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Phytoplankton and Temperature Control Seasonal Dynamics of Greenhouse Gases in a Large River

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Abstract Rivers are a dynamic source of greenhouse gases (GHGs), yet the temporal variability and controlling mechanisms of their CO_2:CH_4:N_2O ratios remain poorly constrained. We monitored the three GHGs in the German river Elbe over 5 years at two sites to identify seasonal controls as well as travel time related and site-specific mechanisms driving GHG concentration ratios and fluxes. CO_2 concentrations ranged from 2.8 to 125 µmol L^{-1} and showed a clear seasonal pattern with minimum values below saturation in summer, mainly correlating with indicators of planktonic photosynthesis, light availability, and chlorophyll concentration. CH_4 concentrations ranged from 0.0006 to 0.85 µmol L^{-1} and showed an opposite seasonal dynamic with maximum values in summer, correlating with temperature and particulate organic carbon. N_2O concentrations were between 0.007 and 0.07 µmol L^{-1}, mostly near saturation and mainly determined by temperature dependent solubility. We did not observe large differences between the two study sites except for elevated CH_4 concentrations at the downstream site during summer. While CO_2 was regulated by the metabolic balance of the water column, CH_4 was more locally controlled, probably by hydrodynamic conditions affecting particle sedimentation. The total GHG-potential of the three gases in terms of CO_2 equivalents was dominated by CO_2 and its seasonal cycle. Higher CH_4 emissions during summer were compensated by CO_2 uptake. Data-driven models based on machine-learning methods revealed that in the Elbe River, it is probably possible to predict GHG concentrations based on seasonal indicators without the need for water quality parameters.

Plain Language Summary Three different greenhouse gases (GHGs) carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) are emitted from rivers, contributing to global warming. We investigated the concentration of the three gases in a large German river to determine which gas is important under which conditions. We found that gas concentrations in the river were primarily influenced by the season. In summer, photosynthesis by the river plankton consumed CO_2, leading to very low CO_2 concentrations. Contrary to CO_2, the concentration of CH_4 was highest during summer when it was warmer. The concentration of CO_2 was similar at upstream and downstream sites. In contrast, CH_4 was elevated at the downstream site where the river was flowing slower. The concentration of N_2O was very low and limited by its water temperature dependent solubility. We developed a statistical model which could predict the measured gas concentrations from factors such as day length and nutrient concentrations with high precision. Regarding GHG emissions from the Elbe River, CO_2 was by far the most important gas, followed by CH_4 and N_2O.

Key Points:

- CO_2 and CH_4 exhibit opposite annual patterns, with CH_4 peaking in summer and CO_2 reaching its highest levels in autumn and winter
- CO_2 dynamics were primarily regulated by phytoplankton activity, whereas CH_4 concentrations were mainly controlled using local processes
- N_2O concentrations were low and largely governed by temperature-dependent solubility

Supporting Information:

Supporting Information may be found in the online version of this article.

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1. Introduction

Rivers are not only transporting dissolved and particulate matter from the continents to the oceans but also emit a substantial fractions of their load in form of greenhouse gases (GHG) to the atmosphere (Battin et al., 2009). They are exchanging all three major GHGs, CO_2, CH_4, and N_2O with the atmosphere. Depending on whether or not the temperature dependent atmospheric equilibrium concentration is exceeded, rivers can act either as source or sink of a respective gas. In most cases, rivers are over-saturated, which makes them a globally significant source of GHGs. Globally, streams and rivers emit 8,200 Tg CO_2 (Li et al., 2021), 27.9 Tg CH_4 (Rocher-Ros et al., 2023), and 0.07 Tg N_2O (Marzadri et al., 2021) per year. Thus, global emissions are dominated by CO_2 and CH_4, while N_2O emissions are of minor importance (Lauerwald et al., 2023). The ratio between the three gases is relevant because they differ in their global warming potential, with CH_4 and N_2O being 28 and 273 times more climate

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active than CO_2, respectively. On a global scale, the median molar concentration ratio of CO_2, CH_4, and N_2O is 4806:12:1 (Stanley et al., 2023), resulting in a relative global warming effect of the three GHGs annually emitted from global rivers in terms of CO_2-equivalents of 429:41:1. However, in a particular river, the relative contribution of the three gases to the overall climate effect can be highly variable because GHG concentrations typically have a high spatio-temporal variability.

On large scale, GHG concentrations depend on stream order with CO_2 (Hotchkiss et al., 2015) and also N_2O emission (Marzadri et al., 2021; Turner et al., 2015) generally decreasing with stream size because external GHG input from the catchment becomes less important in larger streams and rivers (Leng et al., 2022). For CH_4 such large-scale pattern is less clear (Stanley et al., 2023). However, there is not only heterogeneity of GHG concentrations on the catchment scale but also at the reach scale. While a lot of research has been done on smaller streams, little is known about spatio-temporal dynamics of GHGs in rivers. It has been shown that spatial variability in the German River Elbe is especially important for CH_4, while diurnal variability is more relevant for CO_2 emissions (Koschorreck et al., 2024). Stream GHG concentrations also vary seasonally with different seasonal patterns for different gases. In temperate streams CH_4 concentrations are typically elevated in summer, while CO_2 or N_2O concentrations are often highest in winter (Mwanake et al., 2023). Thus, there is considerable spatial and temporal variability of GHG concentrations in rivers, but patterns are different for the three GHGs.

Because dissolved gases equilibrate with the atmosphere within a rather short time or flow distance, respectively (Crawford et al., 2014), GHG concentrations in the water are regulated locally by in-stream processes, interaction with the floodplain, and gas exchange with the atmosphere (Leng et al., 2022). Since European rivers are typically heavily anthropogenically modified and often uncoupled from their floodplains, in-river processes become even more important (Machado dos Santos Pinto et al., 2020). In larger rivers, GHG concentrations are mostly regulated using internal processes (Hotchkiss et al., 2015). One consequence of this is that, similar to lakes, water residence time becomes an important factor.

CO_2 concentrations are regulated by the balance between gas exchange, respiration and photosynthesis but also chemical buffering (Leng et al., 2025; Nguyen et al., 2025). Since a large part of terrestrial organic matter entering the stream network is already mineralized in the headwaters, the supply of easily degradable allochtonous organic material is limited in downstream rivers and respiration depends largely on biomass produced in the river itself (Hotchkiss et al., 2015). Thus, there is typically a negative correlation between indicators of photosynthesis such as chlorophyll or oxygen and CO_2 concentration (Carter et al., 2022). The development of phytoplankton is a common phenomenon in large rivers and was described already in the River Continuum Concept (Vannote et al., 1980). This concept predicts the development of riverine phytoplankton at higher stream orders, and an increase in the production to respiration ratio more than 1 towards autotrophic conditions. Regarding both phytoplankton densities and related autotrophic processes (e.g., primary production, nutrient retention), highest biomasses and productions is usually reached in mid-sized to large rivers as phytoplankton development depends on water residence time (Reynolds & Descy, 1996). In addition, nutrient availability and light exposure (dependent on solar radiation as well as water depths and turbidity) are important factors which determine phytoplankton density in rivers (e.g., Reynolds et al., 1994). The concentrations of nutrients often show a longitudinal decrease inversely to an increase in phytoplankton biomass (Bowes et al., 2012; Minaudo et al., 2015; Rode et al., 2007). Furthermore, different mechanisms for phytoplankton loss can occur, including sedimentation under reduced flow conditions (e.g., Köhler et al., 2002; Reynolds & Descy, 1996) and grazing by both planktonic and benthic filter feeders depending on the development of particular grazer communities (Gosselain et al., 1998; Welker & Walz, 1998). Most of the controlling factors for phytoplankton are superimposed by discharge. Low discharge during summer droughts enhances residence time and increases light exposure of suspended algae and thus improves growth conditions unless discharge-related loss processes occur (e.g., Houser et al., 2015; Weitere & Arndt, 2002). On the other hand, in the lowland, downstream, and estuarine parts of rivers, water depth and turbidity often limit light penetration and hence primary production. While there is a clear link between phytoplankton and CO_2 concentration, possible links between phytoplankton and CH_4 are less clear.

