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Dissolved methane in Indian freshwater reservoirs

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Abstract

Emission of methane (CH₄), a potent greenhouse gas, from tropical reservoirs is of interest because such reservoirs experience conducive conditions for CH₄ production through anaerobic microbial activities. It has been suggested that Indian reservoirs have the potential to emit as much as 33.5 MT of CH₄ per annum to the atmosphere. However, this estimate is based on assumptions rather than actual measurements. We present here the first data on dissolved CH₄ concentrations from eight freshwater reservoirs in India, most of which experience seasonal anaerobic conditions and CH₄ buildup in the hypolimnia. However, strong stratification prevents the CH₄-rich subsurface layers to ventilate CH₄ directly to the atmosphere, and surface water CH₄ concentrations in these reservoirs are generally quite low (0.0028-0.305 μ M). Moreover, only in two small reservoirs substantial CH₄ accumulation occurred at depths shallower than the level where water is used for power generation and irrigation, and in the only case where measurements were made in the outflowing water, CH₄ concentrations were quite low. In conjunction with short periods of CH₄ accumulation and generally lower concentrations than previously assumed, our study implies that CH₄ emission from Indian reservoirs has been greatly overestimated.

Keywords: Methane, Eutrophication, Stratification, Dams, Reservoirs, India

1. Introduction

Several recent studies have shown that tropical reservoirs, built for hydroelectric power generation, irrigation or flood control, are significant contributors of methane (CH₄) to the atmosphere (Keller and Stallard 1994; Galy-Lacaux et al. 1997; 1999; Fearnside 2002; Lima 2005; Abril et al. 2005; Ramos et al. 2006; Kemenes et al. 2007). In stratified systems, organic matter decomposition leads to anoxia enhancing CH_4 accumulation in bottom waters (Guérin et al. 2006; Guérin and Abril 2007). However, CH₄ accumulation in reservoirs depends on environmental factors that affect CH₄ production, oxidation or transport. These factors include the type and amount of organic matter, the dominant organic matter decomposition pathway, temperature, hydrological conditions and vegetation. Methane accumulated in the bottom waters may be eventually released to the atmosphere across the air-water interface depending on physical processes such as the wind-induced or convection-driven mixing (Liu et al. 1996; Guérin and Abril 2007), at the turbines of hydroelectric projects and downstream of the dams from the outflowing subsurface waters (Abril et al. 2005). However, during stratified conditions the diffusive flux of surface CH₄ is not very large due to rapid oxidation of CH₄ as it diffuses upwards to the oxygenated surface waters (Borges et al. 2011). Consequently, CH_4 concentrations in surface waters are generally low even though CH_4 is also reported to be produced within oxygenated water columns of lakes (Schulz et al. 2001; Grossart et al. 2011).

Methane flux from a reservoir depends on several factors such as the prevailing meteorological conditions, the quantity and nature of the organic carbon, surface area and age of the reservoir (Saint Louis et al. 2000). An initial spike in CH₄ emission appears to occur after a few years of flooding, due to the decomposition of labile organic matter, followed by a considerable decrease in emission usually within 20 years (Galy-Lacaux et al. 1999).

Natural wetlands are known to contribute substantially to global CH₄ emission. Combining bottom-up and top-down fluxes, Chen and Prinn (2006) reported that the southern and tropical regions account for >70% of total global wetland emissions, while other studies (Li et al. 2002; Yan et al. 2003) found lesser emissions from the tropical rice agriculture. Since methane emissions from these sources depend on various environmental factors, the uncertainties associated with the estimations are quite large. In a recent re-evaluation of CH₄ emission Bastviken et al. (2011) argued that the tropics account for about 49% of the total CH₄ emission from freshwater ecosystems. Based on CH₄ data from Lake Kiwu, Borges et al. (2011) reported that the CH₄ emission from natural tropical lakes, particularly those experiencing permanent stratification, was rather limited. This was in sharp contrast to earlier estimates made by Saint Louis et al. (2000) who suggested that 90% of

the CH₄ emissions were from reservoirs in the tropics. Moreover, in the compilation by Bastviken et al. (2011) only 9 out of 36 publications and only 7 out of 106 data entries deal with tropical lakes. This suggests that the tropical freshwater ecosystems have been greatly under sampled and thus it is important to get additional CH_4 data from these regions.

