



Ecosystem bioelement variability is associated with freshwater animal aggregations at the aquatic-terrestrial interface

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Abstract

The impacts of animals on the biogeochemical cycles of major bioelements like C, N, and P are well-studied across ecosystem types. However, more than 20 elements are necessary for life. The feedbacks between animals and the biogeochemical cycles of the other bioelements are an emerging research priority. We explored how much freshwater mussels (Bivalvia: Unionoida) were related to variability in ecosystem pools of 10 bioelements (Ca, Cu, Fe, K, Mn, Na, Mg, P, S and Zn) in streams containing a natural mussel density gradient in the US Interior Highlands. We studied the concentrations of these bioelements across the aquatic-terrestrial interface—in the porewater of riverine gravel bars, and the emergent macrophyte *Justicia americana*. Higher mussel density was associated with increased calcium in gravel bars and macrophytes. Mussel density also correlated with variability in iron and other redox-sensitive trace elements in gravel bars and macrophytes, although this relationship was mediated by sediment grain size. We found that two explanations for the patterns we observed are worthy of further research: (1) increased calcium availability in gravel bars near denser mussel aggregations may be a product of the buildup and dissolution of shells in the gravel bar, and (2) mussels may alter redox conditions, and thus elemental availability in gravel bars with fine sediments, either behaviorally or through physical structure provided by shell material. A better understanding of the physical and biogeochemical impacts of animals on a wide range of elemental cycles is thus necessary to conserve the societal value of freshwater ecosystems.

Keywords Ionome · Calcium · Trace element · Redox · Metals · Bivalve · Freshwater mussel

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We used a multi-element approach to examine relationships between animal aggregations and ecosystems. This approach has potential to generate hypotheses regarding animals' biogeochemical impacts.

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Introduction

Bioelements constitute the material portion of the ecological economy: they construct the various structures of life and perform all its complex chemical reactions. Decades of study have revealed the ecological importance of three of the most abundant bioelements: carbon (C), nitrogen (N), and phosphorus (P). Together, we classify C, N, and P alongside oxygen (O) and hydrogen (H) as macronutrients, as they are ubiquitous for life and combine to make up > 99% of most biological systems (Kaspari 2021). Macronutrient use drives many ecological patterns and processes and organismal behaviors, so understanding the biogeochemical cycles of these elements is necessary for ecological comprehension and forecasting. However, around 20 other bioelements are also key drivers of ecological and physiological function. For instance, calcium (Ca) works with P to construct bone in vertebrates and shells in mollusks; iron (Fe) forms hemoglobin in mammals and can limit primary production in marine ecosystems (Boyd et al. 2000); zinc (Zn), manganese

(Mn) and other transition metals bind to proteins to catalyze metabolic reactions; magnesium (Mg) is the central atom of chlorophyll molecules and helps support the phosphate backbone of DNA. To unravel ecological patterns and processes, we must explore the exchanges of matter underlying ecosystems and the organisms within them across the full suite of bioelements.

Animals can directly and indirectly influence elemental cycles in distinct ways from plants, fungi, and microbes (Schmitz et al. 2018). Compared with these other taxa, animals exhibit more complex behaviors and larger scales of movement and produce chemically distinct specialized tissues. Animals directly influence the forms and distributions of bioelements in the ecosystem when they aggregate to breed, rest, or feed, and when they move or migrate across ecosystems (Polis and Hurd 1996; Subalusky and Post 2019). Mobile animals with large body size or high abundances can quickly transport large pools of bioelements through space, and can cross ecosystem boundaries within and between marine, freshwater, and terrestrial environments (Ben-David et al. 1998; Roman et al. 2014; Bump 2018). Further, animals' behavior can create indirect impacts on elemental cycles. Animals may alter the physical environment, for example by trampling soils and creating grazing lawns in terrestrial systems (McNaughton 1985; Schmitz et al. 2018) or through bioturbation—the reworking of sediments by burrowing that occurs across ecosystem types (Meysman et al. 2006).

The impacts of animals on the biogeochemical pools and fluxes of macronutrients, especially C, N, and P, are now recognized across terrestrial, marine, and freshwater ecosystems (McNaughton 1985; Vanni 2002; Allgeier et al. 2017; Schmitz et al. 2018; Parr et al. 2019). Animal effects on the cycles of the other bioelements, and the ecological consequences of such effects, have received less attention, but have also been documented across a range of taxa and ecosystem types. Grazing ungulates increase bioavailable sodium (Na) concentrations in African savannah soils (McNaughton et al. 1997), and appear to increase concentrations of several other metals, including copper (Cu) and chromium (Cr) in North American grasses and forbs (Kaspari et al. 2021). In coral reefs, grazing fish impact the Ca cycle by ingesting and redistributing calcium carbonate as they scrape the reef for algae (Morgan and Kench 2016). Aquatic insects recycle Ca and potassium (K) in streams, and can transfer these bioelements across the aquatic-terrestrial interface upon emergence as flying adults (Webster and Patten 1979). Vertebrates, corals, and mollusks concentrate large amounts of Ca and P in their skeletons and shells respectively and release these elements slowly into the environment upon their deaths (Barnes and Devereux 1984; Strayer and Malcom 2007; Subalusky et al. 2017). All animals also rely on a range

of electrolytes—metals such as Ca, Mg, Na, and K that dissociate in solution to form ions that conduct electrical currents—and trace elements to maintain homeostasis and perform physiological processes such as biosynthesis, immune responses, and metabolism (Harrison et al. 1936; Yattoo et al. 2013). Because animal-generated impacts on biogeochemical cycles depend on the habitat, behavior, and physiology of the focal animal species, an integrated perspective on an animal's ecology is needed to predict which bioelements they may interact with most strongly in the environment.

