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Spatial and temporal (annual and decadal) trends of metal(loid) concentrations and loads in an acid mine drainage-affected river

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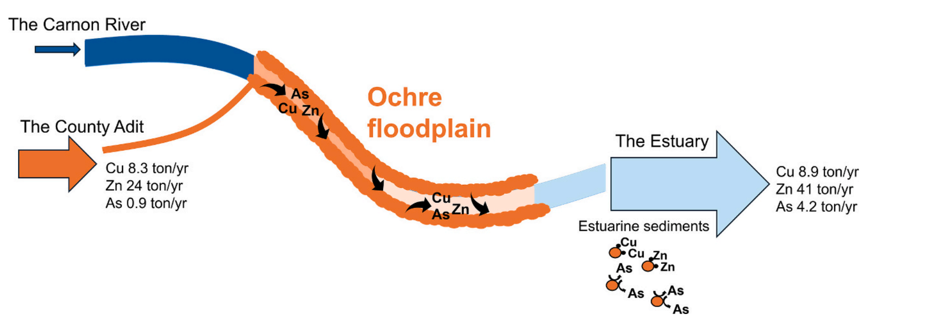
HIGHLIGHTS

- Legacy AMD discharges can cause long-term liabilities for receiving rivers.
- 22 years of aqueous data reveal increasing As and Fe export to the coastal zone.
- Discharge drives Cu and Zn release, while pH and Eh influence Fe, S and As mobility.
- Carnon River metal(loid) yield into the estuary is comparable to other AMD rivers.
- Diffuse sources are key contributors of metal(loid)s to the Carnon River.

GRAPHICAL ABSTRACT



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ABSTRACT

Acid mine drainage (AMD) is a worldwide problem that degrades river systems and is difficult and expensive to remediate. To protect affected catchments, it is vital to understand the behaviour of AMD-related metal(loid) contaminants as a function of space and time. To address this, the sources, loads and transport mechanisms of arsenic (As), copper (Cu), zinc (Zn), iron (Fe) and sulfur (S) in a representative AMD-affected catchment (the Carnon River in Cornwall, UK) were determined over a 12-month sampling period and with 22 years of monitoring data collected by the Environment Agency (England) (EA). The main source of metal(loid)s to the Carnon River was the County Adit which drains AMD from approximately 60 km of underground historical mine workings. Maximum aqueous concentrations of Fe, Cu and Zn occurred immediately downstream of the County Adit confluence with the Carnon River, whereas maximum As and S concentrations occurred further downstream, suggesting the presence of diffuse sources. Discharge and concentration relationships suggested that discharge drove Cu and Zn release, whereas pH and Eh influenced Fe, S, and As mobility. Total loads (represented by unfiltered sample contaminant concentrations) to the coastal zone were high, ranging from 183 to 354 kg/month As, 307–742 kg/month Cu, 189–1960 kg/month Fe, 53,400–125,000 kg/month S and 1280–3320 kg/

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month Zn. The longevity and increasing amounts of contaminant discharge were confirmed with 22 years of EA monitoring data. This study highlights the complex and multifaceted behaviour of contaminant metal(loid)s within AMD-affected riverine systems and the fact that point and diffuse sources can constitute significant long-term liabilities for such environments.

1. Introduction

Acid mine drainage (AMD) is the outflow of acidic water caused by the oxidation of pyrite and other redox-active sulfidic minerals typical of mining metal and coal ores (Akcil and Koldas, 2006; Crane and Sapsford, 2018). AMD can generate ecotoxic conditions due to low pH (<6) and high concentrations of sulfate (SO_4^{2-}), iron (Fe) and metal(loid)s including arsenic (As), copper (Cu) and zinc (Zn) (Environment Agency, 2008; Nordstrom et al., 2015). Approximately 20–50 thousand mines worldwide discharge AMD into surrounding river systems (Rezaie and Anderson, 2020). AMD treatment is challenging and expensive (Johnson and Hallberg, 2005; Akcil and Koldas, 2006) estimates for total global AMD remediation cost are often in the order of US$100 bn, and as a result, AMD-affected rivers are frequently left untreated (Hudson-Edwards et al., 2011; Lottermoser, 2015; Tremblay and Hogan, 2016).

AMD-derived metal(loid)s can be concentrated in aqueous and sediment phases, posing spatial and temporal environmental hazards (Johnson and Thornton, 1987). River sediment-borne As, Cu, Zn and Fe, for example, can be remobilised due to both physical (e.g. enhanced erosion during a storm event) and/or geochemical processes (e.g. reductive dissolution of metal(loid)-bearing Fe (oxy)hydroxides) (Balistrieri et al., 2007; Lynch et al., 2014; Cánovas et al., 2014).

The major controls on the spatial and temporal variabilities of aqueous metal(loid) behaviour in mining-affected rivers have been shown to be source type (Lottermoser, 2010), pH (Hierro et al., 2014; Jarvis et al., 2019), redox potential (Lynch et al., 2014), discharge (Byrne et al., 2013; Onnis et al., 2023), dilution from sources and streams with low metal(loid) concentrations (Olías et al., 2020), and rainfall (Sarmiento et al., 2009). For example, an inverse relationship between pH and metal(loid) concentrations has been recorded in the AMD-affected Huelva Estuary (Spain) (Hierro et al., 2014) and Coledale Beck (UK) (Jarvis et al., 2019). Jarvis et al. (2019) observed increased metal(loid) release at higher river discharge due to inputs of low pH runoff from acid peat soils in Coledale Beck (UK). AMD metal(loid)s can also be mobilised during stormflow events as a result of dissolution of efflorescent metal sulfates (Sarmiento et al., 2009) and flushing of soil and sediment porewaters (Byrne et al., 2013).

Monitoring metal(loid) loads is fundamental for source apportionment (Kimball et al., 2002; Byrne et al., 2020). Spatial sampling and synchronous discharge (tracer injection and salt dilution gauging) measurement methods were used in Nant Cwmnewyddion (UK) over a hydrological cycle to identify diffuse and point sources of aqueous metals under different discharge conditions (Onnis et al., 2023). A synoptic discharge monitoring method (velocity-area) was used by Banks and Palumbo-Roe (2010) to identify previously unknown point, discrete and diffuse sources, along with Zn sinks in rivers in the northern Pennines (UK). Source apportionment is especially important in identifying diffuse sources, which may become more prominent with increased flooding from predicted increased rainfall due to climate change (Foulds et al., 2014; Arnell et al., 2015).

Despite detailed studies like these, there remains a relatively limited understanding of the annual (seasonal) and decadal (10s of years) trends of riverine geochemistry, metal(loid) concentration and load in AMD-affected catchments, often due to a lack of monitoring data. Such

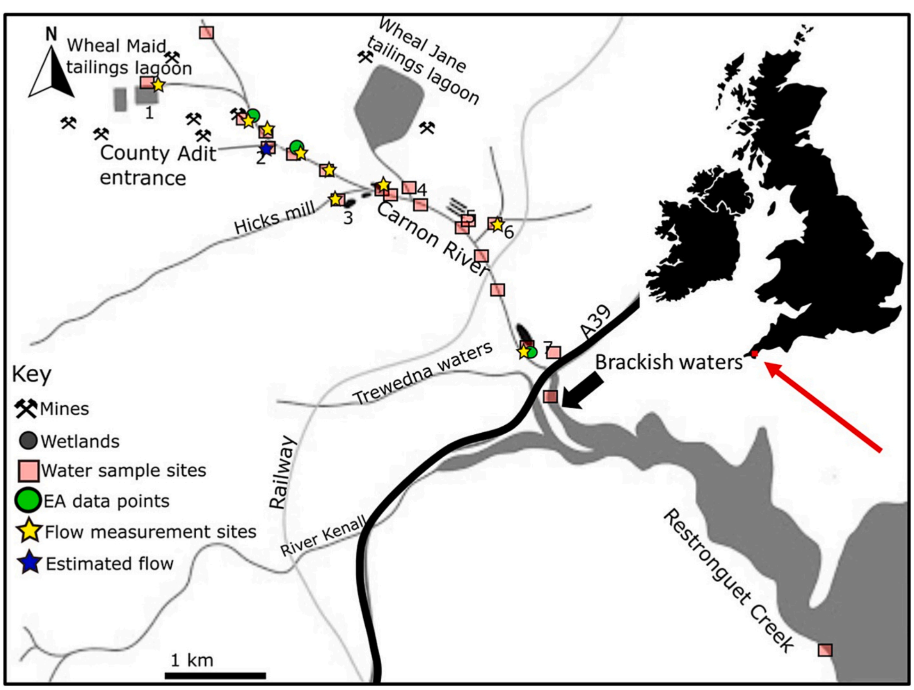

Fig. 1. Location of the Carnon River and Restronguet Creek sample sites used in this study. Sample locations from the Environment Agency are indicated as circles. For this study, squares stars represent water samples and flow measurements. EA data points are monitoring sites. Numbered inputs refer to adit inputs and tributaries of the Carnon River. Input 1 – Wheal Maid sites. Input 2 – County Adit (Wellington and Nangiles Adit) (discharge estimate taken) Input 3 – Hicks Mill (historic As calciner) (discharge measured) Input 4 – Wheal Jane Adit (no discharge measured) Input – 5 Potential Adit (no discharge measured) Input 6 – Grenna Lane Bridge (discharge measured) Input 7 – Downstream Devoran Bridge wetland (no discharge measured). Downstream of the A39 road is the fresh- and seawater mixing zone (4.6 km). Sample details are provided in the supplementary information (S.I.) in S1.

