

Fate of groundwater-derived nutrients in tidally influenced coastal aquifers: numerical simulations

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Introduction

The flow, transport and transformation processes in a subterranean estuary strongly control the exit conditions for groundwater-derived nutrients discharging to coastal waters. While several studies have examined the fate of nutrients in subterranean estuaries [e.g., 1, 2], the impact of oceanic fluctuations including tides is often neglected. These water level fluctuations however can induce a highly dynamic surficial mixing and reaction zone in the near-shore aquifer and significantly alter the subsurface flow paths for discharging nutrients. In this study the variable density groundwater flow model SEAWAT-2005 is used in combination with the reactive multi-component transport model PHT3Dv2.10 to examine the influences of tide on the transport and transformation of nutrients (ammonium, nitrate, and phosphate) in this dynamic zone. Reactions considered in the model include denitrification, nitrification, aerobic degradation of dissolved organic carbon, iron oxidation and reduction, and phosphate adsorption [1].

Results and Conclusion

SEAWAT combined with PHT3D provides a powerful modeling platform for simulation of the multi-component reactive transport processes occurring in a tidally-influenced subterranean estuary. Simulations reveal that tidal fluctuations significantly alter the transport pathways of the groundwater-derived nutrients and the mixing between the groundwater and recirculating seawater in the near-shore aquifer. This alters the biogeochemical reactions occurring in this region and thus impacts the nutrient transformations and subsequent loading rates to coastal waters (e.g., Figure 1). Tide-induced recirculation also leads to the precipitation of iron oxides around the upper mixing zone and this may act as an important geochemical barrier for accumulating chemicals including phosphate in the intertidal sediments. A sensitivity analysis is presented for the governing parameters.

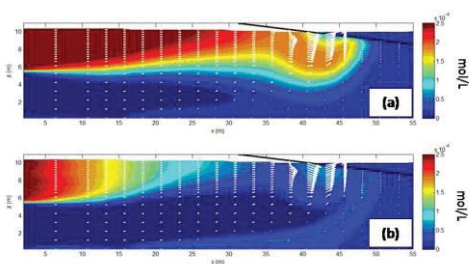


Figure 1: Nitrate concentrations in a nearshore aquifer exposed to tidal fluctuations (amplitude 0.5 m) (a) without, and (b) with reactions considered.

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An *Ab Initio* and Raman Investigation of Aqueous Cu(I) and Cu(II) Chloride Complexes

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Abstract

Thermodynamic properties of metals with common ligands under hydrothermal conditions are needed to model the geochemistry metal ore deposits and the chemistry of Generation IV super-critical water nuclear reactor designs. While the thermodynamic stability of copper (I) and copper (II) chloro complexes are quite well established over a wide temperature range [1,2], the structure of some of these species is a subject of active investigation [3].

This study uses Raman spectroscopy as a tool to identify the structure, speciation and thermodynamic properties of copper complexes. Briefly, polarized Raman spectra, collected parallel and perpendicular to the orientation of the exciting beam as a function of molality and temperature, relative to an internal standard (ClO_4^-), were used to determine reduced isotropic spectra [4]. The spectra are very weak, and this technique yields an accurate baseline correction. *Ab initio* calculations, using methods similar to those for Zn-Cl [5], have been used to predict the stability, structures and Raman spectra of all the possible chloro and aquo complexes with Cu^+ and Cu^{2+} . The Cu-Cl vibrational frequency for Cu^+ complexes was sensitive to the hydration number and the type of calculation (HF,MP2,B3LYP).

Based on these *ab initio* calculations, and the temperature dependent spectra in H_2O and D_2O , vibrational bands were assigned to the copper (II) species Cu^{2+} , CuCl^+ , CuCl_2^0 and CuCl_3^- . While the spectra for copper (I) species were much less intense, there is strong evidence for CuCl_2^- and CuCl_3^{2-} .

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