

## ANNUAL REPORT ON GEOTRACES ACTIVITIES IN INDIA

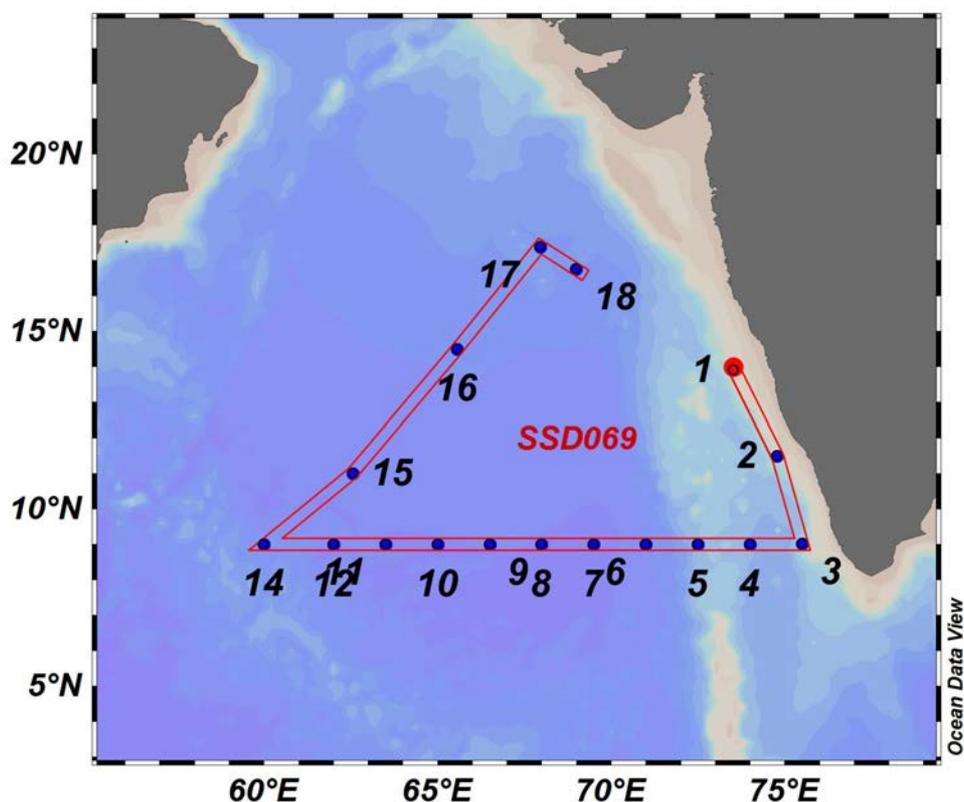
May 1st, 2022 to April 30th, 2023

### *New GEOTRACES or GEOTRACES relevant scientific results*

- Biogeochemical cycling of micronutrients in the Arabian Sea

The Indian Ocean is unique in terms of its geographical position, physicochemical conditions, and the existence of numerous sources and sinks of micronutrients. The biogeochemical cycling of the micronutrients in the Indian Ocean has received little attention. The current study demonstrates the sources, sinks, and internal cycling of the micronutrients, as well as their influence on the ecological distribution in the Indian Ocean.

To determine the distribution of micronutrients such as Fe, Ni, Cd, Co, Cu etc. in the Indian Ocean and to identify the sources, sinks and internal cycling of these micronutrients in the Indian Ocean, seawater from the Arabian Sea has been analysed.



**Figure IN-1:** Study area showing the stations of the water sampling along the cruise track of G110 in the Arabian Sea from Jan to Feb 2020.

