# Pathways of dissolved organic matter in the subterranean estuary: Evaluation of organic geochemical tracers

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The mixing zone of fresh terrestrial groundwater and recirculating seawater in a coastal permeable aquifer, the so-called “subterranean estuary”, is a powerful bioreactor which determines the fate of dissolved compounds as they are transported into the ocean via submarine groundwater discharge (SGD). Dissolved organic matter (DOM) plays a crucial role in driving microbial remineralization processes, and through its breakdown contributes to the groundwater nutrient pool. Until recently, DOM in the subterranean estuary was mostly determined as bulk dissolved organic carbon, providing limited information on sources and degradation states. Studies of chromophoric DOM (CDOM) and biomarkers such as lignin provide information on DOM origin. Other traditional parameters, such as amino acid D/L ratios and degradation indices, and stable isotopic composition (e.g. $\delta^{13}C$), can be used to track the processing of DOM. Emerging analytical techniques, e.g. ultra-high resolution Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR-MS), improve our understanding of the chemical composition of DOM by providing molecular fingerprints. We investigated two intertidal subterranean estuaries, in Hampyeong Bay along the Yellow Sea coast of South Korea and on Spiekeroog Island, a barrier island in the German Wadden Sea. The major objective was to characterize pathways of DOM as it travels through the aquifer. In Hampyeong Bay, amino acid and CDOM data pointed to a mostly marine DOM source, whereas on Spiekeroog, $\delta^{13}C$ values indicated both a marine and a terrestrial DOM source. Molecular fingerprinting showed that a large amount of DOM was processed in the aquifer of Spiekeroog Island, whereas several components were passing the subterranean estuary unaltered, possibly forming a source of refractory DOM.

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# Is your clean lab full of zinc?

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Contamination of samples with extraneous zinc is likely much more common and severe than many metal isotope geochemists expect. Bottles, tubes, pipette tips, and especially disposable gloves are often produced with Zn stearate as the mold release agent. By far the largest amount of zinc is introduced by gloves. Dilute HCl will effectively rid other items of Zn, but gloves cannot be cleaned easily, and their use can lead to surface contamination throughout the lab.

We recently conducted experiments in which dissolved Zn was partly adsorbed onto Mn-oxide particles. The dissolved and adsorbed pools were separated by filtration, and isotope ratios were analyzed by MC-ICP-MS. A commercial ICP solution was both our standard ($\delta^{66/64}Zn = 0$) and the source of Zn in the experiments. When gloves were worn for sample handling, blanks contained as much as 150 ng Zn, and both the dissolved and adsorbed pools came out enriched in heavy isotopes relative to the starting pool, in apparent violation of mass balance. Without gloves, blanks were lower, but still variable, and mass balance was more closely satisfied. Zinc leached from two brands of allegedly low-zinc vinyl gloves was +10‰ relative to our standard ($\delta^{66/64}Zn$). We conclude that glove Zn in our lab contaminated our samples, even when gloves were not worn for sample processing.

We were only able to see clear evidence of contamination because (1) we had an expectation of mass balance, and (2) we happened to use a standard strongly enriched in light isotopes relative to our gloves. We caution others who measure unknown, natural samples that most natural samples are similar in isotopic composition to the gloves we measured and to JMC-Lyon Zn, which is becoming an accepted Zn isotope standard. Knowing whether variable amounts of glove zinc are contaminating samples is therefore a challenge. We recommend very careful monitoring of blanks and column chemistry yields, and we plan to designate and clean a glove-free workspace within the clean lab for further zinc isotope work.