Estimation of Atmospheric CO_2 Pressure from River and Ground Water Composition

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Abstract

The carbon cycle has important applications in monitoring global climate change. Atmospheric CO_2-pressure is a major component of this cycle. It is possible to calculate the partial pressure of CO_2 in the atmosphere from a geochemical interpretation of temperature, pH and bicarbonate alkalinity of a river. This is known as the "effective" or "apparent" CO_2 pressure. Such calculations across the world have shown that rivers have pCO_2 higher than the atmospheric value which varies from 300 to 400 ppm i.e. $\log pCO_2$ is between -3.5 and 4.0. Many suggestions have been made to explain this paradox. The major ones are: (a) perennial rivers have a Base Flow which is essentially high-CO_2 groundwater, (b) the rate of dissolution of CO_2 in river water is faster than the rate of release of excess CO_2 back to the atmosphere, (c) human activities like burning of fossil fuels and deforestation have resulted in an increase of CO_2 in the atmosphere which in turn has favored photosynthesis and given more plant cover on land. It is obvious that interaction between various sinks and sources of CO_2 has resulted in the lack of equilibrium between rivers and the earth's atmosphere. This effect is possibly temporary but deserves further investigation.

Data recently collected along the course of the Mahanadi river in Odisha show that the apparent $\log pCO_2$ in this river ranges from -3.4 to -2.8 at temperature 25.0 to 32.5 °C. In other words, the pCO_2 is slightly higher than the atmospheric value. At those stations where earlier data were available, there is a decreasing trend over the past few years. This paper attempts to verify this observation in terms of the different hypotheses listed above.

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Introduction

- Atmospheric CO_2 is a major component of the global carbon cycle. Its dissolution at the atmosphere-hydrosphere interface acts as a carbon sink.
- Rivers are major exporters of C from continents to coastal waters.
- The partial pressure of riverine carbon dioxide (pCO_2), an important parameter in estimating CO_2 evasion, as it represents the direction and intensity of gas exchange at the water to air interface and reflects whether a river is a sink or source of atmospheric CO_2.
- Recent studies found that most of the river systems actively degasses CO_2 into the atmosphere and a net sources of atmosphere CO_2.

Major sources of CO_2 concentrations in the river

- Inorganic carbon fixation via aquatic primary production
- Organic matter decomposition,
- Import via groundwater
- Exchange with the atmosphere

Factors influencing pCO_2

- Intensity of precipitation
- Hydrological flow path
- Land use composition (i.e. percentage of forest and agriculture)
- Dam Construction

Land use in Mahanadi Basin

Analysing land-use changes from 1972 to 2003, it may be concluded that the total forest cover has declined by 5.71% of the total area of the basin. A reduction in barren land (0.64%) is followed by increase in areas of surface water bodies (0.47%), built up land (0.22%), river bed (0.11%) and most prominently agriculture (5.55%). This implies that the total forest cover and barren land has declined at the expense of increase in water body, river bed, agriculture and built up land in a span of 30 years.

Methodology

- Water samples collected from mainstream of the Mahanadi and its major tributaries and
- Data for three groundwater samples were taken from ground water year book of CGWB
- Temperature and pH were measured at field by Orion 5star multiparameter.
- HCO_3 by titration.

The equilibrium constant for this solubility reaction:

$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-$

$K_{CO2} = mH_2CO_3/pCO_2$ (1)

