Hydrodynamic and Primary Production Effects on Seasonal DO Variability in the Danube River

Jan Maier[1], Anna-Neva Visser[1], Christina M. Schubert[1], Simon T. Wander[1], Johannes A. C. Barth[1]

[1]Applied Geology, GeoZentrum Nordbayern, Friedrich-Alexander-University Erlangen-Nürnberg, Erlangen 91054, Germany

Correspondence to: Jan Maier (jan.m.maier@fau.de)

Abstract

Dissolved oxygen (DO) is a fundamental indicator for water quality and ecosystem health, particularly in the context of anthropogenic impacts and climate change. This study presents the first large-scale dataset of DO concentrations combined with its stable oxygen isotope ratios (expressed as $\delta^{18}O_{DO}$), particulate organic carbon concentrations (POC) and respiration/ photosynthesis (R/P ratios) from five seasonal campaigns along the entire Danube River in 2023 and 2024. Our findings reveal pronounced seasonal DO dynamics driven by temperature, biological activity and hydrodynamic conditions. During spring and summer, enhanced photosynthesis increased DO up to 0.40 mmol/L, with $\delta^{18}O_{DO}$ values down to +12.1 ‰ and POC up to 0.25 mmol/L in two highly productive river sections. Low R/P ratios of up 0.1 further indicated strong net autotrophic conditions. ~~The s~~Strong correlations between $\delta^{18}O_{DO}$ and POC further confirm~~s the dominant~~ influence of primary producers (i.e., photosynthetic organisms) in a river section where a reduced slope led to slower flow and lower turbulence. Notably, $\delta^{18}O_{DO}$ values were~~ significantly~~ lower than those expected for atmospheric equilibrium (+24.6 ‰ ± 0.4 ‰), a pattern rarely documented in large river systems. In contrast, tributary inflows from the Tisa and Sava R~~r~~ivers diluted biomass and organic material inputs and led to declines in DO and POC. By late summer, intensified respiration reversed photosynthetic signals, led to the lowest DO concentrations down to 0.16 mmol/L and raised $\delta^{18}O_{DO}$ up to +23.7 ‰, particularly in the Sava River. In fall, DO levels partially recovered despite continued respiration, as also indicated by the highest observed $\delta^{18}O_{DO}$ values of 25.9 ‰ and the highest R/P ratios of the entire season, that reaching up to 8.9. ~~, while i~~In winter, oxygen input from the atmosphere became ~~the ~~dominant ~~control ~~with minimal biological influences. Overall, this study provides new insights into dynamics~~ interplays~~ between oxygen sources and sinks across the river continuum over seasons. These new insights underscore the need for continuous DO monitoring, particularly in late summer when oxygen levels can become critically low. Understanding these interactions can help to establish efficient aqueous ecosystem management and conservation strategies in the face of land use ~~environmental ~~and climate change.

1. Introduction

Freshwater ecosystems are increasingly threatened by complex global stressors (Borgwardt et al., 2019; Vörösmarty et al., 2013) Beyond climate change, anthropogenically-induced alterations of river morphology (Belletti et al., 2015), disrupted flow regimes (Acreman and Dunbar, 2004; Poff and Zimmerman, 2010), nutrient input (Fowler et al., 2013; Seitzinger et al., 2006; Sutton et al., 2011), and pollution from urban and industrial sources (Nyenje et al., 2010; Qing et al., 2015; Suthar et al., 2009; Xia et al., 2016) continue to degrade water quality and stability of aquatic habitats. Land use changes further intensify these pressures, thus often jeopardizing river basin health. Such influences can also amplify the impacts of environmental stressors~~disasters~~ (Honisch et al., 2002; Hua, 2017). Consequently, between 2015 and 2021, only 37 % of all European surface water bodies achieved a 'good' ecological status and only 29 % a 'good' chemical status (EEA, 2021). These numbers ~~which~~ highlight~~s~~ the urgency to address environmental~~these~~ challenges for terrestrial aqueous systems. Particularly excessive agricultural nutrient inputs from mostly agriculture land use, primarily phosphorus and nitrogen, threaten aquatic life and can trigger algal blooms that lead to eutrophication, oxygen depletion and ultimately a decline in biodiversity (Carpenter et al., 1998; Dudgeon et al., 2006; Grizzetti et al., 2017).

Among many consequences of these stressors, disruptions of dissolved oxygen (DO) sources and sinks can ~~significantly~~ impact freshwater habitats and influence biodiversity, biogeochemical cycles and overall environmental health (Franklin, 2014; Killgore and Hoover, 2001; North et al., 2014). Primary producers, such as phytoplankton, serve as a key source of DO via photosynthesis, whereas respiration by heterotrophic organisms ~~acts as~~provide major sinks that consume DO (Heddam, 2014; Wetzel, 2011). However, DO concentrations are not solely regulated by biological activity.~~, but~~ They are also influenced by atmospheric exchange and environmental factors such as temperature, light availability and nutrient levels (Benson et al., 1979; Odum, 1956; Stumm and Morgan, 1995). In addition, chemical processes, such as redox reactions and the mineralization of organic carbon under stratified or eutrophic conditions, can also serve as important DO sinks, particularly in hypolimnetic lake environments, anoxic groundwaters and rivers with elevated groundwater input (Jurgens et al., 2009; Piatka et al., 2021; Rosecrans et al., 2017).

In the context of fluvial systems, a better understanding and prediction of DO distributions and their controlling processes are essential to assess aquatic health and to prevent or at least manage potential anoxic events. This is especially important for the Danube River, Europe's second-longest waterway. While the river provides important services for agriculture and energy production, these activities also impose significant pressures on its natural system. Additionally, the Danube serves as a crucial ecological corridor that promotes biodiversity across central and eastern Europe (Habersack et al., 2016; ICPDR, 2015; Sommerwerk et al., 2009). Although the ecological quality improved in the last 30 years, the Danube River still faces ongoing threats, particularly from organic pollution downstream of major cities and after confluences of key tributaries (Mănoiu and Crăciun, 2021; Wachs, 1997).

Despite the critical role of DO in freshwater ecosystems, research has primarily focused on DO concentration patterns as an indicator of water quality, while the relative contributions of biological and atmospheric inputs often remain poorly quantified. In particular, photosynthesis and community respiration drive DO dynamics in fundamentally different ways, yet their individual effects cannot be fully distinguished through concentration measurements alone. Traditional approaches lack a ~~clear~~ framework to separate DO sources and sinks, thus leaving significant gaps in our understanding of aqueous DO cycling. Stable isotope measurements of DO provide a powerful tool to overcome these limitations by distinguishing between three key processes that govern DO dynamics in aqueous environments: photosynthesis, respiration and atmospheric exchange. Aquatic photosynthesis, by splitting water molecules, transfers a typically ^{16}O-enriched signature into the DO pool (Guy et al., 1993; Limburg et al., 1999). However, under low DO concentrations, concurrent DO consumption can lead to ^{18}O-enrichments even during photosynthesis (Eisenstadt et al., 2010). Similarly, aerobic respiration preferentially consumes ^{16}O, leaving the remaining DO enriched in ^{18}O (Mader et al., 2017). This study is among ~~the~~ few to apply DO isotopes to river systems and contributes to a still limited body of research on DO dynamics in aqueous systems (e.g., Parker et al., 2010; Quay et al., 1995; Tobias et al., 2007; Wassenaar et al., 2010) ~~and contributes to a still limited body of research~~.

With increasing environmental pressures~~Given these challenges~~, a comprehensive understanding of DO sources and sinks in the Danube is essential for assessing and managing river health. To address this issue, we conducted the first large-scale study of the DO budget of the entire Danube main channel and its key tributaries (e.g., Inn, T~~h~~isa~~,~~ and Sava) (Figure 1), based on five sampling campaigns between 2023 and 2024. By integrating spatial high-resolution DO measurements with $\delta^{18}O_{DO}$ analyses, particulate organic carbon (POC), and ratios between respiration and photosynthesis (R/P), we were able to reveal DO sources and sinks along the river continuum together with its seasonal dynamics. This approach could identify critical periods and regions characterized by elevated or depleted DO levels and also disentangled variable contributions by photosynthesis, respiration and atmospheric exchange. Together, ~~T~~these ~~novel~~ findings contribute to a more comprehensive ~~enhance our~~ understanding of the Danube~~'s~~ River`s functioning. ~~and contribute to a strong scientific foundation for river management and conservation strategies amid growing environmental pressures.~~

2. Material and methods

2.1 Study area

The Danube has a total length of 2,857 km and a mean annual discharge of 6486 m^3/s (Sommerwerk et al., 2009). Its catchment area of 807,827 km² hosts a population of approximately 83 million people in 10 different countries and serves as a vital freshwater resource for Central and Eastern Europe (Habersack et al., 2016; ICPDR, 2015; Sommerwerk et al., 2009). In ~~Between July~~ 2023 and ~~September~~ 2024, five sampling campaigns were conducted on the main river and its major tributaries (e.g., Inn, Tisa and Sava), covering the following key seasons: summer (July 2023), fall (late October to early November 2023), winter (February 2024), spring (April 2024) and late summer (late August to early September 2024). ~~in spring, summer, late summer and fall and winter were conducted on the main river and the main tributaries (e.g., Inn, Tisa, Sava).~~ During each sampling campaign, between 54 to 89 sampling locations along the entire mainstream were surveyed (Figure 1~~; dataset will be uploaded on PANGAEA~~). The coordinates of the sampling sites were recorded in the field by Google Maps and confirmed bywith a Garmin eTrex HC-series GPS device., and eElevation data were determined with a barometric altimeter via the mobile Elevation App from Mapnitude Company Limited (https://mapnitude.com/elevation).(Supplementary Material Table 1). Discharge data were provided by the International Commission of the Danube River (ICPDR database, https://www.danubehis.org, (ICPDR, 2025; last access: 11. March. 2025).

