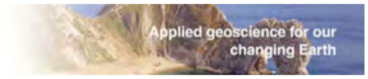
British Geological Survey



Tracing sources and fate of zinc in a mining-impacted river catchment:

insights from flow measurements, synoptic sampling and zinc isotopes

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Outline

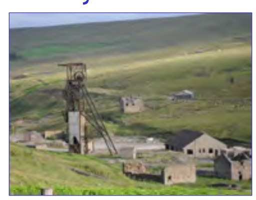
Findings of a project which uses a catchment-based approach to determine the importance of point and diffuse sources of zinc contamination and natural attenuation processes in a mining-impacted catchment in the UK.

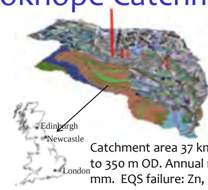
Drivers

•Effective remediation requires an understanding of all the sources responsible for the contaminant loading in a catchment.

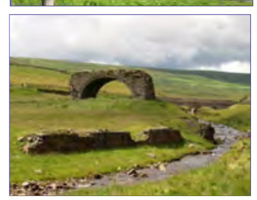
•Catchments are not homogeneous and the contaminant loading may be subject to a combination of point and diffuse inputs, non-conservative behaviour, dilution where the stream passes through contaminant-free stretches of the catchment, and seasonality.

Study Site: the Rookhope Catchment

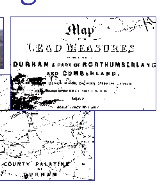




Catchment area 37 km^2. Elevation 600 to 350 m OD. Annual rainfall ~ 1000 mm. EQS failure: Zn, Pb. Cumulative zinc load 5.6 to 18.5 kg/day



Metal Ore and Mining

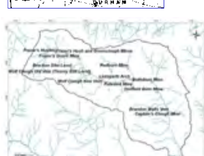


•Fracture-hosted mineralisation in Carboniferous late Dinantian to early Namurian platform carbonates.

•Galena and fluorite are the main ore minerals, accompanied by subsidiary baryte, sphalerite, witherite and chalcopyrite.

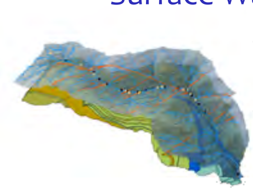
•The majority of the lead mines were exploited during the period 1692 to 1882.

•Fluorspar mining continued until 1999, when the last mine, Grove Rake, closed.



Map of Mining Centres

Surface Water Monitoring

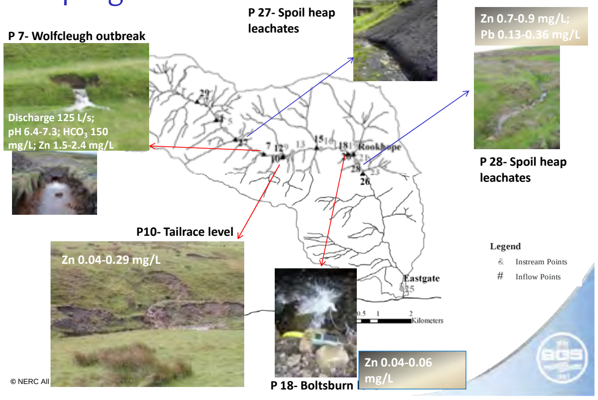


- Synoptic water sampling and flow monitoring in May 2007, June 2007, Jan 2008 and Apr 2009.
- to cover water stretches upstream and downstream of visible mine water discharges or at the confluence of major tributaries.

✓ 12 instream sampling points on the Rookhope Burn + 11 inflow sampling points;

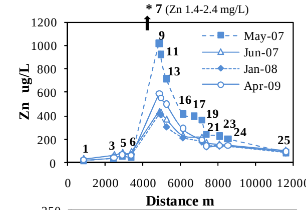
✓ Flow monitoring (Columbia 2 Digital Stream Meter- discharge determined using the velocity-area method (Shaw, 1999)) + field measurements of physico-chemical parameters and ICP-AES/ICP-MS analysis of major and trace elements.

Sampling Points

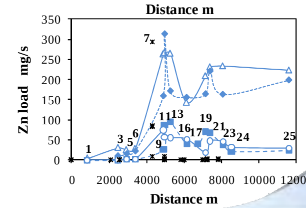


Results of the surface water monitoring

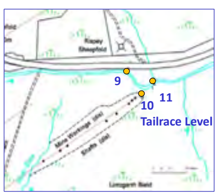
- Major changes in the Rookhope Burn stream chemistry occurred downstream of the location of the mine water outburst at Wolfcleugh point 7 (stretch 6-9)



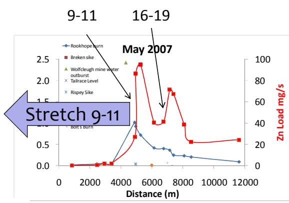
- The Zn load profile differs from the concentration profile in that it displays two distinct peaks in load



Sub-surface contributions



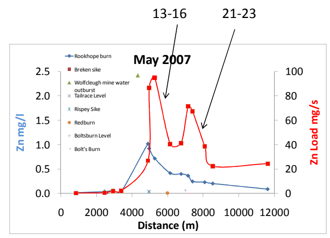
Contribution from mine workings
Clear discharge contribution d/s point 10, identified by closely spaced flow monitoring, aligns with a series of mine workings/northeast to southwest-trending mineral vein.



