SOURCE APPORTIONMENT OF METAL MINE POLLUTION IN WANLOCK WATER USING TRACER INJECTION AND SYNOPTIC SAMPLING

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Executive Summary

- Four rivers in the Leadhills/Wanlockhead area are classified as 'less than Good Status' under the EU Water Framework Directive due to pollution from historical metal mines. As identified by previous studies, the contaminants of concern are cadmium (Cd), lead (Pb) and zinc (Zn), with the Cd impact extending up to 68km downstream from the source.

- Previous investigations conducted by SEPA and the Coal Authority (CA) established stream metal loading estimates for some mine pollution sources in the Wanlock Water. While these estimates provide a foundation for further study, for many inflows they were not considered robust enough to guide and inform engagement with landowners and the development of remedial solutions in the watershed. Detailed source apportionment was recommended to provide confidence in the location and relative importance of both point and diffuse sources.

- High spatial resolution monitoring of simultaneous metal concentrations and streamflows are required to undertake detailed source apportionment. To do this, a tracer injection and sampling experiment was conducted in a 2km long reach of the Wanlock Water in September 2019 in order to: (i) locate and rank the loading contribution from principal sources of mine pollution, and; (ii) identify the relative importance of point and diffuse sources of mine pollution under steady-state flow conditions. Twenty-one stream sites and eighteen inflow sites were sampled.

- The principal sources and the contribution from each for the contaminants of concern as identified by the tracer study are presented in the table below:

Principal Metal Sources in the Study Reach		
Cadmium (dissolved)	**Zinc (dissolved)**	**Lead (total and dissolved)**
Bay Mine Adit: 26%	Bay Mine Adit: 18%	Wetland area: 48% (48% dissolved)
Glenglass Level No 2: 19%	Glenglass Level No 2: 18%	Queensbury Tailings Ponds: 35% (14 % dissolved)
Glenglass Level: 14%	Glenglass Level: 16%	
Queensbury Tailings Ponds: 9%	Queensbury Tailings Ponds: 9%	
	Wanlock Water u/s of Bay Mine Adit: 9%	

- Most of the dissolved Zn and Cd loading was attributed to point sources (67% and 75%, respectively) of mine water in the upper part of the study area (for example, mine drainage from Bay Mine Adit, Glenglass Level and Glenglass Level No. 2). In contrast, the majority of total and dissolved Pb loading

originated from more diffuse sources of mine waste (78% and 74%, respectively) in the lower part of the study reach (for example, the wetland area and Queensbury Tailings Ponds).

- Based on the results of the source apportionment study, mass balance calculations suggested treatment of mine water from Bay Mine Adit, Glenglass Level and Glenglass Level No. 2 could achieve a 50% decrease in Zn and Cd stream concentrations. Combining mine water treatment with capping of the Queensbury Tailings Ponds could achieve a >70% decrease in Zn and Cd concentrations. Capping of the Queensbury Tailings Ponds would likely substantially reduce Pb loading from this area also, however the potential change in stream concentrations could not be estimated by mass balance due to the non-conservative behaviour of Pb.

- A number of recommendations for next steps and potential scientific studies are made to further aid understanding of stream metal loading and the development of remedial measures. These are:

  1. Water quality modelling to estimate the potential impacts of reductions in Zn and Cd in downstream river systems (Crawick Water and the River Nith) and in the Wanlock Water downstream of the mines and mine wastes.
  2. Investigate potential variability in metal concentrations and loads over time in different flow conditions by monitoring during medium and / or low flow conditions, and undertake a detailed review of existing data using modelled flow predictions.
  3. Liaise with Natural Resources Wales and summarise the latest position with regard to their research on remediation solutions.
  4. Solute transport modelling to more accurately represent physical and chemical transport mechanisms in mine pollution remediation scenarios, in particular for Pb.
  5. Sampling and analysis of the geochemical and mineralogical properties of sediment in the wetland to establish the mechanisms of Pb attenuation and release in this area.
  6. Bespoke tracer injections in the stream channel above Bay Mine Adit to establish where stream water is being lost and if this stream water is flowing through mine strata and emerging at downstream adits.
  7. Undertake a detailed remedial options appraisal to consider the costs and appropriateness of various treatment systems and engineering solutions.

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1.   Introduction

Many years of metal mining in the United Kingdom (UK) has left behind miles of abandoned underground mines and significant quantities of waste that can contaminate watercourses (Byrne et al. 2012; Jarvis and Mayes 2012). Contamination from abandoned metal mines is recognised as a major cause of failure to achieve environmental objectives set out in Water Framework Directive (WFD) River Basin Management Plans (Jarvis and Mayes 2012). As such, identification and remediation of mine pollution sources is one of the major challenges facing environmental regulators.

Metalliferous deposits in Scotland are generally small scale and scattered throughout the country (EnviroCentre Ltd & Pleydell Smithyman 2015). Due to the presence of significant and accessible galena and sphalerite veins in the surrounding rock formations, the villages of Leadhills and Wanlockhead are well known for being the centre of lead production in Scotland for many hundreds of years, with evidence of this industrial activity remaining prominent in the landscape. The importance of its prominence is demonstrated by the Inventory for Scotland of Closed Mining Waste Facilities which are, or could be, causing serious environmental impact. Despite coal mining being the most significant extractive industry in Scotland, 85 of the 91 sites listed are associated with lead mining activity in the Leadhills/Wanlockhead area (EnviroCentre Ltd & Pleydell Smithyman 2015).

The Water Framework Directive requires EU member states to develop River Basin Management Plans (RBMP) driven by monitoring and classification of waterbodies in line with common methodologies and standards. In 2018 SEPA has classified nineteen surface waterbodies as 'less than Good Status' due to pressures from mining and quarrying in Scotland. These are predominantly linked to former coal mining activity but five are due to metal mining, four of which are associated with the Leadhills/Wanlockhead area, with three directly impacted by the study area. The Wanlock Water is classified as Moderate Status due to failures of Cd, Pb and Zn environmental quality standards (EQS).

SEPA has assigned measures on itself under the RBMP to understand the sources of the pollution. This included a partnership project with the Coal Authority (CA), which estimated that two point sources of mine drainage (Bay Mine Adit and Glenglass Level) were providing approximately 25% of Pb, 53% of Cd and 40% of Zn loading to the Wanlock Water. An additional 8% of Pb, 6% of Cd and 11% of Zn loading were attributed to point source drainages from the Queensbury Tailings Ponds. However, some loadings were based on estimations of streamflow rather than field measurements and a considerable amount of stream loading was not captured in this study. It was considered likely that diffuse sources could be responsible for the loading and that further high spatial and temporal resolution monitoring of synchronous metal concentrations and streamflows was necessary to provide confidence in the location and relative importance of both point and diffuse sources.

Since the completion of the CA report in 2014 SEPA has increased the monitoring network to improve the knowledge of the scale of the impact. This has shown that the pollution originating from the various former mining features in the Wanlock Valley has an impact downstream into the Crawick Water (Zn & Cd) and River Nith (Cd). The location and setting are illustrated in Figure 1.
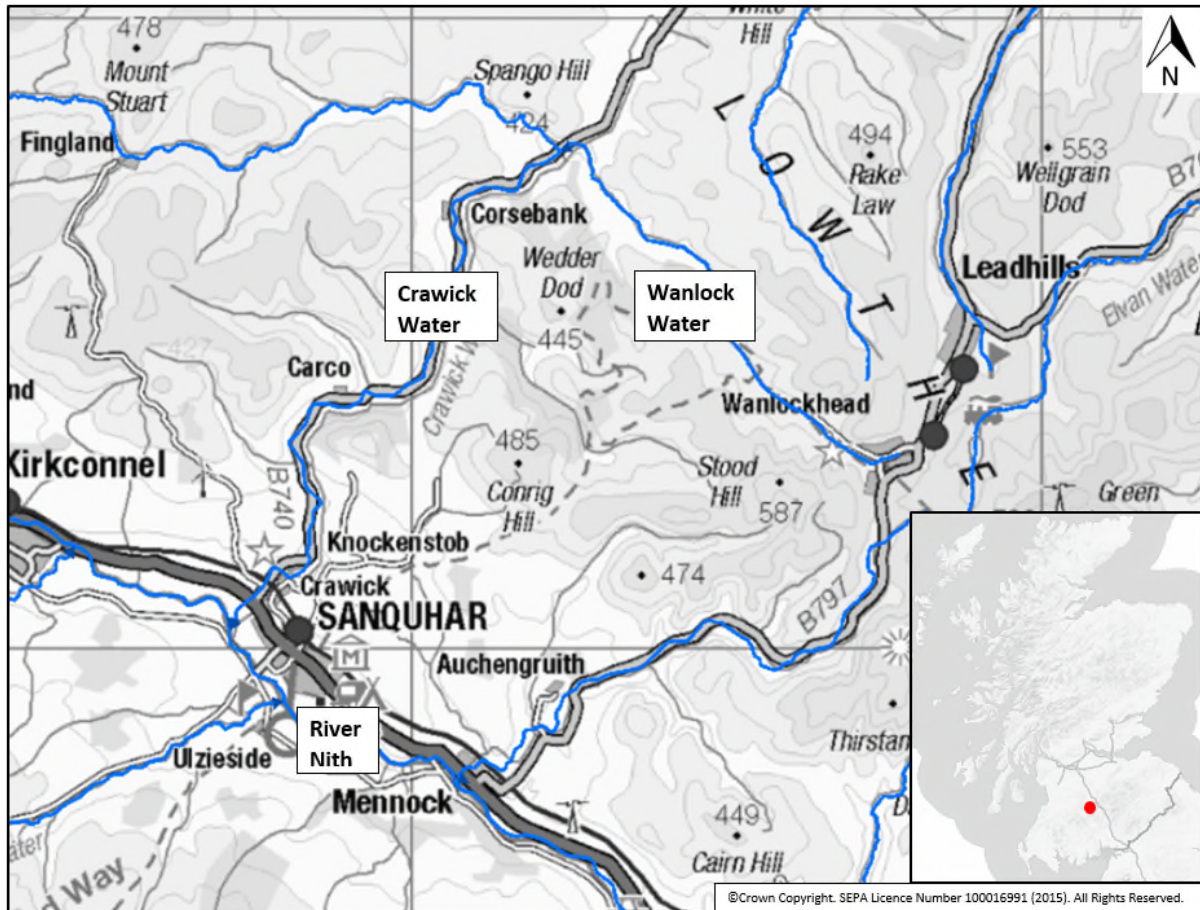
Figure 1. Overview of area and waterbodies of interest.

With multiple potential sources of pollution across a watershed and the extensive nature of historical mining operations, the task of identifying and quantifying sources of mine pollution in river watersheds is complex (Byrne et al., 2012). For the purposes of this report, point sources are defined as direct discharges of mine water to the river such as drainage levels, pipes or adits, whilst diffuse sources are considered as mine spoil (associated with locations of historic activities or transported by flood events), small episodic surface run-off during rainfall, groundwater contaminated by leaching processes, and the hyporheic zone. This is consistent with the definitions in the joint agency paper on Abandoned Mines and the Water Environment (Environment Agency 2008). Point sources of mine pollution are generally easily identified and quantified in the field. However, while evidence of potential diffuse sources can often be garnered from field observations and historic records or maps, the exact location of these

features and quantification of their contribution to stream metal loading remains problematic.

There is currently no systematic approach in the UK for identifying diffuse sources of mine pollution or for discriminating the relative importance of point and diffuse sources at the river watershed scale (Jarvis and Mayes 2012). Recognising the limitations of existing methodologies, a major recommendation of the Defra *Prioritisation of abandoned non-coal mine impacts on the environment* project was to develop a methodology for systematic scoping of river watersheds impacted by mine pollution for more informed decision-making (Jarvis and Mayes 2012).

The tracer dilution and synoptic sampling approach for source apportionment of mine pollution was developed by the U.S. Geological Survey (USGS) and has been extensively used in the USA to inform remediation under the Abandoned Mine Lands Initiative (Kimball et al. 2002; Runkel et al. 2017; Walton-Day et al. 2007). It uses high spatial resolution synchronous (or synoptic) water quality and flow measurements at multiple stream and inflow locations across a watershed to provide spatially detailed assessments of pollutant fluxes. Flow is measured using a conservative (or stable) tracer (typically sodium bromide or lithium chloride) that is injected into the stream above mine workings at a constant rate and concentration. Over time, all portions of the stream (including the hyporheic zone) become fully mixed with the tracer to reach a plateau concentration. Decreases in plateau concentrations with distance downstream reflect dilution by point and diffuse source inflows. The advantage over typical methods of streamflow estimation (e.g. velocity-area, weir, gulp-injection) is that flow measurement is based on dilution of a tracer that is fully mixed in the stream. Physical flow measurement in high-energy mountain streams is compromised by irregular stream cross-sections and failure to capture hyporheic flow, potentially leading to significant errors in flow estimates. In addition, because streamflow is quantified by tracer concentration, there is no need to measure flow at each location and therefore, sampling effort per location is substantially reduced. This allows sampling at many more locations and / or over a much larger area for the same effort, thereby increasing both accuracy and detail of loading estimates for decision-making purposes. The results provide greater spatial coverage, better resolution (samples are closer together) and more accurate streamflow (and therefore metal loading) estimates, allowing discrimination and quantification of point and diffuse source inputs.

The overall aim of this project was to build on previous work and provide sound scientific evidence to inform decisions aimed at improving the WFD water body status of rivers impacted by historical mining activities at Wanlockhead. To achieve this, we apply the tracer dilution and synoptic sampling methodology for the first time in a Scottish watershed impacted by historical mining activities. The project also aims to demonstrate the effectiveness of this technique in delivering a detailed understanding of pollutant sources in the upper Wanlock Valley. The specific objectives were to: (i) locate and rank the principal sources of mine pollution including those identified by the CA (The Coal Authority, 2014) and SEPA (SEPA, 2016), and; (ii) discriminate the

relative importance of point and diffuse sources of mine pollution under steady-state flow conditions.

2.   Field Setting

The Wanlock Water rises to the east of the village of Wanlockhead at an elevation of approximately 435mAOD. From there, the river flows approximately 8km to its confluence with the Crawick Water at Spango Bridge, which then flows approximately 12km to the confluence with the River Nith at Sanquhar (Figure 1). The study area encompasses a 2km long section of the Wanlock Water from upstream of the Bay Mine Adit inflow to downstream of the Sowen Burn inflow (Figure 7).

SEPA has developed a Conceptual Site Model (CSM) covering the former mining areas of the Wanlock catchment following completion of the CA Scoping Study (SEPA, 2016). Both reports recommended various actions including this source apportionment study, the need for a further detailed walkover of the site, and additional desk-based research. The following sections summarise existing knowledge and presents the findings of the additional research and walkover carried out by SEPA and LJMU in July 2019. The maps presented in this section have been reproduced with the permission of the National Library of Scotland (NLS).

2.1 Legacy mine drainage in the study area

The village of Wanlockhead in Dumfries and Galloway was historically the centre of lead mining in Scotland with the peak in mining activity occurring between the 1600s and the 1930s. The SEPA funded CA report of 2014 provides a detailed review of the various mining features in the Wanlock Valley. The CA identified three low lying adits present within the study area and include the Bay Mine Adit (at approximately 345mAOD), Glenglass Level (at approximately 335mAOD) and Meadowfoot Adit (at approximately 340mAOD). The CA report indicated that water flowing from the Bay Mine Adit may include resurgence of the Wanlock Water (which infiltrates the riverbed above Bay Mine Adit during lower flows) along with groundwater present in the Bay (or Charles) Mine and Straitsteps Mine to the north of the Wanlock Water. The Glenglass Level drains the southwest side of the Wanlock Water and is connected to Glencrieff Mine. The Meadowfoot Adit is partially blocked but the small discharge is believed to drain workings from the small Meadowfoot Mine on the north side of the valley (CA, 2014).