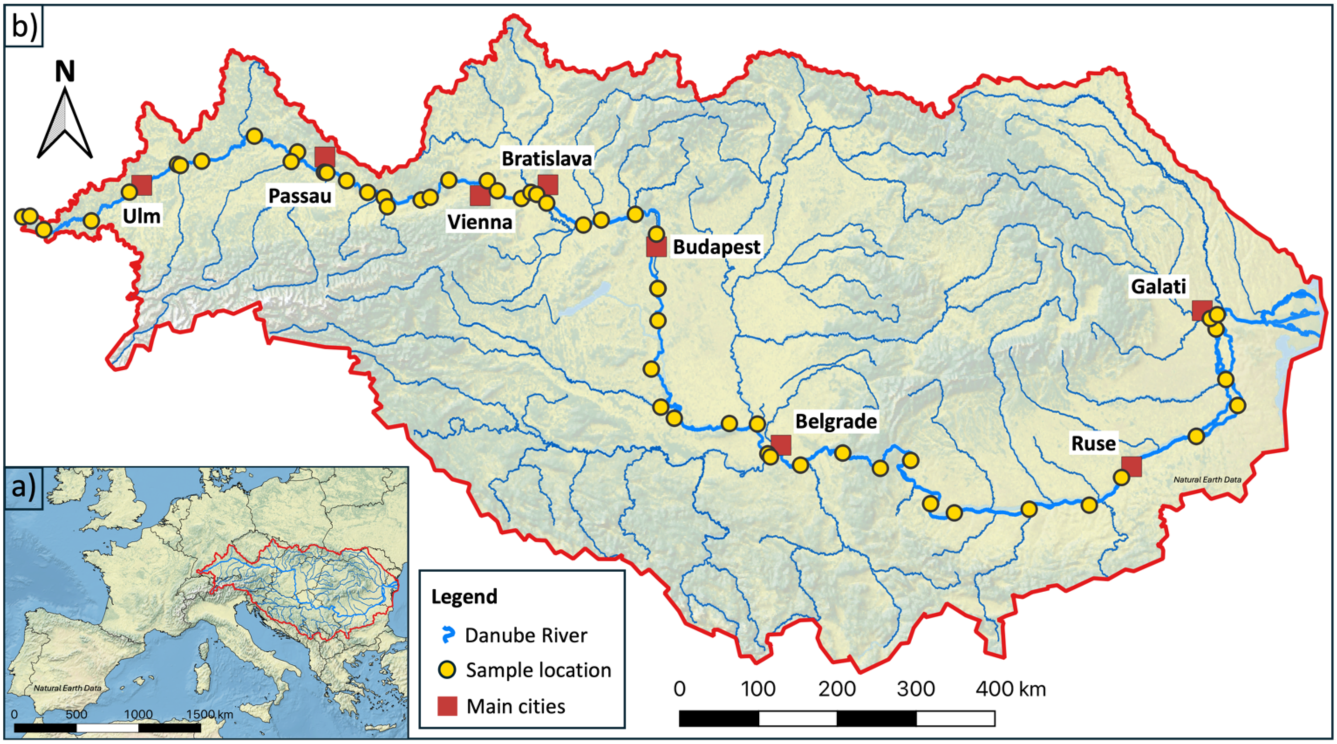

Figure 11: a) Overview map of Europe and b) detailed view of the Danube River Basin (red outline), including the Danube River (thick blue line) and its major tributaries (thin blue lines), data provided by the ICPDR (data source ICPDR, 2025, last access: 11 March 2025).Map of the Danube River Catchment and its most important tributaries. Danube River Basin District (red), as well as the Danube River and tributaries, data provided by the ICPDR (data source ICPDR, 2025, last access: 11. March 2025 ICPDR, 2025). Yellow dots represent the sampling locations of lLate summer 2024 sampling campaign;, red squares show main cities along the Danube. Sampled tributaries include the Brigach, Breg, Lech, Isar, Inn, Enns, March, Váh, Dráva, Tisa, Sava and Siret. The map was created using QGIS v 3.28.3 with raster data from © natural earth data (raster data (version 3.2.0, (last access: 11 December 2024): https://www.naturalearthdata.com/downloads/10m-raster-data/10m-cross-blend-hypso/) and shapefiles from geoBoundaries (shapefile data (last access: 11 December 2024): https://www.geoboundaries.org/globalDownloads.html).

2.2 Field methods

Samples were collected using a weighted narrow mouth 2--L polyethylene sampling bottle that was submerged between 1 and 2 meters below the water surface to obtain well-mixed water and to minimize influences of by rain and evaporation. Sampling took place either from the center (via bridges or passenger boats) or occasionally from the riverbank. In each case, well-mixed water samples were obtained from flowing section of the river. To ensure that the samples represented the entire river section, two cross-sectional profiles were sampled~~taken~~ during each sampling campaign and in all cases, they confirmed homogeneously mixed and representative water of each location. ~~mixing.~~

In situ measurements of temperature (T), DO, and oxygen saturation (DO %) were performed with a multiparameter instrument (HQ40d, HACH™, Loveland, CO, USA). This instrument was calibrated daily. Measurement standard deviations were ± 0.1 mg/L for DO, ± 0.42 % for DO %, and ± 0.07 °C for T.

For $\delta^{18}O_{DO}$ analyses, samples were filtered through 0.45 µm pore size nylon syringe filters (Sartorius™) into pre-poisoned 12-mL vials (Labco LTD. Lampeter Exetainer™). These vials contained 10 µL of a saturated $HgCl_2$ solution to inhibit microbial activity after sampling. Vials were filled completely and sealed with screw caps and butyl septa for efficient sealing ~~-off~~ against atmospheric influences. Triplicate samples were stored in the dark at 4 °C. To evaluate potential diel effects on DO, nighttime samples were collected in the main river channel at two sites during the campaign of late summer 2024 and reveal minor differences in DO concentration (< 0.01 mg/L) and $\delta 18O_{DO}$ (<1‰).

For water isotopes (expressed as $\delta^{18}O_{H2O}$), necessary for R/P calculations, water samples were collected in identical 12-mL exetainers however without poisoning by $HgCl_2$ ~~poisoning~~.

For the determination of POC, 500 mL of unfiltered water ~~samples~~ were collected in acid-washed high-density polyethylene Nalgene bottles. Before sampling, the bottles were thoroughly rinsed three times with sample water. Preparation for POC analysis involved filtering the collected water through pre-weighed glass fiber filters (GF-5, pore size 0.4 µm; Macherey-Nagel, Düren, Germany). To eliminate residual organic carbon, these filters were pre-heated at 400 °C for 4 h and stored under sterile conditions until sampling.

2.3 Laboratory methods

$\delta^{18}O_{DO}$ measurements were performed using a modified automated equilibration system (Gasbench II, ThermoFisher Scientific™) connected in continuous flow mode to a DELTA V Advantage isotope ratio mass spectrometer (IRMS, ThermoFisher Scientific™). The analytical approach was based on methods described by Barth et al. (2004) and Wassenaar and Koehler (1999). Briefly, a 3 mL pure helium headspace was established in the sample vial, and dissolved gases were extracted by shaking these sample vials on an orbital shaker at 250 rotations per minute for 30 minutes. The extracted O_2 in the headspace was separated from nitrogen (N_2) and other trace gases using a gas chromatography column (CP-Molsieve 5 Å, 25 m length, 0.53 mm outer diameter, 0.05 mm inner diameter; Agilent™, Santa Clara, CA, USA) before introduction into the isotope ratio mass spectrometer (IRMS) for analysis. Results are reported as averages of triplicate measurements, with an external reproducibility better than ± 0.2 ‰ (1σ).

Values of $\delta^{18}O_{H2O}$ were determined by infrared spectroscopy (IRIS) with a Picarro™ analyzer (L 1102-i WS-CRDS, Santa Clara, CA, USA). The analysis was conducted following the protocol outlined by van Geldern and Barth (2012).

All stable isotope values are reported in the standard δ-notation relative to the Vienna Standard Mean Ocean Water (VSMOW) and are calculated as:

$$\delta = (R_{sample} / R_{reference} - 1) \quad (1)$$

and then multiplied by 1000 to express them in per mille (‰). R represents the molar ratio of the heavy to light isotopes ($^{18}O/^{16}O$ for oxygen; $^{2}H/^{1}H$ and $^{18}O/^{16}O$ for H_2O) in the sample and the reference (Coplen, 2011). The ratio of VSMOW is 2005.20 ± 0.43 ppm (Baertschi, 1976). For $\delta^{18}O_{H2O}$, external reproducibility was better than ± 0.1 ‰ (1σ).