knowledge is essential in understanding and predicting metal(loid) fate and designing effective remediation strategies. To address this gap, this work investigated metal(loid) behaviour along the length of an AMD-affected river over different hydrological conditions over one year. To address the temporal controls on metal(loid) distribution, an analysis of instream concentration and discharge data collected between 2000 and 2021 by the Environment Agency (England) (EA) was also conducted. The outcomes of this study are intended to provide a fundamental mechanistic understanding of the dynamic behaviour and fate of key AMD-generated metal(loid) contaminants (As, Cu, Fe and Zn) within riverine systems as a function of changing hydrological conditions and time. Such detailed knowledge is essential for accurately informing river management policy in the future.

2. Methods and materials

2.1. Area of study

The Carnon River in Cornwall, SW England, is 14 km long, has a catchment area of 31 km^2, and discharges into the tidally affected Restronguet Creek (Environment Agency, 2020a, 2020b) (Fig. 1). The river is underlain by silt and sandstones from the Mylor Slate Formation and hosts mineral veins containing As-Cu-Fe-Pb-Zn sulfides, cassiterite (SnO_2) and wolframite ($(Fe, Mn)WO_4$) (Embrey and Symes, 1987; Pirrie et al., 2002). Mining in the Carnon River catchment began in the Bronze Age and continued intermittently until the closure of Wheal Jane in 1991 (Embrey and Symes, 1987; Pirrie et al., 2003; Rainbow, 2020). The river receives AMD from legacy mining sources, including the County Adit, Nangiles Adit, and Wellington Adit (Pirrie et al., 2002). The County Adit is an underground gallery connecting over 60 km of historical mine workings and is one of the most contaminated water bodies in the UK, estimated to provide 26 % of Fe (together with the Dolcoath Adit) and 67 % of As to England and Wales's overall load from abandoned mines to estuaries (Mayes et al., 2010). At its operational peak in the 1890s, the County Adit discharged over 65 million L daily of metal(loid) contaminated water into the Carnon River (Buckley, 1992; Rainbow, 2020). The river has also been affected by infrequent large-scale events, such as the flooding of the Wheal Jane Mine in January 1992 when 50 million L of pH 3.1, metal(loid)-bearing mine water was accidentally discharged (Banks et al., 1997; Pirrie et al., 2002). Since 1994, water from the former underground workings at Wheal Jane Mine has been treated before release to the Carnon River (near input 4, 2.17 km; Fig. 1) (Environment Agency, 2022).

The Carnon River is recognised as AMD-affected and has been investigated for many decades (e.g., Bryan and Gibbs, 1983; Pirrie et al., 2003; Meyer et al., 2019). However, a full understanding of the temporal and spatial trends and sources of metal(loids) in the Carnon River has yet to be established. Additionally, discharge data have been recorded at very few sites along the river, and contaminant loads have been recorded only for Restronguet Creek and the County Adit (Mayes et al., 2010; Mayes et al., 2013). The lack of discharge data compromises the reliability of source apportionment exercises, since mass input and export of metal(loid)s cannot be quantified by concentration data alone (Kimball et al., 2002; Runkel et al., 2018). The mining history and short length (14 km) of the Carnon River allowed for an extensive investigation into the behaviour of the aqueous metal(loid)s from source to sink.

2.2. Water sampling and discharge measurements

To determine the months that best represented the hydrological cycle captured by low (Q75), medium (Q50) and high-discharge (Q25) Carnon River behaviour, an analysis of river flow archive data (NRFA) was conducted (NRFA, 2021) (S.I. section S2). Meteorological data were not included in determining the sampling months due to its limited ability in representing site specific hydrological conditions (Stewart, 2015; Frassl et al., 2018). As a result of the analysis, the months chosen were April 2021 (lower mid Q50–75), August 2021 (low Q75), November 2021 (upper mid Q25–50) and February 2022 (high Q25). Discharge monitoring data from the NRFA were collected at Bissoe (1.6 km, Fig. 1 input 3), and low, medium, and high discharge were defined as <330 L/s, 330–552 L/s and >948 L/s, respectively.

Water samples and discharge and aqueous geochemical measurements were taken at 21 sites in the Carnon River catchment in each of the four sampling months. The sampling sites were selected to capture inputs from all main tributaries and adits while having regular spacing to account for diffuse metal(loid) inputs or attenuation, where inputs could not be seen (Fig. 1). The number of accessible sampling sites varied throughout the year, as some became either accessible or inaccessible due to seasonal or logistical constraints. During the sampling campaigns river discharge, water turbidity and embankment shape and colour data were collected.

At each site, two water aliquots were taken. One aliquot was filtered through a cellulose 0.45 μm filter, and the other was unfiltered. Both were collected in 30 mL clean polyethylene bottles and acidified with 2 mL of 5 M HNO_3. Unfiltered samples were defined as comprising suspended particulate and dissolved aqueous phases and filtered samples were defined as comprising <0.45 μm suspended particles and dissolved aqueous phases (Buffle and Leppard, 1995a, 1995b). Locations influenced by the tide (south of the A39; Fig. 1) were sampled at the same tidal height (mid-tide) during each sampling campaign to minimise tide-induced geochemical variability. Additional samples were taken at a wetland near Hicks Mill stream (input 3, 1.8 km) and from the Grenna Lane Bridge tributary (input 6, 3.12 km) in November 2021 and February 2022 (see S3 in S.I.). For quality assurance, two sites (representing 10 % of the sites) were selected randomly in each sampling campaign for field blanks and field duplicates. Field blanks were used to assess potential atmospheric contamination and were made by exposing deionised water to environmental conditions at the allocated site and preparing aliquots as per the filtered and unfiltered samples. Field duplicates were taken to assess the precision of sampling and analysis. In total, 172 samples were collected, comprising 86 unfiltered and 86 filtered samples. Sample locations and names are detailed in Table S1 in S.I.

Field measurements of pH and temperature (HACH sensION +mm156 multiprobe), electric conductivity (EC) (Fisherbrand Traceable Conductivity/TDS Meter Pen), and GPS (GARMIN etrex 10) were taken at each sampling site. The pH and EC were calibrated using Hanna Instruments pH 4.01, 7.01, 10.01, and EC 1413 μS/cm calibration solutions.

The salt dilution gauging method (slug injections; Moore, 2004; Jarvis et al., 2019) was chosen to measure river discharge velocity. This method was appropriate for this study because the Carnon River has a narrow width, deep cross-sections, varying velocities and an irregular riverbed (Moore, 2004). Nine of the twenty-one sample sites had discharge measured (Fig. 1). The other sites did not have the required length for the salt dilution method or were flooded. The load was calculated from the discharge measurement and concentration recorded at that time. The County Adit's discharge was estimated by subtracting the flows of the upstream (50.234 N, −5.139 W) and downstream (50.234 N, −5.139 W) sites of the County Adit confluence with the Carnon River, and by assuming that there were no diffuse sources in this segment. The latter site did not have any discharge recordings during November and February due to limited access to the site and issues with performing the slug injection, such as high suspended solids interfering with the EC recordings. The August 2021 discharge measurement was not taken at the 1.9 km site due to inaccessibility. Details on salt dilution gauging methods, source apportionment, effective inflow concentration calculations, attenuation and load calculations are given in S4 of the S.I.

