**Final Report**

# ARI: Towards Long-term Monitoring of the $CO_2$ System in Arctic Rivers

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## 1. Why do we care?

Most natural waters, such as river water and seawater, contain carbonate species, including dissolved carbon dioxide,$CO_2$ (including $CO_2$ gas and carbonic acid, $H_2CO_3$), bicarbonate ($HCO_3^-$), and carbonate ($CO_3^{2-}$) ions in various amounts. Collectively, we refer to them as the $CO_2$ or inorganic carbon system in natural waters. Most of these carbonate species are products derived from weathering of rocks, degradation of organic matters, and respiration. The aqueous $CO_2$ system can be defined by any two of the four measurable variables: pH, partial pressure of $CO_2$ ($pCO_2$), total dissolved inorganic carbon (DIC), and total alkalinity (TA). The concentrations of these carbonate species define the state of the $CO_2$ system and determine how much $CO_2$ will either be taken up from or released to the atmosphere. Such an air-water exchange of $CO_2$ plays a fundamental role in regulating the atmospheric $CO_2$ level, and thus the Earth's climate.

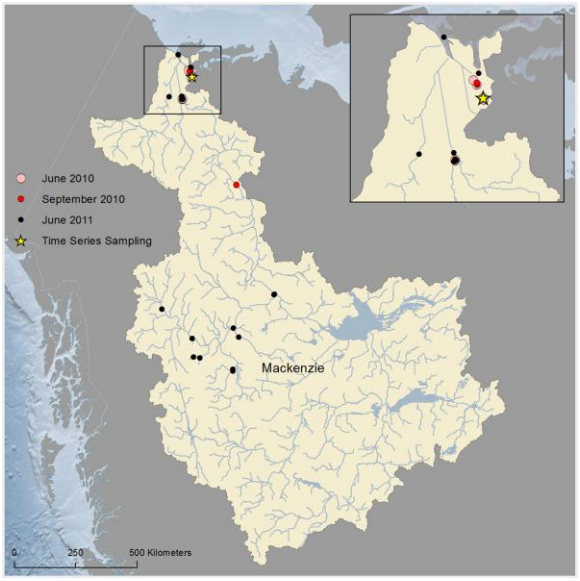

Fig. 1. Mackenzie River basin and sampling stations

The Arctic Ocean receives large riverine fluxes of organic and inorganic matter, suspended material, and nutrients from surrounding rivers, with this riverine influence being the most substantial among all major ocean basins. The Arctic is also considered particularly sensitive to global climate change. The $CO_2$ system and associated inorganic carbon fluxes in Arctic rivers will likely undergo significant and observable changes in the coming decades. Such changes may have significant impacts on riverine and coastal carbon cycles and related ecosystems, which may ultimately affect atmospheric $CO_2$ levels and the climate. To identify and study these potential changes in Arctic rivers, both long-term and short-term measurements are critical. The fundamental scientific questions we intend to address through this study are: 1) what are the natural variabilities (e.g. seasonality and diel cycles) of the riverine $CO_2$ system and inorganic carbon fluxes in the Mackenzie River? 2) What are the major drivers to their natural variabilities? The answers to these questions are important to study so that we will be able to predict geochemical changes in Arctic rivers.

## 2. What did we do?

Through the support of this project, we have established monthly time-series measurements of DIC and TA in the Mackenzie River, the major Arctic river in North America, located near Inuvik, Canada (Fig. 1). DIC is a measure of the total concentration of carbonate

Fig. 2. Sampling at the Mackenzie River.
Upper left: Z. Aleck Wang, Assistant Scientist, is crossing the Mackenzie River on a ferry.
Upper right: Charles Zhu, a visiting student from Yale University, is taking water samples during the first sampling trip.
Middle left: Donald Ross, Technician from Aurora Research Institute, Inuvik, Canada, helps to take monthly water samples from the river.
Middle right: William Hurst, Technician from Aurora Research Institute, is in charge of monthly sampling.
Lower left: Katherine Hoering, Research Assistant, is taking water samples from upper stream of the Mackenzie River.
Lower right: Sampling on a boat in the main channel of the river.

