# 23. Stream sediment background concentrations in mineralised catchments in Northern Ireland: assessment of 'pressures' on water bodies in fulfilment of Water Framework Directive objectives

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An approach for deriving sediment background metal and metalloid element concentrations using systematically collected geochemical survey data is demonstrated in the mineralised area associated with the Ordovician-Silurian rocks in counties Down and Armagh in Northern Ireland. Operationally-defined background ranges can be used for improving the assessment of the environmental pressures posed by historical mining on impacted catchments and establishing feasible catchment restoration goals. Deriving pre-mining baselines provides essential information for any proposed mineral development project, with direct benefit to the mineral sector and industry.

## Introduction

In mineralised areas, the local background concentrations of metal and metalloid elements in stream sediments, derived from the weathering and dispersion of metalliferous mineralisation, are often higher than the regional backgrounds. This is in fact the same as the central precept of geochemical exploration for economic ore deposits, where sediment anomalies may indicate the presence of an ore deposit. From an environmental perspective,

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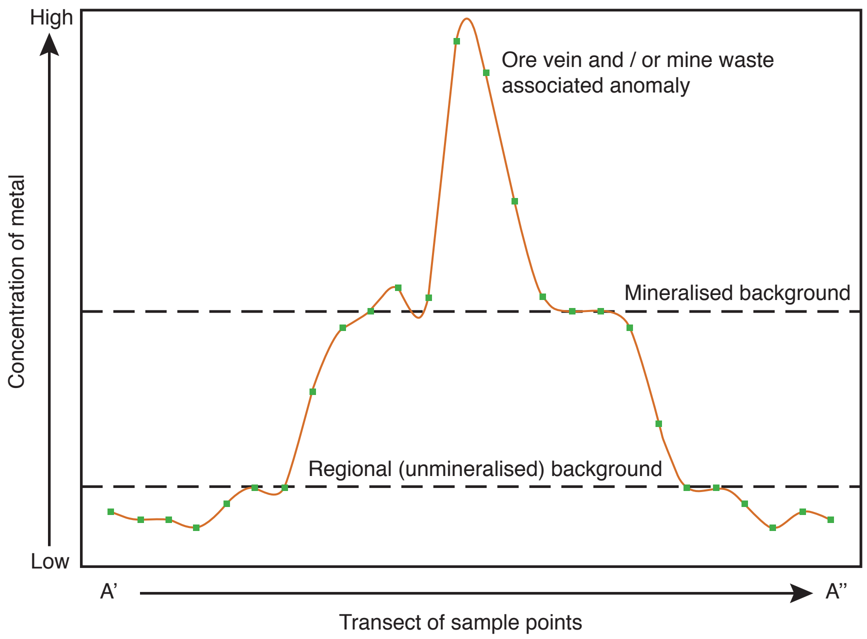


Figure 23.1. Idealised illustration of the naturally elevated baseline occurring over an area of mineralisation, and an anomaly associated with a mineral vein or mine wastes.

defining these anomalies and background thresholds in sediments may be needed for the assessment of 'pressures' on the condition of water bodies, as required by the EU Water Framework Directive (WFD).

Sediments, often enriched in metal(loid)s, are well recognised among the diffuse pollution pressures impacting mineralised water bodies, typically in heavily mined landscapes. For these areas, metal(loid) element background concentrations may be present at substantially higher levels than generic risk-based quality standards (MacDonald *et al.*, 2000), suggesting the need for remedial action. In such circumstances, case-by-case evaluations are required to deal with sediment contamination and clean-up goals, as it may not be technically feasible to bring these sites to standards that are lower than natural background concentrations.

A number of methods may be used to distinguish background concentrations, including the use of historical records, geochemical analogues and statistical approaches (Runnels *et al.*, 1992). Statistical methods used to distinguish between anomalous and background concentrations in geochemical exploration of mineral deposits all converge on various methods of discriminating outliers of normally or log-normally distributed populations and making estimates of central tendency, spread and identification of upper thresholds of background. The statistical method used in this study is that of Sinclair (1976), and is applied using the 'Probplot' code (Stanley, 1987), reproduced in an 'R' script environment.

The method provides a procedure for estimating the constituent populations from polymodal populations, once plotted on cumulative probability plots. This overcomes the problem that often background thresholds are estimated based on data derived from more than one population. Upper and lower thresholds are then calculated as mean ± 2 standard deviations (SDs) for each constituent population.