To compare the Carnon River metal(loid) loads with other AMD systems, metal(loid) yields (tonnes/year/km^2) were calculated by dividing the load by the river's catchment area. The catchment area was calculated using the watershed feature on GIS (ArcGIS online ESRI).

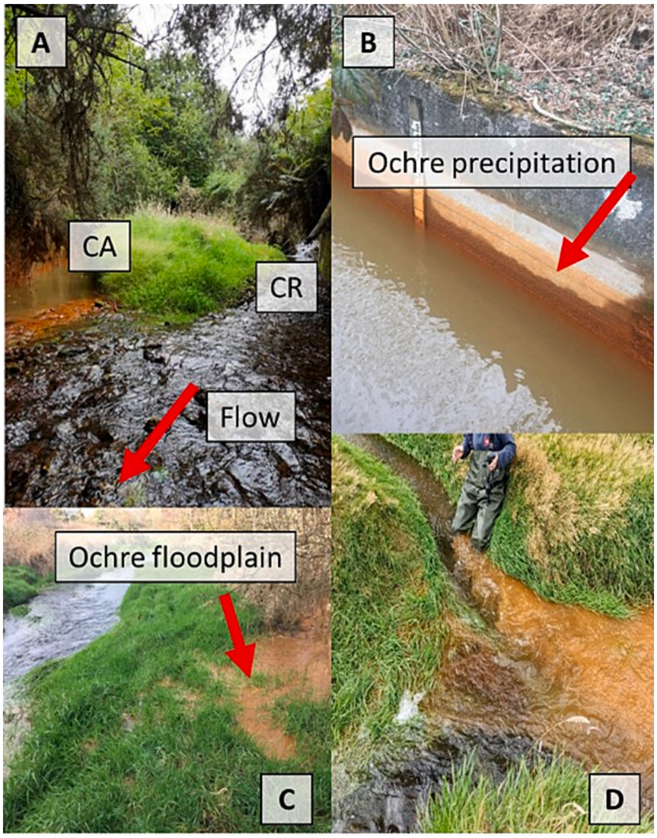

Fig. 2. Photographs of the Carnon River and County Adit taken between April 2021 and February 2022. (A) The confluence of the County Adit (CA) and Carnon River (CR); (B) Iron (oxy)hydroxide (ochre) precipitation on the culvert wall downstream of the confluence of the CR and CA; (C) Iron (oxy)hydroxide (ochre) rich floodplain; (D) Physical release of floodplain Fe (oxy)hydroxides (ochres) downstream of Bissoe (1.6 km) by agitation.

2.3. Geochemical analysis

Filtered acidified samples were analysed for As, Cu, and Zn by Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS; Agilent 7700×) and for Fe and S by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES; Agilent 5110 Series). Unfiltered acidified samples were analysed for As, Cu, Zn, Fe and S metal(loid) concentrations using the ICP-OES. Sulfur was analysed to interpret mechanisms in the Carnon River and is not a focus in this study.

The accuracy of the analysis was assessed using certified reference materials (CRM) for trace (QC1488_LRAC1572 Trace metals WS20mL) and major metal(loid)s (QC3041_LRAA8648 Mineral whole volume 500 mL) (1640a Trace metals in water). Accuracy was calculated as the coefficient of variation (CV%) between analysed and certified concentrations using Excel (2016) (see S5 in S.I. for CV% values and lower limit of detections). Concentration and load error bars were calculated from field duplicate CV% results due to inaccuracies (large CV%) in the CRM analysis described in S5 in S.I.

2.4. Chemodynamic and chemostatic relationships

The relationship between discharge and concentration was examined by plotting the power law relation (Eq. (1)) against the coefficient of variation of concentration (CV_C) and discharge (CV_Q) (Godsey et al., 2009; Koger et al., 2018):

$$C = aQ^b \tag{1}$$

where C is concentration, a is a constant, Q is discharge, and b is the log-log slope.

The concentration and discharge analysis can uncover the degree to which hydrology controls chemistry, and the concentration-discharge relationship can help to discern possible sources. The relationship between the discharge and concentration of each metal(loid) can be either chemostatic or chemodynamic. Chemostatic (defined as slope $b > \pm 0.1$ and CV_C/CV_Q is >0.5) indicates that the metal(loid) concentration is constant over the range of discharge values, while chemodynamic ($CV_C/CV_Q < 0.5$) behaviour indicates that concentration changes with changing water parameters (pH, alkalinity, redox, dissolved oxygen (%), temperature and EC) and discharge (Musolff et al., 2015). The power law relation can be documented as either a 'flushing' (concentration increases with increasing discharge) trend (slope $b > 0.1$) or a 'dilution' (concentration decreases with increasing discharge) trend (slope $b < -0.1$) (Godsey et al., 2009). Statistical analysis was performed using Origin Lab Pro. Simple linear regression fits between discharge and concentration were done to obtain the coefficient of variation (R^2). The standard error of the slope (S_b) was calculated to quantify how accurate the slope estimates are based on the sample data. Results of the statistical analysis (p-values) are presented in Table S6 (S.I.).

2.5. Environment agency (EA) data analysis

To examine decadal metal(loid) concentration trends in the Carnon River, time-series plots of unfiltered and filtered As, Fe, Cu, and Zn instream concentrations were produced using data collected between January 2000 and December 2021 (Environment Agency, 2021). Unfiltered Cl was also plotted to determine if the downstream part of the Carnon River was affected by sea water (Devoran Bridge, ~4.3 km). The data were collected at three sample points: upstream of the County Adit (50.234 N, −5.139 W) (unaffected by the County Adit) (0.65 km), downstream of the confluence of the County Adit and the Carnon River (50.234 N, −5.138 W) (directly affected by the County Adit) (0.94 km), and a downstream site which discharges into the estuary (50.214 N, −5.10 W) (4.3 km) (Fig. 1). Discharge data were also collected for Twelveheads and the County Adit – Carnon River confluence (from 2009) but none were available for the downstream estuary site. The selected sites and timeframe were extracted, summarised, and concatenated into a CSV file using Python (3.11). Discharge data were grouped and averaged for daily flow readings using Python (3.11). These data were then analysed with Origin Lab Pro (2023). The Mann-Kendall (MK) statistical test was used to determine temporal trends in EA time series data (2000−2021) (Hirsch and Slack, 1984) and was executed using a multitest (version 6.1) VBA macro on Excel (2016) (see Table S7 in S.I.).

Table 1
Unfiltered and filtered (<0.45 μm) concentrations of As, Cu, Fe, and Zn in the Carnon River from this study and earlier works. All concentrations are in mg/L.

	Bryan and Gibbs (1983) (n = 3)		Environment Agency (2021) (2000–2021) (n = 695)		This study (n = 172)	
	Unfiltered	Filtered	Unfiltered	Filtered	Unfiltered	Filtered
As	0.03–0.2	0.031–0.082	0.01–0.67	0.01–0.15	<0.0004–0.21	0.004–0.2
Cu	0.053–0.68	0.054–0.68	0.03–1.17	0.03–1.17	0.02–0.53	0.02–0.6
Fe	0.137–25	0.05–18.5	0.08–13	0.03–4.9	0.05–2.6	<0.003–0.9
Zn	0.93–12	0.95–12	0.29–3.4	0.78–2.6	0.42–1.95	0.4–2.2

