Variability of dissolved aluminum and manganese in the Gulf of Alaska.

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Background

•The Northern Gulf of Alaska (GOA) is a marine system that receives large quantities of freshwater input from rivers and glaciers. These rivers and glaciers provide many different particulate and dissolved metals to the system; most notably to this study, aluminum and manganese (1,2).

•Insight into the input of aluminum and manganese can be gained from the relationship between the metals' concentrations and salinity (3).

•Manganese is used in a proteins essential for a wide variety of global phytoplankton species; however, aluminum is not as widely necessary (4).

•Some work has been done tracking riverine input of aluminum and manganese in the GOA (3), and with my research I am adding information about the vertical concentrations of these metals.

•The Northern Gulf of Alaska Long Term Ecological Research project (NGA LTER) provides the infrastructure for my work. NGA LTER consists of three lines (Fig. 1) sampled during spring, summer, and fall. The NGA LTER Site is approximately the size of Wisconsin.

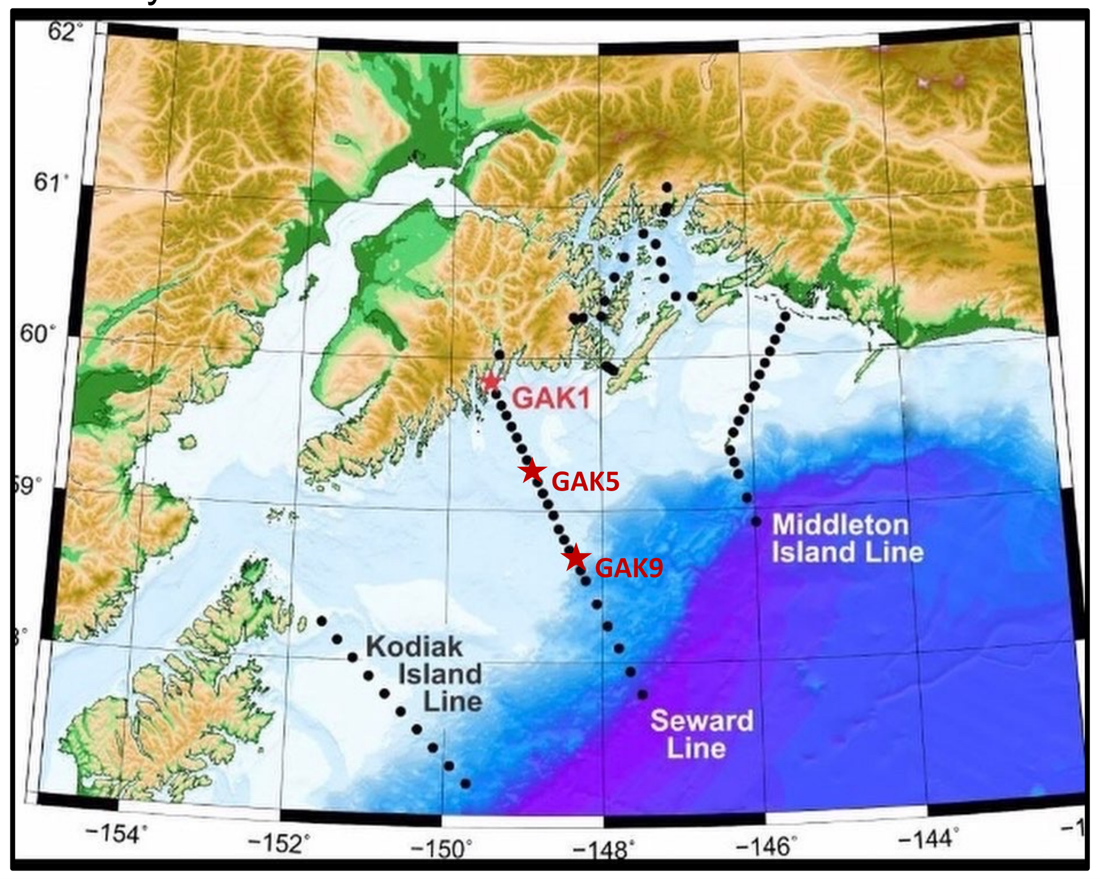


Figure 1. The NGA site, including Stations GAK1, GAK5, and GAK9 along the Seward Line. Color shows depth

My Story

I got started with the NGA LTER in July of 2022, when Dr. Ana Aguilar-Islas brought me on board as a volunteer assistant alongside her PhD student, Emily Ortega. It was aboard the *R/V Sikuliaq* that my interest for chemical oceanography and trace metal chemistry bloomed. I have since volunteered aboard the *M/V Tiglâx* for the NGA LTER fall 2022 cruise, and will be aboard the *R/V Kilo Moana* for the 2023 summer cruise.

