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# Mining Impact on Stream Sediment Quality in County Antrim, Northern Ireland

TELLUS/ TELLUS BORDER GEOCHEMISTRY

PROGRAMME COMMISSIONED REPORT CR/13/130 N



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BRITISH GEOLOGICAL SURVEY

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PROGRAMME COMMISSIONED REPORT CR/13/130N

# Mining Impact on Stream Sediment Quality in County Antrim, Northern Ireland

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*Editor*

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*Keywords*

Stream sediment quality, mining,  
metals

*Bibliographical reference*

LASS-EVANS, S. 2013. Mining  
Impact on Stream Sediment  
Quality in County Antrim,  
Northern Ireland. *British  
Geological Survey  
Commissioned Report*,  
CR/13/130. 26pp.

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# Foreword

This report documents a two-month pilot project investigating potential mining impacts on stream sediment quality in County Antrim, Northern Ireland.

# Acknowledgements

This research is supported by the European Union INTERREG IVA-funded Tellus Border project.

Tellus Border is a €5 million cross-border project to map the environment and natural resources in the border region of Ireland and continue the analysis of data in the border counties of Northern Ireland. It is a joint initiative between the Geological Survey of Northern Ireland (GSNI), the Geological Survey of Ireland, Queen's University, Belfast and Dundalk Institute of Technology.

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Dr. Diarmad Campbell (British Geological Survey (BGS)), Mike Young (GSNI), Dr Marie Cowan (GSNI) and Fiona Fordyce (BGS) are thanked for their help and support. Diego Diaz Doce (BGS) and Alex Donald (GSNI) are thanked for their assistance with GIS.

# Disclaimer

The views and opinions expressed in this research report do not necessarily reflect those of the European Commission or the Special EU Programme Body (SEUPB).

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# Summary

Historical mining activity has in some cases released large quantities of heavy metals into the fluvial environment of many settings around the world. County Antrim is one of the main areas in Northern Ireland known for historical mining, where 780 shafts and adits are associated with iron ore exploration, and where historically, ca. 700,000 tonnes of bauxite were produced. In order to assess the legacy of mining operations, it is important to understand the present (baseline) chemistry of the natural environment. Heavy metals resulting from mining activities need to be distinguished from products of natural variation and geological processes.

Using geographic information systems (GIS) and multi-element diagrams ("spidergrams") for analysis, the project modelled the geological background of the area, and was able to distinguish whether high metal concentrations in stream sediments were of mining or of natural origin. Sub-catchments with enhanced sediment element concentrations relative to the geological background were identified; and enrichment factors (EFs), as a classification of the degree of enhancement above natural geological background due to mining activities, were calculated.

Results of this study reveal that stream sediment compositions are mainly determined by the underlying geology. Sediment quality guidelines for As, Cd, Cu, Pb and Zn were exceeded by <10% of the samples in most sub-catchments, although 31% of the samples exceeded the guideline for As in the north-eastern coastal Glendun River sub-catchment. By contrast, more than 80% of the samples exceeded the sediment quality guidelines for Cr and Ni in most sub-catchments within the study area. However, these high, Cr and Ni (and also Cu) concentrations do not result from mining activities, and most likely reflect the association with their geological parent material.

Mining (mainly iron ore and bauxite) has had no detectable impact on sediment quality in nine sub-catchments, while three coastal sub-catchments showed slight enrichments of either As and Sn or As, Ag, Co, Sb and Sn. However, as the EFs do not exceed 1.5, their enrichment can be classified as minor.

# 1 Introduction

Chemical pollution of the natural environment is one of the legacies of mining activities. The release of potentially harmful elements, notably high concentrations of heavy metals, are of particular concern, as their occurrences could have long-term implications for ecosystems, agriculture and possibly human health.

Historical mining activities are known to have released large quantities of heavy metals into the fluvial environment of many settings around the world (Hudson-Edwards, 2003). At the time of the mining operation, the potential consequences of such industrial development may not have been fully understood; even if a mine has been closed for many years, its impact on the environment might still be present today. Heavy metals, if released into rivers or streams at mining sites, will be either stored in river bed sediments, seep into underground water courses, or will be transported along the water body and deposited downstream. Over time, they might remain buried in sediment and soil, but could also become remobilised and redeposited elsewhere. In order to assess the legacy of mining operations, it is of fundamental importance to understand the present (baseline) chemistry of the natural environment. Heavy metals present as a consequence of mining activities need to be distinguished from the products of natural variation and geological processes.

Northern Ireland has over 2000 abandoned mine workings, mostly dating from the 18<sup>th</sup> to early 20<sup>th</sup> Centuries (NIEA, 2009). One of the main areas known for historical mining sites is Co. Antrim, where 780 shafts and adits are associated with iron ore exploration, and where historically ca. 700,000 tonnes of bauxite have been produced (Lusty *et al.*, 2012). In order to assess the potential impact of these mining activities on sediment quality, this project modelled the geological background of the area and was able to distinguish whether high metal concentrations were of natural origin or affected by mining activities.

More precisely, the project assessed the following aspects in Co. Antrim:

- (1) Identification of the spatial distribution of sediment element concentrations;
- (2) Assessment of sediment quality with respect to sediment quality guidelines;
- (3) Geological background model on a sub-catchment scale;
- (4) Assessment of whether historical mining had an impact on sediment quality.

This project helps to inform implementation of the regulations transposing the Water Framework Directive (WFD) and the European Mining Waste Directive (MWD), and thus helps government to comply with the requirements on the assessment and monitoring of natural sources of pollutants.

