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Article

Observations of River Solute Concentrations during Ice Formation

Ella L. DeGrandpre, Michael D. DeGrandpre,* Benjamin P. Colman, and H. Maurice Valett

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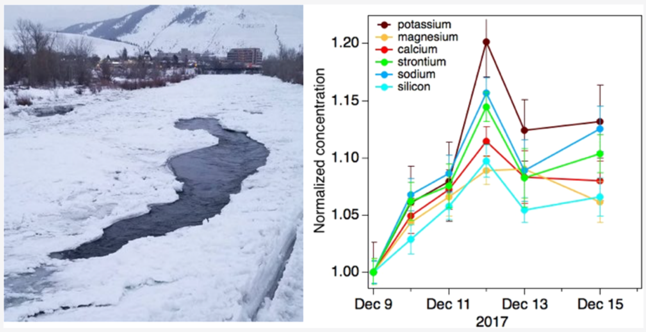
ABSTRACT: It has been observed in some aquatic systems, such as lakes and oceans, that when ice forms solutes are excluded from the ice, increasing their concentrations in the water. This process, known as solute ice exclusion, could be important in rivers and streams where ice can be a significant fraction of the total volume, potentially significantly increasing chemical concentrations in the water. There have been no reported observations of solute dynamics during ice formation in rivers and streams, however, even though the freeze−thaw cycle is a common phenomenon for lotic systems in cold regions. To investigate this process, a variety of solutes were measured during three ice formation events in a mine-waste-polluted river in western Montana. A laboratory study was also conducted to determine how different metal cations partition when ice forms. It was found that solute concentrations significantly increase during the early stages of ice formation. Correlations with ion size and changes in temperature support the idea that ice exclusion was controlling solute dynamics during these periods. These observations could have important implications for predicting the environmental impacts of toxic solutes in rivers and streams subject to seasonal ice formation.



KEYWORDS: *river ice, solute exclusion, solute rejection, dissolved metal concentrations, river pollution*

1. INTRODUCTION

Understanding the processes that control toxic solute concentrations in aquatic ecosystems is of great importance. Ice formation is one process that could increase pollutant concentrations in aquatic environments. As ice forms, it excludes ions and other solutes from its crystalline structure, leaving them in the water.[1] This process of solute exclusion, also known as solute rejection, has been shown to have important physical and geochemical consequences in some aquatic environments. For instance, solute exclusion can drive stratification and inhibit vertical mixing in freshwater lakes.[2] Studies have found higher concentrations of ions and organic matter in lakes and ponds during the winter and related these findings to the exclusion of solutes from ice.[3−5] Solute exclusion can increase chloride concentrations to toxic levels in wetlands where concentrations are already high due to road salt runoff.[6] Ice formation can also change seawater−carbonate chemistry because of selective retention of total alkalinity in ice relative to total dissolved inorganic carbon.[7] In addition, ice formation in the Arctic Ocean has been observed to increase the dissolved oxygen concentration in the underlying seawater.[8]

Many temperate and high-latitude rivers experience seasonal ice formation,[9] and solute exclusion presumably occurs in these systems. In fact, rivers might be more sensitive to solute exclusion than deep lake and marine environments because pollutants could be more effectively concentrated due to higher ice:water ratios.[10] From a biogeochemical and ecological perspective, however, river ice has primarily been considered as a barrier for gas exchange (e.g., ref 11) and as a source of habitat or ecological disturbance.[9,12,13] Few studies have evaluated ice solute exclusion in rivers. Osterkamp et al.[14] attributed an increase in electrical conductivity in a small stream to solute exclusion during ice formation. In their three studies, conductivity increased 15% to 20% during initial ice formation and then decreased to pre-ice levels after continuous ice cover formed. Guo et al.[15] estimated large seasonal changes in Yukon River solute export due to ice formation by estimating the total volume of ice formed and the solute exclusion factor between ice and water. They attributed higher fall and winter levels of dissolved organic and inorganic carbon to ice formation and found a higher exclusion of inorganic species than of organic carbon. In contrast, Xiao et al.[16] studied the retention of pollution in river ice after a chemical spill. Residual nitrobenzene retained in the ice was quickly released during spring melt, increasing the pollutant concentrations above background levels. Stable isotopes of water have been found to selectively partition during ice formation, providing insights into ice formation processes.[17] Except for Osterkamp

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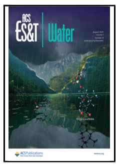

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et al.,[14] we have not found examples in which solute dynamics have been studied in rivers during initial ice formation, when solute and pollutant concentrations could increase rapidly above background levels.

