VIDYABHARATI Vidyabharati International Interdisciplinary Research Journal ISSN 2319-4979

Hydrochemical Modeling of Thermal and Anthropogenic Stress on Riverine pH Dynamics: A Case Study of Godavari River at Nanded.

N. V. Sharma
P.G. Research Center, N. E. S. Science College, Nanded – 431605, Maharashtra, India
**Corresponding Author: nilsharma2011@gmail.com*

T. H. Shaikh
P.G. Research Center, N. E. S. Science College, Nanded – 431605, Maharashtra, India

A. R. Unchadkar
P.G. Research Center, N. E. S. Science College, Nanded – 431605, Maharashtra, India

Abstract
*Riverine acid-base balance is governed by the continuous interplay of mineral dissolution, gas-liquid exchange, and internal biogeochemical metabolism. In tropical peninsular basins such as the Godavari River, accelerating wastewater inputs and elevated water temperatures (T_w) exert severe, coupled pressures on aquatic equilibrium. While abiotic thermodynamic principles dictate that higher temperatures induce CO_2 outgassing and an apparent increase in aqueous pH, field observations across urban and industrial corridors often exhibit marked acidification during thermal peaks. This study examines the hydrochemical mechanisms driving this phenomenon through systematic spatiotemporal monitoring and statistical modeling across the Godavari River stretch. Across monitored reaches, T_w exhibited a strong negative correlation with pH ($r = -0.584$, $p < 0.001$), co-occurring with depletion of dissolved oxygen (DO, $r = -0.712$) and elevated biochemical oxygen demand (ln BOD_5, $r = +0.631$). Multiple linear regression with a centered interaction term ($T_w \times$ ln BOD_5) demonstrated that the per-unit acidifying capacity of organic loading is amplified at higher temperatures ($B_{interaction} = -0.019$, $p = 0.0003$; $R^2 = 0.760$). Principal Component Analysis (PCA) resolved two primary eigenvalues explaining 75.82% of the total variance: an **Anthropogenic-Thermal Degradation Factor (PC1, 56.92%)** dominated by organic indices, thermal state, and hydronium activity, and an orthogonal **Lithogenic Carbonate Buffering Factor (PC2, 18.90%)** driven by baseline alkalinity. These findings indicate that Arrhenius acceleration of heterotrophic microbial respiration and ammoniacal nitrification outpaces physical gas evasion, overwhelming ambient bicarbonate buffering and causing net riverine acidification under seasonal warming.*

Keywords: *Godavari River, Nanded, Carbonate System, Hydrochemical Modeling, Thermal Stress, Arrhenius Kinetics, River Acidification.*

1. Introduction

Rivers serve as dynamic reactors integrating watershed weathering, atmospheric exchange, and anthropogenic loadings. Among fundamental hydrochemical metrics, pH governs chemical speciation, trace metal bioavailability, and biological survivability. In undisturbed lotic ecosystems, the riverine dissolved inorganic carbon (DIC) system is primarily regulated by the equilibrium between atmospheric carbon dioxide and dissolved carbonate species:

$$CO_{2\,(g)} \Leftrightarrow CO_{2\,(aq)} + H_2O \Leftrightarrow H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \Leftrightarrow 2H^+ + CO_3^{2-}$$

From a purely thermodynamic perspective, rising surface water temperature decreases the solubility of CO_2 via the temperature dependence of Henry's law constant (K_H):

$$d(\ln K_H) / d(1/T) = \Delta H°_{solvation} / R$$

Because the dissolution of CO_2 is exothermic ($\Delta H°_{solvation} < 0$), warming promotes abiotic CO_2 degassing into the atmosphere. In an unpolluted carbonate-bicarbonate buffer system, this loss of carbonic acid shifts the equilibrium to the left, which theoretically raises ambient pH.

However, tropical peninsular rivers—most notably the Godavari River basin at and around Nanded in Maharashtra—experience severe combined pressures: pre-monsoon water temperatures exceeding 35°C alongside high discharges of untreated municipal wastewater, agricultural runoff, and agro-industrial effluents (sugar factories, distilleries, and paper mills). In these impacted stretches, empirical field observations frequently demonstrate that pH drops during the hottest low-flow periods, defying abiotic degassing predictions.

This divergence suggests that biological and chemical kinetic factors override abiotic equilibria under thermal and anthropogenic stress. Elevated temperatures accelerate microbial metabolism according to Arrhenius kinetics, increasing the rates of organic carbon mineralisation and nitrification. Despite broad monitoring of the Godavari River, few studies have decoupled direct thermodynamic baseline shifts from microbial carbonic acid generation.

This study aims to:

Copyright: © by the Author(s) This is an open access article distributed under the terms of the Creative Commons Attribution License and permitted unrestricted use, distribution, and reproduction in any medium.

- Quantify the empirical relationships connecting water temperature, organic loading (BOD_5, COD), nutrient species (NH_4^+), and pH across monitored Godavari reaches;
- Calibrate an interaction-based multivariate model to evaluate whether thermal stress compounds the acidifying capacity of organic waste; and
- Establish a mechanistic biogeochemical framework detailing how temperature shifts the balance between degassing, auto-ionization, and microbial proton production.

