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TITLE: Quantifying and correcting the impacts of freezing samples on dissolved organic matter absorbance

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ABSTRACT BODY: The use of optical measurements as proxies for organic matter concentration and composition has become increasingly popular in recent years. Absorbance of chromophoric dissolved organic matter (CDOM) can be used to estimate concentrations of dissolved organic carbon (DOC), as a qualitative assessment of dissolved organic matter (DOM) average molecular weight and is often used to calibrate satellite remote sensing of organic matter. However, there is evidence that preservation of samples can lead to significant changes in CDOM absorbance spectra. Freezing is a popular means of preservation, but can result in flocculation of DOM when samples are thawed for analysis. We hypothesize that the particles generated as a result of a freeze/thaw cycle lead to increasing absorption in visible wavelengths (400–800 nm). Yet, absorbance in the UV spectra should remain similar to original values. These hypotheses are tested on CDOM spectra collected from two large Arctic watersheds (the Mackenzie and Yukon rivers) and four smaller Texas watersheds (the Colorado, Guadalupe, Nueces and San Antonio rivers). In addition, we experiment with additional filtering and sonication to correct for flocculation from frozen samples. Preliminary data show that short wavelengths are relatively well preserved (200-300 nm). However, CDOM absorption changes unpredictably from 350-450 nm, the wavelengths most commonly used to estimate DOC. Absorption coefficients tend to be higher in these wavelengths after a freeze/thaw cycle, but the magnitude of this increase varies. Some of these impacts can be corrected for with sonication. For instance, when comparing experimental treatments to initial absorption at 365 nm from Mackenzie River samples, R2 increases from 0.60 to 0.79 for samples undergoing one freeze/thaw cycle to those that were also sonicated. Regardless of treatment, however, no spectral slopes were well preserved after a freeze/thaw cycle. These results reinforce earlier work that it is best for all CDOM samples to be measured immediately, without preservation. CDOM measured on frozen samples, particularly after sonicating, can be used as a proxy for bulk DOC concentrations and specific UV absorbance (SUVA), but freeze/thaw effects confound our ability to examine DOM composition from spectral slopes.