Some mineralised areas have a long history of mining, which raises the problem of distinguishing between anomalous populations due to the weathering/dispersion of mineral veins and anomalous populations related to mineral spoil heaps/mining (Fig. 23.1). Once the geochemical populations, defined using the methods described, are mapped in a GIS framework, integration of spatial information regarding drainage, known mineral occurrence and mine shafts can help to distinguish enriched populations with anthropogenic sources (mining) from those with natural sources (mineralisation). Although the task of searching for breaks and extracting thresholds from cumulative probability curves is subjective and not exempt from ambiguity, when it is evaluated in terms of independent information, for example from maps, it becomes a powerful tool for helping to understand the data (Reimann and Garrett, 2005).

Here the approach was demonstrated in the mineralised areas associated with the Ordovician-Silurian rocks in counties Armagh and Down. The Tellus geochemical stream sediment data were used for this scoping study (Flight and Lister, 2013).

## The Longford–Down geology, mineralisation and mining

The Longford–Down Massif, an area of some 6000 km$^2$, extends across counties Down and Armagh in Northern Ireland and over the border into Louth, Monaghan, Cavan and Longford in the Republic of Ireland. It forms part of the Southern Uplands – Down–Longford terrane that extends into Scotland. The bedrock of this terrane is mainly Ordovician–Silurian greywacke sandstone, siltstone and mudstone arranged in fault-bound packages or 'tracts' (Anderson, 2004). In Northern Ireland these rocks are known as the Gala and Hawick Groups (GSNI, 1997). They are believed to have been brought together during closure of the Iapetus Ocean in an accretionary prism that formed during subduction of oceanic plate beneath the Laurentian continental margin. Associated regional-scale magmatism at that time resulted in the formation of Late Caledonian intrusive bodies such as the Newry Igneous Complex (Cooper and Johnston, 2004a; Cooper *et al.,* Chapter 11, this volume). Palaeogene magmatism, related to the opening of the North Atlantic, is also represented through the Slieve Gullion Complex in County Armagh and the Mourne Mountains Complex in County Down (Cooper and Johnston, 2004b).

The study area includes the South Armagh–Monaghan mining district, historically an important area of mineral extraction for lead, centred on the town of Keady in South Armagh. Mineralisation is principally galena, sphalerite, pyrite and chalcopyrite with calcite and barytes gangue (Arthurs and Earls, 2004).