Riverine CH_4 is primarily produced in anoxic sediments although phytoplankton-mediated CH_4 production has also been reported (Patel et al., 2024). In River Elbe, it has been shown that areas with reduced flow velocity and thus, sediment accumulations either in the litoral, harbors or upstream of dams are a major source of riverine CH_4 (Bussmann et al., 2022). Production of CH_4 in sediments is primarily controlled by organic matter availability and

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temperature (Stanley et al., 2016). Methane can also be consumed by microbes, but the rates of methane oxidation in flowing water are usually low compared to outgassing (Matoušů et al., 2019).

Different to CO_2 and CH_4, N_2O is not an end product of organic matter mineralization but rather an intermediate of a variety of nitrogen cycling processes such as nitrification and denitrification (Quick et al., 2019). Thus, N_2O in aquatic systems depends on the availability of inorganic nitrogen species (Baulch et al., 2011) as well as oxygen conditions (Rosamond et al., 2012), both of which are related to phytoplankton growth and activity. It appears that all three gases are potentially affected by temperature, trophic state and the activity of phytoplankton.

While much is known about the effect of trophic state and plankton on particular processes, there are few studies investigating the effects on all 3 GHGs in parallel over a longer period (Stanley et al., 2023). We can expect that the concentrations of the 3 gases are affected by the growth and activity of plankton in different ways. This would lead to distinct spatio-temporal patterns of GHG ratios. We hypothesize that (H1) a longitudinal plankton gradient increases CH_4 relative to CO_2 and N_2O downstream. This should be especially pronounced in the growing season. Thus, we also hypothesize that (H2) the CH_4 to CO_2 ratio is higher in summer. To test these hypotheses, we monitored 2 sites at a large German river over 5 years for the concentration of CO_2, CH_4, and N_2O. To explain the observed pattern and eventually predict GHG concentrations, we measured potential influential parameters to feed statistical/machine-learning models.

2. Materials and Methods

2.1. Study Sites and Sampling

River Elbe is a large, lowland river in Central Europe, flowing from the Krkonoše Mountains in the Czech Republic through Germany to the North Sea, and is characterized by a diverse catchment that includes urban, agricultural, and forested landscapes (Figure S1 in Supporting Information S1). Previous studies have shown that the river develops a longitudinal plankton gradient with high plankton biomass and nutrient depletion further downstream (Kamjunke et al., 2022).

To assess the effect of water residence time, we chose two sites separated by a 129 km river reach. The average water travel time between the two sites is 2 days, and the average discharge at the upstream site Magdeburg is 554 m^3/s. There is one major tributary (river Havel), which contributes an average of 108 m^3/s, representing 16% of the total discharge at the downstream site Wittenberge. Due to small hydraulic gradients, groundwater influence on the river is small (Zill et al., 2023).

The two sites at Magdeburg (German river km 326) and Wittenberge (km 455) were sampled from bridges monthly in 2020–2024. To assess lateral variability, we took three samples at Magdeburg (left, middle, and right side of the main stem) and two at Wittenberge (left and right side in the main stem). Samples were taken during the morning hours between 7 and 11 a.m. At each sampling, water physicochemical parameters (temperature, O_2, pH) were measured immediately (WTW, Weilheim, Germany). Water samples for the analysis of major solutes were filled in flasks and transferred to the lab.

For CO_2, CH_4, and N_2O analysis, 30 mL water samples were collected in 60 mL plastic syringes. A headspace of 30 mL ambient air was added, avoiding any contamination by breathed air. After vigorous shaking for 1 minute the headspace was transferred to pre-evacuated 12 mL exetainers (Labco, UK) and water temperature in the syringe (=equilibration temperature) was measured. Ambient air samples for headspace correction were taken on each occasion.

Discharge data from official gauges were kindly provided by the German Federal Waterways and Shipping Administration (WSV). Meteorological data were obtained via the Meteostat portal and contained the variables air temperature, wind speed, relative humidity and precipitation from two weather stations of the German Weather Service at Magdeburg (https://meteostat.net/de/station/10361) and Seehausen (https://meteostat.net/de/station/10261) near our water sampling sites.

2.2. Analysis

Water-chemical variables were measured using standard methods as described in Kamjunke et al. (2021): In the laboratory samples were filtered onto quartz fiber filters (MN QR10, Macherey-Nagel) or glass fiber filters (GF-F, Whatman). Filtrates were stored at 4°C until further analyses and filters were frozen. We used the

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segmented flow technique for the photometric determination of nitrite (NO_2^-), nitrate (NO_3^-), and silicate (Si). The ammonium molybdate spectrometric method was used to measure soluble reactive phosphorus (SRP) and after persulfate digestion total phosphorus (TP). Organic carbon concentration in the filtered and unfiltered original water samples was analyzed based on high-temperature oxidation using nondispersive infrared sensor detection (DIMATOC 2000, Dimatec Analysentechnik GmbH, Essen, Germany). Chlorophyll a concentration was measured by high performance liquid chromatography after calibration with commercial standards (Kamjunke et al., 2021).

The mixing ratio [ppmv] of CO_2, CH_4, and N_2O in the exetainers was measured by a gas chromatograph (SRI 8610, SRI Instruments, Torrance, USA) equipped with a flame ionization detector + methanizer for CH_4 and CO_2 and an electron capture detector for N_2O. The carrier gas was N_2. Certified calibration gas was used to convert peak areas to ppmv. Mixing ratios were converted to concentrations using equilibration temperature dependent Henry coefficients (Sander, 2015) and CO_2 data were corrected for alkalinity as explained in Koschorreck et al. (2021).

2.3. Calculation and Statistics

Water depth (z) at that specific river region was calculated using a discharge (Q)-depth relationship measured at different discharge conditions (Kamjunke et al., 2021):

$$z = -10^{-6} \times Q^2 + 0.0046 \times Q + 0.8478 \left(n = 7, R^2 = 0.99\right)$$

Diffusive fluxes of GHGs [mmol m^{-2} d^{-1}] were calculated as

$$F_{gas} = k_{gas} \times \left([gas_{water}] - [gas_{air}]\right)$$

where k_{gas} is the gas transfer velocity for the respective gas (m d^{-1}), $[gas_{water}]$ is the gas concentration in water (μmol L^{-1}), and $[gas_{air}]$ is the gas concentration in equilibrium with ambient air (μmol L^{-1}). We used atmospheric concentrations of 400 ppm CO_2, 2 ppm CH_4, and 0.4 ppm N_2O. Gas transfer velocities for the particular gases (k_{gas}) were calculated as:

$$k_{gas} = \left(\frac{Sc_{gas}}{600}\right)^{-1/2} \times k_{600}$$

where Sc_{gas} is the Schmidt number for the respective gas at the water temperature calculated following the coefficients summarized in Raymond et al. (2012) and k_{600} [m d^{-1}] was calculated from water depth using an empirical relation from Leng et al. (2025):

$$k_{600} = z \times 1.2 + 1.4$$

The correlation between water depth and k_{600} was highly significant ($R^2 = 0.99$, $p < 0.05$) and k_{600} values were consistent with common empirical relations (Leng et al., 2025). We used the same k_{600} model for both sites since hydrodynamic conditions in river Elbe are rather consistent between Magdeburg and Wittenberge and water depth and flow velocity vary in a small range (Kamjunke et al., 2021). To compare the climate effect of the three gases, we converted fluxes to CO_2 equivalent fluxes [gCO_2eq m^{-2} d^{-1}] using a global warming potential (100 years time horizon) of 28 for CH_4 and 273 for N_2O (IPCC, 2021).

Annual emissions were computed for the two sites by calculating mean diffusive fluxes for each site and sampling date and then linearly interpolating data between sampling dates to obtain flux data for each day. Annual emissions were then calculated by summing up daily fluxes over the respective years. Missing data during the first and last few days of the study period were gap filled with data from the first and last sampling, respectively.

