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Sub-hourly changes in biogeochemical properties in surface waters of Zuari estuary, Goa

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Abstract Processes in natural waters are highly variable in time and space. Although changes are expected in short-time scales, how short one could get to measure reliably is subjective to sampling strategies and methodologies. Here, we show that sub-hourly changes in surface waters dissolved oxygen, nutrients, and pigments are measurable and significant in an estuarine system. Tidal circulation has been found to strongly influence the observed changes and has implications to material fluxes in and out of estuaries.

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Introduction

Time and spatial scales for various processes will be different depending on the nature of the ecosystem/environment. For instance, molecular processes will be the fastest (<1 min) and occur in shortest spaces (<10 cm), whereas processes associated with gyral circulation in the ocean can be at scales of >100 km and over 1 year. To understand the changes in the environment, one should be able to make measurements at appropriate time and spatial scales using the appropriate gadgets. Measurements at hourly intervals or more are common to study changes in properties with diurnal and/or tidal variability, but sub-hourly changes have not been attempted. One limitation comes from the assumption that sub-hourly changes may not be significant. Here, we attempted to check if sub-hourly changes in some fundamental biogeochemical parameters are measurable and magnitudes of their variability.

Materials and methods

Study area

The study was conducted at a station at the mouth of Zuari estuary, Goa, which has a bay of 10 km in the

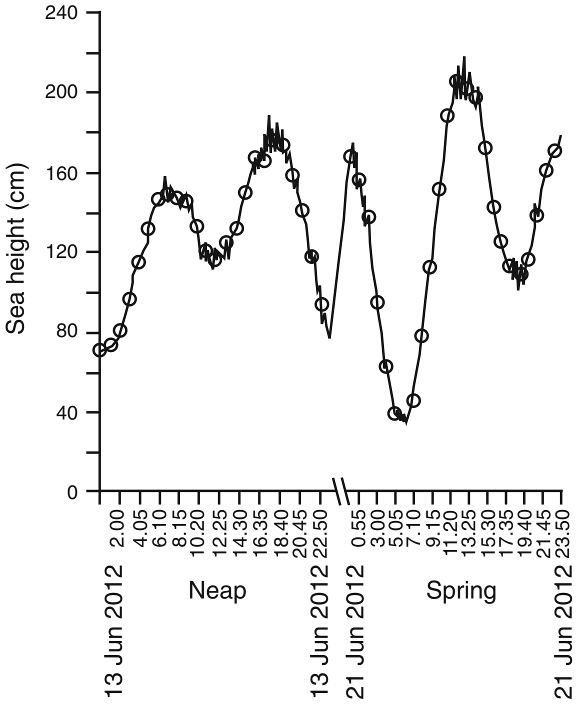

Fig. 1 Figure shows sea level during the two short time scale experiments covering neap and spring tides. The *shaded* portions show the periods of sampling during the experiments

upstream direction from the mouth. The station is ~5 m deep and is on one side of the 5-km wide estuarine mouth. The bay is surrounded by Dona Paula in the north, Mormugao port in the south, and Arabian Sea in the west. Rainfall and runoff in Goa estuaries are highly seasonal. The maximum rainfall occurs during the southwest monsoon when maximal runoff of about $2,190\times10^6$ m^3 is estimated (Shetye et al. 2007; Suprit and Shankar 2008). During summer monsoon period, the estuary is flushed with freshwater. Strong winds, waves, and tides facilitate turbulence and biogeochemical processes and consequent variability in properties.

Sampling strategies

Experiments were conducted twice; experiment 1 during flood phase of neap tide on June 13, 2012 and experiment 2 during ebb phase of the spring tide on June 21, 2012.

Sample collection and analysis

Water samples were collected at 10-min intervals for 1 h (Fig. 1). Only surface water (from 1 m depth) was collected using a 5 L Niskin sampler. Samples were collected for salinity, dissolved oxygen, dissolved inorganic nutrients, and pigments (chlorophyll a and phaeopigments). Salinity samples were collected in precleaned small glass bottles and measured using Autosal salinometer. Temperature was measured by using a bucket thermometer. Both salinity and temperature were measured once at the beginning of each experiment. Sea level was measured by a tide gauge of our Institute placed at Verem, a few kilometers from the present sampling station. All the samples were collected and preserved immediately. Dissolved oxygen and nutrients were analyzed following the methods of Grasshoff et al. (1983). Chlorophyll a and phaeopigments were measured according to Parsons et al. (1974). All the samples were analyzed, in duplicates, immediately after bringing them to the laboratory.