This study investigates short-term variation in solute concentrations during ice formation in the mine-waste-polluted Clark Fork River (CFR) in western Montana. The CFR is one of the most mining-impacted rivers in the United States with exposure to flood plain mine tailings for more than a century.[18] For this study, complementary efforts were conducted to quantify and understand solute concentration changes during ice formation. To verify that solute exclusion occurs, a laboratory study compared ice exclusion of different metal cations, including mine-related contaminants. In an initial field study, alkalinity and major anions were measured in the CFR ice and compared to concentrations in the water. Two subsequent field studies quantified solute concentrations in the river water during ice formation events. The laboratory and field studies found that solute concentrations significantly increased during ice formation and that the relative increase correlates with ion size. These results indicate that the observed increase in concentrations was due to exclusion of solutes from the ice matrix during ice formation, resulting in conditions that may present additional stress to aquatic biota in polluted waters.

2. METHODS

2.1. Laboratory Study. A laboratory study was conducted to determine the extent to which different metal cations partition between ice and water. The metal salts potassium chloride, barium chloride, magnesium chloride, strontium chloride, zinc chloride, cupric chloride, lithium bromide, cobalt chloride, and calcium chloride were prepared in deionized water. Halide salts were chosen because of their availability and lack of strong metal complexation. The combined solution was diluted to ~5 mg L^{-1} for each salt (actual molar metal concentrations ranged from 24 to 67 μM). Three beakers were filled with 300.0 mL of the salt solution and placed covered in a freezer for 5 h, resulting in ~50% ice formation by volume. The frozen portions of the samples were separated from the water and melted. Both the melted ice and the remaining water were analyzed using inductively coupled plasma atomic emission spectrometry (ICP-AES, PerkinElmer OPTIMA 5300) with EPA Method 200.7 and a single-point calibration.[19]

2.2. Clark Fork River Studies. Samples were collected from the Clark Fork River in Missoula, MT (Figure 1). The CFR is a high-gradient, cobble-bed river with a long history of impacts from mining and smelting activities once located in the river headwaters. The river mean depth and width at the sampling site are ~1 and ~50 m, respectively, with mean peak and base flows of 260 and 40 m^3 s^{-1}, respectively. The initial study was undertaken to determine if river ice formation results in solute exclusion. A sample was collected from surface ice and from a nearby open channel on January 10, 2016. Ice was thawed in the laboratory, and all samples were analyzed for total alkalinity and the major anions fluoride (F^-), chloride (Cl^-), and sulfate (SO_4^{2-}). All samples were filtered prior to analysis (Gelman Supor 37 mm 0.22 μm syringe filter). The anions were quantified by ion chromatography using EPA Method 300.0[22] with a Dionex ICS-2100 instrument. Alkalinity was determined by Gran titration with standardized hydrochloric acid[20] and was assumed to be comprised solely of the bicarbonate anion, which is a good approximation (>97%) at the typical pH of the CFR.[21]

Figure 1. Partially ice-covered Clark Fork River near the study site in Missoula, MT, during the December 2016 ice formation event.

A subsequent study in December 2016 determined if solute concentrations change in river water during ice formation with a focus on major abundant metals. The study was repeated during an ice event in December 2017 to verify the 2016 results. In these studies, field sampling was initiated when regional forecasts predicted extended periods of frigid temperatures (Figure 2). Sampling spanned initial ice formation, when minimal ice coverage existed, through the period when the river became ice covered (Figures 1 and 2). Water samples were taken from open areas close to shore because of hazardous conditions. Samples were collected daily over four (2016) and six (2017) days during the ice formation events (Figure 2). Discharge was ~42 m^3 s^{-1} prior to ice formation for both events, near the 91-year median of 40 m^3 s^{-1} [U.S. Geological Survey gaging station above Missoula (https://waterdata.usgs.gov/nwis/uv?site_no=12340500)].

