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Physicochemical effects on Zn sediment cycling

INDIRECT EFFECTS OF CLIMATE CHANGE ON ZINC CYCLING IN SEDIMENTS: THE ROLE OF CHANGING WATER LEVELS[1]

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Abstract

Increased variability in lake and river water levels associated with changing climate could impact the fate and effects of metals in redox-sensitive sediments through the alteration of microbial communities and of acid–base and redox chemistry. The objective of the present study was to determine the influence of water level fluctuation on metal speciation in porewater and predict environmental risk to high-carbonate systems. Using experimental microcosms with sediments collected from 4 metal-contaminated coastal freshwater wetlands in Michigan, USA, we conducted water level fluctuation experiments. Porewater and sediment metals (Ca, Cu, Fe, Mg, Mn, Ni, Zn) and important metal binding phases (iron-oxide speciation, acid-volatile sulfide) were quantified. In a short-term drying (seiche) experiment, there were decreases in all porewater metals after inundation of saturated sediments. During a drought experiment, re-inundation of oxidized sediments increased porewater Cu, Zn, Mg, Ca for most sites. Porewater Zn increased after inundation to levels exceeding the US Environmental Protection Agency threshold for chronic toxicity. These data show that the dissolution of metal carbonates and metal sulfates contributes to metal release after re-flooding and indicate that we might expect increased ecological risk to organisms present in drought-sensitive regions where altered hydroperiods are likely to increase metal bioavailability.

Keywords: Metals, Ecotoxicology, Sediments, Wetlands, Climate change, Redox, Biogeochemistry, Zinc cycling, Water level fluctuation

This article includes online-only Supplemental Data.

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INTRODUCTION

Climate change is affecting regional hydrology, with collateral effects on the biogeochemistry of aquatic systems [1]. Although climate is variable in nature, the magnitude, frequency, timing, and duration of precipitation or flooding events (hydroperiod) are expected to be altered significantly on a regional basis by warming global temperatures [2]. Increased water level fluctuation affects coastal ecosystem biogeochemistry by altering sediment acid–base chemistry, redox potential, and microbial community response, which can facilitate release or sorption of metal contaminants [3]. These processes are relevant to several hydrologic types, such as streams and wetlands.

The fate and release of metal contaminants are controlled primarily by the abundance and reactivity of ligands that bind metals, thereby reducing their ecotoxicity. Many metals of concern (Zn, Cu, and Ni) are primarily toxic to organisms in their +2-oxidation state, when dissolved. The primary objectives of the present study were to determine the influence of water level fluctuation on metal speciation in porewater and sediments, to identify the key binding ligands associated with metal flux, and to discuss potential effects to benthic macroinvertebrate populations.

Many ligands are sensitive to redox, pH, or microbial changes associated with water level fluctuations, including Fe/Mn-oxyhydroxides, metal sulfides, and metal carbonates. Oxygen fluxes affect the formation and dissolution of Fe/Mn-oxyhydroxides, which can release or bind metals [4]. Another primary fate process of these metals is binding to sulfide complexes under reduction and release after oxidation of sediments [5]. In this reaction, sediment microbes kinetically mediate the production and oxidation of sulfide. Although the formation of metal carbonates is less influenced by redox or microbial activity, it is highly a function of pH, which

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has been shown to increase after reduction of oxidized sediments [6]. Yet another primary binding phase is organic carbon, which is thought to be less affected by redox state and varies in importance, depending on the metal of interest [7]. Predicting sediment toxicity in hydrologically dynamic watersheds is nuanced because of the complexity of formation of these compounds.

Sediments with low acid neutralizing capacity (such as acid-sulfate or low-carbonate systems) are very sensitive to hydrologic pulses. In one study in Hamburg Harbor, Germany, oxidation of reduced sediments led to a decrease in pH from 8 to 4, leading to release of metals into the water column [8]. Recent work investigating effects of flooding on the drought-induced floodplain of Australia's Lower Murray River similarly showed a sudden decrease in pH after inundation, attributable to release of iron sulfate, with acidity persisting in sediments for more than 3 yr after the initial inundation [9,10]. Further studies of sulfide oxidation focus on treatment of acid mine drainage, more specifically using the Global Acid Rock Drainage guide to predict geochemical behavior of waste rock [11].

Work investigating the role of hydroperiod on metal dynamics in medium-high–acid neutralizing capacity freshwater systems has focused primarily on nutrient availability and has not been linked to metal toxicity. Reflooding of oxidized sediment as a part of a wetland restoration led to eventual reduction of Fe and release of phosphate into surface water [12]. Steinman et al. [13] showed similar results in a controlled laboratory testing of coastal Great Lakes wetland sediments after 8 wk of soil desiccation. These studies suggest Fe oxidation plays an important role in hydrologically dynamic sediments, which may influence the fate of other metals.

One metal-centric study of a high–acid neutralizing capacity floodplain forest along the upper Mississippi River (La Crosse, WI, USA) found an increase in porewater Zn and other

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metals during a 4-mo oxidation period [14]. In a freshwater tidal wetland in Virginia, USA, Seybold et al. [15] showed a direct correlation of oxidation and acidification, which helps explain why metal flux is being observed in low-acid systems. Further evidence is needed to show whether metal flux associated with water level fluctuation in high-carbonate sediments are likely to induce effects to macroinvertebrate populations.

We predict that inundation of oxidized sediments will lead to a release of previously sediment-bound metals; that long-term drought events will produce higher porewater metal bioavailability and theoretical toxicity than short-term, seiche events, as a result of an increase in oxidized sediment fraction; and that sulfide, iron/manganese oxides, and carbonate-binding ligands will be the primary controls on metal flux. These data will help predict the effect of climate-induced water level fluctuation on metal cycling and toxicity in the freshwater systems, such as the Great Lakes, and inform continued management and protection of wetland and shallow-water ecosystems.