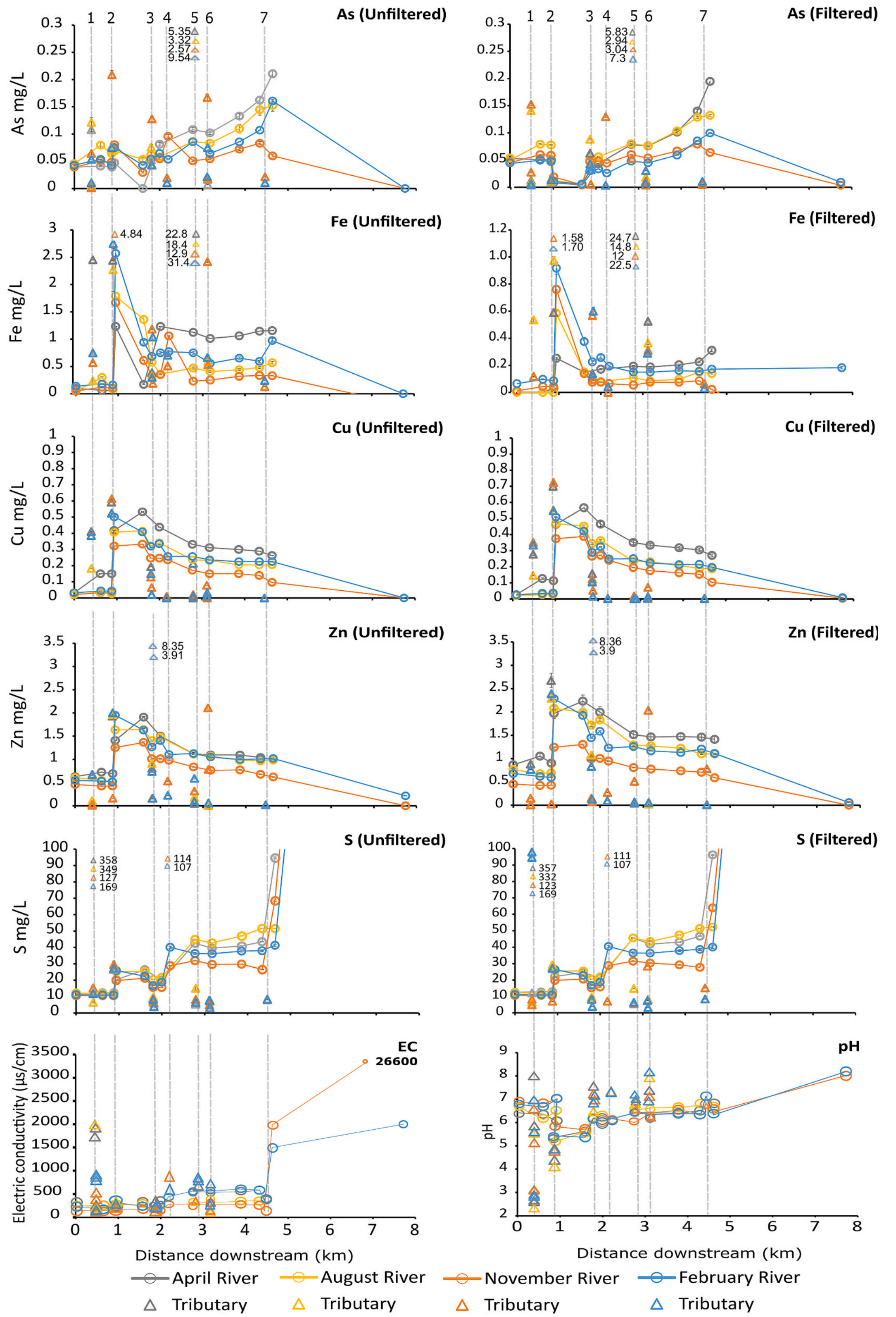

Fig. 3. Filtered (<0.45 μm suspended particulate and dissolved phases) and unfiltered (suspended particulate (>0.45 μm) and dissolved phases) metal(loid) concentrations and water parameters (pH and EC) vs distance downstream in April, August, November (2021) and February (2022). Locations of numbered incoming tributary sites (numbered vertical lines in Fig. 1) are as follows: input 1 is Wheal Maid (0.4 km), input 2 is the County Adit (0.88 km), input 3 is Hicks Mill stream (1.8 km), input 4 is Wheal Jane (2.17 km), input 5 is potential adit (2.79 km), input 6 is Grenna Lane Bridge tributary (3.12 km) and input 7 is the Devoran Bridge wetland (4.64 km)). 0 km is an unaffected site upstream of the County Adit – Carnon River confluence. Input 1 has been marked as 0.4 km to avoid confusion with the County Adit distance and placed in the correct position in the Carnon River.

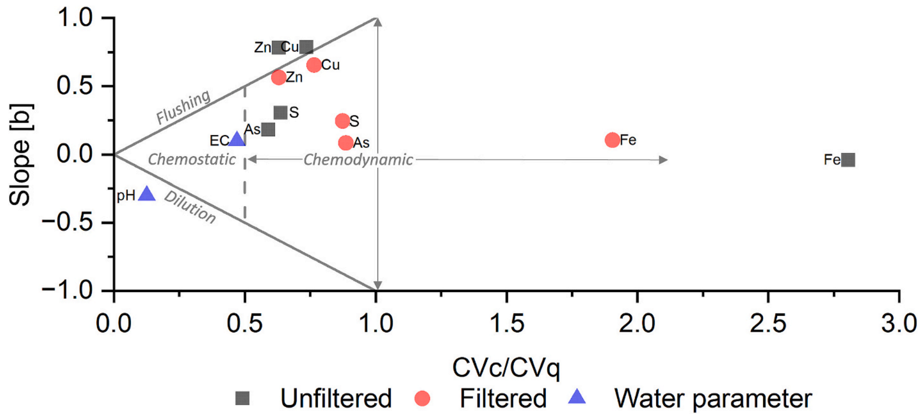

Fig. 4. Power law relation (slope [b]) vs coefficient of variation of concentration divided by the coefficient of variation of discharge (CVC/CVQ). The dashed line shows the definition between chemostatic and chemodynamic behaviour. The 0 to +1 line defines the 'flushing' trend. The 0 to −1 line defines the 'dilution' trend.

3. Results and discussion

3.1. Annual instream metal(loid) concentrations and loads, downstream trends, and sources in the Carnon River

3.1.1. Aqueous and geomorphological observations of the Carnon River catchment

The Carnon River underwent changes in river discharge, water turbidity and embankment shape and colour throughout the sampling year. The water changed from clear to cloudy after the County Adit – Carnon River confluence (0.94 km) and remained cloudy downstream (Figs. 2.A, 2.B). Iron (oxy)hydroxides (possibly including oxyhydroxysulfates but referred to in this paper collectively as Fe (oxy) hydroxides) (ochre) were volumetrically most abundant after the County Adit - Carnon River confluence and at Bissoe (1.6 km). The Fe (oxy)hydroxides were deposited onto floodplains between the confluence and 4.6 km (ochre floodplain in Fig. 2.C). During the sampling campaigns, they were physically mobilised from riverbanks and riparian areas during rainfall events and after agitation (Fig. 2.C, 2.D).

3.1.2. Annual downstream trends of instream metal(loid) concentrations and water parameters in the Carnon River catchment

Instream metal(loid) concentrations, pH and EC exhibited large ranges along the Carnon River (Table 1, Fig. 3), similar to those found in earlier studies (Bryan and Gibbs, 1983; Environment Agency, 2021). This variability was likely due to differing sampling times and riverine discharge throughout the year (discussed further in Section 3.2.).

The Carnon River EC was 142–250 μS/cm upstream of the County Adit – Carnon River confluence (0.94 km) and increased consistently throughout the sampling year at the confluence to 167–335 μS/cm, likely due to the input of aqueous ions including metal(loid)s from the County Adit (input 2, 0.88 km) (Fig. 3). Similarly, the increase in the Carnon River EC (279–443 μS/cm) at 2.19 km downstream was likely due to inputs of higher EC (567–850 μS/cm) waters from the Wheal Jane Adit (input 4, 2.17 km) Fig. 3). The EC further increased downstream of this confluence (2.19 km) to the estuary (7.74 km) to a maximum of 26,600 μS/cm (Fig. 3), likely due to the mixing with seawater at 4.6 km and inputs from tributaries with higher EC values (Fig. 3).

The pH in the Carnon River upstream of its confluence with the County Adit (0.94 km) was 6.04–7.02 and consistently decreased downstream of this point to 5.17–5.84 throughout the sampling year (Fig. 3). It then rose and remained constant (average pH 6.28) until the estuarine point (7.74 km), increasing further to 8–8.17. Water temperatures in the Carnon River ranged from 10 to 15.5 °C and 9.7 to 20.7 °C in the inputs (adits and tributaries) (Fig. S8 in S.I.). Throughout the sampling campaign, the river temperatures increased downstream of the County Adit confluence and of the Hicks Mill stream (input 2, 1.8 km) at 2 km (Fig. S8 in S.I.).