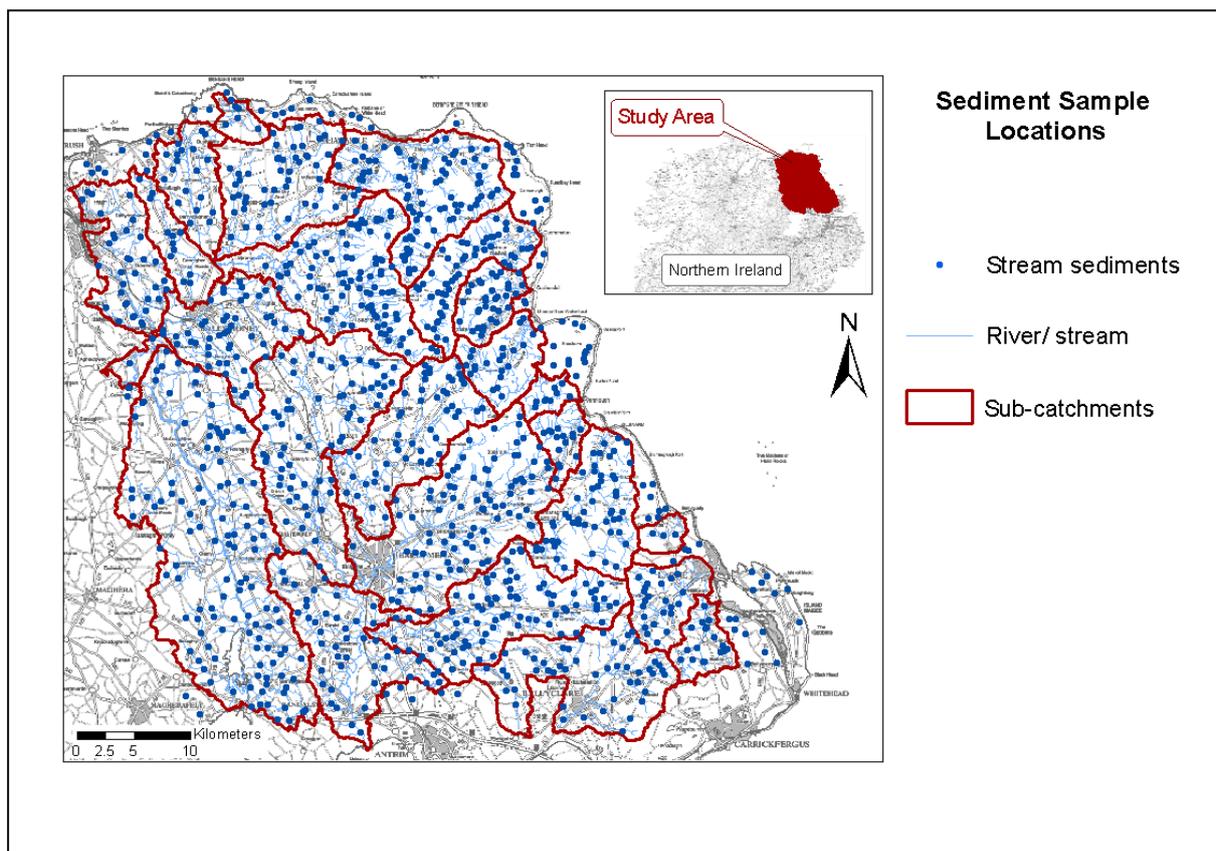
## 2 Material and Methods

### 2.1 DATA SOURCES

#### 2.1.1 Tellus Stream Sediment Data

The Tellus Project was implemented to provide high resolution regional datasets to underpin government and private body decisions regarding sustainable economic development, social infrastructure, environment and health. The project, managed by the Geological Survey of Northern Ireland (GSNI), comprises detailed geochemical surveys of soils and streams, as well as a low-level airborne geophysical survey.

The geochemical surveys of Northern Ireland were carried out in three phases by GSNI and the British Geological Survey (BGS). The Tellus sampling programme followed the procedures of the BGS's Geochemical Baseline Survey of the Environment (G-BASE) programme. A comprehensive description of the G-BASE sampling, analysis and quality control procedures is given by Johnson *et al.* (2005), while additional information on GSNI's Tellus survey is presented in Smyth (2007). Stream sediments on the eastern side of Northern Ireland were collected in the summers of 2005 and 2006, at an average sampling density of 1 site per 2.4 km<sup>2</sup> from 1<sup>st</sup> or 2<sup>nd</sup> order streams (Fig. 1). The <150µm fraction material was analysed for major and trace elements by Wavelength Dispersive X-Ray Fluorescence (WD-XRF) Spectrometry and Energy Dispersive (Polarised) X-Ray Fluorescence (ED(P)-XRF) Spectrometry, while Au and Platinum Group Elements (PGE) were analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).



**Fig. 1.** Map of the Co. Antrim study area showing the Tellus stream sediment sample locations.

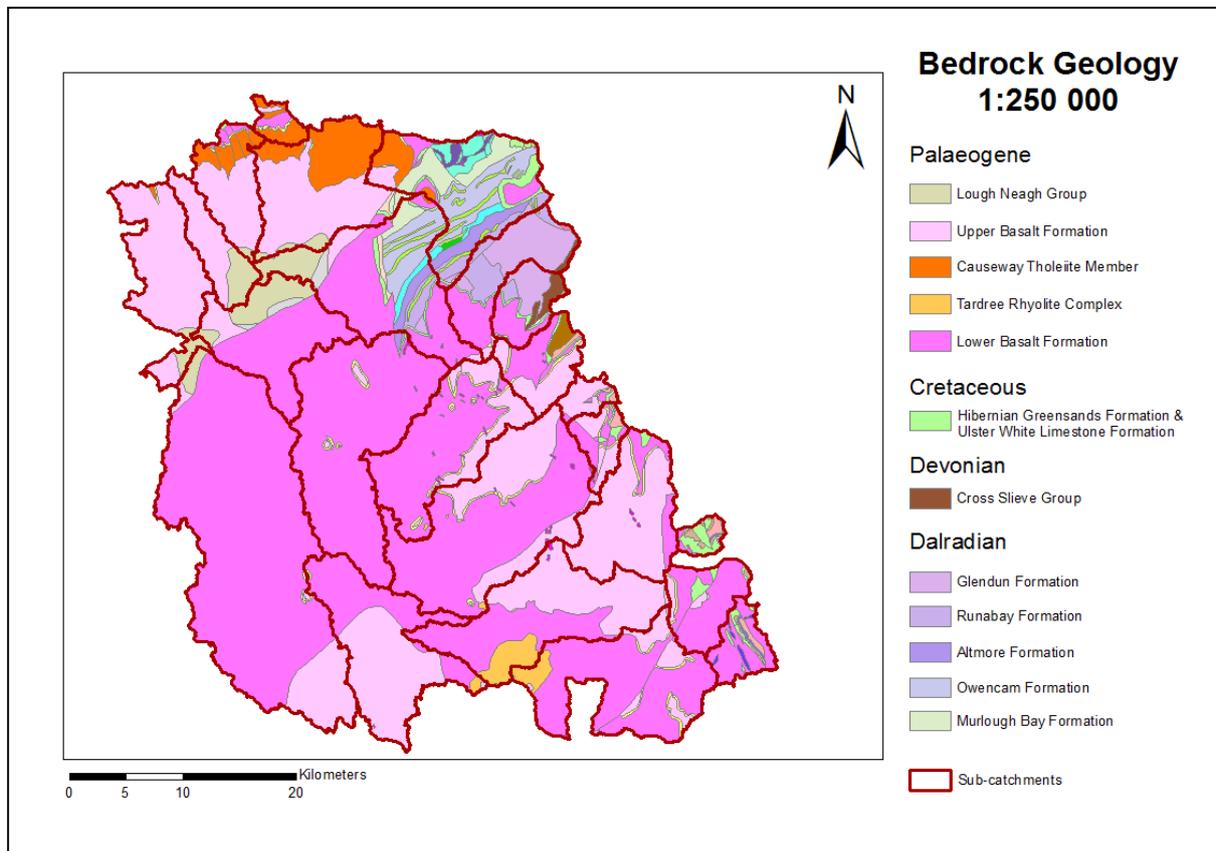
### 2.1.2 Current and Historic Topographic Maps

Current topographic maps of 1:10,000, 1:50,000 and 1:250,000 scales and historical maps of 1:10,000 were available under license from the Land & Property Services (LPS), Northern Ireland.

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### 2.1.3 Geological Map

A digital 1:250,000 scale map of the bedrock geology of the area was available from GSNI (Fig. 2).



