Sources and cycling of vanadium in a tropical coastal lagoon system and the Bay of Bengal

A Thesis

submitted in partial fulfilment of the requirements for the MSc Programme

by

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under the guidance of

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This thesis is dedicated to all my well-wishers.

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Certificate

This is to certify that this dissertation entitled **Sources and cycling of vanadium in a tropical coastal lagoon system and the Bay of Bengal** towards the partial fulfilment of the MSc programme at the Indian Institute of Science Education and Research, Pune, represents study/work carried out by **Raniria Mitra** at IISER Pune under the supervision of **Dr. Gyana Ranjan Tripathy**, Chair and Associate Professor, Department of Earth and Climate Sciences, during the academic year 2023-2024.

Dr. Gyana Ranjan Tripathy
(Supervisor)

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Declaration

I hereby declare that the research work presented in the report entitled **Sources and cycling of vanadium in a tropical coastal lagoon system and the Bay of Bengal** has been carried out by me at the Department of Earth and Climate Sciences, Indian Institute of Science Education and Research, Pune, under the supervision of Dr. Gyana Ranjan Tripathy and the same has not been submitted elsewhere for any degree.

Raniria Mitra

(MSc Student)

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List of abbreviations

BoB – Bay of Bengal

CEC – Cation exchange capacity

CPS – counts per second

GRASP - Geochemical Research for Aquatic and Sedimentary Processes

IMD - Indian Meteorological Department

Kyr – Kilo-years

NIST 1640a - National Institute of Standards & Technology 1640a

OC – organic carbon

OMZ – Oxygen minimum zone

PPE - Precleaned high-density polypropylene

PSU – Practical Salinity Unit

Q-ICP-MS – Quadrupole Inductively Coupled Plasma Mass Spectrometer

SGD – Submarine groundwater discharge

V – Vanadium

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Abstract

The aim of this study is to constrain coastal behavior and chemical budget of vanadium (V), a bio-essential element, in a tropical lagoon system (Chilika lagoon, India) and the Bay of Bengal. The Chilika lagoon, the largest brackish-water lagoon in Asia, is located on the east coast of India within the delta of the Mahanadi River. In this study, dissolved vanadium along the salinity gradient of the lagoon and its possible sources (river, ground water and Bay of Bengal) were measured using a Quadrupole Inductively Coupled Plasma Mass Spectrometer (Q-ICP MS) instrument. The V concentrations and salinity of the Chilika samples showed a wide range of variations during four distinct seasons, pre-monsoon (April-May, 2017; 34.9-69.4 nmol/L), onset of monsoon (June 2016; 26.8-46.5 nmol/L), monsoon (August 2017; 32-62.4 nmol/L), and post-monsoon (January 2018; 32.1-84.5 nmol/L) seasons. These concentrations are intermediate to that of the riverine input (16.9 ± 16 nmol/L), and groundwater (86.05 ± 126 nmol/L) samples. The average vanadium concentration for the BoB samples in this study is 45 ± 8 nmol/L (n = 45), for an average salinity of 34 ± 1 psu (n = 45). Surface seawater V concentrations of the west of the Bay of Bengal varies from 25.3-51.1 nmol/L with a mean of 41.2 ± 5.9 nmol/L. Considering the general trend, the variations in surface waters compared to depths is minimal with a few prominent deviations from conservative behavior. The vanadium-salinity data for the Chilika during the pre-monsoon and post-monsoon periods do not fall on the theoretical mixing between rivers and seawater. It depicts a non-conservative mixing behavior of vanadium in the Chilika lagoon, pointing to additional source of V to the lagoon. Although we hypothesize V supply through submarine groundwater discharge and/or desorption, our preliminary data are not sufficient to constrain the exact source for this system.

1 Introduction

1.1 Biogeochemistry of trace elements

Trace elements, despite their low crustal abundance, exert substantial control over the oceanic and continental biogeochemical processes. These elements, often masked by the presence of major elements, are essential in unfolding biotic and abiotic interactions. These elements serve as catalysts, cofactors, and structural components for numerous biological and biochemical reactions. Their interactions with major elements (such as, carbon, nitrogen, phosphorus, and sulfur) modulate the nutrient cycles, energy transfer pathways, and ecosystem productivity (Falkowski et al., 2008). Trace elements reflect physical, geological, chemical and biological information of an ecosystem; thereby, acting as proxies for paleo-climatic and -oceanographic studies. The cycling of trace elements varies among elements and within the chemical forms of these elements. The processes controlling the cycling of these elements progress with energy from the sunlight and nutrient supply, significantly affecting the environment.

Trace elements in seawater are classified into four types: conservative, scavenged, nutrient, and redox-controlled (Nozaki, 1997). The conservative elements are characterised with higher residence time (with respect to ocean mixing time ~1.6 kyr) and hence, have uniform concentrations (with depth and space) in global ocean. The nutrient-type elements get depleted in the surface water because of biological uptake, and are enriched in the bottom water by regeneration from particulate matter. The nutrient-type trace elements, such as Fe, Zn, Co, Cu, Mn, Ni, and Cd, often serve as cofactors for enzymes related to photosynthesis and respiration (Morel and Price, 2003; Sunda 2012; Twining and Baines, 2013; Lohan and Tagliabue, 2018). These elements show a range of concentrations in the photic zone of the water column in oceans and lakes owing to high biological activity and ocean circulation pattern. Phytoplanktons in this zone involve these elements for their cell structure and growth. So, a decreasing trend in concentration is seen for these elements in the photic zone (Bruland 1983; Fisher et al. 1984). The scavenged-type elements, namely, Fe, Mn, Co, Cr, Pb, Pu, Sn, Pa, and Th (Balistrieri et al. 1981; Santschi et al. 1980) undergo removal from the water column by forming nuclides in dissolved phases when particles settle through a lake, estuary or ocean. Scavenging depends on the chemical nature of the particle surface.

Trace element distribution in the modern ocean is controlled by their sources (continental fluxes, atmospheric deposition, hydrothermal activities and sea-floor alteration) and sinks (authigenic and biogenic mineralization) (Murray, 1987; Anderson and Henderson, 2005).

However, additional processes of release (submarine groundwater discharge-SGD, desorption, mineral redissolution) and removal (biological uptake, clay/sediment adsorption, mineral coprecipitation) of trace elements complicate their coastal inventory. The impact of these processes at the fresh-sea water interfaces is mostly controlled by chemical (pH, salinity, and ionic strength), physical (sediment load and tidal cycles), and biological factors (Charette et al., 2016; Samanta and Dalai, 2016).

The SGD is a process by which continental groundwater discharges directly into the sea, when connected to a coastal aquifer. Sometimes these aquifers have fractures and cracks which permeate groundwater into the sea (Cho et al., 2018). The SGD-driven flux is an important source of trace elements, nutrients, carbon and metals to coastal waters (Moore, 2010). The SGD flux vary according to tidal cycles on a diurnal scale, water table elevation changes on a seasonal scale based on rainfall and evapotranspiration effects, and aquifer heterogeneity on a spatial scale (Knee and Paytan, 2011). Ion-exchange processes like desorption (release of adsorbed molecules from a substrate) and adsorption (metal ion adsorption on inorganic and organic substrates based on their surface reactivity) also contribute to the coastal trace element inventory (Coeffy et al., 1997). The cation-exchange-capacity (CEC) of an oxide substrate favors adsorption in higher pH (7-9) of natural waters compared to higher salinity. Clays have higher CEC and hence, higher potential for participation in adsorption (Carrillo, 1998).

Increasing order of timescale (T_c) for equilibration of trace elements depends on the dissolved organic carbon peptization and particulate organic carbon coagulation, $T_c = 10^{-2}$ to 10^2 d (Huang et al., 2015). This process can regulate the concentration of organically complex elements such as Cu, Pb and Hg. These reactions are important for coastal system because of high organic loading and in estuarine system large gradient of ionic strength (Kerndorf and Schnitzer 1980). Other process like clay reconstitution maintains element concentration in sediments having higher affinity for clay minerals, $T_c = 10^1$ to generally > 10^5 d, e.g., Si, Al, and B (Mackin 1986, 1987; Mackenzie and Garrels 1966). The cycling of redox-sensitive and nutrient-type elements depends on organic carbon degradation by bacterial action (Bacterial Degradation) of subsurface water and sediments. Some of these redox-sensitive elements (Co and Mn) are mobilised in a reducing (anoxic) environment, and others like Cr, Se, U, Pu, and V are mobilised in an oxidising (oxic) environment.

1.2 Vanadium cycling

Vanadium (V) is a nutrient-type element with redox-sensitive properties. The average crustal abundance of vanadium, owing to its lithophile nature, is 97-230 μg/g (Taylor and

McLennan, 1981; Condie, 1993; Taylor and Mclennan,1995; Gao et al., 1998b; Rudnick and Gao, 2003). Generally, vanadium is found as a refractory element in igneous (e.g., granites, rhyolites, basalts) and sedimentary rocks (sandstone, shale, limestone) types. Volcanic emissions, continental dust and marine aerosols are the major natural sources of vanadium to the atmosphere (Huang et al., 2015). Post-industrial revolution, vanadium concentration drastically increased due to burning fossil fuels, mining, smelting, and coal production, which acted as the primary anthropogenic sources. These aerosols mix with rainwater and precipitate on the crust, enriching the soil vanadium concentration (global average ~90 μg/g; Hope, 2008). Weathering and soil erosion release vanadium from the crust, mobilise through fluvial action and deposit this sediment-rich vanadium in lakes, estuaries and oceans. This initiates the primary cycle of vanadium distribution in water bodies. The cycle of vanadium in dissolved phases is largely controlled by Eh, pH and oxygen availability. In neutral pH, V(V) is the dominant species, whereas in acidic conditions, VO_2^+ dominates and VO_4^{3-} in extremely alkaline conditions (Wehrli and Stumm, 1989; Wanty and Goldhaber, 1992).