This URSA grant does not mark the end of my journey with trace metal chemistry– I will be continuing this research over the summer and as a senior capstone project. After graduation, I plan to continue with UAF for a master's degree in Chemical Oceanography. I also hope to continue working with the NGA LTER over the course of these pursuits.

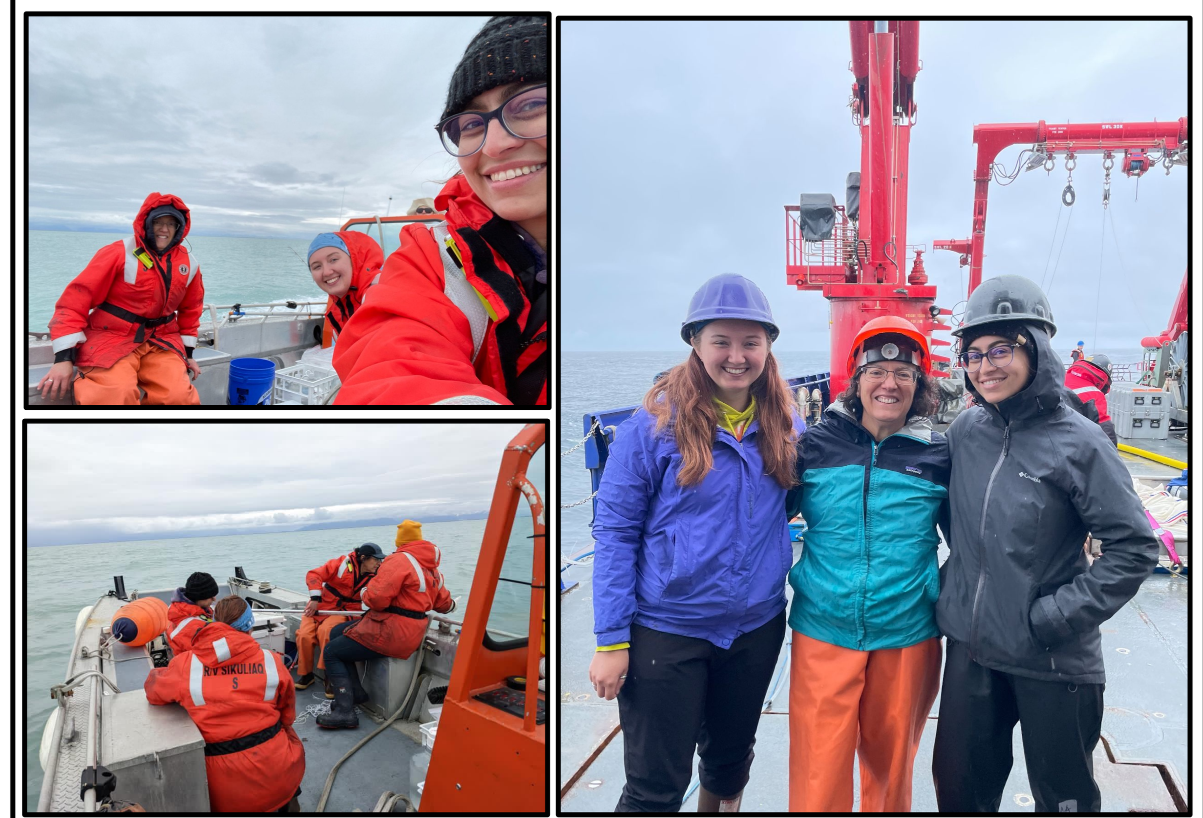


Figure 2. (Right) "Team Trace Metals". (Left: top and bottom) Small Boat Operations: Copper River Outflow Sampling from during the *Sikuliaq* Summer 2022 cruise.

