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Rapid recovery of benthic invertebrates downstream of hyperalkaline steel slag discharges

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Abstract

This study assesses the physical and chemical characteristics of hyperalkaline steel slag leachate from a former steelworks on two streams in England and their impacts on benthic invertebrate communities. Using multivariate methods (CCA), we related invertebrate richness and diversity with chemical parameters along the environmental gradient from point sources to less impacted sites downstream. Point discharges are characterised by high pH (10.6-11.5), high ionic strength (dominated by Ca-CO_3-OH waters), elevated trace elements (notably Li, Sr and V) and high rates of calcium carbonate precipitation. This combination of stressors gives rise to an impoverished benthic invertebrate community in source areas. The total abundance, taxonomic richness and densities of most observed organisms were strongly negatively correlated with water pH. Analysis using biological pollution monitoring indices (e.g. BMWP and Functional Feeding Groups) shows the system to be highly impacted at source but when pH approaches values close to aquatic life standards, some 500m downstream, complex biological communities become established. In addition to showing the rapid

recovery of invertebrate communities downstream of the discharges, this study also provides a baseline characterisation of invertebrate communities at the extreme alkaline range of the pH spectrum.

Keywords: invertebrates; hyperalkaline; steel slag; leachate; community analysis; monitoring

INTRODUCTION

Natural systems with very high alkalinity are rare and usually associated with thermal springs (e.g. Khoury et al., 1985). However, numerous globally important industrial processes can give rise to extremely alkaline drainage waters that can create an enduring pollution legacy around residue disposal sites (Mayes et al., 2008). These residues include steel slags (Roadcap et al., 2005), coal combustion residues (Dellantonio et al., 2010), chromite ore processing sites (Stewart et al., 2007), Solvay Process residues from the manufacture of soda ash (Effler et al., 2001), lime spoil (e.g. Burke et al., 2012) and bauxite processing residue (e.g. Mayes et al., 2011). Many of these wastes and by-products are being produced in increasing quantities globally, so an understanding of their broader environmental impact, either in disposal sites or during afteruse (e.g. as aggregates for road fill: Chaurand et al., 2007), is much-needed to facilitate their effective management.

The weathering products of alkaline residues often have high pH due to the dissolution of oxide and hydroxide minerals which gives rise to high alkalinity and pH beyond the range routinely encountered in natural systems. Some studies have suggested that the hydroxyl ion (OH^-) can be directly toxic to some fish in high concentrations (Wilkie and Wood, 1996). Furthermore, increased bioavailability of some metals or metalloids, particularly those that form oxyanions at high pH (e.g. aluminate, arsenate, chromate, vanadate) can pose additional threats to aquatic organisms (e.g. Cornelis et al., 2007). Beyond these chemical stressors, there can also be physical stressors in hyperalkaline environments. Many calcium-rich highly alkaline waters are characterised by rapid rates of carbonate precipitation, as waters take in atmospheric carbon dioxide to regain equilibrium (Roadcap et al., 2005). The physical smothering of benthic habitats and hardpan formation can impose additional impacts on benthic environments (Mayes et al., 2008), and case studies monitoring the benthic recovery of limed rivers suggested that powdered limestone may clog substrates and be detrimental to filter feeders (Fjellheim and Raddum, 1995). While extensive research efforts have characterised toxicological thresholds and both species and ecosystem response under the acidic range of the pH spectrum (e.g. Monteith et al., 2005), given the far greater number of acid-affected freshwater environments, comparatively few studies have addressed the impacts of hyperalkaline industrial waters on freshwater communities.

The most comprehensive ecosystem assessments to date of alkaline industrial pollution have been made at the Solvay waste-impacted Onondaga Lake (NY, USA) and associated streams. Discharges during plant operation and residual leachate from soda ash beds were of high pH (>10), moderately saline and rich in Ca^{2+} as well as some other metals including mercury (Effler, 1987; Effler et al. 1991; 2001; Auer et al. 1996). The excess Ca^{2+} in highly alkaline waters leads to rapid precipitation of carbonate crusts as atmospheric CO_2 in-gasses into the waters as they regain equilibrium (Roadcap et al., 2005). Since the closure of a soda ash plant at Onondaga Lake, marked increases in the diversity of the lake zooplankton assemblage were reported (Auer et al., 1996; Effler et al., 2001) as a consequence of decreased calcite loadings, which fell from 23.2 g/m^2/d before plant closure to 12.8 g/m^2/d eight years after plant closure (Effler and Brooks, 1998). Increases in the abundance of large-bodied cladocera (*Daphnia* spp.), were cited as an indication of improvements in the state of the zooplankton community in the lake as the impact of the soda ash leachate was gradually attenuated (Effler and Brooks, 1998). Preliminary studies on a steel slag impacted stream in Pennsylvania, USA, cited a similar combination of stressors including high pH and carbonate smothering of benthic zones as a control on invertebrates and fish populations in a stream which had a pH in excess of 10 (Koryak et al., 2002). The formation of calcareous hardpans on the stream-bed has also been observed to be detrimental to aquatic macrophyte diversity and abundance at sites receiving Solvay bed leachate (Madsen et al., 1996) and lime spoil leachates (Mayes et al., 2005).

Evidence from sudden, extreme releases of highly alkaline residues also highlight demonstrable short-term impacts of hyperalkalinity on instream biota (Cairns et al., 1972; Klebercz et al. 2012). However in all cases there are multiple synchronous potential stressors impacting on the stream (e.g. extreme pH, high metal(loid) concentrations, physical effects of a flood wave and scouring) and it is therefore difficult to isolate the individual variables most important in affecting invertebrate abundance and diversity. For example, after the accidental release of 1 million m^3 of highly alkaline bauxite processing residue liquor in Ajka, Hungary in 2010, studies showed a short term decline in planktonic rotifer diversity and abundance some 250 km downstream in the Danube (Schöll and Szövényi, 2011), while studies focussing on source areas showed adverse effects on sediment-dwelling ostracods such as *Heterocypris incongruens* in bioassays when exposed to the alkaline substrates (Klebercz et al., 2012). However, the combination of high pH, salinity, mineral precipitation and high metal mobility (notably vanadium: Burke et al., 2012) were encountered at all impacted sites.

Through integrating biological, physical and chemical monitoring, this study aims to assess the impacts of industrial drainage on benthic invertebrate communities at two streams in northern England subject to long-term leaching of hyperalkaline waters from steel slag disposal sites. This study provides (1) a detailed assessment of the physical and chemical environment of hyperalkaline streams, (2) an assessment of the ecological impacts of hyperalkaline waters using standard biometric indices routinely used to monitor freshwater systems, and (3) scarce information on the controls on aquatic biota in streams affected by this enduring form of post-industrial pollution.