During the site walkover, most of the locations identified by the CA were confirmed, however, a notable sized inflow was identified, located opposite the Meadowfoot Adit flowing from a small manhole type structure within the Glencrieff Tailings. It is not clear what the source of this is and the historic Ordnance Survey and geology maps above noted a spring shown on the 1860 map in the vicinity of the outflow. There are a number of historic channels and old shafts/mine drainage levels that are shown on historic maps discussed in Section 2.2 and it is possible that this could be the source of the discharge. However, the location of the outflow is very close to the Glenglass Level (Figure 2). Potential sources are mine water from the Glencrieff Mine via fracture

flow or additional shaft/adit, alternatively, given the significant change to the valley floor in this area, it also has potential to carry some of the resurgent Wanlock Water lost in the upper valley. It may also include a portion of groundwater seepage from the tailings, and at times of rainfall, runoff from the tailings. For ease of reference and given the vicinity of the Glenglass Level, this study will refer to this discharge as Glenglass Level No.2. Further discussion on its source will be given in the results analysis.
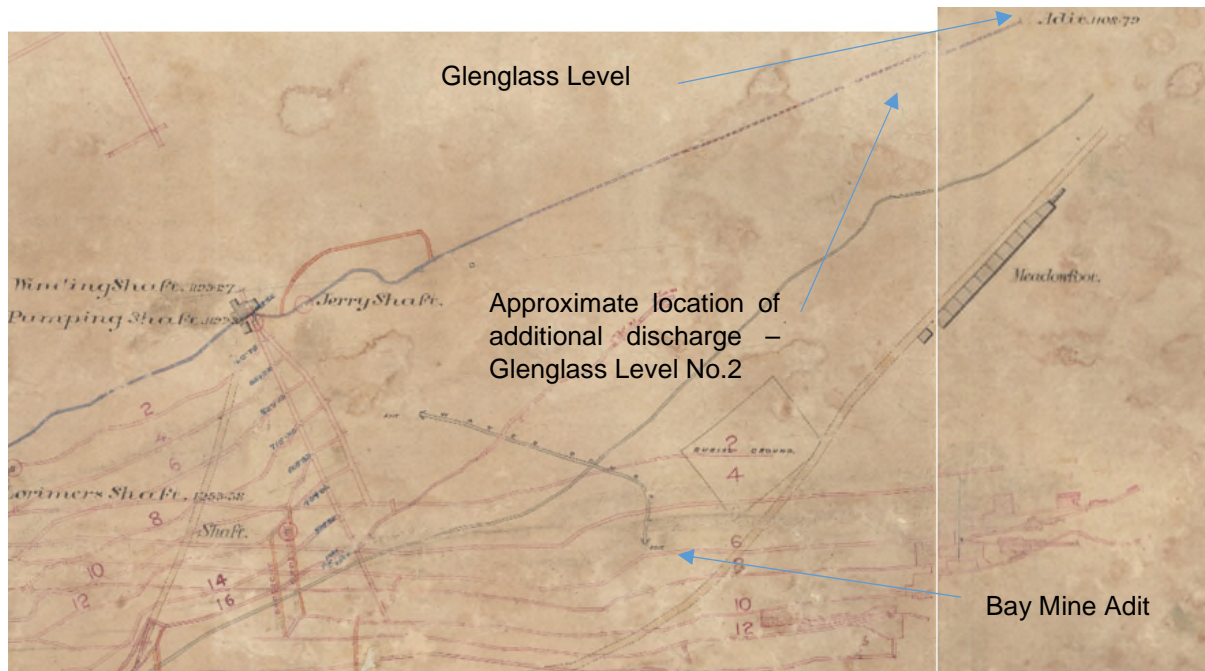
Figure 2. Extract from Wanlockhead Lead Mines Plan and Transverse and Longitudinal Sections. Courtesy of Buccleuch Estates through the Dumfries Archival Mapping Project.

2.2 Geological and mineralogical setting

Wanlockhead is situated in the Southern Uplands Terrane, a glaciated landscape comprising the Kirkcolm Formation (sandstones and siltstones), Crawford Group (mudstones, cherts and lava flows), Moffat Shale Group (dark mudstones), and the Portpatrick Formation (volcaniclastic greywacke sandstones) (Floyd 2003). The primary ore mineralisation is related to the Caledonian Orogeny resulting in hydrothermal veins predominantly of metal sulphides including galena (PbS) and sphalerite (ZnS). These are mainly located within the Portpatrick Formation with some localised extension into the Kirkcolm Formation. The mineral veins generally trend north-northwest to south-southeast. These were well mapped due to the historic mining and are shown in gold in Figure 3 below.

Figure 3. Extract from Geological Survey of Scotland, Dumfriesshire Sheet VII, 1870 (not to scale).

Superficial deposits of post-glacial alluvium are present on the valley floor with glacial till present on the lower slopes of the surrounding hills, shown as yellow and black dots respectively in Figure 3. Localised areas of peat are also present in areas in the valley floor and on the hillsides shown in yellow and annotated in Figure 3.

The superficial deposits are overlain by variable depths of made ground deposits in large parts of the upper Wanlock valley floor and lower hillsides. Made ground is likely to largely comprise mining and lead production wastes including tailings, crushed rock and slags, some of which remain un-vegetated due to the concentrations of metals in the soils. Two major mine waste features previously identified are the uncapped Queensbury Tailings Ponds (covering approximately 9000 m^2) in the lower part of the study area and the capped Glencrieff Tailings Ponds in the upper part of the study area. The change in these features, and thus extent of made ground in the flood plain is clear from the historic map extracts presented in Figures 4, 5 & 6. Mine wastes are also present in other areas including around the former Smelting Mill between the Sowen Burn and Wanlock Water, and at the distinctive mine waste mountain at the Glencrieff Mine.

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In 2014, samples of made ground collected by the CA from the Queensbury Tailings Ponds in the north-western end of the upper valley had concentrations of Pb around 6% by weight and 1.3% Zn by weight. SEPA and the CA have identified such materials as more diffuse sources of pollution. These have been eroded and washed out into the floodplain and river bed over time by natural processes where exposed. Evidence of the tailings deposits, and of the erosion were clearly visible during the walkover and sampling positions selected to identify any significant loading from these features.

Likely locations of made ground can be identified by review of historic Ordnance Survey maps. Particular areas of interest are shown in Figure 4 and the changes in the mapping over time, visible in Figures 5 & 6, represent development of the made ground which has potential to be a significant diffuse source of pollution to the water environment.
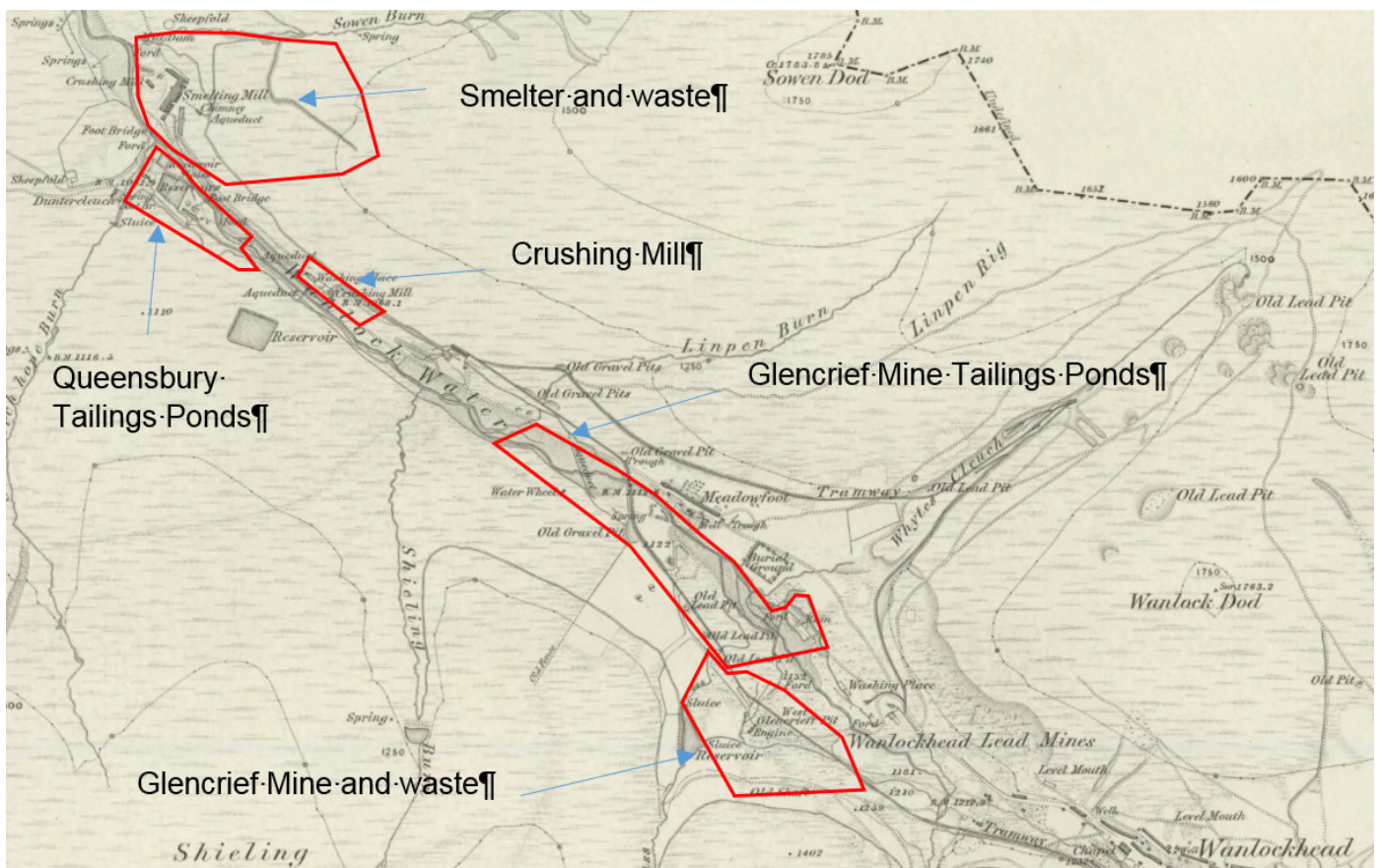
Figure 4. Extract from Ordnance Survey Dumfriesshire Sheet VII, 1860 (not to scale).

Figure 4 shows that extensive mining infrastructure is already well developed by 1860, including the Smelting Mill and reservoirs of the Queensbury Tailings Ponds. Also notable is the presence of various artificial water channels and significant braiding of the Wanlock Water in the vicinity of Meadowfoot.

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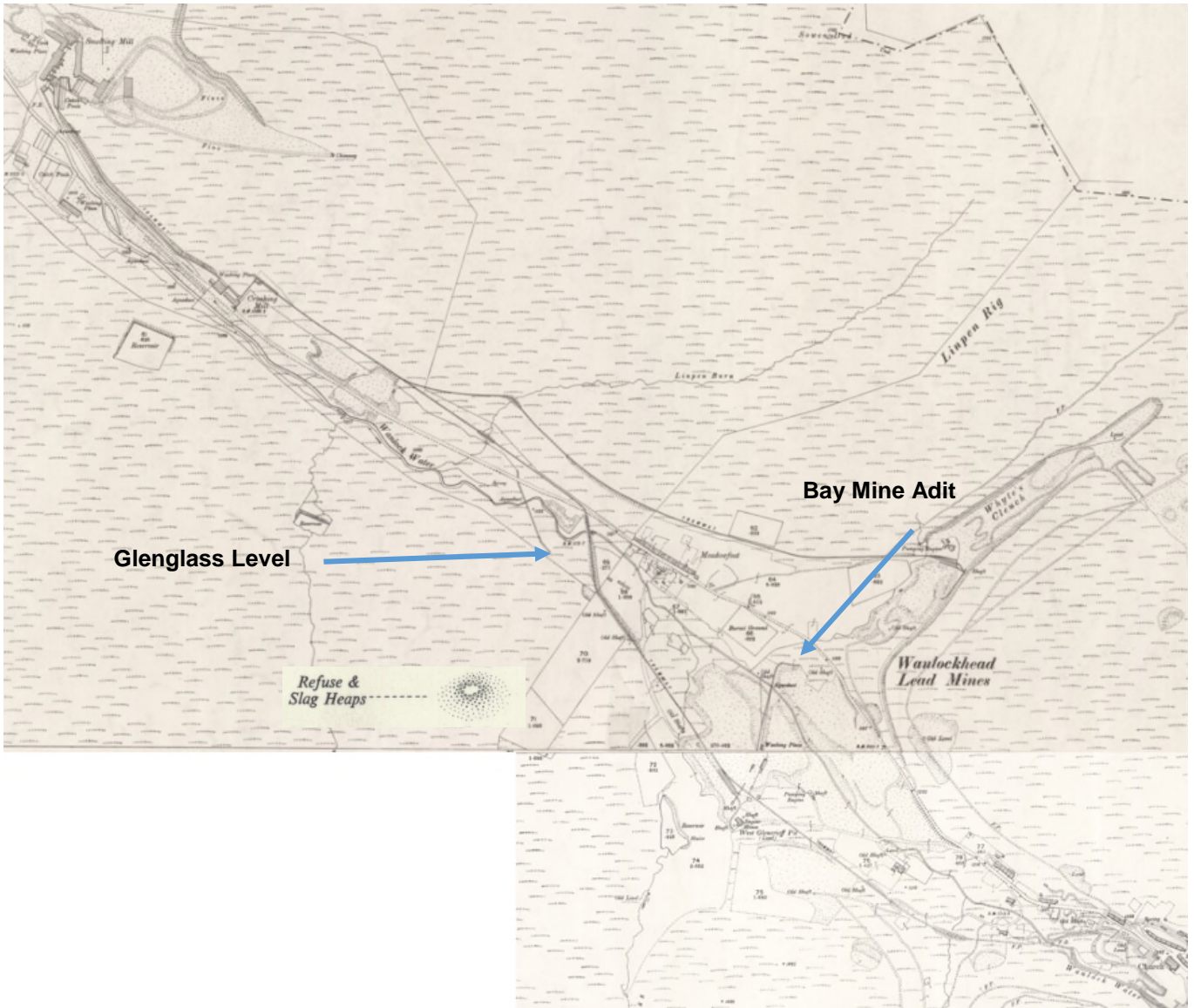
Figure 5. Extract from Ordnance Survey Dumfriesshire Sheet VII(2) & (6), 1899 (not to scale).

