

## **Impact of physical processes on oxygen loss and production of hydrogen sulphide and methane in a tropical freshwater reservoir**

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### **Abstract:**

Carbon neutrality of tropical reservoirs is a big concern in recent years as some estimates project high methane emission from these reservoirs. While there are studies available on the impact of physical processes (stratification and mixing) on the biogeochemistry of tropical reservoirs, not much information is available on the inter-annual variability in the low oxygen conditions and production/accumulation of hydrogen sulphide (H<sub>2</sub>S) and methane (CH<sub>4</sub>) during summer. This paper presents time series data based on monthly *in situ* observations from a tropical reservoir (Tillari, Maharashtra) situated in the Western Ghats in India. Sampling was carried out for temperature, dissolved oxygen (DO), H<sub>2</sub>S and CH<sub>4</sub> at a fixed location from March 2010 till June 2014. The reservoir experiences stable stratification during summer (March to June) with complete loss of oxygen and production of H<sub>2</sub>S (max. ~9 µM) and CH<sub>4</sub> (max. ~185 µM) in the profundal zone. During the summer stratification, the hypolimnion acted as a pool of CH<sub>4</sub> with integrated values ranging between 3502 and 41632 mg m<sup>-2</sup>. However, the intensity and duration of anoxia varied during different years, influencing H<sub>2</sub>S and CH<sub>4</sub> production. Mixing in the reservoir was observed between July and September in association with the monsoonal runoff, which increased the DO concentrations in the sub-surface layers. Besides, complete mixing was observed between December and February due to winter convection. This, however, was found to play an important role, as weaker mixing in the preceding year was associated with severe oxygen loss in the profundal zone during the following summer with a production of H<sub>2</sub>S and CH<sub>4</sub>. In contrast, more robust mixing during winter led to moderate low oxygen conditions with less production of these gases in the subsequent summer. Based on our observations and considering a large number of reservoirs in the tropics, we hypothesize that with the present trends of global warming and less cold winters, low oxygen conditions in the profundal zone may be more severe in future with positive feedback on H<sub>2</sub>S and CH<sub>4</sub> production during summer.

**Keywords:** Tropical reservoirs, stratification, mixing, dissolved oxygen, hydrogen sulphide and methane

## 1. Introduction:

While dams have been an asset to society in general, their credentials as being carbon neutral have come under suspicion in recent years. This is mainly because oxygen is lost from the stored water in the sub-surface layers during stratification leading to the production of H<sub>2</sub>S and CH<sub>4</sub> (Galy-Lacaux et al., 1999; Fearnside, 2002, Lima, 2005; Ramos et al., 2006; Kemenes et al., 2007; Narvenkar et al., 2013). While CH<sub>4</sub> is a potent greenhouse gas with a warming potential far greater than carbon dioxide (Ramaswamy, 2001), H<sub>2</sub>S is known for its environmentally toxic nature (Rubright et al., 2017). The loss in oxygen also impacts the quality of the water and the release of such hypoxic waters can have a deleterious effect on the ecosystem within the reservoir as well as downstream (Winton et al., 2019). H<sub>2</sub>S concentrations above 5 ppm have been found to result in the mortality of prawns and fishes (Smith et al., 1976; Grizzle, 1981). CH<sub>4</sub> release to the atmosphere occurs through surface diffusion, ebullition and discharge at the outlets. Release through bubbling was observed as an important process in shallow lakes (Bastviken et al., 2004). In contrast, surface diffusion and degassing at the outlet were seen as important escape mechanism in deeper reservoirs (Keller and Stallard 1994; Abril et al., 2005). Galy-Lacaux et al. (1997) estimated that about 10% of the stored carbon in inundated soil is lost to the atmosphere as CH<sub>4</sub> and carbon dioxide (CO<sub>2</sub>) during the first two years of burial. India is one of the six largest dam-building nations (Nick van de Giesen, 2010) and presently, the Ganges–Brahmaputra basin (mainly India and Nepal) is reported to face significant dam construction activity (Zarfl et al., 2014). An earlier report suggested that the Indian dams annually emit as much as 33.5 MT of CH<sub>4</sub> to the atmosphere (Lima et al., 2008). However, this report was based on assumptions as studies on CH<sub>4</sub> from Indian reservoirs are somewhat limited. In the first report from Indian reservoirs, Narvenkar et al. (2013) observed that CH<sub>4</sub> emission from Indian reservoirs had significantly been overestimated. In one of the reservoirs (Tillari, Western Ghats, India) where seasonal measurements were carried out, a high concentration of CH<sub>4</sub> (as much as 156 µM) was observed in the bottom waters during the summer season. However, stable stratification did not allow the CH<sub>4</sub> to vent into the atmosphere but was instead oxidised in the upper epilimnion with limited emission to the atmosphere (Narvenkar et al., 2013).

A variety of factors govern oxygen consumption in lakes and reservoirs. The supply of organic matter to the dark sub-surface layers and the resultant microbial decomposition plays a significant role in the formation of low-oxygen zones in reservoirs. Also, irregularities in reservoir morphometry have been found to influence oxygen consumption. On depletion of dissolved oxygen, the microbes continue the process of decomposition by utilizing oxygen from reactive nitrogen (nitrate) reducing it to molecular nitrogen (N<sub>2</sub>; Naqvi et al., 2018). On exhaustion of reactive

nitrogen, the process is then carried out by reducing sulphate and carbon dioxide resulting in the production of  $\text{H}_2\text{S}$  (Muyzer and Stams, 2008) and  $\text{CH}_4$  (Balch et al., 1979) respectively. Kreling et al. (2017) observed higher oxygen uptake in cases where the slopes of meta limnetic shore were gentle in comparison to those which were steeper. In the temperate latitudes, lakes and reservoirs undergo stratification (summer and winter) and mixing (spring and fall) twice during the year. Considering the existing warming trend ( $0.85^\circ\text{C}$  between 1880 and 2012; IPCC, 2014), studies on stratification and mixing in reservoirs are necessary as reduced mixing will impact the oxygen replenishment in the deeper layers of the reservoirs changing biogeochemistry and ecosystem (Nurnberg, 1995; Rabalias et al., 2001). Modelling studies on Lake Tahoe showed that the lake became more stable with warming, impacting the mixing and water quality of the reservoir over time (Sahoo and Schladow, 2008). In a time-series study conducted in Lake Biwa in Japan, Yoshimizu et al. (2010) observed that warmer winters could impede circulation and oxygenation of the bottom waters of warm monomictic lakes. Studies on Indian reservoirs focusing on stratification and mixing processes are rather sparse, with a majority focused on the ecology and fishery potential of these freshwater systems (Sugunan, 2000). Nevertheless, few studies focusing on the hydrological conditions of the reservoirs in southern India are available. These studies have reported weak thermal stratification during summer with oxygen deficiency in the hypolimnion. However,  $\text{H}_2\text{S}$  was observed only during specific years of the study period (Sreenivasan, 1964; Sreenivasan et al., 1964; Sreenivasan, 1970). In a study conducted on nine lakes of Jammu and Kashmir, summer stratification was observed to last through to autumn with isothermy setting in during the winter months (Vass, 1980; Zutshi et al., 1980). In a majority of the reservoirs in India, summer stratification is most intense during May-June, which is eroded by the southwest monsoonal inflow and by convective mixing during winter (Sugunan, 2000; Desai and Singh, 2000; Narvenkar et al., 2013). Kurian et al. (2012) reported the occurrence of anoxygenic photosynthesis in the hypolimnion of the Tillari Reservoir and attributed light as the primary factor in addition to the availability of  $\text{H}_2\text{S}$ . However, not much information is available on the mode/impact of stratification and mixing in tropical reservoirs (Winton et al., 2019). While it is observed that annual summer stratification leads to oxygen depletion in the deeper layers, higher concentrations of  $\text{H}_2\text{S}$  and  $\text{CH}_4$  were observed only during certain years, which brings out the need to understand the finer scale physical control in the tropical reservoirs. The present study uses the first-ever time series data from a tropical freshwater reservoir to unravel the controls on annual stratification and mixing and the resultant production of  $\text{H}_2\text{S}$  and  $\text{CH}_4$ .

