Supplementary Material

Tellus regional stream water geochemistry: environmental and mineral exploration applications

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Supplementary maps and plots

The following figures are as referenced in the main text.



Figure 1 Subsoil map of the northern part of Ireland, based on Teagasc Subsoil map (Fealy *et al.* 2009). Basemaps © Ordnance Survey Ireland Licence No. EN 0047221.



Figure 2 Location of known base metal and gold mineralization in study area. Basemaps © Ordnance Survey Ireland Licence No. EN 0047221.



Figure 3 Land use / cover in the study area (Corine 2012). Basemaps © Ordnance Survey Ireland Licence No. EN 0047221.

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Figure 4 Piper plots of major ions in Tellus stream water samples, classified by bedrock type.



Figure 5 Distribution of pH in Tellus stream water. Basemaps © Ordnance Survey Ireland Licence No. EN 0047221.



Figure 6 Biplots of pH vs. NPOC, Al, Fe, Mg, Ca, Sr, U and Cu.



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Figure 7 Distribution of Zn in Tellus stream water. Basemaps © Ordnance Survey Ireland Licence No. EN 0047221.

Comparison of Cation/Anion Associations using Piper Plots and Principal Component Analysis

Introduction

The use of Piper plots has traditionally been a graphical way of expressing the relationships of groups of cations/anions [Ca-Mg-(Na+K)], [Cl+F+NO3], [(Na+K)-(SO4+Cl)-(Ca+Mg)-(HCO3)], which reflect conditions influenced by pH and eH.

Figure 4 shows the Tellus waters data plotted on a standard Piper plot (Piper, 1944). The figure shows a range of cation/anion compositions classified by underlying rock type. Limestones show a distinct clustering where there is corresponding relative enrichment in Ca-Mg- HCO_3^- . Other water sampling sites associated with granites, clastic sediments, mafic rocks and felsic intrusive rocks show relative depletion in Ca-Mg- SO_4^{2-} - HCO_3^- and a range of values for Cl⁻-F⁻- NO_3^- , HCO_3^- and Ca-Mg.

One of the problems with ternary diagrams and other graphical forms of data presentation that restrict the space of presentation is the degree of distortion that patterns exhibit near the limits of the diagrams. This effect is due to the compositional nature, specifically, of ternary diagrams. A way of expressing this is through the use of a software package CoDaPack (Comas-Cufí and Thió-Henestrosa, 2011). CoDaPack software enables the projection of data in ternary diagrams by centring the mass of data in the ternary diagram. The corresponding triangular grid is re-projected to illustrate the amount of distortion in the grid. Figure 8a shows a ternary diagram of Mg-Ca-K classified by the lithologies underlying the waters sampling sites. Due to the low amount of K relative to Ca and Mg, the data are compressed along the Mg-Ca side of the triangle. Centring the data, using CoDaPack, as shown in Figure 8b, reveals much more information about the relationship of the different lithologies relative to the cations Mg-Ca-K. Note that the ternary grid is highly distorted, emphasizing the significant problem that can be encountered when using ternary diagrams.



Figure 8 (a) Ternary diagram of Mg-Ca-K classified by the lithologies underlying the waters sampling sites. (b) Ternary diagram of Mg-Ca-K classified as per Figure 7a, with the data centred using CoDaPack. Note that the Ternary grid for the centred plot is distorted.

As an alternative to a ternary diagram, principal component analysis (PCA), after a method used by Grunsky (2001), was applied to a log-centred transform of the cations/anions from the Piper diagram of Figure 4. The first two components account for more than 75% of the overall variation and PCA biplots of the first two components are shown in Figures 9 to 12, where the scores of the components are classified by rock type, SRF Domain. Teagasc subsoil class and Corine land cover, respectively. Figure 9 shows that bicarbonate (HCO₃⁻), Ca and F⁻ are associated with the underlying limestone lithology. Na-Cl⁻ (brine) have an inverse association with HCO₃⁻-Ca-F⁻ reflecting a very different environment, which is influenced by the nature of the intrusive and sedimentary (non-carbonate) rocks and the proximity to the Atlantic Ocean. Magnesium appears to be neutral between the two extremes along the first principal component, reflecting its presence in waters overlying limestones and intrusive/sedimentary rocks. Potassium is also neutral relative to HCO₃⁻-Ca-F⁻ and Na-Cl⁻ and shows a significant loading along the negative PC2 axis. High negative PC2 values appear to be associated with Ordovician-Silurian deep marine sediments in the eastern part of the sample area, Silurian-Devonian granitic rocks in the western part of the sample area and Neoproterozoic sediments in the northern part of the sample area.



Figure 9 Biplot of PCA1 vs. PCA2 for Tellus stream water samples, classified by bedrock type.

Figure 10 shows the scores of the components classified by SRF Domains. Domain2 (D2) shows a relative enrichment of Ca- HCO_3^- along the negative PC1 axis. Domain 5 (D5) occupies the negative PC2 and positive PC1 axis. The other domains appear to be mixed along the positive PC1 axis and negative to positive PC2 axis.



Figure 10 Biplot of PCA1 vs. PCA2 for Tellus stream water samples, classified by SRF Domain.

Figure 11 shows the PC1-PC2 scores classified by Teagasc subsoil types. Till derived sediments ("T" Teagasc subsoil classes) have relative enrichment of Ca- HCO_3^- -F⁻ suggesting that these sediments overlay the carbonate terrain. Blanket peat appears to dominate the positive PC1 and positive PC2 region of the biplot, which occurs predominantly in the western part of the sampling area. However it is important to note that both classes (till and peat) are spread across the entire biplot indicating significant overlap of the classes in terms of the cation/anions of the waters.



Figure 11 Biplot of PCA1 vs. PCA2 for Tellus stream water samples, classified by Teagasc subsoil class.

Figure 12 shows the PC1-PC2 biplot coded with land cover classes. Relative enrichment of Ca- HCO_3^- -F⁻ along the negative PC1 axis corresponds to land cover that is dominated by pasture, while the positive PC1 axis region is dominated by the land cover class of peat bog. These two land cover classes also extend into the positive and negative PC2 axis regions.



Figure 12 Biplot of PCA1 vs. PCA2 for Tellus stream water samples, classified by Corine land cover class.

Summary

It is evident from the biplots shown in Figures 9 to 12, there is more information about the relative associations of the cations/anions and the corresponding attributes of rock type, Teagasc, subsoil classes, SRF Domains and land cover than that shown in the Piper diagram in Figure 4. Thus, a preferred method for studying the characteristics of the Tellus stream water is through the use of multivariate statistical methods based on a logratio transform.

References

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