Diurnal fluctuation of zinc concentration in metal polluted rivers and its potential impact on water quality and flux estimates

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ABSTRACT

Diurnal fluctuations of metals have been observed in the South Tyne river catchment, UK, in both upland tributaries and major river reaches. Zinc exhibits the most pronounced cyclicity, with concentrations increasing during the night to a maximum near 05:00 before decreasing during the day. This trend is the inverse of pH and temperature observations, which are thought to be the predominant drivers behind the cyclicity. Photosynthetic reactions of biomass and algae alter the pH within the river systems, therefore promoting hydrous metal oxide precipitation during the daylight which consequently allows divalent cations including zinc to sorb onto them. This mechanism may be supported by direct uptake of zinc by algae and other biogeochemical reactions which combine to create large differences in zinc concentrations; during base flow zinc concentrations increased by 326% from the minima over 48 hours. Maximum concentrations are not being captured during routine water quality analysis resulting in inaccurate and misleading EQS results and total flux estimations, for example the annual total zinc flux in a small tributary increases from 17 to 76 tonnes/year when routine grab sample data are supplemented with 24-hour sampling results.

Key words | diurnal, flux, monitoring, water quality, zinc

INTRODUCTION

Heavy metals in aqueous systems are problematic for environmental, economic and aesthetic reasons. Although there are continuing point and diffuse sources of metal pollution from contemporary sources such as highway runoff and industrial effluents, a significant proportion of all metal pollution in England and Wales originates from historic mining activity; it has recently been calculated that 50% of the total metal flux to the freshwaters of England and Wales arises from abandoned mines alone (Mayes et al. 2010). Of the metals typically present in metal mine drainage zinc is the most prevalent, and is the focus of this paper.

In order to ascertain a clear understanding of the potential impact of elevated zinc concentrations, and to calculate fluxes of metals to downstream locations, it is necessary to appreciate the influence of possible dynamic fluctuations in metal concentrations due to hydrological and biogeochemical processes. Specifically, previous research indicates zinc concentration is subject to diurnal variation in heavily contaminated rivers (Bourg & Bertin 1996; Nimick et al. 2005). The aim of the current work is to investigate the magnitude and spatial extent of such diurnal fluctuations in the River South Tyne catchment and evaluate the impact these fluctuations may have on the determination of the absolute flux to the lower parts of the river catchment.

METHODS

Site location

The investigation was conducted on the South Tyne River catchment (~800 km²), which drains the North Pennines, UK. The North Pennines were heavily mined until the late 1980s for lead and zinc. The ungauged River Nent (29.1 km²) is a known Zn-rich river which drains the Nent-head area, one of the most heavily worked mining locations.
A site on the Nent (Blagill) is used here as the most upstream location, nearest the source of contamination. Downstream of this are two further monitoring points, Featherstone (~18 km downstream of Blagill) and Haydon Bridge (~40 km downstream of Blagill), located on the main South Tyne channel in close proximity to Environment Agency gauging stations. Figure 1 illustrates the location of the monitoring sites within the catchment.

**Sample collection and analysis**

Semi-continuous monitoring of temperature, pH, dissolved oxygen, conductivity and turbidity using YSI sondes (multi-parameter water monitors, model number 6820) commenced in April 2010. The sondes were installed at the three monitoring locations and programmed to record data at 15 minute intervals. The sondes were calibrated <24 hours before deployment following YSI procedure and installed in the rivers in flowing water of the main channel. Aquamatic autosamplers were deployed at the three sites, programmed to sample 750 ml every 2 hours over 48 hour periods. Samples were collected in acid-washed polypropylene bottles which were completely rinsed with de-ionised water before use. Prior to each sample intake the samplers tubing was automatically flushed with river water to prevent cross-contamination. Samples were collected from the field site at regular intervals, remaining in the sampling bottle for up to 48 hours. Upon return to the laboratory, samples were acidified with 1% v/v HNO₃ to ensure the metals remained in solution. Subsamples were taken for total cations, filtered cations (<45 μm) and anions, with subsequent analysis of cation (Al, As, Ca, Cd, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Si, Zn) and anion concentrations undertaken using Inductively Coupled Plasma-Optical Emission Spectometry (Varian Vista MPX CCD ICP-OES) and ion chromatography (Dionex DX-320) respectively. Although anions (SO₄²⁻, Cl⁻, HCO₃⁻) are routinely analysed as part of the wider research pertaining to this investigation, they are not the primary elements of concern therefore for logistical reasons not all anions were analysed in the autosampling procedure. Blanks comprising of 1% v/v HNO₃ (Primar Plus), standards (prepared from NIST traceable 1,000 mg/L stock solution purchased from VWR/Fisher Scientific) and certified reference material (River Water – River Thames LGC6019) were analysed accordingly. The installation of autosamplers and subsequent analysis has been repeated on six separate occasions to evaluate the extent of diurnal variations during different hydrological situations and also the potential intra-annual variability. The January (2011) steady-flow sampling was carried out during a low flow that was slightly decreasing due to a small amount of rain the previous day which ceased 18 hours prior to sampling. It proceeded to be dry and cold during sampling; these conditions caused the water in the inlet pipe of the River Nent autosampler to freeze and prevented the intake of some samples.