In both freshwater and marine ecosystems, bivalves alter macronutrient cycles and possess physiological and behavioral characteristics that may uniquely influence the cycling of a wide range of bioelements (Vaughn and Hoellein 2018). Where they occur, freshwater mussels (Bivalvia: Unionoida, hereafter “mussels”) can be the dominant component of freshwater benthic zone biomass, especially in streams (Strayer and Smith 1994). Mussels create biogeochemical hotspots of macronutrient storage and recycling via assimilation, egestion and excretion of N and P (Atkinson and Vaughn 2015; Atkinson et al. 2018). Mussels also sequester Ca within their calcium carbonate-based shells, even in Ca-poor waters (Strayer 1993). Mussel shells may thus create hotspots of Ca storage and flux via sequestration and subsequent release from the shell as it decays. Mussels also create bioturbation effects that increase oxygen penetration into aquatic sediments. Bioturbation alters the oxidation states of redox-sensitive metals, inhibiting the buildup of reduced states such as the divalent cations Fe^{2+} and Mn^{2+} , in favor of more oxidized states— Fe^{3+} and Mn^{4+} —which are less soluble (Matisoff et al. 1985; Aller 1990). Dead, empty shells also create structure in the sediment and may increase oxygen penetration by creating larger pore spaces (Vaughn and Hoellein 2018; Bódis et al. 2014). Mussels' relationships with bioelement pools even extend beyond stream ecosystems into adjacent terrestrial habitats (Allen et al. 2012; Lopez et al. 2020). In eastern North America, dense aggregations of mussels, known as mussel beds, are found near gravel bars formed by the emergent macrophyte *Justicia americana*. At high flows, these gravel bars are submerged, and mussels can be dislodged from their beds and washed onto the gravel bar surface. When the water retreats, mussels laterally burrow through the sediment to escape emersion and track the receding water line (Newton et al. 2015; Lymbery et al. 2021; Curley et al. 2022). Yet many mussels die, and their shells decay into the gravel bar sediment (Sousa et al. 2012). Mussel bioturbation (as they burrow) and subsequent mortality (once flows recede) may therefore alter gravel bar sediment structure and influence porewater biogeochemistry. In turn, changes to porewater chemistry may impact the elemental composition of the macrophytes deriving nutrients from the porewater and potentially impact

the macrophytes' nutritional quality for terrestrial herbivores that feed on these plants (Lopez et al. 2020, 2022).

Before hypotheses can be formulated and tested regarding mussel-bioelement interactions at the aquatic-terrestrial interface, exploratory studies are needed to quantify covariation between the characteristics of mussel beds and environmental bioelement pools. We conducted an observational field study to test for relationships between the density of freshwater mussel aggregations and the concentrations of a suite of bioelements in both gravel bar porewater and the macrophyte *J. americana* (Fig. 1). We focused primarily on Ca because of its importance in mussel shell formation, but also sampled for six redox-sensitive bioelements (metals Cu, Fe, Mn, Zn, as well as S and P) and three other electrolyte-forming metals (K, Mg, Na). Two research questions guided our study. **Q1**—How much do gravel bar and macrophyte Ca concentrations relate to mussel density? We expected to observe a positive relationship between Ca concentrations and mussel density because the buildup and decay of shell material in the ecosystem will increase proportionally with the number of mussels in an aggregation. **Q2**—How much do the concentrations of redox-sensitive bioelements (Cu, Fe, Mn, Zn, S, and P) in gravel bar porewater and macrophytes covary with mussel density? We expected to observe these relationships due to sediment oxygen penetration caused by mussel effects on substrate structure. We answered these questions by conducting two field studies across a naturally occurring mussel density gradient. First,

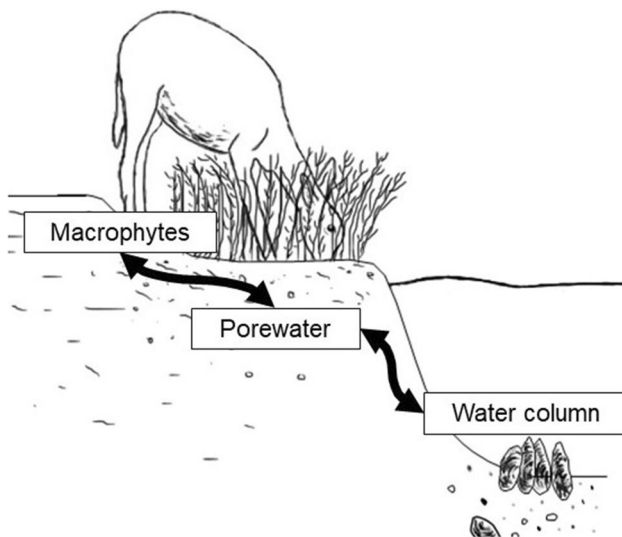


Fig. 1 Freshwater mussels interact with the environmental concentrations of bioavailable minerals and micronutrients in stream ecosystems. Mussels directly interact with the overlying water column and with gravel bar sediments during high flows. Emergent aquatic plants such as *Justicia americana* inhabit riverine gravel bars and acquire nutrients directly from the porewater. Plants may reflect variation in porewater chemistry in their tissues. Changes in plant nutritional status may affect herbivores that consume aquatic plants

we used ion probes designed to assess the concentrations of plant-available nutrients in soils to conduct a pilot study of nutrient availability in gravel bar sediments across the mussel density gradient. Then, we conducted a follow-up study to quantify bulk nutrient concentrations in the water column, the gravel bar porewater, and in emergent macrophytes. We subsequently generated testable hypotheses that could explain the patterns that we observed in the field, and to guide further research.

Materials and methods

We studied associations between freshwater mussel aggregations and ecosystem bioelement concentrations in the Ouachita Highlands and Gulf Coastal plain regions of Oklahoma, USA, in three adjacent rivers within the Red River drainage. The Kiamichi and Little Rivers are tributaries to the Red River, and the Glover is a tributary of the Little River. The Little River is the largest drainage at 10,720 km², the Kiamichi has a drainage area of 4500 km², and the Glover has a drainage area of 828 km². These rivers have similar physicochemical conditions (OWRB 2017) and well-studied mussel communities from a shared regional species pool (Vaughn 2003; Allen et al. 2013). Mussels have similar effects on ecosystem function across the three drainages (Atkinson and Vaughn 2015; Hopper et al. 2018). To test the predicted associations between mussel density and environmental bioelement concentrations we conducted a pilot study using soil ion exchange probes, followed by a stream reach-scale study of major bioelement pools. Bioelement concentrations and references to the elements in this study refer to the total soluble or exchangeable element concentrations; specific oxidation states were not measured. We had 15 sites across the two field studies, and each consisted of stream reaches of approximately 100 m in length, with either no mussels (0 ind m⁻²) or a mussel bed occupying the channel surrounding the gravel bar with a density of ~10–38 ind m⁻² (Fig. S1; Table 1). Mussel density was quantified using 0.25 m² quadrat surveys described in Hopper et al. (2018). Sites less than 1 km apart were blocked together and defined as a “site block” during data analysis to account for autocorrelation. Both studies were conducted at baseflow to minimize the potential for temporal variation in discharge to drive differences in elemental concentrations within sites.