Further detail of mining infrastructure is given by the larger scale map in Figure 5. Previous braiding of the Wanlock Water no longer apparent, it is likely that the river has been straightened and canalised to accommodate mine waste on the valley floor south of Meadowfoot. The locations of the Glenglass Level and Bay Mine Adit discharges are annotated.
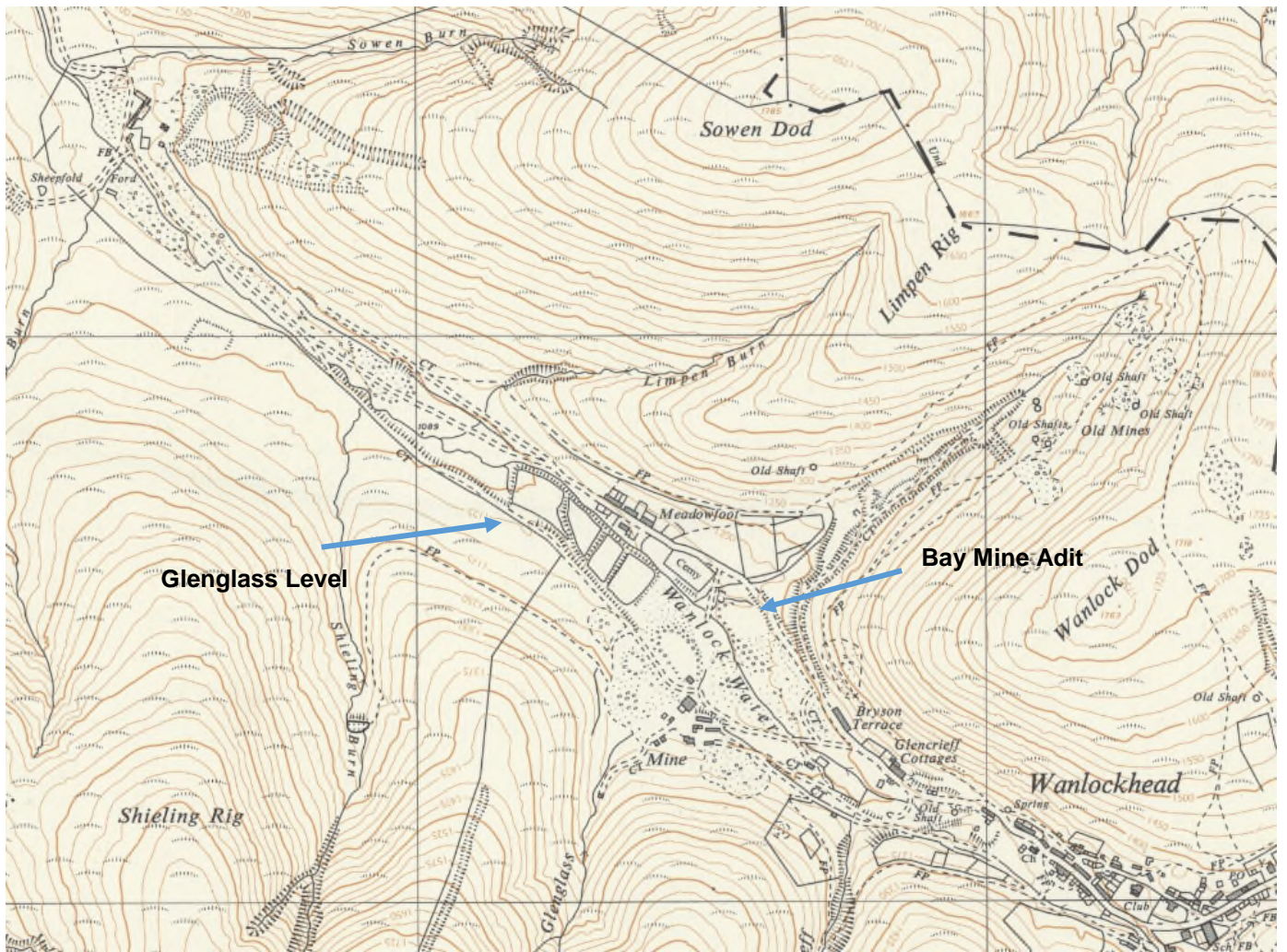
Figure 6. Extract from Ordnance Survey Sheet NS81SE 1962 (not to scale).

Mining has all but ceased by 1862 (Figure 6) and some features are no longer mapped. Extensive waste, bunds and slope features are now present at Meadowfoot on the valley floor, with the Wanlock Water further canalised along its northeastern edge. These features are former tailings ponds associated with the Glencrieff Mine that have since been landscaped and vegetated. The Queensberry Tailings Ponds are now shown as waste ground or spoil.

2.2 Hydrology, hydromorphology and hydrogeology

Within the study area, major tributary and mine water inflows are the Bay Mine Adit, Whyte's Cleuch, Glenglass Stream, Glenglass Level, Limpen Burn, Shieling Burn, Glenmarchhope Burn and Sowen Burn (The Coal Authority, 2014). Sections of the river within the study area are within a relatively confined and straightened channel, particularly when flowing past potential diffuse sources of the Glencrief and Queensbury Tailings Ponds, and the sites of the former crushing mill and smelter. It becomes less confined and more meandering between Glencrieff Tailings and

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Queensbury Tailings Ponds. There is a notable feature between the Limpen Burn and the former crushing mill where the river flows through a boggy wetland area and the channel becomes braided for approximately 170m. The wider landscape in the study area comprises upper moorland with steep side slopes rising to 588mAOD. Annual rainfall exceeds 1500 mm a^{-1} (Rowan et al. 1995).

Groundwater discharging from mine adits is an important component of the flow in the Wanlock Water. The area is located in the Upper Nithsdale groundwater body and the underlying geology is generally a low permeability matrix. Fracture planes are therefore the primary groundwater pathways in the bedrock and productivity will be higher local to fractures where present, and in the heavily mined strata where the voids provide significant pathways for groundwater flow and increased productivity. Following cessation of mine dewatering, groundwater is present in the former workings below the water table. In the superficial soils and made ground, groundwater flow may be limited to alluvial and peaty deposits, with some flow also likely in the glacial till, particularly where it is of a less cohesive nature. Permeability in soils can be anticipated to be highly variable.

During the walkover carried out in July 2019, the Wanlock Water was largely dry from the north-eastern edge of Wanlockhead village down to below the Bay Mine Adit. As noted in Section 2.1, this occurrence has been previously reported and typically occurs when dry weather is predominant. Given the uncertainty surrounding the exact flow path for water lost to the ground, uncertainty of travel times for lost water to reach the Bay Mine Adit or alternative resurgence location, limitations of one week of fieldwork allowance and potential excess dilution of the tracer it was agreed to base this study on the Wanlock from the point of the Bay Mine Adit. This study does not aim to address the question on the location of resurgence of lost water from the upper Wanlock Water.

2.4   Sampling plan

Following the completion of further desk based research and site walkover the sampling sites were selected by SEPA and LJMU. These are shown in detail in Figure 7. They have been selected to identify as many of the diffuse and point source loading contributions from the known sources of mine waste or former activities in the study area, in combination with loading from inflows that were deemed to be viable for sampling. In addition locations known to have episodic inflows such as those from the Queensbury Tailings Ponds were noted and scheduled for sampling if possible. The samples locations are described in Table 1.

The nomenclature used is as follows:

- WW – Wanlock Water
- LBI – Left Bank Inflow (compared to stream flow direction)
- RBI – Right Bank Inflow (compared to stream flow direction)
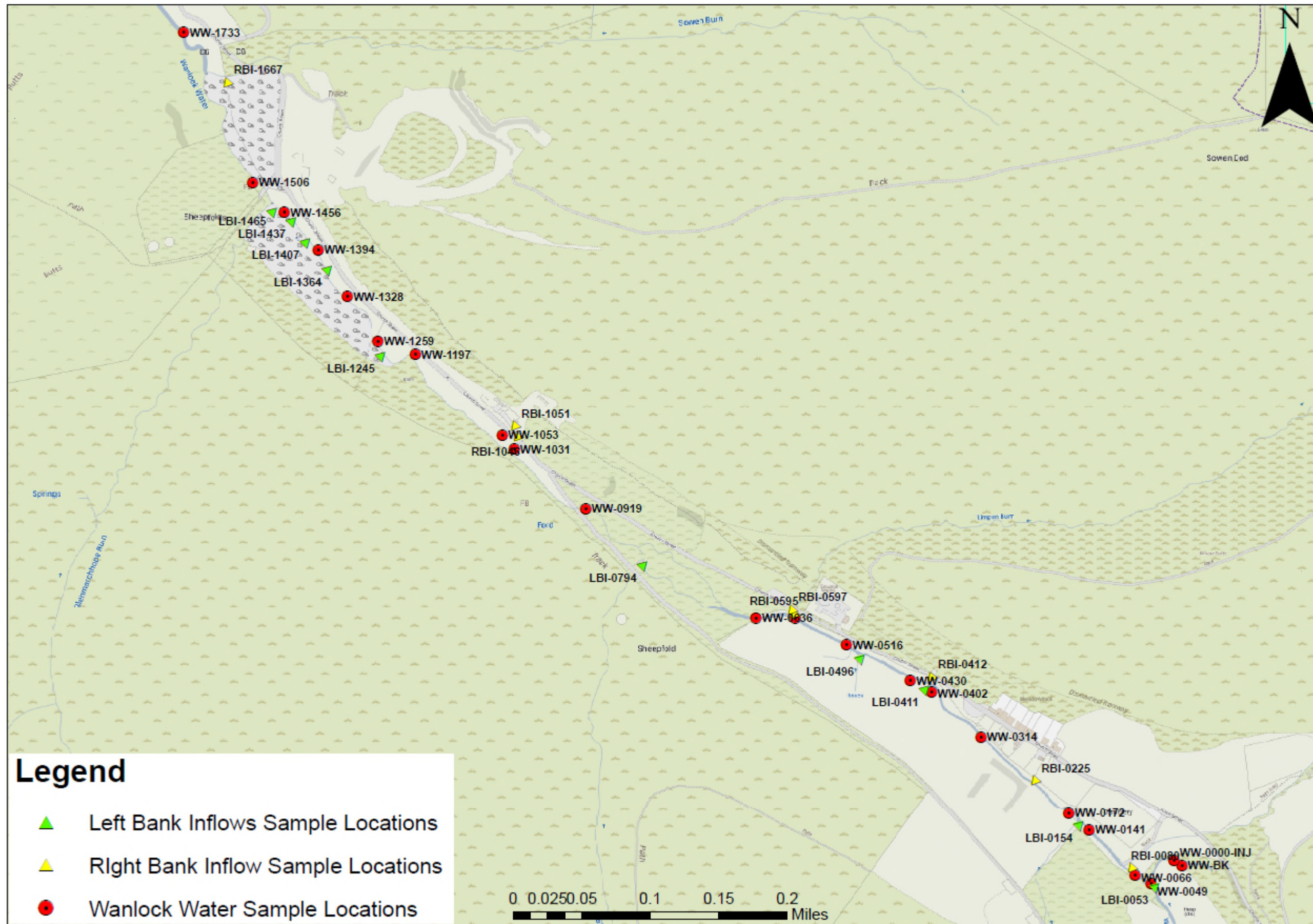- X – Additional sample collected on sampling day.

Figure 7. Stream and inflow sample sites. Numbers associated with samples represent distance (in metres) below the tracer injection point (WW-0000).

Site ID	SEPA ID	Source	Distance [m]	Easting	Northing	Description
WW-BK	571545	STR	0	286553	613530	Above injection point
WW-0000-INJ						Injection point on Bay Mine Adit, tank position below pool on RB, 2-3 m from stream.
WW-0049	562186	STR	49	286517	613509	1st synoptic site on BMA
LBI-0053	571546	LBI	53	286522	613506	Wanlock Water u/s of BMA, probably dry when sampling
WW-0066	557476	STR	66	286498	613519	Wanlock Water d/s of BMA in rock channel
RBI-0080	571570	RBI	80	286493	613526	Whytes Cleuch, old dry channel to right on BMA, probably dry when sampling
WW-0141	571547	STR	141	286444	613572	Wanlock Water d/s Whytes Cleuch, u/s Glenglass stream (Glencrief Mine discharge)
LBI-0154	571548	LBI	154	286433	613579	Glenglass stream (Glencrief Mine discharge)
WW-0172	571549	STR	172	286420	613592	Wanlock Water d/s Glenglass stream (Glencrief Mine discharge)
RBI-0225	572199	RBI	225	286379	613628	U/T (intermittent) at Meadowfoot, u/s of Wanlock Water conf
WW-0314	120447	STR	314	286317	613681	Wanlock Water d/s LB tailings embankment, opposite last house on RB
WW-0402	571550	STR	402	286259	613734	Wanlock Water u/s Meadowfoot Adit and LB inflow draining tailings
LBI-0411	571551	LBI	411	286252	613738	LB inflow draining mine tailings
RBI-0412	571552	RBI	412	286258	613750	Meadowfoot Adit
WW-0430	571553	STR	430	286234	613747	Wanlock Water d/s Meadowfoot Adit, u's Glenglass Level
LBI-0496	571554	LBI	496	286176	613774	Glenglass Level
WW-0516	551960	STR	516	286159	613789	Wanlock Water d/s Glenglass Level, road drainage pipe on RB, STW on RB
WW-0586	477682	STR	586	286099	613821	Wanlock Water u/s Limpen Burn and STW outfall
RBI-0595	571555	RBI	595	286097	613824	STW outfall
RBI-0597	571556	RBI	597	286094	613829	Limpen Burn
WW-0636	571557	STR	636	286053	613821	Wanlock Water d/s Limpen Burn and STW outfall, u/s marshy wetland
LBI-0794	571558	LBI	794	285921	613883	Shieling Burn, inflow draining marsh
WW-0919	536512	STR	919	285853	613949	Wanlock Water d/s marshy wetland, at footbridge
WW-1031	120824	STR	1031	285769	614019	Wanlock Water u/s RB inflow draining marsh and crushing mill
RBI-1046	571559	RBI	1046	285772	614032	inflow draining marsh and part of crushing mill
RBI-1051	571560	RBI	1051	285769	614045	minewater next to crushing mill
WW-1053	571561	STR	1053	285755	614036	Wanlock Water d/s RB inflow draining marsh and crushing mill
WW-1197	571562	STR	1197	285653	614130	Wanlock Water d/s crushing mill, u/s tailings ponds
LBI-1245	572200	LBI	1245	285613	614127	Drainage (intermittent) to Wanlock Water, u/s of Queensbury Tailings
WW-1259	553443	STR	1259	285609	614146	Wanlock Water u/s tailings ponds
WW-1328	553444	STR	1328	285573	614198	Wanlock Water opp tailings ponds
LBI-1364	571563	LBI	1364	285551	614231	LB dry channel draining tailings, may be dry when sampling
WW-1394	571564	STR	1394	285539	614253	Wanlock Water opp tailings ponds
LBI-1407	571565	LBI	1407	285525	614263	LB dry channel draining tailings, may be dry when sampling
LBI-1437	572198	LBI	1437	285508	614287	Queensbury Tailings Drainage No.3 to Wanlock Water
WW-1456	553446	STR	1456	285499	614297	Wanlock Water u/s Glenmarchhope Burn
LBI-1465	571566	LBI	1465	285486	614298	Glenmarchhope Burn
WW-1506	571567	STR	1506	285462	614332	Wanlock Water d/s Glenmarchhope Burn, opp smelter/washer, u/s braided section
RBI-1667	571568	RBI	1667	285431	614448	Sowen Burn
WW-1733	481028	STR	1733	285381	614508	Wanlock Water d/s Sowen Burn and braided channel

Notes: **Green**   **d/s = downstream; u/s = upstream; RB = Right Bank; RBI = Right bank inflow; LB = Left Bank;**
shading = inflow   **LBI = Left Bank Inflow; STR – Main Stream Sample; STW-= Sewage Treatment Works;**

Table 1. Wanlock Water Synoptic Sampling Sites

3. Methodology

3.1 Tracer injection, synoptic sampling and analysis

Metal loads were quantified under steady-state flow conditions using the tracer-dilution (to estimate streamflow) and synoptic sampling method (Byrne et al. 2017; Runkel et al. 2013). Sampling was undertaken under approximately Q30 flow conditions based on scaling from Hall Bridge gauging stations on the River Nith downstream of the study site. A continuous tracer injection of sodium bromide (NaBr) was initiated with an automated pump delivering 152 ml min^{-1} of the tracer from a secure 1000L IBC tank into the Bay Mine Adit discharge (WW-0000-INJ in Figure 7) at 15:45 on 9th September 2019. The injection was terminated at 16:10 on 13th September 2019 following completion of synoptic sampling. The injection site was located on the Bay Mine Adit inflow to the Wanlock Water. Upstream of the Bay Mine Adit, the Wanlock Water was not present in the river channel when the injection began. During the study a multi-parameter probe was installed in the river to record electrical conductivity, DO and pH for the duration of the injection.