Located between 8°N and 37°N latitudes and experiencing largely tropical/subtropical climatic conditions. India has around 4300 dams (http://www.rivernet.org/general/wcd/wcd_overview_english.pdf), ranking third globally in terms of numbers after China and the USA. It has been suggested that the combined CH₄ emission from these dams, estimated to reach 33.5 megatonne (MT) per annum, could be higher than similar emissions from any other country (http://www.sandrp.in/drp/May_June 2007.PDF). This estimate, which includes emissions from reservoirs (1.1 MT), spillways (13.2 MT) and turbines of hydropower dams (19.2 MT), is however based on assumed values since there have been no measurements of CH₄ in Indian reservoirs so far. The only published data on CH₄ fluxes from Indian aquatic systems come from lakes and rivers (Purvaja and Ramesh (2001) and Rajkumar et al. (2008) in the Adyar River; Verma et al. (2002) from the Vembanad Lake and Shalini et al. (2006) from the Pulicat Lake). In addition, Biswas et al. (2007) studied CH₄ dynamics in the Sundarban mangrove ecosystem of Northeast India. We provide here results of the first ever study of CH₄ from a number of reservoirs covering a wide latitudinal range that allow us to assess the validity of the above estimate.

2. Study sites and methodology followed

Eight dams, located within a wide latitudinal band (9.8°N-31.4°N), were selected for the present study (Table 1 and Fig.1). Six of these dams are located in or close to the Western Ghats, a mountainous tropical region close to the Indian west coast that receives heavy rainfall during the southwest monsoon (SWM). The seventh – the Rihand Dam over the river by the same name that originates in peninsular India is situated at the southern edge of the central part of the Indo-Gangetic Plain just north of the Tropic of Cancer. The eighth – the Bhakra-Nangal Dam is built over the Sutlej River at the foothills of the Himalayas. The reservoirs of these dams vary greatly in size from very small systems such as Selaulim to very large ones such as Bhakra-Nangal and Rihand (Table 1). They also experience widely different climatic conditions. Thus, our data should be representative of reservoirs of South Asia as a whole. All of these reservoirs were sampled in summer when the water column was well stratified. Additional observations were made in winter in some reservoirs to study the seasonal variations.

Water sampling was carried out using 5-litre Niskin samplers mounted on a nylon rope and fitted with reversing thermometers to measure the temperature at the sampling depth. Sub-samples for dissolved oxygen (DO), hydrogen sulfide (H₂S) and CH₄ were collected carefully avoiding atmospheric contamination. While samples for DO were analyzed at site following the Winkler procedure, those for CH₄ were preserved with mercuric chloride and carried to the National Institute of Oceanography, Goa, and analyzed within a week following Mc Auliffe (1971). Briefly, 25 ml of the sample was equilibrated successively three times with an equal volume of ultra-high-purity grade helium in a gas-tight syringe for 5 min, and the extracted moisture-free headspace was analyzed on a gas chromatograph (Shimadzu 2010) equipped with a flame ionization detector. Separation was achieved on a stainless steel column (1.5 m length, 2.2 mm diameter) packed with molecular sieve (5A 80/100 mesh). Calibration was carried out using standard gas mixtures and air samples were frequently run to monitor the detector response. Samples for H₂S were analysed by the spectrophotometric method as described by Cline (1969). Nutrients (NO₃⁻, NO₂⁻ and PO₄⁻³⁻) were measured using a SKALAR autoanalyzer. For estimation of Chlorophyll a, a known volume of water was filtered through a Whatman GF/F filter paper (47mm diameter, 0.7 µm pore size) under low vacuum. Chlorophyll a was extracted in 10 ml of 90% acetone in the dark for 24 hours in the refrigerator and the fluorescence was measured using a Turner Designs fluorometer (10-AU).

3. Results

Vertical profiles of temperature, DO and CH₄ in all reservoirs are shown in Figures 2, 3, and 4. All reservoirs showed strong stratification during summer (Fig. 2). While the water temperature at the surface ranged between 26.5°C and 32.9°C, it varied between 21.7°C and 26.5°C with the exception of the Bhakra-Nangal Reservoir where the hypolimnion was much cooler (to a minimum of 14.4°C) reflecting the glacial source of water. Thus, the surface-to-bottom temperature difference was much higher in summer (ranging from 4.7°C in Idukki to 14.4°C in Bhakra-Nangal) as compared to the fall/winter (1.2°C in Tillari and 3°C in Idukki). The quasi time series measurements in the Markandeya reservoir showed an increase in this gradient from 3.6°C in April to 5.1°C in May 2007 (Fig. 3 a-c).

The epiliminia were well-oxygenated at all times in all reservoirs. In summer, DO decreased sharply within the thermocline reaching hypoxic levels in the hypolimnion of Supa, suboxic (denitrifying) levels in Markandeya and Koyna, and completely anoxic (sulphidic) levels in Idukki, Tillari and Selaulim reservoirs (Fig. 2, 3 and 4). The two northern reservoirs (Bhakra-Nangal and Rihand) remained oxic throughout the water column (Fig. 2a and 2b). Observations in Markandeya

in 2007 showed temporal development of hypolimnetic O_2 deficiency and the waters turned from hypoxic to suboxic within 51 days from spring to summer (Fig. 3).