The solubility of vanadium is dependent on its several oxidation states. Vanadium occurs on the Earth's surface in +3, +4, and +5 oxidation states. Vanadium's nature of chemical speciation produces different complexes according to its oxidation state. V (V) is present in oxic conditions as HVO_4^{2-} and $H_2VO_4^-$. Usually, V(IV) species are VO^{2+}, $VOOH^+$, and insoluble $VO(OH)_2$ (Rehder, 2008a; Rehder, 2008b). In anoxic conditions, V(III) forms from vanadyl species, which forms solid oxides like V_2O_3 and $V(OH)_3$ that accumulate in sediments (Fig. 1). V(V) is the dominant species of vanadium in oxic and alkaline aqueous conditions. Hence, vanadium accumulation in marine sediments drastically changes with f_{O_2} in the ocean (Shaw et al., 1990; Wanty and Goldhaber, 1992; Tribovillard et al., 2006). An increase in salinity decreases the adsorption of V(V) (Huang et al., 2015). Further, environmental setting is an essential factor in the chemistry of vanadium in solution and its control on the ecological aspects. Phytoplanktons like green algae and diatoms stimulate growth by utilising vanadium. Soluble vanadium is generated through the interaction of source materials, the solution's chemical composition, and sorbing colloids. The global concentration of vanadium in rivers is ~ 36.2 nmol/L (Shiller and Boyle, 1987). Low dissolved vanadium concentrations in the streams signify a strong iron (Fe) association in particulate or colloidal forms (Wällstedt et al., 2010). However, the concentration of dissolved vanadium in rivers is mostly related to weathering of source rocks. In regions similar to Wyoming River, U.S.A., the concentrations are as high as ~30-220 mg/L (Schroeder, 1970; Shiller and Boyle, 1987), attributing to active mining actions. Vanadium concentrations in water are regulated seasonally. A study in Long Island Sound (Wang and

Sañudo Wilhelmy, 2009a), Toyko Bay and Shimizu Port, Biwa Lake (Sato and Okabe, 1978; Sato and Okabe, 1982) and Florida Bay (Caccia and Millero, 2003) reported high concentrations of dissolved vanadium during summer in fresh and marine waters. There are multiple factors that cause seasonal variability in vanadium concentration. Eh, and pH are two major factors playing a vital role in vanadium's association with particulates in the water. Vanadium concentrations could also be attributed to photoreduction in an acidic stream, showing diel variation (Kay et al., 2011).

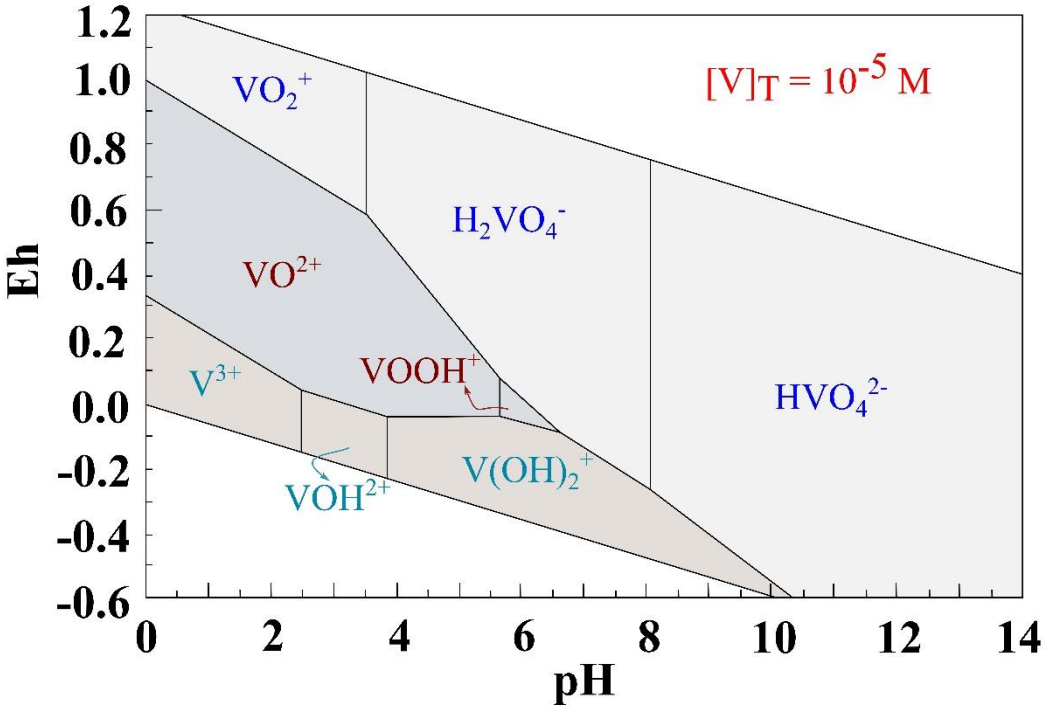

Fig. 1 Eh-pH predominance for vanadium speciation in soluble form [modified from Huang et al., 2015]

Vanadium is one of the most abundant trace elements (like molybdenum) in marine settings. Its concentrations in the open ocean are ~35-45 nmol/L (Emerson and Huested,1991). Additionally, marine hydrothermal vents also supply vanadium to the oceans. Mid-oceanic ridge sediments have a concentration of ~400 µg/g of V (Bostrom and Fisher, 1971). Vanadium shows conservative behaviour in open oceans, but in coastal waters, it behaves non-conservatively with relatively lower concentrations (Wang and Sañudo Wilhelmy, 2009b). Studies highlight the affinity of vanadium in the open ocean to stay in the dissolved phase compared to the particulate phase (>0.45 µm). Estimates for the global ocean depict the dissolved vanadium reservoir at 2.7 × 10^{15} g V compared to that of the suspended particulate reservoir (1.8 × 10^{10} g V; Hope, 2008). Considering its global circulation, ocean bed sediments are the largest and ultimate sink of vanadium, with an estimated reservoir at 1.7 × 10^{20} g V. This vanadium is stored mainly in carbonaceous sediments and marine shales (Ekstrom et al., 1983). Chemical signatures of

vanadium are preserved in these marine sediments, serving as a paleo-proxy.

As a nutrient element, vanadium is also used for biological uptake in microbes, phytoplanktons and aquatic plants. Microorganisms are responsible for vanadium transformations. Chemoautotrophic *Thiobacillus species* change insoluble V(III) and V(IV) to soluble V(V). Silicate bacterium like *Bacillus mucilaginous* cause bioleaching of vanadium from muscovite and quartz (Dong et al., 2020). Studying the geochemical behavior of vanadium helps to understand the accretion of the Earth and the interface of its inner layers. Other processes like weathering, diagenesis and biological uptake regulate the concentration of vanadium in every biosphere interface.

1.3 Importance of coastal ecosystems

Coasts are the interface region between the ocean and the continent. Multiple processes act on the coastal ecosystem, making it rich in biodiversity. Rivers and sea mixing zones create a range of salinity suitable for fisheries and shrimp cultivation. Sediments deposited by the rivers have a variety of nutrient-rich minerals. The physical behavior of oceans and fluvial action associated with the riverine sediments form certain geomorphological features like estuaries and deltas. These ecosystems are crucial for the habitability of mangroves and wetlands. Mangroves and wetlands play a significant role in global warming. They both release (source) and take up (sink) CO_2 (carbon sequestration), a major greenhouse gas (Twilley et al., 2017). Generally, the carbon is stored in soils and their biomass, wherein processes like respiration and decomposition release CO_2. Trace elements and the biogeochemical cycle in this region also enhance the productivity and biological uptake, contributing to the organic carbon (OC) cycle. Vanadium has lower concentration and shows non-conservative behavior in coastal environments (Wang and Sañudo Wilhelmy, 2009b).

Comprehending the behavior of trace elements, such as vanadium, in coastal ecosystems is essential to assess the related biogeochemical processes. This shall enhance understanding of these shallow and semi-restricted coastal lagoons, which influence the ultimate nutrient delivery to the oceans. The Chilika lagoon (India) is situated in one such ideal environment, consisting of peculiar habitats, intense productivity patterns, large biodiversity (heterotrophy), and numerous geological processes, making it a unique environmental setting with a higher carbon burial efficiency. Investigations on the trace element biogeochemistry of this large tropical lagoon system (Danish et al. 2019, 2020, 2021) are sparse. In this thesis, an attempt has been made to evaluate the distribution of vanadium in the Chilika lagoon and the Bay of Bengal. This shall provide insights into the budget of vanadium along this coast by evaluating the ultimate

delivery of vanadium to the Bay of Bengal. In this contribution, an assessment of the dominant sources and sinks of this element shall enhance the understanding of coastal behavior. In this regard, the following objectives have been structured.

1.4 Objectives

The main objectives of the thesis work are as follows:

- To identify the source, sink and processes of the biogeochemical cycle of vanadium in the Chilika lagoon, India.
- To estimate the vanadium budget of the Chilika lagoon and identify the associated biogeochemical processes that regulate this budget.

1.5 Structure of the thesis

The overall structure of the thesis can broadly be divided into the following sections:

Chapter 1 introduces the biogeochemical cycling of vanadium and its importance in coastal and open oceans.

Chapter 2 describes the study area (Chilika lagoon, India), its geohydrological settings. It also provides the analytical protocol adopted during this study.

Chapter 3 presents the spatial and seasonal data for the Chilika and the Bay of Bengal. These data are also discussed to establish the sources and cycling of this trace element in these settings.

Outcomes from this thesis work are summarized in the **Chapter 4**. It also highlights the future scope of this research in identifying and quantifying the elemental budget associated with these biogeochemical cycles.

2 Material and Methods

2.1 Study area

The Chilika lagoon is the largest brackish water lagoon in Asia and located on the eastern coast of India (Sahu et al., 2014). This is a pear-shaped lagoon with a basinal areal of 4300 km^2 and shallower water depth (< 2 m). The water spread in monsoon (August-October) is 1020 km^2 (Gupta et al., 2008), which reduces by 60% in the pre-monsoon (April-May) season. It receives 14,331 million km^3 of freshwater annually from several rivers and rivulets, namely Daya, Bhargavi and Nuna (Panigrahi et al., 2009). The lagoon can be divided into three sectors (Fig. 2). The northern sector mainly receives the freshwater via the distributaries of Mahanadi. This lagoon is a Ramsar wetland site in India (declared in 1981). It is an important area for breeding, wintering and staging for various waterbirds. During the annual migration season, the Chilika is also the abode of various migratory birds like pelican flamingos and herons. It also acts as a refuge for endangered species like the Irrawaddy dolphin and Olive Ridley sea turtle. Unique habitats like mudflats, marshes, sandbars, and islands form a breeding and feeding ground for these species. Thousands of fishermen rely on Chilika for fishery, aquaculture and tourism.

