ANNUAL REPORT ON GEOTRACES ACTIVITIES IN TURKEY

May 1st, 2024 to April 30th, 2025

GEOTRACES or GEOTRACES relevant cruises

As a GEOTRACES-relevant cruise, In July 2024, a comprehensive southwestern Black Sea Cruise was conducted with R/V Bilim-2 funded by the ERC DeepTrace Project. 15 stations on the southwestern shelf and western basin were sampled comprehensively including dissolved, particulate and total metals. On-board dissolved manganese, and hydrogen sulfide measurements were conducted. Additionally, on board and in-situ voltammetry was conducted for redox important species. The nanoparticulate phase from the seawater and the sediment interface was collected with innovative methodologies. Some of the first results on manganese biogeochemistry are featured below in this report.

New GEOTRACES or GEOTRACES relevant scientific results

Manganese Biogeochemistry in the Black Sea

Mn(II) was previously thought to be the only soluble manganese species. However, studies have shown that Mn(III) concentrations can reach to µM levels under dynamic redox conditions. In our project, we optimized a novel porphine method, to measure both Mn(II) and Mn(III) in sediment pore waters and the water column. In the western Black Sea in July 2024, Mn(II) was at a maximum concentration of 10 µM in the water column and 80 µM in the sediment porewaters. In the water column, Mn(III) concentrations increased to a maximum of 0.46 µM while inside the sediment cores Mn(III) was as high as 3.46 µM. Next steps in our research include a comparative assessment of our findings with existing Mn speciation work in the Black Sea and improve the representation of the Mn cycles in 3D biogeochemical models.

Sample collection and filtration

Manganese (Mn) measurements were performed on 12 stations, 9 water column and 3 sediment porewater (Figure 1), in samples collected from July 14th to July 22nd, 2024 in order to decide soluble Mn species, Mn(II) and Mn(III)-Ligand (Mn(III)-L). All samples were immediately filtered upon arrival on deck using 0.2 µm syringe filters in a glove-bag to prevent oxygenation. Acid was not added to any samples because acid precipitates humic substances and effects the complexation of Mn(III) with humic ligands as Mn(III)-L (Oldham et al., 2017). Samples were kept in dark until analyses.

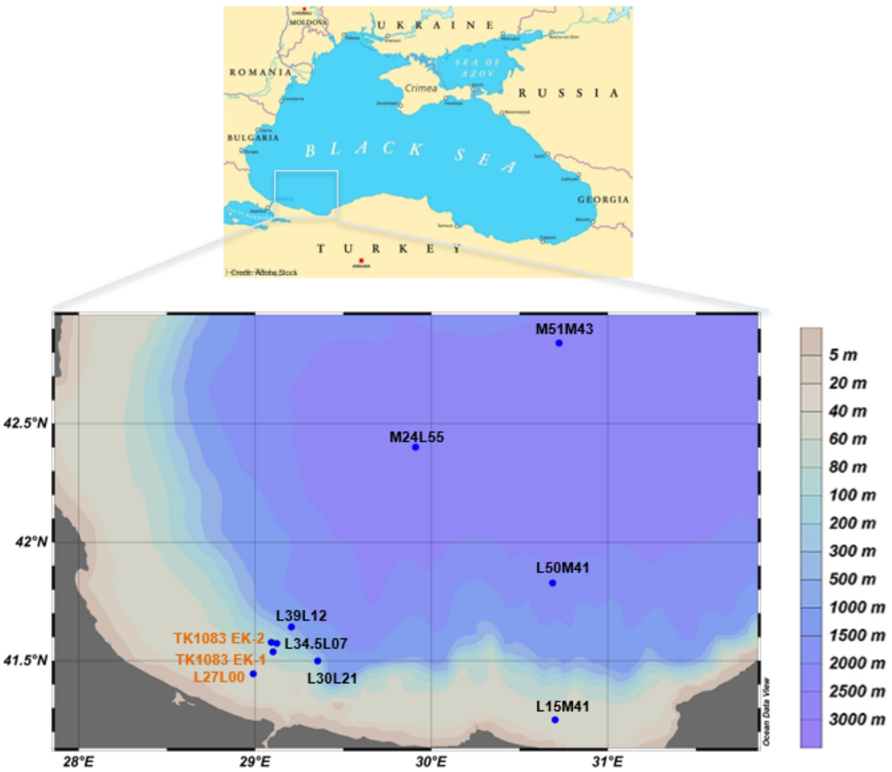
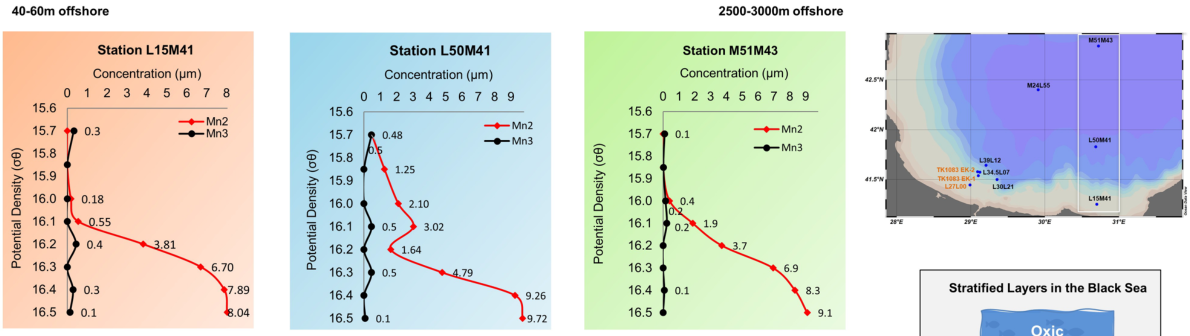