Rainfall records from SEPA's rain gauge at Meadowfoot Sewage Works in the catchment indicated that during the injection period 21.2 mm of rain fell during the study period. Approximately 70% of this rainfall occurred on the 10th September, with the remainder falling over the 11th and 12th September. This caused flow in the river to fluctuate throughout the injection period and this was observed both visibly and on the in-stream bromide probe used to monitor the progress of the tracer injection. Rainfall also caused the point at which the Wanlock Water was lost to migrate downstream approximately 100m, but it was not present in the riverbed at its the confluence with the Bay Mine Adit inflow. No rainfall occurred when the sampling was carried out with the bromide probe, and bromide analysis and post injection slug sampling indicating that the river remained in a sufficiently steady state throughout the 4 hour sampling period on the 13th September.

Synoptic samples were collected at 21 stream sites, 17 inflow sites and 1 mine water site (Figure 7) on the morning of 13th September when tracer concentrations had reached a steady-state plateau. Inflow sites included visible tributary-type inflows and more ill-defined flows such as riparian seeps and springs. In addition to the synoptic samples, a water sample was collected from ponded water in the basement of the former building next to the crushing mill (RBI-1051). All but three sample locations were pre-selected from the previous investigations and site walkover in July 2019.

Upon collecting samples from between 4-7 sites, dependant of the proximity of sampling locations, the bottles were immediately transported to an on-site processing centre. Processing included filtration (0.45 µm), measurement of pH and electrical conductivity, and preservation of samples for metals analysis. pH and electrical conductivity were also determined in the SEPA laboratory. Anion concentrations were determined from filtered, unacidified samples by ion chromatography. Anion concentrations are reported for Cl, Br, and SO_4 (Appendix 1). Aliquots for cation

analysis were acidified to <pH 2 with ultrapure HNO_3. Total recoverable and dissolved (some colloidal material may have passed through the 0.45 µm filter) cation concentrations were determined from unfiltered and filtered samples, respectively, by inductively coupled plasma–mass spectroscopy (ICP-MS). Trace element concentrations are reported for Al, As, Ca, Cd, Cu, Cr, Fe, K, Mg, Mn, Na, Ni, Pb, and Zn (Appendix 1, 2 and 3). Alkalinity as $CaCO_3$ was determined from filtered, unacidified samples.

All laboratory analysis was initially conducted by SEPA with the exception of bromide which was completed by National Laboratory Services (NLS). Bromide concentrations are relatively predictable due to the known concentration of the tracer and estimates of streamflow from salt slug experiments upon completion of the synoptic sampling. However, unexplained issues with the bromide analysis reported by NLS meant that the results did not correlate with anticipated concentrations. The remaining samples were subsequently returned to LJMU within the appropriate holding times who carried out duplicate analysis and returned results that were more consistent with expectations. The streamflow calculations have been calculated using the bromide results obtained by LJMU.

During the accreditation checks of the filtered trace element analysis SEPA chemists highlighted an issue with the filtered Zn results. While most filtered results for trace metals were within the laboratory accreditation limits, the Zn results reported apparent inaccuracies with filtered results noted to have significantly higher concentrations than the corresponding unfiltered result. Inaccuracies ranged between 25-1000% higher in filtered samples. This issue was specific to the filtered Zn results and although the exact source has not been investigated, it is considered to be a result of the on-site filtering and acidification process. Laboratory analysts reported that previous issues have occurred with on-site filtration and suspect that Zn may have been present in the filters or equipment used to carry out filtration. This should be considered in detail for any similar tracer injection studies carried out by SEPA for WFD or pollution identification purposes.

3.2 Estimating streamflow

Decreases in the concentrations of plateau tracer concentrations with distance downstream reflect dilution of the tracer as surface and/or subsurface (groundwater) drainage results in increases in streamflow. Streamflow estimation at each synoptic site relates the injected tracer characteristic to the observed dilution (Kimball et al. 2002):

$$Q = Q_{INJ} C_{INJ} / (C_P - C_B)$$

where Q_{INJ} is the injection rate, C_{INJ} is the tracer injectate concentration, C_P is the tracer plateau concentration at the synoptic site, and C_B is the tracer background

concentration in the stream water. Streamflow estimates and observed tracer dilution are illustrated in Figure 8.

3.3 Loading analysis and source apportionment

The study reach was divided into 22 segments demarcated by the 21 stream synoptic sampling sites. Metal (Pb, Zn, Cd) loads were calculated as the product of the streamflow estimate and the metal concentration. Dissolved concentrations of Cd are used in the loading analysis due to the close correspondence between total recoverable and dissolved concentrations. Total recoverable and dissolved concentrations of Pb are used due to the large differences observed for this element.

As a result of the issues noted in Section 3.1, total recoverable concentrations of Zn are used and assumed to reflect dissolved concentrations. SEPA holds a significant time series data of dissolved and total analysis for various metals from 2012. Comparison of the dissolved and total Zn results from long term monitoring locations in the Wanlock shows Zn is almost entirely present in the dissolved phase. Therefore, total recoverable Zn concentrations are referred to as 'dissolved' concentrations from here onwards.

Cumulative instream load is equal to the sum of all increases in metal load (Kimball et al. 2002). For a given stream segment, the cumulative instream load is increased if the metal load increased, and held constant if the metal load decreased. The cumulative instream load provides an estimate of the total metal load added to the stream over the entire study reach whereas the metal loading represents the net amount of loading after chemical reaction such as adsorption and precipitation. A net increase in cumulative instream load suggests addition of metal mass to the stream. The percent contribution of each source is given by:

$$\%contribution = 100 \; \Delta load \; / \; (L2 - L1)$$

where $\Delta load$ is the within-segment increase, and L1 and L2 are the cumulative instream loads at the upstream and downstream ends of the study reach, respectively. Percent contributions from multiple segments were grouped to represent the total contributions from the main source areas within Wanlock Water. Comparison of cumulative instream load with instream load provides a means of estimating net attenuation of metals over the length of the study reach.

Where stream segments show an increase in metal load, calculation of 'effective inflow concentrations' provides a means to determine if an observed inflow is representative of all inflow waters entering the segment (Kimball et al. 2002). If observed inflow concentrations exceed effective inflow concentrations, there are likely more dilute inflow waters entering the stream segment in addition to the sampled inflow. Conversely, high concentration waters are entering the stream segment when effective inflow concentrations exceed observed inflow concentrations. Under the

assumption of conservative transport, effective inflow concentrations (C_L) can be calculated as:

$$C_L = (Q_D C_D - Q_U C_U) / (Q_D - Q_U)$$

where Q is discharge, C is concentration, and U, D, and L represent upstream, downstream, and lateral inflow values, respectively.

4.   Results and Interpretation

The following sections focus on streamflow, pH and three metals (Pb, Zn and Cd) that have been identified as a potential cause for concern in the Wanlock Water. Copper concentrations were not considered in this study as existing SEPA analysis has shown this metal to be below the calculated bioavailable EQS when classifying the river.

4.1 Streamflow, pH and metal concentrations

Streamflow estimates increased linearly with distance downstream from ~137 L s^{-1} just downstream of the tracer injection site on the Bay Mine Adit to ~270 L s^{-1} downstream of Sowen Burn (Figure 8). The Wanlock Water upstream of Bay Mine Adit accounted for just 5% of the increase in streamflow along the reach.   Four major inflows accounted for 56% of the increase in streamflow at the time of sampling. These were Meadowfoot Adit (RBI-0412) and Glenglass Level No. 2 (LBI-0411) (12.3%), Limpen Burn (RBI-0597) (16.8%), Shieling Burn (LBI-0794) including diffuse drainage from the wetland (18%) and Glenmarchhope Burn (LBI-1465) (9.4%).   Minor inflows (~5% contribution or less) included Whytes Cleuch (RBI-0080), Glenglass Stream (LBI-0154), Glenglass Level (LBI-0496), Sowen Burn (RBI-1667) and various drainages from the crushing mill (RBI-1046) and Queensbury Tailings Ponds (LBI-1245; LBI-1364; LBI-1407; LBI-1437).   Together, stream reaches with sampled inflows comprised 88% of the total streamflow indicating some unidentified or unknown dispersed surface and/or groundwater inputs entering the stream in reaches with no sampled inflows.

Spatial profiles of pH for stream sites and inflows are illustrated in Figure 9. Stream pH values ranged from 7.4 to 7.7 with higher values generally occurring at sites opposite the Glencrieff Tailings Ponds. Inflow pH values were typically lower than stream values (range = 6.6 to 7.9) and possibly represent lower pH water sources from mine workings and organic-rich and saturated soils.
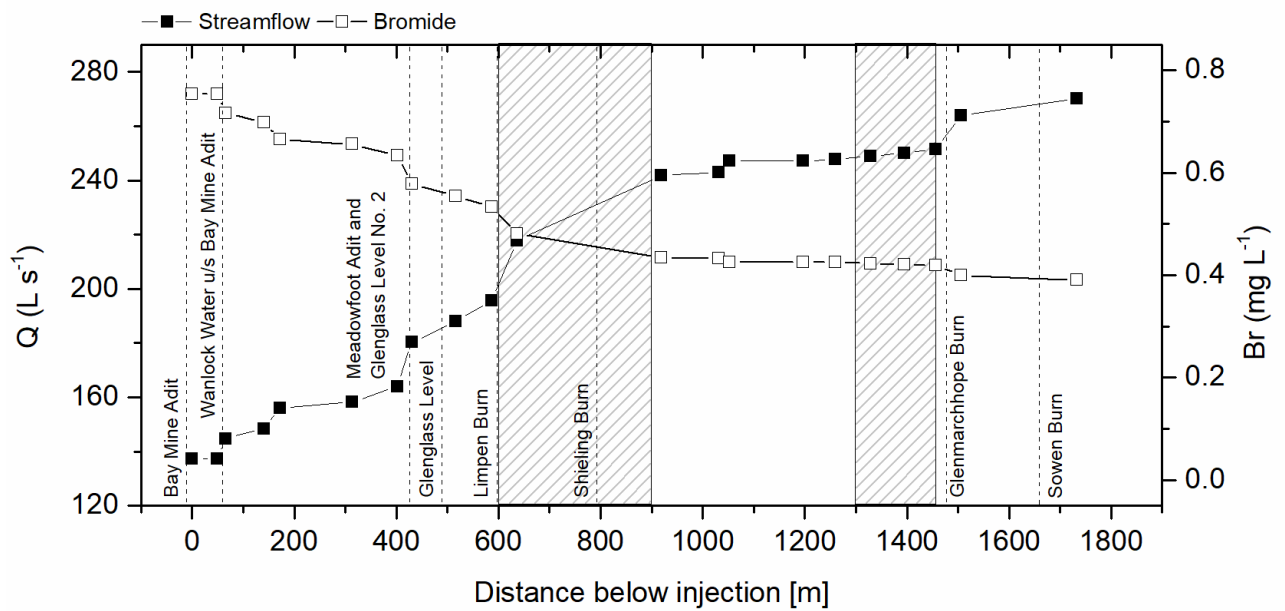
Figure 8. Bromide concentrations and streamflow estimates (derived from the tracer-dilution method) in Wanlock Water, Dumfries and Galloway, September 2019. Shaded areas = wetland (~600-900 m) and Queensbury Tailings Pond (~1300-1450 m).
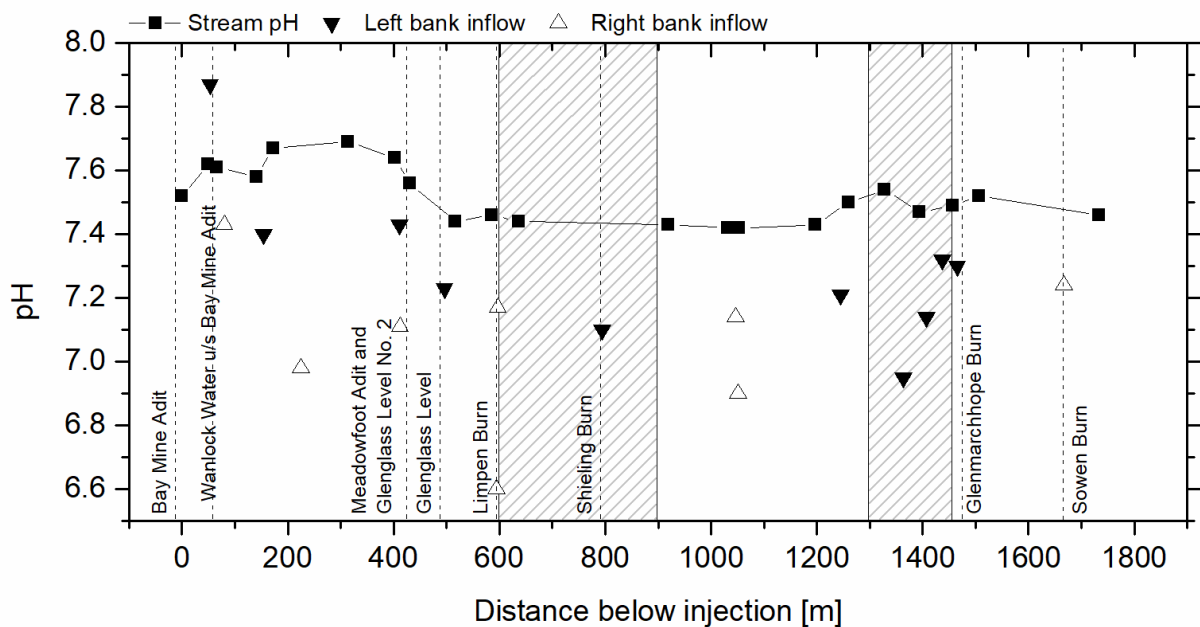

Figure 9. Spatial profile of pH at stream and inflow sites in Wanlock Water, Dumfries and Galloway, September 2019. Shaded areas = wetland (~600-900 m) and Queensbury Tailings Pond (~1300-1450 m).

As part of ongoing WFD classification process SEPA has calculated the EQS for Cd, Pb & Zn for the Wanlock Water as detailed below:

- Cd = 0.09 µg L^{-1}, based on hardness of 50-100 mg L^{-1} CaCO$_3$;
- Pb = 1.2 µg L^{-1}, based on bioavailability;
- Zn = 11.3 µg L^{-1} based on bioavailability.

Instream dissolved Zn, Pb and Cd over the entirety of the study reach are shown in Figures 10, 11 & 12. Mean dissolved concentrations over the long study reach were:

- Cd = 2.4 µg L^{-1} (range = 1.4 – 3.1 µg L^{-1}).
- Pb = 8.2 µg L^{-1} (range = 1.0 – 24 µg L^{-1}),
- Zn = 217 µg L^{-1} (range = 102 – 300 µg L^{-1}).

Concentrations of Pb generally increased with distance downstream (Figures 10). Superimposed on this trend were marked increases associated from the wetland (~600 to 900 m) and the Queensbury Tailings Ponds (~1300 to 1450 m). This pattern was particularly evident for total concentrations but was also found in the dissolved concentration data. The increase associated with the wetland does not appear to be related to Shieling Burn and instead is thought to be related to other unsampled inflows and / or re-suspension of Pb-rich sediments in the wetland area. The increase in Pb concentrations next to the Queensbury Tailings Ponds corresponded to very high total and dissolved concentrations in the left bank inflows (LBI-1245; LBI-1364; LBI-1407; LBI-1437) draining this area.