Soil probe pilot study

In 2018, we evaluated the plant-available concentrations of the selected bioelements in gravel bar sediments within *J. americana* beds at 8 sites in the Kiamichi and Little Rivers using Plant Root Simulator (PRS)[®] soil probes (Western Ag Innovations, Saskatoon, SK, Canada). PRS[®] probes

Table 1 Mussel density and median sediment grain size of the gravel bars at each of the 15 sites used in the two field studies

Site	Mussel density (ind. m ⁻²)	Median sediment grain size (mm)	Soil probe pilot study	Stream reach study
GLM	29	<2		x
GLN	0	35		x
KMU	0	23		x
KBD	11	42		x
K2N	0	<2	x	x
K2M	9	<2	x	x
K3C	34	23		x
KTM	38	15	x	x
KTN	0	49	x	x
KSM	24	48	x	x
KSN	0	–	x	
K7M	24	27		x
K7B	0	35		x
LYM	22	–	x	
LYN	17	–	x	

Mussel densities are rounded to the nearest whole number. Sediment grain size data was not collected at sites during the soil probe pilot study. Whether each site was sampled in the soil probe pilot study, or the stream reach study is indicated by an “x” if the site was sampled

(hereafter “soil probes”) consist of a resin ion exchange membrane encased in plastic and provide a time integrated measurement of ion adsorption designed to simulate the availability of nutrients in the sediment to plants. 6 sites were in the Kiamichi River and 2 were in the Little River (Fig. S1; Table 1).

We buried the soil probes from 06-Aug-2018 to 30-Aug-2018. We randomly placed three soil probe samples < 0.5 m from the water’s edge at each site, along a transect running parallel to the upstream edge of the gravel bar. Intended burial duration was 7 d, based on a test burial conducted in May-2018 and consultation with the probe manufacturer (E. Bremer, pers. comm.; J. Lopez, unpubl. data) However, a storm event, which peaked at ~300 times baseflow occurred on the scheduled day of removal (13-Aug-2018) for half of the sites (USGS Gage #07335790). These probes were subjected to different hydrologic conditions, and we were forced to extend the burial duration until conditions allowed for retrieval (23 d). We statistically accounted for potential flooding effects (e.g., groundwater or allochthonous inputs; see “Data analysis” section). Upon retrieval, soil probes were rinsed with deionized water and refrigerated until shipping to Western Ag Innovations for analysis via inductively coupled plasma optical emission spectrometry (ICP-OES) for Ca, Cu, Fe, K, Mg, Mn, P, S, and Zn. The ICP-OES analysis was conducted by eluting all the ions from the resin surface using 17.5 mL of 0.5 M HCl, then analyzing the resultant

eluant using ICP-OES (Optima ICP-OES 8300, PerkinElmer Inc., USA).

Stream reach study

In 2020 we sampled bioelement concentrations in the stream water column, gravel bar porewater, and *J. americana* above-ground biomass at 12 sites in the Kiamichi and Glover Rivers. This included 10 sites on the Kiamichi River and 2 sites on the Glover River (Fig. S1; Table 1). We used Wolman pebble counts to determine the median sediment grain size in each gravel bar (Wolman 1954). Sediment grain size is an important covariate that affects the activity and availability of some bioelements in porewater by altering redox conditions and sediment binding sites (Horowitz and Elrick 1987). Wolman’s method uses categorical classifications for grains ≤ 2 mm (“sand”) and grains ≥ 257 mm (“boulders”), so we coded these categories as 0 mm for sand and 257 mm for boulders while calculating medians. There were no sites with median sediment size ≥ 257 mm. When the median sediment size value for a site was ≤ 2 mm (sand), we assumed the functional difference between 0 and 2 mm to be negligible at the scale we sampled and coded these values as 0 during statistical analyses.

We sampled water column elemental concentrations by taking duplicate water samples from the center of the stream channel using a syringe filter and glass fiber filters (GF/F; 0.7 μm pore size) and stored them frozen until processing. GF/F filters may introduce some minor contamination to samples, especially from the Na₂O found within borosilicate glass. To account for this, all water samples were analyzed alongside filter blanks using deionized water (see “ICP-OES analysis” section). Duplicate sample results were averaged prior to statistical analysis. We sampled gravel bar porewater by inserting a porewater sampler into the gravel bar in two locations: the upstream end and the downstream end. We took duplicate samples at each location. Bioelement concentrations in samples from upstream and downstream ends did not differ statistically, so we averaged them to get composite concentrations for gravel bar porewater. Porewater samples were too high in sediment to filter in the field and were stored unfiltered and frozen until just prior to analysis, at which point we thawed and decanted them into a syringe filter. We filtered the decanted samples using cellulose acetate membrane filters (CA; 0.7 μm pore size). All water samples were analyzed using ICP-OES.

We also quantitatively sampled the bioelement content of *J. americana* at each site. We placed transects perpendicular to the direction of flow in the adjacent river. We sampled one transect per 10 m of river length when *J. americana* beds were greater than 20 m long, and every 5 m when beds were 20 m or less. On each transect we placed three equidistant 0.25 m² quadrats spanning the entire breadth of the

macrophyte bed and harvested the aboveground biomass in each plot. The biomass from each plot was dried at 70 °C for 72 h and ground in preparation for acid digestion and ICP-OES analysis.