In-Stream Zn load during May sampling (close to base flow conditions) - inflow Zn loads plotted for comparison.

No obvious inflow can account for the gain in zinc load along **stretch 9-11 and 16-19:** *Sub-surface contributions of contaminated groundwater to the river bed of Rookhope Burn.*

Loss in Zinc Load



- Along **stretch 13-16** Zn concentration decreases: attenuation by chemical precipitation
- Along **stretch 21-23** reduction in flow (decrease in concentration less significant): flow loss below the river bed or karstic loss?

- Min cumulative Zn loading 128 mg/s
- Min cumulative Zn attenuation 104 mg/s

Hyporheic Zone Sampling

- From the loading profile the existence of sinks of zinc with cumulative **Zn attenuation** ranging between **80 to 140 mg/s** has been established.
- The Hyporheic Zone (HZ) , the water saturated region at the interface of surface water (SW) and groundwater (GW), was sampled to assess its metal attenuation capacity.
- Focus on a river stretch with dissolved Zn and Mn attenuation.
- Sediments highly contaminated in Pb (Zn).
- Black-coated boulders in the river bed.

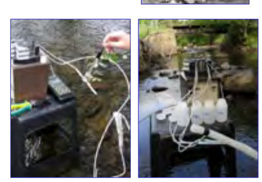
Sediment Composition

- Galena, cerussite, sphalerite, fluorite, dolomite, siderite, feldspar, mica, Qz

pH 6.84
Fe 8.7 %
Mn 4580 mg/kg
Pb 29500 mg/kg
Zn 1690 mg/kg
S 6570 mg/kg
OM 4.24 %

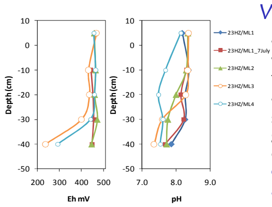
Multilevel Sampler

Installation



Pore water sampling

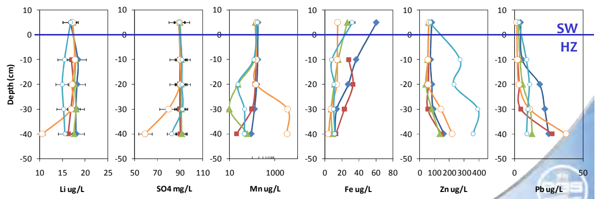
Vertical Gradients in the HZ



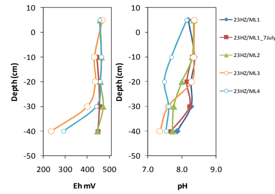
•Oxidising conditions in the shallow HZ (0-30 cm) with Eh decrease at 40 cm depth. pH decreases in the HZ.

• Conservative elements Li, (B , Cl not shown) show small vertical gradients compared to the greater difference with measured GW-MW concentrations (Li_{GW} ~50 ug/L) : **negligible GW contribution to the HZ.**

•Mn, Fe, Zn and Pb do not behave conservatively.



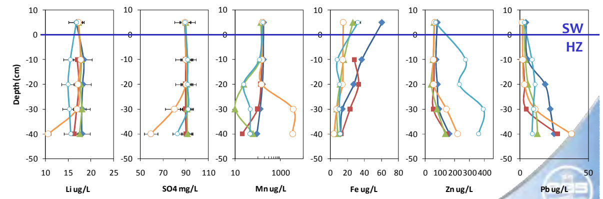
Manganese Attenuation in the HZ



•Mn_{HZ} and Fe_{HZ}< Mn_{SW} and Fe_{SW} in the shallow HZ

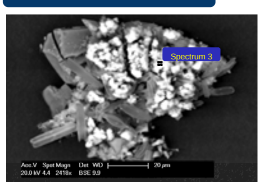
= >**Attenuation by Mn precipitation** from Mn-rich SW in the oxidised pore waters (Eh 400 mV) of the shallow HZ.

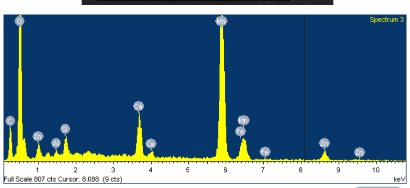
•Down the HZ profile dissolved Mn increases: influence of more reducing conditions enhancing Mn solubility.