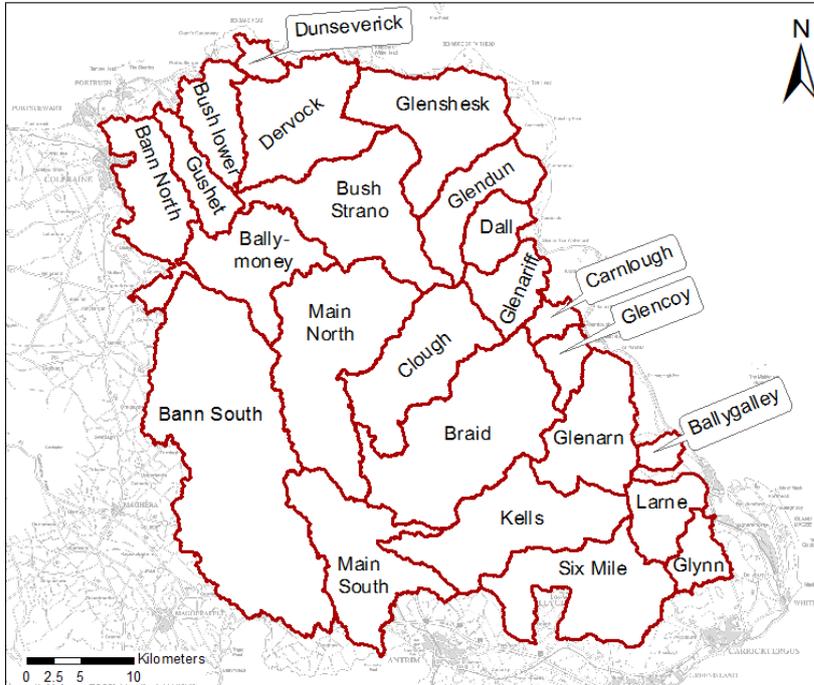
**Fig. 2. Overview of the bedrock geology (1:250,000) in the Co. Antrim study area. Geological lithologies that have an area <math><5\text{km}^2</math> are not included in the legend.**

### 2.1.4 Ordnance Survey Irish National Grid

The Ordnance Survey (OS) Irish National grid was available from LPS.

### 2.1.5 River Catchments

River and stream catchment boundaries were provided by the Northern Ireland Environment Agency (NIEA). For the purpose of this study, some sub-catchments were merged and named after the main river/ stream within the sub-catchment (Fig. 3). As a result, 24 sub-catchments were used for the analysis with catchment sizes between 11 and 307km<sup>2</sup>.



**Fig. 3. Study area sub-catchments<sup>1</sup>**

### 2.1.6 Water Courses

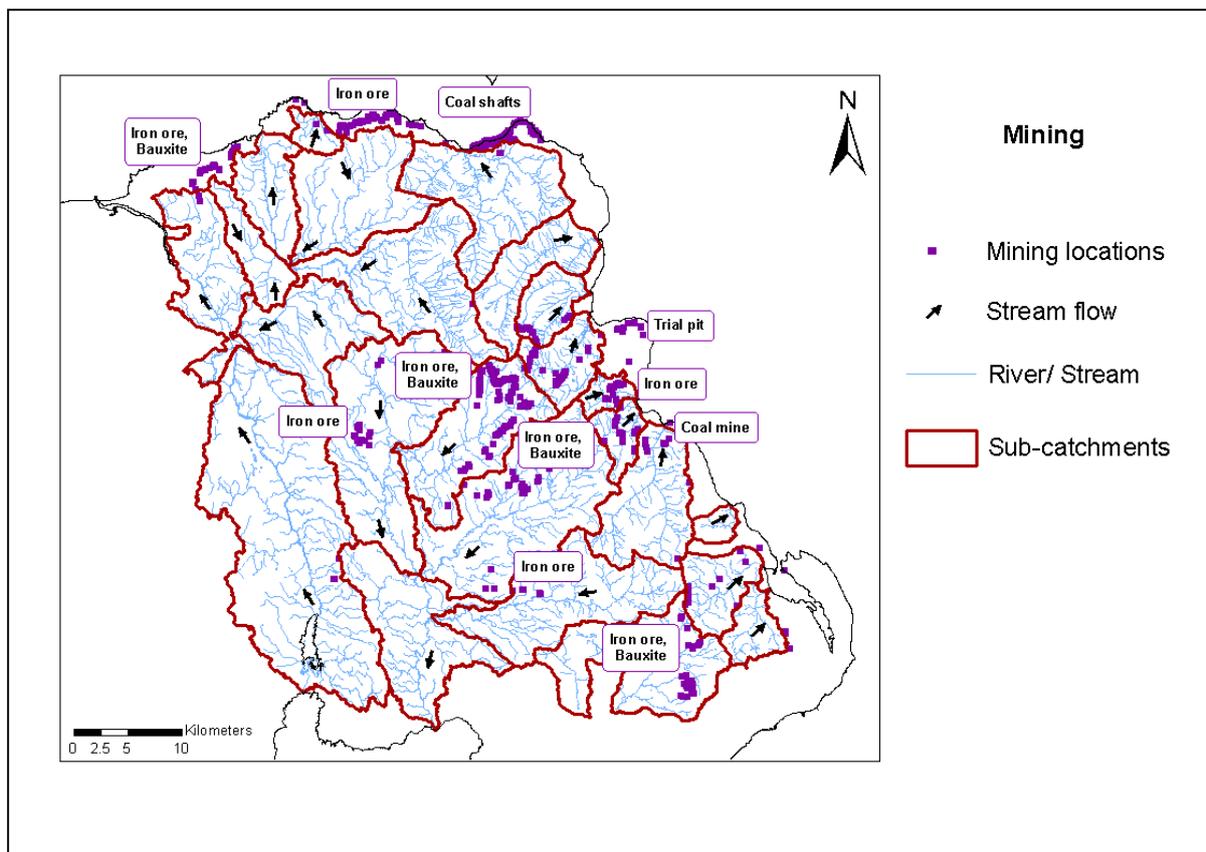
Water courses data were provided by LPS.

### 2.1.7 Mining Locations and Mineral Occurrences

Mining locations and mineral occurrences data in the study area were provided by GSNI (Fig. 4).

---

<sup>1</sup> The sub-catchment names are shortened in the diagram - full names are as follows: Ballygalley Burn; Ballymoney River; Braid River; Burn Gushet River; Carnlough River; Clough River; Dervock River; Dunseverick River; Glengariff River; Glenarn River; Glencoy River; Glendun River; Glenshesk River; Glynn River; Kells Water; Larne River; River Bann North; River Bann South; River Bush Lower; River Bush Stranocum; River Dall; River Main North; River Main South; Six Mile Water.



**Fig. 4. Mining locations in Co. Antrim according to GSNI records.**

Iron ore was extensively worked in Co. Antrim (mainly in Parkmore, Glenravel, Skerry Hill, Newtowncrommelin, Cargan, Glenarriff, Ballylig, Carnlough and Shane’s Hill) up to the 1920s (Lusty *et al.*, 2012). According to GSNI records, 780 shafts and adits are associated with iron ore, worked in open-cast or room-and-pillar underground operations with a cumulative production of five million tonnes (Eyles, 1952). Historically, around 700,000 tonnes of bauxite are estimated to have been produced in Co. Antrim, with the principal mining areas located around Newtowncrommelin, Cargan, Ballylig, Lyle’s Hill and Straid Hill (Lusty *et al.*, 2012).

In terms of precious metals, gold occurs alloyed with silver and other elements, and has been explored over the Precambrian age metamorphic rocks in north-east Co. Antrim, while weakly mineralised copper with minor enrichment of gold, platinum group elements and nickel occurs close to Rasharkin (Lusty *et al.*, 2012). Small amounts of native copper have been recorded in basalt lavas of the Antrim Lava Group as a mineralogical curiosity (Frances, 1972).

## **2.2 SEDIMENT QUALITY ASSESSMENT**

The stream sediment geochemical and field observational data were entered into a GIS using ESRI®Arc v. 9.2 and 10.