METHODS

Site/sediment selection

We selected 4 coastal lacustrine wetlands of high sediment metal content, variable hydrology, and diverse sediment chemical composition and grain size (all minerotrophic). By selecting several sites, we can compare effects of sediment type and improve relatability to multiple field conditions. The sites selected were Quanicassee Wildlife Refuge (QC), East Bay Park (EB), Little Black Creek (LBC), and Lake Erie Metropark Wetlands (DRW). A map of sediment collection sites is provided in Figure 1, with additional site description in the Supplemental Data. We also collected nonpolluted sediments as a control from the River Raisin (RAIS) in Manchester, Michigan. A detailed comparison of site characteristics is provided in

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Table 1.

Experimental design

Sediment columns were extracted intact with a trenching shovel from each site and placed in 3 replicate microcosm chambers per site (November 2014). Sediments were irrigated and remained saturated at room temperature to support microbial life until experiments began in January 2015. Microcosm design is depicted in Figure 2. Input water chemical composition is similar to Great Lakes surface water, with an average of 152.9 ± 1.4 mg L^{-1} $CaCO_3$, 6.2 ± 0.02 mg L^{-1} O_2, 7.6 ± 0.1 pH, 40.7 ± 0.4 mg L^{-1} Na, 3.4 ± 0.3 mg L^{-1} K, and approximately 0.15 mg L^{-1} Cl. Concentrations of other metals in input water were below detection (~5 μg L^{-1}). The flow rate was constant at 1.55 ± 0.5 cm^3 s^{-1} during water additions.

Two experiments mimicking a seiche (short-term drying) and a month-long drought were conducted, both with sediment drying followed by sediment rewetting (15 h and 32 d for seiche and drought, respectively). The seiche and drought hydroperiod were chosen due to their frequency of occurrence in Great Lakes systems. Seiches occur during storm events, when wind pushes water to one side of a lake, causing a basin-wide standing wave. The month-long drought was designed to mimic seasonal low water (dry season) and high water (wet season).

Surface water was drained from microcosms with a 250-μm mesh syringe during drying, with additional drainage from a small 1-cm hole in the bottom of each chamber. An over-head drip system was used to re-inundate sediments, and the drainage hole in the bottom of each chamber was left open (seiche) or closed (drought). This irrigation system emulated precipitation and may have slightly different results than a groundwater-fed system because of the potential for trapped air in microcosm sediments. Excess water overflowed into a drainage basin and was discarded. During the seiche and drought experiments, water was refreshed for 10 min every 6 h

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or for 4 min every 24 h, respectively.

Sampling and lab analysis

Porewater metals were sampled at all depths before and after 15 h of reflooding (for seiche) or after 1, 11, 16, 32 d of reflooding (for drought). Additional sampling for redox parameters (dissolved oxygen and reduced Fe) occurred on days 3, 9, and 24 (for drought). Water was extracted with a nitrogen-purged syringe. A maximum volume of 15 mL porewater was filtered through Rhizon samplers to 0.19 µm, and surface waters were filtered with a 0.45-µm Millipore syringe-attachable filter. Dissolved oxygen in porewater was immediately measured using a 100-µm-diameter oxygen microelectrode. Filtered samples were then acidified with trace metal grade nitric acid to 2%, stored in the dark at 4 °C, and analyzed within 1 mo on an inductively coupled plasma–optical emission spectrometer (ICP-OES) for metals Cu, Ni, Zn, and other important metals associated with binding (Ca, Fe, Mg, and Mn). Metal detection limits were ~5 to 10 µg L^{-1} (Cu, Ni, Zn) or 50 µg L^{-1} (Ca, Fe, Mg, Mn). Concentrations were corrected using a procedural blank (run for every 30 samples). Additional porewater was sampled and quickly analyzed for reduced iron (Fe^{2+}) concentration using a colorimetric (ferrozine) method [16]. Porewater dissolved organic carbon (DOC) was analyzed after acidification (with 6M HCl to a pH of 2) on an Aurora 1030 TOC Analyzer (OI Analytical).

Dry and wet phase sediment cores were extracted from each microcosm on the day prior to re-inundation, 15 or 24 h after inundation, and (for drought experiment) 11 and 32 d after inundation. Sediment cores were sectioned with an acid-cleaned plastic spatula into 1.5-cm increments in a N_2 filled, continuous-flow purging bag. Sediment was processed for acid volatile sulfide (AVS) content and simultaneously extracted metals (SEM) [17], iron oxide crystalline and amorphous content [18], dry weights, and loss on ignition (6-h combustion at 450°C) for

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organic carbon content. Replicate procedural blanks and reference sediments were run with digestions to verify >80% recovery between iron oxide extractions and to correct for reagent-associated metals. Extracted metal solutions were analyzed on an ICP-OES. Sediment pH was measured using a sediment probe.

Statistical analysis

Significance testing was conducted on 2 levels: a multi-site level, including all microcosms as one sample, and a single-site level, looking at individual sites (QC, EB, DRW, and LBC) separately. Most data were not normally distributed, with a right skew attributable to natural heterogeneity (mottling of metals) in sediments. For nonparametric data, Kruskal-Wallis tests were used for multiple variable comparisons, and the median or sign test was used for paired analysis. Where distributions were found to be normal, the equivalent analyses of variance and paired *t*-tests were used. Pearson correlations between porewater metal content and chemical parameters were used when assumptions were met (normality, linearity, homoscedasticity). For non-parametric data, Spearman's rank test was used to determine correlations. All statistical tests were conducted in RStudio, ver 0.98.1102.

The Biotic Ligand Model (BLM) program (Ver 3.1.2.37; Windward Environmental) was used to calculate Zn-BLM chronic 5% hazardous concentrations for *Ceriodaphnia dubia.* Assumptions included sulfide concentrations ranging from 0.001 mg L^{-1} on day 1 to 0.00599 mg L^{-1} on day 32 to reflect increases in measured AVS. Alkalinity was calculated using a pCO^2 of 3.5 assuming an open system. Due to insufficient porewater samples sizes, unmeasured parameters (Na, K, SO_4, and Cl) needed to be estimated and were done so per BLM recommendations with reference to Appendix C of the US Environmental Protection Agency's (USEPA's) aquatic life ambient freshwater quality criteria for Cu [19]. These parameters were a

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lower priority for analyzing from the limited sample volume because they are less influential in predicting Zn toxicity than other inputs, such as pH and Ca [20].

