Supplement of Biogeosciences, 22, 4923–4951, 2025
https://doi.org/10.5194/bg-22-4923-2025-supplement

Biogeosciences
Open Access

Supplement of

Multidecadal trends in CO_2 evasion and aquatic metabolism in a large temperate river

An Truong Nguyen et al.

Correspondence to: An Truong Nguyen (truongan9393@yahoo.com)

S1. Map of study site

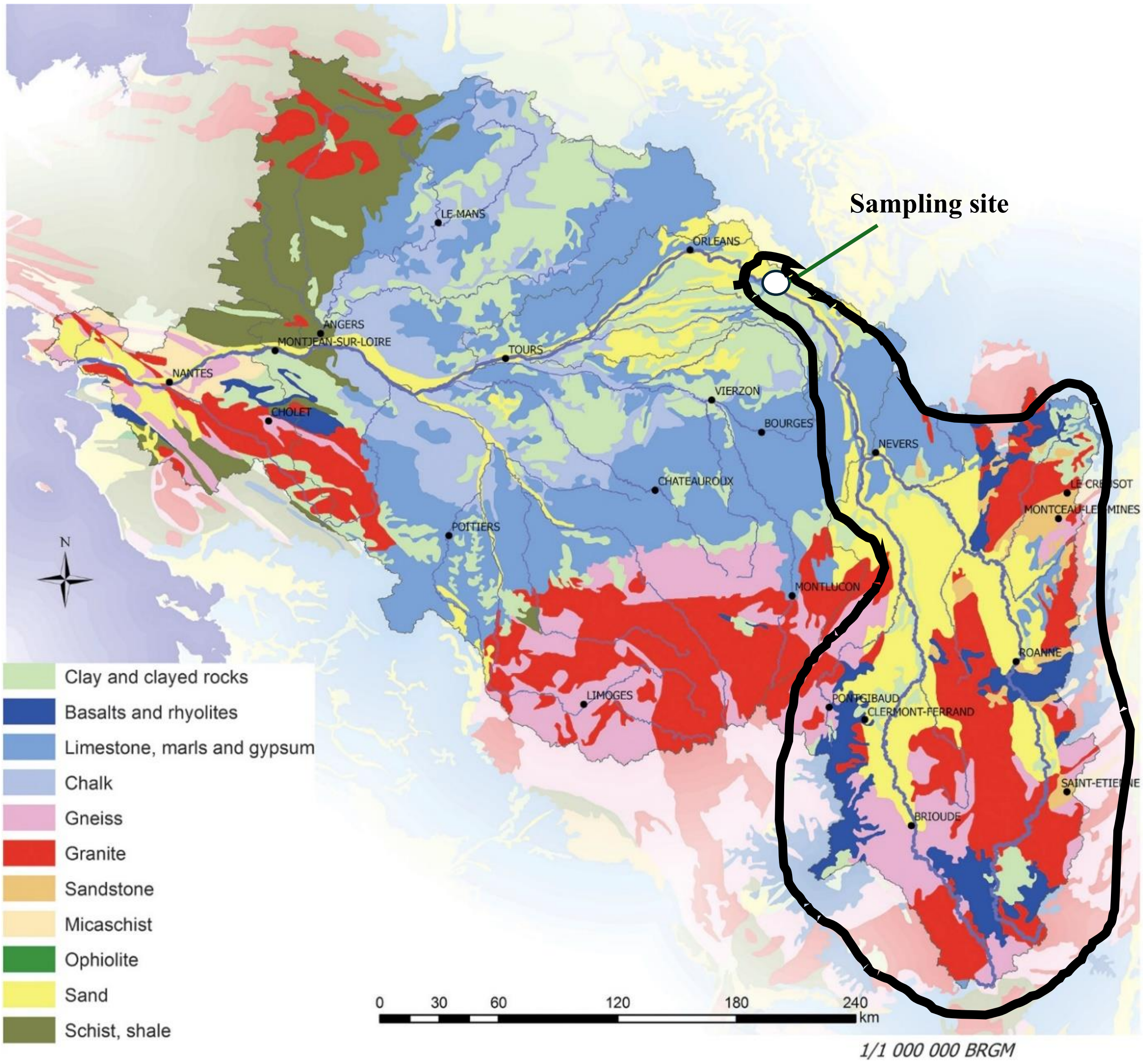

Figure S1. The sampling site and the lithology in the Loire basin (Moatar et al., 2022).

