Abstract

The chemical properties of river water are an important environmental component determining shell chemistry for bivalves living in the river. This study focuses on river water chemistry determined from samples collected from a 13 mile section of the Cannon River in southern Minnesota. Water samples were collected from three sites in the sample area (Faribault, Dundas, and Northfield) in the spring of 2005, and analyzed to determine the alkalinity, ion concentrations, and oxygen and hydrogen isotopic ratios ($\delta^{18}O$ and $\delta^{2}H$). This analysis led to general observations and about the extent and variability of these properties over the river section studied. Isotope analyses of the river water were also compared to isotope data of meteoric water from the area.

Ion and Alkalinity concentrations increased dramatically between Faribault and Dundas, but remained relatively constant between Dundas and Northfield, indicating a possible anthropogenic input source between the Faribault and Dundas locations. Oxygen isotopic composition between the three sample sites was fairly constant ($\delta^{18}O \pm 0.5\ ^{0}/_{00}$) but was more enriched in ^{18}O than local rainwater. This may indicate groundwater interaction. Similar $\delta^{2}H$ enrichment was seen in adjusted river water samples when compared to that observed in meteoric water. This is most likely the result of evaporative fractionation processes.

Introduction

Accretionary skeletons of bivalves retain information indicative of the growing conditions they were subject to during the lifetimes of the bivalves. Comparisons of data from bivalve compositions and the waters in which they grow enhance conceptions of contemporary climactic conditions (Goodwin, D.H. et al. 2001). Bivalves are especially useful because they incorporate oxygen isotopically in equilibrium with the ambient water and they generally exhibit species-consistent physiological fractionation of $^{12}C/^{13}C$ with respect to local carbonates (Werfer, G. and Berger, W.H. 1991). Furthermore, compositional comparisons of mussels and the waters they live in can also yield interesting results regarding the paleotemperature variation, seasonality, and paleoproductivity (Hendry, J.P. et al. 2001).

This study aims to determine the chemical properties of water samples from the Cannon River to provide a basis for comparison with the chemical compositions of mussels collected from the Cannon River.

Water samples were collected in April, 2005 from three sites along the Cannon River near the towns of Faribault, Dundas, and Northfield, Minnesota. An additional rain water sample from the Carleton College campus in Northfield, MN was collected in October, 2004. Samples were analyzed for major anion (fluoride, chloride, nitrate, nitrite, phosphate, bromide, and sulfate) and major cation (lithium, ammonium, sodium, potassium, calcium, and magnesium) content, as well as isotopic ratios of hydrogen and oxygen. As the river water sample sites are in the same watershed and are subject to the same climactic conditions, similar relative ion concentrations and isotopic ratios from each river sample are expected. Similar relative values are also expected between the rain water and river water samples.

Methods

Ion Chromatograph

A Dionex 600 Ion Chromatograph was used to determine the presence of 7 anions and 6 cations. The anions tested for include fluoride, chloride, nitrate, nitrite, phosphate, bromide, and sulfate and major cation lithium, ammonium, sodium, potassium, calcium, and magnesium. The cations the ion chromatograph tested the water for consist of. This included anion and cation analysis

Preparation for oxygen analysis

Water samples were prepared by equilibration of 0.5 ml of water in a 1 dram vial with a gas containing a 9/1 ratio of N_2 to CO_2. Equilibration was carried out by shaking and warming the samples in an incubating shaker at 20°C for 24 hours. 25 μL injections of the headspace gas were injected into a 2 meter long porous-layer open tubular column at 60°C with a flow rate set by adjusting the pressure of the incoming He carrier gas to 5 PSI. Injections were performed at 200 second intervals with an approximate elution time of 300 seconds. Following these procedures provided sufficient separation of the N_2 and CO_2 peaks before insertion to a Finnigan MAT 252 IRMS.

$\delta^{18}O$ values of the unknowns were calibrated relative to the measured values of three internal standards: UU DI (University of Utah Deionized water, $\delta^{18}O$= -16.5‰ $_{VSMOW}$), EVIAN ($\delta^{18}O$= -10.5‰ $_{VSMOW}$), and UU ZERO ($\delta^{18}O$= -0.2‰ $_{VSMOW}$). These standards were prepared and analyzed using the same methods as the unknown samples. A correction was applied to unknown samples to account for the linear increase in the difference between the measured and known values of standards at decreasing $\delta^{18}O$ values. Multiple injections of each sample and multiple preparations of each standard yielded a standard deviation of ~ 0.5‰. Care was taken to include all analysis of standard material in this run calibration. Multiple injections of each sample yielded a standard deviation of less than 0.2‰ after exclusion of samples with obvious memory effects. Analysis of reference tanks showed some machine drift over the course of three 5000 second runs, thus a correction factor to account for this drift was included.

