# Impact of water-particle interactions on molybdenum budget in humid tropical rivers and estuaries: insights from Nethravati, Gurupur and Mandovi river systems

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## ARTICLE INFO

## ABSTRACT

The study presents the seasonal and inter-annual monitoring of molybdenum (Mo) distribution and variability in humid tropical riverine and estuarine systems (Nethravati, Gurupur and Mandovi estuaries) of west coast of India. The study investigates the geochemical behaviour of Mo in the river and estuaries, and their ultimate fluxes into the ocean. The riverine flux of dissolved Mo (DMo) to the Nethravati, Gurupur and Mandovi estuaries are 1800 mol yr$^{-1}$ (4.88 mol day$^{-1}$), 195 mol yr$^{-1}$ (0.53 mol day$^{-1}$) and $10.5 \times 10^3$ mol yr$^{-1}$ (28 mol day$^{-1}$) respectively, and the riverine particulate Mo (PMo) flux to Nethravati estuary is $10.8 \times 10^3$ mol yr$^{-1}$. The DMo in river (~30 to 40%) is scavenged onto particles under oxidized acidic river water conditions and subsequently released in the estuary, impacting the solute budget of Mo to the sea.

In the estuaries, under low salinity conditions, DMo is sequestered onto particles during pre-monsoonal season. The DMo sequestration in the estuary is estimated to be ~2 mol day$^{-1}$ in the Nethravati estuary and ~1.9 mol day$^{-1}$ in the Mandovi estuary. During this season sequestration in the estuary is higher than the riverine supply, indicating the sequestration of both marine and river borne DMo. However, the mechanisms involved in the removal process are different in these estuaries viz. oxidative adsorption process in the Nethravati-Gurupur estuary and microbial utilization in the Mandovi estuary. The lower salinity region during monsoon and post-monsoon season shows slight excess of DMo, river borne particulate Mo could release up to 3 to 4 nmol L$^{-1}$ by desorption under alkaline higher ionic strength conditions. At higher salinity (>20 psu) in both the estuaries and in all the seasons, DMo gain is systematic (~1 to 37 nmol L$^{-1}$). Mo release from river borne particles could contribute only up to 3 to 4 nmol L$^{-1}$, which is not sufficient to balance the observed Mo excess. On the other hand, the reductive Mo remobilization from bottom sediments (Mo = 4 mg kg$^{-1}$) during sediment diagenesis and subsequent tidal activity, release up to 28 nmol L$^{-1}$ of DMo to the estuarine water. Mo release to water column is supported by the gradual enrichment of DMo with depth in the estuary. Therefore, diagenetic release of DMo forms the potential source of DMo excess in the estuary.

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## 1. Introduction

In the ocean, molybdenum is sequestered in organic-rich sediments under reducing conditions. The degree of sequestration depends on the prevailing redox conditions of the overlain water (Algeo and Lyons, 2006). As a consequence, molybdenum and its isotopic ratios form a useful tracer in paleoceanographic reconstruction studies (Algeo, 2004; Algeo and Rowe, 2012; Tribovillard et al., 2006; Pearce et al., 2008; Nägler et al., 2011; Dickson et al., 2012). However, the knowledge on the geochemical behaviour, source and sink pathways of Mo, and the internal cycling of Mo in the coastal and marine environment needs to be refined.

Mo primarily exists in solution as a relatively stable molybdate ion, $(MoO_4^{2-})$ in well oxygenated seawater. It is one of the most abundant transition metals in seawater (~105 nmol L$^{-1}$; Emerson and Huested, 1991) with a residence time of 0.44 Myrs (Miller et al., 2011). Primary sources of Mo in seawater are continental rock weathering and hydrothermal activity. The major sink for Mo is removal to anoxic sediments (McManus et al., 2006) or ferromanganese oxides deposited in