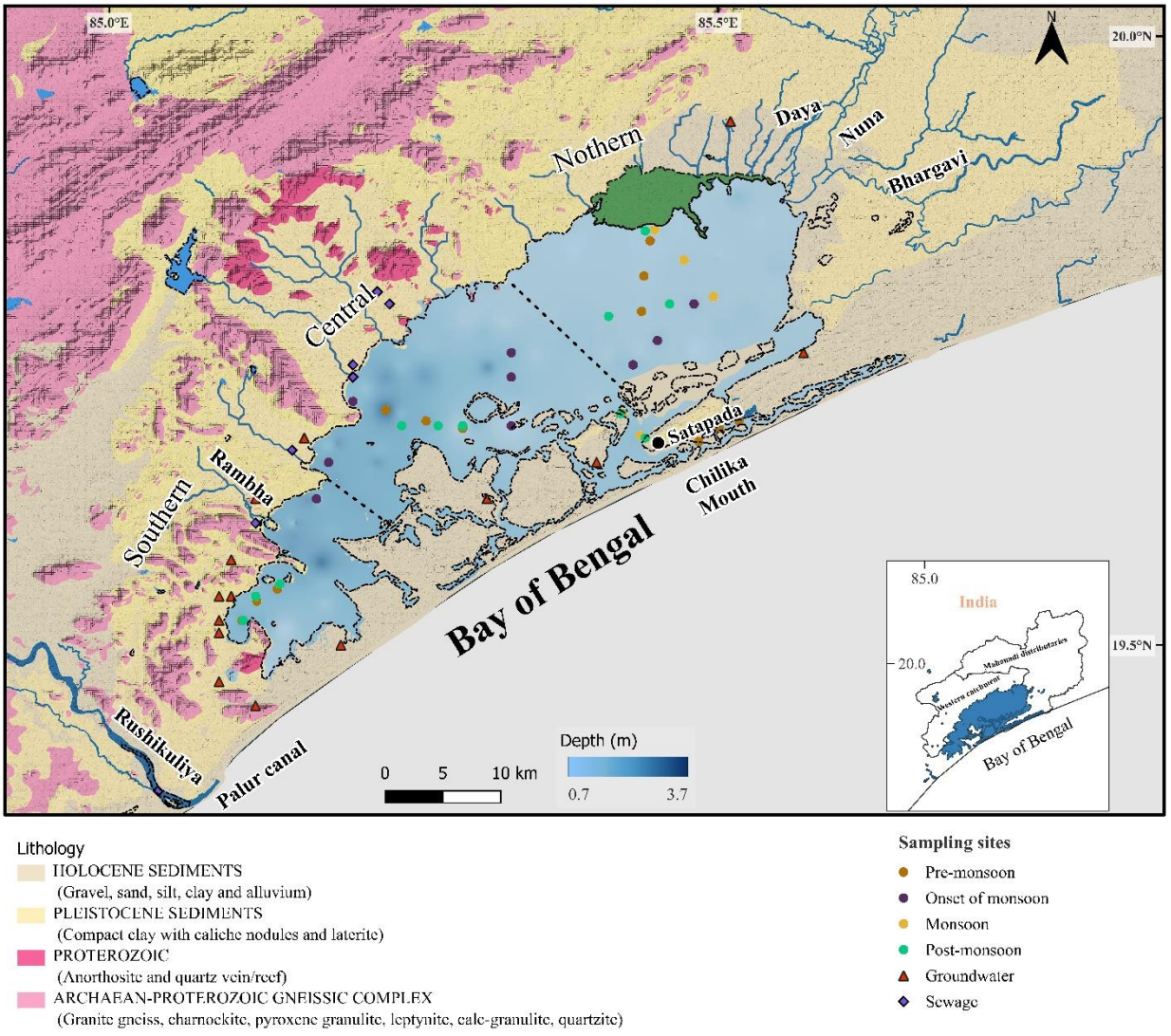

Fig.2 Lithology, geology, geomorphological features, and sampling locations of Chilika in spatial and temporal resolutions.

2.2 Climatic conditions

The Chilika lagoon basin typically has a sub-humid, and tropical monsoon climate. The average annual temperature varies between 14.0º C and 39.9º C (Fig. 3). It receives about 75% of its annual rainfall during the monsoon period. The average rainfall in the catchment is 1300 mm during the monsoon season (June – September; Fig. 4). The wind speed along the coastal track shows seasonal and diurnal variations. The speed is high from March to July and decreases during winter. The wind speed varies from 5.3 km/hour to 16.0 km/hour due to the southwest monsoon's influence (Sarkar et al., 2012; Tomy et al.,2022). Usually, the wind blows from the south and southwest direction from February to September. The wind blows north and northwest for the remaining months (October to January) (Tripathy et al., 1995). This process creates a clockwise wind circulation in the lagoon during winter (Panigrahi et al., 2007). Rapid variation

in wind speed and temperature often contributes to many high-order magnitude cyclones on the east coast of India. Wind stress, tides, and freshwater input also influence the water circulation in Chilika.

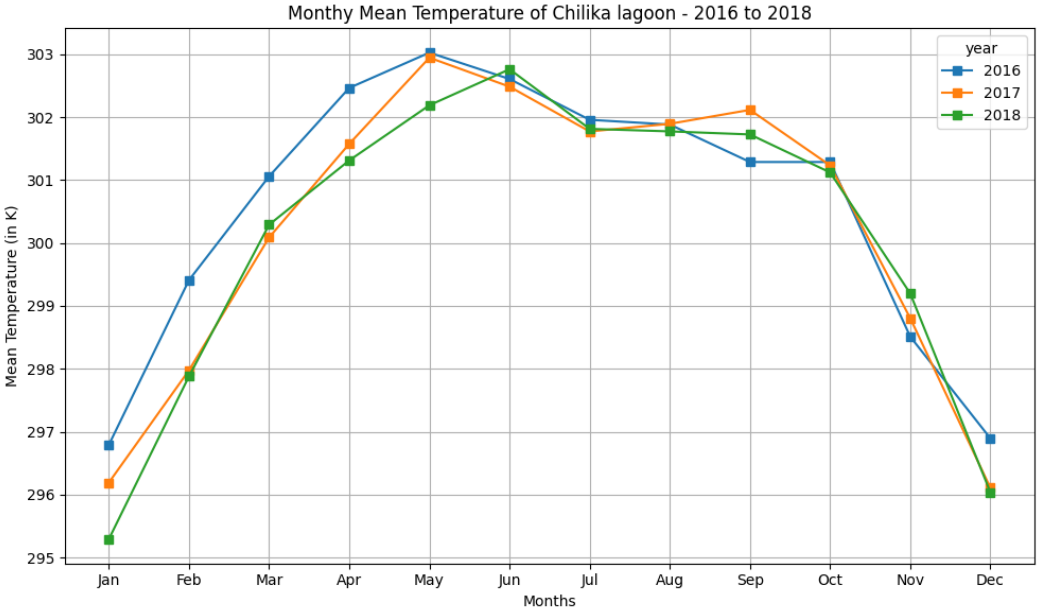

Fig. 3 Monthly mean average temperature (in Kelvin) of the Chilka lagoon for 2016, 2017, and 2018 (Data collected from ERA 5).

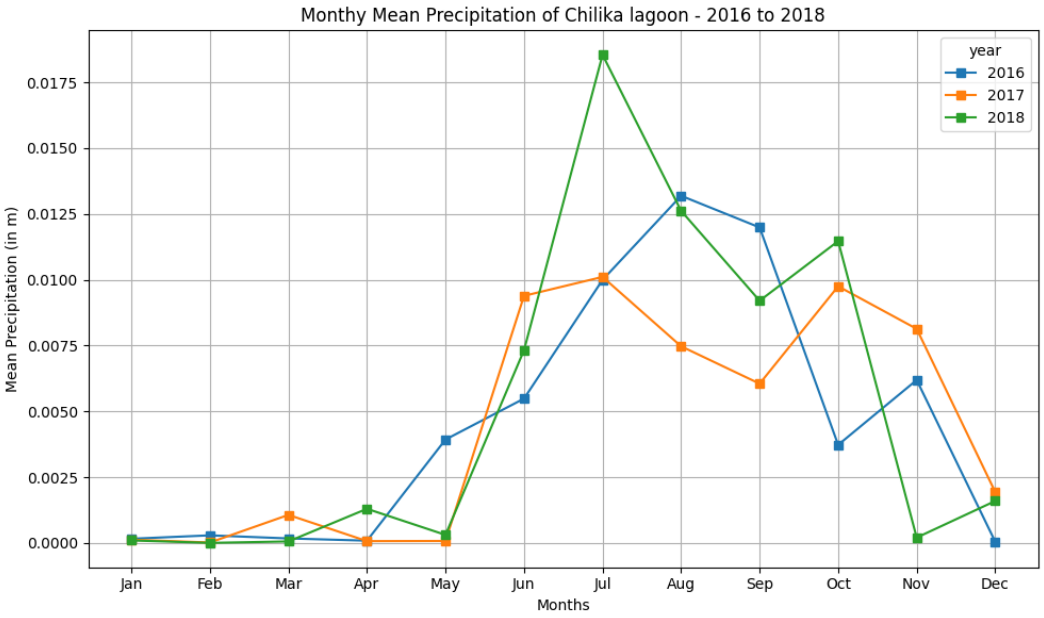

Fig. 4 Monthly mean average precipitation (in meters) of the Chilka lagoon for 2016, 2017, and 2018. (Data collected from ERA 5).

2.3 **Hydrology**

A coastal lagoon like Chilika mostly receives water from rivers (freshwater) and sea. During monsoon, this lagoon swells up to 1020 km^2, due to which freshwater discharge increases by

two orders of magnitude (170×106 m^3 d^{-1}) compared to the pre-monsoon period (4×10^6 m^3 d^{-1}) (Kumar and Pattnaik, 2012). Several rivers and rivulets act as a source of freshwater in the lagoon. In the northern catchment, 75% of freshwater is brought by Mahanadi distributaries, namely Daya and Bhargavi. The remaining 25% of freshwater input is from the western catchments (Kumar and Pattnaik, 2012). The annual discharge of freshwater from Daya and Bhargavi is 5.1 x 10^{12} L/yr (Muduli et al., 2012). Besides the freshwater sources, the hydrology of the Chilika is also controlled by seawater influx. Due to its location on the east coast of India, Chilika is seawater fed from the Bay of Bengal through a 32 km opening in the central sector. An artificial channel, the Palur canal, has been created in the southern section for the mixing of saline water and fresh water. Fortnightly (12 days) and semi-diurnally (12.4 hours), the tidal cycle also plays a significant role in the water exchange between the lagoon and the Bay of Bengal.