MATERIALS AND METHODS

Study site

Two watercourses draining extensive slag mounds associated with the former Consett Iron and Steel works in northern England (54°50′32.9386″N, 001°51′32.5752″W and 54°51′11.7661″N, 001°51′38.0473″W) were sampled in July 2011, November 2012 and May 2013 under baseflow conditions. The sites have been previously characterised by elevated pH (9.0-12.5) both during workings operation (when the waters were dosed with sulphuric acid) and in the three decades since the closure of the steel mill in 1980

(Mayes et al., 2008). Under baseflow conditions, the Dene Burn (sample prefix DB) receives around half of its flow from a subterranean drainage network beneath the Grove Heaps area of the site. These heaps were tipped up until the closure of the workings in 1980 and consist of blast furnace bottom and steel slag (Mayes et al., 2008). The slag is deposited with other site wastes (e.g. ashes and site demolition waste) over superficial alluvium and glacial till in the valley floors above Lower Coal Measures of Carboniferous (Westphalian) age. Sample DB7 lies on a tributary of the Dene Burn unaffected by slag leachate and is therefore considered a reference site. The Howden Burn (sample prefix HB) drains an area north of the Dene Burn previously occupied by the workings blast furnaces, power station and steel plant, again emerging from a large subterranean drainage system (Figure 1). A series of monitoring stations were sampled along the Howden Burn and Dene Burn to allow characterisation of invertebrate communities along the pH gradient from source to their respective confluences with the River Derwent, a major tributary of the River Tyne. Both the Howden Burn (width: 0.6-2.2m) and Dene Burn (width: 0.6-1.9m) follow steep longitudinal profiles (average slopes 0.09 and 0.05 respectively) following incised valleys with minimal or no floodplain (Figure 1).

Water analyses

Major physical and chemical parameters (pH, Oxygen Reduction Potential(ORP), electrical conductivity (at 25^{o}C), temperature) were measured in-situ at all sample stations using a Myron L Ultrameter® calibrated using pH 4, 7, 10 and 12.4 standards, while dissolved oxygen was measured using a YSI850 meter. Sample alkalinity was assessed in the field using a two-stage titration of filtered (0.45-μm) sample with a Hach digital titrator. The field alkalinity titration follows the fixed endpoint method (Hach reference 8203) against 1.6N H_2SO_4 with phenolphthalein (to pH 8.3, where required) and bromocresol green-methyl red indicators (to pH 4.6) to facilitate estimation of the constituents of sample alkalinity (i.e. hydroxyl, carbonate and bicarbonate alkalinity) using the USGS Alkalinity Calculator (http://or.water.usgs.gov/alk/). Physical and chemical samples were taken at the same time as all invertebrate samples.

Stream flow rate was measured at each sample site to compute chemical mass loadings (which facilitate precipitation rate estimates through assessing Ca^{2+} loss between consecutive sample stations). A Valeport 801 velocity meter with a flat electromagnetic sensor was deployed during base-flow sampling at all sites. This device was particularly suited to measuring velocity in the streams studied given the typically shallow depth of water (generally <0.05m). The velocity measurements (which ranged between 5-8 per site cross-section) were also coupled with stream dimension measurements and a visual assessment of the substrate composition (in terms of % cover of clay-silt, gravel, pebbles and boulders within an area defined horizontally by the stream width and vertically by a distance of 3m upstream of the station). This describes the stream bed from which the invertebrates were sampled. Three water samples were taken at each sample station in acid-washed 50mL polyethylene sample bottles. One of these was left unamended for anion analysis, one was filtered (0.45µm) and acidified to pH 2, and the final sample acidified to pH 2 for total elemental analyses. Total metal and metalloid concentrations were analysed using a Perkin Elmer Elan DRCII Inductively Coupled Plasma-Mass Spectrometer (ICP-MS; for As, Cr, Li, Mo, Sb and V: detection limits: 1-5 ppb) and an Optima 5300 DV ICP-OES (all other elements: detection limits: 10-100 ppb). Anions (sulphate and chloride) were measured using a Dionex 100 Ion Chromatograph . Saturation indices for calcite were determined using the geochemical code PHREEQC v.1.5.10 (Parkhurst and Apello, 1999) with the WATEQ4F (Ball and Nordstrom, 1991) database based on filtered samples.

Ecological sampling

In order to determine if invertebrate community composition varied with both site and season, five sample stations from the source of input (which were well defined by pipe drainage from subterranean drainage systems) to the main river were sampled at HB and DB in July 2011 (summer samples). Invertebrates were sampled in triplicate across both riffles and pools at each station through kick sampling (3 minute duration) using a 25cm wide and 22cm deep 1mm mesh net in accordance with the macro-invertebrate sampling methods outlined in WFD UK TAG (SNIFFER, 2008). Large macrophytes and edge vegetation were absent from both streams although small patches of blue-green algae were evident on the precipitated material in the upper reaches of the streams. Both streams flowed through wooded areas which were the source of the organic detritus found throughout. No aquatic invertebrates were found at HB, so both autumn (November 2012) and spring (May 2013) samples were only collected from DB using the methods outlined above. The number of stations sampled during autumn was increased to incorporate an additional downstream site (DB10) to determine the extent of the effects of the hyperalkaline water on invertebrate communities. Samples were preserved in 4% formalin and all taxa, apart from Oligochaeta, were identified to family level and counted in the laboratory (Pawley et al., 2011), with further identification of Ephemeroptera, Plecoptera and Trichoptera to genus/species using the relevant keys. The invertebrate taxa were then assigned to one of five functional feeding groups (Gathering Collectors, Filtering Collectors, Predators, Shredders and Scrapers; Cummings and Klug, 1979) using the appropriate information for each taxon residing in the freshwaterecology.info data base (Schmidt-Kloiber and Hering, 2012) in order to examine the trophic organisation of stream communities.

Statistical analyses

Canonical Correspondence Analysis (CCA) was used to model the response of the invertebrate taxa to the environmental variables and was chosen as there was a high turnover of taxa along the gradient (Zuur et al., 2010). As the invertebrate data set contained double zeros a Chord transform was applied to the invertebrate abundance data prior to analysis. Cleveland dotplots were used to check for outliers and multi-panel scatterplots were used to determine if there was any collinearity (Zuur et al. 2010). As alkalinity was highly correlated with conductivity and the % cover of boulders was highly correlated with the other stream bed variables (% cover sand, clay and pebbles), the variables alkalinity and % boulders were removed from the analysis. The following reduced set of environmental variables were used to constrain the ordination; pH (code: PH), electrical conductivity (COND), oxygen reducing potential (ORP), dissolved oxygen (O2), and the percentage cover of sand (SAND), clay/silt (CLAY) and pebbles (PEBB) on the stream bed; season (SEA) was included as a factor in the model (three levels spring (Sp), summer (Su), autumn (A)). A forward selection procedure was used to determine the significant environmental variables using a permutation test (10000 permutations) to compare the significance of the ratio of the constrained and unconstrained total inertia (F) for each variable (as outlined in Zuur et al., 2010), and a table wide Bonferroni test was applied to the results in order to reduce Type I errors.

In order to determine if ecological impacts due to hyperalkaline conditions could be detected using biological indices routinely used for monitoring purposes we applied the following to the dataset. Firstly, the Biological Monitoring Working Party index (BMWP), average score per taxon (ASPT) and number of taxa (NTAXA) were calculated according to SNIFFER (2008). As we were also interested in the functional ecology of the communities we assigned each taxon to a functional feeding group (FFG) by applying the following indices; ratio of Shredders to Total Collectors (Sh:C), the percentage of Ephemeroptera, Trichoptera and Plecoptera (% EPT), ratio of filtering collectors to gathering collectors (FC:GC) as these have been applied to a variety of stream systems (e.g. Ross et al., 2008; Rawer-Jost et al., 2000). The relationship between environmental variables and biological indices was examined using Spearman Rank correlations as much of the data was discontinuous or did not conform to a normal distribution even after log transformation (Kolmogorov-Smirnov: $p < 0.05$). All statistical analyses were undertaken in the software package R version 2.15.0 (R Development Core Team, 2012)

RESULTS

Physical and chemical characterisation of the streams

Both streams were characterised by Ca-CO_3-OH-dominated waters at source with pH well above ambient aquatic life limits (pH 9). The Howden Burn had far greater ionic enrichment than the Dene Burn, with major ions dominated by Ca^{2+}, OH^- and SO_4^{2-} (Table 1). This difference between the streams is due to relative dilution of the Dene Burn slag drainage with uncontaminated surface waters, while the sulphate enrichment reflects the dumping of sulphur-rich wastes (such as fly ash, flue gas waste and coke works waste) over what were the headwaters of the Howden Burn. Source samples showed the slag leachate to be slightly anoxic on occasion (Table 1), however the streams are characterised by consistently high dissolved oxygen (range 82 to >100% saturation) facilitated by the cascading, high gradient longitudinal profiles of both streams (Table 1). This buffering was pronounced in the Dene Burn, with a fall in pH from 10.5 to less than 8 (Figure 2). These precipitation processes were apparent in the conductivity data for the Howden Burn, but pH showed only a modest fall from source to the confluence with the River Derwent (from 11.5 to 11.0) due to the excess OH^- in this system. Macronutrient concentrations in the waters were modest and reflect the groundwater-dominated sources for both streams, which themselves rise from predominantly made-ground (i.e. waste heaps associated with the former steelworks) with only a sparse cover of low-intensity grazing throughout the catchments (Table 1).

