Spatial and temporal variability in the $\delta^{18}\text{O}_w$ and salinity compositions of Gulf of Maine coastal surface waters

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Abstract

Hydrographic variability and dynamics in the Gulf of Maine are examined through the investigation of $\delta^{18}\text{O}_w$ and salinity properties of coastal surface waters. Data from Gulf of Maine waters sampled over a decade, from 2003 to 2015, including a suite of samples that were collected monthly from April 2014 to March 2015, are presented. These water samples fall on a mixing line between Maine River Water (MRW) and Scotian Shelf Water (SSW). However, slope waters likely also contribute to these surface waters. The seasonal variability in water samples collected during 2014 and 2015 indicates the strong influence of river runoff on coastal Gulf of Maine surface water properties. The coastal surface Gulf of Maine mixing line presented in this paper is a needed baseline for reconstructing hydrographic variability in bicarbonates using oxygen isotopes.

Keywords: Gulf of Maine, oxygen isotopes, conservative water mass tracers, mixing line, salinity, hydrographic variability

1. Introduction

The Gulf of Maine, a semi-enclosed sea on the eastern continental shelf of North America, sits near the intersection of two major North Atlantic currents: the Gulf Stream and the Labrador Current. Gulf of Maine hydrographic properties are therefore influenced by the dynamics and composition of these major

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currents. Reconstructing these hydrographic properties using proxy climate archives such as corals (Sherwood et al., 2011) and ocean quahogs (Wanamaker et al., 2008) has the potential to be a valuable indicator of the past behavior of these important North Atlantic currents. Before past and current hydrographic changes in the broader region can be interpreted from hydrographic changes seen in the Gulf of Maine, Gulf of Maine hydrographic dynamics and the influence of these dynamics on water properties must be comprehensively understood, both for off-shore and coastal locations. The composition (temperature, salinity and oxygen isotope values) and origin of water masses contributing to the Gulf of Maine water properties, as well as the water properties of several off-shore sites have been described in detail by numerous authors (Bigelow, 1927; Gatien, 1976; Fairbanks, 1982; Smith, 1983; Chapman et al., 1986; Chapman and Beardsley, 1989; Brown and Irish, 1993; Smith et al., 2001; Houghton and Fairbanks, 2001). Here, we focus on the use of oxygen isotopes and salinity in determining the hydrography of the Gulf of Maine coastal system.

1.1. $\delta^{18}\text{O}$ and salinity as conservative water mass tracers

Because the oxygen isotopic signature of the water ($\delta^{18}\text{O}_w$) depends on the latitude of origin (Craig, 1961) and is not changed by biological processes during transport, $\delta^{18}\text{O}_w$ is considered a conservative property of water masses. $\delta^{18}\text{O}_w$ has a positive linear relationship with salinity, which is another conservative property of water masses. This relationship between salinity and $\delta^{18}\text{O}_w$ (referred to as a “mixing line” in this paper due to its indication of the mixing of two or more water masses) can therefore be used to determine water mass origin and mixing in any given region, such as the Gulf of Maine (Fairbanks, 1982).

There have been numerous studies that use oxygen isotopes and salinity as conservative tracers of water masses that are thought to contribute to the composition of Gulf of Maine waters. We will first review this work before discussing specific oxygen isotope and salinity studies within the Gulf of Maine.

1.2. Regional water mass composition

The Gulf of Maine is fed by several different water masses which have been described by their temperature, oxygen isotope and salinity signatures (Table 1). The general origin of these water masses is shown in Figure 1. Deep waters in the Gulf of Maine have been shown by numerous authors to be composed of Labrador Slope Water (LSW) and Warm Slope Water (WSW). LSW is generally considered deep (greater than 100 meters) water that is transported by the southwestward flowing branch of the Labrador Current after it has split to divert some water into the Gulf of St. Lawrence (Chapman and Beardsley, 1989; Gatien, 1976). WSW is found at 0-400 meters depths adjacent to the Gulf Stream and is warmer and more nutrient rich than LSW (Townsend and Ellis, 2010; Gatien, 1976). Both slope waters enter the Gulf of Maine via the Northeast Channel.

Shallow waters in the Gulf of Maine are composed of Scotian Shelf Water (SSW), which flows from the Scotian Shelf into the Gulf of Maine over

Water Mass	Temperature (°C)	$\delta^{18}\text{O}_w$ (‰)	Salinity	Citation
Warm Slope Water (WSW)	10	0.4	35.2	Houghton and Fairbanks, 2001
	11.11 (potential)	0.36	35.16	Khatiwala et al., 1999
Labrador Slope Water (LSW)	6	0.22	34.9	Houghton and Fairbanks, 2001
	3.28 (potential)	0.22	34.80	Khatiwala et al., 1999
Scotian Shelf Water (SSW)		-1.09	32.35	Chapman et al., 1986
Labrador Shelf Water (LSHW)	0	-1.62	32.6	Houghton and Fairbanks, 2001
St. Lawrence River Water (SLRW)		-10.3	0	Khatiwala et al., 1999
Arctic River Water (ARW)		-21	0	Khatiwala et al., 1999
Maine River Water (MRW)		-10.89	0	Fairbanks, 1982
Gulf Stream Water		1.15	36.2	Fairbanks, 1982
	16	1.05	35.95	Houghton and Fairbanks, 2001

Table 1: Properties of water masses composing Gulf of Maine waters. Bolded numbers are those chosen for figures and discussion in this paper. These water mass property definitions were largely determined from the end-members of salinity and $\delta^{18}\text{O}_w$ mixing lines derived from water samples collected on research cruises during the 1980s and 1990s. It is important to note that not all of these definitions take into account annual and monthly changes to the water masses but are meant to give rough estimates.