2.4 Geology

The Chilika is located on the coast of the Eastern Ghat mobile belt. Its lithology comprises of metamorphic and igneous rocks such as charnockites, garnets, khondalites, leptynites, and gneiss (Kumar and Pattnaik, 2012). These rocks are rich in quartz, feldspar, orthoclase and pyroxene. The felsic component is dominant in these rocks. The Gondwanas also contribute rocks like sandstone, shale, and limestones. Coastal processes and sediment input from rivers make this region rich in alluvium. The basin lithology consists of 34% granite suite, 7% khondalite, and 15 % charnockite suite. The remaining 44% is sandstone, shale, limestone and alluvium (Chakrapani and Subhramanian,1990). The eastern mobile belt is also rich in coal, limestone, dolomite, bauxite, lead, copper and iron deposits.

2.5 Sampling

Spatial collection of water and sediment samples from the Chilika lagoon was carried out during four different seasons (Danish, 2021). The spatial sampling was conducted in four field trips: during the onset of monsoon (June 2016), pre-monsoon (April-May 2017), monsoon (July-August 2017), and post-monsoon (January 2018) seasons. These samples were collected as part of several field excursions by GRASP (Geochemical Research for Aquatic and Sedimentary Processes) laboratory members and are stored in sample archive at IISER-Pune. Selected samples from this collection were used in this study. These water samples are from all four sectors of the Chilika lagoon and its possible sources (e.g., the Bay of Bengal (BoB), rainwater, rivers and groundwater). As the tidal cycles play a major role in changing the water chemistry, one-day spatial sampling of the whole lagoon at two-hours interval was also carried out during

monsoon (16th August, 2017) and post-monsoon (10th, January 2018) seasons for comparison. There were two significant rainfall events (during mid-November, BOB-06 cyclone and early-December, BOB-08 cyclone; Indian Meteorological Department - IMD) caused by low depression developed over the BoB during the post-monsoon sampling. Freshwater sources (rivers and groundwaters) were sampled from the Mahanadi distributaries in the northern catchment and small rivers/rivulets in the western catchment that contribute to Chilika.

Additionally, seawater samples were also collected by GRASP laboratory members from the surface and various depths at 5 stations during September - October 2021 onboard ORV Sagar Kanya, cruise SK -373 (Fig. 5). The sampling was carried out in the BoB along a trajectory off the coast of Chennai, India, along ~80° - 95°E meridians of longitude and ~11° - 14°N parallels of latitude.

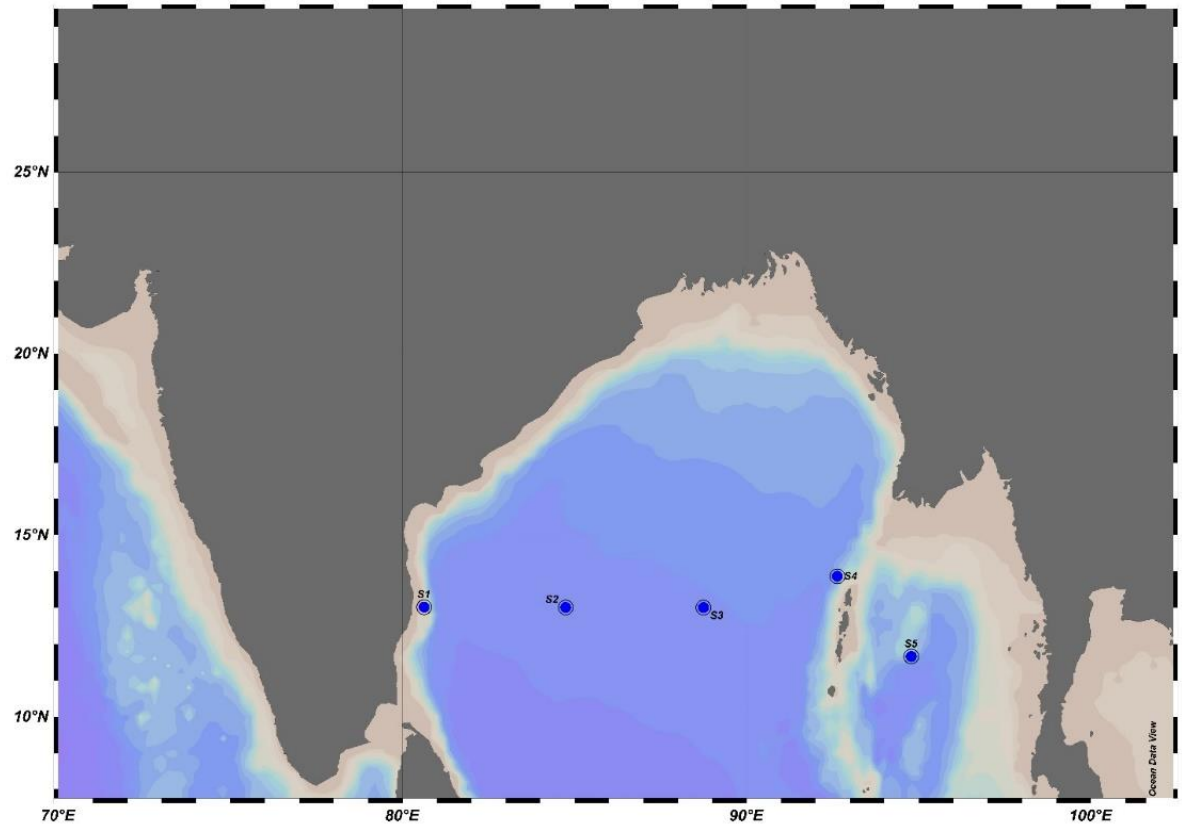

Fig. 5 Sampling locations in the Bay of Bengal collected during September - October 2021 onboard ORE (Ocean Research Expedition) Sagar Kanya, cruise SK-373 [Figure created using Ocean Data View}.

Portable multi-parameter probes were utilised onboard to monitor the water temperature, pH, salinity, and dissolved oxygen (DO) of the samples. All the collected samples were filtered within 24 hrs using a vacuum filtration system and 0.45 μm nylon filters. This ensured the removal of the suspended particles and micro-organisms. All the filtered samples were stored in precleaned high-density polypropylene (PPE) bottles and acidified with high-purity HNO_3 to

reduce the pH to ~2. Acidification allows the dissolved ions to stay in their mobile phase and aids in arresting additional biological growth in the water samples.

2.6 Quadrupole – Inductively Coupled Plasma Mass Spectrometer (Q-ICP MS):

In this study, the quadrupole inductively coupled plasma-mass spectrometer (Q-ICP MS; Thermo iCAPQ) was used to analyze the trace element. This mass spectrometer uses a quadrupole mass analyser to separate and detect ions. There are four major principal components in ICP-MS: sample introduction, ionisation, separation of ions and detection (Potts, 2012).

2.6.1 Sample introduction

The sample introduction system of this instrument is designed for liquids. An autosampler injects ~100 μL of the sample to be analysed for a single measurement. A peristaltic pump system delivers the sample from the autosampler to a nebuliser. The nebuliser aerosolises liquid samples before being introduced to ICP. The aerosolised samples from the nebuliser enter the spray chamber, where it selectively filters out the large aerosol droplets (>10 μm diameter) by gravity. A constant temperature of 2°C is maintained in the spray chamber to reduce the formation of oxides and prevent solvent overloading in the plasma. Because of its inert behaviour, argon (Ar) is used for plasma generation to reduce chemical interference. The ionisation energy of Ar is 15.75 eV, which is higher than any other element so that it can detect a wide range of elements. The job of plasma is to ionise the samples. The plasma is formed at the opening of the torch (three concentric quartz tubes). The injector or the inner tube contains the sample (aerosol phase) in a stream of Ar, which is delivered to the plasma. The other tubes act as a coolant by giving a constant flow of Ar to keep the torch from melting, and it stabilises the plasma. A load coil (made of copper) is connected to the RF generator at the end of the torch. The coil has two to three turns, which pass water for cooling.

2.6.2 Ionisation

The load coil gets a power supply from the RF generator, creating a high frequency of alternating current. However, the power is not supplied to the torch if a few electrons from the tesla coil do not form Ar gas. These electrons undergo extreme oscillations; the collisions from the electrons and atoms cause further ionisation of the argon gas. These rapid collisions and ionisation rapidly increase the temperature to 10000 K. After this process, samples are introduced into the plasma in aerosol form. The free electrons generated in the plasma collide with the sample atoms, forming positive charges. These sample atoms follow the same process of rapid collision and further ionisation. An electric field removes neutral materials through the

rapid acceleration of the ionised sample atoms within the plasma.

2.6.3 Separation of the ions

The samples pass through the sample cones made of platinum or nickel (1 mm diameter) and then through the skimmer cones (0.45 mm diameter). The sudden influx of samples causes a dramatic change in pressure, which causes a free jet to enter the vacuum chamber. To maintain the vacuum, 7×10^{-5} - 1×10^{-3} Pa pressure is generated by the turbomolecular pump. The electrostatic lens guides the sample ions to the Qcell (quadrupole cell). The Qcell consist of the quadrupole flat rods in a semi-contained region. The Qcell can remove undesirable molecule ions by pressurising through chemical reactions in kinetic energy mode (KED mode). The ions are separated by the mass-to-charge ratio by a quadruple mass filter depending on the RF and DC voltage. The transmitted ions are transferred to the dual-mode Secondary Electron Multiplier (SEM) for detection.

2.6.4 Detection of ions

The ions transmitted from the mass quadrupole are distinguished with the help of a detector. Earlier instruments worked with a fluorescent screen as a detector. In modern days, four categories of devices are known. These are the Faraday cup, Daly detector, electron multiplier and photographic plate. A detector measures the counts/abundance of ions. This instrument makes the use of an electron multiplier setup. When the ion reaches the detector, it causes the emission of multiple electrons from the surface, which strikes the dynode. This process is called secondary emission. In this way, the electron multiplier measures the impact of a single ion on the detector.