Surface CH_4 concentrations were generally very low, varying between 0.0028 and 0.305 μ M in all reservoirs (Table 2). However, CH_4 accumulated within the hypolimnion with its concentration increasing rapidly with depth once DO was completely depleted (Fig. 2, 3, and 4). High CH_4 concentrations were observed in the southern reservoirs which experience severe DO depletion in summer. In comparison, significant CH_4 accumulation was not seen in the more oxygenated waters of the Bhakra Nangal and the Rihand reservoirs located in North India (Fig. 2a and 2b).

The aforementioned transition from hypoxic to suboxic states during March-May 2007 in the Markandeya Reservoir was accompanied by increases in CH₄ concentrations from close to zero in March to 30 μ M in April and 55 μ M in May. The observed CH₄ concentrations yield a rate of accumulation around 0.7 μ M d⁻¹ between March and April, and 2.8 μ M d⁻¹ between April and May. Observations in the subsequent years showed similar distribution patterns as in 2007 but with lower buildup of CH₄ (maximum 7 μ M in April 2008 and 27 μ M in May 2009, Fig. 3).

In order to further illustrate seasonal contrast in CH₄ cycling, we have used data from the Tillari Reservoir collected during July and December 2010 (Fig. 4a and 4b). In July the hypoliminion was strongly anoxic with the H₂S concentration reaching up to ~9 μ M with a maximum CH₄ concentration of 156 μ M (the highest observed in the present study). Despite its buildup below the thermocline, CH₄ concentration within the epilimnion was quite low (<0.10 μ M, Fig. 4a). The water column was very weakly stratified in December with a surface-to-bottom temperature difference of only 1.2°C. However, the DO in the hypoliminion was still quite low (hypoxic but not suboxic). The corresponding CH₄ content was low as well; it was, in fact, lower than the concentrations recorded in the upper 20 m (Fig. 4b).

Concentrations of the two major macronutrients – phosphate and NO_3^- – were low to moderately high (Table 2). Inorganic phosphate concentration in the epilimnion varied from 0.072 to 3.17 μ M. Nitrate was also present at low levels (<3.2 μ M) except in Markandeya and Idukki reservoirs where its concentrations reached up to 36.9 and 23.9 μ M, respectively. The peak Chlorophyll *a* concentration, an indicator of biological productivity, varied over a wide range (from 0.71 mg m⁻³ in Rihand to 8.05 mg m⁻³ in Markandeya, Table 2). The moderate nutrients and chlorophyll *a* concentrations indicate that the reservoirs sampled were not severely eutrophied.

4. Discussion

Seasonal data available from the few reservoirs indicate that the water column gets vertically mixed at least once during the winter season. For example, our observations together with recently published data from the Tillari Reservoir, (Madhan et al. 2012; Kurian et al. 2012), show the temporal development of water column stratification with a decline in the DO within the hypolimnion through spring/summer with subsequent reoxygenation during winter mixing. Observations in Markandeya and Koyna (not presented) in late winter/early spring follow the same pattern.

Methane is produced in anoxic sediments/water column and oxidized in aerobic/anaerobic zones (Panganiban et al. 1979; Eller et al. 2005); hence, anoxia is the primary factor required for CH_4 production and anoxic bottom waters of stratified reservoirs are well known for high methane accumulation (Guérin et al. 2006; Guérin and Abril 2007). In the present study too, significant CH_4 buildup (>1 μ M) was observed when water column DO and NO_3^- were completely consumed (Idukki, Tillari and Selaulim) and sulphide was detected. However, there were instances of moderate CH_4 accumulation in non sulphidic waters (Markandeya and Koyna) in the presence of NO_3^- but only when the latter showed a decreasing trend. This is exemplified by the data from Markandeya collected on 22^{nd} April 2008 (Fig. 3f). On this occasion, NO_3^- profile indicated a mid-depth maximum (33.5 μ M at 12.5 m) below which the concentration fell to a minimum of 28.7 μ M at 24 m. Apparently, in such systems methanogenesis and denitrification occur concurrently (Xie et al. 2012)