The calculation of day length and daily global radiation is based on data obtained from the ICOS RI station Hohes Holz (Germany), which is located in representative proximity to the study sites (Rebmann et al., 2025). Day length was determined as the difference in hours between the times of sunset and sunrise for each day. Daily global radiation was calculated by integrating the incoming shortwave radiation measured over the course of each

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respective sampling day. Light availability under water was approximated to $1/z$. All data are published by Koschorreck et al. (2025).

To explore relationships between relevant variables, pairwise Pearson correlations were computed for all numerical columns in the data set using Python library pandas, and the results were visualized as a heatmap with the seaborn library. A diverging colormap with a masked upper triangle was applied to highlight the strength and direction of the correlations in a clear and interpretable format.

We used ensemble models such as random forest (RF) or Gradient Boosting (GB) to investigate the relationships between potential environmental drivers and individual greenhouse gas saturation levels (CH_4 and CO_2). The models were trained to predict gas saturation using physicochemical and biogeochemical variables as input features. The data set covers the full period from 2020 to 2024; for model training, data from 2021 to 2024 were used. Feature importance was assessed using the ensemble models' built-in importance measures, and overfitting was addressed through hyperparameter tuning with 5-fold cross-validation followed by evaluation on a temporal hold-out data set using the year 2020 data for independent prediction. This approach ensures that the model is evaluated on completely unseen data, providing a robust test of its generalization capability. Hyperparameter tuning was conducted using randomized search with 5-fold cross-validation (Schütze, 2025), and model performance was evaluated using R^2 and error-based metrics (e.g., MAE).

3. Results

3.1. GHG Concentration: Seasonal Dynamics and Site Comparison

The concentrations of the 3 GHG gases spanned 4 orders of magnitude, with CO_2 having by far the highest concentration ($33.3 \pm 33\ \mu mol\ L^{-1}$) followed by CH_4 ($0.07 \pm 0.1\ \mu mol\ L^{-1}$) and N_2O ($0.02 \pm 0.02\ \mu mol\ L^{-1}$) (Table S1 in Supporting Information S1). The concentrations of all 3 GHGs showed consistent seasonal cycles (Figure 1).

CO_2 concentrations were highest during autumn and winter and low during summer. During the summers of 2021, 2022 and 2023, the river was even under-saturated, becoming a CO_2 sink during these periods. CO_2 concentrations did not differ between sites.

In contrast CH_4 concentrations differed significantly between sites (Wilcoxon rank-sum test, $p < 0.05$) with higher concentrations at the downstream site Wittenberge during summer. The seasonal pattern of CH_4 was contrary to that of CO_2—highest CH_4 concentrations were always observed during summer. The river was permanently oversaturated with CH_4 (Figure 1, Figure S5 in Supporting Information S1).

The seasonal pattern of N_2O was similar to that of CO_2. There were no differences between sites and the observed concentrations closely followed the atmospheric equilibrium concentration (Figure 1, Figure S2 in Supporting Information S1). There was one sample with extraordinary high N_2O concentration in Magdeburg in 2024, which we treated as an outlier and did not consider in further analysis.

As a consequence of the seasonal change of CH_4 and CO_2, the molrar ratio of CH_4/CO_2 changed with season (Figure 2). During autumn and winter, it was close to zero, while between April and August higher ratios up to 0.1 were observed. The CH_4/CO_2 ratio during that time depended on site: It was about twice as high at the downstream site Wittenberge compared to Magdeburg.

3.2. Drivers of GHG Concentrations

Potential drivers of GHG concentrations (Table S1 in Supporting Information S1) also showed clear seasonal patterns and only small differences between sites (Figure 3). Chlorophyll as an indicator of plankton abundance was high during the summer season when nutrient concentrations were low. The annual amplitude of these parameters was similar between sites with slight differences with respect to timing: The plankton summer peak lasted a few days longer in Wittenberge than in Magdeburg and recovery of the SRP concentration started earlier in Magdeburg. All in all, water quality was similar between sites, which is in contrast to the difference in CH_4 concentration between sites. The summary statistics of all parameters are in Table S1 in Supporting Information S1.

Linear correlation of potential drivers with GHG concentrations give a first hint about the role of different drivers for GHG concentrations (Figure 4a). CO_2 was negatively correlated with parameters indicating season and

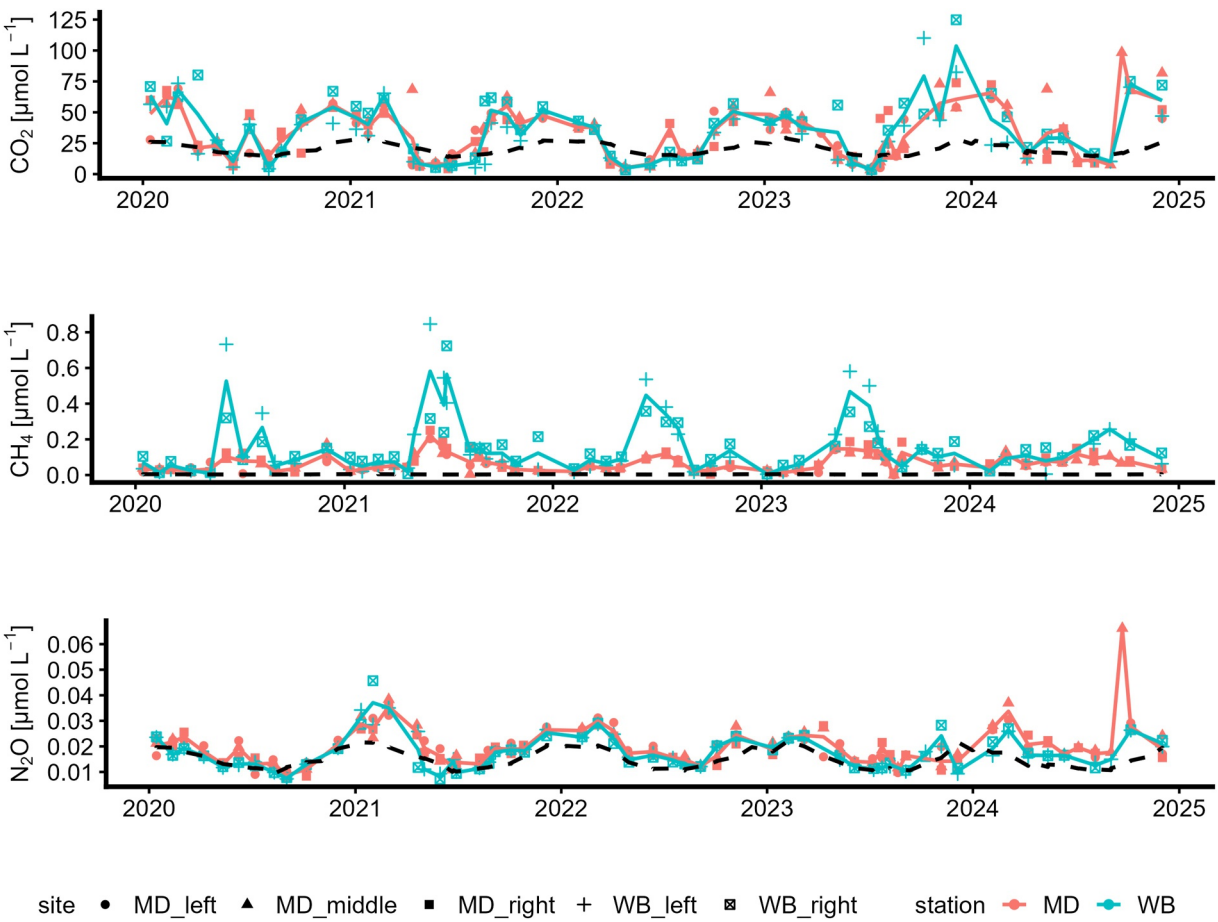


Figure 1. Time series of GHG concentrations in the River Elbe at Magdeburg (MD) and Wittenberge (WB) [µmol L^{-1}]. Dotted lines indicate atmospheric equilibrium concentrations, Dots indicate individual measurements, lines represent site means.