For POC determination, filters previously loaded with particulate material were freeze-dried for 60 minutes under vacuum conditions (<10 mbar) using a freeze-dryer (Lyovac GT 2 GT 2-E, FinnAqua, Gemini BV, Apeldoorn, Netherlands). The dried filters were then pulverized for 60 s using a ball mill (CryoMill, Retsch, Verder, Vleuten, Netherlands). To ensure complete removal of potential carbonate residues, the powdered filter material was fumigated with a concentrated HCl in a desiccator for 24 h. After fumigation, aliquots of the prepared filter material were ~~carefully~~ weighed into tin capsules (5×9 mm, IVA Analysentechnik GmbH & Co. KG, Meerbusch, Germany). ~~The~~ ~~c~~Carbon contents and $^{13}C/^{12}C$ isotope ratios of the samples was then determined with an elemental analyzer (Costech ECS 4010, NC Technologies, Bussero, Italy) coupled in helium continuous flow mode to an IRMS (Delta V plus, ThermoFisher, Bremen, Germany).

2.4 Isotope calculations

~~Evaluations~~ Ratios of respiration to photosynthesis (R/P~~) ratios~~ were determined according to Quay et al. (1995) with:

$$\frac{R}{P} = \frac{\left(\frac{18}{16}O_w * \alpha_p - \frac{18}{16}O_g\right)}{\left(\frac{18}{16}\mathrm{O} * \alpha_r - \frac{18}{16}O_g\right)} \quad (2)$$

where $\frac{18}{16}\mathrm{O_w}$ and $\frac{18}{16}\mathrm{O}$ represent the isotope ratios of oxygen in water and in DO, respectively. The photosynthesis fractionation factor (α_p) was assumed to be 1.000 ± 0.003 (Russ et al., 2004; Stevens et al., 1975) and the respiration fractionation factor (α_r) is commonly assumed with a value of 0.982 for community respiration (Quay et al., 1995).

The parameter $\frac{18}{16}O_g$, described in equation 3, accounts for the isotope ratio of net air-water fluxes and is calculated as:

$$\frac{18}{16}O_g = \frac{\alpha_g * \left(\frac{18}{16}O_a * \alpha_s - \frac{O_2}{O_{2s}} * \frac{18}{16}O\right)}{\left(1 - \frac{O_2}{O_{2s}}\right)} \quad (3)$$

With α_g being the fractionation factor for gas transfer velocities (0.9972 at 20 °C; Knox et al., 1992) and α_s the fractionation factor for oxygen dissolution in water (1.0007 at 28 °C) as calculated by Benson and Krause, (1984). The atmospheric oxygen isotopic ratio $\left(\frac{18}{16}O_a\right)$ is known with a value of + 23.9 ‰ (Dordoni et al., 2022). The $\frac{O_2}{O_{2s}}$ ratio represents the concentration of DO in the sample relative to the maximum temperature-dependent equilibrium concentration after Henry's law. Multiplying this ratio by 100 is equal to DO saturation (DO %) as measured in the field.

This model assumes isotopic steady-state conditions, constant α_r, and simplified gas exchange. Although it cannot resolve short-term variability such as diel cycles, these effects appear minor in the entire Danube mainstream and renders the model suitable for this broad-scale seasonal and spatial assessment.

2.5 Statistical analyses

All statistical analyses were conducted in R (v.4.3.2; R Core Team, 2023) using the lm() function to create the linear model and anova() for variance analysis. The coefficient of determination (R^2) was reported to evaluate the proportion of variance in $\delta^{18}O_{DO}$ explained by DO concentration (Figure 6a, b) and POC concentration (Figure 6c, d). To assess the effect of DO/POC concentration on $\delta^{18}O_{DO}$, we performed a one-way analysis of variance (ANOVA; Fisher, 1932) based on the following linear model:

$$\delta^{18}O_{DO} = \beta_0 + \beta_1 DO/POC + \varepsilon \quad (4)$$

where β_0 is the intercept, β_1 the regression coefficient, and ε the error term. ANOVA was used to determine whether DO/POC concentration explains a significant proportion of the variance in $\delta^{18}O_{DO}$. The p-value from the F-test was used to assess statistical significance with a commonly accepted threshold value α of 0.05.

3. Results

To investigate seasonal variations in DO, $\delta^{18}O_{DO}$ and POC concentrations, data were analyzed along the Danube River for the five different sampling campaigns in spring, summer, late summer, fall and winter. DO concentrations showed clear seasonal fluctuations and variations, that ranged ranging from 0.16 mmol/L to 0.40 mmol/L (5.1 and 12.8 mg/L) (Figure 2a-d). The highest mean DO concentrations occurred during winter (0.36 mmol/L ± 0.01), while the lowest mean occurred in late summer (0.25 mmol/L ± 0.03). Spatial variability was most pronounced in summer 2023, late summer 2024 and spring 2024 (Figure 2a, d). In contrast, concentrations during fall 2023 and winter 2024 showed little variation over the entire course of the river and ranged from ca. 0.30 to 0.35 mmol/L (Figure 2b, c). As indicated by the red arrows in Figure 2a, two distinctthree DO maxima occurred during summer with two being the most pronounced: the first in the mid Danube (~1220 km; 0.35 mmol/L) and the second in the lower Danube (~440 km; 0.40 mmol/L). Similar but less pronounced patterns were also observed in spring and late summer. However, in these seasons, here the downstream maximum did not exceed the upstream one and blue arrows mark the DO minima.

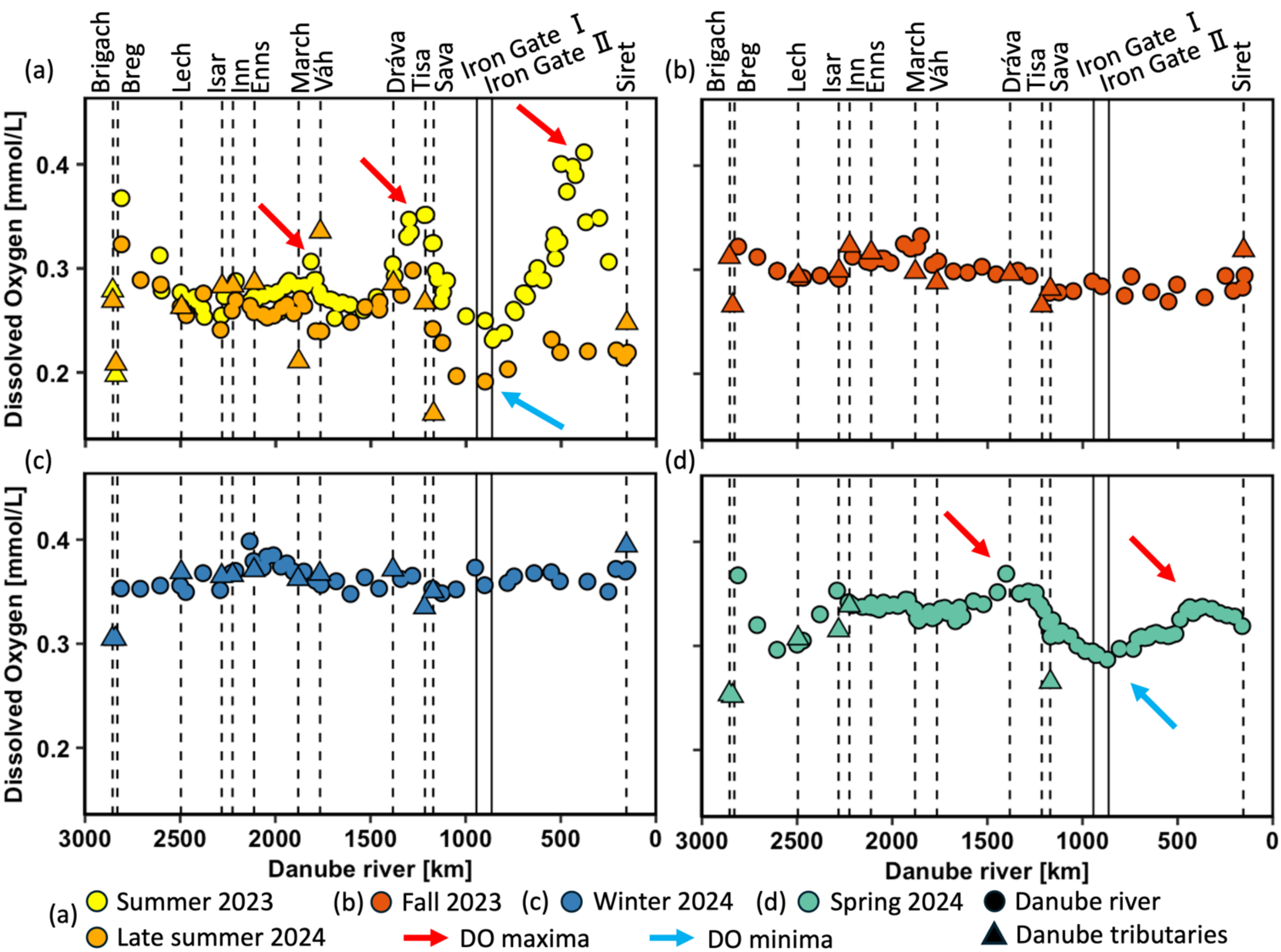

Figure 2: Dissolved oxygen (DO) concentrations (mmol/L) in the Danube River at various distances from the river mouth. Standard error bars are within the symbol size. Circles represent Danube River samples, ~~T~~triangles denote tributary samples, and dotted lines indicate the river km where tributaries enter. Vertical solid lines represent the Iron Gate I and II dams. The red arrows show DO maxima and blue arrows DO minima.

