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Baseline

Bioavailable dissolved organic matter and its spatio-temporal variation in a river dominated tropical brackish water Lagoon, India

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ABSTRACT

Bioavailable dissolved organic carbon (B_{DOC}), nitrogen (B_{DON}) and their degradation rate constants were measured for the Chilika Lagoon, India. Long-term laboratory incubation experiments (90 days) were conducted at a constant temperature (25 °C) to quantify the bioavailable dissolved organic matter (DOM) and the possible degradation rate coefficients. The results showed that 41 ± 12% of dissolved organic carbon (DOC) and 47 ± 17% of dissolved organic nitrogen (DON) were B_{DOC} and B_{DON} respectively, with their stoichiometry found to be higher than the Redfield ratio. A first order exponential non-linear fitting routine was used to estimate pool sizes. The degradation rate constant (k) for the B_{DOC} varied from 0.127–0.329 d^{-1} and B_{DON} from 0.043–0.306 d^{-1} during the study period. Half-lives of the B_{DOC} and B_{DON} ranged from 2.1–5.4 and 2.2–15.9 days, respectively. Overall, the results showed that a fraction of the labile DON was transported from the lagoon to the adjacent coastal sea.

Carbon and nutrient dynamics in the ocean margins are of global significance. Despite contributing only 7% of the global ocean area, coastal lagoons and estuaries occupy a unique position between the land and ocean in its functions of material exchange and nutrient cycling (Gattuso et al., 1998; Wollast, 1998). Dissolved organic matter (DOM) is an important source of carbon and other nutrients for aquatic microorganisms in these environments. DOM therefore has a substantial impact on aquatic food webs and nutrient dynamics (Azam, 1998). DOM plays an important role in a wide range of biogeochemical reactions, such as bacterial uptake, and the mobility of metals, radionuclides, and hydrophobic organic compounds (Chin et al., 1997; Tipping, 1998). DOM also affects the function of ecosystems during the photochemical modification and is known to alter trophic status (Herndl, 1997; Jeffrey et al., 2000; Moran and Zepp, 2000). Terrestrial input (allochthonous material) and indigenous primary production (autochthonous material) are the major sources of DOM in aquatic ecosystems. The DOM behaves as non-conservative in nature, as it undergoes various biological and photochemical transformations before a residual of the DOM is eventually discharged into the oceans (Miller and Zepp, 1995; Amon and Benner, 1996a, 1996b; Opsahl and Benner, 1997; Tranvik, 1998).

In addition to production of particulate organic matter (POM), some of the phytoplankton-derived organic C may accumulate as DOM. DOM is derived either from excretion by phytoplankton or through trophic interactions (i.e., grazing, viral lysis) (Carlson, 2002). In contrast to the export of POM via sinking flux, export of DOM is largely limited to advective processes (i.e., transport of material) except in the case of formation of transparent exopolymer particles (Passow and Carlson, 2012). In coastal systems (viz., lagoons and estuaries), C-rich DOM has been shown to accumulate over timescales ranging from days to months (Álvarez-Salgado et al., 2001; Hill and Wheeler, 2002). Most of the DOM consists of humic, fluvic and non-humic compounds but their bioavailability depends on their chemical structure (Sun et al., 1997). They may be recalcitrant or labile to the heterotrophic degradation (Münster and De Haan, 1998). Depending on the lability of the DOM, the magnitude of DOM exported to oligotrophic offshore surface waters

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from coastal ecosystems may be sufficiently large and alters the balance between heterotrophy and autotrophy. Thus, for understanding the biogeochemical cycling of DOM, factors that regulate DOM degradation in coastal ecosystems need to be studied in detail to ultimately understand DOM export fluxes, degradation rates and flushing time. The fact that DOM accumulates in lagoons suggests that its rate of production must be greater than its rate of removal over the timescale of interest. However, no significant studies have addressed the extent to which bacterial production will allow DOM accumulation in the Chilika lagoon.

DOM is composed of a complex mixture of various organic compounds with turnover times ranging from seconds, days to years (Coffin et al., 1993; Cherrier et al., 1996). Knowledge of the sizes and turnover times of discrete DOM pools is essential for accurate budgeting and modeling of regional as well as global carbon budgets. Because of the differential C and N content of various organic compounds, differences in their degradation rates and turnover times might be expected along with their relative proportions of discrete pools (i.e., labile, semi-labile and refractory). Gupta et al. (2008) and Muduli et al. (2012) have focused on the carbon budgeting of the Chilika lagoon, showing that the system is a source of CO_2 to the atmosphere driven by strong heterotrophic activity via transforming riverine organic carbon to CO_2. Kanuri et al. (2013) studied the role of plankton metabolic process in the production and mineralization of recently produced organic carbon and showed that 80% of the freshly produced organic carbon was mineralized within a day. Some recent studies have also focused on the source and fate of organic matter (N), as well as the new production and mineralization process in the Chilika lagoon (Patra et al., 2017; Mukherjee et al., 2018). To this end, there is a need to have a complete understanding of the biological transformation of organic matter (allochthonous and autochthonous). The absence of this information on the transformation rate of organic matter in Chilika lagoon substantially effects the budgeting of organic matter and its fate. Precise measurements of organic matter degradation rate (by bacteria) and its spatio-temporal variability may resolve the fate of allochthonous organic matter and its transport to the adjacent Bay of Bengal.

In this study, results were obtained from experiments at four stations representative of the four ecological sectors (i.e. Southern Sector (St.1), Central Sector (St.2), Norther Sector (St.3) and Outer Channel (St.4)) of the lagoon during the two meteorologically different periods (May and October 2009). Experiments were designed to quantify DOM degradation rates at the study site. Enclosures containing only DOM (i.e., with POM removed) were either left unaltered or exposed due to the bacterial degradation during the 90 days incubation period.