### Iron:

The present study shows the dissolved Fe (dFe) concentration in the surface waters from 0.1-0.5 nM, which gradually increases with depth up to 1nM. A slightly high concentration is observed in the surface waters of the south-eastern Arabian Sea, which is due to the inflow of the Bay of Bengal Low Saline Water (BBSW) transported by the East India Coastal Current (EICC). Pronounced supply of dFe is observed (~3nM) in the coastal sub-surface water of the Eastern Arabian Sea due to the lateral advection of Fe from the reducing shelf margin. Towards

the south-western Arabian Sea, a relatively higher concentration of dFe (~2nM) marked in deep and intermediate waters, which reaches up to ~200-300 meters signify hydrothermal input, could be sourced from the active hydrothermal vents over the Carlsberg Ridge. This large supply of dFe up to such height in the water column may reach the surface due to the strong upwelling (during SW monsoon) and can be bio-available, hence increases the productivity. The release of dFe (1 to 1.8 nM) to the water column in the Oxygen Minimum Zone of the Arabian Sea acts as another valuable source. Distinctive physicochemical processes in different depths of the water column add to or remove dFe working as a source or sink in the marine realm, controlling its biogeochemical cycle.

#### Nickel:

The concentration of dNi in the Arabian Sea varies from 1.9-2.7nM in the surface waters to 10.2-11nM in the deeper waters. In the coastal waters the dNi concentration varies from 2.2nM-5nM. We have collected water samples throughout the water column depth in 8 stations in the zonal transect of 90N (90N,740E-90N,620E). The concentration of dNi in this transect in the surface waters ranges from 2.2-2.4nM, in the intermediate waters (100m-1000m) ranges from 2.3nM to a maximum of ~7nM at depth of 1000m. Deeper waters (>1000m) have a range of 6.8nM to ~10nM of dNi. Three stations from SSD069 (station 16-18) were done in the perennial oxygen minimum zone of the Arabian Sea. The concentration of the dNi in the surface waters varies 2-2.4nM whereas in depth the concentration reaches up to a maximum of 11nM. dNi concentration values in the deeper waters are seen to be little bit higher in the northern and the perennial OMZ regions than the southern part (9°N transect). Although earlier report conceived the theory of the role of water masses and their mixing of them controls the distribution of dNi in the water column, however in the context of the Indian Ocean, it seen the overpowering role of the OMZ and remineralisation. In the Northern Indian Ocean, the role of OMZ in the intermediate waters depletes dNi wrt Phosphate. The depletion in Ni in the OMZ waters of the Arabian Sea is found to be maximum at SSD069 station 17 and 18 at depth 150 m and 300m of value around 300 pmol/L.

#### Copper:

Biogeochemical cycling and internal circulation play a major role in the distribution of Cu. Reversible scavenging and subsequent sedimentary input are the major processes associated with the Cu distribution. Besides, association of Cu with the Fe-Mn oxy-hydroxides is critical which is not a major source in the open ocean waters but can be a significant source in the continental margins. Though a debate on the hydrothermal vents whether a source or sink, but in our studies we have not seen any significant signature of dCu in the vent areas. In the Arabian Sea along the cruise SSD069 coastal waters shows a high concentration of dCu of 2-2.5nM may be due to the sources from the continents and gradually decreases further towards the open ocean. The profile shows a gradual increase in the concentration with depth unlike other elements of nutrient type. At station 5 a higher signal is seen. And in the OMZ areas the minimum values of dCu persisted up to a greater depth which may be the effect of the change in redox condition in the water column.

#### Cobalt:

Cobalt may act as a primary or secondary limiting nutrient. The requirement of this micro-nutrient in the marine phytoplankton is due to the presence in vitamin B<sub>12</sub> (Cobalamin) and its crucial role as a potential co-factor of Carbonic Anhydrase and Alkaline Phosphatase. In the Arabian Sea the surface concentration remains low except near the coastal areas as probable

sources are the continental margin, riverine input and the atmospheric dust. However, with progressing towards the open ocean surface concentration gradually decreases. As the dCo shows a hybrid type of profile in the water column with scavenging in the surface and then enriching in the intermediate waters. Although the enrichment of dCo in this zone is even more up to 0.11nM in the perennial OMZ.