RESULTS

Site comparison

The most obvious and potentially important difference between sediments is the sediment texture, in addition to loss on ignition (% C), sediment pH, and metal content. Important differences between sites are illustrated in Table 1. Particle size distribution indicates EB and QC are coarse sandy sediments, LBC is a sandy loam, and DRW is a sandy clay loam. Percent by weight of carbon (from loss on ignition) was statistically higher for DRW and LBC than for EB and QC ($p < 0.01$). Three statistical groupings for porewater DOC included high (LBC), moderate (QC), and low (EB and DRW; $p < 0.01$). Sediment pH was statistically different on average between all sites, where LBC was most acidic, followed by DRW, QC, and EB ($p = 0.001$).

Porewater concentrations of Cu, Fe, Mn, and Zn were statistically highest in LBC ($p < 0.004$). For Cu and Zn, there were 2 statistical groupings of high metal content (mean, 3.5 ± 0.6 μg L^{-1} Cu and 159.3 ± 16.5 μg L^{-1} Zn) in LBC and low metal content (mean, 0.6 ± 0.2 μg L^{-1} Cu and 7.0 ± 4.6 μg L^{-1} Zn) in DRW, EB, and QC. For higher-concentration metals Fe and Mn, 3 statistical groupings existed for LBC (mean, 14.8 ± 1.8 mg L^{-1} Fe and 2.2 ± 0.2 mg L^{-1} Mn), DRW (mean, 6.8 ± 0.7 mg L^{-1} Fe and 0.9 ± 0.1 mg L^{-1} Mn), and EB and QC (mean, 1.4 ± 0.1 mg L^{-1} Fe and 0.4 ± 0.03 mg L^{-1} Mn). Reduced Fe concentrations followed this trend as well. Porewater Ca, Mg, and Ni were similar between sites. Total metals analysis showed higher metal concentrations for LBC and DRW than for QC and EB, as shown in Table 1.

When comparing sulfide concentrations in sediments, EB had less AVS on average than

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the other sites (mean, 0.8 ± 0.3 vs 3.4 ± 0.9 µmol S^{2-} g^{-1} dry wt; $p = 0.001$). [SEM-AVS] as normalized for organic carbon varied between most sites. From highest (theoretically most toxic) to lowest (theoretically non-toxic), the 3 groupings were LBC and DRW, EB (and DRW), and QC (and EB) (Table 1; $p < 0.02$).

Higher concentrations of Mn and Fe in LBC and DRW sediments led to higher fractions of Fe oxides, Mn oxides, and Zn bound to Fe/Mn oxides in these sediments than in QC and EB ($p < 0.001$). Average total oxidized concentration for high and low statistical groupings were 71.1 ± 3.8 and 8.6 ± 1.4 µmol Fe g^{-1} dry wt, 3.2 ± 1.7 and 0.9 ± 0.7 µmol Mn g^{-1} dry wt, and 3.0 ± 1.3 and 0.6 ± 0.2 µmol Zn g^{-1} dry wt. Many of the differences between sites are likely related to site hydrology, as LBC and DRW are low-energy (depositional) riverine wetlands, whereas EB and QC are high-energy (less depositional) lacustrine, fringing wetlands.

Seiche experiment

After the 15-h drying period, surface sediments remained partially saturated and chemically reduced. After inundation, sediment moisture content increased by a range of 1% to 15% (average change, 10.0 ± 2.4%), from 39.1 ± 7.5% to 49.0 ± 9.2% on average. Sites with a sandy soil texture (EB and QC) had the highest change in moisture content, compared with sandy loam (LBC) and sandy clay loam (DRW) sediments. After inundation, pH decreased for LBC and DRW microcosms by 0.6 ± 0.05 ($p \leq 0.035$), from 6.8 to 6.3 ± 0.03, but there was no change for QC or EB. The pH remained neutral in all microcosms (range, 6.0–7.4; average, 6.7 ± 0.3). A decrease in porewater Fe^{2+} concentration between saturated and inundated phases suggests sediment oxidation ($p < 0.002$). Although the Fe^{2+} decrease was observed for all microcosms, as individual sites, it was only significant for DRW ($p = 0.04$). We observed no change in porewater dissolved oxygen content (0–1 cm) after inundation.

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All measured porewater metals—including Ca, Cu, Fe, Mg, Mn, Ni, and Zn—decreased in concentration after inundation of sediments (Figure 3). A significant decrease in Zn resulted from inundation ($p = 0.00006$), largely because of decreases of Zn in sandy sediment microcosms (QC and EB). Likewise, a decrease in Ca and Mg ($p \leq 0.02$) occurred from 64.5 ± 6.5 to 47.0 ± 4.7 mg L^{-1} Ca and from 188.0 ± 11.6 to 157.1 ± 9.4 mg L^{-1} Mg for all sites on average. Decreases in Ca and Mg were only significant for LBC and EB on the single-site level ($p < 0.05$). Other decreases (Cu, Fe, Mn, and Ni) were not significant on the multi-site level; however, Fe decreased in LBC from 39.5 ± 4.6 to 21.0 ± 5.0 mg L^{-1} ($p < 0.04$). Nevertheless, results for Cu and Ni may be misleading because concentrations were occasionally below detection.

All sediments from the seiche experiment had a negative average [SEM-AVS] when normalized to organic carbon (Figure 4), indicating theoretically non-toxic sediments as a result of sulfide binding. Increased variability for DRW and QC sediments was likely attributable to wide-ranging AVS values caused by strong vertical redox gradients. In other words, DRW and QC sediments had a strongly defined oxic (≈0–1.5 cm) and reduced layers (≈1.5–3 cm). On average, saturated and inundated sediments showed no differences in [SEM-AVS] on the single-site or multi-site level.