2.7 Trace element analysis

The vanadium concentration (V_{conc}) in the dissolved phases was measured using a quadrupole-inductively coupled plasma mass spectrometer (Q-ICP MS; Thermo iCAPQ) facility at IISER Pune in the kinetic energy discrimination (KED) mode. For this analysis, the filtered and acidified aliquots of the saline water samples were diluted to a salinity of ~1 psu with 2% HNO_3 to minimise the matrix effect. Batch analyses of 150 water samples (50 freshwater, 50 lagoonal, and 50 oceanic) were adopted to evaluate the spatial variations of V along the entire catchment and the open ocean. Background corrections were avoided owing to insignificant blank contribution (avg. ~20 cps; n = 101) to the sample signal (avg. ~7600 cps; n = 150) with an average Signal:Noise (S/N) ratio in orders of 10^2 (Table A2). The instrumental measurement of each sample was undertaken 3 times, the average of which is reported in this work. A standard deviation of ± 5 % (n = 226, including samples and standards) for these 3 runs

per sample confirms the instrumental precision (Table A1); thus, correction for instrumental drifting was avoided.

A standard calibration method was used to assess the accuracy of these analyses. For lagoonal (Chilika) and oceanic (BoB) samples, 1000 µg/mL Vanadium in 2% (v/v) HNO_3 stock solution (I.V. Labs, Inc.) was used for standard aliquot preparations. These standard aliquots were doped with sodium chloride (NaCl) solution (salinity ~1 psu) to account for the matrix effect of the saline samples. Two open ocean samples from BoB (Leg 2-02; salinity = 32.8 psu and Leg 2-03; salinity = 33.1 psu) were also measured (Danish,2021) continuously (n=26) during the analyses. The average V_{conc} (~46 ± 3 nmol/L) of these samples (salinity = 33 ± 0.2 psu), when extrapolated to 35 psu salinity, yields V_{conc} of ~48 ± 3 nmol/L (Table A3), which is consistent with that reported for the global ocean (~40 ± 7 nmol/L; Huang et al., 2015). For freshwater (riverine and groundwater) samples, ICP multi-element standard solution XVI-21 elements in diluted HNO_3 (Merck Supelco. Certipur®) was used for standard calibration. Diluted aliquots of the standard reference material for trace elements in natural water, NIST-1640a (2% HNO_3), were measured with an average V_{conc} = 14.54 ± 0.17 µg/L (n = 3) during the analyses. These measurements are consistent (within ~3 ± 1%) with the reported certificate value (15.05 ± 0.25 µg/L). The average precision of replicate measurements of several samples was ± 4% (n = 15; Table A1).

3 Results and Discussion

Data on water pH, temperature, salinity and vanadium concentration data for Chilika lagoon, rivers are provided in Table A5, and Bay of Bengal samples are provided in the Table A4. These data include spatial and seasonal variation of dissolved vanadium in the Chilika lagoon system.

The average concentration of vanadium in the river is 16.3 ± 14.17 nmol/L (n=10). Outer channel samples were not taken for average as they had higher salinity, indicating seawater intrusion. Similarly, for surface seawater (Bay of Bengal), the average concentration of vanadium is 41.27 ± 5.93 nmol/L (n=24), and the salinity is 32.08 ± 2.15 psu (n=24).

3.1 Distribution of dissolved vanadium in the Bay of Bengal

The average vanadium concentration for the BoB samples is 45 ± 8 nmol/L (n = 45), for an average salinity of 34 ± 1 psu (n = 45). These data when normalized to a salinity of 35 although match well with the global reported value for seawater vanadium (35-45 nmol/L; Emerson and Huested,1991), it falls closer to the higher values of the data spread. Our data are based on analyses with lower (a few hundred cps) counts, but could reproduce the V data reported for NIST-1640a reference material. Hence, these variations although cannot be attributed to analytical issues alone, these samples are planned to measure again to confirm the data. Fig. 6 shows variations in V concentration normalized to salinity 35 psu, $[V]_{norm}$, for the five sampling stations in this study. Surface seawater V concentrations of the west of the Bay of Bengal varies from 25.3 nmol/L - 51.1 nmol/L with a mean of 41.2 ± 5.9 nmol/L, which is comparable to the global average (~40 ± 7 nmol/L; Huang et al., 2015). The salinity ranges from 27 - 34.3 psu, averaged at 32.07 ± 2.14 psu.

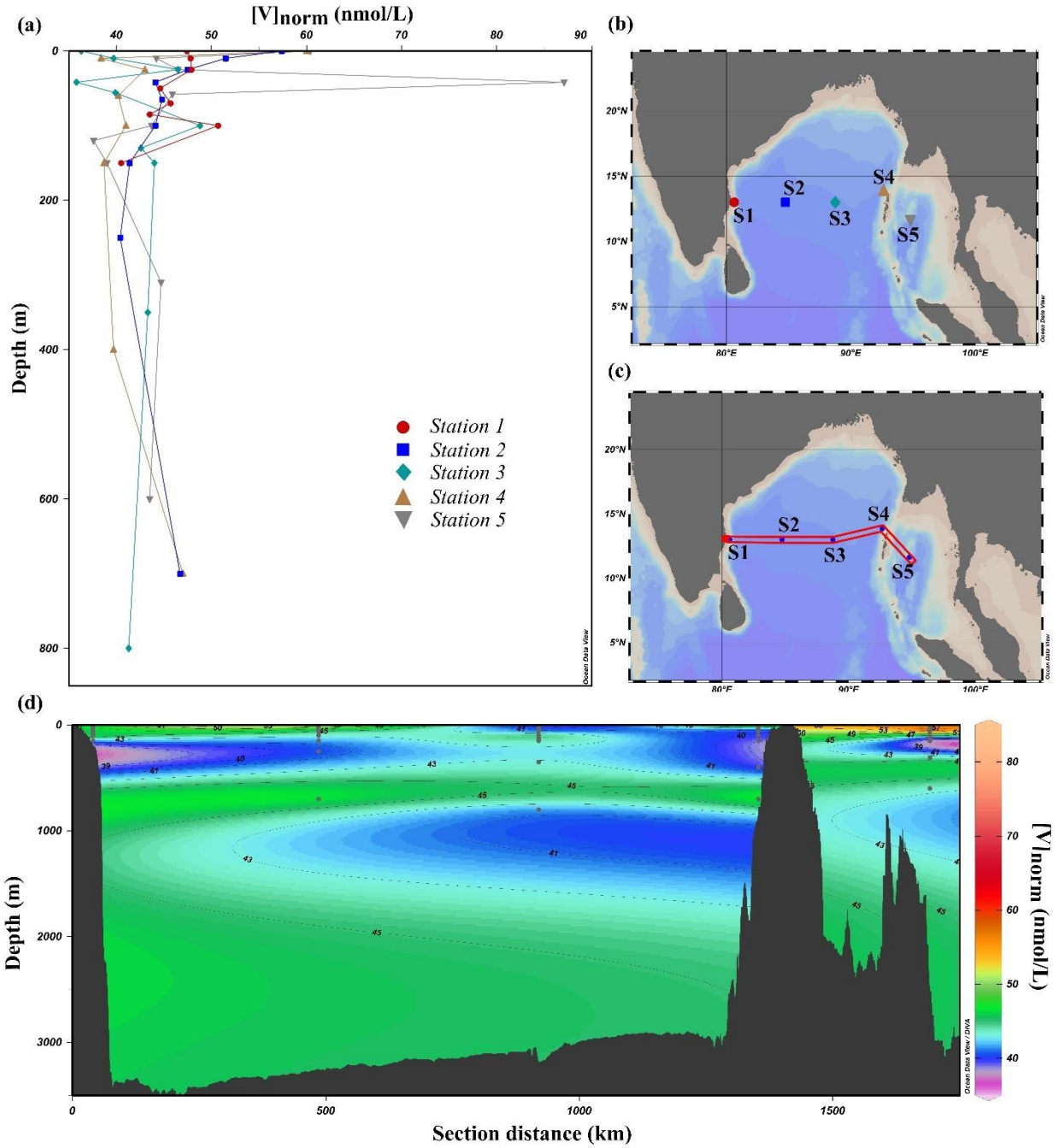

Fig. 6 Distribution of $[V]_{norm}$ along the Bay of Bengal. (a) Station-wise variation of $[V]_{norm}$ with depth; (b) Station locations in the Bay of Bengal across the transect of sampling; (c) Transect (~40km width) considered for the spatial (lateral and vertical profiles) interpolation of $[V]_{norm}$; (d)Spatially interpolated $[V]_{norm}$ across stations and along depths, using variational analysis (figure created using Ocean Data View).

The distribution of $[V]_{norm}$ along the vertical profiles of all the stations depict a general trend of minimal depletion with depth, except for station 3 which portrays otherwise (Fig. 6 (a)). However, considering the variations within stations, no significant spikes in the general pattern of enrichment or depletion is observed between the surface and the bottom waters, except for station 5. The average $[V]_{norm}$ along the vertical profiles of stations 1-4 (46 ± 3, 46 ± 5, 42 ± 4, and 44 ± 7 nmol/L, respectively) are comparable with the global average (~40 ± 7 nmol/L;

Huang et al., 2015). Except the highest observed $[V]_{norm}$ (~87 nmol/L) at a depth of 42 m, the average concentration for station 5 (45 ± 6 nmol/L) also follows a similar trend. These observations tend to agree with the proposed conservative behavior of vanadium in modern ocean owing to its high residence time (~50-100 kyrs; Morris, 1975; Emerson and Heusted, 1991). However, the observed variations in the upper-photic zone of all the stations prompt further investigations to better understand the behavior of vanadium. Towards this, a spatial interpolation of $[V]_{norm}$, using variational inverse model, was adopted to reconstruct a continuous field along the entire stretch of the transect with respect to its depth profile. To achieve this, a section plot was created to represent depth vs. $[V]_{norm}$ with respect to the transect basin (with bathymetry) using the software of Ocean Data View (Fig.6 (d)). The bottom depths of stations (2-5) covered in this study are lower (by value) than the actual bottom water depths of the Bay of Bengal in those regions. Hence, the interpolation adopted uses a quality limit of 14% resolution to account for the entire depth profiles. The section plot highlights higher variation densities within 150 m depth of the water column in all the stations.

