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Impact of water level management on organic carbon availability and nitrogen transformations in wetland sediments

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Abstract: The impact of water level management via water retention on benthic carbon and nitrogen fluxes was studied in a wetland of the Seine estuary. Carbon and inorganic nitrogen fluxes at the sediment-water interface were determined during periods of intermittent and permanent immersion along a lateral gradient. In addition to fluxes, nitrate reduction rates, quantity and quality of both sedimentary and dissolved organic carbon, and organic matter lability via external enzymatic activities were analyzed. During both periods, the sediments subject to water level management facilitated nitrogen removal, with potential NO_3^- fluxes averaging -109 ± 31 nmol NO_3^- cm^{-2} h^{-1} under permanent immersion and -34 ± 13 nmol NO_3^- cm^{-2} h^{-1} under intermittent immersion. During permanent immersion, more water retention favors a higher input of dissolved organic matter including fresh and labile compounds, which most likely explained the significantly higher NO_3^- influxes. Intermittent immersion resulted in a lower quantity of retained dissolved organic matter, which likely explains the low N fluxes. The results of this study indicate the implementation of water retention strategies can markedly enhance NO_3^- removal by increasing the availability of organic matter. This underscores the importance of considering water-level management of wetlands to sustain the ecological functions of these valuable ecosystems, which are often the first barriers against environmental disturbance.

Keywords: Benthic Nitrogen fluxes; Enzymatic activity; Organic carbon quality and quantity; Intertidal wetlands

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1. Introduction

Human activity has considerably disrupted natural biogeochemical cycles and ecosystem functioning, especially the nitrogen cycle (Gruber and Galloway 2008; Galloway et al. 2013), with serious environmental consequences. Excess nitrogen (N) in streams and rivers, often coupled with phosphorus (P), is the main cause of coastal eutrophication (Smith et al. 2006; Conley et al. 2009). Despite efforts to control nitrogen use in agriculture, its prevalence remains high (Bouwman et al. 2013; Mancuso et al. 2021). In this context, natural microbial nitrate elimination is an important ecological function crucial for mitigating excess nitrogen (Meng et al. 2014).

Intertidal wetlands, receiving elevated nitrate concentrations due to intensive agricultural and industrial activities in upstream watersheds (McLusky and Elliott 2004; Barbier et al. 2011), represent crucial areas for nitrate removal and play a significant role in regulating biogeochemical exchanges at aquatic-terrestrial interfaces (Fisher and Acreman 2004; Tanner and Kadlec 2013; Logozzo et al. 2021). These ecosystems, characterized by tidal inundation, create anoxic conditions necessary for microbial nitrate reduction. Moreover, the diverse organic carbon sources present in intertidal wetland sediments, derived from both terrestrial and aquatic origins, exhibit variability in composition and lability, influencing nitrate elimination via dissimilatory nitrate reduction to ammonium (DNRA) and denitrification (Dodla et al. 2008; Stelzer et al. 2014; Morelle et al. 2023).

Hansen et al. (2018) found that wetlands in the Mississippi River Basin are five times more effective, per unit area, at reducing nitrate concentrations in rivers compared to conventional land-based strategies. They suggest that restoring wetlands with consideration for their location in stream networks could greatly improve water quality beyond previous expectations. Indeed, according to a model by Craft et al. (2009), losing 45% of coastal wetlands in Georgia would result in a 23% decrease in soil nitrogen sequestration and a 25% decrease in denitrification. These findings highlight the importance of conserving and restoring wetlands.

However, wetlands in river basins are often associated with large areas of land used for agricultural production and anthropogenic activities that require water management (Downard and Endter-Wada 2013). This management often results in seasonal variations in water levels, mainly permanent immersion in winter and periods of intermittent immersion or even drought in summer, which strongly alter ecosystem dynamics and natural biogeochemical cycles (Friedl and Wüest 2002), including nitrate reduction capacity (White and Kaplan 2017). Seasonal water level changes can disrupt the balance between anoxic and oxic conditions that play a role in the different processes in the carbon and nitrogen cycle (Carey et al. 2022). Permanent immersion is likely to create anoxic conditions favorable for denitrification, whereas intermittent immersion can expose sediments to oxygen, enhancing nitrification (Kuypers et al. 2018). The latter would increase nitrate production and thus potentially decrease the overall nitrate removal efficiency. Furthermore, permanent immersion can impact the availability and composition of organic carbon sources in several ways.

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Immersion can enhance the input of organic matter from allochthonous sources, change the chemical composition of the available OM (Kaiser et al. 2015), and affect decomposition rates (Mckew et al. 2013), especially by influencing aerobic decomposition. Thereby influencing microbial activity and the overall efficiency of nitrate reduction processes (Morelle et al. 2023). These dynamic conditions necessitate a better understanding of how water management practices influence biogeochemical processes and the capacity of wetlands to provide essential ecosystem services, such as water purification and nutrient cycling.

This is especially important considering that water resources are affected by climate change in the form of available water scarcity in watersheds, which will increase the need for water management among different water users, particularly between the agricultural sector and wetland ecosystem services. Field and laboratory studies are needed to complement existing knowledge and more accurately assess these effects in order to enhance management practices.

Within this context, this study aims to investigate the impact of water level management on organic carbon availability and nitrogen transformations in the sediment of a temperate intertidal wetland during two contrasting periods of intermittent and permanent immersion.

The specific objectives were (1) to determine how periods of permanent and intermittent immersion influence the availability and sources of organic carbon in wetland sediments. (2) Determine consequent effects of these water management regimes on nitrogen fluxes, with a focus on nitrate reduction. By addressing these objectives, the study seeks to provide insights that can inform public policies and decision-makers on improving water-level management practices to improve wetland ecosystem services.

We hypothesize that during permanent immersion, organic carbon of aquatic origin from estuarine river water will influence carbon availability, while carbon of more terrestrial

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origin will dominate during intermittent immersion, impacting nitrogen fluxes at the sediment-water interface. To test these hypotheses, four different sites along a lateral gradient of immersion impacted by water management were sampled at both period, which included a non-impacted site to assess natural seasonal variability. To understand the spatial and temporal impacts of water management on these processes, we determined potential benthic nitrogen and carbon fluxes, assessed the quantity and quality of sedimentary and dissolved organic matter, as well as the external enzymatic activities as proxies for organic matter lability.

2. Material and Methods

2.1. Study site and sampling

The wetland under study is located in the northeast of the downstream Seine estuary (49° 26 '50.04 " N; 0° 22' 59.39” E; Normandy, France). It includes agricultural areas, artificial ponds for waterfowl hunting, and a reed bed (Fig. 1). Grazing and mowing are practiced in the agricultural areas, with possible alternation (grazing after mowing) within the same season. Water level is managed by a valve located between the reed bed and the agricultural lands (Fig. 1). When the valve is lowered, water from the estuary enters the wetland at high tides through one-way flaps. In the stagnant waters retained by the valve, the water level, temperature, and conductivity are continuously measured at 1-hour intervals using a self-contained system OTT ecoLog 800 (OTT HydroMet GmbH, Kempten, Germany). In conjunction with the rise in groundwater levels due to the rainy season, the wetland is mainly in permanent immersion from October to April. During the rest of the year, due to the drop in groundwater levels caused by the dry season, the wetland undergoes periods of drought with intermittent immersions during spring tides. From August to October, to increase the water level in the wetland, mainly for anthropogenic activities, the valve is

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lifted by the “national natural reserve of the Seine estuary” (RNNES) 2 hours before and closed 1.5 hours after high tides allowing a higher refill of the wetland.

Four sites were selected based on their distance from the river and the valve. Three sites were influenced by water management, with varying proximity to the valve. The furthest site (S1) was approximately 2,000 meters away from the valve, while the closest (S3) was around 150 meters. The intermediate site (S2) was located at approximately 700 meters (Fig. 1). A fourth site (M), non-impacted by the water management, was located on the riverbank flooded at high tide and uncovered at low tide. Sampling was carried out in September 2020 and March 2021 corresponding respectively to intermittent and permanent immersion periods.

At each site, salinity in overlying water was measured three times using a hand refractometer. Three sediment cores per site (inner diameter: 6 cm, height: 10 cm) were collected within a restricted perimeter (10-15 cm between cores) to minimize spatial heterogeneity and stored at 4°C for 2-4 hours before potential benthic flux determination. Sediment surface samples were also collected using Plexiglass® rings (Inner diameter: 4.2 cm, thickness: 0.4 cm, height: 2 cm) for nitrogen reduction and production rate measurements performed within 24h. Rings with sediment were transported in anoxic bags and stored at 4°C. Additionally, a large core (inner diameter: 9 cm, height: 4.5 cm) was sampled. After being cautiously homogenized, a sub-sample of the large core (2.75 ± 0.02 g) was conserved at -20°C until analyses of external enzymatic activities, and 3 replicates of 10 ml were weighted, stored at -20°C and freeze-dried for 48 h. The moisture content (%) was determined as a percentage relative to the total dry weight. One replicate was then conserved for particle grain size determination, and another was ground for analyses of the elemental composition.