Results and discussion

Salinity was 33.46 during the neap tide and 21.37 during the spring tide experiments. The corresponding temperatures were 29.5 and 28.5 °C. The uncertainties involved in measurements are important and required to give credibility to the observed changes in properties. Table 1 shows the mean deviations of duplicate measurements of

Table 1 Mean deviations of duplicate measurements of various parameters during the short time scale experiments in Zuari estuary, Goa. Experiment 1 was conducted on June 13 and experiment 2 was on June 21, 2012

Parameter	Experiment 1 Neap tide	Experiment 2 Spring tide
Dissolved oxygen (μM)	3.93	2.88
Nutrients (μM)		
Nitrate	0.29	0.40
Nitrite	0.02	0.03
Phosphate	0.06	0.36
Silicate	0.35	2.00
Ammonia	0.18	0.21
Pigments (mg m^{-3})		
Chlorophyll a	0.04	0.11
Phaeopigments	0.79	2.26

Table 2 Ranges of various biogeochemical parameters observed during the short time scale study in Zuari Estuary, Goa

Parameter	Experiment 1		Experiment 2	
	Neap tide		Spring tide	
	Min	Max	Min	Max
Dissolved oxygen (μM)	126.2	181.7	206.9	227.1
Nutrients (μM)				
Nitrate	9.5	10.8	12.7	16.2
Nitrite	0.62	0.74	2.85	3.69
Phosphate	1.03	1.23	0.35	0.91
Silicate	16.3	17.9	14.7	28.7
Ammonia	1.37	1.82	1.63	2.38
Pigments (mg m^{-3})				
Chlorophyll a	0.40	0.50	0.1	0.38
Phaeopigments	0.10	4.10	0.0	10.02

each property during both the experiments. The deviation between duplicates is more during the ebb phase of the spring tide (experiment 2) than the flood phase of the neap tide (experiment 1). Higher deviations in experiment 2 seem associated with higher turbidity of the estuarine waters than in experiment 1. Table 2 contains the ranges of biogeochemical properties observed. But for oxygen, the observed ranges are more significant during the ebb phase of the spring tide that are well above the mean deviations. The ranges were smaller during the neap tide experiment 1. Data in Tables 1 and 2 suggest that it is possible to measure sub-hourly changes in surface waters reliably.

Despite some fluctuations in concentrations of biogeochemical properties with time, some general trends (Figs. 2 and 3) are obvious during both the experiments. The rising sea or tide height during the experiment 1 indicated the flood phase. In general, all nutrient and chlorophyll a concentrations exhibited increasing trends but not clear for oxygen and phaeopigments (Fig. 2). Increases in concentrations of biogeochemical parameters with rising tide suggest that enhanced turbulence facilitated the release of substances from bottom sediments. The sediment resuspension releases dissolved substances from pore water to overlying waters. Such a resuspension must have enhanced phaeopigment levels in water, since the bottom sediments contain higher quantity of degrading pigments. In contrast, concentrations of nutrients and phaeopigments decreased with time in experiment 2, except oxygen and chlorophyll a (Fig. 3). As the ebb current (as indicated by decreasing sea height), which is stronger than the flood current, drains materials from estuary to coastal ocean, the concentrations of these substances have decreased with time in estuarine water. Figures 2 and 3 suggest that dissolved materials in sediment pore waters are released (by diffusion or resuspension) in to overlying water column during the flood tide and that the released materials are carried in to coastal waters by ebb currents. This observation is in conformity with transportation of dissolved carbon dioxide by ebb currents from an intertidal zone (Kumar et al. 1993).

Conclusion

The present study confirms that sub-hourly sampling studies can be carried out with a focus during which discernible changes in surface water properties can be detected for understanding the processes responsible.