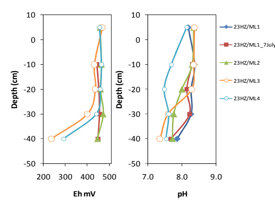
SEM Evidence of Mn precipitation

HZ sediment; black-brown scrapings



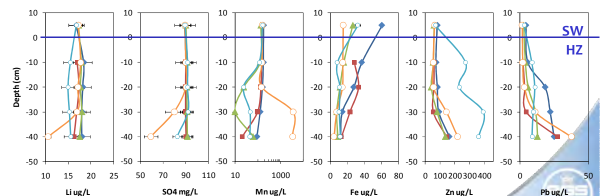


Zinc and Lead in the HZ

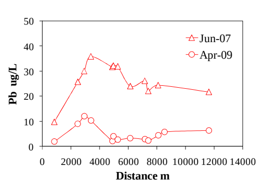


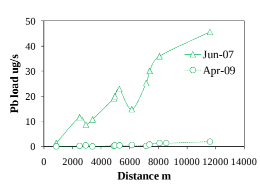
Pb_{HZ} and Zn_{HZ} >> Pb_{SW} and Zn_{SW}

HZ sediment is a potential source of zinc and lead loadings to either the SW or GW depending on the hydrological conditions.



Diffuse Lead Loading from sediment





Feasibility of Zn Isotopes as Environmental Tracers

•The relative abundances of Zn isotopes $\delta^{66/64}$Zn in natural waters may be used to fingerprint sources of this metal and/or to probe important biogeochemical reactions;

•The variation in isotopic ratio of a solute ion can be less ambiguous to interpret than the corresponding variation of water chemistry, because isotopes are affected by a smaller number of processes than chemical concentrations;

•To be successful tracers of anthropogenic and natural sources there should be a sufficient isotope ratio variation among end-members;

•To be effective tracers of weathering reactions there must be a significant contrast in isotope composition among reagent-product.

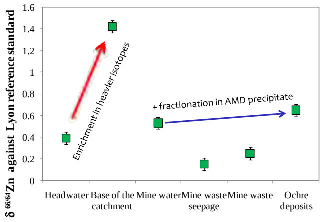
Known isotope fractionation processes:

1. Weiss et al. (2007) demonstrated preferential plant uptake of the lighter Zn isotope, concentrating the heavier isotopes in the pore water and runoff.
2. Balistrieri et al.(2008) experimentally constrained a separation factor for Zn adsorption onto ferrihydrite of +0.53‰ (Δ^{66}Zn adsorbed-solution).

Preliminary Findings

We sampled:

- Headwaters from peat blanket
- Potential Zn sources (mine waste, mine water, mine seepage)
- AMD precipitate ($\delta^{66/64}Zn$ fractionation on iron oxides)
- Water at the base of the catchment



Results

- $\delta^{66/64}Zn$ in mine waste and seepage ~ primary ore (0.15‰);
- Headwater $\delta^{66/64}Zn$ relatively heavier 0.39‰ (Zn-organic complexes?);
- Enrichment in heavier isotopes in iron ochre precipitate from mine water;
- Significant variations in $\delta^{66/64}Zn$ between headwaters and base of catchment.

Conclusive remarks

1. Unknown contributions to the Zn load through the river bed highlight the need for more detailed understanding of the hydrology associated with abandoned workings.

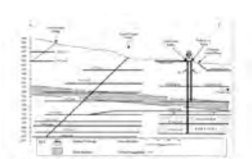
2. The observed triggering of the mine water outburst raises the question of the stability of the underground workings and the risk of designing remediation schemes for a single point in the event of a comparable outburst elsewhere in the catchment.

Conclusive remarks (II)

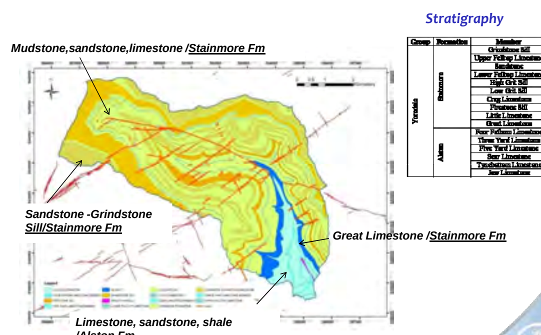
3. We have shown how riverbed sediments may act as a long-term source of zinc, lead to rivers, thereby potentially diminishing the short to medium term benefits delivered by mine water source point remediation.

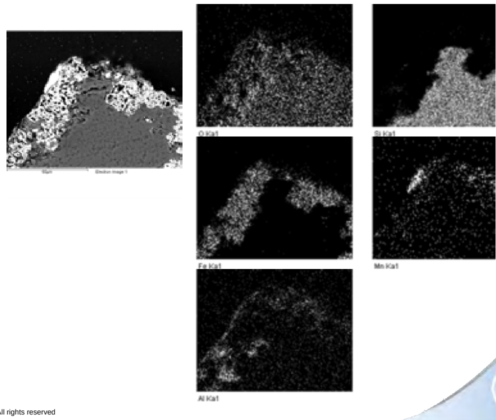
4. We have shown significant differences in $\delta^{66/64}Zn$ in the catchment. Yet, our ability to interpret these measurements in terms of sources and processes is limited because of the paucity of published studies that explore the mechanisms of Zn isotope fractionation. More work is needed to gain further insights on the fractionation behaviours of Zn isotopes to make them strong geochemical probes in biogeoscience.

Thank you for your attention



Geology

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Si Ka1
Fe Ka1
Mn Ka1
Al Ka1