species, while TA represents the total base concentration in the water. By measuring DIC and

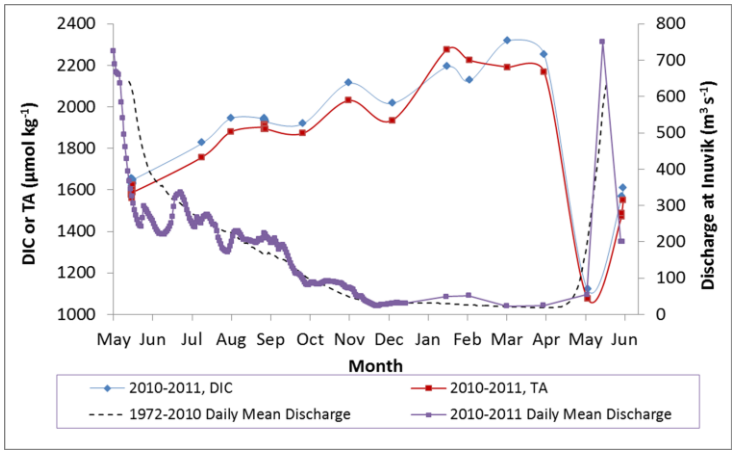


Fig. 3. 2010 -2011 time-series measurements of DIC, TA and discharge in the Mackenzie River near Inuvik, Canada.

TA, all of the carbonate species of the $CO_2$ system and water pH can be calculated.

We have established collaboration with Aurora Research Institute (ARI) at Inuvik through this work, and the technicians there have been taking monthly water samples from the Mackenzie River during the last two years. In addition, we have completed three field sampling campaigns in spring and fall in the Mackenzie River near Inuvik and throughout the river basin (Figs. 1 and 2). It worth pointing out that we have adapted high-precision analytical methods that are used for seawater $CO_2$ system measurements in this study. In the past, direct DIC measurements in river waters were rare, and thus the carbonate chemistry was not well defined. This study was among the first to make high-quality comprehensive measurements of the $CO_2$ system in river waters.

### 3. What did we find?

The new data collected through this project reveals that the $CO_2$ parameters show strong daily and seasonal variations (Fig. 3). We found that the concentrations of DIC and TA are negatively correlated with river discharge for the Mackenzie River (Fig. 3). This means that river discharge has a 'dilution' effect on DIC and TA, where higher river discharge will basically decrease the concentrations of these parameters. Spatially, DIC and TA are more concentrated downstream of the Mackenzie River (Fig. 4). We also found that the Mackenzie River generally releases $CO_2$ to the atmosphere year round because it has a higher $CO_2$ concentration than the atmosphere. There is a small, but significant amount of dissolved $CO_2$ (~5% of DIC concentration) in the river water, as compared to that of seawater which only has about ~1% that contributes to DIC. Fundamentally, this difference determines that the river water has a higher $CO_2$ concentration than normal seawater.

Another important finding in this study is that DIC generation per unit of drainage area (DIC yield) is a strong function of mean air temperature in the Mackenzie (Fig. 5). This result suggests that when temperatures are below zero, DIC yield is almost invariant with temperature; while it increases almost linearly with an increase in temperature after the ice melts

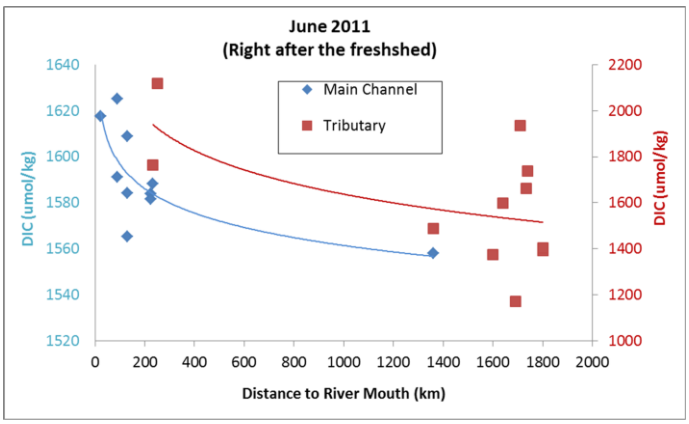


Fig. 4. Spatial distribution of DIC in the Mackenzie River Basin in June 2011.