The Chilika Lagoon, a shallow (mean depth ~1.5 m (0.9–3.5 m)) brackish waterbody is located on the east coast of India (Fig. 1). The lagoon is pear shaped and covers an area of about 1000 km^2 during the monsoon (August–October), which is reduced by nearly 60% during the pre-monsoon (April–May) when evaporation far exceeds precipitation (Gupta et al., 2008). The entire lagoon is classified into four sectors (i.e., northern sector, southern sector, central sector and outer channel) (Muduli et al., 2017). The northern sector is characterized by high turbidity, poor water transparency, high nutrient levels and low water salinity due to the discharge of four rivers (Makara, Daya, Nuna, Bhargavi) running into the system (Barik et al., 2017). The southern sector remains comparatively saline (10.5 ± 3.5) throughout the year, as seawater exchange takes place through a discrete connection (i.e., Palur canal) further south to Rambha Bay. The entire lagoon experiences seawater exchange predominantly through the outer channel (i.e., Gabakunda). The lagoon has a catchment area of approximately 4146 km^2, with an average rainfall of 1238 mm (in 72 rainy days) lasting through June–September (southwest or summer monsoon) and November– December (northeast or winter monsoon); nearly 75% of it occurs during southwest monsoon with a peak intensity during August. The hydrological conditions of the lagoon are significantly affected by the seasonal freshwater runoff and associated material fluxes (such as nutrients, suspended particulate matter) from the rivers.

The sub-surface water samples collected using 5 l Niskin sampler were used for the determination of salinity, pH, dissolved oxygen, inorganic nutrients, chlorophyll-a (*Chl-a*), dissolved organic nitrogen (DON) and dissolved organic carbon (DOC). Salinity was measured by using standard argentometric titration (Grasshoff et al., 1999). pH was measured by using a Metrohm pH meter (accuracy ± 0.005), whilst dissolved oxygen (DO) was measured using the Winkler's titration method described by Grasshoff et al. (1999). The analytical precision, expressed as a standard deviation, was ± 0.07% for DO. Ammonium, nitrite, nitrate and phosphate were measured by using standard spectrophotometric procedures (Grasshoff et al., 1999) and the precision of the analyses were ± 0.02, ± 0.01, ± 0.02 and ± 0.01 μM respectively. Total dissolved nitrogen was measured using the persulfate oxidation method (Korleff, 1999) and the precision of the analysis was ± 0.05 μM. DON was calculated by subtracting dissolved inorganic nitrogen (DIN = ammonium + nitrite + nitrate) from the total dissolved nitrogen. All the analyses were completed within 12 h of the sampling at the shore-based laboratory set up in INS-Chilika. About 150 ml of the water sample was filtered through GF/F filter (Whatman) for the analysis of *Chl-a*. *Chl-a* in the filter was extracted with 90% Acetone, at 4 °C in the dark for 24 h, and then analyzed spectro-photometrically (Parsons et al., 1984). DOC in the water samples was analyzed by means of high temperature catalytic oxidation using a Shimadzu TOC-VCPH analyzer equipped with a platinum catalyst on quartz wool (Gupta et al., 2008). The accuracy of DOC measurements was checked once for every ten samples with Certified Reference Material (supplied by Dr. D. Hansell, University of Miami, USA) and internal standards prepared using potassium hydrogen phthalate (1 and 5 mg l^{-1}). The precision of the analysis was found to be within a deviation of ± 1%.

The filtered water samples were collected in a 250 ml pre-combusted glass bottles and were acidified (pH~2) with 0.1 N HCl and kept at < 4 °C until analysis for the quantification of humic (H_{DOC}) and non-humic (NH_{DOC}) fraction of DOC. The quantification of these two fractions was done using TOC analyzer followed by their adsorption on macroporous non-ionic resin (using column chromatography separation technique) at different pH. To fractionate the DOC, non-ionic amberlite XAD-8 resin (Sigma-Aldrich 40-60mesh) was used. Initially XAD-8 resin was washed and conditioned according to Thurman and Malcolm (1981). It was then packed into a glass column and was washed alternatively (3 times) with 0.1 M NaOH and 0.1 M HCl, and three blanks were collected before loading the sample. The column capacity factor (k′) was maintained at 50 to separate the humic substances using XAD-8 resin. Following this, 200 ml of the filtered sample was allowed to pass through the XAD-8 column at a constant flow rate (Q) of about 1 ml/min. Since the column efficiency is 99%, as per the methodology described by Thurman and Malcolm, 1981, 1% error is expected for H_{DOC} and NH_{DOC} whilst processing through the column. About 25 ml of the eluate (which contains only NH_{DOC}), was collected for the DOC (non-humic) analysis. The eluate was analyzed for NH_{DOC} using high temperature catalytic combustion (HTCO) method using Shimadzu TOC-V analyzer. The difference between total DOC and NH_{DOC} represented the H_{DOC} fraction.

DOM degradation experiments were carried out in the laboratory during May and October 2009 to identify the different pools of organic matter (i.e., labile, semi-labile and refractory) and their degradation rates. Waters samples were collected from 4 stations (Stns. 1, 2, 3 and 4 Fig. 1) located in different sectors of the lagoon with varying hydrographical and hydrochemical conditions.

Water samples from each station were filtered through acid-washed 0.8 μm Teflon membrane filter papers to remove particulate material and collected in two 5 l borosilicate glass bottles (pre-cleaned with extran Extran solution followed by HCl and Milli-Q water), and incubated in the dark at 25 °C temperature for 90 days. The control bottles were also incubated, which were poisoned with 0.1% (v/v) saturated $HgCl_2$ to cease the biological activity at the beginning of the

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