In addition, no differences in total, amorphous, or crystalline oxidized Fe content were observed between saturated and inundated sediments. Average total and amorphous oxidized Fe values between all sediments were 131.8 ± 21.8 and 43.9 ± 7.6 μmol Fe g^{-1} dry wt, respectively. This suggests metal binding to Fe-oxyhydroxides is unchanged during seiche events. As shown in Figure 5, porewater hardness decreased between saturated and inundated phases for EB and LBC ($p < 0.05$), suggesting formation of metal bicarbonates.

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Drought experiment

After 32 d of drying, sediment was oxic with no extractable porewater. Sediment moisture increased after inundation by a range of 8% to 32% (average, 24.8 ± 4.5%), from 17.7 ± 2.5% to 45.3 ± 7.5% on average. The sandy clay loam (DRW) sediments had a very small increase in water content (8.5%) compared with the sandy and sandy loam sediments. Throughout the experiment, sediment pH either increased (for LBC and DRW, from 6.4 to 6.7 ± 0.06) or stayed the same (QC and EB). This suggests that QC and EB have a greater apparent acid buffering capacity than LBC and DRW. The pH stability in QC/EB may also be attributable to lower concentrations of iron sulfides in these sediments. Dissolved oxygen in porewater (0–2 cm depth) decreased on average during the 32-d inundation, whereas Fe^{2+} concentration increased, indicating sediment reduction (Supplemental Data, Figure S1). When considering all sites, Fe^{2+} concentrations increased among days 1, 3, 9, and 16 ($p < 0.001$).

As predicted, inundation of oxidized sediments led to increased porewater Zn and Cu, which then decreased over 32 d (Figure 2). The observed increase in porewater Zn for LBC is especially notable, as it exceeded the USEPA threshold for chronic toxicity (CCC) to freshwater organisms (120 µg L^{-1}) for approximately 30 d [21]. Both EB and QC exceeded the CCC, but only on day 1 after inundation, whereas DRW did not for either experiment (although it did in later trials with increased sediment drying). For Cu, however, LBC and DRW microcosms did not show a significant decrease. These sediments had the highest loss on ignition ($p < 0.05$), which suggests a greater role of organic carbon in controlling Cu partitioning.

We observed the opposite trend for Fe and Mn, where metals started in low concentrations and increased throughout the study (Figure 3). This effect is likely the result of reductive dissolution of Fe/Mn in sediments, as reflected in the formation of reduced Fe. Iron

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and Mn sampling concentrations measured on day 1 after inundation were lower than on days 11, 16, and 32 ($p < 0.00001$). The only exception to this trend was for Mn concentrations in the QC microcosms, which were all similar.

Oxidized sediments pre-inundation and 24 h after inundation had a positive average [SEM-AVS] of 13.6 ± 1.50, as normalized to organic carbon, which suggests potential sediment toxicity to benthic macroinvertebrates (Figure 4). Because all microcosms had AVS concentrations of 0 μmol g^{-1} on day 1 after inundation, [SEM-AVS] became positive. After 32 d of inundation, [SEM-AVS] decreased for all sites except DRW. On the multi-site level, decreases in [SEM-AVS] were not significant (likely because of the small sample size); however, QC's decreases were significant ($p = 0.001$).

No difference in total, amorphous, or crystalline Fe/Mn-oxyhydroxide content occurred between oxidized and inundated sediments at the experiment or site scale. Average total and amorphous oxidized Fe between all sediment types was 98.5 ± 17.6 and 33.2 ± 5.8 μmol Fe g^{-1} dry wt, respectively. In addition, a large fraction of total Zn (63.5 ± 1.4%) was bound to Fe/Mn-oxyhydroxide minerals between all sites. The only phase that decreased after inundation was the amorphous Fe/Mn-oxyhydroxide–bound Zn ($p = 0.055$). Carbonate in sediment and porewater may have also influenced metal flux, as porewater hardness decreased between day 1 and day 32 of inundation (from 477.8 ± 46.3 to 152.1 ± 11.3 mg L^{-1} as $CaCO_3$; $p < 0.0000001$), suggesting precipitation of metal bicarbonates (Figure 5).

Comparison of seiche and drought

Our prediction that metal flux would be greater in the drought experiment than the seiche was correct for several metals. Porewater concentrations of Ca, Cu, Mg, and Zn were greater on average (all days) in the drought experiment than in the seiche experiment ($p < 0.001$). For

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porewater Fe (total and reduced fractions), conversely, seiche-induced sediments had higher concentrations than drought sediments ($p = 0.008$). Reduced Fe concentration was also greater in seiche sediment, with 4.0 ± 0.4 mg L^{-1} Fe^{2+} as compared with 2.3 ± 0.2 mg L^{-1} Fe^{2+} in drought sediment. Porewater concentrations of Ni and Mn were similar between experiments.

The potential for sediment toxicity as [SEM-AVS] normalized to organic carbon was statistically different between the seiche and drought experiments ($p < 0.0001$). Whereas this value stayed mostly negative during the seiche event (mean, –29.8 ± 8.2), it was mostly positive during the drought oxidation event (mean, 8.9 ± 1.9), suggesting that drought-inducing conditions create higher theoretical risk of toxicity. All sediment sampled during both experiments had similar oxidized Fe content. Sediment pH was on average greater in the drought experiment than the seiche experiment (mean, 6.9 ± 0.03 vs 6.6 ± 0.08; $p < 0.000001$).

Some measured parameters, such as DOC in porewater and sediment loss on ignition, were not affected by hydrologic manipulations. Sediment organic matter was similar throughout the seiche and drought experiments (mean, 0.13 ± 0.04% C). Porewater DOC was similar for all microcosms between all experiments; however, one exception was a statistical decrease in DOC for EB during the drought experiment (mean, 1.1 ± 0.3 to 0.5 ± 0.2 mg L^{-1} C; $p < 0.02$).