S2. QA/QC

EDF's environmental monitoring operates under mandatory oversight from ASN (Autorité de Sûreté Nucléaire), France's nuclear safety authority, with comprehensive QA/QC protocols documented for two main periods, including:

1) Historical QA/QC Framework (1990-2008): Moatar et al. (2001) Methodology

During 1990-2008, DO was measured with electrochemical membrane sensors and pH with combination electrodes; these were calibrated at scheduled intervals (using two-point pH buffer solutions and air-saturation for DO) and checked against laboratory benchmarks. The measurement accuracy achieved (including routine calibration and laboratory cross-comparisons) was about ±0.3 pH units for pH and ±8% for DO (in mg O2 L-1). Sensors were inspected, cleaned (to prevent biofouling or sediment clogging), and had consumables (e.g. DO membranes) replaced as needed in accordance with the manufacturer's recommendations and agency protocols.

The monitoring system implemented the quality control methodology developed by Moatar et al. (2001), including: (1) Multi-level automated validation with specific range checks (pH: 6.0-10.0, DO: 0-20 mg L-1), persistence testing (>48 hours constant values), and rate-of-change detection (±0.5 pH units, ±3 mg L-1 DO hourly limits); (2) Cross-station validation comparing upstream and downstream measurements with acceptance criteria of ±0.2 pH units and ±1 mg L-1 DO; (3) Systematic drift correction with linear correction applied when bias exceeded 0.1 pH units over 7-day periods; (4) Expert review integration incorporating discharge patterns to eliminate false anomaly detection; and (5) Performance monitoring maintaining >95% data recovery with documented calibration procedures.

In our study, we specifically employed the open-source pyhydroqc toolkit (Jones et al., 2022) to automate anomaly detection (range, persistence, spike, and drift checks) and then visually inspected flagged periods in conjunction with discharge and the downstream station as an extra safeguard. Through this process, approximately 10% of the hourly pH and O2 data (mostly in the early 1990s) were removed. Short gaps (<6 h) were linearly interpolated, while longer gaps were filled using data from the paired station or smoothed via a seasonal Kalman filter, as detailed sections below.

2) Modern QC Framework (2008-present)

Since 2009, all monitoring laboratories must comply with ISO 17025:2005 international standards, requiring: (1) Documented calibration procedures using certified reference standards traceable to national standards (LNE - Laboratoire National de Métrologie et d'Essais); (2) Staff competency verification through annual testing and training programs; (3) Method validation with comprehensive quality management systems; (4) Regular external audits by COFRAC (Comité Français d'Accréditation) every 15 months; and (5) Inter-laboratory comparison testing organized by ASN to ensure measurement quality.

The 2008 sensor upgrade from membrane to optical technology occurred within this consistent regulatory framework, with both sensor generations operating under identical mandatory ASN oversight requirements.