ICP-OES analysis

We subsampled approximately 50 mg of *J. americana* biomass for each plot and combusted it for 4 h at 500 °C to remove complex hydrocarbons such as lignin that interfere with plant tissue digestion. We combusted *J. americana* tissue in pre-weighed, sealed aluminum foil packets, then transferred the combusted matter into polypropylene tubes. To prevent loss of sample mass during the transfer, we opened one side of the square foil packet and carefully dumped the combusted matter from the packet into the mouth of the tube. We gently tapped the opposite, sealed side of the packet with a pencil to knock any residual matter that may have been clinging to the foil surface into the tube, then re-weighed the foil to ensure that the final mass of the packet matched the initial mass. We also watched closely for any visible mass loss around the mouth of the tube during the sample transfer and restarted the combustion process for any sample where we saw mass loss. Thus, we assume any mass lost in the transfer was negligible. We then digested the remaining mineral ash in a 2:1 v/v solution of HNO₃:H₂O₂ (BDH Aristar® Plus, VWR International, Radnor, PA) within polypropylene tubes and diluted the digested sample to 3–5% HNO₃. We analyzed digested *J. americana* samples using ICP-OES (Thermo Scientific iCAP 7400, Waltham, MA). Sample elemental concentrations were quantified using standard curves from two externally certified multi-element reference standards (CCV standards 1A & 1B, CPI International, Santa Rosa, CA) and calibrated using an internal yttrium standard (Peak Performance Inorganic Y Standard, CPI International, Santa Rosa, CA). We verified bioelement recovery in the samples by including additional replicates of the CCV1 standard throughout each run of the ICP-OES instrument (~5% of each run, or one standard for every twenty samples). Filtered water samples were also diluted to 3–5% HNO₃; GF/F filtered samples and CA filtered samples were analyzed separately using filtered deionized water blanks for each filter type. We analyzed water samples and GF/F and CA filter blanks using the same standards and instruments listed above. Of the 10 elements that we sampled, we removed those that had analytical uncertainties (i.e., those with CCV standard concentration values that drifted over a given sample run) or interferences that caused the instrument to return an “N/A” value from further analysis. Values below the method detection limit (<MDL) during ICP OES analyses were coded as 0 during statistical analysis.

Data analysis

To determine which bioelements drove the most spatial variation in each set of samples—the soil probes, the water column, gravel bar porewater, and macrophytes—we first conducted principal components analyses (PCA) on the site-level mean square root-transformed bioelement concentration values in each sample set. We square root transformed all concentration data to bring the distributions to approximate normality and to achieve homogeneity of variance for linear model residuals (see below). For the soil probes, gravel bar porewater, and macrophytes, we decided which bioelements to test for the predicted associations with mussel density by using the loadings for each principal component with an Eigenvalue ≥ 1 . We considered a bioelement worthy of further analysis if (i) it had one of the k highest absolute values for its loading on any of the k components with an Eigenvalue ≥ 1 , and (ii) it was one of the elements that we predicted to covary with mussel density. Based on the results of the soil probe study, we decided post hoc to test for an association between mussel density and porewater Fe concentration, even though Fe was not one of the drivers of site-level variation in bioelement concentrations in the porewater PCA (see “Results” section).

We then used a series of linear models to evaluate the predicted associations between mussel density and bioelement availability and concentrations. Gravel bar porewater samples were collected at the site level, so we tested how much bioelement concentrations were related to mussel density using ordinary least squares (OLS) regression. When we tested how much redox-sensitive elements in porewater and macrophyte samples were related to mussel density, we also included median sediment grain size and its interaction with mussel density as covariates in our linear models. In the soil probe study and in macrophyte samples we modelled bioelement associations with mussel density using linear mixed effects (LME) models. We included site block (sites <1 km apart) as a random intercept in the models (package: *lme4*). For our soil probe study, we also included fixed effects for the flooding event and the interaction between the flood event and mussel density. For each linear model we verified that residuals did not deviate strongly from normality based on a Shapiro-Wilks test and histogram inspection.

When reporting these analyses, we use P values to determine whether further investigation is warranted in the case of each potential mussel-bioelement association. For mussel-bioelement relationships with $P << 0.05$, we generate specific hypotheses explaining why these relationships may exist. For relationships with $P \leq 0.10$ we suggest further exploration is warranted and provide a broader discussion of possible mechanisms for these relationships. We generated P values for LME fixed effect slopes with Satterthwaite’s t tests and for random effect variances with likelihood ratio

Fig. 2 **a** Estimates of plant-available Ca in eight gravel bars spanning a gradient of freshwater mussel density in the Kiamichi and Little Rivers, Oklahoma ($N=24$). **b** Gravel bar porewater calcium concentrations ($N=12$) and **c** calcium content of *Justicia americana* above-ground biomass at 12 sites spanning a gradient of freshwater mussel density in the Kiamichi and Glover Rivers, Oklahoma, USA ($N=99$). Solid lines indicate that $P < 0.05$ for the mussel-bioelement slope of the associated linear mixed effects model

tests. We used F tests for OLS regression models with t tests for individual parameter slopes. We conducted all analyses in R v4.2.3 (R Core Team 2021).

Results

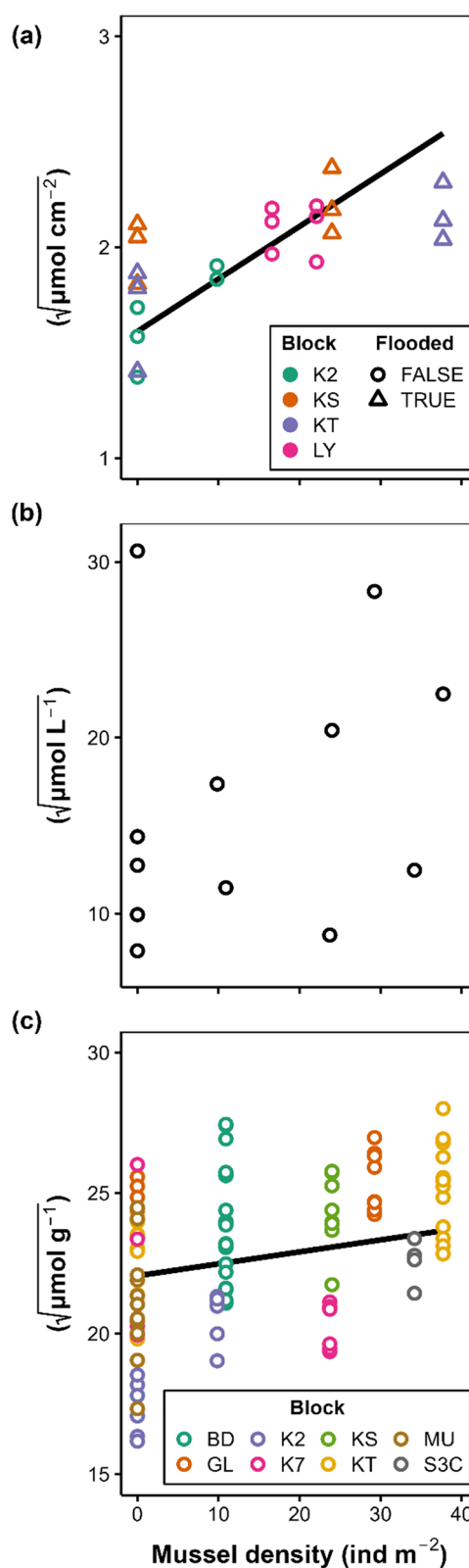
Plant-available calcium and macrophyte calcium content increased with mussel density

