Characterization of dissolved organic matter (DOM) from diverse oceanic environments by reverse osmosis and electrodialysis

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The oceans contain approximately 685×10^{15} g of dissolved organic carbon (DOC), a pool similar to current atmospheric CO2 of \sim 861 x 10¹⁵ g C, and is thus a major component of the global carbon cycle. However, only a small fraction of marine DOM is readily identifiable. Determining the chemical nature of the remaining fraction of oceanic DOM has been impeded by the lack of efficient and non-fractionating methods of isolation/desalting. Here, reverse osmosis- electrodialysis (RO/ED) [1] was used for isolating a representative DOM fraction (~75%) for analysis by advanced solidstate 13C- NMR, UV-vis spectroscopy and wet chemical techniques. Samples were obtained from biogeochemically diverse environments; i.e., photobleached surface gyre, productive coastal upwelled, oxygen minimum, deep Atlantic, and old deep Pacific waters. NMR spectral editing revealed new insights into carbohydrate biodegradation, and preservation of carboxyl groups and condensed aromatic structures (deep sea samples). Quaternary anomeric carbons were identified as an important component of biorefractory carbohydrates. However, despite some differences, these diverse samples yielded remarkably similar DOM compositions. Our results support the 3-pool DOM model (labile, semi-labile, and refractory) [2]. Evidence of 'background' refractory carbon was seen throughout the ocean DOM samples, and the high carboxyl signal in the deep Pacific sample supports the hypothesis that a major fraction of the refractory pool consists of carboxylic-rich alicyclic molecules (CRAM) [3].

RO/ED appears to be the most promising method to date for DOM isolation from seawater; as it can isolate up to 95% of marine DOM (average 75%; compared to 15-40% for other methods) and the extracted DOM has properties closely resembling the unextracted DOM [1,4]. As the method is capable of processing large volumes of seawater, it can potentially be used to collect marine DOM reference material from different oceanic environments, which currently do not exist and would be useful for comparison to terrestrial DOM reference materials.

[1] Koprivnjak et al. (2009). *Geochim. Cosmochim. Acta* 73, 4215-4231. [2] Hansell& Carlson (2001) *Oceanogr.* 14, 41-49. [3]
Hertkorn et al. (2006) *Geochim. Cosmochim. Acta* 70, 2990-3010.
[4] Mopper et al. (2007) *Chem. Review* 107, 419-442.

Groundwater vulnerability to climate change in high elevation catchments of the Sierra Nevada

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Study Design

Snowmelt is an important component of groundwater recharge in high elevation watersheds of the western United States. In these watersheds, the predicted climate change impacts on snowmelt will likely alter the amount and timing of groundwater recharge, which may lead to reduced groundwater production, declining water tables, and reduced baseflow to streams.

We apply dissolved noble gas tracers to answer questions about recharge location and aquifer residence times in two catchments of differing size in the northern Sierra Nevada. The Olympic Valley near Lake Tahoe is a 22 km² alpine catchment while the Upper Merced catchment has an area of 465 km² and drains through Yosemite Valley. In both valleys, deep, high capacity production wells located in the upper portion of the valley draw groundwater from over much of the sediment thickness. These wells were sampled for tritium and dissolved noble gases in order to determine recharge temperatures (used to esimate to recharge elevation), and tritium-helium groundwater ages.

Results

Noble gas recharge temperatures point to the lower slopes of the mountains, just above the valley floor, as important recharge areas for both catchments. Tritium-helium aquifer residence times are somewhat greater in Yosemite Valley wells (10-28 years) than in Olympic Valley wells (<1-23 years), but in both areas the results indicate relatively rapid turnover of groundwater in the coarse alluvium of the upper valley reaches. The much larger Upper Merced catchment thus supplies only somewhat greater buffering to perturbations in recharge and runoff that would be expected due to warmer temperatures. Using the information gathered from these tracers, differing scenarios characterized by earlier snowpack melting and a higher proportion of precipitation as rain are evaluated with regard to potential impacts to recharge.