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Methane in Estuarine Discharges to Coastal Ocean – A Study at Ashtamudi Estuary, Kerala, India

E.J. Zachariah* and C.J. Johny[1]

Atmospheric Sciences Division, Centre for Earth Science Studies
PB 7250, Thiruvananthapuram - 695 031, India
[1]Global Change Centre, National Physical Laboratory, New Delhi, India
✉ ejzach@vsnl.com

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Abstract: Wetlands are major natural source of atmospheric methane, a strong greenhouse gas. Methane fluxes from the Ashtamudi Estuary in Kerala, India (Ramsar site no. 1204), to the atmosphere as well as to the coastal ocean were obtained and are reported here. Concentration of methane in water was estimated by extraction and GC analysis. The water exchanges between the estuary and ocean was estimated by LOICZ Modeling Guidelines. Water to air fluxes of methane from the estuary surface was measured by collecting the emissions. Average water to air flux from this estuary with a water cover area of 5500 ha is 0.57 mg/m^2/hr. The estuarine water is super saturated with methane. The average concentration of methane in the estuary is 420 nMol/L. This study indicates that the discharge of methane rich water from estuaries to coastal ocean need be taken into account when methane budgets are prepared.

Key words: Estuaries, estuarine discharges, dissolved methane, methane fluxes, Ashtamudi estuary.

Introduction

Methane is a strong greenhouse gas, with a long atmospheric residence time. It has been estimated (IPCC, 2001) that methane is about 23 times more potent than carbon dioxide in global warming, when compared on a molar basis over a 100-year time horizon. The relative contributions of CH_4 and CO_2 to global warming are estimated to be 18% and 50% of the total. Methane also plays a key role in atmospheric chemistry. The atmospheric concentration of methane has been increasing steadily during the past 250 years or so, from 0.75 ppmV to its 1998 value of 1.75 ppmV (IPCC, 2001). A number of natural and anthropogenic sources of this gas in our environment have been identified. Methane is produced during anaerobic decay of any biological matter. The major known sources of methane are wetlands, enteric fermentation in the guts of ruminants and termites, mining, combustion of fossil fuels, agriculture under waterlogged conditions, etc. Wetlands are a significant natural source of methane (Fung et al., 1991), contributing around 21% of global methane emission.

Estuaries are partially enclosed wetland bodies of water where saltwater from the sea mixes with freshwater from rivers, streams and creeks. These areas of transition between freshwater and the saline water are tidally driven. The salinity of estuarine water varies depending on the tide and the strength of the freshwater inflow. In addition to freshwater, rivers bring silt and nutrients to the estuary. Methane concentrations in estuarine water are generally orders of magnitude higher than the atmospheric equilibrium, and depend on the balance between various sources and sinks (Middleburg et al., 2002). Measurements in the North Sea and Humber and Tyne estuaries (Upstill Goddard, 2000) have shown that 7.1×10^8 mol methane is estimated to reach southern North Sea through discharges to ocean. Estuarine dynamics and water properties could also influence the methane

*Corresponding Author

concentration. High turbulence favour methane emission to the atmosphere and methane production decrease with increase in salinity.

Surface waters of ocean are supersaturated with methane (Brooks et al., 1981) and a net source of methane, though their contribution to global methane budget is considered to be small. Continental shelf regions that represent only 15% of total oceanic area contribute 68% of global oceanic methane emission (Bange et al., 1994). It has been found that methane concentration in open ocean surface waters in Arabian Sea is of the order of 2 to 3 nMol/L. Dissolved methane concentration in coastal waters is two to three times more than in the open ocean (Lal et al., 1996). Major known source of oceanic methane is marine sediments and in situ production (Karl and Tilbrook, 1994).

The natural sources and sinks of methane in a typical estuarine system can be represented as shown in Figure 1. Though dissolved methane in the Arabian Sea have been investigated (Owen et al., 1991; Lal et al., 1996; Jayakumar et al., 2001), methane concentrations in estuaries adjoining the Arabian Sea need more detailed investigations. Arabian Sea which constitutes only 0.43% of the global ocean cover has been estimated to contribute more than 1.3% of the global oceanic methane fluxes to the atmosphere (Owen et al., 1991).

