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Critical Shifts in Trace Metal Transport and Remediation Performance under Future Low River Flows

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ABSTRACT: Exceptionally low river flows are predicted to become more frequent and more severe across many global regions as a consequence of climate change. Investigations of trace metal transport dynamics across streamflows reveal stark changes in water chemistry, metal transformation processes, and remediation effectiveness under exceptionally low-flow conditions. High spatial resolution hydrological and water quality datasets indicate that metal-rich groundwater will exert a greater control on stream water chemistry and metal concentrations because of climate change. This is because the proportion of stream water sourced from mined areas and mineralized strata will increase under predicted future low-flow scenarios (from 25% under Q45 flow to 66% under Q99 flow in this study). However, mineral speciation modelling indicates that changes in stream pH and hydraulic conditions at low flow will decrease aqueous metal transport and increase sediment metal concentrations by enhancing metal sorption directly to streambed sediments. Solute transport modelling further demonstrates how increases in the importance of metal-rich diffuse groundwater sources at low flow could minimize the benefits of point source metal contamination treatment. Understanding metal transport dynamics under exceptionally low flows, as well as under high flows, is crucial to evaluate ecosystem service provision and remediation effectiveness in watersheds under future climate change scenarios.
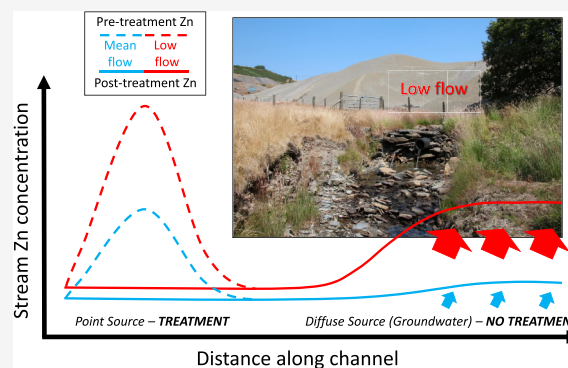
INTRODUCTION

Future changes in stream and river flows worldwide as a consequence of climate change remain uncertain.[1] However, in many global regions, it is likely that river flows will become more variable with more extreme events at the low and high end of the hydrological regime.[1−5] While the effects of high flows on river water quality (mainly nitrogen and phosphorus) have been widely investigated,[6,7] considerably less attention has been paid to the potential effects of more severe and prolonged low flows.[2,8] In the United Kingdom (UK), the most recent climate predictions (UKCP18) indicate a general shift toward aridity from the 2020s to the 2050s.[9] In response, summer river flows are expected to decline and Q95 (flow that is exceeded 95% of the time) may reduce by 26% in central and western Wales and by over 50% in southern England, using the medium emission (P50) scenarios.[10,11] Although the specific effects are unclear, future changes in Q95 in the UK are expected to have negative effects on water quality.[2,12]

Worldwide, millennia of metal mining have produced substantial quantities of potentially toxic metals that contaminate watersheds and ecosystems and cause widespread failure of river water-quality objectives.[13−15] Mine sites are inherently complex systems, and variability in hydrological conditions can dramatically change contamination sources,[16] metal transport and transformation processes,[17] and water-quality improvements from remediation.[18] This is especially relevant in temperate-oceanic regions like the UK where high river flows driven by high rainfall are thought to account for the largest flux of metals in mineralized watersheds through erosion of streamside mine spoil and dissolution of secondary mineral salts accumulated during dry periods.[16,19−21] However, much less is known about metal contamination dynamics at the lower end of the hydrological regime, specifically, extreme low flows. In fact, to the author's knowledge, there are no published studies on this topic. Increased aridity and changes in the magnitude and frequency of Q95 flows would likely decrease the watershed runoff and the surface water component of streams in mineralized watersheds and increase the fraction of (contaminated) subsurface water and groundwater. This could be problematic for monitoring and characterization of mined and mineralized watersheds as dispersed groundwater inputs to mineralized watersheds have proved difficult to locate and quantify.[16] Furthermore, reductions in stream flows would be expected to increase
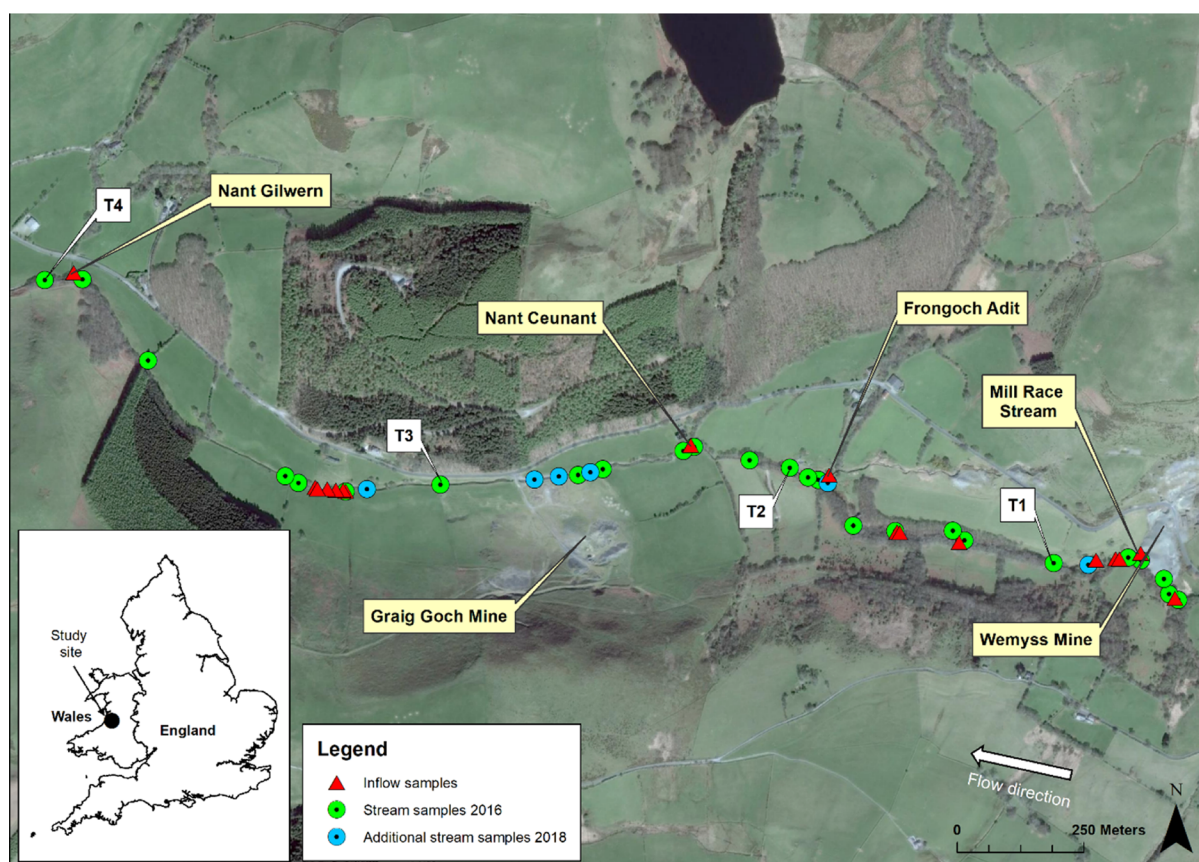
Figure 1. Nant Cwmnewydion study reach showing the location of stream and inflow sample sites. Transport sites for OTIS modelling (at 133, 829, 1610, and 2593 m) are shown as white labels.