A significant increase in both Zn and Cd concentrations occurred between ~400 and 600 m (Figure 11 and 12) and appeared to be associated with left bank inflows (LBI-0411-Glenglass Level No.2 and LBI-0496-Glenglass Level) draining the Glencrieff Mine. It is notable that the general chemistry of LBI-0411 is more consistent with mine water rather than surface drainage. However it is of a lower concentration of Cd and Zn than the Glenglass Level, possibly a function of dilution by surface run-off due to rainfall during the study period. This data supports the earlier hypothesis that the source of this inflow is predominantly mine water, possibly linked to the Glenglass Level or other outflow from the Glencrieff Mine, perhaps with a portion of runoff or drainage/seepage from the tailings area. A slight decrease in concentrations occurred at ~600m possibly due to dilution by water from Limpen Burn. A slight increase in stream concentrations occurred next to the Queensbury Tailings Ponds and appeared to be associated with left bank inflows (LBI-1364; LBI-1407; LBI-1437) draining this area. However, calculation of effective inflow concentrations for the two reaches receiving these three inflows (WW-1328 to WW-1394 and WW-1394 to WW-1456) indicates a significant proportion of the change in stream concentrations was due to unsampled, possible diffuse subsurface, inflows. Although significant attenuation of Pb occurred in places throughout the study reach, elevated Zn and Cd concentrations were maintained throughout the study reach due to the conservative nature of these elements at circum-neutral pH (Byrne et al. 2012; Gozzard et al. 2011; Hermann and Neumann-Mahlkau 1985).

*Figure 10. **[a]** Spatial profiles of total recoverable and dissolved stream Pb concentrations. **[b]** Spatial profile of total recoverable stream and inflow Pb concentrations. **[c]** Spatial profile of dissolved stream and inflow Pb concentrations. Shaded areas in **[a]** = wetland (~600-900 m) and Queensbury Tailings Pond (~1300-1450 m).*

Figure 11. [a] Spatial profiles of dissolved stream Zn concentrations. [b] Spatial profile of dissolved stream and inflow Zn concentrations. Shaded areas in [a] = wetland (~600-900 m) and Queensbury Tailings Pond (~1300-1450 m).

Figure 12. [a] Spatial profiles of total recoverable and dissolved stream Cd concentrations. [b] Spatial profile of dissolved stream and inflow Cd concentrations. Shaded areas in [a] = wetland (~600-900 m) and Queensbury Tailings Pond (~1300-1450 m).

4.2 Metal loads

Changes in metal loads obtained from synoptic sampling of water chemistry and tracer-derived discharge are illustrated in Figures 13 and 14, and Appendix 4. Spatial loading profiles for total Pb loads indicate two stream segments, ending at 1031m and 1446m, accounted for the majority of stream loading (48% and 35%, respectively). These two segments capture the wetland area, with negligible Pb loading coming from

the Shieling Burn, and drainage from the Queensbury Tailings Ponds. The loading profile for dissolved Pb attributes 48% of the loading to the segment capturing the wetland area.

The difference between the instream load and the cumulative instream load can be used to quantify the attenuation that occurred along the study reach. Attenuation of total and dissolved Pb was 72% and 52%, respectively, indicating both physical (settling) and chemical (adsorption and precipitation) processes could be important in the removal of Pb from the water column (Figure 13).
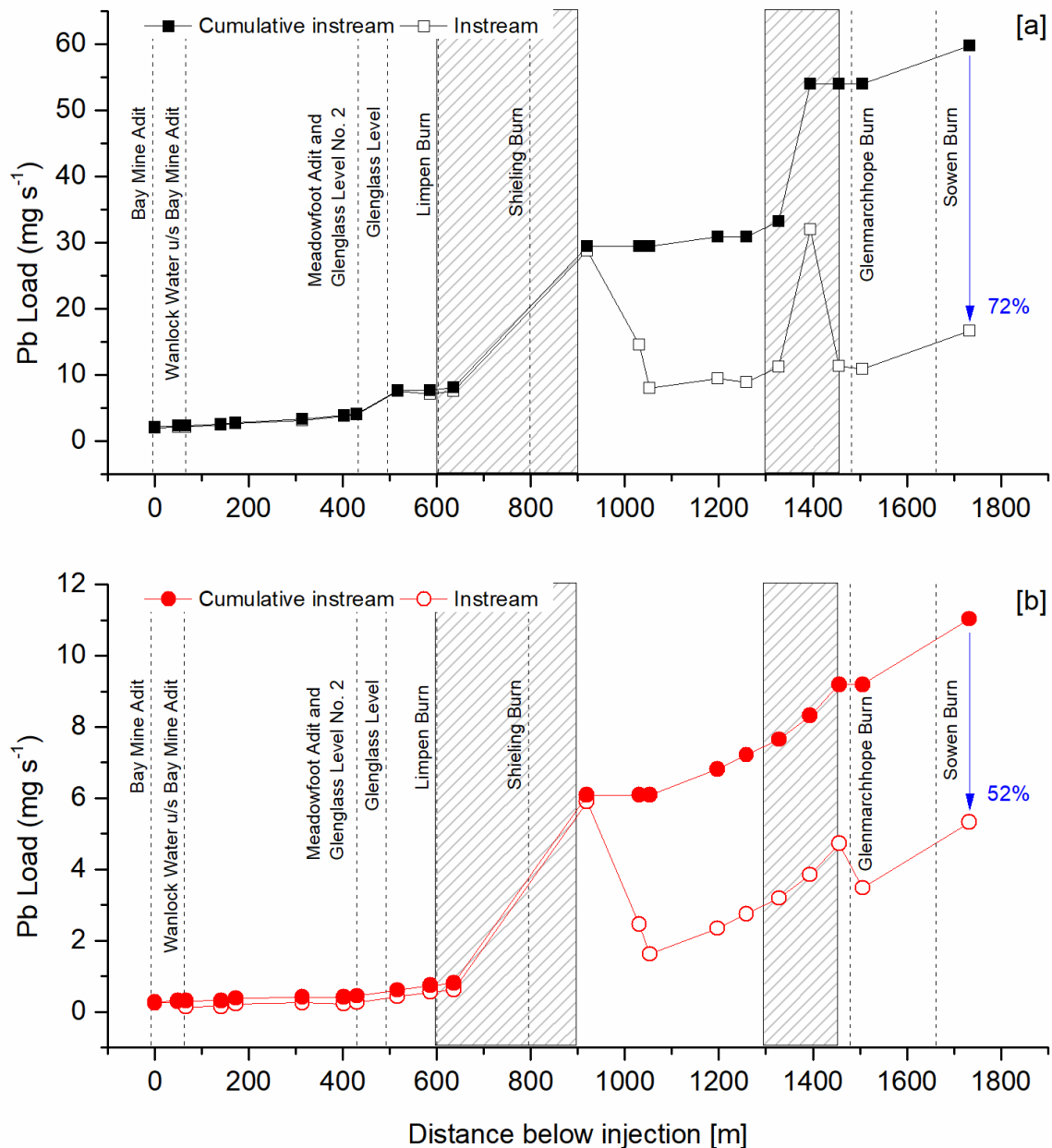
Figure 13. *[a]* Spatial profiles of total recoverable cumulative instream and instream Pb loads. *[b]* Spatial profile of dissolved cumulative instream and instream Pb loads. Shaded areas in *[a]* = wetland (~600-900 m) and Queensbury Tailings Pond (~1300-1450 m). Attenuation indicated by blue arrow in *[a]*.

Attenuation of dissolved Zn and Cd was 11% and 5%, respectively, indicating both of these elements generally behave conservatively in the study reach. The only significant (>1%) zone of Zn attenuation (7%) was in the segment ending at 141m. This segment receives surface inflow from Whyte's Cleuch on the right bank. The pH of this inflow was 7.8 which may account for Zn sorption and/or precipitation at this point. Whytes Cleuch is known to be dry in periods without rainfall and attenuation of Zn may only be intermittent as a result. Geochemical modelling, or spatial and temporal trend analysis of inflow and stream water chemistry, could potentially confirm the mechanisms of attenuation here.
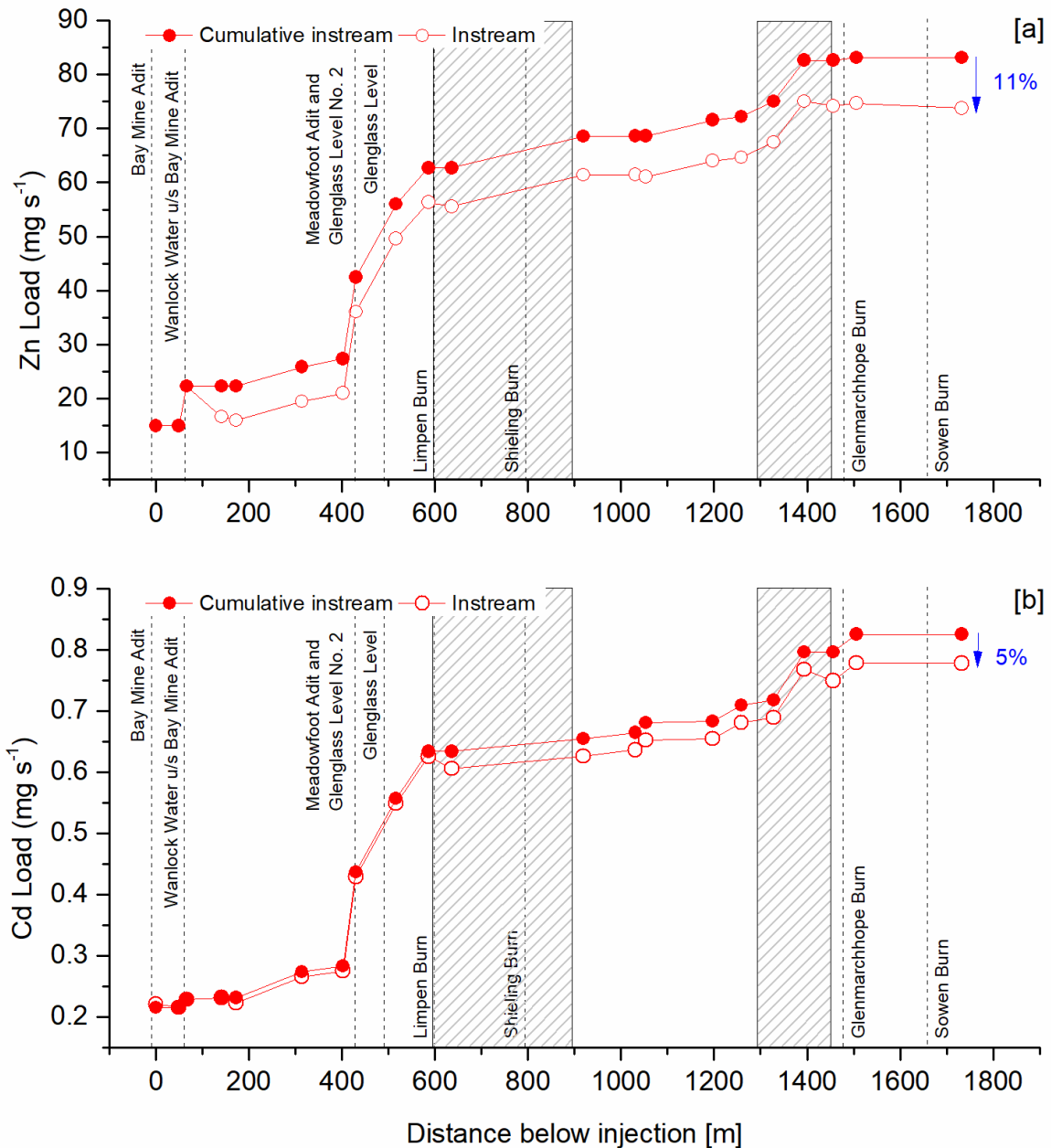
Figure 14. *[a]* Spatial profiles of dissolved cumulative instream and instream Zn loads. *[b]* Spatial profile of dissolved cumulative instream and instream Cd loads. Shaded areas in *[a]* = wetland (~600-900 m) and Queensbury Tailings Pond (~1300-1450 m). Attenuation indicated by blue arrow in *[a]*.

4.3 Ranking of main sources

Calculation of the percent contribution of metals to each stream segment allows identification of the largest sources of individual metals to the study reach. When one or more adjacent segments showed an increase in load, the segments were grouped to reflect loading from a general source area. Six source areas accounted for most of the Pb loading to Wanlock Water along the study reach whereas seven sources accounted for the majority of Zn and Cd loading. Sources and the rankings are shown in Figure 15 below.

For specific metals, the largest source of total Pb was the reach through the wetland (48%) followed by the reaches draining the Queensbury Tailings Ponds (34%). Dissolved Pb loading was also dominated by the wetland area (48%), with significant contributions also from the Queensbury Tailings Ponds (14%) and the Smelter (17%). The relative importance of Shieling Burn versus unsampled inflows in the wetland area warrants investigation, as does a slight increase in iron that was also detected downstream of the wetlands area. However, effective inflow concentrations cannot be calculated for Pb due to its non-conservative behaviour in the study reach. That being said, the very low concentrations of Pb observed in Shieling Burn suggest that the majority of loading in this stream segment reflects mobilisation of particulate and aqueous Pb phases from sediment deposited in the wetland, rather than from Shieling Burn. The Shieling Burn and Limpen Burn do however show higher concentrations of iron than the main stream.

The two largest sources of dissolved Zn were Bay Mine Adit (18%) and the reach including Meadowfoot Adit and Glenglass Level No.2 (18%). The third most important source was the Glenglass Level (16%). The fourth most important source was the Wanlock Water upstream of Bay Mine Adit which accounted for approximately 9% of the overall stream Zn loading. This is significant as the Wanlock Water upstream of Bay Mine Adit was largely dry during our sampling campaign. The resurgence water which was sampled was therefore likely to be groundwater and / or surface water in the hyporheic zine from further upstream which had infiltrated mined strata or made ground in the flood plain and re-emerged at sample point LBI-0053.

