 55 μg l⁻¹ Zn marks outliers of the data that in almost all cases reflect elevated Zn concentrations in streams draining former mine or mineralized areas.

These breaks provide estimates of the background concentrations in stream water for each of these priority substances in the area covered by the Tellus data (Table 2, ‘All’). Generally, estimated background values for As and Cr are well below the stated EQS limits of 25 μg l⁻¹ for As and 3.4 μg l⁻¹ for Cr (III). For Cu, the estimated background of 10 μg l⁻¹ exceeds the stated 5 μg l⁻¹ EQS for water with a hardness ≤100 mg l⁻¹ CaCO₃ eq but is well below...
the corresponding 30 $\mu$g l$^{-1}$ EQS for water with hardness exceeding 100 mg l$^{-1}$ CaCO$_3$ eq. Adding any of these estimated background values to the EQS values to generate ‘corrected’ EQS values would yield higher EQS values. For Zn, the higher estimated background of 34 $\mu$g l$^{-1}$ exceeds the stated 8 $\mu$g l$^{-1}$ EQS for water with a hardness $<$10 mg l$^{-1}$ CaCO$_3$ eq. – adding this value to the stated EQS would eliminate many observed exceedances at the lower end of the scale.

Table 2 summarizes the breakpoints observed on Q-Q plots for stream water samples classified by SRF Geochemical Domain (Gallagher et al. 2021). As may be expected, there is considerable divergence between the estimated threshold or background values for individual elements among the SRF Domains, reflecting the diverse geology of the region. Using EQS concentrations for SPs As, Cr (III), Cu and Zn in surface water without correcting for background will likely lead to many apparent exceedances in monitoring data. Tellus regional stream water data are of sufficient resolution to allow estimates of natural background concentrations at regional or even sub-regional scale.

Surface Water Regulations specify that for some elements the EQS also varies with water hardness, including Cd, Cu and Zn. For example, for Zn the EQS is 8 $\mu$g l$^{-1}$ for water hardness $\leq$10 mg l$^{-1}$ CaCO$_3$ eq.; 50 $\mu$g l$^{-1}$ for hardness $>$10 mg l$^{-1}$ and $\leq$100 mg l$^{-1}$ CaCO$_3$ eq. and 100 $\mu$g l$^{-1}$ for hardness $>$100 mg l$^{-1}$ CaCO$_3$ eq. Water hardness is currently not accounted for in national monitoring programmes in Ireland. As a consequence, surface water is assessed for compliance with EQS values using the lowest or most conservative EQS value for a given element. For Zn, the lowest EQS concentration of 8 $\mu$g l$^{-1}$ can lead to multiple apparent EQS failures.

Water hardness can be calculated for Tellus stream water data from the reported concentrations of Ca$^{2+}$ and Mg$^{2+}$, as measured by ICP-MS. Given the robust nature of ICP analysis, this represents a reliable and consistent means of measuring surface water hardness.

**Table 2. Estimated background concentrations of some elements in Tellus stream water using Q-Q plot breaks**

| Domain     | As $\mu$g l$^{-1}$ | Cr $\mu$g l$^{-1}$ | Cu $\mu$g l$^{-1}$ | Zn $\mu$g l$^{-1}$ |
|------------|-------------------|-------------------|-------------------|-------------------|
| All        | 10                | 1.78              | 10                | 6.5/34            |
| Domain 1   | 0.65              | 0.5               | 4/6               | 7                 |
| Domain 2   | 3                 | 1                 | 5                 | 9                 |
| Domain 3   | 1.9               | 0.8               | 2.1               | 4.8               |
| Domain 4   | 1.8               | 0.7               | 1.9               | 4.7               |
| Domain 5   | 5.6               | 1.5               | 4.4               | 13.8/44           |
| Domain 6   | 0.95              | 0.93              | 1.24/1.82         | 4.7/7.7           |
| Domain 7   | 6                 | 1.14              | 13.5              | 14.2/53.5         |

Data classified according to SRF Geochemical Domains. Some elements have more than one break point on Q-Q plot. SRF Geochemical Domain names: Namurian clastic rocks (D1); limestone (D2); Devonian clastic rocks (D3); Devonian–Carboniferous clastic rocks (D4); Lower Paleozoic sandstone and shale (D5); granitoid rocks (D6) and metamorphic rocks (D7).