2.2.Potential benthic flux determination

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For each period, the 12 sampled cores (4 sites × 3 replicates) were placed together in an opaque tank at controlled temperature (21 °C). To obtain a non-limiting NO_3^- environment, 150 ml of artificial seawater, with the salinity of the sampling site, containing nitrate at a concentration of 500 µM was added on each core. The upper water layer in each individual core was aerated using an air pump allowing the water column to stay oxic throughout the incubation. Then, the surface was protected from light using an opaque cover to avoid photosynthetic activity at the sediment-water interface. At four different incubation times (10, 40, 130, and 250 minutes), 5 ml of the overlying water was sampled from each core using sterile syringes (PP 10 ml) and directly filtered into 5 ml Eppendorf tubes on sterile syringe filter units (0.22 µm; Millex®). For each filtered sample, 2 ml were immediately used for measurement of ammonium (NH_4^+), nitrate (NO_3^-) and dissolved organic carbon (DOC) concentrations while the remaining 3 ml were conserved at 4°C for DOM analyses.

Ammonium (NH_4^+) and nitrate (NO_3^-) concentrations were determined using a Gallery™ Discrete Analyzer (ThermoFisher scientific, Waltham, Massachusetts, USA). The DOC concentrations were determined using a Shimadzu TOC V-CSH total carbon analyzer with the non-purgeable organic carbon method. The calibration was performed using potassium hydrogen phthalate as standard solution. The samples were acidified with 5% of Hydrochloric acid 2N and bubbled with air during 2 min to eliminate inorganic carbon before injection. The uncertainty on the measurement estimated by the 95% confidence interval is 0.4 ppm.

The potential benthic fluxes across the sediment–water interface in each core were assessed by using the change in the molar concentration of the solute and the known volume of overlying water as a function of incubation time and surface area of the sediment core (Aller et al. 1985), expressed in nmol cm^{-2} h^{-1}. NO_3^- fluxes were determined over the entire period (i.e. 0 - 250 min). The NH_4^+ and DOC fluxes were calculated between 10 and 250 min

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of incubation to avoid the effect of the initial elemental desorption. A negative value of potential benthic flux represents an overall decrease in solute concentration in the overlying water during the incubation time while a positive value represents an overall increase in solute concentration in the overlying water. Beside the potential fluxes, *in situ* fluxes were estimated by correcting potential values to correspond with the field temperature by using a temperature to benthic fluxes dependency coefficient (Q_{10}) of 1.8 as determined in aquatic coastal sediments (Laverman et al. 2006).

2.3. Dissolved organic matter spectroscopic analyzes

Dissolved organic matter (DOM) was characterized by fluorescence spectroscopy. Excitation-emission matrix (EEM) fluorescence spectra were acquired in 1 cm path length quartz SUPRASIL® QS cuvettes (Hellma) thermostated at 20 °C, using a Horiba Scientific Aqualog spectrofluorometer in ratio mode equipped with a 150W Xenon lamp and 5 nm bandwidth. EEM spectra were performed using a double-grating monochromator for excitation at wavelengths of 240-800 nm with 5 nm intervals and high CCD detector gain at emission wavelengths of 245-830 nm with approximately 0.58 nm (1 pixel) intervals and 2 seconds integration time. Samples were diluted when necessary to achieve absorbance values below 0.1 to avoid inner filter effects. Sample EEM spectra were obtained by subtracting an ultrapure water (Milli-Q, Millipore) blank spectrum and were instrumentally corrected. Fluorescence intensities were normalized to the area under the Raman peak of the blank spectrum at excitation wavelength 350 nm and expressed in Raman units (RU). Three fluorescence indices were then calculated using the TreatEEM software (Omanović et al. 2023) to obtain information on DOM origin, maturity, and transformation: the humification index (HIX), linked to the aromaticity and maturity of DOM (Zsolnay et al. 1999); the fluorescence index (FI) providing information on microbial *versus* terrestrial sources

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(McKnight et al. 2001); and the biological index (BIX), proxy of fresh DOM production related to biological activity (Huguet et al. 2009).

Then, PARAllel FACtor Analysis (PARAFAC) was used to decompose the EEM spectra for a better identification and assessment of the composition of fluorescent DOM. The multi-way analysis model was run for 3 to 8 components with nonnegativity constraints using the DOMFluor toolbox (ver. 1.7) for MATLAB (R2021b) as described by Stedmon and Bro (2008). The final number of components was validated by split half analysis and residual assessment (Stedmon and Bro 2008; Murphy et al. 2013). Five components C1 to C5 (table 1) were then determined and compared to those identified in other studies through the online spectral library OpenFluor (Murphy et al. 2014). These components successfully matched in the OpenFluor database with Tucker congruence coefficient of over 0.98 on the excitation and emission spectra simultaneously.

To assess the impact of water management on DOM quantitatively, the cumulative fluorescent DOM (FDOM) intensity (ΣF_{max}) was calculated by summing the maximum fluorescence intensity (F_{max}) of the individual components (C1 to C5).

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2.4.Flow-through reactor experiments

Nitrate reduction rates (NRR) and ammonium production rates (APR) in the top sediment layer (0-2 cm) were assessed using flow-through reactor (FTR) experiments (Morelle et al. 2022). A 0.2 µm pore size PVDF (Durapore®) membrane filter and a glass fiber backing filter (1.2 mm thick, 4.7 cm diameter, PALL Corp., NY) were placed on both sides of the sampled Plexiglass® rings. Each ring was enclosed by POM (poly-oxy methylene) Delrin® caps with inflow and outflow channels. Reactors were supplied with an inflow solution containing 5 mM nitrate at a constant flow rate ($Q = 2 \pm 0.15$ mL h^{-1}) using a peristaltic pump (Gilson minipuls) for 24 hours. The salinity of the inflow solutions matched the site salinity, and the pH was adjusted to ambient conditions (pH = 8) using $NaHCO_3$ (0.2 g L^{-1}). To ensure anoxic conditions, input solutions were purged with O_2–free N_2 for 5 minutes before the experiment. FTR experiments were conducted at a constant temperature (21 ± 2°C) and protected from light to prevent photosynthesis. After 16 hours of incubation to stabilize the FTR, reactor outflow samples were collected twice at 4-hour intervals (16h-20h and 20h-24h) and immediately analyzed for ammonium (NH_4^+) and nitrate (NO_3^-) concentrations using a Gallery™ Discrete Analyzer (ThermoFisher scientific, Waltham, Massachusetts, USA). NRR and APR (nmol cm^{-3} h^{-1}) were calculated as $R = (\Delta C \times Q)/V$, with Q the volumetric flow rate, V the reactor volume (27.7 cm^3), and ΔC the absolute difference in concentration of solute between the inflow solution and the outflow sample.

2.5.External enzymatic activities

Potential external enzymatic activities (EEAs) were measured following the method described in Morelle et al. (2023). The enzymes measured were those which catalyze (i) the degradation of organic carbon by converting cellulose into cellobiose (1,4-β-D-cellobiohydrolase [CBH]) and cellobiose into glucose (β-1, 4-glucosidase [GLU]), and (ii) the degradation of organic nitrogen (L-leucine aminopeptidase [LAP]). For each site, the 2.75 ± 0.02 g sediment sample previously stored was homogenized in 91 ml of 50 mM sodium acetate buffer to obtain a sediment solution (SS). Then, in a black flat-bottomed 96-well plate, with two analytical replicates per site and per enzymes, 120 µl SS per replicate was added using an eight-channel pipette. For each SS, standard curves for 4-methylumbelliferone and 7-amino-4-methylcoumarin (60 µl of respectively 0–100 µM and 0–10 µM concentrations), and controls without substrate addition (120 µl SS + 60 µl Milli-Q water), were included. The sediment solutions were incubated with fluorometric substrates for 3-h at 25°C with a resuspension of the mixture within the wells every 30 min using an eight-channel pipette.

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After incubation, fluorescence was measured by a microplate reader (SAFAS Xenius XM, SAFAS Monaco) at 365 nm excitation and 450 nm emission. From fluorescent values and standard calibration curves, each enzymatic activity was calculated and converted in nmol g^{-1} dry sediment h^{-1}.

