

Variability in concentrations and fluxes of methane in the Indian estuaries

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Abstract

In order to examine the fluxes of methane (CH₄) from the Indian estuaries, measurements were carried out by collecting samples from 26 estuaries along the Indian coast during high discharge (wet) and low water discharge (dry) periods. The CH₄ concentrations in the estuaries located along the west coast of India were significantly higher (113±40 nM) compared to east coast of India (27±6 nM) during wet and dry periods (88±15 nM and 63±12 nM respectively). Super-saturation of CH₄ was observed in the Indian estuaries during both periods ((0.18 to 22.3 x10³%). The concentrations of CH₄ showed inverse relation with salinity indicating that freshwater is a significant source. Spatial variations in CH₄ saturation were associated with the organic matter load suggesting that its decomposition may be another source in the Indian estuaries. Fluxes of CH₄ ranged from 0.01 to 298 μmol m⁻² d⁻¹ (mean 13.4±5 μmol m⁻² d⁻¹) which is ~30 times lower compared to European estuaries (414 μmol m⁻² d⁻¹). The annual emission from Indian estuaries, including Pulicat and Adyar, amounted to 0.39 x 10¹⁰ g CH₄ y⁻¹ with the surface area of 0.027 x 10⁶ km² which is significantly lower than European estuaries (2.7±6.8 x 10¹⁰ g CH₄ y⁻¹ with the surface area of 0.03 x 10⁶ km²). This study suggests that Indian estuaries are weak source for atmospheric CH₄ than European estuaries and such low fluxes were attributed to low residence time of water and low decomposition of organic matter within the estuary. The CH₄ fluxes from the Indian estuaries are higher than Indian mangroves (0.01 x 10¹⁰ g CH₄ y⁻¹) but lower than Indian inland waters (210 x 10¹⁰ g CH₄ y⁻¹).

1. Introduction

Methane (CH₄) is an important greenhouse gas having 25 to 40 times greater global warming potential than carbon dioxide (CO₂) and influences the global climate directly or indirectly (Shindell et al., 2009; Khalil et al., 2007). In the marine environment, CH₄ is produced strictly under anaerobic conditions such as those in sediments, interior of suspended particles and in the guts of zooplankton (De Angelies and Lee, 1994; Karl and Tilbook, 1994; Holmes et al., 2000). It is reported that CH₄ can also be produced under aerobic conditions in surface waters under nutrient limiting conditions (Karl et al., 2008; Dammn et al., 2010; Metcalf et al., 2012). Generally estuaries are rich in organic matter and prevalence of anoxic condition in sediments favor the production of CH₄ (Chanton and Whiting, 1995; Heyer and Berger, 2000). CH₄ is also produced as a byproduct during the decomposition of methylphosphonate by aerobic bacteria in phosphate-stressed surface waters (Karl et al., 2008; Metcalf et al., 2012). Under nitrogen limiting conditions, methylotrophic methanogenesis of methane thiol or dimethylsulfoniopropionate (DMSP) leads to formation of CH₄ (Damm et al. 2010). Shallow gassy sediments are also a significant source of CH₄ to the water column (Anderson and Bryant, 1990; Mau et al., 2007; 2015; Treude and Ziebis, 2010). CH₄ is oxidized under anaerobic and aerobic conditions in the sediments and water column (Abril and Iversen 2002; Valentine, 2011). In total marine CH₄ emission to atmosphere, estuaries, coastal areas and continental shelves account a large fraction (75%) (Bange et al., 1994; Middelburg et al., 2002; Abril and Borges, 2004; Bange 2006; Borges and Abril, 2011). Upstill-Goddard and Barnes (2016) estimated that 2.7×10^{10} g of CH₄ emitted annually to the atmosphere from the European estuaries. The CH₄ flux estimations from the estuaries are still sparse and suffer from large uncertainties due to large variability and availability of limited data. It is especially true for South and Southeast Asian estuaries which are highly under-sampled with reference to time and space (Müller et al., 2016).

Estuaries in India are influenced by monsoonal rainfall hence they are called monsoonal estuaries. All these estuaries exhibit non-steady state behavior due to seasonal variations in fresh water discharge (Vijith et al., 2009; Sridevi et al., 2015). Seasonal runoff into these monsoonal estuaries far exceeds the total volume of the estuary during the times of peak discharges and entire estuary turns into river (Sarma et al., 2009; 2010; 2011). The strong stratification occurs during initial phase of discharge for few weeks to month due to low discharge whereas weak stratification or well mixed conditions prevails during other periods (Sridevi et al., 2015). The upstream river almost dries up during dry periods leaving the dominance of seawater in the estuary. Hence, the biogeochemical processes in monsoonal estuaries during wet period could be completely different from that in dry

period. The flux of CH₄ was estimated in the Adyar and Pulicat estuaries in the south east India (40-114 and 54-280 $\mu\text{mol m}^{-2} \text{d}^{-1}$ respectively; Nirmal et al., 2008; Shalini et al., 2006) whereas no information is available from other Indian estuaries. On the other hand, Mangroves are significant source of CH₄ to the atmosphere (Chauhan et al., 2008; Krithika et al., 2008; Dutta et al., 2013) and also source to the adjacent creeks and estuaries through tidal action (Wang et al., 1993; Barnes et al., 2006; Alongi, 2009; Dutta et al., 2013). Mangroves are present at the mouth of some of the Indian estuaries such as Haldia, Mahanadi, Godavari, Krishna, Ponnayyar, Mandovi and Zuari and its impact on estuarine CH₄ is unknown. The objective of this study is to estimate the contribution of Indian estuaries to atmospheric CH₄ and compare the same with other estuaries in the world.

2. Material and methods

2.1. Site description and sampling strategy

Indian estuaries are different from other estuaries in the world with reference timing and magnitude of discharge as they are characterized by seasonal discharge during monsoon period (July to October). The spatial variations in magnitude of discharge in the Indian rivers depend on the monsoonal precipitation pattern over Indian subcontinent (Vijith et al., 2009; Sarma et al., 2009). The precipitation pattern over Indian subcontinent shows strong spatial variations with relatively higher in the southwestern India (~3000mm) followed by northeastern India (1000–2500mm) and the least over the southeast (300–500mm) and northwestern India (200–500mm) (Soman and Kumar, 1990). Hence, the behavior of each Indian estuary may be unique with reference to biogeochemistry and material cycling.