Figure 1: Map of the general area of origin of water masses believed to contribute to the compositions of Gulf of Maine waters. These water masses include Arctic River Water (ARW; Khatiwala et al., 1999), Labrador Shelf Water (LShW; Khatiwala et al., 1999), St. Lawrence River Water (SLRW; Khatiwala et al., 1999), Labrador Slope Water (LSW; Chapman and Beardsley, 1989), Scotian Shelf Water (SSW; Smith, 1983; Chapman et al., 1986), Warm slope Water (WSW; Gatien, 1976), Maine River Water (MRW; Fairbanks, 1982). The justification for choosing the location of origin for these water masses is described in the text. The approximate location of major western North Atlantic currents are also shown: Gulf Stream (white arrow) and the Labrador Current (black arrows), after Chapman and Beardsley (1989) and Loder et al. (1998) and modified from Townsend et al. (2010). Width of arrows indicates the approximate relative strength of currents. Map modified from the NOAA National Geophysical Data Center (maps.ngdc.noaa.gov/viewers/fishmaps).

Cape Sable (Smith, 1983; Chapman et al., 1986). By investigating the $\delta^{18}\text{O}_w$ -salinity relationship of waters on the Scotian Shelf, Khatiwala et al. (1999) determined that SSW was composed of LSW, Labrador Shelf Water (LShW) and St. Lawrence River Water (SLRW).

The majority of the freshwater in the Gulf of Maine originates in locations north of this region. The northern most possible source of freshwater to the Gulf of Maine is considered to be low- $\delta^{18}\text{O}_w$ Arctic River Water (ARW) flowing out of the Labrador Sea (Khatiwala et al., 1999). While Fairbanks (1982), Chapman et al. (1986), and Chapman and Beardsley (1989) all inferred the freshwater end-

members ($\delta^{18}\text{O}_w$ of -21‰) of mixing lines derived from areas in and around the Gulf of Maine to indicate a freshwater source of ARW, Khatiwala et al. (1999) and Houghton and Fairbanks (2001) argue that this freshwater end-member is in fact the result of mixing between SLRW and LShW.

1.3. The $\delta^{18}\text{O}_w$ and salinity signatures of Gulf of Maine waters

Waters within the Gulf of Maine are the result of mixing between the water masses described in Section 1.2 as well as Maine River Water (MRW), which Fairbanks (1982) determined to have an average $\delta^{18}\text{O}_w$ of 10.89‰ (calculated by taking an annual average of the $\delta^{18}\text{O}_w$ composition of the Kennebec and St. John Rivers; Table 1). A brief review of work done on quantifying this mixing using the salinity and $\delta^{18}\text{O}_w$ composition of Gulf of Maine waters, as we do in this study, follows.

Fairbanks (1982) sampled water at various depths in Wilkinson Basin, western Gulf of Maine, in January, May and August of 1981 (Figure S1A in the supplementary material). He found that Wilkinson Basin surface and intermediate waters (above 115 meters depth) fall on a two water mass mixing line:

$$\delta^{18}\text{O}_w = 0.421S - 14.66 \quad (1)$$

This mixing line is very similar to the mixing line the author developed for the Scotian Shelf (Figure S1A in the supplementary material) and therefore suggests that the near surface and intermediate, non-coastal waters of the Gulf of Maine are primarily fed by SSW, as has been described in several other studies (Hopkins and Garfield, 1979; Smith, 1983).

Slope water, the composition of which Fairbanks (1982) determined from samples taken between Nova Scotia and Cape Hatteras, falls on a two-water-mass mixing line (Figure S1A in the supplementary material) between Gulf Stream waters and fresh water that have an $\delta^{18}\text{O}_w$ value of -21.7‰ , which the author took to indicate Labrador Sea origin. Samples of bottom water from Wilkinson Basin fall on this mixing line and suggest that bottom waters in the Gulf of Maine are composed of slope water (WSW and LSW), as separately determined by other authors (e.g. Ramp et al., 1985). The equation for this mixing line is:

$$\delta^{18}\text{O}_w = 0.628S - 21.67 \quad (2)$$

Chapman et al. (1986) also used salinity and $\delta^{18}\text{O}_w$ as a tracer of water masses and found a decrease in the percentage of SSW with depth in the Northeast Channel, indicating the deep inflow of slope water. However, salinity and oxygen isotope data indicate that deep waters in the Northeast Channel were still composed of 20-30% SSW. The authors suggested that this may indicate the mixing of SSW with LSW farther north over the Scotian Shelf, a mixture of water masses that is then transported into the Northeast Channel. The $\delta^{18}\text{O}_w$ data that the authors presented also suggested that slope waters mix with SSW in the Gulf of Maine before leaving around the southern flank of Georges Bank.

