

## TRACE GAS FLUXES IN A POLLUTED SUB-TROPICAL RIVER ESTUARINE CONTINUUM, THE ADYAR, SOUTH INDIA

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**ABSTRACT**



Coastal ecosystems can influence atmospheric chemistry and earth's radiative balance through the transfer of biogenic trace gases such as  $N_2O$ ,  $CH_4$ , and  $CO_2$  to the atmosphere. Recent studies in temperate regions have confirmed that estuarine ecosystems are significant sources to global concentrations. Present estimates of trace gas emissions are difficult to constantise particularly in subtropical and tropical zones due to paucity of data. The aim of this study was to quantify fluxes of  $CO_2$ ,  $CH_4$  and  $N_2O$  in a subtropical polluted river/estuary, the Adyar, South India.

The mean concentration of  $CH_4$  from the Adyar River expressed as % saturation relative to atmosphere was 871388 %, the highest ever reported globally for a riverine environment. The mean  $CH_4$  concentration in upstream and estuarine systems were observed to be around  $2000 \text{ nmol l}^{-1}$ , while the midstream concentrations reached  $> 63,000 \text{ nmol l}^{-1}$ .  $CH_4$  in Adyar River is a function of carbon inputs predominantly in the form of sewage and the highest inputs occur in the middle reaches where highest  $CH_4$  concentrations are observed. The present investigation overall suggest the entire Adyar River/ estuarine system behaves as an atmospheric source of  $CH_4$  and the middle reaches dominate with % saturations ranging from 15,430 to 72,72,539 relative to atmosphere. Strong negative correlations were observed with  $CH_4$  against DO and ORP. The  $CH_4$  concentrations in the Adyar were found to be higher under anoxic conditions ( $DO < 1 \text{ mg l}^{-1}$ ), where the ORP is negative ranging from  $<1$  to  $-301 \text{ mV}$  in the middle reaches (the river stretch running within the city limits i.e., from 16 to 26 km from the source).

The Adyar system overall behaved as a source of  $N_2O$  to the atmosphere with concentrations typically exceeding atmospheric equilibrium concentration with the % saturations ranging from 54 - 4296 and these values are in good agreement with those reported by other authors in other coastal ecosystems. The data illustrate a wide range of concentrations ( $4$  to  $541 \text{ nmol l}^{-1}$ ) however all seasonal data overlap suggesting that seasonal

patterns are either not clear or not significant in this study. The system as a whole behaves as an annual source of atmospheric N<sub>2</sub>O with the highest concentrations observed in the oxygenated upstream and estuarine sections and nitrification is assumed to be the major source. Lowest N<sub>2</sub>O concentrations were observed in the heavily impacted midstream region with negative ORP values (reaching upto - 300 mV) and acts as a sink. It can be deduced that N<sub>2</sub>O is removed from the middle sections of Adyar by denitrification in the absence of oxygen.

The present study in the Adyar estuarine section observed wide range of pCO<sub>2</sub> concentrations higher in dry season with a range of 1140-2690 µatm (mean 2104 µatm) and 675-3379 µatm with (mean 1326 µatm) in the wet season. Variations in gas (CH<sub>4</sub>, N<sub>2</sub>O and pCO<sub>2</sub>) concentrations mirrored strongly to tide level and salinity and the gas maxima concentrations were obtained during low tide and low salinity. Strong linear negative correlations were observed against salinity during wet season (r=-0.72, -0.47, -0.70) and dry season (-0.96, -0.36, -0.71) for CH<sub>4</sub>, N<sub>2</sub>O and pCO<sub>2</sub> respectively.

Considering water to air exchange fluxes, the system behaved as a source of both atmospheric CH<sub>4</sub> and N<sub>2</sub>O throughout the year with an emissions ranging from 49 - 3343 µM m<sup>-2</sup> h<sup>-1</sup> and 0.01 - 0.06 µM m<sup>-2</sup> h<sup>-1</sup> respectively and water to air flux of CH<sub>4</sub> in the present study was higher than any published data. On comparing between direct method and models for estimating these fluxes, the floating gas exchange chamber (direct method) is found to be a reliable technique for measuring water to air fluxes, as it takes ebullition also into account. The highly impacted midstream emits higher CH<sub>4</sub> and oxygenated upstream and estuarine sections emit more N<sub>2</sub>O to the atmosphere. The CH<sub>4</sub> concentrations in the Adyar surface sediments (upto 5 cm) were also high in the middle sections and methanogens were found to be active in decomposition upto 6 days.

To summarise, the Adyar estuary recorded the highest ever reported CH<sub>4</sub> concentration for a riverine environment globally. The heavily impacted middle reaches of the Adyar river registered higher CH<sub>4</sub> and acts a source to the atmospheric CH<sub>4</sub> concentration and lesser N<sub>2</sub>O concentrations acting as a sink. In contrast, the upper and estuarine sections of the Adyar observed higher concentrations of N<sub>2</sub>O. The N<sub>2</sub>O and pCO<sub>2</sub> concentrations of the Adyar were in agreement with other major world rivers, even then the Adyar act as a strong source of trace gases (CH<sub>4</sub>, N<sub>2</sub>O and pCO<sub>2</sub>) to the atmosphere.