The element distribution maps were generated using the Inverse Distance Weighting (IDW) interpolation function with a grid cell size of 250m, a fixed search radius of 1500m and power value of 2. Grids were produced using the Spatial Analyst tool, while the parameters of gridding were based on the methods of the G-BASE programme (Johnson *et al.*, 2005). The geochemical data was classified according to the percentiles (5th, 10th, 15th, 25th, 50th, 75th, 90th, 95th and 99th) of the data distribution using a gradational colour scheme.

For the geological background model (i.e. exclusion of sediment samples close to mining sites; see section 2.3.1 below), coloured dot maps were produced using graduated symbols and the same percentile classification as for the interpolated maps.

Established sediment quality guidelines for metals in river sediments are not available for the UK or the European Union (EU), and hence, element concentrations in the study area were assessed with respect to the Canadian freshwater sediment quality guidelines (MacDonald *et al.*, 2000) to identify the percentage of samples in sub-catchments that exceeded the probable effect concentration (PEC).

## **2.3 ASSESSMENT OF MINING IMPACT ON SEDIMENT QUALITY**

### **2.3.1 Geological Background Model**

In order to assess, monitor and control pollution, anthropogenic sources of metals must be distinguished from natural sources. By following the methods of Ridgway *et al.* (2003), further refined by Lass-Evans *et al.* (in prep), the geological background signature was modelled, and then, in that natural context, the additional influence of potential effects of mining activities was assessed on overall levels of metals in the sediments.

In order to model the geological background, a GIS was developed, incorporating the Tellus stream sediment data, current and historical topographic maps, bedrock geology, river/stream sub-catchment boundaries, mining locations and mineral occurrences.

The observed geochemical signatures for each sub-catchment were calculated by taking the average concentrations from all stream sediments within each of the 24 sub-catchment boundaries.

As the purpose of this study was to assess potential mining impacts on sediment quality, the geological background was modelled by assessing only mining activities, while other anthropogenic sources, such as industrial or urban influences, were not taken into account.

The geological background model was modelled by excluding stream sediments that were either located close to or downstream of a mining site in each sub-catchment. The geological background signature was then calculated as follows: (1) percentage areas of the different geological lithologies in each sub-catchment were computed; (2) average stream sediment element concentrations over each geological lithology were combined on a weight basis, according to the percentage that each geological lithology occupied in each sub-catchment.

In order to compare the observed geochemical signature with the modelled geological background signature, the data were interpreted with the help of spidergrams. Major element values (reported in wt%) were converted into mg/kg (ppm) values; and elements were normalised to the upper continental crust (UCC) (Wedepohl, 1995). These multi-element plots have the advantage that elements with widely different concentrations can be viewed on a single diagram and that the pattern of variations can be compared, even if absolute concentrations are different.

### 2.3.2 Determining Mining Impact

In order to quantify the mining contribution to trace element concentrations in the sediments, element enrichment factors (EFs) for each sub-catchment were calculated by using the following equation (Kuusisto-Hjort & Hjort, 2013):

$$EF = \frac{Metal_{sample}}{Metal_{baseline}}$$

where  $Metal_{sample}$  is the average metal concentration in the sub-catchments (observed geochemical signature) and  $Metal_{baseline}$  is the average metal concentration of the modelled geological background. Heavy metal enrichment was interpreted as suggested by Birch and Davies (2003), in which enrichments are classified from no enrichment ( $EF \leq 1$ ), moderate enrichment ( $1 < EF \leq 5$ ), severe enrichment ( $5 < EF \leq 25$ ) to extremely severe enrichment ( $EF > 25$ ).

## 3 Results and Discussion

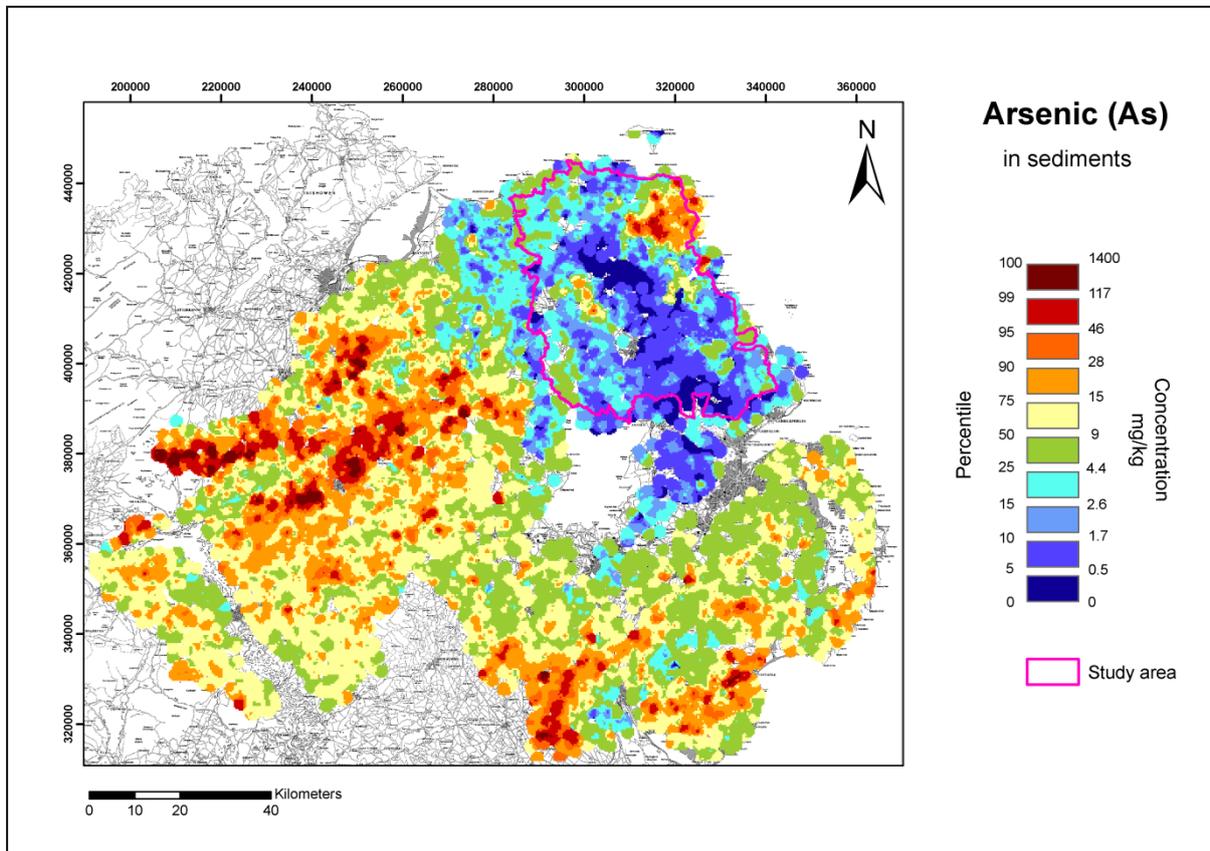
### 3.1 SEDIMENT QUALITY IN COUNTY ANTRIM

Most of Co. Antrim comprises of Palaeocene volcanic rocks, while the north-eastern corner of the study area is underlain by older (Dalradian, Devonian and Cretaceous) sedimentary and meta-sedimentary psammites, sandstones and limestones (see Fig. 2). Sediment element concentrations in Co. Antrim show a strong association with their geological parental material.