Stable isotope values measured for DO ($\delta^{18}O_{DO}$) ranged from +25.9 ‰ to +12.1 ‰ in the entire dataset (Figure 3a-d). Here, the equilibrium with atmospheric oxygen (+24.6 ‰ ± 0.4 ‰) serves as the boundary value between photosynthesis and respiration (Dordoni et al., 2022). Values below this threshold refer to photosynthesis, while values above it refer to respiration. Consequently, samples from summer 2023, late summer 2024, and spring 2024 predominantly showed photosynthesis-driven signals with $\delta^{18}O_{DO}$ values lower than +24.6 ‰ (Figure 3a, d). Conversely, samples from fall 2023 and winter 2024 often fell into the respiration range, even though they were close to the equilibrium (Figure 3b, c). Variability in $\delta^{18}O_{DO}$ was highest during summer (+19.4 ± 3.2 ‰), late summer (+22.4 ± 2.3 ‰) and spring (+21.9 ± 1.4 ‰). On the other hand, fall and winter exhibited lower variabilities with +24.3 ± 1.1 ‰ and +24.7 ± 0.4 ‰. As shown by the red arrows in Figure 3a, four~~two~~ minima in $\delta^{18}O_{DO}$ were observed during summer: one near the source region and three others at the same locations as the ~~where~~ DO maxima. Among these, the two most pronounced occurred in the mid Danube ~~with~~ (+14.8 ‰) and the lower Danube (+12.1 ‰). ~~Spring and late summer showed similar patterns with two $\delta^{18}O_{DO}$ minima, but the downstream minima were smaller than the upstream.~~ In late summer, two $\delta^{18}O_{DO}$ minima occurred, with the upstream minimum being more pronounced than the downstream one. In spring, three smaller minima of $\delta^{18}O_{DO}$ appeared across the upper, middle and lower Danube.

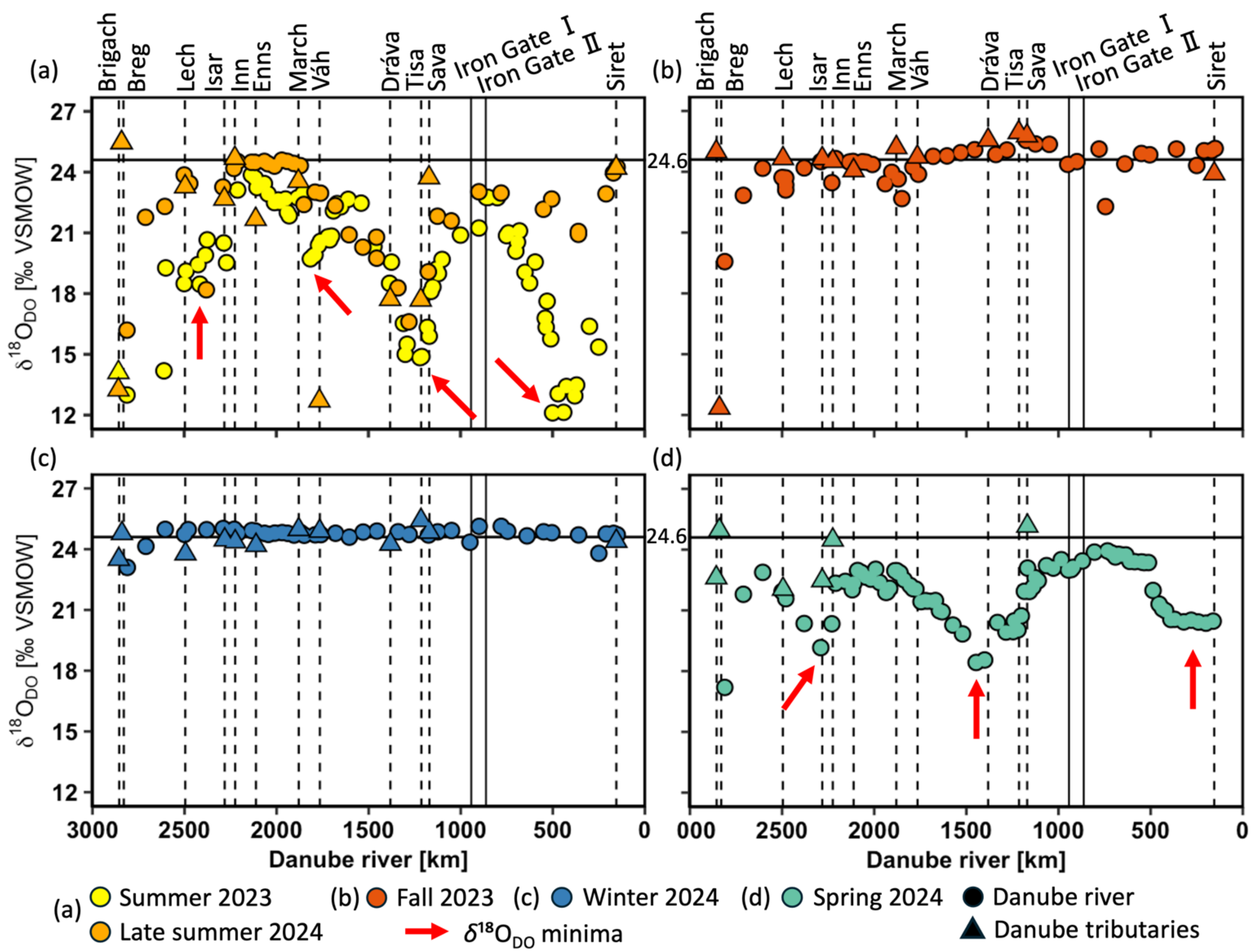

Figure 3: Stable isotopes of dissolved oxygen ($\delta^{18}O_{DO}$) in the Danube River at various distances from the river mouth: Standard error bars are within the symbol size. Circles represent Danube River samples, ~~T~~triangles denote tributary samples, and dotted lines indicate the river km where tributaries enter. Vertical solid lines represent the Iron Gate I and II dams, and the horizontal solid line at +24.6 ‰ is the equilibrium for atmospheric oxygen. Values >+24.6 ‰ indicate respiration and <+24.6 ‰ photosynthesis. The red arrows show $\delta^{18}O_{DO}$ minima.

POC concentrations ranged from 0.01 to 0.26 mmol/L (0.1 to 3.1 mg/L) (Figure 4a-d) with pronounced seasonal fluctuations. Maxima in POC occurred ~~These values largely followed the same trends as DO concentrations and $\delta^{18}O_{DO}$ values~~

~~with considerable fluctuations~~ in summer 2023, late summer 2024 and spring 2024, aligning well with elevated DO concentrations and inversely related $\delta^{18}O_{DO}$ minima. In contrast, POC levels in fall 2023 and winter 2024 were less variable and mostly remained below 0.10 mmol/L. As highlighted by the red arrows in Figure 4a, three~~wo~~ maxima in POC concentrations were also observed during summer, with two being the most pronounced: the first one in the mid Danube (~1210 km; 0.25 mmol/L) and the second in the lower Danube (~500 km; 0.24 mmol/L). Samples from late summer showed a scattered pattern, with slightly elevated values in the upper Danube, ~~a similar trend, with~~ a weaker increase~~maximum~~ in the mid Danube and generally lower values downstream~~Danube~~. Spring samples ~~also~~ showed two peaks in the middle and lower Danube, where the downstream peak was ~~also~~ smaller than the upstream one.