**Tellus Surface Water: Zinc EQS**

- Zn $>$ 8 $\mu$g/l

Zn EQS exceedances v water hardness

- Category III
- Category II
- Category I

Hardness, mg/l CaCO$_3$

- $>$ 100 (Cat III)
- $>$10 - $\leq$100 (Cat II)
- $\leq$ 10 (Cat I)

Fig. 10. Distribution of sites for which the measured Zn concentration in Tellus stream water samples exceeds 8 $\mu$g l$^{-1}$, the minimum Environmental Quality Standards (EQS) value. Exceedances of EQS after correction for water hardness are also shown. Water hardness is classified according to the EQS for Zn: $\leq$10 mg l$^{-1}$, $>$10 mg l$^{-1}$ and $\leq$100 mg l$^{-1}$ and $>$100 mg l$^{-1}$ CaCO$_3$ eq., and for convenience labelled Category I, II and III, respectively. Basemaps © Ordnance Survey Ireland Licence No. EN 0047221.
The equation to convert these concentrations to mole equivalent CaCO₃ concentrations is

\[
\text{Hardness (CaCO₃ equivalent) } = [2.5 \times \text{Ca}^{2+}] + [4.1 \times \text{Mg}^{2+}]
\]  (1)

The Tellus stream water data set includes baseline chemical data for 6835 sites spread across a geologically diverse region. While these data are not directly comparable to monitoring site data, they do provide an insight into the possible impact that accounting for hardness would have on the outcomes of monitoring programmes. The hardness values calculated from the Tellus Ca²⁺ and Mg²⁺ data have been interpolated, using inverse distance weighting, to produce a map of stream water hardness in the study area. Figure 10 also shows the distribution of sites for which the measured Zn concentration in Tellus stream water exceeds 8 μg l⁻¹, the lowest EQS value and the one used to assess EPA monitoring data in the absence of water hardness estimates. Out of 6835 samples, 286 (4.2%) exceed 8 μg l⁻¹ Zn. When allowance is made for hardness (Fig. 10), only 27 samples (0.4%) exceed the EQS.

Fig. 11. Distribution of nitrate concentrations in stream water, showing locations of samples of stream water draining arable land. Basemaps © Ordnance Survey Ireland Licence No. EN 0047221.

Fig. 12. Tukey boxplot (log10) of surface water nitrate concentrations classified by major land cover (Corine 2012) classes.
Application of hardness data reduces the number of Zn exceedances observed in Tellus data, when using the minimum EQS value, by 90%.

A similar exercise has been carried out for Cu and Cd (Gallagher et al. 2021) but the impact of potential EQS exceedances for these elements is lower, if still significant. In the case of Cd, application of hardness data reduces the number of Cd exceedances observed in Tellus stream water data by just under 40%. Unlike Zn, Cd is not widely dispersed in stream water at elevated concentrations in the survey area and relatively high concentrations are typically related to specific non-carbonate bedrock sources. Hence, higher EQS values, based on increased water hardness that is intrinsically related to the presence of carbonate bedrock, do not affect the observed rate of EQS exceedance as strongly as is the case for Zn.

Fig. 13. Comparison of the distribution of As, Sb and Zn concentrations in Tellus stream sediment and stream water samples, with locations of known base metal and gold mineralization highlighted. Colours for element classes as in Figure 11. Basemaps © Ordnance Survey Ireland Licence No. EN 0047221.
the sites that exceed the lower EQS for Cu are in non-carbonate areas, i.e. in the lower water hardness category, so application of the water hardness data has only limited effect.

**Anthropogenic processes influencing stream water**

Potentially Harmful Substances are routinely monitored in stream water for exceedances of EQS values. Tellus data demonstrate that elements such as Cd, Zn and Cr can be present in stream water in relatively high concentrations, reflecting bedrock composition and unrelated to known anthropogenic activity. However, some of the highest concentrations of Cd, Zn and other metals in the Tellus survey area and elsewhere in Ireland can be directly related to historic mining activity (Stanley et al. 2009).

In Ireland, the number of historic mine sites that give rise to significant impacts on stream water chemistry is small. Such sites are well-known, of very limited extent and subject to detailed surveillance monitoring. Of far greater potential concern are the more pervasive impacts on stream water chemistry of agricultural activity. The impact of agriculture on stream water chemistry is readily apparent on the map of nitrate distribution (Fig. 11), which shows two areas, in County Louth and east County Donegal, where high stream water nitrate concentrations occur. These coincide with the two most intensively cultivated areas of the study region (Fig. 11). The median NO$_3^-$ concentration for Tellus stream water draining arable land (21.2 mg l$^{-1}$) is over 18 times higher than for pasture land (1.19 mg l$^{-1}$) and almost 80 times higher than for other land uses (Fig. 12). Similar, if less stark, distinctions were observed for phosphorus. Stream water in areas of well-drained soil had significantly higher concentrations of both nitrate and phosphorus than stream water in areas of soil in other drainage classes (Gallagher et al. 2021).