2.6.Sediment characteristics

The particle grain size distribution was determined for each site by laser diffraction using a Malvern particle size analyzer in combination with a liquid sample autosampler. The mud sediment fraction was estimated as the percentage of silt particles < 63 µm (% of fine). The total organic carbon and total nitrogen contents (C_{org}; N_{tot}) and the stable isotope natural abundances ($\delta^{13}C$; $\delta^{15}N$) were determined with an elemental analyzer (Vario PYRO cube, Elementar, Hanau, Germany) coupled to an isotope-ratio mass spectrometer (Isoprime, Micromass, Manchester, UK). The standard gas was calibrated in relation to the international standard (PeeDee Belemnite-190PDB). The N_{tot} and $\delta^{15}N$ values were determine for each sampled site using a sub-sample of freeze-dried and crushed sediment placed into a tin capsule. Another sub-sample was acid treated with 2N HCl to remove the carbonate and subsequently rinsed with deionized water. After centrifugation, the carbonate-free pellet was dried at 60 °C, and manually crushed before being placed into a tin capsule for determination of C_{org} and $\delta^{13}C$. The coefficient of variation was 0.2‰ for $\delta^{13}C$ and 0.3‰ for $\delta^{15}N$. N_{tot} and C_{org} were expressed as percentage of the dry sediment mass and C_{org}:N ratio (molar:molar) was calculated.

2.7.Statistical methods

Statistical tests were conducted using R V4.3.1 and Sigma-Plot V12. Shapiro-Wilk normality test determined whether the data deviated from a normal distribution, while Bartlett

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or Levene tests assessed homogeneity of variances. Upon validation, differences between sites for each period concerning the measured parameters was evaluated through one-way ANOVA followed by a TukeyHSD test. If normality and variance conditions were not met, a Kruskal-Wallis test followed by a pairwise t-test was performed. Significant differences between periods for each site were determined using a t-test or Mann-Whitney Rank Sum test for non-parametric values. Correlations between variables were assessed using the Pearson correlation coefficient (r). Finally, a principal component analysis (PCA) was conducted using the "FactoMineR" package. The PCA was applied to the entire dataset, with immersion status as supplementary qualitative variable and benthic fluxes (NO_3^-, NH_4^+, and DOC) and rates (NRR, APR) as supplementary quantitative variables.

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3. Results

3.1. Water and sediment characteristics

In accordance with the natural seasonal cycles, the temperature values were higher during intermittent immersion than during permanent immersion. During sampling, water temperature was at 14.2 ± 0.2°C in September (intermittent immersion) and at 8.9 ± 0.2°C in March (permanent immersion) while salinity values (PSU) were respectively between 6.4 and 8.4 and between 0.5 and 1.0 without significant differences between sites.

The percentage of fine particles (< 63 µm) in the sediment showed lower values (<70%) at sites S1 and M than at S2 and S3 (>80%; Table A.1). The moisture content of the sediment varied from 34.3 to 50.7% depending on the site with the lowest values observed at site 2 for both periods. The elemental characterization of the sediment samples showed the lowest $\delta^{13}C$ and $\delta^{15}N$ values at S1 and similar values on the other sites. The total nitrogen content (N; %) and the total organic carbon (C_{org}; %) led to C_{org}:N ratios (molar:molar) lower at S1 and S2 (< 10) located in the wetland than at S3 and M (up to 20) located near to the river, showing a significant positive correlation with the moisture content.

3.2. Dissolved organic matter (DOM) characteristics

The fluorescence of dissolved organic matter (FDOM) released from the sediment to the overlying water was characterized by five components (C1 to C5 – Table 1) explaining over 99.7% of the variability in the entire EEM spectra dataset.

During intermittent immersion, no significant differences on cumulative FDOM intensity were recorded between site, managed or not (fig. 2a). In contrast, during permanent immersion, significantly higher ΣF_{max} values were observed in S1 compared to S3 and M (aov, $p < .01$). Results revealed that ΣF_{max} was significantly lower (t-tests, $p < .05$) during intermittent compared to permanent immersion for sites under water management (S1, S2, and S3). Conversely, there were no difference in ΣF_{max} between the two periods at the non-managed site M (t-test, $p = .97$).

Despite these variations, the relative fluorescence of each FDOM component (Fig. 2c and 2d) was minimally impacted by water management, with only C3 showing a significant lower relative abundance during intermittent immersion, while C4 showed a higher relative abundance.

The FDOM indices (HIX, BIX, and FI) exhibited minor differences between immersion periods and sites (Table A.1). During intermittent immersion, HIX at site M was lower compared to the managed sites (S1, S2, S3), while during permanent immersion, HIX was higher at site M than at the managed sites. Similarly, the BIX index was higher at site M than managed sites at both periods. Furthermore, FI at site M was lower during permanent immersion compared to intermittent immersion, with a significantly higher FI value at site M

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compared to the managed sites during intermittent immersion. No significant differences in FI were observed between sites during permanent immersion.

3.3.Potential enzymatic activity

The lability of C and N-related organic compounds in the sediment samples was evaluated through external enzymatic activities (EEA). Higher EEA values were consistently observed during permanent immersion compared to intermittent immersion across all sites (Table A.1), suggesting increased microbial activity associated with organic matter degradation during permanent immersion. For all EEA, the most terrestrial site (S1) exhibited the highest values during both periods (Table A.1).

A significant positive correlation ($p < .001$) was found among all EEA, suggesting that environmental conditions may similarly influence the degradation of C and N-related organic compounds. Regarding specifically the C-related EEA, the glucosidase-EEA values were, on average, 2.7-fold higher than the cellulase-EEA across all sites.

3.4. Benthic fluxes

The potential benthic NO_3^- fluxes were negative in each core, ranging from -5.8 to -154.5 nmol NO_3^- cm^{-2} h^{-1} (Fig. 3a), showing the potential of all sampled sites to remove nitrate from the overlying water. Sites submitted to water management (S1, S2, and S3), showed higher NO_3^- influxes during permanent compared to intermittent immersion with on average -109.4 ± 31.2 and -33.5 ± 12.6 nmol NO_3^- cm^{-2} h^{-1} respectively. Inversely, lower NO_3^- influxes were observed at the non-managed site M during permanent compared to intermittent immersion with on average -29.9 ± 1.2 and -41.5 ± 3.7 nmol NO_3^- cm^{-2} h^{-1} respectively. During permanent immersion, the NO_3^- influxes for sites 1, 2, and 3 were higher than for the

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non-managed site M. During intermittent immersion, the lowest NO_3^- influxes were recorded at the most terrestrial site (S1) with on average -15.4 ± 6.4 nmol NO_3^- cm^{-2} h^{-1}.

The potential benthic NH_4^+ fluxes, ranging from -0.5 to 15.6 nmol NH_4^+ cm^{-2} h^{-1} were also higher during permanent compared to intermittent immersion for all sites (Fig. 3b). For both periods, the non-managed site M showed lower fluxes (respectively -0.2 ± 0.2 and 0.5 ± 0.4 nmol NH_4^+ cm^{-2} h^{-1}) compared to the sites submitted to the water management (on average 1.1 ± 0.8 and 7.9 ± 4.2 nmol NH_4^+ cm^{-2} h^{-1} respectively). The NH_4^+ fluxes were negatively correlated with the NO_3^- fluxes during permanent immersion ($p < .001$, r = -0.91), such a correlation was absent during intermittent immersion (p = 0.21).

The potential benthic fluxes of dissolved organic carbon (DOC) ranged from -17.5 ± 22.0 nmol C cm^{-2} h^{-1} at site M during intermittent immersion to 36.8 ± 13.2 nmol C cm^{-2} h^{-1} at S1 during permanent immersion (Table A.1). Due to a large variability between replicates, no significant differences between periods or sites were observed. Nevertheless, both for intermittent and permanent immersion, the average DOC fluxes were lower at the intertidal site M (-17.5 ± 22.0 and 0.5 ± 3.0 nmol C cm^{-2} h^{-1} respectively) compared to the managed sites (on average 3.4 ± 22.8 and 25.4 ± 14.5 nmol C cm^{-2} h^{-1} respectively). The DOC fluxes showed a significant positive correlation with the NH_4^+ fluxes ($p < .01$, r = 0.75) and a significant negative correlation with the NO_3^- fluxes ($p < .01$, r = -0.81) for the sediments exposed to a permanent immersion. No significant correlations were observed during intermittent immersion.