Figure 1: Sampling Stations in the Southwestern Black Sea in July 2024.

Spectrophotometric measurements for manganese speciation

Manganese speciation of the filtrated waters were analysed by the addition of a soluble porphyrin ligand (Madison et al., 2011). In this method, firstly, porphyrin complexes with cadmium (Cd) as a porphyrin-Cd complex and then, it undergoes a rapid metal substitution reaction with Mn(II) in the sample, giving a peak at 468 nm as porphyrin-Mn complex. In Madison et al., 2011, Mn speciation is based on the known reaction rate constants "k1" for Mn(II) and "k2" for Mn(III)-L because Mn(III)-L complexes undergo a slow ligand substitution reaction. However, we amended samples with a strong reductant, hydroxylamine, to assess the presence of strong Mn(III)-L complexes (Oldham et al., 2017). The difference between the samples with and without hydroxylamine gives us strong Mn(III)-L complexes using a quartz 1 cm cell in UV/Vis spectrophotometer coupled with OceanView software.

Onset of total dissolved manganese (dMn_t) increases between potential densities ($\sigma\theta$) of 16.0-16.5. Strong Mn(III)-L complexes were generally detected between 15.7-16.1 densities. In water column, max dMn_t was measured as 9.8 µM, while max. Mn(II) was 9.72 µM, and max. Mn(III) was 0.46 µM. In sediment porewaters, max dMn_t was measured as 82.67 µM, while max Mn(II) was also 82.67 µM and Mn(III) was 3.46 µM. The speciation profiles of Mn for three stations, L15M41, L50M41 and M51M43, was shown in Figure 2.



Depth (m)	Density	dO2 (µM)
125	15.7	26.34
131	15.85	20.29
139	16.0	8.71
147	16.1	5.46
157	16.2	3.36
169	16.3	0
185	16.4	0
209	16.5	0

Depth (m)	Density	dO2 (µM)
78	15.7	12.22
87	15.85	11.16
96	16.0	17.33
103	16.1	4.69
113	16.2	19.24
126	16.3	5.08
147	16.4	0
166	16.5	0

Depth (m)	Density	dO2 (µM)
69	15.7	8.61
74	15.85	5.69
82	16.0	5.27
90	16.1	4.26
98	16.2	4.15
112	16.3	0
126	16.4	0
143	16.5	0

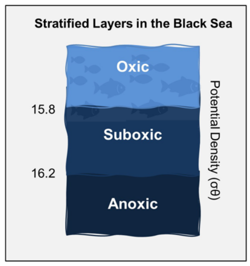


Figure 2: Mn(II) and Mn(III) profiles along offshore gradient in the Black Sea in July 2024.

References

Madison, A. S., Tebo, B. M., & Luther, G. W. (2011). Simultaneous determination of soluble manganese(III), manganese(II) and total manganese in natural (pore)waters. Talanta, 84(2), 374–381. https://doi.org/10.1016/j.talanta.2011.01.025

Oldham, V. E., Mucci, A., Tebo, B. M., & Luther, G. W. (2017). Soluble Mn(III)–L complexes are abundant in oxygenated waters and stabilized by humic ligands. Geochimica et Cosmochimica Acta, 199, 238–246. https://doi.org/10.1016/j.gca.2016.11.043

Other GEOTRACES activities

The establishment of a marine metal nanogeoscience laboratory at METU-IMS was finally completed during this term. It features advanced instruments, including the icpTOF for rapid multi-element analysis with the Quantistar calibration system, the FFF system for nanoparticle fractionation, and the DLS instrument for assessing dispersion stability in environmental matrices. Additionally, essential tools such as a laminar flow hood, fume hood and a deionized water generator have been installed. The acquisition, validation, and successful training on these systems represent a major step forward for the project. This facility will be a key asset in current projects but also future GEOTRACES-related collaborative activities.

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