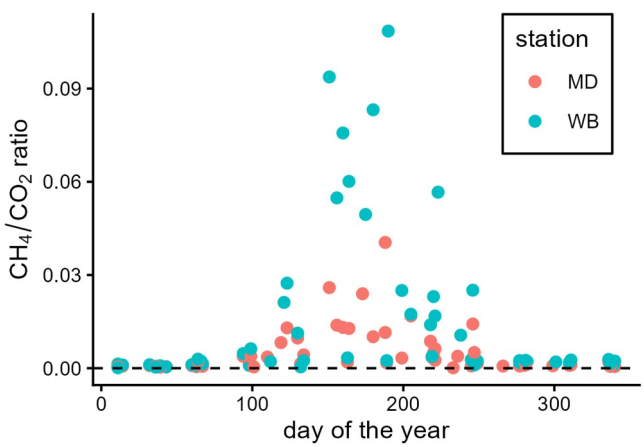


Figure 2. Seasonality of the CH_4/CO_2 concentration ratio in Magdeburg (red) and Wittenberge (blue) for all years.

plankton abundance. CH_4 was poorly correlated with water quality parameters with seasonal indicators like temperature and radiation having a clear effect. Interestingly, CH_4 was correlated stronger with particulate organic carbon (POC) than with chlorophyll, indicating that non-plankton organic matter was important for CH_4 production. N_2O was like CO_2 negatively correlated with seasonal indicators with higher concentration at lower temperature. This correlation disappears when relative saturation instead of absolute concentration is plotted against temperature ($R^2 = 0.07$, not shown), indicating that the seasonality of N_2O was exclusively driven by the temperature dependence of solubility. Interestingly, also the observed strong positive correlation between nitrate and N_2O disappears when we look at N_2O saturation, indicating that the correlation with nitrate is a pseudo correlation. A correlation matrix (Figure S3 in Supporting Information S1) confirmed that several parameters were intercorrelated, like for example, POC and chlorophyll or temperature and day length. These correlations were independent of site (Figure S4 in Supporting Information S1). Based on our correlation matrix (Figure 4a), we summarized the most important correlations in a conceptual scheme of the three GHGs CO_2, CH_4, and N_2O in River Elbe (Figure 4b).

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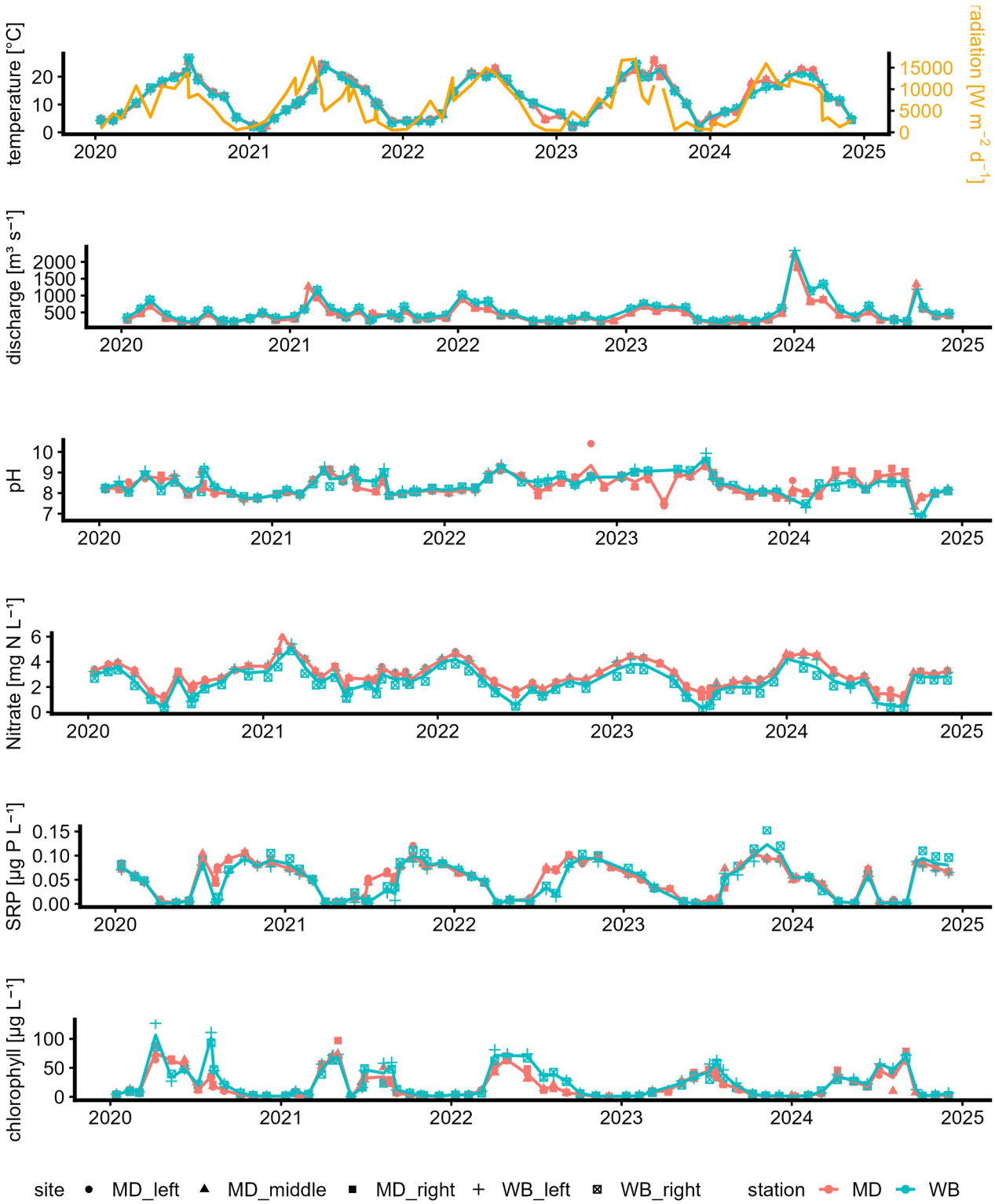


Figure 3. Time Series of relevant parameters temperature, discharge (*Q*), pH, nutrients, and chlorophyll at Magdeburg (MD) and Wittenberge (WB). Dots indicate individual measurements, lines represent site means.