Methods

• Samples collected for this project are from the NGA LTER 2020 Summer cruise, collected by the Aguilar-Islas lab.

• We chose to analyze samples from stations GAK1, GAK5, and GAK9. These stations give us data from the inner shelf, the mid-shelf, and the shelf margin (Figure 1), and provide an idea of cross-shelf transport.

• These samples were processed using a flow injection system adapted from previous systems (3,5). The hardware includes one 12-port valve, two 6-port, 2-position valves, and a peristaltic pump. The 6-port valves direct the flow of sample/reagents, and include a resin column that holds on to the metals and removes the major salts (see below). The 12-position valve is used as an autosampler. The valves are controlled using VICI-VCom software coded with times for loading the sample onto the column that depend on expected metal concentrations.

• To concentrate the metals of interest, samples are passed through a NOBIAS resin column with a high affinity for Al and Mn, then the column is rinsed with water to remove salts. Metals are then stripped from the column using ultra pure nitric acid. Metals can be concentrated up to 20-times their concentration in seawater.

• A standard curve is generated from standard dilutions in seawater with low-metal concentration.

• Samples, standards and blanks are concentrated in the same manner and then analyzed by inductively coupled plasma mass spectrometry.

Figure 3. Filling the resin column for the flow injection analysis system.

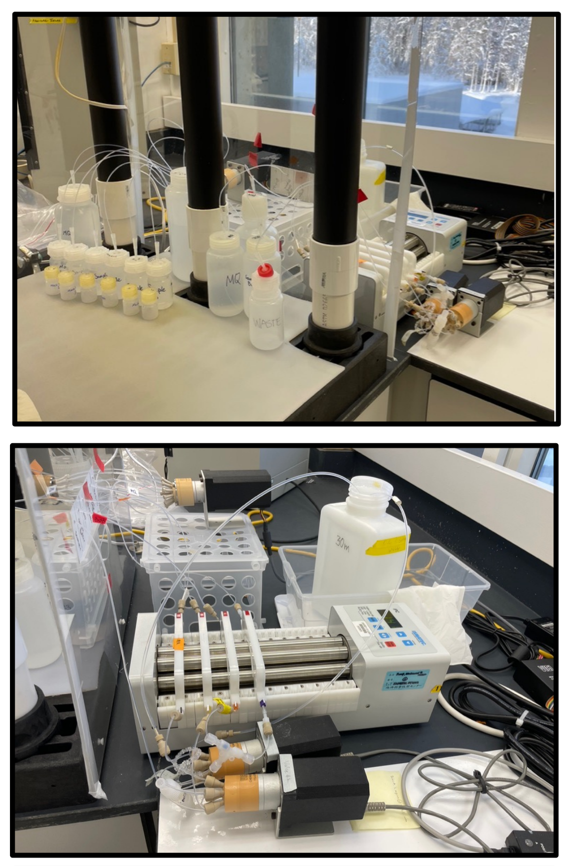
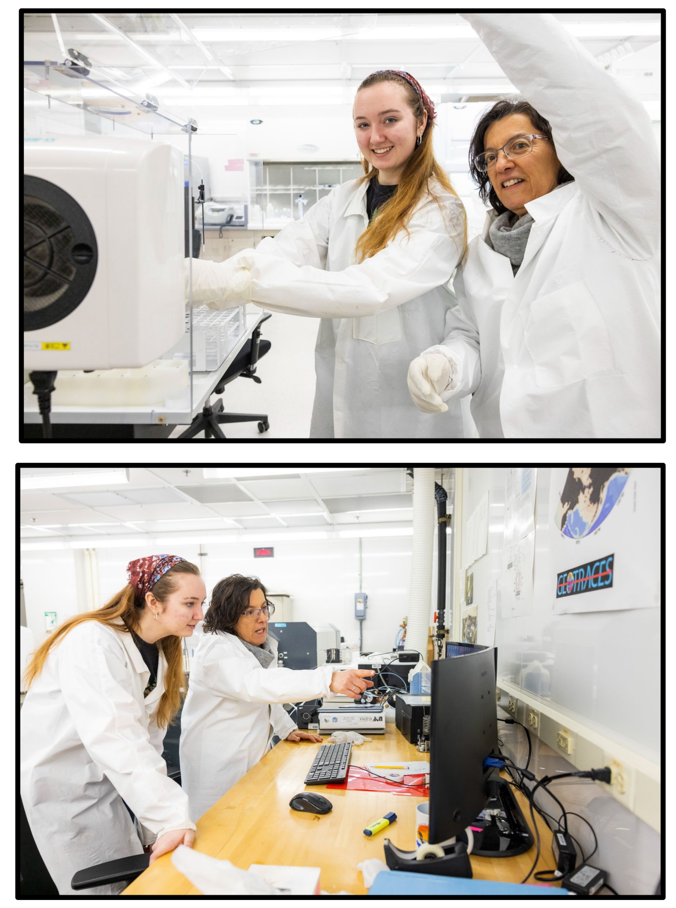