While assessing the causes of the observed variability of CH_4 in the studied reservoirs, we note that the recently built and also smaller reservoirs (Tillari, Selaulim and Markandeya dams) showed the highest CH_4 concentrations. The first two exhibited intense anoxia i.e. sulphate reduction and high CH_4 . We would expect similar conditions in the third one (Markandeya) as well, but the water level fell down drastically in peak summer preventing further observations. The medium-sized reservoirs of Supa, Koyna and Idukki are quite old. They are located amidst dense forests of the Western Ghats, and are not affected by human activities such as agriculture runoff and sewage discharge. However, these reservoirs exhibited wide range of conditions (from hypoxia with no CH_4 accumulation in Supa, the largest of the three reservoirs, to intense anoxia with moderate accumulation of CH_4 in Idukki, the smallest of the three systems; Fig. 2). Bhakra-Nangal and Rihand reservoirs, two of the oldest reservoirs in India did not experience significant CH_4 buildup at all. These are also the largest among those sampled in terms of their storage capacities (Table 1) and thus could have greater buffer capacity for change.

In order to investigate how the trophic state of the reservoirs affects CH₄ production, we sought correlation between the column-integrated Chlorophyll *a* and CH₄ concentrations,

considering only those data sets with significant CH₄ concentrations (Fig. 5). The two parameters appear to be positively related with the correlation coefficient (*r*=0.56, *n*=15) being statistically significant at 95% confidence. However, it may be pointed out that CH₄ production in the hypolimnion is expected to lag behind photosynthetic production in surface waters by several days. For example, the maximal Chlorophyll *a* and CH₄ concentrations observed in the Markandeya reservoir on 23^{rd} April 2007 were 8.1 mg m⁻³ (Table 2) and 30.0 µM, respectively. When the reservoir was visited again ten days later, the respective concentrations had changed to 5.5 mg m⁻³ and 55.4 µM. The greater accumulation of CH₄ observed during the later survey should be better related to higher Chlorophyll *a* measured during the earlier trip. In view of such a decoupling between surface organic production and subsurface CH₄ production, the stage of anoxia determined by time elapsed since the onset of stratification should be taken into consideration. As it is, the data included in Fig. 5 were collected during different redox stages. Despite this limitation, the observed correlation indicates that the trophic state may play a key, if not the dominant, role in CH₄ production in the reservoirs.

Although the Chlorophyll *a* content varied considerably, the observed values do not show abnormally high phytoplankton biomass. The upper water column in any of these reservoirs did not have very high suspended load, and so, it seems reasonable to assume that photosynthesis was macronutrient(s)-controlled. Productivity in freshwater lakes is often limited by inorganic phosphorus (Wetzel 2001). In these systems, however, inorganic phosphate was never completely depleted (Table 2). NO₃⁻ concentrations in surface waters were low in these reservoirs except in Markandeya and Idukki (Table 2). While the elevated NO₃⁻ levels in Marakandeya can be attributed to agricultural activities, as the land surrounding the reservoir is intensively cultivated, the Idukki reservoir is surrounded by dense, pristine forest, and the higher surface NO₃⁻ concentration is perhaps due to natural leaching of nitrogen from forest soil.

Given the large consumption of synthetic nitrogenous fertilizers in South Asia - this region accounts for roughly 20% of the global nitrogen consumption (ftp://ftp.fao.org/agl/agl/docs/cwfto11.pdf) - the measured NO₃ levels in the Indian reservoirs, except for Markandeya, are unexpectedly low and considered together with the moderate chlorophyll a concentration, do not show a high degree of eutrophication. The fate of the nitrogen anthropogenically released to the environment is beyond the scope of this report, but irrespective of the cause, it is reasonable to conclude that agricultural activities do not contribute much to CH₄ accumulation in these reservoirs. Accordingly, CH₄ concentrations in Indian reservoirs are not abnormally high.

Results of previous studies elsewhere in the tropics revealed that most of the carbon stored in the initial organic matter is lost to the atmosphere as CH₄ and carbon dioxide within 20 years of impounding (Galy-Lacaux et al. 1999). For example, in the well studied Petit Saut Reservoir in French Guiana, anoxia with very large accumulation of CH₄ (average ~875 μM) was observed within just one month of impounding; this was estimated to subside to ~20 µM within 17 years (Galy-Lacaux et al. 1999). In the present study, reservoirs ranged from 1-47 years of age when sampled. CH_4 concentration in the young (1-10 years) Indian reservoirs studied are lower than the peak values recorded in most of the young South American reservoirs (3-10 years after construction) and comparable to older (16-37 years) South African reservoirs (Table 3). For instance, even in the youngest reservoir investigated in the present study (i.e., Markandeya), the maximal observed CH₄ concentration was lower by an order of magnitude (Table 3). In addition, this reservoir, which was characterized by the highest NO_3 and chlorophyll *a* concentrations, presumably under anthropogenic influence, among all the reservoirs sampled, did not experience sulphidic conditions in the bottom water during the 3 years of sampling (from 2007 to 2009). The Petit Saut reservoir submerges equatorial forest (soil carbon: 100 MgC ha⁻¹; 1 Mg=10⁶ g) while the African reservoirs submerge equatorial forest and some are also covered by macrophytes (soil carbon: 70 MgC ha⁻¹) (Galy-Lacaux et al.1999). The soil organic carbon content in the upper 30 cm in India ranges from 45 to 143 MgC ha⁻¹ (Bhattacharyya et al. 2000), comparable to the above-mentioned values. Allochthonous organic matter is the major source of greenhouse gas emissions after 10 years of reservoir creation (IPCC 2006). Methane concentrations in the older (21-47 years) Indian reservoirs studied were very low (<11 µM), with the exception of Idukki (80 µM; 30 years). It thus appears that while the quantity of organic matter in the submerged soil is comparable to other tropical systems, CH₄ production in these reservoirs is relatively lower (Table 2), presumably due to lower production of organic matter in the water column.