Preparation for hydrogen analysis

Hydrogen isotope ratios of water samples and standards were obtained by reducing the hydrogen in 2μL of water to ^2H with ~100 mg of Zn reagent in a Pyrex tube at 500° C. The resulting gasses were analyzed using a Thermo Finnegan Delta S isotope ratio mass spectrometer (IRMS) with a dual inlet.

Preparation for Alkalinity Analysis

Alkalinity was determined by means of titration based on the U.S. EPA approved method 310.1 (Ruthenburg, T. 2004). A sample of water was titrated with 0.020 N HCl to pH 4.5, and the total value of the titrant used was recorded. The samples were titrated using a buret and a stirred with a magnetic stir bar. Alkalinity, in units of mg $CaCO_3$ / L was then determined using the following equation:

Alkalinity = (A)(N)(50000) / mL_of_sample

A = mL Titrant Used
N = Normality of Standard Acid

Results
Cations

Sodium levels detected in the Cannon River ranged from 8.33-13.15 mg/L. Potassium levels ranging from 5.54-5.98 mg/L were detected. Magnesium was detected in concentrations ranging from 23.00-30.05 mg/L. Measured calcium levels ranged from 64.10-96.66 mg/L (Table 1).

Measured cation levels, with the exception of potassium, show a pattern of rapid increase of concentration between Faribault and Dundas, and in the cases of magnesium and calcium a slight dropoff in concentration between Dundas and Northfield (Figure 2). Lithium and ammonium were not detected in any of the samples.

Anions

Fluoride was detected only at the Northfield site, which had concentrations of 0.14 mg/L. All other anions were present at all three sampling sites. Chloride was observed in concentrations ranging from 14.03-20.47 mg/L. Nitrate concentrations range from 5.15-23.94 mg/L. Sulfate concentrations are present in a range of 39.43-62.12 mg/L (Table 1). Observed anions show a pattern of dramatic increase in concentration between Faribault and Dundas, followed by a slight dropoff in concentration between Dundas and Northfield (< 1 mg/L, Figure 2). Nitrite, bromide, and phosphate were not observed in any of the samples. The sum of both cations and anions shows a clear increase in total ion concentration is observed between Faribault and Dundas.

Table 1: Ionic Concentrations of Water collected from sample sites.

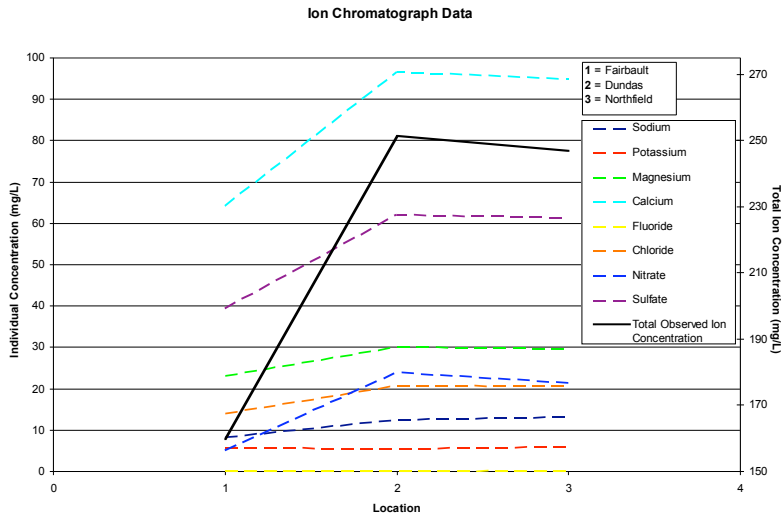| Ion Chromatography			
Location Description	Faribault	Dundas	Northfield
Sodium (mg/L)	8.33	12.42	13.15
Potassium (mg/L)	5.64	5.54	5.98
Magnesium (mg/L)	23.00	30.05	29.65
Calcium (mg/L)	64.10	96.66	95.02
Fluoride (mg/L)	0.00	0.00	0.14
Chloride (mg/L)	14.03	20.82	20.47
Nitrite (mg/L)	0.00	0.00	0.00
Nitrate (mg/L)	5.15	23.94	21.40
Sulfate (mg/L)	39.43	62.12	61.22
Total (mg/L)	159.68	251.55	247.03

Ion Chromatograph Data

Figure 2: Ion concentrations observed in water collected from the Cannon River. Dashed lines refer to individual ion concentrations. The solid black line refers to the total ion concentration, and is quantitated on the right side of the figure.