metal concentrations in mineralized watersheds,[22] which may alter biogeochemical and solute transport processes. These potential changes in metal contamination dynamics could, in turn, increase the ecotoxicity of metal pollutants and affect the efficiency of remedial approaches.

The UK experienced a prolonged period of warm and dry weather over the summer (June, July, August) of 2018. Stream flows across the UK in July 2018 were generally low to notably low (72nd to 95th percentile), compared to long-term data (1981−2010), with exceptionally low flows (>95th percentile) and new July minima in parts of central Wales.[23] This offered a unique opportunity to study trace metal dynamics under stream flows that are currently exceptional but are predicted to become more common in the future. Through comparison of datasets representing average and exceptionally low-flow conditions, our study establishes variability in physical and chemical transport processes and how this might affect remediation effectiveness in hydrologically complex, mined, and mineralized watersheds. This is achieved through a watershed-scale synoptic sampling (using tracer dilution) and solute transport modelling study which has not previously been demonstrated in temperate-oceanic watersheds characterized by variable hydrological regimes. Using spatially detailed stream flow, water quality, and metal loading datasets for average and exceptionally low flows, our specific objectives were to (a) establish the dynamic variability of point and diffuse water and metal contamination sources, (b) investigate differences in the transport and geochemical behavior of key metal contaminants, and (c) establish the potential effectiveness of different remediation scenarios. The results of this study support the development of conceptual and numerical models of trace metal behavior and transport in watersheds and offer critical insights to the potential effects of low flows on processes and remediation.

MATERIALS AND METHODS

Field Setting. The Central Wales Orefield contains numerous headwater streams severely affected by mine contamination.[24] The predominant rock types in the district are Upper Silurian shales, siltstones, and mudstones[25] that were fractured and penetrated by warm brines during the Variscan orogeny to produce barite, fluorspar, and sulfides of Pb, Zn, and Cu.[26] Although calcite is rare, the predominance of monosulfides (galena, sphalerite) means mine wastes are generally not acid generating, and most mine water pH values range from 5.5 to 7.5.[27] Overlying superficial deposits, where present, consist mostly of glacial clays (till) and sometimes peat, with alluvial sediments along river channels.

The Nant Cwmnewydion (52° 20′ 58″ N; 3° 53′ 15″ W) is typical of many upland and mineralized streams in this region and throughout the UK. The watershed contains numerous point and diffuse sources of mine contamination that contribute to substantial breaches of water quality standards (for Pb, Zn, Cu, and Cd).[24,28] In the case of the Nant Cwmnewydion, intensive monitoring by the environmental regulator (Natural Resources Wales) has identified two main sources of contamination (principally of Pb and Zn): erosion and leaching of the large waste tips at Wemyss Mine and contaminated groundwater entering the stream via Frongoch Adit (Figure 1). In 2011, a stream diversion at Frongoch Mine

(north-east of Wemyss Mine) reduced the volume of water and trace metal loads entering the Nant Cwmnewydion via Frongoch Adit but increased the metal concentrations.[29] Remediation of Frongoch Adit (water treatment facility) is being assessed, and remediation of Wemyss Mine (mine spoil erosion control) is currently (2020) in progress.