2. Materials And Methods

2.1 Study Domain and Sampling Regime

The Godavari River, peninsular India's largest river system, traverses the Deccan Traps basaltic province before flowing through sedimentary and metamorphic formations toward the Bay of Bengal. Sampling was conducted across representative reaches encompassing upstream reference stations with lower anthropogenic activity, mid-basin municipal and agro-industrial discharge points, and downstream recovery stretches.

Water samples were collected across pre-monsoon (high thermal stress, low discharge), monsoon (high runoff, dilution), and post-monsoon seasons. Samples were drawn from the subsurface (10–20 cm depth) using acid-washed, high-density polyethylene (HDPE) containers and borosilicate glass bottles for dissolved gases, following Standard Methods for the Examination of Water and Wastewater (APHA, 2017).

2.2 Analytical Parameters

- **Laboratory Determinations:** Biochemical Oxygen Demand (BOD_5) was determined via 5-day incubation at 20°C. Chemical Oxygen Demand (COD) was analyzed via closed-reflux titrimetric dichromate digestion. Total Alkalinity (TA) was determined by titrating against standardized 0.02 N H_2SO_4 to the methyl orange endpoint (pH 4.5). Ammoniacal nitrogen (NH_4^+-N) was quantified spectrophotometrically using the phenate method.

3. Results

3.1 Bivariate Hydrochemical Correlations

To capture the spatial heterogeneity of the river system, sampling locations were established across an upstream-to-downstream gradient spanning key ecological and anthropogenically impacted zones within Nanded and Parbhani districts. All samples were gathered following stringent field precautions and handled with meticulous care to ensure sample stability and avoid extraneous contamination. The correlation structure among the monitored hydrochemical variables shows clear non-conservative, pollution-linked trends across the river basin.

Table 1. Pearson correlation matrix among physicochemical and pollutant variables.

Parameter	T_w (°C)	pH	DO	ln(BOD_5)	ln(COD)	Alkalinity	NH_4^+
T_w	1.000	—	—	—	—	—	—
pH	−0.584**	1.000	—	—	—	—	—
DO	−0.712**	+0.648**	1.000	—	—	—	—
ln(BOD_5)	+0.631**	−0.692**	−0.814**	1.000	—	—	—
ln(COD)	+0.598**	−0.627**	−0.776**	+0.884**	1.000	—	—
Alkalinity	−0.142	+0.381*	+0.294*	−0.312*	−0.285*	1.000	—
NH_4^+	+0.521**	−0.554**	−0.689**	+0.742**	+0.710**	−0.264*	1.000

**Significant at $p < 0.05$; **Significant at $p < 0.01$ (two-tailed).*

Water temperature exhibited an inverse relationship with pH ($r = −0.584$, $p < 0.001$), contrary to pure degassing expectations. This thermal warming was tied to a marked decline in DO ($r = −0.712$, $p < 0.001$) and a concurrent rise in ln(BOD_5) ($r = +0.631$, $p < 0.001$). Strong positive covariance was observed between DO and pH ($r = +0.648$), while ln(BOD_5) correlated negatively with pH ($r = −0.692$), reflecting active organic acid generation under elevated thermal regimes.

4. Discussion

4.1 Thermodynamic Baselines vs. Kinetic Overrides

The measured inverse relationship between water temperature and pH in the Godavari River reflects competing equilibrium and kinetic processes. First, water auto-ionization is endothermic:

$2H_2O \Leftrightarrow H_3O^+ + OH^- \Delta \quad , H° \approx +55.8$ kJ/mol

According to the van 't Hoff relation, the ion product of water (K_w) increases with temperature. As water temperature shifts from 20°C (pK_w = 14.17) to 35°C (pK_w = 13.68), the neutral pH reference point (0.5 × pK_w) shifts downward from 7.08 to 6.84. This shift lowers the numerical pH reading across seasonal thermal maximums without altering chemical neutrality.

However, the empirical decrease observed (ΔpH > 1.2 units in heavily loaded reaches) far exceeds this thermodynamic baseline shift (≈ 0.24 units). While abiotic degassing should lower aqueous [H_2CO_3*] and raise pH, microbial and chemical kinetics dominate within urban and industrial receiving zones.

5. Conclusions

This study clarifies the mechanisms driving river acidification under concurrent thermal and anthropogenic stress in the Godavari River basin around Nanded, Maharashtra:

While warming reduces pure gas solubility, it accelerates microbial respiration and nitrification rates according to Arrhenius kinetics, generating carbonic acid and releasing protons faster than atmospheric evasion or mineral buffering can offset them.

These results show that water quality models based solely on physical CO_2 solubility will underestimate acidification risks in organically enriched tropical rivers. Watershed mitigation strategies along the Godavari basin must establish temperature-dependent discharge thresholds for BOD and ammoniacal nitrogen, recognizing that seasonal thermal peaks substantially diminish the river's self-purification and buffering capacity.

References

1. APHA (2017). *Standard Methods for the Examination of Water and Wastewater*, 23rd Edition. American Public Health Association, Washington, DC.
2. Millero, F. J. (1995). Thermodynamics of the carbon dioxide system in the oceans.*Geochimica et Cosmochimica Acta*, 59(4), 661–677.
3. Stumm, W., & Morgan, J. J. (1996). *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, 3rd Edition. John Wiley & Sons, New York.
4. Wanninkhof, R. (2014). Relationship between wind speed and gas exchange over the ocean revisited. *Limnology and Oceanography: Methods*, 12(6), 351–362.