Isotopes

      Measured levels of δ^2H for water from the Cannon River range from δ^2H–57.4$^0/_{00}$ to δ^2H–43.1$/_{00}$ (VSMOW) on the first run. Variation in δ^2H for the second run ranges between δ^2H-55.3$^0/_{00}$ to δ^2H-53.0$^0/_{00}$. Deuterium composition for rainwater collected in the Northfield area ranges between δ^2H-76.2$^0/_{00}$ to δ^2H-72.6$^0/_{00}$ (Table 2 and Figure 3).

Table 2: δ^2H (VSMOW)

	Run 1	Run 2
Faribault*	-57.4	-53.0
Dundas*	-43.1	-55.3
Northfield*	-56.2	-54.3
Northfield RW	-76.2	-72.6

* units are ‰
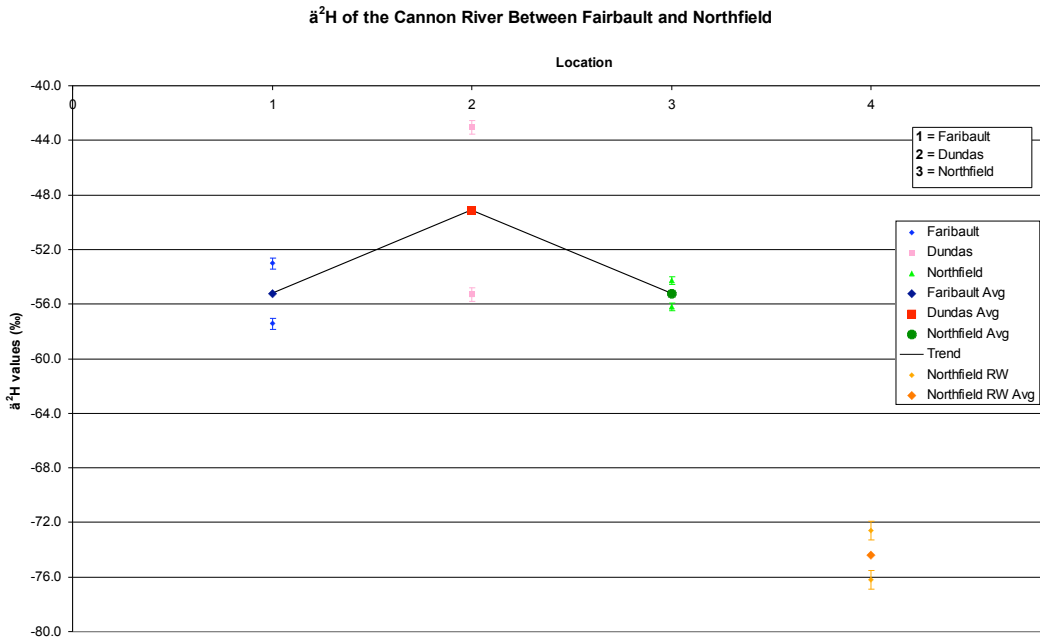
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ä²H of the Cannon River Between Fairbault and Northfield

Figure 3: δ^2H values (‰) of water samples collected from the study area. River water values are connected by a trendline. Rain water plots in the bottom right for comparison. Samples were analyzed on a (Thermo Finnegan) Delta S IRMS with a dual inlet. The error bars were calculated as standard deviations by the instrument.

Measured levels of $\delta^{18}O$ for water collected from the Cannon River range between $\delta^{18}O$-9.09$^0/_{00}$ and $\delta^{18}O$-8.06$^0/_{00}$ (VSMOW). $\delta^{18}O$ values of Northfield rainwater range between $\delta^{18}O$-9.17$^0/_{00}$ and $\delta^{18}O$-8.52$^0/_{00}$ (Table C and Figure C).