Tracer Injection and Synoptic Sampling. Two separate continuous tracer injection and synoptic sampling studies were carried out in the Nant Cwmnewydion in July 2016 and July 2018. The 2016 and 2018 studies were conducted under Q45 and Q99 flow conditions, respectively, based on analysis of a 56 year historical record (1963−2019) from a nearby flow gauge (Figure S1). During both experiments, a concentrated sodium bromide (NaBr) solution was introduced to the stream above known mine workings. Once bromide (Br) in the stream had reached plateau concentrations, spatially detailed synoptic sampling was carried out at 25 stream sites and 18 inflow sites in 2016 and at 31 stream sites and 6 inflow sites in 2018 (Table S1). Inflow sites included visible tributary-type inflows and more ill-defined flows such as riparian seeps and springs. All samples were processed on-site [pH and specific conductance measurement, filtration (0.45 μm), preservation (ultrapure 1% HNO_3 v/v)] and prepared for cation and anion analyses. Bromide and anion concentrations were determined from filtered, unacidified samples by ion chromatography (Tables S2 and S3). Total recoverable and filtered cation concentrations were determined by inductively coupled plasma mass spectrometry (Tables S4−S7). Zinc and Pb are the primary metals discussed in this paper as they are the main elements of concern in the region.

Estimating Stream Flow by Tracer Dilution. As Br is considered to behave conservatively in circum-neutral streams,[30,31] decreases in Br concentrations downstream from the injection point reflect dilution of the tracer as point and diffuse surface and/or groundwater inputs result in increased streamflow. The observed dilution of Br can then be used to calculate stream flows throughout the study reach using the tracer-dilution method (Tables S2 and S3).[30,32−34]

Loading Analysis. For the 2016 study, the study reach was divided into 24 stream segments demarcated by 25 stream sampling sites. For the 2018 study, the study reach was divided into 30 stream segments demarcated by 31 stream sampling sites. Total and filtered Zn and Pb loads were calculated as the product of tracer-derived stream flow and metal concentration (Tables S8−S11). Segments where the load increased represent sources of trace metal mass to the stream. Cumulative instream loads (sum of all increases in the load between stream segments) were calculated to estimate the total metal load added to the stream over the entire study reach.[33] Comparing cumulative instream metal loads with measured instream loads (including stream segments with increases and decreases in load) provides a means of estimating net attenuation of trace metals (after chemical reaction) over the length of the study reach and the proportion of metals attributable to sampled and unsampled locations (Tables S8−S11).

Equilibrium Modelling. Equilibrium modelling, using the measured stream and inflow filtered concentrations, was carried out using the PHREEQC code and the wateq4f thermodynamic database distributed with the code.[35,36] Alkalinity was estimated for the stream and inflow waters as bicarbonate by ion sum calculation (i.e., charge balance was forced with bicarbonate).

OTIS Modelling. OTIS (one-dimensional transport with inflow and storage)[37] has been used widely to describe the hydrologic and geochemical processes controlling solute transport in streams.[38] Applications include investigations of hyporheic zone and nutrient biogeochemical processes through simulation of tracer breakthrough curves and nutrient additions.[39−42] However, application of the steady-state model to simulate watershed-scale solute transport processes is rare, and we are aware of only one existing study that utilized OTIS to simulate remedial alternatives in US montane environments.[43] Our study is therefore the first to adopt this approach in a temperate-oceanic environment and under different stream flow conditions.

The spatially detailed solute concentrations and stream flows obtained during synoptic sampling were used to calibrate OTIS to simulate remediation of metal contamination sources. Four steps were involved in the modelling process.[43] These were (1) estimation of physical transport parameters [dispersion coefficient (D); stream cross-sectional area (A); storage zone cross-sectional area (A_S); storage zone exchange coefficient (α)], (2) calibration of OTIS models for Zn and Pb assuming conservative transport, (3) simulation of non-conservative transport by estimating first-order removal coefficients (λ), and (4) simulation of changes in metal solute concentrations due to planned remediation activities. Further details of the OTIS modeling approach, including sensitivity analysis of the transport parameters, are provided in the Supporting Information.

RESULTS AND DISCUSSION

Variability in Water Chemistry, Streamflow, and Metal Contamination Sources. Spatial pH profiles were different under Q45 (range = 5.8−6.5) and Q99 (range = 6.6−7.6) flow conditions (Figure 2a). The predominance of monosulfides (galena and sphalerite) in this region means mine drainages are generally circum-neutral,[27] and all of the mine drainages in the watershed had pH above 6.0, including Frongoch Adit (groundwater and mine drainage from Frongoch Mine). The lower pH during Q45 flow conditions was possibly due to an increased proportion of peat runoff during higher flows, a pattern that has been observed elsewhere in the UK.[18] Under Q99 conditions, many inflows in the watershed were dry or had extremely low flows, indicating limited hydrological connection to the lower pH water of the peaty areas.