In order to examine the variations in CH₄ concentrations and related atmospheric fluxes from the Indian estuaries, surface water samples were collected in 26 estuaries (8 major, 12 medium and 6 minor based on the rate of discharge of >500, >100 to <500 and <100 $\text{m}^3 \text{s}^{-1}$ respectively) along the Indian coast during wet (28 July – 18 August 2011) and dry periods (2-15 January 2012) (Figure 1). From each estuary, samples were collected from 2 to 5 locations during wet period (135 samples) between mouth and upstream estuary at approximately equal distances due to weak spatial salinity variations, whereas 5 to 9 locations were occupied during dry period (162 samples) by covering different salinity gradients (near zero to 33) (Table 1). Less samples were collected during wet period as the entire estuary is filled with freshwater due to high discharge with weak salinity gradient between upstream and mouth of the estuary. In addition to this, samples were also collected at 5 locations in Dowleiswarm dam reservoir to examine the influence of dam discharge on estuarine CH₄ flux during both dry and wet periods.

2.2. Physical and chemical properties

Temperature and salinity were measured using a CTD system (Sea Bird Electronics, SBE 19 plus, USA) with the analytical precisions of 0.001° C and 0.004 respectively. Dissolved Oxygen (DO) was measured using Winkler titration method of Carritt and Carpenter (1966) with potentiometric detection technique. The analytical precision, expressed as standard deviation, was 0.07% for DO. The suspended particulate matter (SPM) was measured based on weight difference of the matter retained on 0.22 µm pore size polycarbonate filters after passing 1 L of sample. Particulate organic carbon (POC) was measured by filtering about 1 L of water sample through a pre-combusted GF/F filter (combusted at 300 °C for 6 h) at low vacuum and dried at 60° C for at least 24 h. Filters were acid fumigated for 12 h in the desiccator to remove inorganic carbon and POC on filter was measured using an elemental analyzer (Thermo Finnigan, Germany; Sarma et al., 2014). The high purity CO₂ gas was used as working standard for carbon. The gas was calibrated with internal reference material of glutamic acid and marine sediment. The analytical precision was ±0.02% for POC.

2.3. Measurements of CH₄

Dissolved CH₄ in the water was determined by a multiphase head space equilibration technique (McAuliffe, 1971) coupled with Gas Chromatographic (GC) analysis. Briefly, predetermined volume (25 ml) was equilibrated with equal volume of helium in a gas tight syringe by vigorously shaking the syringe at room temperature for 5 minutes using wrist action shaker. After equilibrium, the head space was dried over drierite and then injected through a 5-ml sampling loop into a gas chromatograph (Agilent- 6820, USA) and separated over a Molecular sieve (5A) column (80/100 mesh) at 35°C, and CH₄ peak was detected with a Flame Ionization Detector (FID) (Patra et al., 1998 and Jayakumar et al., 2001). The analytical uncertainty (1σ) for CH₄ measurements was less than ±2%, which was estimated from the analysis of duplicate water samples stored for different periods of time. The precision of CH₄ measurement was always better than 1% (at 1σ level).

2.4. Calculation of CH₄ saturation and water to air flux

The saturation values are expressed in percentage and calculated using formula given below:

$$\% \text{ Saturation} = (\text{measured CH}_4 \text{ concentration} / \text{equilibrium CH}_4 \text{ concentration}) \times 100$$

The equilibrium CH₄ concentrations were computed at *in situ* temperature and salinity using Wiesenburg and Guinasso (1979).

The flux of CH₄ between the water and atmosphere was calculated as

$$F(\text{gas}) = k \cdot S_{\text{gas}} [\Delta\text{gas}]$$

Where $F(\text{gas})$ is flux, k is the gas transfer velocity (m d^{-1}), S_{gas} is the solubility coefficient of CH₄ ($\text{mol m}^{-3} \text{atm}^{-1}$) (Wiesenburg and Guinasso, 1979) and Δgas is the difference of CH₄ between water and air. Seasonal mean wind speed data were obtained from the Indian Meteorological Department (IMD) from the weather stations (at 10m height) close to the respective estuaries from hourly mean wind speed data. Gas transfer velocity (k) depends on many factors such as, primarily wind speed, temperature, turbulence in air and water (eg. Wanninkhof, 1992; Upstill-Goddard, 2006). Wind speed is probably the most important factor controlling the transfer velocity, and different empirical relationships relating k to wind speed have been proposed in literature (e.g. Wanninkhof, 1992; Nightingale et al., 2000; Borges et al., 2004). Though wind speed is one of the most important parameters controlling the transfer velocity, there are several environmental variables, such as wave geometry, sea surface roughness, turbulence, wave breaking, bubble formation, rainfall, surfactants, bottom driven turbulence, biology of the sea surface micro layer and bubble ebullition also influences (Upstill-Goddard, 2006). There is no single equation is developed to account influence of all these processes on transfer velocity. For instance, Borges et al. (2004) measured transfer velocity using closed chamber technique in the European estuaries and the same cannot be adapted to other estuaries as these measurements are site specific. Therefore, the flux estimation may be either under or over-estimated due to not accounting all the influencing factors on transfer velocity. Hence, we used transfer velocity derived from different sources (Wanninkhof, 1992; Nightingale et al., 2000 and Borges et al., 2004) and compared the estimates. We used estimated CH₄ emissions by Wanninkhof (1992) for comparison with other estimated in the literature.

2.5. Measurement of CH₄ fluxes at sediment and submarine ground water interfaces

Sediment fluxes of CH₄ were measured in the Godavari and Krishna estuaries using benthic chambers over 12 h. CH₄ fluxes across the sediment water interface were calculated as the product of the chamber height and slope of linear regression of the variations in CH₄ concentrations with time (Pratihary, 2009). The submarine ground water flux to estuary was computed using the mean CH₄ concentration between ground water (Rao, 2015) and estuary and exchange rates derived using Radium isotopes by Rengarajan and Sarma (2015) in the Godavari estuary. Due to lack of such information, these fluxes in other estuaries could not be estimated.

One way analysis of variance (ANOVA) was used to calculate significance of the seasonal and spatial variation in different physicochemical parameters using STATISTICA software.