Trace elements

Of the trace elements surveyed, none exceeded prescribed aquatic life standards in the European Union at the hardness of the waters sampled (Table 1). Aluminium, which is a determinand of potential concern given mobility (as aluminate) at pH > 8 in surface waters, did not exceed prescribed Environmental Quality Standard (EQS) values. Fe, while present, was also not at concentrations that would warrant regulatory concern (Table 1). Chromium, copper, nickel and zinc were either below prescribed EQS or detection limits in all samples. However, steel slag drainage can be characterised by enrichment in elements that are (a) not typically encountered in polluted wastewaters, and (b) not routinely monitored by regulatory agencies. These include steel additives and/or elements that are mobile under high pH conditions such as antimony, barium, lithium, molybdenum, strontium and vanadium, for which no formal European water quality standards are currently set. Table 1 shows the aggregated aquatic life standards of Buchman (2006) alongside the sample data which serves as an initial screening tool for the potential toxicity of some of these elements. However, it must also be stressed that standard toxicological tests rarely assess the broader chemical matrix of Ca-OH-rich, highly alkaline waters. It is apparent that strontium (Sr) and lithium (Li) exceeded provisional acute EQS, while vanadium (V) was present at source in modest concentrations (< 52 μg/L) in both discharges (Table 1). While no formal ambient aquatic life standards are prescribed for V, concern has been raised for V in drinking waters with a suggested DWS of 15 μg/L (Gerke et al., 2010). Correlations between major parameters and many trace elements showed strong positive relationships (Table 2), which (a) suggests that most of the potential stressors in the streams are sourced from the steel slag (for example, the strong positive relationships between Ca, V and Sr), and (b) highlights how concentrations of many elements decline concomitantly with distance from the sources (Figure 2). Previous studies at the site have shown through mass balance estimates that some of the potentially important trace elements (e.g. Sr and V) are attenuated in the secondary precipitates that are a characteristic feature of the sites (Mayes et al., 2008).

Secondary precipitates

The secondary precipitates themselves were dominated by calcite, but in source areas contain polymorphs of calcite such as vaterite (Mayes et al., 2008) which is indicative of the very rapid mineral precipitation rates. Calcium carbonate precipitation rates, as estimated from mass balance between sequential sample stations and areal estimates of the stream bed from site surveys, generally decreased with distance from the sources and is reflected in the downstream falls in conductivity (as ionic species are lost from solution) across the two streams (Figure 2). In lower reaches of the Dene Burn instream Ca^{2+} load gains were observed (Figure 2) which is most likely ascribable to inputs of Ca^{2+}-rich waters from tributaries draining springs from Coal Measures strata, and is consistent with field observations in showing minimal, if any carbonate precipitation in these lower reaches (from 270m from the source). Although the reach-scale precipitation rate estimates are likely to obscure small scale variations in precipitation rate that will arise with hydrodynamics (for example, between a thin film of water flowing over a carbonate barrage and that in a slow flowing pool), the aggregated estimates highlight the dominant broader significant positive relationship between pH and precipitation rate in these systems (Table 2).

Invertebrate data

No invertebrates were found in the samples from Howden Burn, so analysis is restricted to those collected from Dene Burn. As noted above, the Howden Burn has far higher conductivity (>1563 μS/cm^2) and pH in excess of 11.3; a feature of receiving slag leachate without surface drainage (Table 1). Both of these factors are thought to be highly detrimental to aquatic communities. The drainage from Dene Burn slag is joined by additional tributaries containing uncontaminated surface waters improving the overall water quality, hence invertebrate abundance and diversity increased downstream. Figure 3 is the site conditional CCA plot (i.e. species are plotted close to the stations where they occur) for the Dene Burn with stations plotted at the centroids of the species scores. Overall, 61% of the total inertia (1.62) was explained by the nine environmental variables, with 52% explained by the first two canonical axes. Out of the original nine variables, only two were highlighted as being statistically significant by the forward selection process (Table 3). Season (SEA) was the most important factor separating stations, spring samples were markedly different to summer and autumn samples (Table 3; Figure 3). The other significant variable was pH, which separated stations along the first CCA axis and, whilst not significant after Bonferroni adjustment (Table 3), ORP clearly influenced the distribution of the sites along CCA2. There was a significant negative correlation between taxon richness and % clay-silt content of the stream bed (Spearman Rank Correlation, $r_s = -0.423$, df = 20, $P < 0.05$; Table 4) and taxon Shannon Weiner diversity and pH (Spearman Rank Correlation, $r_s = -0.474$, df = 20, $P < 0.05$; Table 4). Samples near the source had low invertebrate abundance and richness and contained mainly Chironomidae, Simuliidae and Gammaridae (Figure 4; Appendix 1 for more information). The stream bed at stations 1 – 3 mainly comprised of clays, and precipitated $CaCO_3$ which declined rapidly in proportion downstream (Figure 2). As the buffering effects of carbonate precipitation reduced pH levels further downstream, more complex invertebrate communities become established approaching that of the reference site (station DB7), with more sensitive taxa such as Heptageniidae and Philopotamidae occurring at pH <8.7, along with an increased taxon diversity and richness downstream of the source (Figure 4; Table 4 and Appendix 1).

In terms of the FFG composition, samples from stations 1-3 of Dene Burn were dominated by gathering collectors in spring and summer, whilst filtering collectors and shredders were more abundant during the autumn (Figure 5). As pH decreased below 8.5 scrapers became more abundant as did predators in the lower reaches of the system, and a more diverse community became established (Table 3; Figure 5). The only FFG metric correlated with environmental variables was % EPT that has a significant negative relationship with pH (Spearman rank, $rs = -0.462$, $P < 0.05$). BMWP, ASPT and NTAXA all showed a negative correlation with pH (Spearman Rank Correlation, $P<0.01$ in all cases) indicating hyperalkaline waters had a severe impact on invertebrate communities.