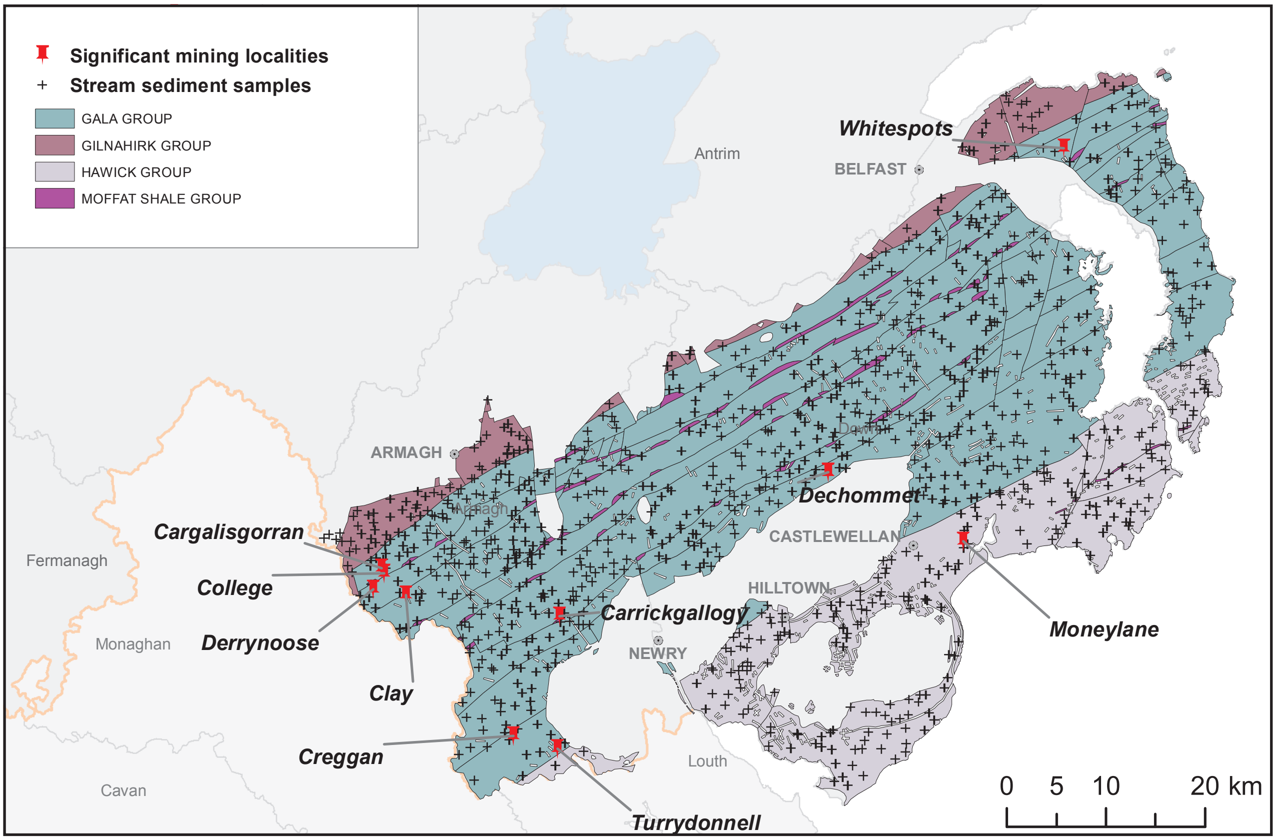


Figure 23.2. Map of the Ordovician–Silurian outcrop area and stream sediment sites.

In South Armagh 57 shafts and adits are recorded by GSNI (http://mapapps2.bgs.ac.uk/GSNI_Geoindex/home.html). Historical mines described by Cole (1922) are the Derrynoose Mine, College Mine, Clay Mine, Carrickgallogy Mine and Creggan Mine. The abandoned mine workings are sufficiently old to predate any waste control legislation and the most modern mineral extraction methods, with Derrynoose lead mine having been abandoned in 1842.

The Longford–Down Massif also hosted major lead mining at the Conlig–Whitespots mines near Newtownards in County Down. These produced an estimated 13,500 t of lead and operated intermittently in the period 1780–1899 (Cole, 1922). This mineralisation is similar to that of the South Armagh–Monaghan mining district.

## Results

In counties Down and Armagh, only sediment samples from above Ordovician and Silurian bedrock were selected and form the basis of our work to define background metal(loid) element concentrations (Fig. 23.2). The regional stream-sediment data set for Down–Armagh reflects the bedrock despite thick glacial cover mostly comprising till (Breward *et al.*, 2011). This concurs with a recent study by Dempster *et al.* (2013), which showed a close geochemical relationship between soils, till and bedrock.