Cadmium sources were almost identical in rank and loading to Zn sources, which reflects the underlying geochemical similarity of these elements. The largest source of total and dissolved Cd loading was Bay Mine Adit (26%). The second and third largest sources were the reaches including Meadowfoot Adit and the Glenglass Level No.2 (19%) and the Glenglass Level (14%). The Wanlock Water upstream of the Bay Mine Adit was not so significant in terms of its significance for Cd.
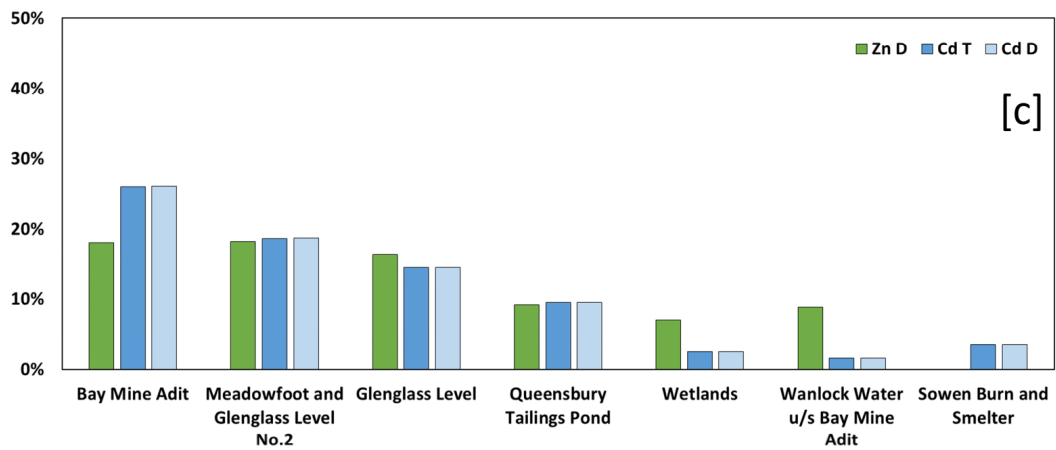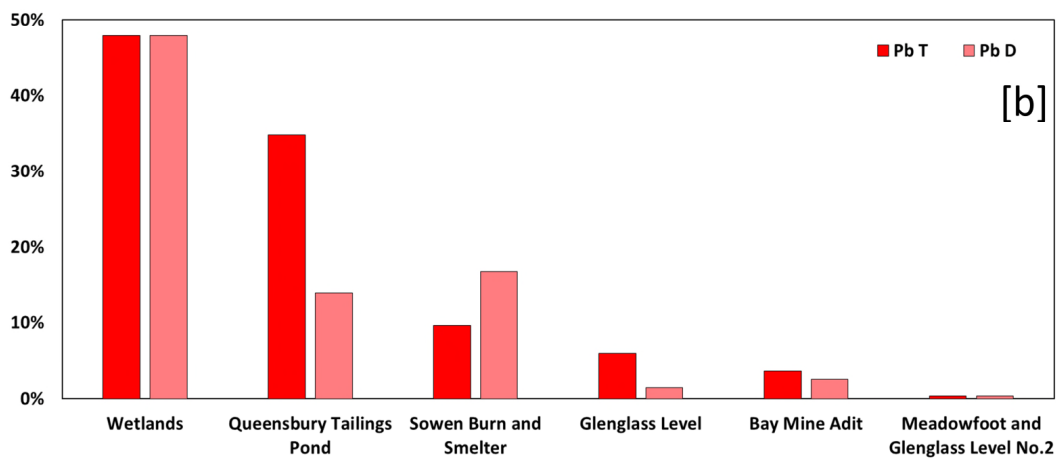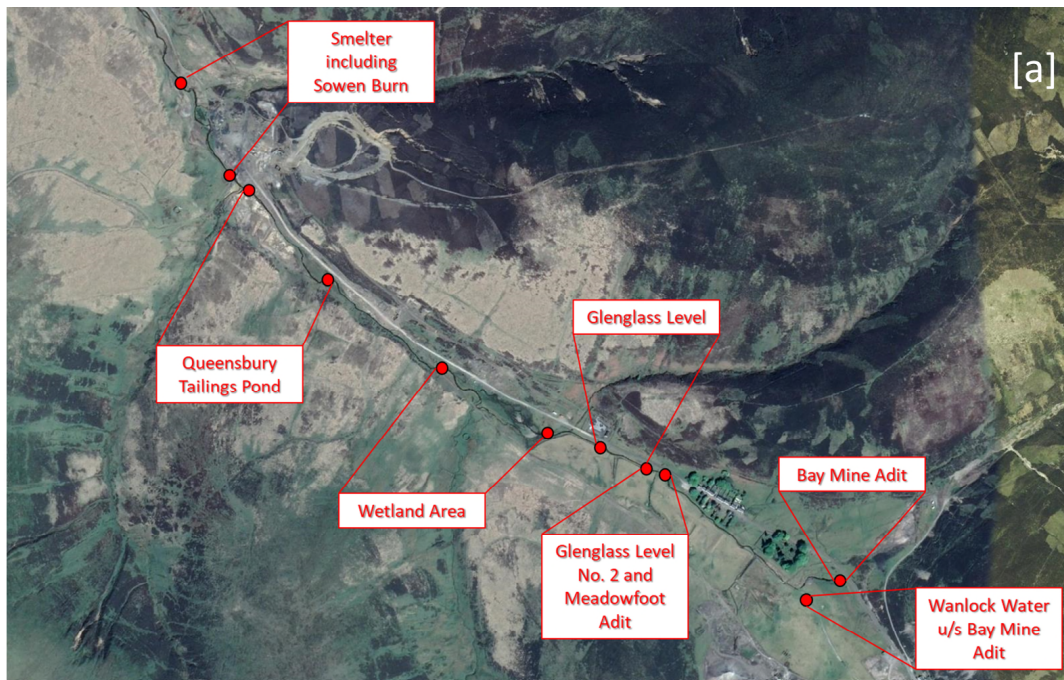
Figure 15. Percent contribution and location of source areas to overall load within the Wanlock Water study reach. [a] Location of the main source areas within the study reach. [b] Pb loading from the six main sources. [c] Zn and Cd loading from the seven main sources. D = dissolved load and T = total recoverable load in the bar chart legends.

Considering the main source areas identified from the loading data, Pb (total and dissolved) was sourced mainly from primary (Queensbury Tailings Ponds) and secondary (wetland area) mine waste deposits. The wetland area may function as a depositional area for aqueous and particulate metals during low flows. The wetland area may also be contaminated by wastes deposited during the operational period of the mines. The dominance of the particulate phase during sampling suggests Pb mobilisation and transport from the wetland is related to high stream velocities that mobilise streambed sediments. Mobilisation from the Queensbury Tailings Ponds would appear to be related to erosion and runoff of tailings following rainfall. In comparison, the loading data suggests that Zn and Cd were mainly sourced from mine water emerging into the Wanlock Water via Bay Mine Adit, Glenglass Level, Meadowfoot Adit and Glenglass Level No. 2, although notable contributions occur from the Queensbury Tailings Pond.

4.4   Point versus diffuse source contributions

Consideration of the relative importance of diffuse and point sources of mine pollution is necessary to inform the design of remedial solutions and to evaluate potential changes in the location and magnitude of sources under different streamflow conditions.

Point sources identified in the study area were discrete discharges of mine water into the stream. In the study area these included drainage from mine adits and levels. Stream water entering the study area above Bay Mine Adit is considered as a point source of entry, however as described in the CA report of 2014, this will comprise a mixture of point and diffuse sources. Diffuse sources identified in the study area included leaching and erosion of mine tailings/waste, remobilisation of mine waste deposited in the wetland area, and possibly groundwater efflux (as demonstrated by effective inflow calculations for the reaches next to Queensbury Tailings Ponds). Other potential diffuse sources include the hyporheic zone, where remobilisation of sediment-bound metals to dissolved phases has been established in other studies (Palumbo-Roe et al. 2012). Diffuse sources can be both persistent and episodic in nature and can vary in importance in response to streamflow and rainfall. For example, drainage from the Queensbury Tailings Ponds might be expected to increase in importance as a source during periods of high rainfall, when erosion and runoff rates may be high (Byrne et al. 2013; Gozzard et al. 2011; Jarvis et al. 2019). The mode of entry to the stream channel could be via a complex combination of episodic point and diffuse source inflows. Conversely, groundwater contaminated by leaching from mine workings and tailings, such as that which may exist where the stream passes the Queensbury Tailings Ponds, may be more persistent (Byrne et al. under review).

Figure 16 illustrates a comparison between cumulative instream metal loads and the cumulative loads from point sources (mine water) and diffuse sources (mine waste) of mine pollution, based on the results of this study. For this analysis, diffuse sources

include the wetland area, the Queensbury Tailings Pond, and stream segments with no observed inflows but where metal load increased. Point sources include all mine water and tributary inflows.

This analysis indicates the dominance of point sources of dissolved Zn and Cd (67% and 75%, respectively) in the upper part of the study area (above ~516m) where mine water discharges are important. Diffuse sources of total and dissolved Pb (67% and 75%, respectively), and to a lesser extent Zn and Cd (9% and 10%, respectively), are most important in the lower part of the study area (below ~516m) where mobilisation in the wetland and drainage from the uncapped Queensbury Tailings Ponds increase stream metal loading.
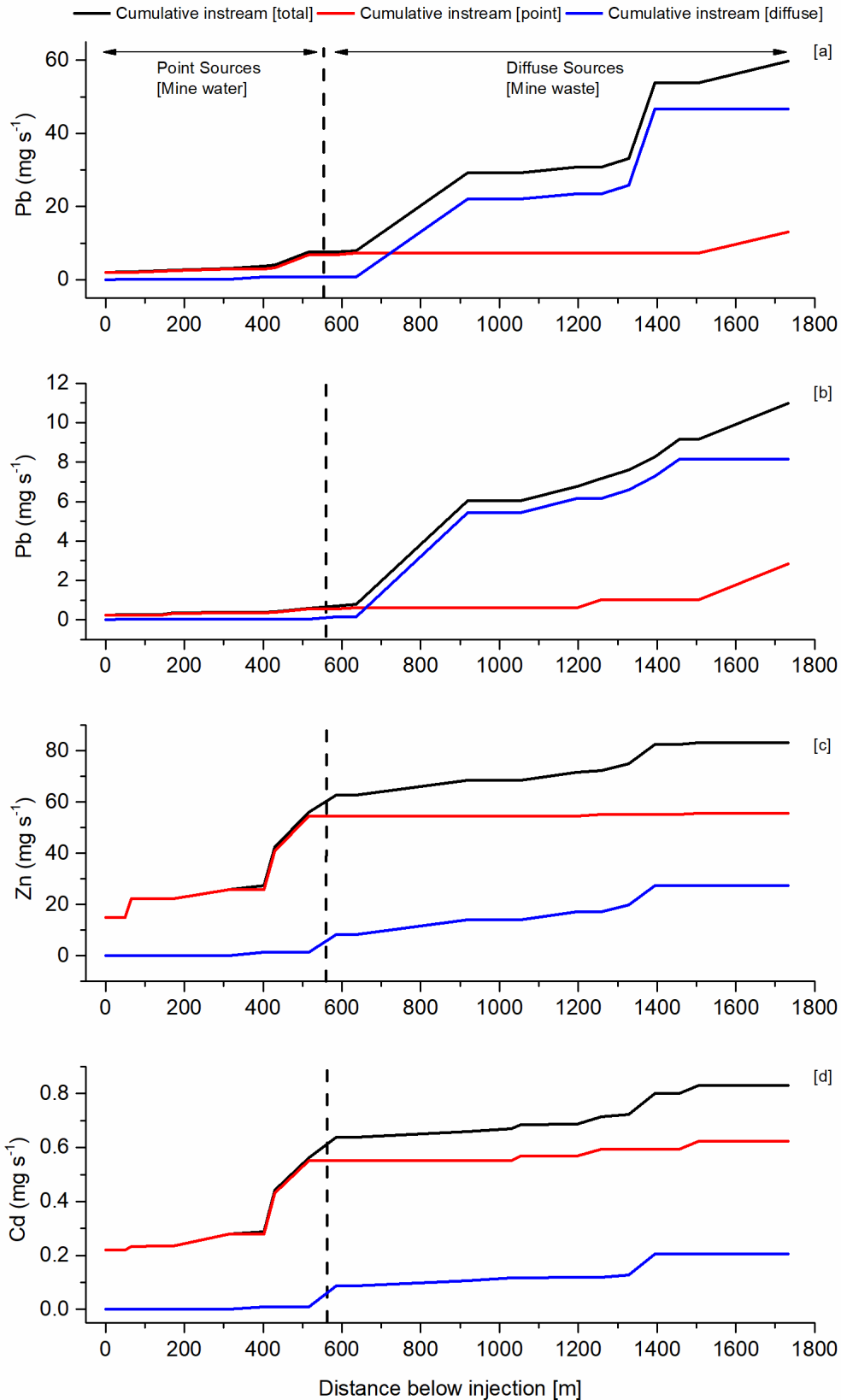
Figure 16. Spatial profiles of cumulative instream (total, diffuse source and point source) loads for [a] total recoverable Pb, [b] dissolved Pb, [c] dissolved Zn and [d] dissolved Cd.

4.5   Implications of remediation and impacts on WFD classification

The effect on stream metal concentrations of treating mine water inflows or minimising mine tailings erosion can be estimated through mass balance calculations. For Zn and Cd that appear to behave relatively conservatively in the study reach, this method can approximate concentration changes from remediation reasonably well. For Pb, this approach may be limited due to the reactive behaviour of this element in the system under study. To investigate the potential impact of remediation on stream Pb concentrations, the use of a reactive solute transport model is recommended that incorporates geochemical processes such as adsorption, precipitation and dissolution (Runkel 1998; Walton-Day et al. 2007).

We consider here five possible remediation scenarios to reduce Zn and Cd concentrations in the Wanlock Water:

1. Treatment of mine water from Bay Mine Adit,
2. Treatment of mine water from Glenglass Level,
3. Treatment of mine water from Glenglass Level No. 2,
4. Capping and re-vegetation of the Queensbury Tailings Ponds to reduce surface erosion and subsurface leaching, and
5. Capping of the Queensbury Tailings Ponds and treatment of all three major adits and drainage levels (Scenario 1, 2, 3 and 4).

Effective inflow concentrations calculated for Zn and Cd for the stream segment encompassing Glenglass Level No.2 (and Meadowfoot Adit) indicate inflow concentrations from the Glenglass Level No.2 are most responsible for the observed increase in loading along this stream segment. As a result, treatment of water from Meadowfoot Adit is not considered here. Remediation of Pb sources is not considered due to the aforementioned problems with using the mass balance approach for this element, however, the above actions, especially capping of the tailings ponds would likely lead to a significant reduction in Pb loading.

A post-remediation load at the end of the study reach (WW-1733) can be calculated by subtracting the load attributed to the remediated source area from the pre-remediation load at the end of the study reach. Dividing this by the flow at the end of the study reach gives a post-remediation metal concentration.   All remediation scenario calculations are shown in Table 2, and are based on results from this synoptic sampling event.

These calculations assume that remediation removes 100% of the metal contaminants from the source area, which is unlikely, and that it does not modify the flow attributed to that zone. They show that even if Scenario 5 could be implemented, the EQS would not be achieved at the end of the study reach due to the presence of other diffuse and point sources in the study reach. WFD classification is based on annual averages over a number of years and as such it would be important to consider the influence of different flow conditions on these calculations.

	Scenario #1	Scenario #2	Scenario #3	Scenario #4	Scenario #5
Dissolved Zn					
Environmental Quality Standard [µg/L]	*11.3*	*11.3*	*11.3*	*11.3*	*11.3*
Pre-remediation concentration [µg/L]	**273**	**273**	**273**	**273**	**273**
Pre- remediation load [mg/s]	73.8	73.8	73.8	73.8	73.8
Load from source [mg/s]	15.0	13.6	15.1	13.1	56.7
Post- remediation load [mg/s]	58.8	60.2	58.7	60.6	17.0
Post-remediation concentration [µg/L]	**217.6**	**222.8**	**217.2**	**224.4**	**63.0**
Concentration change post-remediation [%]	*28*	*15*	*20*	*12*	*75*
Dissolved Cd					
Environmental Quality Standard [µg/L]	*0.09*	*0.09*	*0.09*	*0.09*	*0.09*
Pre-remediation concentration [µg/L]	**2.88**	**2.88**	**2.88**	**2.88**	**2.88**
Pre- remediation load [mg/s]	0.788	0.788	0.788	0.788	0.788
Load from source [mg/s]	0.216	0.120	0.154	0.097	0.586
Post- remediation load [mg/s]	0.563	0.658	0.625	0.681	0.192
Post-remediation concentration [µg/L]	**2.08**	**2.43**	**2.31**	**2.52**	**0.71**
Concentration change post-remediation [%]	*20*	*18*	*20*	*18*	*77*

Table 2. Potential improvements in dissolved Zn and Cd in the Wanlock Water under different hypothetical remediation scenarios. Pre-remediation and post-remediation calculations are for the last synoptic sampling point (WW-1733).

Notwithstanding the scenarios being based on this sampling event, it can be seen that even if 75% of the Cd and Zn sources were eliminated, the Wanlock Water is unlikely to achieve Good chemical status under WFD classification at the end of the study reach. However, some degree of dilution will occur before the Wanlock flows into the Crawick Water and the potentially achievable decreases in the relevant metals should be modelled by SEPA in a SAGIS model (or similar) to assist in the understanding of the potential improvement in the classification in the impacted downstream rivers, the Crawick Water (Cd & Zn) and the River Nith (Cd).

