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Evaluating Rare Earth Element distributions in the Northwestern Mediterranean Sea

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The distribution of Rare Earth Elements (REE) in the ocean is determined by their sources and sinks as well as the physical ocean transport. In the Northwestern Mediterranean Sea, potential sources of REE are rivers, Saharan dust and SGD and water column is generally structured in three main water masses. To evaluate the role of the external inputs versus water mass mixing in the budgets of REE in this area, we delineated a mass balance for dissolved REE (and Neodymium isotopes) with data from three water column profiles (MedSeA cruise). Results show that physical transport governs the REE mass balances in global terms although external exchanges do exert an important role, in particular in surficial and intermediate waters. Among the four identified external sources, atmospheric fluxes are the most important for all the REE, especially for the light REE and namely for Ce. For heavy REE, riverine fluxes become the second input in magnitude. Submarine groundwater discharge fluxes contribute from 3% to 20% of the external REE inputs to the system, competing with the diffusive fluxes from sediments, which account for 6 to 17% of the global external sources.

Calculated missing fluxes for REE are important in surface (Modified Atlantic Waters) and intermediate (Levantine Intermediate Waters) layers where the % of imbalances -with respect to inputs or outputs- ranged from 2 to 30% for all the REE except for Ce. More specifically, missing fluxes represented net LREE (La to Sm) outputs and HREE (Eu to Lu) inputs in surface waters while net output fluxes for all the REE in intermediate waters were required. We consider that the most probable process responsible for these fluxes is an active reversible scavenging, i.e. REE adsorption onto particles with subsequent desorption from dissolution or particle disaggregation. The imbalance for cerium indicates an output missing flux corresponding to the 77% (surface waters) and 96% (intermediate waters) of the cerium flux leaving the system due to water mass advection. The most plausible mechanism is Ce+3 removal by particle scavenging via oxidation to insoluble Ce+4, the thermodynamically stable form. Assuming that, we have calculated the Ce oxidation rates with respect to average Ce concentrations to be 0.33%·d-1 and 0.08%·d-1 for surface and intermediate waters, respectively. The former is in good agreement with previous results by Moffet (1990; from 0.3 to 0.8 % in the first 200 m depth). Cerium oxidation obtained for intermediate waters is remarkably weaker likely because of remineralization taking place at these depths, which acts adding dissolved Ce to the water column. Regarding deep waters, the defined REE balance is well resolved, with a reduced imbalance only representing from 0.1 to 2.6% of the inputs/outputs for all the REE, except for Ce. The missing flux for the latter raised to 6.3% of the outputs, again pointing to Ce oxidation and precipitation onto resuspended particles in bottom waters.

Moffett, J. W., 1990. Microbially mediated cerium oxidation in sea water. Nature 345, 421-423.