Surface depletion indications of $[V]_{norm}$ is not pronounced in stations 1-5 (except 3) which is similar to that observed for the Atlantic Ocean (Morris, 1975; Jeandel et al., 1987) indicating either a minimal effect of biological uptake or a balance between biological uptake by riverine and atmospheric inputs as well as physical exchange with deeper water (Middelburg et al., 1988). Riverine inputs may be attributed to explain surface $[V]_{norm}$ at stations 1,4 and 5 considering their coastal environment. Station 1 is situated on the shelf near the eastern coastal margin of India, off the Godavari basin. The V concentration of clastic sediments in the Godavari basin has been estimated at ~298 µg/g (Vuba et al., 2015) which could be a potential source of enrichment in the basin aquifers. Considering ~10-48% contribution of SGD to the water budget of Godavari estuary (Damodararao and Singh, 2022), it could be a possible source of higher vanadium concentration in the surface water of station 1. A relatively higher surface $[V]_{norm}$ concentrations at stations 4 and 5 may be attributed to the continental input from the Andaman Islands where beach rocks (avg. $[V]_{norm}$ ~340 nmol/L) and suspended load of detrital minerals with vanadium in their lattice sites, could be potential contributing sources (Chandrasekaran et al., 2015). Besides continental input, the lack of surface depletion from station 2 may be attributed to physical exchange with deeper water considering the seasonal impact of mixing during the sampling period (September, 2021) when BoB experiences wind-driven upwelling (Jana et al., 2018). Contrastingly, surface water depletion in $[V]_{norm}$ (~36 nmol/L) at station 3 is observed which is consistent with observations in the Pacific Ocean (Collier, 1984) and could be possibly linked to higher biological uptake in the open BoB during September, with primary productivity (PP) averaged at ~1280 mg Cm^{-2} d^{-1} (Madhupratap et al., 2003).

The $[V]_{norm}$ concentrations along all the stations show a dip between 40-50 m depths except station 5. This sudden dip measures at 35.8 nmol/L for station 3, the lowest observed value in this study. The observed decrease may be attributed to the highly productive mixing zone in the photic depths of BoB resulting in removal by biological uptake (Collier, 1984). Further, this observation could also be attributed to authigenic removal of vanadium due to change in the redox conditions of the water column since cyclonic eddies intensify the oxygen minimum zone (OMZ) of BoB (Sarma et al., 2018). The spike in station 5 at 42 m depth ($[V]_{norm}$ ~87 nmol/L) is the highest observed in this study. Station 5 is located near the western coast of the Andaman Sea and Barren Islands, which has a coral cover on shallow reef flats (Brown et al., 2011). These reefs are subject to semi-diurnal tides (Gibson et al., 2007) which hints at coralline and shelf sediment redissolution of vanadium as causative processes for this abrupt increase in $[V]_{norm}$.

The variation observed within 100-200 m depths for all stations show an increasing trend of $[V]_{norm}$ except for stations 3 and 5. These depths coincide with the average thermocline of BoB (Liu et al., 2023) which impacts the redox states of the water column. The measured salinities along these depths are also higher hinting towards decreasing affinity for adsorption onto organic and inorganic substrates, thereby, increasing the concentrations. However, in stations 3 and 5, scavenging by terrigenous and/or biogenic particulate material is proposed as the causative mechanism of the observed depletion. This is due to the active mixing and circulation zone of water column at these depths of both the stations. The bottom water samples for station 1 show significant depletion in $[V]_{norm}$ which may be attributed to the active authigenic removal, adsorption and scavenging of vanadium by shelf sediment deposits. However, the observations for the other stations cannot be explained with the observed trend alone as those depths do not fall at the particle-water interface. A more thorough investigation is required using particle phase analyses and biological pump of vanadium in BoB, data on which is largely scare in this sector.

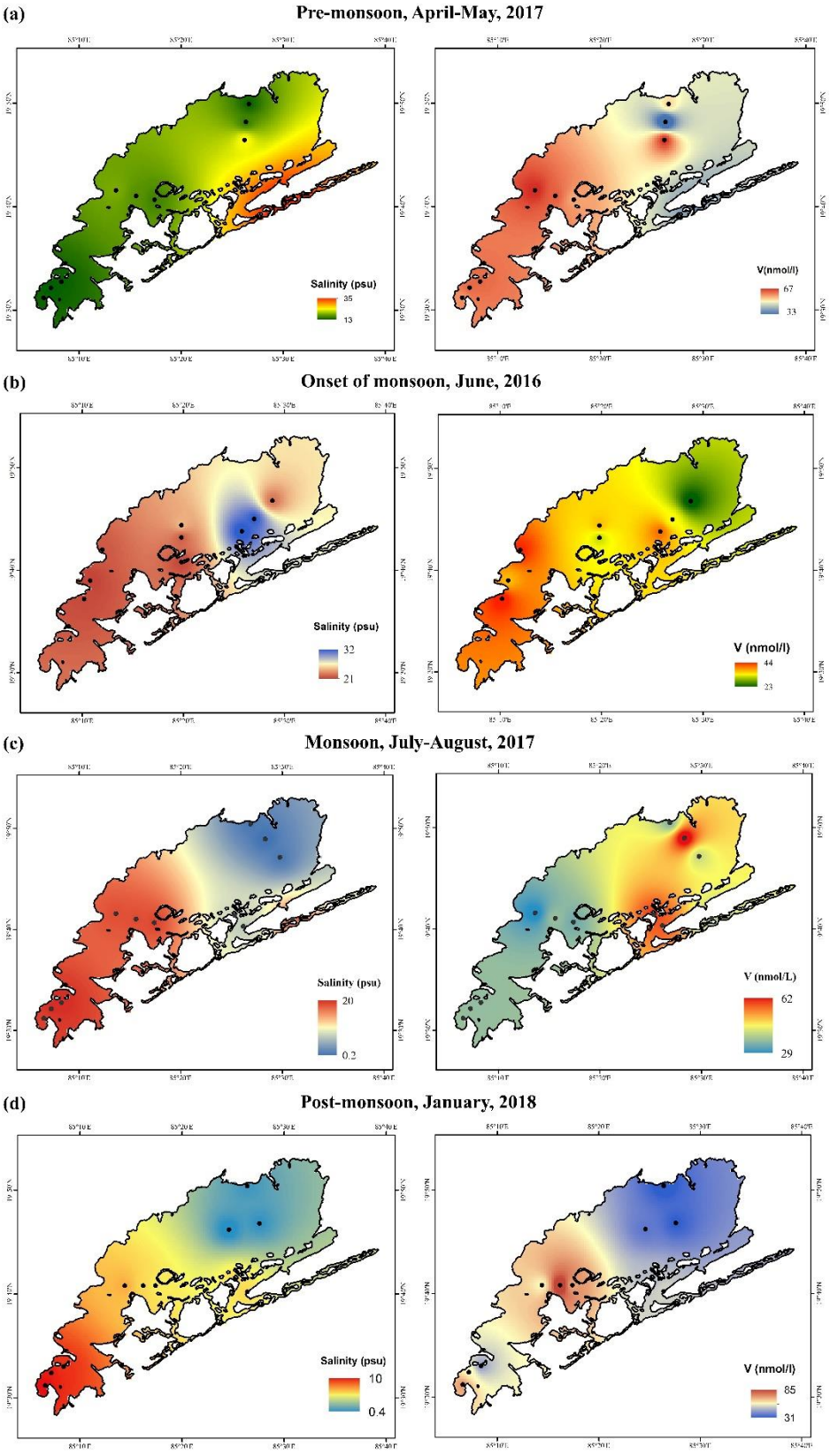

Fig. 7 shows variations in salinity and vanadium concentration in the Chilika lagoon (a) Pre-monsoon, April-May 2017, (b) The onset of monsoon, June 2016, (c) Monsoon, July-August 2017, and (d) Post-monsoon, January 2018. The maps are created by interpolating the salinity and concentration measured from the samples collected in these regions.

3.2 V concentration of the Chilika Lagoon and its coastal behavior

Water pH of the Chilika lagoon varies widely between 7.1 and 9.28, with an average value of 8.1 ± 0.4. The highest pH is observed in the central zone of the lake, whereas the lowest pH is observed near the outflow at Satapada. The Chilika also characterises with large spatial and seasonal variations in salinity (Fig. 7). The average salinity for the monsoon samples studied herein is 12 ± 8 psu (ranges from 0.2 - 20, n = 12). This average value is intermediate to that observed for the pre-monsoon (21 ± 9 psu; range: 13.1 - 35.3; n = 12) and post-monsoon (6 ± 4 psu; ranges from 0.4 - 10.1, n =11) samples. The average salinity at the onset of monsoon is 24.8 ± 3.9 psu (ranges from 21.9 - 31.7, n = 9). Additional to seasonal variation, the spatial samples also exhibit large salinity variation (Fig. 7) with lower salinities mostly being observed for samples from the northern sector.

The average vanadium concentration in the Chilika lagoon is 22.4 ± 17.6 nmol/L, which is comparable to the reported average for Mahanadi (20.55 ± 7.61 nmol/L; Mahanta and Mahananda, 2020). The average concentration of vanadium in the river is 16.3 ± 14.17 nmol/L (n=10). The global average concentration of vanadium in rivers is 22.9 ± 2.03 nmol/L (Schuth et al. 2019; Huang et al. 2015). For groundwater samples, the relatively higher salinity (0.28 - 4.32 psu; avg. 1.2 ± 0.9 psu, n =17) and the V concentration (26.98 - 360.71 nmol/L; avg. 203.60 ± 99.1 nmol/L, n = 17) hints to seawater intrusion or anthropogenic seepage.