Similarly, Houghton and Fairbanks (2001) used oxygen isotope measurements to determine the source of waters on Georges Bank and in the Northeast Channel from 1995-1998. The authors show that water samples collected in the Northeast Channel fall on a single mixing line with WSW and LSW as the saline end-member (Figure S1B in the supplementary material):

$$\delta^{18}O_w = 0.57S - 19.5 \quad (3)$$

While investigations into the oxygen isotopic composition of Gulf of Maine waters have yielded important information on water mass sources and mixing in the Gulf of Maine, there are still large gaps in the research that need to be addressed in order to gain a better understanding of hydrographic variability and dynamics in this region. Specifically, no studies have shown the isotopic composition of coastal, surface waters, how these waters vary from season to season and between regions and what this reveals about hydrographic composition in the Gulf of Maine. In this paper, we seek to fill this gap by presenting $\delta^{18}O_w$ and salinity data from water samples collected along the coastal Gulf of Maine over multiple seasons and years.

2. Methods

Two sets of water sample data are presented in this paper. One set is oxygen isotope and salinity data from water samples collected between 2003 and 2013 at various locations in the Gulf of Maine and termed here the Wanamaker data set (see Figure 2, orange markers, for collection site locations). Some of these data has been published previously but are compiled here for the first time. This data set includes water samples published by Wanamaker et al. (2006), Wanamaker et al. (2007) and Owen et al. (2008), as well as data collected as part of research published by Beirne et al. (2012). The other data set is comprised of surface water samples collected monthly from April 2014 - March 2015 at locations along the coast of Maine (see Figure 2, red and teal markers, for collection site locations) to further expand the spatial and temporal range of the coastal Gulf of Maine mixing line as well as to investigate the seasonal variability in hydrographic composition in these areas. This data set is termed the 2014/2015 data set in this paper.

The Wanamaker data set primarily consists of water samples collected as part of various experiments conducted at the Darling Marine Center in Walpole, Maine. Water samples collected during these experiments were obtained from water pumped into the Darling Marine Center’s flowing seawater laboratory from ~10 meters below mean low tide in the Damariscotta River, an estuarine environment. Additionally, this data set contains data from water samples collected between Seguin Island in the western coastal Gulf of Maine and Isle au Haut in the central coastal Gulf of Maine during July 2011 and from samples collected along the southern Maine and New Hampshire portion of the Gulf of Maine coast during October of 2013.

Figure 2: Map of water sample collection sites in the Gulf of Maine. The map shows water sample collection sites for the Wanamaker and 2014/2015 data sets, as well as freshwater samples collected in 2014/2015. Yellow arrows indicate the locations of select sampling sites mentioned in the text (DMC - Darling Marine Center). White arrows indicate the mouth of five major rivers that empty into the Gulf of Maine. Black arrows indicate surface currents (based on Pettigrew et al. (2005)), including the Eastern Maine Coastal Current (EMCC) and the Western Maine Coastal Current (WMCC). Width of the arrows indicate the relative strength of these currents. Map modified from Google Earth. For a higher resolution map of the sample locations, see Figure S2 in the supplementary material.

Details on data processing of water samples from previously published work are included in those publications. Samples collected in 2010 at the Darling Marine Center and the summer of 2011 (unpublished) were brought to the Stable Isotopes Lab (SIL) at Iowa State University and measured via a Picarro L1102-i Isotopic Liquid Water Analyzer with an attached autosampler. Isotopic standards (OH-1, OH-2, OH-3) were used as reference standards to place samples on the international scale, VSMOW. Samples were injected six times, with only the last 4 injections being used to determine the isotopic value of the sample in order to avoid memory effects. The combined uncertainty (which is derived from taking the square root of the analytical uncertainty estimate squared plus the linear model correction factor squared) was $1\sigma = \pm 0.15\text{‰}$ (for 2010 samples) and $1\sigma = \pm 0.04\text{‰}$ (for 2011 samples). Water samples collected during October 2011 (unpublished) were processed in the same way as water samples from the 2014/2015 surface coastal mixing line data set, as described below.

The salinity of water samples collected in 2010 and 2011 was measured on a YSI Professional Plus salinity meter or equivalent device using methods similar to the ones described below for the 2014/2015 surface coastal mixing line data set.

Collection for the 2014/2015 surface coastal mixing line began in April of 2014 and lasted through March of 2015. Water samples were collected monthly in areas accessible by road, primarily east of Penobscot Bay. An effort was made to visit the same locations each month in order to gain a better understanding of regional seasonal variability in water composition. Additionally, water was collected by scientists from the Mount Desert Biological Laboratory and by citizen-scientist volunteers at locations throughout the Maine coast convenient to where they lived and worked. Freshwater samples were also obtained from the Penobscot River in Old Town, Maine (44.937642° , -68.646260°) on a monthly basis and from the Kennebec River immediately before its confluence with the Androscoggin (44.013367° , -69.831106°) several times throughout the year. It is important to note that while it is fresh water, the Kennebec River is tidal at this location. Water was collected in either 1 oz or 4 oz French square glass bottles with phenolic polycone lined caps. Every effort was made to fill the bottles completely in order to minimize head space in the bottle and consequently evaporation. Water samples were stored in a refrigerator when possible, although this was not always an option.