In County Louth univariate mapping suggests that high concentrations of Ca, Mg, Ba, HCO$_3^-$ and U in stream water are also associated with the high nitrate concentrations. Multivariate statistical analysis (e.g. Figs 4 and 6) confirms these observations, with nitrate associated with HCO$_3^-$, Ca, U, Sr, F$^-$, Mg, SO$_4^{2-}$ and Ba in PC biplots and on cluster dendrograms. In part, this reflects an association with limestone bedrock across the region but in County Louth the bedrock is Lower Paleozoic greywacke. There, the source of Ca and Mg in stream water is more likely to be agricultural activity, including liming and fertilizer application. The associated

![Fig. 14. PC2 v. PC3 for stream water draining Corine land cover peat bog class.](http://geea.lyellcollection.org/Downloaded from http://geea.lyellcollection.org/ by guest on June 27, 2022)
high bicarbonate concentrations may account for the elevated U concentrations since U is commonly associated with HCO₃⁻ owing to the stability in solution of U carbonates and bicarbonates (De Vivo et al. 2006). However, there is the possibility that some of the observed high U in stream water may reflect leaching of fertilizer applied to topsoil in the area (e.g. Khater 2006; Molina et al. 2009).

The Tellus stream water data are comparable to EPA monitoring data (Trodd and O’Boyle 2020), with both indicating that higher concentrations of nitrate and phosphorus occur in surface water draining the more productive agricultural land, both arable land and pasture. However, Tellus data provide a more detailed picture of the impact of agriculture on water quality and, as the samples were collected from first- and second-order streams, they indicate that these impacts are pervasive, occurring in the upper parts of catchments, with few areas of improved agricultural land in the survey area unaffected by nitrate or phosphorus inputs.

**Stream water geochemistry and mineral exploration**

Stream water base metal (Zn ± Pb ± Cd) anomalies can be observed near numerous historic mine sites in the Tellus survey area (Fig. 13). Base metal anomalies in stream water can also be observed close to known but unworked mineralized bedrock occurrences. Mineralization signatures in stream water chemistry are not confined to base metals. Gold pathfinder elements As and Sb are enriched in stream water draining known Au deposits in Counties Donegal, Monaghan and Mayo. Comparison of univariate maps for stream sediment and stream water (Fig. 13) indicate that stream water geochemistry may identify known base metal and Au mineralization as readily as stream sediment geochemistry.

While these univariate maps present clear evidence of spatial association between chalcophile elements such as Zn and Cd, stream water geochemical anomalies and known mineralization, there are clearly numerous stream water samples with ‘anomalous’ concentrations that cannot be readily associated with any known mineral occurrence.

On PC biplots, based on a centred logratio transform, (Fig. 14), stream water classified by the Corine Land Cover ‘peat bog’ class display a distinct absence (negative PC2 and/or PC3) of components typically associated with carbonate rocks and agricultural activities, such as Ca, HCO₃⁻, nitrate and phosphorus. Conversely, these stream water samples exhibit a relative enrichment trend (positive PC2 and/or PC3) in chalcophile elements, including Zn and Pb, that may be ascribed to element adsorption in the organic-rich peat.

Cluster analysis shows that Zn and Cd are closely associated in stream water samples that drain Lower Carboniferous bedrock (Fig. 6) and greywacke of the Longford-Down Inlier (Gallagher et al. 2021), the two bedrock units that host the most significant base metal mineralization in the survey area. These elements have similar atomic radii and form a solid-solution series in sphalerite. Cadmium is a notable trace element in numerous Zn–Pb deposits in Ireland (e.g. Slowey 1986; Wilkinson et al. 2005; Stanley et al. 2009; Torremans et al. 2018). NPOC is part of a larger cluster with both Zn and Cd and may also be interpreted to reflect complexation of metals by organic-rich material. Multivariate statistical analysis thus points to some association of chalcophile elements and organic components. Therefore, it is possible that apparent anomalies of Zn and Cd in stream water may reflect base-metal mineralization or simply enrichment following complexation within organic-rich soil and sediment.