DISCUSSION

The composition of the waters draining from the slag mounds is consistent with previous studies at the site (Mayes et al. 2006; 2008) and studies of slag leachate elsewhere in the world (e.g. Roadcap et al., 2005). The waters showed several unusual features such as (a) hyperalkaline pH, (b) enrichment of metals not routinely monitored by regulatory authorities and (c) very high mineral precipitation rates. The high pH, derived from dissolution of oxide and hydroxide phases in the slag (Roadcap et al., 2005), had both streams exceeding regulatory pH guidelines for large distances and is consistent with high ionic strength of source waters, notably in the Howden Burn (Figure 2). Li, Sr and V were present in concentrations higher than typically encountered in natural surface waters (e.g. Hem, 1985), and were at concentrations similar to those documented due to mineralisation or mining-related enrichment (Kszos and Stewart, 2003; Jones et al., 2013). V should be a particular focus for toxicity studies in hyperalkaline waters, given it is usually observed in its pentavalent, and most toxic, form under high pH conditions (Chaurand et al. 2007; Burke et al., 2012) and retains mobility under circum-neutral pH (Takeno, 2006). Precipitation rates at the source of the Howden Burn (up to 284 g $CaCO_3/m^2/day$) were an order of magnitude above the highest rates documented for natural tufa-precipitating streams, which are typically quoted in the range 0.2-10 g $CaCO_3/m^2/day$ (Zaihua et al., 1995; Miliša et al., 2006). The steep gradient stream morphology also lends itself to buffering of the waters with distance downstream (Figure 2), with thin films of leachate cascading over carbonatecrust barriers enhancing CO_2 in-gassing to the waters and subsequent calcite precipitation (Roadcap et al., 2005). Precipitation rates in the Dene Burn were towards the upper range of those found in natural karstic streams only in source areas (Figure 2). The precipitation rate data were also consistent with calculated calcite saturation indices (Figure 2), with values above +0.3 usually considered the threshold for heterogeneous calcium carbonate precipitation (Ford and Williams, 1998). The Howden Burn retained a high $SI_{calcite}$ throughout its course at values above thresholds where homogeneous calcite precipitation would be anticipated from solution (quoted at +1.5: Ford and Williams, 1998). The high rates of carbonate deposition in source areas of both streams compare with those documented at other Ca-rich alkaline waters (Effler and Brooks, 1998) and are similar to mineral precipitation rates at analogous sites affected by other forms of inorganic post-industrial pollution, notably circum-neutral pH coal mine drainage (Edwards and Maidens, 1995; Jarvis and Younger, 1997).

As such, there are a range of potential physical and chemical variables that could impact on the biological communities of the streams. The absence of any invertebrate populations in the Howden Burn, characterised by higher precipitation rates, greater ionic strength and higher pH waters reinforces this (Table 1). Whilst high conductivity may have severe toxic effect on invertebrates depending on the composition of the ions within solution (Cormier et al., 2013), apart from the ions associated with increased alkalinity (carbonate and hydroxide), trace elements and major ions remained generally below EQS levels where prescribed (Table 1). There has been a suggestion of V toxicity to juvenile benthic invertebrates in marine settings at concentrations of a similar order to those documented here (e.g. Chiffoleau et al., 2004; Fichet and Miramand, 1998), however, there have been few studies on invertebrate response to V pollution in freshwaters and this remains a research need.

ORP and the proportion of pebbles on the stream bed appear to be highly positively correlated as does the proportion of clay-silt and pH levels, suggesting the physical influence of the leachate on the substrate as an important control on the stream bed (Figures 2 and 3). High levels of suspended inorganic material are thought to create unfavourable conditions for filter feeders and cause benthic smothering (Fjellheim and Raddum, 1995). However, the pH values at these stations typically exceeded pH 9.5, far greater than that found in natural headwater stream systems (Cormier et al., 2013; Ross et al., 2008) or even in impacted sites which have undergone alkali-dosing remediation to reduce the impacts of acid mine drainage (AMD: e.g. Bradley and Ormerod, 2002). Some invertebrate taxa can tolerate hyperalkaline environments, and Chironomidae have been recorded in pH 11 waters derived from NaOH exposure (Berezina, 2001). The taxon Chironomidae contains many different species which have differing abilities to tolerate adverse conditions or recolonize areas rapidly (Pires et al., 2000). A series of mesocosm studies by Berezina (2001) indicated that, besides certain species of Chironomidae, ,few invertebrate taxa tolerated exposure to hyperalkaline conditions (pH 11) with most suffering mortality within 48hrs. The larvae of certain species of Chironomidae are thought to be more tolerant of short term exposure to high pH than pupae which lose osmoregulation organs during metamorphosis and suffer higher mortality (Berezina, 2001).

The multivariate analysis (Figure 3) also highlighted the importance of seasonal variations in the observed communities. Summer samples were associated with occurrence of Heptageniidae (Hep), Hydrophilidae (Hydrop) and Empididae (Emp) whereas low numbers of Limoniidae (Lim) and Chironomidae (Chir) with spring. Previous studies have suggested that intolerant taxa emerging in spring will suffer high mortality leaving a low diversity community with only the most tolerant taxa present later in the year (Garcia-Criado et al., 1999). However, the Dene Burn spring samples had a far lower abundance and diversity than those of summer and autumn and probably due to the scouring of the stream bed by high water flow during a period of heavy rainfall earlier in the year. Howden Burn was only sampled during summer and was devoid of macro-invertebrates, however it is possible that this could also be colonised at different times of the year. As such, repeated seasonal assessments of additional hyperalkaline sites would be beneficial to assess such patterns.

While the most common species encountered in the high pH sites of the Dene Burn were of the families Chironomidae, Gammaridae and Simuliidae, these stations in source areas had low diversity and abundance (Figure 5, Table 4). Surprisingly, small numbers of individuals of both Baetidae (*Baetis rhodani*) and Leuctridae (*Leuctra moselyi*) were found at station 3 during autumn at a pH of 9.68. *Baetis rhodani* appears to be quite tolerant of higher pH and has been recorded in abundance post-liming treatment of acidic streams (Bradley and Ormerod, 2003). Both Heptageniidae and Leuctridae have been recorded from both non-polluted and polluted sites in Spanish riverine systems impacted by coalfield and mining run off, albeit at pH values lower than recorded here (Garcia-Criado et al., 1999). While these taxa also have higher BMWP scores due to their sensitivity to organic pollution, they may not be as sensitive to mining discharges (Garcia-Criado et al., 1999) or to hyperalkaline conditions.

Assessment of the invertebrate functional feeding groups offers a good indication of broader community function (Figure 5). In boreal stream systems functional group richness and diversity was shown to increase with increasing pH, but the pH levels did not exceed 8.4 during that study on natural streams (Heino, 2005). As seen in streams impacted by AMD (Ross et al., 2008), herbivores (scrapers) were absent from the most severely impacted sites and gathering collectors predominated (Short et al., 1990). Previous studies on acidic streams have highlighted that acid tolerant taxa may adopt a generalist feeding strategy deriving allochthonous carbon from detritus and autochthonous carbon from biofilms (Layer et al., 2013). At more neutral pH levels, a range of acid sensitive specialist grazers fed on aquatic vegetation but were absent from acidic sites (Layer et al., 2013). This may be the case in this study; the hyperalkaline areas had few taxa, usually classified as detritivores (Figure 5), but these too may be able to adopt a generalist feeding strategy, using biofilms on the clays as a source of autochthonous carbon.

The ratios of key functional feeding groups can also be used as metrics of benthic community health. According to Rawer-Jost et al., (2000) when values of the FC:GC and Sh:C indices are less than 0.5 and 0.25 respectively, this indicates an impacted system. Whilst neither of these indices was correlated with environmental variables they still indicate that the upper reaches of the stream was severely impacted by the physical and chemical conditions of the slag drainage (Table 4). Other indices have been widely applied for biological indicators of pollution (Mason, 2002). The BMWP scoring system primarily reflects the sensitivity of invertebrates to organic enrichment (Czerniawska-Kusza, 2005). However such metrics also reflect the changes in water quality with both AMD (Bradley and Ormerod, 2002) and coalfield run-off (Garcia-Criado et al., 1999). The results obtained from the WFD-TAG (SNIFFER, 2008) approach suggest that the Dene Burn was severely impacted close to the source and water quality improved downstream from the slag leachate discharges (Table 4). The distance over which such improvements were tangible was in the region of 500m from source suggesting relatively rapid recovery (compared with AMD impacts for example: Kruse et al. 2013) due to instream chemical buffering processes. Irrespective of the metric used to measure the structure of the invertebrate community, the overall picture is that the prevailing physical and chemical conditions driven by the hyperalkalinity of the slag drainage have a major impact on the biota of the system near the source.