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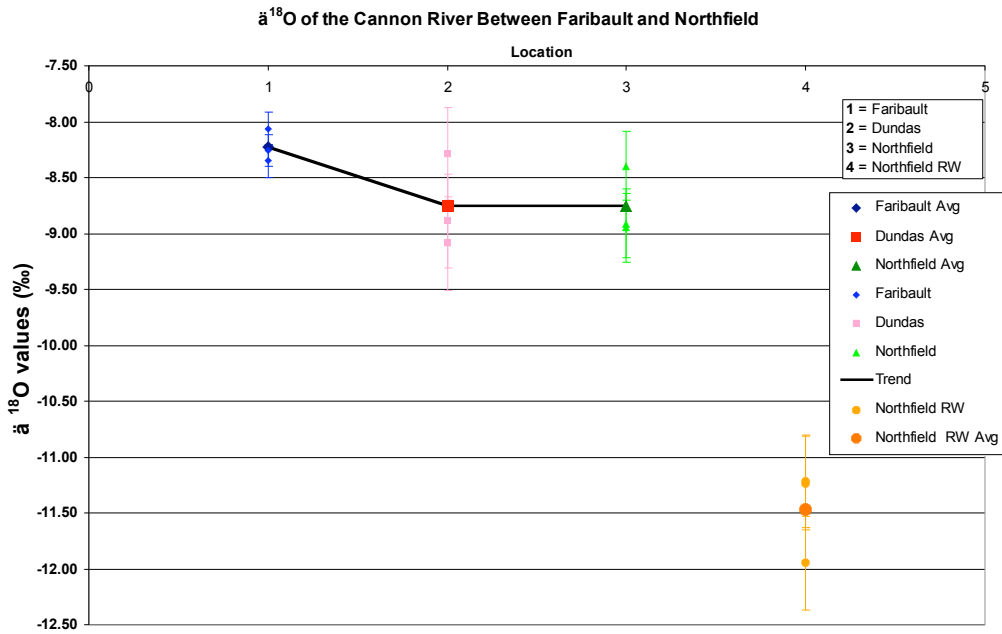Figure 4: This figure uses $\delta^{18}O$ obtained from a Finnigan MAT 252 isotope ratio mass spectrometer. River water samples are connected with a trend line. Rain water values plot in the lower right hand corner, for comparison. Calibrations to account for standards, machine drift, and temperature equilibration were utilized. Error bars represent the standard deviation of the multiple injections

Table 3: $\delta^{18}O$ (VSMOW)

Location	$\delta^{18}O$ ‰
Faribault	-8.35
Faribault	-8.06
Faribault	-8.26
Faribault Avg.	**-8.22**
Dundas	-9.09
Dundas	-8.89
Dundas	-8.29
Dundas Avg.	**-8.75**
Northfield	-8.95
Northfield	-8.91
Northfield	-8.40
Northfield Avg.	**-8.75**
Northfield RW	-11.95
Northfield RW	-11.22
Northfield RW	-11.24

Northfield RW Avg.	-11.47

Alkalinity

Observed levels of $CaCO_3$ range between 133.3 mg/L and 180.0 mg/L. Minimum levels are seen in Faribault, and a maximum concentration is observed at Dundas, with a slight decline in Alkalinity observed at Northfield (Table D).

Table 4: Alkalinity observed at three sites along the Cannon River.

Location	Alkalinity (mgCaCO3/L)
Faribault	133.3
Dundas	180.0
Northfield	169.9

Discussion

The concentration of total ions monitored in the water increased sharply between Faribault and Dundas, and this rate of increase leveled off between Dundas and Northfield. However, there was not a systematic change in concentration of the ions analyzed in relation to one and other. The variance was roughly the same for the following groupings of ions: calcium, sodium and nitrate; magnesium and chloride; and sulfate and potassium. Overall there were no outliers that showed trends drastically different from the overall observed ion concentrations. Anthropogenic sources between Faribault and Dundas could account for the drastic increase in observed ion levels between the first two test sites. Possible sources include agricultural input from farms between Faribault and Dundas. The lack of numerous farms between Dundas and Northfield could account for the stablizing in observed ion concentration. The fact that nitrates follow also increase and stabilize further supports this theory.

Alkalinity concentrations show a pattern similar to those of the major ions observed in that there is a dramatic increase of concentration between Faribault and Dundas followed by a mild drop off in concentration between Dundas and Northfield. In each case the alkalinity observed is approximately twice (2x) the observed dissolved calcium.