## **2. Materials and methods:**

### **2.1. Study area:**

The Tillari Reservoir (15.76°N 74.09°E), constructed on the Tillari River, is located at the foothills of the Western Ghats, India (Figure 1). The dam blocks the original course of the river, and the stored water is released at the western edge with two outlets. The dam construction was completed in 2006 and the reservoir inundated resulting in a total storage capacity of 0.45 billion m<sup>3</sup> (Kurian et al., 2012; Narvenkar et al., 2013). The water level in the reservoir (as observed at station T1) varied between 39 m during the spring inter-monsoon (SIM, March to May) and 59 m during the southwest monsoon (SWM, June to September). The stored water is used for irrigation, generation of electricity and domestic purpose. While one of the outlets is used for overflow, the outflow of the turbines was at 64 m reservoir level. During peak SIM (April-May) the outflow waters smell of H<sub>2</sub>S. The reservoir receives almost all of its rain during the SWM.

### **2.2. Sampling and analysis:**

Monthly sampling was carried out at the deepest point of the reservoir from March 2010 till June 2014 (station T1 in figure 1). A transect (stations T2 to T7) was also sampled to study the variation during peak SWM (July 2012) along the upstream section of the reservoir, where the depth shallowed gradually up to 2.8 m at T7. A portable Conductivity Temperature Depth profiler (CTD, SeaBird Scientific SBE25 plus V2) was used to generate water column temperature data. Water samples were collected using a 5 litre Niskin sampler, at 5 m intervals up to 20 m and thereafter generally every 10 m with the deepest sample taken ~1 m above the bottom. The number of depths sampled varied between 7 and 10 depending on the column depth.

Sub-sampling for dissolved gases (DO, H<sub>2</sub>S and CH<sub>4</sub>) was done carefully using a sampling tube (Tygon tubing fitted with a glass tube). The sampling tube was connected to the nozzle of the Niskin sampler and the water sample was allowed to flow into the sample bottle filling from the bottom up. Care was taken to ensure no bubble was trapped in the sampling tube or the bottle. The samples were fixed with respective reagents after over-flowing three times the sample bottle volume. DO was sampled in 125 mL calibrated ground glass stoppered bottles. It was fixed immediately upon collection by simultaneous additions of 1 ml each of Winkler A and Winkler B reagents. The sample was later analysed in the laboratory following the titration method as detailed in Grasshoff et al. (1983). Samples for H<sub>2</sub>S were collected similarly in 60 ml ground glass stoppered bottles. 4 ml of mixed diamine reagent was added immediately to the sample and gently mixed after replacing the stopper. The absorbance was determined spectrophotometrically at 670 nm (Cline, 1969). For blank,

the surface water sample was treated in the same manner and analysed. CH<sub>4</sub> samples were collected in 125 ml ground glass stoppered bottles, preserved with mercuric chloride and analysed on a Shimadzu Gas Chromatograph-2010, equipped with a flame ionization detector, within a week following the equilibration method of Mc Auliffe (1971), as detailed in Narvenkar et al. (2013).

Nutrient samples (nitrate) were collected in 100 ml high-density polyethylene bottles. The sample bottle was rinsed thoroughly before collection. After collection the samples were stored in ice and later analysed in the laboratory, using the SKALAR autoanalyser following Grasshoff et al. (1983). The nutrient autoanalyser is a segmented flow analyser, where the sample intake and reagent addition is completely automated. The nitrate in the sample was reduced to nitrite by passing it through a Cu-Cd reductor column using NH<sub>4</sub>Cl as a buffer. Sulphanilamide and n-(1-naphthyl)-ethylenediamine dihydrochloride was then added to the sample to develop a pink coloured azo dye, the absorbance of which was measured at 543 nm. Calibration was obtained by using potassium nitrate as a standard. The precision of the above method was 0.6%. For particulate organic carbon (POC), 2 to 5 litres of water were filtered through pre-combusted GF/F Whatman filter paper. POC was analysed using an elemental analyser (EURO3000 Eurovector) connected to an Isotope Ratio Mass Spectrophotometer following the protocol detailed in Bardhan et al. (2017).

The stability of the water column was obtained by computing the stability frequency (or Brunt-Vaisala-frequency) as given in Boehrer and Schultze (2008).

$$N^2 = \frac{g}{\rho} \frac{d\rho}{dz}$$

Where N<sup>2</sup> is the stability frequency squared (s<sup>-2</sup>), g is the gravitational force (9.8 m s<sup>-2</sup>) and ρ is the density at depth z.

The layers of the water column were determined by using the temperature difference. For determining epilimnion and hypolimnion, a temperature difference of less than 0.1°C m<sup>-1</sup> was considered, whereas, in the metalimnion, the temperature difference varied between 0.4 and 1°C m<sup>-1</sup>. DO loss rates for the water column (below 20 m) were derived by plotting the average DO below 20 m against time (in days). Simple linear regression was used to find the slope, which denoted the fall in oxygen over time. The water column integrated methane values were calculated by summation of the average methane concentrations of the adjacent depth intervals. Simple linear regression was also used to understand the correlation between bottom DO and temperature difference between surface and bottom, and to see the correlation between temperature difference of the previous winter with the

extent of anoxia in the subsequent summer as shown in figure 5b. The figures were plotted using Ocean Data View 4, Grapher and Illustrator 10.0.3.

### **3. Results and discussion**

#### **3.1 Stratification and mixing in the Tillari Reservoir:**

In general, the water column temperature during the study period varied between 23.7 and 32.9°C. The general water column stratification and mixing conditions in the Tillari Reservoir during different seasons are shown in figure 2. The epilimnion (mixed surface layer with near-uniform temperature), metalimnion (sharp fall in temperature) and hypolimnion (low uniform temperature) were distinctly visible during the SIM (Figure 2a). As a result of summer stratification, the surface epilimnion was restricted to 5 m, below which the metalimnion extended up to 18 m, followed by the deeper hypolimnion. However, with the onset of the monsoonal rainfall, the surface temperatures decreased from ~ 32°C to ~ 28°C, thus eroding the epilimnion, leaving behind the metalimnion which extended from surface till 15 m (Figure 2b). No stratification was observed during October as the heating was not so intense. In contrast to the SIM, the water column was well mixed from November to January due to winter mixing (Figure 2c).