Major dissolved aqueous species, including potassium (K), magnesium (Mg), calcium (Ca), strontium (Sr), sodium (Na), and silicon (Si), were analyzed using ICP-AES. To obtain trace metal concentrations for copper (Cu) and zinc (Zn), the 2016 samples were also analyzed using an inductively coupled plasma mass spectrometer (ICP-MS, PerkinElmer Elan DRC-e) following EPA Method 200.8.[23] The ICP-MS was calibrated with five standards ranging from ~0.1 to 100 μg L^{-1}. Concentrations of Cu and Zn are not included in the 2017 assessment as the ICP-MS was not available.

2.3. Data Analysis. In the laboratory and field studies in which both ice and water solute concentrations were measured, we compare the ratio of concentrations in water to those in ice (i.e., concentration factor C_{water}:C_{ice}). In the second and third field studies in which solute concentrations were measured only in river water, solute concentrations are presented as a ratio to the initial concentration for each solute

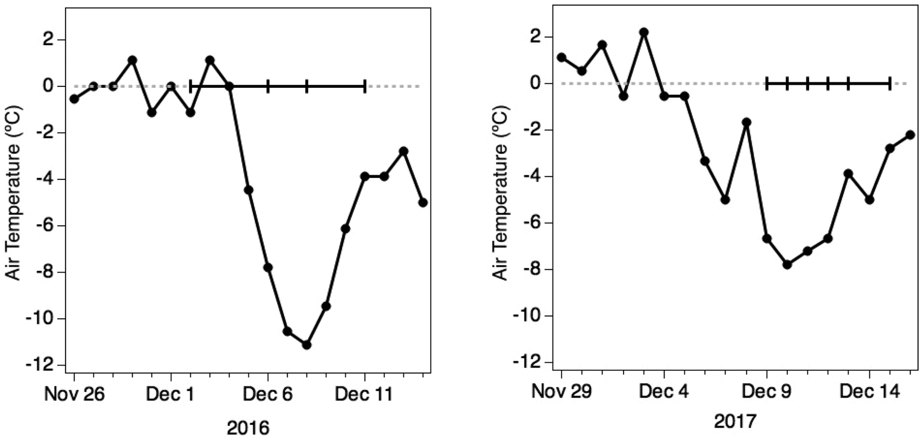

Figure 2. Mean (24 h) air temperature during the 2016 and 2017 sampling dates (●), water freezing point (---), and sampling periods (horizontal line with vertical ticks for each sampling date). Temperature data were obtained from the National Climatic Data Center (www.ncdc.noaa.gov/cdo-web).

and reported as the "normalized concentration". The normalized concentration facilitates comparisons given the large range of concentrations observed across solutes. Ionic radii for the different solutes were obtained from refs 24 and 25. Data were compared using linear regressions with significance levels based on two-tailed probability tests ($\alpha = 0.05$). Analytical uncertainties were computed using either the replicate analyses or the instrument signal precision if replicates were not available.