Although remediation of Pb sources has not been considered here, it is likely that capping of the Queensbury Tailings Ponds would significantly reduce erosion and transport of Pb to the stream, and hence reduce stream Pb concentrations. The role of the wetland area (main source of Pb) in stream metal loading warrants further investigation as it is possible that this is an episodic source, related to higher stream water velocities and flows that mobilise deposited Pb-rich sediments and soils. It would be important to consider whether there are any similar features in the wider catchment as well. Areas of the river where deposition and remobilisation of sediments can occur such as the wetland area may act as significant sources.

Ongoing erosion of Pb-rich made ground soils will result in deposition of particulate Pb downstream and thus the ongoing creation of persistent sources of Pb will occur. Reducing erosion where possible should result in reducing the ongoing creation of persistent sources downstream, especially during high flow events.

5.   Conclusions

The tracer dilution and synoptic sampling approach utilised in this study was successful at establishing streamflow and water chemistry at multiple sites across the Wanlock Water watershed over a timescale of a few hours. These data were then used to establish high spatial resolution loading profiles for mine pollution contaminants in the Q30 flow conditions during the sampling that, in turn, were used to locate and quantify the major point and diffuse sources of mine pollution and estimate improvements that could be achieved by remediation.

Approximately 88% of the streamflow was accounted for by stream reaches with sampled inflows indicating some additional unsampled, most likely dispersed, sources of surface and / or groundwater was entering the study area in reaches with no sampled inflows.

It has confirmed that all three of the major mine contaminants (Pb, Zn and Cd) breach EQS throughout the study reach.   Mean dissolved concentrations of these contaminants over the 2km long study reach were:

- Cd = 2.4 µg L^{-1} (range = 1.4 – 3.1 µg L^{-1}).
- Pb = 8.2 µg L^{-1} (range = 1.0 – 24 µg L^{-1}),
- Zn = 217 µg L^{-1} (range = 102 – 300 µg L^{-1}).

5.1   Zinc and cadmium source apportionment and behaviour

Zinc and Cd were found to display similar patterns, with loading primarily from point sources (67% and 75%, respectively) of mine water from the upper section of the study reach.   The primary sources of dissolved Zn and Cd in the study reach, and their overall importance to stream metal loading, are presented in Table 3 below.

Principal Sources in the Study Reach (% of total load)		
Source	Zinc (dissolved)	Cadmium (dissolved)
Bay Mine Adit	18.0	26.0
Meadowfoot Adit and Glenglass Level No 2	18.1	18.6
Glenglass Level	16.3	14.5
Queensbury Tailings Ponds	9.1	9.5
Wetland Area	7.1	2.5
Wanlock Water u/s Bay Mine Adit	8.8	1.6
Sowen Burn and Smelter	0	3.5

Table 3. Principal sources of dissolved Zn and Cd in the study reach. Contribution to overall stream metal loading is expressed as a percent of the total.

Both Zn and Cd generally behaved conservatively in the study reach with total attenuation along the reach estimated at 11% and 5%, respectively*.*

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5.2   Lead source apportionment and behaviour

Lead loading was found to be largely from more diffuse sources of deposited mine wastes (78% (total) and 74% (dissolved)). The primary sources of dissolved and total Pb in the study reach, and their overall importance to stream metal loading, are presented in Table 4 below.

Principal Sources in the Study Reach (% of total load)		
Source	Lead (total)	Lead (dissolved)
Wetland Area	47.9	47.9
Queensbury Tailings Ponds	34.8	14.0
Sowen Burn and Smelter	9.7	16.7
Glenglass Level	6.0	1.5
Bay Mine Adit	3.6	2.5
Meadowfoot Adit and Glenglass Level No 2	0.4	0.3

Table 4. Principal sources of total recoverable and dissolved Pb in the study reach. Contribution to overall stream metal loading is expressed as a percent of the total.

Attenuation of total and dissolved Pb was 72% and 52%, respectively, indicating both physical (settling) and chemical (adsorption and precipitation) processes could be important in the removal of Pb from the water column.

5.3   Remediation scenarios

Mass balance calculations were used to estimate potential decreases in Zn and Cd stream concentrations in response to hypothetical remediation scenarios. Treatment of mine water from Bay Mine Adit, Glenglass Level and Glenglass Level No. 2 could achieve a 50% decrease in Zn and Cd stream concentrations. Combining mine water treatment with capping of the Queensbury Tailings Ponds could achieve a >70% decrease in Zn and Cd concentrations. However, these interventions would not be sufficient for the Wanlock Water to meet environmental quality standards due to other sources of pollution in the study reach.   Changes in Pb concentrations due to hypothetical remediation were not considered in this study due to the non-conservative behaviour of this contaminant. However, capping of the Queensbury Tailings Ponds would likely lead to a substantial reduction in Pb loading from this area.

6. Recommendations

1. The possibility of extending the predicted changes in metal concentrations over this study reach further downstream (using the SAGIS-SIMCAT water quality model) should be explored to understand if the investigated remediation scenarios could lead to improvements in impacted rivers downstream, specifically in Crawick Water (Zn and Cd) and the River Nith (Cd).

2. This study was conducted under estimated Q30 streamflow conditions based on scaling from a downstream gauge on the River Nith. It is worth noting that mining-impacted watersheds are hydrologically-complex systems and that changes in rainfall, runoff and streamflow could change the location and importance of the identified mine pollution sources. Prior to the Covid-19 outbreak, targeted synchronous flow and concentration monitoring was planned to be undertaken in persistent low flow conditions. This will be carried out if it can be undertaken safely, and budget is available. However, in the meantime a review of existing SEPA water quality data in combination with the data from the CA study and modelled flow rates in the Wanlock Water could be undertaken. This could provide an indication of the variability in concentrations and loads over time in different flow conditions. It would be important to consider other factors that can impact metal mobility as part of this work.

3. In 2016, SEPA commissioned studies to examine the potential economic benefit of improving the water quality of the Wanlock Water to Good WFD status. This indicated the economic value of improving the water quality in the River Nith and Crawick Water could be up to £6.4m. This was based on potential costs to undertake engineering work, such as capping the Queensbury Tailings Ponds, and implementing a mine water treatment scheme similar to that of Force Crag, Cumbria. A mine water treatment scheme such as this involves compost flow beds to reduce metal concentrations that would involve significant land take and continuous maintenance and management. Other treatment methods are currently being trialled by Natural Resources Wales and it would be beneficial to liaise with their specialists and prepare a summary conclusions of their research to inform any choices of remediation solutions and re-assess the potential economic benefits when appropriate.

4. Simple mass balance calculations have been used here to estimate potential water quality improvements that could arise from treatment or remediation of different mine pollution sources. However, this approach cannot be used for reactive contaminants like Pb, nor does it consider how changes in water chemistry, due to remediation of mine pollution sources, might affect the transport and concentration of contaminants. It is therefore recommended that a solute transport model (such as OTIS – One-dimensional Transport with Inflow and Storage) is used to establish more robust predictions of potential

water quality improvements due to remediation. This would require additional data collection to calibrate the transport model. However, the model itself would use the water chemistry data derived from the present study.

5.   The wetland area was identified in this study as the primary source of particulate and dissolved Pb loading to the stream. Our hypothesis suggests that high streamflows and velocities mobilise Pb from residual mine wastes in the wetland, however geochemical processes could also influence the loading identified in this stretch of river. These mine wastes may have been deposited in the wetland during the operation of the mine. Alternatively, the mine wastes may originate upstream of the wetland with the wetland acting as a sink for Pb during periods of low flow. Collection and analysis of sediment cores from the wetland could be undertaken in combination with targeted water sampling to establish the nature and extent of Pb pollution. Geochemical and mineralogical analyses would shed light on the hydrological and geochemical processes that drive both attenuation and release of Pb from these sediments.

6.   It is possible that stream water lost in the channel upstream of the study reach (from the north-eastern edge of Wanlockhead down to below the Bay Mine Adit) during dry periods may flow through fracture planes and mined strata and re-emerge via Bay Mine Adit and, possibly, Glenglass Level No. 2. Interaction of this water with the exposed underground mined surfaces may cause elevated metal concentrations and / or loads at the resurgence points. Identifying the location of water loss in the stream channel, and establishing a hydrological connection between the lost stream water and the emerging mine waters, would provide the information necessary to assess whether a remedial effort (e.g. lining of the stream channel) is warranted or feasible. A hydrological connection could be investigated by injecting a concentrated solution of sodium bromide into the Wanlock Water above Bay Mine Adit and monitoring bromide concentrations at suspected resurgence points (i.e. Bay Mine Adit and Glenglass Level No. 2). The time period of the injection could vary from days to several weeks depending on the tracer transit time. Loss of water in the streambed channel could be located and quantified using a series of gulp (or slug) injections of sodium chloride along the course of the stream where flow loss is thought to occur.

7.   Undertake a detailed remedial options appraisal to consider the costs and appropriateness of various treatment systems and engineering solutions. Opportunities for partnerships and funding for remediation trials can then be examined. Some or all of the other recommendations will be needed to inform this work and a decision will be required to agree the most appropriate way forward given the significant scale of the problem caused by the historic metal mining in this area.

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Appendix 1. Physio-chemistry, tracer (bromide) and major ion concentrations in Wanlock Water, Dumfries and Galloway, September 2019.

SiteID	SEPAID	Source	Distance [m]	pH	SC [µS/cm]	Alkalinity [mg/L CaCO$_3$]	Br [mg/L]	Ca [mg/L]	K [mg/L]	Mg [mg/L]	Na [mg/L]	SO$_4$ [mg/L]	Cl [mg/L]
Stream sites													
WW-BK	571545	STR	-10	7.52	162	49.00	0.016	20.20	0.382	2.25	8.86	6.78	12.90
WW-0049	562186	STR	49	7.62	162	49.00	0.754	20.30	0.380	2.27	9.19	6.70	13.40
WW-0066	557476	STR	66	7.61	161	49.40	0.716	19.80	0.379	2.22	8.92	6.74	13.50
WW-0141	571547	STR	141	7.58	162	49.60	0.699	20.10	0.356	2.25	9.01	6.74	13.10
WW-0172	571549	STR	172	7.67	153	48.20	0.665	18.60	0.357	2.30	8.39	6.70	11.90
WW-0314	120447	STR	314	7.69	154	47.70	0.656	18.90	0.378	2.33	8.43	6.88	12.00
WW-0402	571550	STR	402	7.64	154	47.70	0.634	18.80	0.378	2.31	8.46	6.93	12.50
WW-0430	571553	STR	430	7.56	157	49.50	0.578	20.00	0.393	2.51	8.45	8.72	11.70
WW-0516	551960	STR	516	7.44	161	50.10	0.555	19.90	0.366	2.49	8.16	9.38	11.20
WW-0586	477682	STR	586	7.46	160	49.30	0.534	20.10	0.372	2.54	8.28	9.18	11.20
WW-0636	571557	STR	636	7.44	155	47.80	0.481	19.20	0.381	2.48	7.96	9.03	11.50
WW-0919	536512	STR	919	7.43	147	45.40	0.435	18.30	0.393	2.49	7.68	8.43	9.95
WW-1031	120824	STR	1031	7.42	146	44.00	0.433	18.20	0.359	2.49	7.60	9.22	10.30
WW-1053	571561	STR	1053	7.42	144	44.30	0.426	17.80	0.377	2.45	7.46	8.31	10.10
WW-1197	571562	STR	1197	7.43	143	44.90	0.426	18.20	0.379	2.51	7.62	8.42	10.00
WW-1259	553443	STR	1259	7.50	143	45.10	0.425	17.60	0.360	2.45	7.36	8.42	10.10
WW-1328	553444	STR	1328	7.54	144	44.20	0.423	18.10	0.372	2.53	7.53	8.49	9.51
WW-1394	571564	STR	1394	7.47	143	45.50	0.421	18.10	0.393	2.55	7.56	8.52	10.00
WW-1456	553446	STR	1456	7.49	143	44.50	0.419	17.90	0.370	2.52	7.45	8.67	9.98
WW-1506	571567	STR	1506	7.52	141	42.60	0.400	17.50	0.350	2.52	7.34	8.40	9.70
WW-1733	481028	STR	1733	7.46	132	40.40	0.391	15.90	0.366	2.50	6.84	8.20	9.11
Inflow sites													
LBI-0053	571546	LBI	53	7.87	143	43.40	0.014	16.40	0.328	2.26	9.61	5.24	12.70
RBI-0080	571570	RBI	80	7.43	100	34.50	0.016	12.10	0.335	2.28	4.57	6.12	4.66
LBI-0154	571548	LBI	154	7.40	79.1	26.70	0.016	7.36	0.288	3.05	4.10	5.97	3.60
RBI-0225	WW-ADHOC-X6	RBI	225	6.98	115	37.50	0.015	13.10	0.214	2.20	7.09	4.24	8.32
LBI-0411	571551	LBI	411	7.43	168	52.30	0.014	21.70	0.416	2.86	7.77	12.90	10.10
RBI-0412	571552	RBI	412	7.11	110	36.40	0.014	13.20	0.374	2.18	5.64	5.20	5.80
LBI-0496	571554	LBI	496	7.23	176	55.30	0.016	23.60	0.455	3.10	7.22	14.80	8.89
RBI-0595	571555	RBI	595	6.60	172	no data	0.015	no data	no data	no data	no data	12.30	12.80
RBI-0597	571556	RBI	597	7.17	47.1	10.70	0.014	3.62	0.187	1.73	3.96	3.58	4.57
LBI-0794	571558	LBI	794	7.10	51.6	16.20	0.014	4.65	0.245	1.89	4.24	2.59	3.82
RBI-1046	571559	RBI	1046	7.14	90.5	29.80	0.014	10.30	0.311	2.47	3.93	6.13	4.19
RBI-1051	571560	RBI	1051	6.90	104	27.40	0.015	11.40	0.394	2.95	3.64	12.90	4.36
LBI-1245	WW-ADHOC-X5	LBI	1245	7.21	61.1	22.30	0.016	5.58	0.142	3.11	3.36	0.10	4.11
LBI-1364	571563	LBI	1364	6.95	39.6	9.37	0.015	3.94	0.194	1.62	3.03	0.10	3.70
LBI-1407	571565	LBI	1407	7.14	56.3	20.90	0.016	4.90	0.130	1.98	3.56	0.10	3.98
LBI-1437	WW-ADHOC-X4	LBI	1437	7.32	51.2	18.50	0.016	2.06	0.116	0.75	2.22	3.53	3.08
LBI-1465	571566	LBI	1465	7.30	69.7	23.90	0.014	4.31	0.273	2.31	3.87	2.42	4.15
RBI-1667	571568	RBI	1667	7.24	57.5	13.10	0.014	4.30	0.309	2.80	4.36	5.15	5.42

Appendix 2. Total recoverable metal concentrations in Wanlock Water, Dumfries and Galloway, September 2019.

