Characterization of Naturally Occurring Carbon in Lake Okeechobee Water and its Compositional Change Following Recharge and Storage in the Upper Floridan Aquifer

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INTRODUCTION.

Dissolved organic matter (DOM), the complex organic material resulting from biomass degradation, plays a significant role in the cycling of carbon in the atmosphere. In order to fully understand its impact on the environment or a specific ecosystem, one must analyze it on the molecular level. In this study, the DOM of the Floridian Aquifer System (FAS) was analyzed.

The FAS is one of the most productive groundwater sources in the world. It is composed of the Upper Floridan Aquifer (UFA) and the Lower Floridan Aquifer (LFA), underlies portions of five U.S. states, and provides drinking water to over 10 million residents. Via aquifer storage and recovery (ASR), treated surface water is injected into the aquifer, stored, and then extracted when needed. The process of ASR is an integral component of the Comprehensive Everglades Restoration Plan, which aims to maintain hydrologic flow from Lake Okeechobee to the Everglades. At the confluence of the Kissimme river, surface water is extracted from Lake Okeechobee, treated by sand filtration and ultraviolet disinfection, and is then injected into the LFA. However, these preliminary treatments do not account for any removal of dissolved organic carbon (DOC). The treated recharge water has a DOC concentration of about 15.0 mg/L, and the naturally occurring water of the UFA has a DOC concentration of about 2.0 mg/L (in the area of the injection site). During aquifer storage, the microbial communities’ processes create a significant alteration in the chemistry of the water injected, and those microbial communities in the UFA utilize carbon, nitrogen, and phosphorous substrates. The presence and composition of the DOM may have a significant role in the rates of these microbial processes as the communities consume nitrogen and phosphorous. In order to characterize the DOC present in water samples from the UFA, Fourier Transform Ion Cyclotron Mass Spectrometry (FT-ICR-MS) was used to examine DOC at the elemental level.

RESULTS.

Negative Ion Electrospray Ionization (no modifier) FT-ICR MS at 9.4 Tesla

Tampa Bay UFA Groundwater ~36,000 ppb > 60

METHODS.

Eight one liter samples were collected for this study: two pure end member samples and six 1:1 and 3:1 ratios of the two end members. The two end members were one pure groundwater sample and one pure Kissimme River sample. Native UFA water samples were collected from monitoring well #10 at the Kissimee River ASR facility (located about 8,000 feet upstream of the confluence of the Kissimme River and Lake Okeechobee). Samples were filtered with 0.2 micron polycarbonate filters and collected in one liter borosilicate bottles sealed with silicon septa. The samples were put on ice in the field after filtration and then frozen at -20°C.

The remaining six samples ratios of each member water) were left unfiltered and used to construct one litter microcosms at ratios of 1.1 and 3.1 (v:v). The microcosms were incubated at room temperature in the dark with an argon headspace, which served to maintain anaerobic and reduced conditions. After the incubation periods were completed, the contents of each microcosm were filtered and processed in the same manner as the original filtered samples. Nitrate, nitrates, ammonium, and phosphate were quantified with a SEAL Analytical AutoAnalyzer. After filtration, DOM was extracted from each sample using Solid Phase Extraction (SPE) with PPL as a sorbent. 8 DOC concentration of about 15.0 mg/L, and the naturally occurring water of the UFA has a DOC concentration of about 2.0 mg/L (in the area of the injection site). During aquifer storage, the microbial communities’ processes create a significant alteration in the chemistry of the water injected, and those microbial communities in the UFA utilize carbon, nitrogen, and phosphorous substrates. The presence and composition of the DOM may have a significant role in the rates of these microbial processes as the communities consume nitrogen and phosphorous. In order to characterize the DOC present in water samples from the UFA, Fourier Transform Ion Cyclotron Mass Spectrometry (FT-ICR-MS) was used to examine DOC at the elemental level.

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Figure 1: Maps showing the location of sample retrieval.

Figure 2: Left: the extracted DOM in Groundwater and Kissimme samples, respectively. Right: An example of an original water source juxtaposed with several extracted DOM samples.

Figure 3: Negative ion electrospray ionization FT-ICR mass spectrum at 9.4 tesla of Groundwater sample. ~36,000 peaks were detected and assigned elemental compositions with signal magnitude above six times the baseline ms noise level between m/z 150-950. The Kissimme sample yielded ~34,000 peaks were detected (m/z 150-950).

Figure 4: Hetatom Class distribution for Kissimme River DOM compared to Groundwater DOM from the Floridian Aquifer. The most abundant class in both samples corresponds to compounds that contain O₃H₅ per molecule. Notably, the Kissimme sample contains N₂O₃ compounds that were not detected in Groundwater. Nitrogen compounds likely enter into groundwater through anthropogenic sources (e.g., fertilizer).

Figure 5: Elemental compositions can be rapidly visualized in van Krevelen diagrams, which plot the atomic ratios of hydrogen to oxygen versus oxygen to carbon: van Krevelen Comparison O₃H₅, N₂O₃, and S₂O₃ classes of Groundwater (top) and Kissimme (bottom) samples. These van Krevelen diagrams are comparing the ratios of H/C to O/C. These elemental compositions can be sorted into compound groups such as lipids, proteins, carbohydrates, lignin, and condensate hydration, and each of these compound classes has characteristic H/C and O/C ratios. 10,11 O₃H₅ and N₂O₃ classes exhibited highest abundance in protein and lignin-like compounds, while S₂O₃ compounds indicate a higher abundance of lipids and tower presence of lignin. Lignin is a significant portion of humic substances, that is a major organic fraction of soil. They are also a component of cell walls, thus indicating a terrestrial plant source of the DOM present in the samples. 10,11 Proteins are expected to be derived from insects, which may have terrestrial or aquatic origins. Amino acids are labile components of dissolved organic nitrogen (DON). 10,11

Figure 6: Plots of relative abundance (z-axis), H/C ratio and carbon number for O₃H₅, N₂O₃, and S₂O₃ classes of Groundwater (top) and Kissimme (bottom) samples. Across all classes, the most abundant compounds correspond to compounds that contain CₓHᵧOᵦ and H/C ratios between 0.75-1.0.

Figure 7: DBE (double bond equivalence) illustrations comparing O₃H₅, N₂O₃, and S₂O₃ classes of Groundwater (top) and Kissimme (bottom) samples. DBE relates to the number of double bonds or rings present in a molecule. Atoms are expected to have low H/C ratios and have been shown to be particularly sensitive to photocatalytic degradation. 12 Thus, their persistence may be expected to increase once removed from their original source and moved to the UFA.