Figure 3a shows the variation of surface temperature at the Tillari Reservoir and air temperature at Panaji, Goa, during the study period. As there was no weather station near the study area, we have used air temperature collected by the Indian Meteorological Department at Panaji, Goa, India, which is ~40 km from the study site. Nonetheless, the excellent match between the data sets show the influence of surface atmospheric heating and cooling on the reservoir water temperature. The warming of the reservoir is also influenced by incoming solar radiation. Limited light measurements available during the first year of sampling showed that the metalimnion and part of the hypolimnion received a significant amount of sunlight (Kurian et al., 2012). The reservoir was subjected to heating twice during the year, once in summer (SIM) and second during the fall inter-monsoon (FIM, October-November). The surface heating during summer showed inter-annual variability with the summer of 2010 showing the maximum temperature during the study period (Figure 3b). The maximum surface temperature observed during summer decreased from 32.9 to 31.3°C in the subsequent years. The summer heating resulted in the warming of the top 5 - 10 m of the water column, where the temperature was above 30°C. The second annual heating observed in October also showed inter-annual variability with October of 2011, showing the highest surface temperature of 30.8°C, warming the top 5 m of the water column. In comparison, October during the rest of the years was cooler, with surface temperatures varying between 27.9 and 29.9°C, the lowest being

observed in 2012. The temperatures in the hypolimnion (below 20 m) generally ranged between 24 and 26°C, except during the monsoon of 2012 and 2013, when the temperatures fell below 24°C. The reservoir experienced complete mixing once a year during winter (northeast monsoon (NEM), December to February) when the temperature of the water column was  $\sim 24^\circ\text{C}$ . Inter-annual variation was observed, with 2010-11 and 2011-12 recording better mixing (isothermal temperatures) in comparison to 2012-13 and 2013-14. Near-complete mixing in the reservoir was also observed during the SWM of 2011 and 2013 in comparison to 2010 and 2012.

To understand stratification and mixing processes in the reservoir, we plotted the stability frequency ( $N^2$ ) against time (Figure 3c). The higher frequency indicated vertical stability (stronger stratification), whereas the lower value indicated mixing. In conjunction with the air and surface temperature, the highest stratification was observed during the SIM (April-May) followed by the FIM. On the other hand, the vertical stability was the least during the NEM, enabling convective mixing of the waters from the surface to the bottom. The vertical stability during the winters of 2010-11 and 2011-12 was lower than that of 2012-13 and 2013-14, supporting better vertical mixing during the former years (Figure 3c). However, the vertical stability during the SWM's (August-September) was higher than the NEM's for 2010 and 2011 and was comparable for the years 2012 and 2013. Thus, while both the NEM and SWM resulted in the mixing of the water column, complete mixing was observed only during the NEM's of 2010-11 and 2011-12 as seen from the temperature profiles.

### **3.2. The impact of physical processes on dissolved oxygen, hydrogen sulphide and methane in the reservoir:**

The above stratification and mixing processes have a profound effect on the biogeochemical processes in a reservoir. Figure 4a shows the inter-annual variation of DO in the Tillari Reservoir. In general, the DO concentrations varied between undetectable levels and 10 mg L<sup>-1</sup>. The epilimnetic waters were oxic throughout the study period, with concentrations ranging between 5 and 10 mg L<sup>-1</sup>. However, the metalimnetic and hypolimnetic DO showed strong intra-annual as well as inter-annual variability. During the summer months between March and June, DO below 20 m noticed a sharp fall to undetectable levels. In 2010, 2013 and 2014, the hypolimnetic waters were anoxic for over three months during summer, wherein the case of the latter two years, low oxygen conditions prevailed in the hypolimnion even during the preceding winter months. In contrast, during the summer of 2011 and 2012, the hypolimnetic waters were anoxic for only a month and a half (between June and July). The rate of oxygen loss was higher during 2011 and 2012 (0.04 and 0.03 mg L<sup>-1</sup> D<sup>-1</sup>, respectively) in comparison to 2013 and 2014 (0.02 and 0.01 mg L<sup>-1</sup> D<sup>-1</sup>, respectively). With the onset of the SWM,

DO in the hypolimnetic waters increased to  $> 5 \text{ mg L}^{-1}$ . The SWM of 2012 and 2013 witnessed a better replenishment of DO in the hypolimnion in comparison to 2010 and 2011 by almost  $1.6 \text{ mg L}^{-1}$ . In addition to summer, the hypolimnetic waters also experienced low oxygen conditions towards the fall end of the SWM (September) and during FIM (October). However, the intensity of low oxygen conditions varied between different years with October 2010, showing the least DO concentrations ( $< 1 \text{ mg L}^{-1}$ ), but never anoxic. The second replenishment of DO in the hypolimnion occurred during the winter months (November to February), during which the concentrations rose to  $> 4 \text{ mg L}^{-1}$ . However, the winters of 2010-11 and 2011-12 showed better replenishment of DO in the sub-surface layers in comparison to the winters of 2012-13 and 2013-14. Thus, while the monsoon mixing does inject DO in the hypolimnion, it is consumed during the FIM, and the subsequent replenishment during the NEM due to winter mixing depends on the strength of the winter as seen above.

The variation of  $\text{H}_2\text{S}$  in the Tillari Reservoir is shown in figure 4b. In general,  $\text{H}_2\text{S}$  was observed below 20 m in association with the summer anoxia and varied between 1 and  $9.9 \mu\text{M}$ . The maximum concentration was found during the summer of 2013, followed by  $9.2 \mu\text{M}$  during the summer of 2010. Also, during these years,  $\text{H}_2\text{S}$  was observed in the hypolimnion for more than three months. On the other hand, relatively lower concentrations ( $< 4 \mu\text{M}$ ) were found during the summers of 2011 and 2012 with the occurrence of  $\text{H}_2\text{S}$  for just above a month.  $\text{H}_2\text{S}$  was also observed during the summer of 2014, where the concentration varied around  $5 \mu\text{M}$ .  $\text{CH}_4$  varied similarly to  $\text{H}_2\text{S}$  with maximum concentrations ranging between  $47 \mu\text{M}$  and  $185 \mu\text{M}$  in the anoxic sub-surface layers (Figure 4c). High concentrations of 156 and  $185 \mu\text{M}$  were observed during July 2010 and June 2014, respectively. In comparison, moderate  $\text{CH}_4$  concentrations ( $98 \mu\text{M}$  and  $86 \mu\text{M}$ ) were found during July 2012 and June 2013, respectively. The lowest level of  $\text{CH}_4$  ( $47 \mu\text{M}$ ) in association with the seasonal anoxia was observed during the summer of 2011.

Oxygen depletion in sub-surface waters depends primarily on stratification set in due to heating of the surface water (Hawkins, 1985; Townsend, 1999; Narvenkar et al., 2013; Zhang et al., 2015; Itoh et al., 2015). The anoxia was primarily ascribed to the effect of temperature on the microbial metabolism in the hypolimnion (Townsend, 1999). An eight years time-series study conducted in two tropical reservoirs in Australia revealed long periods of anoxia in the reservoirs with the smaller reservoir experiencing nine months and the larger reservoir experiencing five months of anoxia. While the rates of oxygen loss experienced by Tillari Reservoir is much lower in comparison to these two Australian reservoirs ( $0.11 - 0.24 \text{ mg L}^{-1} \text{ D}^{-1}$ ), they were comparable with those reported for the temperate water bodies ( $0.003 - 0.12 \text{ mg L}^{-1} \text{ D}^{-1}$ , Townsend, 1999; Hudson and Vandergucht, 2015).