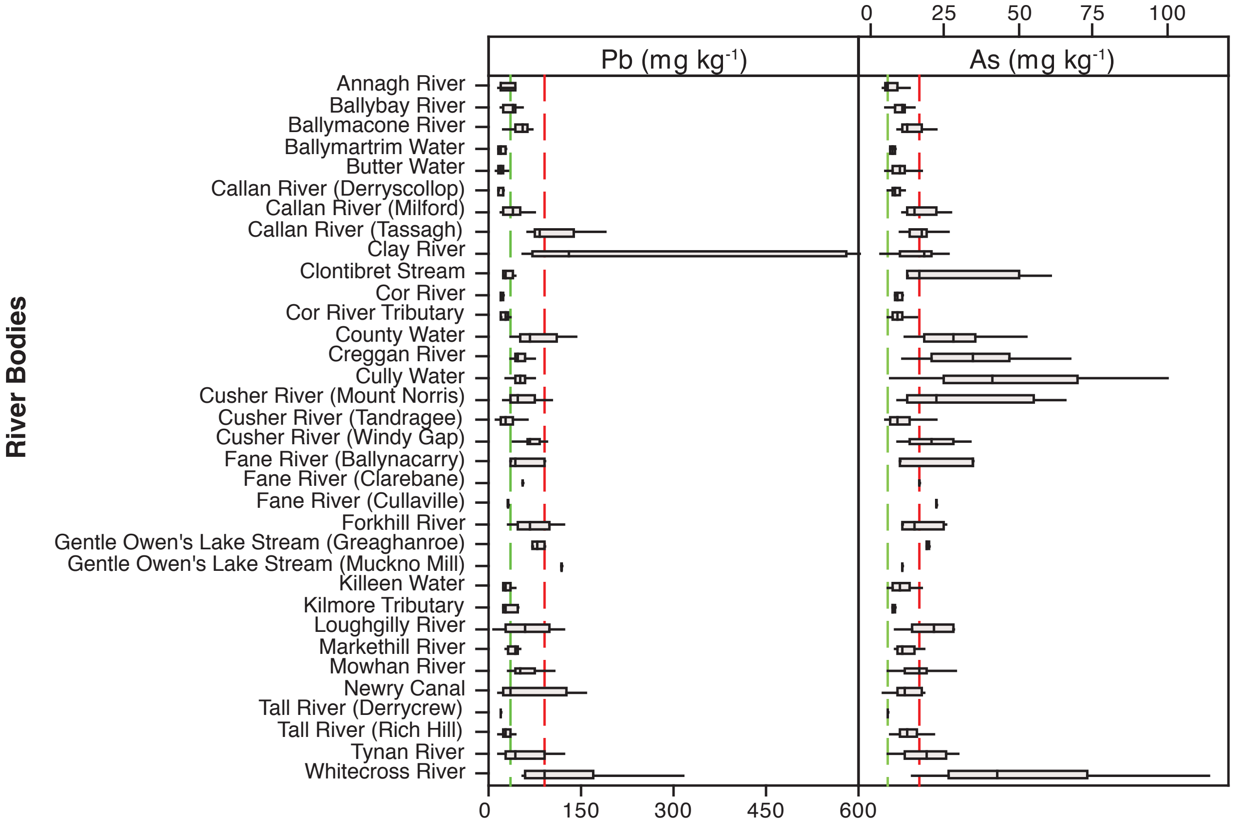


Figure 23.3. Boxplot of stream sediment data with river catchments: Pb and As in County Armagh (green lines: Pb TEL= 35 mg kg$^{-1}$; As TEL= 5.9 mg kg$^{-1}$; red lines: Pb PEL= 91.3 mg kg$^{-1}$; As PEL= 17 mg kg$^{-1}$).

**Table 23.1.** Summary statistics for Pb, Zn, Cd, and As populations and TEL and PEL values as reported by MacDonald *et al.* (2000)

| Variable | *n* | Minimum | Q1 | Median | Q3 | Maximum | Mean | TEL | PEL |
|---|---|---|---|---|---|---|---|---|---|
| | | (mg kg$^{-1}$) | | | | | | | |
| Pb | 1014 | 8 | 25 | *35* | *54* | ***1245*** | *50* | 35 | 91.3 |
| Zn | 1014 | 32 | *124* | *172* | *257* | ***3162*** | *237* | 123 | 315 |
| Cd | 1014 | 0.3 | 0.3 | *0.6* | *1.2* | ***56*** | *1.4* | 0.596 | 3.53 |
| As | 1014 | 0.9 | *7.3* | *11* | ***17*** | ***357*** | *16* | 5.9 | 17 |

Italic data ≥ TEL; bold data ≥ PEL.

Table 23.1 shows the statistics for lead (Pb), zinc (Zn), cadmium (Cd) and arsenic (As), elements that, being hosted in the known mineralisation, are typically high in the Ordovician–Silurian strata locally. These can exert toxic effects on the benthic community living in the environment impacted by these sediments. Table 23.1 also lists the associated toxic effect level (TEL, the concentration below which sediment-associated contaminants are not considered to represent significant hazards to aquatic organisms) and the predicted