DISCUSSION

Assessing ecological risk of seiche and drought

The magnitude of chemical change observed during the simulated seiche is relatively unconcerning from a biological perspective. Metals concentrations did not exceed CCC, with [SEM-AVS]/*f*OC values remaining negative. The pH decrease observed for LBC and DRW may indicate oxidation or increased microbial production after inundation of sediments. Several species of amphipods can be sensitive to acidification with changes to pH of >0.7 units, although

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this is mostly an issue in warmer-temperature water with low pH (<6) [22,23]. Although the magnitude of sediment acidification in LBC and DRW during the seiche was less than 0.7, field-monitoring efforts should consider large-scale changes in sediment pH with water fluctuation events, as the magnitude may vary. Porewater metal concentrations typically increase with acidification, but the opposite was observed in the present study. It is possible that metals leached from the microcosm chambers, as some drainage occurred in attempt to emulate groundwater dynamics. Seiche, tides, and other short-term water level fluctuations raise and lower the water table in accordance with water level. As the water table lowers, porewater leaches from wetland sediment; however, re-inundation would include metal-rich groundwater inputs (which our experimental design did not include) [24]. In field settings, we would still expect porewater metals to increase with a pH decrease, despite these findings.

The increase in porewater Zn after inundation of drought/oxidized sediments is an ecological concern, because it may adversely affect benthic macroinvertebrates inhabiting metal-contaminated sediment. Although QC, EB, and LBC all exceeded the USEPA threshold for chronic toxicity, LBC was the only site in exceedance when compared with the hardness corrected criteria (Figure 6). However, recent studies using a BLM for Zn show that chronic toxicity to organisms is often underestimated using the hardness corrected criteria [20], particularly for *C. dubia*. In the present study, we found the hardness corrected criteria to be somewhat underprotective as compared with the Zn-BLM for 2 of our sites (EB on day 1 and LBC on days 1–16). The BLM is designed to address environmental risk to surface water organisms and not benthic organisms exposed to porewater; however, it is more mechanistic and chemically descriptive than current theoretical models or screening methods for sediments such as SEM-AVS or probable-effects concentrations. A sediment BLM that can accurately predict

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metal bioavailability where organic carbon is the primary binding ligand has been produced; however, it is not yet fully applicable to field settings or designed to account for changing redox conditions [25]. Future model development is needed to accurately incorporate benthic species into the BLM or similar user-friendly and mechanistically driven model.

Although the probability of toxic effects to organisms associated with Zn pulsing is debatable, one study confirmed its occurrence during field sampling in a similar watershed [14]. In Krieling et al. [14], porewater ion content measured by a plant root simulator (PRS) showed increasing Zn concentrations with sediment oxidation in a floodplain of the upper Mississippi River (WI, USA). Further, in White et al. [26], species richness in high-carbonate lakes (in Great Lakes region) was found to be highest when the magnitude of water fluctuation remained unchanged from year to year. The loss of species richness was weakly correlated to water quality (DOC, Ca^{2+}, Conductivity, pH, SO_4^{2-}), although metal analyses were not included in the study. These 2 lines of evidence, in conjunction with findings from the present study, suggest that field studies should be conducted to precisely assess impacts of Zn oxidative release.

In addition to the dissolved Zn porewater concentrations, [SEM-AVS] values are another line of evidence indicating sediments oxidized during drought may have increased theoretical toxicity to organisms. Several studies using Zn-spiked sediments have clearly shown that [SEM-AVS] values >0 are strongly correlated with metal toxicity to several macroinvertebrate species [27,28]. Despite these findings, others suggest it may not be appropriate in nonequilibrium systems because of differences in reaction kinetics of sulfide reduction between sediment types and the preference for less toxic microsites by organisms [29,30]. Regardless, it is still a useful tool to help predict metal binding to sulfide and organic matter in sediments, as well as metal bioavailability.

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Effects of sediment chemistry on redox-induced Zn pulse

During the present experiments, several important metal binding phases were affected during drought conditions, including carbonates and sulfides. Sulfide (as AVS) and carbonate (in porewater) were moderately correlated with Zn in LBC porewater (cc = –0.64, $p < 0.01$; cc = 0.59, $p < 0.001$). This is strong evidence that porewater Zn increased after inundation due to oxidation of Zn sulfides and dissolution of Zn carbonates. A theoretical schematic of these reactions is provided as Figure 7. Zinc sulfides have been well studied and are known to be an important ligand for Zn bioavailability [31,32]. The mechanics of Zn carbonate formation and dissolution are less studied but are of considerable importance in high-carbonate systems [33]. Zinc carbonate precipitation may have increased during sediment drying, leading to increased dissolution after sediment inundation. This effect would be enhanced by the observed increase in sediment acidity on day 1.

It is somewhat surprising that there was not a clear change in sediment Fe/Mn-oxyhydroxide content (crystalline, amorphous, or total), especially in sediments with high Fe (DRW and LBC). Most studies show an overall decrease in sediment Fe/Mn-oxyhydroxide content with reduction, although these studies use homogenized (not heterogeneous) sediment. In more controlled studies, reductive dissolution of Fe/Mn-oxyhydroxides has been found to be important for porewater metal equilibrium [34]. Further evidence using electron microscopy techniques shows the formation of Zn on and in amorphous ferrihydrite and vernadite-like minerals in oxidized sediments [35]. For other metals (Cu and Ni), crystalline Fe/Mn oxide content increases and amorphous Fe/Mn oxide content decreases as oxic and anoxic sediment layers form with aging [36]. Sediment heterogeneity and mottling added to the complexity of this system such that more intensive sampling was likely needed to see effects to Fe/Mn-

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oxyhydroxide content. Further, sediment desiccation likely decreased microbial productivity, which would also decrease kinetic rates of Fe/Mn-oxyhydroxide transformation.