In order to explore the data further, it is necessary to define what an anomalous concentration of Zn or Cd is. The use of inflection points on the Q-Q plot was discussed above. Samples with Zn concentration above the inflection point of 34 μg l⁻¹ (Table 2) are mostly related to known mineralization. To widen the search somewhat for this exercise, values around the 98th percentile of Zn

![Fig. 15. Zn v. Cd in Tellus stream water: magenta colours are points for which both Zn and Cd equal or exceed their respective 98th percentile value. Inset: ternary diagram plotting Zn and Cd with non-purgeable organic carbon.](http://geea.lyellcollection.org/)
and Cd (20 and 0.08 μg l⁻¹, respectively) were selected as the threshold of anomalous concentrations. Figure 15 shows a scatterplot of Zn vs. Cd (here multiplied by 100 for plotting convenience). Points for which both Zn and Cd are equal to or exceed their respective threshold value are magenta-coloured. Figure 15 plots Zn and Cd together with NPOC and again the ‘anomalous’ points are highlighted. This plot suggests that ‘anomalous’ Zn and Cd values typically have relatively low-NPOC concentrations. By excluding those few points with higher-NPOC concentrations it is possible to refine this further, improving the likelihood of avoiding ‘anomalous’ Zn and Cd values that owe their relatively high concentrations to organic complexation rather than mineralization. Figure 16 shows the same data on a map. While the distribution of anomalous points largely coincides with that of known mineralization, some of these points are not known to be associated with mineralization and may thus represent possible exploration targets. Such single ‘anomalies’ can be assessed with reference to Figure 15 to determine the likelihood that they reflect an organic influence.

A principal component analysis of the stream water data enhances the possibility of recognizing processes related to base metal mineralization. A separate principal component analysis was carried out on nine chalcophile elements in the stream water data set: Cu, Zn, Pb, Cd, S, As, Sb, Se and Sn. Biplots were prepared over the first eight principal components with the principal component scores classified by rock type and the SRF Geochemical Domains for classification. Symbol sizes were created based on values of Zn and Cd ≥98th percentile concentration and a distance measure of a stream water sample site to the closest chalcophile mineral occurrence obtained from the GSI Mineral Localities database. Figure 17 shows the plots for samples tagged by bedrock composition. All other plots are included in Gallagher et al. (2021). Figure 17 shows the Zn and 100*Cd values that exceed 20 and 10 ppm, respectively, which occur as distinct outliers in the PC1 v. PC2 biplots for rock type. The corresponding ‘distance to mineral location’ biplot shows the Zn–Cd outliers as having a closer proximity (<2000 m) to mineral occurrence locations.
Tellus stream water geochemistry

Conclusions

The Tellus stream water geochemistry data set has been subject to a range of univariate and multivariate statistical analyses in order to elucidate the factors that influence stream water geochemistry in the survey area.

Univariate geochemical maps indicate that stream water major and trace element chemistry broadly reflects the composition of bedrock and subsoil. Major ion hydrochemistry indicates a broad association between the major bedrock types and stream water composition. Multivariate statistical analysis provides more comprehensive support for geogenic control of stream water geochemistry. Principal component analysis, cluster analysis and RF classification identify specific element associations that reflect contributions from different bedrock and subsoil compositions. Even in areas where peat bog forms the subsoil, stream water chemistry carries a distinct bedrock signature.

Surface Water Regulations set EQS values for individual Priority Substances and Specific Pollutants that may depend on background concentrations and/or water hardness. Interpolation of Tellus stream water data to generate water hardness maps in combination with EDA analysis to define background concentrations allows identification of the most appropriate EQS values for Priority Substances As, Cr, Cu and Zn. Adding estimated background values to the EQS values yields higher applicable EQS values, leading in turn to a significant reduction in the number of observed exceedances of EQS values in the survey area. This reduction is especially notable for Zn, with an estimated reduction of 90%.

The most common source of anthropogenic impacts on stream water chemistry in the survey area is agricultural activity. Two areas of high nitrate concentrations coincide with the two most intensively cultivated areas of the study region. The median NO₃⁻ concentration for Tellus stream water draining arable land (21.2 mg l⁻¹) is over 18 times higher than for pasture land (1.19 mg l⁻¹) and almost 80 times higher than for other land cover classes. High concentrations of Ca and Mg observed in stream water have also been linked to agricultural activity, including liming and fertilizer application. Tellus regional geochemical data provide a more detailed picture of the impact of agriculture on water quality than monitoring site data. As Tellus samples were collected largely from first- and second-order streams, they indicate that these anthropogenic impacts are pervasive, occurring in the upper parts of catchments, with few areas of improved agricultural land in the country unaffected by nitrate or phosphorus inputs.