$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$

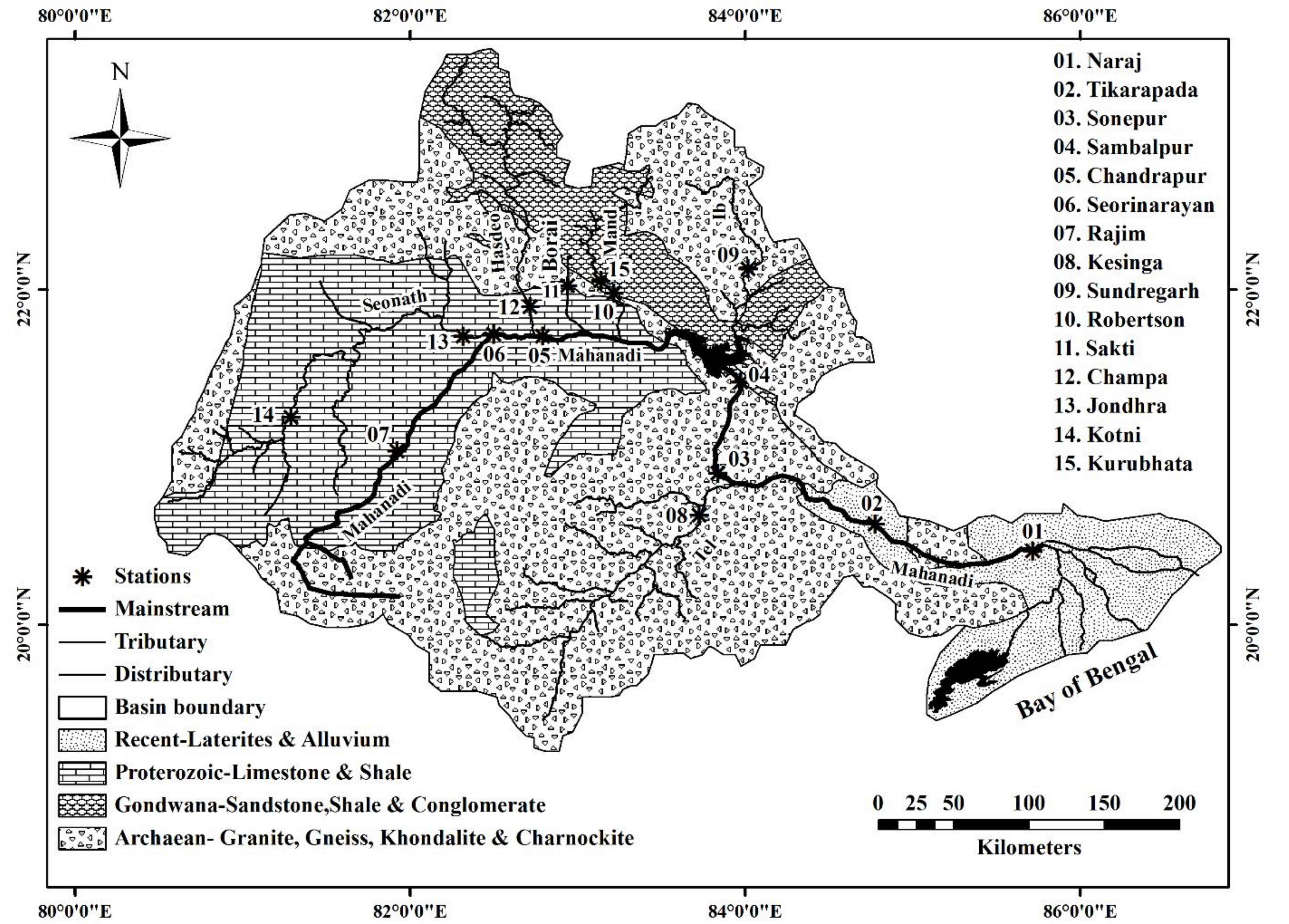
$K_1 = (mH^+.mHCO_3^-)/mH_2CO_3 = (mH^+.mHCO_3^-)/ K_{CO2.}\ pCO_2$ (2)

$K_1.K_{CO2}.\ pCO_2 = mH^+.mHCO_3^-$ (3)

Taking logarithm of both sides of equation (3),

$\log pCO_2 = \log mHCO_3^- - \log (K_{1.}K_{CO2}) - pH$ (4)

For a given temperature, K_1 and K_{CO2} are constant.



80°0'0"E
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22°0'0"N
20°0'0"N
N
01. Naraj
02. Tikarapada
03. Sonepur
04. Sambalpur
05. Chandrapur
06. Seorinarayan
07. Rajim
08. Kesinga
09. Sundregarh
10. Robertson
11. Sakti
12. Champa
13. Jondhra
14. Kotni
15. Kurubhata
Hasdeo
Borai
Mand
Ib
Seonath
Mahanadi
Tel
Bay of Bengal
Stations
Mainstream
Tributary
Distributary
Basin boundary
Recent-Laterites & Alluvium
Proterozoic-Limestone & Shale
Gondwana-Sandstone,Shale & Conglomerate
Archaean- Granite, Gneiss, Khondalite & Charnockite
0 25 50 100 150 200
Kilometers