S3. Figures

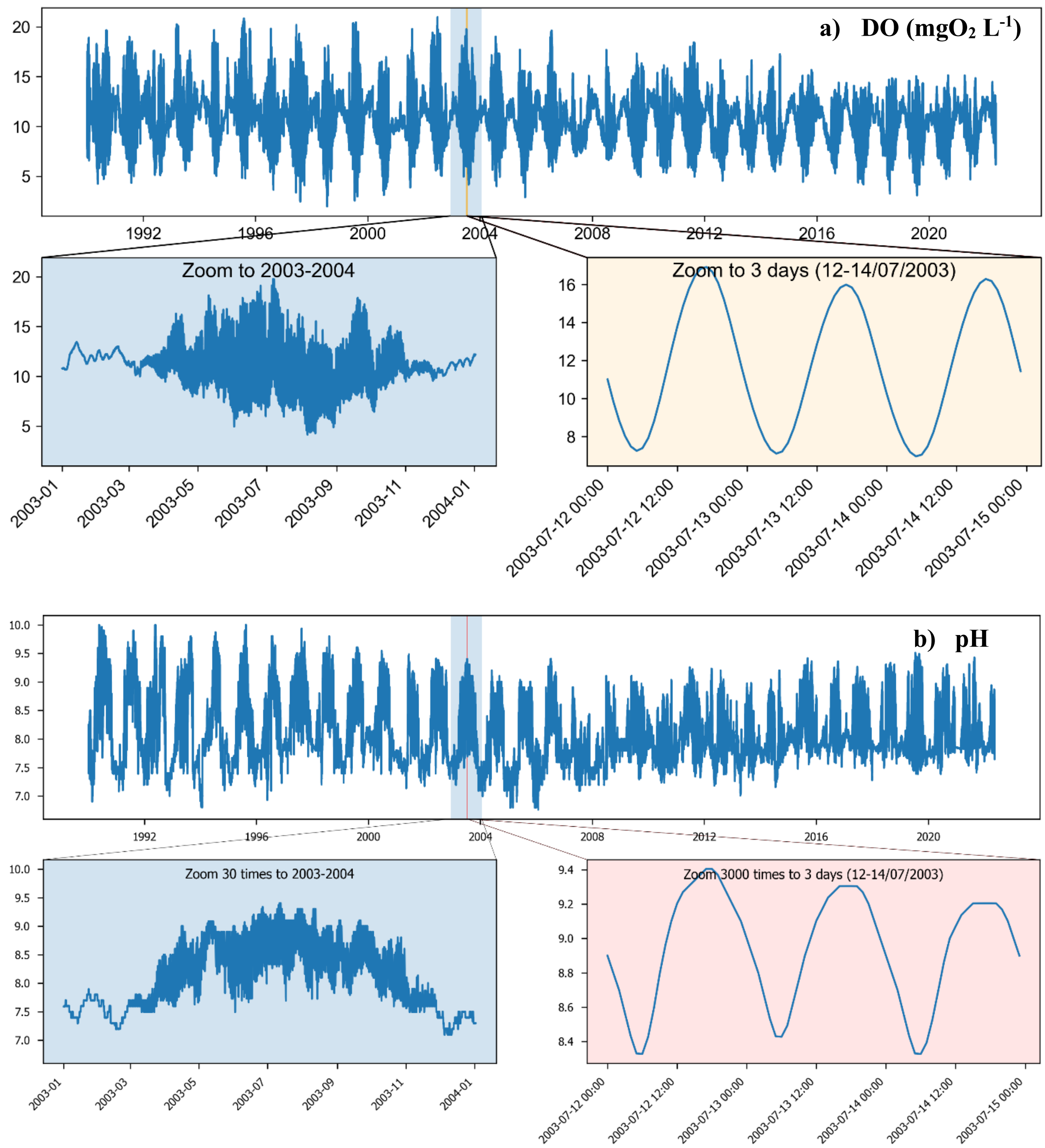

Figure S2: Overview of long-term, high resolution of hourly DO (mgO_2 L^{-1}) and pH in Dampierre station in 1990-2021