CONCLUSIONS

While strict limits are set for the upper limit of ambient water pH in river systems (typically 8.5 or 9), there is a paucity of studies assessing the distribution of invertebrates under highly alkaline conditions. This study highlights that at extreme alkaline pH there are a number of potential physical and chemical stressors that give rise to highly impacted biological communities. High pH at source is coincident with very high rates of mineral precipitation, and increased dissolved metal concentrations (notably Sr, Li and V). The high precipitation rates give rise to a benthic environment dominated by very fine-grained amorphous calcium carbonate smothering at rates far above natural tufa-precipitating streams in source areas. Similar to other sites impacted by inorganic pollution such as coal mine drainage, the benthic smothering may be as important a constraint on invertebrate communities as any chemical variable (Jarvis and Younger, 1997). Once pH falls below 10.5, which is accompanied by falling precipitation rates, the abundance and diversity of invertebrate taxa increases in the impacted streams. These initially include collectors such as members of the families Chironomidae, Gammaridae and Simuliidae. Various biological monitoring indicators and measures of community composition all show the system to be highly impacted. Only in lower reaches of the Dene Burn (>500m downstream) does a diverse invertebrate community become established. These data provide a useful foundation for further studies on what is an increasingly documented pollution problem. With increasing volumes of caustic by-products and wastes arising from industrial processes and being disposed of in landfill sites, there is an increasing need for both accurate impact assessments of alkaline drainage, but also management strategies for addressing such leachates (e.g. Mayes et al., 2009). Future directions should include surveys at other, similar hyperalkaline sites, as well as laboratory studies to isolate the key controls on invertebrate tolerance to highly alkaline waters. The importance of trace elements such as vanadium, for which there are scant toxicological information for freshwaters of this matrix, needs to be assessed alongside other chemical stressors (ionic strength and pH) and the dominating physical factors (elevated carbonate precipitation rate) apparent in these systems.

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Figures and Tables

Table 1. Baseflow major physical and chemical parameters and major and minor elemental constituent of filtered (0.45μm) samples. Source samples (HB1 and DB1) and those furthest from source (HB8 and DB8) on each drainage stream are presented alongside Environmental Quality Standards (EQS), where prescribed.

Determinand	HB1	HB8	DB1	DB8	**EQS**
pH	11.64	11.32	10.72	9.06	6-9
Temperature (°C)	13.0	12.8	12.5	13.4	
Electrical conductivity (μS/cm^2)	3193	1563	452	438	
p.e. (V)	0.037	0.042	-0.018	0.075	
Dissolved oxygen (% sat.)	92.5	96.5	88.0	99.4	50
Distance downstream of source (m)	5	460	5	1660	
Major ions (mg/L)					
Ca	239	110	15	11	
Mg	<1	2	2	1	
K	293	172	18	19	
Na	83	56	25	24	
Cl	42	41	18	18	
SO_4	852	546	36	36	
NO_3	3	4	3	3	
Total P	0.05	0.09	0.03	0.04	
Total Alkalinity (as $CaCO_3$)	332	84	59	66	
OH	29	13	3	<1	
CO_3	139	20	18	2	
HCO_3	9	3	9	37	
Trace elements (μg/L)					
Al	556	13	15	40	750
Ba	42.5	32.8	26.0	4.6	110^
Cd	<2	<2	<2	<2	5
Cr	8.4	6.7	2.5	<1	50*$^+$
Cu	<1	<1	<1	<1	28*$^+$
Fe	980.7	690.4	137.6	88.3	1000$^+$
Li	822.0	703.6	14.2	4.4	260^
Mn	32.2	1.1	17.4	5.4	
Mo	23.4	13.3	10.9	2.8	1600^
Ni	8.9	4.8	10.9	0.3	200*$^+$
Pb	<5	<5	<5	<5	20*$^+$
Sb	1.6	1.1	1.0	0.1	
Si	1290	1160	222	203	
Sr	2610	1140	213	279	15^
V	51.8	34.2	13.9	1.6	60*$^+$
Zn	9	2	4	3	10.9*

* = hardness related, value quoted for hardness values encountered here; + = as dissolved fraction which can pass through a 0.45µm filter. EQS taken from EU WFD with exception of '^' which are from Buchman (2008).

Table 2. Spearman's rank correlation matrix for selected major physical and chemical parameters and metals across the Dene and Howden Burns. n = 57 for all except those including $CaCO_3$ precipitation rate (n = 16). ** = $P < 0.001$. E.C.: Electrical Conductivity.

	pH	*E.C.*	*$CaCO_3$ precipitation rate*	*Ca*	*Sr*
E.C.	0.778**				
$CaCO_3$ rate	0.965**	0.850**			
Ca	0.877**	0.896**	0.885**		
Sr	0.628**	0.781**	0.937**	0.743**	
V	0.761**	0.782**	0.920**	0.788**	0.761**

Table 3. Summary of the results from the CCA showing the contribution of the environmental variables to the first two canonical coefficients. Numbers in bold denote significant p values after table-wide Bonferroni correction of the permutation tests (ns denotes not significant).

	Axis 1	*Axis 2*	*F*	*p value*
Eigen values	0.331	0.185	-	-
% Variation explained	20.4	11.4	-	-
Constrained environmental variable scores				
% Sand (SAND)	-0.133	0.664	1.09	ns
% Pebbles (PEBB)	-0.365	0.265	1.09	ns
% Clay (CLAY)	0.418	-0.349	1.21	ns
Conductivity ($\mu S/cm^2$) (COND)	-0.439	-0.174	1.76	ns
pH (PH)	0.469	-0.549	**2.04**	**0.023**
Oxygen reducing potential (ORP)	-0.574	0.379	2.11	0.026
Dissolved oxygen (% sat.) (O2)	-0.265	-0.626	1.52	ns
Distance from source (km) (DIST)	-0.086	0.072	0.39	ns
Season (SEA)			**2.83**	**<0.001**

Table 4. Summary of the biological indices across seasons (mean (sd)) for stations along Dene Burn (abbreviations as in text). Note: DB7 is a reference site.