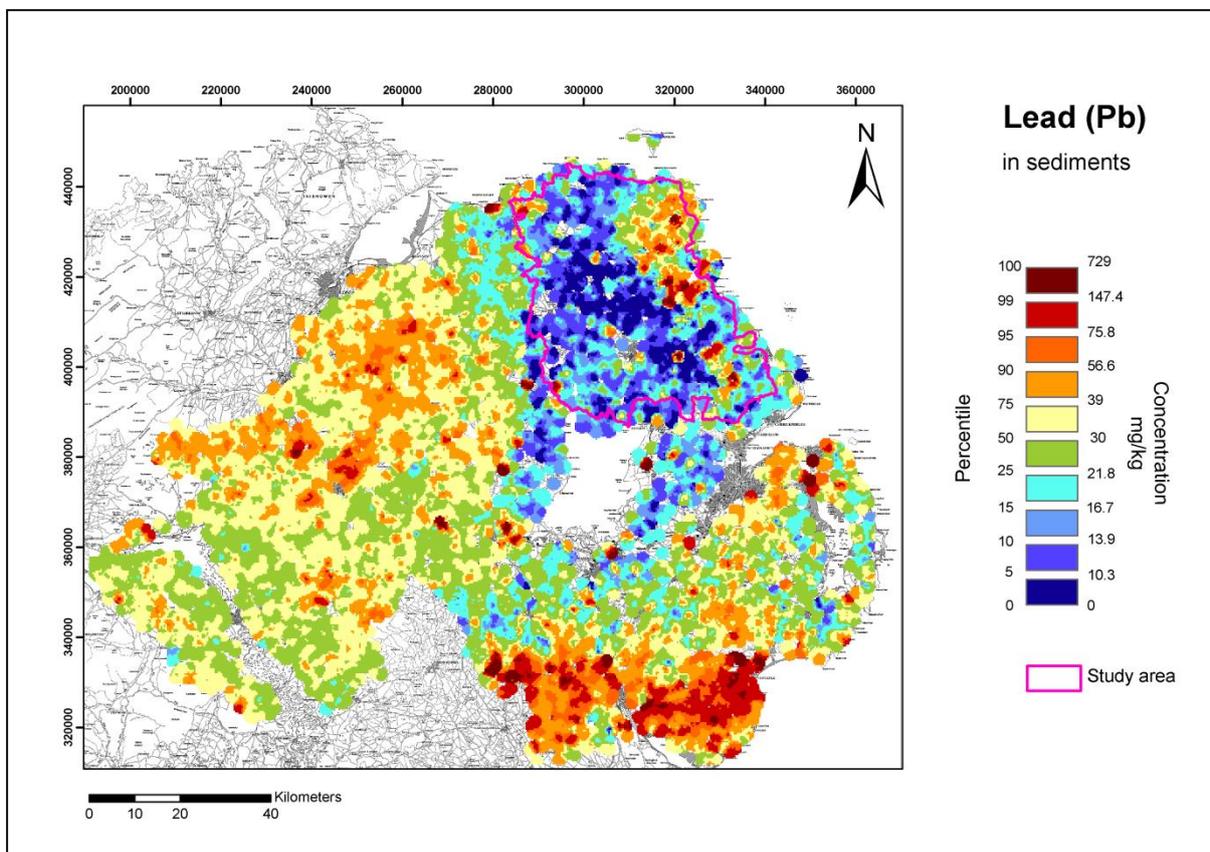
In general, sediments over the Devonian and Dalradian rocks are higher in As, Co, Pb and Sb if compared with the Palaeocene volcanics (Fig. 5a, 5b). Highest concentrations of As (130mg/kg) occur in the Glenshesk River sub-catchment, while highest concentrations of Co (157mg/kg), Pb (729mg/kg) and Sb (19mg/kg) were analysed in the Glendun River sub-catchment (see Fig. 3 for locations). By contrast, areas underlain by the volcanic rocks are characterised by generally higher concentrations of Cr (up to 1751mg/kg in the Glenarn River sub-catchment), Cu (up to 197mg/kg in the Dervock River sub-catchment) and Ni (up to 416mg/kg in the Glenarn River sub-catchment) (Fig. 5c). However, the highest concentrations of Cr were found in the eastern coastal area outside the sub-catchment boundaries (1926mg/kg) and over Cretaceous rocks (1791mg/kg) in the Larne River sub-catchment.

Sediment quality was assessed by determining the percentage of samples that exceeded the Canadian freshwater sediment quality guidelines PEC values (MacDonald *et al.* 2000). Note that these guideline values are based on a <2mm sediment fraction, while the Tellus samples are <150µm fraction sediments. Therefore, the proportion of samples exceeding the guidelines might be slightly overestimated as metals generally concentrate in fine fraction material.

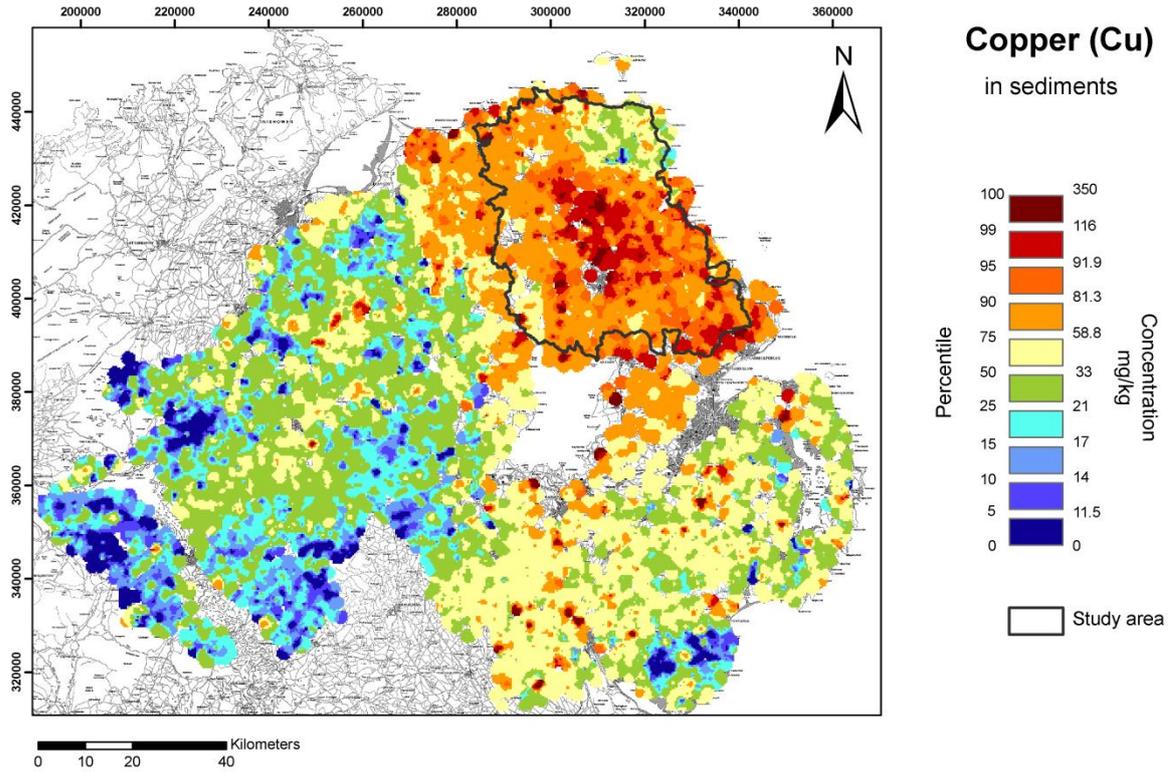
The percentage of samples that exceeded the PEC values are summarised for the elements As, Cd, Cu, Pb and Zn in Fig. 6a and for the elements Cr and Ni in Fig. 6b.



a.)