### Cadmium:

The biogeochemical cycling of dCd is mainly dominated by the biological uptake of the phytoplankton in the photic zone and the regeneration of the particulate Cd which governs the shape of the vertical profile of dCd in ocean, however, water-mass circulation also plays an important role in the distribution of dCd in ocean waters. It has been recently argued that the precipitation of Cd in the form of sulphides also affects its biogeochemical cycling in the Oxygen Deficient Zone (ODZ) and is not restricted to the euxinic basins. Though recent studies reveal the CdS precipitation in the North Atlantic and South Pacific but not in North Pacific. However, in the Northern Indian Ocean it is supposed to be precipitated from the water column but we observed a range of positive and negative Cd anomaly with respect to the phosphate in the OMZ waters of the Arabian Sea. The dCd in the Arabian Sea ranges from 0.01nM to 0.98nM. Recent studies on the sulphide precipitation of metals is observed in the ODZs. The Northern Indian Ocean although experiences the process still its dynamic nature makes some variations in the precipitation of different metals. In case of dNi, the Arabian Sea experiences a depletion with respect to the phosphate but in dCd it is not the case. Arabian Sea experiences an enrichment even in the layers of OMZ. The high productivity of Arabian Sea, its uptake and subsequent regeneration might have overpowered the CdS precipitation process. Also, the intrusion of the Red Sea water and Persian Gulf Water in the water depth of 200m- 800m might have influence it. Further isotopic studies in the dissolved and particulate phases will exactly describe the dominance of the processes in the water column in various part of the Indian Ocean though this CdS precipitation seems to be a regional scale process.

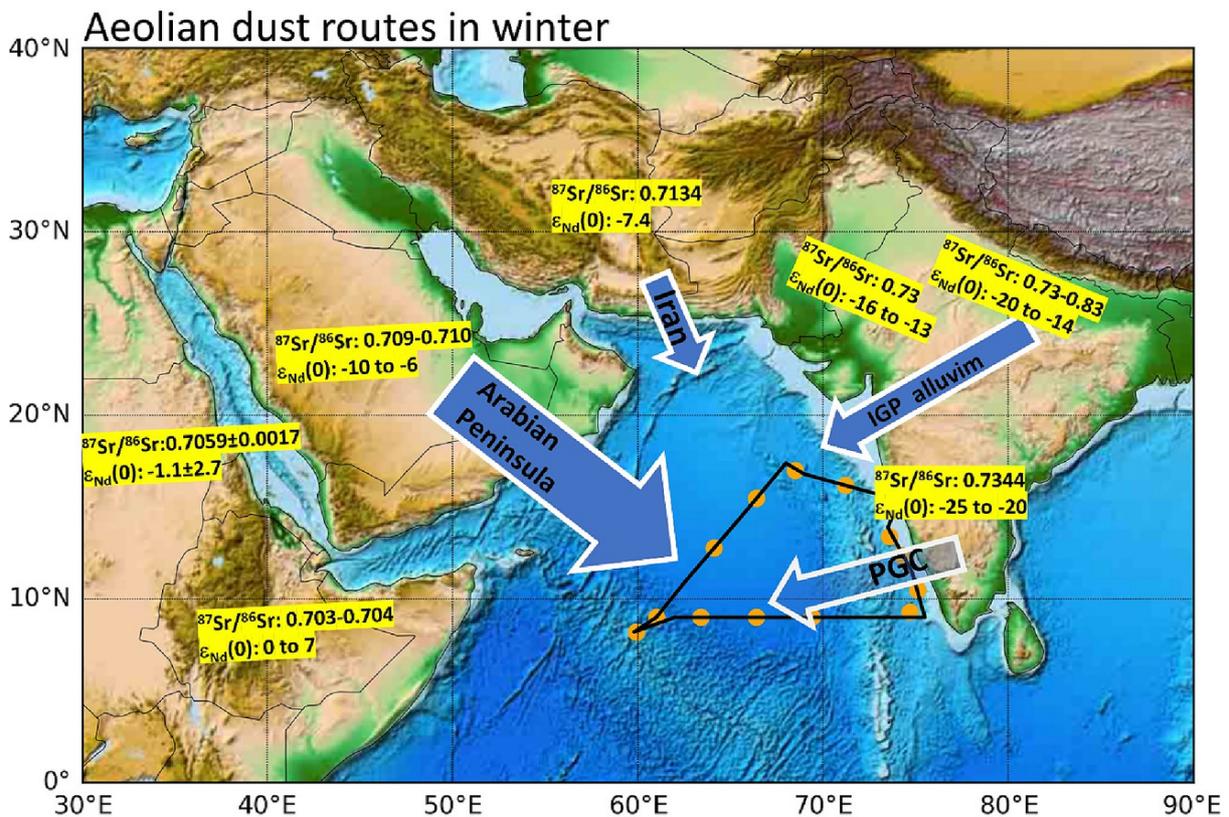
- Link of the short-term temporal trends of Sr and Nd isotopic composition of aeolian dust over the Arabian Sea with the source emissions