AMD-affected river systems have been shown to have elevated concentrations of metal(loid)s after confluences of point sources such as adits. Dilution from less contaminated tributaries typically cause these concentrations to recover to values recorded upstream of the confluence (Kimball et al., 2002; Cánovas et al., 2014). In the Carnon River, however, filtered and unfiltered Cu and Zn concentrations did not recover to those upstream of the confluence of the County Adit (0.94 km), but mostly increased or remained level at 1.6 km and decreased gradually downstream of the confluence to 7.74 km (Fig. 3). This can be explained by the chemodynamic (CV_C/CV_Q = 0.61–0.76) behaviour displayed by unfiltered and filtered Cu and Zn with a flushing trend in the Carnon (b = 0.57–0.79, R^2 = 0.03–0.1, S_b = 1.05E^{-04}-3.88E^{-04}) (Fig. 4, Table S6 in S.I.). This behaviour indicates that concentrations increased with river discharge and explains why the Cu and Zn did not decrease with dilution from tributaries with lower concentrations (Fig. 5). Flushing behaviour has been linked to metal(loid) mobilisation from exposed riverine sediments that can contain legacy mine waste (Byrne et al., 2013) and from erosion of river embankments (Kimball et al., 1995). In the Carnon River, such behaviour is reflected in the erosion of ochre floodplains (Fig. 2.D) that could contain Cu- and Zn-bearing Fe (oxy)hydroxides generated at the confluence with the County Adit.

Decreases in filtered and unfiltered As, Fe and S concentrations downstream of the County Adit – Carnon River confluence (0.94 km) (Fig. 3) likely reflect the formation of As-bearing Fe (oxy)hydroxide and oxyhydroxysulfate ochres. Fluctuations in these concentrations downstream of this point may reflect dissolution, erosion and dispersion of these ochre (Fig. 1.B, 1.D).

The difference between the effective inflow concentration for the stream segment (1.6–1.9 km) receiving the Hicks Mill stream input (input 3, 1.8 km) and the observed concentration of the inflow was mostly large (>41 %) for As, S and Fe. The difference between the effective inflow concentrations of As, S and Fe for the stream segment (1.9–4.3 km) receiving the potential adit input (input 5, 2.79 km) and the observed concentration of the inflow was 76 % (Table S9 in S.I.). This suggests that a portion of unsampled As, Fe and S existed, implying an additional source in the stream segments 1.6–4.3 km which could be groundwater or hyporheic zone water.

Unfiltered and filtered Fe, S and As exhibited a chemodynamic (CV_C/CV_Q = 0.59–2.8) behaviour with very weak flushing (b = −0.04-0.30, R^2 = −0.002-0.41, S_b = 2.39E^{-05}-6.10E^{-05}) (Fig. 4, Table S6 in S.I.). This suggests that although Fe, S and As concentrations vary with discharge, other factors may have more influence on their behaviour (Musolff et al., 2015). These could include pH (Jarvis et al., 2019), ORP (Lynch et al., 2014), groundwater inflow and soil through flow (Byrne et al., 2013).

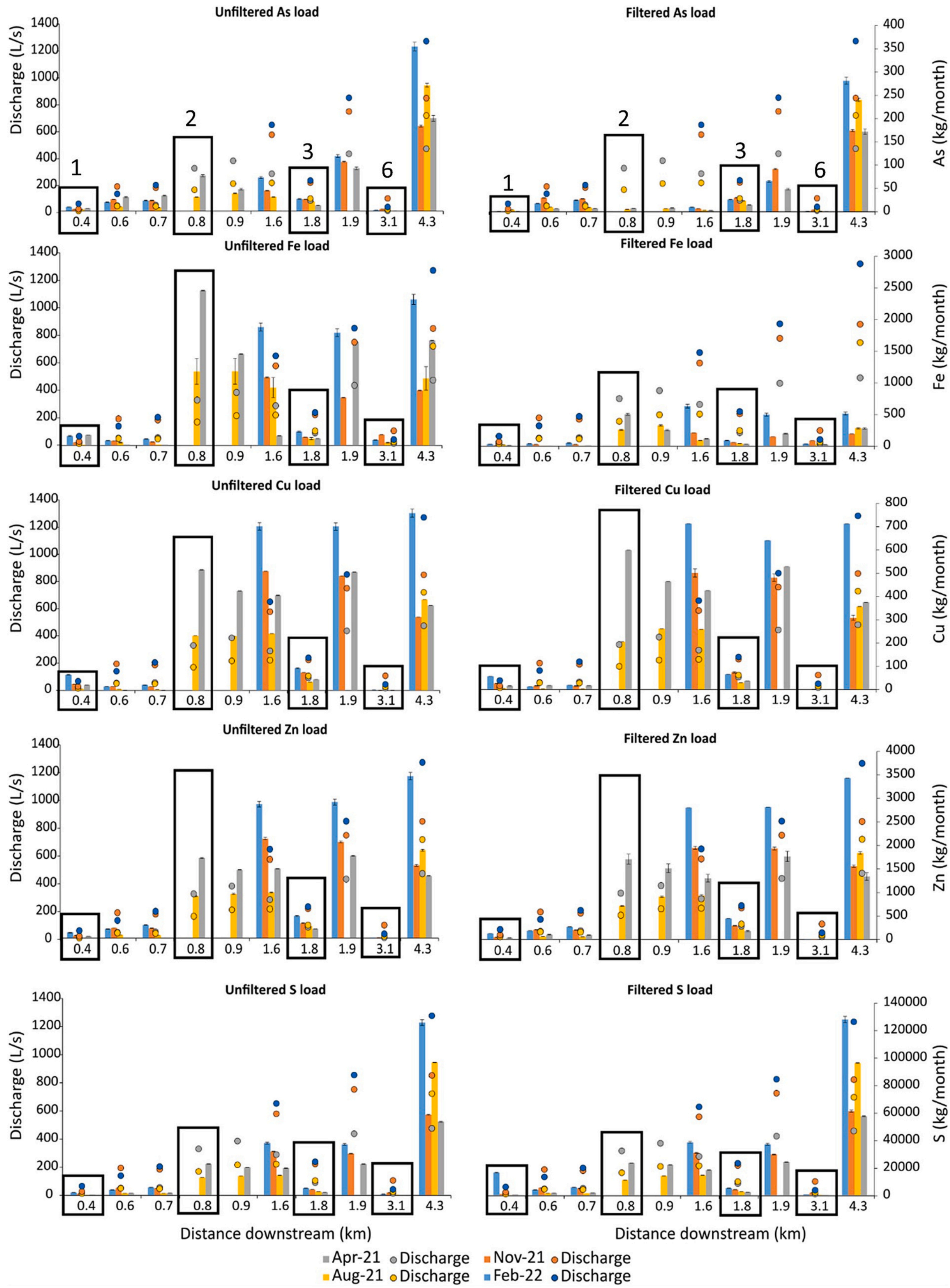

Fig. 5. Unfiltered (comprising suspended particulate and the dissolved phases) and filtered (comprising <0.45 μm suspended particulate and dissolved phases) metal (loid) loads vs distance downstream between April, August, November (2021) and February (2022). Discharge values are shown as circular symbols. Rectangular boxes highlight tributary and adit inputs (Fig. 1). Input 1 (Wheal Maid) has been marked as 0.4 km to avoid confusion with the County Adit distance and placed in the correct entry part of the Carnon River (0.8 km). Input 2 represents the County Adit site (0.8 km). 0 km is an unaffected site upstream of the County Adit. Input 3 is Hicks Mill (1.8 km). Input 6 is the Grenna Lane Bridge tributary (3.1 km).