Water samples were transported to Iowa State University’s SIL. Here samples were measured for isotopes on a Picarro L2130-i Isotopic Liquid Water Analyzer with an attached autosampler. The isotopic values of samples collected in 2014 were calculated using Vienna Standard Mean Ocean Water (VSMOW) and two other reference standards, both of which are calibrated to VSMOW. The uncertainty ranged from $1\sigma = \pm 0.07\text{‰}$ to $\pm 0.18\text{‰}$ and averaged $1\sigma = 0.12\text{‰}$.

The salinity of water samples for the 2014/2015 surface coastal mixing line data set was measured at SIL using a Oakton SALT 6+ handheld salinity meter, which has a reported accuracy of ± 1 . To verify the accuracy of this meter, salinity of several of the water samples was also measured using a YSI Professional Plus salinity meter, which has a reported accuracy of ± 0.1 . Both salinity meters were calibrated using a 45,000 $\mu\text{Siemens/cm}$ solution (~ 29.16 ppt). The calibration was tested on a 32.0 ppt solution composed of deionized water and pure sodium chloride (NaCl). As is seen in Figure 3, the two meters were in close agreement with a slope of 1.0 and a coefficient of determination (R^2 value) of 1.0. The average absolute difference between the two salinity meters was 0.2, indicating that the uncertainty in the salinity measurement is approximately ± 0.2 .

When analyzing the composition and mixing of Gulf of Maine waters, $\delta^{18}\text{O}_w$ values were linearly regressed against salinity values to create mixing lines for coastal surface Gulf of Maine waters. Tidal height during sampling was not considered during these data analyses. While tidal height does change the water composition, previous experiments at the Darling Marine Center have shown that the average change in water $\delta^{18}\text{O}_w$ over one tidal cycle is $\sim 0.26\text{‰}$ (see Figure S3 in supplementary material for these data), which would indicate an

Figure 3: Comparison of salinity measurements of the same water sample by two different salinity meters. The two salinity meters are the Oakton SALT 6+ handheld salinity meter (y axis) and the YSI Professional Plus salinity meter (x axis).

accompanying change in salinity of ~ 0.86 (calculated using the coastal Gulf of Maine mixing line equation - see Section 4). These changes in $\delta^{18}\text{O}_w$ values during a tidal cycle are only slightly above the analytical uncertainty and the changes in salinity values are below the instrumental accuracy. Therefore, tidal effects on water properties are not large enough to warrant factoring tidal height during sampling into our data analysis. When analyzing the monthly data, months will be grouped into seasons using the following scheme: spring - April and May, summer - June, July and August, fall - September, October, November, winter - December, January, February. March is not included in these season classification schemes as data for this month was collected one year after data collected for April and May and therefore grouping it with the spring data (as would be commonly done), would introduce unwanted temporal variability.

3. Results

3.1. Coastal Gulf of Maine $\delta^{18}\text{O}$ -salinity mixing lines

Because both the 2014/2015 and Wanamaker data sets contain water samples from the coastal Gulf of Maine, combining them into one mixing line will give

Figure 4: All water samples used for the Gulf of Maine coastal mixing line (black line). The dashed lines indicate 95% prediction limits for the linear regression model. Pink marker indicates Scotian Shelf Water (SSW) composition as determined by Chapman et al. (1986). As noted by Smith et al. (2001), the oxygen isotope and salinity value of SSW varies from year to year depending on river runoff. The values used here were the composition of SSW found in the spring of 1981.

a better overall understanding of the relationship between $\delta^{18}\text{O}_w$ and salinity of coastal Gulf of Maine waters. In addition, these data together represent the composition of waters in the coastal Gulf of Maine sampled over more than a decade and therefore combining the data reduces the bias towards conditions in any one particular year (Figure 4). The resulting mixing line has the equation:

$$\delta^{18}\text{O}_w = 0.25S - 9.13 \quad (4)$$

Salinity explains 94.5% of the variance in $\delta^{18}\text{O}_w$ values. Water samples with salinities below 5 were not used in these mixing lines so as not to significantly influence the mixing line with a freshwater source specific to a given region of the Gulf of Maine. Equation 4 will be termed the coastal Gulf of Maine mixing line for the remainder of this paper.

3.2. Seasonal variability in coastal Gulf of Maine water properties

As mentioned in Section 2, water samples comprising the 2014/2015 data set were collected monthly from April 2014 to March 2015 at various locations along the eastern coast of Maine. Figure 5 shows month to month changes in salinity and $\delta^{18}\text{O}_w$ composition in select locations along the coast (see Table 2 for specific locations and location descriptions). These data show a large range in oxygen isotope and salinity measurements. In general, oxygen isotope and salinity values at a given site follow similar trends. Most sites show increasingly higher salinity and $\delta^{18}\text{O}_w$ values from spring to winter (excluding December). Salinity and $\delta^{18}\text{O}_w$ values in April were lower than most of the period sampled. Values tended to also be significantly lower in December.