3. Results

3.1. Physico-chemical characteristics of Indian estuaries

The Indian estuaries displayed wide hydrological conditions resulting from variable freshwater discharge, flushing rates and tidal amplitude. The annual mean discharge in the Indian estuaries ranged between ~28 and 3505 m³ s⁻¹ (Table 1). The relatively high discharge and tidal amplitude was found in the estuaries located in the northern than southern part of India (Sarma et al., 2012). The water temperature at the surface of Indian estuaries ranged between 21.5°C to 33.5°C and 25.5°C to 32 °C, whereas salinity ranged from 0.04 to 28.78 and 0.23 to 22.84 during wet and dry periods respectively. The mean dissolved oxygen in Indian estuaries was slightly below saturation levels (90 ±2 %) and relatively lower saturation was observed during dry period (87 ±5 %) compared to wet period (96±3%). The concentrations of POC varied between 29.5-764 µM (mean 233±108 µM) and 29.7-322 µM (mean: 89±47 µM) during wet and dry periods respectively. The concentration of organic carbon to suspended particulate matter (SPM) ranged from 0.4 to 15.2% (4.9±0.5%) and 0.1-18.3% (mean: 3±0.2%) respectively during wet and dry periods.

3.2. Variations in concentration and saturation of CH₄ in the Indian estuaries

The CH₄ showed wide variations in the Indian estuaries (Table 1) and ranged from 4 to 130 (mean±standard error; 27±6) nM in the estuaries located along the east coast and 5 to 573 (113±40) nM in the west coast of India during wet period. CH₄ concentrations ranged from 5 to 179 (63±12) nM in the estuaries located along the east coast and 18 to 488 (88±15) nM in the west coast of India during dry period. The CH₄ concentrations were significantly higher in the west coast (113±40 nM) than east coast estuaries (27±6 nM) during wet period (63±12 and 88±15 nM respectively; p < 0.001, n=40) and this difference was less significant during dry period (p < 0.05; n=61). Nevertheless, the mean concentrations of CH₄ were marginally higher during dry period (74±11 nM) compared to that of wet period (61±17 nM) in the Indian estuaries (Table 2). Similarly higher saturation of CH₄ occurred in the estuaries located along the west coast of India (3.38±0.08 x 10³ and 3.58±0.08 x 10³% during wet and dry periods respectively) than east coast (0.99±0.03 x 10³ and 1.65±0.07 x 10³% during wet and dry periods respectively) (Table 2). Though the CH₄ saturation in different estuaries was variable, however, the mean saturation during wet and dry period was insignificant in the estuaries located along the west coast whereas saturation during dry period is almost double to

that of wet period in the east coast estuaries (Table 2). Exceptionally high super saturation (>5000%) was noticed in Godavari, Cauvery, Vaighai, Cochin Back waters, Chalakudi and Netravathi estuaries during dry period while Ambalyaar, Netravathi, Tapti and Mahisagar estuaries during wet period (Table 1). Relatively high POC concentrations was observed in the estuaries containing high CH₄ saturation (>5.0 x 10³%) during wet and dry periods respectively. Super-saturation of CH₄ in the Tapti estuary has been attributed to high organic carbon load from the upstream river (Nirmalkumar et al., 2010). Though Indian estuaries receive higher organic carbon load during wet period (233±61 µM) than dry period (89±17 µM), the mean CH₄ saturation was higher during latter (2.49±0.07 x 10³%) than former period (1.92±0.06 x 10³%). This suggests that inefficient decomposition of organic matter, higher oxidation of CH₄ and high water-to-air flux of CH₄ during wet than dry period could be potential reasons for lower CH₄ concentrations during former than latter period. The water-to-air flux of CH₄ was relatively lower during wet (6.6 to 20.2 µmol m⁻² d⁻¹) than dry period (7.8 to 23.5 µmol m⁻² d⁻¹; Table 3) due to higher wind speed during latter than former period. This suggests that variations in water-to-air fluxes may not be potential reason for seasonal variations in CH₄ in the Indian estuaries.

4. Discussion

4.1 Source of CH₄ in the Indian estuaries

The major processes responsible for CH₄ in the estuaries are lateral transport from the upstream river, inputs from the sediments, oxidation in the water column and evasion to the atmosphere. In addition to this, the stagnation of water column promotes accumulation of CH₄ and decrease of O₂ leading to existence of favorable conditions for CH₄ production. Several dams had been constructed on all rivers sampled in this study and water is stored in the dam reservoir over 6 month's period to meet irrigation and domestic needs. Sarma et al. (2011; 2012) observed high pCO₂ (partial pressure of carbon dioxide) levels in the Indian estuaries during wet period and attributed to modification of organic matter in the dam reservoir. Recently Prasad et al. (2013) noticed significant modifications in the organic matter through microbial processes in the Dowleswaram dam reservoir on Godavari river during storage period leading to increase in pCO₂ levels to >15000 µatm. Formation of CH₄ is also possible due to degradation of organic matter in the dam reservoir. The mean concentrations of CH₄ in the dam reservoir during storage period (January to June) were 214±60 nM whereas it was lower (73±10 nM) during discharge period suggesting that significant amount of CH₄ is formed during the former period. The concentrations of CH₄ during August (peak discharge period) in the Godavari estuary were 72 nM which is close to that of discharge water from the upstream river (73±10 nM).

Sarma et al. (2011) noticed high $p\text{CO}_2$ (up to 30,000 μatm) associated with initial pulse of discharge (normally in the month of July) in the Godavari estuary due to discharge of modified waters in the dam reservoir during storage period. Dams modify significant amount of organic matter leading to the formation of CH_4 and will be transported to the estuary during initial phase of discharge (Abril, et al., 2005; Guerin et al., 2006; Kemenes et al., 2007; Kemenes et al., 2011; Barros et al., 2011). On the other hand, the residence time of estuary increases during dry period (>30 days) than wet period (<1 day) due to negligible discharge in the former period (Acharyya et al., 2012; Sridevi et al., 2015). It has been noticed that significant amount of organic matter, which was brought to the estuary during wet period, is modified during dry period to support 70-90% of heterotrophic carbon demand in the estuary (Sarma et al., 2009; Sarma et al., 2012). In such conditions, dissolved oxygen concentrations in the water column decreases to undersaturation levels (~80-90%) but anoxic conditions never develop. It has been noticed that production of CH_4 in the water column associated with stratification of water column and anoxic bottom waters in several estuaries, fjords and lagoons (Koné et al., 2010; Borges and Abril, 2011). Salinity stratification is normally observed in the Indian estuaries during low discharge periods, however occurrence of hypoxic or anoxic conditions were never reported (Sarma et al., 2010; Acharyya et al., 2012; Sridevi et al., 2015). Based on the daily observations in the Godavari (Sarma et al., 2010), Mandovi and Zuari (Pedneker et al., 2011), and Krishna (Dr. T.R. Kumari personal communication, 2016) estuaries, the strong stratifications was observed only for a period of two to three weeks during low discharge season when oxygen saturation levels were between 82 to 93%. Hence, stratification may not promote production of CH_4 in the Indian estuaries. Several estuaries, such as Haldia, Mahanadi, Godavari, Krishna, Ponnayaa, Mandovi and Zuari, harbor mangroves at the mouth of the estuaries. Higher concentrations of CH_4 were reported in Mangrove regions (Chauhan et al., 2008; Krithika et al., 2008; Dutta et al., 2013) and its impact of adjacent estuaries and coastal waters was also noticed (Wang et al., 1993; Barnes et al., 2006; Alongi, 2009; Dutta et al., 2013). However, elevated concentrations of CH_4 were not observed in the estuaries that harbor mangroves compared to others suggesting that dilution of estuarine waters or higher rates of evasion to atmosphere may be possible. Therefore the discharge of freshwater from upstream river, the exchange of CH_4 at groundwater-estuary and sediment-water interface may be important source to the Indian estuaries.