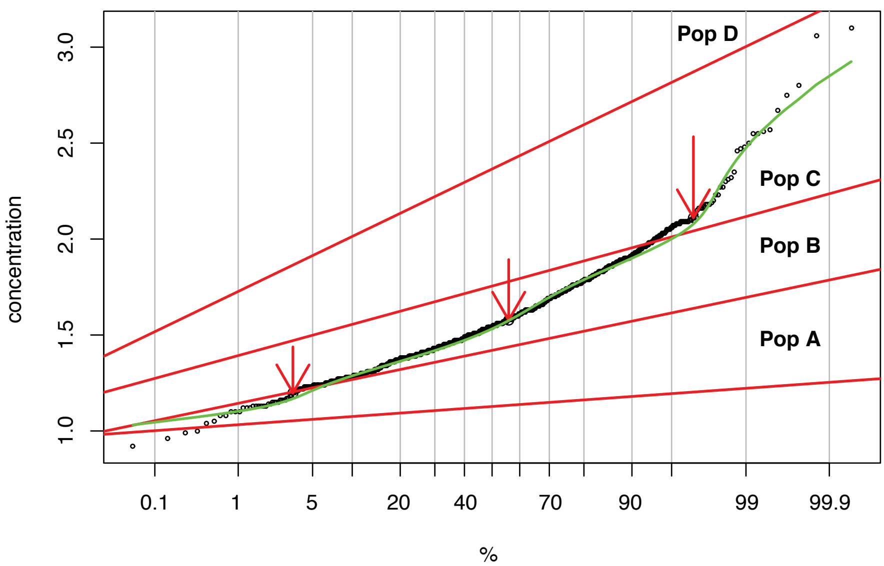


Figure 23.4. Probability plot showing $log_{10}$Pb original data, plotted as black circles, with four populations (red line) partitioned using the partitioning procedures of Sinclair (1976). Red arrows indicate inflection points where the modelled populations join. The modelled populations are recombined proportionally (green line) to compare with the original data.

effect level (PEL, the concentration representing the lower limit of the range of concentrations associated with adverse biological effects), as reported by MacDonald *et al.* (2000).

These data have been examined by river management agencies, as they are the basic management units for reporting and assessing compliance with the WFD environmental objectives. Figure 23.3 shows an example for Pb and As for the catchments over the Ordovician–Silurian of Armagh, demonstrating that some catchments have samples that often exceed the TEL, and, in some instances, also the PEL thresholds. This highlights the need to estimate background concentrations, since there is no suggestion that these 'high' stream sediment metal(loid) element concentrations were not predominantly of natural origin.

While this scoping study has investigated a range of metal(loid) elements, in this brief summary of our methodology we present only our interpretations for Pb, as an example of the approach.

Figure 23.4 shows the partitioning of the cumulative probability plot of $log_{10}$Pb data into four populations, A, B, C and D, with the following mean and threshold parameters (mean ± 2SD) in mg $kg^{-1}$: A (13.2; 10.9–16.0); B (26.4; 15.3–45.6); C (57.3; 27.6–119.3); and D (232.9; 65.4–829.4); and the following proportions, respectively: 2.8%, 53.2%, 41.0% and 2.7%. Some overlapping between populations exists, hence intermediate classes defined as 'overlapping populations' are created where data could form part of the data population above or below, as shown in Table 23.2.