Aeolian transport of continental dust from the Middle East and South Asia to the Arabian Sea (AS) is an important route for delivering key trace metals and nutrients. Despite being surrounded by several deserts, it is not clear which dust source is most likely contributing to mineral aerosols over this marine basin in winter. Substantial information on dust source emissions and transport pathways over the AS is, thus, needed for better constraining the biogeochemical effects in the sunlit surface waters.

Here, we investigated the Sr and Nd isotopic composition ( $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\epsilon_{\text{Nd}}(0)$ ), respectively: characteristic of source material) of dust samples collected over the AS during a GEOTRACES-India expedition (GI-10: 13 January-10 February 2020).

Both tracers,  $^{87}\text{Sr}/^{86}\text{Sr}$  (0.70957–0.72495) and  $\epsilon_{\text{Nd}}(0)$  (–24.0 to –9.3), showed pronounced spatial variability. These proxies were further tagged with their source profiles of surrounding land masses based on the origin of air mass back trajectories (AMBTs). We also encountered two dust storms (DS), one on 27 January 2020 ( $^{87}\text{Sr}/^{86}\text{Sr}$ : 0.70957;  $\epsilon_{\text{Nd}}(0)$ : –9.3) and the second one on 10 February 2020 ( $^{87}\text{Sr}/^{86}\text{Sr}$ : 0.71474,  $\epsilon_{\text{Nd}}(0)$ : –12.5), which showed distinct isotopic signatures. AMBTs and satellite imagery together revealed that DS1 is from the Arabian Peninsula and DS2 is from Iran and/or the Indo-Gangetic Plain. Notably, the Sr and Nd isotope composition of DS1 is further consistent with other dust samples collected over the