3. RESULTS AND DISCUSSION

3.1. Laboratory Study. In the laboratory study, a wide range of metal cations, including alkali, alkali earth, and mining-related transition metals (nine different metal cations), were quantified in both the ice and water phases. The ice had significantly lower ion concentrations than the remaining water, with only 12−17% of the total ion mass remaining in the ice (Table S1), demonstrating the effectiveness of solute exclusion for a wide range of metal solutes. The corresponding concentration factors ($C_{water}:C_{ice}$) ranged from 5.6 to 10.5 and are significantly correlated with solute ionic radii (Figure 3; $r^2 = 0.67$; $p = 0.011$). While the correlation appears to be heavily influenced by the largest ion (K^+), the correlation actually improves if K^+ is removed from the data set ($r^2 = 0.71$; $p = 0.005$). We also found that the concentration factors are more weakly correlated with atomic radius [$r^2 = 0.50$; $p = 0.03$ (not shown)] and not correlated with atomic mass [$r^2 = 0.03$; $p = 0.65$ (not shown)]. Previous laboratory ice studies have focused on narrower suites of cations and other solutes with different experimental objectives. For example, Killawee et al.[26] studied solute and gas partitioning to help interpret ice core data. They found preferential retention of ions on the basis of size ($Mg^{2+} > Na^+ \sim Ca^{2+} > Sr^{2+}$). Other experiments have focused on the fundamental interactions of solutes and ice.[27,28] Studies have found that the extent of exclusion of solutes from ice depends not only on solute size but also on other variables such as the rate of ice formation, temperature, solute concentration, metal carbonate precipitation, and the presence of other solutes.[26,27,29] Because of these interacting effects, there is no reason to assume a linear relationship between concentration factors and ionic radii.[27] These results do, however, support the idea that ions, including contaminant metals like Cu and Zn, will be strongly excluded from ice and can then concentrate in the aqueous phase.

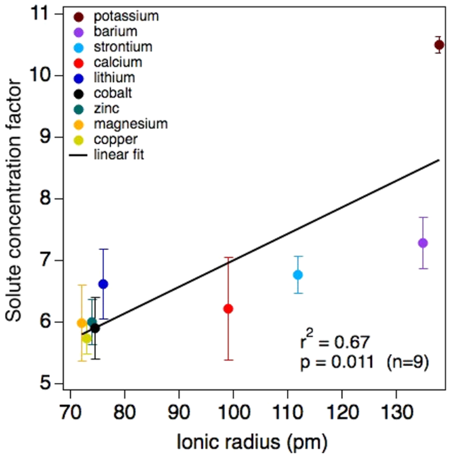

Figure 3. Laboratory evaluation of the relationship of solute concentration factors ($C_{water}:C_{ice}$) with ionic radius. Error bars are based on replicate standard deviations ($n = 3$). Larger ions are more effectively excluded due to size constraints in the ice matrix as shown by previous studies of other aqueous systems.

3.2. Clark Fork River Field Studies. The initial field study in January 2016 found significantly higher concentrations (t test; $p < 0.0001$−0.015) of the major anions (SO_4^{2-}, Cl^-, HCO_3^-, and F^-) in the water relative to the ice (Table S2). Ice concentrations were 7.7−33% of the water concentration, and concentration factors ranged from 3 to 13. The concentration factors significantly correlate with ion size (Figure 4; $r^2 = 0.93$; $p = 0.034$). The concentration of sulfate, the largest molecule quantified, was >13 times greater in water than in ice, whereas the smallest ion (F^-) had an ∼3-fold concentration factor (Table S2 and Figure 4). These field data show that river ice formation excluded solutes from the ice and that the extent of exclusion depended upon the solute size, confirming that the results of the laboratory study extend to other types and sizes of ions.

Comparing Figures 3 and 4, we find the anions are generally larger than the cations (>130 pm) but have comparable concentration factors with the exception of sulfate. The concentrations of anions have been found by others to be higher in ice than the concentrations of cations.[27] It is believed

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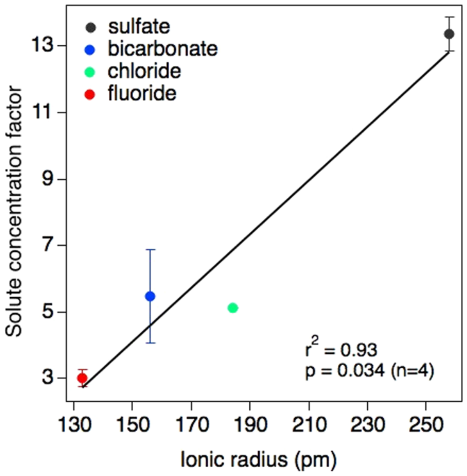

Figure 4. Solute concentration factors (C_{water}:C_{ice}) vs ionic radius for four anions during an ice formation event on the Clark Fork River in January 2016. Data are means ± standard deviations (n = 3) with error bars not visible for the chloride anion.

that monovalent anions are needed to maintain the charge balance of the common divalent cations (e.g., Ca and Mg),[27] especially because sulfate is more excluded because of its large size. Also, specifically in this case, the concentration factors in Figures 3 and 4 were determined under very different freezing and water (stagnant and flowing) conditions that could affect the results.