Although an overall decrease in Zn bound (through complexation or adsorption) to amorphous Fe/Mn-oxyhydroxides (ferrihydrite, lepidocrocite) was observed during the inundation, it was not correlated with porewater Zn concentrations ($p > 0.25$). This may indicate the amorphous Fe/Mn-oxyhydroxide-Zn is being reduced to a non-labile form, or the relationship is confounded by other ligands such as sulfide, carbonates, or particulate organic matter. Our findings agree in that the amorphous Fe/Mn-oxyhydroxides seem more important to Zn bioavailability than the crystalline phases, since we observed a change in Zn binding to amorphous but not crystalline Fe/Mn-oxyhydroxides. This is likely attributable to the large surface area of amorphous compounds, which increases available binding sites [37].

Because porewater DOC did not change during the experiment, it is unlikely it influenced Zn bioavailability. Our sampling design; however, did not allow sampling of porewater particulate organic matter, which we would expect to become more sorptive to metals as pH increases. In future studies, we hope to measure the changes in metal binding to particulate organic matter with water level fluctuation.

Previous studies have shown inundation of oxidized sediment to cause toxicity in low acid-neutralizing capacity systems. Carvalho et al. [38] assessed impacts of resuspension on macroinvertebrate populations in the acid-sulfate sediments of Billings Reservoir, Brazil, in which sediment oxidation caused acute toxicity to *Daphnia similis*. Their findings, however, are only tangentially applicable to high–acid neutralizing capacity systems during water level fluctuations.

This**<ZAQ;5>** study shows that systems with relatively high pH and high buffer capacity

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can also release bioavailable metals into aquatic systems. Sediment pH was strongly correlated to porewater Zn for DRW and LBC sediments only, during the drought experiment (cc = –0.5, $p < 0.0001$). Well-buffered QC and EB sediments did not experience a pH change, allowing Zn to be rapidly re-adsorbed to sediments after the initial inundation. In these experiments, hydrology has proved important in (at least) 2 aspects. First, it shapes sediment characteristics from allotchtonous inputs, which alters grain size, nutrient inputs, and general chemical composition. Second, it directs the chemical equilibrium of sediments and thus the bioavailability of metal contaminants.

Implications for climate research

Our findings suggest additional focus is needed to predict biogeochemical effects of climate variability on affected aquatic systems. Our regional focus was the lower Great Lakes, where increased variability in water levels has occurred in recent years, ranging from record lows (2013) to surges of 0.6 to 1 m in lake water levels (2014) [39]. This hydrologic variability is correlated with surface water temperatures, the duration and coverage of winter lake ice, evaporation, and precipitation, all factors influenced on a regional scale by El Niño climatic events and weakening of the circumpolar vortex [40]. Both of these climatic phenomena are expected to strengthen with continued climatic warming, further increasing variability in Great Lakes water levels [41]. Strong evidence suggests the metal pulse we observed in our experimental microcosms is occurring in coastal sediments of the Great Lakes. If so, this could have important biogeochemical ramifications for these aquatic systems.

As a lab microcosm study, the present research has a few limitations to its field applicability, including the absence of plants and autochthonous inputs. The presence of plants can add new organic carbon to sediments, and plant rhizospheres can alter the oxidation of

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sediments, which influences metal binding [42]. With these important distinctions in mind, the data and results of the present research can be broadly applied to freshwater aquatic systems.

Although the present study shows increased bioavailability of metals in just one aquatic system (high-carbonate coastal freshwater wetlands), similar biogeochemical effects are predicted for riparian and inland freshwater aquatic systems. Our stated predictions were partially correct, in that sediment oxidation led to Zn release; long-term drying (drought) had a larger effect on theoretical toxicity than short-term drying (seiche); and dominant binding ligands associated with Zn-oxidative release were sulfide, carbonate, and amorphous Fe/Mn-oxyhydroxides. The redox-induced pulse of metals into sediment porewaters can lead to changes in nutrient availability, sediment chemistry, and environmental risk; therefore, site-specific hydrochemical parameters should be considered when assessing sediment quality.

Supplemental Data—The Supplemental Data are available on the Wiley Online Library at DOI: 10.1002/etc.xxxx.

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Data Availability—Data, associated metadata, and calculation tools are available from the corresponding author (snedrich@umich.edu).

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Figure 1. Location of wetland sites along the coast of Michigan, USA.

Figure 2. Experimental microcosm design during dry and inundated sediment phases. Rhizon porewater samplers were inserted at depths of 1, 2, 3, 5, and 10 cm.

Figure 3. Average Zn, Cu, Fe, and Mn in porewater for seiche (saturated and inundated) and drought experiments. Averages were calculated, including all depths ± standard error (n = 3) for each sediment type (drought) or all depths and sediment types ± standard error (n = 12) for seiche. Zinc exceeds the US Environmental Protection Agency recommended water quality criteria for aquatic life**<ZAQ;6>** (120 µg L^{-1}). See Figure 1 for definition of site abbreviations.

Figure 4. [SEM-AVS]/fOC**<ZAQ;7>** (± standard error) for seiche and drought experiments. Statistical differences between experiments (*a/b*) and within experiments (*) are shown ($p < 0.05$). Values are mostly negative during seiche experiment but become positive during drought, indicating higher potential toxicity. See Figure 1 for definition of site abbreviations.

Figure 5. Porewater hardness (± standard error) for seiche and drought experiments, with lettering for statistical significance ($p < 0.05$). Porewater hardness shows highest carbonate dissolution on day 1 inundation of the drought experiment and near return to seiche conditions after 32 d. See Figure 1 for definition of site abbreviations.

Figure 6. Porewater Zn concentrations compared to hardness-corrected US Environmental Protection Agency threshold for chronic toxicity (CCC) [21] and Biotic Ligand Model (BLM)-derived chronic 5% hazardous concentration (HC5) values for drought experiment. Exceedance of the CCC was observed in LBC only at the start of the experiment. The chronic HC5 suggests hardness-corrected criteria may occasionally be underprotective for EB and LBC sites. See Figure 1 for definition of site abbreviations.