Ashtamudi Estuary

Ashtamudi estuary in Kollam district of Kerala covers an area 5,500 ha (Sankar et al., 1998). It lies between 76° 31′ and 76° 41′ East and 8° 54′ and 8° 59′ 30″ North.

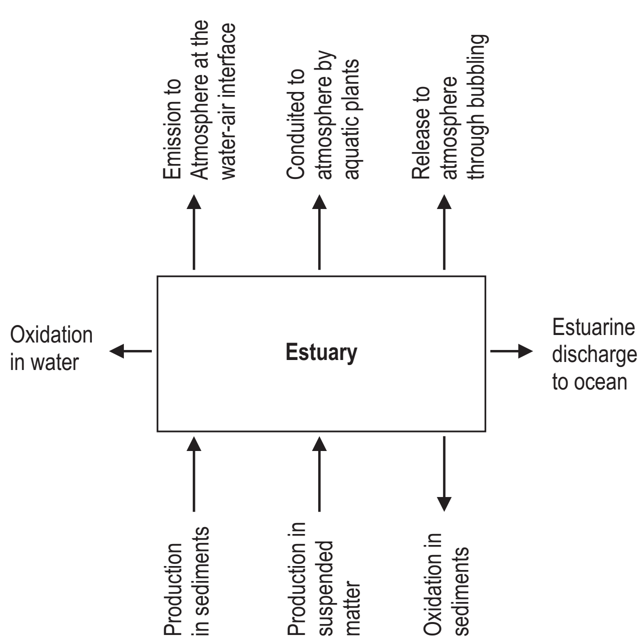

Figure 1: Methane budget in a typical estuarine system.

It has eight prominent arms, adjoining the Kollam town. The arms converge into a single outlet at Neendakara near Kollam, to enter the Lakshadweep Sea. A sketch diagram of the Ashtamudi estuary is available in Figure 2. The lagoon is connected to the sea through a tidal channel at Neendakara. The currents in the estuary are strongly influenced by the flow through this channel. The maximum velocity observed is 100 cm/sec. in the Neendakara inlet area (Joseph Mathew et al., 2001). The depth at the confluence zone is 6.4 m. The deepest point is at a depth of 14 m at Vellimon, in one of the arms of the estuary. The major river discharging into the Ashtamudi estuary is the Kallada River. The Kallada River originates from the Western Ghats, a prominent mountain range in the peninsular India. TS canal, a waterway running along the Kerala coast is another link with the estuary. Annual rainfall in the catchment area of the estuary is 2400 mm and the maximum air temperature range between 35.6 and 31.0°C and minimum temperature range between 23.0 and 20.9°C.

Ashtamudi Lake has been designated as a Ramsar Site in November 2002 (Ramsar site no. 1204). Population density and urban pressures, including pollution from oil spills from fishing boats and from industries in the surrounding area and conversion of natural habitat for

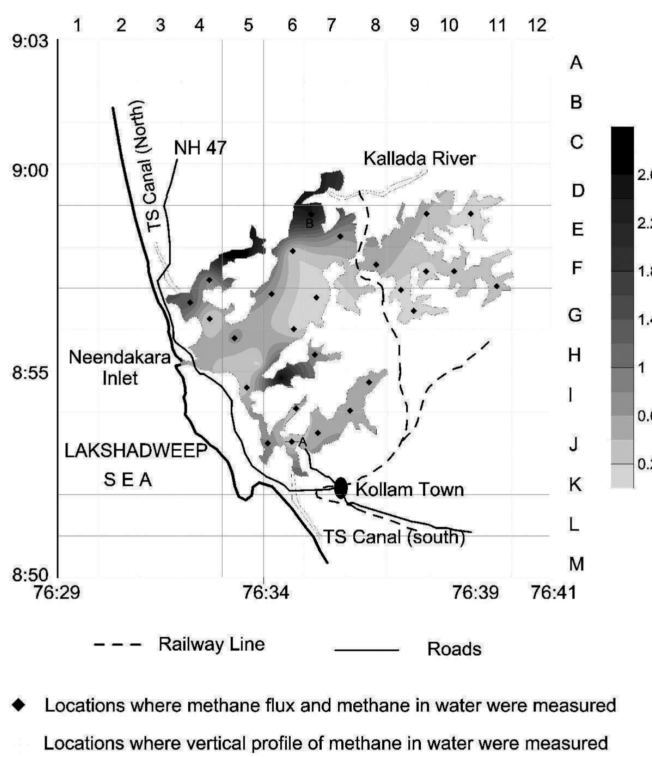

Figure 2: Sketch map of Ashtamudi estuary showing the distribution of water to air methane emission (mg/m^2/hr).