Stream water in the Nant Cwmnewydion is poorly mineralized and buffered (low alkalinity) with low concentrations of major ions, including sulfate (Tables S2 and S3), a general characteristic of watersheds in the region.[44] Zinc and Pb are the major contaminants of concern and breach regulatory standards (15 μg L^{-1} Zn; 1.2 μg L^{-1} Pb)[45] along the entire study reach and under both flow conditions (Figure 2b,c). Stream Zn concentrations were greatest under Q99 conditions (maximum = 8146 μg L^{-1}), reflecting a widespread pattern in mineralized watersheds across the UK during the summer of 2018. Large increases in stream Zn concentration were associated with surface water drainages from Wemyss Mine (Mill Race Stream = 5825 μg L^{-1}) and subterranean drainage from Frongoch Mine (Frongoch Adit = 9000 μg L^{-1}). Stream Zn concentrations under Q45 conditions followed a similar downstream pattern but were lower (maximum = 2901 μg L^{-1}), and increases were again associated with the same inflows draining Wemyss Mine (Mill Race Stream = 4997 μg
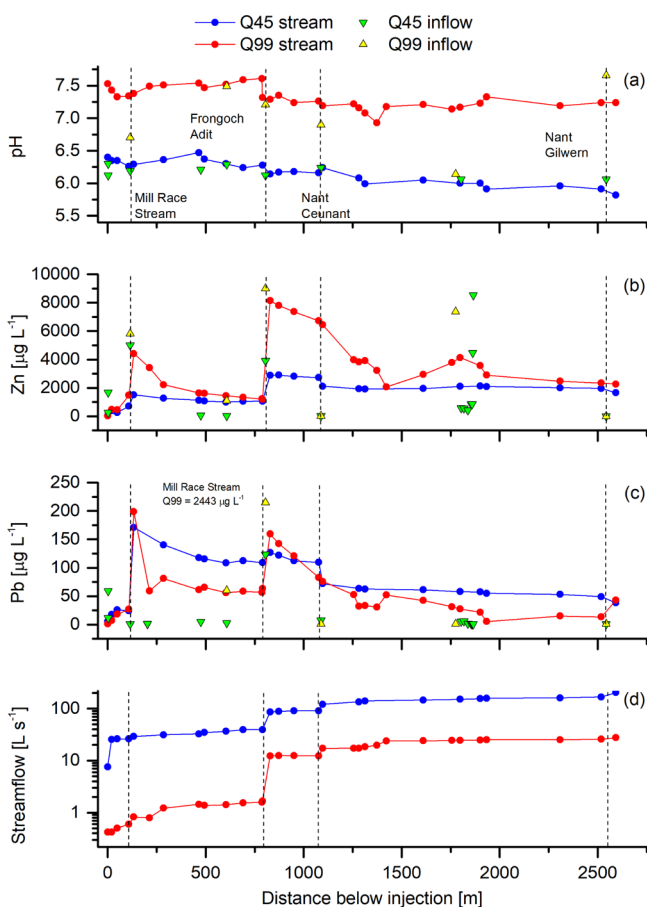
Figure 2. Spatial profiles from synoptic sampling: (a) pH; (b) zinc-filtered concentration; (c) lead-filtered concentration; and (d) streamflow (log scale). Locations of major surface inflows are marked with a dashed vertical line and labelled in (a).

L^{-1}) and Frongoch Mine (Frongoch Adit = 3907 μg L^{-1}). Other substantial Zn concentrations were measured under both flow conditions in water from small diameter pipes (maximum = 7358 and 8514 μg L^{-1} at Q45 and Q99, respectively) opposite Graig Goch Mine and thought to be connected to deep mine workings at the site. In contrast to Zn, stream Pb concentrations were generally highest (maximum = 171 μg L^{-1}) during Q45 conditions, although Q99 inflows from Mill Race Stream (2443 μg L^{-1}) and Frongoch Adit (214 μg L^{-1}) increased the stream concentrations temporarily above Q45 concentrations.

Streamflow increased from 7.5 L s^{-1} (above Wemyss Mine) to 203 L s^{-1} (below Graig Goch Mine) under Q45 conditions and from 0.46 to 27.5 L s^{-1} under Q99 conditions (Figure 2d). For the purpose of examining water and trace metal sources along the study reach, data have been summarized for 11 subreaches as shown in Figure 3 and Table S12. The main point sources of water identified were Mill Race Stream, Frongoch Adit, Nant Ceunant and Nant Gilwern. Under Q45 conditions, approximately 13% of streamflow originated from mining-affected point inflows [mine point source inflows (MPI) in Table S12] (Mill Race Stream = 1.4%; Frongoch Adit = 11.6%). This increased to approximately 36% (Mill Race Stream = 0.8%; Frongoch Adit = 35.4%) under Q99 conditions. Similarly, diffuse water (subsurface and/or ground) inputs from mining-affected reaches [mine diffuse source inflows (MDI) in Table S12] increased from approximately

12% under Q45 conditions to 29% under Q99 conditions. Most of the increase was attributable to Graig Goch Mine and is thought to represent a previously unknown subsurface hydrological connection between the stream and deep mine workings (Graig Goch Deep Adit level). Together, point and diffuse water inputs from known mine areas (MDI and MPI in Table S12) contributed 25 and 66% of water to the stream under Q45 and Q99 conditions, respectively, indicating the importance of ground and mine water in maintaining streamflow under low-flow conditions.