In order to estimate the *in-situ* benthic fluxes, the potential fluxes were transformed using a Q_{10} of 1.8 resulting in predicted *in situ* benthic NO_3^- fluxes ranging from -3.5 to -31.5 nmol NO_3^- cm^{-2} h^{-1} (Table A.1). In contrast to the potential fluxes, the temperature differences between the two periods led to estimated NO_3^- fluxes higher during intermittent than permanent immersion for sites S2, S3, and M. For the site S1, NO_3^- influxes were still higher during permanent than intermittent immersion. The estimated *in-situ* benthic NH_4^+ fluxes ranged from -0.29 to 2.31 nmol NH_4^+ cm^{-2} h^{-1} with no significant difference between periods or sites (Table A.1).

3.5.Nitrate reduction and ammonium production rates

The nitrate reduction rates (NRR; fig. 4a) showed more differences between sites than periods. Only S1 showed a significant seasonal variation, with higher NRR values during permanent (139.5 ± 14.5 nmol cm^{-3} h^{-1}) compared to intermittent immersion (60.9 ± 8.5 nmol cm^{-3} h^{-1}). During the intermittent immersion, significant differences in NRR values were observed among sites, with the lowest values at S1 and the highest values at S3 (176.9 ± 12.8 nmol cm^{-3} h^{-1}). The NRR values at S2 (115.6 ± 2.7 nmol cm^{-3} h^{-1}) were significantly different from S1 and S3 but not different from site M (107.4 ± 10.4 nmol cm^{-3} h^{-1}).

The ammonium production rates (APR; fig. 4b) showed more seasonal than site differences. During the intermittent immersion, S3 showed significantly higher APR values (4.3 ± 0.3 nmol cm^{-3} h^{-1}) than the other managed sites (S1 and S2 with on average 1.3 ± 0.6 nmol cm^{-3} h^{-1}) but not significantly different from site M (2.7 ± 0.8 nmol cm^{-3} h^{-1}). During permanent immersion, the significantly lowest APR were recorded at site 2 (4.1 ± 1.3 nmol cm^{-3} h^{-1}) while the highest values were recorded for S1 and S3 (on average 15.4 ± 0.8 nmol cm^{-3} h^{-1}). Site M was the only site with no seasonal differences; for all managed sites, the APR values were significantly higher during permanent than intermittent immersion.

3.6.Correlations

The principal component analysis (PCA) performed on the dataset explained 56.1% of total inertia considering the two first dimensions and 72.9% by including the third one, each presenting eigenvalue higher than 1 (Kaiser criterion). The 1st dimension was mainly driven

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positively by the C-EEAs (17.3%) and the N-EEA (16.8%), and negatively by the $\delta^{13}C$ (16.1%) and $\delta^{15}N$ (14.7%) which exhibited the highest contribution and proximity to the 1st axis. The 2nd dimension was influenced by both the N content (20.2%) and the BIX (22.6%), while the 3rd dimension was mainly driven by the C_{org} (24.5%) and the C_{org}:N ratio (21.5%). The response variables (benthic fluxes and rates) were negatively oriented with the 2nd axis and positively with the 3rd axis, with NRR particularly close to the 2nd and the 3rd axes. The correlation circle of the 1st and 2nd dimensions (fig. 5) was selected for presentation, while the 3rd dimension was not shown, due to a more contrasted representation of the ellipses. The angles between the response variables related to the fluxes of carbon (F-DOC) and ammonium (F-NH_4^+ and APR) and the structuring variables related to organic carbon (EEA, ΣF_{max}) suggested positive inter-correlation. The ellipses of the analysis enable clear differentiation of the sites where immersion was controlled from the non-managed site M, the latter being mainly positively linked with BIX and negatively to the values of total nitrogen in the sediment (N). Regarding the orientation of the vectors for the managed sites, the analysis revealed that permanent immersion was more favorable for carbon accumulation and lability as well as NO_3^- influxes than the intermittent one (fig. 5).

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4. Discussion

This study aimed to examine how wetland water level management affects nitrogen reduction capacities in relation with sediment organic carbon during intermittent and permanent immersion. Our results support our initial hypothesis that more organic carbon from estuarine river water was retained in the wetland during permanent immersion, enhancing carbon availability and lability, and thus positively impacting nitrogen fluxes and nitrate reduction. Contrary to expectations, intermittent immersion resulted in limited organic carbon supply from the river, thereby constraining carbon degradation and nitrate reduction.

These results underscore the significant influence of water management on dissolved organic matter quantity and quality, as well as on benthic nitrogen fluxes and especially reduction rates.

4.1. Impact of water management on benthic organic matter

The impact of permanent or intermittent immersion on sedimentary organic matter (sedOM) was not evident, as indicated by the lack of seasonal variation in sedimentary parameters. The different sites showed distinct sedOM signatures however, assessed through C_{org}:N ratios and $\delta^{13}C$, which can be used to distinguish the origin of sedOM (Lamb et al. 2006). These signatures were largely explainable based on the hydrological regime of the different sites, which were in turn influenced by water management practices.

The site closest to the valve and most influenced by river input (S3) exhibited a C_{org}:N ratio averaging 17.7 and a $\delta^{13}C$ of -26.5 for both periods, considered as a terrestrial sedOM signature (Lamb et al. 2006). This is most likely the result of the functioning of the valve, which maintains water level equilibrium by overflowing, resulting in low currents and the accumulation of terrestrial debris settling at the valve, as evidenced by high percentages of fine particles. This likely influenced terrestrial sedOM accumulation in sediment.

For sites S1 and S2, the SedOM signature suggested that organic carbon originates mainly from freshwater microalgae, with C_{org}:N ratios lower than 10 (Lamb et al. 2006). At these sites, shallow water with low currents during summer, resulting from intermittent immersion, created favorable conditions for freshwater microalgae growth (Hitchcock 1980; Stal 2010; Hussain et al. 2014). This is further supported by the surrounding agricultural land, which provides ample nutrients through fertilization and presence of cattle, facilitating algal growth (Steinman et al. 2003; Atkinson et al. 2011).

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The sedOM signature at the intertidal and non-managed site M, with C_{org}:N ratios over 13 more related to plant than algae (Lamb et al. 2006), may be attributed to tidal waves and currents preventing the deposition of sinking phytoplankton (Huettel and Rusch 2000), confirmed by a low percentage of fine particles. Currents are also likely to enhance the resuspension of microphytobenthic biofilms exported to the river (Redzuan and Underwood 2021). Furthermore, OM from plants is refractory and well-preserved in mudflat sediments compared to OM from microalgae (Burdige 2007), which degrades rapidly due to its easily degradable structure (Nielsen et al. 2004; Bouillon and Boschker 2006; Kawaida et al. 2019; Morelle et al. 2023). The sedOM signature at site M is thus likely the result of physical removal of algal material and its rapid degradation via mineralization, consistent with previous findings in the Seine Estuary (Thibault et al. 2019).

4.2. Impact of water management on dissolved organic matter

Water management significantly influenced the quantity and quality of fluorescent dissolved organic matter (FDOM) within the studied wetland. During permanent immersion, FDOM intensities were higher compared to intermittent immersion, indicating greater quantities of dissolved organic matter (DOM) in the water. Permanent immersion likely facilitated the transfer of DOM from sediment into the water column, resulting in the accumulation of dissolved organic compounds (Wright and Reddy 2009). Longer water residence times most likely promoted the transformation of complex, terrestrially-derived DOM into more labile components, fueling microbial respiration and production, as has been shown in streams and lakes (Ejarque et al. 2018; Boodoo et al. 2020). Rainfall generally increases terrestrial DOM input, likely contributing to higher FDOM concentrations in winter (Wang et al. 2021). Aquatic DOM from the estuary, entering through the valve, also contributed to the total DOM pool (Wright and Reddy 2009), further increasing FDOM

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intensity at managed sites. The multiple sources and water retention through the valve consistently increases the quantity of FDOM in the overlying water during permanent immersion.

On a lateral basis, sites exhibiting terrestrial FDOM signatures and high FDOM intensities, particularly site S1, also likely received additional DOM input from surrounding agricultural lands. The higher FDOM intensities and external enzymatic activities (EEA) observed at S1 suggest that the microbial community is more active and efficient than at other sites (Miller and Moran 1997; Gonnelli et al. 2013). Differences in DOM composition are most likely related to variations in bacterial community composition and activity (Blanchet et al. 2017). The higher total organic carbon content (C_{org}) at sites 1 and 3, compared to sites 2 and M, showed a sedimentary OM signature mainly of terrestrial plant origin. This could partly explain the lateral differences recorded in EEA, as rhizosphere soil EEA is generally higher than that of bulk soil (Gianfreda 2015).