development purposes, affect the site. Major anthropogenic impacts arise through coconut husk retting and fish farming in some parts of the estuary and fishing in general. Coconut husk retting which used to be a major source of loading into the estuaries in the region is on the decline in recent years (Zachariah and Johny, 2006).

Methodology

Water to air fluxes of methane, dissolved methane in the estuarine water, and water budget of the estuary for the computation of methane in the estuarine discharges, were measured/estimated for the Ashtamudi estuary. Measurements were conducted at a number of locations within the estuary to obtain data representative of the lake. A distance of about 100 m from the shore was maintained, wherever possible, to avoid biases due to non-representative and very localised influences like drains, etc. Disturbing the water and sediments during the collection of samples were minimised by switching off the boat engine in advance and drifting or rowing to the location. Care was exercised to avoid disturbing sediments which might release methane bubbles trapped in it.

Water to Air Fluxes

Methane fluxes at the water air interface were measured by collecting the emissions and analysis by gas chromatography. Methane emission from the water surface was collected using a box type sampler, which is a cylindrical box with one end open. The box was floated on the water surface with its open end pointing downwards and dipping into water bounding an area of water surface. An inflated pneumatic tube of the type used in automobile tyres was used to float the box. When thus floated, the box would enclose some headspace above water surface. Any emission from the water surface enclosed by the mouth of the box would collect in the box and mix with the air above the water surface in it, resulting in an increase of methane concentration inside. Samples of this air methane mixture are withdrawn at known intervals (~ 20 minutes) for analysis, through a septum port on the closed end of the box. The sampler was deployed at locations where measurements were to be made.

Samples were withdrawn from the box into syringes, brought to laboratory and analysed using a Flame Ionisation Detector (FID) on a Gas Chromatograph (NUCON, Model 5765). The FID was calibrated using standard gas mixtures of 3.5, 11.9, 27 and 119 ppm methane in pure nitrogen. A 1/8″ dia X 2 m stainless steel column packed with Porapak Q, maintained at 70°C (isothermal) was used to separate methane. High purity nitrogen gas (30 mL/minute) was used as carrier gas. High purity hydrogen and Zero Air in cylinders were used for the flame.

A sample is withdrawn from the box at the time of deployment of the sampling box and another sample after an interval of time ‘T’. The samples were analysed to obtain their methane concentration. From the change in concentration during the time interval between the initial and second sampling, the quantity of methane emitted during the interval is computed. Water to air flux per unit area (m^2) is computed taking into account the area of the open end of the sampler and the volume of the air space in the sampler.

Methane in Water

Methane in water was determined by analysis of water samples collected from different locations. At each location, samples were collected at 1 m depth intervals, using a water sampler capable of drawing samples without disturbing dissolved gases in the collected sample. The samples were chilled and kept refrigerated (without freezing) till analysis in the laboratory.

Methane contained in the water was measured by extracting it into pure nitrogen gas. This includes the methane dissolved in liquid water, and the gas which might be trapped in the suspended particles in the water. The chilled water samples were slowly brought to room temperature. A known quantity from this (10 mL) was taken into a syringe containing a known volume (30 mL) of pure N_2 gas, closed, and shaken for one minute to extract the dissolved methane into the nitrogen gas. The resulting gas mixture was analysed using an FID on a gas chromatograph to determine the concentration of methane in it. The extraction from same sample was repeated with fresh N_2 gas till the methane concentration in the extracted mixture fell below detectable limit. The total quantity of methane thus extracted was computed to obtain the amount of methane extracted from the 10 mL sample. From this, the quantity of methane in a litre of water was computed and converted to concentration in nMol/L.