Overall, point source mine inflows (Mill Race Stream and Frongoch Adit) accounted for approximately 53 and 48% of Zn and Pb loads (MPI in Table S12), respectively, in the study reach under Q99 conditions (Figure 4a,b). This increased to 64% for Zn and 85% for Pb under Q45 conditions. However, diffuse contributions in mine areas (MDI in Table S12) were greatest under Q99 conditions; Zn increased from 23 to 31%, and Pb increased from 6% loading to 17%. Comparison of cumulative instream and instream (filtered) metal loads (Figure 4c,d) shows that, at the watershed-scale, attenuation of Zn and Pb by chemical reaction was greatest at Q99 (Zn = 68%; Pb = 72%) compared to Q45 (Zn = 8%; Pb = 40%) conditions. The potential processes controlling this pattern are explored in the next section.

Examining discrete changes in metal loads along the study reach, six major source areas of Zn and Pb can be identified under the two different flow conditions (Figure 3). Frongoch Adit was the largest source of both Zn (Q45 = 57% of total Zn; Q99 = 52% of total Zn) and Pb (Q45 = 52% of total Pb; Q99 = 45% of total Pb) (Table S12). The second and third largest sources of Zn under Q45 were diffuse drainage from Graig Goch Mine (20%) and Mill Race Stream (7%), respectively. The second and third largest sources of Zn under Q99 were diffuse drainage from Graig Goch Mine (31%) and the Nant Ceunant (15%), respectively. The second largest source of Pb was Mill Race Stream under Q45 (34%) with the third largest source being Graig Goch Mine (5%). The second and third largest sources of Pb under Q99 were the Nant Gilwern (20%) and Graig Goch Mine (17%). The Nant Ceunant was also an important source of Zn under Q99 conditions. This indicates that metal mobilization from mineralized parts of these tributary watersheds contributed substantially to stream metal loading. The overall contribution from the nonmined tributaries was more significant for both metals under Q99 conditions which could indicate either lower hydrological connectivity between mine workings under Q99 conditions or hydrological changes in the tributary watersheds allowed oxygen to mobilize metals in the regolith.[46,47]

Trace Metal Transport Processes. The filtered fraction (0.45 μm) typically comprised 73% of Pb under Q45 flow conditions and 84% under Q99 flow conditions (although there was a considerable range of 23−97% in the latter (Figure S2), indicating that both the filtered and particulate fractions were important transport vectors for Pb. Zinc was present principally in the filtered fraction (typically >90%) under Q45 flow conditions. However, similar to Pb, the proportion of Zn in the filtered fraction increased (typically >99%) under Q99 flow conditions (Figure S2). This indicates that Zn was behaving in a conservative manner (especially under Q99 flow conditions) and that physical dilution by low Zn concentration inflow waters was the main mechanism driving the decrease in concentrations. It is curious then why comparison of total observed instream and cumulative instream Zn and Pb loads
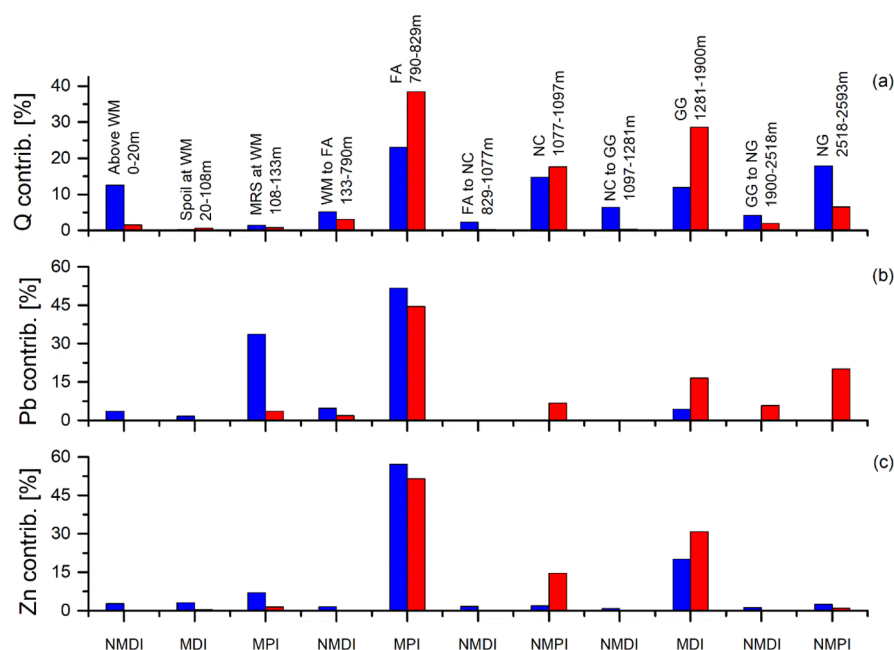
Figure 3. Percent contribution of (a) streamflow, (b) Pb loads, and (c) Zn loads to 11 subreaches. Lead and Zn loads are calculated as a percentage of the cumulative load at the end of the study reach. Subreaches were selected to bracket mine point source inflows (MPI), non-mine point source inflows (NMPI), mine diffuse source inflows (MDI), and non-mine diffuse source inflows (NMDI). Blue bars = stream samples during Q45; red bars = stream samples during Q99. WM = Wemyss Mine; MRS = Mill Race Stream; FA = Frongoch Adit; NC = Nant Ceunant; GG = Graig Goch Mine; and NG = Nant Gilwern.