The concentration in CH_4 in the ground water was measured only along the bank of Godavari and Krishna estuaries and the mean concentration was 1566 ± 81 nM (Rao, 2015). Based on the exchange rates computed using radium isotopes (Rengarajan and Sarma, 2015), the flux of CH_4 from ground

water to estuary was computed as 19.2 and 22.4 $\mu\text{mole m}^{-2} \text{d}^{-1}$ during dry period in the Godavari and Krishna estuaries respectively. The exchange of CH_4 at the sediment-water interface was also measured in the Godavari and Krishna estuaries to examine its impact on estuarine CH_4 . The CH_4 flux at sediment-water interface was 20.9 ± 3 and 25.1 ± 4 $\mu\text{mole m}^{-2} \text{d}^{-1}$ in Godavari and Krishna estuaries respectively. Therefore both submarine groundwater and sediment water exchanges contributed up to 40% of CH_4 in the Godavari and Krishna estuaries. Though such measurements were not made in other estuaries, the contribution from these sources is expected to be significant in other Indian estuaries as well.

The CH_4 saturation showed strong inverse correlation with salinity (r^2 varied between 0.43 and 0.78) during dry period with variable slopes (6.4 to 132) in different estuaries suggesting that freshwater is a significant sources of CH_4 to the estuaries with strong spatial variations (Fig. 2). Decrease in CH_4 saturation with increase in salinity was reported in several estuaries in the world (Jaykumar et al., 2001; Middelburg et al., 2002; Bange, 2006; Zhang et al., 2008; Koné et al., 2010; Borges et al. 2015). Similarly CH_4 saturation showed linear relation with POC during wet ($r^2=0.43$; $p<0.001$) and dry period ($r^2=0.32$; $p<0.001$) in the Indian estuaries (Fig. 3). This suggests that decomposition of organic carbon brought by river discharge may be responsible for higher CH_4 saturation during wet and dry periods. The decrease in both POC and CH_4 with salinity is also possible due to settling on sediment surface and release to the atmosphere or oxidized respectively. The weaker relationship could possibly due to influence of both these processes. The major source of POC to the Indian estuaries were largely contributed by terrestrial organic matter from C3 and C4 plants and also detritus from freshwater algae while the contribution from soil organic matter is minimal (Sarma et al., 2014). The POC showed significant inverse relation with salinity during wet ($r^2=0.59$; $p<0.001$) and dry periods ($r^2=0.32$; $p<0.001$) suggesting that freshwater is a strong source of organic matter to the estuary (Sarma et al., 2012) (Fig. 4). This indicates that the estuaries, which received high organic matter load, are acting as a strong source of CH_4 to the atmosphere. Relatively higher CH_4 saturation was observed in the estuaries located along the west coast of India ($3.38 \pm 0.08 \times 10^3$ and $3.58 \pm 0.08 \times 10^3\%$ during wet and dry periods respectively) than east coast of India ($0.99 \pm 0.03 \times 10^3$ and $1.65 \pm 0.07 \times 10^3\%$ during wet and dry periods respectively) and it is consistent with the POC load. The mean organic carbon in SPM (%) in the estuaries located along the west coast was lower ($4.4 \pm 0.3\%$) than east coast ($5.5 \pm 0.3\%$) during wet period while it was opposite during dry period (2.2 and 4.0% in the east and west coast estuaries respectively). The higher CH_4 concentration in the organic carbon poor estuaries indicating that decomposition of high organic matter is one of the major sources of CH_4 .

It is possible that variable decomposition rates of organic matter might have contributed to variations in CH₄ saturation in the estuaries located along the east and west coasts of India. Relatively lower oxygen saturation was noticed in the west coast estuaries (87%) compared to east coast estuaries (97%) during wet period whereas 96 and 90% during dry period respectively (Table 2). Low mean pH values found in the west coast estuaries (6.82±0.52) than east coast estuaries (7.65±0.57) during wet period further suggesting that higher decomposition rates of organic matter in the former than the latter estuaries (Sarma et al., 2012). In addition to this, relatively higher bacterial activity was noticed in the sediment from the west coast than east coast estuaries (Prasad, 2015) further suggesting that higher decomposition of organic matter in the former than latter estuaries. Therefore, this study suggests that fresh water inputs, decomposition of organic matter, exchange at the sediment-water interface and submarine ground water discharge are the major sources of CH₄ to the Indian estuaries. The oxidation of CH₄ in the water column could be possible sink (Koné et al., 2010; Borges and Abril, 2011) and no such measurements were carried out in this study to examine its contribution on removal of CH₄ from the water column.

4.2 Fluxes of CH₄ to the atmosphere

The seasonal mean wind speed (u_{10}) ranged between 0.31 and 2.66 m s⁻¹ during dry and wet periods respectively in the Indian estuaries. Based on seasonal mean wind speed data, the seasonal mean CH₄ efflux from the Indian estuaries ranged from 6.6 to 20.2 and 7.8 to 23.5 μmol m⁻² d⁻¹ during wet and dry periods respectively using different transfer velocities (Table 3). Relatively higher fluxes were computed using Borges et al. (2004) transfer velocity coefficients and lower using Nightingale et al. (2000). Higher fluxes were noticed in the Ponnayar, Vellar, Netravathi and Tapti during wet period and Tapti, Netravathi, Cochin Back Waters, Cauvery and Penna estuaries during dry period (Table 1). Such high fluxes in these estuaries were driven not only due to higher CH₄ concentrations but also winds. The annual mean flux from the Indian estuaries ranged between 7.4 and 22.5 μmol m⁻² d⁻¹ to the atmosphere. The CH₄ fluxes from the Pulicat estuary (Shalini et al., 2006) and Adyar estuary (Nirmal et al., 2008) were estimated to be 54-280 and 40-114 μmol m⁻² d⁻¹ respectively. Since these estuaries were not sampled in this study, taking these data into consideration, the mean CH₄ flux from the Indian estuaries amounts to 13.4±5 μmol m⁻² d⁻¹.