High EEA and FDOM intensities during permanent immersion indicate stimulated decomposer activity and increased OM lability due to organic carbon supply. This is consistent with higher DOC and NH_4^+ effluxes during this period, which are indicators of organic matter degradation (Gerringa 1990; Grzybowski 2002). Numerous studies have demonstrated that external carbon input significantly and positively increases organic carbon decomposition (Mack et al. 2004; Shaver et al. 2006; Stern et al. 2007), which aligns with the positive response of microbial activity to organic carbon input.

The hypothesis that DOM supply is related to water management is supported by lower FDOM intensities during intermittent immersion. This is also supported by the lack of seasonal total FDOM intensity variation at the non-managed site M, which consistently experiences the same hydrological regime associated with tides. The higher BIX values, along with the increased relative fluorescence intensity of PARAFAC components C2, C3, and C5

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at site M compared to the managed sites, also support this assumption. These results illustrate the presence of more recently produced estuarine FDOM (Huguet et al. 2009) at site M and a more terrestrial signature of FDOM (higher proportion of C1 and C4) at the managed sites. Higher HIX values during intermittent immersion suggest a more degraded and humified organic matter content in the sediment. However, BIX values remain high for the managed sites. Mladenov et al. (2005) reported microbial degradation of fresh OM due to higher leaching of plant litter in seasonal marshes compared to permanent immersed marshes. This finding aligns well with the high values of HIX and BIX obtained during intermittent immersion and elucidates the higher relative fluorescence of the PARAFAC component C4 (terrestrial origin) observed during this period.

Conversely, BIX values remain relatively high during permanent immersion while HIX values are relatively low at managed sites, reflecting potential FDOM transformation processes (Huguet et al. 2009). A similar FDOM composition (Fig. 2d) is observed during permanent immersion for the managed sites, particularly for S1 and S2, contrasting with the PARAFAC component compositions observed during intermittent immersion (Fig. 2c). This could be explained by the rapid DOM flux from sediment to overlying water at the beginning of submersion, followed by a decrease over time (Wright and Reddy 2009), and by the longer residence time of the water, which allows DOM quality to stabilize (Wang et al. 2021).

Overall, the results confirm that spatial and seasonal variations in FDOM is intricately linked to the supply of organic carbon and the dynamics of the ecosystem (Lu et al. 2003; Maie et al. 2006), including water dynamics influenced by management practices. Additionally, the results underscore the significance of such management practices in influencing biological processes and associated ecological functionalities (Richter et al. 2003), particularly in relation to the availability and lability of organic matter.

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4.3. Consequences for nitrogen removal from the overlying water

The nitrate reduction rates (NRR) and NO_3^- fluxes into the sediment demonstrate the capacity of these sediments to remove NO_3^- from the overlying water across all sites and both periods, aligning with measurements from other shallow brackish and coastal wetlands (Tomaszek et al. 1997; Sundbäck and Miles 2002; Racchetti et al. 2011). These results further demonstrate that regular and permanent immersion through river connection enables higher NO_3^- fluxes compared to when the wetland is isolated and receives little to no water from the river, as suggested by Racchetti et al. (2011). This is particularly notable for S1, which experienced the greatest impact due to limited immersion during summer and exhibited the most pronounced seasonal differences in NO_3^- fluxes and NRR. The restriction on OM availability and lability due to intermittent immersion may have decreased the potential for NO_3^- reduction and nitrogen fluxes. These findings overall confirm that continuous immersion in wetland areas leads to increased NO_3^- reduction, as evidenced in other wetlands (Saunders and Kalff 2001; Czuba et al. 2018). On the other hand, the non-managed site M, characterized by a tide-related hydrological regime rather than seasonal water management fluctuations, exhibited no significant seasonal variation in NO_3^- fluxes. Therefore, it can be inferred that the observed seasonal variation, with higher potential NO_3^- fluxes measured at the managed sites in winter (fig. 3), stems from differences in immersion regimes due to management practices between periods.

The observed positive correlations between nitrogen removal factors (NO_3^- fluxes, NRR) and indicators of OM degradation (EEA, DOC and NH_4^+ fluxes, and APR) during permanent immersion imply that the primary NO_3^- reduction process is likely coupled with organic carbon oxidation, such as denitrification, or DNRA (Tiedje 1988; Kuypers et al. 2018). However, DNRA, by reducing NO_3^- to NH_4^+, would result in increased NH_4^+ production and fluxes. Therefore, our results, with relatively low NH_4^+ effluxes and APR values compared to NRR, suggest that DNRA is of minor importance. This supports the assumption that under conditions of prolonged submersion in river-connected wetlands, denitrification predominates in NO_3^- reduction (Racchetti et al. 2011; Zhang et al. 2016).

Overall, our study suggests that water influx into the wetland, particularly through permanent immersion, is essential for the input of DOM, as evidenced by measurements of FDOM. This input includes organic compounds from both surrounding vegetation and decomposed matter from the river, as indicated by the different PARAFAC components (Table 1). The addition of DOM stimulates microbial enzyme production (Fontaine et al. 2003; Schimel and Weintraub 2003), accelerating the breakdown of organic matter into simpler compounds, which leads to the higher extracellular enzyme activity (EEA) measured during the permanent immersion period. These readily available compounds are favored carbon sources for nitrate reduction (Morelle et al. 2023). Consequently, the enhancement of organic matter degradation likely contributes to increased NO_3^- fluxes (Fig. 3a), predominantly through denitrification, which, when complete, recycles NO_3^- to its inert gaseous from, N_2. Therefore, the permanent immersion of the wetland not only improves access to DOM but also enhances degradation activity, thereby improving the ability to reduce NO_3^- by utilizing degraded compounds as a carbon substrate.

However, anthropogenic water management of the studied wetland induces seasonal fluctuations in water levels, with permanent immersion primarily occurring in winter when temperatures are low. Temperature plays a crucial role in activating biogeochemical processes (Veraart et al. 2011; Shen et al. 2020), with lower temperature resulting in reduced NO_3^- removal (Shen et al. 2015). The influence of temperature on NO_3^- removal was evaluated by adjusting measured potential fluxes based on in-situ temperatures to estimate actual fluxes. This adjustment revealed lower *in situ* NO_3^- influxes in winter compared to summer. Nonetheless, NO_3^- influxes during winter remained significantly higher in the managed sites

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compared to the non-managed site M. Consequently, these results suggest that permanent immersion supports NO_3^- removal from the overlying water through the supply of labile OM, but the overall impact on nitrate removal is limited due to low temperature during immersion.

5. Conclusion

The water management of the studied wetland led to stagnant water bodies during several winter months and dewatering during the remainder of the year, resulting in successive summer droughts. The results of this study indicate that permanent immersion, promoted by water management, may have a positive impact on organic carbon accumulation, organic matter degradation, and nitrate removal. However, as permanent immersion mainly occurred during winter, its positive impact was limited due to low temperatures. In contrast, stagnant water combined with summer temperature could potentially lead to high nitrate removal. Nevertheless, despite nitrogen fluxes remaining negative and higher than those in winter, the lack of organic carbon supply in summer appears to limit carbon and nitrogen cycling. These findings underscore the critical importance of considering water level management in wetlands to support essential ecosystem functions. Orienting water management in summer towards water retention and consequent carbon accumulation might enhance nitrate removal from the overlying water in these wetlands. Water resource management policies must fully integrate the potential effects of water-level fluctuations on wetland ecosystems. Maintaining hydrological regimes conducive to both water quality preservation and biogeochemical processes, such as nitrogen reduction in wetland sediments, is essential. An integrated approach to land and water management is needed, considering the complex interactions between surrounding agricultural practices, water quality, biogeochemical cycles, and ecosystem conservation goals. Adopting adaptive wetland management approaches that account for seasonal variability and climate change is crucial.

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The findings of this study provide information to guide public policies and management practices aimed at preserving and restoring wetland ecosystems, while supporting the indispensable ecosystem services they provide, highlighting the importance of collaboration among policymakers, natural resource managers, scientists, and local stakeholders in developing and implementing integrated and adaptive wetland management strategies.

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Figure 1. **Map of the sampling sites located in lateral wetlands of the Seine estuary with water entries during high tides.** Water is held back in the wetland by a valve (white arrow) located between a reed bed and several agricultural lands exploited for mowing and/or grazing. Sites S1, S2, and S3 were located in the wetland where water accumulates. Near the river, the reed bed, non-impacted by water management and naturally flooded by tide, has several maintained ponds for hunting and a mudflat located on the riverbank where site M was located. Water level, temperature, and conductivity are continuously monitored using a self-contained probe.