(Figure 4c,d) indicates greater reactive loss under Q99 (Zn = 68%; Pb = 72%) than Q45 (Zn = 8%; Pb = 40%) flow conditions.

Modelling of mineral phases and saturation indices at selected stream and inflow samples sites was performed to investigate if there were any spatial (along the stream) or temporal (between flow types) differences that could explain the observed patterns of instream metal loading (Tables S13 and S14). Generally, Pb- and Zn-bearing minerals [including anglesite ($PbSO_4$), cerussite ($PbCO_3$), and smithsonite ($ZnCO_3$)] were found to be undersaturated throughout the watershed and under both flow conditions. Ferrihydrite [$Fe(OH)_3$] was predicted to be undersaturated during Q45 flow conditions, but most sample sites were supersaturated during Q99 flow conditions. This is important as freshly precipitated iron (hydr)oxides such as $Fe(OH)_3$ have an adsorption capacity 10 times that of aged oxides, which has been found to correspond to a 10-fold difference in the cation exchange capacity and surface area.[48,49] Very little freshly precipitated $Fe(OH)_3$ is therefore needed to sorb high concentrations of Pb and Zn.[50] A probable vector for Zn removal at low flow was therefore sorption directly to the streambed sediments.[51] This would account for the occurrence of Zn almost exclusively in the filtered fraction under Q99 flow conditions, despite the large-scale attenuation observed in the loading data. Sorption of Pb directly to streambed sediments may also have occurred; however, sorption or coprecipitation with particulate Fe was likely the dominant Pb removal mechanism. In addition to increased sorption capacity of freshly precipitated $Fe(OH)_3$, there were also hydraulic differences at low flow which probably encouraged metal sorption to the streambed sediments. Stream velocities were substantially lower under Q99 flow conditions, meaning contact time between stream water and sediment was higher. In addition, there was much less water in the stream channel,

meaning a greater volume of the water was in contact with the streambed and the bank surface. It is also possible the sorption process may have been biologically mediated, as has been observed in other arid, low-flow settings.[52]

Remediation Effectiveness. Plans for remediation of metal contamination from Frongoch Adit and Wemyss Mine are progressing; however, the preliminary target for filtered Pb and Zn removal is 94% based on the performance of other treatment systems.[53] Therefore, remediation scenarios tested using the calibrated models included reductions in metal loadings from Wemyss Mine and Frongoch Adit and an aggregate of both sources. The Pb and Zn concentration changes presented here represent the maximum possible from elimination of the mining-related sources identified in the watershed. The sensitivity analysis of the OTIS transport parameters showed a less than 1% uncertainty in the predicted stream Pb and Zn concentrations (Table S17).

The initial conservative model simulations of Q99 flow conditions showed both the Pb and Zn simulations plotting above the observed data (Figure S3), indicating that removal of both of these metals by chemical reaction is important under low flows. Conservative model simulations plotted closer to the observed data under Q45 flow conditions, especially for Zn, indicating chemical processes of attenuation were less important at higher streamflows. Subsequent reactive modelling incorporating first-order decay produced good fits with the observed solute data (Figure S3).

Remediation scenario modelling indicates that the largest changes in both stream Pb and Zn concentrations could result from remediation of both Wemyss Mine and Frongoch Adit for Q45 flows and Frongoch Adit alone for Q99 flows (Figure 5). For Pb under Q99 flows, simulation results indicate that remediation of Frongoch Adit could result in 67% reduction at the farthest downstream synoptic sampling site (2593 m) (Table S15), which is equal to the value for remediation of
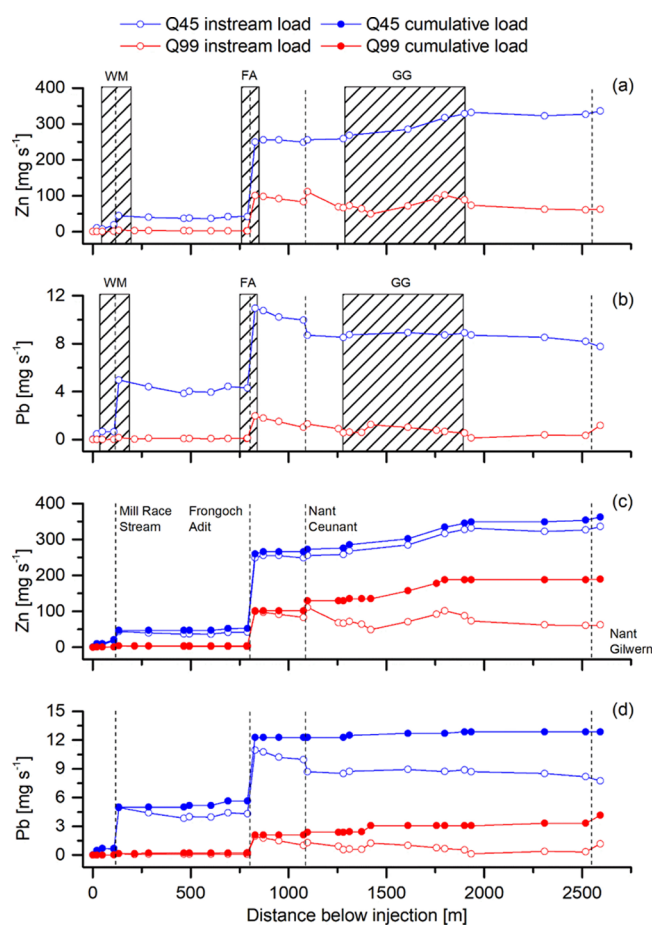
Figure 4. Spatial profiles from synoptic sampling: (a) Filtered Zn instream loading; (b) filtered Pb instream loading; (c) filtered Zn cumulative (closed circles) and instream loading (open circles); and (d) filtered Pb cumulative (closed circles) and instream loading (open circles). Locations of major surface inflows are marked with a dashed vertical line and labelled in (c). Locations of mine sites are labelled with hatched boxes in (a,b): WM = Wemyss Mine; FA = Frongoch Adit; and GG = Graig Goch Mine.