India houses 14 major, 44 medium and 162 minor estuaries and the total surface area of Indian estuaries amounts to 0.027×10⁶ km² calculated from the mouth of the estuary to the region where

tidal oscillations are almost negligible (Qasim, 2003). The annual emissions of CH₄ to the atmosphere amounted to, including Pulicat and Adiyar estuaries, 0.39×10^{10} g CH₄ y⁻¹ (based on Wanninkhof 92 coefficients) from the Indian estuaries. The annual mean CH₄ flux from European estuaries estimated to be 414 ± 493 $\mu\text{mol m}^{-2} \text{d}^{-1}$ (Upstill-Goddard and Barnes, 2016) which is about ~30 times higher than emissions estimated from the Indian estuaries (13.4 ± 5 $\mu\text{mol m}^{-2} \text{d}^{-1}$). The residence time of the Indian estuaries varied between 2 and 10 days and it is lower than European estuaries (2-70 days; Upstill-Goddard and Barnes, 2016). On the other hand, the population density in the basin varied from 137 to 319 persons per square kilometer in the Indian estuaries (Central Water Commission, 2012) and it was lower in the European estuaries sampled (73 to 368 persons per square kilometer; Caraco and Cole, 1999). Hence this study suggests that low CH₄ fluxes in the Indian estuaries are attributed to lower residence time of water in the estuary and less human settlement along the most of the riverine banks compared to developed countries in the world. Exceptions for few estuaries, such as Mahanadi, where the population density and port activities contribute while industrial and domestic pollution responsible in Narmada and Tapi. Nevertheless Indian estuaries emit relatively lower CH₄ to the atmosphere than elsewhere in the world than hitherto hypothesized (Table 4).

Mangroves are a strong source of trace gases to the atmosphere (Chauhan et al., 2008; Krithika et al., 2008; Dutta et al., 2013; Barnes et al., 2006; Biswas et al., 2007). Chauhan et al. (2008) estimated mean CH₄ fluxes from the mangroves in India to be 5.9 $\mu\text{mol m}^{-2} \text{d}^{-1}$. The total flux of CH₄ from the Indian mangroves to the atmosphere amounts to 0.01×10^{10} g CH₄ y⁻¹. The CH₄ flux measurements from inland water in India (lakes, ponds, rivers, open wells, reservoirs, springs, and canals) including ebullition and diffusion ranged from 10 to 52100 $\mu\text{mol m}^{-2} \text{d}^{-1}$, with a mean of 7800 ± 12700 $\mu\text{mol m}^{-2} \text{d}^{-1}$. Conservative extrapolation to whole India yielded emissions of 2.1×10^{12} g CH₄ y⁻¹ from India's inland waters (Selvam et al., 2014). Therefore the fluxes of CH₄ from Indian estuaries and mangroves were an order of magnitude less than that of from the Inland waters of India.

5. Conclusions

Contribution of CH₄ fluxes from the Indian estuaries to the atmosphere is estimated through collection of samples from the 26 estuaries along the Indian coast during wet and dry periods. The mean CH₄ concentrations and saturation values were ranged from 4 to 573 nM and 0.18 to 22.34 x 10³% in the Indian estuaries with super-saturation in all estuaries sampled. Spatial variations in the CH₄ saturation in the Indian estuaries were related to organic matter load and salinity suggesting that decomposition of organic matter and riverine inputs seem to be the major sources. The contribution

from the ground water exchange and benthic fluxes are highly significant to the estuarine CH₄ concentrations. The fluxes of CH₄ from the Indian estuaries ranged from 7.4 to 22.5 μmol m⁻² d⁻¹ using different transfer velocity coefficients. The annual mean flux of CH₄ from the Indian estuaries, including Pulicat and Adiyar estuaries, comes to 13.4±5 μmol m⁻² d⁻¹ using Wanninkhof 92 formulation. The total flux of CH₄ from the Indian estuaries amounted to 0.39 x 10¹⁰ g CH₄ y⁻¹ using Wanninkhof 92 which is an order of magnitude less than that of inland waters from the Indian subcontinent as well European estuaries (414 μmol m⁻² d⁻¹).

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Estuary	Size	Latitude (°N)	Longitude (°E)	Surface Area (km ²)	Annual discharge (m ³ s ⁻¹) ^{&}	Salinity	DO-Sat (%)	POC (μM)	CH ₄ (nM)	CH ₄ Saturation (x10 ³ %)	Flux- W92 (μmol m ⁻² d ⁻¹)
Rivers Flowing towards Bay of Bengal											
Haldia(5)[5]	***	22.02	88.05	18.15	1600	(0.71) 4.72	(84) 88	(429) 231.8	(5) 6	(0.21)0.23	(0.12)0.08
Subarnalekha(2)[3]	**	21.57	87.53	23.15	392	(3.97) 4.31	(98) 98	(335) 103.5	(6)24	(0.26) 0.98	(0.01) 0.22
Baitarani(2)[9]	**	20.78	86.94	22.69	903	(0.09) 18.33	(63)91	(254)135.4	(14) 5	(0.62)0.22	(1.23) 0.24
Mahanadi(3)[9]	***	20.33	86.67	13.56	2121	(0.07) 20.41	(88) 93	(165) 57.1	(44)16	(1.85) 0.73	(0.37) 0.12
Rushikulya(2)[3]	*	19.38	85.08	12.57	ND	(20.70) 7.35	(104) 99	(166) 59.9	(7) 23	(0.34) 0.98	(0.05)0 .17
Vamsadhara(2)[5]	**	18.35	84.12	15.05	ND	(13.26)12.45	(99) 97	(144) 59.4	(4) 13	(0.18) 0.59	(0.08) 0.42
Nagavali(2)[3]	**	18.22	83.93	13.94	ND	(28.78) 6.43	(101) 87	(201) 63.8	(14) 18	(0.74) 0.73	(0.61) 0.55
Godavari(5)[7]	***	16.72	82.03	241.1	3505	(0.16)21.31	(74)102	(480) ND	(72)144	(3.15) 6.39	(2.29) 4.38
Krishna(3)[8]	***	16.03	81.07	36.49	2213	(5.27) 20.55	(98)103	(94)54.3	(11) 9	(0.49) 0.43	(1.11) 0.15
Penna(2)[5]	**	14.57	80.16	27.97	200	(9.27) 12.11	(105)101	(66) 63.7	(10) 46	(0.47) 1.97	(1.06) 19.2
Ponnayaar(2)[5] [§]	*	11.77	79.79	9.89	ND	(0.29) 7.67	(84) 98	(93) 107	(43) 60	(1.81) 2.66	(11.8) 1.61
Vellar(2)[5]	*	11.49	79.76	20.63	ND	(11.57) 6.92	(98) 119	(116) 207	(35) 23	(1.56) 1.02	(10.23)0.58
Cauvery(3)[7]	***	11.14	19.84	20.63	677	(12.04) 5.25	(96) 72	(143) 124	(38) 15	(1.70) 17.43	(1.05) 10.9
Ambalayar(2)[3]	*	10.03	79.23	4.57	28	(4.20) 3.86	(105) 77	(431) 95	(130) 9	(5.88) 0.43	(4.03) 0.74
Vaigai(3)[6]	*	9.34	78.94	0.22	36	(27.89)12.41	(104)105	(51) ND	(6) 179	(0.29) 7.94	(2.1) 35.3