Figure 4. (Top) Inside the hood with the samples and fluids used in the flow injection analysis. (Bottom) A view of the valves and peristaltic pump used.

Conclusions and Future Work

- To quantify trace metals in seawater, it is necessary to remove the major salts and to concentrate the metal.
- The sediment resuspension near the bottom indicates disturbance of surface sediment and a likely source of dMn.
- There is evidence of a surface source of dM at all stations.
- More work is required to quantify aluminum.
- More work is required in order to increase precision.
- I will continue this work during the rest of the semester and in summer. . . Stay tuned.



Results

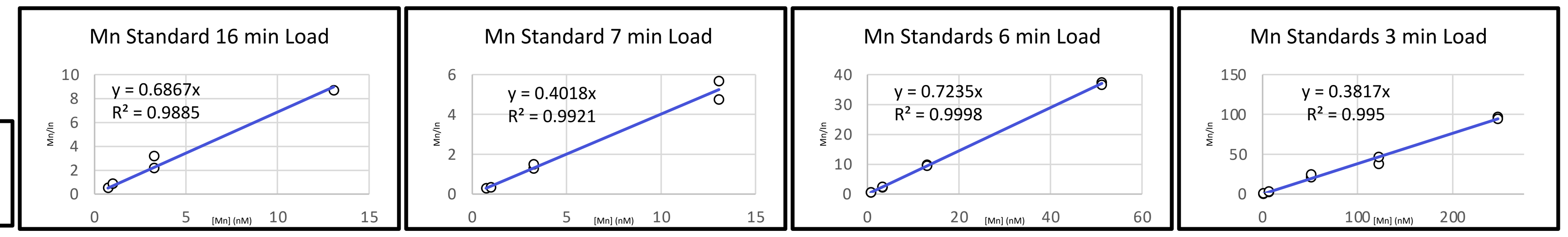


Figure 5. Standard curves for manganese.