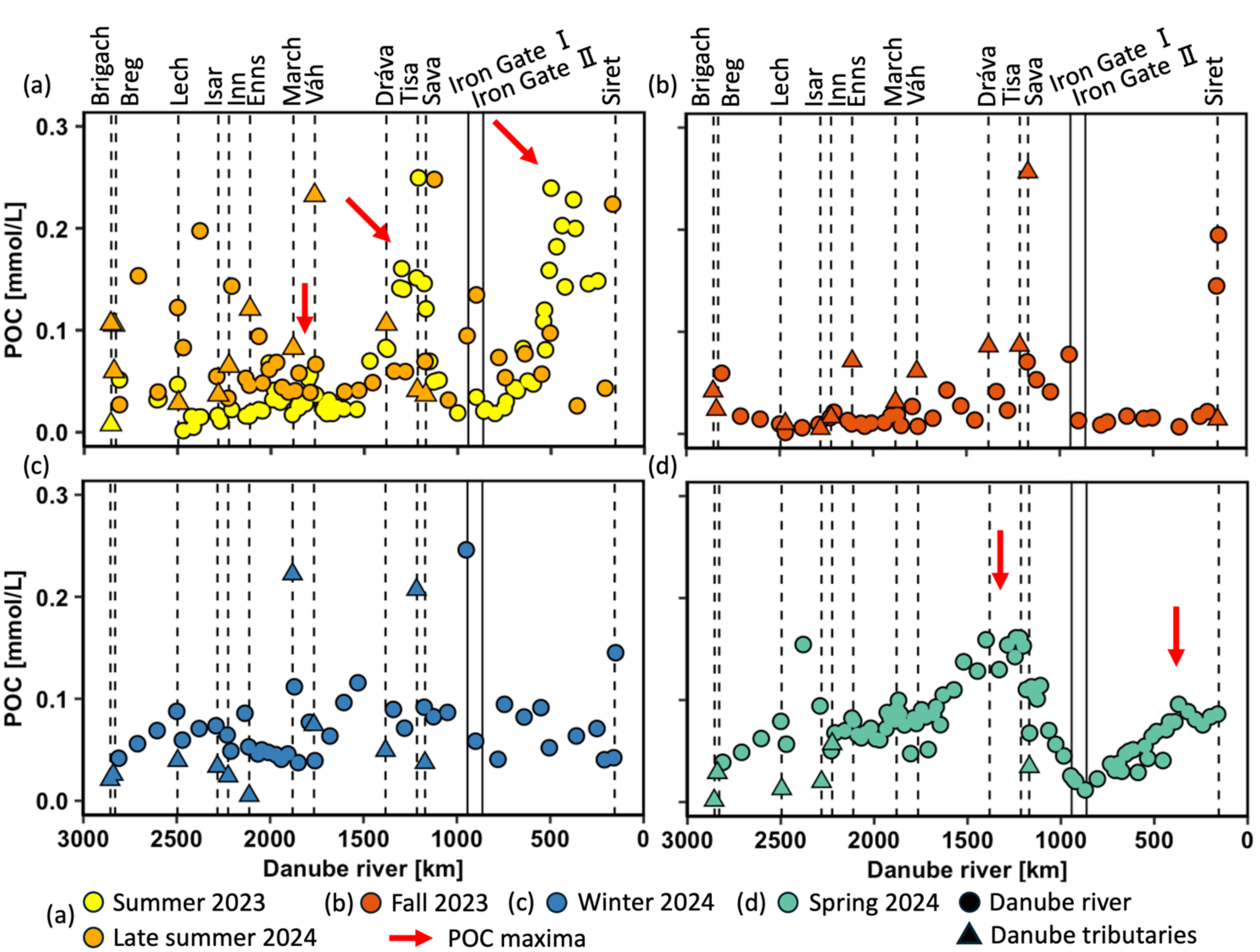

Figure 4: Particular organic carbon (POC) concentrations (mmol/L) in the Danube River at various distances from the river mouth. Standard error bars are within the symbol size. Circles represent Danube River samples, ~~T~~triangles denote tributary samples, and dotted lines indicate the river km where tributaries enter. Vertical solid lines represent the Iron Gate I and II dams. The red arrows indicate POC maxima.

R/P ratios were not plotted here over the entire range of the river but showed similar trends as shown for DO, $\delta^{18}O_{DO}$ and POC (Figure S1). However, a cross plot between $\delta^{18}O_{DO}$ and R/P ratio showed a non-linear relationship of both parameters (Figure 5). R/P ratios ranged from 0.1 in summer to 8.9 in fall. Spring and summer samples were more dominated by photosynthesis, with R/P ratios smaller than 1, while winter and fall samples were more dominated by respiration, with R/P ratios larger than 1. Late summer samples exhibited a mixed signal, with most values in a range of overlapping photosynthesis and respiration and R/P values mostly larger than 1.

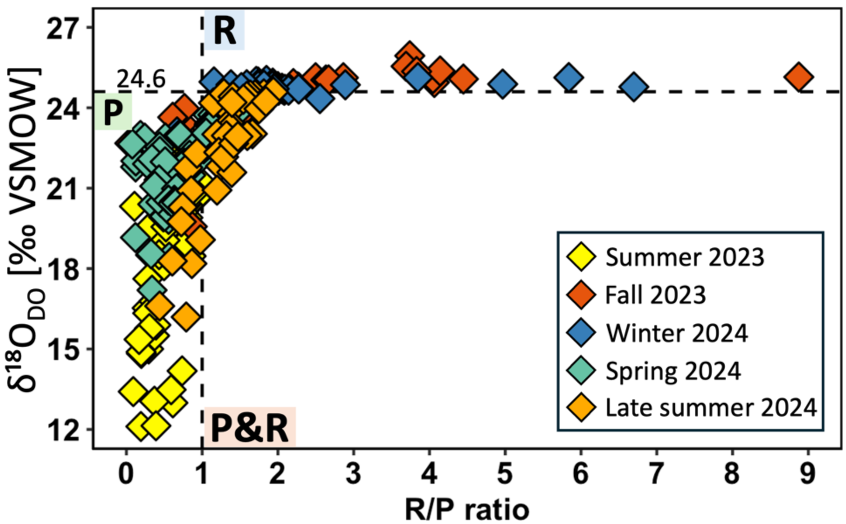

Figure 5: Cross plots of $\delta^{18}O_{DO}$ versus~~.~~ respiration/photosynthesis (R/P) ratios of the Danube River~~. sampling locations.~~ The horizontal dotted line at +24.6 ‰ marks the equilibrium for atmospheric oxygen. Values with >+24.6 ‰ indicate respiration and <+24.6 ‰ photosynthesis. The vertical dotted line at R/P = 1 denotes the transition between photosynthesis and respiration. R/P values <1 indicate dominance by photosynthesis, and R/P >1 dominance by respiration.

Correlation plots between $\delta^{18}O_{DO}$ and DO concentrations are shown~~were created~~ for spring and summer (Figure 6a), and for late summer, fall and winter (Figure 6b). Here the strongest and statistically significant correlations were observed in spring ($R^2 = 0.52$, $p < 0.05$) and summer ($R^2 = 0.75$, $p < 0.05$)~~ which were both statistically significant~~. In spring, higher DO coincided with lower $\delta^{18}O_{DO}$, while in summer, this relationship was even stronger. In contrast, correlations weakened in late summer ($R^2 = 0.14$, $p < 0.05$) and fall ($R^2 = 0.33$, $p < 0.05$), even though they were still statistically significant. This suggests that while $\delta^{18}O_{DO}$ and DO are still related, other factors such as respiration, chemical processes or elevated groundwater input likely contributed to $\delta^{18}O_{DO}$ variability. In winter ($R^2 = 0.04$, $p > 0.05$), no significant correlation was observed between both parameters.

To further investigate potential biological influences on $\delta^{18}O_{DO}$, it was correlated with POC concentrations at selected areas of high DO contents (ca. 1600 to 200 km) that were found during spring and summer (Figure 6c) and for late summer, fall, and winter (Figure 6d). The strongest and statistically significant correlations were observed in spring ($R^2 = 0.60$, $p < 0.05$) and summer ($R^2 = 0.88$, $p < 0.05$)~~ which were both statistically significant~~. In spring, this correlation was moderately strong, and increasing POC concentrations coincided with decreasing $\delta^{18}O_{DO}$ values. However, no direct biological influence on

$\delta^{18}O_{DO}$ values could be identified in late summer ($R^2 = 0.16$), fall ($R^2 = 0.06$), and winter ($R^2 = 0.13$), as reflected by weak, non-significant correlations ($p > 0.05$). ~~These results suggest that POC does not exert a clear influence on $\delta^{18}O_{DO}$ during these three seasons, although other environmental or biological factors may contribute.~~