Our data support the view that most of the CH₄ produced in the hypolimnion is oxidized aerobically by the methanotrophs (Liu et al. 1996; Striegl and Michmerhuizen 1998). For instance, monthly observations in the Tillari reservoir during 2011 revealed highest concentrations of 0.15-0.35 μ M at the surface during the period of stratification (when the concentration in the hypoliminion reached up to 17 μ M). Even lower concentrations (0.02 μ M) occurred throughout the water column in winter. In other reservoirs too, surface CH₄ levels did not exceed 0.305 μ M at any time. Vigorous mixing during the periods of turbulence (e.g. during storms) or convective overturning during early winter may lead to entrainment of CH₄-rich water into the upper water column. However, the ongoing time series observations in Tillari reservoir (Narvenkar et al. manuscript in preparation) suggest that with the advent of winter, the hypolimnion appears to be renewed slowly presumably allowing CH₄–oxidation to keep pace with mixing such that the surface layer CH₄ concentrations

remain quite low. This also happens during the SWM season when the region is subjected to strong winds and intense rainfall. Recent measurements have confirmed that during this period reoxygenation of hypolimetic waters occurs through lateral advection of oxygen rich waters (Narvenkar et al. manuscript in preparation). Thus, CH₄ accumulated in the hypolimnion during the preceding dry season is oxidized before it can ventilate to the atmosphere. Methane emission from shallower reservoirs through ebullition is another important pathway of its emission to the atmosphere (Abril et al. 2005). While we did not directly measure CH₄ efflux to the atmosphere, we did not notice significant ebullition on any occasion, which is not very surprising as the highest CH₄ concentration (~156 µM; Fig. 4a) was well below saturation. Moreover, all reservoirs are deeper than 10 m (*http://www.cwc.nic.in/main/downloads/ National Register of Large Dams 2009.pdf*), and thus emission via this process also may not be very large.

High CH₄ emissions have been reported from water exiting dams through deep outlets (Abril et al. 2005; Kemenes et al. 2007) raising concerns about the green credentials of hydroelectricity (Giles 2006). We carried out CH₄ measurements in water immediately after it was discharged from the Koyna reservoir in May 2010. The concentration was <0.5 μ M. Moreover, in all reservoirs (except Tillari and Selaulim, two of the smallest systems sampled) significant increase in CH₄ concentration occurred below the depth of water outflow. Also, CH₄ levels in the four largest reservoirs in the present study did not rise much above the background. While the reservoirs sampled constitute a small fraction of all man-made reservoirs in India, and it is possible that there are some systems that behave differently from those in the present study, based on the available information alone, it seems that emission of CH₄ from Indian reservoirs cannot be as high as assumed so far. Direct measurements of CH₄ efflux from the reservoir surface and measurements in outflows from major dams are however needed to accurately quantify such emissions.

5. Conclusions

Our study revealed that although waters of the hypolimnia of the majority of the reservoirs examined turn anaerobic during summer, dissolved CH_4 accumulation in these systems is much smaller than assumed previously (which is consistent with modest eutrophication). Moreover, substantial accumulation of CH_4 mostly occurs below the depths of water intake for power generation and irrigation. Most of the CH_4 produced in Indian reservoirs appears to be consumed by methanotrophs within the reservoirs.

Despite the use of enormous amounts of synthetic nitrogen fertilizers and large reactive nitrogen release from other sources such as sewage and fossil fuel combustion in India, our study, the first of

its kind, shows that the reactive nitrogen concentrations in freshwater reservoirs are much lower than expected.

Further work addressing mechanisms of nitrogen removal, characterization of the organisms involved in nitrogen and CH₄ cycling, and direct measurements of CH₄ emissions is needed for a better understanding of the biogeochemical processes occurring in these reservoirs.