Our exploratory PCA indicated that Ca was an important driver of variation in the nutrient composition in all sets of samples—the soil probes, water column, porewater, and macrophytes (Tables S1–S4). In the soil probes, plant-available Ca ranged from 1.92 to 5.65 $\mu\text{mol cm}^{-2}$ and increased in association with mussel density ($t=2.9$, $P=0.017$), with a weak site effect ($\chi^2=3.2$, $P=0.076$) (Fig. 2a). In water column samples, dissolved Ca concentrations ranged from 35.2 to 129 $\mu\text{mol L}^{-1}$. In porewater samples, dissolved Ca concentrations ranged from 62.1 to 938 $\mu\text{mol L}^{-1}$. Porewater Ca concentrations did not have a clear relationship with mussel density ($t=0.8$, $P=0.423$; Fig. 2b). Macrophyte tissue Ca content ranged from 262 to 785 $\mu\text{mol g}^{-1}$, and also increased with mussel density ($t=2.56$, $P=0.012$) and varied between sites ($\chi^2=37.3$, $P < 0.001$) (Fig. 2c).

Redox-sensitive metals covaried with mussel density in macrophytes

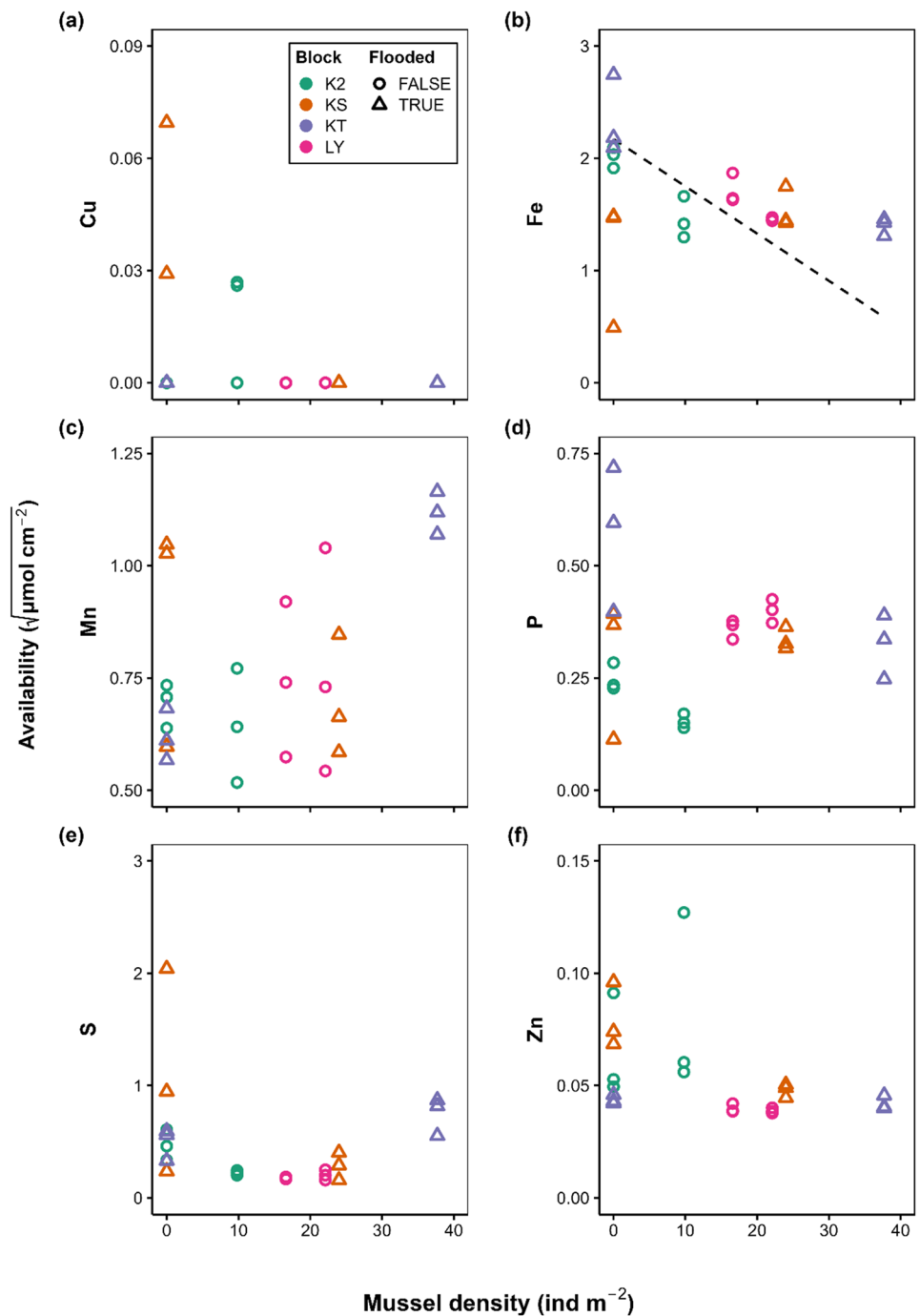
PCA suggested that Cu, Fe, Mn, S, P, and Zn drove variation in soil probe nutrient availability between sites (Table S1). Cu concentrations were consistently lower than the method detection limit in the soil probe samples. Among the predicted mussel-bioelement relationships, soil probe Cu (range: $< \text{MDL} - 0.00483 \mu\text{mol cm}^{-2}$), Mn (0.268–1.36 $\mu\text{mol cm}^{-2}$), P (0.0129–0.517 $\mu\text{mol cm}^{-2}$), S (0.0249–4.16 $\mu\text{mol cm}^{-2}$), and Zn (0.00142–0.0161 $\mu\text{mol cm}^{-2}$) availability were not associated with mussel density ($P > 0.10$; Fig. 3a, c–f), but our models did suggest Fe availability (0.242–7.53 $\mu\text{mol cm}^{-2}$) may have been weakly negatively associated with mussel density ($t=-2.0$, $P=0.070$), and this relationship varied by site ($\chi^2=4.6$, $P=0.031$) (Fig. 3b).