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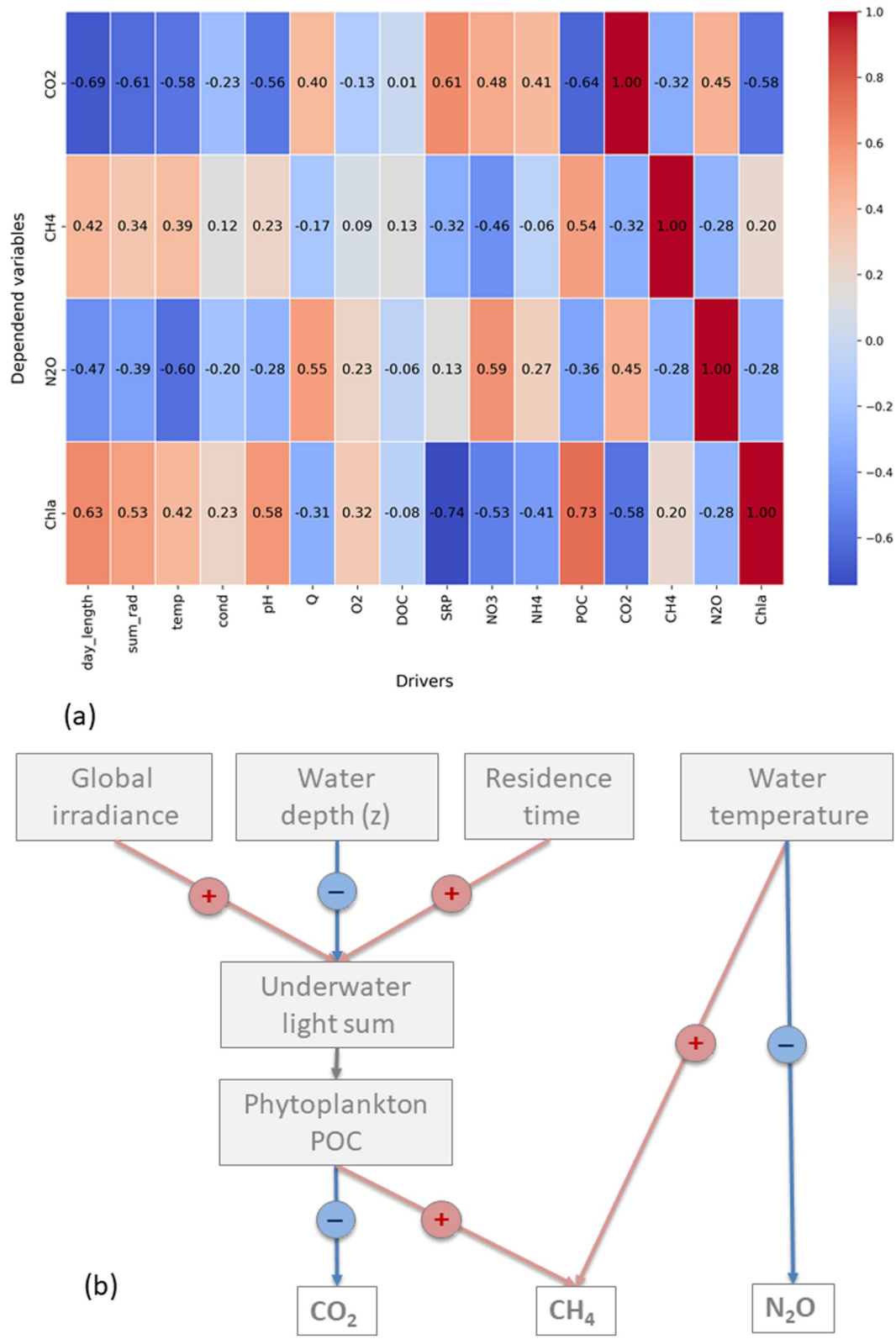


Figure 4. (a) Linear Pearson correlation of greenhouse gas concentrations with different drivers. Statistical significance was assessed using the Pearson correlation *p*-value, while the magnitude of R was interpreted as effect size. Correlations with $|R| > 0.15$ were therefore considered weak, despite being statistically significant. (b) Scheme correlation of the 3 GHGs with drivers in the River Elbe.

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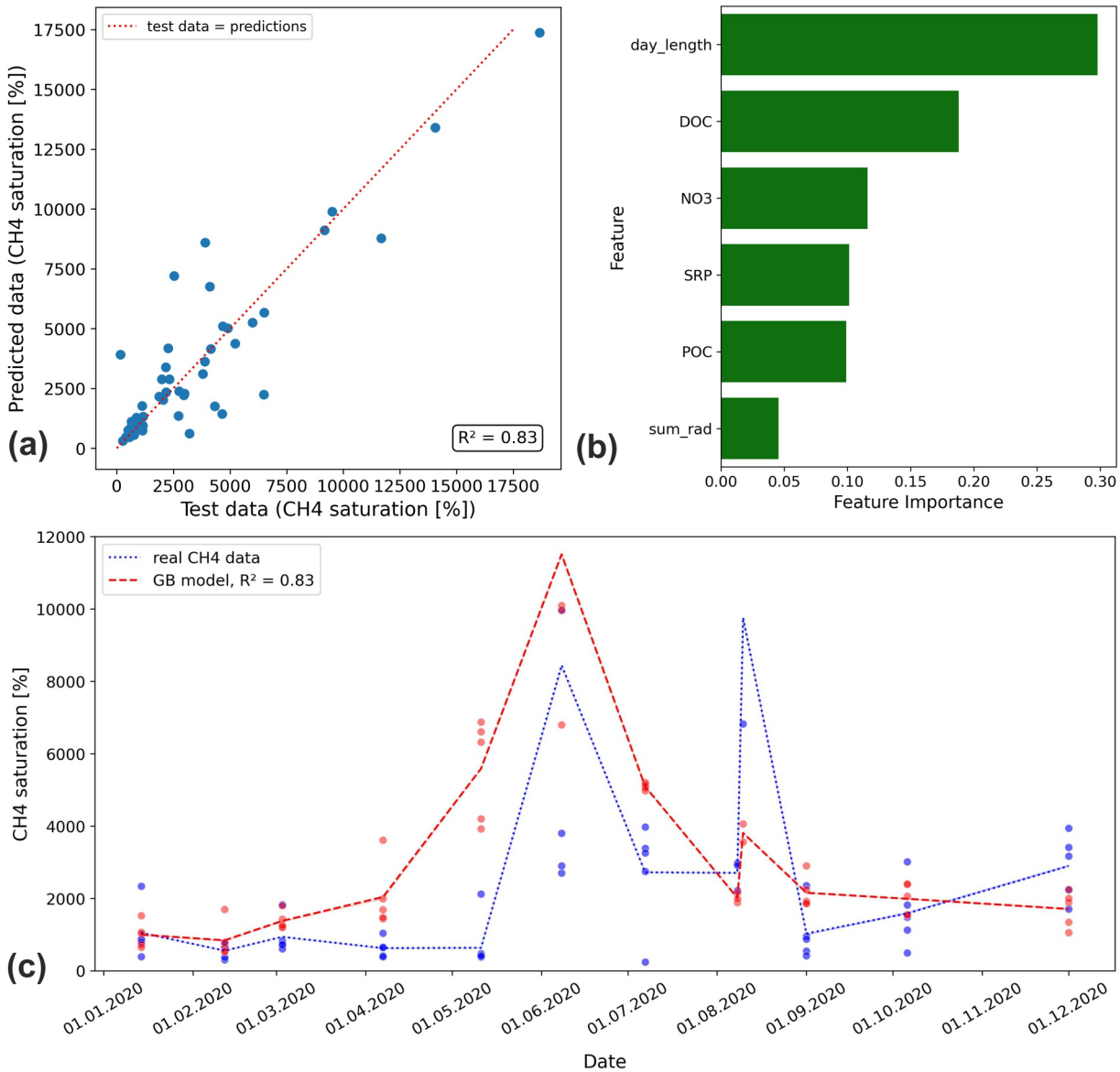


Figure 5. Performance of a Machine Learning model approach: Gradient Boosting (GB) ensemble model to predict the relative CH_4 saturation in River Elbe. (a) Comparison of 2020 test data with predicted data for CH_4 saturation from GB model ($R^2 = 0.83$). (b) Feature Importance analysis shows the most important variables for the prediction of CH_4 saturation: daylight hours (day_length), DOC, soluble reactive phosphorus, NO_3^-, particulate organic carbon and daily radiation sum. (c) Comparison of measured and predicted data for CH_4 saturation in the year 2020. The GB model approach exhibits a slight tendency to overestimate methane saturation during spring. Nevertheless, it achieves robust coefficients of determination, with values exceeding 0.83.