Station	*Distance from source (km)*	*Shannon Weiner Diversity, H'*	*Taxon richness, S*	*BMWP score*	*ASPT*	*NTAXA*	*%EPT*	*FC:GC*	*Sh:C*	*% P*
DB1	0.38	0.97 (0.35)	3.33 (1.53)	11.4 (10.6)	4.2 (1.46)	1.7 (0.6)	1.8 (3.0)	0.33(0.56)	0.03 (0.02)	0 (0)
DB2	0.46	1.41 (0.39)	5.00 (1.0)	34.6 (9.1)	5.77 (0.2)	6.0 (2.1)	57.7 (23.1)	0 (0)	0.09 (0.11)	0 (0)
DB3	0.59	1.81 (0.46)	11.0 (4.1)	23.6 (19.3)	6.0 (1.31)	8.0 (3.1)	36.9 (14.6)	0.51 (0.29)	0.05 (0.1)	2.0 (0.74)
DB4	0.67	1.24 (0.59)	7.0 (4.6)	48.3 (10.6)	4.83 (1.31)	4.3 (3.0)	6.6 (8.1)	0.34 (0.59)	0.04 (0.03)	0.85 (0.72)
DB5	0.70	0.99 (0.22)	8.7 (4.9)	24.6 (18.0)	5.01 (0.71)	4.7 (3.1)	2.9 (4.6)	1.01 (1.0)	0.02 (0.02)	0.63 (0.87)
DB6	0.75	1.16 (0.31)	5.0 (2.8)	14.6 (8.8)	4.18 (0.03)	3.5 (2.1)	5.6 (7.9)	0.09 (0.15)	0.01 (0.01)	1.0 (1.4)
DB7	0.2	1.54 (0.08)	9.0 (4.2)	67.8 (19.4)	6.13 (0.24)	11.0 (3.1)	56.0 (22.9)	0.46 (0.66)	0.49 (0.16)	9.0 (12.8)
DB8	0.97	1.68 (0.11)	14.0 (3.1)	40.7 (7.6)	5.83 (0.9)	7.0 (1.4)	22.6 (23.4)	1.58 (0.76)	0.09 (0.04)	3.1 (1.6)
DB9	1.46	1.27 (0.52)	10.0 (7.0)	51.5 (32.2)	6.06 (0.22)	8.3 (5.0)	17.0 (14.9)	0.44 (0.73)	0.47 (0.22)	1.39 (1.62)
DB10	1.66	1.59 (0.19)	11.0 (3.4)	51.1 (22.1)	5.68 (0.61)	9.0 (3.6)	13.7 (4.1)	0.94 (0.73)	0.46 (0.39)	3.6 (2.2)

FIGURE CAPTIONS

Figure 1. Location map for the former Consett Steelworks and associated drainage streams (colour ramp indicates topography: from brown (low elevation) to green (high elevation))

Figure 2. Baseflow patterns in selected major physical and chemical parameters and elemental concentrations along the Howden Burn and Dene Burn.

Figure 3. CCA site conditional scaling plot for the Dene Burn samples with sites (A) and taxa (B) plotted separately.

Figure 4. Overall abundance of key taxa (number per 3 minute kick sample plotted on a log scale) along Dene Burn transect showing change in overall abundance and dominant taxa.

Figure 5. Abundance and structure of invertebrate communities with season. Data shown for Dene Burn only as no invertebrates were present in the Howden Burn. Symbol size is proportional to the log of the total invertebrate abundance (the raw values of which displayed adjacent to symbols).

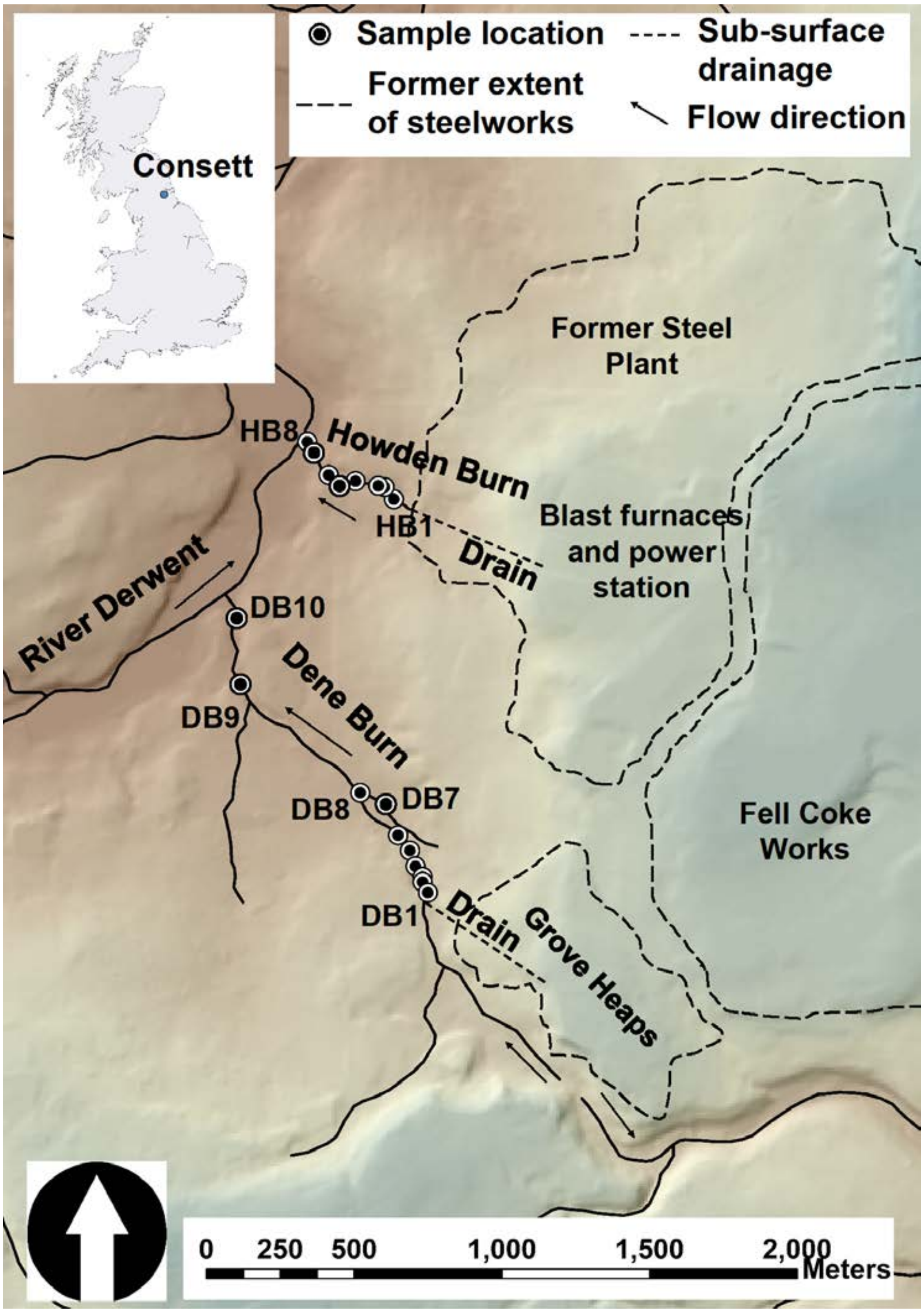
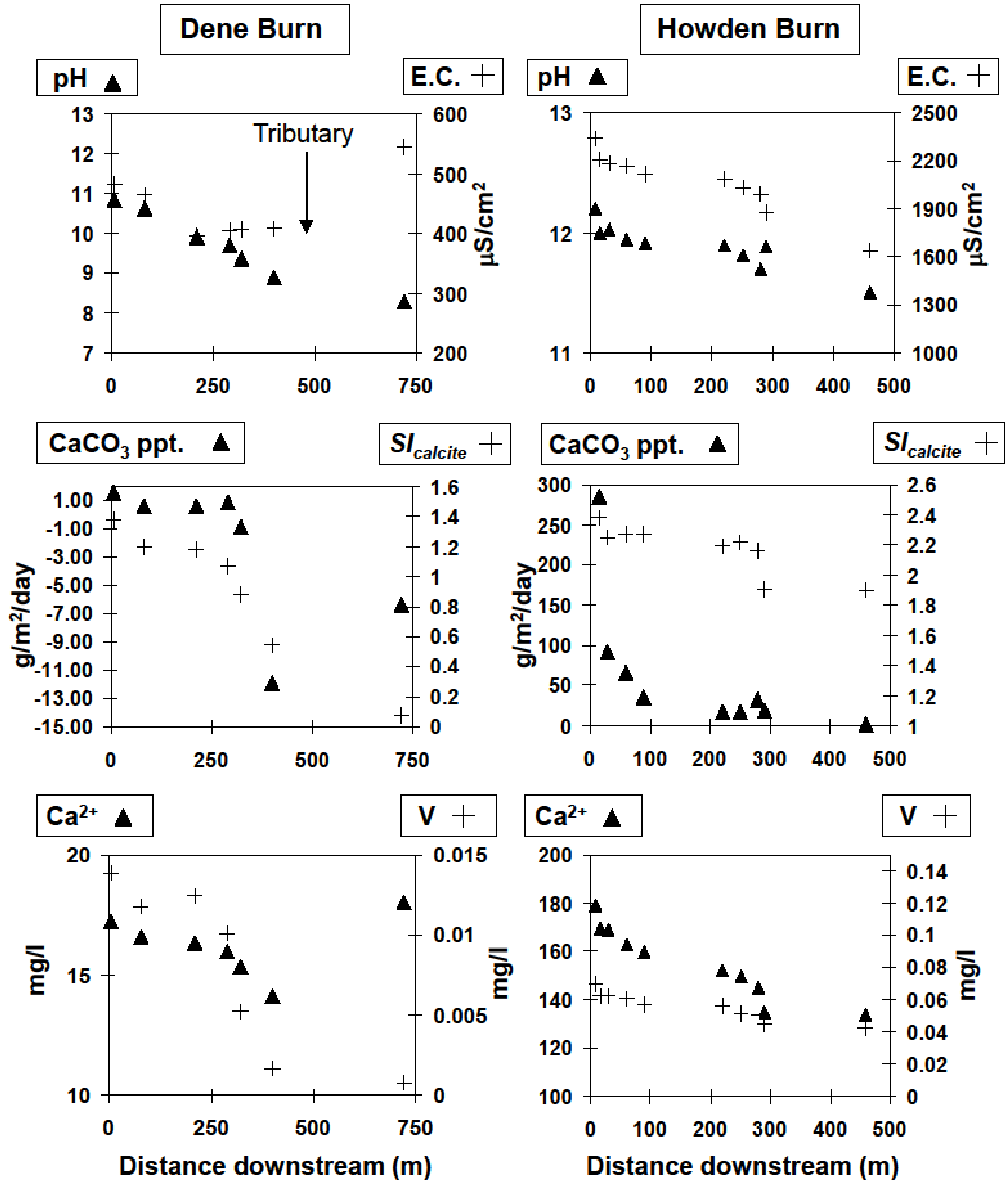