Water Budget of the Estuary

In order to estimate the methane fluxes to the coastal ocean through estuarine discharges and water exchanges, water budget calculations of the estuary was done according to LOICZ biogeochemical modelling guidelines (Gordon et al., 1996). It is estimated that 4986 million m^3 of water exchange through tidal flow take place annually between estuary and sea. Average salinity in the ocean was 34.9 (Gopalakrishna et al., 2005), and corresponding annual average value for the estuary was 26.9, based on the measured data. Annual freshwater runoff into the estuary from Kallada River is 1300 million m^3 (Nair and Azis, 1987). This water flows through the estuary and finally reaches the coastal waters. Annual water loss from estuary through evaporation process is calculated using the evaporation rate of 1.2 m/year (Baungatner and Reichel, 1975). Annual precipitation to the estuary is calculated using monthly rainfall data. Different components in the water budget are shown in Figure 3.

Results

Water to air flux was measured at 27 locations in the estuary during the pre-monsoon period of 2004 and the values are given in Table 1. The values ranged from 0.06 to 2.73 mg/m^2/hr with a mean value of 0.57 mg/m^2/hr. Figure 2 shows the distribution of flux values measured during the pre-monsoon period in 2004. Anthropogenic sources like coconut husk retting and fish farming are present in the regions which show higher methane fluxes. The central lobe of the lake, which is under a greater influence of tidal flow and mixing and where the salinity is higher, shows relatively lower emission. It is also noted that the methane fluxes are moderate though this is a tropical site. The high salinity in the lake could be the reason for moderate fluxes.

A plot of dissolved methane in the surface water in the estuary is shown in Figure 4. Lower concentration of methane is observed near the confluence zone and

Table 1: Methane flux measured from Ashtamudi estuary

Location		*pH*	*Salinity*	*CH_4 in water*	*Emission*
No	*Ref**			*(nMol/L)*	*(mg/m^2/hr)*
1	J6	8.03	31.8	934	0.173
2	J7	7.78	31.5	808	0.554
3	I8	7.53	31.2	1211	0.548
4	I8	7.28	31.7	1492	0.533
5	I5	8.04	31.3	266	0.294
6	H7	7.71	33.2	600	0.695
7	J6	7.99	32.0	654	0.854
8	I6	7.90	32.2	323	0.245
9	H6	8.03	30.7	71	0.145
10	G7	7.99	30.1	108	0.094
11	F8	7.92	29.0	307	0.576
12	G9	7.99	28.5	239	0.101
13	G9	7.90	28.7	122	0.108
14	F9	8.00	28.6	206	0.139
15	F10	8.00	28.7	90	0.331
16	F11	7.82	28.6	228	0.241
17	E9	7.82	27.5	54	0.381
18	E10	7.97	27.7	351	0.064
19	E7	7.97	27.9	256	0.650
20	E7	8.01	27.0	302	2.416
21	F6	8.03	29.4	261	0.191
22	G6	8.07	30.1	207	0.620
23	H5	8.11	31.8	72	0.725
24	G4	7.92	32.0	115	0.133
25	G4	7.69	30.8	204	1.329
26	F4	7.79	30.0	263	0.736
27	F5	7.55	30.7	1057	2.728

*Reference to grid in Figure 2.

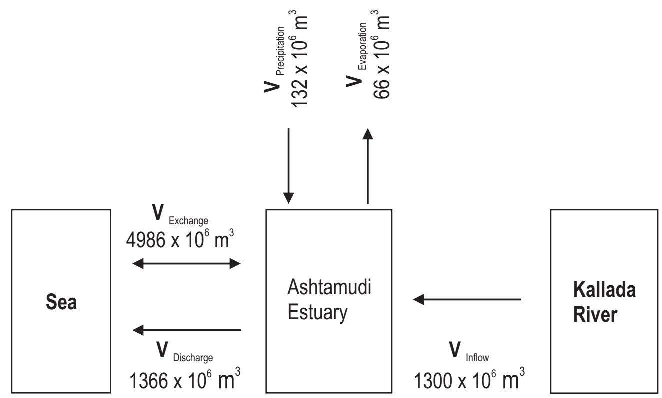

Figure 3: Annual water budget of Ashtamudi estuary.