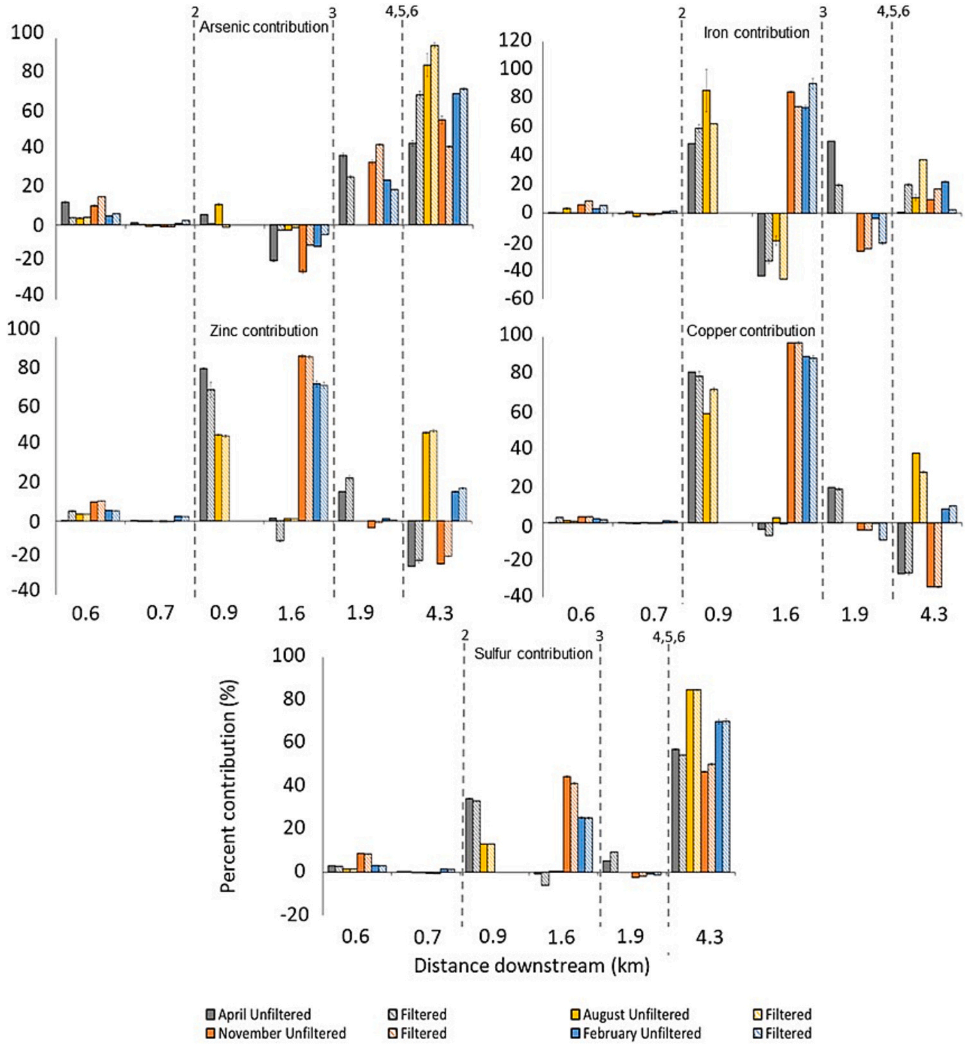

Fig. 6. Percentage contributions of As, Cu, Zn, Fe and S to the cumulative metal(loid) load of the Carnon River. Dashed lines indicate inputs of tributaries and adits. Solid coloured bars represent unfiltered and hashed colour bars represent filtered. Input 2 – County Adit (Wellington and Nangiles Adit nearby (0.88 km)) Input 3 – Hicks Mill stream (1.8 km) Input 4 – Wheal Jane Adit (2.17 km) Input – 5 Potential Adit (2.79 km) Input 6 – Grenna Lane Bridge tributary (3.12 km). Negative percentage contributions suggest site-specific attenuation, where no contributions of contaminants to the metal(loid)load were observed.

3.1.3. Annual downstream trends of instream loads in the Carnon River catchment

Contaminant loads for metal(loid)s (excluding filtered As) increased after the confluence of County Adit and Carnon River (0.94 km) (Fig. 5) (0–7.15 to 47–1515 kg/month). In April and August 2021, the County Adit contributed high unfiltered and filtered loads of Cu (59–81 %), Zn (46–83 %), and Fe (49–86 %) (Fig. 6, Table S10 in S.I.) to the cumulative load of the Carnon River. The highest contributions of unfiltered and filtered As (42–96 %) and S (47–85 %) to the cumulative load (Table S10 in S.I.) of the Carnon River occurred at 4.3 km (Fig. 6) where a secondary source of these elements has been proposed (Section 3.1.2). Decreases in some of the loads in the 1.6 to 4.3 km segment (e.g., unfiltered Fe in November 2021; Fig. 5) indicate metal(loid) attenuation that is reflected in processed such as the deposition of the Fe (oxy)hydroxides in the ochre floodplain (Fig. 1.D).

The calculated maximum filtered and unfiltered loads into the estuary were Cu 710 and 742 kg/month Cu, 3430 and 3320 kg/month Zn, 281 and 354 kg/month As, 513 and 1960 kg/month Fe and S 128,000 and 125,000 kg/month S, respectively. These metal(loid)s and S were likely transported and deposited in aqueous or sediment form to the estuary or open ocean (Pirrie et al., 2002), where they could, in turn, be remobilised by physical (high discharge and tides, rising sea levels) and chemical processes (pH, EC, ORP, temperature, ocean acidification) (Turley and Findlay, 2009; Erickson and Brase, 2019).

3.2. Seasonal and decadal trends in metal(loid) concentrations and load

3.2.1. Seasonal trends in instream metal(loid) concentrations and loads in the Carnon River

The downstream trends of metal(loid) concentrations for the sampling year remained constant, with a few outliers (e.g., unfiltered Fe loads in April and November) (Fig. 3) which can be attributed to differing hydrological and climatic conditions. For example, the highest metal(loid) concentrations were recorded in April 2021 (Fig. 3). These could be due to reduced rainfall in the sampling week that reduced dilution (Table S11 in S.I.), as observed in other AMD-affected catchments (e.g., Rio Odiel and Rio Tinto, Spain) (Braungardt et al., 2003; Sarmiento et al., 2009). In contrast, some of the highest metal(loid) concentrations from the County Adit (input 2, 0.88 km) were recorded in November 2021 (excluding Zn), coinciding with a period of high rainfall (see Table S11 in S.I. for rainfall data) recorded in the sampling week (18.6–25 mm). This likely led to high discharge which in turn could have flushed higher amounts of metal(loid)s out of the County Adit (input 2, 0.88 km).

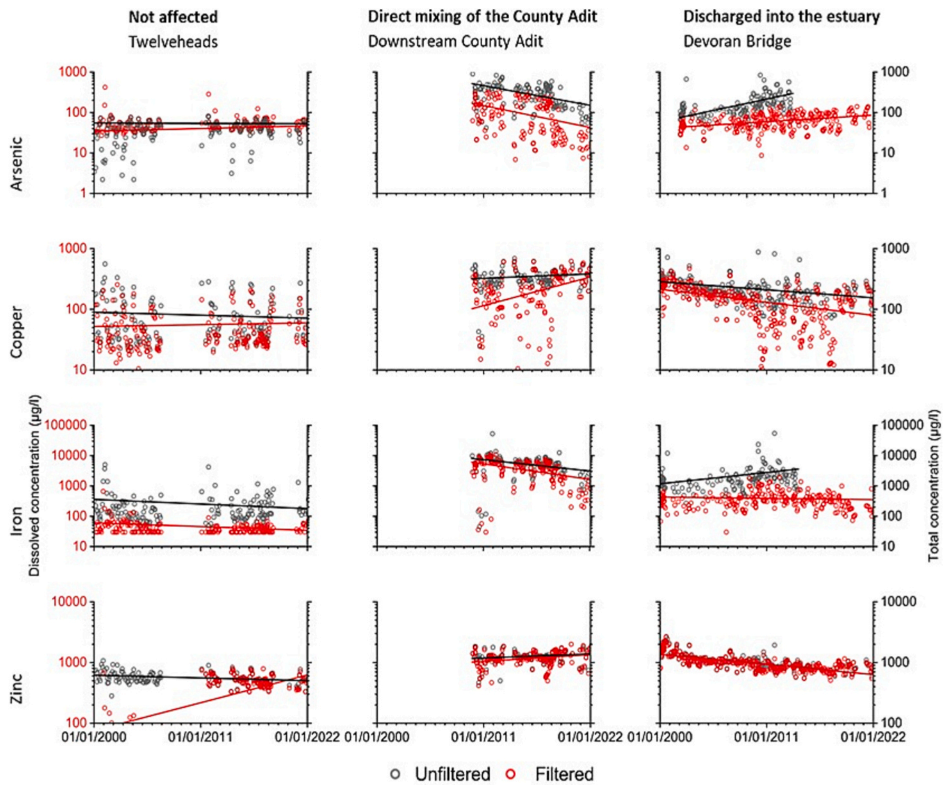

Fig. 7. Unfiltered (black) (comprising suspended particulate and the dissolved phases) and filtered (red) (comprising <0.45 µm suspended particulate and dissolved phases) As, Cu, Fe and Zn concentrations between 01/01/2000 and 02/12/2021 at Twelveheads, Confluence of the County Adit (CA) and Carnon River (CR), and Devoran Bridge in the Carnon River (green circles on Fig. 1).
(Data from Environment Agency monitoring sites (Environment Agency, 2021). Lines are linear curve fits extracted using Origin Lab Pro.)