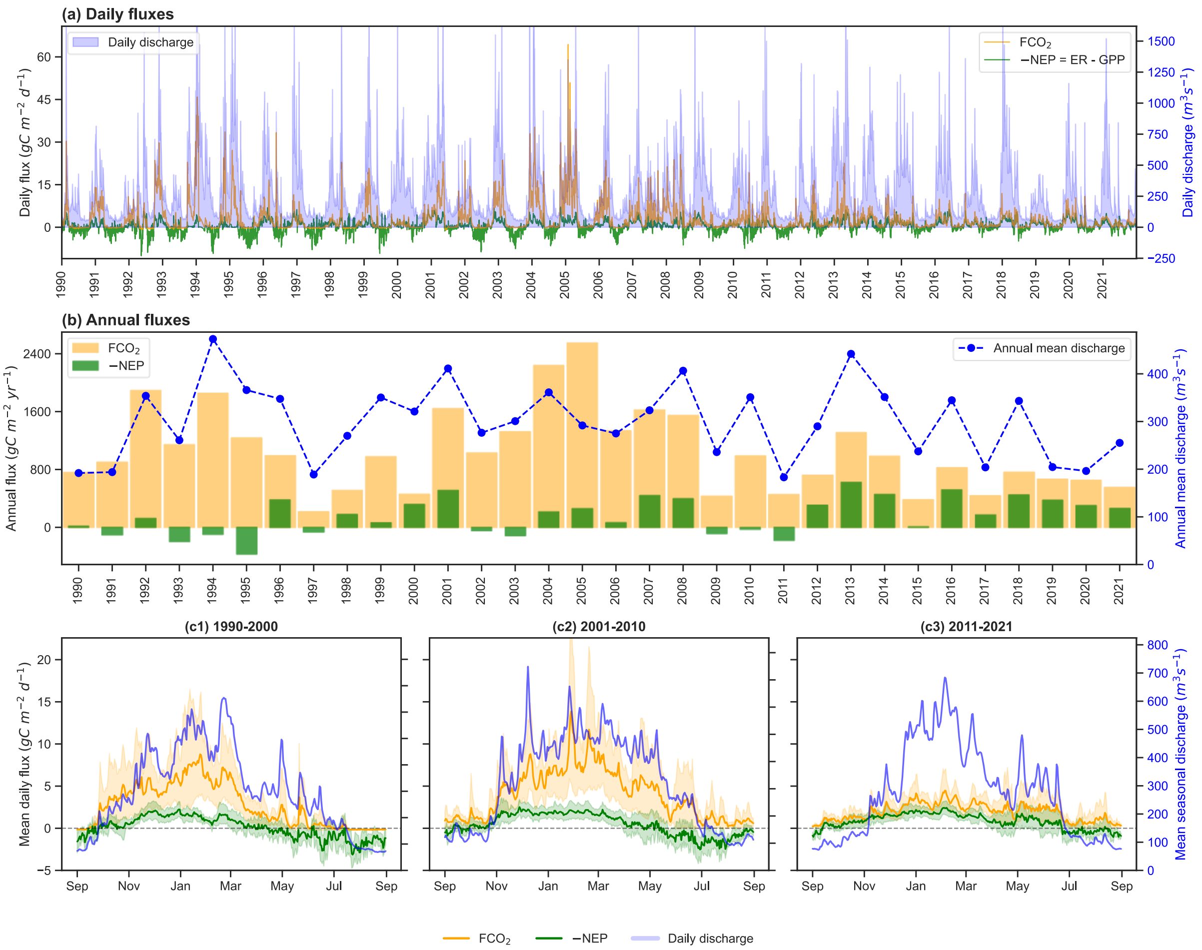

Figure S3: Comparison of carbon fluxes (-NEP and FCO_2) with river discharge across daily, annual, and seasonal timescales.

References

Jones, A. S., Jones, T. L., & Horsburgh, J. S. (2022). Toward automating post processing of aquatic sensor data. Environmental Modelling and Software, 151, 105364. https://doi.org/10.1016/j.envsoft.2022.105364

Moatar, F., Descy, J.-P., Rodrigues, S., Souchon, Y., Floury, M., Grosbois, C., Minaudo, C., Leitao, M., Wantzen, K. M., & Bertrand, F. (2022). Chapter 7—The loire river basin. In K. Tockner, C. Zarfl, & C. T. Robinson (Eds.), Rivers of Europe (Second Edition) (pp. 245–271). Elsevier. https://doi.org/10.1016/B978-0-08-102612-0.00007-9

Moatar, F., Miquel, J., & Poirel, A. (2001). A quality-control method for physical and chemical monitoring data. Application to dissolved oxygen levels in the river loire (france). Journal of Hydrology, 252(1–4), 25–36. https://doi.org/10.1016/S0022-1694(01)00439-5

Raymond, P. A., Zappa, C. J., Butman, D., Bott, T. L., Potter, J., Mulholland, P., Laursen, A. E., McDowell, W. H., & Newbold, D. (2012). Scaling the gas transfer velocity and hydraulic geometry in streams and small rivers. Limnology and Oceanography: Fluids and Environments, 2(1), 41–53. https://doi.org/10.1215/21573689-1597669