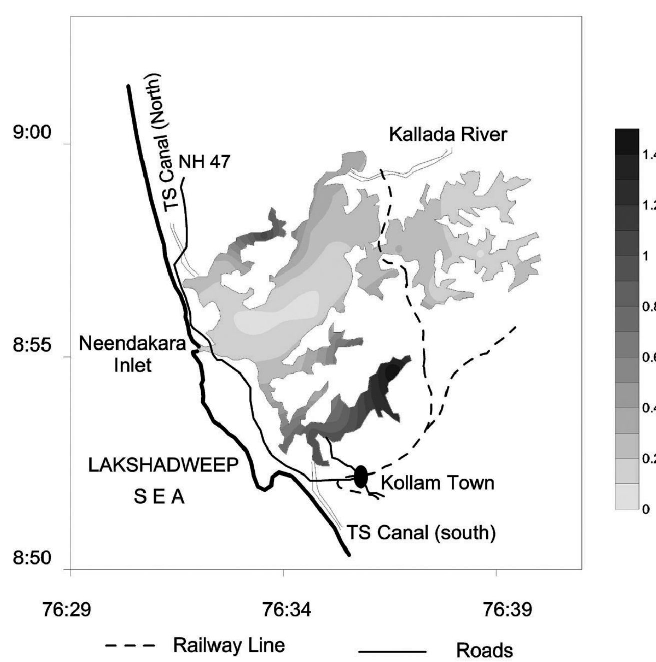

Figure 4: Distribution of dissolved methane (µmol/L) in surface water of Ashtamudi estuary.

adjoining regions than in far away regions. This suggests the mixing of methane-rich water in the estuary with sea water under the influence of the tidal flow. The values ranged from 54 nMol/L to 1490 nMol/L. The average was 420 nMol/L. The methane concentration in the estuary water is significantly higher than in the ocean. The water to air methane fluxes and the dissolved methane in the water does not correlate closely with each other as is seen from Figures 2 and 4. The currents in the estuary could be a contributing factor for this.

Methane emission and methane in water at different locations within the estuary and corresponding salinity and pH values are given in Table 1.

The vertical distribution of methane in the estuary was measured. Figure 5 is a plot of the vertical distribution of methane in water, as measured at two locations in the estuary during pre-monsoon 2005. Since most regions of the estuary were shallow, only representative data from two locations which were deep enough are presented. The locations are marked in Figure 2. Earlier measurements in the vicinity of these sites (Joseph Mathew et al., 2001) have recorded higher current velocities in the middle layers than in the top and bottom layers in the estuary. Lower spread of values of methane in water in the middle layer than in the lower and upper layers as seen in Figure 5, indicates more uniform mixing in the middle layers than in the top and bottom layers.

The water budget of the estuary was computed as described in an earlier section here. The estuary receives 1300 million m^3 as river run-off, 132 million m^3 as precipitation in the estuary, and loses 66 million m^3 through evaporation, annually. This fresh water mixes in the estuary and flows out to the sea. Another 4986 million m^3 sea water flows in and out as a result of tidal influences. Hence total annual water discharge to the sea is 6352 million m^3.

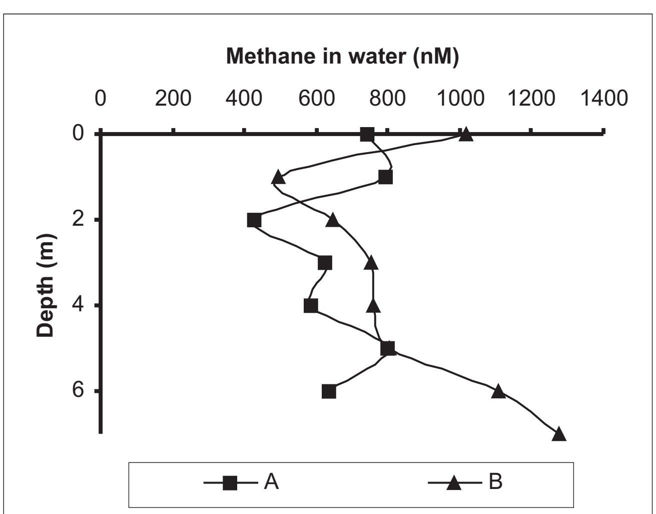

Figure 5: Vertical profile of methane in water at some locations in the estuary.