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oxygenated waters (Scott et al., 2008). Despite the vital biological role of dissolved Mo (DMo) in ocean (Howarth and Cole, 1985), it shows conservative behaviour in open ocean (Morris, 1975; Collier, 1985; Quiby-Hunt and Turekian, 1983) and non-conservative distribution near coastal margins (Tuit, 2003). Until recently, the DMo in estuaries was believed to be conservative (Audry et al., 2007; Stardy et al., 2009) as a result of mixing between Mo-rich seawater and depleted river water. However, some studies reported the non-conservative behaviour of DMo (Waeles et al., 2013; Wang et al., 2016; Rahaman et al., 2010; Rahaman et al., 2014). This non-conservative behaviour has implications in the oceanic Mo budget because the riverine influx is adversely affected by the estuarine processes. Current DMo oceanic budget is based on the assumption that Mo behaves conservatively during estuarine mixing and is least affected by biogeochemical transformation and sedimentary processes. Recent studies suggest that Mo biogeochemical cycle is influenced by several factors. This includes anthropogenic activity (Rahaman et al., 2010), submarine ground water discharge fluxes (Beck et al., 2010), and diffusion from sediment pore water (Dalai et al., 2005; Dellwig et al., 2007). These processes lead to Mo enrichment in estuaries, whereas oxidative scavenging onto Fe-Mn oxy-hydroxides (Morford and Emerson, 1999), algal uptake (Cole et al., 1993; Glass et al., 2012; Wang et al., 2016), uptake by mangrove vegetation (Rahaman et al., 2010) lead to DMo depletion in the estuaries. The dissolved Mo geochemistry of tropical riverine and estuarine systems are studied to understand the anthropogenic stress on Mo cycle and to estimate the ultimate flux to ocean (Rahaman et al., 2010; Miller et al., 2011).

In this study, we present geochemical data in dissolved and particle phase from the monthly monitoring of a humid tropical river (Nethravati River), and the seasonal and inter-annual monitoring of estuarine systems (Nethravati, Gurupur and Mandovi estuaries) of west coast of India. The paper discusses the Mo distribution in the rivers and estuaries to gain insights into processes contributing to the source-sink of Mo, and the possible anthropogenic influence on the Mo cycle in these tropical catchments. This study provides new insights in to the ultimate geochemical flux of DMo from tropical rivers to the open ocean.

## 2. Materials and methods

### 2.1. Study area and sampling:

The Nethravati-Gurupur and Mandovi rivers originate in the Western Ghats, and flow westwards into the Arabian Sea. These rivers are among the major contributors of water and sediments to the eastern Arabian Sea. The Nethravati-Gurupur river basins predominantly drain granite-gneiss, granulites, metasediments and laterites, whereas Mandovi river basin drains basalts, granites and gneisses, coastal alluvium and laterites. The geological characteristics of these river basins have been described elsewhere (Kessarkar et al., 2009; Rahaman and Singh, 2012; Rahaman et al., 2010; Rao et al., 2011; Gurumurthy et al., 2012; Prajith et al., 2016). The annual discharge of Nethravati-Gurupur River is 388 m$^3$ s$^{-1}$ and Mandovi River is 264 m$^3$ s$^{-1}$ (Central Water Commission, Government of India; http://www.cwc.nic.in/). All these rivers have similar demographic and morpho-climatic settings with humid equatorial tropical climate. In the last two decades, the west coast of India has been the hub of major industrial projects and has seen rapid economic growth over the years. As a consequence, the downstream of these basins are now facing significant anthropogenic stress. The estuarine systems formed by the confluence of these rivers with Arabian Sea are classified as monsoonal estuaries (Vijith et al., 2009) as about 75 to 85% of the total annual discharge occurs during the monsoon. Hydrodynamics of the estuaries is controlled by both river runoff and tides during monsoon (June to September) and semi-diurnal tidal range of 0.2 to 2 m during the non-monsoonal months.