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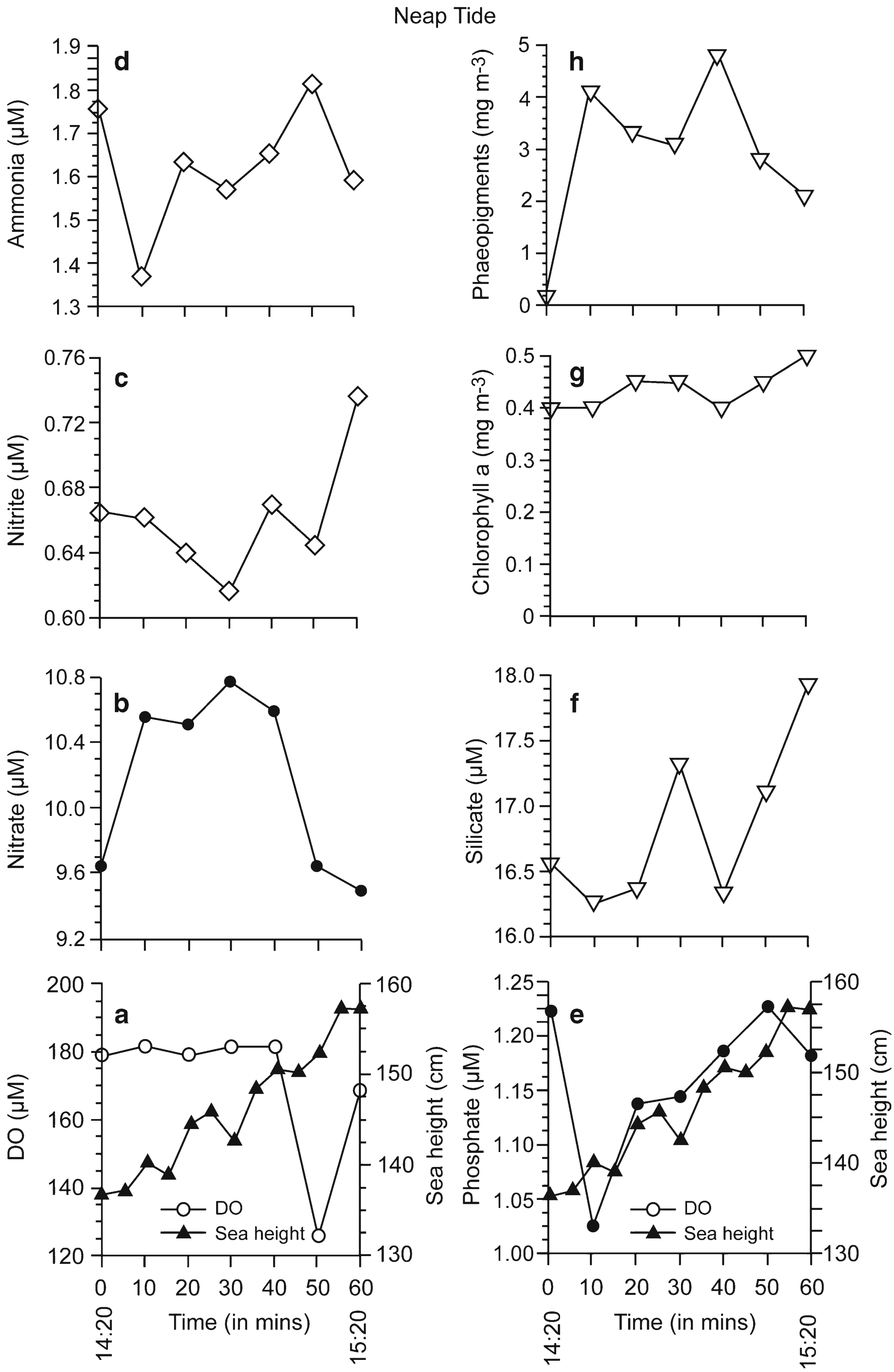

Fig. 2 Sub-hourly variations in sea height, dissolved oxygen (*DO*), nutrients, and pigments during experiment 1 (neap tide on 13 June 2012)