Figure 2. Average fluorescence intensity of the fluorescent dissolved organic matter (FDOM) at the sediment-water interface. The intermittent immersion sediments are shown on the left, the permanent immersion period on the right. The cumulative fluorescence intensities (RU) of the five components determined by PARAFAC were indicated on the top panel **(a and b)**, and their relative fluorescence intensity (%) on the lower panel **(c and d)**.

Figure 3. Potential nitrate (a) and ammonium (b) fluxes measured at the water-sediment interface. The error bar indicates the standard deviation (n = 3). Black bar referred to the intermittent immersion period while gray bars referred to the permanent immersion period. Lower-case letters refer to statistical differences obtained after a comparison test performed with both sites and periods included

Figure 4. Boxplot of the nitrate reduction (a) and ammonium production (b) rates measured in the top sediment layer (i.e. 2 cm). The error bar indicates the standard deviation (n = 6). White boxes referred to the intermittent immersion period while gray boxes

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referred to the permanent immersion period. Lower-case letters refer to statistical differences obtained after a comparison test performed with both sites and periods included.

Figure 5. Principal Component Analysis. The values of the water-sediment interface characteristics (temperature (T°C; °C), content in fine particles (%Fine; %), moisture content (MC; %), total nitrogen content (N; %), total organic carbon content (C_{org}; %), C:N ratio (C_{org}:N; molar:molar), $\delta^{13}C$ and $\delta^{15}N$ (‰)) were used as structural variables, as well as the parameters related to the dissolved organic carbon (sum of the maximum fluorescence intensity of all five PARAFAC components (ΣF_{max}; RU), humification index (HIX), fluorescence index (FI), biological index (BIX)), and the carbon and nitrogen related external enzymatic activities (C-EEA, N-EEA; nmol g^{-1} dry sediment h^{-1}). The benthic fluxes (NO_3^- influxes (nmol NO_3^- cm^{-2} h^{-1}), NH_4^+ effluxes (nmol NH_4^+ cm^{-2} h^{-1}), and DOC effluxes (nmolC cm^{-2} h^{-1})) as well as the nitrate reduction rates (NRR; nmol cm^{-3} h^{-1}), and ammonium production rates (APR; nmol cm^{-3} h^{-1}) were used as supplementary quantitative variables while the immersion status, relative to the water management (permanent, intermittent, non-managed) was used as supplementary qualitative variable and for ellipses.

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Figure 1

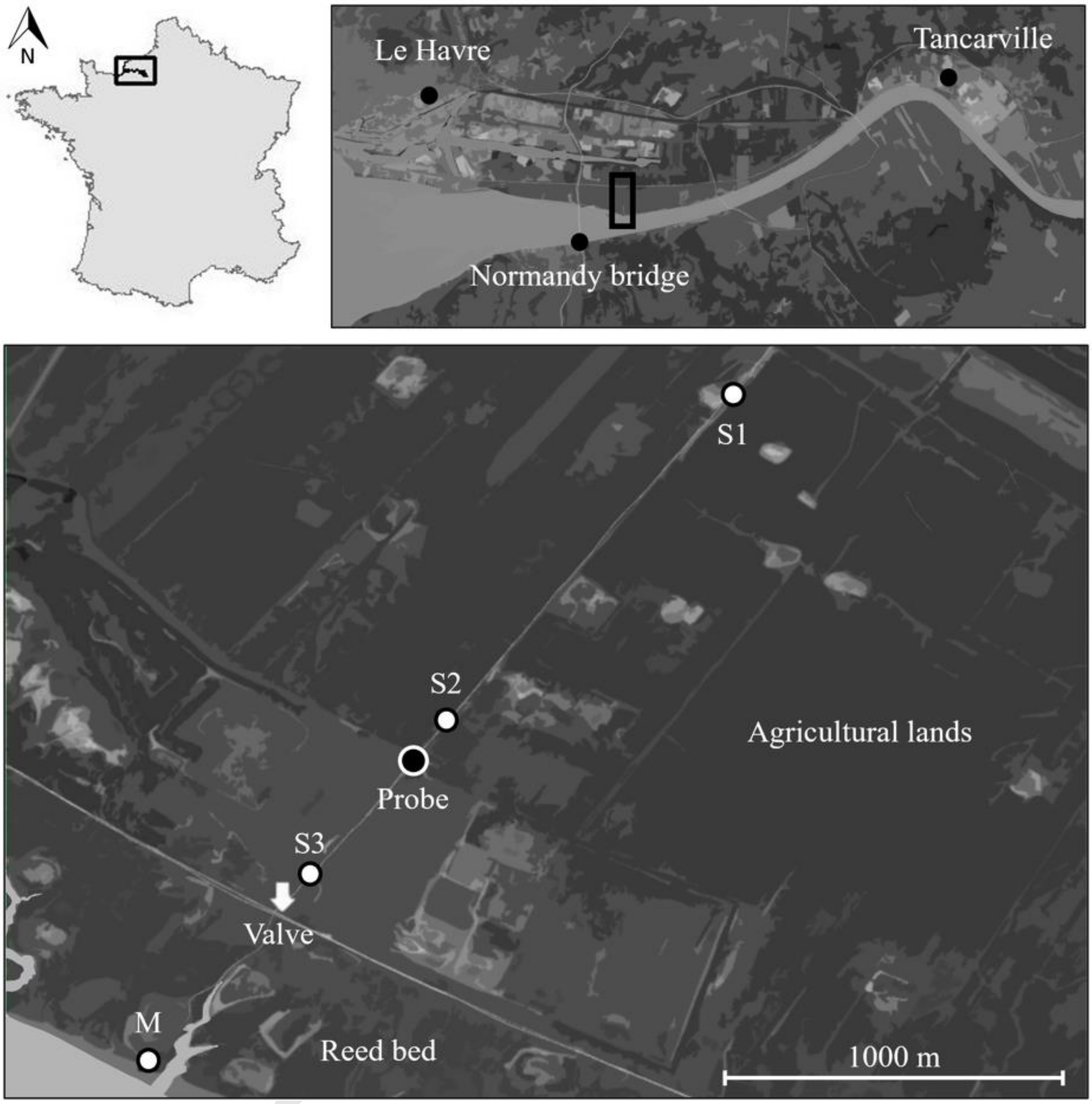
N
Le Havre
Tancarville
Normandy bridge
S1
S2
Probe
S3
Valve
Agricultural lands
M
Reed bed
1000 m

