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Vertical distribution of Mn(II) and Mn(III) in the Black Sea's water column and sediments during the July 2024 R/V Bilim Expedition

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Understanding the vertical distribution and speciation of manganese across redox interfaces is crucial, as it plays an essential role as a catalyst in many biogeochemical processes. For many years, soluble Mn was thought to consist only of Mn(II). However, in the last two decades, it has been shown that soluble Mn also includes Mn(III)-L complexes across water column redoxclines and sediments. The Black Sea provides a unique natural laboratory as the largest anoxic-sulfidic water body on Earth. Although oxygen supports rich marine life in the oxic zone down to a density layer (sigma-theta) of 16.2-16.4 (80-150 m depth), it becomes either depleted in the anoxic zone or present at low concentrations in the suboxic zone. Stressors such as warming and eutrophication contribute to declining oxygen levels in the water column. As a result, different forms of redox-sensitive metals can be observed, such as Mn(IV) oxide particles in oxic waters and Mn(II)/Mn(III) species in suboxic and sulfidic waters. Here, we report on the distribution of Mn(II) and Mn(III) in the Black Sea in July 2024 using the porphyrin method, based on samples collected by R/V Bilim-2 in July 2024. Our study focuses on the western part of the basin. Mn(II) onset density (sigma-theta) was observed between 16.0 and 16.5, with a maximum concentration of approximately 10 μM in the water column and 80 μM in the sediments. In the water column, Mn(III) concentrations increased to a maximum of 0.46 μM while inside sediment cores sampled from the redoxcline, Mn(III) was observed in the top 8 cm with concentrations ranging from 0.58 to 3.46 μM. Our research provides a general perspective on the vertical distribution of manganese in both the water column and sediment in the Black Sea. It also correlates manganese distribution with oxygen levels and hints at how it responds to anthropogenic stressors and climate change. The next steps in our research include a comparative assessment of our findings with other existing Mn speciation studies in the Black Sea and using this comparative analysis to develop the Mn cycles in recently developed, three-dimensional biogeochemical models of the Black Sea.