The temporal dynamics of solute exclusion during ice formation in December 2016 and December 2017 are shown in Figure 5. All solute concentrations increased in the CFR in both events compared to their initial values (Tables S3 and S4). Concentrations then leveled out or eventually decreased as the freezing events progressed and temperatures moderated (Figure 2).

Normalized concentrations for Cu and Zn in 2016 were significantly higher than those of the other species following initial ice formation (Figure 5A). The concentrations of both Zn and Cu declined after the sampling on December 6, 2016, and the concentration of Cu had a large unexplained drop on the sixth day of the ice formation period (Figure 5A). Zinc exhibited the largest change in relative concentration, initially increasing 2-fold; the actual concentration changed from 46 to 92 nM (Table S3). When Zn and Cu were excluded from the analysis, changes in normalized concentrations were closely related to changes in temperature (Figure 6; r^2 = 0.68; p = 0.012). Over the monitoring periods, solute concentrations did not return to their original values, suggesting a continued influence of ice formation on river water chemistry.

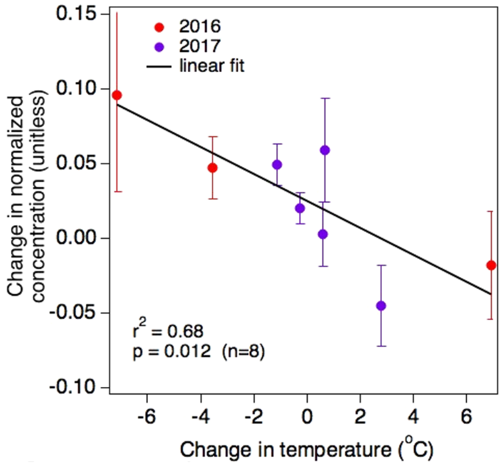

Figure 6. Relationship between changes in normalized concentration and changes in temperature averaged for each day for the species shown in Figure 5. Zn and Cu were excluded from the averages (see the text). The error bars are the standard deviations of the average normalized concentrations. Changes were calculated between sequential samples (dates in Figure 2). The linear fit is for all data (2016 and 2017).

Across the combined ice formation events, averaged normalized concentrations are significantly correlated with ionic radii (Figure 7; r^2 = 0.80; p = 0.016), supporting the idea that the observed increase in concentration is due to ice formation. The normalized concentrations of Cu and Zn do not correlate with the free cation radii (73 and 74 pm for Cu

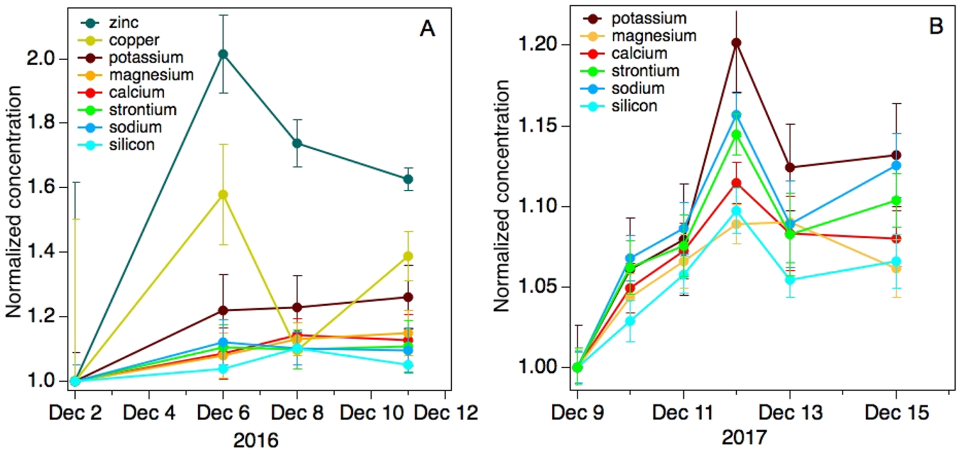

Figure 5. Normalized solute concentrations in the CFR throughout ice formation events in December 2016 (A) and 2017 (B). Associated temperatures are shown in Figure 2. Concentrations are presented as ratios with initial concentrations (normalized concentration) to show the relative changes of different metal solutes during the freezing period. Cu and Zn were not measured in 2017. Note that the x and y ranges are different for the two plots. Error bars are the standard deviations of the atomic emission signal precision recorded by the ICP during the measurements. See Tables S3 and S4 for metal concentrations.