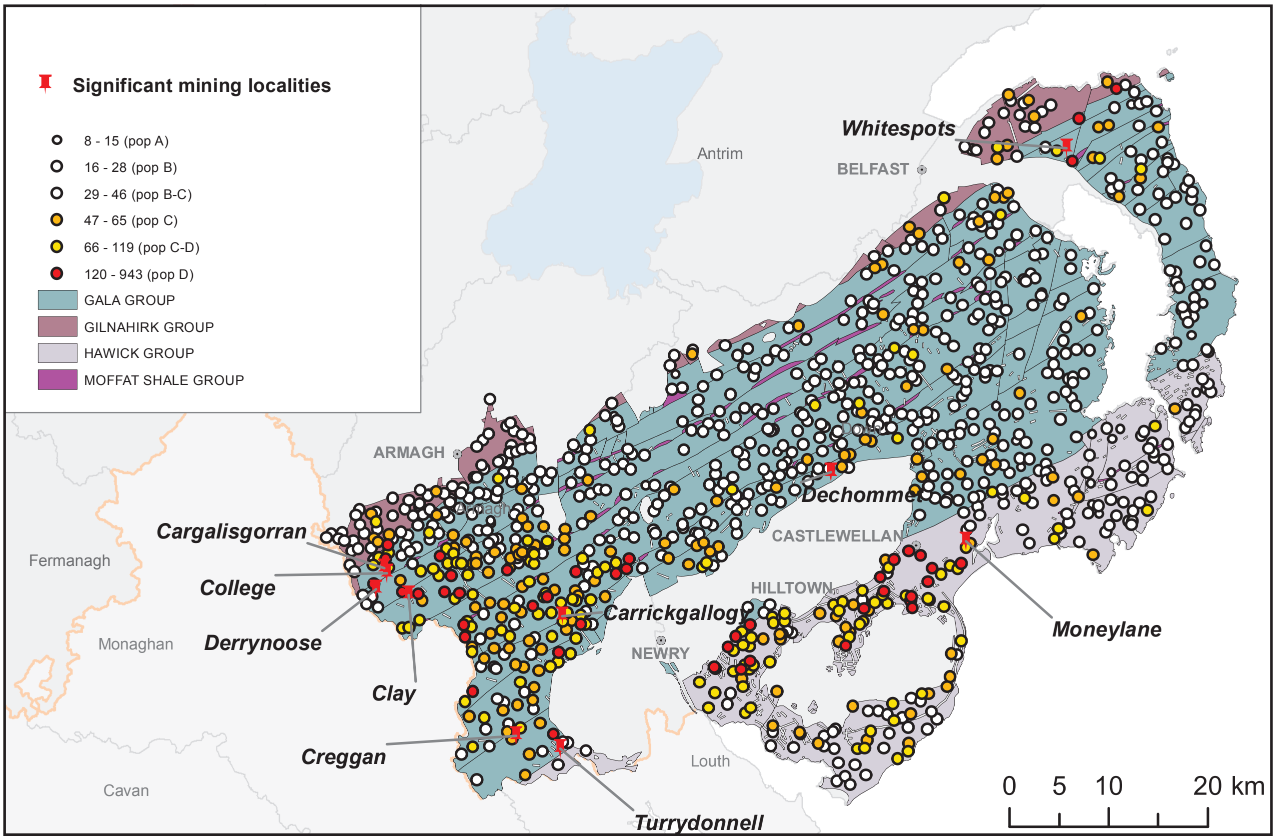


Figure 23.5. Map of classification of Pb stream sediment concentrations: based on modelled populations shown in Table 23.2 with additional 'overlapping' populations reflecting data that may be drawn from either of the surrounding data populations.

**Table 23.2. Thresholds of partitioned populations including overlapping populations, Pb (mg kg$^{-1}$) in stream sediments**

| Pb population | Thresholds | |
|---|---|---|
| | Min. | Max. |
| A | 11.0 | 15 |
| B | 15 | 27.6 |
| B–C | 27.6 | 45.6 |
| C | 45.6 | 65.4 |
| C–D | 65.4 | 119.3 |
| D | 119.3 | 829.4 |

The population with the highest concentrations of Pb, D, with a lower threshold of 119 mg kg$^{-1}$, corresponds to the two most significant historic mining localities of the study area, the South Armagh–Monaghan mining district and the Conlig–Whitespots base metal mining area (Fig. 23.5). This population also includes several sites over the Hawick Group,