Although the highest metal(loid) concentrations were recorded in April 2021, the loads were highest in February 2022 (during Q25 flow conditions) (Fig. 5). The latter could have resulted from high rainfall in the week preceding the sampling period (83.4 to 87.2 mm) (Table S11 in S.I.) and the high discharge (Q25, 852 L/s) recorded in the February campaign. The latter could have caused river embankment erosion and suspension of metal(loid)-bearing Fe (oxy)hydroxides (Fig. 2.D). The low attenuation (difference between the cumulative load and the instream measured load (eq. 4 in S.I.)) of unfiltered and filtered Fe, Cu, Zn, S and As in February 2022 (<21 %; Fig. S12 in S.I.) suggests that the elevated discharge conditions may have reduced the retention of metal (loid)s within the Carnon River sediments.

3.2.2. *Decadal trends in instream metal(loid) concentrations in the Carnon River*

Temporal aqueous changes in unfiltered and filtered As, Cu, Fe and Zn concentrations from 2000 to 2021 in the Carnon River upstream of the County Adit at Twelveheads, at the confluence of the County Adit and the Carnon River, and in the estuary (Devoran Bridge) are shown in Fig. 7. Concentrations at the Carnon River – County Adit confluence were higher than those at Twelveheads, highlighting the substantial metal(loid) inputs from the County Adit (Fig. 7). At Twelveheads, most concentrations did not change significantly over the 22-year sampling period, except for unfiltered and filtered As and pH (which increased) and filtered Fe and unfiltered and filtered Zn (which decreased; Fig. 7).

At the County Adit – Carnon River confluence, statistically significant increases in Cu (Mann Kendall (MK) 1357 to 2110, n 149, $p < 0.05$) and Zn (MK 1220 to 1417, n 149, $p < 0.05$) and decreases in pH (MK -1766, n 149, $p < 0.05$) occurred over time (Fig. 7, Table S7 in S.I.). These trends differ from those in other AMD-affected systems, including the Afon Ystwyth (UK) (1919–2005) and Rookhope Burn (UK) (1977–2008) (Mayes et al., 2010). In these systems, metal(loid) concentrations reached asymptotic values, and pH increased between 10 and 20 years after the cessation of mining. The Carnon River's increasing Cu, Zn and acid generation over time could have been due to the continuous and perhaps increasing discharge of AMD from the County Adit and to a lack of buffering capacity in the underlying silts and sandstone (Embrey and Symes, 1987; Scrivener and Shepherd, 1998; Pirrie et al., 2002). Discharge at the EA monitoring sites (Twelveheads and the County Adit – Carnon River confluence (Fig. S13 in S.I.)) increased between 2000 and 2021, as shown by Mann Kendall (MK) analysis (Table S7 in S.I.; MK 298217 to 686,489, n 4557–4567, $p < 0.05$). If the trend of increasing discharge continues, the resulting higher water levels in the underground County Adit could cause more frequent flushing of Cu and Zn, mobilising these metals from the heavily mineralised area into the river system due to their chemodynamic behaviour (Fig. 4).

In contrast, at the confluence, statistically significant decreases in filtered and unfiltered As and Fe concentrations occurred between 2000 and 2021. Arsenic (MK -2255 to −2672, n 149, $p < 0.001$), Fe (MK -2295 to −2932, n 149, $p < 0.001$), and pH (MK -1766, n 149, $p < 0.05$), exhibited a significant negative trend indicated by Mann Kendall statistics, implying an inverse temporal relationship. The decline in As and Fe could be due to the increased precipitation of As-bearing Fe (oxy) hydroxides from Fe (II) oxidation and hydrolysis (Dold, 2014) of the County Adit AMD over the 20 years of data collection. The distinct geochemical behaviour of Fe, compared to Cu and Zn, reflects its tendency to precipitate as Fe oxides under low pH conditions (Dold, 2014), even in the absence of neutralizing rock materials. This precipitation process explains the observed differences in their temporal evolution.

At Devoran Bridge, Mann Kendall test results (Table S7 in S.I.) indicated a significant positive trend with time for As (MK 4083 to 5606, n 357, $p < 0.001$), unfiltered Fe (MK 2892, n 357, $p < 0.001$), and pH (MK 8783, n 357, $p < 0.001$). This trend implies a direct temporal

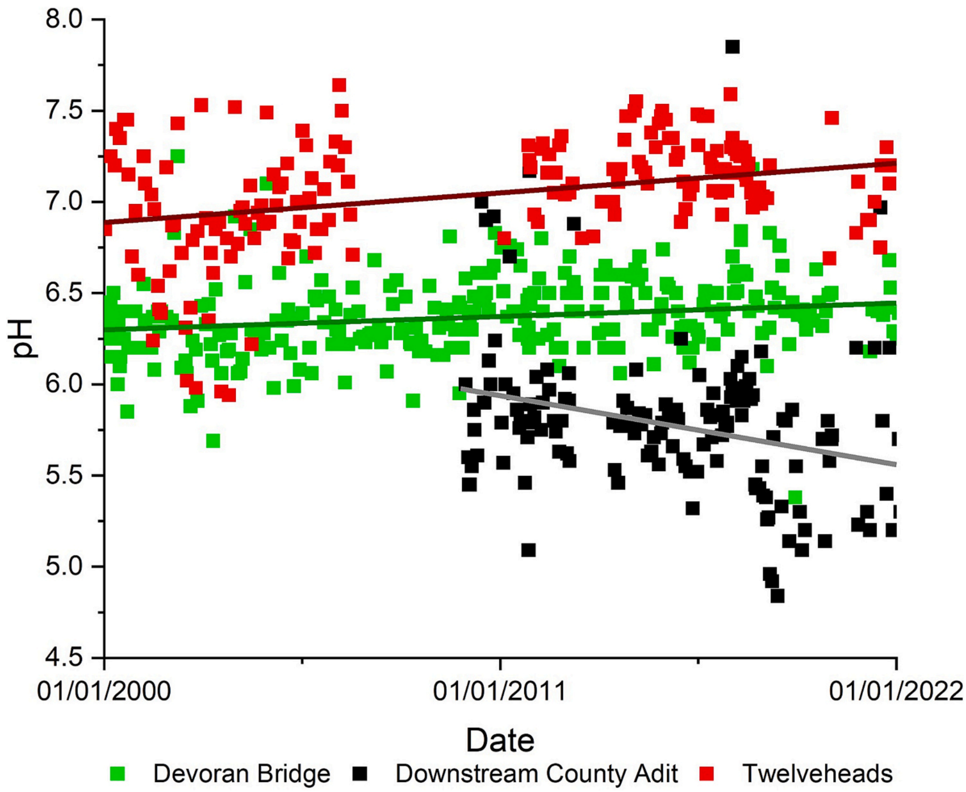

Fig. 8. pH data collected between 01/01/2000 and 02/12/2021 at Twelveheads, immediately downstream of the County Adit – Carnon River confluence and Devoran Bridge in the Carnon River (green circles in Fig. 1).
(Data from Environment Agency monitoring stations (Environment Agency, 2021).)

Table 2
Filtered 'dissolved' concentrations (mg/L) in AMD-affected rivers after mixing with unaffected river water. n.r. = not reported.