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References

Abril, G., Guérin, F., Richard, S., Delmas, R., Galy-Lacaux, C., Gosse, P., et al. (2005). Carbon dioxide and methane emissions and the carbon budget of a 10-years old tropical reservoir (Petit-Saut, French Guiana). *Global Biogeochemical Cycles*, 19, GB4007, doi:10.1029/2005GB002457.

Bastviken, D., Tranvik, L. J., Downing, J. A., Crill, P. M., Enrich-Prast, A. (2011). Freshwater Methane Emissions Offset the Continental Carbon Sink. *Science*, 331, 50.

Bhattacharyya, T., Pal, D. K., Mandal, C., & Velayutham, M. (2000). Organic carbon stock in Indian soils and their geographical distribution. *Current Science*, 79, 655-660.

Biswas, H., Mukhopadhyay, S.K., Sen, S., Jana, T.K. (2007). Spatial and temporal patterns of methane dynamics in the tropical mangrove dominated estuary, NE coast of Bay of Bengal, India. *Journal of Marine Systems*, 68, 55-64.

Borges, A.V., Abril, G., Delille, B., Descy, J-P., Darchambeau, F. (2011). Diffusive methane emissions to the atmosphere from Lake Kivu (Eastern Africa). *Journal of Geophysical Research*, 116:G03032. doi: 10.1029/2011JG001673.

Chen, Y. -H., & Prinn, R. G. (2006). Estimation of atmospheric methane emissions between 1996 and 2001 using a three-dimensional global chemical transport model. *Journal of Geophysical Research*, 111, D10307, doi:10.1029/2005JD006058.

Cline, J.D. (1969). Spectrophotometric determination of hydrogen sulfide in natural waters. *Limnology Oceanography*, 14, 454-458.

Eller, G., Känel, L., & Krüger, M. (2005). Co-occurrence of Aerobic and Anaerobic Methane Oxidation in the Water Column of Lake Plußsee. *Applied and Environmental Microbiology*, 71(12), 8925-8928.

Fearnside, P. M. (2002). Greenhouse gas emissions from a hydroelectric reservoir (Brazil's Tucurui´ Dam) and the energy policy implications. *Water, Air and Soil Pollution*, 133, 69-96.

Galy-Lacaux, C., Delmas, R., Jambert, C., Dumestre, J. F., Labroue, L., Richard, S., et al. (1997). Gaseous emissions and oxygen consumption in hydroelectric dams: A case study in French Guyana. *Global Biogeochemical Cycles*, 11 (4), 471-483.

Galy-Lacaux, C., Delmas, R., Kouadio, G., Richard, S., & Gosse, P. (1999). Long term greenhouse gas emission from a hydroelectric reservoir in tropical forest regions. *Global Biogeochemical Cycles*, 13 (2), 503-517.

Giles, J. (2006). Methane quashes green credentials of hydropower. Nature, 444, 254-255.

Grossart, H-P., Frindte, K., Dziallas, C., Eckert, W., & Tang, K. W. (2011). Microbial methane production in oxygenated water column of an oligotrophic lake. *Proceedings of the National Academy of Sciences*, 108, 49, 19657-19661.

Guérin, F., Abril, G., Richard, S., Burban, B., Reynouard, C., Seyler, P., et al. (2006). Methane and carbon dioxide emissions from tropical reservoirs: significance of downstream rivers. *Geophysical Research Letters*, 33, L21407, doi: 10.1029/2006GL027929.

Guérin, F., & Abril, G. (2007). Significance of pelagic aerobic methane oxidation in the methane and carbon budget of a tropical reservoir. *Journal of Geophysical Research*, 112, G03006, doi:10.1029/2006JG000393.

International Panel on Climate Change (IPCC), (2006). *IPCC Guidelines for National Greenhouse Gas Inventories. Prepared by the National Greenhouse Gas Inventories Programme,* Eggleston, H. S., Buendia, L., Miwa, K., Ngara, T. & Tanabe , K. (eds.). published: IGES, Japan.

Keller, M., & Stallard, R. F. (1994). Methane emission by bubbling from Gatun Lake, Panama. *Journal of Geophysical Research*, 99 (D4), 8307-8319.

Kemenes, A., Forsberg, B. R., & Melack, J. M. (2007). Methane release below a tropical hydroelectric dam. *Geophysical Research Letters*, 34, L12809, doi:10.1029/2007GL029479.

Kurian, S., Roy, R., Repeta, D.J., Gauns, M., Shenoy, D.M., Suresh, T., et al. (2012). Seasonal occurrence of anoxygenic photosynthesis in Tillari and Selaulim reservoirs, Western India. *Biogeosciences*, 9, pp. 2485-2495.