Potentially Harmful Substances are routinely monitored in stream water for exceedances of EQS values. Tellus data demonstrate that elements such as Cd, Zn and Cr can be present in stream water in relatively high concentrations, reflecting bedrock composition and unrelated to known anthropogenic activity. However, some of the highest concentrations of Cd, Zn and other metals in the Tellus survey area and elsewhere in Ireland can be directly related to mineralization and historic mining activity. Current EQS values for several Potentially Harmful Substances vary according to water hardness but lack of water hardness data means that the most conservative threshold values are employed. The high-resolution Tellus data allow generation of interpolated water hardness maps that can be used to assign the correct hardness value to any monitoring site, potentially reducing the number of reported exceedances, especially for Zn.

Stream water base metal (Zn ± Pb ± Cd) anomalies and gold pathfinder element (As ± Sb) anomalies can be observed near numerous historic mine sites and close to known but unworked mineralized bedrock in the Tellus survey area. They are also evident in areas where mineralization has not been reported. On PC biplots stream water classified by the Corine Land Cover ‘peat bog’ class exhibits a relative enrichment trend in chalcophile elements, including Zn and Pb, that may be ascribed to element adsorption in the organic-rich peat, suggesting that at least some apparent metal anomalies are unrelated to mineralization but instead reflect complexation of metals by organic-rich material. This is supported by cluster analysis that shows organic carbon measured in stream water (NPOC) to be part of a larger cluster with both Zn and Cd.

Analysis of background threshold values was employed to define anomalous Zn and Cd concentrations. Those anomalous concentrations linked with known mineralization generally have low NPOC concentrations. Principal component analysis reinforces this...
distinction. Maps of PC3 and PC4, illustrating the positive scores of PC3 and PC4 principal components that have chalcophile enrichment without corresponding NPOC enrichment, may be useful for targeting exploration strategies.

Acknowledgements
This work is published with the permission of the Director of Geological Survey Ireland.

Author contributions
VG: conceptualization (supporting), formal analysis (supporting), visualization (equal), writing—original draft (lead); ECG: formal analysis (lead), methodology (lead), visualization (supporting), writing—original draft (supporting), writing—review & editing (supporting); MMP: conceptualization (lead), project administration (lead), supervision (lead), writing—original draft (supporting), writing—review & editing (supporting); MAB: data curation (lead), formal analysis (supporting), writing—review & editing (supporting); SL: writing—review & editing (supporting), formal analysis (supporting); JS: data curation (supporting), formal analysis (supporting)

Funding
This work is funded by the Government of Ireland. Tellus Border data collection was part-funded by the EU INTERREG IV A programme.

Data availability
The data sets analysed during the current study are available in the Geological Survey Ireland repository: https://www.gsi.ie/en-ie/data-and-maps/Pages/default.aspx.

Scientific editing by Scott Alan Wood

De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A., De Vos, W., V., Gallagher, A.
Tellus stream water geochemistry

O’Connor, P.J., Reimann, C. and Kürzl, H. 1988. A geochemical survey of Inishowen. Co. Donegal. Geological Survey of Ireland Report Series, RS88/1, https://secure.decc.gov.ie/goldmine/docpage.html?id=0&id2=0536596&id3=0536075

Peters, A., Merrington, G. and Crane, M. 2012. Estimation of Background Reference Concentrations in UK Freshwaters. Water Framework Directive – UK Technical Advisory Group (WFD-UKTAG). Sniffer Environment Agency, https://www.wfuk.org/sites/default/files/Media/Environmental%20standards/Backgrounds%20Final%20Report.pdf

R Core Team 2021. R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria, https://www.R-project.org/

Simpson, P., Edmunds, W., Breward, N., Cook, J., Flight, D., Hall, G. and Lister, T. 1993. Geochemical mapping of stream water for environmental studies and mineral exploration in the UK. Journal of Geochemical Exploration, 49, 63–88, https://doi.org/10.1016/0375-6742(93)90039-O

Slowey, E.P. 1986. The zinc-lead and barite deposits at Keel, County Longford. Irish Association for Economic Geology, Dublin, 319–330.