**RESULTS AND DISCUSSION**

**In stream zinc fluctuation**

Figure 2(a) shows the amplitude of zinc concentration variation during a 48 hour period in June 2010, when almost 100% of the total zinc concentration was present in the dissolved (<45 μm) fraction. The high proportion on zinc in the dissolved phase was also observed at the downstream locations, with an average of 93% in the dissolved phase at Featherstone and 77% in the dissolved phase at Haydon Bridge during the June 2010 autosampling period. This partitioning of total versus dissolved zinc concentrations remained similar in each event sampled during steady flow conditions.

Figure 2(c) also shows the total zinc concentration at the two downstream sites of Featherstone and Haydon Bridge. These show simultaneous changes in zinc concentration, albeit at smaller magnitudes than those observed on the...
the increase from the minimum to maximum zinc concentration in the Nent is 326%, whereas at Featherstone it is 160% and at Haydon Bridge 140%. As the distance downstream increases noise from additional inflows slightly distorts the smooth variation observed upstream in the Nent. At all three sites the zinc concentrations rise during the night, reaching maximum concentrations at approximately 05:00. After the peak the concentrations of zinc start to decrease during the day, reaching minimum concentrations at approximately 17:00. Diurnal variation of zinc is observed consistently during each monitoring period undertaken in steady flow conditions except in the January 2011 exercise in which Zn shows no discernible cyclicity in the Nent, even though other parameters do. This is seen in Figure 2(d) and discussed in a later section.

The largest single increase in total Zn concentration observed in an investigation by Gammons et al. (2007) on a similar sized zinc rich creek in Montana (USA) was 109% over a 24 hour period. However, their research was carried out after a period of heavy rainfall, which may have flushed some of the particulate zinc downstream.

**Cyclicity of labile parameters**

In addition to zinc, other water quality parameters and constituents exhibit diurnal cyclicity. Figure 2(a) and (b)
illustrates the changes in temperature, pH and dissolved oxygen saturation in relation to the zinc concentration over a 48 hour period. Over the sampling period the stream discharge is relatively stable (0.09 < 0.13 m³/s) and there was no precipitation. Temperature and pH show synchronous diurnal variation which is known to be a consistent instream occurrence. A clear inverse relationship between zinc and pH and zinc and temperature can be seen. Dissolved oxygen also displays consistent cyclicity. However, its timing is offset from the other variables, falling midway between the two cycles of pH and zinc and temperature and zinc.

In sampling of the Nent undertaken in January 2011, no clear diurnal fluctuations of zinc are observed. However, cyclicity of pH is still apparent (Figure 2(d)), albeit at a smaller magnitude than during the June sampling. The missing zinc data are a consequence of the autosampler failure, as discussed previously.

**Variation of other trace metals**

Cadmium (Cd), Manganese (Mn), Nickel (Ni) and Silicon (Si) consistently mirror zinc fluctuations in all the observation periods in both the total and dissolved phase (Figure 3) for the Nent. In contrast, Aluminium (Al), Iron (Fe) and Potassium (K) showed no discernable trends during 3 out of 4 steady flow events. The exception was observed during January (2011) sampling in the Nent where Fe and Al appear to show the inverse trend of zinc. Arsenic (As), Copper (Cu) and Lead (Pb) are routinely below detection limits on almost all the samples and therefore any trends present are not evident.

Several of the sampling events were undertaken during periods of rainfall (November 2010 and a second event in January 2011). During these events there is no evidence of the same diurnal variation trends as exhibited in the low flow conditions of any of the elements or variables. The observed concentration variations instead correlate with the hydrographs, indicating the dilution is masking any diurnal cyclicity. In addition the partitioning between total and dissolved Zn concentrations appears to increase during initial rainfall.

**Diurnal mechanisms**

The diurnal fluctuations of temperature and pH are well understood. Temperature rises during the day as solar radiation heats up the river water and drops during the night as the river loses its heat. pH steadily increases during the day as a function of photosynthesis; consumption of dissolved CO₂ by aquatic plants and algae occurs during daylight followed by the subsequent release at night. Photosynthesis is also responsible for the amount of oxygen in the water; O₂ is produced during daylight which prompts an increase in Eh, with the reverse occurring during the night. The cause of the observed metal fluctuations within river systems is a widely debated topic. Hydrological and biogeochemical mechanisms have both been postulated with the majority now favoring the latter (Bourg et al. 2000; Nimick et al. 2003; Jones et al. 2004; Shope et al. 2006; Parker et al. 2007).