Li, C., Qiu, J., Frolking, S., Xiao, X., Salas, W., Moore III, B., Boles, S., Huang, Y., & Sass, R. (2002). Reduced methane emissions from large scale changes in water management of China's rice paddies during 1980-2000, *Geophysical Research Letters*. 29, doi:10.1029/2002GL015370.

Lima, I. B. T. (2005). Biogeochemical distinction of methane releases from two Amazon hydroreservoirs. *Chemosphere*, 59, 1697-1702.

Liu, R., Hofmann, A., Gülaçar, F.O., Favarger, P-Y., & Dominik, J. (1996). Methane concentration profiles in a lake with a permanently anoxic hypolimnion (Lake Lugano, Switzerland-Italy). *Chemical Geology*, 133, 201-209.

Madhan, R., Dabholkar, N., Navelkar, G., Desa, E., Afzulpurkar, S., Mascarenhas A., et al. (2012). Autonomous profiling device to monitor remote water bodies. *Current Science*, 102, 169-176.

Mc Auliffe, C. (1971). GC determination of solutes by multiple phase equilibration. *Chemical Technology*, 1, 46-50.

Panganiban, A.T. Jr., Patt, T. E., Hart, W., & Hanson, R.S. (1979). Oxidation of methane in the absence of oxygen in Lake water samples. *Applied and Environmental Microbiology*, 37, 303-309.

Purvaja, R., & Ramesh, R. (2001). Natural and anthropogenic CH₄ emission from Coastal wetlands of south India. *Environmental Management*, 27, 547-557.

Rajkumar, A. N., Barnes, J., Ramesh, R., Purvaja, R., Upstill-Goddard, R.C. (2008). Methane and nitrous oxide fluxes in the polluted Adyar River and estuary, SE India. *Marine Pollution Bulletin*, 56, 2043-2051

Ramos, F. M., Lima, I. B. T., Rosa, R. R., Mazzi, E. A., Carvalho, J. C., Rasera, M. F. F. L., et al. (2006). Extreme event dynamics in methane ebullition fluxes from tropical reservoirs. *Geophysical Research Letters*, 33, L21404, doi: 10.1029/2006GL027943.

Rosa, L. P., Santos, M. A., Matvienko, B., Sikar, E., & Santos, E. O. (2006). Scientific errors in the Fearnside comments on greenhouse gas emissions (GHG) from Hydroelectric Dams and response to his political claiming. *Climatic Change*, 75, 91-102, doi: 10.1007/s10584-005-9046-6.

Saint Louis, V., Kelly, C., Duchemin, E., Rudd, J. W. M., & Rosenberg, D. M. (2000). Reservoir surface as sources of greenhouse gases to the atmosphere: A global estimate. *BioScience*, 20, 766-775.

Schulz, M., Faber, E., Hollerbach, A., Schröder, H. G., Güde, H. (2001). The methane cycle in the epilimnion of Lake Constance. *Archiv fuer Hydrobiologie* 151,157-176.

Shalini, A., Ramesh, R., Purvaja, R., & Barnes, J. (2006). Spatial and temporal distribution of methane in an extensive shallow estuary, south India. *Journal of Earth System Science*, 115, 451-460.

Striegl, R. G., & Michmerhuizen, C. M. (1998). Hydrologic influence on methane and carbon dioxide dynamics at two north-central Minnesota lakes. *Limnology and Oceanography*, 43, 1519-1529.

Verma, A., Subramanian, V., & Ramesh, R. (2002). Methane emissions from a coastal lagoon: Vembanad Lake, West Coast, India. *Chemosphere*, 47, 883-889.

Wetzel, R.G. (2001). Limnology: Lake and river systems (3rd ed). Academic Press, Orlando, FL.

Xie, L., Chen, J., Wang, R., Zhou, Q. (2012). Effect of carbon source and COD/NO₃⁻-N ratio on anaerobic simultaneous denitrification and methanogenesis for high-strength wastewater treatment. *Journal of Bioscience and Bioengineering*, 113 (6), 759-764.

Yan, X., Ohara, T., & Akimoto, H. (2003). Development of region-specific emission factors and estimation of methane emission from rice fields in the East, Southeast, and South Asian countries. *Global Change Biology*, 9, 237-254.

