Investigation of Hydrochemical Anomalies of the Roe Valley Catchment, Northern Ireland

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Abstract

Anomalies in stream water concentrations for several metals (Al, Cr, Cu, Ni, Pb, Zn) over the Roe Valley, Co. Londonderry, were detected in 1996. The catchment has a variety of geological formations, with base-rich and base-poor lithologies, and peat dominated headwaters. A selection of stream water sites was re-sampled (2009) to compare with the older survey sampling (1996), and to try to elucidate the hydrochemical processes. Additionally, some of the sites had concentrations close to, or exceeding those, of the Water Framework Directive (WFD) Environmental Quality Standards (EQS). Since 1996, chromium, nickel and zinc concentrations have changed only moderately. Copper concentrations have decreased significantly between 1996 (median 2.7 µg/L) and 2009 (median 1.3 µg/L). The trace element concentrations can be related to local natural sources (such as mineralisation in the Sperrin Mountains), and solubility controls related to pH and dissolved organic carbon. The change in copper concentrations is not completely understood, but may relate to subtle variations in solubility controls, or a decline in the sources of copper to the catchment.

Aims and Objectives

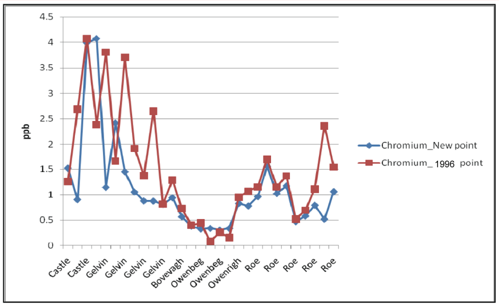
- To investigate the origin of anomalous concentrations of trace elements in the Roe Valley recorded in 1996,
-To explain the significance of elevated metals from the 1996 data with respect to Environmental Quality Standards (EQSs) of the Water Framework Directive (WFD),
- To resample and analyse water samples in the Roe Valley to check if elevated metal concentrations still exist.

Methodology and Results

Filtered stream water samples were acidified and analysed using ICP. All sampling and analysis was done in accordance with BGS Sampling Strategy (Johnson et al. 2007). Chromium (Figure 1), nickel and zinc concentrations have changed only moderately, and their relative abundance within the overall dataset is very similar - nickel concentrations are significantly correlated; chromium and zinc are positively correlated, but individual outliers distort the relationship.

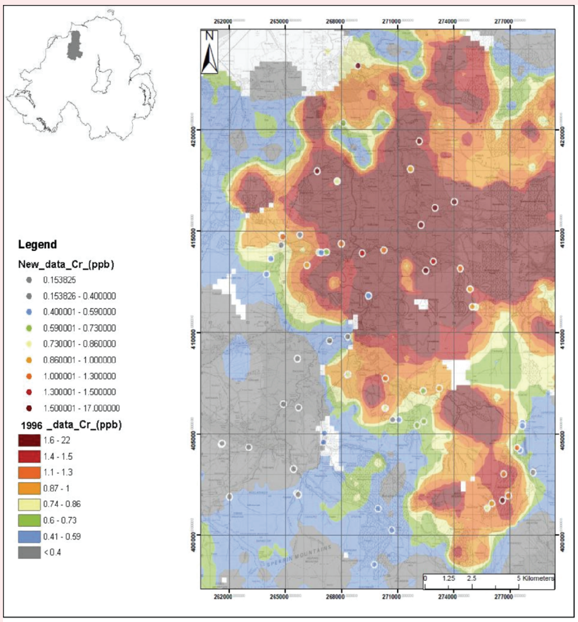
Figure 1

Plot of re-sampled sites showing chromium stream water results



Copper concentrations have decreased from a median of 2.7 µg/L in 1996 to a median of 1.3 µg/L in 2009. Elevated chromium concentrations source from the east of the catchment (Figure 2). Elevated nickel, copper and zinc concentrations are located to the centre of the catchment along the River Roe and where major tributaries join the river. The 1996 results show two sites which exceed EQS; however no new results exceed the standards.