In water column samples, Cu (0.00851–0.0672 $\mu\text{mol cm}^{-2}$), Fe (2.82–14.5 $\mu\text{mol cm}^{-2}$), K (13.0–30.0 $\mu\text{mol cm}^{-2}$), Mg (40.3–71.7 $\mu\text{mol cm}^{-2}$), Mn



(0.0883–0.544 $\mu\text{mol cm}^{-2}$), Na (81.4–190 $\mu\text{mol cm}^{-2}$), and Zn (0.178–1.012 $\mu\text{mol cm}^{-2}$) drove variation in nutrient concentrations (Table S2). In porewater samples,

Fig. 3 Estimates of plant-available ion concentrations (**a** copper, **b** iron, **c** manganese, **d** phosphorus, **e** sulfur, and **f** zinc) in eight gravel bars spanning a gradient of freshwater mussel density in the Kiamichi and Little Rivers, Oklahoma, USA ($N=24$). Intercepts of the lines shown were calculated using the average intercepts across site blocks from linear mixed-effects models. Dashed line presence indicates that $P \leq 0.10$ for the mussel-bioelement slope of the associated linear mixed effects model. Key in panel **a** corresponds to all panels

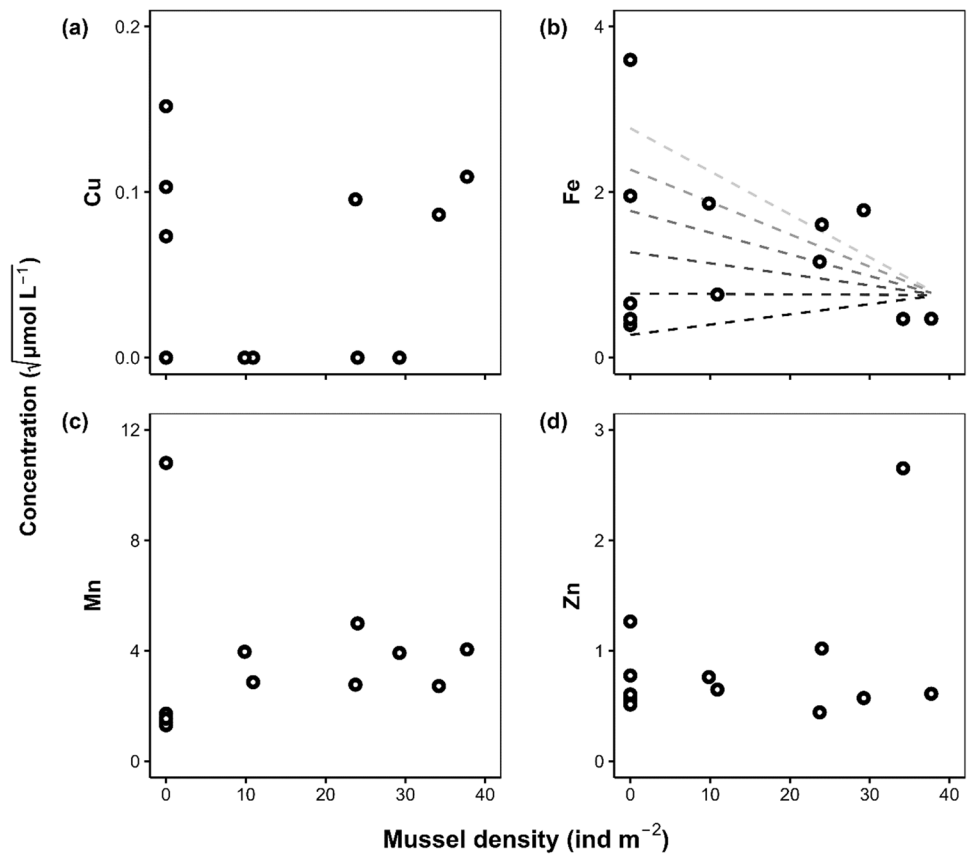


Cu ($0\text{--}0.023 \mu\text{mol L}^{-1}$), K ($20.9\text{--}77.6 \mu\text{mol cm}^{-2}$), Mg ($29.7\text{--}347 \mu\text{mol cm}^{-2}$), Mn ($1.70\text{--}117 \mu\text{mol L}^{-1}$), Na ($88.5\text{--}250 \mu\text{mol cm}^{-2}$), and Zn ($0.196\text{--}7.05 \mu\text{mol L}^{-1}$) drove variation in nutrient concentrations (Table S3), but there was no evidence for any of the predicted mussel-bioelement relationships (Cu, Mn, Zn) ($P > 0.10$; Fig. 4a, c, d). However, our post hoc analysis of the relationship between mussel density and Fe concentration ($0.157\text{--}12.9 \mu\text{mol L}^{-1}$) indicated there may be a similarly weak negative association

between mussel density and Fe concentrations in porewater as was observed in the soil probes ($t = -1.9$, $P = 0.100$; Fig. 4b). Porewater Fe concentrations also decreased as sediment grain size increased ($t = -2.9$, $P = 0.020$; Fig. 4b), although there was not a significant interaction between mussel density and sediment grain size ($t = 1.5$, $P = 0.161$).