Figure 5. Observed and simulated (WM = Wemyss Mine; FA = Frongoch Adit) filtered Pb concentrations during Q45 (a) and Q99 (b) flow conditions. Observed and simulated filtered Zn concentrations during Q45 (c) and Q99 (d) flow conditions. Simulations consider 94% reduction in metal concentrations from WM and FA. Locations of major surface inflows are marked with a dashed vertical line and labelled in (a).

Wemyss Mine and Frongoch Adit. However, remediation of both Wemyss Mine and Frongoch Adit could be required to achieve the greatest reduction of Pb under Q45 flows (79%) because of increased loading from Wemyss mine under Q45 flow conditions. A decrease in Zn concentrations of 62% under Q45 flow conditions could be achieved from remediation of both Wemyss Mine and Frongoch Adit, whereas remediation of Frongoch Adit alone could achieve the same reduction (17%) as remediation of both Wemyss Mine and Frongoch Adit under Q99 flows. The smaller reductions in Zn concentrations compared to Pb are in part explained by the reactivity of Pb in the system under study, which results in substantial removal by instream chemical processes under both flow conditions. An additional important factor is high Zn concentration water entering the stream via diffuse subsurface pathways, which increases stream Zn concentrations along an approximately 600 m length of channel adjacent to Graig Goch Mine.

It is interesting to note that, in general, remediation of Wemyss Mine alone could result in less than 2 and 11% reduction in Pb and Zn concentrations, respectively, under Q99 and Q45 flows. This is due to (1) the greater overall loading from Frongoch Adit a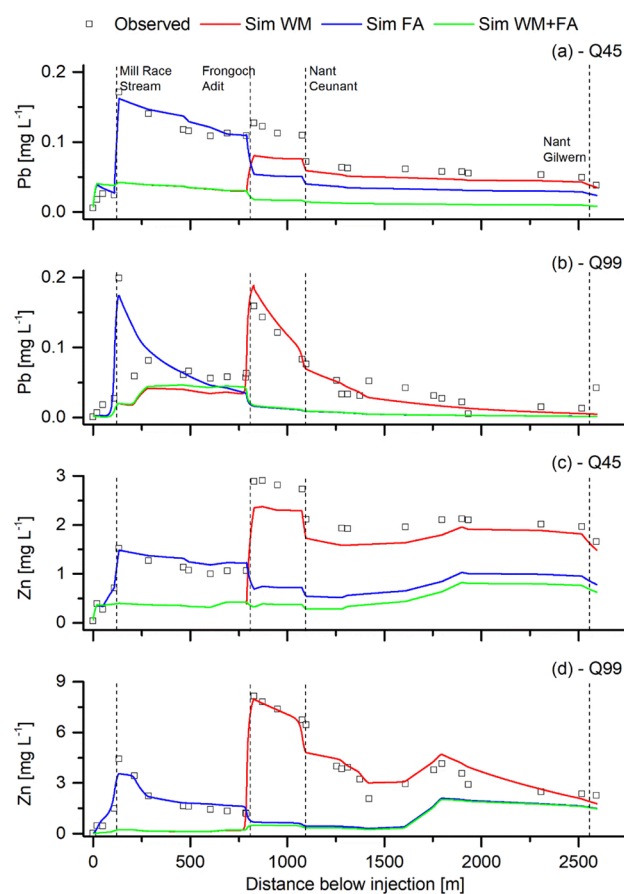nd (2) the fact that this source is farther downstream than Wemyss Mine, and much of the solute loading from Wemyss Mine is removed by instream chemical reactions.

Implications. The latest UK climate change scenarios (UKCP18) indicate that precipitation could decrease by almost 50% in summer by 2070.[9] Data from many other nations with substantial mining legacies and/or mineralized regions demonstrate an increasing trend toward aridity, with some regions such as the western USA and Chile currently experiencing decade-long megadroughts.[54,55] In this context, there are three primary implications of this work.