Figure 2 Chromium - 1996 and new data (Crown Copyright and Database Rights 2009)



Discussion

Tributaries to the east of the catchment rises from the Upper Basalt Formation and flow over the Sherwood Sandstone Group towards the centre of the catchment. Chromium concentrations are thought to be governed by the Upper Basalt Formation. Significant concentrations of chromium exist in olivines (Mg_2SiO_4) and pyroxenes ($MgSiO_3$), which occur in basalt, with chromium incorporated into these rocks through magnesium (or iron) minerals. The chromium is thought to be mobilised by means of organic complexation with fulvic acid in peat.
Elevated nickel concentrations also appear to the east and centre of the catchment. Basalt is known to contain high levels of nickel which may be responsible for elevated nickel concentrations to the east of the catchment.
Anomalously high copper and zinc concentrations appear throughout the Dalradian Formation which contains areas of mineralisation. Mineralisation is strongly linked to the presence of sulphide compounds which are available in vein systems throughout the Dalradian Formations. It is thought that these copper and zinc anomalies are reaching the centre of the catchment by means of metal chelation with sulphides or peat (Figure 3).

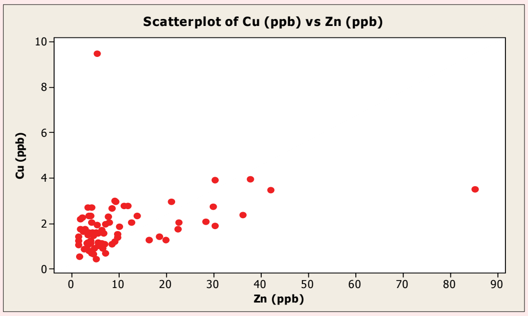


Figure 3
New stream water copper (µg/l) varies sympathetically with new stream water zinc concentrations (µg/l)

Another possibility for elevated nickel, copper and zinc concentrations may be due to groundwater which could be recharging the River Roe. There is a relationship between high metal concentration and low pH concentration due to the stabilisation effect pH has on metals in solution. With low pH, metals are less likely to sorb to organic matter or precipitate from solution (Simpson et al. 1993).

Parameter	WHO Drinking Water Standards (mg/l)	Environmental Quality Standards (Hardness band: >250 mgCaCO$_3$/l)
Chromium	0.05	250
Nickel	0.02	200
Copper	2	28
Zinc	3	125

Table 1

WHO Drinking Water Standards and Environmental Quality Standards for selected parameters

High levels of certain metals in drinking water are known to be potentially harmful to human health. Symptoms such as kidney and liver damage, birth defects, vomiting and diarrhoea are common from ingesting chromium, nickel and copper respectively. Factors such as bioavailability affect the consumption of metal enriched waters. In order to protect human and aquatic life, concentration limits have been set in place for a wide range of inorganic contaminants; such an example can be seen in Table 1 where WHO drinking water standards are listed. Table 1 also lists Environmental Quality Standards of the Water Framework Directive indicating limits for these parameters in surface waters.

Certain concentrations of these metals are essential to human health. For example, chromium III is an essential nutrient for humans and a shortage in the diet may lead to heart conditions, diabetes and disruptions of metabolisms.

Conclusion

Elevated chromium concentrations are probably sourced geologically from the Upper Basalt Formation. It also appears that nickel may source from the Upper Basalt Formation. Copper and zinc anomalies are thought to originate from isolated areas of mineralisation in the Dalradian Formation. Groundwater recharge, as a source of nickel, copper and zinc anomalies, is another potential explanation for these elevated metal concentrations.

Recommendations

- Review existing rainfall abundance and composition data from both sampling periods to determine if rainwater composition had an effect on results,
- Investigate complexes in which these metals exist; this would have an effect on their bioavailability and thus EQSs,
- Resample areas showing elevated copper and zinc concentrations as these may lead to potential areas of mineralisation in the Dalradian Formations,
- Analyse groundwater samples to determine the potential introduction of these metals through groundwater recharge of the River Roe,
- Determine the oxidation state of chromium to determine toxicity to aquatic life,
- Study contaminated land maps and investigate old industries in the area as possible sources of these metal anomalies.

References

Johnson, C.C., Breward, N., Ander, E.L. and Ault, L. (2007) 2005 G-Base Field Procedures Manual: Second Revision, BGS.
Simpson, P.R., Edmunds, W.M., Breward, N., Cook, J.M., Flight, D., Hall, G.E.M, and Lister, T.R. (1993) 'Geochemical mapping of stream water for environmental studies and mineral exploration in the UK', *Geochemical Exploration*, 49(1993), 63-88.
Thornton, I. (1983) Applied Environmental Geochemistry, London: Academic Press.

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