The Nethravati-Gurupur estuary, located in the Karnataka coast, is formed by the confluence of Gurupur River with Nethravati River at Mangalore. The Gurupur River merges with the Nethravati River after taking the direction - parallel to coast, for about 5 km (Fig. 1a). The estuary is very shallow and has almost reached deltaic stage. It is characterized by mixed type of diurnal tides (Reddy et al., 1979). During the low tide period, the alluvial bed is usually exposed. During the monsoon season the freshwater flow influence the currents in the estuary while tidal influence dominates during the rest of the year although it is barely seen beyond 15–20 km inland (Manjunatha and Harry, 1994). About 93% of the total river discharge occurs between June and October. The river discharge during non-monsoonal months is low and the freshwater input to estuary is almost stopped at the Thumbe dam (located 5 km upstream of Farangipet) which provides water to Mangalore city. The Gurupur estuary receives the treated domestic sewage water ($4.8 \times 10^6$ m$^3$ yr$^{-1}$) from Mangalore. An industrial cluster of large-medium-small scale industries (MRPL, BASF, MCF, etc.) is located near the Gurupur estuary. However, none of these industries discharge waste directly to river-estuary (CPCB, 2010).

The Mandovi estuarine system (Fig. 1b) in the central west coast of India, in Goa, is a monsoonal estuary with an average depth of 5 m and width of the river mouth of 4 km. At the end of the monsoon, the Mandovi estuary becomes an extension of Arabian Sea with tidal currents. Tides in the Mandovi are mixed, semi-diurnal dominant (Sundar and Shetye, 2005). Detailed estuarine characteristics is reported by Vijith et al., (2009). Many mechanised fishing boats and barges carrying Fe and Mn ores may induce turbidity within the estuarine system. Anthropogenic activities in the estuary include industries, mining and discharge of domestic sewage (Alagarsamy, 2006 & Ramaiah et al., 2007).

### 2.2. Sample collection and analysis:

Estuarine water samples were collected along the salinity transects of Nethravati-Gurupur and Mandovi estuaries during pre-monsoon, monsoon and post-monsoon season. Nethravati estuary was monitored for two years (2010–11 and 2014–15) on a seasonal basis. In addition, vertical depth samples were collected during the post monsoon season from the estuarine and coastal region. The sampling was carried out during the low tide cycle with a fishing motor boat. Water and suspended particles were collected along the salinity gradient from freshwater endmember to seawater endmember. pH, dissolved oxygen (DO; mg L$^{-1}$), and salinity (psu) were measured on-site through a portable multi-parameter probes (HACH®). The salinity was cross checked for few samples at laboratory using Elico® salinity meter and salinity refractometer. Water samples were filtered in situ through 0.22 μm pore size polycarbonate filters (Nuclepore®). Filtered solutions for trace elements measurements were acidified with double distilled HNO$_3$ or HCl to pH < 2 and stored in pre-cleaned polypropylene (PP) bottles until analysis. Concentrations of major dissolved species were determined by ion-chromatography, alkalinity through auto-titrator, dissolved silica through spectrophotometer at the Indo-French Cell for Water Sciences, Indian Institute of Science, Bangalore.

The DMo concentrations in the estuarine water were determined by voltammetry-polarography (Metrohm VA797) at MIT, Manipal. The working electrode was set on a static mercury drop electrode (SMDE) mode with a mercury drop size 0.52 mm$^2$, silver electrode as reference electrode, and a platinum electrode as auxiliary electrode. Analysis was conducted by differential pulse adsorptive voltammetry. The method is based on adsorption of Mo complex 8-hydroxy-7iodo-quinoline 5 sulphonic acid (Sigma Aldrich, CAS547911), and 96% Suprapure sulphuric acid (Merck), potassium chloride (Merck, Suprapure) at the mercury drop. The samples were UV-irradiated in presence of H$_2$O$_2$ for one and half hours before analysis. An electrolyte (0.2 mmol L$^{-1}$ of Ferron, 0.7 mol L$^{-1}$ KCl, and 0.1 mol L$^{-1}$ H$_2$SO$_4$) of 2 ml was added to 10 ml of UV irradiated sample. The sample was then deaerated with