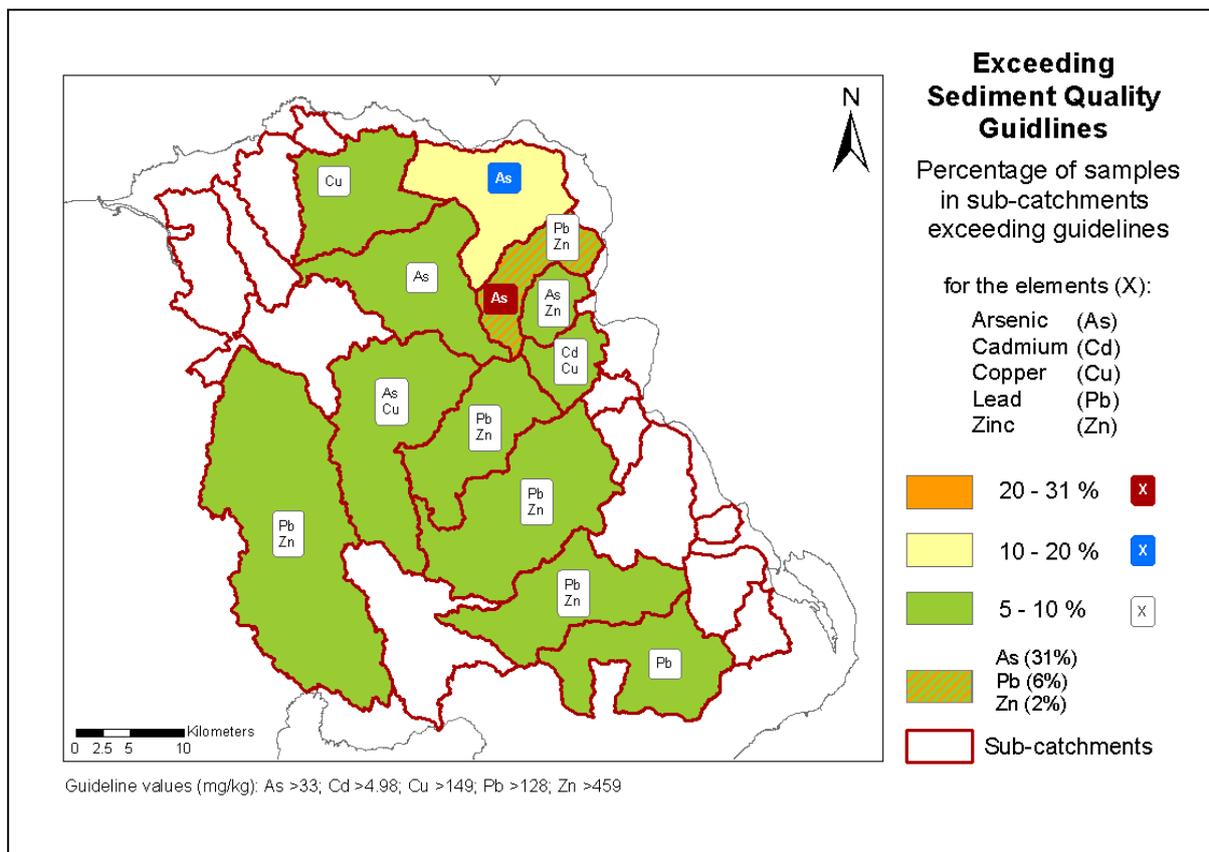
b.)



c.)

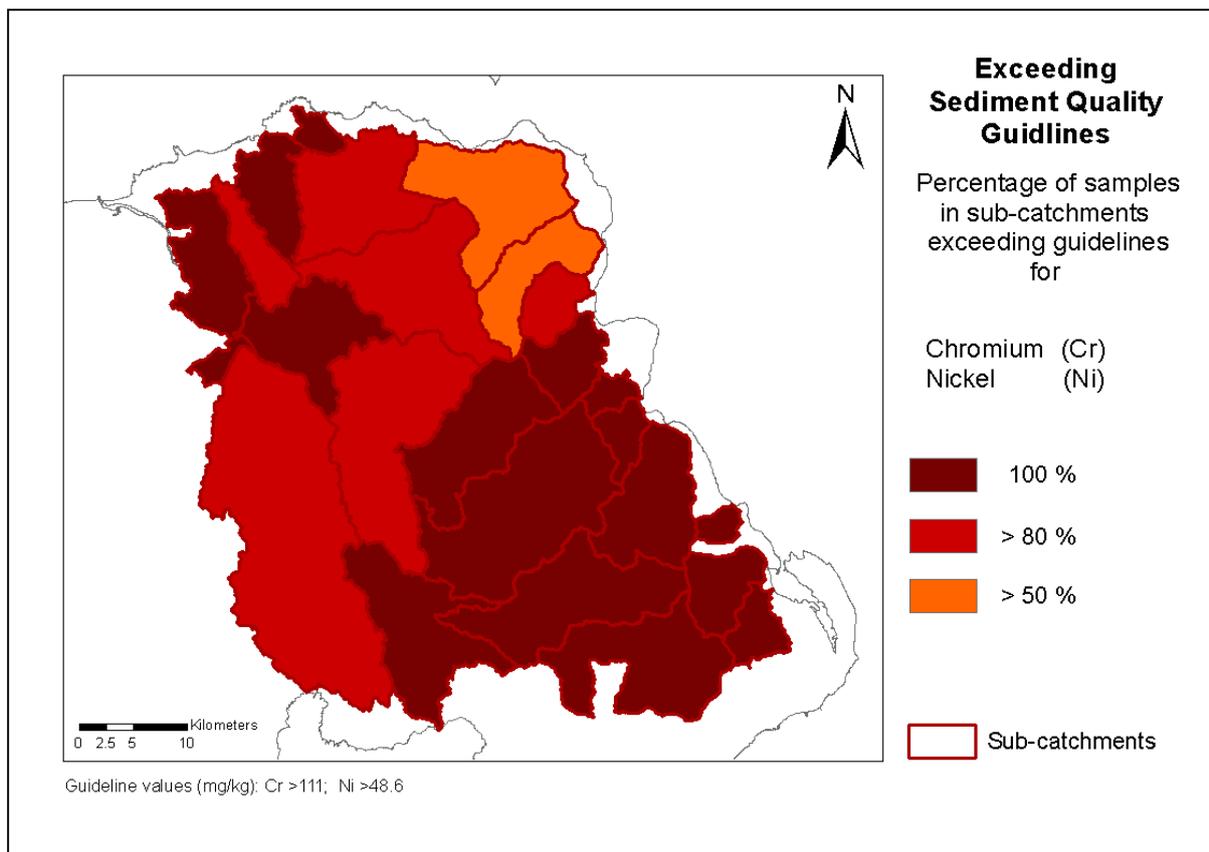
**Fig. 5. (a) Arsenic, (b) lead and (c) copper distribution in Northern Ireland stream sediments<sup>2</sup>.**

<sup>2</sup> The study area is marked with a pink or black outline. The distribution map for chromium and nickel looks very similar to the copper distribution map with high concentrations over the Palaeocene volcanic rocks and lower concentrations over the Devonian and Dalradian rocks.