Figure 2

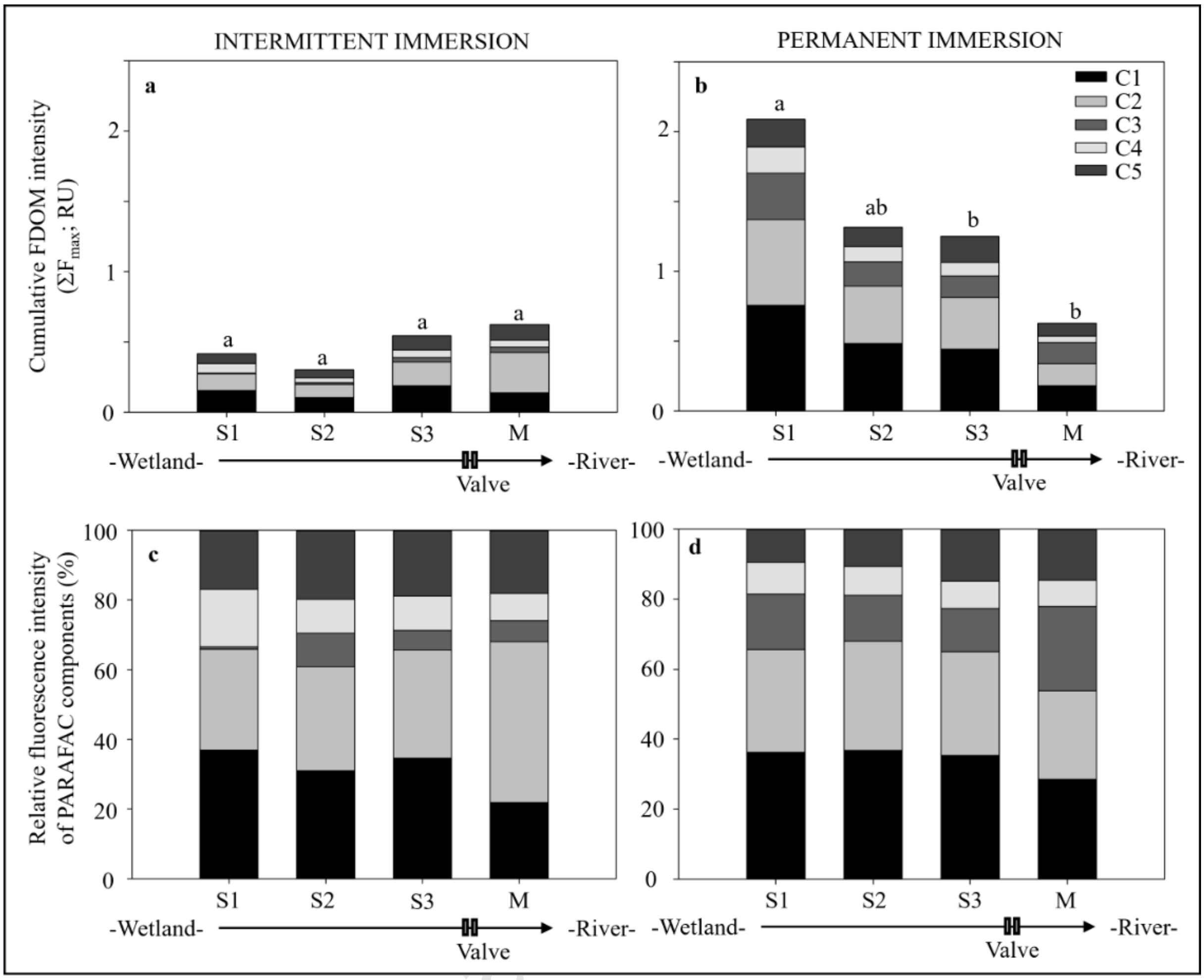

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Figure 3

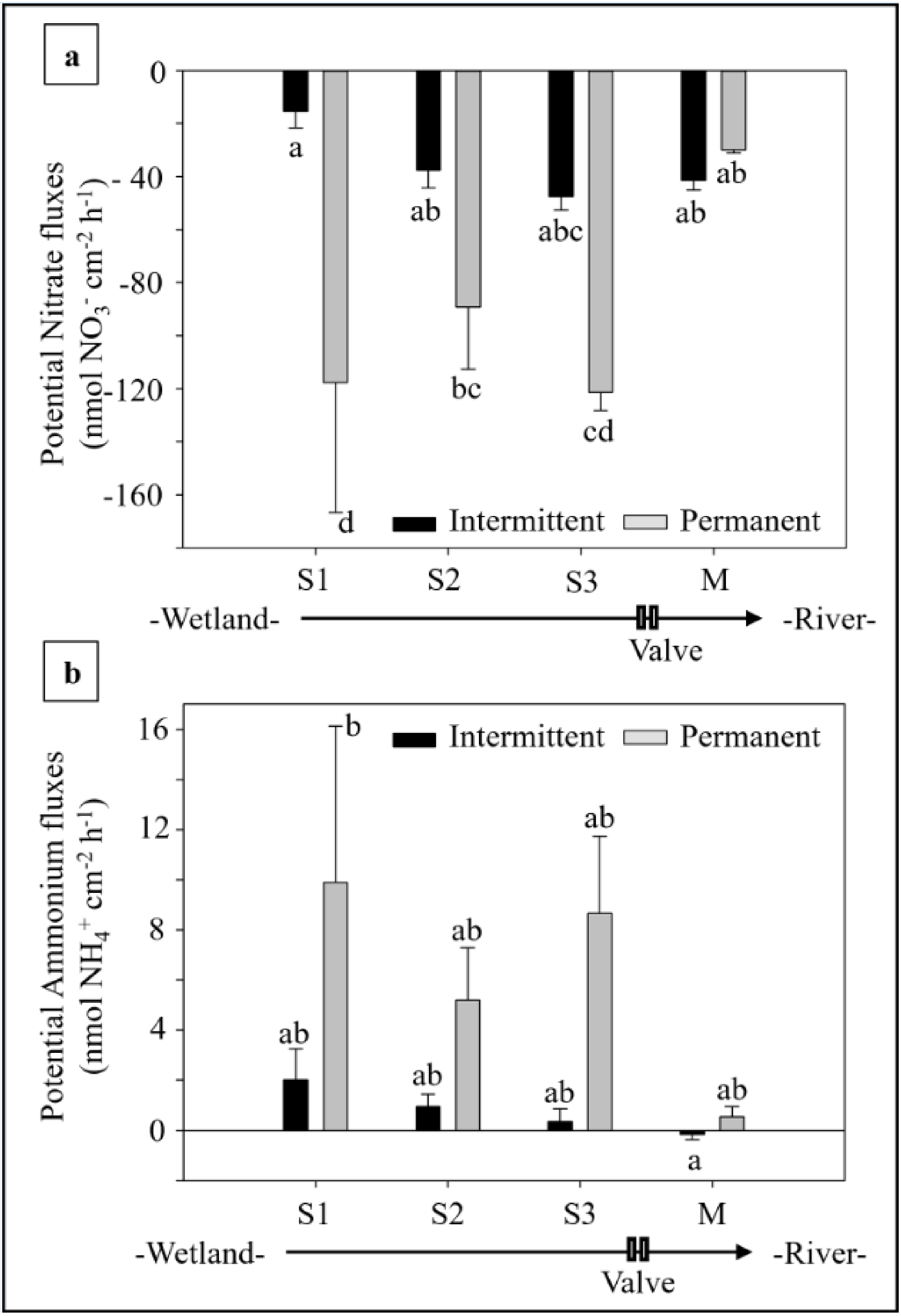
a
Potential Nitrate fluxes
(nmol NO_3^- cm^{-2} h^{-1})
0
- 40
-80
-120
-160
a
d
ab
bc
abc
cd
ab
ab
Intermittent
Permanent
S1
S2
S3
M
-Wetland-
Valve
-River-
b
Potential Ammonium fluxes
(nmol NH_4^+ cm^{-2} h^{-1})
16
12
8
4
0
b
ab
ab
ab
ab
ab
ab
a
Intermittent
Permanent
S1
S2
S3
M
-Wetland-
Valve
-River-