With a focus on Zn, several hypotheses are discussed, many of which are interlinked.

**Hydrological**

Within the research that promotes hydrological mechanisms there are also several possible causes. For example Sullivan & Drever (2001) advocate that diurnal variations in stream discharge promote variable dilution and consequently diurnal Mn and Zn concentration fluctuations. Hydraulic exchange as discussed in Choi et al. (2000) has also been hypothesized (Brick & Moore 1996), as has the hydraulic conductivity of the streambed changing due to fluctuating temperatures (Constantz et al. 1994). Data from this research indicate discharge fluctuations are asynchronous to the observed diurnal metal cycles. Theoretically, if it was a hydrological control all waterborne constituents should be equally affected, yet this research indicates that this is not the case, with zinc showing a consistently large diurnal fluctuation whilst other metals show inconsistent trends.
Geochemical

A common theory is the adsorption of divalent metal cations (Zn$^{2+}$) onto hydrous metal oxides (Shope et al. 2006; Parker et al. 2007). The rise in pH, Eh and temperature during the day (due to solar radiation and photosynthesis) encourages the precipitation of hydrous Fe and Mn oxides, and therefore enhances the rate of sorption of cations such as Zn$^{2+}$ onto these surfaces (Gammons et al. 2007). This results in a reduction in the concentration of dissolved Zn during the daylight. During darkness, these processes reverse. The anticipated inverse correlation of metals with pH, water temperature and solar radiation resulting from possible increased adsorption is seen throughout the results shown here (Figure 2). An investigation by Parker et al. (2007) observed that sorption of Cu, Fe(II) and Zn with hydrous Fe and Al oxides occurred progressively as the pH of the water increased from 5.3 to 7; this suggests that it may be a plausible mechanism in the River Nent given a fluctuation of up to 2 units of pH has been observed (Figure 2).

Another theory regarding zinc cyclicity is proposed by Shope et al. (2006) who noted that both Zn$^{2+}$ and Mn$^{2+}$ were adsorbed onto secondary Mn-Zn oxide surfaces. This is also driven by pH and temperature variation and would therefore produce diurnal cycles. In Shope et al. (2006), the Mn-Zn oxides were observed as thick black crusts on the stream substrate; no such observations have been observed on the Nent during this investigation.

In order to ascertain the potential phases and associations of the minerals, saturation indices (S.I.) were calculated using PHREEQC for the samples taken at 19:00 and 05:00 during the June sampling, which represent the minimum and maximum zinc concentrations. The results indicate only iron oxides and oxyhydroxides are consistently supersaturated to any substantial degree. In both samples, zinc and carbonate phases show too little variance around the point of equilibrium to confidently support any conclusion regarding dissolution and precipitation and therefore any mechanisms influencing zinc diurnal cyclicity. However, the continual presence of iron oxides and oxyhydroxides suggests they may potentially act as a sorbent for zinc.

Biological uptake

Laboratory studies such as that discussed in research by Morris et al. (2005) assess the viability of biological uptake causing diurnal metal cycles. These indicate that photoautotrophs can accumulate and release cationic metals during photosynthetic cycles, i.e. biofilms and algae sorb metals during light periods and release metals during the dark periods. Algae observed in the Nent partially cover the substrate year-round, although it is abundant during the summer months. This has been identified as various zinc-tolerant species such as Stigeoclonium pp. (Armitage et al. 2007), which is known to remove zinc from the water column via intracellular accumulation (Pawlik-Skowron 2003). As Figure 2 suggests, in contrast to the summer events sampled there appears to be no diurnal zinc variation during the January sampling. As there is considerably less algae in winter than summer, it is possible the algae is a dominant control on the cyclicity as less algae means there is less available to uptake zinc. It also means there is less algae available to photosynthesize, which may consequently influence the magnitude of the pH cycle. This is evident in these results as during June, when algae is prolific, the pH increases almost two-fold yet during January, with reduced algae quantities, the pH increase is near 0.2. Lower temperatures observed during the winter sampling may also affect the rate of photosynthesis. In the downstream locations in the River South Tyne less algae is observed on the substrate. These locations are deeper and faster flowing than the Nent so light sensitive algae may not thrive or be able to photosynthesize as vigorously.