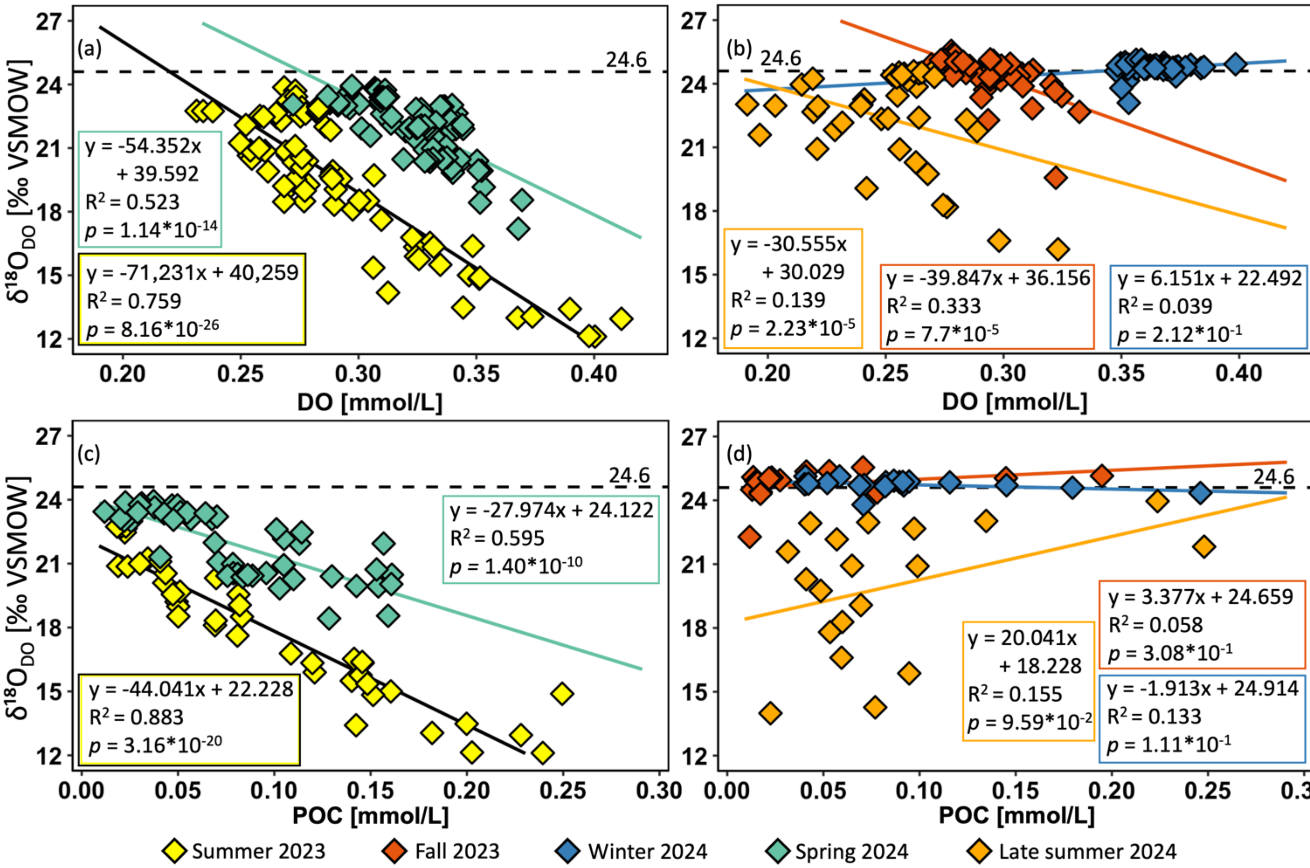

Figure 6: Correlation plots for all Danube sampling locations of $\delta^{18}O_{DO}$ and dissolved oxygen (DO) in summer and spring (a), in late summer, fall, and winter (b). High productivity areas (~1600 to ~200 km) related correlation plots of $\delta^{18}O_{DO}$ and particulate organic carbon (POC) for the same periods are presented to highlight potential biological inputs (c, d). The negative correlation indicates that as POC increases as $\delta^{18}O_{DO}$ values decrease. This pattern is consistent with biological oxygen production (<+24.6 ‰) and consumption (>+24.6 ‰), as oxygen produced by algal activity is usually ~~isotopically lighter~~enriched in ^{16}O when compared to ~~than that of~~ the atmosphere. These results support the role of algae-derived organic matter in influencing the $\delta^{18}O$ signature of dissolved oxygen.

4. Discussion

4.1 Seasonal Dynamics

Seasonal variations in DO and $\delta^{18}O_{DO}$ along the Danube River are primarily influenced by temperature, biological activity, and atmospheric exchange. During winter, colder water temperatures decreased to 6.5 °C and thereby enhanced~~ing~~ O_2 solubility (Figure S2c) (Rettich et al., 2000). Additionally, higher river discharge and associated turbulence likely accelerated atmospheric oxygen exchange ~~further increased O_2 solubility~~ and ~~led~~ contribute to the highest DO concentrations measured throughout the year (Figure 2c; Figure S3, S4c) (Vautier et al., 2020). The associated $\delta^{18}O_{DO}$ data support this interpretation because ~~of an atmospheric oxygen source as~~ values remained consistently close to those expected for atmospheric equilibrium (±24.6 ‰ ± 0.4 ‰) (Figure 3c; Figure S5). Although respiration must have occurred as well, its overall impact on the DO budget was likely minimal and largely masked by continuous atmospheric equilibration (Figure 3c, 6b). At first glance, associated R/P ratios might contradict this interpretation with values larger than 1 (Figure 5, Figure S1c). However, according to Dordoni et al. (2022), true dominance of respiration only becomes evident when R/P ratios exceed 2. Therefore, winter conditions reflect a mixed signal, with minor respiration influences and dominant atmospheric exchange.

With rising temperatures and longer daylight in spring, biological activity became more prominent and led to moderate to high DO concentrations (Figure 2d; Figure S2d, S3) (Wetzel, 2011). The associated $\delta^{18}O_{DO}$ values indicated enhanced photosynthetic activity, as they gradually shifted from atmospheric equilibrium toward less positive values (Figure 3d; Figure S5). Such a photosynthesis increase was further confirmed by slight rises in POC concentrations when compared to winter. While some of this POC may have originated from external sources, such as soil material washed into the river (Aramaki et al., 2010; Reddy et al., 2021), the concurrent buildup of POC, DO, and $\delta^{18}O_{DO}$ suggests an accumulation of algae biomass driven by in-river photosynthetic activity (Figures 2d, 3d, 4d). ~~Direct influences of photosynthesis on DO dynamics were further supported by a~~A moderate but statistically significant correlation between DO concentration and their $\delta^{18}O_{DO}$ values ($R^2 = 0.52$, $p < 0.05$) further supported direct influences of photosynthesis on DO, thus highlighting the link between oxygen production and its photosynthetic source. Although photosynthesis predominantly influenced DO in spring, atmospheric exchange likely remained a significant contributor. This process was likely supported by cool temperatures that remained below 18 °C and elevated discharge rates that also increased turbulent flow (Figures S2d, S3d). Moreover, the interplay between biological and physical processes was also reflected by R/P ratios (Figure 5, Figure S1d). Most of these ratios remained below 1 and indicated shifts towards photosynthesis. However, occasional mixed signals, with R/P ratios around and larger than 1, suggest that both atmospheric exchange and respiration processes also influenced the river's DO budget.

The intensification of biological activity in summer was most evident by $\delta^{18}O_{DO}$ values that decreased to +12.1 ‰ (Figure 3a; Figure S5). This distinct shift marks the time of peak photosynthetic activity in the Danube and is particularly notable because such pronounced deviations from atmospheric equilibrium are typically observed in standing waters (e.g., Quay et al., 1995; Wassenaar, 2012)~~. However, similar deviations caused by photosynthesis have also been recorded in smaller streams~~or smaller streams (e.g., Parker et al., 2010; Wassenaar et al., 2010), but rarely in larger river systems (Quay et al., 1995) ~~observed in standing waters (e.g., Quay et al., 1995; Wassenaar, 2012). However, similar deviations caused by photosynthesis have also been recorded in smaller streams (e.g., Parker et al., 2010; Wassenaar et al., 2010)~~and support our finding that rivers~~even running waters~~ are capable of strong photosynthetic DO input. The strong photosynthetic signal was further reflected in the increases of POC concentrations, that indicat~~ing~~e an accumulation of organic matter. Overall, the simultaneous increases of POC and DO, along with parallel decreases in $\delta^{18}O_{DO}$ and characteristic fluctuations in R/P ratios that also consistently fell below 1 in summer, ~~clearly~~ underscore intensified photosynthetic activity (Figures 2a, 3a, 4a, 5;

Figure S1a). The strong linear correlation and statistical significance between $\delta^{18}O_{DO}$ and DO further confirm this relationship ($R^2 = 0.76$, $p < 0.05$; Figure 6a). These indicators reflect the preferential input of ^{16}O via photosynthetic water splitting, a process that proceeds without isotopic fractionation (Mader et al., 2017). Interestingly, despite such strong biological DO inputs, DO concentrations were often lower in summer when compared to winter and spring (Figure S3). These declines in DO concentrations can be attributed to higher water temperatures (Figure S2), which reduce O_2 solubility (Rettich et al., 2000). Another factor that may have reduced DO could have been the simultaneous decomposition of POC by respiration. If so, and Wwhile this process likely contributed to DO depletion, its impact on POC levels must have been minor.was minimal. In fact, POC input appeared to outperform its consumption, as indicated by rising concentrations (Figure 4a). However, it is possible that short term fluctuations in POC were not fully captured by the sampling frequency and implies that elevated POC levels do not necessarily contradict intensified decomposition activity under warmer conditions. Although DO levels were higher in winter, photosynthetic DO production likely played an important ecological role during warmer periods when atmospheric O_2 exchangecontributions were was less effective. However, such photosynthetic DO increases may also associate with declines during nighttime due to ongoing respiration. In riparian zones and in headwaters as this process may have been more important than in the main river, where our limited night measurements indicated only minor diel variations. Notably, recent research has shown that $\delta^{18}O_{DO}$ responds more sensitively to metabolic shifts than DO concentrations, as it can detect transitions between photosynthesis and respiration before they become evident in net DO concentrations (Dordoni et al., 2024). Such observations justify the additional application of stable isotopes.