Figure 6 shows water samples from the 2014/2015 surface coastal mixing line data set plotted in terms of location and colored in terms of $\delta^{18}\text{O}_w$ composition and salinity. The figure reveals little discernible patterns for the spring and winter with a range of $\delta^{18}\text{O}_w$ values present. However, similarities emerge in the summer and fall maps. The majority of samples collected during the fall have higher $\delta^{18}\text{O}_w$ values than those collected during the summer. In both seasons, there are no discernible spatial patterns and all samples have similar intraseasonal $\delta^{18}\text{O}_w$ values. The several samples that have significantly lower $\delta^{18}\text{O}_w$ values than other samples for summer and fall were collected directly from rivers. Seasonal salinity averages for coastal Gulf of Maine waters follow a similar pattern to those of $\delta^{18}\text{O}_w$: no dominant spatial pattern exists for winter and spring months but coastal waters have spatially similar salinity values for both the summer and fall months. Coastal waters are more saline in the fall compared to the summer.

3.3. Temporal changes in the oxygen isotopic composition of Maine rivers

The temporal variability of $\delta^{18}\text{O}_w$ values from water samples collected on the Kennebec and Penobscot Rivers is shown in Figure 7. The average $\delta^{18}\text{O}_w$ value for the Penobscot River is -10.5‰. The average $\delta^{18}\text{O}_w$ value for the Kennebec River is -9.2‰. However, it is important to note that these rivers were not sampled in all months (partially due to these rivers being frozen during parts of

Figure 5: Temporal changes in salinity (A) and $\delta^{18}\text{O}_w$ (B) composition of coastal Gulf of Maine waters in 2014 and 2015. Refer to Table 2 for the specific location and location description where data were collected.

ID	Location	Latitude	Longitude	Location Description
A	N Lubec	44.862308°	-66.983883°	north side of headland at mouth of Cobscook Bay
B	S Lubec	44.854854°	-66.981424°	south side of headland at mouth of Cobscook Bay
C	Cutler	44.657318°	-67.207298°	protected harbor; no immediate fresh water input
D	N Great Waas Island	44.51627°	-67.590607°	north side of island in Alley Bay; fresh water input on other side of bay
E	SW Great Waas Island	44.480140°	-67.598422°	southwest side of island; no immediate fresh water input
F	Jonesport	44.528216°	-67.620356°	near entrance to small estuary
G	Prospect Harbor	44.399638°	-68.02334°	harbor with fresh water input
H	Sorrento	44.471798°	-68.182030°	end of headland on Frenchman Bay; fresh water input into bay near headland
I	Hancock	44.467197°	-68.224646°	end of headland on Frenchman Bay; fresh water input into bay near headland
J	Bar Harbor	44.392267°	-68.204079°	east side of island on Frenchman Bay; no immediate fresh water input
K	Bass Harbor	44.221642°	-68.336743°	mouth of harbor on island; fresh water input into harbor

Table 2: Table of monthly water sampling location descriptions. The locations correspond to locations represented in Figure 5 and the letter ID correspond to the letters labeling the red markers in Figure S4 of the supplementary material.

Figure 6: Seasonal maps of the $\delta^{18}\text{O}_w$ composition (left column) and salinity (right column) of coastal Gulf of Maine waters from water samples collected for the 2014/2015 data set. Data is organized based on what time of year the sample was collected: spring (April and May), summer (June, July, August), fall (September, October, November), winter (December, January, February). Data collected in March was not included as it was collected the year following the year that the other spring data was collected. Data from water samples collected at the same location during the same season were averaged together. The locations of Penobscot Bay and several major rivers are denoted to be used as spatial references.

Figure 7: Temporal variability of $\delta^{18}\text{O}_w$ composition of Maine river water from samples collected in 2014/2015. See text for specific locations.

the winter and early spring) and that the Kennebec River was sampled in fewer months than the Penobscot. The average $\delta^{18}\text{O}_w$ of the Penobscot for the months in which the Kennebec was also sampled (July, October, November and December) was -9.9‰ . As shown by these averages and Figure 7, the $\delta^{18}\text{O}_w$ values of water samples from the Kennebec River consistently have higher $\delta^{18}\text{O}_w$ values than those from the Penobscot River. Both rivers show strong differences in $\delta^{18}\text{O}_w$ composition between seasons, with a more than 2‰ difference in Penobscot River waters over the course of a year. Additionally, both rivers follow similar $\delta^{18}\text{O}_w$ trends to those seen in the coastal water samples, with lower $\delta^{18}\text{O}_w$ values in April and May and higher $\delta^{18}\text{O}_w$ values during the summer, with peak values in November.