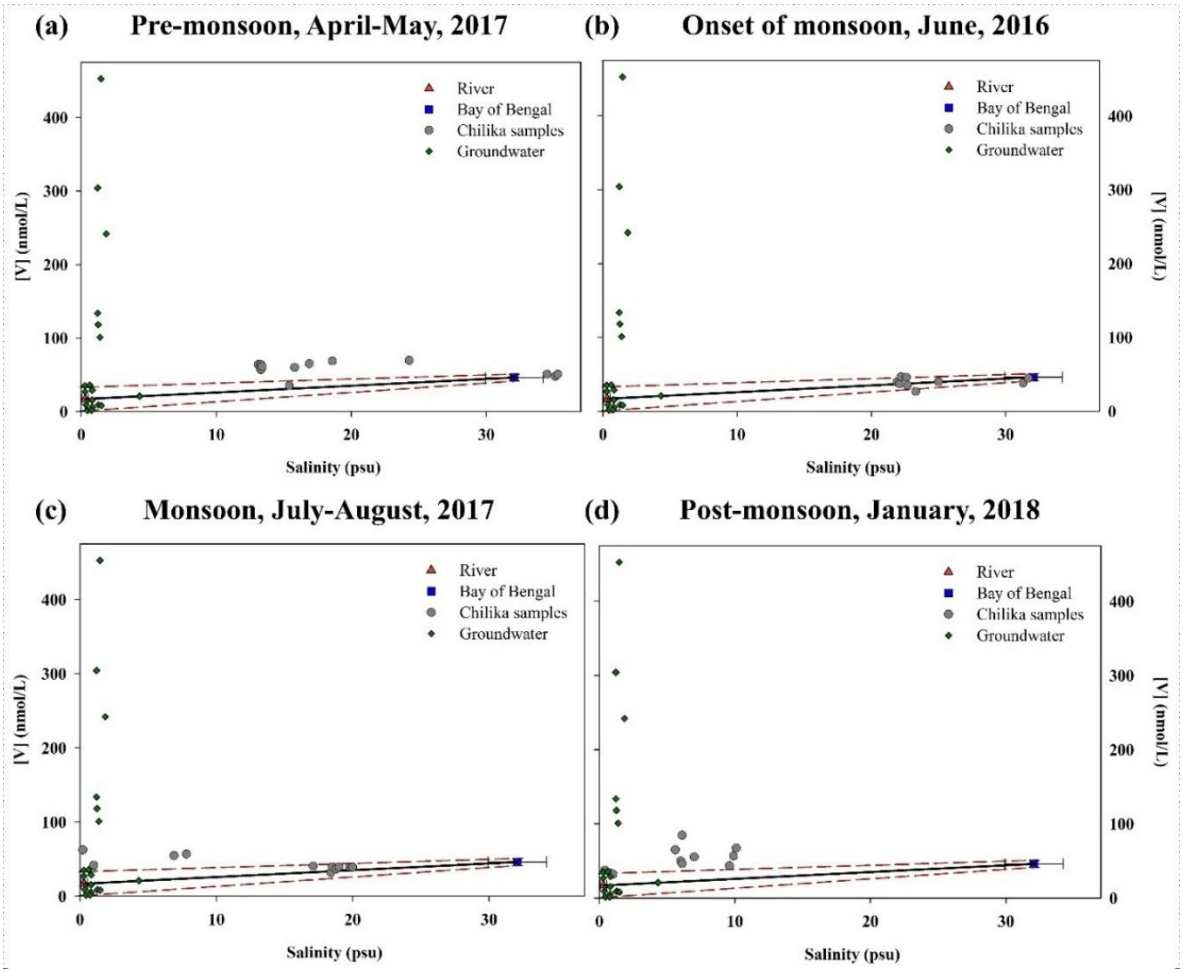

Fig. 8 shows variation in concentration of dissolved v*anadium in four different seasons* (a) *Pre-monsoon, April-May 2017, (b) The onset of monsoon, June 2016, (c) Monsoon, July-August 2017,* and *(d) Post-monsoon, January 2018 across* an *endmember mixing zone.*

3.3 Seasonal variation of dissolved vanadium concentration with salinity gradient in Chilika lagoon

The V concentrations of the Chilika samples during the onset of the monsoon vary between 26.8 and 46.5 nmol/L, with an average concentration of 39 ± 6 nmol/L. The concentration variation broadly follows the salinity trend with the lowest concentrations being observed in the northern sector and the highest in the southern sector. The vanadium concentration follows the trend of the mixing zone, indicating conservative behavior. One point in the northern sector (salinity = 23.3 psu; concentration = 26.8 nmol/L), which falls out of the mixing line, indicates removal processes. It can be biological uptake or adsorption by clay particles. However, during pre-monsoon, the sample concentration falls above the mixing zone, indicating an addition process. The concentration ranges from 34.9 nmol/L (northern) to 69.4 nmol/L, with an average of 57.6 ± 10.1 nmol/L (n = 12). During pre-monsoon season, higher salinity in the northern sector, due to evaporation and low water discharge from the rivers, plays a role in concentrating

the water. Vanadium's concentration also increases due to desorption from clay particles, increases turbidity and shallow depth (<2m), and rapidly releases vanadium from the sediments to the water column.

In the monsoon season, the northern samples and outer channel samples (near Satapada) show higher vanadium concentration and fall above the mixing zone, showing non-conservative behavior. The average concentration of vanadium is 43.2 ± 9.4 nmol/L. The concentration ranges from 32 nmol/L in the central sector to 62 nmol/L in the northern sector. During monsoon, the concentration of the northern sector is higher due to high submarine-groundwater discharge (SGD). This process is more dominant in the northern sector because all the major feeding rivers of Chilika are situated in the northern sector.

All the post-monsoon samples show non-conservative behaviour. The samples fall above the mixing zone, indicating the dominance of addition processes. The vanadium concentration may increase due to submarine groundwater discharge and desorption processes. The average concentration is 51.9 ± 16 nmol/L, ranges from 32.1 nmol/L to 84.5 nmol/L. The highest is in the central zone, indicating high submarine groundwater discharge.

3.4 Variation of vanadium with salinity

Samples from all four seasons were investigated to determine the variation in vanadium concentration and salinity of the Chilika lagoon. A theoretical mixing line with river and seawater as endmembers for salinity and vanadium concentration to assess their source contribution. The average river water (salinity = 0.3 + 0.2 psu, V_{conc} =16.9 ± 16.2 nmol/L) and seawater (salinity = 32.1 ± 2.1 psu, V_{conc} = 46 ± 4.8 nmol/L) were used for the mixing line generation. However, observations highlight the offset from the trend of the binary mixing line for most of the samples of all the four seasons (Fig. 8). The data points within the theoretical mixing zone reflect the conservative nature of vanadium, whereas, those that fall above the theoretical mixing zone show the non-conservative behavior. This can be explained by the incorporation of additional sources other than rivers and seawater. Groundwater vanadium (86.05 ± 125.9 nmol/L) contribution could be a possible additional source for this variation in the V-salinity trend of Chilika via submarine groundwater discharge (SGD) or through desorption processes (ion exchange mechanism of vanadium).

3.5 Possible causes for the addition of vanadium in Chilika lagoon

Multiple reasons can contribute to the addition of Vanadium to the Chilika lagoon. The main source of V addition can be due to the submarine groundwater discharge and/or ion-exchange processes. Vanadium concentration in groundwater was relatively high, with an

average concentration of 86.05 ± 125.9 nmol/L. The high concentration of vanadium in groundwater can be caused by water-particulate interaction in the subsurface zone. The leaching of surrounding rocks, mostly silicate rocks, has a high concentration of Vanadium. The constant interaction of these rocks with groundwater causes chemical reactions and leaches the rock. Chilika Lagoon is situated in a terrain with higher granitic rock, so it can be a factor in enriching the groundwater with Vanadium. Another possible reason for this is the desorption of clay minerals. Heavy siltation occurs in Chilika Lagoon; the lagoon gets shallower every year. Clays deposited in the lagoon are enriched with Vanadium; over time, the constant interaction of water and clay causes the desorption of Vanadium. Moreover, Vanadium in waterbodies prefers to stay in dissolved phases than in particulate phase, as stated by Hope (2008). The Eh and pH play a crucial role in regulating Vanadium desorption. The available data in this thesis work, however, is not enough to constrain the exact process for the mid-salinity V enrichment in the Chilika.

The Vanadium and salinity budget of Chilika Lagoon is calculated during monsoon season following the approach adopted by Danish et al. (2019) for boron in this lagoon. We have taken all hydrological data from Danish et al. (2019). The average salinity of the lagoon during monsoon season is 12.4 psu, which corresponds to 30% of the seawater influx to the Chilika. The average Vanadium concentration is 43.0 nmol/L. The total inventory for Vanadium is 4532.01 kg. The salinity and Vanadium budget of Chilika Lagoon during monsoon are presented in Fig. 9.

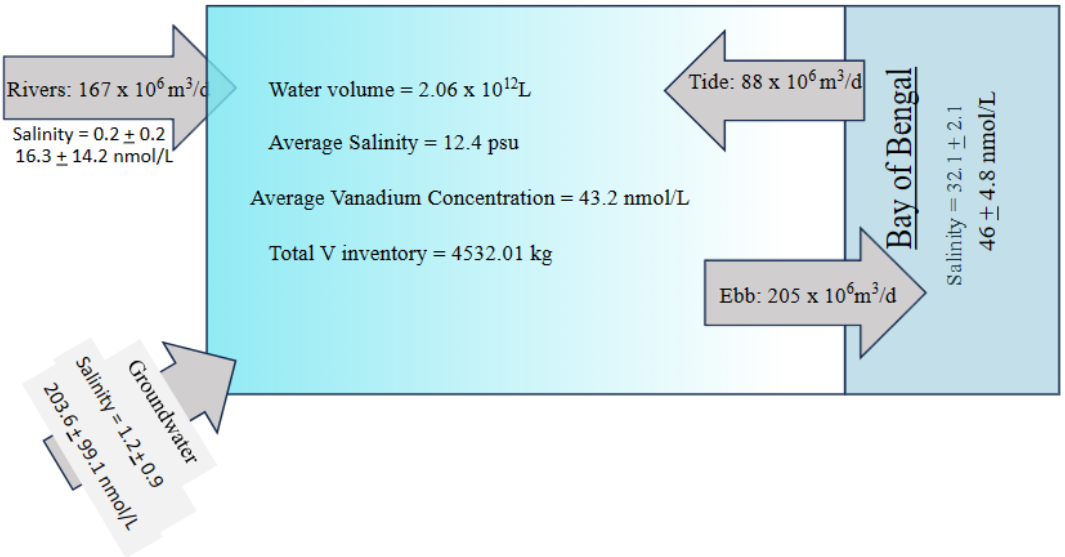

Fig. 9 Vanadium budget of the Chilika lagoon during monsoon.