Discussions

Methane in water and water to air fluxes of methane measured in the Ashtamudi Estuary are given in Table 1. The methane concentration range between 54 and 1492 nMol/L, which shows super saturation at all locations in the estuary. The methane concentration in the estuary shows no significant correlation ($R^2 = 0.19$) with salinity. It may also be noted that the spread of salinity values in this estuary is relatively low. The water to air fluxes of methane and methane concentration in the water do not show correlation, which implies that the major source of methane out-gassing could be emission from sediments rather than from the overlying water. The water to air fluxes of methane were in the range 0.064 to 2.728 mg/m^2/hour. It is seen that methane concentrations are relatively lower in the main lobe of the estuary, which is under the direct influence of the tides and mixing as seen in Figure 2. The grids F4, F5, I8, J7 in Figure 2 are regions under anthropogenic influences like coconut husk retting (Zachariah and Johny, 2006) and have recorded high concentration of methane in water as well as water to air fluxes.

Measurements at other estuaries under the influence of coconut husk retting have also recorded high methane fluxes. Methane fluxes from Vembanad lake in the west coast of India (Verma et al., 2002) are anomalously high at 193.2 ± 24.5 mg/m^2/hour at Kumaragom, which they have attributed to coconut husk retting activity in the lake.

Records of methane fluxes from different ecosystems in India are available. The daily methane fluxes from Cauvery Delta mangrove ecosystem in South India (Krithika et al., 2008) is reported to be in the range between 18.99 and 37.53 mg/m^2/day [*i.e., 0.79 to 1.56 mg/m^2/hr, average*]. The corresponding dissolved methane concentration ranged between 182.75 ± 3.2 nMol/L and 267.69 ± 3.65 nMol/L. Methane fluxes from the Sundarban biosphere (Mukhopadhyay et al., 2002) ranges from 4.53 to 8.88 μg/m^2/sec [*i.e., 16.31 to 31.97 mg/m^2/hr*]. The overall annual estimate of methane fluxes from this ecosystem to atmosphere was estimated as 184.0 Gg. Dissolved methane in the surface water in the Hooghly estuarine system (Mukhopadhyay, 2007) was 35.99 ± 16.9 nMol/L during the monsoon season. The post- and pre-monsoon values were 32.89 ± 14.99

nMol/L and 35.6 ± 9.48nMol/L respectively. The higher concentration during monsoon period is interpreted as due to discharge from the mangrove areas. The bottom water concentrations were higher at 43.6 ± 6.84 nMol/L, 53.95 ± 5.68 nMol/L, and 56.1 ± 4.52 nMol/L respectively during monsoon, post-monsoon and pre-monsoon periods respectively. However, the sediment pore water concentrations of dissolved methane showed a different trend with highest concentration of 1877.8 ± 1689.1 nMol/L during the post-monsoon period. The corresponding monsoon and pre-monsoon values were 788.6 ± 530.6 and 1297.8 ± 844.1 nMol/L respectively.

Methane fluxes from various coastal wetlands in the eastern coast of South India shows wide variability ranging from 3.1 mg/m^2/hour adjoining Bay of Bengal to 21.56 mg/m^2/hour in the Adayar river (Purvaja and Ramesh, 2001). The methane fluxes show a strong negative correlation to dissolved oxygen, sulphates and salinity. It is also reported that fluxes are influenced by tidal fluctuations. Methane in the surface water measured at Pulicat Lake adjoining Bay of Bengal in South India (Shalini et al., 2006) ranged from 94.14 to 500.62 nMol/L, which exhibited a weak, negative, correlation with salinity. They have observed low methane concentrations in the sea water mixing zones, implying dilution of the estuarine water by the seawater. It is reported that tidal flushing could be playing a major role in the spatial variation of dissolved methane in the Pulicat lake. It is noted that the concentration of dissolved methane in the Bay of Bengal as measured in this study was 50 nMol/L, which is lower than the range of values reported for the estuary but significantly higher than oceanic methane concentrations reported elsewhere. The methane concentration gradient reported here has been interpreted as an indication that the Pulicat system might be a source of methane to the surrounding coastal waters. Average methane fluxes from other estuaries in this region are also of the same order. The average values reported range from 0.2 to 0.9 mg/m^2/hr (Zachariah and Johny, 2006).