Rivers Flowing towards Arabian Sea												
CBwaters(3)[8] [§]	***	10.05	76.27	231.1	391	(3.50) 8.87	(92) 65	(ND) 51	(32)159	(1.33) 7.43	(5.32) 29.3	
Chalakkudi(3)[7]	**	10.19	76.21	9.69	ND	(0.05) 14.71	(90) 86	(93) 51	(25)106	(1.03) 5.02	(1.27) 6.8	
Bharatakulza(2)[6]	*	10.81	75.96	19.12	ND	(0.10) 17.56	(85) 79	(68) 98	(26) 19	(1.11) 0.92	(1.39) 0.51	
Netravathi(2)[7]	**	12.87	74.96	18.54	ND	(0.06) 9.94	(78) 79	(400) 81	(573) 120	(22.34) 5.82	(114.25)24.3	
Kali(2)[6]	**	14.85	74.15	17.59	152	(5.86) 9.45	(95) 63	(212) 55	(7) 48	(0.29) 2.04	(0.25) 1.20	
Zuari(3)[8]	**	15.41	73.92	14.62	103	(7.32) 20.71	(93) 83	(81) 66	(11) 29	(0.49) 1.33	(1.13) 4.2	
Mandovi(2)[8]	**	15.50	73.90	27.68	105	(0.42) 22.84	(95) 82	(110) 45	(28) 22	(1.09) 1.03	(2.96) 3.14	
Narmada(2)[4] [§]	***	21.69	72.00	115.5	1447	(0.14) 3.82	(75) 90	(750) ND	(5) 18	(0.19) 0.74	(0.11) 1.2	
Tapti(2)[3] [§]	***	21.24	72.80	41.04	472	(0.10) 9.33	(74) 98	(402) ND	(489) 488	(19.67) 0.56	(298.6)14.2	
Sabarmathi(2)[3] [§]	**	22.99	72.56	66.29	120	(0.04) 13.51	(82) 77	(621) ND	(562) 38	(0.13) 1.59	(0.14) 0.3	
Mahisagar(2)[3]	**	22.44	73.07	14.28	ND	(0.11) 0.23	(78) 89	(468) ND	(175) 54	(6.89) 2.08	(8.16) 0.38	

Table 1: Surface area (km²), annual mean discharge (m³ s⁻¹), salinity, DO-Sat (%), POC (μM), CH₄ concentration (nM), saturation (%) and flux (μmol m⁻² d⁻¹) in the Indian estuaries.

Data in the bracket and open represents during wet and dry periods respectively. ND denotes no data. Data in square bracket in 1st Column represents the number of sampling points in dry period where as other in parenthesis represents the wet period.

&Discharge data was obtained from Sarma et al., 2012.

§denotes estuaries which are highly polluted due to local industrial or another anthropogenic activities. CB water represents Cochin Back Waters ***represents major estuaries (>500 m³ s⁻¹), ** represents medium estuaries (>100 to<500 m³ s⁻¹) and * represents minor estuaries (<100 m³ s⁻¹)

Table 2: Mean \pm SE concentrations of several biogeochemical properties in the east and west coast estuaries during wet and dry periods.

Property	East coast estuaries		West coast estuaries		Indian estuaries	
	Dry period	Wet period	Dry period	Wet period	Dry period	Wet period
DO sat (%)	90 \pm 2	97 \pm 4	96 \pm 3	87 \pm 5	93 \pm 4	90 \pm 3
OC (%)	4.0 \pm 0.5	5.5 \pm 0.3	2.2 \pm 0.2	4.4 \pm 0.3	3.0 \pm 0.2	4.9 \pm 0.5
POC (μ M)	105 \pm 8	205 \pm 28	68 \pm 6	301 \pm 40	89 \pm 17	233 \pm 61
CH ₄ conc (nM)	63 \pm 12	27 \pm 6	88 \pm 15	113 \pm 40	74 \pm 11	61 \pm 17
CH ₄ sat (x 10 ³ %)	1.65 \pm 0.07	0.99 \pm 0.03	3.58 \pm 0.08	3.38 \pm 0.08	2.49 \pm 0.07	1.92 \pm 0.06

Table 3: The seasonal and annual mean water-to-air fluxes of CH₄ (μ mol m⁻² d⁻¹) in 26 Indian estuaries using different transfer velocity formulations

Transfer velocity model	Flux of CH ₄ in μ mol m ⁻² d ⁻¹		
	Wet season (Mean \pm SE)	Dry season (Mean \pm SE)	Annual (Mean \pm SE)
Wanninkhof (1992)	9.7 \pm 3.3	14.8 \pm 5.7	11.3 \pm 4.1
Nightingale et al. (2000)	6.6 \pm 2.1	7.8 \pm 1.4	7.4 \pm 1.2
Borges et al. (2004)	20.2 \pm 5.9	23.5 \pm 3.4	22.5 \pm 3

Table 4: The range of concentrations, saturation and fluxes of CH₄ to the atmosphere from the various estuaries in the world.