**Fig. 6a. Arsenic, cadmium, copper, lead and zinc distribution with respect to freshwater sediment quality guidelines (MacDonald *et al.*, 2000).**

The sediment quality guidelines for As, Cd, Cu, Pb and Zn were exceeded by <10% of the samples in most sub-catchments, while 31% of the samples exceeded the guideline for As in the north-eastern coastal Glendun River sub-catchment (Fig. 6a). By contrast, more than 80% of the samples in most sub-catchments within the study area exceeded the sediment quality guidelines for Cr and Ni, apart from the coastal Glenshesk River and Glendun River sub-catchments, where 50% of the samples exceeded the guideline values (Fig. 6b).



**Fig. 6b. Chromium and nickel distribution with respect to freshwater sediment quality guidelines (MacDonald *et al.*, 2000).**

### 3.2 GEOLOGICAL BACKGROUND MODEL

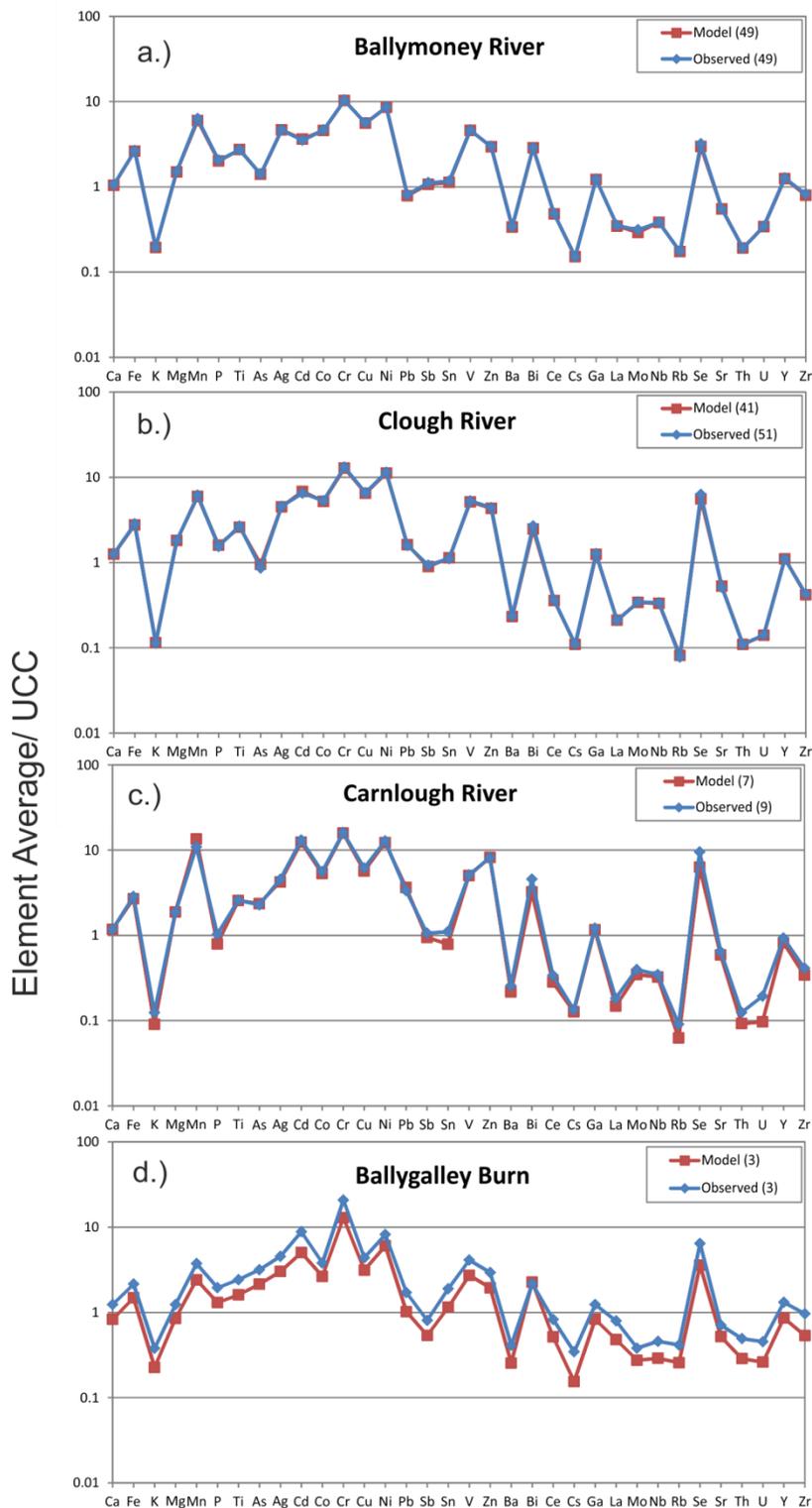
In order to assess potential mining impacts on sediment quality in Co. Antrim, the modelled geological background signature was compared to the observed signature by plotting both signatures on spidergrams. In sub-catchments where no mining has occurred, the sediment composition is largely determined by the underlying rock types. Therefore, the observed and modelled geological background signatures should follow the same pattern in the spidergrams. The observed and geological background signatures in Co. Antrim showed very similar patterns for the Ballymoney River, Burn Gushet River, Dervock River, Glendun River, River Bann North, River Bann South and River Main South sub-catchments. The Ballymoney River sub-catchment is given as an example (Fig. 7a).

In sub-catchments where mining (mainly iron ore and bauxite) has taken place, the observed and geological background model signatures also showed similar spidergram patterns indicating that mining had no impact on sediment quality. This was the case for Braid River, Clough River, Glenarn River, Kells Water, River Main North, Six Mile Water. The Clough River sub-catchment spidergram is given as an example (Fig. 7b).

Slightly higher concentrations of some elements in the observed signature, when compared to the geological background signature, indicate that mining might have had an impact on sediment quality. Spidergrams from the Carnlough River, Glenariff River, Glencoy River and Glenshesk River sub-catchments show slight enhancement of some heavy metal concentrations (Fig. 7c.). However, apart from the Glenshesk River, in addition to heavy metals, a large number of non-metals are slightly enhanced. Therefore, attributing this metal enrichment to mining alone may not be correct, as other processes might have caused the slight offset of the observed signature in

the spidergram patterns for these sub-catchments. For example, it was noted that if only a small number of samples were available to represent a geological lithology, the observed and modelled geological background signatures could be slightly offset. This may be a consequence of poorer accuracy in determining the modelled geological background on the basis of a small number of samples. The Ballygalley Burn, Dunseverick River, Glynn River, Larne River, River Bush Stranocum, River Bush Lower and River Dall sub-catchments had fewer than three samples collected over some geological lithologies and the spidergram patterns of the observed and geological background model signatures were slightly offset in each case (Fig. 7d.).

One way to overcome the problem of having only a small number of samples available over a particular geological lithology is to add to the original data set sediment samples that were collected over the same lithology but from one or more neighbouring sub-catchments. This procedure was carried out successfully in a study of the Clyde catchment around Glasgow in the west of Scotland (Lass-Evans *et al.*, in prep). It was attempted in this study, but as the rock formations of Devonian and Dalradian age in the north-eastern coastal area are rather limited in geographic extent, samples from the same lithology in neighbouring sub-catchments were often not available. Consequently, the geological background for sub-catchments with a small number of samples could not be remodelled in this study.