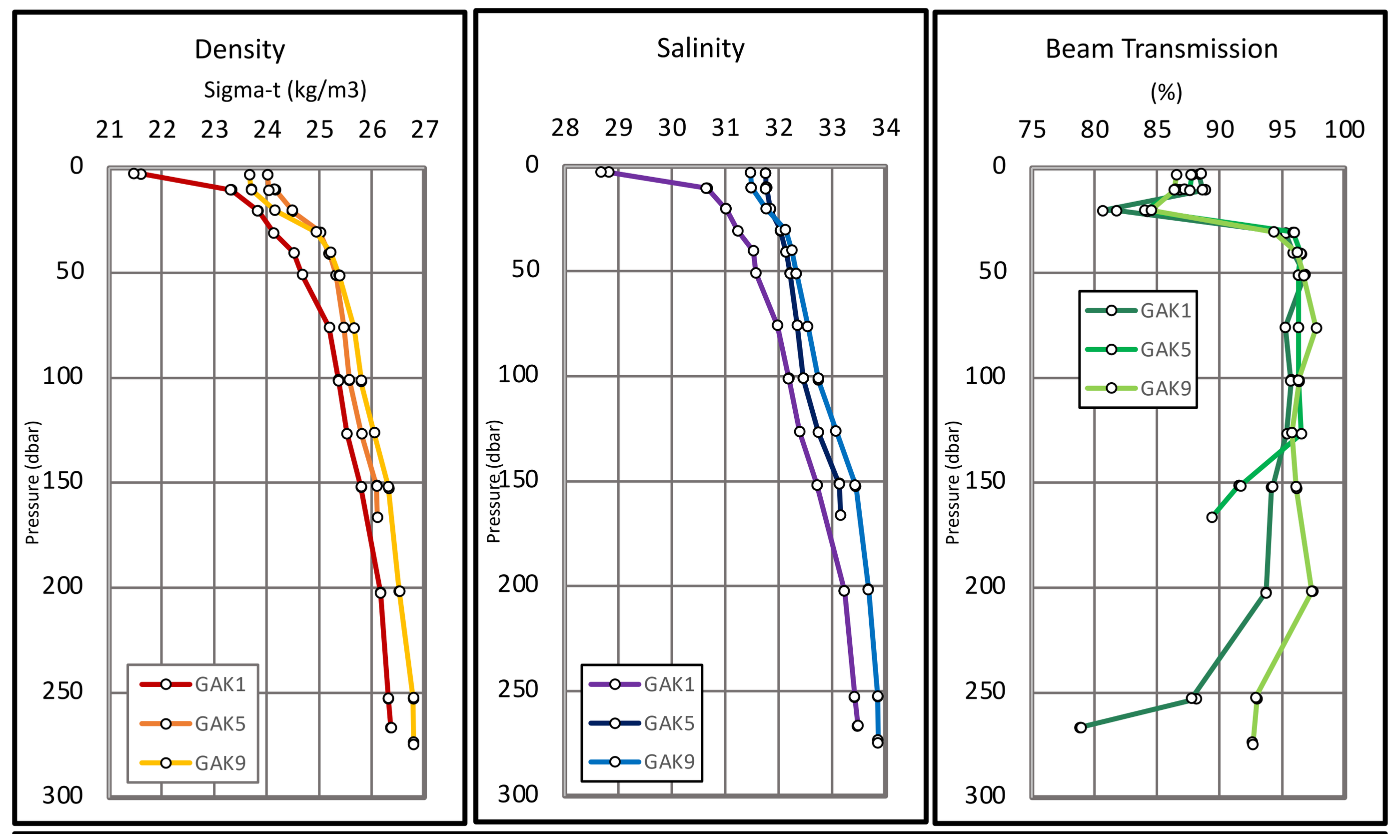


Figure 6. Oceanographic figures depicting density, salinity, and beam transmission (particle content).

- The resin has been unable to capture aluminum in large enough quantities to draw conclusive results. I will continue to refine my methods in order to acquire the ideal conditions for aluminum retention on the system.
- [Mn] was shown to increase at the bottom of each station. This indicates a benthic source from disturbed sediment (see beam transmission, Figure 6).
- At GAK9, [Mn] was highest at the surface, and was still relatively high at GAK5. This indicates a surface source of Mn (fresh water or atmosphere, Figure 7)).
- The decreased levels at the surface versus at 15 meters depth found at GAK5 may indicate some biological uptake of Mn at the surface.
- Another notable feature is the signal from approximately 100-175 m at GAK9. This is likely a sedimentary signal from the bottom at GAK5 and GAK6, as those stations are about 150 meters deep.