*Median values: ^sBased on Wanninkhof (1992) transfer velocity coefficient

Estuary	CH ₄ (nM)	CH ₄ Saturation (x10 ³ %)	Flux (μ mole m ⁻² d ⁻¹)	Reference
Alesa (US)	5.7-697	0.30-29.0	180	De Angelies and Lilley, 1987
Hudson (US)	50-940	2.10-39.0	350	De Angelies and Scranton, 1993
Bodden (Germany)	2.4-370	0.10-15.5	30-210	Bange et al., 1998
Tomales Bay (US)	8-100	0.30-4.10	7-10	Sansone et al., 1998
Tyne (UK)	13-654	0.45-20.0	-	Upstill-Goddard et al., 2000
Humber(UK)	15.5-669	0.56-21.05	-	Upstill-Goddard et al., 2000
Randers Ford (Denmark)	41-420	1.70-17.50	70-410	Abril and Iversen, 2002
Temmesjoki (Finland)	240-506	10.20-21.1	-	Silvennoinen et al., 2008
European estuaries (9)	2-3600	0.07-150.0	130	Middelburg et al., 2002
Danube (UK)	131	5.34	470	Amouroux et al., 2002
Weser River (Germany)	40-1860	2.20-81.9	-	Grunwald et al., 2009
Rio san Pedro Bay(Spain)	12-87	0.51-5.0	34-150	Ferron et al., 2007
Yangtze (China)	13-27	0.52-1.28	35-114	Zhang et al., 2008
Pearl (China)	6.9-173.7	0.33-7.89	63.5	Zhou et al., 2009
Guadalete Estuary (Spain)	21.8- 3483	1.10- 130.3	20.3 - 3645	Burgos et al., 2014
Brisbane Estuary (Australia)	31to 578	1.21 to 26.43	18.7- 1725	Musenze et al., 2014
Tay estuary (UK)	4.5-361	0.10- 13.13	-	Harley et al., 2015
Lupar Estuary	2- 61	0.09- 2.79	61.3	Muller et al., 2016
Saribas Estuary	8.3- 68	0.39- 3.05	63	Muller et al., 2016
Brisbane (Australia)	48-687	2.16-26.9	--	Strum et al., 2016
European Estuaries (6)	--	0.58-26.35	34.2-1253	Upstill-Goddard and Barnes, 2016
Pulicate (India)	94-500	4.0-21.30	54-280	Shalini et al., 2006
Adiyar (India)	5-6500	0.20-27.0	40-114	Nirmal Rajkumar et al., 2008
Indian Estuaries (26)	4-573 (69.8)*	0.18-22.34 (3.13)*	0.01-298 (13.4) ^s	Present Study

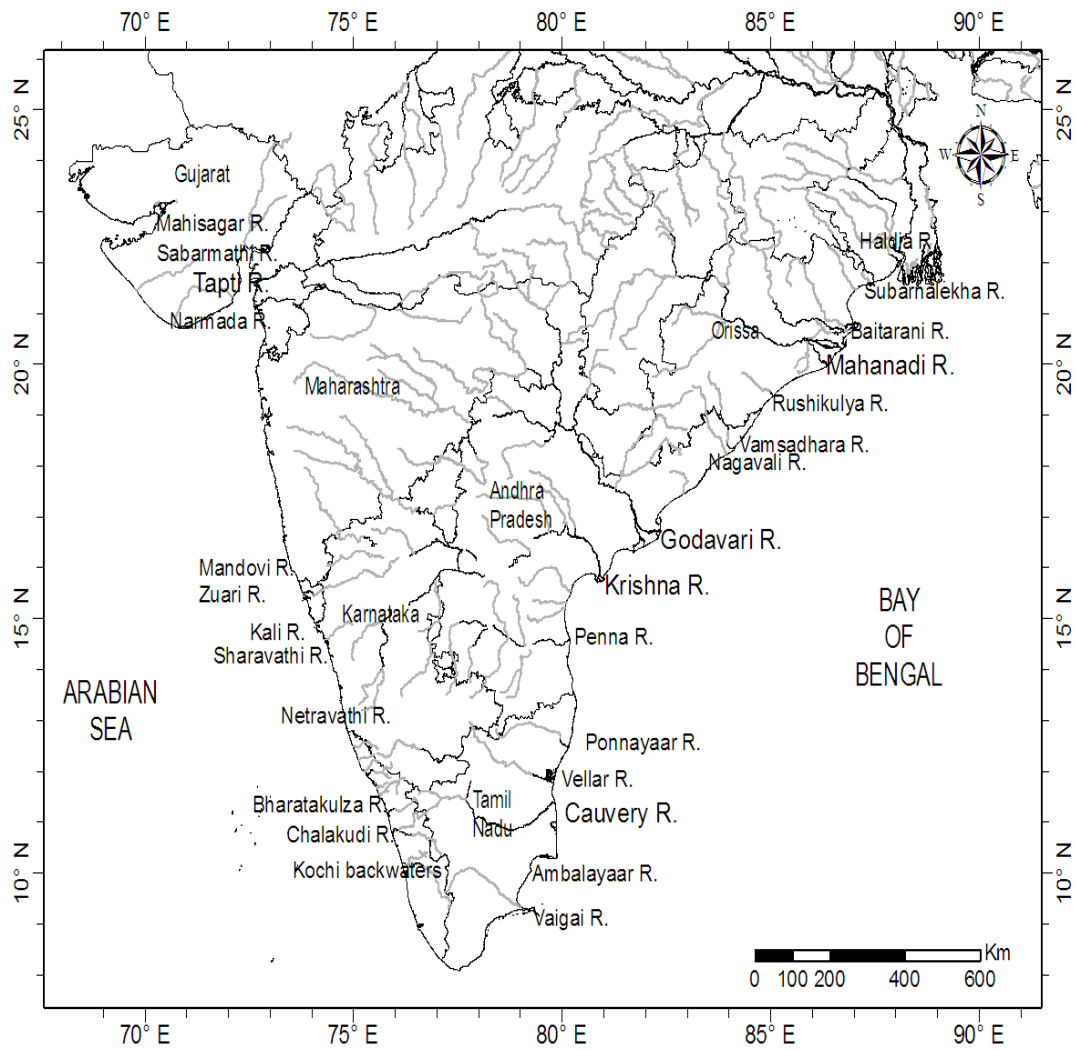


Figure 1: Station locations map where major rivers are shown with larger font letters. The main course of the river is shown as dark line while tributaries were shown in grey color.