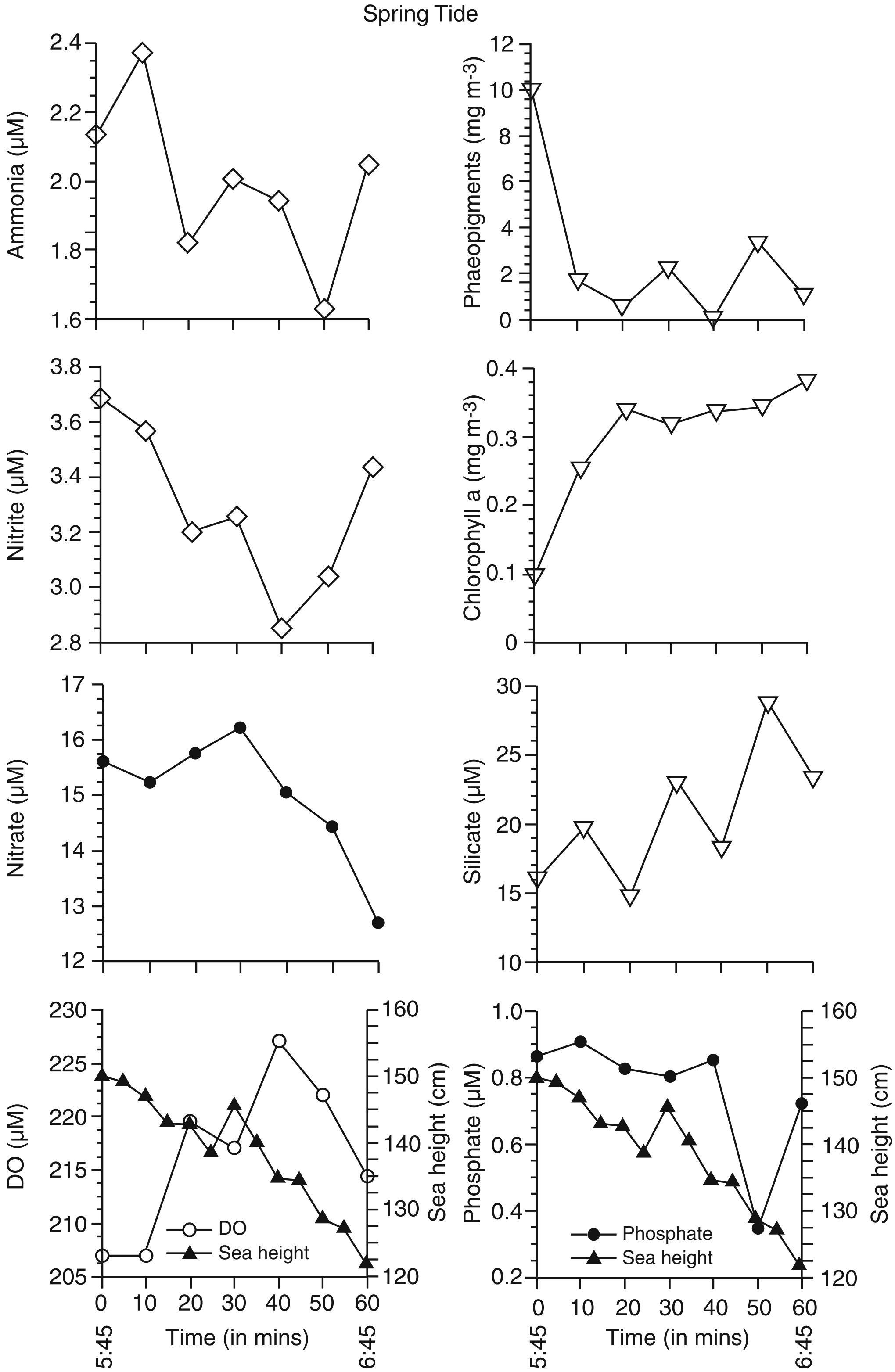

Fig. 3 Sub-hourly variations in sea height, dissolved oxygen (*DO*), nutrients, and pigments during experiment 2 (spring tide on 21 June 2012)

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