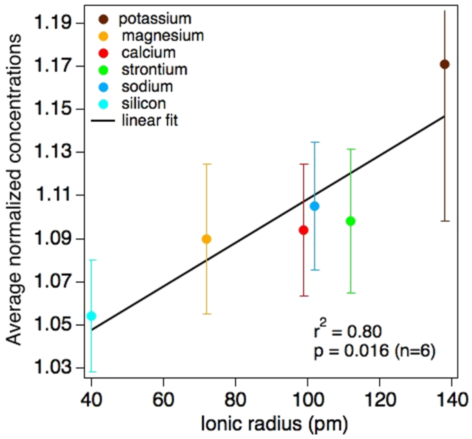

Figure 7. Average normalized concentrations for each metal solute from the 2016 and 2017 field studies (from Figure 5 data) vs ionic radius in picometers. Error bars are based on standard deviations of the averaged normalized concentrations.

and Zn, respectively) and were not included in the regression analysis in Figure 7. As noted above, changes in the normalized concentrations for these two trace metals were not tied to changing temperatures. The deviations displayed by Cu and Zn could arise from a number of sources. The transition metals, including Cu and Zn, typically form complexes in natural waters. Alkali (Na and K) and alkali earth (Mg, Ca, and Sr) metals, on the contrary, exist primarily as uncomplexed cations, on the basis of equilibrium modeling calculations.[30] At the typical pH (8.4) and alkalinity (2400 μmol L^{-1}) of the CFR in December,[21] Cu and Zn are predicted to be complexed as $Cu(OH)_2°$ (100%), $ZnCO_3°$, and $Zn(CO_3)_2^{2-}$ (60%) with the remaining Zn comprised of free Zn^{2+} and $Zn(OH)_2°$. Copper may also be strongly complexed by organic molecules in natural waters.[31] The ion size alone, however, cannot account for the large change in concentrations. As shown in Figures 3 and 4 and Tables S1 and S2, larger ions like sulfate and potassium had large concentration factors and were mostly excluded from ice; consequently, the linear relationship with ionic radius (Figure 7) should break down (plateau) with larger molecules because very little solute will remain in the ice. Concentrations can further increase as the ice volume increases, but this study suggests the river ice discharge was no greater than 25% ice, assuming 100% of potassium was excluded; i.e., the maximum normalized K concentration was 1.25 in Figure 5. The higher normalized concentrations of Zn and Cu may be associated with increased levels of suspended solids from ice scouring.

As suggested by the normalized concentrations in Figure 5, ice comprises 5−25% of the total discharge. Although quantifying ice volume in rivers is difficult[32,33] and was not in the scope of this study, the large amounts of ice observed in the CFR are consistent with these estimations (Figure 1). During the ∼1 week sampling periods, the CFR transitioned from no ice to nearly complete ice cover. Small ice floes coalesced into large ice and slush rafts that soon spanned the river from bank to bank while rapidly flowing downstream until ice jamming occurred and complete static ice cover formed (Figure 1). Guo et al.[15] in their study of the biogeochemistry of the Yukon River assumed a 20% ice:water discharge ratio; thus, our estimated ice volumes and observed concentration increases appear to be reasonable.