Sample location
Sub-surface drainage
Former extent of steelworks
Flow direction
Consett
Former Steel Plant
HB8
Howden Burn
HB1
Drain
Blast furnaces and power station
River Derwent
DB10
Dene Burn
DB9
DB8
DB7
Fell Coke Works
DB1
Drain
Grove Heaps
0
250
500
1,000
1,500
2,000
Meters

Fig 1



Dene Burn
Howden Burn
pH
E.C.
Tributary
µS/cm²
13
12
11
10
9
8
7
600
500
400
300
200
0
250
500
750
2500
2200
1900
1600
1300
1000
100
200
300
400
$CaCO_3$ ppt.
$SI_{calcite}$
g/m²/day
1.00
-1.00
-3.00
-5.00
-7.00
-9.00
-11.00
-13.00
-15.00
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
250
150
50
2.6
2.4
2.2
2
1.8
Ca^{2+}
V
mg/l
20
15
0.015
0.01
0.005
180
160
140
120
0.14
0.12
0.1
0.08
0.06
0.04
0.02
Distance downstream (m)

Fig 2

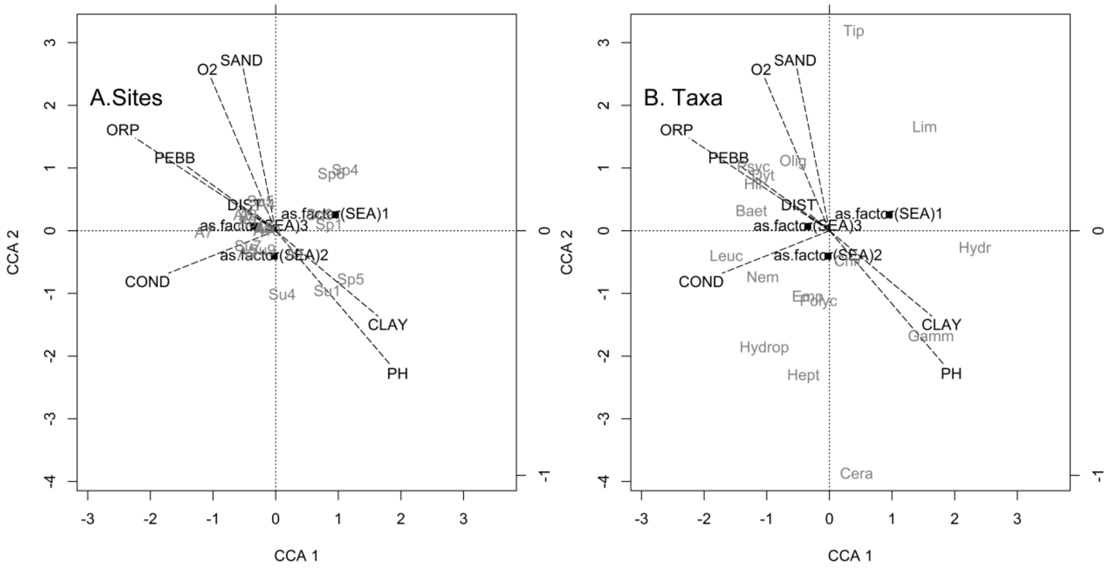

A.Sites
B. Taxa
CCA 1
CCA 2
O2
SAND
ORP
PEBB
DIST
as.factor(SEA)1
as.factor(SEA)3
as.factor(SEA)2
COND
CLAY
PH
Sp4
Sp1
Sp5
Su1
Su4
Tip
Lim
Olig
Baet
Leuc
Nem
Hydr
Hydrop
Hept
Gamm
Cera

Fig 3

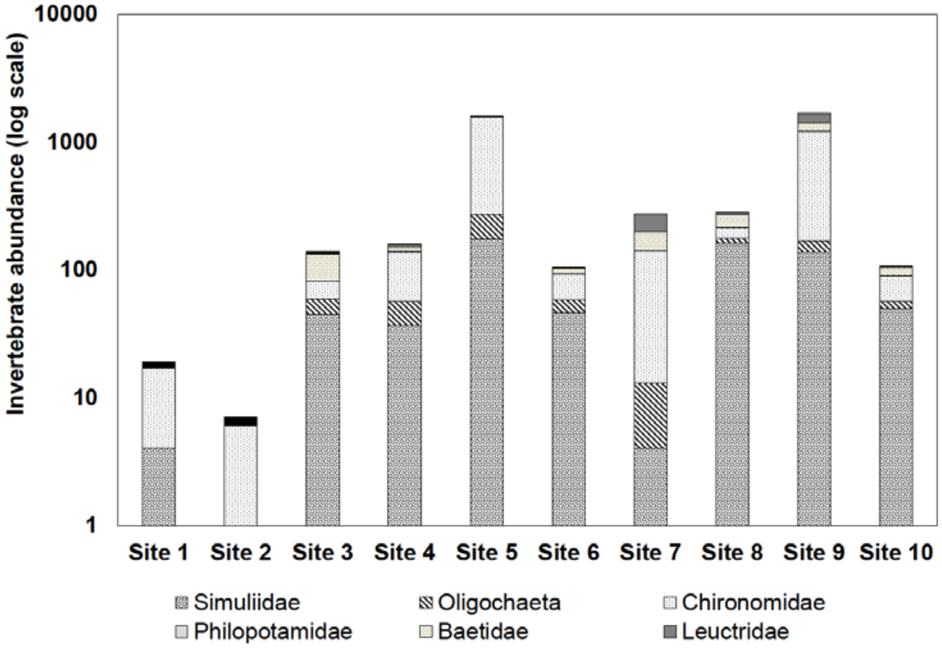

10000
1000
100
10
1
Invertebrate abundance (log scale)
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6
Site 7
Site 8
Site 9
Site 10
Simuliidae
Oligochaeta
Chironomidae
Philopotamidae
Baetidae
Leuctridae