4. Discussion

4.1. Seasonal variability

The seasonal variability seen at most of the locations sampled, of relatively low salinity and $\delta^{18}\text{O}_w$ during the spring months and progressively increasing values of salinity and $\delta^{18}\text{O}_w$ through the rest of the sampling period, with the exception of the month of December (Figures 5 and 6), indicates a significant influence of local river water on coastal Gulf of Maine waters, as would be expected. As was described in Section 3.3, the $\delta^{18}\text{O}_w$ compositional variability of Penobscot and Kennebec Rivers show similar patterns to $\delta^{18}\text{O}_w$ compositional variability of Gulf of Maine coastal seawater (Figure 7). The lower $\delta^{18}\text{O}_w$ values in April and May are the result of snow melt influences. Because snow forms at colder temperatures, the proportion of heavy to light isotopes within the snow tends to be lower when compared to liquid precipitation due to higher fractionation factors and increased condensation of water vapor at lower latitudes, which decreases the $\delta^{18}\text{O}$ value of the water vapor that reaches the Gulf of Maine. Therefore, when the snow melts in spring, rivers carry waters that have lower $\delta^{18}\text{O}_w$ values when compared to non-snowmelt flows to the Gulf of Maine, clearly influencing Gulf of Maine waters.

Figure 8: 2014-2015 monthly average discharge of select major rivers that empty into the Gulf of Maine. Data taken from the closest available stream gauge to the coast for five rivers: the Penobscot River (45.236111°, -68.651389°), St. John River (47.038889°, -67.739722°), the Kennebec River (44.472222°, -69.683889°), the Androscoggin River (44.072222°, -70.208056°) and the St. Croix (45.136944°, -67.318056°). It is important to note that some of the rivers were frozen for parts of December so the average plotted is an average of those days when the water was flowing. Missing data for some rivers in January-March is the result of those rivers having frozen surfaces for the majority of those months. Data obtained from the Water Survey of Canada (St. John River; <http://wateroffice.ec.gc.ca/report/>) and the United States Geological Survey (<http://waterdata.usgs.gov/usa/nwis/>). See Figure 2 for the location of each river mouth.

However, as salinity shows similar seasonal changes to $\delta^{18}\text{O}_w$, it is likely that the seasonal changes in river discharge rates have a significant influence on coastal Gulf of Maine water properties as well. 2014-2015 average monthly discharges of 5 of the major rivers that empty into the Gulf of Maine are shown in Figure 8. Discharges for all rivers were high in the spring, as a result of snow and ice melt, before significantly diminishing in the summer and fall months. Discharges again increased in December. Changes in river discharge would be expected to affect both salinity and $\delta^{18}\text{O}_w$ of coastal waters as rivers bring fresh, low $\delta^{18}\text{O}_w$ value (in comparison to seawater) waters to the coast (Fairbanks, 1982; Houghton and Fairbanks, 2001).

This seasonal variability in $\delta^{18}\text{O}_w$ values of river water along with changes in river flow can also explain the low $\delta^{18}\text{O}_w$ values of Gulf of Maine water in December at some locations. During December 2014, there were several significant rain events in the two weeks prior to and including the date of sampling (December 17), totaling 9.93 centimeters, as recorded in Bangor, Maine (44.7978°, -68.8185°) which is on the southern end of the sampling region and is the precipitation record closest to the sampling sites. These precipitation totals are significantly higher than those for the two weeks leading up to and including other sampling days, which averaged 4.72 cm and did not exceed 9.32 centimeters (this next highest value occurred in October; data available at <http://www.usclimatedata.com/climate>). The combination of higher river flows (see Figure 8) as a result of these rain events as well as a lower $\delta^{18}\text{O}_w$

value freshwater input as the result of reduced temperatures likely led to the significant deviances from the seasonal trend seen at some locations in December (Figure 5).

It is also important to note that it was raining when December water samples were collected (Bangor, Maine got 1.63 cm of rain that day). Because water samples were collected at the surface, it is possible that this precipitation contributed to the lowering in $\delta^{18}\text{O}_w$ values and freshening of December water samples compared to the overall seasonal trend. However, in general, water property variability in coastal Gulf of Maine waters does not follow precipitation trends for 2014 and 2015 as recorded in Bangor, Maine (not shown).

While there is not enough data available to be able to analyze whether variability in river discharge or river $\delta^{18}\text{O}_w$ composition plays a larger role in the variability of coastal Gulf of Maine waters, it is clear that rivers emptying into the Gulf of Maine have a strong influence on these waters. Because salinity changes so closely follow $\delta^{18}\text{O}_w$ changes in coastal waters, it seems likely that river discharge variability is the dominant influence on seasonal changes in coastal water properties.

4.2. Spatial variability

The influence of rivers on coastal Gulf of Maine waters is also evident when looking at the spatial variability of $\delta^{18}\text{O}_w$ values (Figure 6). During the spring, there seem to be few spatial similarities or patterns in the $\delta^{18}\text{O}_w$ composition of coastal Gulf of Maine waters. The $\delta^{18}\text{O}_w$ composition of water samples collected during these high freshwater discharge periods is likely dependent on proximity of the sampling site to a freshwater source and the $\delta^{18}\text{O}_w$ of that freshwater source (see Table 2 for description of sampling location including proximity to freshwater source). There are also few spatial patterns for the winter season but this is likely due to the anomalous month of December, in which water samples from several sites had salinity and $\delta^{18}\text{O}_w$ values well below the seasonal trend as has been stated earlier (see Figure 5). If December data are ignored, water samples collected in the winter have spatially similar $\delta^{18}\text{O}_w$ and salinity values. These values are similar to those of water samples collected in the fall (Figure 5).