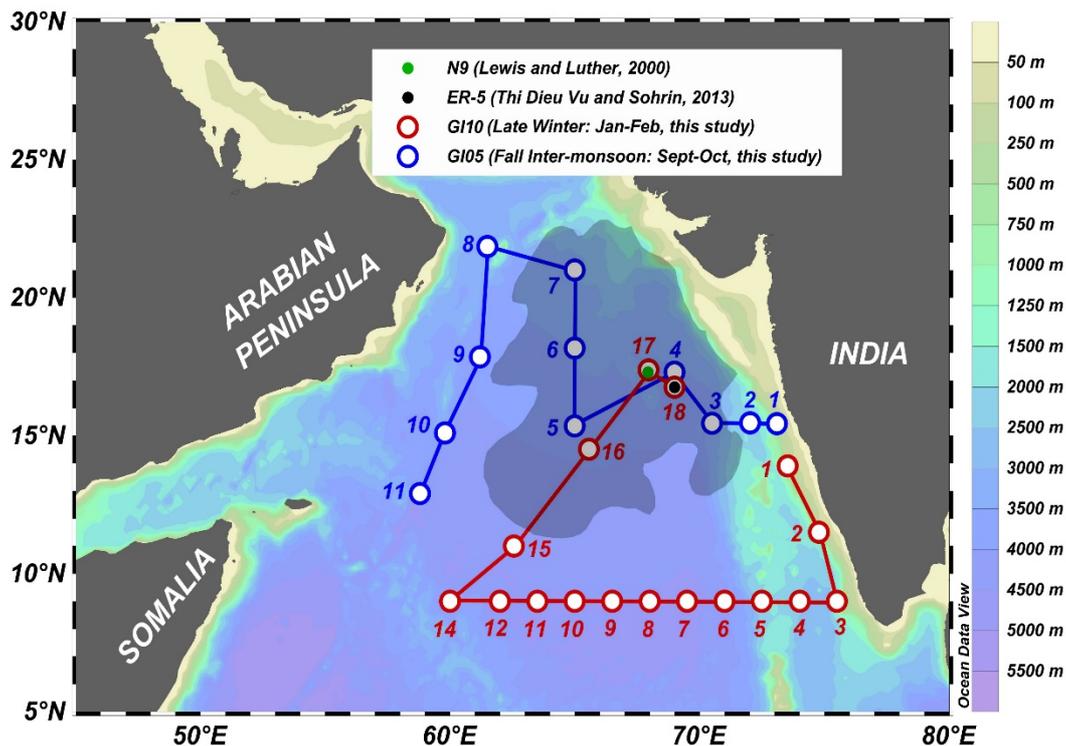
pelagic waters, suggesting the impact of dust outbreaks from the Arabian Peninsula during winter season. Such documentation based on the  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\epsilon_{\text{Nd}}(0)$  over the Arabian Sea, hitherto, is lacking in literature and, thus, highlights the need for more measurements.



**Figure IN-2:** Study area in the Arabian Sea showing aerosol dust pathways in the winter season, with characteristic radiogenic isotopic composition ( $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $\epsilon_{\text{Nd}}(0)$ ) of source regions.