Late summer samples differed from those of mid-summer, despite similar water temperatures (Figure S2a). During this later period, DO concentrations reached their lowest levels, particularly in the Sava River, where oxygen levels decreased to 0.16 mmol/L (see blue arrow in Figure 2a). After its confluence with the Danube, DO levels showed a slight recovery but remained depleted toat around 0.20 mmol/L (see blue arrow in Figure 2a). Given that healthy aquatic systems should maintain DO levels above 0.156 mmol/L (WHO, Atlas Scientific), these late summer values raise concerns about critical oxygen depletion. This concern is further supported by a shift in R/P ratios from a photosynthesis-dominated signal (R/P<1) to a mixed signal (R/P>1) (Figure 5; Figure S1a), thus indicating that respiration rates had begun to exceed those of photosynthesis. In parallel, DO saturations increasingly fell below 100%, thus suggesting net oxygen production and further supporting the interpretation of enhanced respiration. Additionally, compared to mid-summer, the weakening correlation between DO and $\delta^{18}O_{DO}$ ($R^2 = 0.14$) suggests a reduced influence ofby photosynthesis and a relatively greater contribution of respiration or atmospheric exchange, both of which can introduce more variable isotopic signatures and alter the relationship (Figure 6b). A combination of declining primary production, enhanced respiration, and potential organic matter decomposition likely contributed to the observed decrease in DO concentrations. With rising temperatures due to climate change, further DO declines can be expected, particularly during periods of reduced photosynthetic activity, such as late summer. This trend may also apply to other temperate large river systems, when late summer and early fall become the most critical periods for DO depletion (Piatka et al., 2021; Zhi et al., 2023). Although water quality in the Danube has improved over the last three decades,

~~these findings highlight the need for continuous oxygen monitoring, especially in the Sava and Lower Danube regions (Mănoiu and Crăciun, 2021).~~

In fall, declining water temperatures increased O_2 solubility and led to a moderate rise in DO concentrations when~~as~~ compared to late summer (Figure 2b; Figure S2b) (Rettich et al., 2000). These temperature decreases also contributed to a more homogeneous DO distribution along the entire river system, which showed a large-scale seasonal effect that contrasted with the localized areas of high DO production in summer. This seems plausible because such temperature shifts by changing seasons are able to affect an entire river system. As a result, $\delta^{18}O_{DO}$ values shifted towards more positive values and approached those of atmospheric exchange (Figure 3b; Figure S5). ~~Additionally~~On the other hand, reduced light intensity and a decline in photosynthetic activity during fall also affected the entire river system (Aruga, 1965; Collins and Boylen, 1982). With the decline in photosynthesis, respiration became the dominant process, as also reflected by R/P ratios that were mostly above 2, especially in the lower section of the Danube (Figure 5; Figure S1b). This transition from a photosynthesis to a respiration-dominated river~~system~~ was likely further enhanced~~can be attributed to the~~ by accumulation of organic material over the summer, which provided fresh biomass for decomposition by~~through~~ respiration in fall. (DeNicola, 1996; Uehlinger et al., 2000). Although in fall increased respiration was evident in the R/P ratios, $\delta^{18}O_{DO}$ levels ~~values themselves~~ remained close to atmospheric equilibrium (Figure 3b; Figure S5). This pattern suggests that during this time the Danube system is buffered by atmospheric O_2 exchange ~~and~~ which serves as a crucial DO source~~ that~~ prevent~~s~~ing DO depletion despite the dominance of respiration.

Overall, seasonal fluctuations in DO and $\delta^{18}O_{DO}$ along the Danube River were primarily influenced by temperature, associated atmospheric exchange and biological activity. In spring and summer, photosynthesis was an important process that increased DO and lowered $\delta^{18}O_{DO}$, while in late summer, enhanced respiration became more important predominant and caused lower DO levels and higher $\delta^{18}O_{DO}$, particularly evident in the Sava tributary. With cooler temperatures in fall, DO levels recovered, although respiration remained an important driver. In winter, oxygen solubility was the dominant control, with minimal biological influence.

4.2 Areas of increased primary production

~~In addition to~~Beyond the seasonal dynamics~~ observed throughout the year~~, our data revealed three~~wo distinct~~ areas of increased DO production~~., emerged~~ They occurred during the warm season~~.~~, with one area~~One~~ located in the middle and the other in the~~the second in the~~ lower section of the river. These areas were characterized by elevated~~exhibited pronounced increases in all three parameters:~~ DO~~, $\delta^{18}O_{DO}$~~ and POC concentrations, while $\delta^{18}O_{DO}$ showed corresponding decreases (Figures 2a, d; 3a, d; 4a, d; Figure S6a-c). ~~Here, the pronounced shifts in $\delta^{18}O_{DO}$ values down to +12.1 ‰ are most remarkable, because such large deviations from atmospheric equilibrium are typically observed in standing waters (Quay et al., 1995; Wassenaar, 2012) or smaller streams (Parker et al., 2010; Wassenaar et al., 2010), but rarely in larger river systems (Quay et al., 1995).~~ ~~These~~Especially the pronounced decline in $\delta^{18}O_{DO}$~~shifts clearly~~ indicated enhanced photosynthesis, which has already been identified as the primary driver of oxygen production during the warmer months (Figure 6a, b). The strong photosynthetic impact is further supported by clear correlations between $\delta^{18}O_{DO}$ values and POC concentrations (Figure 6c). This relationship indicates the importancedominance of autotrophic organisms as key DO sources in these highly productive river sections during spring and summer and is supported by previous studies on the Danube, which also emphasized the importance of autotrophic activity (Hein et al., 1999; Riedler P. and Schagerl M., 1998).

As the warm season progressed, the correlation between $\delta^{18}O_{DO}$ and POC strengthened, thus reflecting the increasing role of autotrophic production, with a moderate correlation in spring ($R^2 = 0.60$) that became even stronger in summer ($R^2 = 0.88$). These positive correlations indicate that a substantial portion of the organic material must have originated from primary producers and directly contributed to the formation of these maxima. This pattern aligns well with the composition of the Danube´s phytoplankton community, which is primarily composed of diatoms, alongside notable co-occurrence of Cyanobacteria, Chlorophyta and Cryptophyta. In particular, the downstream shift from benthic to planktonic diatoms, observed by (Liška et al., (2021), likely supported enhanced primary production in the middle and lower Danube and supports the isotope signals. Although the same areas of elevated productivity did not change in late summer (Figure 2a, 3a, 4a), the previously strong no significant correlation disappearedcould be observed during this period (Figure 6d). This lack of correlation may result from the gradual depletion stabilization of high DO and POC values during this transition period, thereby suggesting a weakening of autotrophic activity. At the same time, or the increasing influence of allochthonousexternal POC sources (i.e., , such as material transported into the river) may have further decoupled the relationship between $\delta^{18}O_{DO}$ and POC. Despite the continued occasionally elevated DO levels, this seasonal shift likely reflects a decline in primary production as environmental conditions changed and led to reduced relative contributions of autotrophic materialprimary producers to the overall organic mattererial pool decreased.

The link between primary producers and DO dynamics observed in this study is further supported by previous research on the Danube. For instance, phytoplankton data from Literáthy et al. (2002) showed that the highest biomass occuredoccurred in the middle section of the river, thus aligning with the area identified inby our study and supportsindicating the connection between increased primary production and DO-rich zones. Furthermore, Dokulil, (2015) highlighted findings from several chlorophyll-α studies in the Danube that indicated peak algae growth during summer with significant temporal variations in both the intensity and timing of algae blooms across several years (e.g., 1988, 1998 and 2001). The agreement between these findings and our data suggests that algal blooms occur regularly in this section of the Danube, thus contributing to and reinforcing seasonal variations.

One key factor that influences these areas of increased productivity is the decreasing changing flow gradient of the Danube (Figure S6d). According to Habersack et al. (2016), the riverbed slope decreases in its middle section from a steeper gradient of about 0.4 % in the upper Danube to a much flatter gradient of about 0.1 %. The observed decrease in slope already begins in the region of the first lower productivity area and becomes increasingly pronounced towards the second and third high productivity area in the middle and lower Danube. This reduction in slope decreases the velocity of the river and creates flow conditions that favor primary producers. In addition,The resulting slower water flow velocities enhances the sedimentation, which in turn decreases turbidity and light penetration and further supports photosynthetic activity. These conditions also align with findings of Dokulil (2006, 2015), who identified the middle reach of the Danube as an optimal zone for primary production due to moderate flow velocities and increased light availability. Moreover, the Danube had low to ~~exhibited only~~ moderate discharge levels during summer that could further intensify these effects (Figure S4a). While not at its lowest, this discharge still enables longer water residence times that increase light exposure for algae and create favorable growth conditions (Kamjunke et al., 2021; Weitere and Arndt, 2002).

Another factor that may have contributed to the observed productivity patterns is the proximity of Budapest (Figure S6a-d). Located upstream of the productivity maximum in the mid ~~-~~Danube, it could influence primary production through nutrient inputs. Urban areas such as Budapest are known sources of nutrient pollution due to wastewater discharge (Nyenje et al., 2010; Xia et al., 2016), while agricultural activities further contribute to nutrient loading. However, our analyses ~~did not~~ were unable to reveal ~~clear~~ links between nutrient concentrations, POC, DO levels or $\delta^{18}O_{DO}$ values. For instance, nitrate concentrations ranged around a mean value of 0.10 mmol/L ± 0.0025 (standard error) throughout the year and along the entire river (Figure S7a-d), while phosphate levels remained consistently below the detection limit. These results align well with previous findings published by Liška et al. (2021), who reported ~~almost~~ stable nitrate concentrations in the Danube over the past decades without noticeable peaks from potential point sources. One possible explanation is that primary producers rapidly absorb and utilize available nutrients and prevent their accumulation in measurable concentrations (Joint et al., 2001; Wetzel, 2011). This mechanism could explain the observed productivity patterns, despite minimal variance in nutrient levels and may particularly account for undetectable phosphate concentrations, because this nutrient ~~at~~ is rapidly taken up by primary producers. ~~However, t~~ To further investigate this possibility, more detailed studies on aquatic biomass and nutrient uptake processes would be required.