As stated above, rivers in the eastern Gulf of Maine tend to have water with lower $\delta^{18}\text{O}_w$ values than those in the western Gulf of Maine and therefore one might expect to see $\delta^{18}\text{O}_w$ values increase to the west. However, small rivers that do not have large watersheds extending into higher latitudes, which is the case for many of the rivers that empty into the Gulf of Maine near where water samples were collected, will not have $\delta^{18}\text{O}_w$ values as low as those rivers with larger watersheds. Therefore, the data collected in the spring and winter months likely reflects the influence of local river $\delta^{18}\text{O}_w$ composition and shows little spatial patterns due to the large variety of watershed sizes for these local rivers.

Figure 6 clearly shows that water samples collected during the fall had higher $\delta^{18}\text{O}_w$ values than those collected during the summer and that water samples from both seasons had higher $\delta^{18}\text{O}_w$ than samples collected during spring and

winter. In the previous section, we suggested that these seasonal differences were evidence of less influence of fresh water on coastal water properties during the summer and fall months due to decreased river discharge. The fact that water samples collected during the summer and fall seasons show spatial similarities also suggests decreased local river water influence. With decreased local river influence, coastal seawater composition is primarily determined by the composition of waters carried by ocean currents, specifically the Eastern Maine Coastal Current (EMCC) in this case. As that composition is fairly uniform throughout the area sampled, water samples collected along the eastern Maine coast show similar composition for seasons when river discharge is low.

4.3. *Gulf of Maine coastal mixing line*

The coastal Gulf of Maine mixing line that we present in this paper indicates mixing between two distinct end-members, MRW and SSW, with possible slope water influences. As can be seen in Figure 4, the Wanamaker data set has a slightly higher $\delta^{18}\text{O}_w$ values for fresher waters than the 2014/2015 surface coastal mixing line and a slightly lower $\delta^{18}\text{O}_w$ values for more saline waters. The reasons for this difference in mixing line end-members is likely both the result of differences in the general sampling locations as well as year-to-year difference in the composition of the end-members.

Most of the samples collected for the Wanamaker data set were collected in the western Gulf of Maine while most of the samples for the 2014/2015 data set were collected in the eastern Gulf of Maine (Figure 2). The differences in latitude between these general locations leads to differences in the $\delta^{18}\text{O}_w$ signature of the water feeding these regions as rivers flowing into the eastern Gulf of Maine tend to have watersheds at higher latitudes and therefore have lower $\delta^{18}\text{O}_w$ values. These differences can be clearly seen from the rivers sampled for this study (Figure 7). The Kennebec River had consistently higher $\delta^{18}\text{O}_w$ values than the more eastern Penobscot. While these spatial differences in $\delta^{18}\text{O}_w$ are not seen when looking at locations sampled for the 2014/2015 data set (Figure 6), this lack of latitudinal differences is likely due to the relatively small area where samples were collected (i.e. almost exclusively from the eastern Gulf of Maine), and the obvious influence from small local rivers, as discussed in Section 4.2 (see the supplementary material for a further discussion of the influence of coastal location on water sample end-members).

The differences in mixing line end-members, particularly the saline end-member, can also be attributed to the differences in years when the samples were collected. As pointed out by Smith et al. (2001), the composition of SSW changes from year to year as a result of changes in river runoff onto the Scotian Shelf. Figure 4 shows the estimated composition of SSW, as measured in the spring of 1981 by Chapman et al. (1986), to be the saline end-member of the Gulf of Maine coastal mixing line. However, the Wanamaker data have slightly lower $\delta^{18}\text{O}_w$ values for saline water than the 2014/2015 data do, which is likely due to differences in SSW composition in the Gulf of Maine between 2014/2015 and the years the samples collected for the Wanamaker data set were taken (2003-2013). A lower $\delta^{18}\text{O}_w$ value for SSW would likely indicate less river runoff onto

the Scotian Shelf so that a greater percentage of the fresh water contributing to SSW composition was from higher latitudes with a lower oxygen isotopic signature.

However, the fact that SSW seems to be the dominant saline end-member for coastal Gulf of Maine waters does not rule out the influence of slope waters on coastal surface regions. Due to yearly compositional variations similar to those of shelf waters, it is conceivable that WSW and LSW could have had similar compositions to SSW at the time that water samples were collected for the coastal Gulf of Maine mixing line. Therefore, it is likely that all three water masses influence Gulf of Maine coastal surface waters, at least to some extent.

4.4. *Gulf of Maine mixing lines*

When comparing the Gulf of Maine coastal mixing lines to other mixing lines found for waters in the Gulf of Maine and surrounding regions (equations 1, 2, and 3; Figure 9), the coastal mixing line has the highest $\delta^{18}\text{O}_w$ value for the freshwater end-member. This result is consistent with the general conclusion of this and previous studies: coastal Gulf of Maine surface waters are influenced by local river runoff while waters found at deeper depths and farther from the coast are influenced by freshwater sources originating in the Gulf of St. Lawrence, the Labrador Shelf, and the Labrador Sea, which have lower $\delta^{18}\text{O}_w$ values due to their origin at higher latitudes (Houghton and Fairbanks, 2001).