- Biogeochemical cycling of dissolved manganese in the Arabian Sea

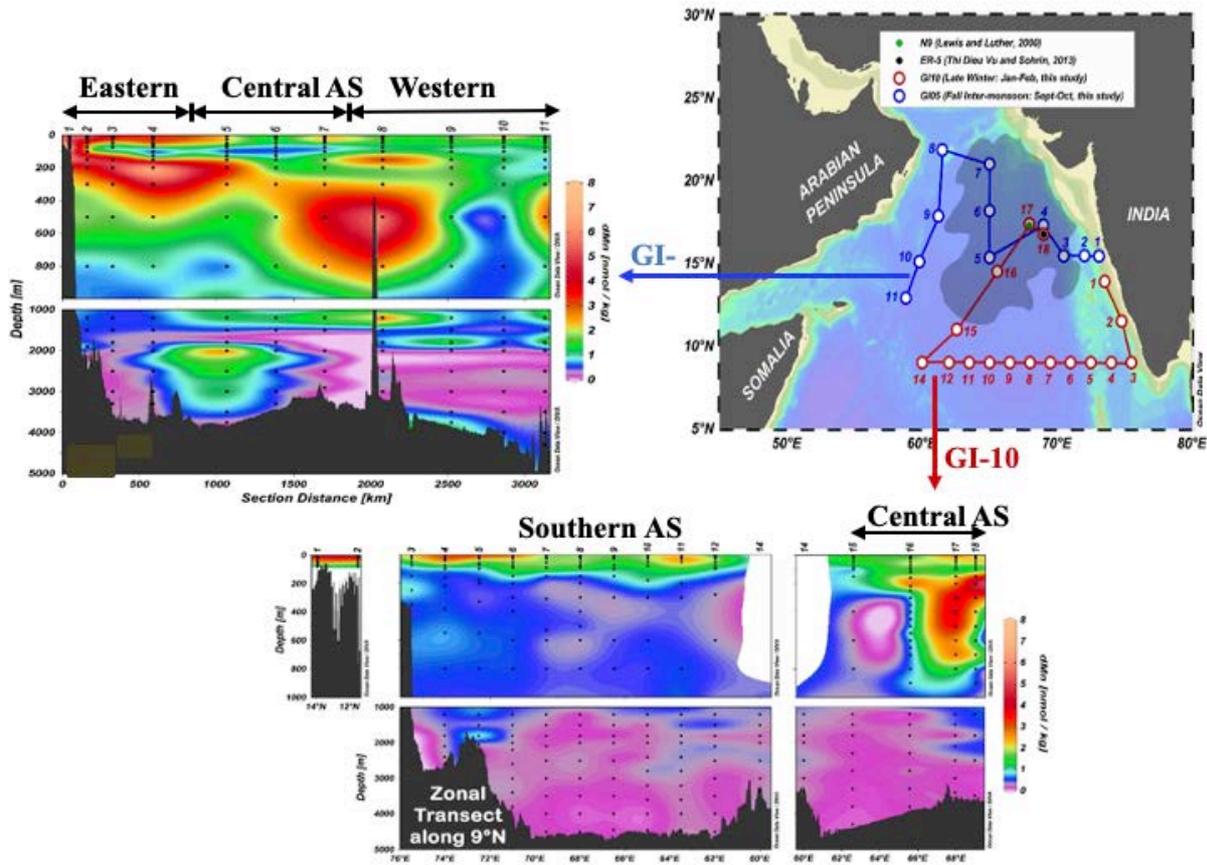
Manganese (Mn) acts as a bio-essential trace metal and its availability in seawater may impact the productivity and diversity of marine phytoplankton (Coale, 1991; Raven, 1990; Sunda, 2012). Particulate authigenic Mn oxides and oxyhydroxides formed in the ocean water column may act as important sink for other bio-essential trace metals (e.g., Co, Zn, Ni, etc.) and, therefore, the Mn redox cycling in seawater can impact the bio-availability of these micro-nutrients. We measured dissolved Mn (dMn) in the water column along the GEOTRACES-India transects, GI-05 and GI-10 (Figure IN-1), to understand the control of diverse biogeochemical processes, including atmospheric dust deposition, biological cycling, water mass mixing, redox changes in the sediment and water column, on dMn distribution in the coastal and open Arabian Sea regions. The study presents important implications for the Mn and other trace nutrient bio-availability in the AS euphotic waters.



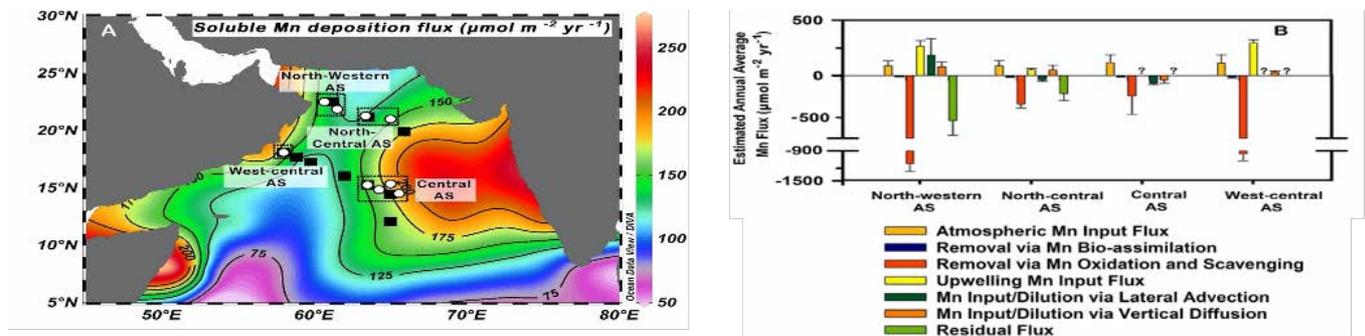
**Figure IN-3:** Sampling locations along the GI05 (blue circles) and GI10 (red circles) cruise transects where vertical dMn profiles are measured. The shaded area represents the AS denitrification zone identified by Naqvi (1991), where  $[\text{NO}_2^-] > 1\mu\text{M}$  at the secondary nitrite maximum depth. Crossover stations from earlier studies, ER-5 (black circle) and N9 (green circle), are also marked.