First, although changes in stream water chemistry and metal contamination sources during high river flows have been widely documented,[16,18,19] the present study highlights, for the first time, modification of water chemistry, metal loads, and sources during exceptionally low flows. Metal loads (from point and diffuse sources) were substantially lower under low-flow conditions, but the relative importance of mine workings drainage to overall flow in the study reach increased from 24% under Q45 flow conditions to 64% under Q99 flow conditions (Table S12). The relative importance Zn and Pb loads from diffuse sources (predominantly groundwater) also increased (Zn, 23−31%; Pb, 6−17%) under Q99 flow conditions (Table S12). The effect on water chemistry was stark. Stream pH was typically 1 unit higher under Q99 flow conditions; this is

thought to reflect reduced hydrological connectivity with lower pH peatland water.[56] The decrease in stream pH under high-flow conditions has been postulated to increase stream metal loads because of remobilization of weakly bound sediment metal phases.[18] It is difficult to attribute this process to specific locations of, or changes in, stream metal loading in the present study; however, it may account for some of the Zn loading (approximately 2%) observed in this study that was not sourced from any known mining-affected stream reaches. It is perhaps expected that metal concentrations would be higher under lower-flow conditions because of decreased dilution;[22] however, our data indicate that the relative importance of different metal sources is also an important determinant of metal concentrations across streamflows. For example, stream Zn concentrations were highest under Q99 flow conditions, reflecting both the importance of mine water as a source of Zn and its strong influence on stream chemistry at low flow. However, Pb concentrations were generally lower under Q99 flow conditions despite elevated inflow concentrations from the Mill Race Stream and Frongoch Adit, probably reflecting high rates of chemical attenuation, perhaps influenced by the higher stream pH. It is worth noting that Pb and Zn loadings from non-mined tributary watersheds (Nant Ceunant and Nant Gilwern) contributed more to streamflow under low-flow conditions and reflect a wider global pattern of elevated metal concentrations in mineralized watersheds experiencing a general increase in aridity.[46,57] With this in mind, potential increases in metal concentrations and loading from mineralized (nonmined) watersheds, due to climate change, warrant consideration when evaluating water quality and remediation targets.

Second, this work highlights different mechanisms of metal transport during exceptionally low-flow conditions, with likely implications for stream ecosystem health and services in upland watersheds. Specifically, chemical attenuation of Pb and Zn was higher under low flows, with sorption directly to streambed sediments likely a dominant removal mechanism for Zn.[51] Furthermore, saturation of ferrihydrite during low flow possibly increased Pb attenuation through sorption and/or coprecipitation reactions. These process changes are important and could potentially increase the concentration of sediment-bound toxic metals in the upper parts of watersheds under low-flow conditions; these sediment-bound metals would eventually be flushed to downstream flood plain areas during high-flow events.[19] Upland environments (mountains, moorland, and heath) cover approximately 18% of the UK[58] and provide an estimated 68% of the UK's drinking water,[59] as well as contributing substantially to the biological and genetic diversity of the UK's native flora and fauna. Increased levels of contamination of streambed sediments and stream water are likely in UK mineralized watersheds as a result of an increase in the frequency and severity of prolonged dry spells. This could have substantial negative consequences for biodiversity and ecosystem service provision in upland environments.

Third, this study highlights how tracer injection, synoptic sampling, and solute transport modelling of watersheds, prior to consideration of remediation options, could inform and guide remediation efforts to deliver the best possible environmental and socio-economic outcomes. Simulation of metal concentrations under exceptionally low flow indicates that remediation could be less effective (<20% reduction in Zn concentrations) than under average-flow conditions. In our study reach, this was largely due to increased stream Zn concentrations driven by higher concentration and untreated ground and subsurface waters entering the system, principally from Graig Goch Mine. Other studies have shown the importance of diffuse mine contamination sources for increasing stream metal loads and concentrations during rainfall-driven high-flow events.[16,19,60] Furthermore, a study in northern England demonstrated that remediation of a major point source of contamination could be less efficient at high flows due to the greater importance of untreated diffuse sources.[18] In the context of remediation planning and design, the findings from our study are important for two reasons: (1) they indicate that remediation could be less efficient at extremely low flows (as well as at high flows)[18] in some settings where untreated diffuse groundwater exerts a disproportionate influence on streamflow and metal concentrations; (2) they suggest that discharge−concentration relations for metals may be highly context-dependent, and remediation design which considers only sources active during rainfall events may be too simplistic and miss key sources which increase in importance under low flows. In this context, application of the synoptic sampling and solute transport modelling approach over a broader range of the hydrological regime may be highly beneficial in mined watersheds to improve the efficacy of remediation schemes, especially as flow extremes (low and high) are predicted to become more frequent and severe during the 21st century. In watersheds affected by both surface mine wastes and mine water sources, remedial strategies that minimize flow over and through mine wastes and treat point and (where possible) diffuse mine water sources, including groundwater, are likely to be required to meet the challenges of climate change.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.0c04016.

> Details of tracer injection, metal loading analyses, and OTIS modelling methods; data from water sampling, streamflow, and metal loading analysis; OTIS and PHREEQC modelling; plots showing a flow duration curve for Afon Ystwyth; comparison between total and filtered stream metal concentrations; and OTIS conservative and reactive model results (PDF)

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