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Figure 7. A schematic of the chemical equations associated with Zn oxidative release and subsequent reduction in high alkalinity sediments.

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<<ENOTE>> AQ2: Please spell out *f*OC

<<ENOTE>> AQ3: Does “SEM-AVS” differ from “[SEM-AVS]”?

<<ENOTE>> AQ4: Please define cc. (Correlation coefficient?)

<<ENOTE>> AQ5: Please clarify: Does “This” refer to the present study or to [38]?

<<ENOTE>> AQ6: Figure 3: Please add a citation for this source. (Is it [21]?)

<<ENOTE>> AQ7: Figure 4: Please define [SEM-AVS] ad *f*OC <!--<query><!--<query></query>--><**<ENOTE>> AQ8:** Table 1: Please define [SEM-AVS] and *f*OC.</query>-->

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Table 1. Physical and chemical properties of sediment types used in the present experiment show more similarity between sites QC and EB as compared with sites LBC and DRW for sediment texture, total metal content, and total Fe-oxide content[a]

Site[b]	Texture	pH[c]	LOI (% C)	DOC (mg L^{-1} C)	[SEM-AVS]/*f*OC	Total Fe-oxides (μmol Fe g^{-1} dry wt)	Total Metals (mg kg^{-1})				
							Cu	Fe	Mn	Ni	Zn
QC	Sandy	7.3A	8.0A	0.65A	–0.9A	30.5A	6.1A	3640A	68.5A	ND[d]	27.4A
		±0.03	±1.4	±0.20	±8.0	±1.3	±1.8	±268	±11.9		±2.2
EB	Sandy	7.4B	7.0A	0.37B	3.5A/B	36.4A	4.6A	3010A	71.9A	ND[d]	18.0A
		±0.04	±2.4	±0.10	±3.7	±7.7	±3.3	±720	±20.8		±9.8
LBC	Sandy	6.2C	13.0B	1.07C	16.5C	212.0B	48.5B	14 300B	609.8B	24.6A	195.9B
	loam	±0.05	±1.2	±0.21	±4.4	±18.7	±21.6	±5400	±326.4	±12.3	±83.3
DRW	Sandy clay	6.8D	25.1C	0.21B	11.7B/C	198.0 B	66.1B	22 100	285.5B	34.4A	263.2
	loam	±0.06	±1.0	±0.03	±11.2	±10.8	±2.8	B±459	±23.2	±0.5	B ±6.6
RAIS	Sand	7.5B	2.0D	—	–119.8E	88.3C	ND[d]	8600C	386.0B	ND[d]	14.6A
		±0.05	±0.4		±59.8	±2.7		±1370	±105.9		±4.5

[a] Parameters that vary between 3 or more sediment types include pH, loss-on-ignition (LOI), dissolved organic carbon (DOC), and

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<ZAQ;8>[SEM-AVS]/*f*OC (± standard error). Different upper-case letters indicate statistical differences between sites ($p < 0.05$)

[b] See Figure 1 for definitions of site abbreviations.

[b] Calculated from drought experiment data only.

[c] Not detected (detection limits = 19 µg L^{-1} or ≈17.9 mg kg^{-1} for Ni and 0.5 µg L^{-1} or ≈0.5 mg kg^{-1} for Cu).

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EB	Sandy	7.4B	7.0A	0.37B	3.5A/B	36.4A	4.6A	3010A	71.9A	ND[d]	18.0A
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LBC	Sandy	6.2C	13.0B	1.07C	16.5C	212.0B	48.5B	14 300B	609.8B	24.6A	195.9B
	loam	±0.05	±1.2	±0.21	±4.4	±18.7	±21.6	±5400	±326.4	±12.3	±83.3
DRW	Sandy clay	6.8D	25.1C	0.21B	11.7B/C	198.0 B	66.1B	22 100	285.5B	34.4A	263.2
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[a] Parameters that vary between 3 or more sediment types include pH, loss-on-ignition (LOI), dissolved organic carbon (DOC), and **<ZAQ;8>**[SEM-AVS]/*f*OC (± standard error). Different upper-case letters indicate statistical differences between sites ($p < 0.05$)

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[b] Calculated from drought experiment data only.

[c] Not detected (detection limits = 19 µg L^{-1} or ≈17.9 mg kg^{-1} for Ni and 0.5 µg L^{-1} or ≈0.5 mg kg^{-1} for Cu).

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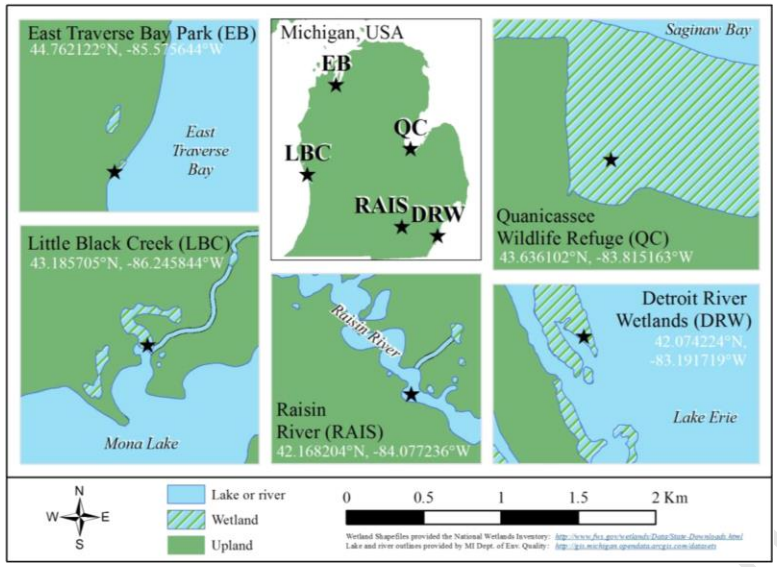