A strong east-west concentration gradient was observed in the surface dMn distribution in the AS (Figure IN-2). Higher dMn input from atmospheric dust deposition and, presumably, from riverine discharge and/or shelf sediments resulted in increased dMn levels ( $1.6\text{--}5.7\text{ nmol kg}^{-1}$ ) in the surface waters of the eastern AS. While, strong removal of dMn via Mn-oxidation and scavenging led to relatively lower dMn levels ( $1.3\text{--}2.2\text{ nmol kg}^{-1}$ ) in the surface waters of the open western AS.

A mass-balance of dMn in the euphotic waters of different open AS regions was done considering the input (atmospheric deposition), removal (bio-assimilation, and Mn-oxidation and scavenging) and internal redistribution (water mass mixing) of dMn (Figure IN-3). Significant contribution (14–99%) from atmospheric Mn deposition to the total estimated dMn input flux is estimated. In terms of removal, Mn-oxidation and particle scavenging are found to be the predominant processes, contributing 61–99% of the total estimated output fluxes. Removal via Mn bio-assimilation and subsequent export plays a secondary role. Water mass mixing (via lateral and vertical advection-eddy diffusion) is found to predominantly contribute (~70–80% of the total input flux) to the dMn inventory in the euphotic zone of the coastal regions of the western AS.



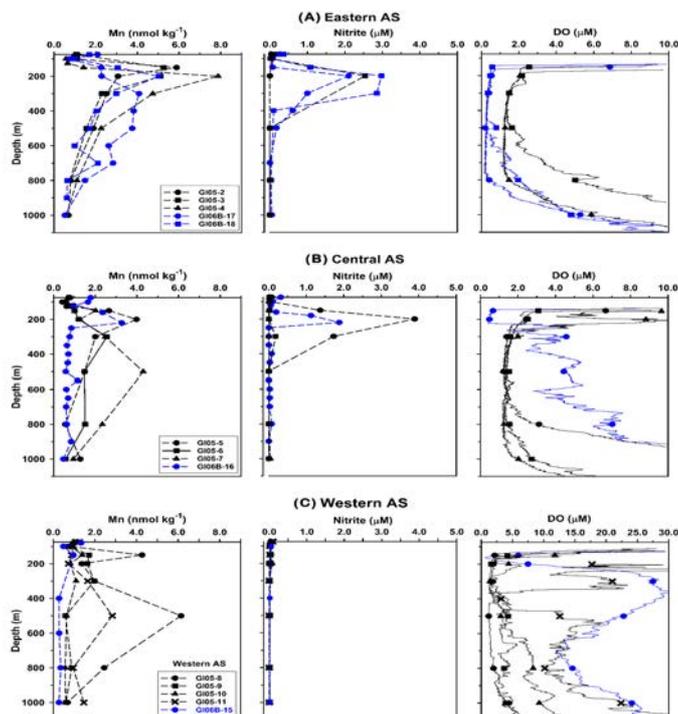
**Figure IN-4:** Dissolved Mn distribution along the GI05 (top left) and GI-10 (bottom) cruise transects.



**Figure IN-5:** (A) Estimated soluble Mn deposition flux from atmospheric dust deposition. (B) Mass-balance of dMn in the euphotic waters (upper 100m) of different AS regions.