The $\delta^{18}O$ concentration of the Cannon River decreases downstream between Faribault and Dundas, at which point the $\delta^{18}O$ concentration becomes constant. River isotopic fractionation processes are the most likely mechanisms depleting the river of ^{18}O as the water travels down stream, although the concentration change is less than .5‰. A significant difference in $\delta^{18}O$ was observed for rain water and river water. The fact that the rain water was more ^{18}O depleted than the river water. This can likely be attributed to groudwater being introduced to the river upstream of Faribault. Ground water is often heavier in ^{18}O because the water has had time to equilibrate with the rocks and soils of the aquifer which have a higher concentration of ^{18}O (Drever, J.I. 1997). Another variable that might be affecting relative $\delta^{18}O$ values is the source of the rain water. The rain water was collected in Octobr 2004, while the river water was collected in April 2005. Seasonal

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variations in the source of the waters (Pacific Ocean in winter, Gulf of Mexico in summer) each have different isotopic signatures that could be causing the differences that were observed.

Isotopic δ^2H data for samples collected at the Dundas location in the first run show an enrichment of δ^2H (in the order of ~ +15 ‰) when compared to δ^2H observed in Faribault and Northfield samples, as well as δ^2H values observed in Dundas run 2. While more samples are needed to conclude that the value obtained for Dundas run 1 is an anomaly, it is likely that the value observed for Dundas in run 2 is the more accurate datum. Based on this assumption, run 2 is likely the most representative of the δ^2H concentration of the Cannon River at Dundas, and indicates that the δ^2H of the Cannon River is fairly constant (Figure 5).
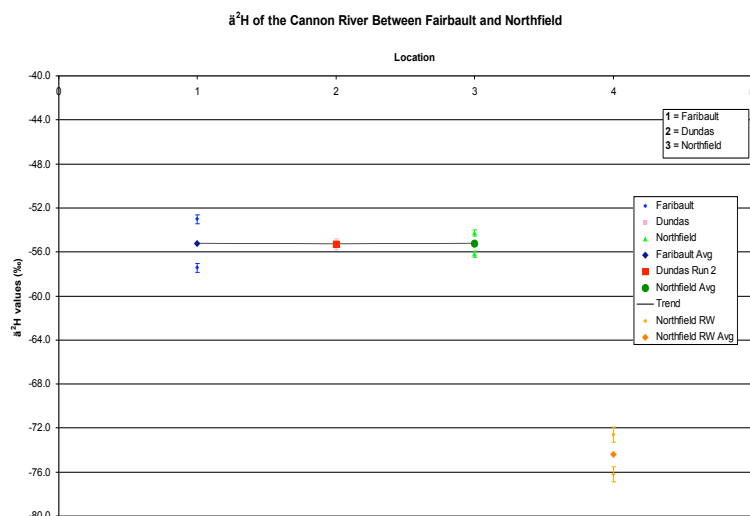

Figure C: Adjusted δ^2H values (‰) of water samples collected from the study area. The probable anomalous value obtained for Dundas in the first run is removed, resulting in a smoother trend line of river water values. Rain water plots in the bottom right corner for comparison.

Conclusion

The increase of concentration of ions observed between Faribault and Dundas is likely the result of anthropogenic input between the sites. More detailed sampling is necessary to pinpoint the source of the additional ions. The overall similarity in characteristics of the three river water data points in terms of isotopic ratios ($\delta^{18}O$ and adjusted δ^2H) indicate that little fractionation occurs between the three sites, likely because of their proximity and similar climatic conditions. Differences in isotopic composition between the river water and rain water are most likely the result of fractionation processes and the introduction of ground water into the river. Seasonal

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variations in the source of meteoric water may also result in the discrepancy in isotopic values observed between river and rain waters.

Increasing the number of samples examined at each site will increase the reliability of data collected in the future. This will decrease the chances of a statistical outlier obscuring trends and increase the odds of a representative data set. Furthermore, adding new sample sites will create a more comprehensive analysis of river chemistry conditions. Performing comprehensive studies during multiple seasons could assist in identifying the effect of snow melt and moisture source on the $\delta^{18}O$ and δ^2H values, among other effects. Studying isotopic trends of groundwater could also shed further light on observed trends in this data set. Future collaborations could include comparisons of trends in isotopic ratios with indigenous species such as the pink heelsplitter (*Potamilus alatus)*. Such studies could reveal information about isotopic fractionation within biological processes as well as the isotopic composition of the bivalve's growing environment in recent times.

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