Figure 1

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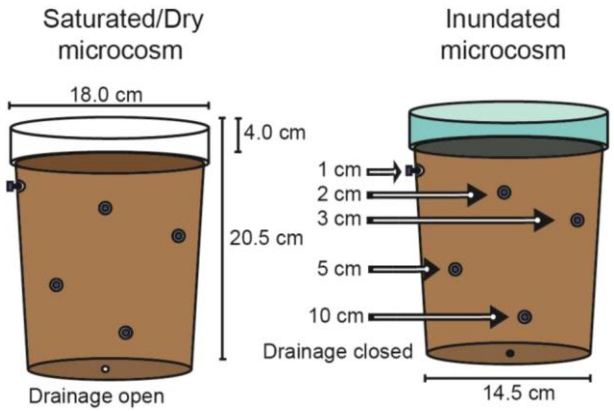

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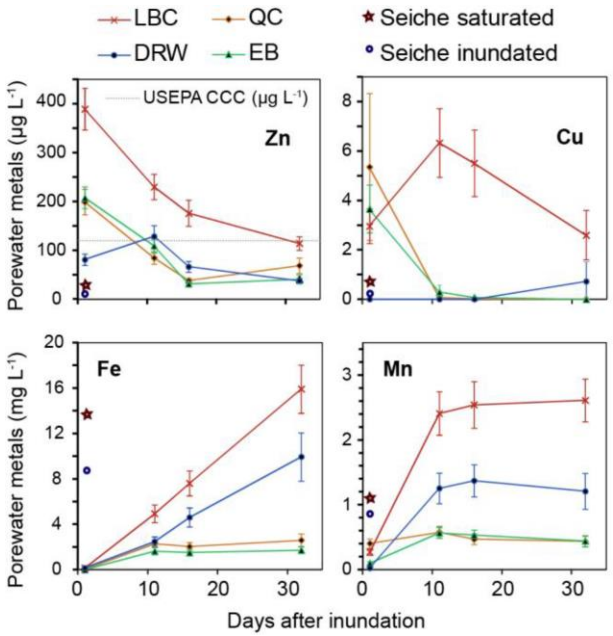

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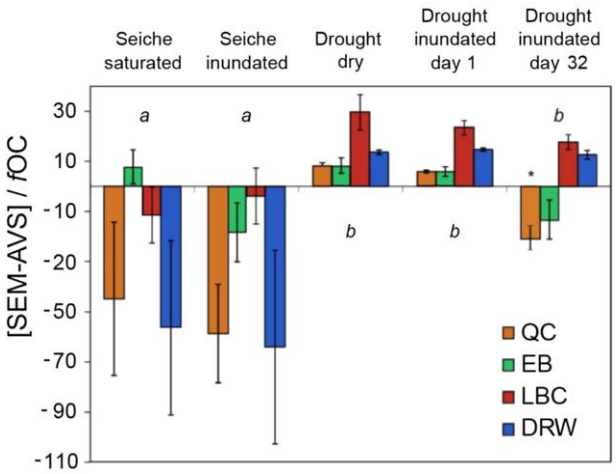

Figure 4

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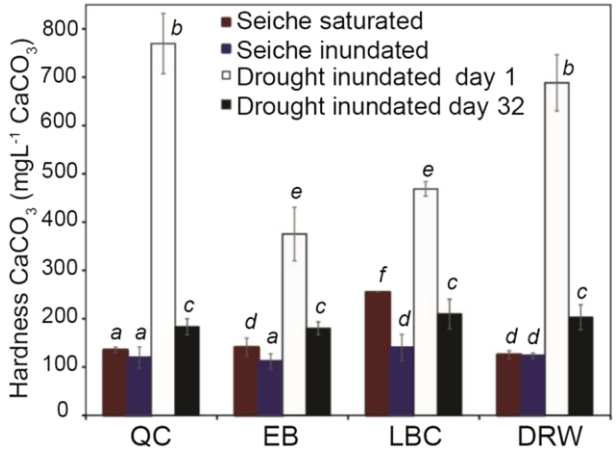

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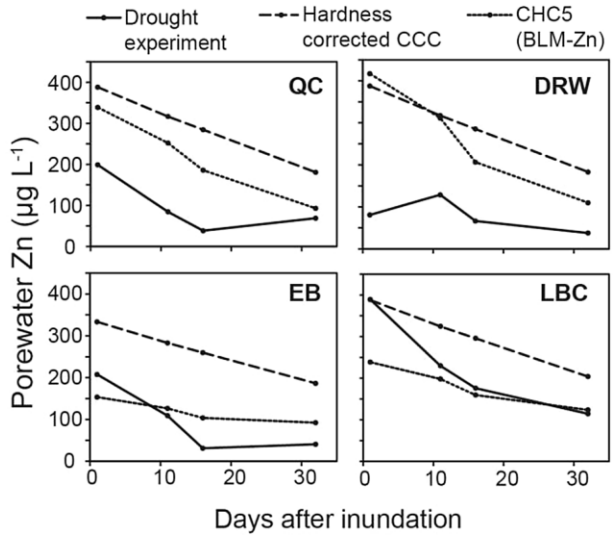

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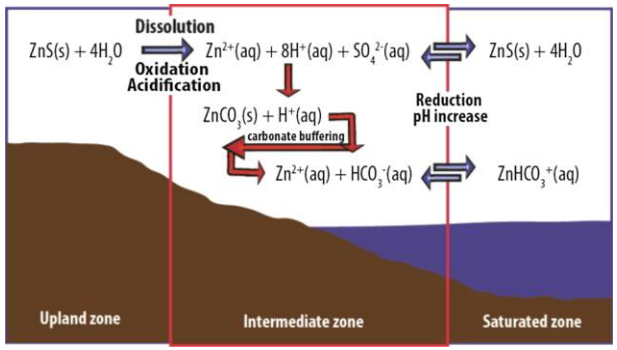

Figure 7

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