Figure 4

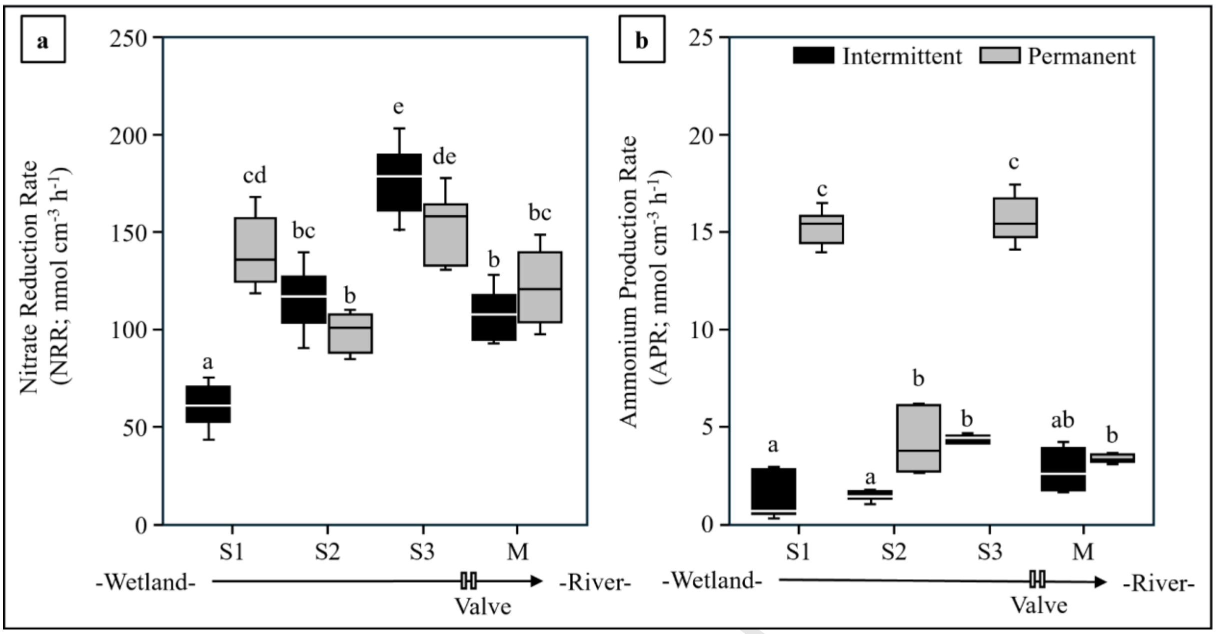

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Figure 5

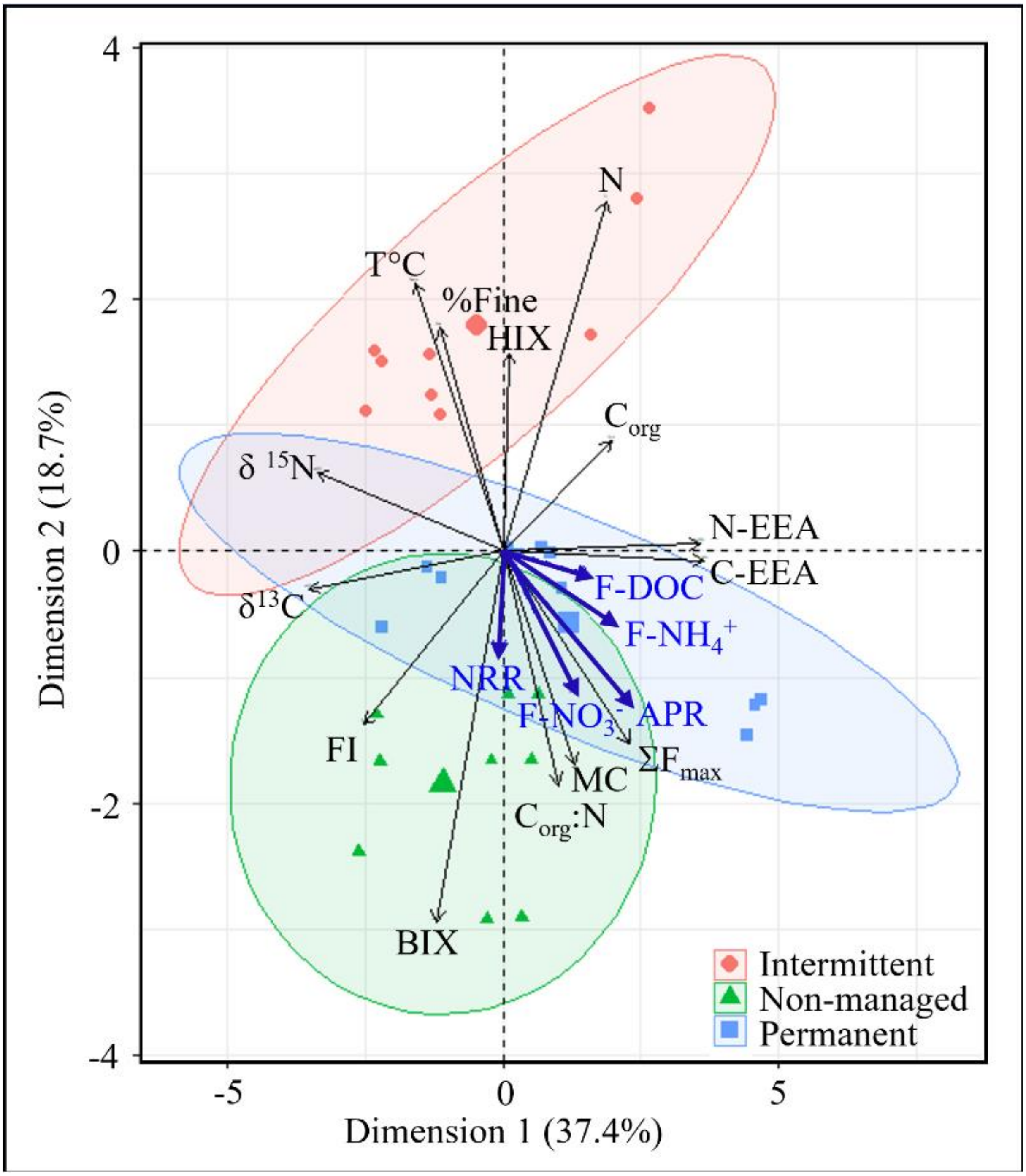
4
2
0
-2
-4
-5
0
5
Dimension 2 (18.7%)
Dimension 1 (37.4%)
N
T°C
%Fine
HIX
C$_{org}$
δ ^{15}N
N-EEA
C-EEA
δ^{13}C
F-DOC
F-NH$_4^+$
NRR
F-NO$_3^-$
APR
FI
ΣF$_{max}$
MC
C$_{org}$:N
BIX
Intermittent
Non-managed
Permanent

Table 1. Components modelled by PARAFAC. Peak wavelengths: Excitation (Ex) and Emission (Em) maxima; description according to literature references. Secondary excitation band is given in brackets. Component contour plots are presented in supplement (Fig. S1).

Component	Ex(max)/Em(max)	Potential origins and characteristics	References
C1	< 240 (340) / 455	Terrestrial substances[a, b]; Lignin-derived[a]; Highly conjugated aromatic material[c]; Nutrient-rich agricultural catchments[d]	[a]Queimaliños et al. (2019); [b]Yamashita et al. (2010); [c]Osburn et al. (2016); [d]Marcé et al. (2021)
C2	< 240 (310) / 390	Biological/Microbial origin[e, f, g]	[e]Parlanti et al. (2000); [f]Murphy et al. (2011); [g]Du et al. (2021)
C3	300 (< 240) / 340	Protein-like[b, h, i, j]; Generated by microbial communities[h], periphyton[j] and leachates from higher plants[h, j]	[h]Coulson et al. (2022); [i]Calderó-Pascual et al. (2021); [j]Eder et al. (2022)
C4	270 (245) / 505	Terrestrial substances[c, k, l]; High molecular weight and aromatic carbon[k]; Reduced quinone-like[k]; Lignin phenol-like[m]	[k]Kowalczuk et al. (2009); [l]Kothawala et al. (2014); [m]Walker et al. (2013)
C5	280 / 335	Protein-like[j, k, n, o]	[n]Graeber et al. (2021); [o]Guéguen et al. (2014)

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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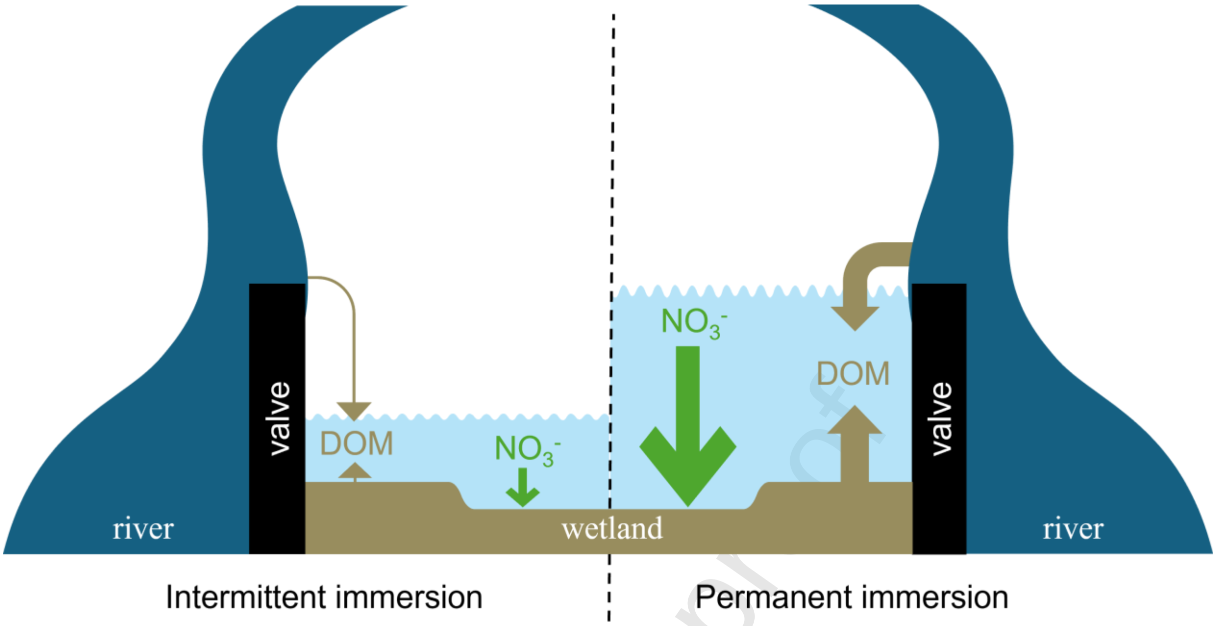
Graphical abstract



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Highlights

- Permanent immersion enhances nitrate reduction via input of fresh organic matter
- Intermittent immersion decreases input of organic matter, limiting nitrate removal
- Low temperatures in winter limit the positive impacts of permanent immersion
- Favoring wetland immersion during summer may enhance ecosystem services

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