To relate stratification and mixing to the oxygen loss, H<sub>2</sub>S and CH<sub>4</sub> production, we plotted the temperature difference between surface and bottom waters with the bottom oxygen concentrations (Figure 5a). The temperature difference was negatively correlated to bottom oxygen, indicating oxygen loss during stratification and gain during mixing. We also plotted the number of days the oxygen concentration in the hypolimnion was less than 0.14 mg L<sup>-1</sup> during SIM (summer) with the temperature difference of the previous NEM (winter, Figure 5b). The figure showed a positive correlation between the two indicating whenever winter mixing was intense as observed during the winters of 2010-11 and 2011-12, oxygen was replenished in the hypolimnion, and the following summers (2011 and 2012) observed shorter periods of anoxia and lower H<sub>2</sub>S and CH<sub>4</sub> concentrations (Table 1). On the other hand, when the winter mixing was weak as seen during the winters of 2012-13 and 2013-14, oxygen replenishment to the hypolimnion was weaker, leading to extended periods of anoxia and higher H<sub>2</sub>S and CH<sub>4</sub> during the subsequent summers. In the latter, this was observed despite high DO in the hypolimnion during the SWM of 2012 and 2013. Replenishment of DO in the hypolimnion was also observed in association with the monsoonal runoff (Figure 4a), due to the lateral advection of dense cooler rainwater from the upstream section of the river as shown in figure 6. Thus, while DO was replenished in the bottom waters during the SWM, its concentration in the deeper layers was controlled by the injection of DO during winter convection. Similar results were observed by Yoshimizu et al. (2010) in Lake Biwa, a warm monomictic lake in Japan, where milder winters were associated with loss of oxygen, resulting in lower oxygen saturation in the bottom waters, the difference being that Lake Biwa never went anoxic, unlike the Tillari Reservoir.

Oxygen consumption in the water column depends on the supply of oxygen by diffusion/advection and the amount of organic matter available for degradation. In the case of the Tillari Reservoir, one can reasonably assume minimum or no replenishment of oxygen by diffusion to the deeper layers during summer as stratification was strong enough to allow any vertical diffusion. The sampling was done in the deepest portion of the original riverbed, close to the dam, where there is no outlet. Thus, one may safely assume minimum lateral advection in the sub-surface layers of the reservoir before the SWM. Nonetheless, the anoxia during peak summer was well spread, covering a significant portion of the reservoir as observed from the H<sub>2</sub>S smell from the outgoing waters of the powerhouse (Figure 1). The Tillari Reservoir does not have any agricultural activities in the catchment area and receives most of its rain during the SWM. Nitrate concentrations observed in the reservoir (16 μM during SWM, an annual average of 3.4 μM) were modest when compared to the nitrate concentration observed in the Markandeya Reservoir (~ 37 μM in March, Narvenkar et al., 2013), located just ~70 km northeast of Tillari on the Deccan plateau in peninsular India, which receives agricultural runoff.

Chlorophyll *a* concentrations observed in the reservoir were also modest with maximum concentrations (up to 6.6 mg m<sup>-3</sup>) found during the SWM (June-July) and NEM (December, Ayaz Ahmed, personal communication). Recently Bardhan et al. (2017) have attributed higher POC in the epilimnion to primary productivity and high POC in the metalimnion during the SWM to runoff (allochthonous) in the Tillari Reservoir. In any case, the average POC below 20 m in the reservoir was ~ 0.34 mg C L<sup>-1</sup> indicating that carbon did not limit the consumption of oxygen through remineralization.

Another mechanism that has an impact on water quality in a reservoir is the changes in the water level (Wang et al., 2009; Braga et al., 2015; Wang et al., 2020). During summer stratification when the hypolimnion turns anoxic, reduced soluble compounds such as NH<sub>4</sub><sup>+</sup>, Fe<sup>2+</sup>, Mn<sup>2+</sup> and H<sub>2</sub>S will be released from the anoxic sediments to the overlying waters which can deteriorate the water quality of the reservoir. Besides, phosphorus released from anoxic sediments can stimulate phytoplankton growth when hypolimnetic waters are entrained into surface waters during mixing events. This internal nutrient loading can aggravate eutrophication through cyanobacterial bloom and subsequent hypolimnetic anoxia in the summer (Beutel et al., 2007). The water level in the Tillari Reservoir was maximum during the SWM and least during the SIM. Interestingly, the lowest water level during the SIM's of 2011 and 2012 was observed with low concentrations of H<sub>2</sub>S and CH<sub>4</sub> (Figure 4) and vice-versa for 2010, 2013 and 2014. However, since we do not know the morphometry of the reservoir, assessing the impact of water level changes and sediment oxygen demand is difficult. The oxygen depletion in the metalimnion not only hosts a variety of nitrogen transformation processes (nitrification, denitrification and ammonification, Bardhan et al., 2017) but also supports sulphate reduction and methanogenesis. While the oxic surface hosts phytoplankton taxa belonging to desmids, green algae, blue-green algae and diatoms (Ayaz Ahmed, personal communication), brown sulphur bacteria occur under low light conditions in the sulphidic layer during the seasonal anoxia (Kurian et al., 2012).

The high concentration of sub-surface CH<sub>4</sub> observed during the summer of 2010 has been reported in Narvenkar et al. (2013), which is the first-ever study on CH<sub>4</sub> distribution from eight reservoirs of India. The study revealed that the CH<sub>4</sub> emission from Indian reservoirs had significantly been overestimated. Recently Bansal et al. (2015) reported enhanced CH<sub>4</sub> flux (172 mg m<sup>-2</sup> d<sup>-1</sup>) from a subtropical reservoir (Okhla, located on the river Yamuna), which was attributed to high organic and nutrient loadings to the reservoir, high percentage of shallow areas and presence of dense aquatic vegetation. They also found that the summer season exhibited significantly higher CH<sub>4</sub> flux as compared to monsoon and winter seasons due to favourable water and sediment conditions.

Hypolimnetic CH<sub>4</sub> build up in a reservoir mainly depends on the autochthonous production, nature of organic matter, surface area, age of the reservoir and temperature (Saint Louis et al., 2000; Narvenkar et al., 2013 and references therein). Reports suggest that CH<sub>4</sub> emission from the reservoirs decreases significantly within 20 years of inundation, with significant emission being observed within a few years of flooding (Galy-Lacaux et al., 1999). Tillari Reservoir was inundated in 2006, and the water column integrated CH<sub>4</sub> ranged from 0 - 41632 mg m<sup>-2</sup> in the present study. Our observations over five years showed large inter-annual variability in the CH<sub>4</sub> and H<sub>2</sub>S (Table 1). During the summer anoxia, the hypolimnion acted as a reservoir of CH<sub>4</sub>, and the integrated values ranged between 3502 and 41632 mg m<sup>-2</sup>. Recent studies have provided information on concentrations of CH<sub>4</sub> and H<sub>2</sub>S in the hypolimnion and reported that the Indian reservoirs may not be significant emitters of these gases as predicted previously since they are oxidised at depths by micro-organisms (Narvenkar et al., 2013; Naqvi et al., 2018). Naqvi et al. (2018) have demonstrated experimentally that accumulated CH<sub>4</sub> gets consumed through a widespread methanotrophy-denitrification coupling, potentially mitigating eutrophication and, controlling emissions of not only CH<sub>4</sub> but also N<sub>2</sub>O to the atmosphere. However, since H<sub>2</sub>S smell was prevalent at the outlet of the power plant (Figure 1), some amount of CH<sub>4</sub> would have fluxed out, but this needs to be estimated.

