CHEM 6001: MSc Departmental Seminar

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Title

Characterizing iron complexing ligands in marine environments using FPLC-IMAC

Abstract

Iron plays an active role in aquatic environments, acting as a key micronutrient for microorganisms such as phytoplankton. Iron is difficult for these organisms to access in oceanic water due to its two redox states (II and III). The II redox form is soluble in water under anoxic conditions; however, it is easily oxidized to its III in the presence of oxygen and precipitates as Fe2O3(s). As a result, dissolved iron concentrations are sub-nanomolar in seawater. Microorganisms have evolved strategies to keep iron in solution, namely via the production of siderophores, specialized iron-chelating molecules. 99% of the dissolved iron in the ocean is bound to organic ligand complexes, which help to maintain the bioavailability of the metal. These ligands are considered part of dissolved organic matter (DOM), a complex carbon pool containing eclectic water-soluble compounds of varying chemical compositions. The vast majority of DOM is uncharacterized and often referred to as humic substances (HS), which originate from the breakdown of organic matter of biological origin. A subset of HS can bind selectively to iron, and retain it in its dissolved form in marine waters. Humic-derived ligands are prevalent in coastal regions due to the influx of terrestrial organic matter, especially in boreal regions where rivers contain high concentrations of both iron and DOM. Recent publications have theorized that these ligands may play an essential role in the marine iron cycle, and as such, further investigation is needed.

To further investigate the specific origin and influence of these ligands on aquatic iron cycling, the ligands need to be extracted from the ocean's complex matrix, isolated from the rest of the DOM. A method for this extraction was developed using immobilized metal affinity chromatography (IMAC). The method works by charging a column containing Sepharose beads with iron. The iron ligands in our sample bind to the column, while other compounds pass through. A series of different eluants is then used to elute the retained ligands from the column based on different structural and chemical properties. The eluted ligands are then collected in fractions for further analysis. The optimized IMAC method results show three distinct regions of ligand classes of varying binding strength and structural composition.

To validate the method solutions of known ligands were used as validation samples. These specific ligands were chosen due to their likely presence in aquatic environments. By testing these ligands using the optimized method, we could further infer how the humic-iron ligands

would interact with our iron-charged column. The findings of the model ligands suggested that binding to the column was typically bidentate, with two coordination sites needed for retention to occur. After testing and validation, the method was implemented for riverine, coastal, and open ocean samples. Comparison of the behaviour of natural water samples with the model ligands reveals potential binding characteristics and origins of HS ligands