While there are other possible explanations for increased solute concentrations during ice formation, our laboratory and field observations, data analysis, and river discharge (see below) support ice formation as the cause of these observed patterns. Anchor ice can inhibit groundwater input[10] that could change solute concentrations, but this process would not lead to the observed size-dependent concentration increases (Figure 7). Correlations with discharge could indicate that a change in groundwater or tributary input is driving the concentration changes. While no discharge data are available for December 2017 because the gage stopped recording during the ice event, no correlation exists between solute concentrations and river discharge recorded during 2016 at the USGS gage located near the sampling site (USGS 12340500, data not shown). Disturbance due to ice scour could increase solute concentrations during ice formation by enhancing exposure and dissolution of metals;[34] while this may have contributed to the larger observed values of Zn and Cu (which are present in high concentrations in CFR sediments),[18] ice scour also fails to generate size-dependent concentration changes as observed for all other solutes. Ice formation in the hyporheic zone or soils[35,36] could lead to size-dependent ion exclusion, but these explanations are also improbable. It is unlikely that hyporheic and soil water, insulated to some extent from the sub-zero air temperatures, are freezing sufficiently to alter solute concentrations in a large river such as the CFR.[37,38] Importantly, during the two freezing events massive ice formation was observed to occur (Figure 1), supporting our contention that proximal in-stream freezing and solute exclusion were the controlling processes.

Lastly, it is notable that solute concentrations did not return to baseline levels observed before the freezing events (Figure 5). We assume that soon after continuous ice cover is achieved solute concentrations will return to baseline levels (as observed for conductivity by Osterkamp et al.[14]). Ice formation slows with the insulating ice cover,[32] which would slow accumulation of solutes in the river water. The duration of our studies was not long enough to observe if this occurs.

4. CONCLUSIONS

This study shows that solute exclusion during ice formation significantly increased aqueous concentrations in a riverine system. This conclusion is supported by the high concentration factors (C_{water}:C_{ice}) (Figures 3 and 4), the increase in solute concentrations during ice formation (Figure 5), the relationship between the change in concentration and the change in temperature (Figure 6), and the correlation between river solute concentrations and ionic radii (Figure 7). The extent of solute exclusion and its dependence on ionic radii were verified by the laboratory study and initial field study (Figures 3 and 4). The laboratory study supports the idea that ice exclusion will affect a wide range of metal contaminants. The extent of exclusion of contaminant metals like Cu and Zn likely depends upon the complexation of the metal species, but even if uncomplexed, significant increases in concentration could be expected from ice formation.

While we found small increases in concentration for most solutes relative to those for stagnant natural waters,[6] these changes could still have important consequences. Past studies on the CFR have shown that dissolved metals are near toxic thresholds. A study by Nimmo et al.[40] used the zooplankton *Ceriodaphnia dubia* to measure both chronic and acute effects of the mine-affected CFR waters on aquatic organisms. In a number of instances, conditions were acutely toxic to *C. dubia*. Increased toxic metal concentrations due to ice formation could increase overall toxicity to aquatic invertebrates with potential for propagation through the food web.[41] Solute exclusion could also be more important in smaller streams that may have higher ice:water ratios.[39] Moreover, the extent of river ice is decreasing globally,[42] and freeze−thaw periods are expected to become more frequent as the temperate zone moves to higher latitudes.[10] Freeze−thaw cycles could lead to more frequent periods of increased levels of toxic solutes relative to a river that remains ice covered for most of the winter. These results suggest that solute concentration and dilution (freeze−thaw) events could be an important factor in the health of rivers and streams. Further studies are needed to quantify these effects for a wide range of stream types and freezing conditions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsestwater.1c00064.

> Solute concentration data from this study in four tables that comprise the four different experiments described in the text (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Michael D. DeGrandpre − *Department of Chemistry and Biochemistry, University of Montana, Missoula, Montana 59812, United States;* orcid.org/0000-0003-1969-6709; Email: michael.degrandpre@umontana.edu

Authors

Ella L. DeGrandpre − *Department of Chemistry and Biochemistry, University of Montana, Missoula, Montana 59812, United States*

Benjamin P. Colman − *W.A. Franke College of Foresty & Conservation, University of Montana, Missoula, Montana 59812, United States*

H. Maurice Valett − *Division of Biological Sciences, University of Montana, Missoula, Montana 59812, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acsestwater.1c00064

Notes

The authors declare no competing financial interest.

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