Smedley, P.L., Bearcock, J.M., Fordyce, F.M., Everett, P.A., Chenery, S. and Ellen, R. 2017. Stream-water geochemical atlas of the Clyde Basin. Nottingham, UK, British Geological Survey, 168pp. (OR/16/015), http://nora.nerc.ac.uk/id/eprint/519332/

Stanley, G., Gallagher, V., Ni Mhaíirtín, F., Brogan, J., Lally, P., Doyle, E. and Farrell, L. 2009. Historic Mine Sites – Inventory and Risk Classification. Volume 1: A Joint Study Carried Out by The Environmental Protection Agency and The Geological Survey of Ireland. Environmental Protection Agency, Wexford, Ireland, https://www.epa.ie/publications/monitoring-assessment/assessment/inventory-and-risk-classification-volume-1.php

Strahler, A.N. 1957. Quantitative analysis of watershed geomorphology. Transactions of the American Geophysical Union, 38, 913–920, https://doi.org/10.1029/TR038i006p00913

Strahler, A.N. 1964. Quantitative geomorphology of drainage basins and channel networks. In: Chow, V.T. (ed.) Handbook of Applied Hydrology. McGraw-Hill, New York, 439–476.

Thompson, S.J., Shine, C.H., Cooper, C., Halls, C. and Zhao, R. 1992. Shear-hosted gold mineralization in Co. Mayo, Ireland. In: Bowden, A.A., Earls, G., O’Connor, P.G. and Pyne, J.F. (eds) The Irish Minerals Industry 1980–1990. Irish Association for Economic Geology, Dublin, 21–38.

Torremans, K., Kyne, R., Doyle, R., Given, J.F. and Walsh, J.J. 2018. Controls on metal distributions at the Lisheen and Silvermines deposits: insights into fluid flow pathways in Irish-type Zn-Pb deposits. Economic Geology, 113, 1455–1477, https://pubs.geoscienceworld.org/segweb/economicgeology/article/113/7/1455/566507, https://doi.org/10.1130/0891-8378(2018)1455.4598

Trodd, W. and O’Boyle, S. 2020. Water Quality in 2019 An Indicators Report. Environmental Protection Agency, Wexford, Ireland, https://www.epa.ie/publications/monitoring-assessment/freshwater-marine/Water_Quality_2019.pdf

Wall, B., Cahalane, A. and Derham, J. (eds). 2020. Ireland’s Environment – An Integrated Assessment 2020. Environmental Protection Agency, Wexford, Ireland, https://www.epa.ie/our-services/monitoring-assessment/assessment/irelands-environment/

Wallace, L., Schroder, I. et al. 2020. Northern Australia Hydrogeochemical Survey, Data Release, Preliminary Interpretation and Atlas – Tennant Creek, McArthur River and Lake Woods Regions. Geoscience Australia Record 2018/48 (eCat 122089).

Wang, B., Wanty, R. and Vohden, J. 2005. Geochemistry of stream-waters in mineralized and non-mineralized areas of the Yukon-Tanana Uplands. Impacts of Global Climate Change.

Ward, J.H.Jr 1963. Hierarchical grouping to optimize an objective function. Journal of the American Statistical Association, 58, 236–244, https://doi.org/10.1080/01621459.1963.10500845

Webb, J.S., Nichol, I., Foster, R., Lowenstein, P.I. and Howarth, R.J. 1973. Provisional Geochemical Atlas of Northern Ireland (Technical Communication 60). Applied Geochemistry Research Group, Imperial College of Science and Technology, London, http://www.researchgate.net/publication/265457227_Provisional_Geochemical_Atlas_of_Northern_Ireland

Wilkinson, J.J., Eyre, S.L. and Boyce, A.J. 2005. Ore-forming processes in Irish-type carbonate-hosted Zn-Pb deposits: evidence from mineralogy, chemistry, and isotopic composition of sulphides at the Lisheen Mine. Economic Geology, 100, 63–86, https://pubs.geoscienceworld.org/segweb/economicgeology/article-abstract/100/1/63/151075, https://doi.org/10.1016/0012-620x(05)00963

Young, M.E. (ed.) 2016. Unearthed. Impacts of the Tellus Surveys of the North of Ireland. Royal Irish Academy, Dublin.

Young, M.E. and Donald, A.W. (eds). 2013. A Guide to the Tellus Data. Geological Survey of Northern Ireland, Belfast, http://nora.nerc.ac.uk/id/eprint/509171/