As explained in section 3.1, the winters of 2010-11 and 2011-12 were well mixed due to convective mixing of the waters from the surface to the bottom. Subsequent observations during January – March of 2011 and 2012 witnessed a better-oxygenated water column with very low CH<sub>4</sub> concentration in the hypolimnion. During these years, the CH<sub>4</sub> build up in the anoxic hypolimnion started only in April/May. In contrast, the winters of 2012-13 and 2013-14 experienced less mixing, and subsequently, suboxic conditions and CH<sub>4</sub> build up in the hypolimnion started as early as January. Time series measurements in the reservoir showed a decreased intensity of summer stratification during 2010-2014 (Fig. 5), which is said to affect the water column redox condition and in turn, affects the CH<sub>4</sub> build-up. As seen from Figure 4 and Table 1, anaerobic conditions were developed every summer, but with varying intensity. The year 2010 was the most intense with reducing conditions persisting for 113 days (with ~29 m anaerobic hypolimnion) and resulted in a CH<sub>4</sub> concentration of 156 μM (41632 mg m<sup>-2</sup>) in the bottom waters (Table 1). As expected from the physical parameters, the water column CH<sub>4</sub> (46 μM) and H<sub>2</sub>S (3.1 μM) concentrations were the lowest during the summer of 2011. In 2012, the anaerobic hypolimnion persisted for a longer time (85 days), and probably resulted in higher CH<sub>4</sub> concentrations (97 μM) as compared to 2011 (Table 1). The hypolimnetic CH<sub>4</sub> accumulation during 2013 was comparable (86 μM) to 2012 despite highly reducing conditions (H<sub>2</sub>S ~9.8 μM), probably due to low autochthonous production (annually

averaged integrated Chl *a* 48 mg m<sup>-2</sup> as compared to 63 mg m<sup>-2</sup> during 2012) or the coupling between methanotrophy and denitrification (Naqvi et al., 2018). In the subsequent year (2014), the CH<sub>4</sub> concentration was the highest (185 μM; June), however, the measurements were very sparse (only 3 observations were carried out) to derive a conclusion. Overall, our observations showed that physical processes (mixing and stratification) play a significant role in controlling the redox conditions and in turn, the H<sub>2</sub>S and CH<sub>4</sub> build up in the reservoir.

In a study on the subtropical reservoir in Taiwan (Fei-Tsui Reservoir), Itoh et al. (2015) found a similar impact of atmospheric forcing on the biogeochemistry of the reservoir. They reported higher production of CH<sub>4</sub> in summer when the preceding winter mixing was weak and vice-versa. Very few studies on Indian reservoirs have focused on the role of physical processes on the biogeochemistry of the reservoir (Sugunan, 2000). In a study on nine lakes in Jammu and Kashmir, Zutshi et al. (1980) reported that the lakes situated at 2000 m altitude were dimictic, whereas the lakes located below this altitude were monomictic with the deeper lakes exhibiting loss of oxygen in the subsurface layers during summer. Narvenkar et al. (2013) observed that higher latitude reservoirs in India, such as Rihand (24.2 °N) and Bakhra Nangal (31.4°N) remain well oxygenated throughout the year in comparison to lower latitude reservoirs (between 10 and 17.5 °N) which experienced hypoxic to anoxic conditions during summer. Estimates show high CH<sub>4</sub> emissions from the tropical reservoirs especially from the Indian reservoirs (Lima et al., 2008). However, these emission estimates, which were based on assumptions, have been proven otherwise by actual measurements carried out by Narvenkar et al. (2013). In the present study, the extent of stratification and mixing varied during different years with a resultant impact on DO concentrations and the production of H<sub>2</sub>S and CH<sub>4</sub> in the deeper layers of the reservoir. It was observed that the extent of oxygen depletion in the deeper layers during summer depended on the intensity of winter mixing in the preceding year, emphasizing the role of physical processes in controlling the biogeochemistry of the reservoir. Under the present scenario of global warming, winters may not be as cold as previously observed with possibly decreased duration of cold periods. Such a scenario will impact the mixing and over-turning of water bodies thereby decreasing oxygen supply to the deeper layers of freshwater reservoirs. With more warming, the above result has important implications for the production of H<sub>2</sub>S and CH<sub>4</sub> and in turn the green credentials of these reservoirs. Since studies addressing physical processes and their impact on biogeochemistry in tropical reservoirs are sparse, more studies are needed to understand the mechanism of oxygen loss and H<sub>2</sub>S and CH<sub>4</sub> production in these reservoirs.

## **5. Conclusion:**

In the present study, we have reported annual variation for over four years focusing on stratification and mixing with the resultant impact on biogeochemistry in a tropical reservoir. The study details the variation of temperature, DO, H<sub>2</sub>S and CH<sub>4</sub> in a pristine (agriculture-free and domestic effluent free) reservoir in India. The reservoir experiences stratification during summer, which results in anoxia in the profundal zone with the production of H<sub>2</sub>S and CH<sub>4</sub>. The intrusion of cooler oxygen-rich monsoonal runoff replenishes the deeper layers during the SWM. The reservoir is monomictic (mixing during winter), during which the water column gets well-mixed, and oxygen is replenished in the deeper layers of the reservoir. Importantly, the severity of oxygen depletion during summer was observed to be intricately linked to the extent of winter mixing seen in the preceding year, which may be a typical feature for tropical reservoirs. Global warming may worsen this condition causing more severe oxygen depletion and production of CH<sub>4</sub> in the profundal zone.

## **Declarations:**

- Ethics approval and consent to participate : Not applicable
- Consent for publication: Manuscript is cleared by CSIR-NIO for publication
- Availability of data and material: Data available at NIO data site
- Competing interests: Not applicable
- Funding: included in the acknowledgement

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### Authors contribution:

DMS, SK, HU, MU and SWAN designed the study. DMS conceptualised and wrote the manuscript, compiled most of the data and drew all graphs. SK and GS helped in writing the manuscript. GS generated part of the CH<sub>4</sub> data and prepared table 1. HN helped in data compilation. All authors have approved the article.

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### Figure Captions:

Figure 1: Station locations in the Tillari Reservoir, T1 is the time series station. Stations T2 to T7 were sampled in July 2012 to study the variation along the upstream section of the river. The dotted line shows the original river bed and the flow of the river. T1: 15°45'30.00"N, 74° 5'30.00"E; T2: 15°45'34.80"N, 74° 6'12.80"E; T3: 15°45'38.90"N, 74° 6'55.60"E; T4: 15°45'43.00"N, 74° 7'39.50"E; T5: 15°45'56.90"N, 74° 8'17.60"E; T6: 15°46'4.20"N, 74° 8'48.90"E; T7: 15°46'10.00"N, 74° 9'18.10"E. Base map downloaded from Google maps.

Figure 2: Typical temperature variation in the Tillari Reservoir depicting the various layers during different seasons (2a. SIM (May), 2b. SWM (August) & FIM (October) and 2c. NEM (January)).

Figure 3a) Time-series variation of surface water temperature (black) at the Tillari Reservoir and air temperature (red) collected at a meteorological station ~40 km from the reservoir. 3b) Time-series variation of water column temperature in the Tillari Reservoir. 3c) Time-series variation of the stability frequency at the Tillari Reservoir. X axis shows the month and year from 31/3/2010 to 11/6/2014. The dashed line indicates end of year. The southwest monsoon is from June to September (JJAS).

Figure 4: Time-series variation of dissolved oxygen (4a), hydrogen sulphide (4b) and methane (4c) in the Tillari Reservoir. X axis shows the month and year from 31/3/2010 to 11/6/2014. The dashed line indicates end of year. The southwest monsoon is from June to September (JJAS).

Figure 5: a) Scatter plot of bottom DO versus temperature difference between surface and bottom at the Tillari Reservoir. b) Plot of number of days the water column (below 20 m) was suboxic against the least temperature difference during the preceding winter (November to February).