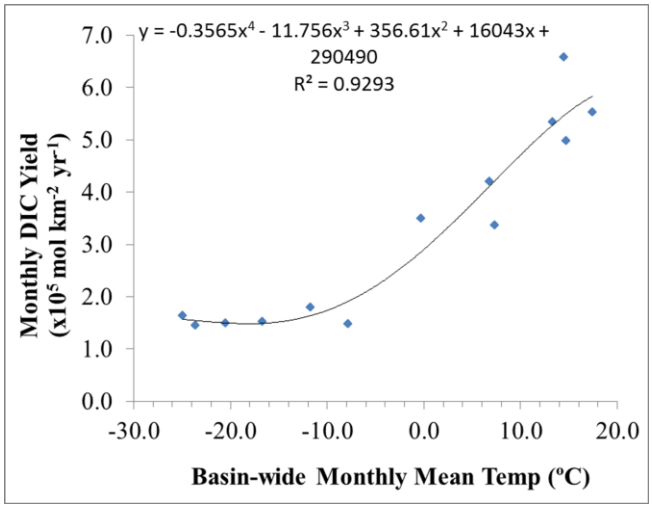


Fig. 5. Monthly DIC yield vs. monthly basin-wide mean air temperature in the Mackenzie.

(temperature > 0°C). This has important implication on how the inorganic carbon flux and the $CO_2$ system will respond with respect to climate change. It means that as the Arctic temperature increases, more carbonate species (including dissolved $CO_2$) will end up in the river. This will increase DIC and TA concentrations, as well as the amount of $CO_2$ released from the river to the atmosphere. If we assume that Fig. 5 holds and there is 4°C warming in the Arctic region by the end of this century, as suggested by model projection, such a temperature increase will translate into a ~20% increase in DIC and TA, and ~17% increase in dissolved $CO_2$ in the river. These changes will result in a higher rate of $CO_2$ release from the Mackenzie River and more carbonate species will be transported to the ocean. If other Arctic rivers behave similarly to the Mackenzie, these $CO_2$ and carbonate flux increases may have global significance.

**4. What is the next step?**

It is critical to continue our time-series measurements at the Mackenzie River so that we can observe long-term changes. We have discussed this aspect with the staff members at ARI, and they have agreed to continue the monthly sampling for us after the completion of this project. We envision that this research project will evolve to a long-term monitoring program that will document changes of the riverine $CO_2$ system in the Arctic region and provide valuable data that will allow for better prediction of future changes in river chemistry and their influence on the ecosystem and climate. The findings from this project warrant further investigation as to why there is a strong relationship between how much carbonate species are generated in the basin and the air temperature (Fig. 5). There are many possible biogeochemical mechanisms that may explain such a relationship. To understand the mechanism behind this relationship is important to be able to predict how the riverine $CO_2$ system will change in the Arctic and thus how the climate will respond to these changes. Adaptation and mitigation strategies can then be made if we know these changes well enough. We will actively seek funding to continue our research in the Mackenzie River basin. The data collected through this project provides us the leverage in this regard.

We have presented this work during the 2012 Ocean Science Meeting at Salt Lake City, UT, Feb. 19 – 24, 2012 (Title: 'Temporal and Spatial Variabilities of the Riverine Inorganic Carbon System in the Mackenzie River and Beyond'). We are currently preparing a peer-reviewed paper to be submitted this year.