3.3. Machine Learning Models

Applying simple linear regressions is problematic when drivers are not independent of each other. To better consider interactions between parameters, we applied ensemble modeling approaches (GB and RF) to predict GHG concentrations in river water using physicochemical parameters as input features. The primary focus of our investigation was on the performance and interpretability of the GB model, given its ability to sequentially correct model errors and often achieve higher predictive accuracy in structured environmental data sets. The GB model was trained using measured variables which were identified as main predictors for the CH_4 concentration variability based on Pearson correlation coefficients (shown in Figure 4). The GB model yielded R^2 of 0.83 and MAE of 890 (Figure 5a), outperforming the RF model ($R^2 = 0.75$). The reported mean absolute error refers to methane saturation expressed in percentage (%), consistent with the target variable CH_4 saturation. The coefficient of

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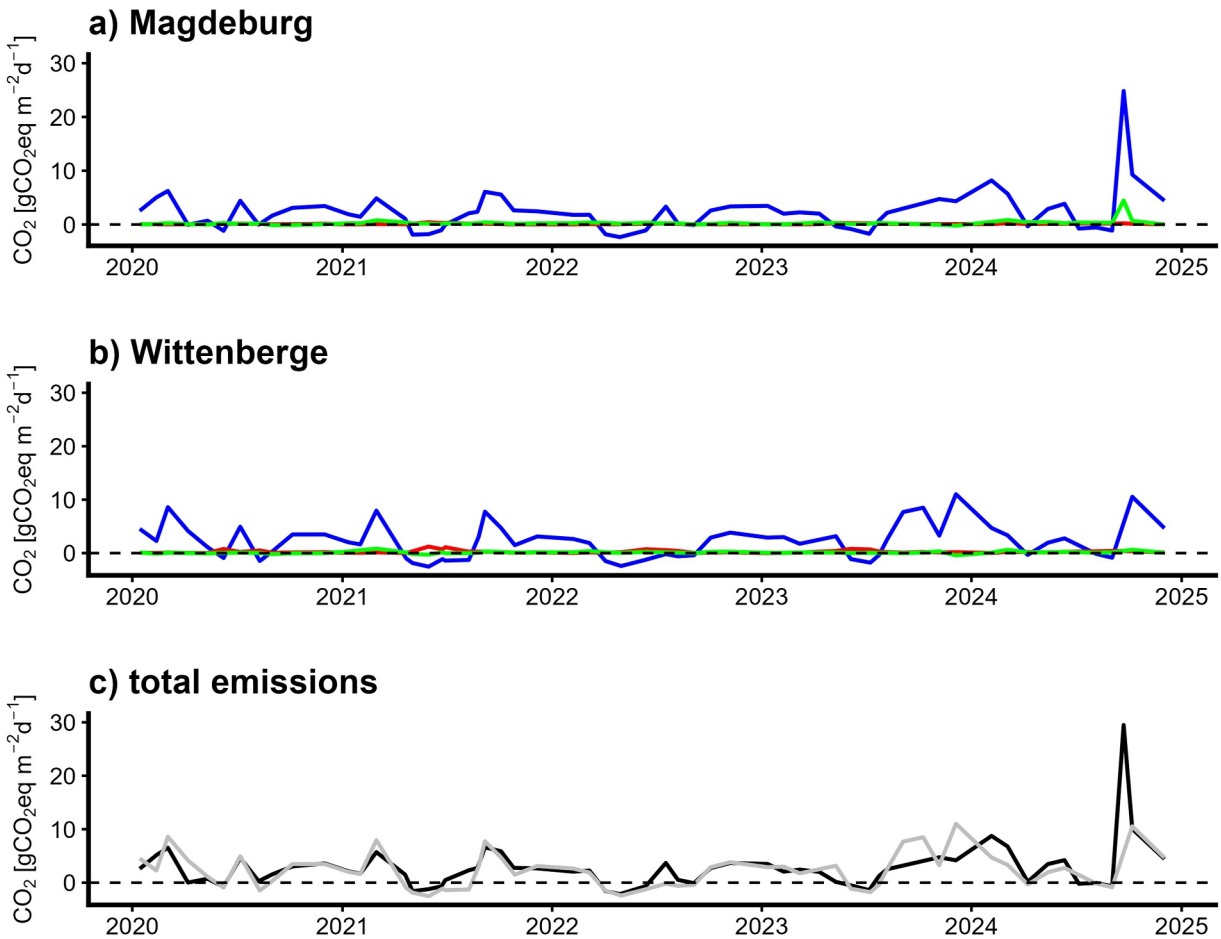


Figure 6. Diffusive GHG emissions in terms of CO_2-equivalents (CO_2 = blue, CH_4 = red, N_2O = green) at (a) Magdeburg and (b) Wittenberge. (c) Total GHG emissions at Magdeburg (black) and Wittenberge (gray).

determination was calculated based on independent test data, using a hold-out split (20%) that was not involved in model training or hyperparameter optimization. Cross-validation was used exclusively for hyperparameter tuning, while model performance metrics reported in the manuscript reflect generalization performance on unseen data. In addition, an independent temporal test set (year 2020) was used to further assess model robustness. Feature importance analysis indicated that the available daylight hours, DOC, SRP, NO_3^-, POC, and daily radiation sum were among the most influential variables driving the model predictions (Figure 5b). The result of this prediction is shown in Figure 5c. The GB model reproduces the seasonal trend of CH_4 saturation with a tendency to slightly over predict saturation during summer.

An analogous modeling approach was used to predict CO_2 concentrations, following the same training and validation strategy (Figure S5 in Supporting Information S1). The performance of the GB CO_2 model was also good ($R^2 = 0.65$), with SRP, pH, POC, O_2, and Q being the most influential parameters. The model reproduced the seasonal cycle of CO_2, although CO_2 saturation is under-estimated in winter and spring and over-estimated in summer and especially autumn.

3.4. Diffusive Fluxes and Annual Budget

From GHG concentrations and gas transfer velocities, we calculated median diffusive fluxes of 46, 0.3, and 0.01 mmol m^{-2} d^{-1} for CO_2, CH_4, and N_2O respectively (means ± SD: 52 ± 83, 0.41 ± 0.47, and 0.02 ± 0.04). As a consequence of the observed seasonality of GHG concentrations, diffusive GHG emissions also changed with season. To make the climate impact of the three gases comparable, we express their fluxes in terms of CO_2 equivalents (Figure 6). At Magdeburg, emissions were nearly exclusively in the form of CO_2 (Figure 6a). Thus,

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Table 1
Annual Emissions of CO_2, CH_4, and N_2O [g CO_2 eq m^{-2} y^{-1}] at Magdeburg (MD) and Wittenberge (WB)

year	MD total	MD CO_2	MD CH_4	MD N_2O	WB total	WB CO_2	WB CH4	WB N_2O
2020	940	888	28	24	1,146	1,075	69	3
2021	930	781	46	103	904	711	120	73
2022	510	406	27	77	489	341	84	64
2023	925	843	42	40	1,517	1,406	94	17
2024	2,018	1,754	48	216	1,499	1,333	84	82
Mean	1,065 (53)	934 (53)	38 (26)	92 (83)	1,111 (39)	973 (46)	90 (21)	48 (74)

Note. One row for each year plus one row with 5 years mean (CV in % in brackets). Calculated from linear interpolation of data in Figure 6a + Figure 6b.

emissions occurred primarily during autumn and winter. The pattern was the same at Wittenberge, but here lower summer CO_2 emissions were partly compensated by elevated CH_4 emissions (Figure 6b). However, even considering CH_4 emissions, at Wittenberge the river was a net GHG sink in summer.

However, compared to GHG emissions during the rest of the year, this summer GHG uptake was rather short and uptake fluxes were rather low. Thus, in an annual perspective River Elbe was a net source of all three gases (Table 1). At Magdeburg CO_2, CH_4, and N_2O contributed 87%, 3%, and 10% to the total annual emission in terms of CO_2 equivalents. At Wittenberge, these numbers were 87%, 9%, and 4%. These patterns were similar between years but there was considerable variability between absolute annual emissions, with the year with the highest emissions having about 3 times higher emissions than the year with the lowest emissions. Interestingly, at Magdeburg, the highest annual emissions were observed in 2024, while in Wittenberge emissions were highest in 2023. The year 2022 had the lowest emissions at both sites.

4. Discussion

4.1. Mechanisms Regulating CO_2, CH_4, and N_2O Concentrations

The CO_2 concentration in the river was primarily correlated with factors related to the phytoplankton. Photosynthesis depleted CO_2 during the growing season. Benthic primary production and macrophytes can be ruled out as important contributors to primary production in the lowland part of river Elbe (Deutsch et al., 2009; Kamjunke et al., 2021) and there is little lateral inflow of potentially CO_2 rhich groundwater (Koschorreck et al., 2022; Zill et al., 2023). Under nutrient-rich conditions in the river, phytoplankton photosynthesis was most likely regulated by factors affecting light availability, global irradiance and water depth. A control of chlorophyll a concentration by global irradiance was detected in River Elbe before (Kamjunke et al., 2021), and a seasonal CO_2 cycle was also observed in other rivers (Hassan et al., 2024). The correlation of the CO_2 concentration with light makes it possible to model and predict CO_2 from data such as day length and water depth without knowing the detailed processes in the catchment—at least in nutrient rich rivers. This is probably also an explanation for the observed rather small interannual variability of the CO_2 concentration. The apparent contradiction to a rather high interannual variability of CO_2 observed in the French river Loire (Nguyen et al., 2025) can be explained by our much shorter study time, which did not include large changes in trophic state.