Sambalpur

Tikarapada

Kotni

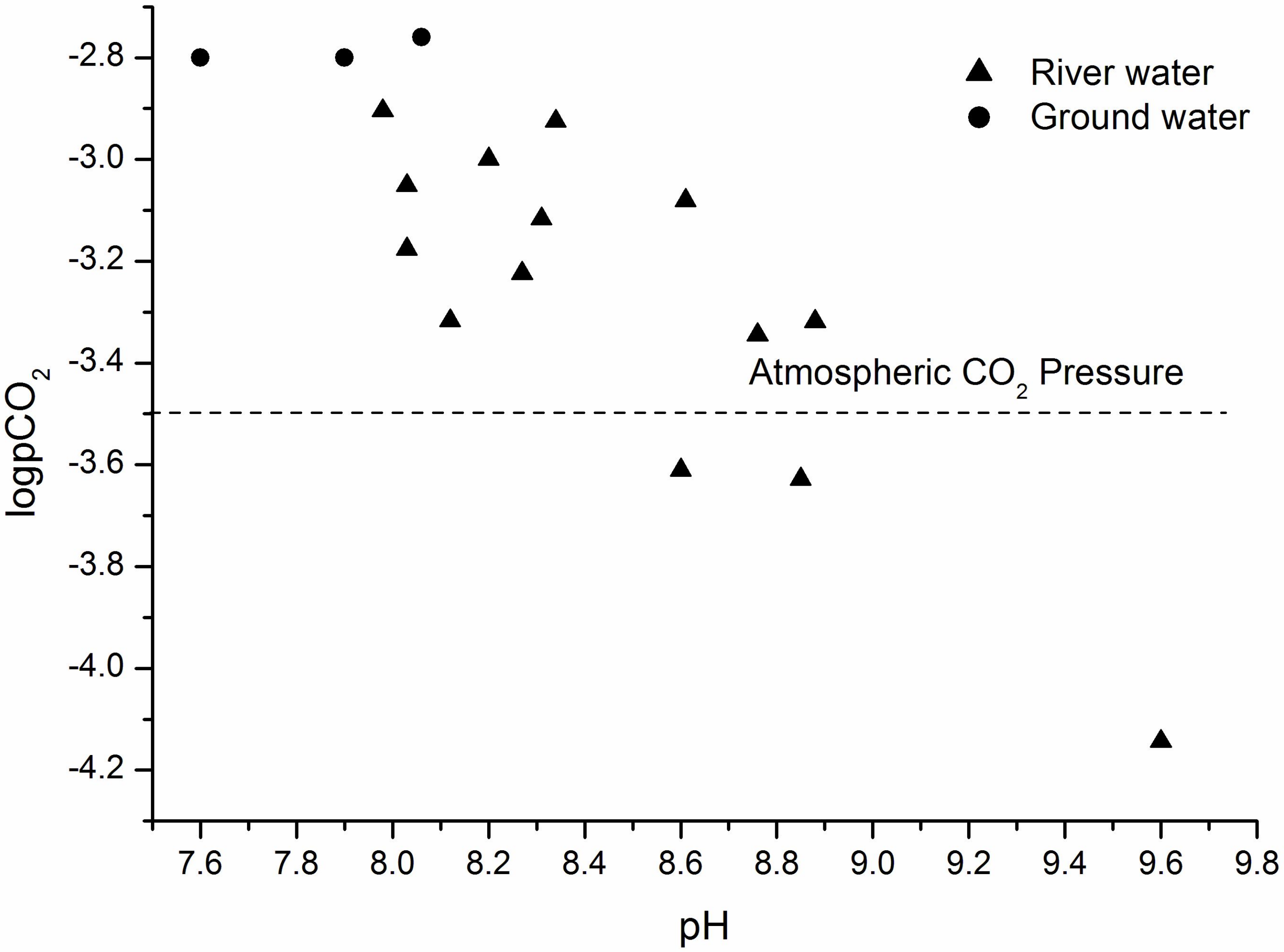
Naraj

Result and Discussion

- The pH of river water varies from 7.98 to 9.6
- Concentration of HCO_3^- in river water varies from 48.81 to 280 mg/L .
- High alkalinity and pH is associated with the upper part of the Mahanadi dominated by limestone.
- The pCO_2 in the basin ranges between $10^{-2.90}$ and $10^{-4.14}$.

pCO2 in Ground water

Location	Date	pH	HCO_3 (mg/L)	logpCO2
Tikarapada	April, 2014	8.06	183	-2.76
Sundargarh	April, 2015	7.6	61	-2.8
Kurubhata	May, 2015	7.9	128	-2.8



- At most locations apparent pCO_2 is higher than the atmospheric value
- At each location pCO_2 in ground water is not only higher than the atmospheric value but also higher than the corresponding river water value.
- Similar trend has been observed in all the rivers in the world
- River water contain significant fraction of high-CO2 ground water as base flow during pre-monsoon period.
- The rate of release of excess CO_2 is much slower
- The interaction among various sources and sinks of CO_2 has resulted in the lack of equilibrium between rivers and the earth's atmosphere.