Concentration (mg/L)	Chinaman Creek, Australia (pH 3.2) (Lottermoser and Ashley, 2006)	Rio Tinto, Spain (pH 1.6–7.6) (Hudson-Edwards et al., 1999)	Heng Shi, China (pH 2.6–7) (Zhao et al., 2012)	Tamar, UK (pH >5) (Mighanetara et al., 2009)	Carnon River, UK (pH 4.3–7.1) (This study) (Filtered)
As	0.019	0.5–25	0.03	0.082–0.34	0.004–7.3
Cu	7.77	0.05–240	0–7.7	0.0036–0.65	<0.0009–0.72
Fe	13.7	n.r.	116	0.055–3	0.02–25
Zn	23.1	0.3–420	35	0.0038–0.32	0.096–2

relationship with concentration, indicating that As and unfiltered Fe concentrations and pH increased with time (Figs. 7, 8). These trends could be explained by the transport downstream of the As-bearing Fe (oxy)hydroxides and their storage in floodplains and subsequent physical and chemical remobilisation. Copper (MK -12,871 to −15,929, n 357, $p < 0.001$) and Zn (MK -18,078 to −21,028, n 357, $p < 0.001$) exhibited a significant negative trend at Devoran Bridge, implying an inverse temporal relationship. This relationship could be due to sorption or ion exchange of Cu and Zn on estuarine minerals as a response to increased pH with time (Figs. 7, 8) (Dzombak and Francois, 1990; Wołowiec et al., 2019). This in turn could be related to rising sea levels, suggested by increasing aqueous Cl concentrations recorded at Devoran Bridge over the 20 years (Fig. S14 in S.I.) and recorded rising sea levels at Newlyn, SW England (~36 km from the estuarine mouth of the Carnon river) that have been documented as 3.8 mm/year from 1993 to 2014 (Bradshaw et al., 2016).

3.3. Global importance of the Carnon River

Metal(loid) concentrations in the Carnon River are compared with other AMD-affected river systems in Table 2. The Carnon River As, Cu, Zn, and Fe concentrations determined in this study are higher than the Tamar River (UK) (Mighanetara et al., 2009). By contrast, Cu, Fe and Zn concentrations in the Carnon River are mostly orders of magnitude lower than those of Chinaman Creek (Australia) (Lottermoser and Ashley, 2006), Rio Tinto (Hudson-Edwards et al., 1999) and the Heng Shi River (China) (Zhao et al., 2012) (Table 2). Arsenic concentrations in the Carnon River exceed those of Chinaman Creek (Australia) and the Heng Shi River (China) (Table 2). The varying degrees of AMD-related metal (loid) contamination in these river systems underscore the importance of tailored environmental management strategies and the need for comprehensive monitoring and remediation efforts worldwide.

Yields of As from the Carnon River determined for this study are higher than those of the other AMD-affected rivers reported in Table 3. Although most of the rivers reported in Table 3 have higher yields of Cu, Fe and Zn, the Carnon also exports considerable amounts of these metals to the coastal zone. The yields for As, Cu, Fe and Zn recorded at the County Adit by Mayes et al. (2010) are higher than those reported in this study, likely due to the former study reporting unfiltered loads and the latter reporting filtered loads (Table 3). Using yield to estimate a river catchment's metal(loid) export could highlight key contaminating sites and better develop treatment and management strategies for AMD-

Table 3
Filtered 'dissolved' yields (tonnes/year/km^2) of metal(loid)s by adits and coastal outputs in AMD-affected catchments and their estimated watershed area (km^2). n.r. is not reported.

Catchment	Tamar, UK (Mighanetara et al., 2009)	Tyne, UK (Mayes et al., 2013)	Coledale beck, UK (Jarvis et al., 2019)	River Ystwyth, UK	
Yield tonnes/year/km^2				Nant Cwmnewyddion, UK (Onnis et al., 2018; Onnis, 2020)	Frongoch stream, UK (Mayes et al., 2008)
Coastal or Adit load	Coastal	Coastal	Adit	Adit	Adit
Watershed area (km^2)	967	2280	3.12	4.54	3.75
As	0.00252	n.r.	n.r.	n.r.	n.r.
Cu	0.01344	0.00132	n.r.	0.00336	0.0054
Fe	0.06024	n.r.	0.0054	0.04308	n.r.
Zn	0.0072	0.04104	1.0242	0.01356	3.97572

Catchment	Ria Del Huelva, Spain			La Réole, France		Carnon River, UK		
Yield tonnes/year/km^2	Ria Del Huelva, Spain (Sainz et al., 2004)	Rio Tinto, Spain (Cánovas et al., 2014)	Rio Odiel, Spain (Cánovas et al., 2021)	La Réole, France (Audry et al., 2005)	Rio Morte, France (Audry et al., 2005)	Restronguet Creek* (This study)	County Adit (Mayes et al., 2010) (unfiltered)	County Adit (This study)
Coastal or Adit load	Coastal	Adit	Adit	Coastal	Adit	Coastal	Adit	Adit
Watershed area (km^2)	3760	807	891	51,200	172	50.9	20.7	20.7
As	0.00816	0.00444	n.r.	n.r.	n.r.	0.05124	0.13056	0.0036
Cu	0.44628	0.68808	0.09696	0.00156	n.r.	0.10284	0.04356	0.261
Fe	n.r.	6.15264	0.08484	n.r.	n.r.	0.07428	6.78636	0.2436
Zn	1.0902	0.84564	0.11304	0.00492	0.26376	0.4818	1.64148	0.783

affected rivers.

4. Conclusions

This study has highlighted the importance of using contemporary and historical data to investigate metal(loid) behaviour within an AMD-affected river catchment as a function of spatial and temporal variability over one year and over two decades. Annual (2021−2022) and decadal (+20 years) trends in metal(loid) concentration, pH, EC, and temperature from the Carnon River showed that legacy underground mining adits continue to discharge contaminant metal(loid)s even after cessation of mining for several decades. Historical (+20 years) metal(loid) concentrations changed significantly ($p < 0.05$) downstream to the estuary, with Cu and Zn showing a slight downward trend and As and Fe exhibiting a slight increase. These trends may be due to the erosion and dissolution of As-bearing Fe (oxy)hydroxides and sorption or ion exchange of Cu and Zn onto estuarine minerals as a response to the increase in pH over time, which may be due to rising sea levels. Loadings of metal(loid)s in April, August and November 2021 and February 2022 increased downstream with recorded maximum unfiltered loads at Cu 742 kg/month, Zn 3320 kg/month, As 354 kg/month, Fe 1960 kg/month and S 125,000 kg/month discharging into the estuary (Fig. 5). Arsenic, Cu, Fe, S, and Zn concentrations exhibited a chemodynamic behaviour (CV_C/CV_Q = 0.59–2.8) and flushing behaviour suggesting that they were susceptible to changes in river discharge and were likely mobilised from historically contaminated riverine sediments. Iron, S and As exhibited very weak flushing (b = −0.04-0.30, R^2 = −0.002-0.41, S_b ≤0.05) behaviour, indicating that their concentration varied with discharge and that other factors (pH, ORP, groundwater inflow, soil through flow; Jarvis et al., 2019; Lynch et al., 2014; Byrne et al., 2013) may be more critical in controlling their behaviour (Musolff et al., 2015).

The research presented in this paper confirms earlier studies that proposed that the County Adit was a main contributor to metal(loid) contamination in the Carnon River. Importantly, this work also highlighted the role of diffuse sources to the metal(loid) loads to the river and coastal zone. Such sources may have been overlooked in other AMD-affected catchments.

Overall, this study illustrates the importance of monitoring AMD-affected rivers due to their highly variable behaviour as a function of space and time and their potential to contaminate fluvial and coastal environments for 10s to 100 s of years after mining has ceased. Only using a multifaceted and dual approach of comprehensive water sampling as a function of changes in riverine discharge regime and historical trend data can we gain a strong understanding of the environmental behaviour of AMD-affected rivers. Such knowledge is vitally important to design remediation strategies and understand how their vulnerability and likely change in the future due to climate change.

CRediT authorship contribution statement

Elin Jennings: Writing – original draft, Data curation, Conceptualization. **Patrizia Onnis:** Writing – review & editing, Methodology, Conceptualization. **Rich Crane:** Writing – review & editing, Methodology, Conceptualization. **Sean D.W. Comber:** Writing – review & editing, Methodology. **Patrick Byrne:** Writing – review & editing, Methodology. **Alex L. Riley:** Writing – review & editing, Methodology. **William M. Mayes:** Writing – review & editing, Methodology. **Adam P. Jarvis:** Writing – review & editing. **Karen A. Hudson-Edwards:** Writing – review & editing, Methodology, Conceptualization.

Declaration of competing interest

The authors affirm that no apparent financial conflicts of interest or personal associations could have conceivably influenced the findings presented in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2025.178496.

Data availability

Data will be made available on request.

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