Different from CO_2, concentrations of CH_4 were only weakly correlated with measured parameters. The GB model was mainly driven by parameters indicating season. This is consistent with the view that CH_4 in rivers is less driven by processes in the water but by either production in the sediment or import from the riparian zone (Bussmann et al., 2022; Stanley et al., 2016). Independent of the location of CH_4 production, methanogenesis in the environment depends on temperature, resulting in higher concentrations during summer. Correlation of stream CH_4 concentration with temperature is a common observation (Wiemann Olsen et al., 2025), supporting the view that CH_4 in rivers is mainly controlled by the rate of methanogenesis, either in the river itself or the riparian zone. Our data show that CH_4 is probably much less affected by processes in the water of the river than CO_2.

The concentration of N_2O in the River Elbe was always close to atmospheric equilibrium (Figure S5 in Supporting Information S1). Seasonality was exclusively caused by the temperature dependence of N_2O solubility. N_2O concentrations close to equilibrium are actually typical for surface waters (Aho et al., 2023), even under-

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saturation is frequently observed. This means that N_2O exchange between the river and atmosphere was likely the fastest process in the river N_2O cycle. Obviously, N_2O turnover by denitrification or nitrification, which are thought to be the major processes of N_2O turnover in rivers (Quick et al., 2019), was too slow. This is consistent with a meta-analysis which showed that water residence time in rivers is too short for significant microbial N_2O production (Maavara et al., 2019). That is also an explanation why we did not find the often-observed negative correlation between N_2O and O_2. A theoretical option is that N_2O producing and consuming processes in the river were active at exactly the same rate, resulting in zero net productions of N_2O. However, such a scenario is highly unlikely. Thus, we conclude that N_2O turnover in the river was slow compared to gass exchange at the water surface, leading to temperature dependent close to equilibrium concentrations all the year round. Interestingly, we observed a correlation with nitrate although the N_2O concentration was exclusively controlled by temperature.

Correlation of N_2O with nitrate is a common observation in the literature (Baulch et al., 2011; Quick et al., 2019) and is attributed to the regulation of microbial nitrogen turnover by inorganic nitrogen availability. However, there are other studies showing a correlation between N_2O and temperature but not nitrate (Venkiteswaran et al., 2014). N_2O emissions from rivers are often estimated from inorganic nitrogen concentrations using emission factors, although the statistical relation between nitrate and N_2O is often weak (Zhang et al., 2020). Our results show that correlations between nitrate and N_2O need to be interpreted with care and are not necessarily caused by a direct mechanistic link between inorganic nitrogen and N_2O. The indirect emission factor calculated by dividing the N_2O concentration by the nitrate concentration was 0.00012 ± 0.00009 for our data set, indicating that the standard emission factor of 0.0025 cannot be used for River Elbe. This confirms observations by Turner et al. (2015) that emission factors decrease with stream order and probably need to be revised downward (Hama-Aziz et al., 2017).

Thus, we observed considerable seasonal variability in GHG concentrations. To better understand the mechanisms driving that variability, we compared two sites separated by about 2 days of water travel time.

4.2. Spatial Variability and Site Comparison (Hypothesis 1)

We hypothesized that a longitudinal plankton gradient would increase CH_4 relative to CO_2 and N_2O downstream (H1). In contrast to the initial expectation of different chlorophyll and nutrient concentrations at the two sites, our data did not show a pronounced longitudinal difference in most measured parameters, and we did not see higher chlorophyll concentrations in combination with lower nutrient concentrations at the downstream site. Although we detected longitudinal gradients along the river in previous studies (Kamjunke et al., 2022, 2023), the travel time of 2 days was too short to result in pronounced differences. Thus, hydraulic residence time was insufficient to generate substantial longitudinal gradients of CO_2 and N_2O. Interestingly, the only parameter clearly differing between the two sites was CH_4. Thus, we disproved our first hypothesis for CO_2 and N_2O but not for CH_4.

We can calculate the theoretical residence time of a gas in the river by multiplying its concentration by water depth and divided by the flux between water and atmosphere. The theoretical residence times for CO_2 ranged from −49 to 7 (median 1 d), for CH_4 0.5–4.4 d (median 0.7 d), and for N_2O −180–136 (median 3 d). This is comparable to the travel time of water between the two sites. In other words, the travel time between the sites was long enough for equilibration of the water with the atmosphere under the assumption of no net production during travel. The similarity of CO_2 concentrations between sites (which means the CO_2 pool in the water was rather constant) suggests that CO_2 production and atmospheric exchange were in equilibrium along river Elbe. This is consistent with no change in chlorophyll concentration, indicating no net primary production between the two sites. This is plausible given the strong light limitation of primary production in the river (Kamjunke et al., 2021). Thus, rather similar CO_2 concentrations along the river are caused by a combination of constant flow conditions (and thus similar k_{600}), little import of CO_2 from the catchment, and low net-primary production by the phytoplankton.

Contrary to CO_2, we clearly found elevated CH_4 concentrations at the downstream site. It is the question whether this is an effect of longer water residence time or if other factors play a role. Since flow velocity as well as river morphology were uniform between Magdeburg and Wittenberge, different CH_4 concentrations were most probably not caused by different gas transfer velocity and emissions. Another argument supporting this conclusion is that CO_2 and N_2O concentrations, which are affected by k_{600} in a similar way, did not differ between the two sites. The inflow of the River Havel 17 km upstream of Wittenberge might have contributed to high CH_4 concentrations. This tributary is flowing very slowly and has CH_4 concentrations higher than River Elbe

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(Bussmann et al., 2022). Applying equ.4 from Crawford et al. (2014) we estimate that in river Elbe after 25 km, 50% of dissolved gases would equilibrate with the atmosphere, provided that outgassing is the only process affecting dissolved gas concentrations. Thus, most of the CH_4 found at Wittenberge should originate from the reach directly upstream of Wittenberge. Applying a combination of hydrological methods, Zill et al. (2023) found evidence for an effect of agricultural drainage ditches on the river Elbe in the region of Wittenberge. Such drainage ditches are known to have high CH_4 concentrations (Peacock et al., 2021). However, the fact that we did not observe a correlation between CH_4 and discharge is not supporting this argumentation.

Previous research provided strong evidence that CH_4 in river Elbe primarily originates from near shore sediments in flow reduced areas like groyne fields (Bussmann et al., 2022; Koschorreck et al., 2024). In fact, the reach 25 km upstream of Wittenberge contained nearly twice as many groynes (414) compared to the reach upstream of Magdeburg (242). Also, the average flow velocity was lower upstream of Wittenberge (0.8 m s^{-1}) compared to Magdeburg (0.94 m s^{-1}). Thus, conditions for sediment accumulation, and thus potential CH_4 production, were better at Wittenberge than at Magdeburg. We conclude that water residence time of the order of a few days does not have a strong effect on GHG concentrations in this light limited lowland river and that CO_2 is mainly controlled by metabolic processes in the river water while CH_4 depends on local factors. Thus, we could not confirm H1.

4.3. Seasonal Controls (Hypothesis 2)

While our data do not support H1, we found clear evidence supporting our second hypothesis (H2). In H2, we predicted that the CH_4 to CO_2 ratio is higher in summer. Our data show, that season was the dominant factor regulating GHG concentrations and ratios in River Elbe, confirming results from other nutrient rich temperate rivers in Belgium (Borges et al., 2018), the US (Carter et al., 2022) and France (Nguyen et al., 2025). Such seasonality can be driven by hydrology and residence time (Borges et al., 2018) as well as the balance between photosynthesis and respiration (Carter et al., 2022; Nguyen et al., 2025), leading to the common observation of low CO_2 concentration during the growing season in summer. Consistent with our observation that low net primary production probably led to little differences between sites, the observed seasonal fluctuation of CO_2 can be explained by the seasonal shift of the ratio between gross photosynthesis and respiration, which is influenced by a combination of light availability and temperature (Figure 4b).