Figure captions:

Fig. 1 Map of India showing locations of the reservoirs sampled in the present study

Fig. 2 Vertical profiles of temperature, dissolved oxygen and methane in the Reservoirs; (a) Rihand - May 2009, (b) Bhakra Nangal - August 2008, (c) Supa - May 2008, (d) Koyna - May 2010, (e) Idukki - May 2008, (f) Selaulim - May 2010

Fig. 3 Vertical profiles of temperature, dissolved oxygen and methane in the Markandeya Reservoir in (a) March 2007; (b) April 2007; (c) May 2007; (d) April 2008; and (e) May 2009. Vertical profiles of nitrate and methane in Markandeya Reservoir in April 2008 (f)

Fig. 4 Vertical profiles of temperature, dissolved oxygen and methane in the Tillari Reservoir in (a) July 2010; (b) December 2010

Fig. 5 Correlation between column-integrated chlorophyll *a* and CH_4 (mg m⁻²) in the reservoirs experiencing significant CH_4 increase during summer samplings. The data points are labelled as follows. The letter identifies the reservoir (I = Idukki, K = Koyna, M = Markandeya, S = Selaulim, T = Tillari) while the remaining digits give the month and year of sampling (e.g. 05/10 for May 2010)









Fig 4



Fig 5



Table 1: Details of reservoirs sampled

Reservoir	Location	Observations	Purpose	Gross Storage capacity (10 ⁹ m ³)	Year of completion /filling
Idukki, Kerala	9.79° N, 76.93° E	November 2006, May 2008, and June 2009	Hydroelectric	2.0	1974
Markandeya, Karnataka	16.02°N, 74.64°E	March, April, May 2007, April 2008, May 2009	Irrigation	0.1	2006
Supa, Karnataka	15.34°N, 74.39°E	April, May 2008	Hydroelectric	4.1	1987
Selaulim, Goa	15.21°N, 74.18°E	May 2010	Irrigation/Storage	0.23	2000
Tillari, Maharashtra	15.76°N, 74.09°E	July, 2010 and Dec, 2010	Irrigation/Storage	0.45	2006
Koyna, Maharashtra	17.51°N, 73.86°E	May 2010	Hydroelectric	2.8	1964
Rihand, Uttar Pradesh	24.20°N, 83.00°E	May 2009	Irrigation/ Hydroelectric	10.6	1962
Bhakra-Nangal, Himachal Pradesh	31.41°N, 76.43°E	August 2008	irrigation/ Hydroelectric	9.3	1963

Reservoir	Date of sampling	NO ₃ ⁻ +NO ₂ ⁻	PO ₄ ³⁻	CH ₄	Max. Chl.
	Nov-06		0.48	0.0184	4.4
	May-08	23.87	0.66	0.2355	3.5
Idukki	Jun-09	12.49	1.02	0.048	1.8
	Mar-07	36.85	3.17	0.2513	6.2
	Apr-07	12.52	1.55	0.2629	8.1
	May-07	9.94	1.63	0.2521	5.5
	Apr-08	22.51	1.73	0.1606	4
Markandeya	May-09	8.26	0.18	0.1108	4
	Apr-08	1.33	2.11	0.0259	2.1
Supa	May-08	0.06	0.55	0.0565	3.1
Bhakra- Nangal	Aug-08	3.1	0.15	0.305	2.8
Rihand	May-09	11.98	0.22	0.0028	0.7
Selaulim	May-10	0.13	-	0.1002	2.8
	May-10	0.18	-	0.1257	1.3
Koyna	Feb-11	2.78	0.07	0.0354	1.2
	Jul-10	1.21	0.08	0.0562	6.4
Tillari	Dec-10	0.69	0.2	0.0293	1.8

Table 2: Surface $(NO_3^{-}+NO_2^{-}, PO_4^{-3-}) \mu M$, CH₄ (μM) and maximal chlorophyll *a* concentrations (mg m⁻³) in Indian reservoirs.

Reservoir name	CH ₄ μM	References	
Idukki, Kerala	80.3	present study	
Markandeya, Karnataka	55.4	-do-	
Supa, Karnataka	0.11	-do-	
Selaulim, Goa	125.4	-do-	
Tillari, Maharashtra	156.3	-do-	
Koyna, Maharashtra	11.6	-do-	
Rihand, Uttar Pradesh	0.08	-do-	
Bhakra Nangal, Himachal Pradesh	1.3	-do-	
Other tropical Reservoirs	СН4 μМ	References	
The Petit Saut, Brazil	800	Guerin et al. 2006	
Samuel, Brazil	220	-do-	
Balbina, Brazil	440	-do-	
Balbina, Brazil	240	Kemenes et al. 2007	
Tucurui, Brazil	375	Rosa et al. 2006	
Buyo, Africa	93.75	Galy-Lacaux et al.1999	
Taabo, Africa	37.5-43.75	-do-	
Ayame I, Africa	62.5	-do-	

Table 3: Comparison of methane concentrations in Indian and other tropical reservoirs