In macrophyte tissues, Cu, Fe, and Zn drove variation in nutrient content (Table S4). The predicted mussel-bioelement associations for Cu, Fe, and Zn were mediated by

Fig. 4 Gravel bar porewater concentrations of bioelements (**a** copper, **b** iron, **c** manganese, and **d** zinc) at 12 sites spanning a gradient of freshwater mussel density in the Kiamichi and Glover Rivers, Oklahoma, USA ($N=12$). Dashed line presence indicates that $P \leq 0.10$ for the mussel-bioelement slope of the associated linear regression model. Line shading indicates sediment grain size. Lighter shaded lines indicate model predictions for finer sediments, while darker shaded lines indicate predictions for coarser sediments (range = 0–50 mm)



sediment grain size. Macrophyte Cu content ($0.0710\text{--}0.342 \mu\text{mol g}^{-1}$) increased with mussel density ($t=3.1$, $P=0.003$; Fig. 5a). However this relationship was constrained by a positive relationship between Cu content and median sediment grain size ($t=4.4$, $P<0.001$; Fig. 5a). Macrophyte Cu content was also constrained by an apparent interaction between sediment grain size and mussel density ($t=-4.2$, $P<0.001$), and varied across sites ($\chi^2=68.8$, $P<0.001$) (Fig. 5a). Fe content ($4.82\text{--}202 \mu\text{mol g}^{-1}$) also increased with mussel density ($t=6.0$, $P<0.001$) (Fig. 5b). Fe content was negatively associated with sediment grain size ($t=-3.3$, $P=0.002$) (Fig. 5b). Fe content was also constrained by an interaction between mussel density and sediment grain size ($t=-5.7$, $P<0.001$), and varied across sites ($\chi^2=98.3$, $P<0.001$) (Fig. 5b). Macrophyte Zn ($0.206\text{--}0.911 \mu\text{mol g}^{-1}$) was also positively associated with mussel density ($t=5.0$, $P<0.001$) and was positively associated with sediment grain size ($t=2.7$, $P=0.009$) (Fig. 5c). The Zn macrophyte model also suggested an interaction between mussel density and

sediment grain size ($t=-5.1$, $P<0.001$), and varied by site ($\chi^2=38.3$, $P<0.001$) (Fig. 5c).

Discussion

Calcium availability

Mussel density was associated with elevated Ca concentrations in the gravel bar substrate and in emergent macrophytes, supporting the prediction that mussel aggregations covary with Ca at the aquatic-terrestrial interface (Q1). Plant-available Ca and Ca in *J. americana* tissues both increased in association with mussel density, although dissolved Ca in gravel bar porewater had no association with mussel density. We conclude it is most likely that the observed patterns in plant-available Ca and macrophyte Ca are due to the buildup and dissolution of Ca from mussel shells, followed by uptake and assimilation

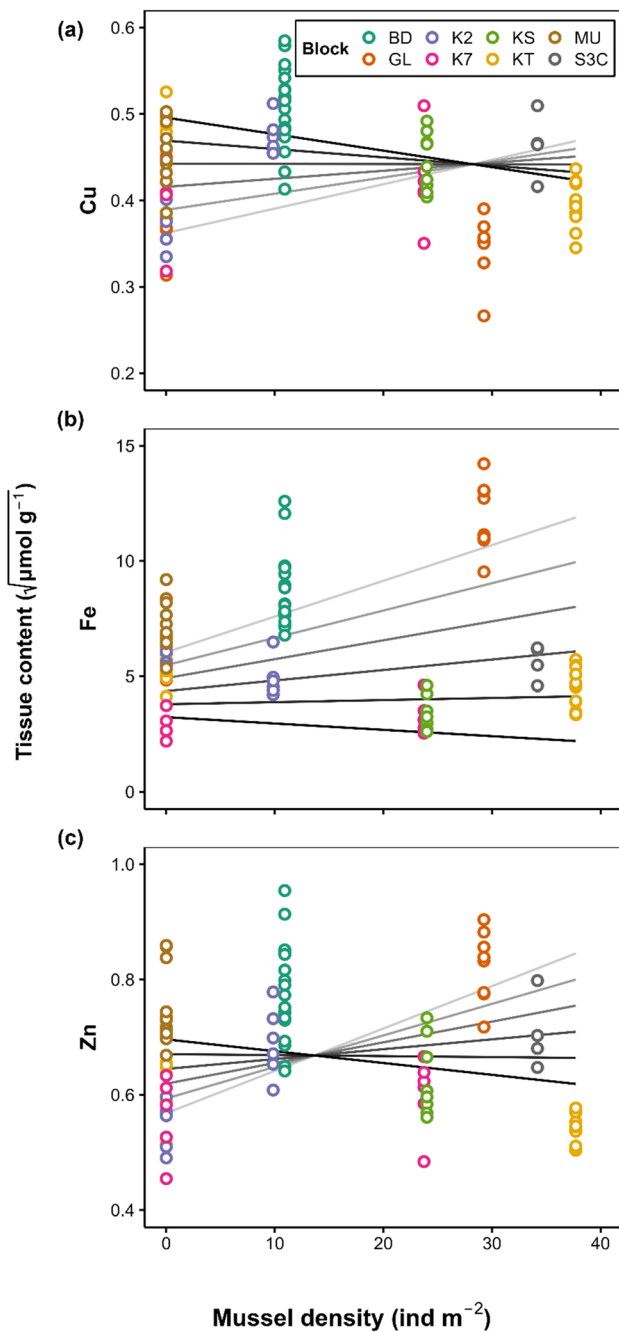


Fig. 5 Tissue bioelement content of *Justicia americana* aboveground biomass (**a** copper, **b** iron, and **c** zinc) at 12 sites spanning a gradient of freshwater mussel density in the Kiamichi and Glover Rivers, Oklahoma, USA ($N=99$). Panels with multiple lines show the interaction between sediment size (indicated by darkness of the line shading) and mussel density. Intercepts of the lines were calculated using the average intercepts across site blocks from linear mixed-effects models. Solid lines indicate that $P < 0.05$ for the mussel-bioelement slope of the associated linear mixed effects model. Line shading indicates sediment grain size. Lighter shaded lines indicate model predictions for finer sediments, while darker shaded lines indicate predictions for coarser sediments (range = 0–50 mm). Key in panel a corresponds to all panels

into macrophyte tissues. We suggest this positive relationship occurred because Ca is relatively bioavailable when dissolved as a divalent cation (Ca^{2+}) and plants have a high demand for Ca, so it benefits the plant to take up and store as much Ca as possible (i.e., luxury consumption; Sterner and Elser 2002). While we did not detect a clear association between mussel density and dissolved Ca in gravel bar porewater, we suspect our failure to detect such a relationship stemmed from small sample size incurred by our site-level sampling scheme. Indeed, post hoc outlier removal suggested this apparent lack of a relationship may be the byproduct of a single site with zero mussel density which also had the highest observed porewater Ca concentrations. Our study was not designed to disambiguate whether mussel density was driving elevated Ca concentrations versus responding to naturally elevated Ca concentrations. Alternative explanations for the observed positive correlation could include that mussels tend to aggregate in areas with Ca-rich groundwater inputs that might alleviate Ca limitation or demand. However, waters in the Kiamichi River are well above the water hardness and acidity thresholds that might limit mussel distributions (Haag 2012; OWRB 2017). Further, the Kiamichi River has relatively few reaches that gain groundwater in the portion of the river we studied, and most reaches lose surface water to groundwater recharge (Brewer et al. 2019). As such, we find it more likely that mussels are driving the observed associations with Ca.