The Arabian Sea waters have been reported to be supersaturated with methane, by various investigators. Owen et al. (1991) have reported super saturation ranging between 157 and 268% at depths less than 200 m in the Arabian Sea. Lal et al. (1996) reported methane concentration ranging between 2 and 9 nMol/L, with peak concentration at depths around 100-200 m. Lal et al. (1996) have reported that the Arabian Sea is super-saturated with methane at all depths down to 400 m, with peak concentration ranging from 200 to 400%. It is also reported that there is a large variation in supersaturation from the coast to open sea, with maximum near the coast. High concentration of methane in the coastal waters of the Arabian Sea was observed by Jayakumar et al. (2001). The concentration during the South West monsoon period in the surface waters along the coastal region ranged from 2.6 to 20.3 nMol/L. Near-shore surface saturations of methane have been very high. Average saturations reported off mouth of Mandovi were 1818±1396%. Such super saturations have been attributed to fluxes from adjoining wetlands.

Observations elsewhere also show the same trend of methane super saturation in the estuaries and coastal ocean. The Rhine estuary methane concentration range up to 1437 nMol/L in the freshwater regime and up to 125 nMol/L in the marine end of Rhine (Middelburg et al., 2002). Humber and Tyne estuaries adjoining the North Sea have methane concentrations in the range 190-670 nMol/L and 650 nMol/L (Goddard et al., 2000) respectively. Corresponding methane concentrations in the Humber river and Tyne river were reported as 33-152 nMol/L and 3-62 nMol/L, with strong correlation with salinity. Sediment pore water measurements show significantly higher methane concentrations. In the Scheldt Estuary, a tidal freshwater marsh in the Netherlands, methane in pore water in the top layers of the sediment was in equilibrium with the overlying water and increased significantly at lower layers (Van der Nat and Middelburg, 2002). Measurements in a non-tidal estuary in the Denmark (Abril and Iversen, 2002) show 600 nMol/L methane in the sediment pore water at a depth of 10 cm. Water to air methane fluxes from the Scheldt Estuary in the Netherlands range from 0.13 to 5.91 mol/m^2/yr [*corresponds to average value of 0.24 to 10.79 mg/m^2/hr*] (Van der Nat and Middelburg, 2000). Surface water methane concentrations in the Gulf of Mexico (Brooks et al., 1981) ranges from 37-12,700 nL/L [*ie., ~ 26-9070 nMol/L*]. They have observed maximum concentration at a depth of around 50 m.

In general, methane concentration in the sediment pore water is highest and orders of magnitude higher than even the overlying estuary water. Methane concentrations in the estuary water are significantly higher than that in the adjoining ocean, and the coastal ocean contains a higher concentration than the open ocean. This gradient from the estuary to coastal ocean to open ocean appears to be significant and suggests that estuarine discharges could be one of the major sources of methane in the coastal ocean. The role of estuarine discharges in enriching the coastal ocean with dissolved methane has been suggested by other investigators also (Jayakumar et al., 2001; Shalini et al., 2006, Mukhopadhyay, 2007). Methane concentration in water as well as water to air fluxes in estuaries show fairly wide variability at locations within each estuary as well as among different estuaries. The values observed at the Ashtamudi estuary are in general agreement with the values available from elsewhere. It is also noted that though this is a tropical site, the methane export from the estuary is only moderate. The major reason for this could be the relatively high salinity in the estuary due to mixing with seawater. The export of methane from the estuary to the coastal ocean in the form of estuarine discharges has been estimated based on the methane concentration in the estuary and the water budget of the estuary.

Conclusions

It is estimated that 270×10^6 g methane is emitted to atmosphere annually from the Ashtamudi estuary having a water cover area of 5500 ha. The amount of methane reaching the coastal ocean through water discharge from the estuary is estimated to be 42×10^6 g annually. It is noted that the methane fluxes to the coastal ocean from the estuary, as a result of tidal mixing and water flow through, is nearly 15% of the fluxes from the estuary to the atmosphere. This indicates the need to consider estuarine discharges also into account when methane budgets for coastal regions are worked out.

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