The coastal Gulf of Maine mixing line falls farther away from WSW and LSW end-members than any of the other mixing lines found for the region, indicating less influence on coastal Gulf of Maine surface waters by slope waters compared to offshore and deeper regions. However, as stated earlier, WSW and LSW composition change slightly on a yearly basis and it is likely that these slope waters influence coastal Gulf of Maine surface waters, at a least to a small degree.

It is important to note that previously constructed mixing lines from the Gulf of Maine and surrounding regions were composed of water samples with salinities of no less than 30, since fresher samples were not present in the regions where water samples were collected for these mixing lines. Therefore, the freshwater end-member of these mixing lines is less constrained than it is for the coastal Gulf of Maine mixing line.

4.5. *Implications for Gulf of Maine paleoclimate*

Understanding the relationship between $\delta^{18}\text{O}_w$ and salinity in the Gulf of Maine is useful for both understanding hydrographic dynamics in the region today but also in reconstructing this hydrography in the past. Specifically, using oxygen isotopes archived in *Arctica islandica* shells (Wanamaker et al., 2011; Wanamaker et al., 2008) or other carbonate material to reconstruct water temperatures requires knowledge of the $\delta^{18}\text{O}_w$ composition in which that material formed. While these data are generally not available, understanding the relationship between $\delta^{18}\text{O}_w$ and salinity in a region and using local instrumental records of salinity at least provides an estimate of the $\delta^{18}\text{O}_w$ composition of

Figure 9: $\delta^{18}\text{O}_w$ -salinity mixing lines for the Gulf of Maine along with data from the Gulf of Maine coastal mixing line. Mixing lines include the Gulf of Maine coastal mixing line (equation 4); the Fairbanks (1982) Wilkinson Basin surface and intermediate water mixing line (equation 1); the Fairbanks (1982) Scotian Shelf mixing line; the Houghton and Fairbanks (2001) Northeast Channel mixing line (equation 3); the Fairbanks (1982) slope water mixing line (purple; equation 2). Water masses are plotted using the bolded values in Table 1.

waters in the area of reconstruction. As can be seen in Figure 9, there is a significant difference in mixing lines between waters in coastal and more offshore regions. Therefore, previous mixing lines available for the Gulf of Maine region are not particularly skillful in representing coastal Gulf of Maine situations and would do a poor job in reconstructing $\delta^{18}\text{O}_w$ based on salinity records. Consequently, depending on where the proxy material is collected from, the mixing line used for approximating $\delta^{18}\text{O}_w$ when reconstructing water temperatures must be carefully considered. A more comprehensive understanding of present day hydrographic dynamics gained from $\delta^{18}\text{O}_w$ -salinity mixing lines is also useful when interpreting these reconstructed temperature records in terms of hydrographic dynamics.

4.6. *Conclusions and future work*

$\delta^{18}\text{O}_w$ and salinity values measured in water samples collected along the coastal Gulf of Maine from 2003-2015 are presented. These data reveal that coastal Gulf of Maine waters fall along a mixing line between MRW and SSW. The freshwater end-member of this mixing line varies depending on the location that the water sample was collected, with a higher $\delta^{18}\text{O}_w$ value end-member for samples collected in the western Gulf of Maine. From 2003 to 2015, these coastal surface waters do not appear to be greatly influenced by slope water input, although it is likely that slope waters do contribute to coastal surface water properties to some extent.

The $\delta^{18}\text{O}_w$ and salinity composition of these waters are influenced primarily by changes in river discharge and $\delta^{18}\text{O}_w$ variability of Maine rivers, as evident from the seasonal trends in salinity and coastal $\delta^{18}\text{O}_w$, with lower salinity and $\delta^{18}\text{O}_w$ values in spring, following trends in river discharge and $\delta^{18}\text{O}_w$ composition. The effect of changes in river discharge on coastal Maine water properties is also evident from looking at spatial differences in $\delta^{18}\text{O}_w$ values: large spatial differences in spring and winter indicate the increased influence of local rivers (due to higher river runoff) while few spatial difference in summer and fall indicate larger ocean water influences (due to lower river runoff).

This study is a start to understanding $\delta^{18}\text{O}_w$ -salinity relationships as well as hydrographic variability and major driving influences of water properties in coastal Gulf of Maine waters. However, more work is needed in order to develop a comprehensive view of the spatiotemporal variability in water properties in the region. To date, little to no work has been done to look at changes in the $\delta^{18}\text{O}_w$ -salinity relationship with depth in the Gulf of Maine except for a few select locations (Wilkinson Basin - Fairbanks, 1982; the Northeast Channel - Houghton and Fairbanks, 2001). Understanding how these water properties change with depth and time throughout the Gulf of Maine will facilitate a much better understanding of hydrographic dynamics at depth as well as providing appropriate mixing lines for reconstructing past oceanic conditions using oxygen isotopes biocarbonates collected at depth.

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