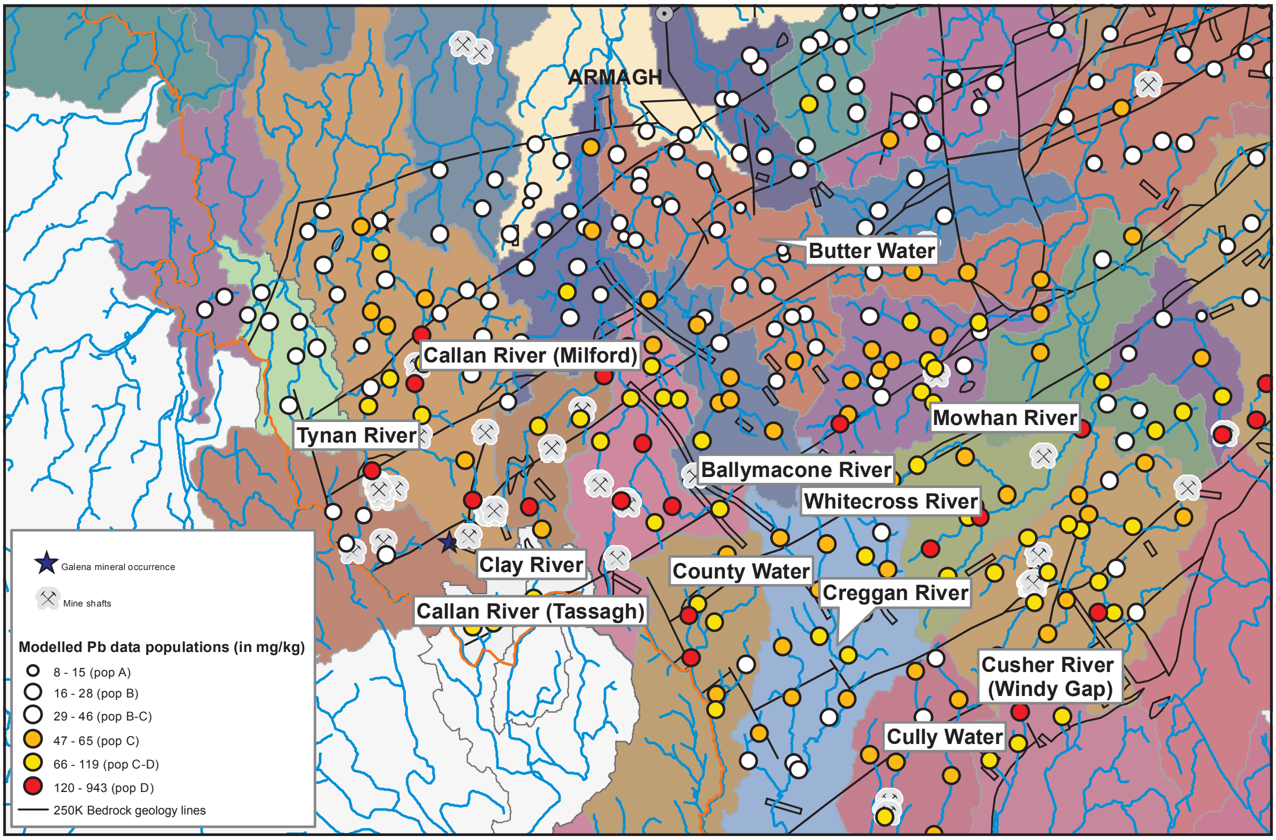


Figure 23.6. Distribution of Pb modelled populations in the water bodies of the mining district in County Armagh.

in the northern drainage from the Mourne Mountains Complex, in which, although there are no extensive mineral workings, high Pb levels are ubiquitous in stream sediments.

Figure 23.6 shows in greater detail the modelled population distribution in the South Armagh area, in river bodies highlighted to exceed the PEL levels (Fig. 23.3). Population D is scattered around the known and worked mineral veins, such as in the Clay River and the Callan River (Tassagh) water bodies. Population C is more evenly distributed over the Creggan or the Ballimacone river bodies, where no known shafts are recorded, and is interpreted as representative of high natural background concentrations. Separation of these more widespread, potentially natural, high concentrations from the anomalous data populations, perhaps more likely to arise from point sources, could help in targeting key sites for further investigation.

## Using stream sediment data in environmental assessments

The integrated river basin approach of the European WFD requires contamination in sediments to be addressed, as they are an essential part of our river basins. The presence of contaminated sediments may be one of the obstacles to achieving good ecological status for a water body.

Regional geochemical surveys such as Tellus can contribute to the assessment of environmental pressures on water bodies by establishing baseline values and monitoring anomalous concentrations in metals and metalloids, considered potentially harmful elements.

The derivation of background concentration ranges presented in this chapter is based on well-established methods such as statistical probability plotting techniques presented in exploratory data analysis, integrated with spatial analysis in a GIS framework. Where data exceed sediment quality standards, this procedure gives some assistance in identifying where natural background concentrations (due to mineralogical variations in the catchment geology) may contribute more of the 'contaminant'.

This is designed to aid the decision-making process in relation to why quality standards may have failed, or in consideration of a remediation strategy for a natural ecosystem. The methodology provides a consistent approach for investigating the background populations of any element and can be applied to other areas affected by mineralisation in Northern Ireland and the Republic of Ireland for which there is a consistently high-quality and high-density stream sediment data set.

Information on the baseline conditions of catchments prior to mining is also needed to provide a reference point against which changes can be measured and can be used by industry and regulators in considering future mining proposals.

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