Dissolved Mn and secondary nitrite maxima are observed to be correlated in the upper thermocline water in the denitrification zone of the (DNZ) eastern and central AS (Figures IN 4A and 4B), indicating an important role of *in situ* reductive dissolution of Mn oxides and oxyhydroxides. However, the strength of dMn maximum increases from the central AS coast to the eastern AS, suggesting additional dMn input from the reducing shelf and slope sediments of the western Indian margin to the open AS through lateral advection.

Outside the DNZ, in the north-central and western AS, dMn maxima is observed to show a relative shift to the lower thermocline waters (~500 m, Figure IN-4C). This shift is attributed to the change in source region of the dMn input to the western and north-central AS, from the reducing margins of the north (Pakistan Margin) and north-western AS (Oman Margin), where core of the oxygen minima intersects the margin sediments at depth range of 400–600 m.



**Figure IN-6:** Vertical profiles of  $dMn$ , dissolved nitrite and oxygen in the (A) eastern, (B) central and (C) western AS regions.

- Impact of weathering, lithology and fluvial transport on  $\delta^{98}Mo$  in a tropical river (Narmada)

Stable molybdenum (Mo) isotopes ( $\delta^{98}Mo$ ) were measured in the waters from the Narmada River to understand the impact of various processes on the Mo supply to the ocean. Results show that the Mo isotopic composition ( $\delta^{98}Mo$ ; relative to NIST SRM-3134 = 0.25‰) of the Narmada river water vary significantly, from 0.30 to 0.92‰, considerably heavier than the crustal components. The measured  $\delta^{98}Mo$  in the Narmada river water show significant control of continental weathering, soil organic matter cycling, secondary mineral formation, and surface-ground water interactions.

#### ***GEOTRACES or GEOTRACES relevant cruises***

- There was no new sample collection done through the last year. However, various water and sediment/particulate samples are being analysed currently for their trace element and isotopic composition and other key parameters.

***New GEOTRACES or GEOTRACES-relevant publications (published or in press)***

- Naman Deep Singh, Sunil Kumar Singh, Nirmalya Malla, Venkatesh Chinni, Biogeochemical cycling of dissolved manganese in the Arabian Sea, *Geochimica et Cosmochimica Acta*, Volume 343, 2023, Pages 396-415, ISSN 0016-7037, <https://doi.org/10.1016/j.gca.2022.12.030>.
- Karri Damodararao, Sunil Kumar Singh, Substantial submarine groundwater discharge in the estuaries of the east coast of India and its impact on marine strontium budget, *Geochimica et Cosmochimica Acta*, Volume 324, 2022, Pages 66-85, ISSN 0016-7037, <https://doi.org/10.1016/j.gca.2022.03.002>.
- Rakesh K. Tiwari, Tarun K. Dalai, Saumik Samanta, Waliur Rahaman, Sunil K. Singh, Tristan J. Horner, Geochemistry of uranium in the Ganga (Hooghly) River estuary, India: The role of processes in the water column and below the sediment-water interface, *Marine Chemistry*, Volume 247, 2022, 104173, ISSN 0304-4203, <https://doi.org/10.1016/j.marchem.2022.104173>.
- Naman Deep Singh, Sunil Kumar Singh, Distribution and cycling of dissolved aluminium in the Arabian Sea and the Western Equatorial Indian Ocean, *Marine Chemistry*, Volume 243, 2022, 104122, ISSN 0304-4203, <https://doi.org/10.1016/j.marchem.2022.104122>.
- Vineet Goswami, Sunil K. Singh, Ravi Bhushan, Vinai K. Rai, Spatial distribution of Mo and  $\delta^{98}\text{Mo}$  in waters of the northern Indian Ocean: Role of suboxia and particle-water interactions on lighter Mo in the Bay of Bengal, *Geochimica et Cosmochimica Acta*, Volume 324, 2022, Pages 174-193, ISSN 0016-7037, <https://doi.org/10.1016/j.gca.2022.03.010>

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