Figure 6: Temperature section along the Tillari River. The isotherms in the deeper layers indicate intrusion of cooler dense waters from the upstream part of the river.

Figure 1.

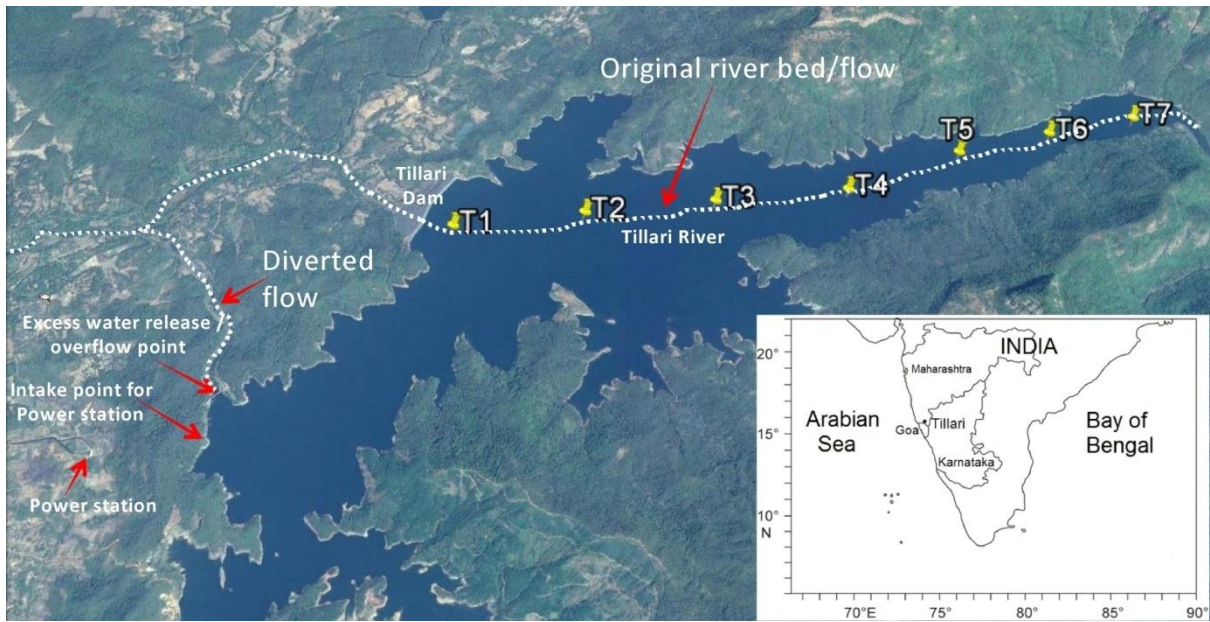


Figure 2:

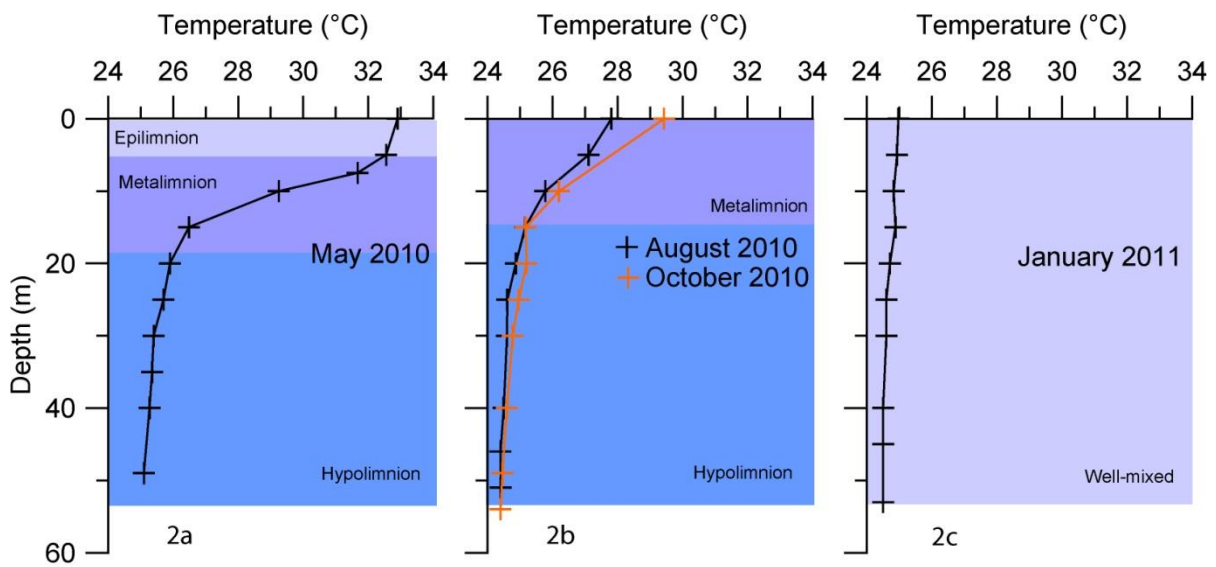


Figure 3

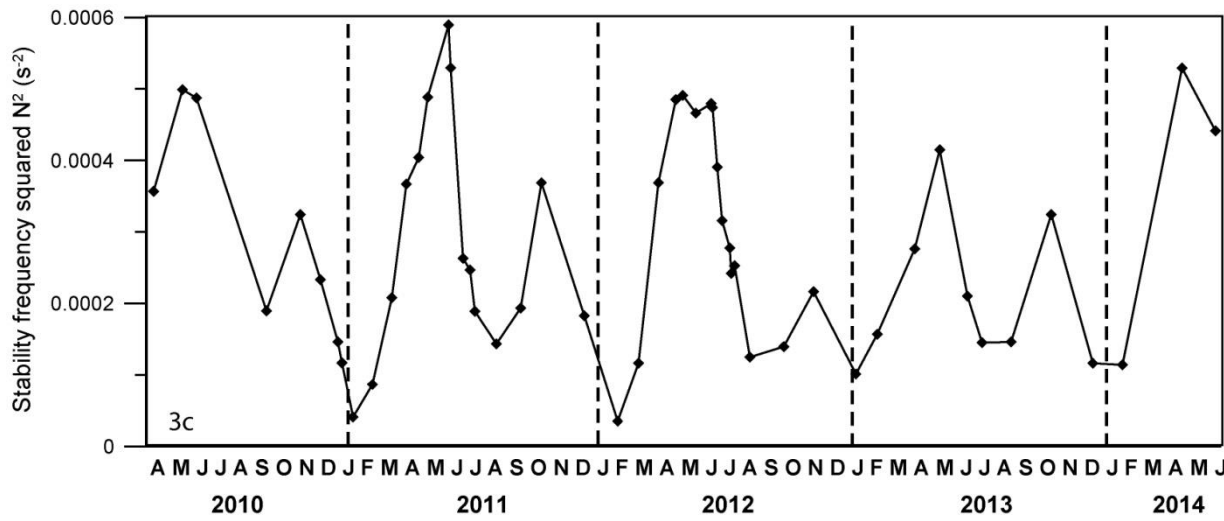
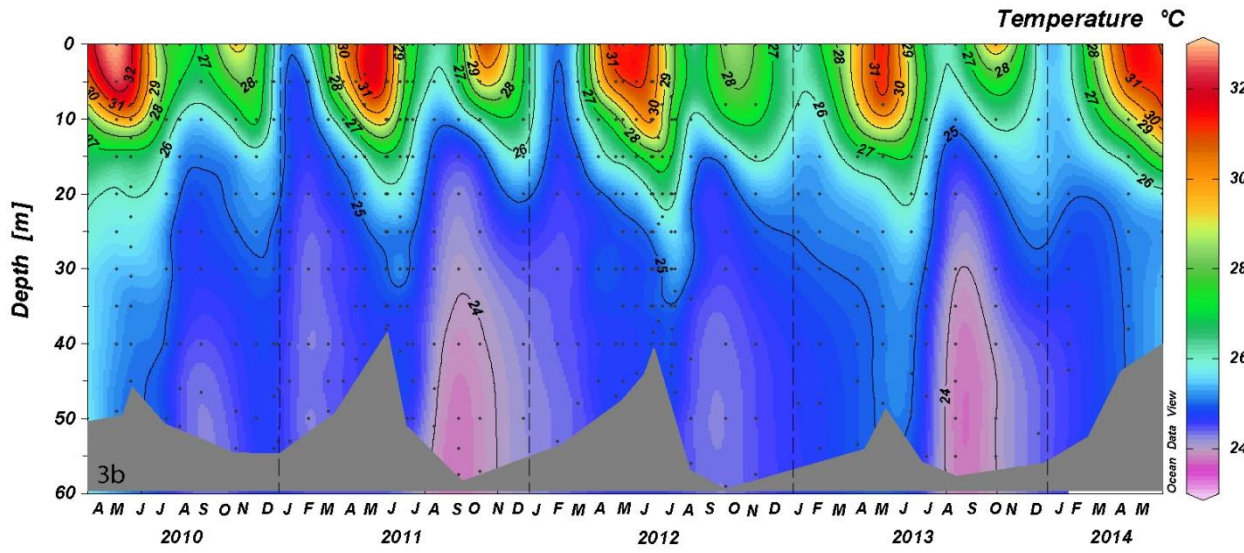
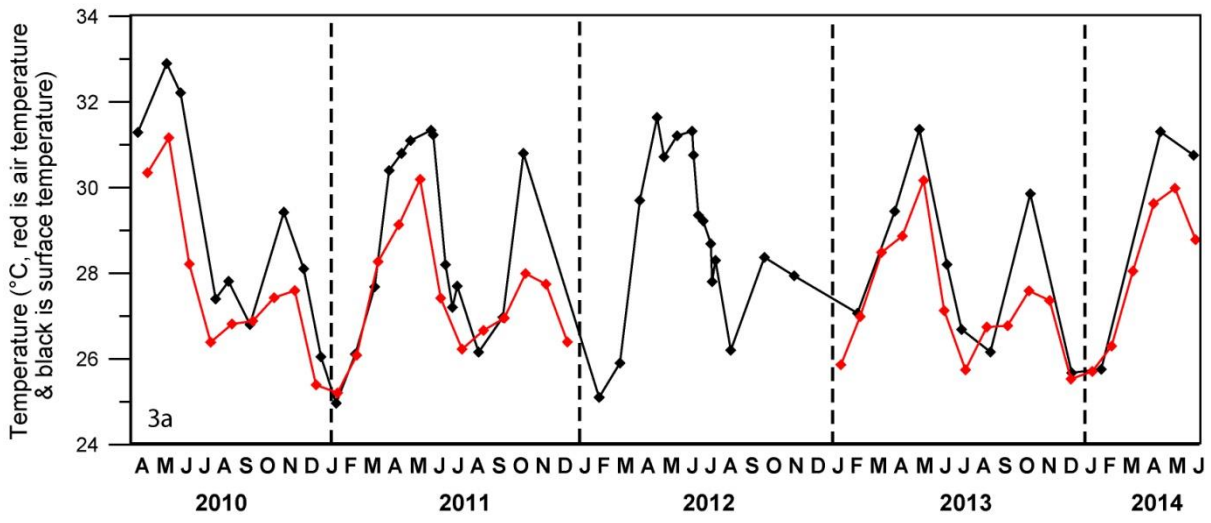