Following the upstream productivity maximum near Budapest, DO concentrations declined abruptly, together with decreases in POC and increases in $\delta^{18}O_{DO}$ values (Figures 2a, d; 3a, d; 4a, d). Previous studies have also documented reductions in phytoplankton biomass and chlorophyll-α concentrations in this region (Dokulil, 2006, 2015; Dokulil and Kaiblinger, 2008; Literáthy et al., 2002). These patterns suggest that external factors, particularly the inflows of the Tisa and Sava rivers, play a role. Both tributaries introduce large volumes of water and contribute substantial dilution to the main course of the Danube. Although the Tisa and Sava rivers could not be sampled during all campaigns, data from late-summer and spring indicate that they contain lower DO concentrations (~~blue arrow~~ Figure 2a, d), higher $\delta^{18}O_{DO}$ values, and reduced POC levels compared to the main stem of the Danube (Figure 3a, d; 4a, d). This observation supports dilution as a plausible mechanism for the observed decrease. Further evidence arises from previous studies, which estimated that this confluence with the Danube becomes ~~is being~~ diluted by approximately 27 % during average discharge conditions (Dokulil, 2015). Discharge data from summer and spring confirm this effect and ~~,~~ show~~ing~~ a substantial increase in total river discharge following the confluence with these tributaries (Figure S4a, d). Additionally, the inflow of the Morava River (not analyzed in this study) likely added further dilution effects (Dokulil, 2015). Moreover, a similar dilution effect likely occurred between the smaller upstream increase and the mid Danube productivity maximum. In this case it was influenced by the March and Váh Rivers. Although not sampled during summer, both tributaries contribute substantial discharge and likely carry water with lower DO and POC and higher $\delta^{18}O_{DO}$, thereby contributing to the observed decline.

Beyond these hydrological factors, land use including agriculture and urbanization across the basin may act as key drivers on DO dynamics. Although nitrate levels remain relatively low, and indicate no critical eutrophication risk, these inputs still support the observed productivity maxima. To better trace and understand sources and transformation of land use and associated nutrient influences on DO dynamics, further investigations with detailed GIS mapping and other tracers such as nitrogen isotopes may be necessary.

Further downstream, the Danube featured a second and even more intense productivity zone with similar patterns to the upstream peak area. While this area shows increased chlorophyll-α and suspended solids (Dokulil, 2015; Dokulil and Kaiblinger, 2008), phytoplankton biomass does not rise accordingly (Literáthy et al., 2002), thus suggesting an unconventional productivity pattern. On the other hand, a pronounced decrease in $\delta^{18}O_{DO}$ indicated active photosynthesis despite potential phytoplankton growth limitations (Wetzel, 2011). Notably, this region exhibited the lowest $\delta^{18}O_{DO}$ values in the study, along with R/P ratios close to 0 in summer, thus underscoring the significance of photosynthetic activity (Figure 5; Figure S1a). These findings align with those of Dokulil (2006, 2015), who reported that despite significant increases in chlorophyll-α, primary production remained low due to poor light availability in the water column that in turn have been caused by elevated turbidity. Similar to the upstream peak, the emergence of this second productivity zone coincided with a decrease of the ~~flattening~~ river gradient (0.05 – 0.01 %) that likely fosters favorable hydrodynamic conditions for algae (Habersack et al., 2016).

The spatial patterns observed also coincide with the above-discussed seasonality. They enhance spatial DO dynamics and play a crucial role, as the second most productive area is clearly visible in summer, but weakens and~~or~~ even disappears by late summer (Figure 2a, 3a). Initially, the peak was driven by primary production, but as the season progressed, it declined rapidly. This decrease was also reflected by the absence of a pronounced $\delta^{18}O_{DO}$ peak and a shift in R/P ratios toward respiration in late summer (Figure 5b; Figure S1a) and highlights growing influences of heterotrophic processes, particularly in the lower section of the river. Additionally, the decreasing correlation between $\delta^{18}O_{DO}$ and POC concentration in late summer suggests a shift towards~~in dominant~~ respiration ~~processes~~ (Figure 6d). While~~ such~~ a strong correlation in summer indicated active primary production, this link weakened as phytoplankton started to decompose, thus leading to organic matter accumulation and increased microbial respiration. This transition further supports the interpretation~~dea~~ that the second peak ~~i~~was initially fueled by photosynthesis during slow flow but shifted~~s~~ toward organic matter degradation as the season progressed.~~later in the season.~~ Therefore, areas with shallow gradients not only promote algal growth but also facilitate biomass accumulation and subsequent respiration, making them key zones of enhanced biogeochemical activity in the river.

~~This study identified two areas of high productivity in the Danube, as marked by elevated DO concentrations, $\delta^{18}O_{DO}$ stable isotopes and POC levels. These maxima occurred in regions with reduced slopes, where slower flow velocities and lower turbulence likely promoted increased autotrophic activity. In these sections of the river, primary producers emerged as key drivers of DO input, with a strong correlation between $\delta^{18}O_{DO}$ and POC concentrations in spring and summer. Notably,~~

~~$\delta^{18}O_{DO}$ values reached as low as +12.1 ‰, a deviation from atmospheric equilibrium rarely observed in larger river systems.~~ Connecting these findings with previous research underscores the critical role of primary producers in shaping oxygen dynamics and in influencing organic material distribution across the Danube River. ~~However, t~~The persistence of intensive ~~high~~ alga~~e~~l growth also highlights the need for stricter compliance with EU regulations on water quality. Since DO serves as a key parameter for assessing ecosystem health, further monitoring ~~and regulation are~~is essential to mitigate human-induced impacts and maintain balanced aquatic conditions in the Danube system.

5. Conclusions

Our study demonstrated that seasonal variations in temperature, biological activity and hydrodynamic conditions drive complex seasonal and spatial DO dynamics in the Danube River. In spring and summer, enhanced photosynthesis raised ~~DO and~~ POC and DO levels, while lowering associated $\delta^{18}O_{DO}$ values. This precise source identification is novel in the Danube River and serves as a crucial indicator of ecosystem health. ~~The p~~Photosynthetic effects were particularly evident in two areas of higher productivity where reduced slopes resulted in slower flow velocities and lower turbulence. In these zones, where river conditions approached those of standing waters, primary producers played a critical role, as shown by strong correlations between $\delta^{18}O_{DO}$ and POC. These findings underscore the importance of autotrophic DO production in the Danube and suggest that with rising temperatures and resulting reduced DO solubility the ecosystem may increasingly rely on this internal form of oxygen input. However, tributary inflows from the Tisa and Sava R~~r~~ivers diluted biomass and organic material inputs and contributed to declines in DO and POC levels downstream.

Although the Danube River´s water quality has improved over last three decades, vulnerable sections such as the Sava and Lower Danube continue to face the risk of further DO depletion. This risk is especially pronounced during late summer and early fall, when photosynthetic oxygen production declines and respiration intensifies while the river is often still too warm to dissolve sufficient atmospheric O_2. With ongoing climate warming, these potential DO deficits are expected to worsen, a trend likely to extend to other temperate large rivers systems.

~~In terms of seasonality, late summer emerged as the most critical season of the Danube River, especially the lower part of the Danube River. In contrast, colder seasons of fall and winter facilitated DO recovery and emphasized atmospheric O_2 input as another key and temperature-dependent source. With rising global temperatures and warmer cold seasons, future DO budgets could be at risk during these periods.~~ By integrating high-resolution measurements of DO, $\delta^{18}O_{DO}$, POC and R/P ratios, our study identified new arrays of biogeochemical processes that regulate DO~~ dynamics~~. Notably, DO concentrations alone are often insufficient to identify their sources, but when combined with $\delta^{18}O_{DO}$ values, relative contributions of different sources (photosynthetic and atmospheric input) and sinks (respiration) become ~~much~~ clearer. Such knowledge is crucial for future river management and may help to plan ecological conservation amid increasing environmental pressures. ~~Thus,~~ W~~w~~e therefore recommend high-resolution monitoring of DO and its sources and sinks, with a particular focus on vulnerable regions with critically low DO in late summer. The potential to identify DO sources and sinks ~~in other aquatic systems~~ with the application use of stable isotopes in other aquatic systems, offers a powerful tool for understanding and conserving diverse aquatic ecosystems globally.

Data availability

We already submitted our data sets from this manuscript to PANGAEA in March 2025. U, until its publication all data are available upon request.

Author contributions

JM: sampling, conceptualization, formal analysis, investigation, methodology, visualization, and writing (original draft preparation). ANV: conceptualization, formal analysis, investigation, methodology, visualization, and writing (original draft preparation). CMS: investigation, methodology, visualization, and writing (original draft preparation). STW: investigation, methodology, visualization, and writing (original draft preparation). JACB: conceptualization, resources, supervision, and writing (original draft preparation).

Competing interests

The contact author has declared that none of the authors has any competing interests.

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