Since most river variables follow a seasonal pattern, it is not straight forward to derive mechanistic relationships from statistical analysis. Statistical models can be used to predict GHG concentrations with surprising accuracy but do not provide conclusive information about the sources of CH_4 in rivers. We conclude that models driven by physical seasonal drivers such as day-length, temperature, or daily light sum offer a good potential to predict GHG concentrations in large rivers. The same probably applies to emissions, since seasonal CO_2 emissions from river Elbe are mostly controlled by seasonal changes in concentration rather than k_{600} (Leng et al., 2025).

We show that both CO_2 and CH_4 concentrations followed a reproducible seasonal cycle, which in the case of CO_2 was linked to net primary production while in the case of CH_4 it was probably controlled by temperature regulation of methanogenesis. As a consequence, we observed a pronounced seasonal shift of GHG ratios with higher CH_4/CO_2 ratios during summer, confirming our second hypothesis.

4.4. GHG Ratios

To put the data into perspective, we compiled river GHG ratios from the literature (Table 2). Molar ratios between the three GHGs in rivers cover a broad range. However, in all studied systems CO_2 had the highest concentration or flux, followed by CH_4 and N_2O. River Elbe had lower concentrations of CO_2 and CH_4 compared to N_2O in comparison to the median of all studies in Table 2, which is 3091:25:1. Our median CO_2/CH_4 ratio of 476 was in the range of literature values but variability within our data set was extremely high (range 10–15226) and was larger than variability between the systems in Table 2. Thus, GHG ratios in rivers might be primarily controlled by season rather than geographical factors.

According to the "anaerobic scaling hypothesis" the CO_2 to CH_4 ratio is constrained by the relative contribution of methanogenesis to organic matter mineralization in a system and is highest in anthropogenically affected systems (Stanley et al., 2016). Thus, it is an option to identify sites and moments with especially high climate impact. The observed high temporal variability of the CO_2 to CH_4 ratio shows that it is very important to consider

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Table 2
Molar Ratios of GHGs (Either Concentration or Flux) Normalized to N_2O and CO_2/CH_4 Ratios in Various Rivers

System	Ref	Data type	Unit	CO_2	CH_4	N_2O	CO_2/CH_4
Elbe	This study	Conc	µmol/L	1666	4	1	476
German rivers	Mwanake et al. (2025)	Flux	mmol/m^2 d	14250	26	1	545
Global rivers	Diverse	Flux	Tmol/year	94286	1096	1	86
3 German rivers	Mwanake et al. (2023)	Flux	mmol/m^2 d	1847	3	1	633
Global rivers	Stanley et al. (2023)	Conc	µmol/L	4806	12	1	409
Global rivers	Stanley et al. (2023)	Flux	mmol/m^2 d	16000	79	1	203
Czech Stream	Mach et al. (2016)	Flux	kmol/year	2787	3	1	1102
Czech Stream	Hlavácová et al. (2006)	Conc	µmol/L	1435	8	1	169
20 streams New Hampshire	Herreid et al. (2020)	Conc	µmol/l	3091	12	1	250
Low gradient stream US	Carter et al. (2022)	Conc	µmol/L	4792	25	1	195
River Kongo	Borges et al. (2019)	Flux	mmol/m^2 d	112227	571	1	197
Rhine river	Mwanake et al. (2024)	Conc	µmol/L	2007	27	1	74
Rhine river	Mwanake et al. (2024)	Flux	mmol/m^2 d	808	37	1	22
Median				**3091**	**25**	**1**	**203**
Min				808	3	1	22
Max				112227	1096	1	1102

temporal variability when comparing the climate impact of different rivers. Although the ratio is affected by a large number of environmental factors, the numbers in Table 2 are surprisingly uniform. Whether this is due to a general regulator similar in different systems (like e.g. reaeration) remains to be investigated.

5. Conclusions

By analyzing GHG concentrations over 5 years, we identified season as the major factor influencing GHG ratios in a large German river. This also means that season is a dominant factor determining the climate impact of a river–probably more important than geographical factors. Thus, approaches to scale up riverine GHG emission should have a stronger focus on seasonality rather than spatial aspects. If we consider CO_2 emissions as climate neutral (because CO_2 derives mostly from new organic matter), periods with high CH_4 to CO_2 ratios (in our case summer) are interesting with respect to monitoring schedules as well as the timing of management options.

Interestingly, seasonal patterns were rather consistent between years. Although the seasonal pattern was similar for the different years, there was some inter-annual variability in emissions. When comparing annual mean GHG concentrations with annual means of different drivers (Figure S6 in Supporting Information S1) no clear relations emerge. Thus, to explain GHG concentrations in rivers, simple correlation analysis is not suitable.

The interactions between water and atmosphere influenced by the complex interplay of hydrological and biochemical processes are often nonlinear and context-dependent, making them difficult to capture with traditional models. Recent studies demonstrated that RF machine-learning models can be used to predict CH_4 (Rocher-Ros et al., 2023) or N_2O (Marzadri et al., 2021) concentrations globally. Brown et al. (2025) and papers therein present successful application of such models for predicting riverine gross primary production and ecosystem respiration from physical and chemical parameters, while a recent study by Mwanake et al. (2025) applied machine learning models to predict riverine GHG emissions across Germany using a combination of in situ water quality measurements and remotely sensed vegetation indices. Their approach showed that data-driven models can successfully capture spatial patterns and key drivers of emissions, even in complex and heterogeneous river networks. Our analysis confirms those observations—we could successfully predict riverine GHG conditions with high predictive power.

The value of such a model lies in its ability to reconstruct historical emissions from periods with data gaps, to identify seasonal or interannual trends, and to forecast future changes under varying environmental conditions. Moreover, the model provides insights into the key drivers of GHG dynamics and supports the development of

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scalable, data-driven approaches for riverine GHG monitoring and management. However, it is important to keep in mind that feature importance derived from ensemble models reflects predictive relevance within the selected feature set rather than direct mechanistic causality. Some predictors identified as important (e.g., day length) primarily represent seasonal co-variation of multiple environmental processes such as temperature, radiation, and biological activity, rather than acting as direct drivers of CH_4 dynamics. Similarly, SRP should be interpreted as an indirect indicator reflecting catchment inputs and trophic status, potentially linked to carbon cycling via primary production or carbonate chemistry, rather than a direct control on gas saturation. Consequently, feature importance results should be interpreted in a relative and context-dependent manner, complementary to correlation analyses and process-based understanding. We conclude that models driven by seasonal physical variables such as day length, temperature, and radiation can provide good predictive performance for GHG concentrations, especially at a certain study site. However, these variables primarily act as proxies for seasonal co-variation of multiple processes and should not be interpreted as universal mechanistic drivers across river systems. Mechanistically more constrained model variants focusing on gas-specific drivers (e.g., pH and DIC-related variables for CO_2, redox and organic matter proxies for CH_4) may provide improved generalizability across river systems, even if their statistical performance is lower than that of purely data-driven models.

Our results indicate a higher climate impact of the river under future global warming conditions. Climate change with longer and warmer summers probably extends the period of elevated CH_4 to CO_2 ratios in rivers. During previous decades, long-term trends of water temperature ranged between 0.13 and 0.92°C per decade in streams and rivers (Niedrist, 2023; Scott et al., 2023), and droughts are predicted to occur more frequently in the future (Spinoni et al., 2018). Shifting aquatic CH_4 to CO_2 ratios upwards under such conditions is a positive feedback mechanism further driving global warming.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Availability Statement

The data of this study are available at Koschorreck et al. (2025). The phyton code used for statistical modeling is available at Schütze (2025).

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