Fig 4

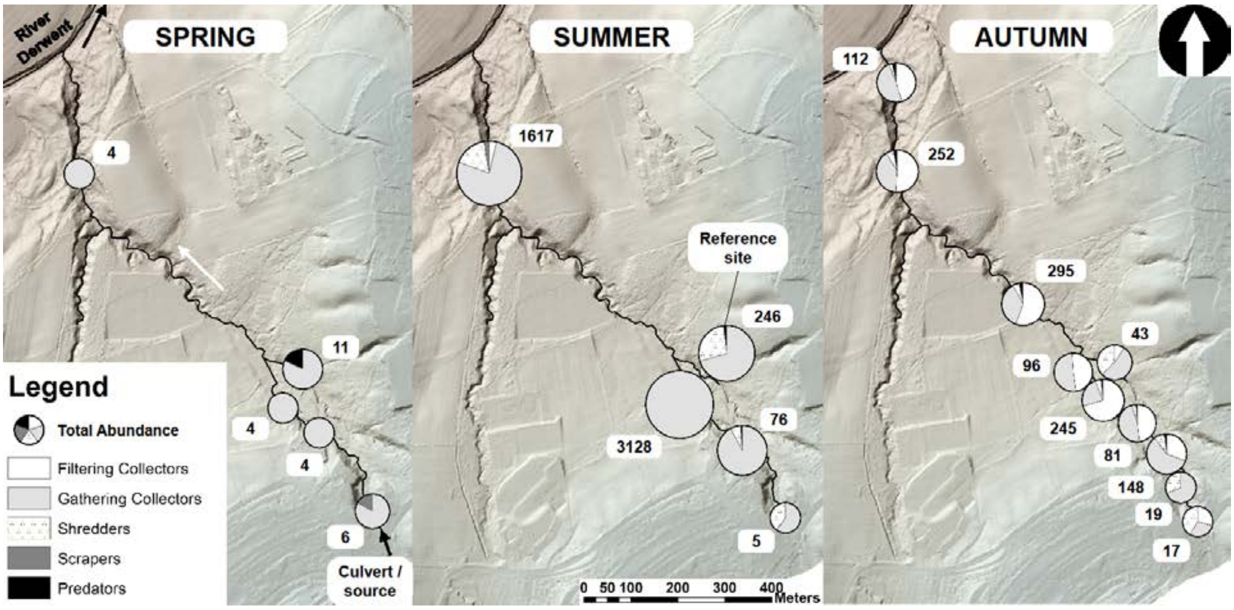

River Derwent
SPRING
SUMMER
AUTUMN
4
11
4
4
6
Culvert / source
1617
Reference site
246
3128
76
5
112
252
295
43
96
245
81
148
19
17
Legend
Total Abundance
Filtering Collectors
Gathering Collectors
Shredders
Scrapers
Predators
0 50 100 200 300 400 Meters

Fig 5

Appendix 1. Total invertebrate taxon abundance (pooled from three 3-minute kick samples) for each station and season (Sp=spring, Su=summer, A=autumn) and the pH conductivity (µS/cm^2) recorded during sampling.

Station	DB1			*DB2*	*DB3*	*DB4*			*DB5*			*DB6*		*DB7*		*DB8*	*DB9*			*DB10*
Season	Sp	Su	*A*	*A*	*A*	*Sp*	*Su*	*A*	*Sp*	*Su*	*A*	*Sp*	*A*	*Su*	*A*	*A*	*Sp*	*Su*	*A*	*A*
pH	10.1	11.9	10.6	9.9	9.7	9.6	10.2	9.5	9.9	10.3	9.3	8.3	8.9	8.5	8.1	8.3	8.9	8.7	8.0	7.8
Conductivity (µS/cm^2)	445	561	463	397	399	443	445	404	441	427	406	443	409	1404	1125	576	450	669	545	543
Hydrobiidae *Potamopyrgus* sp.	0	0	0	0	0	0	0	0	0	4	0	0	0	0	0	2	0	10	2	0
Planorbidae	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	4	0	0
Oligochaeta	0	0	0	0	14	0	5	15	0	89	9	0	12	6	3	15	0	19	11	7
Gammarus pulex	0	2	2	2	4	0	0	1	0	4	5	0	1	1	0	0	0	0	0	2
Baetidae (*Baetis rhodani*)	0	0	0	7	51	0	0	11	0	6	15	0	11	42	15	55	0	116	43	14
Heptageniidae (*Ecdyonurus* sp.)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	16	0	0
Heptageniidae (*Rhithrogena* sp.)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	12	0	0
Nemouridae (*Amphinemoura* sp.)	0	0	0	3	6	0	0	0	0	0	1	0	0	6	1	3	0	24	9	0
Leuctridae (*Leuctra moselyi*)	0	0	0	1	2	0	5	2	0	5	5	0	0	60	15	11	0	244	5	1
Dytiscidae	0	0	0	0	1	0	0	0	0	0	3	0	0	2	0	4	0	0	3	1
Noteridae	0	0	0	0	0	0	1	1	0	1	1	0	0	1	0	0	0	1	1	1
Rhyacophilidae	0	0	0	0	1	0	0	0	0	7	0	0	0	2	0	2	0	11	2	0
Philopotamidae	0	0	1	0	0	0	0	2	0	4	0	0	0	0	0	2	0	37	1	1
Hydropsychidae	0	0	0	0	0	0	0	0	0	0	0	0	0	2	0	0	0	12	0	0
Tipulidae	0	0	0	0	1	0	0	0	0	0	0	2	0	0	0	3	0	4	2	1
Chironomidae	5	3	5	6	23	4	65	12	4	1245	33	9	26	124	5	37	4	985	46	33
Simuliidae	0	0	4	0	45	0	0	37	0	2	173	0	46	0	4	161	0	10	127	50
Empididae	0	0	1	0	3	0	12	3	0	0	0	0	2	8	0	7	0	2	0	2

Limoniidae	2	0	1	0	12	8	1	10	2	3	6	10	1	11	0	11	2	16	6	3
Psychodidae	0	0	0	0	0	0	1	1	0	19	2	0	0	4	0	9	0	0	5	0
Chaoboridae	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	3	0	0
Ceratopogonidae	0	0	0	0	0	0	19	0	0	3	0	0	0	2	0	0	0	0	0	0
Ostracoda	0	0	0	0	0	0	3	0	0	3	0	0	0	6	0	0	0	23	0	0
Copepoda	0	1	0	0	0	0	7	0	0	5	0	0	0	0	0	0	0	0	0	0