In the Nent the vast quantities of algae and photosynthetic material may be a major control, driving the pH and oxygen changes which in turn promote biogeochemical mechanisms causing diurnal fluctuations. Geochemical analysis indicates the Nent is supersaturated only in iron compounds suggesting the formation of hydrous ferric oxides (HFO), and possibly sorption of divalent cations to the HFO. However, there is no visible evidence of an oxide crust on the substrate, or of zinc or iron precipitate in the rivers. At the downstream locations, any diurnal fluctuations may not be as pronounced due to the lack of algae available to influence the photosynthetic cycles or to accumulate metal during daylight hours, but is difficult to be conclusive since simple dilution effects may reduce the amplitude of the cycles.

Implications

Water quality standards

Environmental quality standards (EQS) as regulated by the Environment Agency (England and Wales) are the current statutory guidelines regarding water quality of surface water bodies. The average total zinc concentration observed
in the Nent (April 2010–February 2011) is 1.42 mg/L (range of 0.50 < 4.21 mg/L), of which an average of 94% is in the dissolved fraction. The annual average zinc concentration permitted in the Nent is 0.05 mg/L, based on the classification of the Nent according to EQS guidelines. The average value was obtained using concentrations from low and high flows through periods of semi-continuous monitoring; this a more accurate reflection of the water quality than assessments undertaken by regulators as they sample routinely yet infrequently. Analysis of historic water quality data provided by the Environment Agency (April 1979 to May 2010) indicates routine sampling times do not correspond to the times of peak zinc concentrations; approximately 33% of sampling is undertaken between 11:00–12:00 at the Nent (and similarly across the catchment), at which point the maximum zinc concentration would be under-represented on average by ~38%. This is illustrated in Figure 4. It is clear from Figure 4 that water quality sampling is undertaken during times when Zn is not at its peak, therefore missing the highest zinc concentrations resulting in potentially inaccurate water quality assessments.

**Flux estimates**

As seen in Figure 4, routine water quality sampling is undertaken in daylight hours. Current mass flux estimates for zinc in the River South Tyne (and likely other rivers), and measurements of zinc concentration in general, are likely to be underestimates as the maximum zinc concentrations are missed. For example, using the lowest zinc value observed during the June sampling, the calculated total zinc flux at Featherstone would be 3,050 kg/year. However, if the maximum zinc concentration from the June sampling is used the flux increases by 60%. The same situation occurs at Haydon Bridge where the annual flux would be 40% higher if the peak values are utilized. As the Nent is ungauged, discharge to calculate flux has been calculated through a stage discharge relationship ($r^2 = 0.97$). During the June sampling event, the average daily total zinc flux is calculated as 23.5 kg/day. If the mean is calculated for the same period using equivalent Environment Agency zinc concentration data, the flux would be 7.5 kg/day, ~68% less. Similar underestimates become magnified on an annual scale: the total annual zinc flux on the Nent is calculated as 17 tonnes/year if grab samples alone are used (taken fortnightly between 09:00–17:00). If the grab sample data are supplemented by data recorded using autosampling equipment (i.e. full 24 hour periods in low and high flow) the total annual zinc flux estimate for the Nent increases to approximately 76 tonnes/year. This substantial difference in a small catchment would have numerous implications on water quality and any remediation scheme designs.

**CONCLUSIONS**

Diurnal variations of instream metals, in particular zinc, are prevalent across the South Tyne river catchment. The magnitude of the cyclicity becomes less pronounced as the distance from the source of the zinc increases. Zinc (and Cd, Mn and Si) increases at night reaching a maximum near 05:00 before decreasing throughout the day; in a 48 hour monitoring period during low flow zinc increased by a maximum of 325%. The cyclic nature of zinc concentration is the inverse to that of pH and temperature, which are predominantly controlled by photosynthetic processes of instream biomass (such as algae) and solar radiation. These pH and temperature changes appear to be the main drivers behind the diurnal variation of the metals as they alter the CO2 and Eh concentrations, therefore encouraging the precipitation of hydrous metal oxides during daylight which can subsequently sorb the divalent metals. However, given the magnitude of the changes it is possible that more than one mechanism may be responsible for the diurnal fluctuation. In particular biological uptake may play an important role.

As a consequence of these diurnal fluctuations water quality monitoring and flux estimations may be inaccurate, since regulatory bodies predominantly sample during times of decreasing concentrations (i.e. the middle of the day) and therefore miss the maximum metal concentrations.
Flux estimates for the River Nent vary by almost 60 tonnes/year depending on sampling procedure and frequency; for a small catchment this is a significant difference. Remediation schemes, annual flux estimates and water abstraction all require an accurate understanding of temporal changes in water quality. The findings of this work improve understanding of these temporal trends in water quality with respect to metals concentrations, and will result in improved estimates of metal flux and more effective management of freshwater systems affected by metals pollution.

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