4 Conclusions

In this study, spatial and seasonal distribution of dissolved vanadium concentrations along the salinity gradient of the Chilika lagoon and its possible source waters (Mahanadi distrutaries, groundwater, and the Bay of Bengal) have been investigated. During the onset of monsoon, the V concentrations indicate a conservative mixing between river and seawater in this coastal regime. However, the pre-monsoon and post-monsoon samples showed non-conservative behavior of vanadium with significant positive deviation from the mixing zone. This has been attributed to some additional processes of release of vanadium via SGD (post-monsoon) and/or ion exchange processes (pre-monsoon). During the monsoon season, the outer channel (near Satapada) and northern sector samples show a non-conservative mixing due to surge in freshwater and subsurface discharge, intensified tidal cycles, and reduced effect of adsorption on the sediments. However, these estimates are preliminary and shall be confirmed with future investigations on the corresponding particulate and biogenic phases. Constraining the processes in this coastal regime is complex and requires additional analyses. Further, the observations from the Bay of Bengal highlight the fate of vanadium in the oceanic environment. A slight deviation from the expected conservative behavior has been observed in BoB compared to other world oceans. Some important processes such as continental input, biological uptake, scavenging by terrestrial sediments, mineral and/or coral redissolution, and changes in redox conditions along the water column affecting the vanadium solubility have been proposed to explain these deviations from the conservative behavior. However, the changes are extremely minimal and impacts of these major processes shall be confirmed with a better insight into the dataset governing the biological pump of the ocean along with reactions at the particle-water interface.

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Annexure

Table A1: The relative standard deviation (%) during the analyses accounting for the instrumental and analytical precision.

Sample Type	Instrumental precision		Analytical precision	
	RSD %	n	RSD %	n
Chilika lagoon	5	97	5	5
Freshwater sources	6	71	4	6
Bay of Bengal	6	58	4	4
Average	5 ± 1		4 ± 1	

Table A2: The background contribution during analysis with signal:noise ratio *[cps refers to (instrumental) counts per second]*.

	Sample		Blanks		Signal:Noise
Sample Type	cps	n	cps	n	
Chilika lagoon	1605	50	15	42	108
Freshwater sources	20582	50	16	30	1256
Bay of Bengal	574	50	18	29	31

Table A3: Reproducibility of vanadium concentrations of standard reference materials and open ocean samples during the analyses.

Reference Material	Reported value	Measured value	
	[V]	[V]	$[V]_{norm}$
	(nmol/L)		
NIST-1640a	15.05 ± 0.25		
Leg2-02		45 ± 3	48 ± 3
Leg2-03		46 ± 3	49 ± 3
Open ocean[$]	40 ± 14		

$: Data sourced from Huang et al., 2015; [V]norm: vanadium concentration normalized to salinity 35 psu.

Table A4: Data on cruise stations, station depths, water depths, salinity, dissolved vanadium, vanadium normalised, and geographical coordinates of Bay of Bengal samples collected onboard ORV Sagar Kanya, cruise SK-373.

Station	Date	Latitude	Longitude	Location	Station depth	Sample ID	Water depth	Salinity*	[V]	[V]norm
		°N	°E		m		m	psu	nmol/L	
S1	24-Sep-21	13° 1.033'	80° 37.610'	Bay of Bengal	205	BB21/8	0	33.3	45±6	47±7
						BB21/1	10	33.6	46±11	48±11
						BB21/2	25	33.6	46±12	48±13
						BB21/3	50	33.5	43±5	45±5
						BB21/4	70	34.7	45±4	46±4
						BB21/5	85	34.8	43±4	43±4
						BB21/6	100	34.6	50±7	51±8
						BB21/7	150	34.9	40±13	40±13
S2	26-Sep-21	13° 0.461'	84° 44.377'		3255.7	BB21/12	0	32.6	53±6	57±7
						BB21/9	10	33.2	49±6	52±7
						BB21/10	25	33.2	45±6	48±6
						BB21/11	42	34.0	43±7	44±8
						BB21/13	65	34.6	44±8	45±9
						BB21/14	100	34.8	44±1	44±1
						BB21/15	150	34.9	41±4	41±4
						BB21/16	250	35.0	40±4	40±4
						BB21/17	700	35.0	47±12	47±12
S3	28-Sep-21	13° 0.281'	88° 44.674'		3069	BB21/25	0	32.7	34±6	36±7
						BB21/18	10	32.8	37±9	40±10
						BB21/19	25	32.8	44±5	46±6
						BB21/24	42	33.3	34±2	36±2
						BB21/20	56	35.0	40±6	40±6

						BB21/26	100	34.7	48±0	49±0
						BB21/21	130	34.9	42±5	43±5
						BB21/27	150	34.9	44±11	44±11
						BB21/22	350	35.0	43±8	43±8
						BB21/23	800	35.0	41±9	41±9
S4	30-Sep-21	13° 52.022'	92° 38.108'	Bay of Bengal	941	BB21/35	0	32.0	55±6	60±7
						BB21/28	10	32.1	35±10	38±11
						BB21/29	25	32.2	40±10	43±11
						BB21/30	60	33.8	39±5	40±5
						BB21/31	100	34.5	40±6	41±6
						BB21/32	150	34.9	39±7	39±7
						BB21/33	400	35.0	40±3	40±3
						BB21/34	700	35.0	47±7	47±7
S5	3-Oct-21	11° 39.544'	94° 46.982'	Andaman Sea	1855	BB21/45	0	29.0	50±6	60±7
						BB21/36	10	29.7	37±11	44±13
						BB21/37	25	32.3	43±5	47±6
						BB21/38	42	33.6	84±6	87±6
						BB21/39	58	34.1	45±5	46±6
						BB21/40	100	34.6	43±6	44±6
						BB21/41	120	34.7	37±9	38±9
						BB21/42	150	34.8	39±6	39±6
						BB21/43	310	35.0	45±6	45±6
						BB21/44	600	35.0	44±9	44±9

**average of values recorded ± 0.5m of sampling depth*

 # collected with a metal (Fe) bucket and a rope from the main deck of the ship

Table A5: Data on geographical locations, depth, pH, temperature, salinity, and dissolved vanadium concentration for the Chilika lagoon water samples collected during four field trips (January-2018, May-2017, June-2016, August-2017).

	Sample ID	Latitude	Longitude	Depth	Temperature	pH	Salinity	[V]
		°N	°E	m	°C		p.s.u.	nmol/L
PRE-MONSOON	CLK17-05	19.54	85.12	2.0	29.8	8.3	13.1	64±4
	CLK17-72	19.83	85.44	0.9	28.6	8.0	13.3	57±4
	CLK17-06	19.55	85.14	2.1	29.7	8.3	13.3	64±2
	CLK17-04	19.52	85.11	2.0	29.6	8.4	13.4	61±1
	CLK17-73	19.80	85.44	1.2	28.8	8.3	15.4	35±6
	CLK17-30	19.68	85.29	1.2	26.8	8.3	15.8	60±4
	CLK17-29	19.68	85.26	2.1	26.8	8.3	16.9	65±2
	CLK17-28	19.69	85.23	4.6	28.5	8.1	18.6	69±3
	CLK17-74	19.77	85.44	1.4	28.9	8.4	24.3	69±2
	CLK17-109	19.68	85.52	-	29.2	7.4	34.5	51±7
	CLK17-111	19.67	85.48	-	32.3	7.6	35.1	48±10
	CLK17-110	19.68	85.50	-	30.7	7.5	35.3	50±7
ONSET OF MONSOON	CLK16-03	19.65	85.18	2.7	30.8	7.8	21.9	39±3
	CLK16-16	19.68	85.33	0.8	31.7	7.5	22.1	37±4
	CLK16-04	19.62	85.17	2.0	30.7	7.8	22.2	47±2
	CLK16-02	19.70	85.20	2.5	30.5	7.6	22.6	46±1
	CLK16-17	19.72	85.33	1.9	31.3	7.6	22.7	35±3
	CLK16-29	19.78	85.48	1.7	32.6	7.7	23.3	27±6
	CLK16-18	19.74	85.33	2.0	31.1	7.8	25.0	40±4
	CLK16-28	19.75	85.45	1.8	32.4	8.1	31.3	38±6
	CLK16-27	19.73	85.43	2.0	32.7	8.1	31.7	45±7

MONSOON	CLK17-M72	19.82	85.47	1.6	31.0	8.7	0.2	62±3
	CLK17-M71	19.84	85.45	1.5	30.2	8.7	0.9	37±3
	CLK17-M73	19.79	85.50	1.5	31.9	8.1	1.0	42±0
	CLK17-M108	19.67	85.44	-	30.9	8.3	6.9	55±3
	CLK17-M107	19.69	85.42	-	31.1	8.4	7.8	57±1
	CLK17-M109	19.68	85.52	-	31.0	8.2	17.1	40±5
	CLK17-M27	19.69	85.23	2.8	30.5	8.0	18.4	32±3
	CLK17-M28	19.68	85.26	2.8	30.2	8.1	18.5	39±2
	CLK17-M29	19.68	85.29	1.2	30.0	7.9	18.8	37±3
	CLK17-M04	19.52	85.11	3.2	30.4	8.0	19.0	39±3
	CLK17-M05	19.54	85.12	2.6	29.9	8.1	19.8	39±5
	CLK17-M06	19.55	85.14	2.7	30.3	8.1	20.0	39±6
POST-MONSOON	CLK18-Ja67	19.77	85.41	-	20.0	8.3	0.4	37±1
	CLK18-Ja68	19.78	85.46	-	20.5	8.2	0.8	33±1
	CLK18-Ja66	19.84	85.44	-	19.4	8.1	1.0	32±1
	CLK18-Ja39	19.68	85.29	-	21.5	9.3	5.6	65±4
	CLK18-Ja104	19.67	85.44	-	22.7	8.2	6.0	50±3
	CLK18-Ja103	19.69	85.42	-	22.5	8.0	6.1	46±3
	CLK18-Ja38	19.68	85.27	-	21.0	9.2	6.1	84±5
	CLK18-Ja37	19.68	85.24	-	21.5	8.5	7.0	55±1
	CLK18-Ja06	19.55	85.14	-	21.7	8.5	9.6	43±1
	CLK18-Ja05	19.54	85.12	-	21.7	8.5	9.9	57±3
	CLK18-Ja04	19.52	85.11	-	22.0	8.5	10.1	67±1