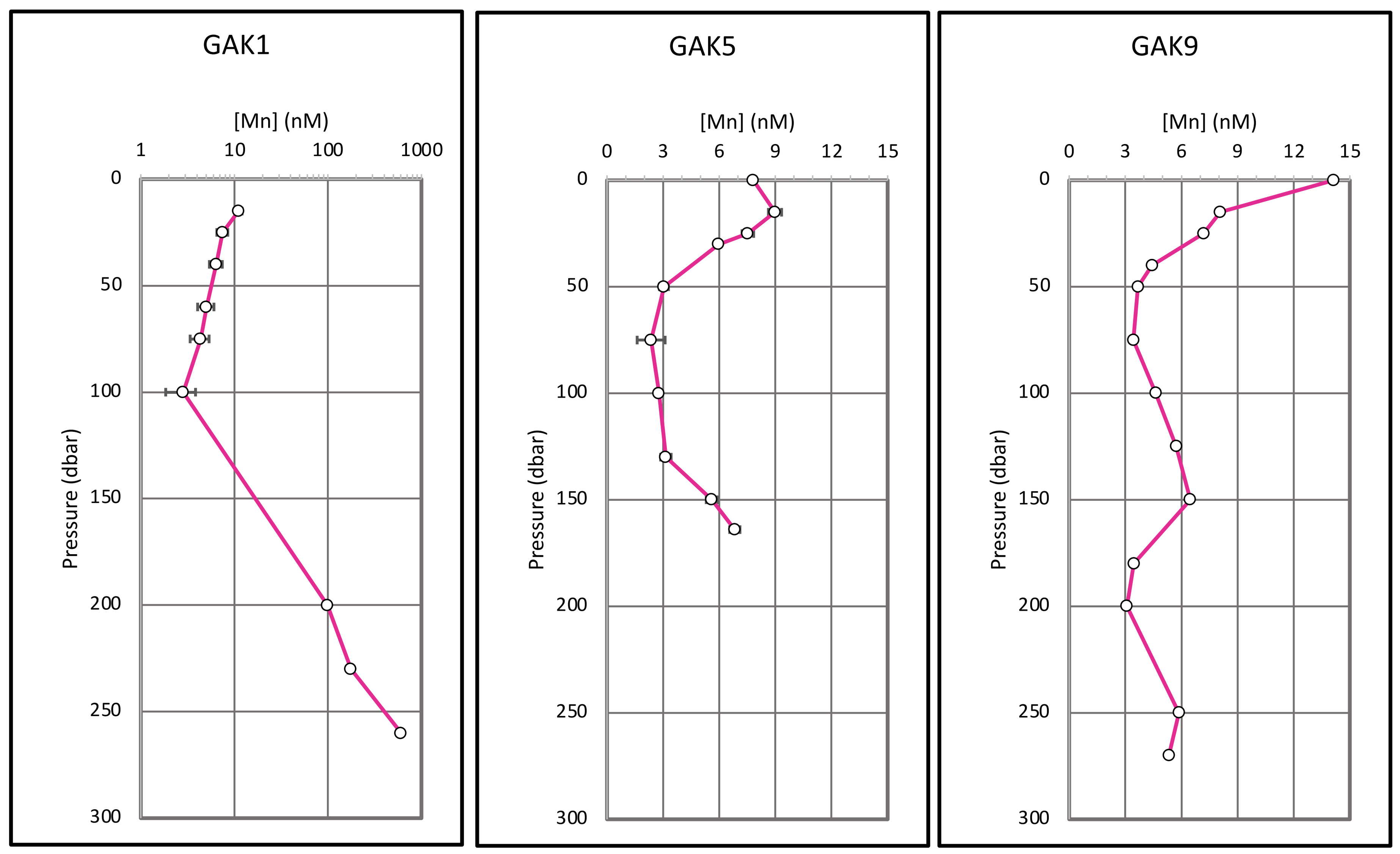


Figure 7. The manganese profiles for GAK1, GAK5, and GAK9.

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References: (1) Beamer,J.P.,Hill,D.F.,Arendt,A.,Liston,G.E.,2016.High-resolution modeling of the coastal freshwater discharge and glacier mass balance the Gulf of Alaska watershed.Water Resour.Res.52,3888–3909.; (2) Brown, M. T., Lippiatt, S. M., & Bruland, K. W. (2010). Dissolved aluminum, particulate aluminum, and silicic acid in northern Gulf of Alaska coastal waters: Glacial/riverine inputs and extreme reactivity. *Marine Chemistry*, *122*(1), 160–175. https://doi.org/10.1016/j.marchem.2010.04.002; (3)Kandel, A., & Aguilar-Islas, A. (2021). Spatial and temporal variability of dissolved aluminum and manganese in surface waters of the northern Gulf of Alaska. *Deep-Sea Research Part II, 189–190*. https://doi.org/10.1016/j.dsr2.2021.104952 (4) Twining, Benjamin S., and Stephen B. Baines. "The Trace Metal Composition of Marine Phytoplankton." *Annual Review of Marine Science*, vol. 5, no. 1, 3 Jan. 2013, pp. 191–215., https://doi.org/10.1146/annurev-marine-121211-172322. (5)Brown, M. T., & Bruland, K. W. (2008). An improved flow-injection analysis method for the determination of dissolved aluminum in seawater. *Limnology & Oceanography, Methods*, *6*(1), 87–95. https://doi.org/10.4319/lom.2008.6.87; (6) "Northern Gulf of Alaska LTER." *University of Alaska Fairbanks.* January 30, 2018. https://nga.lternet.edu/.