SiteID	SEPAID	Al [µg/L]	As [µg/L]	Cd [µg/L]	Cr [µg/L]	Cu [µg/L]	Ni [µg/L]	Pb [µg/L]	Zn [µg/L]	Fe [µg/L]	Mn [µg/L]
Stream sites											
WW-BK	571545	<11	<2.0	1.55	<0.5	1.00	<0.35	14.6	109.0	5.0	2.5
WW-0049	562186	<11	<2.0	1.57	<0.5	1.05	<0.35	15.7	109.0	5.0	2.5
WW-0066	557476	<11	<2.0	1.58	<0.5	no data	<0.35	15.0	154.0	5.0	2.5
WW-0141	571547	<11	<2.0	1.56	<0.5	1.05	<0.35	16.4	112.0	5.0	2.5
WW-0172	571549	<11	<2.0	1.43	<0.5	1.05	<0.35	17.1	102.0	15.0	2.5
WW-0314	120447	<11	<2.0	1.68	<0.5	1.20	0.36	20.0	123.0	5.0	2.5
WW-0402	571550	<11	<2.0	1.68	<0.5	1.34	<0.35	23.0	128.0	15.0	2.5
WW-0430	571553	<11	<2.0	2.38	<0.5	1.84	0.61	22.1	200.0	12.0	2.5
WW-0516	551960	<11	<2.0	2.92	<0.5	2.06	0.72	40.2	264.0	13.0	2.5
WW-0586	477682	<11	<2.0	3.20	<0.5	2.30	0.79	36.2	288.0	12.0	2.5
WW-0636	571557	<11	<2.0	2.78	<0.5	2.00	0.74	34.5	255.0	18.0	2.5
WW-0919	536512	<11	<2.0	2.59	<0.5	2.14	0.79	119.0	254.0	33.0	9.0
WW-1031	120824	<11	<2.0	2.62	<0.5	2.09	0.84	60.1	253.0	35.0	9.0
WW-1053	571561	<11	<2.0	2.64	<0.5	1.99	0.78	32.3	247.0	35.0	9.0
WW-1197	571562	<11	<2.0	2.65	<0.5	1.93	0.79	38.4	259.0	33.0	10.0
WW-1259	553443	<11	<2.0	2.75	<0.5	2.04	0.85	35.9	261.0	35.0	10.0
WW-1328	553444	<11	<2.0	2.77	<0.5	2.05	0.85	45.1	271.0	43.0	13.0
WW-1394	571564	26.8	<2.0	3.07	<0.5	3.09	0.95	128.0	300.0	86.0	14.0
WW-1456	553446	11.1	<2.0	2.98	<0.5	3.36	0.88	45.1	295.0	46.0	13.0
WW-1506	571567	21.3	<2.0	2.95	<0.5	3.11	0.88	41.3	283.0	60.0	13.0
WW-1733	481028	13.8	<2.0	2.88	<0.5	3.37	1.07	61.7	273.0	54.0	17.0
Inflow sites											
LBI-0053	571546	<11	<2.0	0.49	<0.5	0.82	<0.35	19.8	30.2	5.0	2.5
RBI-0080	571570	<11	<2.0	0.67	<0.5	2.70	0.39	33.8	53.4	24.0	2.5
LBI-0154	571548	12.8	<2.0	0.35	<0.5	0.68	0.41	7.9	40.4	54.0	5.0
RBI-0225	WW-ADHOC-X6	11.8	<2.0	0.15	<0.5	0.70	0.37	7.1	10.1	16.0	2.5
LBI-0411	571551	<11	<2.0	4.63	<0.5	3.67	1.36	32.3	426.0	10.0	2.5
RBI-0412	571552	<11	<2.0	0.14	<0.5	0.43	<0.35	3.5	10.5	5.0	2.5
LBI-0496	571554	<11	<2.0	7.03	<0.5	4.30	1.76	68.7	741.0	5.0	6.0
RBI-0595	571555	70	<2.0	0.39	<0.5	2.50	0.67	22.7	89.8	110.0	5.0
RBI-0597	571556	27.2	<2.0	0.05	<0.5	0.48	0.68	13.6	3.6	94.0	7.0
LBI-0794	571558	31.7	<2.0	0.03	0.57	0.49	0.67	3.0	4.1	133.0	14.0
RBI-1046	571559	<11	<2.0	2.94	<0.5	2.44	1.77	23.5	421.0	14.0	16.0
RBI-1051	571560	49.7	<2.0	10.40	<0.5	3.72	1.11	314.0	1150.0	125.0	23.0
LBI-1245	WW-ADHOC-X5	153	<2.0	0.07	<0.5	0.69	0.93	32.6	12.4	393.0	10.0
LBI-1364	571563	229	<2.0	4.39	0.57	14.90	2.18	1060.0	669.0	316.0	74.0
LBI-1407	571565	137	<2.0	4.28	<0.5	15.50	1.11	685.0	561.0	163.0	23.0
LBI-1437	WW-ADHOC-X4	226	<2.0	4.09	0.66	21.20	1.46	3100.0	457.0	351.0	39.0
LBI-1465	571566	31.9	<2.0	0.03	<0.5	1.73	0.84	21.3	4.4	140.0	19.0
RBI-1667	571568	24.2	<2.0	0.68	<0.5	2.11	1.92	13.4	61.5	104.0	27.0

Appendix 3. Dissolved metal concentrations in Wanlock Water, Dumfries and Galloway, September 2019.

SiteID	SEPAID	Al [µg/L]	As [µg/L]	Cd [µg/L]	Cr [µg/L]	Cu [µg/L]	Ni [µg/L]	Pb [µg/L]	Zn [µg/L]	Fe [µg/L]	Mn [µg/L]
Stream sites											
WW-BK	571545	<11	<2.0	1.61	<0.5	0.978	<0.35	1.78	109	5	2.5
WW-0049	562186	<11	<2.0	1.59	<0.5	0.95	<0.35	2.02	109	5	2.5
WW-0066	557476	<11	<2.0	1.52	<0.5	1.34	<0.35	1.02	154	5	2.5
WW-0141	571547	<11	<2.0	1.57	<0.5	0.923	<0.35	1.02	112	5	2.5
WW-0172	571549	<11	<2.0	1.43	<0.5	0.901	<0.35	1.44	102	5	2.5
WW-0314	120447	<11	no data	no data	no data	no data	no data	no data	123	5	2.5
WW-0402	571550	<11	<2.0	1.61	<0.5	1.11	<0.35	1.39	128	5	2.5
WW-0430	571553	<11	<2.0	2.4	<0.5	1.41	0.625	1.47	200	5	2.5
WW-0516	551960	<11	<2.0	3.01	<0.5	1.7	0.733	2.27	264	5	2.5
WW-0586	477682	<11	no data	no data	no data	no data	no data	no data	288	13	2.5
WW-0636	571557	<11	<2.0	2.83	<0.5	1.62	0.758	2.85	255	5	2.5
WW-0919	536512	<11	<2.0	2.56	<0.5	1.76	0.8	24.4	254	17	8
WW-1031	120824	<11	no data	no data	no data	no data	no data	no data	253	16	8
WW-1053	571561	<11	<2.0	2.66	<0.5	1.61	0.819	6.57	247	16	8
WW-1197	571562	<11	<2.0	2.71	<0.5	1.64	0.845	9.51	259	18	9
WW-1259	553443	<11	<2.0	2.53	<0.5	1.73	0.829	11.1	261	20	10
WW-1328	553444	<11	<2.0	2.81	<0.5	1.68	0.857	12.8	271	21	11
WW-1394	571564	<11	<2.0	2.84	<0.5	2.02	0.87	15.4	300	23	11
WW-1456	553446	<11	<2.0	3.07	<0.5	1.78	0.875	18.8	295	23	11
WW-1506	571567	<11	<2.0	2.8	<0.5	1.71	0.893	13.2	283	24	12
WW-1733	481028		<2.0	2.92	<0.5	1.8	1.01	19.7	273	34	16
Inflow sites											
LBI-0053	571546	<11	<2.0	0.471	<0.5	0.788	<0.35	1.59	30.2	5	2.5
RBI-0080	571570	<11	<2.0		<0.5	2.65	0.387	7.76	53.4	14	2.5
LBI-0154	571548	<11	<2.0	0.314	<0.5	0.633	0.411	3.36	40.4	18	2.5
RBI-0225	WW-ADHOC-X6	<11	<2.0	0.114	<0.5	0.626	0.371	0.634	10.100	5	2.5
LBI-0411	571551	<11	<2.0	4.41	<0.5	2.6	1.4	3.36	426	5	2.5
RBI-0412	571552	<11	no data	no data	no data	no data	no data	no data	10.5	5	2.5
LBI-0496	571554	<11	<2.0	7.37	<0.5	3.61	1.88	10	741	5	5
RBI-0595	571555	<11	<2.0	0.281	<0.5	1.44	0.493	4.56	89.8	20	2.5
RBI-0597	571556	12.1	<2.0	0.028	<0.5	0.455	0.688	5.88	3.6	52	6
LBI-0794	571558	18.8	<2.0	0.023	<0.5	0.466	0.602	1.9	4.14	77	12
RBI-1046	571559	<11	<2.0	3.04	<0.5	2.34	1.78	2.37	421	5	14
RBI-1051	571560	<11	<2.0	10.3	<0.5	1.7	0.973	11.6	1150	12	16
LBI-1245	WW-ADHOC-X5	128	<2.0	0.05	<0.5	no data	0.966	19.3	12.4	300	7
LBI-1364	571563	207	<2.0	0.138	<0.5	0.41	<0.35	0.351	669	277	71
LBI-1407	571565	<11	<2.0	4.12	<0.5	9.33	0.838	114	561	34	20
LBI-1437	WW-ADHOC-X4	108	<2.0	3.94	<0.5	17	1.25	1860	457	218	38
LBI-1465	571566	18	<2.0	0.019	<0.5	0.477	0.85	10.1	4.44	82	17
RBI-1667	571568	11	<2.0	0.597	<0.5	0.632	1.89	4.7	61.5	39	25

Appendix 4. Metal loads calculated in Wanlock Water, Dumfries and Galloway, September 2019.

L = instream load. ΔL = change in load. CL = cumulative instream load.

SiteID	SEPAID	Cd Dissolved [mg/s]			Cd Total [mg/s]			Pb Total [mg/s]		
		L	ΔL	CL	L	ΔL	CL	L	ΔL	CL
WW-BK	571545	0.22	0.22	0.22	0.21	0.22	0.22	0.24	0.28	0.28
WW-0049	562186	0.22	-0.01	0.22	0.22	0.00	0.22	0.28	0.03	0.31
WW-0066	557476	0.23	0.01	0.23	0.23	0.01	0.23	0.15	-0.13	0.31
WW-0141	571547	0.23	0.00	0.23	0.23	0.00	0.23	0.15	0.00	0.31
WW-0172	571549	0.22	-0.01	0.23	0.22	-0.01	0.23	0.22	0.07	0.39
WW-0314	120447	0.27	0.04	0.27	0.27	0.04	0.28	0.25	0.03	0.41
WW-0402	571550	0.28	0.01	0.28	0.28	0.01	0.29	0.23	-0.02	0.41
WW-0430	571553	0.43	0.15	0.44	0.43	0.15	0.44	0.27	0.04	0.45
WW-0516	551960	0.55	0.12	0.56	0.55	0.12	0.56	0.43	0.16	0.61
WW-0586	477682	0.63	0.08	0.63	0.63	0.08	0.64	0.56	0.13	0.74
WW-0636	571557	0.61	-0.02	0.63	0.61	-0.02	0.64	0.62	0.06	0.81
WW-0919	536512	0.63	0.02	0.65	0.63	0.02	0.66	5.90	5.28	6.09
WW-1031	120824	0.64	0.01	0.67	0.64	0.01	0.67	2.45	-3.45	6.09
WW-1053	571561	0.65	0.02	0.68	0.65	0.02	0.68	1.62	-0.83	6.09
WW-1197	571562	0.65	0.00	0.68	0.65	0.00	0.69	2.35	0.73	6.81
WW-1259	553443	0.68	0.03	0.71	0.68	0.03	0.71	2.75	0.40	7.21
WW-1328	553444	0.69	0.01	0.72	0.69	0.01	0.72	3.19	0.44	7.65
WW-1394	571564	0.77	0.08	0.80	0.77	0.08	0.80	3.85	0.67	8.32
WW-1456	553446	0.75	-0.02	0.80	0.75	-0.02	0.80	4.73	0.87	9.19
WW-1506	571567	0.78	0.03	0.83	0.78	0.03	0.83	3.48	-1.24	9.19
WW-1733	481028	0.78	-0.00	0.83	0.78	-0.00	0.83	5.32	1.84	11.03

Appendix 4 continued. Metal loads calculated in Wanlock Water, Dumfries and Galloway, September 2019. L = instream load. ΔL = change in load. CL = cumulative instream load.

SiteID	SEPAID	Pb Dissolved [mg/s]			Zn Dissolved [mg/s]		
		L	ΔL	CL	L	ΔL	CL
WW-BK	571545	2.00	2.16	2.16	14.97	14.97	14.97
WW-0049	562186	2.16	0.15	2.31	14.97	0.00	14.97
WW-0066	557476	2.17	0.02	2.32	22.29	7.33	22.29
WW-0141	571547	2.43	0.26	2.58	16.62	-5.68	22.29
WW-0172	571549	2.67	0.24	2.82	15.93	-0.69	22.29
WW-0314	120447	3.17	0.50	3.32	19.47	3.55	25.84
WW-0402	571550	3.77	0.60	3.92	20.99	1.51	27.36
WW-0430	571553	3.98	0.21	4.14	36.06	15.07	42.43
WW-0516	551960	7.56	3.57	7.71	49.63	13.57	56.00
WW-0586	477682	7.08	-0.48	7.71	56.34	6.71	62.71
WW-0636	571557	7.52	0.44	8.15	55.57	-0.77	62.71
WW-0919	536512	28.78	21.26	29.41	61.43	5.86	68.57
WW-1031	120824	14.60	-14.17	29.41	61.48	0.05	68.62
WW-1053	571561	7.98	-6.62	29.41	61.05	-0.43	68.62
WW-1197	571562	9.49	1.51	30.91	64.01	2.97	71.58
WW-1259	553443	8.89	-0.60	30.91	64.67	0.65	72.24
WW-1328	553444	11.23	2.33	33.25	67.47	2.81	75.04
WW-1394	571564	32.03	20.80	54.05	75.06	7.59	82.63
WW-1456	553446	11.34	-20.69	54.05	74.18	-0.88	82.63
WW-1506	571567	10.90	-0.44	54.05	74.68	0.50	83.14
WW-1733	481028	16.67	5.77	59.82	73.77	-0.91	83.14

Glossary

Conservative transport – The transport of an element or compound in a stream without chemical reaction.

Cumulative instream load – The cumulative instream load for an element or compound in stream water is the total amount of mass added to the stream.

Diffuse source – A dispersed and possibly episodic discharge of water or mine water from a mine feature to a stream. Diffuse sources could include surface and subsurface drainage from mine spoil during rainfall, groundwater efflux through a streambed, or remobilisation of particle bound metals to dissolved phases in the hyporheic zone.

Effective inflow concentration – Effective inflow concentration represents the average element or compound concentration entering a stream segment via surface and / or subsurface flow.

Hyporheic zone – Typically defined as a zone of ground (including subsurface) water and surface water interaction in a stream corridor. The hyporheic zone can encompass the streambed and streambanks.

Instream load – Instream load is the mass load of an element or compound at any point in a stream calculated as the product of the constituent concentration and streamflow.

Non-conservative transport – Also termed 'reactive transport', non-conservative transport refers to an element or compound in a stream that is undergoing chemical transformations that can change its stream concentration.

Plateau – In a tracer dilution and synoptic sampling experiment, this is the point where there is no, or very small, changes in the tracer concentration, as measured at a fixed point in the study area.

Point source – A direct and clearly identifiable discharge of water or mine water from a mine feature to a stream that may also be episodic. Point sources could include drainage from a pipe, adit or shaft, as well smaller tributary-type surface flows from mine wastes.

Steady-state – This refers to a system where a key parameter determining the behaviour of the system remains constant in time. In this report, steady-state refers to the flow rate of the tracer injection pump and streamflow in the Wanlock Water.

Synoptic sampling – Synoptic sampling is the collection of multiple water quality and streamflow samples at the same time (or within a window of a few hours during steady state conditions) from the same locations.

Tracer dilution – The observed dilution of an injected conservative tracer in a stream used to derive streamflow estimates.