Figure 4

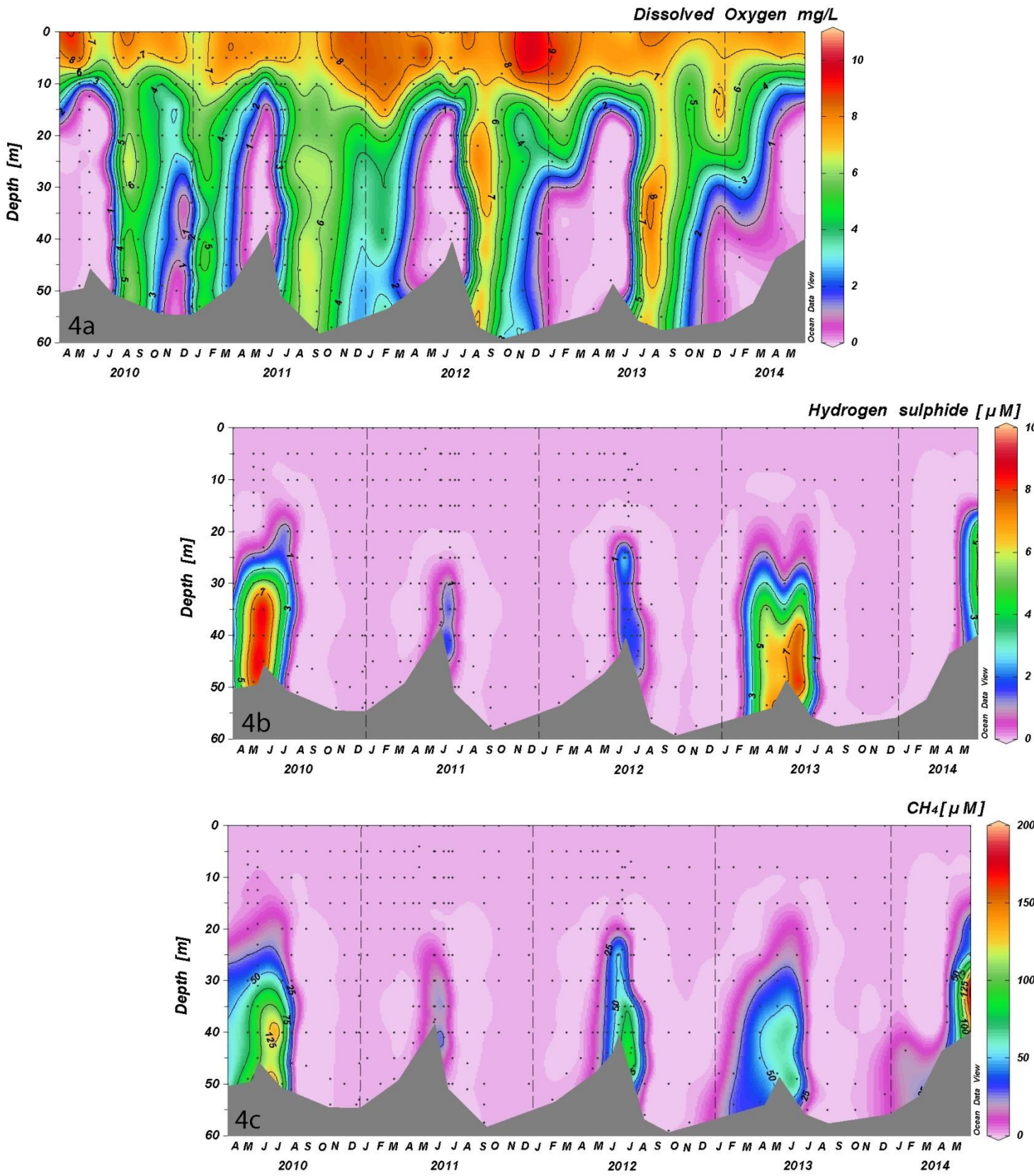


Figure 5

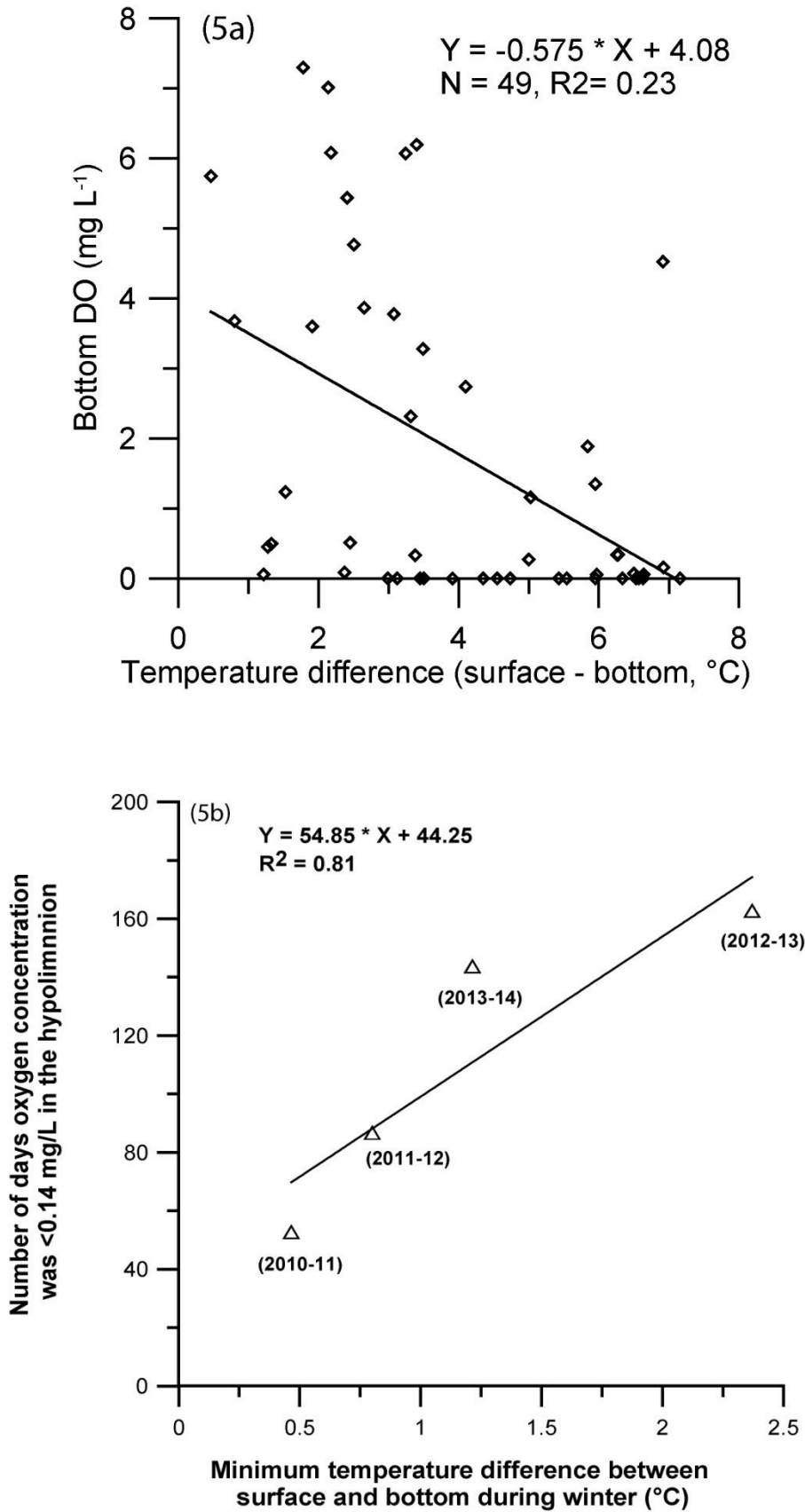


Figure 6.

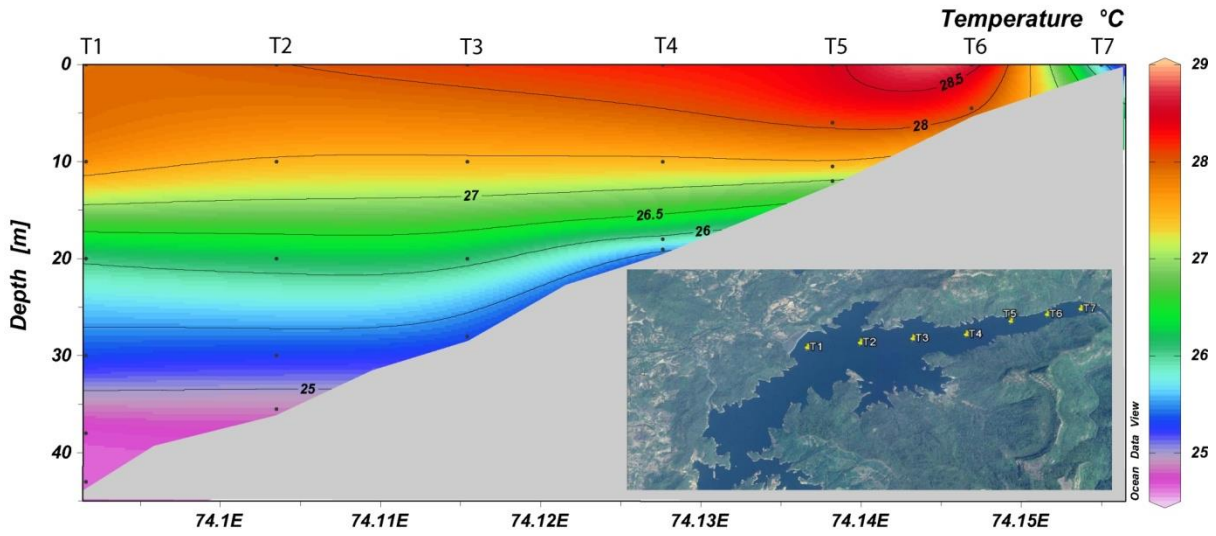


Table 1: Methane and H<sub>2</sub>S levels within the anaerobic (O<sub>2</sub><0.14 mg L<sup>-1</sup>) hypolimnion of the Tillari reservoir during 2010-2014.

Year	No. of days of anaerobic (O <sub>2</sub> < 0.14 mg L <sup>-1</sup> ) hypolimnion (depth m)	Maximum H <sub>2</sub> S (μM)	Maximum hypolimnetic CH <sub>4</sub> (μM)	Water column integrated CH <sub>4</sub> (mg m <sup>-2</sup> )	Bottom temperature range (°C)
2010	113 (29.7)	9.2	156.3	24225-41632	25.75-24.95
2011	51 (12.9)	3.11	46.6	222-7692	24.77-24.53
2012	85 (15.8)	3.43	97.8	1857-17919	24.87-24.62
2013	161 (22.4)	9.88	86.2	1773-20653	25.08-24.45
2014	142 (14.5)	5.49	185.0	1092-17473	25.33-24.35