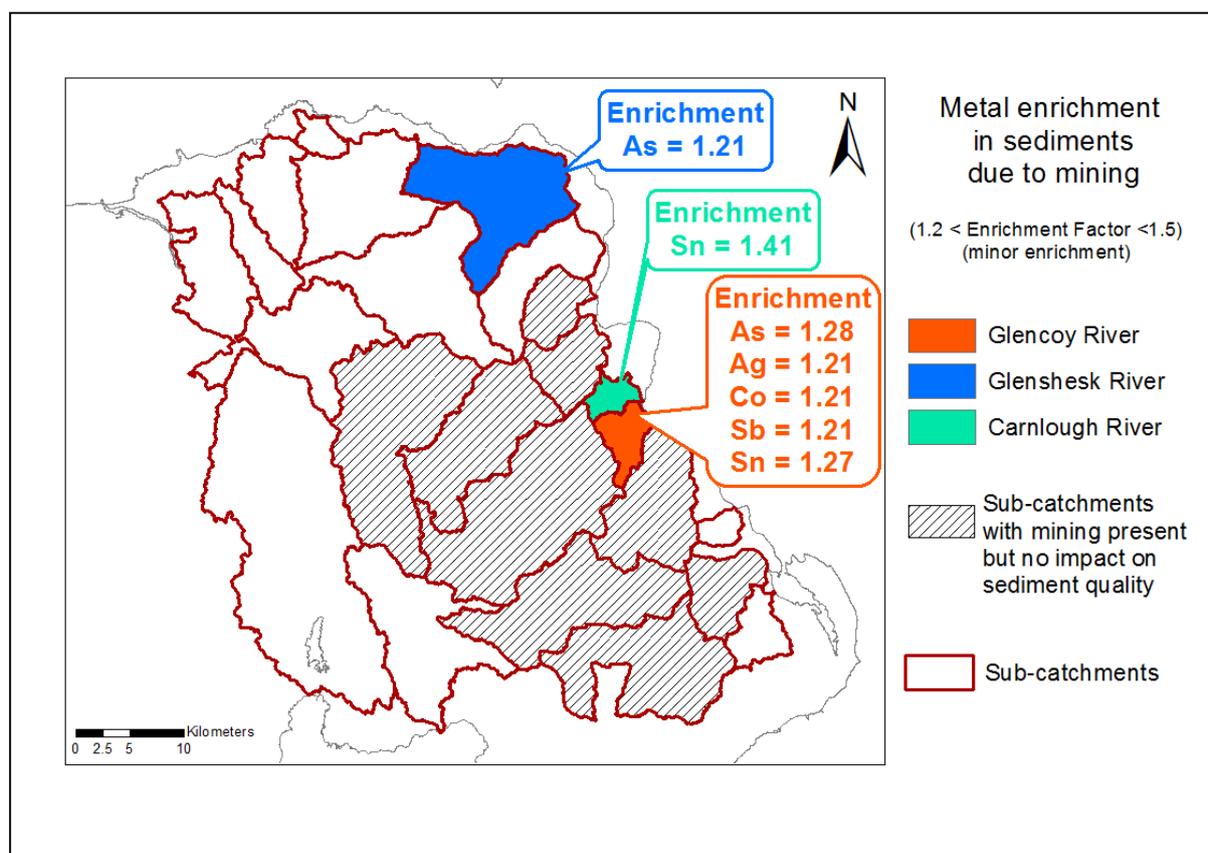


**Fig. 7. Example spidergrams of (a) a sub-catchment where no mining was present (Ballymoney River); (b) a sub-catchment where mining was present, but the spidergram indicated that mining had no impact on sediment quality (Clough River); (c) a sub-catchment where mining might have had an impact on sediment quality (Carnlough River); (d) a sub-catchment, where less than three samples represented a geological lithology, resulting in a slight offset of observed and geological background signatures (Ballygalley Burn).**

### 3.3 MINING IMPACT ON SEDIMENT QUALITY

In Co. Antrim, mining (mainly iron ore and bauxite) had no detectable impact on sediment quality in nine sub-catchments, while three coastal sub-catchments are slightly enriched in some elements (Fig. 8). The Carnlough River sub-catchment has an EF of 1.41 for Sb, while the Glencoy River sub-catchment shows enrichment of As, Ag, Co, Sb and Sn with EFs of 1.28, 1.21, 1.21, 1.21 and 1.27, respectively. However, as pointed out in section 3.2, fewer than three samples were collected over some lithologies; and thus, these slight enrichments cannot be attributed to mining impacts alone.

The Glenshesk River sub-catchment has an EF of 1.21 for As. Only one sample was excluded to model the geological background, as it was located close to a mining site (coal colliery/shafts). However, as the stream is also draining from a small urban area (Ballyvoy), the slight As enrichment could also be related to urban pollution.



**Fig. 8. Enrichment factor map of Co. Antrim showing the sub-catchments in which mining had (or had not) an impact on sediment quality.**

Overall, sediment sub-catchment EFs in Co. Antrim do not exceed a value of 1.5. As their enrichment is less than three times the natural background, it can be classified as minor (Birch and Davies, 2003).

The high Cu, Cr and Ni sediment concentrations in the study area (see section 3.1) do not result from mining activities and most likely reflect an association with their geological parent material (Palaeogene Lower and Upper Basalt Formation and Causeway Tholeiite Member).

## 4 Conclusions

Northern Ireland has over 2000 abandoned mine workings, mostly dating from the 18<sup>th</sup> to early 20<sup>th</sup> Century. Co. Antrim is one of the main areas known for historical mining, where 780 shafts and adits are associated with iron ore exploration, and where historically ca. 700,000 tonnes of bauxite were produced. In order to assess the potential impact of these mining activities on sediment quality, the project modelled the geological background of this area and was able to distinguish whether high metal concentrations in stream sediments were of natural origin or were impacted by mining activities.

Sediment quality guidelines for As, Cd, Cu, Pb and Zn were exceeded by <10% of the samples in most sub-catchments, while 31% of the samples exceeded the guideline for As in the north-eastern coastal Glendun River sub-catchment. By contrast, more than 80% of the samples exceeded the sediment quality guidelines for Cr and Ni in most sub-catchments within the study area, apart from the coastal Glenshesk River and Glendun River sub-catchments, where 50% of the samples exceeded the guideline values.

In order to assess potential mining impacts on sediment quality in Co. Antrim, the geological background for each of the 24 sub-catchments was modelled. Sub-catchments with enhanced element concentrations relative to the geological background were identified; and enrichment factors (EFs), as a classification of the degree of enhancement above natural geological background due to mining activities, were calculated.

Mining (mainly iron ore and bauxite) had no impact on sediment quality in nine sub-catchments, while three coastal sub-catchments showed slight enrichments of either As and Sn or As, Ag, Co, Sb and Sn. However, as the EFs do not exceed 1.5, their enrichment can be classified as minor.

The high Cu, Cr and Ni sediment concentrations in the study area do not result from mining activities and most likely reflect an association with their geological parent material.

# Glossary

BGS	British Geological Survey
G-BASE	Geochemical Baseline Survey of the Environment
GIS	Geographical Information System
GSNI	Geological Survey of Northern Ireland
ED (P)-XRF	Energy Dispersive Polarised X-Ray Fluorescence Spectrometry
EF	Enrichment Factor
ESRI	Environment Systems Research Institute
EU	European Union
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IDW	Inverse Distance Weighting
LPS	Land & Property Services
MWD	Mining Waste Directive
NIEA	Northern Ireland Environment Agency
OS	Ordnance Survey
PEC	Probable Effect Concentration
PGE	Platinum Group Elements
UCC	Upper Continental Crust
WD-XRF	Wavelength Dispersive X-Ray Fluorescence Spectrometry
WFD	Water Framework Directive

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