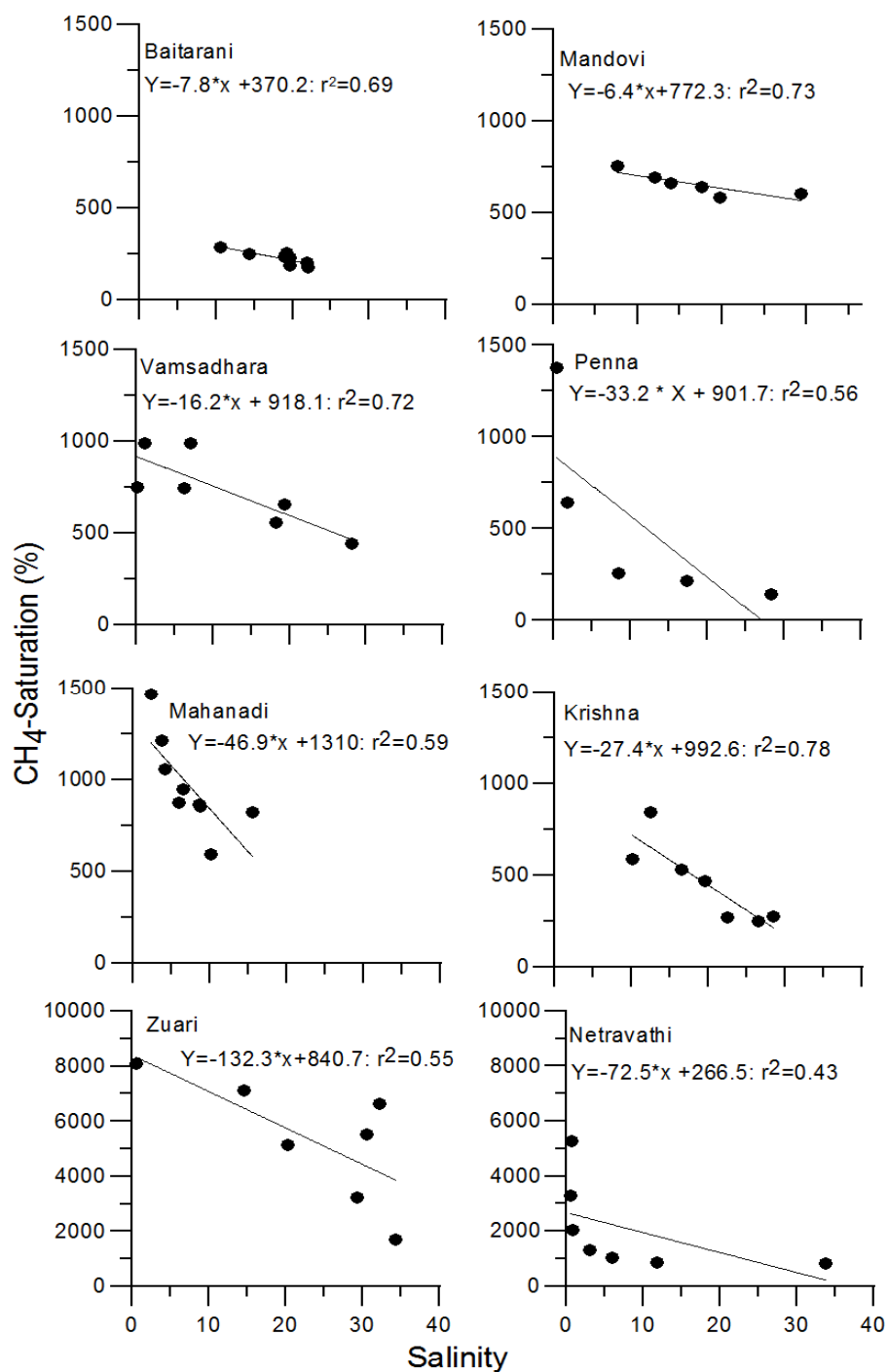


Figure 2: Relationship of CH₄ saturation (%) with salinity in the selected Indian estuaries.

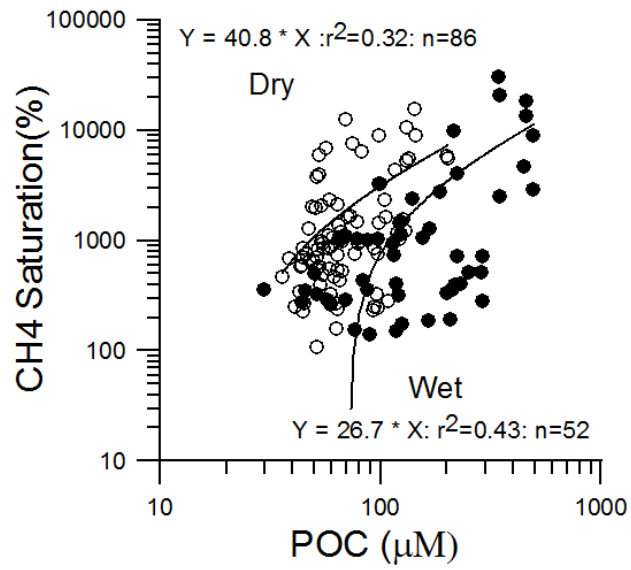


Figure 3: Relationship of CH₄ saturation (%) with POC (µM) in the Indian estuaries during wet (closed circles) and dry (open circles) periods.

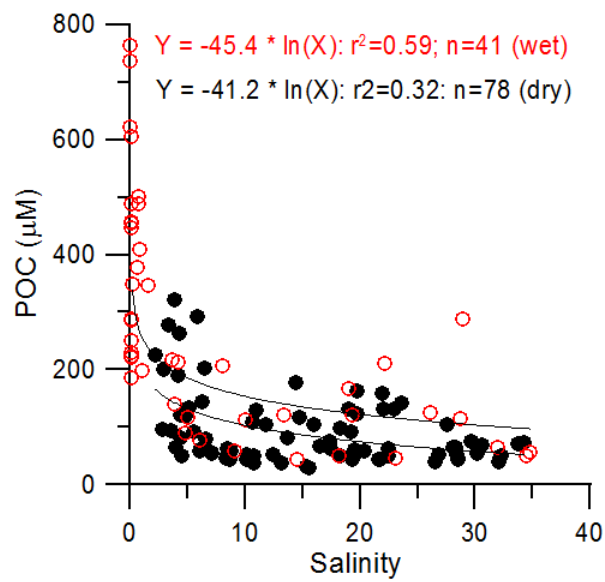


Figure 4: Relationship of POC (µM) with salinity in the Indian estuaries during wet (red open circles) and dry periods (closed circles).