The Ca content (~ 1–3% Ca by weight) of our study macrophyte, *J. americana*, well exceeded the Ca content found in most terrestrial vegetation ($\leq \sim 1\%$) (Fashingbauer and Moyle 1963; Kreulen 1975; Pabian et al. 2012; Kaspari et al. 2021). Ca concentrations in aquatic vegetation may be up to twice as high as those in terrestrial vegetation, and Ca-rich plants are thought to confer nutritional benefits to herbivores (Kreulen 1975; Freeland and Choquenot 1990; Ceacero et al. 2014). As mussel shells are deposited onto gravel bars, the shells may essentially lime the gravel bar sediments, and enhance the nutritional benefits that herbivores receive from eating these plants (Pabian et al. 2012). Based on the findings of the present study, we suggest the following hypothesis: gravel bar sediment and macrophyte Ca concentrations are positively related to a site’s mussel density in gravel bars due to the buildup and dissolution of shell material in the environment. To test this mechanism experimentally may be difficult, as mussel shells decay slowly. The average decay rate for one common North American mussel species (*Amblema plicata*) has been estimated at $k = -0.0001 \text{ day}^{-1}$, taking as long as 31 y to decay completely (Atkinson et al. 2018). Testing this hypothesis would thus require more targeted field studies that explicitly focus on Ca pools and fluxes, while accounting for alternative sources of Ca.

Availability of redox-sensitive metals

The prediction that mussels were associated with variability in redox-sensitive trace metals in gravel bar sediments was not well-supported, but we still suggest that future research on the relationship between mussels and redox-sensitive bioelements in gravel bars is warranted (Q2). The weak negative associations we observed between mussel density and plant-available Fe in the soil probe study and dissolved Fe in the porewater samples could be consistent with physicochemical structuring where mussel burrowing or shell deposition increases oxygen penetration into sediment pore spaces (Matisoff et al. 1985; Aller 1990; Bódis et al. 2014). Increases in oxygen penetration to the substrate may preclude microbial reduction of Fe, thus causing Fe to precipitate as solid Fe oxides (Zhang et al. 2014). CaCO₃ from shell decay could also decrease Fe plant-availability by buffering the acidity of gravel bar sediments (Graham and Stangoulis 2003). Ultimately, however, the weak relationship between mussel density and Fe availability and concentrations in gravel bars should be viewed as equivocal unless additional—ideally experimental—evidence suggests otherwise.

Compared to gravel bar sediments, variation in the trace metal content of *J. americana* tissues was more strongly associated with mussel density (Q2). If the weak negative association of gravel bar sediment Fe concentrations with mussels does represent a real ecological pattern, then the contrasting patterns in Fe concentrations between gravel bar sediments or porewater and macrophytes could be explained by the hypothesis that plants preferentially adsorb bioelements that are scarce in the environment (Kaspari 2021). Plants increase Fe uptake when they are deficient, suggesting that the macrophytes may preferentially take up Fe as it becomes scarcer in the porewater. The same mechanisms that plants use to upregulate Fe adsorption also promote the uptake of Cu, Zn and other metals as a byproduct—regardless of their concentrations (Graham and Stangoulis 2003). Decreases in porewater Fe could have thus caused *J. americana* to acquire excess Fe, Cu, and Zn, resulting in increased macrophyte Fe, Cu, and Zn content.

Verifying whether the observed relationships between mussels and gravel bar Fe concentrations are causal will require additional research, especially since we found that *J. americana* metal concentrations covaried not only with mussel density, but sediment grain size. Our study sites varied considerably in sediment grain size, and relationships between mussels and macrophyte metal concentrations tended to be strongest at sites with finer sediments. If mussels introduce gaps for oxygen penetration through burrowing or shell deposition, these effects should be stronger at sites with finer sediments that have lower oxygen penetration. Indeed, we found that the mussel-bioelement

relationship for macrophyte tissue was predicted to be positive when sediment size was finest, and negative when sediment size was coarsest. This type of potential animal-environment interaction highlights the environmental context-dependency of observational field studies such the one presented here. A factorial approach where mussel density, shell presence, and sediment grain size are systematically varied could begin disentangling how mussels may alter the cycles of redox-sensitive elements like Fe at the aquatic-terrestrial interface. Aquatic mesocosms or self-contained benthic field enclosures would provide ideal settings for such an experiment.

Conclusions

Taken together, our findings support the notion that freshwater animal aggregations impact elemental cycles beyond the well-studied C, N, and P pathways. Animals' biogeochemical impacts may be especially strong for elements that are more concentrated in animal tissues than in plants. We focused primarily on calcium concentrated in bivalve shells, but animals also disproportionately accumulate—and hence may redistribute—other elements such as Na, Cr, lithium, nickel, arsenic and cobalt (Kaspari 2021). Our study represents the type of exploratory ecosystem research that is needed to develop an improved understanding of how animals interact with a broader range of biogeochemical cycles in freshwater ecosystems. Once patterns in elemental availability such as the ones we have quantified here are identified, the mechanisms that drive them can be more rigorously tested (Tredennick et al. 2021). These mechanisms may be direct (e.g., assimilation and subsequent release via decay or in excreta) or indirect (e.g., physical effects on ecosystem structure). The diversity of elemental cycles that animals interact with and the diversity of mechanisms by which animals may impact these cycles therefore represent a fruitful direction for both exploratory and experimental research.

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Author contribution statement JWL and CCV designed the field studies. RNH conducted and advised on ICP-OES analyses. TBP assisted with the PRS[®] probe study and consulted on data analysis and interpretation. JWL wrote the initial manuscript and revised with input from all authors.

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Data availability The datasets used and analyzed during the current study are uploaded to Open Science Framework and can be found here (<https://osf.io/dahytr/>).

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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